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Environmental Implications of Higher Order Fullerenes and Conjugated Nanostructures

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Environmental Implications of Higher Order Fullerenes and Conjugated Nanostructures

by

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Dedication

My Parents

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Environmental Implications of Higher Order Fullerenes and Conjugated Nanostructures

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In quest of harnessing emergent properties and achieving multifunctionality in the materials realm, synthesis and manipulation at the nano-scale has moved its focus from simple passive nanomaterials (NMs) to hierarchical nanostructures. Such nanostructures include higher order fullerenes (HOFs), carbon allotropes composed of more than 60 carbon atoms per fullerene cage, and conjugated nanohybrids (NHs), prepared from materials of multiple chemical origin. The advantages in their electronic, optical, physicochemical, and magnetic properties have inspired their research and use in photovoltaics, nano-electronics, biomedical imaging and drug delivery, catalysis, energy generation and storage, and environmental remediation and sensing. Not only as research grade materials, a global market of bio-imaging and fuel-cell applications have been integrating use of HOFs, and NHs, respectively. Thus it is an exciting time for materials engineering to expand the spectrum of these 'horizon materials' by putting together a variety of chemical 'building blocks' and build a wide range of multifunctional hierarchical structures. However, such conjugation leading to complex hierarchical structures also introduces unknown environmental risks. The emergent properties of these hierarchical structures necessitate careful assessment of their environmental health and safety.

This dissertation is one of the first organized efforts to identify hierarchical nanostructures and assess their environmental implications. This research, through extensive literature review of these novel nanostructures, proposes a working definition of NH from environmental perspective, classifies a wide array of NHs based on chemical origin, and identifies their emerging and altered physicochemical properties with potential to generate unprecedented environmental fate, transport, transformation, and toxicity. Furthermore, this dissertation makes an effort to address three major data gaps: i.e., a) challenges in aqueous solubilization of HOFs, b) possible correlation of carbon numbers on fullerene molecules with their aggregation behavior, and c) influence of hybridization on aggregation kinetics and antimicrobiality of an important electrocatalyst NH (metal-carbon). To address the first data gap, aqueous suspensions of nC_{60}, nC_{70}, nC_{76}, and nC_{84} were prepared using a calorimetry-based solvent exchange method. Non-aggregating and size-specific aqueous nC_{60} and nC_{70} fullerene clusters also were prepared using a non-ionic polymer, pluronic acid (PA). The environmental processes section of this research assessed aggregation kinetics of nHOFs and NHs as well as antimicrobiality of TiO_2 conjugated oxidized multiwalled carbon nanotube (OMWNT-TiO_2) NH.

Aqueous solubilization of C_{70}, C_{76}, and C_{84} was performed being guided by molecular dynamics (MD) simulations. Increased energy demand reflects favorability of HOF-water interaction. The experimental findings suggest that nHOF clusters obtained via solvent-exchange solubilization method remains stabilized by electrostatic repulsion. Similarly, non-ionic triblock co-polymer PA F-127 stabilized aqueous C_{60} and C_{70}s were prepared. Experimental results suggest that size uniformity of aqueous fullerenes increased with the increase in PA concentration, yielding optimum 58.8±5.6 and 61.8±5.6 nm nC_{60}s and nC_{70}s, respectively (0.10 %w/v PA). Fullerene aqueous suspensions also manifested colloidal stability even in presence of 1 M NaCl or in biological media, i.e., DMEM and RPMI. MD simulations results indicate encapsulation of fullerene clusters by PA molecules and subsequent steric stabilization. The results from this study may facilitate mechanistic environmental and toxicological studies with size-specific fullerenes that do not aggregate in high ionic strength biological media.

Aqueous suspensions of nC_{60} and three nHOFs (i.e., nC_{70}, nC_{76}, and nC_{84}) obtained via solvent-exchange method were systematically studied to determine their aggregation kinetics in a wide range of mono- (NaCl) and divalent ($CaCl_2$) electrolytes. Experimentally obtained critical coagulation concentration (CCC) values of nC_{60} and nHOFs displayed a strong negative correlation with the carbon number in fullerenes. The aggregation mechanism was dominated by van der Waals interaction as enumerated via MD simulation and modified Derjaguin-Landau-Verwey-Overbeek (DLVO) model. Natural macromolecules profoundly stabilized all fullerene clusters, even at 100 mM NaCl concentration. The results from this study can be utilized to predict aggregation kinetics of nHOFs other than the ones studied here.

To understand the aggregation behavior of carbon-metal NHs, oxidized MWNTs were hybridized sequentially with undoped or Nb-doped TiO_2 and Pt NPs. OMWNT-TiO_2, OMWNT-$TiNbO_2$, OMWNT-TiO_2, and OMWNT-$TiNbO_2$-Pt and the component materials were characterized and their aggregation behavior was studied systematically. Experimental findings show that CCC values OMWNT were reduced by TiO_2 attachment; however, Nb-doping and Pt attachment increased their colloidal stability and CCC values. The aggregation mechanism was elucidated by modified DLVO energy calculations using composition-averaged Hamaker constants for NHs. Natural macromolecules stabilized all the NHs and the component materials. Antimicrobiality of OMWNT-TiO_2 NH was studied via *in vitro* cell viability tests. Opportunistic pathogen *Pseudomonas aeruginosa* PAO1 strain was exposed to OMWNT, TiO_2, and OMWNT-TiO_2 NH at different concentrations in dark and UV-irradiated conditions. OMWNT-TiO_2 NH showed higher antimicrobial activity compared to the component materials under UV-irradiation. Extracellular reactive oxygen species (ROS) measurement by using fluorescence molecular probes for H_2O_2 identifies UV-induced enhanced ROS generation by the NH as a likely antimicrobial mechanism.

The research presented in this dissertation takes the first attempt toward EHS assessment of complex and hierarchical nanostructures. The research findings present new insights into these ‘horizon materials’ and likely will spark interests on this necessary line of research to better understand the environmental fate, transport, and effects of HOFs and NHs. As nanotechnology is advancing from passive singular nanostructures to active and complex nano-systems; such undertakings become imperative to evaluate implications of material complexity at the environmental interface.

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Chapter 1: Introduction

1.1 Introduction

Material manipulation at the nano-scale, initiated by the discovery of C_{60} fullerenes in 1985,[1] has advanced as the most multidisciplinary and transformative field of research over the last three decades. Advancement in material synthesis has impacted the fields of electronics,[2] conventional and renewable energy sources,[3] catalyst based industrial production,[4] infrastructure,[5] transportation,[6] food,[7] textile,[8] biomedical imaging and medicine,[9] environmental remediation and water treatment[10], profoundly. Commercialized nano-enabled products have increased dramatically over the last decade grossing more than trillion dollars in global revenue and more than $370 billion within the US in 2013. The continuous pursuit of superior performance from nano-enabled products and technologies have recently driven the focus to shift from single passive nanomaterials (NMs) to multifunctional hierarchical nanostructures.[11] This new material class includes hierarchical structures in the fullerene family with more than 60 carbon atoms (e.g., C_{70}, C_{76}, C_{78}, C_{84}, C_{90}), which are known as higher order fullerenes (HOFs). The more complex structures within this material class include conjugated multi-component nanostructures or nanohybrids (NHs). Potential for numerous combinations among various NM types (including carbon-based, metallic, and/or organic) with different dimensions and physicochemical properties may lead to an ever expanding array of hierarchical nanostructures (Figure 1.1).

HOFs offer several advantages compared to C_{60} fullerenes including low energy band gap,[12] ambipolar electronic properties,[13] higher redox potentials[14] and electron affinities, [15] etc. HOFs are attractive due to their advantageous properties for applications mostly in the fields of photovoltaics[16, 17] and nanoelectronics.[18-20] Larger cages of HOFs are able to incorporate rare earth metal atoms creating endohedral metallofullerenes.[21] These novel NHs with as high as ~500 times increase in water relaxivity are awaiting approval from Food and Drug Administration (FDA) to enter the multibillion dollar magnetic resonance imaging (MRI) contrast agent market.[22]

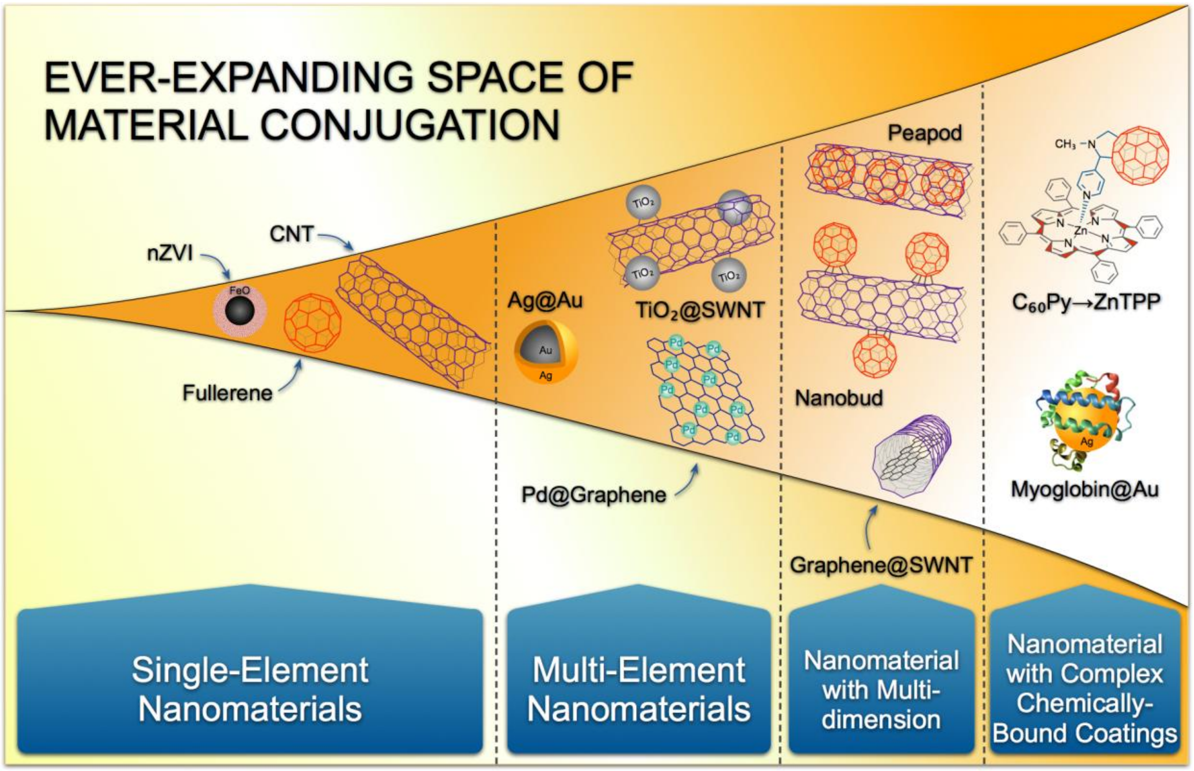

FIGURE 1.1. Schematic showing the ever-expanding space of nanomaterial conjugation and the resulting permutations of nanomaterials. (adopted from Saleh and Aich et al. 2015[23])

HOFs can further be conjugated with carbon nanotubes (CNTs) or nanohorns (CNHs) endohedrally or exohedrally to formulate a subset of NHs that can manifest similar properties and bring unique advantages to solid state electronics and biomedical imaging.[24] Similarly, other NHs are prepared by conjugating multiple nano-scale entities of unique origins and functionality that lead to either enhanced or multifunctional properties. For example, when paramagnetic iron oxide coats plasmonic gold to form shell-core bimetallic NHs, it can be used simultaneously for biomedical imaging and photodynamic therapeutics.[25] The same iron oxides when deposited on 2-dimensional graphene-oxide sheets, are able to catalytically degrade organic pollutants.[26]

Similarly, titanium dioxide (TiO_2) nanoparticles when deposited on CNTs or graphene can act as a photocatalyst for solar cells or organic pollutant degradation[27] and also as support material for platinum (Pt) electrocatalysts in electrochemical fuel cells.[28] Thus assemblages of different NMs can lead to various combination types including carbon-carbon, carbon-metal, metal-metal, and organic molecule based NHs.[11] Detailed descriptions of different NH classes and their multidirectional applications are reviewed in later sections of this dissertation. The benefits emanating from HOFs and NHs are evident and are likely to widen the hierarchical nanostructure domain and relevant applications with the potential of release in natural environments.

Environmental release and exposure pathway of these hierarchical nanostructures can vary depending on their applications. For example, photovoltaic cells and fuel cells containing HOFs and NHs may be disposed in landfills and will cause nano-contamination of the aquatic environment through leaching and seepage to the ground water. On the contrary, MRI agents and nano-medicines can directly end up in the waste water treatment systems. Upon release to the natural environment, these hierarchical nanostructures will undergo various environmental processes. The most common processes include interfacial interactions (e.g., aggregation, deposition, sedimentation, transport), chemical transformations (e.g., dissolution, redox, sorption), and biological consequences (e.g., organismal uptake and toxicity, bio-transformation). Though environmental health and safety (EHS) of the component materials of most NHs have been studied extensively, uncertainty in their environmental behavior persists due to unique and emergent properties that are manifested upon hybridization.[11, 23, 29] Thus there is a critical need to systematically assess EHS of hierarchical nanostructures.

This dissertation is the first organized effort in defining and identifying hierarchical nanostructures and assessing their environmental behavior. This work first undertakes an extensive literature review on hierarchical nanostructures and proposes an environmentally relevant definition of these NHs and also establishes a framework for classification.[11] Guided by the extensive literature review the dissertation then selects HOFs and a metal-carbonaceous NH and evaluates aggregation and antimicrobial behavior of these materials.

Assessing inter-particle aggregation is a key aspect in determining environmental fate and toxicity of NMs. Surface water and groundwater contain various dissolved ionic species, which influence aggregation behavior of NMs by modulating their electrostatic interaction. The state-of-the-art nano-EHS literature extensively assessed aggregation behavior of simple carbonaceous or metallic NMs including C_{60},[30] CNTs,[31, 32] graphene,[33] TiO_2,[34] ZnO,[35] Ag,[36] and nano iron,[37] under various environmental conditions. However, the aggregation propensity of complex hybrid nanostructures, i.e., of HOFs and NHs, has not been systematically assessed. For example, nC_{60} (aqueous C_{60} colloid) is known to be highly stable in aqueous environments dominated by electrostatic contributions from negative surface charge.[30] HOFs possess lower band-gap and higher electron affinity than does C_{60}, which may alter the surface charge characteristics and solvent affinity of nHOFs.[12] Increase in carbon numbers in fullerene structures have shown to increase inter-molecular binding energy,[38] which might translate to increased van der Waals (vdW) attraction forces in the nHOFs. Thus nHOFs might manifest altered aggregation and mobility in aqueous environment as compared to nC_{60}s.

Similarly, hybridization of multiple NMs alters the physicochemical properties and manifests unique emergent properties relevant to their environmental behavior. These may include: electronic band-gap reduction of semi-conducting TiO_2 or ZnO when deposited on highly conductive CNTs or graphene;[27] change in vdW attraction forces upon fullerene insertion in CNTs;[39] altered dimensionality upon exohedral conjugation of fullerene and CNTs (1-D CNT to 3-D CNT-fullerene NH);[40] decreased dissolution of Ag when coated with inert Au NMs.[41] NHs act as independent units rather than mixtures and thus their properties are not equal to the summation of the parent material properties. These altered properties will likely change NHs' aggregation behavior and interactions with microorganisms. Modified surface chemistry, vdW attraction forces, and dimensionality of NHs also will change their colloidal stability. Photoactivity of TiO_2 enhanced by conjugation with CNTs can lead to enhanced light-induced reactive oxygen species (ROS) production[42] – a key mechanism contributing to antimicrobiality. Thus NHs might pose uncertain environmental implications that are unique from their parent material behavior. Exponential growth in synthesis and application of this novel material class necessitates careful evaluation of their environmental behavior and underlying mechanisms. The dissertation is framed in this space and is the first attempt to address such critical nano-environmental data gap.

1.2 Research Objectives

This dissertation has the following specific aims: first, critical review of the existing HOF and NH literature from an environmental context to identify data gap and establish a layout for future environmental studies; second, preparing stable aqueous suspensions of HOFs intended for use in environmental implication studies; third, understanding inter-particle interactions, i.e., aggregation behavior of HOFs and NHs in aqueous systems; and finally, investigating the antimicrobiality of NHs. Three different HOFs, i.e., C_{70}, C_{76}, and C_{84}, were selected as HOFs while oxidized multiwalled carbon nanotubes (OMWNT) were hybridized with titanium dioxide (TiO_2) and platinum (Pt) to prepare metallic-carbonaceous NHs.

1.3 Research Hypotheses

Hypothesis 1: Classical solvent extraction method for solubilization of C_{60}s will be applicable for aqueous solubilization of HOFs.

Hypothesis 2: Non-ionic triblock co-polymer functionalization will enable cluster size control and result in highly stable C_{60}s and C_{70}s.

Hypothesis 3: Increase in carbon number in the fullerene structure will increase van der Waals attraction and thereby increase aggregation propensity of HOFs in aquatic environment.

Hypothesis 4: Hybridization with metal nanoparticles (TiO_2 and/or Pt) will enhance aggregation propensity and UV-mediated reactive oxygen species (ROS) generation and antimicrobiality of the OMWNTs.

1.4 Approach and Methodology

The proposed research was accomplished by completion of the following tasks.

Task 1. Literature review to determine data gap regarding environmental implications of HOF and NH

Task 2. (a) Aqueous solubilization of HOFs using solvent-exchange method.

(b) Aqueous solubilization of C_{60} and C_{70} using non-ionic biocompatible polymer.

Task 3. Aggregation kinetics of HOFs in aqueous systems.

Task 4. Role of hybridization on aggregation kinetics and antimicrobiality of OMWNT-TiO_2 NHs.

1.5 Organization of the Dissertation

This dissertation is organized in eight chapters and five appendices. Chapter 1 introduces this dissertation with a brief overview on current status of the hierarchical nanostructure research, their environmental importance, key data gaps, research objectives, and hypotheses. Chapters 2-

7 consist of literature review and original research articles either published or currently in review or in preparation for publication as book chapters and peer-reviewed articles.

Chapter 2 presents a literature review on the C_{60}, HOFs, and their NHs. The review includes: a historical perspective; synthesis, characterization, and applications in energy production and storage; and environmental implication of these carbon allotropes. This review identifies the knowledge gap in regard to HOFs' environmental behavior. This work was led by Nirupam Aich and was published in 2015 as a book chapter titled 'Fullerenes, higher fullerenes, and their hybrids: Synthesis, characterization, and environmental considerations' in the book titled '*Carbon Nanomaterials for Advanced Energy Systems*' edited Wen Lu, Jong-Beom Baek, and Liming Dai.[3]

Chapter 3 critically reviews the current status of multicomponent nanohybrid research. In an attempt to isolate true NHs from mixtures, a working definition for NHs was proposed. Through a systematic literature search using keywords in ISI Web of Knowledge, environmentally relevant NHs were identified and their synthesis and applications were discussed. Moreover, this chapter identifies altered and emergent properties of NHs and discusses the potential unknown environmental implications origination from NHs. This work was led by Nirupam Aich and was published in 2015 as a cover article in *Environmental Chemistry* titled 'A critical review of nanohybrids: synthesis, applications and environmental implications'.[11]

Chapter 4 tests the first hypothesis by solubilizing three different HOFs, i.e., C_{70}, C_{76}, and C_{84}, in water using a sonic-energy based modified liquid-liquid extraction technique. Guided by molecular dynamics (MD) simulations, incremental sonic energies for the increasing carbon number of HOFs were employed to produce their stable aqueous suspensions. Nirupam Aich was the primary author of this article, which was published in 2012 as peer-reviewed article in *Nanotechnology* and was titled 'Preparation and characterization of stable aqueous higher-order fullerenes'.[38]

Chapter 5 tests the second hypothesis. This study uses a non-ionic biocompatible polymer, pluronic acid (PA) F-127, to prepare size-tuned and non-aggregating aqueous nC_{60} and nC_{70} clusters. PA-coated fullerenes showed enhanced stability in highly saline solution and biological culture media. MD simulations were performed to elucidate the mechanisms behind PA-induced colloidal stability. Nirupam Aich was the lead author of a peer-reviewed article, published in 2013 in *Nanotechnology* titled 'Preparation of non-aggregating aqueous fullerenes in highly saline solutions with a biocompatible non-ionic polymer'.[43]

In Chapter 6, aggregation kinetics of aqueous nC_{60}s and nHOFs was systematically studied to test the third hypothesis. Aggregation kinetics was measured experimentally and the underlying mechanism of aggregation was deciphered via analysis with a modified Derjaguin-Landau-Verwey-Overbeek (DLVO) theory and MD simulations. The influence of natural organic matter on nHOF aggregation also was assessed. This work has been submitted as an original research article to *Environmental Science and Technology* with the title 'Aggregation kinetics of higher order fullerenes in aquatic systems',[44] with Nirupam Aich as the lead author.

Chapter 7 presents results from tests of the fourth hypothesis. This chapter presents experimental aggregation kinetics data of OMWNTs-TiO_2-Pt NHs and their components materials in the presence of mono- and di-valent electrolytes. The effect of natural macromolecules on NH aggregation also was examined. This study also evaluates the role of hybridization on photo-induced antibacterial activity of OMWNT-TiO_2 NHs and that of the component materials. This chapter is in preparation for submission as a peer-reviewed article with a tentative title 'Aggregation kinetics and antimicrobiality of TiO_2-multiwalled carbon nanotube nanohybrids', with Nirupam Aich as the lead author.

Chapter 8 is the final chapter in the dissertation that summarizes the results of this dissertation work, discusses environmental implications of the obtained results and presents future recommendations.

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Chapter 2: Fullerenes, Higher Fullerenes, and their Hybrids - Synthesis, Characterization, and Environmental Considerations*

2.1 Introduction

The search for alternative and renewable energy sources has become one of the major thrusts of the 21st century researchers due to the increasing demand for energy. Innovations and development of photovoltaics, dye-sensitized or polymer solar cells, high-efficiency lithium ion batteries, super-capacitors, transparent conductors, hydrogen productions and storage systems, microbial fuel cells, catalyst driven proton exchange membrane fuel cells, thermoelectric power generation, etc. have come to the forefront in alternative energy research.[1, 2] In hunt for effective energy transfer, distribution, and storage, improved materials are being synthesized since the 1990s. Nano-scale manipulation of materials has fueled such development.[3] Improved surface area at the nano-scale and targeted molecular placement or alteration in nanomaterials resulted in desired band gap tuning, effective electron transfer, storage, and surface activity.[4] One of the key challenges that eluded energy researchers for decades was an efficient photo-electron acceptor with high structural stability and chemical reactivity; a spheroidal carbon allotrope, known as fullerene addressed this critical gap in alternative energy research and development.[4, 5]

60 carbon atoms, organized following isolated pentagon rule (i.e., 20 hexagons and 12 pentagons), forming a truncated icosahedron structure is known as Buckminsterfullerene—the first member of the fullerene family, discovered by Sir Harry Kroto, Robert Curl, and Richard Smalley in 1985.[6] Fullerenes' ability to effectively function in donor-acceptor heterojunctions

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has popularized its synthesis, derivatization, and supramolecular assembly for photovoltaic applications.[5] Later, detection and effective isolation of higher order fullerenes,[7] i.e., C_{70}, $C_{76,}$ C_{82}, C_{84}, etc., have encouraged their studies and use in energy applications. Changes in electron hole-pair generation ability and electronic band-gap with the changing number of atoms in the fullerene structures have continued to evoke interest in these higher fullerenes.[8, 9] Electronic structure could be further tuned by conjugation of fullerenes with other carbon allotropes, e.g., carbon nanotubes, graphene, etc.; which has encouraged synthesis of hierarchical assemblages of fullerenes with other nano-scale structures, resulting in nano-scale hybrid materials (NHs).[10-14]

C_{60}s, especially its polymeric derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM), have been known to be the most effective electron acceptor for organic photovoltaics.[5] Recent advances in this field have proposed a novel donor-acceptor blend for electron-hole transfer. By photo-exciting the donor, electron moves from the lowest unoccupied molecular orbital (LUMO) of the donor's to the acceptor's, where the hole gets transported to the donor's. C_{60}'s excellent electron accepting ability has presented it as an ideal candidate for photovoltaic solar cell construction. Their applications in organic field effect transistors[15] and lithium or hydrogen storage[16] also depend on its high electron affinity and high charge transferability. C_{60}s also act as promising catalytic composites and electrode materials for nafion-based proton exchange membrane fuel cells.[17] Similarly, higher order fullerenes such as C_{70}, C_{76}, C_{84}, C_{90} and their derivatives also are being utilized as higher efficiency transistors and have shown promising solar cell efficiencies.[18-20] Moreover, hybridization of fullerenes to formulate concentric fullerene clusters or carbon nano-onions[21], fullerene nano-peapods[11] or nano-buds(fullerene-carbon nanotube hybrids),[22, 23] and endohedral metallofullerenes[24] enhance their promises in energy storage devices. However, such demand of fullerenes requires higher quantity to be synthesized and purified. Such high demand for this material requires unique synthesis and preparation processes, which in conjunction with fullerenes' inherent attributes can invoke toxic responses to the environment, hence necessitate careful consideration.[25]

C_{60} and its derivatives such as C-3, fullerol $C_{60}(OH)_{24}$, bis-methanophosphonate fullerene, tris carboxyl fullerene adduct tris-C_{60}, dendritic C_{60} mono adduct, malonic acid C_{60} tris adduct, etc. are found to be responsible for inducing toxicological impacts in soil and aquatic microbes,[26-30] invertebrates,[31] and fish[31] as well as in human cell lines,[32-34] and rats and mice.[35] Such environmental and biological toxic potential are known to have resulted from fullerenes' ability to penetrate cell membranes and generate oxidative stresses. Similarly, C_{70}s also have shown to adversely affect aquatic species, when C_{70}-gallic acid derivative at less than quantifiable concentration cause significant reduction in diaphnia magna fecundity after 21 day exposure. It also has demonstrated generation of oxidative stress through inhibition of enzymatic activities.[36] The demonstrated toxicity of fullerenes resulted in systematic evaluation of its fate, transport, and transformation in natural environment; which include fundamental aggregation,[37] deposition and transport in porous media,[38] photo-induced transformation,[39] etc. C_{60}s, synthesized using different techniques,[40, 41] have been studied to evaluate role of synthesis on their potential risk. However, very few studies have focused on systematic investigations of higher fullerenes and fullerene-based NH's fate, transport, transformation, and toxicity.[10, 14, 25, 42]

This chapter discusses synthesis, characterization, and application of fullerenes, higher fullerenes, and their NHs. The chapter identifies the potential risk of these carbon allotropes when used in energy applications and discusses possible strategies for pursuing green synthesis of these materials. The discussion in this chapter will potentially highlight the relevant risk of using fullerenes in energy applications and help establish an understanding of environmental considerations.

[The planning and completion of the work was led by Nirupam Aich. He was primarily involved in writing the sections discussing the introduction, historical perspective, synthesis and characterization, and environmental considerations. Jaime Plazas-Tuttle helped in reviewing energy applications and producing the schematics. Dr. Navid Saleh supervised the work.]

2.2 Fullerene, higher fullerenes, and nanohybrids: Structures and historical perspective:

2.2.1 C_{60} fullerene

C_{60} fullerene is an all carbon and perfectly symmetric molecule made from 60 carbon atoms (Figure 2.1a). It was the first ever discovered regular truncated icosahedral molecule.[43, 44] The carbon atoms on the vertices of the polygons in C_{60}s possess SP^2 hybridization and become bonded through 6:6 double bond between hexagons and 6:5 bonds between hexagons and pentagons.[45] One carbon atom is bonded to 3 other carbon atoms with a bond length of 0.14 nm. The total spherical diameter of a C_{60} molecule becomes 0.71 nm, giving rise to the perfect symmetric cage.[46] Though such molecules possess high structural stability,[43, 44, 47, 48] these were found to be highly reactive, where acceptance of electrons makes them strongly reductive.[49, 50] Such conjugate reactivity and structural stability help them to produce various derivatives as shown in Figure 2.1b.

The discovery of fullerene was rather extraordinary.[51] A research lab in Exxon group in 1984 had first seen carbon soot presenting similar time of flight (TOF) mass spectra for even numbers of carbon atoms starting from 40 to 200,[52] however they were unable to identify the abundance of C_{60}s in that mixture. In similar timeframe, while searching for the mechanism of interstellar long chain carbon molecule formation, an unusual TOF spectral signature of carbon soot was observed by Sir Kroto, Smalley, and Curl, while synthesizing carbon soot through laser irradiation of graphite[6] at Rice University in 1985. The group hypothesized that the spectral signature was generated due to the formation of C_{60}s, the probable aromatic icosahedron structure with remarkable stability. Later on, nuclear magnetic resonance (NMR) experiments were performed to conclude that the molecules obtained by Kroto and others truly resulted in C_{60} molecules.[53] Kratschmer, Huffman, and Fostiropoulos on the other hand, came up with synthesis technique for macroscopic amount C_{60} and C_{70} in 1989[54]. In 1995, Harry Kroto, Richard Smalley, and Robert Curl were awarded Nobel Prize in chemistry for the discovery of C_{60}. The afore-mentioned scientists later named the first discovered carbon allotrope as 'Buckminsterfullerene' or 'fullerene' to pay homage toward the renowned American architect Buckminster Fuller, who designed geodesic dome shaped structures resembling fullerenes.

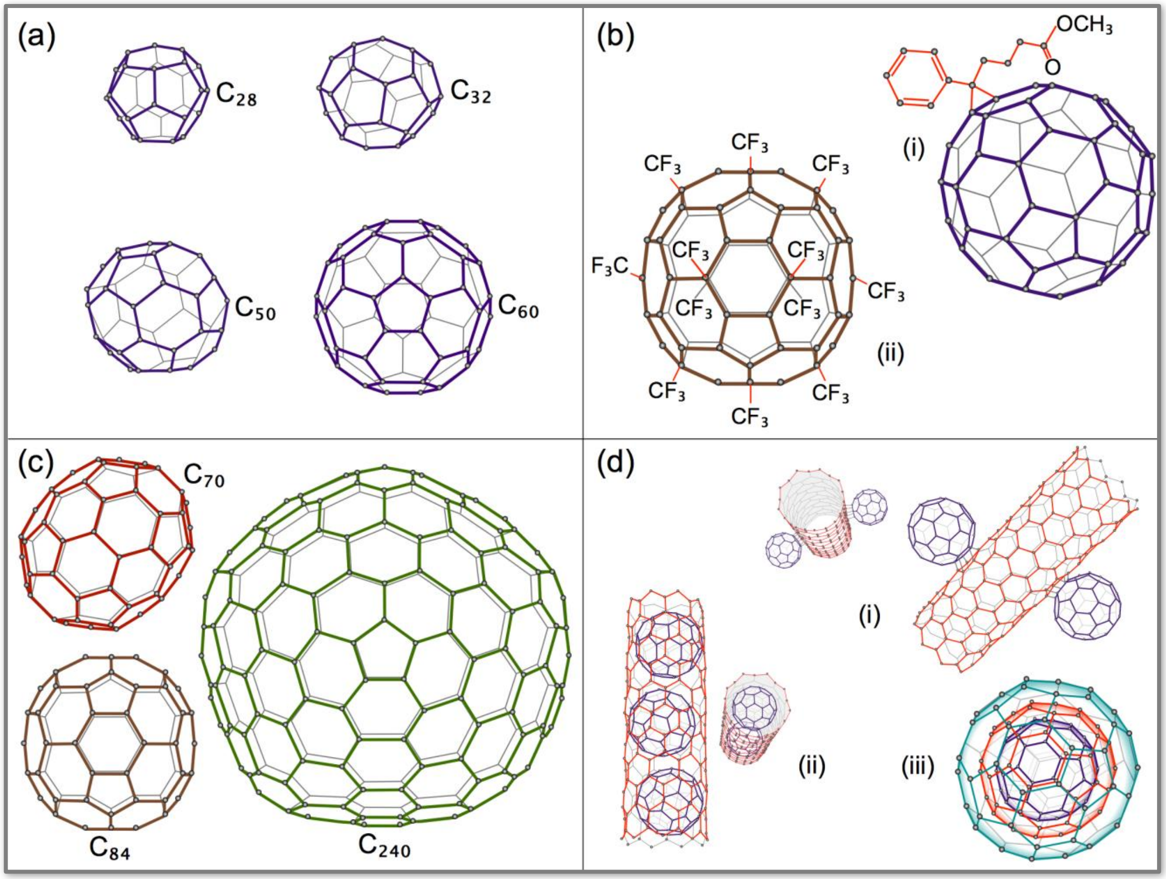

FIGURE 2.1. (a) fullerenes, (b) fullerene derivatives, (i) C_{60}-derivative [6,6]-Phenyl C61-butyric acid methyl ester (PCMB), (c) higher order fullerenes, and (ii) Trifluoromethyl derivative of C_{84} ($[C_{84}](CF_3)_{12}$), (d) (i) nanobud (fullerenes covalently bound to the outer sidewalls of single-wall carbon nanotube), (ii) peapod (fullerenes encapsulated inside a single-wall carbon nanotube), and (iii) nano-onion (multi-shelled fullerenes).

2.2.2 Higher fullerenes

Members of fullerene family possessing more than 60 carbon atoms are known as higher order fullerenes (Figure 2.1c). They are generally found in the same carbon soot obtained during C_{60} synthesis. C_{70} being the first member of the higher order fullerene family, is always found in abundance with the C_{60}s. However, the other members, i.e., C_{76}, C_{78}, C_{84}, C_{92}, (up to fullerenes with more than hundred carbon atoms) are found in much smaller quantities in the soot. Diederich et al. first found mass spectroscopic evidence for existence of C_{76}/C_{78} and C_{84} and isolated them through extraction technique employment during reproduction of Kratschmer method for producing C_{60} and C_{70} fullerenes.[55] During the same time, theoretical prediction of their existence, isomerism, and chemical stability was presented by Fowler and Manolopolous.[56-59] With the help of the newer chromatographic techniques, fullerenes with a wide range of composition, i.e., C_{20} to C_{400}, were extracted, isolated, and characterized alongside with identification of isomeric forms of several higher order fullerenes.[7, 60, 61]

2.2.3 Fullerene-based nanohybrids

When C_{60} and higher fullerenes are conjugated either exohedrally or endohedrally with carbon and metal-based nanomaterials, the ensemble materials are known as fullerene-based nanohybrids (NHs) (Figure 2.1d).[10, 14] The overall scope of this chapter will limit the discussion to carbon only NHs. Endohedral NHs can be formed via fullerene and higher fullerene encapsulation within carbon nanotubes and larger fullerenes structures. These structures are called peapods[62] and carbon nano-onions,[63] respectively (Figure 2.1d). Nano-peapods, prepared in 1998 by Luzzi et al., was one of the first NHs synthesized.[62] Growing interests in fullerene and NH chemistry, encouraged development of other NH assemblages, either with carbon nanotubes[64] and graphene.[65] The conjugation is performed using both non-specific short-ranged interaction[66] and via covalent bonding[64, 67] with the use of functional linking molecules or polymers.

2.3 Synthesis and Characterization

2.3.1 Fullerene and higher fullerene synthesis

Commercial production of C_{60}s and higher fullerenes involve a two-step process.[68] First: carbon soot containing fullerene mixtures are synthesized via carbon vapor generation methods. Second: fullerene separation and purification from the carbon soot is performed to obtain individual fractions of the carbon allotropes. Based on the raw materials and precursors, vaporization methods, and processing techniques various soot generation processes have been developed. Most of the synthesis techniques were developed during the 1985-1995 timeline, when fullerene discovery and techniques for primary isolations and separation were innovated.[51] Later, chemical synthesis processes to form fullerenes from aromatic hydrocarbons were developed.[69] A brief discussion on the major fullerene and higher fullerene production techniques is described in this section. Figure 2.2 shows a flow diagram demonstrating steps involved in carbon soot synthesis and fullerene extraction and purification.

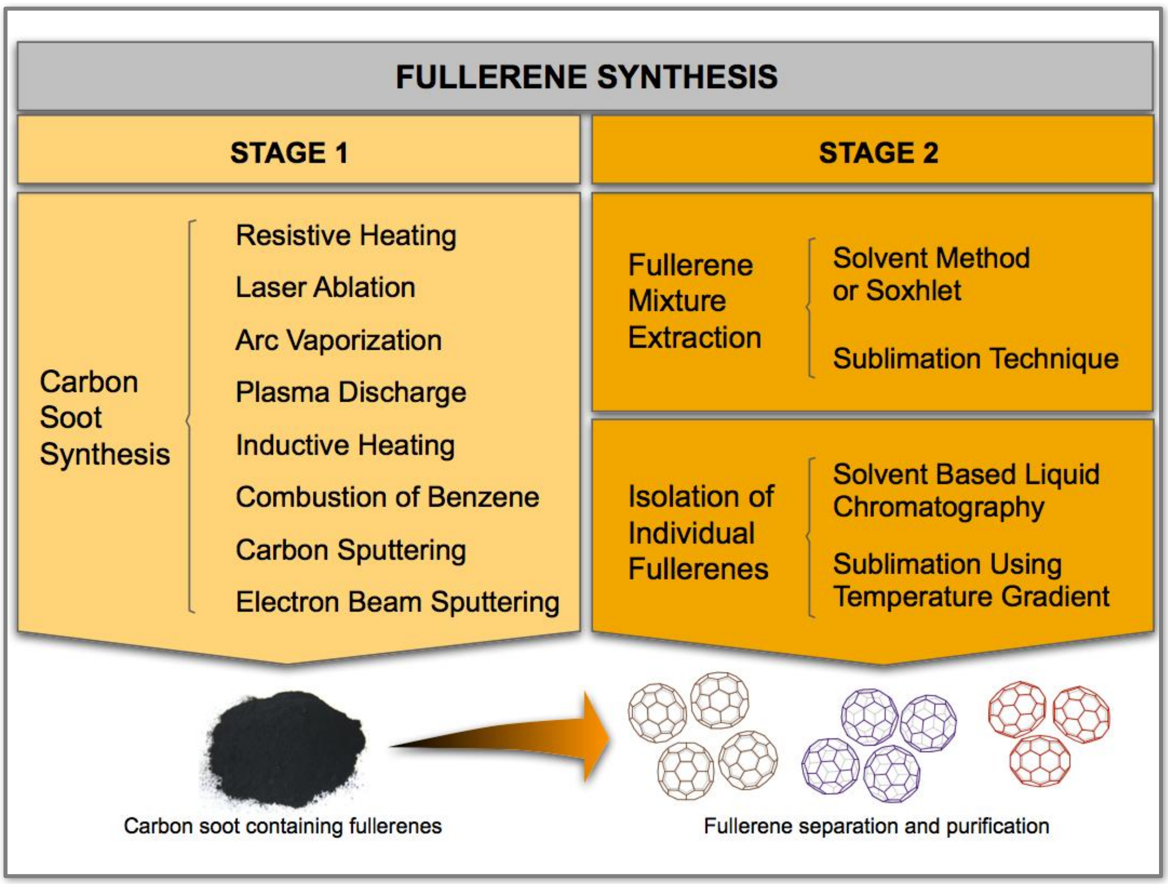

FIGURE 2.2. Flow diagram showing steps for fullerene synthesis via carbon soot formation and fullerene separation and purification.

2.3.1.1 Carbon soot synthesis

Arc vaporization methods. Arc vaporization methods are the most effective ones for carbon soot synthesis. The process of resistive heating of graphite rods in helium environment, developed by Kratschmer et al., was the first step to produce carbon soot containing fullerenes in macroscopic amounts.[70] The method was furthered into AC- or DC-arc based carbon vaporization processes to produce gram quantities of fullerenes,[71] this technique reduced loss of carbon rods through complete heating of the electrodes. Figure 2.3 shows a typical arc process for fullerene soot generation. Two graphite rods are separated from each other by 1-10 mm in a helium-filled chamber under 100-200 torr pressure. An arc is discharged to generate 100-200 amps current at a voltage of 10-20 V. This process causes the graphite rods to evaporate and form soot containing fullerene products. Copper jacket covering the chamber wall and circulating cooling water control the temperature to allow carbon soot vapors to condense and deposit on the chamber walls, which can later be extracted for purification and processing. Modifications of these methods were performed to achieve several advantages. Such modifications include: arc via contacting with the graphite[61, 72] or demineralized coal electrodes,[73] employment of plasma discharge for high yield,[60, 74] application of DC power rather than AC,[61, 72, 73] and low current rather than high AC current.[75] to achieve better fullerene yield, formation of tapered apparatus for gravity based collection of carbon soot,[75] etc.

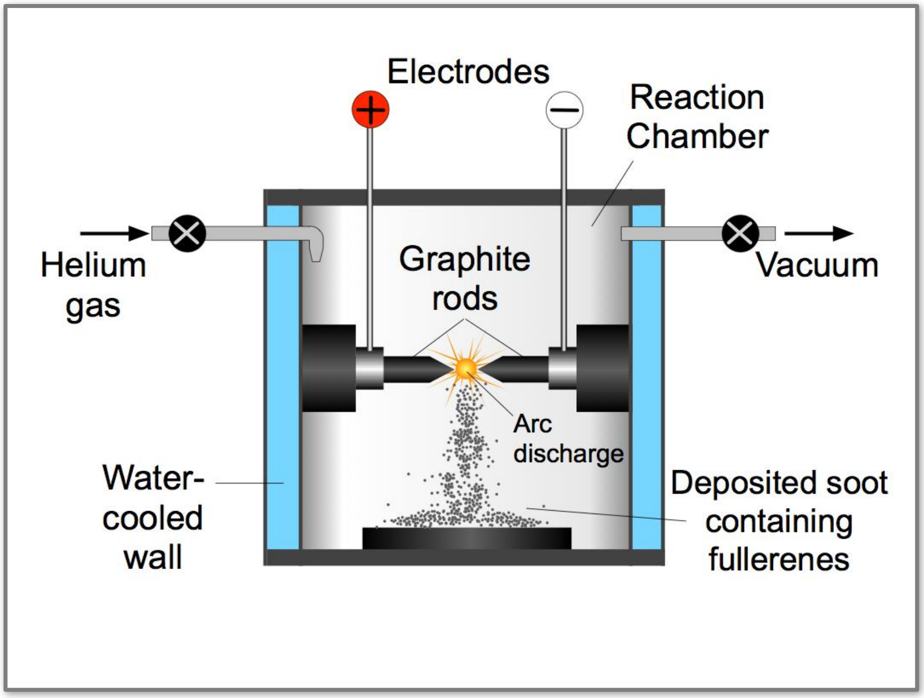

FIGURE 2.3. Arc discharge process for fullerene synthesis (adapted and modified),[72, 76]

Laser ablation method. This technique was first adopted by Smalley group in 1985;[6] which involves a laser, such as neodymium-doped yttrium aluminum garnet (Nd:YAG), irradiated on a graphite rod causing the carbons to evaporate via heating and produce carbon plasma. Afterwards, controlled cooling of the carbon plasma takes place to form fullerene clusters. Later ablation at elevated temperature or inside of heated furnace resolved the issue by slowing down the cooling process.[55, 76] Around 1000-1200 °C was found be most efficient for fullerene cluster formation.[76] A high temperature furnace containing such laser ablation arrangement is shown in Figure 2.4. Operating parameter modulation, such as changing laser intensity, wavelength, buffer gas pressure, and temperature in the furnace, can offer better control over fullerene formation and yield.

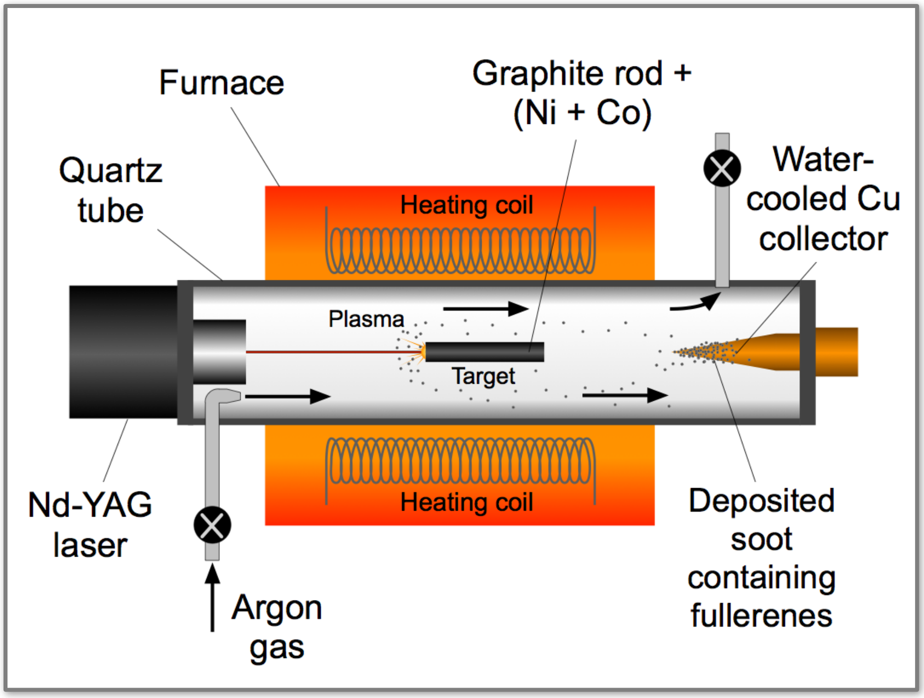

FIGURE 2.4. Laser ablation process for fullerene synthesis (adapted and modified)[76].

Other methods. Versatility in fullerene synthesis processes has been achieved through adoption of different innovative approaches. A thermal vaporization method by inductively heating the graphite rods in a high frequency furnace at 2700 °C was developed for soot production at large quantities.[77] Moreover, combustion method was employed where laminar flames of premixed benzene and oxygen with argon diluents were used to produce C_{60} and C_{70}.[78, 79] Gram quantities of fullerenes were produced using this process with potential for easy scale-up, continuous process operations, and easy dopant addition in the flame mixture, and changes in flame properties for controlling the fullerene size distribution.[76, 78] Efficient production of large quantity higher fullerene soot with minor C_{60} presence was developed by Bunshah et al. in 1992.[80] Two different experimental setups were devised—one for carbon sputtering and the other using electron beam sputtering. In the carbon sputtering method, a magnetron sputtering cathode was attached to a graphite target and carbon black was sputtered from the target by helium ions. In the other method, an electron beam was used to evaporate carbon from a graphite target. Efficiencies of fullerene synthesis methods along with their extraction methods, yield, operating conditions, such as pressure, temperature, mode, etc. have been summarized in several review papers.[81, 82]

2.3.1.2 Extraction, separation and purification

Fullerene extraction and purification involve a two-step process.[68] First: fullerene mixtures are isolated from the carbon soot using a solvent extraction, followed by a separation of individual fullerene molecules using chromatography or sublimation processes. Details of these processes are described below.

Fullerene mixture extraction from carbon soot. In the solvent extraction method, fullerene mixtures along with some soluble hydrocarbons from the soot are dissolved in toluene or similar solvents and then filtered or decanted to remove the insoluble residue to recover extractable fullerenes at 10 to 44% mass.[81] Toluene soluble extracts generally contain 65% C_{60}, 30% C_{70}, and 5% higher fullerenes.[81] Tetrahydrofuran (THF) also is used to ultrasonicate soot at room temperature, followed by filtration.[83] Evaporation of the filtrate in a rotary evaporator is employed to obtain fullerene powder mixture. A Soxhlet apparatus also can be used for efficient solubilization of fullerenes.[60, 68] In this process the solvent is first boiled and evaporated which is condensed down through a carbon soot matrix, extracting the fullerenes. The cycle is repeated for maximizing the fullerene extraction.[60] Sublimation process in contrast, involves heating the raw soot in a quartz tube under helium gas or in vacuum followed by condensing the mixture.[84] Fullerene mixtures accumulate at the bottom leaving the residue products from soot in the vapor phase.

Separation and purification of individual fullerenes from mixture. There are two major processes for purification or isolation of individual fullerenes. These are solvent-based liquid chromatography (LC) and sublimation using temperature gradient.

Liquid Chromatography (LC). This is the primary technique for separation of individual C_{60}, C_{70}, and other higher fullerenes from the extracted mixture.[81] In this process a solution of fullerene mixture is passed through a packed porous column. The solution is known as mobile phase and the solvent as eluent; while the solid surface is called the stationary phase. Based on the molecular weight, fullerenes undergo chromatographic separation.[85] Selective separation of individual fullerenes with highest purity can be achieved by changing the stationary phase and eluent constituent and compositions.[81] Historically, a wide variety of mobile phases and stationary phases have been used for successful separation of fullerenes. The eluents include: toluene,[86] hexane,[87, 88] toluene-hexane mixture,[53, 71] pi-basic groups, etc. On the other hand, alumina,[89] silica gel,[71] graphite,[90] C18 reverse phase,[91] pi-acidic Pirkle phase,[92] etc. have been reported to be used as developed stationary phases. Soxhlet method also has been combined with the purification process to have a one-step extraction-purification technique for fullerene separation from raw soot.[93] This process loads fullerene mixture from top and separates individual structures employing a chromatographic column. Higher fullerene separation is achieved using high pressure liquid chromatography (HPLC), which involves repeated and reversed chromatographic methods. The process utilizes solvents like carbon disulfide for achieving enhanced solubility of higher fullerenes. Gel-permeation based chromatographic techniques also have been used for fullerene separation.[94] Commercially available HPLC systems have been found to use pyrenylpropyl and pentabromobenzyl groups as stationary phases for fullerene isolations.[95] Toluene and toluene-acetonitrile mixture have been found to be the most commonly used mobile phase for C_{60} and C_{70} separation while chlorobenzene and dichlorobenzene are used for higher fullerenes.

Sublimation with temperature gradient. Differences in sublimation temperature and artificially created thermal gradient are used as the driving forces for the separation process.[96, 97] The raw soot containing fullerene mixture is directly added to a quartz tube under vacuum and heat is applied at the center of the tube to raise the temperature to 900-1000 °C. The tube containing the fullerene mixture has its one end at the center of the quartz tube and the other is protruded outside of the tube in the ambient environment. Thereby, a temperature gradient is created from the center of the tube (hottest) to the outermost end. Individual fullerenes based on their sublimation temperatures deposit at different locations of the tube. Generally, higher fullerenes deposit closer to the center as they possess higher sublimation temperature compared to C_{60}s. Such spatial distance allows for purification of the individualized structures.[98] Several modifications have been performed on this method to improve separation efficiencies, which are elaborately described in literature.[68]

2.3.1.3 Chemical synthesis processes

Fullerene synthesis using chemical methods has been sought for obtaining large quantity of isomerically pure fullerenes. However, only a couple of attempts have been successful developing such method, with only one that has realized into large-scale production so far.[99] Pyrolysis of naphthalene and its derivatives to obtain C_{60}s and C_{70}s through patching of C_{10} fragments encouraged researchers to adopt chemical pathways for fullerene synthesis.[100] Inspired by Barth and Lawton's,[101] Scott and co-workers presented their pioneering work of chemically synthesizing bowl-shaped corannulene molecules ($C_{20}H_{10}$) using flash vacuum pyrolysis (FVP) process.[102] Later, the same group developed a rather ground-up chemical synthesis method where commercially available precursors, such as bromomethylebenzene and 2-naphthaldehyde, were used to form C_{60}s.[103] Successive chemical reactions and modifications of these precursors lead to formation of polyarenes and their derivatives, such as $C_{60}H_{30}$, $C_{80}H_{40}$, and $C_{60}H_{27}Cl_{3}$.[103, 104] Finally, employing FVP at 1100 °C can cause cyclodehydrogenation and cyclodehalogenation of these intermediates to produce notable quantities of isomerically pure C_{60}s.[103, 104] However, the yield of this process is typically low (i.e., less than 0.4%), which restricts the use of this method for commercial production of fullerenes.[69] Newer techniques for fullerene fragment production and their conjugation processes have been proposed which require further investigations and research to fully realize.[99]

2.3.2 Fullerene-based nanohybrid synthesis

Fullerenes can be hybridized with carbonaceous materials both endohedrally and exohedrally. Endohedral hybrid examples include nano-peapods[62] and nano-onions.[63] Fullerene molecules when entrapped within carbon nanotubes are called nano-peapods while multi-layered concentric fullerenes are known as carbon nano-onions. Such encapsulations are performed through thermal annealing,[62, 105] carbon vapor deposition (CVD) based growth processes,[106] water assisted electric arc,[105, 107] or wet capillary filling processes.[108] Exohedral conjugations of fullerenes with carbon nanotubes[109] and graphene[65] require non-covalent functionalization; □-□ interaction between functionalized molecules can hold the carbon allotropes together. However, covalent functionalization also can be performed. For example, porphyrin derivatized fullerenes can provide bonding through amination reaction with the carboxy-functionalized carbon nanotubes.[110] Moreover, harsh chemical reactions forming seamless bonds can give rise to special form of hybrids named ‘nano-buds’.[23, 64]

2.3.3 Characterization

With the advancement of nanotechnology, various techniques have been developed to characterize fullerenes and their hybrids.[10, 14, 42, 111] From production of soot to the formation of individual fullerenes, several characterization methods are employed to determine the composition, morphology, and concentration.[68, 76] Such techniques include mass spectroscopy, nuclear magnetic resonance (NMR), optical spectroscopy, HPLC, electron microscopy (TEM), etc. We have limited our discussion to fullerene characterization only; NHs in the literature have mostly followed similar characterization tools. However, spectral, physical, and chemical signatures of NHs will differ significantly from fullerenes. This section will briefly describe key characterization techniques for fullerenes.

2.3.3.1 Mass spectroscopy

Mass spec has been one of the primary identification tools of the first fullerenes. Several mass spec methods have evolved over the years.[82] The key process in this characterization involves ionization and charged-separation of neutral molecules according to their mass-to-charge (m/z) ratio. It is a highly sensitive method which can detect as low as 10 ions, enabling detection of trace concentrations of fullerenes.[112] The ionization and desorption of molecules are generally done by laser induced methods.[113] Other methods of ionization include: thermal desorption,[114] fast atomic bombardment,[60, 115] electronspray ionization,[116] etc. For detection of the ionized fullerene samples and their spectral recording, time-of-flight (TOF),[54] or Fourier transformed mass spectrometry[68, 82] (FTMS) methods are used.

2.3.3.2 Nuclear magnetic resonance (NMR)

NMR is also very useful in determination of fullerene and higher fullerene purity.[7, 53, 117, 118] 13C-NMR has been proven to bear the first evidences of fullerene structures, which led to the conclusion of C_{60}'s ability to follow the isolated pentagonal rule.[54] It is interesting to notice that the highest obtainable spherical symmetry of C_{60}, when produced or characterized in its purest form, presents with a singular peak around 142-143 ppm in the resonance spectra.[53, 76] On the other hand, five resonance peaks are obtained for the ellipsoidal shape of C_{70} fullerenes.[119] Stability of fullerenes in different reactive environment also has been understood employing NMR method.[118]

2.3.3.3 Optical spectroscopy

The ability of light absorption by individual fullerenes differs based on the molecular weight and band structure of the fullerenes. While solubilized in toluene, C_{60} suspensions appear to be magenta or deep purple, whereas C_{70}s exhibit a color close to the red wine.[68] Other higher fullerenes show colors ranging from yellow to green with the increase in molecular weight of the fullerene molecules.[7, 120] Similarly, their light adsorption in infrared and UV region also differs that are utilized for spectral characterizations of fullerenes.[76] For example, Figure 2.5 shows UV-vis spectral signatures of C_{60} and C_{70} aqueous suspensions. The suspensions were prepared by sonicating powdered fullerenes in a biocompatible polymer solution. UV peaks appeared at 275 and 350 nm for C_{60}, while C_{70} showed widening and broad shoulders at those wavelengths, lacking in distinct peaking behavior. C_{70}s showed peaks close to 410 nm, consistence with published literature.[42, 111]

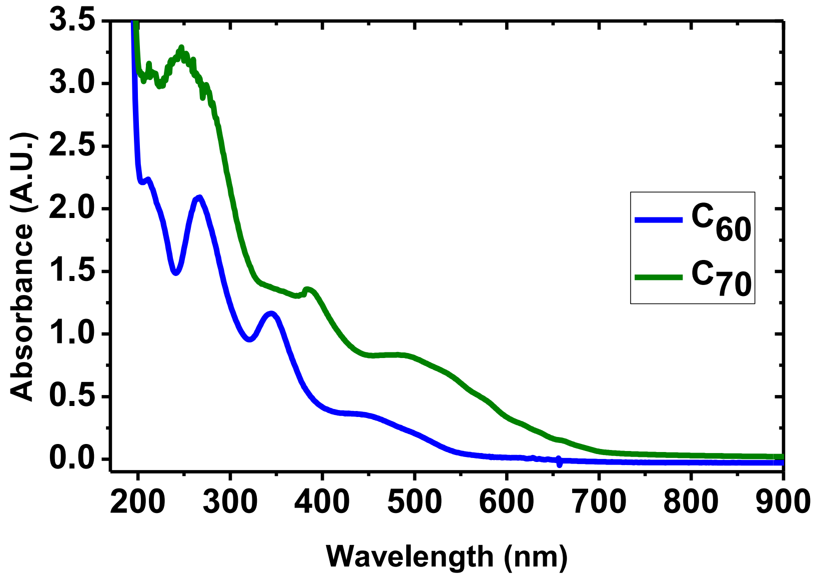

FIGURE 2.5. UV-Visible spectra of pluronic modified C_{60} and C_{70} aqueous suspensions.

2.3.3.4 HPLC

HPLC is one of the key techniques for fullerene separation, as discussed earlier. Besides, HPLC also can serve as an effective analytical tool for purity assessment of C_{60}s, C_{70}s, and higher fullerenes.[7, 76] Moreover, HPLC also can be utilized for detection of fullerenes using the well-established elution times, proved to be reliable in literature.[76] Such detection has been performed in commercial applications also. For example, in a 4.6 mm ID × 250 mm standard commercial column, using toluene as mobile phase at 1.0 mL/min flow rate, UV peaks at 312 nm wavelength for C_{60}, C_{70}, C_{76}, and C_{84} fullerenes can be observed at 8, 12.5, 17, and 23 min respectively allowing for their individual characterizations.[95]

2.3.3.5 Electron microscopy (EM)

Since the evolution of scanning tunneling microscopy, fullerene structures were confirmed through visual observation.[121] Development of electron microscopic (EM) techniques over the years has allowed for detailed characterization of fullerenes during synthesis and during their postproduction application. EM techniques enable evaluation of size and morphological characteristics of molecular and clustered fullerenes.

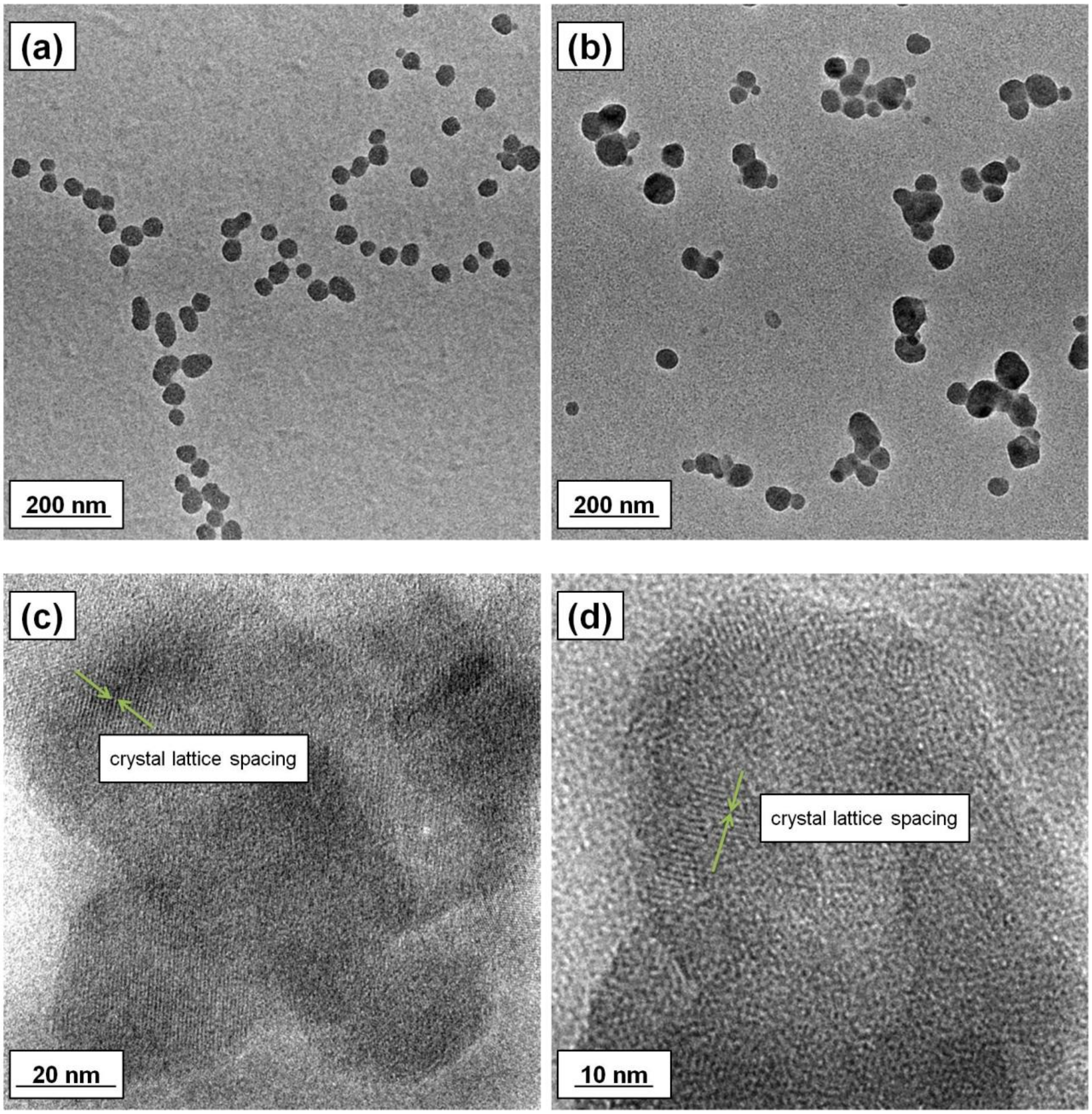

FIGURE 2.6. HRTEM micrographs of pluronic modified (a) C_{60} and (b) C_{70} aqueous suspensions. Zoomed in micrographs showing (c) C_{60} and (d) C_{70} crystalline features.

For example, Figure 2.6 shows high resolution transmission electron micrographs (HRTEM) obtained for aqueous fullerene clusters, solubilized via sonication in polymeric aqueous suspension as mentioned earlier.[111] Figures 2.6 (a and b) show C_{60} and C_{70} clusters, respectively. They morphology appear to be spherical. Figure 2.6(c-d) present higher magnified images, confirming fullerene lattice fringes, proving the crystalline nature of the clusters.

2.3.3.6 Static and dynamic light scattering (SLS and DLS)

Fullerene clusters in suspension are characterized using light scattering techniques. Dynamic and static light scattering (DLS and SLS) are the most popular tools that are employed to evaluate time dependent cluster size, fractal dimension, and aggregation propensity of fullerenes and other nanomaterials.[42, 111, 122, 123] Such methods are particularly useful for environmental implication studies, where interaction of fullerene clusters in water under varying chemical conditions can be systematically studied.[111, 124] Here we will discuss measurement of aggregation kinetics of C_{60}s using DLS technique; detailed description of the SLS technique for determination of aggregate structure of carbonaceous nanomaterial is presented in a previous work by our group.[123]

Time dependent dynamic light scattering (TRDLS) intensity measurement can be performed on C_{60} aqueous suspension against different environmentally relevant concentrations of NaCl salt. The C_{60} aqueous suspension here was prepared by a well established solvent exchange method.[42] An ALV/CGS-3 compact goniometer system (ALV-Laser Vertriebsgesellschaft m-b.H., Langen/Hessen, Germany) equipped with 22 mW HeNe Laser 632 nm (equivalent to 800 mW laser at 532 nm) and high QE APD detector with photomultipliers of 1:25 sensitivity was used for this purpose. The obtained scattering data for each condition were used to profile time dependent aggregation profile of fullerene nanoparticles at each electrolyte condition as shown in Figure 2.7a. It is observed that with no salt addition and at low ionic concentration of NaCl (up to 10 mM), the hydrodynamic radius of C_{60} clusters remained unchanged over time. However, increased aggregation is observed at higher salt concentrations.

The initial slope of this profile is the initial rate of aggregation which is proportional to the initial rate constant (k_{in}) and also to the initial concentration of the fullerene suspension (Equation 2.1)[125].

$$k \propto \frac{1}{N_0}\left[\frac{dR_h(t)}{dt}\right]_{t\to 0} \ldots (2.1)$$

Attachment efficiency (α) of fullerene clusters at each solution condition can then be obtained through dividing the initial aggregation rate at each solution condition by the initial aggregation rate at favorable condition for aggregation (which is obtained at high salt concentration). The theoretical formulation is expressed in equation 2.2.[125]

$$\alpha = \frac{\left[\frac{dR_h(t)}{dt}\right]_{t\to 0}}{\left[\frac{dR_h(t)}{dt}\right]_{t\to 0, fav}} \ldots (2.2)$$

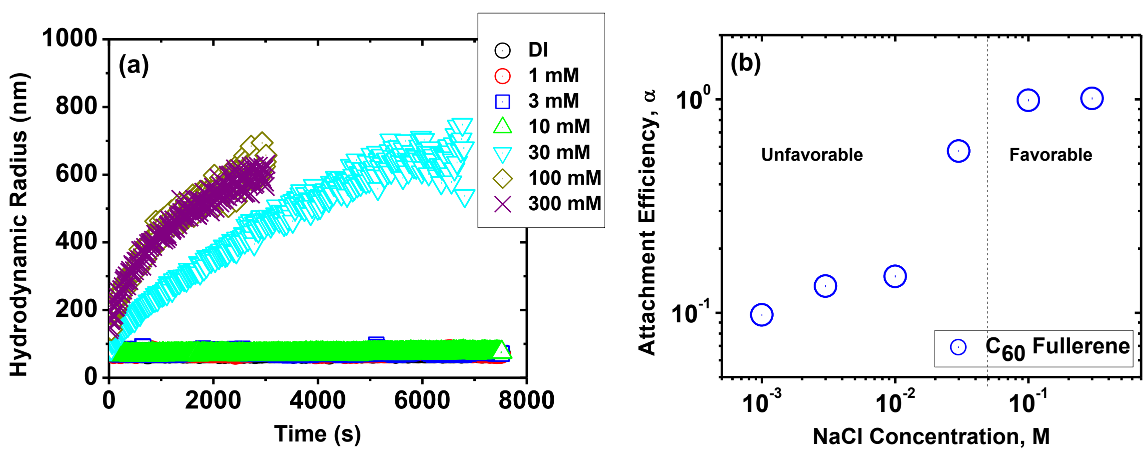

FIGURE 2.7. (a) Time dependent aggregation profile of C_{60} at different NaCl concentrations. (b) Stability plot for C_{60} aqueous suspension at different NaCl concentration.

The attachment efficiencies can then be plotted against corresponding salt concentrations (Figure 2.7b), known as stability plot. Figure 2.7(b) shows that C_{60} aqueous suspension follows classical Derjaguin-Landau-Verwey-Overbeek (DLVO) behavior.[124, 125] Further quantitation of the aggregation propensity of the fullerenes can be obtained analyzing the stability plot.

2.4 Energy Applications

A large number of fullerene-related publications offering insights into energy applications can be found in the literature. A recent literature search in Web of Science® has resulted in a total of 1626 publications from 1991-2012 that are concerned on energy applications. The search was performed using a glossary of energy terms and a search algorithm designed with wild-cards and Boolean operators. Title field tag and article only document type also was combined in the search criteria to limit the obtained results. The literature search reveals that the energy application sector of fullerenes and related materials is at an early stage; however there is a rather rapid increase in fullerene energy application literature over the past decade (Figure 2.8a). Most publications focus on fullerenes (89.2%), while less than 10% of the yearly publications are devoted to HOFs (0.3%), fullerene derivatives (6.1%), and/or hybrids (2.6%). The advantages of fullerenes and related materials on the energy application sector are derived from their fascinating characteristics: good acceptors of electrons and exceptionally low reorganization energies in electron transfer,[89] superconductivity,[126] absorption of light throughout the visible region,[127] and their stability due to rigid spherical carbon framework.[128]

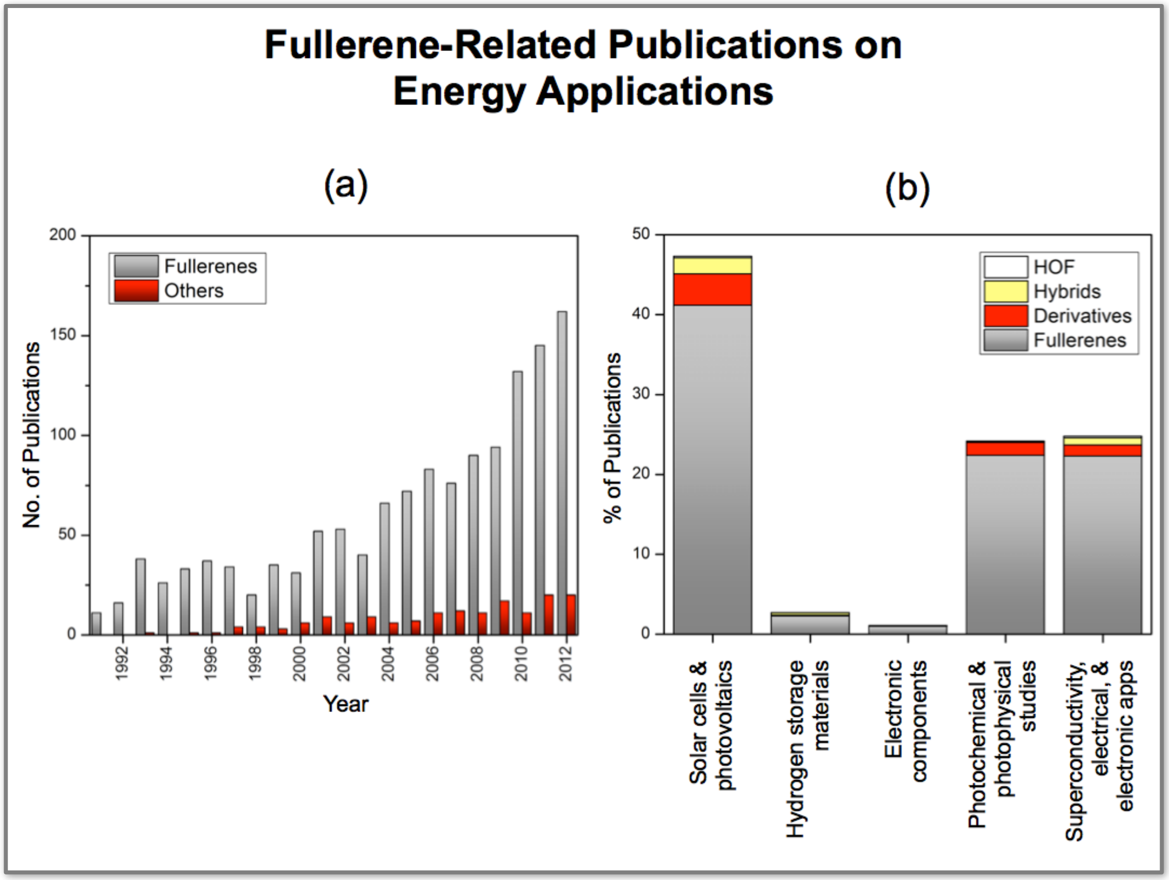

FIGURE 2.8. (a) Total number of publications on fullerene and related materials on energy topics. Note: Others correspond to HOFs, derivatives, and hybrids. (b) Energy applications of fullerenes, HOFs, hybrids, and its derivatives. (Source: ISI Web of Science, Sept 2013).

The retrieved publications also have provided information regarding the various practical applications, which can be generally categorized as follows: i) solar cells and photovoltaic materials, ii) hydrogen storage materials, and iii) electronic components. The technical literature also contains information on properties fullerenes and related materials relevant to energy applications: iv) superconductivity, electrical, and electronic properties, and v) photochemical, photophysical, and photocatalytic studies (Figure 2.8b). The following section will briefly describe the different aspects and relevant properties of energy applications with fullerenes.

2.4.1 Solar cells and photovoltaic materials

One of the most promising applications for fullerene-related materials is *solar cells and photovoltaic materials* (~47% of the publications, Figure 2.8b). The increased demand for low-cost renewable energy sources and the photo excitation properties of C_{60}s and related materials, have generated interest for their application as novel photovoltaic materials, and have motivated new approaches to production of efficient and inexpensive solar cells and photovoltaic devices.

Solar cells convert the energy of light into electricity by photovoltaic effect, and consist of an electron donor and an acceptor material arranged in a bilayer structure of interpenetrating network. Organic materials, e.g., conjugated polymers, have been explored as economic alternatives to inorganic semiconductors (silicon, amorphous silicon, gallium arsenide, selenide, etc.) currently used.[129] The discovery of photo-induced electron transfer from conjugated conducting polymers (as donors) and C_{60}s (as acceptors) provided the first highly efficient plastic photovoltaic cell.[129, 130] C_{60} doped polymers, e.g., polyvinylcarbazole (PVK), poly(paraphenylene-vinylene) (PPV) and phenylmehtylpolysilane (PMPS), have been reported to exhibit exceptionally good photoconductive properties.[131, 132] Organic photovoltaic materials of poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene-vinylene] (MEH-PPV)/C_{60} exhibit an enhancement in the photovoltaic effect with increasing C_{60} concentration.[133] Several studies report the use of other C_{60}-doped polymer combinations for photovoltaic cells: methyl-ethyl-hydroxyl-polypropylvinyl (MEH-PPV)/C_{60} thin film,[134] poly(4-vinyl pyridinated) fullerenes (PVPyF)[135], ITO/Polyaklythiophene(PAT)/C_{60}/Al,[136] poly(3-alkylthiophenes)/C_{60}.[137] However, material stability was found to be a persistent problem for applications of conjugated polymers that are simultaneously exposed to light and oxygen, causing rapid degradation of the materials.[138] Fullerene and high fullerene derivatives (e.g. oligophenylenevinylene (OPV) group attached to C_{60} through a pyrrolidine ring,[139] mono- and multi-adducts of C_{60} derivative [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) and MDMO-PPV,[140] PPV and PCBM,[141] C_{70}/poly(2-methoxy-5-(3,7'-dimethyloctyloxy)-*p*-phenylenevinylene)(MDMO-PPV),[142] poly(2,7-(9-(2'-ethylhecyl)-9-hexyl-fluorene)-alt-5,5-(4'7'-di-2-thienyl2',1',3'-benzothiadiazole)) (PFDTBT) and PCBM,[143] C_{70}-PCBM[144]) are also been studied for incorporation in photovoltaic devices; however, such research is only in preliminary stages.

The use of hybrids for efficient solar energy conversion is also emerging. Studies have looked at chemically linked CdSe quantum dots (QDs) with thiol-functionalized C_{60} hybrids. The photo-induced charge separation between CdSe QDs and C_{60}s opens up new design strategies for developing light harvesting assemblies.[145] Other studies have looked into the effects of incorporating carbon nanotubes (CNTs) in a polymer-fullerene blend host. Nanobuds (C_{60} functionalized CNTs) were found to be disadvantageous and somewhat detrimental to overall photovoltaic device performance.[146]

The use of fullerenes and other related materials has also been focused on enhancing the thermal stability of solar cells,[147] improving the performance and efficiency of polymer-fullerene conjugates,[148] photovoltaic properties of new blends,[149] and optimizing polymer-fullerene solar cells.[150] Driven by technology advances, a better understanding of fullerenes, their synthesis and processing techniques will likely allow to lower the cost of the material to meet the exponential demand of the energy industry.[151]

2.4.2 Hydrogen storage materials

Hydrogen is a clean and renewable source of energy that could be generated by electrolysis of water. Only a small percentage of the publications surveyed here report on fullerene and related materials as storage devices for molecular hydrogen (~3%, Figure 2.8b). However, it appears that fullerene and related materials may be promising towards storage capacities for hydrogen. In its gaseous form, hydrogen has a low specific volumetric energy density, compared to other liquid fuel sources. To increase its energy density, compressed hydrogen should be stored in a hydrogen-storage material such as hydrogen storage alloys and CNTs.[152] Because of low efficiency from high frictional power loss, an electrochemical compressor using a membrane electrode assembly (MEA) film of proton (H+) conductor is more effective than the conventional mechanical compressing methods.[153] However, humidity affects the proton conductivity and has to be removed from the compressed hydrogen. New fullerene composite membranes have been synthesized and have demonstrated enhanced proton conductivity under low relative humidity conditions.[17, 154, 155] $C_{60}H_{36}$ has been under scrutiny as the source of hydrogen for the in situ hydrogenation of $(C_{59}N)_2$. It has led to $C_{59}NH_5$ as the main reaction product, identified by negative-ion mass spectrometry and providing evidence of the usage of C_{60}s as a storage device for hydrogen.[156] The electrochemical compression and hydrogen storage capacity using the MEA of fullerene related materials (hydrogensulfated fullerenol) has been confirmed.[153] Studies also show that hydrogenation of carbon materials (fullerenes) requires activation centers.[156, 157] While considering these aspects, heteroatoms such as N, P, and S seem to be promising to behave as activators in heteroatom containing carbon materials for hydrogen storage applications. Boron atoms have also been identified for low energy hydrogenation.[157]

It has been demonstrated that coated fullerenes are ideal for many practical hydrogen storage applications. A single Ni-coated fullerene can store up to three H_2 molecules (storage capacity up to 6.8 wt %).[158] The capacity of charged fullerenes C_n ($20 <= n <= 82$) as hydrogen storage media has been found to be up to 8.0 wt %.[159] Hydrogenated silicon-fullerene has also been proposed for hydrogen storage with up to 9.48 wt % storage capacity.[160] Calcium has been proposed as a desirable metal coating to functionalize fullerenes and obtain high-capacity hydrogen storage materials with a hydrogen uptake up to 8.4 wt %.[161] Ti-decorated doped silicon fullerene, Ca-coated boron fullerenes, and Mg-decorated boron fullerenes with storage capacities up to 5.23, 8.2, and 14.2 wt %, respectively have also been reported.[162-164]

2.4.3 Electronic components (Batteries, capacitors, And open-Circuit voltage applications)

The incorporation of fullerene and related materials to improve the electrochemical performance of electronic components is scarcely reported by specific research groups, with publications in the last 10 years, dealing mostly with batteries,[165-173] capacitors,[174-177] and open-circuit voltage studies.[178-192] However, the demands of these components with higher capacity will likely increase to meet future energy demands.

2.4.4 Superconductivity, electrical, and electronic properties relevant to energy applications

Superconductivity is the event of exactly zero electrical resistance and expulsion of magnetic fields, occurring in certain materials when cooled below a critical temperature $T_{c.}$[193] Zero resistance and magnetic field exclusion have a major impact on electric power transmission and also enable the development of much smaller electronic components that are more reliable, efficient, and environmentally benign for energy applications.[193, 194] Fullerene-based superconductors have drawn enormous scientific interest towards energy applications (~25% of the publications, Figure 2.8b). In 1991, research on semiconducting technology found that alkali-metal-doped films of C_{60} leads to metallic behavior.[195] Shortly thereafter, these alkali-doped C_{60}s are found to be superconducting at T_c that is only exceeded by the cuprates.[126, 196, 197] It was also found that potassium-doped C_{60} becomes superconducting at 18 K, making it the highest transition temperature for a molecular superconductor.[126] It has been discovered that the superconducting transition temperature in alkaline-metal-doped fullerene increases with the unit-cell volume.[198] Cesium-doped fullerene (Cs_3C_{60}) has been reported to lead to superconductivity at 38 K under applied pressure in 1998,[199] but the highest superconducting transition temperature of 33 K at ambient pressure was reported for cesium-rubidium-doped fullerene (Cs_2RbC_{60}) in 1991.[200]

One of the biggest limitations of superconducting fullerenes is their instability in air; exposing the materials to air for a fraction of a second can completely compromise the superconductivity. Investigations in superconducting fullerenes continue as new combinations surface and other fullerene-related materials are synthesized.[201] HOF analogues of the alkali-doped fullerenes have also been investigated; however, results indicate absence of superconductivity above 5K.[202] A vast body of literature can be found on superconducting fullerenes and on the electrical and electronic properties of these materials. However, more research on superconductors using other fullerene related materials is necessary.

2.4.5 Photochemical and photophysical properties pertinent for energy applications

The photoactivity and the ability to 'tune' fullerenes[203] and related material properties (i.e. band gap, chemical environment, conductance, thermal storage, etc.) are fundamentally important to fabricate devices for the collection, conversion and storage of renewable energy (solar energy). Photochemical and photophysical properties of fullerenes and related materials result in the distinctive switching of chemical reactions, electrical energy, luminescence, degradation, absorption, thermal, and electrical properties of functional composites, which is crucial for novel devices with excellent performance.

In general terms, research in photochemical and photophysical properties of fullerenes revolves around optical absorption,[204-206] photo luminescence and fluorescence,[207, 208] excited state dynamics and properties of the singlet and triplet states,[209-213] photochemical reactions,[214-216] synthesis,[217-220] photocatalyst degradation,[215, 221-223] singlet oxygen production, and charge-transfer reactions.[224-229] A fair number (24.2%) of the retrieved publications deal with photochemical and photophysical information on fullerenes (Figure 2.8b). However, additional progress is required given the diversity of fullerene and related materials and the necessity to functionalize and "tune" their properties for specific energy applications.

2.5 Environmental Considerations for Fullerene Synthesis and Processing

Sustainable use of materials for energy applications not only demands for a renewable alternative with a small energy footprint but also necessitates low risk-involvement in the usage and disposal of such materials. Fullerenes, one of the most attractive nanomaterials for energy applications, should present minimum environmental risk to be considered truly sustainable. However, fullerenes' unique electronic properties are also known to be responsible for reactive oxygen species generation, resulting in environmental toxicity. Moreover, synthesis and solubilization process of fullerenes and the soft polymeric and surfactant surface coatings (used for processing) will likely contribute to altered environmental risk. Thus synthesis and processing of fullerenes, higher fullerenes, and their hybrids necessitates careful consideration for choosing potentially greener options.[10, 14, 25, 111]

For example, organic photovoltaics, a major fullerene-based device, is an assemblage of multiple layers containing electron donor and acceptors, electrodes, and electron-hole transporters packaged within plastic materials such as poly(ethylene-terephthalate) or PET.[230] These organic photovoltaics at the end of their usage will likely be disposed off to landfills.[231, 232] Though PET packagings are non-biodegradable, their fragmentation through abrasion and photodegradation under long-term exposure to sunlight are likely.[233, 234] Such degradation can lead to potential release of fullerene derivatives PCBM from the interior of these solar cells.[235] During their residence in landfills, the material exposure to soil surfaces and water (after being carried via surface run-offs) these fullerene, their derivatives, and associated solvents will inevitably interact with the aquatic environment and terrestrial ecosystems. Thus, true sustainable energy generation require a thorough understanding of material energy cost as well as environmental risks associated with environmental fate, transport, and exposure.

2.5.1 Existing environmental literature for C_{60}

C_{60} and its several derivatives, including PCBMs, have been systematically studied to better understand their fate and transport, environmental transformations, and toxicity towards aquatic species. It is important to note here that fullerene preparation methods and the chemical identity of the surface moieties of their derivatives can play a significant role in their environmental behavior. Fullerene cluster size and surface chemistry is known to impact their environmental behavior.[41, 124, 236] Importantly, the initial cluster sizes and surface chemistry are found to differ based on fullerene processing techniques; while extended mixing of water result in larger fullerene clusters with rough irregular edges, solvent exchange using toluene or THF as intermediate can produce smooth round edge crystalline structures.[237] Similarly, surface charge of the aqueous suspension using THF as intermediate was found to be significantly more negative compared to that produced via extended mixing.[40] Systematic evaluation of aqueous C_{60} and their derivatives showed such process technique dependent behavior; the OPV-containing PCBM and corresponding butyl (PCBB) and octyl (PCBO) esters showed exceptionally higher stability compared to pristine aqueous C_{60}.[238] Mobility of fullerenes in porous media and their interfacial interaction are also highly dependent on the preparation methods,[27] stabilizing agents,[236] and particle size.[27] For example, toluene dissolved aqueous C_{60}

was found to show higher toxicity to Japanese Medaka fish compared to C_{60}s solubilized with dimethyl sulfoxide (DMSO) by extended stirring.[239] Toluene dissolved C_{60} suspension exhibited spherical aggregates while the other methods formed mesoscale aggregates. Thus synthesis and preparation techniques of fullerenes can allow for environmentally friendly alternatives.

C_{60} aqueous suspensions are known to show toxicity to microbial entities in aquatic[29, 41] and soil[28] media, other invertebrates,[240] and fish.[240] There have been evidences of genotoxicity[241] and developmental toxicity[242] induced by C_{60} aqueous suspensions. Several mechanisms for fullerene toxicity are postulated that include: ROS mediated oxidative damage,[32] lipid peroxidation of cell organelles,[243] direct contact with the cell membrane, and consequent membrane protein oxidation. Such toxic potential depends on the physicochemical characteristics such as surface charge and aggregate sizes[27, 41] as well as on preparation methods[29, 41] or solvents used.[41] For example, continuous sonication and separation through filtration of fullerene suspensions yield smaller aggregates that tend to produce more ROS leading to increased antibacterial effects.[27] Solvent effects on C_{60} toxicity evaluations on the other hand, have created controversies in the literature.[244, 245] Toluene and THF based fullerene suspensions have shown significantly higher toxicity compared to solvent free ones.[31, 244, 245] In some cases residual toluene or THF and their degradation by-products were also found to be more responsible for the enhanced toxicity than the pristine C_{60} aqueous suspension.[244, 245] It is also important to note that fullerene and its derivatives are often coated with polymers or surfactants to attain desired properties. Many of such synthetic molecules possess either non-biodegradable poly-aromatics or cyclic organic compounds. Such moieties have already reported to exhibit toxic behavior. For example, gamma-cyclodextrine-C_{60} aqueous suspension showed higher photodynamic activity under UV illumination than poly-vinyl pyrollidone (PVP) dissolved C_{60}.[246] Similarly tween-80 induced higher toxicity to *E. coli* when compared to *N,N*-dimethylformamide in solubilizing C_{60}.[247] Thus not only solvents used for fullerene synthesis but also chemical moieties used to functionalize these carbon allotrope surfaces need careful evaluation to reduce environmental risk. However, it has been found that the solvents' inherent toxicity is increased when it is associated with fullerenes.[248]

Environmental transformation of C_{60}s through reaction with atmospheric oxygen[249] or ozone, or via photochemical reactions under sunlight or UV-irradiation, or by adsorption of bio- and geo-macromolecules (e.g. humic and fulvic acids) are also inevitable. Such transformations, that are likely going to be influenced by their synthesis and processing techniques, will also influence their subsequent environmental interactions. Sunlight or UV exposure to fullerenes are inevitable in the natural environment, which is known to cause chemical transformation of fullerenes by surface alteration via oxidation.[250] Such functionalization can enhance their stability in water, thus making them more persistent[251] in aqueous environment. Similarly, dissolved organic matter (NOM), generated from degradation of flora and fauna, can coat fullerene surfaces and stabilize their colloidal presence in water.[252] Dissolved organic matter in wastewater effluent was also found to inhibit fullerene aggregation by providing similar steric stabilization.[253] Thus, alteration of fullerene interaction in water can occur as a result of a combined presence of sunlight and NOMs;[254] where sunlight induced functionalization can inhibit humic adsorption of fullerenes,[254] humics can reduce UV-inflicted oxidation via scavenging of ROS[39]. Transformations of C_{60}s by ozonation or UV-irradiation have shown to increase ROS production and subsequent *E. coli* inactivation.[255, 256] NOMs when interact with fullerene suspensions can affect the triplet-exited state, an intermediate state responsible for ROS generation.[257] While NOMs can quench such photoactivity of pristine C_{60} suspensions, they can enhance it for fullerenol.[257] Therefore, a complex interplay of both NOM and sunlight exposure will determine the environmental fate of the fullerenes and necessitate systematic evaluation.

2.5.2 Environmental literature status for higher fullerenes and fullerene-based NHs

Unlike C_{60}s, environmental considerations of higher fullerenes (e.g. C_{70}, C_{76}, C_{78}, C_{84}, C_{90}, etc.) and NHs have mostly been ignored.[10, 14, 25, 42] A limited number of studies evaluated colloidal properties[42, 258, 259] and toxicity[36] of C_{70}s. One of our previous studies incorporated additional higher order fullerene (i.e. C_{76} and C_{84}) colloidal property evaluations upon aqueous solubilization.[42] These studies show that higher fullerene hydrodynamic radii and surface potential differ substantially from those of C_{60}s.

Toxicity studies on daphnia magna, an aquatic organism, showed acute toxicity in presence of gallic acid stabilized C_{70} suspensions; mechanism identified was oxidative stress generated from fullerenes.[36] It is also to be noted that higher fullerene isomers possess smaller band gap, which can make them more reactive[8] compared to C_{60}s and C_{70}s, influencing ROS generation and subsequent toxic potential of the materials. Such band gap modulated toxicity mechanism is already demonstrated in case of metal nanoparticles.[260] NHs, on the other hand, have not yet been studied for environmental fate or toxicological implications. However, it can be safely argued that fullerene, their derivatives, and higher fullerenes when conjugated to form NH ensembles will likely present altered electron charge transfer, band-gap, photo-activity, sorption properties, morphology, etc., which will result in unique environmental behavior. The state-of-the-art literature shows a major gap in knowledge for risk and safety evaluation of higher fullerenes and fullerene-based NHs.[10, 14, 25, 42]

2.5.3 Environmental considerations

Based on the existing literature it is clearly evident that advantages of fullerenes do not come without associated environmental risk. Figure 2.9 presents a schematic showing probable release of fullerene and its homologues from energy applications to the environment as well as their fate, transport, and transformation, leading to potential environmental risk. Therefore, choice of synthesis and processing techniques as well as chemical functionalization of fullerenes should be considered keeping environmental risk factors in mind. C_{60}s, higher fullerenes, and NHs will likely, if not already being used in commercial energy applications. Exposure of these materials during manufacture, use, or end of life is thus likely and should be considered for their design and production. This section discusses key considerations of fullerene use in energy applications and identifies some relevant aspects critical to ensure environmental safety.

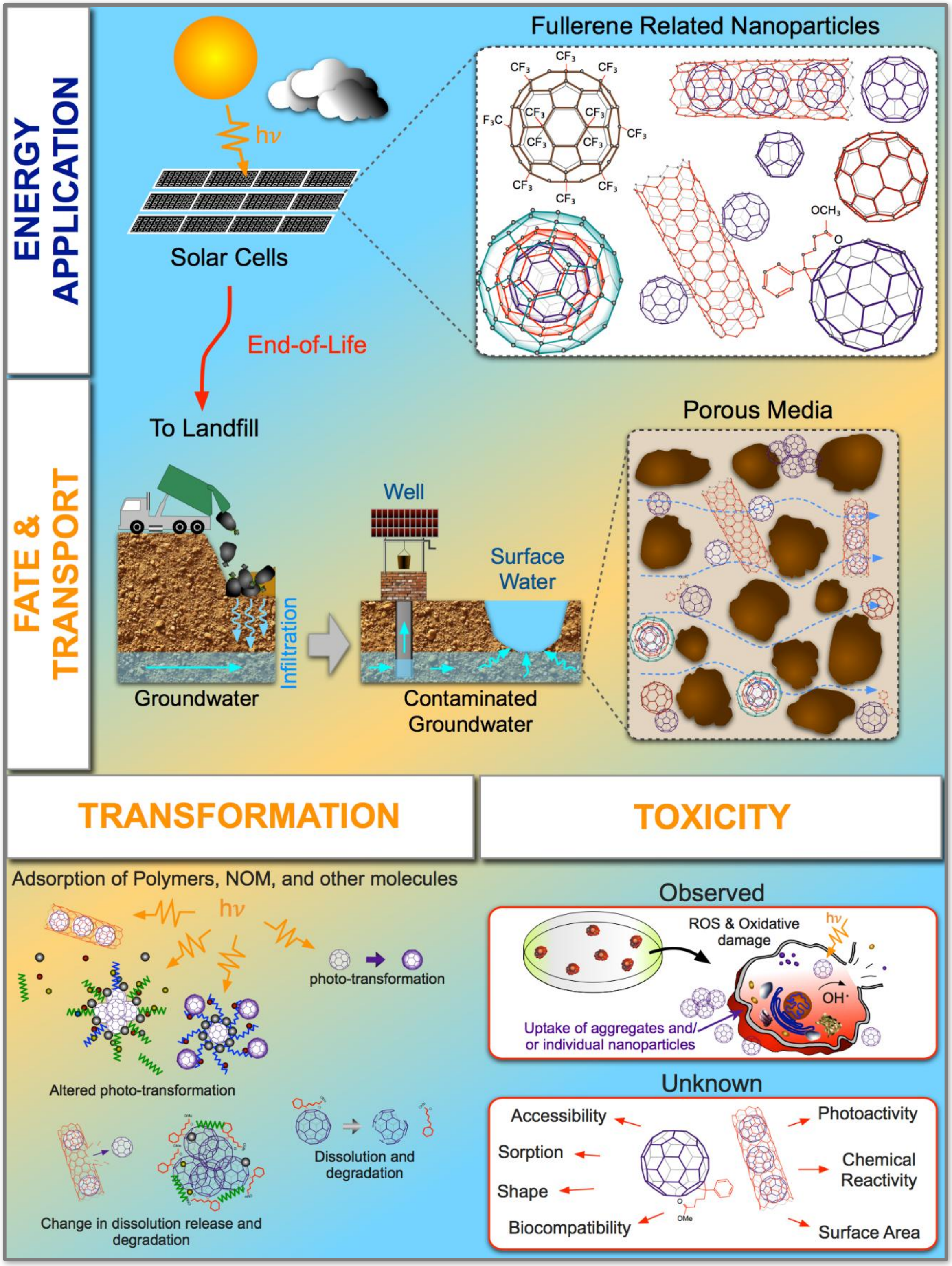

FIGURE 2.9. Likely environmental fate, transport, transformation, and toxicity of fullerenes and related nanomaterials.

2.5.3.1 Consideration for solvents

Solvents used to formulate the electron donor-acceptor (P3HT:PCBM) blends or thin films, generally consist of chlorobenzene,[261, 262] dichlorobenzene,[261, 262] ortho-xylene,[261] mixture of chloro- and nitro-benzene,[261] chloroform,[263] and toluene[264] (Figure 2.10). Most of these solvents possess aromatic groups and are halogenated, which are known as non-biodegradable as well as toxic.[265] Thus choosing these solvents may compromise environmental safety due to the residual in the solar cells. Similarly, solvents used for fullerene processing, e.g., aqueous solubilization, may also pose such risks; e.g., THF or toluene. For greener synthesis of energy devices, comparatively benign, short-chain substituted alkanes (e.g., chloroform) can be opted;[265] or novel solvent-free methods for blend formation can also be developed.[266] Thermal annealing process for morphological control of the P3HT:PCBM film can be chosen over solvent-evaporation annealing to reduce solvent use. However, such alternative decisions require systematic studies comparing solvent effects with energy efficiencies of synthesized and/or processed fullerenes.

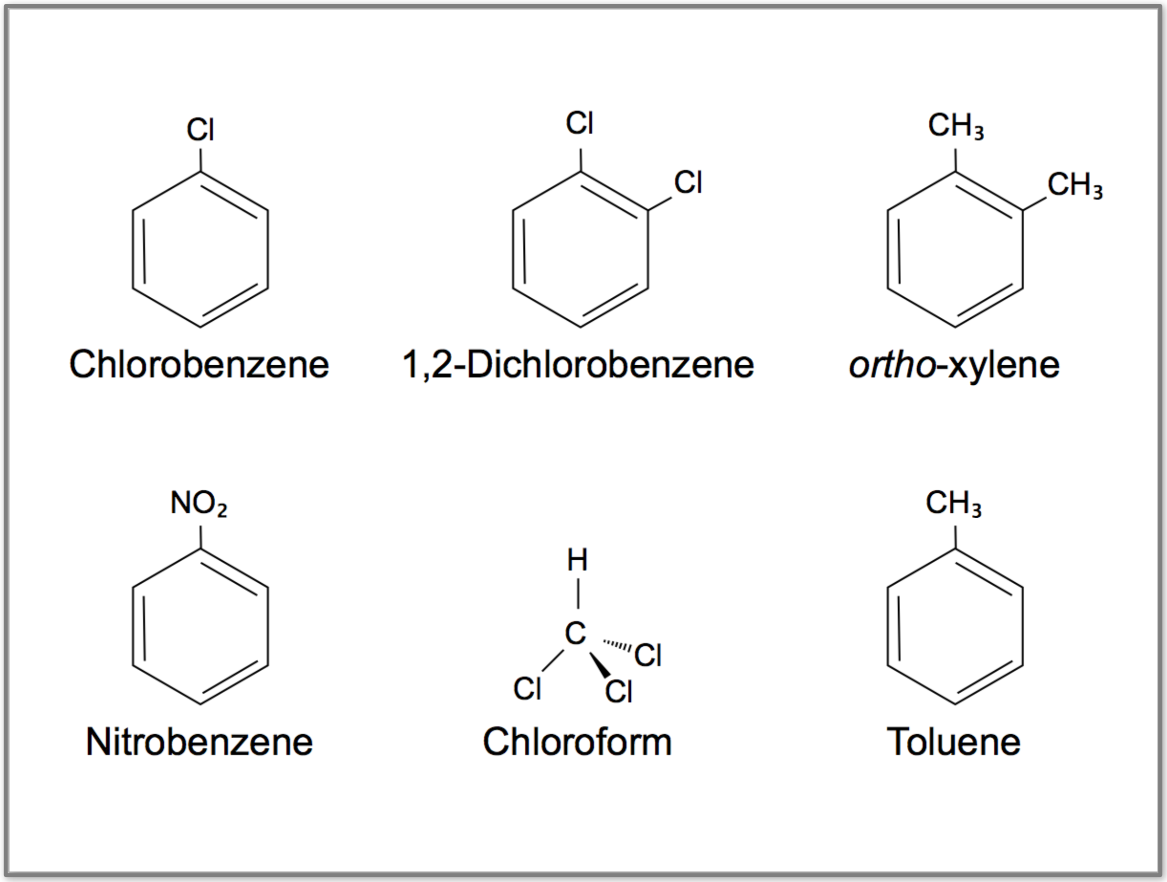

FIGURE 2.10. Structures of commonly used solvents for fullerene synthesis and processing.

2.5.3.2 Consideration for derivatization

Fullerene derivatives, e.g., PCBM, can have C_{60} and C_{70} as origins; which are mostly employed as the electron acceptors.[5] Recently, higher fullerene, i.e., C_{84}-based PCBM derivatives are as also been studied for solar cell applications.[18] Methanofullerenes like PCBM have shown toxic effects to *daphnia magna*,[267] which can be reduced through substitution with low toxicity derivatives. Substitutions of phenyl-group with thienyl-groups and other alkyl analogues can also present lower risk alternatives. Other fullerene derivatives used should also be carefully considered, since many of such possess aromatic rings and/or cyclic chemical structures with less biodegradability. For example, indene-fullerene,[268] 1,4-Di(organo) fullerenes,[269] dihydronaphthyl fullerenes,[270] penta(organo)fullerenes,[271] etc. contain such non-degradable chemical structures, whereas fulleropyrrolidines[272] can be more bio-friendly. Moreover, derivatization is also performed using certain chromophores to enhance photo-induced charge transfers; such as porphyrin, phthalocyanines, etc.[273] Such chromophores with potential safe usage for fullerene derivatization, should be carefully evaluated for their biodegradability.

2.5.3.3 Consideration for coatings

Moreover, fullerene processing involves use of polymers or surfactants to enhance their dispersion as well as photo-physical properties. However, it has been determined in studies that biocompatibility and aggregation behavior depend significantly on the coating characteristics on fullerenes or other nanomaterials[274]. For example, fullerene suspensions stabilized with sodium dodecyl sulfate (SDS) and Triton X 100 produced higher ROS compared to pure fullerene-water suspensions.[275] Furthermore, transformation processes in the environment can become complex as overcoating of these coated fullerenes with geo- and bio-macromolecules will alter their environmental persistence as well as potential risk.[276]

Fullerene synthesis, processing, and separation thus require an underlying risk consideration. Properties of the solvents used, relative degradability of the derivatives and coatings, contribution of coatings on environmental safety, and such similar issues should be considered for safer usage of fullerenes in energy applications. A few critical questions that should be asked to pursue lower risk in fullerene's energy applications are listed below.

1. Are the solvents chosen for fullerene synthesis and separation relatively less toxic?
2. Are there environmentally safer alternatives while derivatizing or hybridizing fullerenes?
3. Are the chemical moieties used to coat fullerene surfaces environmentally benign?
4. Can the fullerenes be immobilized to reduce their release from the devices or processes?

However, environmental considerations should pose these questions at a minimum, encouraging a more systematic and complete environmental study. Effective and sustainable use of fullerenes in energy applications requires attaining environmentally safe usage of these materials; which has been a missing link in most material science research and development.

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Chapter 3: A Critical Review of Nanohybrids - Synthesis, Applications, and Environmental Implications**

Abstract

Nanomaterial synthesis and modification for applications have progressed to a great extent in last decades. Manipulation of physicochemical properties of a material at the nano-scale has been extensively performed to produce materials in novel applications. Controlling size, shape, surface functionality, etc has been a key to success in implementation of nanomaterials in multidimensional usage for electronics, optics, biomedical, drug delivery, and green fuel technology. Very recently, focus has been on the conjugation of two or more nanomaterials to achieve increased multifunctionality as well as creating opportunities for next generation materials with enhanced performance. With incremental production and potential usage of such nanohybrids come the concerns about their ecological and environmental impact which will be dictated by their not-yet-understood physicochemical properties. While environmental implication studies concerning the single materials are yet to give an integrated mechanistic understanding and predictability in their environmental fate and transport, the importance of studying the novel nanohybrids with their multi-dimensional and complex behavior in environmental and biological exposure systems are immense.

Aich, N.; Plazas-Tuttle, J.; Lead, J. R.; Saleh, N. B., A critical review of nanohybrids: synthesis, applications and environmental implications. *Environmental Chemistry* **2014, *11,* (6), 609-623.

3.1 Introduction

Materials development at the nano-scale has progressed from single particle synthesis to multi-component assemblies or hierarchical structures, where two or more pre-synthesized nanomaterials (NMs) are conjugated to extract multifunctionality.[1] These ensembles are termed as nanohybrids (NHs).[2, 3] The underlying focus of NH synthesis is property modulation, which results in alteration to inherent physicochemical properties, i.e., size, shape, composition, and surface chemistry. Such changes also give rise to novel emerging properties[4] that are not observed during classical NM health and safety (EHS) evaluation. This new direction in NH synthesis and use, thus presents unique challenges and necessitates systematic evaluation of nano EHS.

Demand for multifunctionality has resulted in physical and chemical modification to nanomaterials, in general. Size and shape modulation alongside with physical or chemical functionalization are used to achieve hierarchical[5] and hetero-structures.[6] Such functionalization has altered inherent surface attributes and extracted novel electronic configuration, intrinsic hydrophobicity, dissolution properties, etc., from nano-scale materials. The successes on such manipulation have further encouraged to achieving a higher degree of functionality by combining multiple nanomaterials; each possessing unique and novel advantages. For example, nano-scale iron oxide, nanogold, and graphene nanosheets, individually possess paramagnetism, plasmon resonance, and superior charge carrying capability, respectively. However, careful combination of two or more of these materials enhanced their functional performance as observed in development of the first sets of bimetallic NHs. Iron oxide when conjugated with gold to form core-shell particles, provided inherent magnetism of the iron oxide shell, while preserved the surface plasmon resonance of the gold core.[7] Such multifunctional bimetallics were used as magnetic resonance imaging agent with added nanoheating capabilities, useful for laser irradiated drug delivery systems.[8] Similarly, gold when intercalated within layered clay, was used for protein or organic molecule immobilization, applicable as biocatalysts and sensors.[9, 10] Paramagnetic iron oxides on the other hand, when combined with novel graphene-oxides, resulted in unique drug delivery systems with superior drug release and targetability.[11] Again, graphene nanosheets are also combined with porphyrins, titanium dioxide (TiO_2), carbon nanotubes, quantum dots, etc., and have generated NHs for enhanced optical emitting[12] and limiting[13] devices, supercapacitors,[14] lithium-ion batteries,[15, 16] or transparent conductors.[17] It is evident that benefits of conjugation and ensembles of multiple materials are well realized and thus will likely to widen the NH material domain, impacting a much larger application space and in large amounts. For example, it is projected that by the year 2050, at least 100 million kg of platinum carrying titania-modified-MWNT NHs will be deployed in fuel cells for vehicles alone, assuming 20% platinum in the NH by mass.[18, 19]

Development of novel materials comes with an intrinsic uncertainty in regard to their potential environmental and biologic consequences. Material release can occur from nano-laden products and devices as well as during their manufacturing and use phases.[20] Upon release, nanomaterials undergo transport and transformation in either occupational or environmental setting.[21] Such processes are highly influenced by the material attributes and the form of release; e.g., nanomaterial release from personal care products and medicinal applications will possess distinctive physicochemical properties compared to their release from solid-state optoelectronic systems. As material complexity increases with conjugation and assemblages of materials with uniquely different properties, their environmental processes will also be altered and likely present higher uncertainty when predicted using their parent material classes. To date, environmental fate, transport, and transformation literature of nanomaterials have systematically generated a critical information-mass—by measuring physicochemical properties and their influence on environmental behavior manifestation—that has begun to effectively determine material safety and risk.[22, 23] However, uncertainty of environmental behavior for hierarchical and conjugated materials continues to prevail. The uncertainty emanates from the knowledge-gap of 'conjugated materials' in environmental setting—since, ensemble of multiple materials will most likely behave differently compared to their parent components. For example, carbonaceous nanomaterials, such as fullerenes[24] and carbon nanotubes,[25] show high aggregation propensity due to their inherent hydrophobicity and strong van der Waals interaction forces; whereas, metallic nanoparticles (such as silver or zinc oxide), possess unique dissolution and complexation properties.[26, 27] When combined, behavioral manifestation of metal-carbonaceous conjugates can either present dominant hydrophobicity or dissolution/complexation reactions; which will be influenced by the nature of conjugation. Thus risk evaluation of these hierarchical NHs will require systematic environmental studies.

This chapter presents an EHS-relevant definition of hybrid nanomaterials, classifies the NHs, reviews NH literature, and discusses the need for environmental studies. Probable environmental exposures of NHs and relevant altered fate, transport, and toxicity due to transformed physicochemical and emergent properties are discussed. Challenges regarding prediction of environmental behavior of NHs from their individual component characteristics are also delineated. Overall, this chapter will serve as an environmentally relevant summary of the ever-expanding class of NHs, and hopefully will accentuate the importance of evaluating these nano-ensembles for enhanced risk assessment.

[The planning and completion of the work was led by Nirupam Aich. He was primarily involved in writing the sections discussing introduction; NH definition; classification, synthesis and application; and environmental implications of NHs. Jaime Plazas-Tuttle helped in reviewing the extensive literature and producing the schematics. Dr. Navid Saleh supervised the work. Dr. Jamie Lead provided intellectual input on the environmental behavior of the NHs.]

3.2 Defining Nanohybrids

Definitional ambiguities are evident in NH literature[28] similar to the debate that exists for singular nano-scale materials.[20, 29, 30] We attempt to clarify the nuances in NH literature and also to make way for defining NHs from EHS perspective. A strong tendency of claiming simple surface modification—with inorganic, organic, and soft molecules—as hybridization has been observed in the material science literature. For example, attaching a monomer or polymeric molecule onto a metallic nano-scale material has been claimed to be a NH;[31, 32] similarly, large polymeric structures with conjugated inorganic/organic atoms/molecules are claimed to be a NHs as well.[33] Such minor surface modifications, however, can though enhance material performance yet most likely will preserve their parent physicochemical properties and thereby should not be considered as novel NHs for environmental evaluation purposes. Our rendition of environmentally unique NH definition can be formulated as follows: *more than one nanomaterial of unique chemical origin or differing dimensionality when conjugated together via molecular or macromolecular links or physicochemical forces or when one nanomaterial overcoats another possessing unique chemical identity, or when complex soft molecules are engineered to chemically bind to nanomaterial surfaces, all to enhance existing functionality or achieve multifunctional usage, can be defined as NHs.* This definition concurs with the literature definition of NHs,[2-4] however, confines the material class to those NHs that will likely result in unpredicted and unique environmental fate, transport, and toxicity.

3.3 Classification, Synthesis, and Applications of Nanohybrids

The growth of NH literature in the recent decade has been noticeable. To assess the importance of this emerging material-class, a comprehensive literature search using the Web of Science® database was performed (Figure 3.1). A list of 758 peer-reviewed journal articles and 123 additional publications on specialty carbonaceous NHs (peapods, nano-onions, nano-buds, nano-horns, etc.) during the years 1998-2012 were identified. After careful screening on the basis of the NH definition, 752 articles dealing with NHs of environmental importance were selected and classified (Table A-1). The remaining 129 articles were not considered as they were deemed beyond the definitional scope. Overall, the literature search shows an exponential increase in publication number over the last decade (Figure 3.1). This substantial published body of literature thus makes a strong case to carefully evaluate their physicochemical properties, relevant to environmental safety. The environmentally relevant classification of NH is established based on the primary constituents. Four major classes of NHs are identified, namely: *Carbon-Carbon, Carbon-Metal*, *Metal-Metal,* and *Organic molecule coated* NHs (Figure 3.2a).

The simple classification above should not deceive the readers of the inherent complexity of each of these NH classes; e.g., *Carbon-Carbon* NHs include rather simple carbonaceous nanomaterials such as single-walled and multiwalled carbon nanotubes (SWNTs and MWNTs), fullerenes, and graphene sheets as the primary components, which are then conjugated with other carbonaceous entities[34, 35] to form hierarchical structures. Similarly, *Carbon-Metal* NHs are formed via conjugation of carbonaceous materials with metallic nanoparticles.[36, 37] *Metal-Metal* NHs, on the other hand, are assemblages of individual metallic nanoparticles[38] or are formed as core-shell structures of different metals[39] and metal oxides.[40] When metallic nanomaterials combine with long chain polymers,[41] drug molecules,[42] cell-synthesized proteins,[43] DNA,[44] long chain organic molecules,[45] etc. they form *Organic molecule coated* NHs.

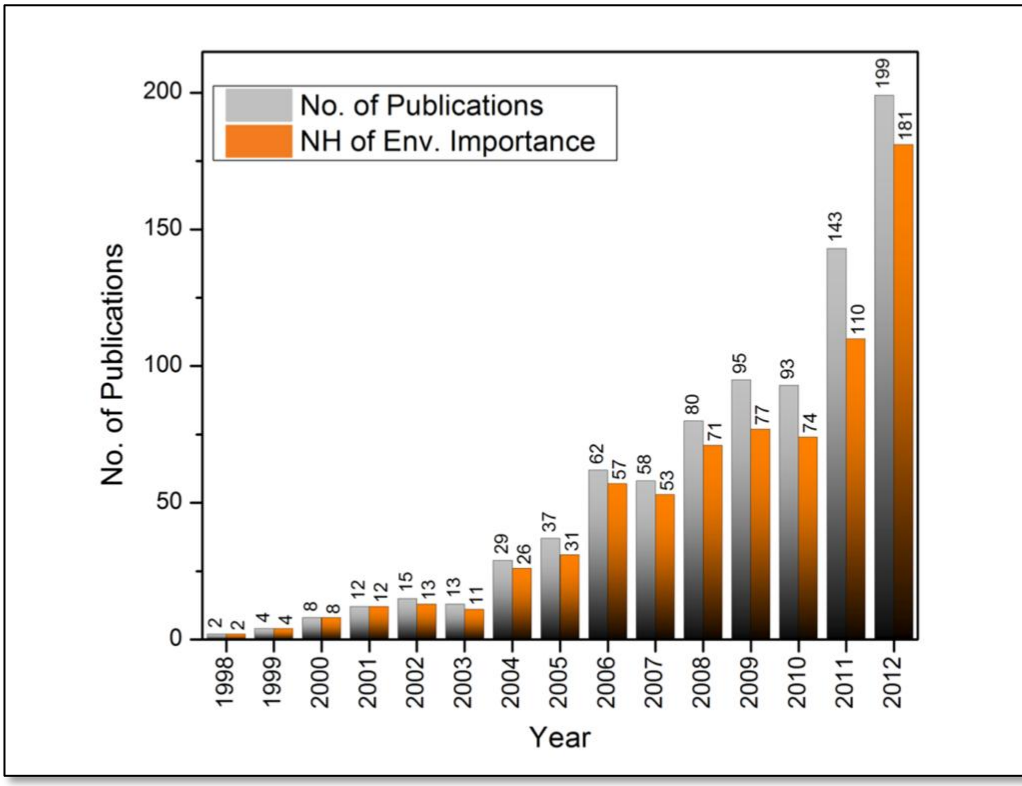

FIGURE 3.1. Total number of publications per year from 1998 to 2012 using the Web of Science® search engine searching for "nanohybrid" or "nano-hybrid", and total number of nanohybrids of environmental importance. Literature was selected when it originated from scientific articles and referred specifically to the following combination of keywords, special character (*), and search field (Title): "Title=(nano-hybrid*) OR Title=(nanohybrid*)". Title was selected as the search criteria to try and limit the results to those articles dealing particularly with NH research. Meeting abstracts, reviews, and proceeding papers, were not included. Moreover, few more search combinations "Title=(nano-horn* OR nanohorn*) AND Title=(hybrid*)", "Title=(peapod* OR pea-pod*) AND Title=(hybrid*)", "Title=(nanobud* OR nano-bud*) AND Title=(hybrid*)", and "Title=(nanoonion* OR nano-onion*) AND Title=(hybrid*)" were used to identify some popular carbonaceous nanohybrids having specialty names because of their interesting morphologies.

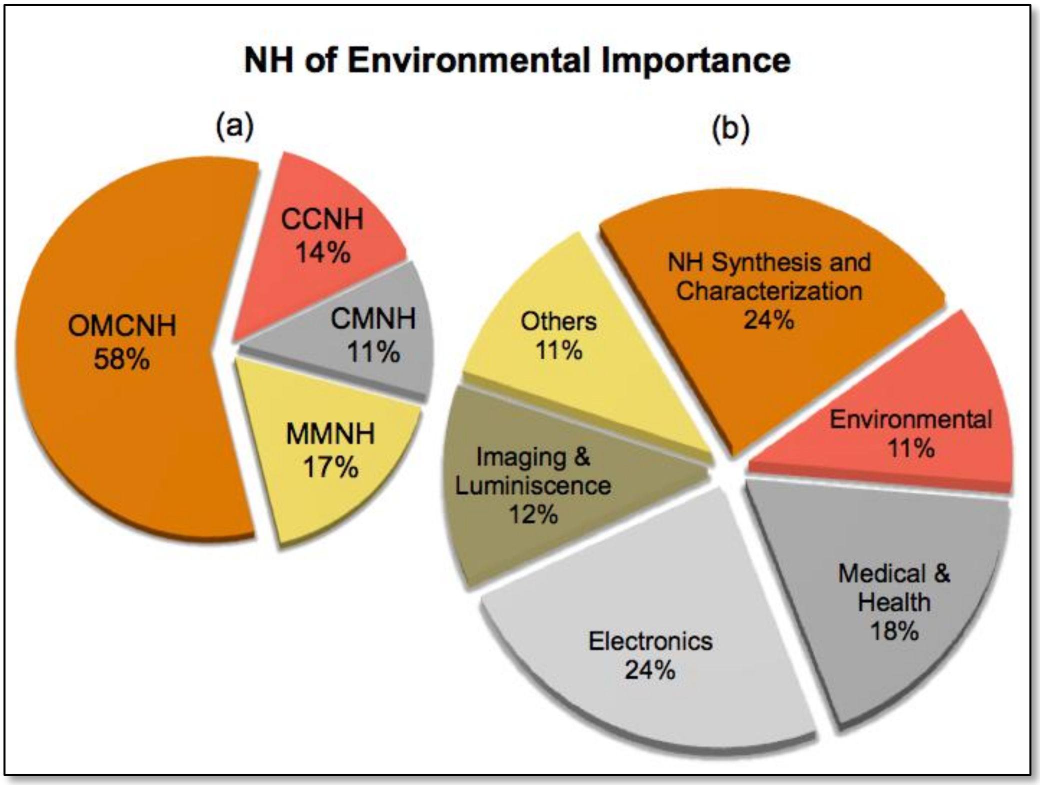

FIGURE 3.2. Distribution of research article publication based on (a) environmental classification of nanohybrids and (b) relevant application premise.

The retrieved literature also provided information in regard to the application potential of the NHs (Figure 3.2b and table A-2). NH applications are categorized as follows: electronic: solar and fuel cells, Li-ion batteries, semiconductors/superconductors/conductive materials, imaging and sensing applications; environmental: contaminant sorption, membrane technology, catalytic/photocatalytic/electrocatalytic applications, and antimicrobial/antibacterial processes and devices; medical: cancer treatment and detection, biomaterial/biohybrids, delivery carriers and drug compound controlled release, UV protection, etc. Detailed and more specific usage of NHs alongside with their synthesis processes (table A-3 through A-5) will be discussed in the following section in context of their environmental release and interaction.

3.3.1 Carbon-Carbon Nanohybrids (CCNH)

Carbon based NHs include combinations of three major carbon nanostructures–zero dimensional fullerenes (Figure 3.3a), 1-D carbon nanotubes (CNTs, SWNT and MWNT), and 2-D graphene and carbon nano-horns (CNHs). Open ended hollow structures of CNTs or CNHs and cage like fullerenes offer unique advantages to produce endohedral NHs as well as allow for generation of their exohedral forms.[46] Fullerenes/graphene (pristine or functionalized) when encapsulated within the CNTs/CNHs via thermal annealing,[35] in situ growth from vapor-based deposition reactions,[47] or dispersion assisted cavity filling processes, are called 'nano-peapods'.[48] Similar synthesis processes as well as water-assisted electric arc process can create an exotic multi-layered hybrid fullerene structure named 'carbon nano-onion.[49-52] On the other hand, exohedral conjugation of CNTs, graphene, and fullerenes employ long-range electrostatic or short-ranged specific interaction;[53] where conjugating molecules or polymers and/or covalent functionalities[54] drive the ensemble process. Such functionalization include: oxidation of CNTs and graphene to attach polar carboxyl or hydroxyl surface groups (-COOH or –OH)[53, 55] and attachment of chemically active molecules[56] or polymeric assemblies.[57] For example, fullerenes functionalized with porphyrin-derivatives are refluxed with acid-treated CNT-COOH suspensions to generate fullerene-CNT hybrid via reaction between the carboxy functionality on CNT and amine-groups on the porphyrin molecules.[58] Producing seamless exohedral bonding between CNT-graphene[54] or CNT-fullerene[59] (nanobuds) through covalent modification is typically achieved via catalytic reaction processes involving vapor phase reactant molecules. Moreover, drop-cast,[60] spin-cast,[61] and dipping[62] methods of these graphitic NMs can produce layered assemblies of NH-based thin films via electrostatic and non-covalent interaction.

The usefulness of hybridization among carbonaceous nanomaterials (CNMs) has been obtained from multifunctional and improved properties emanating from individual species. While graphene brings in high reactive surface area, mechanical/thermal stability, and high electrical conductivity, CNTs present unique electrical, mechanical, optical, and charge carrying properties. Fullerenes on the other hand provide high electron density and photoactivity. Thus, fullerenes when conjugated with graphene or CNTs can lead to improved organic photovoltaics[63] and optoelectronic devices, optical limiting and switching,[64] field effect transistors[65] via enhancement of the photo-induced electricity production, charge transfer and electron/hole shuttling,[65] singlet excited state quenching,[56] non-linear optical properties,[64] band gap tenability,[46] etc. Hybridized graphene can act as a major candidate for transparent conducting films for optoelectronic and photovoltaic devices, which possess high surface area, conductivity, transmittance, and low physical thickness as they conjugate with CNTs and/or fullerenes.[66, 67] Such modifications also render their applications in various avenues; such as in electrochemical and biomolecular sensing,[68] structural health monitoring,[69] etc.

3.3.2 Carbon-Metal Nanohybrids (CMNH)

Carbon-Metal nanohybrid (CMNH) synthesis processes involve combination of carbonaceous nanomaterials (CNTs, graphenes, and fullerenes) with different metallic or metal oxide nanoparticles[70] (Figure 3.3b). CMNHs include assemblages with a variety of metallic nanoparticles (MNPs) ranging from noble metals like Ag, Au, Pt, Pd, Ru, Rh, etc. to lanthanide series metals (La, Sc, Gd, etc), metal oxide NPs (ZnO, TiO_2, SiO_2, Fe_3O_4, CuO, etc), semiconducting quantum dots (CdSe, CdTe, etc), and ligand-based metallic compounds (ferrocene). CMNHs can be synthesized following four key pathways—(i) filling the inner cavities of CNTs/fullerenes with MNPs using vapor deposition,[71] arc discharge,[72] thermal annealing,[73] and wet chemical approach;[74] (ii) attaching MNPs onto CNT surfaces functionalized with pyrene, porphyrin derivatives[75] and similar linking molecules;[76] (iii) decorating CNM surfaces with MNPs by sol-gel,[77] hydrothermal,[78] and aerosol-based processes;[79] and (iv) in-situ growth of MNPs on CNM surfaces via electrochemical,[80] eletroless deposition,[81] and redox reactions.[82]

Combinations of graphitic and metallic nanostructures result in emergence of unique and synergistic electrical, optical, mechanical, catalytic, sensing ability, magnetic properties, which can be utilized for applications in various fields; e.g., chemical reactivity and catalysis,[83, 84] organic photovoltaics and solar cells,[85] optoelectronics,[86] supercapacitors[87] and batteries,[88] proton exchange fuel cells,[89] gas and chemical sensing,[90] biomedical imaging,[91] environmental pollution monitoring and mitigation,[92, 93] etc. Thermal and mechanical stability of CNTs and graphene with high active surface area are particularly promising in the development of Li-ion storage units with high efficiency, capacity, and durability.[78] Similarly, antibacterial activities of TiO_2, ZnO, or Ag are enhanced when conjugated with carbonaceous nanomaterials and thus facilitate their use in water treatment and other purification or detoxification applications.[93] Better sensors for gas, protein, or chemicals (H_2O_2[90], trinitrotoluene[90], etc) are being prepared using CMNHs utilizing their enhanced sorption and electrical sensitivity. On the other hand, endohedral metallofullerenes by themselves[94] and/or when encapsulated inside CNTs or CNHs[95] have great potential to be used as MRI contrast agents with extremely high water relaxivities—a holy grail in MRI contrast agent research. Such a wide range of application of CMNHs has encouraged major research efforts in material development and their application necessitating extensive environmental implications studies.

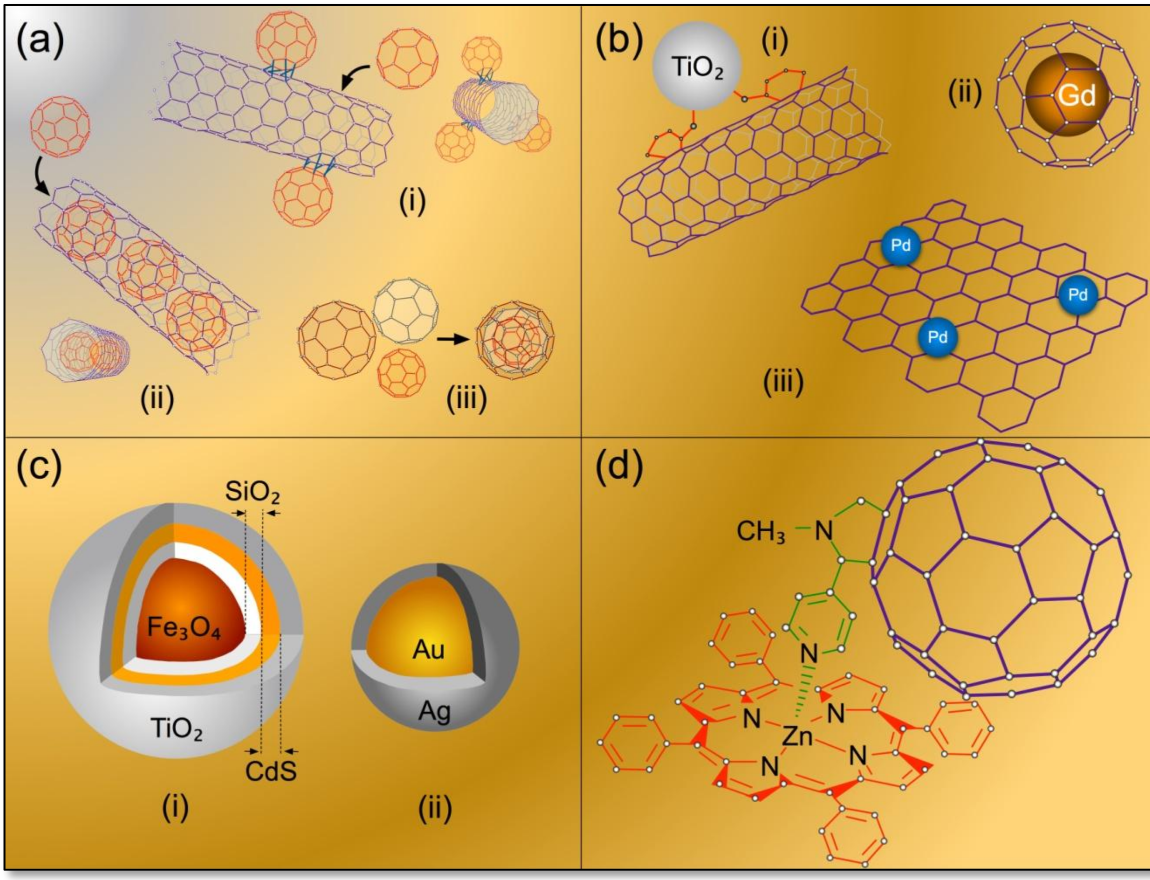

FIGURE 3.3. Schematic representations of NHs. (a) Carbon-carbon: (i) nanobud (fullerenes covalently bound to the outer sidewalls of single-wall carbon nanotube), (ii) peapod (fullerenes encapsulated inside a single-wall carbon nanotube), and (iii) nano-onion (multi-shelled fullerenes); (b) Carbon-metallic: (i) titanium dioxide nanoparticle conjugated with single-wall carbon nanotube, (ii) gadolinium encapsulated within a fullerene, and (iii) graphene decorated with palladium; (c) Metal-metal: (i) multimetallic core-shell structure of TiO_2-CdS-Fe_3O_4@SiO_2 and (ii) bimetallic Au-Ag core-shell; (d) Organic molecule coated: zinc tetraphenylporphyrin coordinated with pyridyl fulleropyrrolidine (C_{60}Py-ZnTPP) dyad.

3.3.3 Metal-Metal Nanohybrids (MMNH)

Metal NMs, i.e., metals and metal oxides when conjugated to form multi-metallic ensembles are classified as metal-metal nanohybrids, MMNHs (Figure 3.3c). Metals can be grouped based on their functionalities; e.g., plasmonic (Au, Ag, Pt),[96] magnetic (Fe_3O_4, Fe_2O_3)[97] and semiconducting oxides (TiO_2),[98] quantum dots (CdSe, ZnS, CdTe, ZnO, PbS),[99] etc. Synthesis processes to prepare conjugated metallic NMs depend on the desired hybrid properties, structures, and applications. Wet chemical processes involving reduction or thermal decomposition of metal salts are the most used synthesis techniques.[100] Wide variations of wet chemical processes include: polyol methods,[101] photochemical deposition,[102] electroless plating,[103] solvothermal,[104] hydrothermal,[105] sol-gel,[40] ion-implantation,[106] epitaxial growth,[107] etc. Vapor/gas phase processes, such flame aerosol,[108] and plasma-assisted deposition[109] are also commonly used. Core-shell based nanostructures can be formed by co-reduction[110] or sequential reduction,[101] where a metal NM previously formed can act as 'seed' for subsequent growth of another NM with different chemical origin. Optical lithography is also combined with the common methods to obtain patterned growth.[111] Template-based growth processes can be used to obtain hollow spherical,[112] porous,[113] or tubular[114] structures. Matrix bound methods on the other hand utilizes inorganic silica, oil-water interface, and polymer or block-co-polymer matrices, where co-precipitation,[115] ion implantation,[106] emulsification,[116] reverse micellization[117] processes grow NHs. Core-shell metallic layers sometimes include inorganic[118] or organic[119] linkers or spacers between them. Biogenic or green synthesis approaches for MMNH have also been developed using natural extracts as solvents or reducing agents.[120] This is a synopsis of MMNH synthesis processes. Careful review of the existing literature will further elaborate on such techniques.

Property synergies in MMNHs allow their application in diverse fields of photovoltaics and solar cells,[104] biomedical engineering and nano-therapeutics,[121] catalysis,[122] chemical sensing[123] and degradation,[122] and bactericidal applications.[124] For example: co-axial Ag/TiO_2 core-shell nanowire arrays with high specific surface area and rapid electron transport can improve the electron collection efficiency for application in dye-sensitized solar cells.[104] Bioapplications such as: enhancement of contrast in MRI for disease[125] and pathogen detection,[126] photo-thermal destruction of these cells by near-IR irradiation,[125] and separation of cancer cells from cell-mixtures[8] have begun to employ plasmonic, semiconducting, and magnetic metal NP based MMNHs.[121] Plasmonic properties of Au and Ag are combined to produce high efficiency localized surface Plasmon resonance (SPR) and surface enhanced Raman scattering (SERS) to detect disease-specific biomolecules.[100] Photoluminescent properties of semiconducting quantum dots have been shown to be enhanced when combined with magnetic (e.g. Fe_3O_4.CdS[127]) or plasmonic particles (e.g. Au-CdSe/Zns[128]) and can be used for bioimaging or fluorescence microscopy. Conjugating TiO_2, Ag, or ZnO with other metal NPs has also shown to enhance photocatalytic activities and band-gap modulation combined with excellent charged separation and charge transfer processes have made them excellent candidates for organic contaminants degradation[113] and bacteria inactivation under UV to visible light irradiation.[124] Such diverse applications, particularly in biomedicine, increase MMNHs' environmental relevance.

3.3.4 Organic Molecule Coated Nanohybrids (OMCNH)

A wide body of literature identifies metallic, carbonaceous, or polymeric NMs coated with organic molecules, biomolecules, or polymers as NHs (Figure 3.3d). Layer-by-layer hierarchical thin films have also been called NHs. Though such identification can be debatable, environmental evaluation of NHs in this category should be pursued with reflection on already existing classical coated-NM studies. The literature on OMCNH involves a wide range of synthesis processes that include: physisorption of organic molecules,[129] electrochemical immobilization of protein, enzyme, or DNA molecules,[45] polymer grafting from or grafted to NM surfaces,[130] emulsification,[41] and ion-exchange.[131] Such coated NMs are researched in the application areas of nanoelectronics,[129] photovoltaics,[129] chemical and bio-sensing,[132] bio-imaging,[133] controlled drug delivery,[134] and cancer therapy.[135] CNMs are surface functionalized with porphyrin,[129] phthalocyanine,[129] and other molecules to attain higher efficiency in charge transfer for photovoltaics and dye sensitized solar cells. Similarly, magnetic or plasmonic particles are grafted or coated with organic polymers, such as PEG[136] and PVP[137] to enhance their solubility for enhanced bio-imaging, drug delivery, or sensing. MNMs are also attached to organic fluorophores for enhanced tagging and contrasting.[133]

Most of these materials appear to be merely coated-NMs for environmental purposes, thus might not require systematic and independent environmental evaluation for accurate risk estimation. Already established environmental fate and toxicological literature have focused on physisorbed coatings. For example, citrate, PVP, PEG, gum Arabic, copolymers, etc. are typically adsorbed onto the NMs to enhance dispersion in a desired solvent and have been studied for environmental implications.[138-141] However, the recent surface modification of nanomaterials are performed with rather complex supramolecules or heterocyclic structures (e.g., porphyrin), which are covalently bound to the NM surfaces.[142-144] As per the NH definition, chemically bound coatings of this nature will lead to altered nano-EHS behavior. For example, heterocyclic porphyrins not only provide stabilization to NH dispersions but will also provide excellent electronic charge transfer properties[142] and antimicrobial capabilities.[145] Moreover, conformational differences of organic molecules or polymers present on the NM surface are known to present unique fate, transformation, and toxicity behavior.[146] Systematically evaluating nano-EHS behavior of such complex chemically coated NHs is thus imperative. Existing environmental literature on NMs with physisorbed coatings will enhance understanding of OMCNH environmental behavior.

3.4 Environmental Interaction of Nanohybrids

The novelty in NH ensembles lies in multifunctionality, resulting from a nonlinear combination of advantageous properties of each of the component nanostructures.[46, 79] Such assemblages not only contribute to enhanced functionality but also present unknown and unique physicochemical properties, which will likely cause unpredictable environmental behavior from their release and exposure. However, while researchers focus on the merits of such NHs, their potential toxic and environmental implication studies have gained attention only recently and require significant systematic approach.

Eco-toxicity of singular nanomaterials and their microbial and organismal uptake are known to be influenced by material-specific physicochemical properties such as size,[147] shape,[148] aggregation state,[149] surface functionality and coating,[150] ROS generation capability,[151, 152] photo-activity,[153] crystallinity[154] and dissolution[26, 149] of metal NMs and band-gap[155] of metal oxide NMs. When NMs are exposed to the environment they experience aggregation in aqueous media[25] and deposition onto solid surface[156] and porous media,[157] which contribute to their mobility in the aqueous environment. Moreover, transformation of NMs[158] can occur via sorption of geo- and bio-macromolecules, reaction with chemical species (presence of reactive ions, ozone, or oxygen), and also by solar irradiation in case of photoactive NMs—contributing towards NM fate and toxicological effects. Fate, transport, and transformation of NMs in the environment are also highly dependent on the intrinsic NM properties. As these nanomaterials conjugate to form hierarchical ensembles, their physicochemical properties alongside with their environmental behavior and toxicity response will likely be altered. How such alteration will occur, depends on the mode of conjugation as well as the application type, influencing their release and exposure. Here altered fate, transport, transformation, and toxicity of some common NHs will be discussed to lay out the uncertainties in nano-EHS.

3.4.1 Fate and Transport

Singular NMs, either carbonaceous or metallic, have been studied extensively to evaluate their aggregation, deposition, and transport behavior. Such behavior has been characterized in relation to their physicochemical properties and major mechanisms are elucidated in terms of electrostatic interactions,[24, 156] van der Waals attraction forces, steric hindrances contributed by physical morphology, and unique material-specific forces, such as magnetism (in case of iron-based NMs[159]) or chirality.[160] However, conjugation of two or more NMs will likely alter contributions from these forces, resulting in uncertain stability and mobility of the NHs.

Carbon nano-peapods, that are highly attractive for solid state electronics[161] or MRI contrast agents,[95] are prepared by encapsulation of fullerenes (C_{60}, C_{70}, or higher order fullerenes) inside carbon nanotubes or carbon nanohorns. Such conjugation exhibit band-gap tuning[162] and electron density differences.[163] Such alteration occurs due to single walled carbon nanotube (SWNT) diameter changes upon conjugation as well as due to entrapment of fullerenes that causes overlap of electron cloud.[162, 164] Peapod formation often involves SWNT oxidation in presence of acid mixtures that forms surface defects and also causes shortening of SWNT length.[164] Such surface property changes will likely influence van der Waals and electrokinetic interactions of nano-peapods (Figure 3.4a). For example C_{60}@SWNT peapod bundles can have stronger van der Waals forces compared to C_{70}@SWNT bundles as demonstrated by spectral characterization.[163] Moreover, other higher order fullerenes also induced size-dependent electronic structure variation in peapods followed by van der Waals disparity.[165] Furthermore, fullerene encapsulation may also result in increased mechanical strength of SWNTs,[166] resulting in stiffer tubules.[167] Altered van der Waals forces and shorter, while stiffer tubes, will likely demonstrate unique environmental behavior compared to the component fullerenes and SWNTs.

Similarly, emergent properties, such as dimensional modifications, occur due to hybridization. For example, nano-peapods mask the presence of zero-dimensional fullerene[163] and two-dimensional graphene[168] inside one-dimensional CNTs; while their exohedral conjugation results in unique three-dimensional configurations. Covalently bonded fullerenes on the surface of the graphene[64] or CNTs[34] (in case of nano-buds) can have debundling or intercalating effects and can result in enhanced stability. However, such dispersion enhancement can also be compromised via superimposed or combined inherent hydrophobicity of the carbonaceous nanomaterials.[46] Exohedrally attached fullerenes may increase physical straining during their transport through porous media (Figure 3.4b). Altered stability and porous media transport will likely lead to uncertain NH fate and transport in natural environment.

Understanding of NH aggregation and transport necessitates resolving the following key questions. Will altered electrostatic or van der Waals forces dictate aggregation or deposition of exohedrally hybridized nanotube-fullerene conjugates? How will metal NPs change NH surface interaction? What will be the roles of the linking molecules? How will overcoating influence aggregation and deposition behavior of metallic NHs? Such questions require immediate attention to address uncertainties from the emerging properties of NHs.

3.4.2 Transformation

Upon environmental release, NMs characteristics get altered via various transformation processes. For example, fullerenes and CNTs can undergo various transformation processes that include: reaction with atmospheric oxygen or ozone,[169] ultraviolet (UV) or solar light mediated photochemical change,[170] adsorption of macromolecules,[171] and natural organic matter

(NOM).[170, 172, 173] Similarly, TiO_2 and ZnO transformation can also occur under UV-exposure and during interaction with geo- and bio-macromolecules.[174] These transformations take place due to NMs' inherent photoactivity, chemical reactivity, and sorption ability; which are functions of their size, shape, surface charge and chemistry.

NOM sorption on carbonaceous and metallic NMs showed enhanced stability in aqueous media.[171, 174] TiO_2 after NOM sorption has exhibited reduced photoactivity and suppressed reactive oxygen species (ROS) production.[174] However, unknown alteration in transformation results may be experienced by hybridized NMs. For example, photoactivity of TiO_2 (under visible light) has been shown to enhance upon conjugation with CNT or graphene, due to lowering in band gap energy.[77, 175] Such enhancement is attributed to the synergy in electronic properties between titania and carbon nano-structures; e.g., small-sized TiO_2 particles on CNT surfaces reduce electron-hole pair recombination rate thus enhancing photoactivity.[77] Moreover, high electron transport ability through hollow CNT structures and conductive graphene—e.g., photoactivity transfer from UV region to visible range—is also known to improve photodynamic activity.[176, 177] Similarly, a substantial increase in the available surface area during hybridization can also invoke excellent sorption properties;[79] as demonstrated in the case of flowerlike hierarchical structures of TiO_2 on CNTs.[93] Sorption of geo- and bio-macromolecules on CNTs can also be enhanced by exohedral attachment of fullerenes, which will likely add to available sorption sites (Figure 3.4c).[59] Increased adsorption can enable higher coverage of the NH surfaces with geo- and bio-macromolecules and thus can alter subsequent fate, transport, and toxicity.

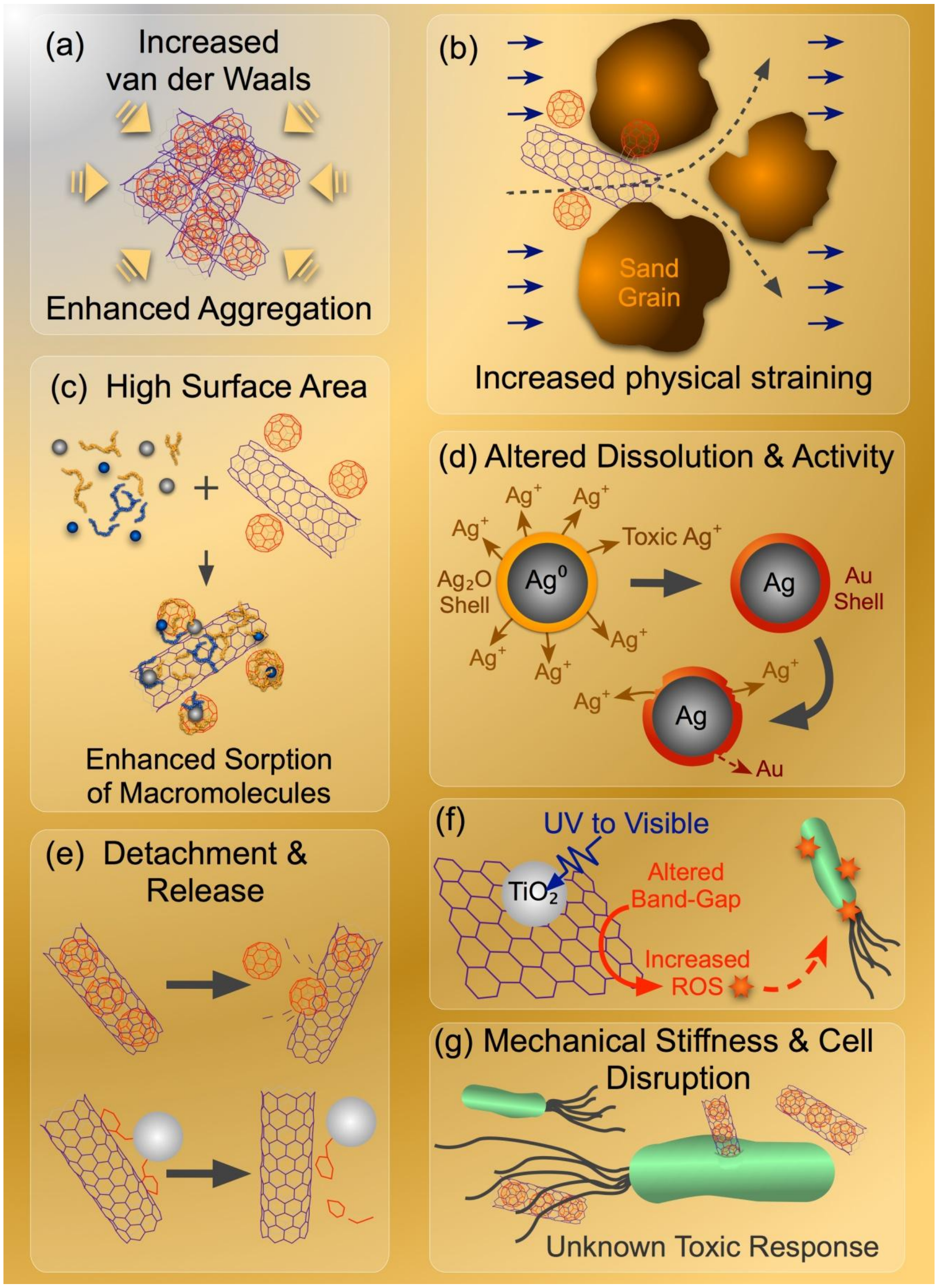

FIGURE 3.4. Plausible environmental interactions of nanohybrids. (a) Increased van der Waals attraction forces in fullerene-CNT peapods may lead to enhance the aggregation. (b) Exohedrally conjugated fullerenes with CNTs may enhance physical straining during transport through porous media. (c) Ag-Au core-shell NHs may show decreased dissolution and enhanced chemical stability. (d) Exohedral conjugation of CNT and fullerene may provide more surfaces for sorption of geo- and bio-macromolecules. (e) Fullerenes may be released from nano-peapods during transformation and result in different surface chemistry compared to components NMs. (f) Band-gap alteration of TiO_2 by conjugation with graphene can increase ROS production under visible light, leading to enhanced nanotoxicity. (g) Increased stiffness due to hybridization may induce greater cellular interaction, uptake, and membrane disruption.

Dissolution and/or reaction with inorganic species such as sulfide (S^{2-}) or chloride (Cl^-) ions in the aquatic environment are two important transformation processes for metallic NMs, such as Ag[26, 149](or ZnO[27] and CuO[178]). These transformations are governed by inherent solubility, reactivity, and sorption ability of AgNPs, influenced by physicochemical characteristics such as: size,[179] shape,[26] surface structures,[26] surface chemistry,[180] or coatings.[138] However, hybridization of chemically active AgNPs with relatively inert gold overcoating can reduce Ag^+ dissolution (Figure 3.4d).[181] Electron transfer properties of Ag-core thru Au-shell has shown to increase oxidative and chemical stability for these NHs.[182] On the contrary, 18 times larger catalytic activity was observed for Ag-Au core-shell structures when compared to monometallic Au particles.[183] Thus, overlapping of chemical or electronic characteristics can have unprecedented impact on the transformation behavior of Ag-Au hybrids.

In addition to the above discussed probable uncertain alterations of transformation behavior, some key questions arise that necessitate systematic transformation studies of NHs. What will the relative roles of parent materials be in such transformation? Will there be new transformation processes resulting from instability of NHs in the environmental matrices—e.g., detachment of TiO_2 from CNT surfaces or release of fullerenes from nano-peapods (Figure 3.4e)? How the NMs released from NHs will alter their previously predicted environmental interactions? Such questions need to be researched to better understand NH environmental transformation.

3.4.3 Toxicity

A substantial literature exists regarding toxicity of singular NMs, delineating mechanisms and correlating the effects with physicochemical properties. Several carbonaceous (fullerene,[184, 185] CNT,[186] or graphene oxide[187]) and metallic NMs (Ag,[26] TiO_2,[154, 188] ZnO,[188] CuO[188]) are known to illicit toxicological effects on biological species. The key mechanisms associated with such toxic responses include: ROS mediated oxidative stress,[147] direct interaction of metal NPs with cell membrane,[148] lipid peroxidation,[189] ROS independent protein oxidation,[190] dissolution and relevant reactive membrane or enzymatic damage,[26] asbestos-like inflammation by CNT,[191] and physical rupture of cell membrane.[187] Material characteristics such as size and surface area,[192] shape,[148] crystalline structure,[148] surface coatings,[193] aggregation state,[149, 194] and electronic properties,[155] have been known to influence NM bioaccumulation and toxicity. However, likelihood of alteration of toxicity following NM hybridization has not been well-studied. Among few recent efforts, most are directed towards beneficial antimicrobial applications while only a handful studies report concerns regarding NHs' harmful implications.[4, 195] For example, bimetallic conjugation of non-toxic parent materials Au and Pt with variable compositions has generated anti-microbial responses against *E. coli*, *Salmonella choleraesius*, and *Pseudomonas aeruginosa* via cell membrane damage and increment in the intracellular level of adenosine triphosphate (ATP).[196] Recent studies involving graphene-ZnO[197] and graphene-Cu[198] NHs showed increased toxicity than their parental components towards a model organism transgenic *Drosophila melanogaster* as demonstrated by enhanced lipid peroxidation and apoptosis. On the contrary, presence of a silica-based shell structure reduced ZnO towards E. coli.[199] A comprehensive toxicity evaluation of E. coli on exposure to iron(Fe)- based bimetallic NHs has shown differences in toxicity based on the presence and type of the second metal.[195] Component dependent toxicity was observed as bare Fe, Fe-Cu, and Fe-Ni showed comparable toxicity while Fe-Pd and Fe-Pt presented with significantly lower toxicity. These differences were attributed to diverse interactions of these NHs with cellular membrane due to differences in surface charge, particle size, and reactivity, caused by conjugation. These evidences of altered bio-compatibility hint towards the necessity of systematic and mechanistic exploration of NH toxicity.

A recent study[200] involving colloidally stable graphene-TiO_2 NHs showed enhancement in photocatalytic ROS generation under visible light irradiation, while pristine TiO_2 showed photoactivity, only in the UV spectrum (Figure 3.4f). This has been possible due to excellent charge separation abilities of graphene; which could reduce TiO_2's band gap in the hybridized form. However, the NHs didn't exhibit enhanced toxicity compared to singular TiO_2 to model aquatic organisms, *Daphnia magna* and *Oryzias latipes* (Japanese Medaka fish). The lack of toxicity may be explained by ROS quenching, which resulted from rapid aggregation of the NHs in high ionic strength culture media. Hybridization of NMs thus has shown to alter nanotoxicity. Emergent properties, such as, changes in surface roughness and mechanical stiffness, have shown to be responsible for differential cell-NH interaction; as was observed in case of multicomponent hierarchical NHs prepared by sequential coating of functionalized CNTs with Ag, DNA, and polyvinyl alcohol (PVA).[201] Similarly stiffness increase due to fullerene encapsulation inside CNTs may also have physical interaction mediated toxicological consequences (Figure 3.4g).

Thus questions may arise while combining graphitic nanostructures with metallic ones. Will emergent mechanical properties dominate the NH toxicity? How will metal dissolution be altered and will mediate nanotoxicity? Will alteration of dimensionality, e.g., from 2D (graphene) to 3D (fullerene-graphene), influence shape-dependent toxicity? Thus potential environmental interaction of emerging nanoscale hybrid materials are ostensibly unique, complex, and may not be predictable from simple one or two parametric combinations of physicochemical characteristics; addressing the aforementioned questions can be a starting point for NH toxicity evaluation.

3.5 Conclusions and Perspectives

The discussion in this chapter has reviewed the NH literature and has highlighted the emergent properties of this new ensemble material class. The novel properties already emerging from conjugation and overcoating are altering fundamental physicochemical properties. Such differences will alter EHS behavior of NHs, thereby warranting careful consideration and strategizing for systematic evaluation. Their environmental exposure appears to be more eminent when NH-laden real-world applications are marketed in electronics (e.g. silicon oxycarbide-CNT[202] and CNF-Lithium nitrate[203] NHs for Li-ion electrodes), in dentistry related products,[204, 205] antimicrobial coatings,[206] and protective devices[207] (e.g. Ag-TiO_2), and in bio-imaging or graphene-based MRI contrast agents.[208, 209] On one hand, NHs, such as Ag-Cu, Fe-Ni, or Ag-In, are being commercially synthesized as research-grade materials,[210] while invention disclosures and patents[14, 211, 212] on lithium-ion batteries (graphene-VO_2), supercapacitors (graphene-Mn_3O_4), and solar cells (CNT-fullerenes), are enabling active technology transfer. The key issue is not about NHs' unique EHS behavior, but about how and by which attribute, will such alteration impact nano-risk determination. The chapter identifies the following concerns in regard to NH EHS: Do the NHs of concern possess unique properties to behave unpredictably in the environment? What will be the form of release for these NHs? Are these NHs going to be environmentally stable; i.e., will these retain their hybrid ensemble entities or detach to individual NM components during environmental exposure? What functionalities or derivatives of these NHs should be studied?

The next generation NHs are headed toward further complicated hierarchical structures, where NMs from more than two chemical origins are being conjugated; e.g., CDS/ZNS-Au, [128] MWNT/Ag-TiO_2,[213] or CDS-TiO_2-Fe_3O_4.[214] Thus a possibility of infinite combinations and functionalization of NMs presents with an almost unmanageable matrix to evaluate their environmental risk. Thus robust strategies for handling this large material set are necessary. Strategy formulation can choose material properties, their structural integrity during environmental exposure, or target a specific groups based on aggravated risk potential realized from the component behavior. However, such strategies necessitate detailed and systematic studies prior to formalization.

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Chapter 4: Preparation and Characterization of Stable Aqueous Higher Order Fullerenes***

Abstract

Stable aqueous suspensions of nC_{60} and individual higher fullerenes, i.e., C_{70}, C_{76}, and C_{84} are prepared by a calorimetric modification of commonly used liquid-liquid extraction technique. The energy requirement for synthesis of higher fullerenes has been guided by molecular scale interaction energy calculations. Solubilized fullerenes show crystalline behavior by exhibiting lattice fringes in high resolution transmission electron microscopy images. The fullerene colloidal suspensions thus prepared are stable with a narrow distribution of cluster radii (42.7±0.8 nm, 46.0±14.0 nm, 60±3.2 nm, and 56.3±1.1 nm for nC_{60}, nC_{70}, nC_{76}, and nC_{84}, respectively) as measured by time resolved dynamic light scattering. The ζ-potential values for all fullerene samples showed negative surface potential with similar magnitude (-38.6±5.8 mV, -39.1±4.2 mV, -38.9±5.8 mV, and -41.7±5.1 mV for nC_{60}, nC_{70}, nC_{76}, and nC_{84}, respectively), that provide with electrostatic stability to the colloidal clusters. This energy-based modified solubilization technique to produce stable aqueous fullerenes will likely aid in future studies focusing on better applicability, determination of colloidal properties, and understanding of environmental fate, transport, and toxicity of higher order fullerenes.

Keywords: Higher order fullerenes, colloidal stability, aqueous solubilization of fullerenes

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4.1 Introduction

Geodesic dome structured C_{60} fullerene's innovation in 1985[1] and its popular use in various fields thereafter,[2-5] encouraged isolation and characterization of similar structures with carbon atom numbers in the order of 70's, 80's and 90's.[6] Higher fullerenes formed with more than 60 carbon atoms in accordance with the isolated pentagon rule, are being extensively investigated in recent years in the fields of solar energy,[7, 8] nanoelectronics,[9-11] and biomedical engineering.[12, 13] The potential importance of these isolated higher structures are primarily attributable to their low energy band gap[14] and ambipolar electronic transport characteristics.[15] Moreover, the larger cage of such higher fullerenes also act as a scaffold to impregnate a wide array of metals that generate endohedral metallofullerenes,[16] a potentially transformational contrast agent for magnetic resonance imaging (MRI) with more than one order of magnitude higher water relaxation time.[17] Multi-billion dollar MRI contrast agent market alongside with solid state electronics industries necessitate aqueous solubilization of stable higher order fullerenes, not only for appropriate processing and applications but also for evaluating environmental impact, i.e., eco-toxicity and environmental fate and transport.

Significant differences in the molecular structure and stability originating from the increased number of carbon atoms have intrigued researchers to isolate and characterize higher order fullerenes.[18] Higher fullerenes (C_{74} to C_{96}) were first identified as synthesis/processing byproducts from resistive heating of graphite rods.[19] High performance liquid chromatography with recycling was employed for the successful isolation of several stable higher fullerene isomers[20] (i.e. one C_{76} isomer,[21] three C_{78} isomers,[22-24] nine C_{84} isomers[25-27] etc.) though less in numbers than the theoretical prediction[28, 29] and their characterization was performed using ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy,[24, 30] UV-Visible absorption measurements,[6,

[31] Raman spectroscopy,[32] etc. High performance liquid chromatography (HPLC) with recycling was employed for successful isolation of several stable higher fullerene isomers.[21, 25, 26, 33, 34] Such emerging higher fullerenes, e.g., C_{76}, C_{78}, C_{80} and C_{84}, have smaller bandgaps between the highest and lowest unoccupied molecular orbitals (HOMO and LUMO) compared to that of the more common C_{60} and C_{70} fullerene structures. The smaller band gap properties of the higher fullerene structures along with their ambipolar characteristics is hypothesized to be the defining factor in production of organic solid semiconductors (with no internal or external doping)[14] and in future applications such as photodetectors[15] with widespread market demand. Moreover, intriguing relationships are found for electron affinities,[35] redox potentials,[36] electrochemical energy gaps,[37] and electrodeposited thin solid films[38] of fullerenes with increasing carbon numbers; which demand exhaustive electrochemical studies in a variety of solvents including water. Furthermore, aqueous solubilization of higher and endohedral fullerenes becomes more important for biomedical applications, particularly, in cases of MRI contrasting agents[39, 40] (effect of shape, size, and symmetry of fullerenes on relaxation characteristics in solution [41]) and drug delivery systems.[42]

Previous efforts to produce colloidally stable fullerenes have been limited mostly to C_{60} fullerenes—pristine[43] and derivatized.[44] The most common processes for suspending nC_{60} include liquid-liquid extraction using organic solvent-fullerene-water mixtures,[45] extraction by distillation of organic solvents,[46] nitrogen purging through fullerene-water-organic solvent mixtures,[43] and solvent free direct ultrasonication[47] or month long magnetic stirring of fullerene-water mixtures.[48] Such nC_{60} solubilization techniques contributed at large in the development of improved photovoltaic devices [49] and film electrodes.[50] Moreover, the aqueous solubilization of nC_{60} enabled detailed implication studies of such materials focusing on colloidal stability,[51, 52] aggregation and deposition behavior,[53, 54] and cyto- and eco-toxicity.[55, 56] To-date, no technique has been proposed to produce stable aqueous suspensions of higher fullerenes with the only exception in the case of C_{70} [43, 57] and mixtures of higher fullerenes[58] and their derivative.[59] Such a gap in literature for individual higher fullerene aqueous suspension may have restricted the use of these higher fullerene structures in applications as well as constrained the implication studies relevant to human health and natural environment.

The objective of this study was to develop a systematic protocol based on calorimetric principles for generating stable aqueous suspensions of commonly used higher fullerenes, i.e., C_{70}, C_{76}, and C_{84} individually. Liquid-liquid extraction of fullerenes by ultrasonication of fullerene-toluene-ethanol-water mixture was performed in a systematic manner to generate colloidally stable higher fullerenes in appreciable quantities. Interaction energies of fullerene pairs were calculated using density functional theory (DFT)[60] within a polarizable continuum model (PCM) of water.[61] Such molecular scale interaction energy differences guided the experimental modifications for calorimetric requirements of higher fullerenes and enabled successful solubilization with scaled-up energy needs. The water solubilized higher fullerenes were then characterized to obtain their physicochemical and electrokinetic properties using transmission electron microscopy (TEM), UV-visible spectroscopy, and electrophoretic mobility measurements. Colloidal stability of the solubilized fullerene clusters was evaluated using time resolved dynamic light scattering (TRDLS). To the best of our knowledge, this study is the first to develop a systematic calorimetric method for generating stable aqueous suspensions of higher fullerene structures with future applicability in electronics, and environmental health and safety studies. Since isomeric separation of higher fullerenes poses significant experimental challenges,[62] effect of isomers on solubilization and subsequent physicochemical properties were considered beyond the defined scope of this research.

[The planning, experimental data collection and writing of the work were led by Nirupam Aich. Dr. Joseph Flora performed molecular modeling. Dr. Navid Saleh supervised the work.]

4.2 Materials and Methods

4.2.1 Molecular Modeling

The initial geometry of the fullerene molecules was obtained from Yoshida[63] and the isomers used for the calculations were C_{60}-Ih, C_{70}-D5h, C_{76}-D2, and C_{84}-D2. The coordinates of each fullerene molecule were optimized[64] with dispersion corrected Density Functional Theory (DFT-D)[65, 66] using the BLYP functional and the 6-31+G(d) basis set as implemented in TeraChem.[67] To obtain an initial geometry for each fullerene pair, the effective fragment potential (EFP) of the single fullerene molecule was generated using GAMESS[68-71] with the STO-3G basis set. A small basis set was used because subsequent geometry optimization at a higher level was performed and also because of the large system memory requirements for large basis sets—e.g., generating the EFP for C60-Ih required 24 GB RAM distributed memory plus 7GB RAM per core and 39 GB RAM distributed memory plus 14 GB RAM per core using the 6-31G(d) and 6-31+G(d) basis sets, respectively. The second fullerene molecule was completely randomly located and rotated around the first, keeping the initial smallest distance between the atoms of the fullerene pair constrained between 1.5 and 5 angstroms. Geometry optimization of the fragment pair was performed using GAMESS and the first 10,000 optimized fullerene fragment pair geometries that successfully converged to a tolerance of $10^{-5}$and within 500 iterations were collected. The geometry of the lowest energy fullerene pair was further optimized using DFT-D/BLYP/6-31+G(d) using TeraChem. The energy of the optimized single and paired fullerene molecules in water was calculated at the same level using the PCM model[61] implemented in GAMESS. The interaction energy between fullerene molecules in water was calculated as

$$Interaction\ energy = E_{PCM}(fullerene\ pair) - 2E_{PCM}(single\ fullerene) \qquad (4.1)$$

4.2.2 Preparation of the Aqueous Fullerene Suspensions

Aqueous suspensions of the higher fullerenes are prepared modifying the existing Andrievsky's method,[45] guided by molecular energy calculations. The fullerenes were obtained from commercial sources, i.e., C_{60} (99.9%) from MER Corporation (Tucson, AZ), C_{70} (98%) from Cheap Tubes Inc. (Brattleboro, VT), C_{76} (98.1%) from BuckyUSA (Houston, TX), and C_{84} (>98%) from SES Research Inc. (Houston, TX). The isomeric distribution of the higher fullerenes were reported by the manufacturers as C60-Ih, C70-D5h, C76-D2, and C84 a mixture of D2 and D2υ. All fullerene samples (24 mg of C_{60}, 30 mg of C_{70}, 2 mg of C_{76}, and 4 mg of C_{84}) were dissolved separately in HPLC grade toluene (30, 30, 10, and 20 mL respectively, Sigma-Aldrich, St. Louise, MO) through magnetic stirring. The toluene suspension of each fullerene was then mixed with deionized water (Barnstead) at a fullerene-water ratio of 4 mg: 60 mL in presence of a co-solvent, HPLC grade ethanol (Sigma-Aldrich, St. Louise, MO) at 2 mL volume. Ultrasonic dismembrator S-4000 (Misonix, Inc. Farmingdale, NY) was used to sonicate these mixtures under fume hood for 3.0, 5.5, 7.5, and 13.0 hours respectively which correspond to the calorimetric energy input of 3.5, 6.3, 8.2, and 13.9 kJ/mL of water respectively (on calorimetry-basis as discussed in results and discussion section) to completely evaporate the organic solvents and thereby successfully extract stable fullerene clusters into water (Table S1). Such increased energy requirement for higher fullerene structures was guided by the enhanced interaction energy between higher fullerene pairs as demonstrated through the *ab initio* calculations. The single phase solution was then quiescently kept aside at room temperature for a few hours to allow any unlikely settling. Each solution was then filtered through a vacuum filter system containing 0.22 µm cellulose acetate membrane filter to obtain clear aqueous suspensions of the fullerenes. All the aqueous suspensions were subsequently stored at 4 °C.

4.2.3 Physicochemical Characterization of the Aqueous Fullerenes

The aqueous fullerene suspensions were characterized to obtain their size distributions and key physicochemical properties using electron microscopy, electrophoresis, and dynamic light scattering. A high resolution transmission electron microscope (HRTEM) JEM-2100F, Jeol, Tokyo, Japan (Electron Microscopy Center of University of South Carolina) was used to image the fullerene nC_{60} and nC_{70} in suspension at an accelerating voltage of 200 kV for samples at different magnifications. The specimens for these micrographs were prepared by placing two to three drops of the aqueous suspension of the prepared fullerene stock on the copper TEM grids coated with carbon film. The drops were then allowed to air dry for a few minutes. A similar specimen preparation procedure was followed for imaging nC_{76} and nC_{84} fullerene suspensions under an H-9500 Hitachi High Technologies America, Inc, Pleasanton, CA HRTEM (Clemson University microscope facilities) with the exception of sonicating the suspensions in the a bath sonicator for 5 min before putting them on the grid. In this case accelerating voltage of 300 kV was used to image the samples at different magnifications and in a number of grid sections to obtain representative images for each sample.

To validate the structure specific chemical signatures of the fullerene samples, UV-vis spectroscopy was performed at room temperature using Agilent 8453 UV-visible spectroscopic system (Santa Clara, CA). For each fullerene sample, a 2 mL volume of the aqueous suspensions at full strength for nC_{76} and nC_{84} and at a 10-fold dilution for nC_{60} and nC_{70} was added to a pre-cleaned quartz cuvette. Background baseline was established for each case in presence of identical cuvette with deionized water prior to each spectral scan. At least 3 spectral scans were collected for each specimen and the triplicate samples were tested for the spectroscopic measurements. Each spectral scan was collected for the entire spectral range (i.e., 200 to 1050 or 1100nm).

A Brookhaven ZetaPALS (Brookhaven Instrument Corporation, Holtsville, NY) electrophoresis technique was used to measure the ξ-potential of the aqueous nC_{60} and higher fullerenes. Each sample was introduced at 2 mL volume to the disposable cuvettes with a 10-fold dilution for nC_{60} and nC_{70} suspensions and with no dilution for nC_{76} and nC_{84}. At least 10 electrophoretic mobility measurements were performed for each sample and samples were run in at least triplicates for each fullerene. The ξ-potentials of the fullerenes were obtained by converting the average values of the electrophoretic mobilities using Smoluchowski relationship.[72]

Time resolved dynamic light scattering (TRDLS) was used to determine colloidal stability of the prepared fullerene suspensions. These measurements were performed using an ALV/CGS-3 compact goniometer system (ALV-Laser Vertriebsgesellschaft m-b.H., Langen/Hessen, Germany) equipped with 22 mW HeNe Laser 632 nm (equivalent to 800 mW laser at 532 nm) and high QE APD detector with photomultipliers of 1:25 sensitivity. Detailed protocol of the TRDLS is described elsewhere.[73, 74] In short, 2 mL of diluted fullerene suspension (nC_{60} and nC_{70} with dilution factor of 10, nC_{76} and nC_{84} fullerenes with dilution factor of 1) was added to a rigorously cleaned borosilicate glass vial[73, 74] and vortex mixed (using VWR Vortexer, Henry Troemner LLC., Thorofare, NJ) prior to initiating the TRDLS measurements. The 632 nm red laser was operated at 33% (for nC_{76} and $nC_{84}$with dilution factor of 1) and 100% attenuation (for nC_{60} and C_{70} with dilution factor 10 , respectively) and scattering data was collected at 90° scattering angle for 15 seconds to generate each average hydrodynamic radius data point. A continuous measurement with each fullerene sample was thus performed for at least 40 min. Such scattering data was then used to generate fullerene cluster size distribution profiles with built-in 'cumulant algorithm' of the ALV software.

4.3 Results and Discussion

4.3.1 Calorimetry-based Solubilization Technique

Individual higher fullerene aqueous solubilization was achieved through a calorimetric modification of the well-established liquid-liquid extraction technique, originally developed by Andrievsky and co-workers.[45] This modification was adopted on the basis of molecular modeling results for fullerene-fullerene interaction in water continuum model. The PCM model showed a linear increase of the interaction between two fullerene molecules with increasing carbon number as demonstrated in Figure 4.1a. That is, the interaction between a fullerene molecule pair become increasingly favorable with the increase in carbon number—resulting in larger energy demand to solubilize higher ordered fullerenes in water as obtained experimentally (Figure 4.1b). It is to be noted here that theoretical computation for interaction energies between two like fullerenes are restricted to 'molecular interaction' instead of 'cluster interaction', i.e., nC_m (where, m is carbon number), due to computational limitations. The higher fullerene solubilization protocol thus involved input of higher energy with the increase in carbon number in the fullerene molecules (Figure 4.1b) guided by the theoretical trend of energy increase. Additional information on the geometry of the optimized configuration can be found in Appendix B (Figure B-1).

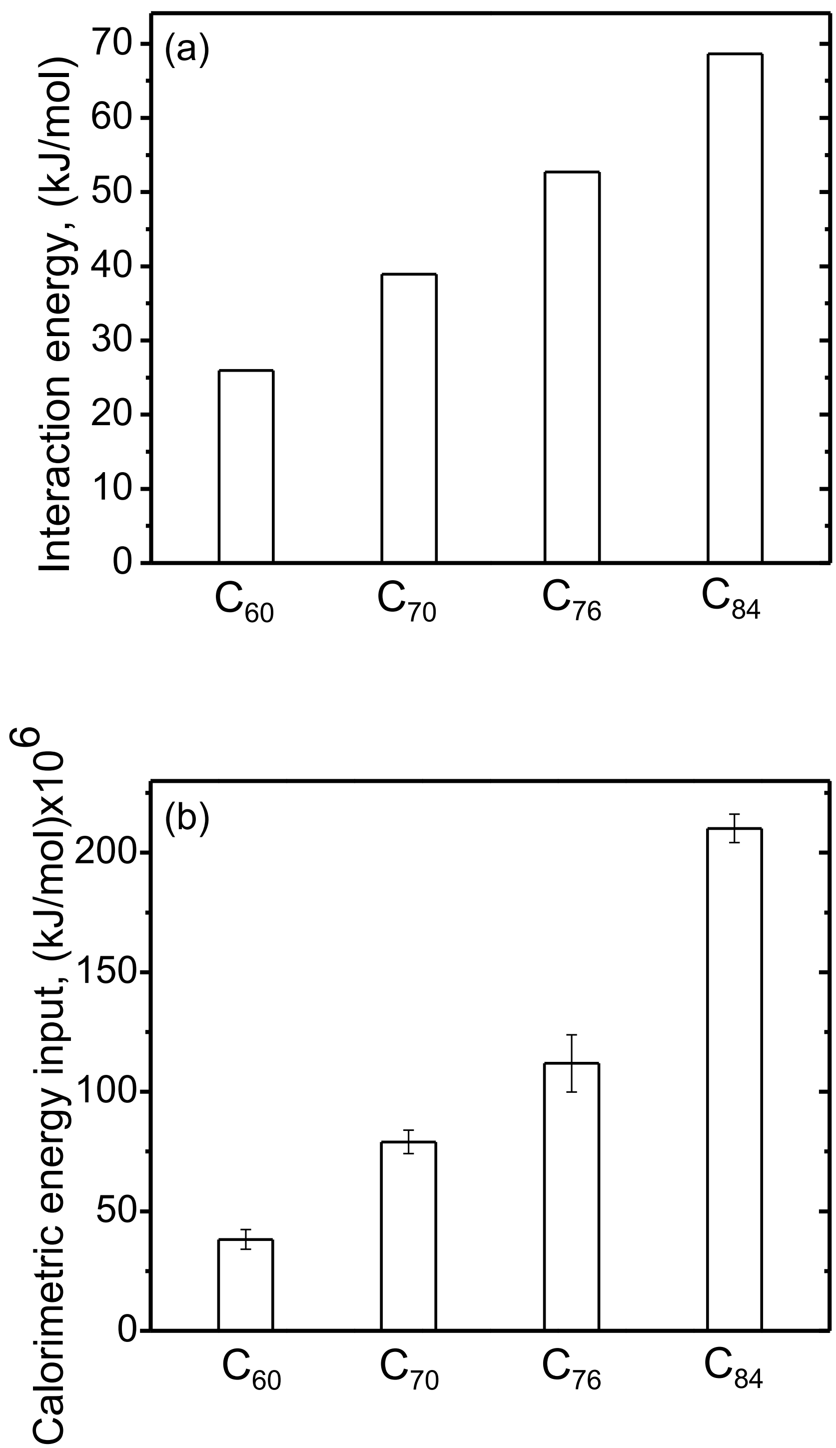

FIGURE 4.1. (a) Variation of interaction energy between two similar fullerene molecules in water calculated by PCM model and (b) Variation of energy input with carbon number of higher fullerenes.

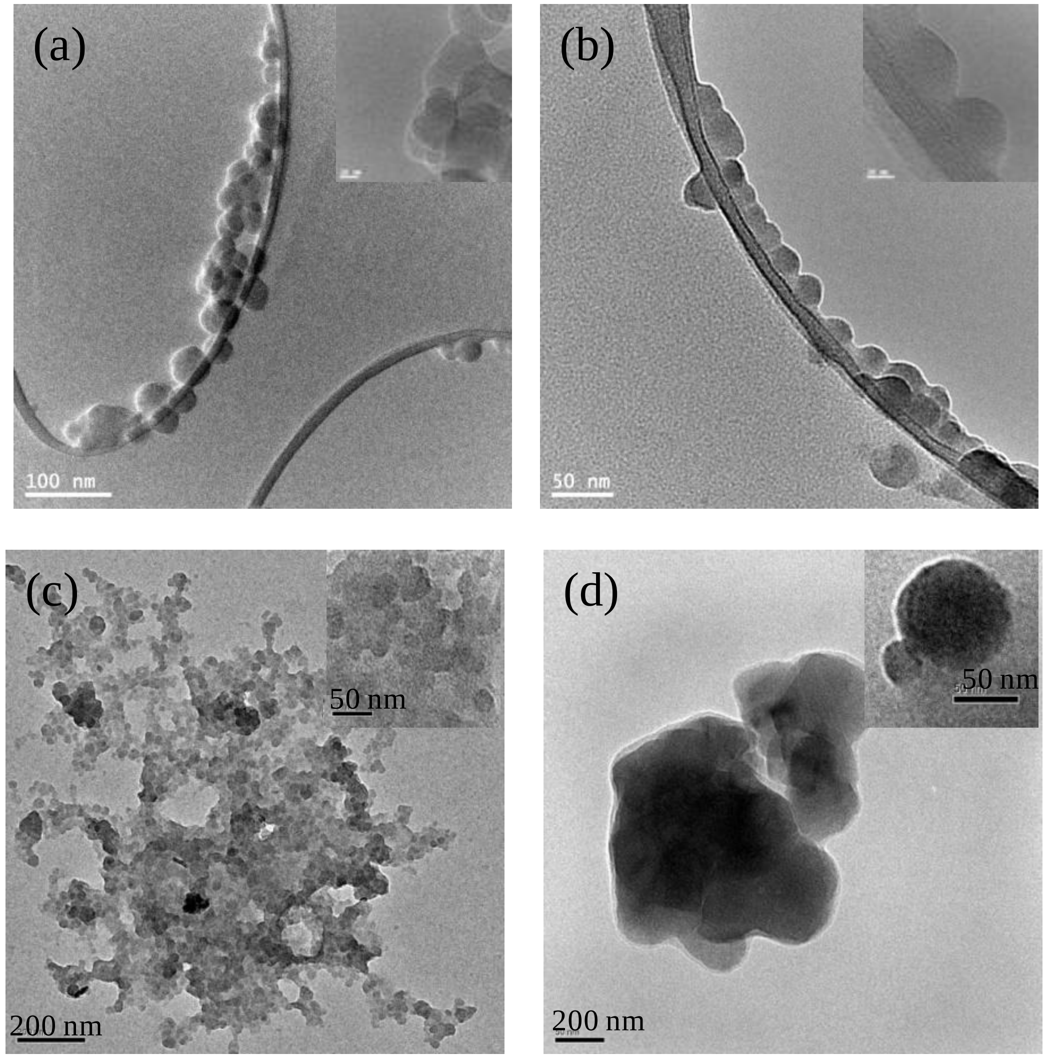

FIGURE 4.2. Representative HRTEM micrographs of aqueous (a) nC_{60}, (b) nC_{70}, (c) nC_{76}, and (d) nC_{84} fullerene clusters. Inset represents higher magnification of the fullerene clusters.

The resulting colloidal suspensions of nC_{60}, nC_{70}, nC_{76}, and nC_{84} acquired are brown yellow, purple, almost transparent, and light yellow colors respectively as presented in Figure B-2(a-d). High resolution transmission electron micrographs (HRTEM) of these fullerenes presented in Figure 4.2 (a-d) show fairly uniform-sized fullerene clusters. The clusters for all four fullerenes appeared to be spherical in shape with relatively rounded edges. The relative uniformity in size of the fullerene clusters as observed in the electron micrographs are further demonstrated through dynamic light scattering, presented later in this section. The higher magnification of the nC_{60} and nC_{70} samples as presented in the inset of Figure 4.2 also provides evidence of possible crystalline nature of the fullerene clusters, consistent with the previously presented micrographs for nC_{60} and nC_{70} aqueous suspensions.[43, 75]

The energy vs. carbon number aspect of this aqueous solubilization technique used in this study is derived from sonochemistry literature[76] where transfer of acoustic energy to the solution through such ultrasonication is commonly referred to as calorimetric energy. The energy estimation involves temperature monitoring with time (Figure B-3) and the use of specific heat principle of water to obtain the power input from the dismembrator. Subsequently, the total time of sonication involved in each synthesis procedure is taken into account by converting the input-wattage to calorimetric-energy (joules). The detailed step by step process of this estimation is described in supporting information (section B-1) for clarity. The energy provided to synthesize aqueous nC_{60} in this study was 38200±4100 MJ/mol, which was increased with the increase in carbon number to 79000±4900 MJ/mol for nC_{70}, 103450±11950 MJ/mol for nC_{76}, and 210170±5990 MJ/mol for nC_{84}. This increasing energy profile was successfully performed to accommodate the high energy requirement for separating and suspending thousands of fullerene molecules in water.

This calorimetric energy approach not only helps generate a protocol with consistency, but also can eliminate the equipment variability from the synthesis process—which is essential for a standardized synthesis protocol. The existing literature in fullerene synthesis does not avail of such controlled synthesis environment.[43, 46, 48] The adaptation of the well-established liquid-liquid extraction method[45] in the literature with such lack of control in the sonication aspect of synthesis, generated inconsistencies in the synthesized fullerene colloids, including difference in size due to variation of sonication time.[77]

4.3.2 Chemical Characterization of the Fullerenes—UV-visible Spectroscopy

Ultra violet-visible (UV-vis) spectroscopic observation of the aqueous fullerene samples is presented in Figure 4.3 that confirms the chemical signature of each fullerene type. Strong absorbance peaks at 216 nm, 264 nm, and 341 nm are observed for nC_{60} suspension.

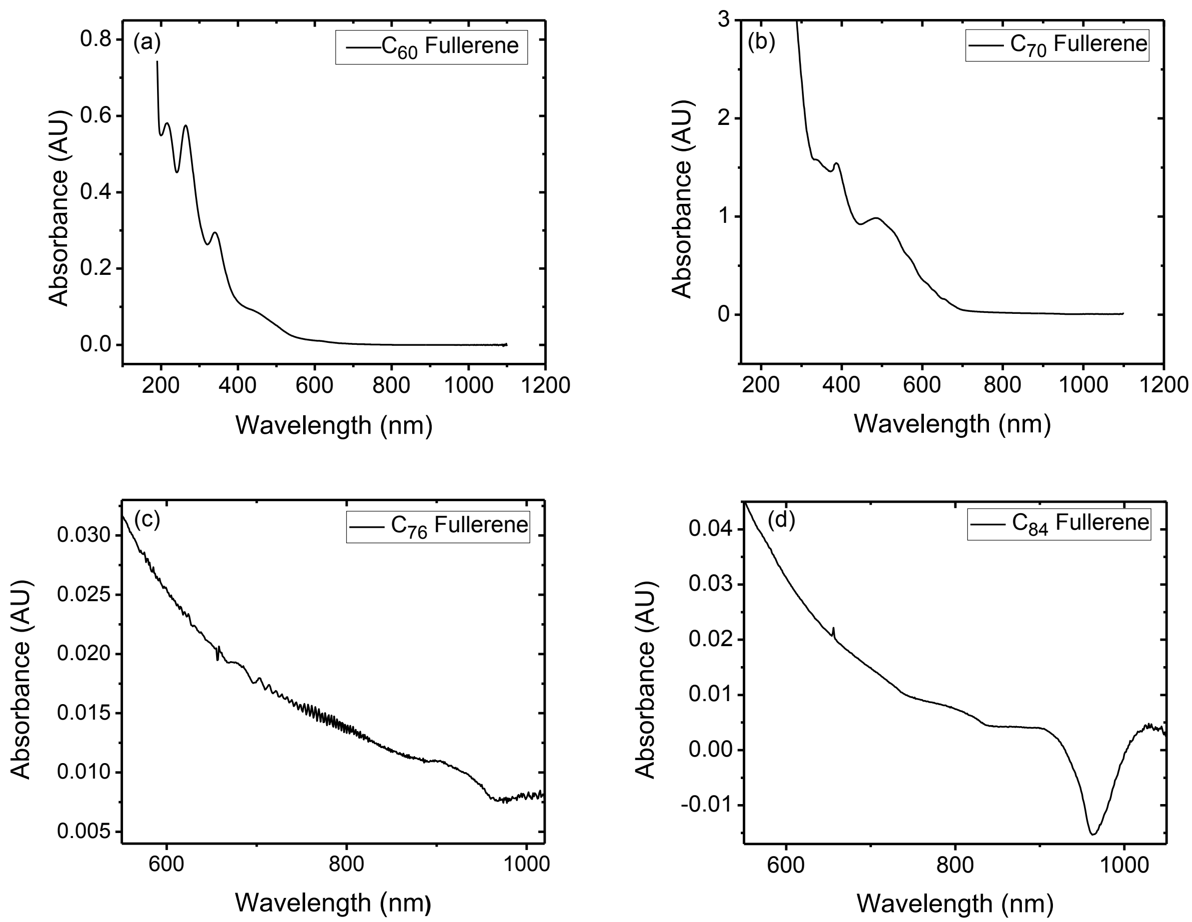

FIGURE 4.3. UV-vis spectra of (a) nC_{60}, (b) nC_{70}, (c) nC_{76}, and (d) nC_{84} aqueous suspensions. The spectra for nC_{60} and nC_{70} fullerenes are presented for a spectral range of 200-1100 nm, while nC_{76} and nC_{84} spectra are presented for 600-1050 nm wavelength. All measurements are performed at 21±0.5 °C temp.

For nC_{70} aqueous suspension, peaks are observed at 386 nm and 480 nm in the UV region. The observed peaks are consistent with literature observation for nC_{60} and nC_{70} in water[43, 78] and also in other solvents such as in THF[43] and hexane.[79] The spectra for nC_{76} and nC_{84} fullerenes showed very weak peak amplitudes in the 600-700 nm wavelength region that are otherwise observed as stronger peaks in the literature in organic solvent, such as benzene.[6] This attenuated peak response might have been caused due to low particle number concentration in the aqueous suspension.

4.3.3 Surface Charge Properties of Higher Fullerenes

All the stable fullerene suspensions showed negative surface potential in deionized water at a pH range of 4.9-5.5 (Figure 4.4). Fullerenes nC_{60}, nC_{70}, and nC_{76} showed similar surface charge properties with ζ potential values of -38.6±5.8 mV, -39.1±4.2 mV, and -38.9±5.8 mV at pH of 5.5, 5.0, and 5.4, respectively. The nC_{84} higher fullerene exhibited a slightly higher ζ potential of -41.7±5.1 mV at pH 5.0. The measurements reported in this study are consistent with the literature findings for nC_{60} (-30 to -70 mV)[43, 51, 80-83] and nC_{70} (-47 to -63 mV).[80, 83] The nC_{76} and nC_{84} surface potential values are reported for the first time in this study. Surface charge properties presented here (>-30 mV) indicate a presence of significant electrostatic barrier to aggregation for nC_{60} and all three higher fullerenes.[72] However, the origin of such high negative surface charge for all-carbon structures like fullerenes is still unknown. Some proposed hypothesis to describe such charging phenomena in water include presence of electron dense surface groups in fullerene surface,[43] clathrate formation,[43] charge transfer, hydrolysis reaction,[81] and interaction between water and fullerene shell.[83] Increasing electron affinity of fullerenes with higher carbon numbers[36] might also be an influencing factor for their stabilization in water.

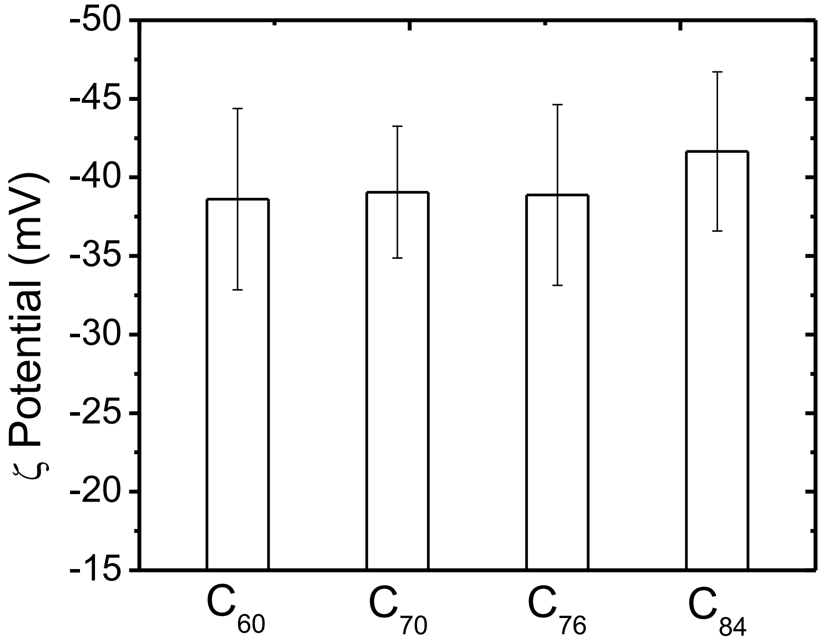

FIGURE 4.4. ξ-potential values for nC_{60} and aqueous higher fullerenes (nC_{70}, nC_{76}, and nC_{84}). All measurements are performed at 22±0.5 °C. The pH values were in the range of 4.9 to 5.5 for the entire set of fullerene samples.

4.3.4 Colloidal Stability of Higher Fullerenes

TRDLS studies for the higher fullerene samples immediately after synthesis show stable profiles with narrow standard deviation for nC_{60}, nC_{70}, nC_{76}, and nC_{84} up to ~40 min immediately after synthesis (Figure 4.5a) which showed a very stable profile with time. The average hydrodynamic radii of nC_{70}, nC_{76}, and nC_{84} were 42.7±0.8 nm, 46.0±14.0 nm, 60.0±3.2 nm, and 56.3±1.1 nm, respectively (Figure 4.5b). The scattering information collected over this period was used to analyze cluster size distribution. The higher fullerenes demonstrate narrow particle size distribution with polydispersity index (PDI) of 0.30±0.03, 0.33.±0.04, 0.18±0.08, and 0.22±0.06 for nC_{60}, nC_{70}, nC_{76}, and nC_{84} respectively (Figure B-4). The data for nC_{60} are consistent with the literature presented range of 45 to 62 nm size, and narrow size distribution with PDI of 0.23-0.28.[43, 51, 55, 81]

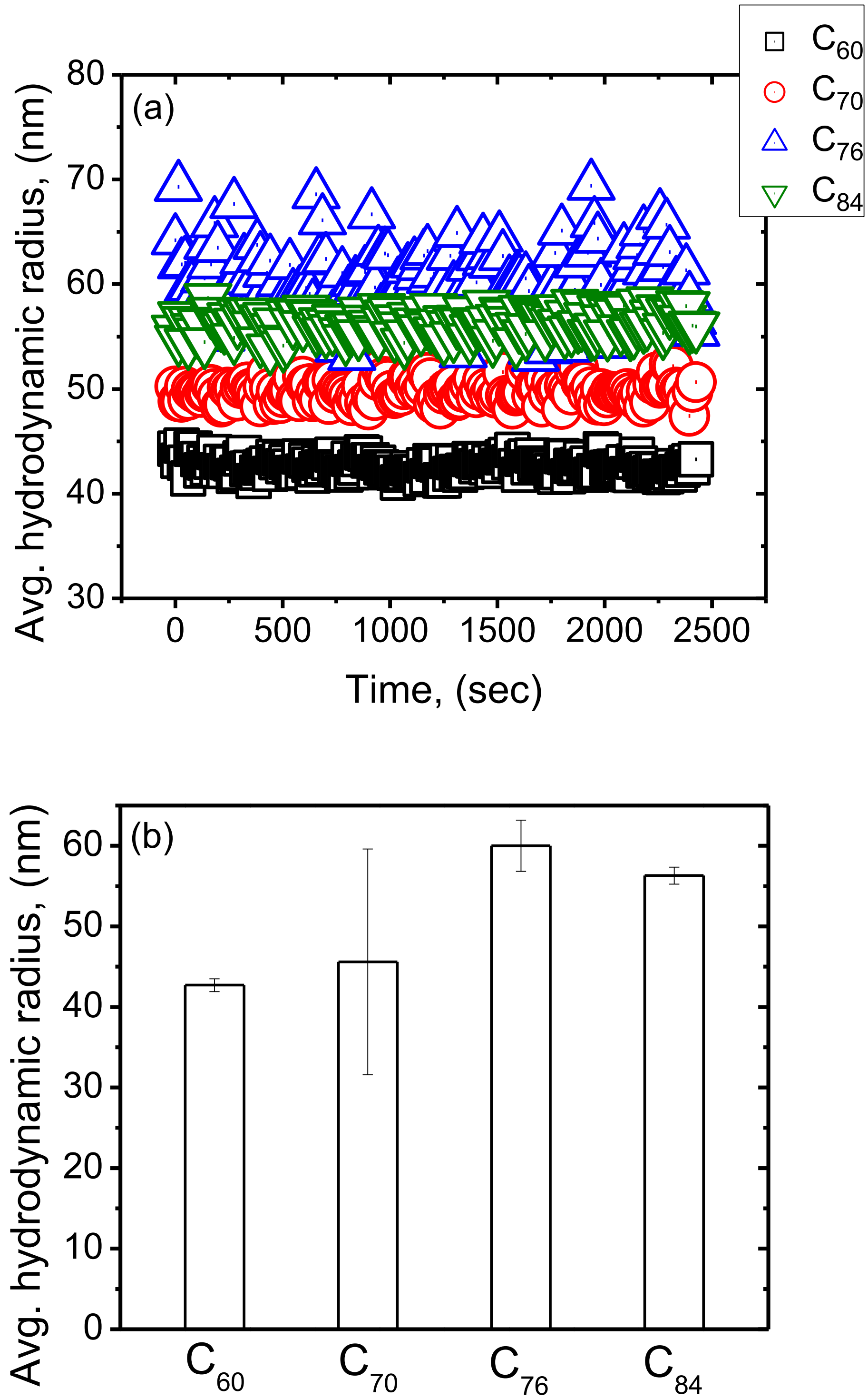

FIGURE 4.5. (a) Profile of hydrodynamic radii with time of higher fullerenes, immediately after synthesis. The profiles are representative of multiple stability runs. (b) Average hydrodynamic radii dataset for nC_{60}, nC_{70}, nC_{76}, and nC_{84} after synthesis. Error bars in (b) represents one standard deviation of the data collected for each case. All experiments are performed at 22±0.5 $^{\circ}$C temp.

The nC_{70} aqueous stability and size range of the clusters was also consistent with the literature presented data of 45 to 63 nm.[43, 51, 58] The nC_{76} and nC_{84} higher fullerene aqueous stability data are not presented prior to this study. The nC_{60} and the higher fullerene average cluster sizes are similar to each other.

4.4 Conclusions

Aqueous suspension of individual higher fullerenes, i.e., C_{70}, C_{76}, and C_{84}, have been successfully prepared using an energy based modification guided by *ab initio* calculation of interaction energy. Density functional theory simulation showed linear increase of interaction energy between fullerene pairs with the increase of carbon number. The enhanced energy need as observed in the experiments was in strong agreement with the favorable interaction energy obtained from first principles. The modified liquid-liquid extraction method produced stable colloidal suspensions of nC_{76} and nC_{84} fullerenes for the first time along with stable nC_{60} and nC_{70} suspensions. The stable nC_{60}, nC_{70}, nC_{76}, and nC_{84} clusters are similar in size (43-60 nm). The primary contribution of the paper include preparation of nC_{76} and nC_{84} stable aqueous suspensions as well as development of a systematic solubilization technique of higher fullerenes that is guided by molecular scale interaction energy estimations. This technique has potential to resolve the uncertainty involved in fullerene solubilization for size variation and varied stability with the change in simple parameters, such as sonicator variability. Such systematic energy-based solubilization technique of higher fullerene solubilization will likely aid in pursuance of future studies that focus on better applicability, determination of colloidal properties, and understanding of environmental fate, transport, and toxicity of such higher order fullerenes.

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Chapter 5: Preparation of Non-Aggregating Aqueous Fullerenes in Highly Saline Solutions with A Biocompatible Non-Ionic Polymer[****]

Abstract

Size-tunable stable aqueous fullerenes were prepared with different concentrations of biocompatible block-copolymer pluronic (PA) F-127, ranging from 0.001% to 1% (w/v). Size uniformity increased with the increase in PA concentration, yielding optimum 58.8±5.6 and 61.8±5.6 nm nC_{60}s and nC_{70}s, respectively (0.10 %w/v PA), as observed using dynamic light scattering technique. Fullerene aqueous suspensions also manifested enhanced stability in saline solution, Dulbecco's Modified Eagle Medium (DMEM), and Roswell Park Memorial Institute (RPMI) culture medium. Transmission electron microscopy was performed to elaborate on the morphology and size specificity of fullerene clusters. Physicochemical characterizations of the suspended fullerenes were performed through UV-Vis spectroscopy and electrophoretic mobility measurements. PA molecules showed size restriction by encasement, as observed via molecular dynamic simulation. Such solubilization with controllable size and non-aggregating behavior can facilitate application-enhancement and mechanistic environmental and toxicological studies of size-specific fullerenes.

Keywords: Fullerene; pluronic; biocompatible; size-tunable; stability

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5.1 Introduction

Fullerenes with 60 carbon atoms organized in a geodesic dome shaped structure—popularly known as buckyballs or buckminsterfullerenes[1] —as well as its homologues (e.g. C_{70}, C_{76}, C_{80}, C_{82}, C_{84}, etc.) and derivatives possess unique physicochemical, electronic, optical, and reactive properties.[2, 3] Such properties largely emanate from geometric orientation of the atoms that necessitate sp^2 hybridization and bond-bending to occur during the spheroid formation.[4] These novel properties encouraged their use in a wide application premise that include: nano-electronics,[5] biomedicine and drug delivery,[2] electrochemical, optical, and gas sensing,[6] industrial catalysis processes,[7] hydrogen storage and fuel cell technologies,[8] and environmental remediation.[9] Moreover, the near-symmetric higher fullerene structures are also known to enclose metal atoms, thus forming metallofullerenes[2] with novel medical, electronic, and structural reinforcement applications. Despite such a wide application premise, the fullerenes are also known to cause toxic responses while interacting with biological entities.[10] Dispersing these all-carbon fullerene molecules in water has been identified as a key challenge for their effective use in applications[11] as well as for mechanistic evaluation of their environmental and biological interactions.[12]

Buckyballs possess strong van der Waals[13] attraction between adjacent solubilized clusters and thus exhibit high aggregation propensity, resulting in a wide size range of agglomerated nC_{60}s. Such variations in size as well as the lack in stability are known to compromise fullerene applicability; e.g., in photovoltaic devices,[14] drug delivery systems,[2] and MRI contrast agents.[15] In photovoltaics, size specificity plays a key role in electron transport ability.[14] Absence of control over size and aqueous stability also reduces effectiveness of drug delivery and release—through differential uptake and uneven distribution[16] — while results in decreased water relaxivity for MRI imaging.[15] In addition, fullerenes' antitumor or antimicrobial potential faces limitations as their ability to produce reactive oxygen species (ROS) gets quenched due to aggregation.[17] ROS generation capability differs not only with aggregate size and degree of agglomeration but also varies between solubilization techniques.[18] In the contrary, this advantageous feature of ROS generation is identified as one of the key mechanisms for fullerene toxicity.[19] Fullerene's toxic effects have also been observed during *in vitro* studies on bacterial community,[19] soil microbes,[20] and human cell lines,[21] as well as *in vivo* exposures to aquatic species,[22] rats, and mice.[23] The identified mechanisms of toxicity include: ROS production, singlet oxygen generation, membrane oxidation, ROS-independent protein oxidation, etc.; which are largely influenced by aggregation of fullerenes.[19, 23] To extract most benefits from applications and to perform mechanistic evaluation of its biological interactions, preparation of stable fullerene suspensions with narrow size distribution is of immense importance.

Mechanochemical solubilization of fullerenes in water from apolar solvents is established as the primary technique to prepare aqueous colloidal fullerenes.[24] Other techniques for solubilization include: solvent exchange with toluene, tetrahydrofuran (THF), etc.;[24, 25] functional group (e.g., –OH, -COOH, -$CONH_2$, etc.) incorporation;[26] surface modification with solubilizing agents such as, triton X, polyvinyl pyrrolidone (PVP), cyclodextrine, polyethylene glycol (PEG), etc.;[27] and mechanochemical solubilization with magnetic stirring of dry fullerenes in water.[28] A substantial body of literature utilized soluble colloidal nC_{60} and studied their stability as well as interaction with biological and environmental interfaces.[19, 29] However, the field of fullerene application and implication has been continually challenged with the unresolved issues of size-specific effects. Moreover, inherent toxicity of the hazardous solvents used in solubilization, e.g., THF,[30] as well as the lack of biocompatible surface coatings continues to convolute fullerene toxicity mechanisms. Recent attempts of size control employing a mixture of relatively non-toxic volatile solvents, such as ethanol, hexane, and isopropyl alcohol,[31] are limited to organic solvent type and fail to be transferred to aqueous fullerene solubility. Similarly, a few biocompatible surfactants were successfully employed to solubilize fullerenes in water, however, failed to demonstrate control over size and stability.[32] The key data gap in the state-of-the-art literature is a preparation technique of size-specific biocompatible fullerenes and its derivatives, which will not only allow for maximizing their potential in applications but will also allow for evaluation of size-dependent toxicity and delineating mechanisms of their environmental and biological interactions. A recent study that presents preparation of pre-crystalized titanium dioxide nanoparticle suspensions stabilized with proteins and other biocompatible coatings[33] inspires this work. Biocompatible stabilization has been extended to carbonaceous nC_{60}s and nC_{70}s in this work.

This study presents a novel sonochemical technique that prepares size-specific aqueous nC_{60}s and nC_{70}s with high colloidal stability, even at elevated background ionic conditions. Biocompatible non-ionic poly(oxyethylene)-poly(oxypropylene) tri-block copolymer, pluronic acid (PA) F-127—recently been used in safe drug design and stabilization of carbon nanotubes and graphene[34] — is employed as the solubilizing agent. Carefully measured fixed mass of dry fullerene powders (C_{60} or C_{70}) were added individually to aqueous PA solutions at 0.001 to 1 (%w/v) concentration range and subjected to controlled ultrasonication. A subsequent centrifugation at 2500 ×g was performed on the sonicated samples to remove unsolubilized fullerenes and later decanted to obtain stable colloidal nC_{60}s and nC_{70}s. Controlled sonication and relative PA concentrations served as primary parameters to generate size-specific nC_{60}s and

nC_{70}s. Controlled size stable suspensions of fullerenes were tested under saline conditions (1 M NaCl) and in biological exposure medium, i.e., in Dulbecco's Modified Eagle Medium (DMEM) and Roswell Park Memorial Institute (RPMI) culture medium. Colloidal morphology and size determination were performed by transmission electron microscopy (TEM). The chemical characteristics are determined with ultraviolet-visible (UV-vis) spectroscopy, while surface charge properties are evaluated through electrokinetic measurements. Mechanisms of fullerene solubilization were evaluated with molecular dynamic (MD) simulation studies and utilizing classical polymer literature. Such tunable fullerene clusters with non-aggregating characteristics will enable enhanced application in nano-biomedicine and also in enumeration of size-specific toxicity mechanisms.

[The planning, experimental data collection and completion of the work was led by Nirupam Aich. Drs. Linkel Boateng and Joseph Flora performed the molecular dynamics simulations. Dr. Navid Saleh supervised the work.]

5.2 Materials and Methods

5.2.1 Preparation of PA modified Aqueous Fullerenes

C_{60} (99.9%) and C_{70} (98%) fullerene powders were procured from MER Corporation (Tucson, AZ) and Cheap Tubes Inc. (Brattleboro, VT), respectively; while commercially available pluronic acid (PA) F127 was obtained from Sigma Aldrich (St. Louise, MO). PA powder was added to filtered deionized water (DI) (Barnstead) to produce 0.001, 0.005, 0.020, 0.10, 0.50, and 1.00 (%w/v) solutions. 5 mg of dry C_{60} or C_{70} was added to 10 mL of PA solution and sonicated for 30 min with ultrasonic dismembrator S-4000 (Misonix, Inc. Farmingdale, NY) at controlled input energy of 31-33 kJ. The sonicated samples were then transferred to 15 mL centrifuge vials and centrifuged at an acceleration of 2500 ×g for 4 h with Eppendorf 5810R (Eppendorf, Hamburg, Germany) and decanted to separate colloidal fullerenes from undissolved ones. The resultant supernatant suspensions were yellow and wine colored in appearance for C_{60} and C_{70} suspensions, respectively. The color intensity showed gradual increase with the increase of PA concentrations. The solubilization procedure was replicated at least once for each case under identical conditions and. The prepared suspensions were stored at 4 °C.

5.2.2 Physicochemical Characterization of Aqueous Fullerenes

Electron microscopy, UV-visible spectroscopy, electrophoresis, and dynamic light scattering were performed to characterize the colloidal fullerenes in terms of their morphological and chemical properties, electrokinetic properties, and stability and size distribution.

Transmission electron microscopy (TEM) of nC_{60} and nC_{70} suspensions was performed using an H-9500 Hitachi High Technologies America, Inc, Pleasanton, CA TEM (Clemson University microscope facilities). Two or three drops of the aqueous suspensions were added to copper TEM grids, coated with carbon film (Ted Pella Inc, Redding, CA) and allowed to air dry for a few min prior placing in the vacuum chamber. Imaging was performed at 300 kV accelerating voltage and at different magnifications and in a number of grid sections to obtain representative micrographs.

Agilent 8453 UV-visible spectroscopic system (Santa Clara, CA) was used to characterize chemical signatures of colloidal fullerenes. A 2 mL fullerene suspension (with no dilution) for each PA concentration was introduced to a clean quartz cuvette. Deionized water was used to establish a baseline prior to fullerene absorbance measurements. Representative spectrum was obtained for 200-1000 nm spectral range from at least three spectral scans for each fullerene suspension.

Electrokinetic measurements were performed on a Brookhaven ZetaPALS (Brookhaven Instrument Corporation, Holtsville, NY) instrument. 2 mL sample was introduced to the disposable cuvettes with no dilution for low pluronic concentrations (0.001 %w/v). For nC_{60} suspensions prepared at 0.005 and 0.020 %w/v PA concentrations, a dilution factor of 5 was used while the rest of the samples were diluted at least 10 times prior to measurement. Triplicates of each sample were run for at least 10 measurements for each replicate. The ξ-potentials of the fullerenes were obtained by converting values of the electrophoretic mobilities using Smoluchowski relationship.[35]

5.2.3 Colloidal Stability of PA-modified nC_{60}s and nC_{70}s

Colloidal size distribution of the PA solubilized nC_{60}s and nC_{70}s in various media conditions were determined using time resolved dynamic light scattering (TRDLS) technique. ALV/CGS-3 compact goniometer system (ALV-Laser Vertriebsgesellschaft m-b.H., Langen/Hessen, Germany) equipped with 22 mW HeNe 632 nm Laser was used to perform such measurements. Detailed description of the equipment and the measurement protocol can be found elsewhere.[36] Highly saline background, i.e., 1 M NaCl solution, Dulbecco's Modified Eagle Medium (DMEM) obtained from Gibco (Life Technologies Inc, Grand Island, NY), and Roswell Park Memorial Institute (RPMI) culture medium at 1× strength were used to evaluate fullerene aggregation characteristics in elevated electrolyte and biologically relevant media conditions. Briefly, 2 mL of fullerene suspensions, diluted at least 100 times either with filtered DI water or with respective biological media was added to pre-cleaned borosilicate glass vials[29] and vortexed with a VWR Vortex mixer (Henry Troemner LLC., Thorofare, NJ). A Perking Elmer (Dumberry, Canada) photon counter in the goniometer was set a scattering angle of 90 °C, which detected scattered light from in every 15 s for at least 15 min duration. The average hydrodynamic radii of fullerenes were estimated from the scattering data with built-in cumulant algorithm.

5.2.4 Molecular Dynamics Simulation

Interaction energies between single fullerene molecules and sections of the PA polymer were calculated using procedures outlined in Zaib et al.[37] An 8-chain ethylene oxide polymer and a 10-chain propylene oxide polymer were constructed using Gaussview[38] to represent the edge and center sections of the larger PA molecule. The initial geometry of the fullerene molecules was obtained from Yoshida[39] and the isomers used for the calculations were C60-Ih and C70-D5h. The geometries of the polymer sections and fullerenes were optimized with dispersion-corrected density functional theory[40] using the BLYP functional and the 6-31++G(d,p) basis set using TeraChem.[41] The effective fragment potential of the polymer sections and fullerenes were generated in GAMESS at the STO-3G level using numerical distributed multipole analysis and neglecting charge transfer.[42, 43] Geometry optimization of the fragments of the molecules was also performed using GAMESS. The initial geometries of the fragments were obtained by randomly locating the center of the individual fullerenes between 1.5 to 5 Å around the center of each polymer section. A total of 10,000 optimized configurations were collected and the lowest energy configuration was selected for further geometry optimization at the BLYP-D3/6-31++G(d,p) level.

Initial geometries of dimmers of ethylene oxide and propylene oxide were generated in Gaussview and residues were generated using the antechamber and preen modules of Amber tools.[44] The full PA polymer was constructed by sequencing the residues in tleap. Twelve and ninety-six molecule clusters of C_{60} and C_{70} were generated by optimizing fragment geometries as described in the previous paragraph.

An explicit solvent molecular dynamics (MD) simulations of the PA polymer with $12C_{60}$ and $12C_{70}$ fullerene clusters was conducted using the AMBER 12 MD package[44] to investigate the effect of PA on fullerene cluster sizes in aqueous solution. The force fields for the PA, C_{60}, and C_{70} were generated using the antechamber module in AMBER with AM1-BCC charges. A 20 ns simulation was conducted to equilibrate the PA polymer and the fullerene clusters in vacuo. The PA was subsequently solvated with a TIP4P water box of dimensions 70 × 72 × 73 $Å^3$ and further equilibrated for 20 ns to ensure structural relaxation of the sections. Simulations of the PA-12C_{60} and PA-12C_{70} complexes were conducted under the NPT ensemble with periodic boundary conditions. The thermostat was regulated using Langevin dynamics with a collision frequency of 2 ps^{-1}. The solvated PA-12C_{60} and PA-12C_{70} complexes were initially optimized to remove bad contacts and further heated to 300 K over a period of 100 ps while restraining the complexes with a force of 2.0 kcal/mol-$Å^2$. This was followed by a 100 ps constant pressure simulation to set the system density to that of bulk water. The restraint on the complexes was subsequently removed and the system was further equilibrated for 10 ns. A final NPT simulation was conducted at 300 K and 1 atm pressure for 200 ns and the coordinates were saved every 100 ps for post-processing. The long-range electrostatic interactions were computed using Particle Mesh Ewald approach and the non-bonded interactions were subjected to a cutoff of 8 Å.[45] 2000 snapshots were obtained from the sampled trajectory and the last 50 ns were used to calculate the binding free energies by means of the molecular mechanics Poisson-Boltzmann surface area (MM/PBSA)[46] approach.

5.3 Results and Discussion

5.3.1 Morphology and Chemical Characteristics

nC_{60}s and nC_{70}s were characterized with TEM to evaluate their physical morphology, while UV-vis spectra were obtained for probing the chemical nature of these aqueous fullerenes. Figure 5.1 shows representative TEM micrographs of nC_{60} (a-c) and nC_{70} (d-f) with increasing percentage of PA usage—from left to right of image sequence—during solubilization. Overall, the micrographs showed crystalline fullerenes that are relatively spherical with rounded edges.

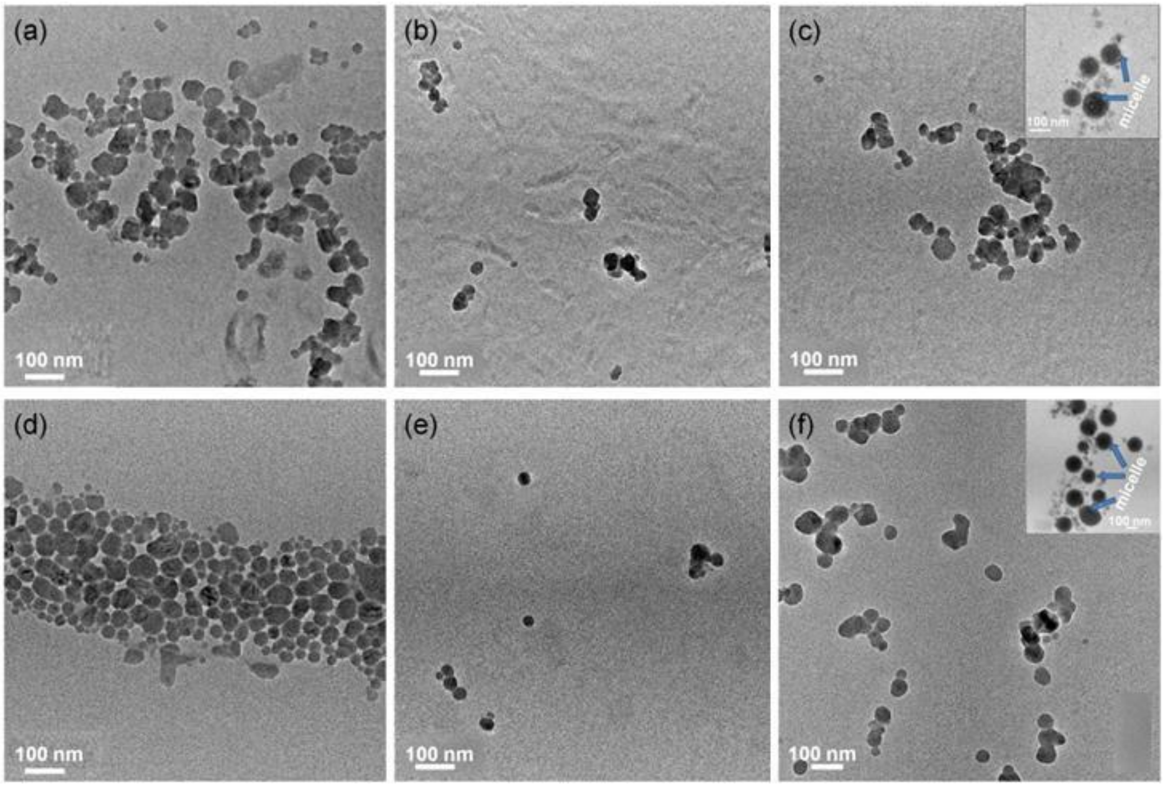

FIGURE 5.1. Representative TEM micrographs of (a-c) nC_{60} and (d-f) nC_{70} with low, medium, and high PA concentrations (0.001-0.005, 0.02-0.10, and 0.5-1.0 % w/v). Inset images in (c) and (f) show PA micelle structures as observed at the high concentration cases.

nC_{60}s and nC_{70}s showed relatively uniform size distribution, however, with noticeable clustering. TEM images in Figure 5.1(a) and (d) showed the largest clusters of nC_{60}s and nC_{70}s when solubilized with the lowest percentage of PA (0.001-0.005 %w/v). These particles have average sizes of 75-80 and 70-80 nm respectively for nC_{60}s and nC_{70}s, with relatively wider distribution. The minimum average sizes for nC_{60}s were observed with the use of moderate PA concentration (0.02-0.1 %w/v) and for nC_{70} with 0.1 %w/v PA. Clusters in these categories averaged 50-55 and 55-60 nm with narrow size distribution, as shown in Figure 5.1 (b) and (d), respectively. A slight increase in size—i.e., 55-65 nm for both fullerenes—was noticed with elevated PA use (0.5-1.0 %w/v). Relatively higher uniformity in size of the fullerenes were also observed for higher PA cases; as represented in Figure 5.1 (b-c) and (e-f) compared to (a) and (d). In addition, perfectly spherical features were also observed with higher PA amount (0.5-1.0 %w/v) as shown in Figure 5.1c and f insets. These uniquely circular structures are believed to be micelles formed when PA molecules were used above their critical micelle concentration (CMC). Commonly reported TEM images showed crystalline fullerenes with wide size variation.[47] Earlier literature reports also presented similar spherical features with internal porosity—as observed with contrasted density—representing PA micelles.[48]

The chemical signatures of fullerenes were studied with UV-vis spectroscopy as shown in Figure 5.2. The spectra showed two peak occurrences at 267 and 346 nm for nC_{60}, for all PA concentrations (Figure 5.2a). However, the relative magnitudes of the peaks, likely representing relative concentration of solubilized fullerenes,[49] showed consistent increase with the increase of PA percentages. Higher solubility of fullerenes with increased PA amounts was also observed, qualitatively, in Figure C-1. In addition, the nature of the peaks appeared to be more defined with the increased PA concentrations. A secondary peak at 207 nm was observed for low PA cases (0.001-0.005 % w/v), which showed a rightward shift to 217 nm for the moderate and higher PA concentrations. The peak broadening in the lower PA percentages suggested presence of larger sized fullerenes in the suspension.[50] On the other hand, nC_{70}s showed strong characteristic absorbance at 386 nm at all PA concentrations. A wide lower-absorbance peak at 210-300 nm was observed to occur, acquiring a more defined feature at moderate and high PA percentages. UV-vis absorbance spectra for nC_{70} also showed a wide shoulder, above 486 nm wavelength. Literature reported peak values are consistent with these observations showing range of 216-218, 264-265, and 339-341 nm for nC_{60}[24, 25] and 386 and 480 nm for nC_{70}[25] aqueous fullerenes.

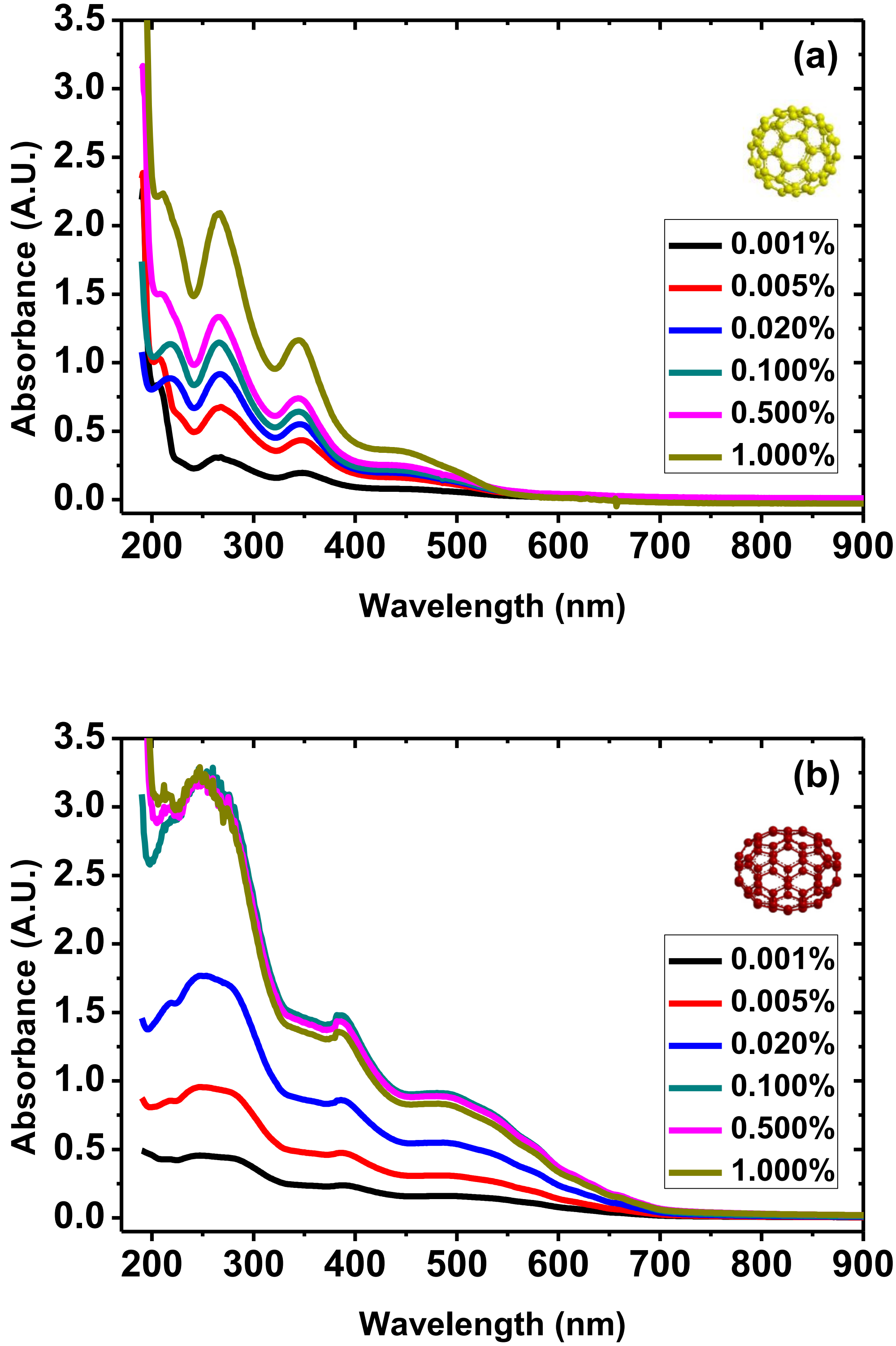

FIGURE 5.2. Representative UV-vis spectra of stable (a) nC_{60} and (b) nC_{70} aqueous suspensions, prepared with a range of PA concentration. All measurements were performed at 21±1 °C.

5.3.2 Electrokinetic Properties

The surface potentials of PA solubilized fullerenes were characterized with □-potential measurements, as presented in Figure 5.3. nC_{60} and nC_{70} showed similar ζ-potential values with a range of -35.4±7.2 to -42.9±7.9 mV and -30.5±6.2 to -41.1±11.3 mV, respectively (Figure 5.3); with no dependence on relative PA concentrations. The values are in good agreement with the literature reported range of -30 to -70 mV for nC_{60}[24, 25, 51] and -39 to -63 mV for nC_{70}[24, 28] fullerene suspensions.[24, 29] The reported surface potential range (i.e., > -30 mV) represented substantial electrostatic stabilization of fullerenes.[25] Though the origin of surface charge on such all-carbon structures are not definitive, possible mechanisms, such as functional group formation, electron cloud distortion, fullerene and water-shell interaction, etc., are postulated in the literature.[52] At elevated background ionic strength (≥30 mM NaCl) the electrostatic potential values of fullerenes showed significant decrease as presented in Figure 5.3(b). Overall, the ξ-potential in these conditions had a small range—with values in the range of -11.2±4.7 to -15.3±6.4 mV and -11.1±4.3 to -14.1±4.5 mV for nC_{60} and nC_{70}, respectively—with no dependence on relative PA concentration. Such decrease in ξ-potential had likely occurred from electrostatic screening in presence of cationic electrolytes, as consistently observed in the earlier literature.[29]

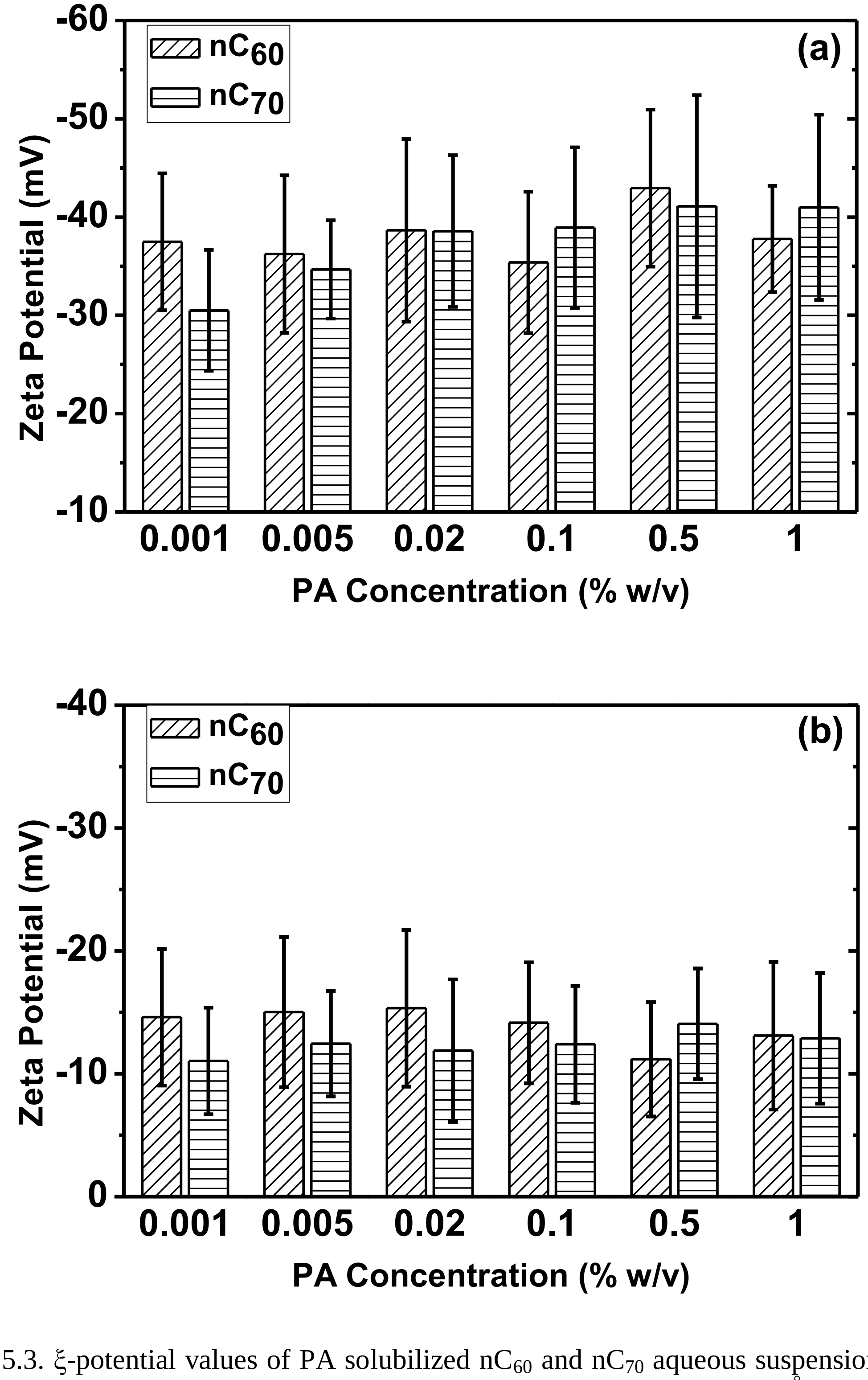

FIGURE 5.3. ξ-potential values of PA solubilized nC_{60} and nC_{70} aqueous suspensions in (a) DI water and (b) with 30 mM NaCl. All measurements are performed at 22± 0.5 °C. The pH values were in the range of 6.9-8 for all the measurements.

5.3.3 Effects of PA on Fullerene Size

PA F-127 modification yielded highly stable aqueous nC_{60}s (Figure C-1a) and nC_{70}s (Figure C-1b). The aqueous suspensions of fullerenes showed consistent hydrodynamic radii over time, an additional testament to their stability (Figure C-2). Increase in PA concentration profoundly affected the cluster sizes and distributions of solubilized nC_{60}s (Figure 5.4a-b) and nC_{70}s (Figure 5.4c-d). Overall, average hydrodynamic radii of nC_{60} (Figure 5.4a) and nC_{70} (Figure 5.4c) decreased from 89.6±8.7 nm to 58.8±5.6 nm and 85.9±7.3 nm to 61.8±5.6 nm, respectively, with the increase in PA percentages from 0.001 to 0.100 %. However, further increase in PA concentration, i.e., to a range of 0.5-1.0 %w/v, resulted in a plateau for average size—showing values of 59.3±3.4 nm to 61.4±3.3 nm and 62.3±2.9 nm to 60.9±4.3 nm for nC_{60}s and nC_{70}s, respectively. Higher PA concentrations not only impacted the size but also enhanced uniformity of clusters for both nC_{60} (Figure 5.4b) and nC_{70} (Figure 5.4d). The fullerene size distributions appeared to be relatively wider for low PA concentrations (Figure 5.4b and d) indicating to a lower size-specificity. This was consistent with the observations in TEM imaging (Figure 5.1) and with the higher standard deviation for the colloidal sizes (Figure 5.4a and c). Interestingly, the narrowest distribution was observed for 0.10 %w/v PA cases, which slightly widened with further increase in PA concentration. The relative uniformity of fullerenes was also demonstrated with extremely low polydispersity index, i.e., 0.06±0.02 to 0.25±0.03, as presented in Table C-1. Such size uniformity, and aqueous solubilization with PA had been observed elsewhere for other graphitic nanomaterials; i.e., for graphene,[53] single-walled[54] and multi-walled[55] carbon nanotubes (SWNTs and MWNTs).

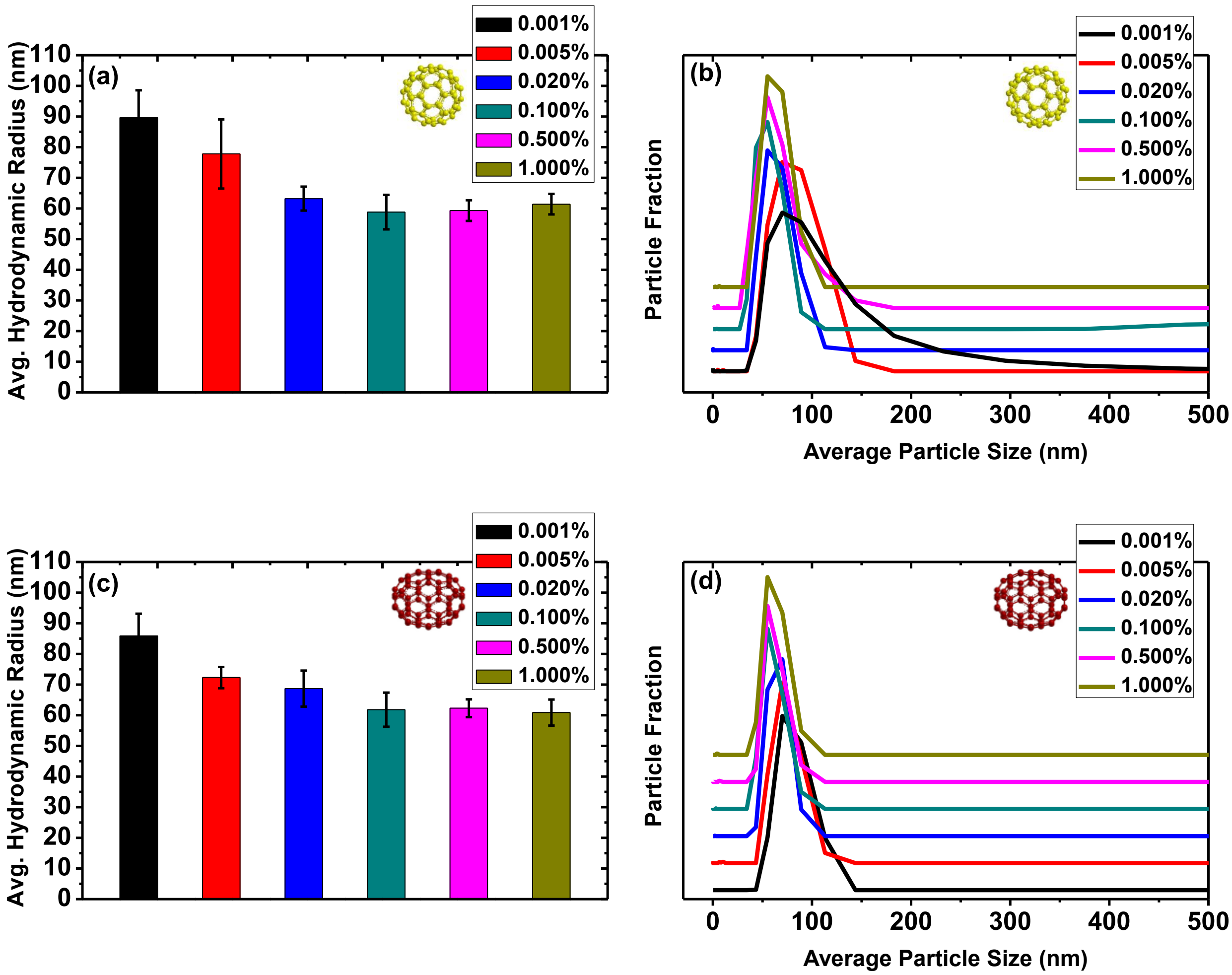

FIGURE 5.4. Average hydrodynamic radii of aqueous (a) nC_{60} and (c) nC_{70} prepared with a range of PA concentration. Particle size distributions of (b) nC_{60}s and (d) nC_{70}s for each of the synthesis conditions. The average and standard deviation values are estimated from two individually synthesized samples, replicated under identical conditions. The size distributions represent representative profiles of fullerene cluster sizes obtained with cumulant fit analysis. Experiments were performed at 22±0.5 °C.

The most effective cleaving of graphite layers as well as debundling of SWNTs and MWNTs occurred with 1-5 %w/v PA addition.[53, 54] At such conditions, a minimum layer thickness of ~4 nm for cleaved nano-graphite was achieved;[53] while optimized length was reported to be 140 and 150 nm for SWNTs[54] and MWNTs,[55] respectively. Moreover, relative increase in solubilized nanotube mass was consistently observed with the increase in PA concentrations;[54] where optimization of relative PA amounts as well as choice of preparation techniques, i.e., between sonication, stirring, and their combinations,[56] were pursued. However, systematic studies for fullerene solubilization with biocompatible PA have not been reported to date.

5.3.4 Mechanisms of PA Solubilization

Water serves as a 'bad-solvent' for the all-carbon fullerene structures[57] and thus results in aggregation and virtual insolubility for these molecules. Fullerene compatibility with water is usually improved with either organic solvents[24] or imparting functional groups onto their surfaces,[24] as discussed earlier. Surfactants and polymers are also employed to minimize unfavorable interaction energy between hydrophobic fullerene surfaces and surrounding water molecules through introduction of an adsorbed lyophilic layer.[27] Applying the latter strategy, non-ionic amphiphilic block copolymer, pluronic acid (PA), with 12,500 Da average molecular weight,[58] served to create such apparent lyophilicity. This was possible because PA contains hydrophobic polypropylene oxide (PPO) middle-blocks, flanged with equal length of polyethylene oxide (PEO) hydrophilic side-blocks. Earlier literature reporting confirmed specific hydrophobic (or lyophilic) interactions between the central PPO blocks and all-carbon structures, such as graphene[34] and carbon nanotubes.[54]

The amphiphilic nature of PA block copolymer probably allowed similar hydrophobic interactions with both C_{60} and C_{70} molecules, where the PEO blocks provided necessary water compatibility. The lower concentration of PA amphiphiles allowed for adsorption of these molecules onto both C_{60} and C_{70} surfaces and enabled their aqueous solubilization. As the PA concentration was increased, the surface coverage of the block copolymers also increased and thus enabled cluster formation with lower average size. Plateauing of cluster size above in the range of 0.5-1.0 %w/v PA indicates potential surface saturation of the block co-polymers. Such size-plateau, interestingly occurred near and above the CMC of PA F-127, which is 0.79 mM or

1 %w/v (measured at 24.5 °C).[59] Approximately, 100 nm sized micelle formation was observed in higher concentration cases, i.e., for 0.5-1.0 %w/v or 0.7 to 1.0 ×CMC of PA (Figure C-3). Such shift in CMC was previously reported in presence of additional sorption surfaces.[59] A relative competition between micelle formation and adsorption to fullerenes probably caused PA macromolecules to slightly widen fullerene size distributions. This was observed in Figure 5.4 (b) and (d) with PA concentrations near or above the CMC. Moreover, classical polymer sorption literature identifies surface curvature as a key parameter influencing PA interaction energy and thereby its sorption density[60] on surfaces. PA surface conformation was further probed with MD simulation (Figures C-4 to C-6 and Figure 5.5).

Figure C-4 showed that the edge and center sections of the PA molecule interacted favorably with the individual fullerenes. Despite the short sections simulated, the edge with ethylene oxide remained linear after geometry optimization while the central polypropylene oxide block developed a slight curvature due to the presence of the methyl groups. The curvature became pronounced in both sections when interacting with the fullerene molecules. The edge block had more favorable interaction energy with the fullerenes than the center block. It's likely that the methyl groups of the central block limited the interaction of the fullerene with the polymer backbone. These calculations at the BLYP-D3/6-31++G(d,p) level demonstrate that the PA polymer will favorably adsorb to the fullerene cluster. MD simulations were performed to evaluate the interaction of fullerene clusters with PA polymer in the presence of water and at room temperature.

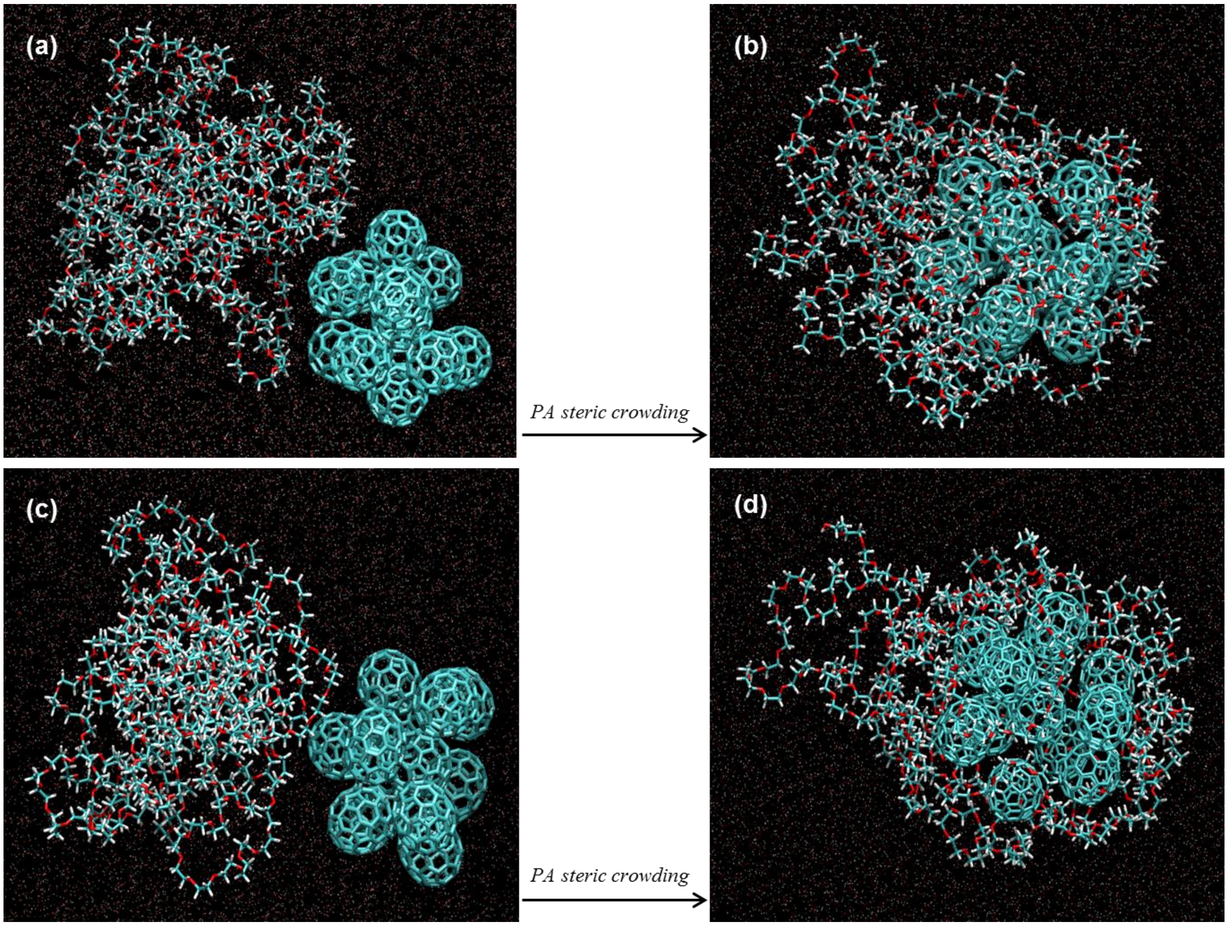

FIGURE 5.5. Representative MD snapshot of (a) PA-12C_{60} starting configuration (b) PA-12C_{60} configuration after 200 ns simulation (c) PA-12C_{70} starting configuration (d) PA-12C_{70} configuration after 200 ns simulation. (Visualized using Visual Molecular Dynamics).

Representative MD snapshots presented in Figure 5.5, showed the conformations of the PA-12C_{60} and PA- 12C_{70} complexes obtained after a 200 ns NPT simulation at 300 K and 1 atm pressure. The PA polymer tended to envelope the smaller 12C_{60} and 12C_{70} fullerene clusters and maximizes hydrophobic interactions between the fullerenes and the PA segments. The simulation indicates that interaction of PA-12 C_{60} and PA-12C_{70} in aqueous solutions was quite strong with interaction energy values of –92.3 ± 12.8 and –106.5 ± 15.3 kcal mol^{-1}, respectively. Such strong interaction indicates preferential binding affinity of the PA molecules to fullerenes and thus potentially restricting the size by physical encasement. Moreover, time-dependent van der Waals interaction energies calculated for PA molecules and $96C_{60}$ and $96C_{70}$ clusters also indicates that PA had highly favorable interaction even with this larger fullerene set (Figure C-5). The free energy associated with the binding of PA molecules with $96C_{60}$ and $96C_{70}$ were determined as –158.6 ± 20.0 kcal mol^{-1} and –186.4 ± 21.5 kcal mol^{-1}, respectively. Moreover, conformation of PA-$96C_{60}$ and PA- $96C_{70}$ shown in Figure S6 indicated that the PA molecules were associated closely with the 96 fullerene clusters. However, the relatively low PA to fullerene ratio likely resulted in steric crowding of the PA molecules and thus disallowed effective encasement of the larger fullerene set (Figure C-6). This result allowed explaining effective size control of nC_{60} and nC_{70} clusters in presence of higher PA to fullerene ratio through physical encasement. Such size restriction via PA coverage failed to occur at low PA to fullerene ratio and resulted in steric crowding of PA around the fullerenes.

5.3.5 Effect of Media Conditions on Fullerene Stability

Fullerene aggregation potential was tested not only with time but more importantly under high electrolyte concentrations. Average hydrodynamic radii of both nC_{60}s (Figure 5.6a) and nC_{70}s (Figure 5.6b) did not show any aggregation in presence of either 1 M NaCl, or with concentrated RPMI and DMEM biological exposure media over 15-25 minute period. Such resistance to elevated electrolyte conditions was demonstrated with unchanged aggregate size (with time) under all the above-mentioned conditions (Figure C-7). This indicated their potential suitability in the cytotoxic assay which will be evaluated for longer time periods (i.e. over 24 to 48 hours); however will require systematic evaluation of stability for longer time periods in the future. The PA amphiphiles, possessing strong hydrophilic side-blocks, did not respond to electrolytes due to the lack in charged functional group presence along the backbone.[58]

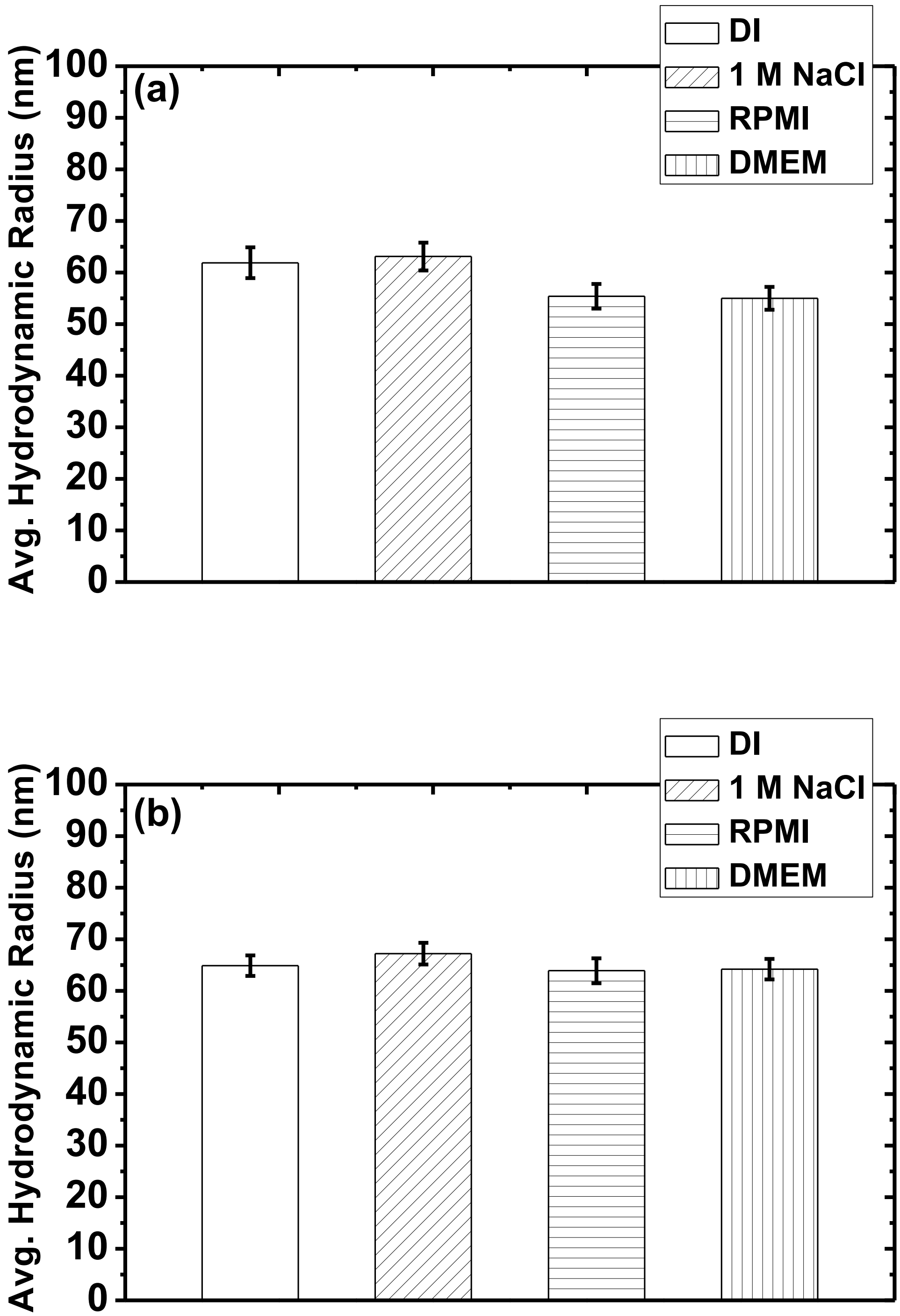

FIGURE 5.6. Average hydrodynamic radii of aqueous (a) nC_{60} and (b) nC_{70} under saline and biological media conditions. Only 0.02% w/v PA concentration cases are presented in this figure. Replicate measurements were performed at 22±0.5 °C.

Such electrolyte resistance was reported earlier for other all-carbon structures, e.g., PA modified graphene[34] and nanotubes.[54] The enhanced non-aggregating behavior of the fullerenes under high electrolyte conditions had likely resulted from steric repulsive interaction, imparted by the adsorbed PA molecules; consistently observed earlier in the literature.[34] In presence of low electrolytes, electrosteric repulsion has favorably contributed to fullerene stability; which shifted to steric contribution only at higher electrolyte cases. This mechanism can also be supported from the demonstration of substantial ξ-potential lowering with ionic strength elevation, as presented in Figure 5.3. Such steric repulsion mediated non-aggregating clusters of nC_{60}s and nC_{70}s will likely aid in toxicological studies. Achieved control over the particle size homogeneity will allow avoiding convolution of toxicity mechanisms (due to aggregation) and thereby will enable systematic evaluation of size-dependent biological uptake and toxicity. Moreover, aqueous suspension preparation of fullerenes with biocompatible PA coatings will offer eliminate complication from solvent induced toxicity.

5.4 Conclusion

Aggregation and lack of homogeneity in particle size distribution have limited the applicability of aqueous fullerenes and convoluted understanding of their toxicity mechanisms. This chapter describes a novel method for synthesis and characterization of nC_{60} and nC_{70} fullerenes using pluronic acid (PA) – a biocompatible triblock copolymer. Resultant fullerenes achieved stable sizes with narrow size distributions. They presented non-aggregating behavior when exposed to elevated electrolyte concentrations due to PA-induced steric hindrance. Such control over size-specificity as well as increased colloidal stability will allow for their use in various applications, such as: targeted drug delivery, photovoltaic devices, high contrast MRI agents, etc.

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Chapter 6: Aggregation Kinetics of Higher Order Fullerenes in Aquatic Systems[*****]

Abstract

Aggregation kinetics of nC_{60}s and higher order fullerenes (HOFs), i.e., nC_{70}, nC_{76}, and nC_{84}, was systematically studied under a wide range of mono- (NaCl, 10-650 mM) and di-valent ($CaCl_2$, 1-38 mM) electrolytes, using time-resolved dynamic light scattering. Suwannee River Humic Acid (SRHA) was used to examine the effect of natural organic matter on nHOF aggregation. Increases in electrolyte concentration resulted in electrical double layer compression of the negatively charged fullerene clusters, and the nC_{60}s and nHOFs alike displayed classical Derjaguin-Landau-Verwey-Overbeek (DLVO) type interactions. The critical coagulation concentration (CCC) displayed a strong negative correlation with carbon number in the fullerenes, and was estimated as 220, 150, 100, and 70 mM NaCl, and 10, 12, 6, and 7.5 mM $CaCl_2$ for nC_{60}, nC_{70}, nC_{76}, and nC_{84}, respectively. The aggregation mechanism, i.e., van der Waals interaction domination, was investigated via molecular dynamics simulation and modified DLVO model. The presence of SRHA (2.5 mg TOC/L) profoundly influenced the aggregation behavior by stabilizing all fullerene clusters, even at 100 mM NaCl concentration. The results from this study can be utilized to predict aggregation kinetics of nHOFs other than the ones studied here. The scaling factor for van der Waals interaction also can be used to model nHOF interaction.

[*****]Aich, N.; Boateng, L. K.; Sabaraya, I. V.; Das, D.; Flora, J. R. V.; Saleh, N. B., Aggregation kinetics of higher order fullerenes in aquatic systems. *Environ. Sci. Technol.* **2015.** (In Review)

6.1 Introduction

Carbon allotropes that form truncated icosahedrons following the isolated pentagon rule (IPR) are known as fullerenes.[1] Highly stable structures of fullerenes display unique electronic, chemical, optical, and thermal properties, thus encouraging their synthesis, derivatization, and use.[2] Fullerenes with 60 carbon atoms are the most separated and used; similar structures with higher number of carbon atoms are known as higher order fullerenes (HOFs), and these larger fullerene cages display unique advantages over C_{60}s.[3] The increase in carbon number modulates their band gap,[4] introduces ambipolar electronic transport characteristics,[5] and increases electron affinity,[6] making HOFs highly desired for use in cosmetics,[7] electronics and energy,[2] and biomedical[8, 9] applications. The attractive applications of HOFs necessitate assessment of environmental health and safety (EHS) of this important carbon allotrope class.[2, 10]

HOFs possess unique physicochemical properties. With the increase in carbon number, the symmetry of the HOF cages shifts from spherical or truncated icosahedrons (for C_{60}) to ellipsoidal (for C_{70}) to irregular (for C_{76}).[4] Larger carbon structures of HOFs with altered geometric shapes lead to differences in electronic properties and solvent interactions (compared to C_{60}s).[3, 4] Improved electrical properties of these higher carbon structures, i.e., lower band gap, ability to simultaneous display n- and p-type junction behavior, higher electron affinities, and charge mobility, are considered valuable in organic field-effect transistors (OFETs), solar-cells, and photovoltaics.[2, 11, 12] Such properties also are shown to lead to the generation of reactive oxygen species (ROS).[13] HOFs have been utilized to encase transition and rare earth metals and form endohedral metallofullerenes (EMFs). For example, EMFs produced by stabilization of Gd, Sc, or Lu metal atoms inside C_{60} and other HOF cages have shown to provide 20-500 times higher proton relaxation in magnetic resonance imaging (MRI) applications, when compared to commercially used chelated-Gd.[14, 15] Furthermore, these EMFs have shown ROS-scavenging ability to protect cells from tumour growth and are attractive as chemotherapeutics.[16] With a multibillion dollar future market for MRI agents,[17] nanomedicine,[18] and photovoltaics,[19] understanding the environmental implications of HOFs is imperative.

Upon release to the aquatic environment, nC_{60}s and nHOFs will undergo aggregation, a key interfacial process, which influences environmental mobility, bioavailability, and ecotoxicity.[2] Aggregation studies of fullerenes have primarily been restricted to nC_{60}s. Aqueous solubilization of C_{60}s was achieved via solvent extraction and mechanochemistry, where the nC_{60}s have shown to possess negative surface potential.[20] Though the origin of surface charge of nC_{60} colloids is largely unresolved,[21] aqueous stability and aggregation kinetics of these fullerene clusters have been studied extensively under a wide range of environmental conditions, which include electrolyte concentration and type,[22] and presence of geo- and bio-molecules[23]. These nC_{60} clusters have shown to follow classical Derjaguin-Landau-Verwey-Overbeek (DLVO) type interaction[21] where surface potential is found to be uniformly distributed to allow the DLVO theory to adequately capture the aggregation process. Derivatives of C_{60}s also have been studied, where the stability of photochemically transformed fullerols and chemically reacted fullerene derivatives has been assessed.[24, 25] However, studies of the aqueous solubilization and stability of HOF clusters are limited[10, 26], thus leaving a critical data gap in assessing aggregation behavior of these higher carbon allotropes.

HOFs, due to increased carbon number and unique atomic orientation have displayed different electron affinities[6] and electron transfer capabilities[27] compared to the C_{60}s and will likely lead to changes in their surface potential. Non-spherical geometry of the HOFs have shown to decrease band gap and also reduce their solvent affinity.[4] The van der Waals attraction of fullerenes also has been shown to follow a $n^{2.2\sim2.75}$ scaling law (n represents carbon number).[28] Such increased particle-particle attraction, higher binding energies,[10] and altered electrokinetics of nHOFs will likely have a strong influence on their aggregation propensity and thus necessitate systematic assessment of such interfacial behavior.

This is a fundamental study that systematically assessesed nC_{60} and nHOF aggregation kinetics in an aquatic environment. A toluene-ethanol-water solvent extraction method was employed to solubilize nC_{60}, nC_{70}, nC_{76}, and nC_{84} clusters. Morphological, chemical, and electrokinetic characteristics of the aqueous nC_{60} and nHOFs were determined using transmission electron and atomic force microscopies (TEM and AFM), UV-visible spectroscopy, and electrophoretic mobility (EPM) measurements, respectively. Aggregation rates of nC_{60}s and nHOFs were measured with time-resolved dynamic light scattering (TRDLS) under a wide range of mono- and di-valent electrolyte concentrations and also in the presence of Suwannee River humic acid (SRHA). Mechanisms of aggregation were deciphered using physicochemical characterization, molecular-scale interaction energies determined via molecular dynamics (MD) simulations, and modified DLVO theory.

[The planning, experimental data collection, analyses, and completion of the work was led by Nirupam Aich. Drs. Linkel Boateng and Joseph Flora performed molecular dynamics simulations. Indu Venu Sabaraya helped in writing the introduction section. Dipesh Das helped in performing electrokinetic property measurement. Dr. Navid Saleh supervised the work.]

6.2 Materials and Methods

6.2.1 Aqueous Fullerene Suspension Preparation

A modified calorimetric technique was utilized to prepare the aqueous suspensions of the fullerene clusters.[10] Each of the commercially available fullerene molecules, i.e., 99.9% pure C_{60} (MER Corporation, Tucson, AZ), 98% pure C_{70} (Cheap Tubes Inc., Brattleboro, VT), 98.1%

pure C_{76} (BuckyUSA, Houston, TX), and >98% pure C_{84} (SES Research Inc., Houston, TX) were first dissolved in HPLC grade toluene (Sigma-Aldrich, St. Louise, MO). The amounts of dry fullerenes to toluene proportion used were 1:1.25 (mg:mL) and the mixtures were magnetically stirred for 30 min. Each toluene suspension was then transferred to a mixture of 60 mL deionized water (DI) and 2 mL ethanol (Sigma-Aldrich, St. Louis, MO). This mixture with a fullerene-water proportion of 1:15 (mg:mL) was sonicated in a fume hood using an ultrasonic dismembrator Q700 (Qsonica, LLC. Newtown, CT) for 3.0, 5.5, 7.5, and 13.0 h, to accommodate for the energy need in solubilizing C_{60}, C_{70}, C_{76}, and C_{84} fullerenes,[10] respectively. Upon complete evaporation of the organic solvents and after leaving the prepared suspensions quiescently for a few hours, vacuum filtration through 0.22-µm cellulose acetate membrane filters (Corning Life Sciences, Corning, NY) was performed to attain clear fullerene aqueous suspensions. The suspensions were stored in the dark (wrapped in aluminum foil) at 4 ºC to avoid any potential photoreaction.

6.2.2 Solution Chemistry

A wide range of mono- (NaCl from Lonza, Rockland, ME) and di-valent ($CaCl_2$ from Teknova, Hollister, CA) salts was used to simulate common aquatic conditions. 5M NaCl and 1M $CaCl_2$ solutions were diluted with filtered deionized (DI) water to attain appropriate ionic strength, which ranged from 10-650 mM NaCl and 1-38 mM $CaCl_2$. To understand the role of natural organic matter (NOM) on HOF aggregation, a mixed electrolyte condition, i.e., 7 mM NaCl and 1 mM $CaCl_2$, was used in the presence of standard II Suwannee River humic acid, SRHA (International Humic Substances Society, Denver, CO) at a concentration of 2.5 mg TOC/L.

6.2.3 Aqueous nHOF Cluster Characterization

TEM, AFM, UV-Visible spectroscopy, and electrophoresis techniques were employed to characterize the physicochemical properties of the aqueous nHOF suspensions. Electron micrographs were obtained at various magnifications and at an accelerating voltage of 200 kV with a JEOL 2010F (JEOL USA, Inc., Pleasanton, CA) high resolution TEM, located at the Texas Materials Institute. The carbon-coated copper TEM grids were prepared by adding two to three drops of each fullerene suspension and air dried over a few minutes. Several micrographs were taken for each fullerene type to obtain representative images.

A Bruker MultiMode 8 AFM equipped with Nanoscope V controller (Bruker Corporation, Santa Barbara, CA) was used to characterize the size uniformity of nC_{60} and nHOFs in aqueous media. For sample preparation, a few drops (~40μL) of individual nC_{60} and nHOF aqueous dispersions were added on freshly cleaved mica surfaces attached to stainless steel SPM discs of 1-cm diameter (Bruker Corp.) and were kept in desiccators for drying. The samples were then examined in ScanAsyst tapping mode using a silicon probe (with resonance frequency of 150 Hz and spring constant of 6 N/m). NanoScope version 9.1 software was used to analyze the images.

An Agilent 8453 UV-visible spectroscope (Santa Clara, CA) was used to characterize the fullerenes both in toluene and aqueous suspensions for their unique UV-vis spectroscopic signature. Baseline was established with toluene and deionized (DI) water (in respective cases), introduced to a pre-cleaned quartz cuvette. Fullerene suspensions (in toluene or in water) were then introduced to a similar cuvette to collect several spectral scans (3 scans per sample) for the entire spectral range of 200 to 1100 nm.

The electrokinetic behavior of the fullerene clusters was monitored by measuring electrophoretic mobility (EPM) utilizing a Malvern Zetasizer Nano ZS (Malvern Instruments

Inc., Westborough, MA), located at the Texas Materials Institute. Appropriate dilutions of NaCl and $CaCl_2$ salts were added to 2 mL fullerene suspensions to generate the desired background chemistry. Dilution factors (diluting from stock suspensions) used for nC_{60}, nC_{70}, nC_{76}, and nC_{84} were 20, 20, 10, and 8, respectively. At least 3 replicate measurements were taken for each sample at each solution condition. The measured EPM values were then converted to ξ-potential utilizing the Smoluchowski relationship.[29] The pH for all samples was left unadjusted (ranged between 5.5-5.8) to avoid introduction of additional ionic species.

6.2.4 Aggregation Kinetics Studies

Time resolved dynamic light scattering (TRDLS) was used to measure aggregation kinetics of the prepared fullerene suspensions at various environmentally relevant conditions. An ALV/CGS-3 compact goniometer system (ALV-Laser Vertriebsgesellschaft m-b.H., Langen/Hessen, Germany) equipped with 22 mW HeNe 632 nm laser (equivalent to 800 mW laser at 532 nm) and high QE APD detector with photomultipliers of 1:25 sensitivity was employed. The details of the experimental protocol have been laid out earlier.[30-34] In short, 2 mL of nC_{60}, nC_{70}, nC_{76}, and nC_{84} suspensions at appropriate dilutions with added salt and/or SRHA were mixed in pre-cleaned borosilicate vials, vortexed, and placed inside the DLS chamber after which scattering intensity was monitored over time.[32] Attenuation of the laser was kept at 100% for all the samples and scattering data was collected at 90º at 15 s intervals. Twenty minutes to one hour of continuous measurements were performed to allow for at least 30% increase of the initial average clusters sizes (for most cases).[32]

The initial aggregation rates (equation 6.1) were determined from the aggregation history (i.e., time vs. hydrodynamic radii plots).[29, 32] The criteria set forth to estimate these rates are described elsewhere.[22, 30, 31, 33, 34] For most conditions, the initial slope was calculated by linear regression of the cluster sizes up to 1.3 times the initial hydrodynamic radius measured by the instrument at time t=0. For relatively low ionic strength cases (in the reaction limited regime), i.e., up to 45-75 mM NaCl or 3-5 mM $CaCl_2$, attainment of a 30% increase of the initial cluster sizes was not achieved during the entire DLS run. In such cases, the slope of the initial linear region of the hydrodynamic radius vs. time plot was calculated. Attachment efficiency of the fullerene suspension at each solution condition was then obtained by normalizing the aggregation rate at each solution condition by the favorable aggregation rate (equation 6.2).[29]

$$k \propto \frac{1}{N_0}\left[\frac{dR_h(t)}{dt}\right]_{t\to 0} \qquad (6.1)$$

$$\alpha = \frac{\left[\frac{dR_h(t)}{dt}\right]_{t\to 0}}{\left[\frac{dR_h(t)}{dt}\right]_{t\to 0,fav}} \qquad (6.2)$$

6.2.5 Molecular Dynamics (MD) Simulations

The interactions between C_{60}, C_{70}, C_{76} and C_{84} fullerene clusters were simulated by means of umbrella sampling simulations to investigate the aggregation behavior of the fullerene pairs in water. The initial configurations for the fullerenes were generated and optimized by following procedures outlined in a previous study.[10] The atomic charges for all molecules were based on the charges generated using the semi-empirical AM1 charge model with bond charge correction (AM1-BCC) and the antechamber module in Assisted Model Building with Energy Refinement (AMBER12).[35] The optimized geometry of each fullerene pair was solvated in Transferable Intermolecular Potential 3P (TIP3P) water and equilibrated. The equilibration of the system consisted of an initial 10,000 cycles of energy minimization followed by a 1 ns molecular dynamics simulations. The umbrella sampling simulations procedure described elsewhere[36] was followed to study the strength of the interactions between the fullerene pairs. A total of 1 ns simulation was performed per window under the constant pressure and temperature (NPT) statistical ensemble, and data were saved every 10 ps for analysis. The output of the simulations was analyzed, and free energy profiles subsequently were subsequently generated using the weighted histogram analysis method.[37]

6.2.6 Net Interaction (DLVO) Energy Calculation

The net interaction energy between a pair of fullerene cluster was calculated following classical DLVO theory; i.e., as the sum of the van der Waals attraction $V_A(h)$ and electrostatic double layer repulsion $V_{EDL}(h)$, using the following equations:

$$V_A(h) = -\frac{A_{121}a}{12h} \text{.........(6.3)}$$

$$V_{EDL}(h) = 64\pi \frac{n_b K_B T}{\kappa^2} \frac{a^2}{(h+2a)} [\tanh\left(\frac{ze\varphi}{4K_BT}\right)]^2 \exp(-\kappa h) \text{......(6.4)}$$

$$V_T = V_{DLVO} = V_A(h) + V_{EDL}(h) \text{.......(6.5)}$$

where, 'a' is the hydrodynamic radius of the particle in m, 'A_{121}' is the Hamaker constant (J) of individual fullerene clusters in aqueous media, 'h' is the separation distance between the particle in m, 'n_b' is ionic concentration, 'K_B' is the Boltzmann's constant (1.38×10^{-23} m^2 kg s^2 K^{-1}), 'T' is temperature in K, 'z' is valence of ions, 'e' is isolated unit electron charge (1.602×10^{-19} C), 'φ' is the surface potential in V, and '$1/\kappa$' is the Debye length in m.

A literature reported Hamaker constant of nC_{60}s in water, i.e., A_{121} (6.7×10^{-21} J) was used for calculating V_A attraction energies between nC_{60} fullerene clusters.[22] Since Hamaker constants for nHOFs are not yet reported in the literature, a scaling factor (β_m) was used to appropriately adjust V_A energies for these nHOFs (where, m represents the number of carbon atoms in HOFs, i.e., 70, 76, 84). β_m is defined as the ratio of the favorable interaction energies (energy minimum values obtained from MD simulations) estimated for each HOF-pair ($IE_{m,net}$) to that of C_{60}-pair ($IE_{60,net}$), obtained under identical simulation conditions. The underlying assumption in estimating this scaling factor was that interaction energies between C_{60} and HOF clusters equivalently scale with those of their molecular counterparts. Translation of molecular behavior to multi-molecular clusters had previously been reported for nC_{60} solubility estimation.[38] These ratios were then utilized to modify the V_A energies as follows.

$$V_{A,m}(h) = \beta_m V_{A,60}(h) \ldots\ldots\ldots (6.6)$$

$$\beta_m = \frac{IE_{m,net}}{IE_{60,net}} \ldots\ldots\ldots (6.7)$$

Here, $V_{A,m}(h)$ and $V_{A,60}(h)$ are the vdW energy values for a nHOF with m number of C atoms and nC_{60} fullerenes, respectively. $IE_{m,net}$ and $IE_{60,net}$ represent the net interaction energies estimated for HOFs and C_{60} fullerenes, respectively, using MD simulations.

6.3 Results and Discussion

6.3.1 Chemical Identity and Morphological Characteristics

The chemical identity of the fullerenes was confirmed via UV-vis spectroscopy as presented in Appendix D, Figure D-1. The spectra obtained for nC_{60} dispersed in toluene shows a characteristic absorbance peak at 335 nm (Figure D-1a) while nC_{70} exhibits peaks at 333, 383, and 473 nm (Figure D-1b), which are all consistent with literature observations.[39] nC_{76} shows a shoulder around 333 nm and undulation near 407 nm (Figure D-1c) and nC_{84} presents a broad shoulder centered around 400 nm with undulation near 474 nm (Figure D-1d); such behaviors follow literature-reported evidences.[40, 41] Aqueous nC_{60}s and nHOFs also were characterized (Figure D-2), and show spectral signatures consistent with the literature.[20, 26, 42]

The crystallinity and morphology of fullerene clusters were determined via HRTEM and AFM. Figure 6.1(a-d) presents representative HRTEM micrographs of nC_{60}s and the nHOFs. Spherical clusters with relatively uniform sizes are observed for all the samples. Inset micrographs show defined crystalline structures of the clusters. Previous literature reports similar nC_{60} and nHOF cluster morphology obtained using solvent-exchange processes.[10, 22, 26]

Moreover, AFM micrographs presented in Figure 6.1(e-h) show spherical aggregates of nC_{60} and nHOFs, similar to those observed via HRTEM. Similar AFM images were presented earlier for nC_{60}s,[43] but these are the first reports for nHOFs.

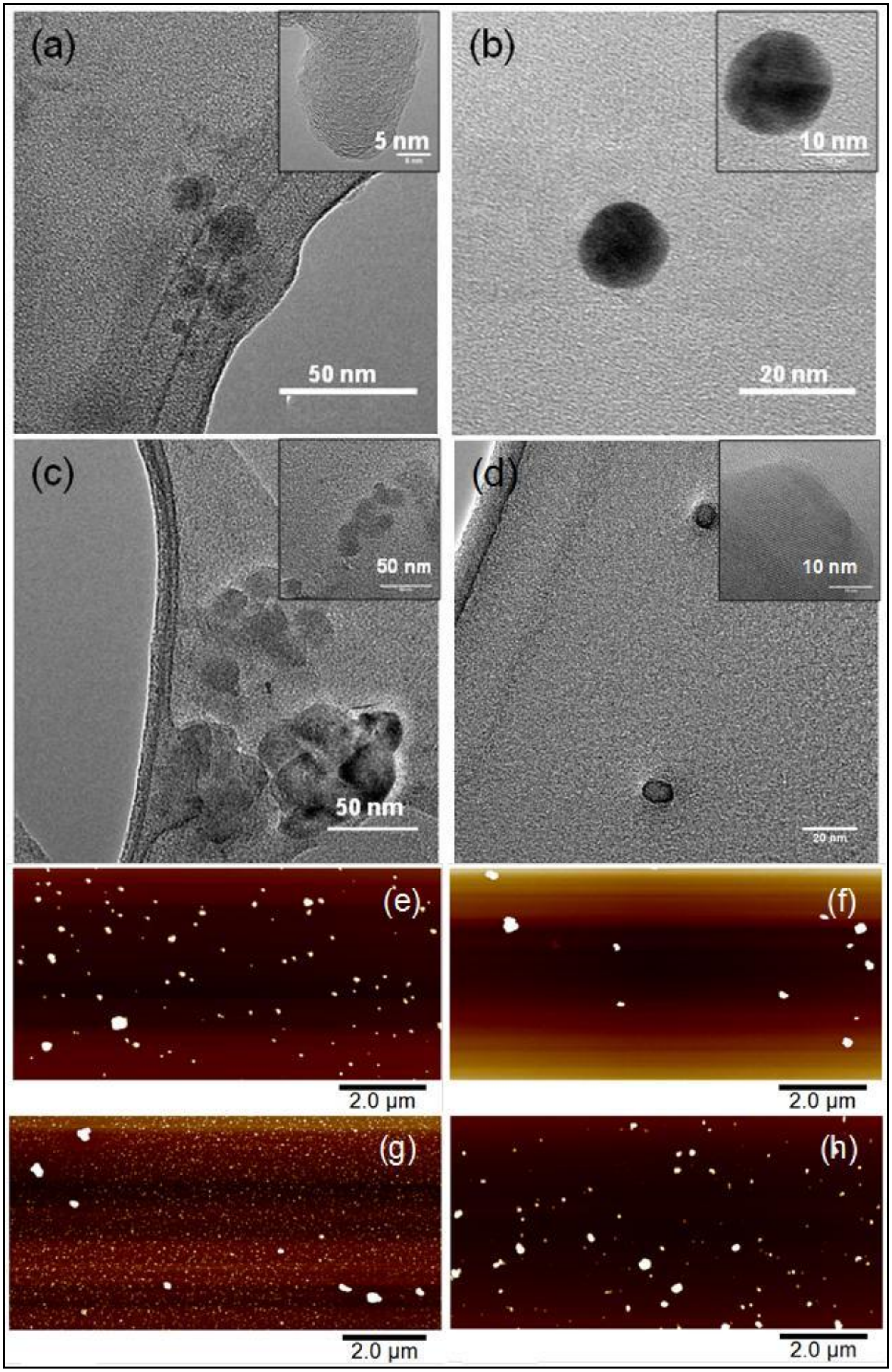

FIGURE 6.1. Representative HRTEM (a-d) and AFM (e-f) micrographs of nC_{60}, nC_{70}, nC_{76}, and nC_{84}, respectively. Insets in (a-d) presents high resolution TEM micrographs.

6.3.2 Electrokinetic Properties

Figure 6.2 presents the electrokinetic properties of the nC_{60}s and nHOFs over a wide range of mono- and di-valent cations. All fullerene clusters exhibit negative surface charge. The existing literature for nC_{60} aggregation and colloidal properties hypothesize hydroxylation,[43, 44] surface oxidation,[21] charge transfer from water and hydrogen bonding,[44] and clathrate-like water-fullerene cluster formation,[44] as potential mechanisms for origin of surface charge for these all-carbon structures; however, the underlying mechanism continues to remain elusive. Acquisition of negative surface charge has been manifested irrespective of the suspension preparation method or type of fullerenes (nC_{60} and nHOFs).[10, 45] Electrokinetic measurements determined in this study show nC_{70}s to possess the highest EPM, closely followed by nC_{60}s; while the larger caged nC_{76} and nC_{84} clusters exhibit notably lower EPM values compared to nC_{60}s. Higher surface charge for aqueous nC_{70}s (-51±2.4 mV) compared to nC_{60}s (-47±4.9 mV) has been reported previously.[44] The differences in surface charge for nC_{60} and nC_{70} likely have originated from the differences in charge distribution on the surface of spherical C_{60} and ellipsoidal C_{70} molecules.[44] However, the mechanism of charge acquisition of the nC_{60}s and nHOFs can be attributed to electron affinity values of these materials, which vary between 2.65-3.07 for C_{60}s to C_{84}s.[6]

The absolute values of EPM decrease with the increase in cation concentration, displaying classical electrokinetic behavior. Compression of electrical double layer is dominant at higher concentration of mono-valent Na^+ (beyond 30 mM) and di-valent Ca^{2+} (beyond 3 mM).

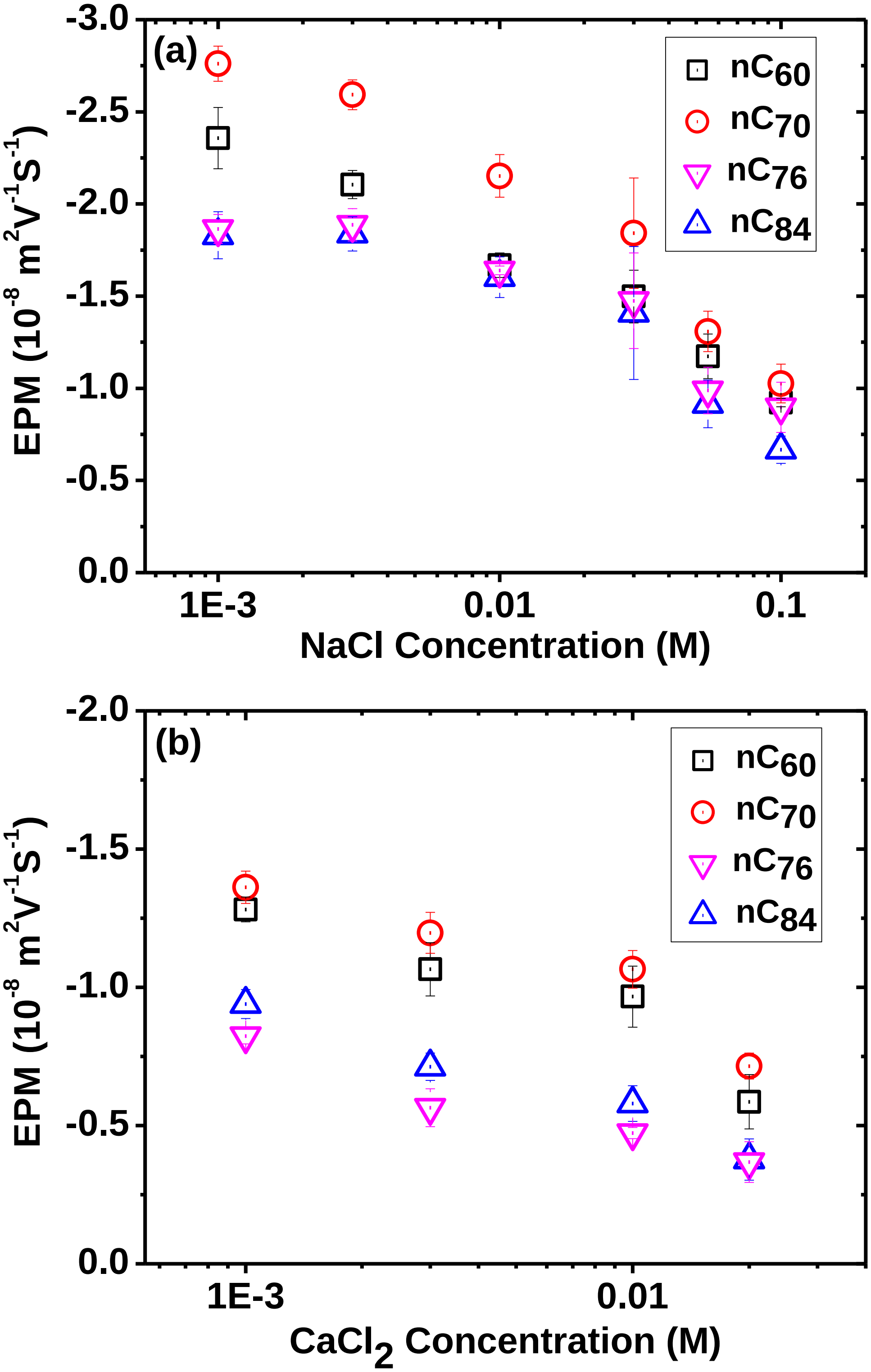

FIGURE 6.2. Electrophoretic mobility (EPM) values of aqueous nC_{60}, nC_{70}, nC_{76}, and nC_{84} suspensions as a function of (a) mono-valent NaCl and (b) di-valent $CaCl_2$ electrolyte concentrations. Measurements were carried out at 5.5-5.8 pH with no additional buffers and at 25 °C.

For mono-valent (NaCl) electrolytes at low salt concentration (0.001M), nC_{70}s presents significantly higher EPM values (-2.76±0.09 $\times 10^{-8}$ $m^2V^{-1}S^{-2}$) as compared to nC_{60}s (-2.35±0.17 $\times 10^{-8}$ $m^2V^{-1}S^{-2}$); while both nC_{76}s and nC_{84}s show significantly lower surface charges (-1.86±0.08 $\times 10^{-8}$ and -1.83±0.13 $\times 10^{-8}$ $m^2V^{-1}S^{-2}$, respectively) compared to nC_{60}s and nC_{70}s. With increasing salt concentration, i.e., at 0.1M NaCl, the EPM for all fullerene cluster types collapse between -0.67±0.07 $\times 10^{-8}$ to -1.03±0.11 $\times 10^{-8}$ $m^2V^{-1}S^{-2}$. Such changes in EPM in the presence of mono-valent salt have been previously reported for nC_{60};[22, 46] however, systematic EPM measurements for nHOFs are reported in this study for the first time. Similarly, the presence of di-valent ($CaCl_2$) electrolytes reduces EPM with the increase in counter ion concentration. The nC_{60} and nC_{70} show similar EPM magnitude while nC_{76} and nC_{84} behave alike electrokinetically throughout the entire range of Ca^{2+} concentrations. At low $CaCl_2$ concentration (0.001M), nC_{60} and nC_{70} display EPM values within the range of -1.28±0.04 $\times 10^{-8}$ to -1.36±0.06 $\times 10^{-8}$ $m^2V^{-1}S^{-2}$, while nC_{76} and nC_{84} show lower EPM ranging between -0.82±0.0.03 $\times 10^{-8}$ to -0.94±0.0.05 $\times 10^{-8}$ $m^2V^{-1}S^{-2}$. At high $CaCl_2$ concentration (0.02M), EPM values for all the fullerene clusters decrease significantly. Overall, nHOFs display classical electrokinetic behavior, similar to nC_{60}s.

6.3.3 Aggregation Kinetics

Aggregation kinetics of nC_{60}s and nHOFs has been analyzed from their aggregation history profiles as presented in Figure D-3. The initial hydrodynamic radii of nC_{60}, nC_{70}, nC_{76}, and nC_{84}, as determined by TRDLS, are 57.6±2.1, 64.6±2.3, 76.6±2.8, and 73.2±1.94 nm, respectively. The hydrodynamic radii were observed to have increased over time with an increasing rate as the cation concentration increased. Similar increasing trend in the initial cluster size for nHOFs has been reported earlier.[47]

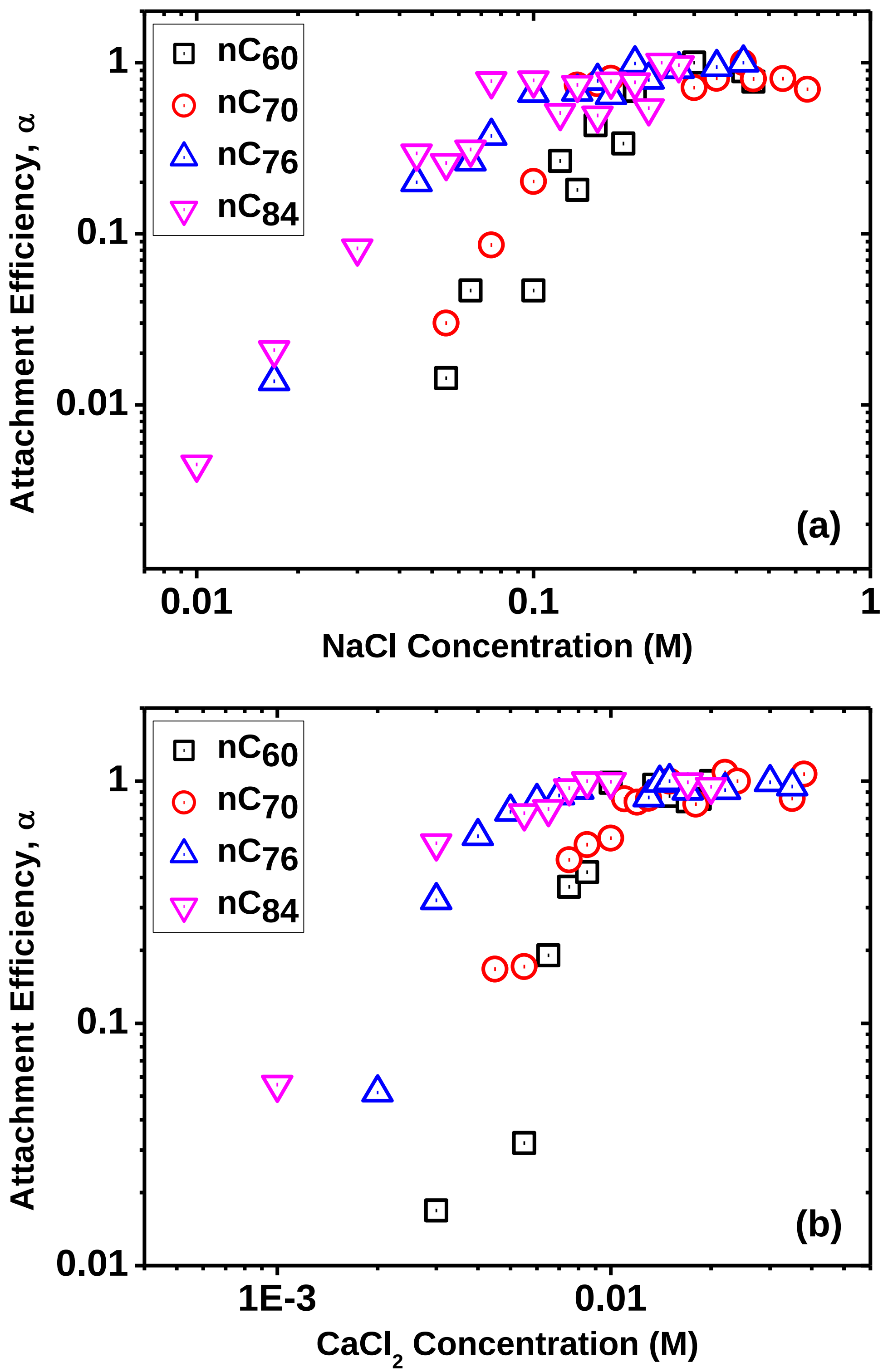

FIGURE 6.3. Stability plots of aqueous nC_{60}, nC_{70}, nC_{76}, and nC_{84} suspension as a function of (a) mono-valent NaCl and (b) di-valent $CaCl_2$ electrolyte concentrations. Measurements were carried out at 5.5-5.8 pH with no additional buffers and at 25 °C.

Attachment efficiencies estimated by normalizing initial aggregation rates at any condition with that at the favorable regime showed classical Derjaguin-Landau-Verwey-Overbeek (DLVO)-type interaction (Figure 6.3). The stability plots of nC_{60} and nHOFs in presence of mono- and di-valent salts (NaCl and $CaCl_2$) exhibit distinct unfavorable or reaction limited (RLCA) and favorable or diffusion limited regimes (DLCA), where the transition is characterized by critical coagulation concentration (CCC). The CCC values in case of mono-valent electrolyte is estimated to be 220, 150, 100, and 70 mM NaCl for nC_{60}, nC_{70}, nC_{76}, and nC_{84}, respectively. The estimated CCC values illustrate a systematic decreasing trend—i.e., higher aggregation propensity—with the increase in carbon number in the fullerene cages. However, stability plots generated for divalent ($CaCl_2$) electrolyte show smaller differences between CCC values, likely resulting from profound compression of electrostatic double layer. The CCC values in the presence of di-valent electrolytes are estimated to be 10, 12, 6, and 7.5 mM $CaCl_2$ for nC_{60}, nC_{70}, nC_{76}, and nC_{84}, respectively. Though an overall decrease in CCC values is observed with a 0.97-1.34 right log-shift, the trend is less systematic when compared to mono-valent NaCl. However, the stability of nC_{60}s and nHOFs follow the Schulze-Hardy Rule; i.e., the ratio of CCC under mono-valent to di-valent electrolyte conditions follow a z^n (where z=2 and n=2-6) rule where n=-4.46, -3.65, -4.06, and -3.22 for nC_{60}, nC_{70}, nC_{76}, and nC_{84}, respectively. nC_{60}s and other carbon allotropes have earlier been shown to follow Schultz-Hardy Rule.[22, 32, 33]

While literature reports CCC values for nC_{60} in presence of NaCl and $CaCl_2$, there is no reported aggregation behavior for nHOFs. The nC_{60}s have shown to exhibit 120-260 mM NaCl and 4.8-6.1 mM $CaCl_2$ as CCC with variation in solubilization method.[22, 46, 48] The estimated stability of nC_{60}s in this study is consistent with the literature reports and systematic monitoring of nHOF aggregation behavior show predictability of CCC using a single parameter, such as carbon number within a HOF cage. The CCCs estimated are linearly correlated with carbon number (Figure 6.4) and show more than 50% reduction in CCC with an increase in carbon number from 60 to 84. The results were statistically significant (R^2 of 0.9699, Pearson's correlation co-efficient r of -0.9899, and F-value of 0.01). The correlation between CCC values and carbon number for $CaCl_2$ shows an overall decreasing trend; however, the there was no linear correlation, likely due to higher degree of compression of electrical double layer and possible coordination from di-valent cations (Figure D-4).[49] Similar observation of enhanced aggregation propensity for higher-order carbon structures was demonstrated, e.g., by single-walled carbon nanotubes, where CCC decreased with the increase in nanotube diameter.[33] The underlying mechanisms of such aggregation behavior have further been probed with MD simulations and modified DLVO analysis.

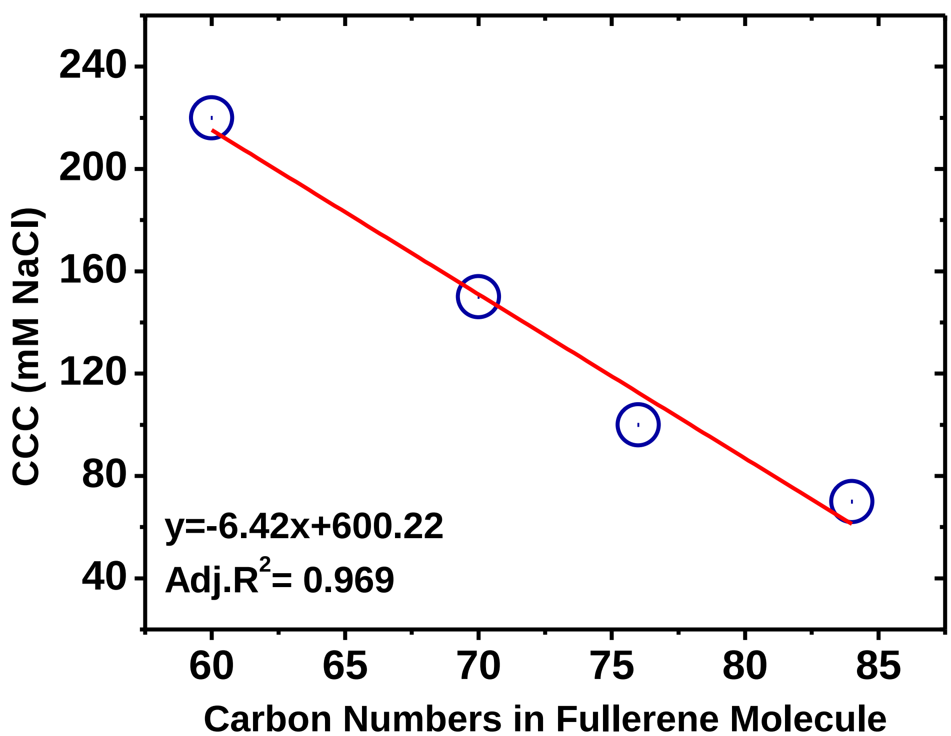

FIGURE 6.4. Linear regression of CCC values with carbon numbers in fullerene molecules for mono-valent NaCl electrolyte.

6.3.4 Aggregation Mechanisms and Role of Carbon Number

Results from the current study and previous literature show that nC_{60} aggregation behavior can be well captured by DLVO theory. Delineation of the nHOF aggregation mechanism from DLVO theory requires understanding of the contributions from vdW attractive interaction from these higher-order carbon structures. To address this issue, MD simulations were performed in explicit water using pair-wise interaction of each fullerene type. Figure D-5 shows a MD snapshot of C_{60} pair visualized using visual molecular dynamics software.[50] Figure 6.5a shows interaction energy as a function of separation distance. It is observed that the interaction between the fullerene pairs is most favorable near an intermolecular separation of 10.5 Å and become less significant at and beyond 13 Å. It is important to note that as the carbon number increases the depth of the interaction energy well increases indicating more favorable interaction between higher carbon-number fullerenes. The net interaction energy for the most favorable interaction of each fullerene pair in aqueous media is then obtained from the difference between the energies at the lowest point of the curves and the average of the plateau. The net interaction energies are -3.7, -4.30, -5.19, and -6.21 kcal/mol for C_{60}-C_{60}, C_{70}-C_{70}, C_{76}-C_{76}, and C_{84}-C_{84}, respectively. These results when plotted against carbon atom numbers in fullerenes as shown in Figure 6.5b display a strong linear correlation[33] with adjusted R^2 value of 0.9399, Pearson's correlation coefficient r of 0.9798, and F-value of 0.02. This is in excellent agreement with linear decrease in CCC values for fullerenes with increasing carbon numbers in the presence of mono-valent NaCl (Figure 6.4), thus reinforcing a strong dominance of vdW interaction between fullerene clusters in the aggregation process. As demonstrated through vacuum phase MD simulations in the previous literature, intermolecular vdW interaction energy between fullerene pairs increase with the increase in carbon numbers–leading to an enhancement in the binding energy.[10, 51]

To further illustrate the aggregation mechanism, total interfacial interaction energies between nC_{60} and nHOF clusters at different NaCl and $CaCl_2$ salt concentrations are estimated using modified DLVO theory (Figures 6.6a-b and D-6 to D-7). Higher fullerenes show decreasing trend in DLVO interaction energies with increasing carbon number at high ionic strength. Figure 6.6(c) shows the net interaction energy values with increasing mono-valent salt concentrations at a separation distance of 2 nm (distance where V_{max}/K_BT occurs). nC_{70} on the other hand shows the highest positive interaction (repulsion) energies at low ionic strength (likely due to the high negative surface charge as discussed earlier). However, at high ionic strength (0.055-0.1 M NaCl) the lowering of electrostatic double layer interaction resulted in dominance of vdW interaction, where the interaction energy curves follow the carbon number trend. Thus at high concentration of mono-valent NaCl, the overall trend of DLVO energies is as follows: nC_{60}> nC_{70}>nC_{76}>nC_{84}; which is consistent with the trend in CCC values. Figure 6.6(d) demonstrates the ability of divalent Ca^{2+} to compress electrical double layer repulsion and shows complete dominance of vdW interaction for nC_{60} and nHOF alike. The DLVO interaction energy shows a rather systematic increase in attractive interaction energies with the increase in carbon number for the entire range of the divalent Ca^{2+} concentration. Such observation confirms that vdW interaction controls the nC_{60} and nHOF aggregation in presence of mono- and di-valent electrolytes.

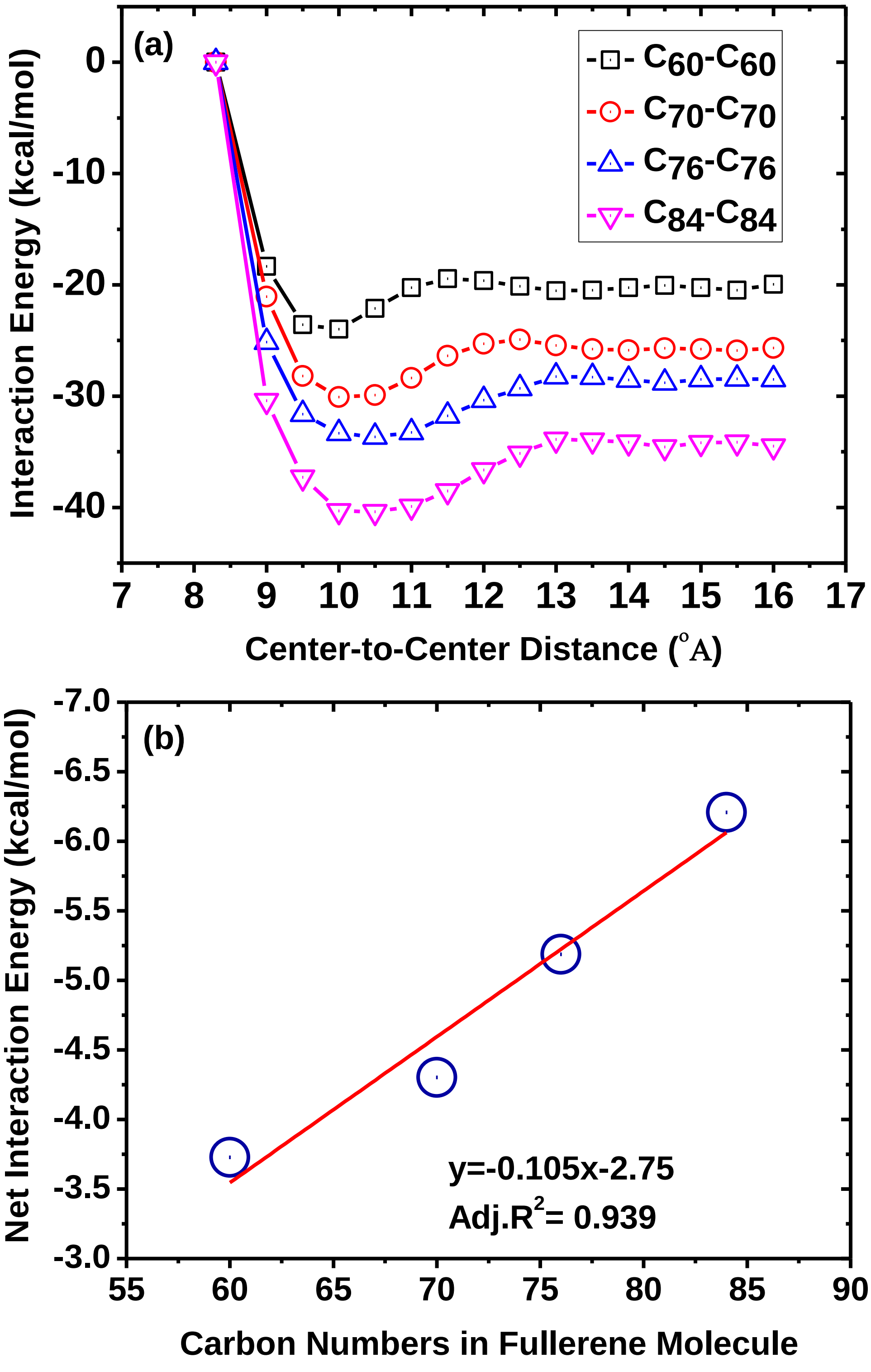

FIGURE 6.5. (a) MD simulation derived pair-wise interaction energies of the like-fullerene molecule pairs (C_{60}-C_{60} or HOF-HOF) as a function of separation distance. (b) Most favorable net interaction energies between like-fullerene molecule pairs with carbon number in fullerene molecules.

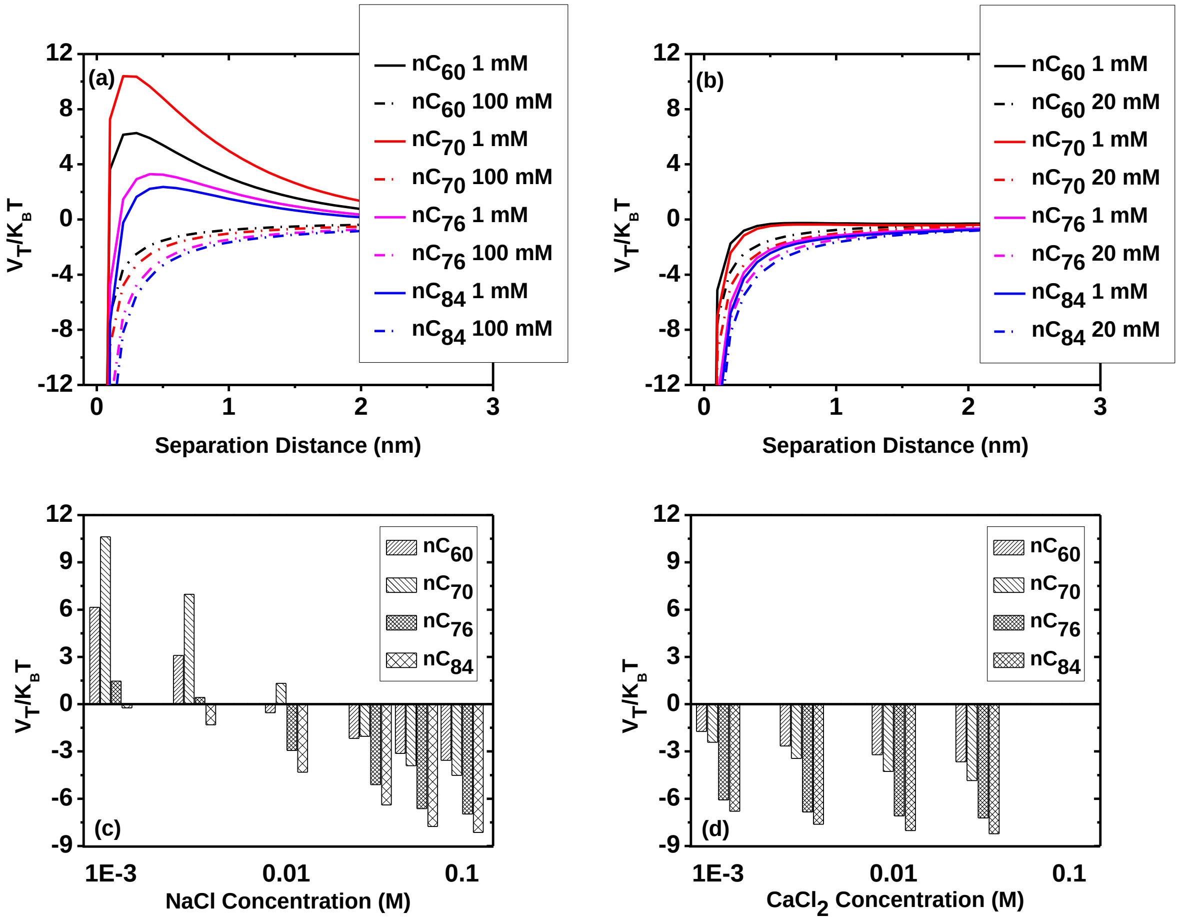

FIGURE 6.6. Estimated total interaction energy (V_T/K_BT) with separation distance using modified DLVO theory for aqueous nC_{60} and nHOFs in the presence of (a) mono-valent NaCl and (b) divalent $CaCl_2$ electrolytes. Bar chart presenting estimated favorable (at separation distance of 2 nm) DLVO interaction energy (V_T/KT) values of nC_{60} and nHOF aqueous suspensions in the presence of (c) mono-valent NaCl and (d) divalent $CaCl_2$ electrolytes.

6.3.5 Role of Humic Acid on Aggregation

The presence of SRHA at 2.5 mg TOC/L concentration stabilizes nC_{60}s and nHOFs at 10 mM total ionic strength (7 mM NaCl and 1 mM $CaCl_2$). No appreciable aggregation of any of the fullerene clusters could be measured; hence the aggregation rates could not be reported. Such stabilization indicates probable adsorption of SRHA to the fullerene clusters, which likely have stabilized these clusters via steric stabilization. Similar stabilization in presence of natural macromolecules was observed in case of nC_{60}s and other carbon allotropes (e.g., single-walled and multiwalled carbon nanotubes) earlier.[33, 46, 52, 53] At elevated ionic strength, i.e., in presence of 100 mM NaCl, SRHA continues to show dominance in nC_{60}s and nHOFs. In these cases, aggregation rates were measurable and are hence reported in Figure 6.7. The presence of SRHA has decreased the aggregation rates of nC_{60}, nC_{70}, nC_{76}, and nC_{84} fullerenes by 94.3, 80, 89.3, and 88.7%, respectively–a more or less uniform stabilization irrespective of the carbon numbers. Such stabilization can have profound environmental implications due to enhanced mobility of these carbon allotropes.

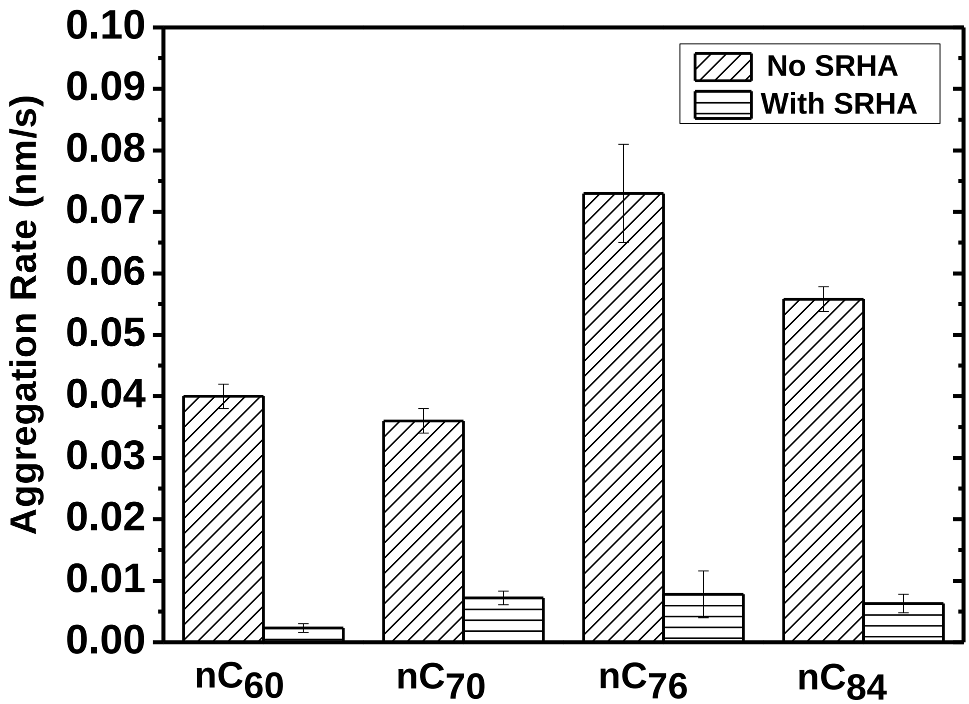

FIGURE 6.7. Aggregation rates of nC_{60} and nHOFs without and with the presence of 2.5 mg/L TOC SRHA. 100 mM NaCl electrolyte was present in each case.

6.4 Environmental Implications

Findings from this study strongly imply that carbon number in fullerene molecules will likely dictate the aggregation behavior of their clusters in natural environment. The aggregation propensity and vdW interaction energies are strongly correlated with carbon number resulting in potential predictability of the fate of other nHOFs in aquatic conditions relevant to the ones used in this study. The higher the carbon number in the fullerene cage the higher will be the aggregation propensity and thus will result in restricted mobility in natural systems. However, such colloidal destabilization behavior will likely lead to increased sedimentation from the water column (in a surface water release scenario) and lower mobility in the subsurface. The aggregation propensity can also lead to increased mass deposition and thereby interaction of larger masses of nHOFs with aquatic organisms.[54] However, the presence of geo- and bio-macromolecules will likely reverse such environmental fate because they will profoundly reduce aggregation propensity and thereby significantly enhance environmental mobility. Such enhanced mobility can present substantial environmental risk, even in water bodies with elevated ionic strength (e.g., marine and estuarine systems). Thus systematic EHS assessment of nHOFs is necessary.

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Chapter 7: Aggregation Kinetics and Antimicrobiality of TiO_2-Multiwalled Carbon Nanotube Nanohybrids[******]

7.1 Introduction

Material synthesis and property manipulation at the nano-scale have achieved a paradigm shift towards multi-component hierarchical structures and nano-systems.[1] Nanohybrids (NHs), ensembles obtained by conjugating two or more individual nanomaterials (NMs), have recently gained increased attention to extract enhanced properties or multifunctionality through alteration of their electronic, optical, physical, and chemical properties.[1-4] An expanding array of NHs is being synthesized and used in various applications, such as biomedicine,[5] biomedical imaging,[6] nanoelectronics, supercapacitors,[7] optoelectronics,[8] solar cell technology,[9] electrochemical fuel cells,[10] electrocatalysis,[11] nano-bio[12] and chemical sensing.[13] These novel nano-assemblages possess either altered properties or present emergent physicochemical and interfacial properties, which did not surface previously for individual NMs and will likely pose uncertainty in predicting their environmental health and safety (EHS),[1, 4] where existing literature on singular NM EHS literature might become inadequate.

Among different NH classes (described in Chapter 3)[1] carbon-metallic NHs (CMNHs) are being researched extensively. This NH class is composed of small metal/metal oxide nanoparticles (MNPs) deposited on large extended surfaces of nanocarbons including one dimensional carbon nanotubes (CNT) or two-dimensional graphene. Nanocarbons provide high mechanical stability, unique interfacial interaction, and excellent thermal conductivity rendering

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control over size, structure, distribution, and morphology of the conjugated MNPs.[14] Moreover, nanocarbons' exceptional charge transfer and ambipolar properties can alter the band gap of the deposited MNPs, improving the catalytic- and photo-activity.[15] Such unique property alterations lead to numerous applications including enhanced heterogeneous catalysis (using Pd, Rh, or Au NPs),[16, 17] photocatalytic energy production and pollutant degradation (TiO_2, ZnO, nano-zero valent Fe),[15, 18] electrocatalysis for fuel cells (Pt, Pd),[19] environmental sensing (using Ag),[20] biomedical imaging, tissue engineering, and drug delivery (using quantum dots CdSe, super-paramagnetic Fe_3O_4, etc.)[21, 22]. Further details of such NHs can be found in Chapter 3 and Appendix A.

Electrocatalysis is one of the most promising areas for CMNHs, which provide faster electron transfer in fuel cells. Traditional fuel cells involve Pt as electrocatalysts that are supported on carbon black to perform the water-splitting reaction and generate hydrogen to harness electricity. Recently, multiwalled carbon nanotubes (MWNTs) conjugated with TiO_2 NPs (undoped or Nb-doped) have been developed as hierarchical NH-support for Pt electrocatalysts, which achieved increased energy conversion efficiency.[23] MWNTs provide reduced corrosion, improve mechanical properties, and enhance high electrical conductivity,[24, 25] while TiO_2 stabilizes Pt against diffusion, detachment, and dissolution[26-29] as well as prevents H_2 and CO chemisorption.[30, 31] Incorporation of Nb as dopant in TiO_2 further enhances n-type conductivity.[32-34] OMWNT-TiO_2-Pt NHs are thus the future of electrocatalytic fuel cells with a potential for 100 million kg NHs being incorporated by 2050.[35] Such increased use necessitates systematic assessment of EHS of this important class of NHs.

OMWNT-$TiNbO_2$-Pt NHs are composed of two NMs with elevated EHS concerns, i.e., TiO_2 and MWNTs. Aggregation behavior of CNT and TiO_2 in aquatic systems has been extensively investigated as a function of environmental conditions and particle properties.[36] On the contrary, studies regarding aqueous aggregation of Pt NPs are limited.[37] Both CNT and TiO_2 NPs show classical DLVO-type aggregation behavior.[38] CNT aggregation kinetics is mostly influenced by length,[39] aspect ratio,[40] chirality or diameter differences,[41, 42] surface oxidation,[43] and surface chemistry.[44] The mechanisms of such interfacial interactions are dependent on the van der Waals forces[42] or electrostatic repulsion (for surface functionalized carbon nanotubes).[43] Similar to CNT, TiO_2 has its unique aggregation characteristics and is primarily influenced by size,[38] surface area,[38] composition,[38] shape,[38] surface charge,[45] as well as surface coatings[46] and synthesis processes[47]. Mechanisms behind aggregation of TiO_2 have been elucidated as interplay between electrostatic, van der Waals, and steric (for polymer coated TiO_2) interactions.[38, 46] For TiO_2 or Pt hybridized MWNTs, the interfacial and environmental interaction likely will be dominated by MWNTs due to their higher surface presence. However, hybridization of MWNTs will likely modulate their physicochemical properties. Surface oxidation of MWNTs shortens the lengths and creates defects with carboxylic or hydroxyl groups.[48] Upon deposition of TiO_2 and Pt NPs, the surface chemistry of OMWNTs as well as the band gap and electrokinetic properties are altered.[49, 50] Moreover, Pt deposition has shown to increase MWNTs' mechanical stiffness.[19] Such altered and emergent properties of metal conjugated OMWNT NHs will likely impact their aggregation behavior. A recent study investigated aggregation kinetics of a similar CMNH (graphene-TiO_2 NH) in aqueous systems, where the NH was found to show aggregation propensity in between literature reported aggregation tendency of graphene and pristine TiO_2.[51] However, no component materials were examined to experimentally compare with the NH.

TiO_2 NPs and MWNTs both display some toxic effects to microorganisms and aquatic species.[52-54] Mechanistically, MWNTs are known to exhibit cell membrane oxidation and generation of reactive oxygen species (ROS) along with 'asbestos-like' inflammatory effects.[55] TiO_2 toxicity involves mostly ROS and oxidative stress mediated cytotoxicity;[56, 57] although a few studies suggest that protein nitration and immune modulation are key mechanisms.[58, 59] These mechanisms are highly influenced by their physicochemical properties such as size,[60] shape and morphology,[61] surface chemistry,[62] and crystallinity.[63] Hybridization changes the mechanical stiffness and surface chemistry of the OMWNTs[3, 4] and also results in shape differences of TiO_2: e.g., spherical, irregular-shaped, rod-like, tubular, rice-grain shaped,[9] and even hierarchical flower like structures, which in turn influence surface chemistry of the MWNTs.[64] Photoactivity of TiO_2 (under visible light) has been shown to be enhanced upon hybridization, due to a lowering in band gap energy.[50] Moreover, increased ROS formation is observed due to TiO_2 size modulation and retarded electron hole-pair recombination upon conjugation with carbon nanotubes or graphene.[64, 65] Such changes in physical morphology, reactive surface area, and photoactivity will likely result in unknown antimicrobiality of these NHs when compared to the component effects. Relevant evidences have been reported involving a graphene-TiO_2 nanocomposite study that showed visible light mediated toxicity toward model aquatic organisms, i.e., *Daphnia magna* and *Oryzias latipes*.[66] However, to date, no systematic studies have evaluated the antimicrobiality of CMNHs.

This study evaluated the aggregation behavior and antimicrobiality of carbon nanotubes, hybridized with TiO_2 (undoped or Nb-doped) and Pt NPs. First, sequential hybridization of OMWNT with TiO_2 (both doped and undoped) and Pt was performed using wet chemistry. Morphological, chemical, and electrokinetic characteristics of the synthesized NHs and parent materials were determined using high resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM) with electron dispersive x-ray spectroscopy

(EDS), x-ray diffraction (XRD) crystallography, and electrophoretic mobility (EPM) measurements. Aggregation rates of the CMNH and the component materials were measured with time-resolved dynamic light scattering (TRDLS) under a wide range of mono- and di-valent electrolyte concentrations and also in the presence of Suwannee River humic acid (SRHA). The antimicrobiality of OMWNT-TiO_2 NHs and the component materials under UV-irradiation was assessed by exposing the NH and its component materials to the opportunistic pathogen *Pseudomonas aeruginosa PAO1*. Mechanisms resulting in antimicrobiality have been studied using ROS species analysis.

[The planning, major experimental data collection, analyses, and completion of the work were led by Nirupam Aich. Dipesh Das and Dr. William Rigdon helped in synthesizing the NHs. Dr. Rigdon did his part under supervision of Dr. Xinyu Huang. Jaime Plazas-Tuttle helped in performing the ROS measurement and cell viability testing. Dr. Mary J Kirisits provided with intellectual contribution in the antimicrobiality testing. Dr. Navid Saleh suvervised the work.]

7.2 Materials and Methods

7.2.1 Synthesis of NHs

To determine the effect of hybridization and doping on the aggregation kinetics of OMWNTs, five different samples were synthesized and analyzed: oxidized (or functionalized) multiwalled carbon nanotubes (OMWNT), undoped TiO_2 hybridized OMWNT (OMWNT-TiO_2), OMWNT hybridized with niobium doped TiO_2 (OMWNT-$TiNbO_2$), OMWNT hybridized with undoped TiO_2 and Pt (OMWNT-TiO_2-Pt), and OMWNT hybridized with Nb-doped TiO_2 and Pt (OMWNT-$TiNbO_2$-Pt). For the antimicrobiality tests only two sets of samples were used; i.e., OMWNT and OMWNT-TiO_2 NHs. The detailed description of the synthesis protocol of these

NHs has been provided elsewhere.[23] In short, MWNTs with 8-15 nm outer diameter and 10-50 μm length (Cheap Tubes Inc., Brattleboro, VT) were first oxidized in a mixture of nitric and sulfuric acid.[67, 68] The oxidized MWNTs were then added to isopropanol (anhydrous) with titanium (IV) isopropoxide at atomic ratios of C:Ti=10:1 to 5:1 and the mixture was refluxed under N_2 at 80 °C for 2 h. For the Nb-doped cases, niobium ethoxide was added to substitute 10% titanium in the host oxide lattice.[23] An appropriate amount of DI water was then added to slowly control hydrolysis, condensation, and growth of the NHs[26, 69] for two additional hours, followed by evaporation of the solvent. Finally calcination of the obtained sample was performed at 450 ºC for 5 h under N_2.

Subsequent Pt deposition was carried out by a microwave assisted polyol reduction method. Fine powders of OMWNT-TiO_2 were dispersed using an ultrasonic dismembrator S-4000 (Misonix, Inc. Farmingdale, NY) in ethylene glycol followed by choloroplatinic acid hexahydrate addition (8% wt. $H_2PtCl_6 \cdot 6\ H_2O$). pH was maintained at 10 using NaOH to promote Pt nucleation. After stirring, mixtures were rapidly heated in a microwave oven to achieve a critical temperature of 140 °C to stimulate Pt growth.[70, 71] Finally, the suspension was filtered using vacuum filtration and the residue was obtained and washed with acetone and DI water followed by drying to obtain OMWNT-TiO_2-Pt or OMWNT-$TiNbO_2$-Pt NHs.

7.2.2 Preparation of NH Aqueous Suspensions

Uniform aqueous suspensions of the NHs and individual components, i.e., OMWNT, OMWNT-TiO_2, OMWNT-$TiNbO_2$, OMWNT-TiO_2-Pt, and OMWNT-$TiNbO_2$-Pt were prepared using a 2-step ultrasonication process. First, 2.5 mg of each powdered samples were sonicated (Misonix, Inc. Farmingdale, NY) in 25 mL filtered DI water for 15 min (energy amplitude 50, 18-20 W). Then an additional 25 mL of filtered DI water was added to the suspensions followed by a similar 15 min sonication to obtain a stock suspension of 50 mL at a concentration of ~5 mg/L., which were stored in the dark.

7.2.3 Solution Chemistry

For aggregation studies a wide range (10-400 mM) of mono-valent (NaCl from Lonza, Rockland, ME) salt concentrations was used to simulate common aquatic conditions. $CaCl_2$ (Teknova, Hollister, CA) at 1, 3, and 10 mM concentrations also was used to assess the role of di-valent cations on aggregation. 5 M NaCl and 1 M $CaCl_2$ stock solutions were diluted with filtered deionized (DI) water and to attain the desired ionic strength. To understand the role of natural organic matter (NOM) on NH aggregation, a mixed electrolyte condition, i.e., 7 mM NaCl and 1 mM $CaCl_2$, was used in the presence of standard II Suwannee River humic acid, SRHA (International Humic Substances Society, Denver, CO) at a concentration of 2.5 mg TOC/L.

7.2.4 NH Characterization

Electron microscopy and electrophoresis techniques were employed to characterize the physicochemical properties of the synthesized NHs and their aqueous suspensions. A JEOL 2010F HRTEM (JEOL USA, Inc, Pleasanton, CA), located at the Texas Materials Institute was used to image the NHs at various magnifications and at an accelerating voltage of 200 kV. The same equipment was used to obtain high annular angle dark field scanning transmission electron microscopic (HAADF-STEM) images of the NHs at high magnification along with EDS mapping of the elements. Drops of aqueous dispersions of NHs were placed on carbon coated copper TEM grids and air-dried over a few minutes. Several micrographs were taken to obtain representative images.

Crystalline structures of the NHs were investigated by performing XRD crystallography. A Rigaku R-axis Spider diffractometer with an image plate detector and Cu-Kα irradiator (wavelength of 0.154 nm) with a graphite monochromator was used for this purpose. The powdered samples were mounted on a cryo-loop using a minimal amount of mineral oil and were analyzed.

The electrokinetic properties of the NHs and their components were examined by electrophoretic mobility (EPM) measurements using a Brookhaven ZetaPALS instrument (Brookhaven Instrument Corporation, Holtsville, NY). Appropriate dilutions of NaCl salts were added to 2 mL of NH aqueous suspensions to generate the desired background chemistry. The stock was diluted 100 times to generate a working suspension. At least 3 replicate measurements were taken for each sample at each background condition. The measured EPM values were then converted to ξ-potential utilizing the Smoluchowski relationship.[72] The pH for all samples was left unadjusted (6.5±0.3).

7.2.5 Aggregation Kinetics Studies

Time resolved dynamic light scattering (TRDLS) was used to measure aggregation kinetics of the prepared NH suspensions at various environmentally relevant conditions. A highly sensitive ALV/CGS-3 compact goniometer system (ALV-Laser Vertriebsgesellschaft m-b.H., Langen/Hessen, Germany) equipped with 22 mW HeNe 632 nm laser (equivalent to 800 mW laser at 532 nm) and high QE APD detector with photomultipliers of 1:25 sensitivity was employed. The experimental details of the aggregation kinetics measurement have been described elsewhere.[42, 73-76] Briefly, stock suspensions were first diluted 100 times to perform the aggregation experiments. The diluted suspension (2 mL) was mixed with appropriate amounts of electrolytes or SRHA solutions in a pre-cleaned borosilicate glass vial. The vial with the working suspension was immediately vortexed and introduced to the DLS chamber followed by scattering data collection.[75] Laser attenuation was kept at 100% for all the samples and scattering data were collected at 90º at 15 s intervals continuously for 25 min for each sample.[75]

Hydrodynamic radii vs. Time plots were generated from the collected data and the aggregation histories were analyzed to obtain initial aggregation rates of the NHs and their component materials using equation 7.1[72, 75] and following the criteria described elsewhere.[42, 73, 74, 76, 77] For most conditions, the initial slope was calculated by linearly regressing the cluster sizes up to 1.3 times the initial hydrodynamic radius measured by the instrument at time t=0. For a few low ionic strength cases, 10-55 mM NaCl depending on types of NMs, attainment of 30% increase of the initial cluster sizes was not possible during the entire DLS run. In such cases, the slope of the initial linear region of the hydrodynamic radius vs. time plot was calculated. Attachment efficiency of the each of the suspensions at each solution condition was then obtained by normalizing the aggregation rate at each solution condition by the favorable aggregation rate (equation 7.2).[72]

$$k \propto \frac{1}{N_0}\left[\frac{dR_h(t)}{dt}\right]_{t\to 0} \qquad (7.1)$$

$$\alpha = \frac{\left[\frac{dR_h(t)}{dt}\right]_{t\to 0}}{\left[\frac{dR_h(t)}{dt}\right]_{t\to 0,fav}} \qquad (7.2)$$

7.2.6 Net Interaction (DLVO) Energy Calculation

The net interaction energies between OMWNT and OMWNT-TiO_2 pairs were calculated following classical DLVO theory; i.e., as the sum of the van der Waals attraction $V_A(h)$ and electrostatic double layer repulsion $V_{EDL}(h)$, using the following equations:

$$V_A(h) = -\frac{A_{121}a}{12h} \ldots\ldots\ldots(7.3)$$

$$V_{EDL}(h) = 64\pi\frac{n_b K_B T}{\kappa^2}\frac{a^2}{(h+2a)}\left[\tanh\left(\frac{ze\varphi}{4K_B T}\right)\right]^2 \exp(-\kappa h) \ldots\ldots(7.4)$$

$$V_T = V_{DLVO} = V_A(h) + V_{EDL}(h) \ldots\ldots(7.5)$$

where, 'a' is the hydrodynamic radius of the particle in m, 'A_{121}' is the Hamaker constant (J) of individual OMWNT or OMWNT-TiO_2 NH in aqueous media, 'h' is the separation distance between the particle in m, 'n_b' is ionic concentration, 'K_B' is the Boltzmann's constant (1.38×10^{-23} m^2 kg s^2 K^{-1}), 'T' is temperature in K, 'z' is valence of ions, 'e' is isolated unit electron charge (1.602×10^{-19} C), 'φ' is the surface potential in V, and '$1/\kappa$' is the Debye length in m.

The Hamaker constant for OMWNT in water ($A_{121,MWNT}$) was estimated as 2.77×10^{-21}J using equation 7.6 and the literature-reported Hamaker constant of MWNT (i.e. $A_{11,mwnt}=6\times10^{-20}$J)[78] and water ($A_{22,water}=3.7\times10^{-20}$J).[79] Composite Hamaker constant for OMWNT-TiO_2 NH in water ($A_{121,NH}$) was estimated as a weighted average of individual Hamaker constant values of OMWNT and TiO_2 in water. The literature-reported Hamaker constant of TiO_2 in water is $A_{121,TiO2}=5.35\times10^{-20}$J.[38] The weighting was based on atomic percentages of OMWNT (70%) and TiO_2 (30%) in OMWNT-TiO_2 NH obtained from x-ray photoelectron spectroscopic measurements. The Hamaker constant thus obtained was $A_{121,NH}=1.79\times10^{-20}$J for OMWNT-$TiO_2$ NH. However, experimental determination of Hamaker constant of these complex NHs is recommended for future studies.

$$A_{121,MWNT} = (\sqrt{A_{mwnt}} - \sqrt{A_{22,water}})^2 \ldots\ldots\ldots(7.6)$$

7.2.7 Photo-irradiation for Antimicrobial Studies

For the UV-induced ROS generation and antimicrobiality study, a wooden UV-chamber was constructed (Figure 7.1). This facilitated uniform UV irradiation to a 96-well plate from all sides. The UV irradiation was introduced by fours 9-W Phillips 325126 PL-S TUV germicidal light bulbs capable of illuminating at 253.7 nm wavelength.

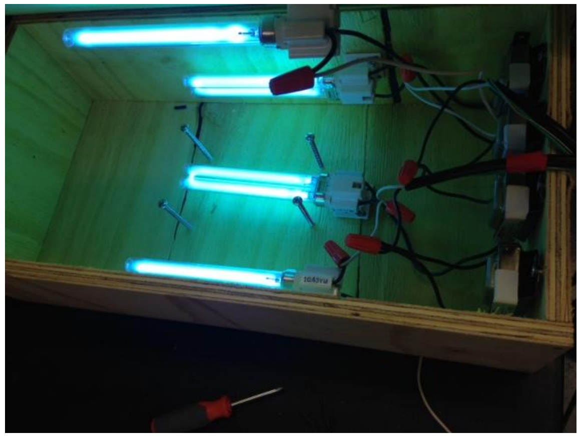

FIGURE 7.1. UV-chamber with 4 9-W Phillips PL-S TUV germicidal light bulbs.

7.2.8 ROS Measurements

Extracellular ROS generation by photo-induced OMWNT, TiO_2, and OMWNT-TiO_2 (5:1) NHs was measured by production of H_2O_2 using molecular fluorescence probes. An Amplex UltraRed hydrogen peroxide/peroxidase assay kit with Amplex Ultrared Stop Reagent was used to capture the ROS-mediated fluorescence produced by the samples. Each of the abovementioned NM or NH samples was first dispersed in DI water by 10 min sonication with ultrasonic dismembrator (Q-Sonica) at two different concentrations, i.e., 1 and 0.1 mg/L. The prepared suspensions were then added to the working solution of the ROS assay kit in a 96-well microtiter plate following the manufacturer's protocol.[80, 81] To evaluate the photo-induced ROS generation, one set of samples (a set of three samples) was irradiated for 10 s with UV-light inside the UV chamber and the another set (control) was kept in the dark for the same time period. Following this step the stop reagent was added to maintain the fluorescence and the plates were wrapped in aluminium foil to avoid interference from ambient light. Finally, fluorescence of the NM samples and the background (only DI reacted with the ROS assay) was measured using a Synergy-HT microplate reader (Biotek, Winooski, VT) with appropriate excitation (485 nm) and emission filters (590 nm). ROS concentrations were determined and reported in relative fluorescence units (R.F.U). Each measurement was performed in triplicate.

7.2.9 Cell Viability Experiments

Antimicrobiality of the OMWNT-TiO_2 NH and the component materials was tested by exposing the Gram-negative opportunistic human pathogen *P. aeruginosa* PAO1. A freezer stock of *P. aeruginosa* PAO1 was stuck on a Luria Betani (LB) agar plate and grown overnight. A single colony from the plate was then used to grow a bacteria culture in 15 mL LB medium at 37 °C with shaking (200 rpm) for 16 h. A 100-μL aliquot of the culture was added to fresh LB medium and was incubated at 37 °C for 4-6 hours until the optical density (O.D.) as measured by the above mentioned microplate reader reached 0.2-0.3, representing mid-exponential growth. The culture suspensions were centrifuged at 2500×g for 15 min using a 5810R Eppendorf centrifuge (Eppendorf AG, Hamburg, Germany). The supernatant was pipetted out and the remaining cell residue was re-suspended in 15 mL 1x Gibco™ phosphate buffer saline (PBS) solution (Fisher Scientific, Pittsburgh, PA). The procedure of centrifugation and re-suspension in PBS media was repeated twice to remove the remaining LB growth medium and prepare the cells in PBS for the NM or NH exposure.

Each NM or its components was sonicated for 10 min in PBS to produce 1 and 0.1 mg/L suspensions, which were subjected to autoclaving in the liquid cycle to ensure decontamination before use. A 10 μL aliquot of the prepared PBS suspension of the sample (OMWNT, TiO_2, or NH) was then added to 90 μL of the bacteria-PBS suspension in a microtiter plate to achieve exposure concentrations of 0.1 and 0.01 mg/L, respectively. For the control, only 10 μL 10x PBS solution was added to the cells. One set of (a set of three samples) exposed samples and controls was then subjected to the UV-irradiation for 10 s, while the other samples were kept in the dark. Each concentration of the NMs was exposed to the cells in triplicates. Then, the cells were incubated at 37 ºC for 2 h and were serially diluted and grown on LB agar plates for cell viability assessment as described in Chambers et al.[82]

7.3 Results and Discussion

7.3.1 Morphological Characteristics and Chemical Identity

Figure 7.2 presents representative EM micrographs of the hierarchical OMWNT-$TiNbO_2$-Pt NHs. Representative bright field HRTEM micrographs in Figure 7.2 (a-d) shows individually separated and un-bundled NHs indicating their uniform aqueous dispersibility and effective oxidative functionalization. Overall, individually separated dark quasi-spherical metallic NPs in the size range of 3-7 nm are observed on the OMWNT surface with exception of few agglomerates. The STEM images are presented in Figure 7.2(e-f), which also show the distribution of bright spherical metallic NPs sitting on the nanotube walls. Figure 7.2 (g-j) shows elemental mapping obtained via EDS spectroscopy to confirm the presence of Ti, Nb, and Pt in the NH. It is important to note that Nb (Figure 7.2i) and Pt (Figure 7.2j) NPs' elemental signatures overlap with the Ti (figure 7.2h) NP position. This indicates that Nb doping and Pt hybridization are closely associated with the TiO_2 NPs on the hybrid structures.

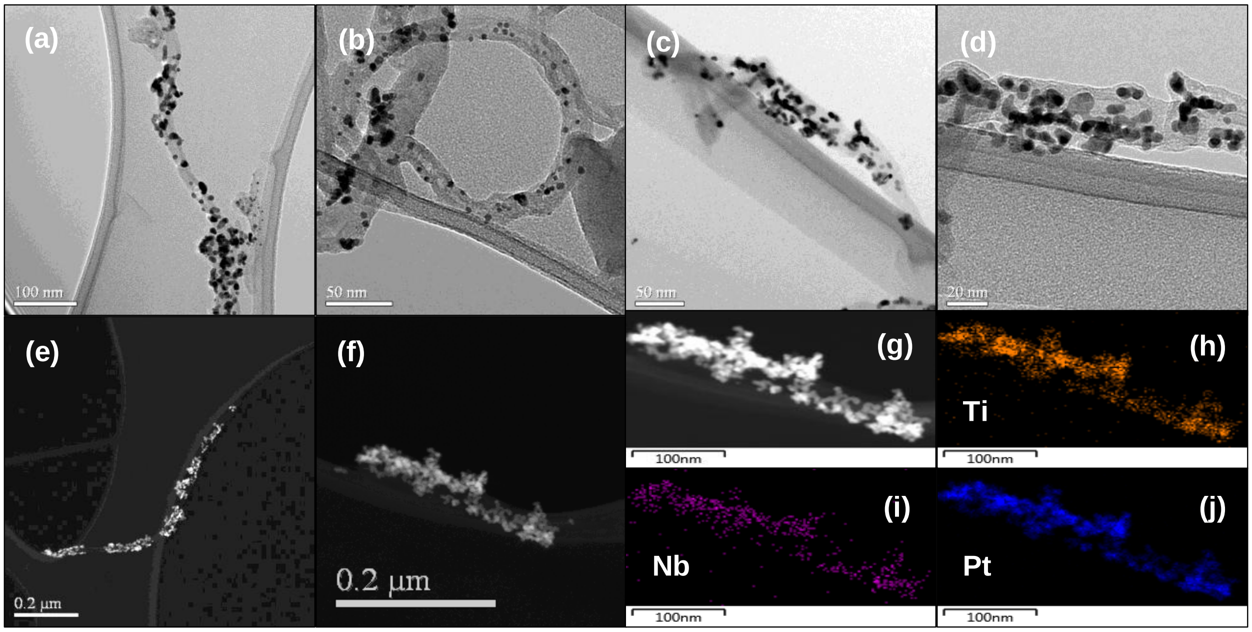

FIGURE 7.2. (a-d) HRTEM micrographs of the OMWNT-$TiNbO_2$ NHs, (e-f) STEM micrographs of the OMWNT-$TiNbO_2$ NHs, and (g-f) STEM micrograph of a short section of OMWNT-$TiNbO_2$ NH with elemental mapping.

The XRD patterns of the OMWNT-TiO_2 and OMWNT-TiO_2-Pt NHs are presented in Figure 7.3. OMWNT-TiO_2 (10:1) NH presents crystalline peaks for both carbon and TiO_2. Besides a strong overlapping C/TiO_2 peak at 25.7° as presented in previous literature,[23] it shows carbon peaks at 43.2°, 53.2°, and 77.8° as well as weaker TiO_2 peaks at 37.5°, 48°, and 62.8°. TiO_2 peaks correspond to pure anatase phase, which is commonly obtained through calcination at a temperature below 500°C.[83] With the increasing TiO_2 concentration in OMWNT-TiO_2 (5:1) NH, carbon peaks disappear and TiO_2 peaks rise in amplitude. OMWNT-TiO_2-Pt NH shows strong occurrence of peaks at 39.7°, 46.2°, 67.4°, and 81.2°; which confirm the presence of Pt and the peak amplitudes overshadow carbon or TiO_2 peaks.[23, 84] Nb-doping reduces TiO_2 and carbon peaks significantly (Figure E-1 in Appendix E) but not the Pt peaks; however, no separate Nb peaks were observed. This confirms that Nb is incorporated within the TiO_2 crystal lattice and not outside.[83]

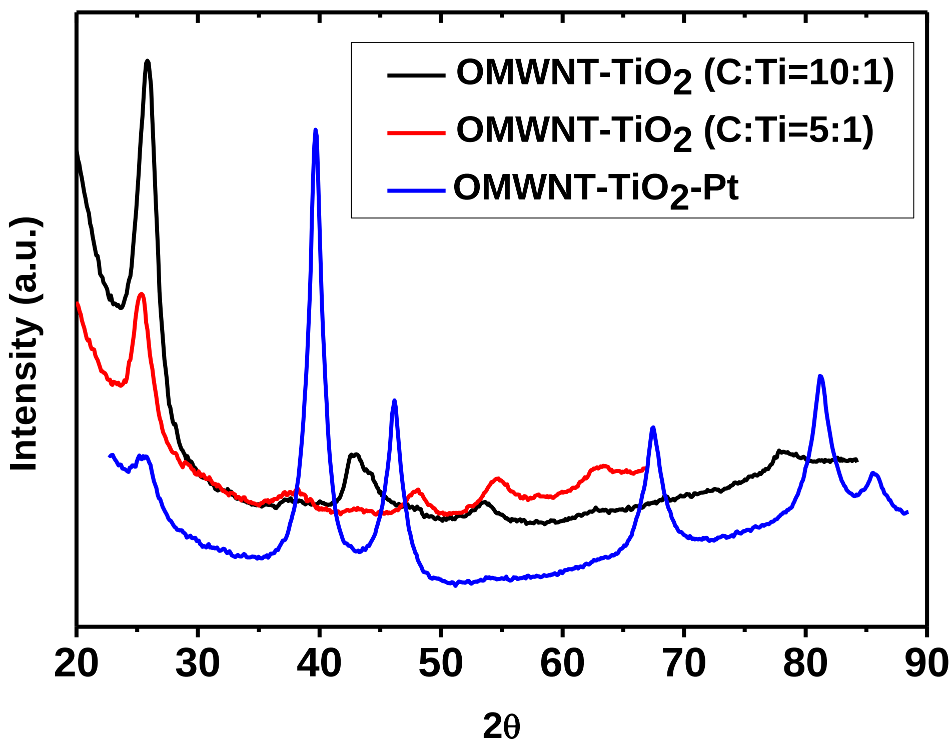

FIGURE 7.3. XRD spectra of OMWNT-TiO_2 and OMWNT-TiO_2-Pt NH.

7.3.2 Electrokinetic Properties

Figure 7.4 presents the electrokinetic properties of the NHs and the component materials in the presence of a wide range of NaCl concentration. All NHs and component materials presented with a high negative surface charge even at high ionic strength of 100 mM NaCl. However, a decreasing trend of the surface charge with increasing salt concentration is observed. OMWNTs possessed the highest EPM values ranging from $-4.3\pm0.5\times10^{-8}$ $m^2V^{-1}S^{-2}$ with no electrolyte addition to $-2.7\pm0.4\times10^{-8}$ $m^2V^{-1}S^{-2}$ in the presence of 100 mM NaCl. OMWNT-TiO_2 NH showed the lowest negative surface charge ranging from $-3.75\pm0.4\times10^{-8}$ to $-2.4\pm0.4\times10^{-8}$ $m^2V^{-1}S^{-2}$. All the other NHs including OMWNT-TiO_2-Pt, OMWNT-$TiNbO_2$, and OMWNT-$TiNbO_2$-Pt exhibit EPM values in between or closer to that of OMWNTs.

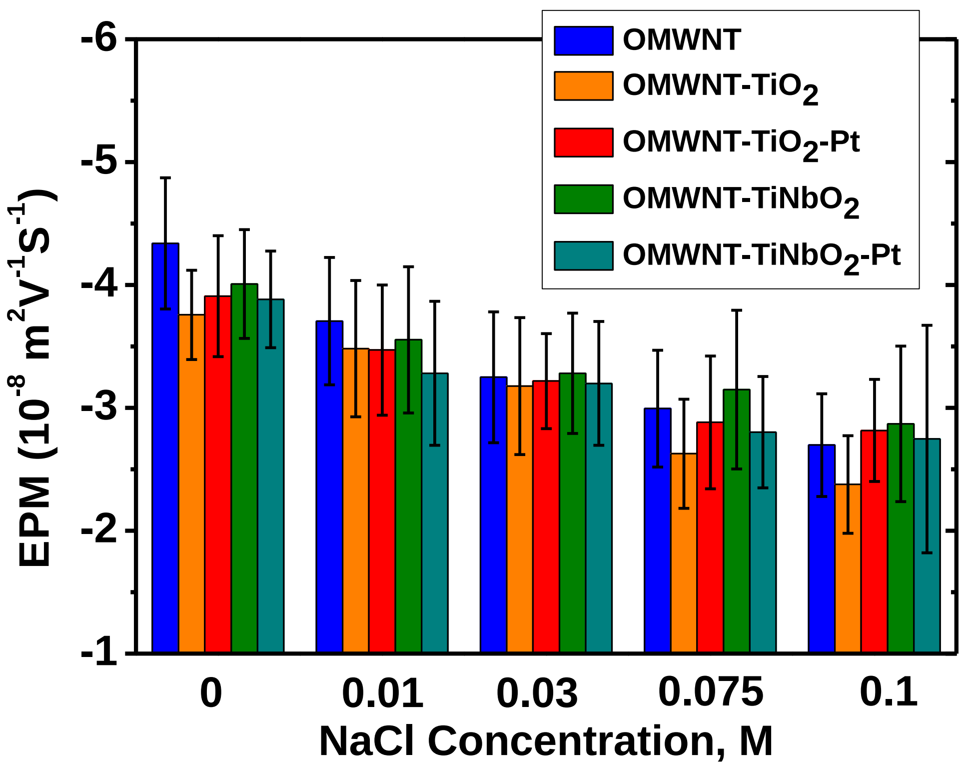

FIGURE 7.4. Electrophoretic mobility (EPM) values of OMWNT, TiO_2, and Pt conjugated NHs at different NaCl concentrations. Measurements were performed at unadjusted pH=6.5±0.3 and 25 ºC.

Strongly oxidized carbon nanotubes have previously been shown to attain such high surface charge because of the carboxyl and hydroxyl functional groups.[43, 85] Decrease of OMWNT surface charge by attachment of TiO_2 has also been shown in the literature.[86] Previous literature shows higher negative surface charge of colloidally stable Pt-TiO_2 conjugate than TiO_2 due to direct charge transfer from Pt to TiO_2.[87] However, EPM values for Nb-doped or hierarchically Pt-conjugated carbon nanotubes have not been reported earlier. Nb dopant donates electrons to enhance the conductivity of the NH[23] and probably contributes to enhanced surface charge.[88] The hierarchical conjugation is a complex phenomenon and will require more systematic investigation to understand the contribution from each of the component materials.

7.3.2 Aggregation Kinetics and Mechanisms

Aggregation kinetics of OMWNT and the four NHs (OMWNT-TiO_2, OMWNT-TiO_2-PT, OMWNT-$TiNbO_2$, and OMWNT were determined over a wide range of mono-valent NaCl concentrations. Three selected materials, OMWNT, OMWNT-TiO_2, and OMWNT-TiO_2-Pt also were exposed to select ranges of $CaCl_2$ salts. The aggregation histories are presented in Figures E-2 and E-3. TRDLS determined initial hydrodynamic radii of OMWNT, OMWNT-TiO2, OMWNT-TiO_2-Pt, OMWNT-$TiNbO_2$, and OMWNT-$TiNbO_2$-Pt are 132±10, 106±9.4, 112±8.8, 107±6.9, and 109±8.3 nm, respectively. The difference in the hydrodynamic radii between OMWNT and the NHs probably occurred due to successive sonication and exposure to reactants during the NH synthesis process. As electrolyte concentrations increase, hydrodynamic radii of OMWNT and NHs increase with time at a faster rate. Figure 7.5a presents the obtained stability plot showing distinct unfavorable or reaction limited (RLCA) and favorable or diffusion limited regimes (DLCA) for OMWNT and NHs. The transition from RLCA to DLCA regime is characterized by critical coagulation concentration (CCC). The CCC values are estimated to be 150, 62, 185, 160, and 280 mM NaCl for OMWNT, OMWNT-TiO_2, OMWNT-$TiNbO_2$, and OMWNT-$TiNbO_2$-Pt, respectively. The estimated CCC values show an intriguing trend. OMWNT-TiO_2 NH shows the lowest CCC value, while OMWNT and other NHs containing Pt and Nb show significantly higher values. The trend of aggregation propensity thus is OMWNT-TiO_2>>OMWNT>OMWNT-$TiNbO_2$>OMWNT-TiO_2-Pt>>OMWNT-$TiNbO_2$-Pt.

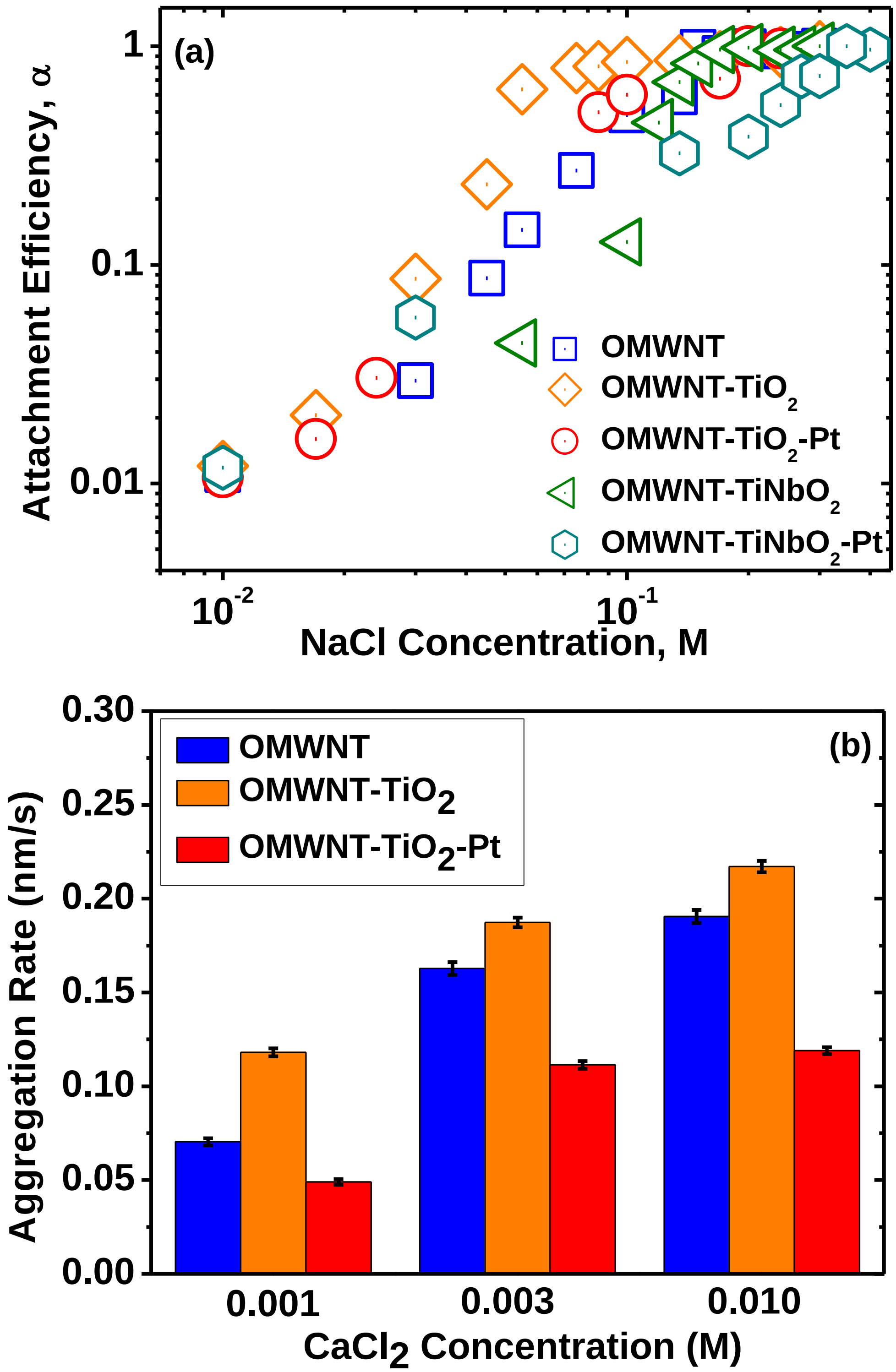

FIGURE 7.5. (a) Stability plots of OMWNT, OMWNT-TiO_2, OMWNT-TiO_2-Pt, OMWNT-$TiNbO_2$, and OMWNT-TiO_2-Pt NHs as a function of mono-valent NaCl concentrations. (b) Aggregation rates of OMWNT, OMWNT-TiO_2, and OMWNT-TiO_2-Pt NH for select divalent $CaCl_2$ concentrations.

Figure 7.6b presents the aggregation rates for OMWNT and their undoped conjugates in the presence of $CaCl_2$. The trend in aggregation propensity remains similar to that in the mono-valent case. The aggregation rates are faster in $CaCl_2$ than in similar NaCl concentration due to larger compression of double layer by the divalent cations.

Literature reports exist for CCC values of OMWNTs and TiO_2, while these are the first reports for the conjugated materials. Depending on extent of oxidation, CCC values of OMWNTs range from 93-210 mM NaCl.[43, 89] Thus CCC of OMWNT obtained in this study falls within the range. TiO_2 (spherical anatase) possesses CCC varying between 25-65 mM NaCl as a function of primary particle size (i.e., ranging from 6-54 nm).[90] A recent study presented CCC value for graphene oxide-TiO_2 nanocomposite as 40 mM NaCl, which shows decline of CCC value of graphene oxide when conjugated with TiO_2.[51] Thus CCC value of OMWNT-TiO_2 NH is probably dominated by the presence of TiO_2 on the OMWNT surface. Further probing with DLVO modeling was performed to understand the mechanism.

To delineate the aggregation mechanisms of OMWNT and conjugated nanostructures, interaction energies were calculated using the DLVO theory. Figure 7.6 shows net interaction energies obtained for OMWNT and OMWNT-TiO_2 NHs at different NaCl concentrations utilizing an average Hamaker constant value for the OMWNT-TiO_2. The model essentially shows that TiO_2 with higher van der Waals energy dominates the aggregation process for the OMWNT-TiO_2 conjugates. This is shown by the change in the net interaction energy, which shows a barrier to aggregation for OMWNT, even at 100 mM NaCl condition, whereas hybridization with TiO_2 eliminates such barrier at electrolyte concentration as low as 30 mM. The EPM values of both OMWNT and OMWNT-TiO_2 NH remain highly negative even at high ionic strength. Thus it can be concluded that van der Waals attraction controls the aggregation process of OMWNT-TiO_2 NH. Similar dominance of van der Waals attraction in graphene oxide-TiO_2 hybrid aggregation has been reported.[51]

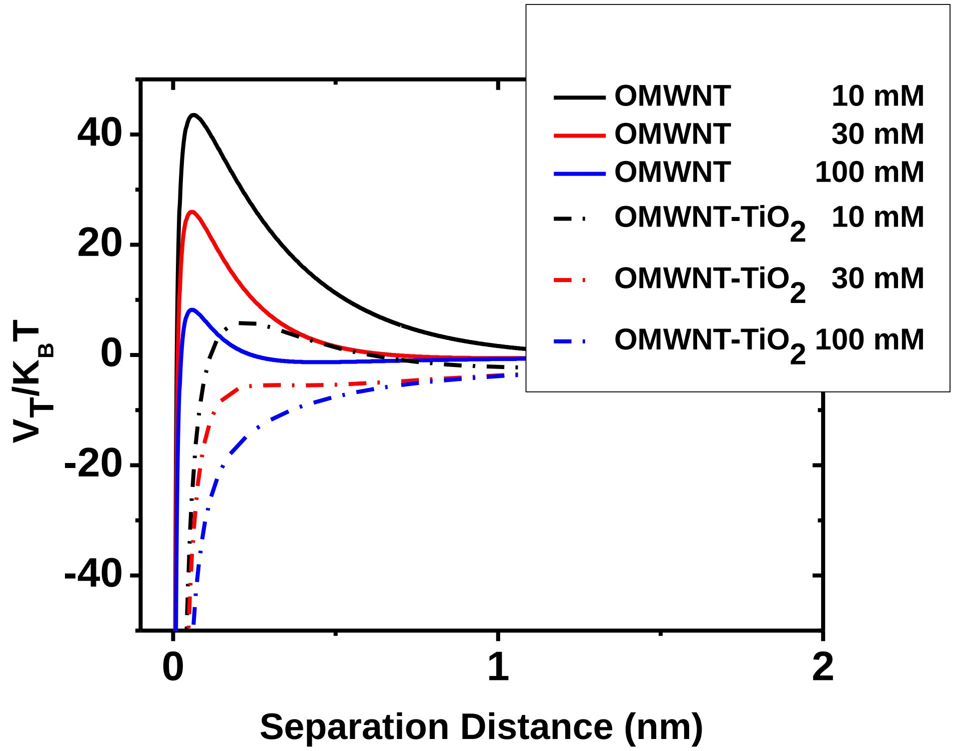

FIGURE 7.6. Estimated total interaction energy (V_T/K_BT) with separation distance using modified DLVO theory for OMWNT and OMWNT-TiO_2 NH in the presence of mono-valent NaCl electrolytes.

Estimation of interaction energies via DLVO theory was not possible for the Pt conjugated and Nb-doped NHs, due to the lack of reports of Hamaker constant values of these materials. The Pt-hybridized and Nb-doped NHs exhibit high stability compared to the undoped TiO_2 NHs. However, the small differences in the EPM values would not seem to explain the large reduction in aggregation propensity of the Pt-hybridized and Nb-doped NHs. Doping with super-valent metal atoms is known to alter the aggregation behavior of TiO_2 by reducing the isoelectric point (IEP). This can partially explain the enhanced stability for Nb-doped TiO_2 stabilization result.[91] The significant increase in CCC for Pt-deposited NHs is most likely controlled by a lowering of van der Waals interaction between the NHs, since EPM values do not show a substantial difference when compared to the OMWNT-TiO_2 NH (Figure 7.4). van der Waals attractive interaction is composed of Keesom, Debye, and London dispersion intermolecular interactions, among which London interaction is the most dominant.[79] London interaction is a strong function of material polarizability (α_p), which is defined as a material's ability to polarize or distort the electron clouds around it in the presence of an external electrical field and allows the creation of an induced dipole of the material in concern; London interaction is proportional to the square of α_p (Equation 7.7). Here, 'V_L' is the energy contribution from London interaction forces between two similar materials (OMWNT-pairs or similar NH-pairs in this context), 'I' is the ionization potential of the material, and 'r' is the separation distance between the materials.

$$V_L = -\frac{3}{4}\frac{\alpha_p^2 I}{r^6} \ldots\ldots (7.7)$$

The α_p values for Pt and Ti are 6.5 and 14.6 F-$m^2$$atom^{-1}$, respectively.[92] Though the presence of Ti presence thus has increased the van der Waals interaction between NHs via increased polarizability of the material (i.e., Ti), introduction of Pt in the NH likely reduces the van der Waals interaction by a substantial reduction in London interaction between the NHs. Besides, Pt deposition has been shown to stiffen the carbon nanotube.[19] Thus, Pt-deposited carbon nanotubes, which show resistance to buckling, might result in reduced interaction. However, such analysis is purely speculation at this point and requires systematic assessment of van der Waals interaction energy measurement and understanding the role of stiffness, if any, on aggregation of colloids.

7.3.3 Role of Humic Acid on Aggregation

Presence of SRHA at 2.5 mg TOC/L concentration stabilizes OMWNT and NHs at 10 mM total ionic strength (7 mM NaCl and 1 mM $CaCl_2$). Aggregation rates of OMWNT and OMWNT-

TiO_2 NH were reduced by 70% and 60%, respectively as presented in Figure 7.7. However, all the other NHs were completely stabilized and showed no measurable aggregation. Such stabilization can be attributed toward steric repulsion produced by adsorbed SRHA on the OMWNT and NH surfaces. Similar stabilization by natural macromolecules in the presence of mono-valent cations was previously observed for oxidized MWNTs and other NMs.[75, 76] NH mobility and fate in the natural environment can be highly influenced by such stabilization. However, high ionic strength and di-valent cation cases should be evaluated for better understanding of their fate in environments with elevated ionic strength.

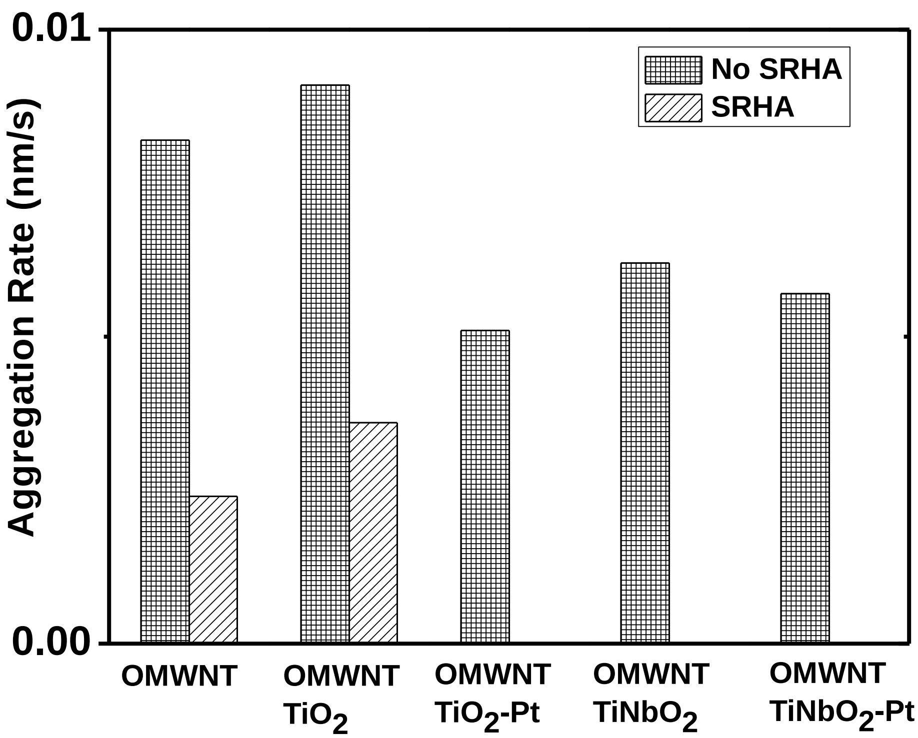

FIGURE 7.7. Aggregation rates of OMWNT and hierarchical NHs without and with the presence of 2.5 mg/L TOC SRHA. 7 mM NaCl and 1 mM $CaCl_2$ was present in each case.

7.3.4 Antimicrobiality of NHs

To evaluate the effect of hybridization on antimicrobiality, standard cell viability tests were performed using *P. aeruginosa* PAO1 bacteria under dark and UV-irradiated conditions. Figure 7.8a presents the cell viability results.

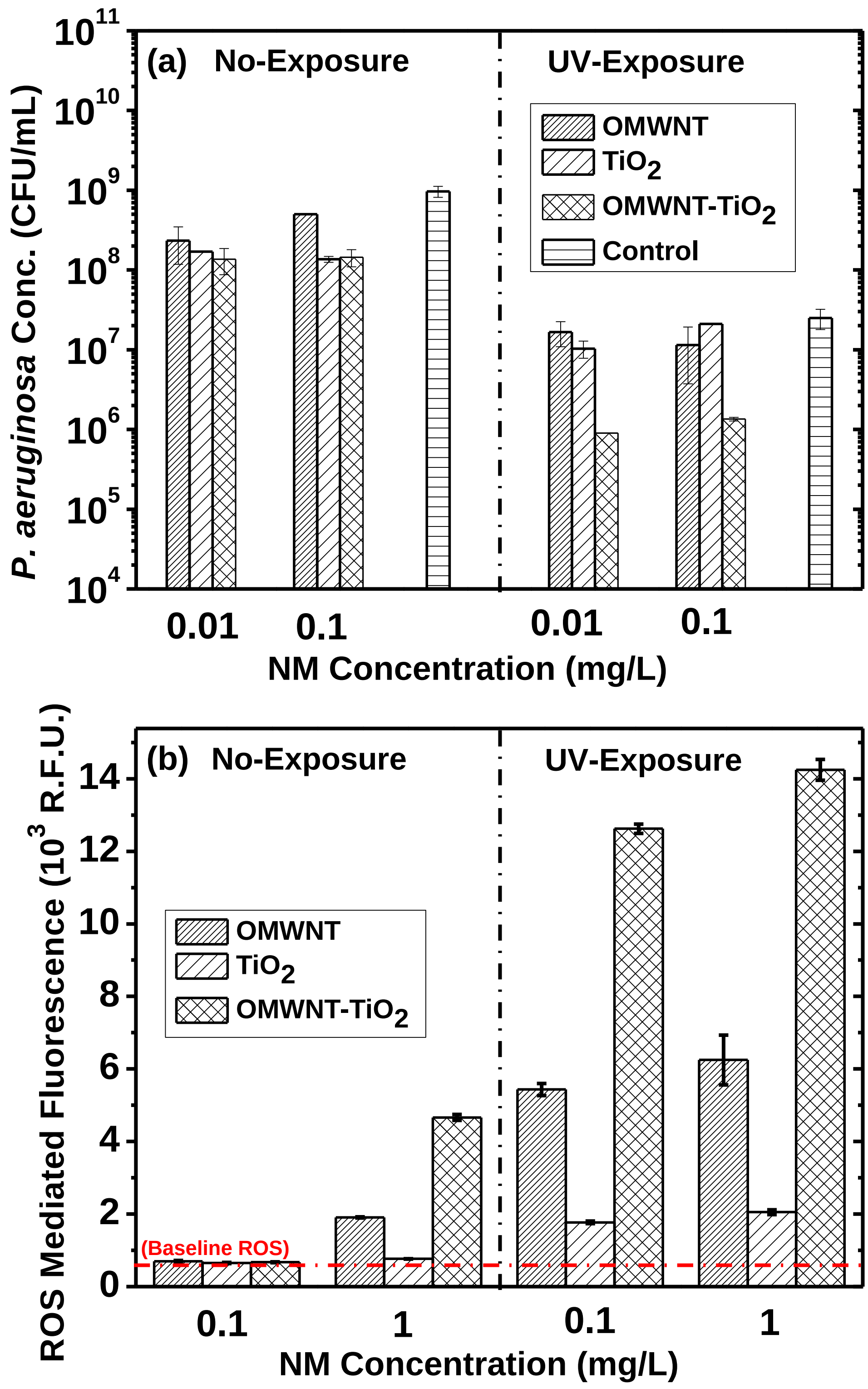

FIGURE 7.8. (a) Viable cell count of *P aeruginosa* under exposure as a function of different concentrations of OMWNT, TiO_2, and OMWNT-TiO_2 NH in dark and under UV-irradiation. (b) ROS generation as a function of OMWNT, TiO_2, and OMWNT-TiO_2 NH concentrations in dark and under UV-irradiation. The horizontal red line shows the baseline fluorescence for deionized water.

In the dark, exposure of the both TiO_2 and the NH shows a slight decrease (less than 1 log) in the bacterial count. However, no effect on cell viability was observed with an increase in the NM concentration from 0.01 to 0.1 mg/L. Under UV-irradiation for 10 s, >1-log inactivation was observed when no NM was present, showing disinfection via UV light only. With exposure to UV and OMWNT or TiO_2, no measurable difference in cell viability is observed as compared to the UV-only control. However, UV and OMWNT-TiO_2 NH at both 0.01 and 0.1 mg/L concentrations produced a 1-log unit decrease in cell viability as compared to the UV-only control. To assess the underlying mechanism behind UV-induced antimicrobiality of the OMWNT-TiO_2 NHs, extracellular ROS measurement with a fluorescence probe to detect H_2O_2 was used. H_2O_2 is an important intermediate (to superoxides and hydroxyl radicals) ROS that has shown to be generated from UV-irradiation of TiO_2 NMs and has been reported to be cause cellular toxicity.[93] However, generation of superoxide and hydroxyl radicals should also be assessed to discern the role of each of the species in antimicrobiality. Figure 7.8b shows ROS-mediated fluorescence for OMWNT, TiO_2, and OMWNT-TiO_2 NH both under dark and UV-irradiated conditions. The horizontal red line shows the baseline fluorescence for deionized water. NH and the component materials at 0.1 mg/L concentration in the dark produce insignificant amounts of ROS (<100 R.F.U). However, with UV-irradiation, ROS production increases and reaches more than 10000 R.F.U. Significant difference was observed between the ROS generation by OMWNT-TiO_2 and its component materials. At 0.1 mg/L under UV-irradiation, OMWNT-TiO_2 NH exhibits ~2.5- and ~10-fold increase in ROS production compared to OMWNT and TiO_2, respectively. Such enhancement in ROS generation corroborates with the increase in antimicrobiality at these conditions. At 1 mg/L concentration of the NMs, ROS increase is observed for the NH and its component materials, with a profound increase in ROS production in case of the OMWNT-TiO_2 NH. This higher NM concentration of 1 mg/L was used to obtain better fluorescence signal. Literature reports have shown band gap reduction of conjugated CNT/graphene-TiO_2 nanostructures resulting in enhanced photoactivity and ROS generation capability.[50] Thus, electronic and photocatalytic property alterations for OMWNT-TiO_2 NH are likely causing the enhanced bacterial inactivation under these conditions. However, the postulated mechanism of ROS-mediated toxicity has been derived based on extracellular measurements and needs to be validated by measurements of intracellular ROS production. Previous literature reported internalization of metal-hybridized carbon nanotubes inside mammalian cells[94]; which can cause generation of intracellular ROS resulting into antimicrobiality. Numerous other potential mechanisms of cellular toxicity remains unexamined including physical interaction of NHs with cell-membrane, lipid oxidation, interactions with transport proteins or intracellular components and enzymatic pathways. Simultaneously, probing emergent properties of the NHs including altered band gap, mechanical stiffness, surface chemistry, also is required to accurately delineate the mechanisms of antimicrobiality.

7.4 Environmental Implications

Results of this study imply that conjugation of multiple nano-entities gives rise to unexpected environmental behavior when compared to their component materials. Aggregation of OMWNT-based NHs is dependent on the type of conjugated materials and is controlled by the van der Waals interaction of the hybridized entities. Pt-hybridized and Nb-doped NHs are highly stable in aqueous environments compared to the OMWNT-TiO_2 conjugates. Thus lowering of the van der Waals interaction by hybridizing with less polarizable metal (Pt) can decrease aggregation propensity and enhance mobility of metal-carbon NHs in the environment. The presence of natural macromolecules will further stabilize the NHs and thus will enhance their mobility. Photo-activation of NHs during their transport in natural aquatic environment, e.g., in shallow surface water conditions, will likely result in increased antimicrobiality, mediated by ROS generation. Such enhanced mobility supplemented by profound photo-reaction can present substantial environmental risks for this important class of metal-carbon electrocatalyst NHs.

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Chapter 8: Conclusions and Future Recommendations

8.1 Conclusions

The research presented in this dissertation identifies data gaps at the frontier of nano environmental health and safety (EHS) and assesses selected environmental interactions of the hierarchical nanostructures. Through extensive literature review (presented in Chapters 2 and 3), relevant hierarchical nanostructures, including higher order fullerenes (HOFs) and conjugated nanohybrids (NHs) have been identified. The detailed literature review also resulted in identifying altered and emergent physicochemical properties of these hierarchical structures and discussed potential significance in presenting uncertainty for assessing environmental fate, transport, transformation, and toxicity of these 'horizon' materials. The key data gaps that this dissertation (Chapters 4-7) addresses include: 1) aqueous solubilization of HOFs for environmental implications studies; 2) size control of C_{60} and HOF aqueous clusters with a non-ionic biocompatible polymer; 3) HOF aggregation kinetics in aquatic environment as a function of carbon number in fullerene cages; and 4) effect of hybridization of metal-oxide nanoparticles with carbon nanotubes on aggregation kinetics and antimicrobiality. State-of-the-art characterization techniques, i.e., electron microscopy, UV-vis spectroscopy, x-ray diffraction, electron-dispersive spectroscopy, atomic force microscopy, electro-kinetic methods, and light scattering, were employed to assess the behavior in the aqueous systems. Modified Derjaguin-Landau-Verwey-Overbeek (DLVO) and molecular dynamic (MD) simulations were utilized to assess mechanisms of interaction. Photo-induced reactive oxygen species (ROS) generation and bacterial cell viability tests were performed to assess antimicrobiality of NHs and the component materials. The major conclusions derived from this research are summarized below.

8.1.1 Fullerenes, higher fullerenes, and their hybrids: synthesis, characterization, and environmental considerations (Chapter 2)

- C_{60}s and HOFs are used in nano-enabled energy applications, e.g., solar cells, photovoltaics, hydrogen storage, batteries, capacitors, etc.
- Environmental implication studies including aggregation, deposition/transport, transformation, and toxicity are mostly limited to C_{60}s and their derivatives.
- State-of-the-art literature lacks in environmental implication studies for HOFs and fullerene-based NHs.
- Environmental considerations for C_{60}, HOFs, and their NHs should also include the influence of the solvents, coatings, or molecules for surface modification.
- The critical data-gap regarding environmental implications of HOFs and fullerene-NHs should be addressed.

8.1.2 A critical review of nanohybrids: synthesis, applications, and environmental applications (Chapter 3)

- Material development in the nano-scale has shifted toward conjugated and hierarchical NHs in the pursuit of enhanced-functionality. This led to exponential growth in research regarding NH synthesis and application. From the environmental perspective a working definition of NHs can be proposed: *more than one nanomaterial of unique chemical origin or differing dimensionality when conjugated together via molecular or macromolecular links or physicochemical forces or when one nanomaterial overcoats another possessing unique chemical identity, or when complex soft molecules are engineered to chemically bind to nanomaterial surfaces, all to enhance existing functionality or achieve multifunctional usage, can be defined as NHs*

- NHs can be classified in four categories: carbon-carbon, carbon-metal, metal-metal, and organic molecule coated NHs.
- NHs introduces altered physicochemical properties and emergent unique properties, relevant to their environmental fate, transport, transformation, and toxicity.
    - NHs can show altered band gap due to change in their electronic properties. This can lead to altered surface chemistry and interfacial interactions influencing aggregation, deposition, or transport.
    - Reduced band gap in NHs can also alter photo-activity leading to enhanced transformation and toxicity.
    - Dimensional alterations due to hybridization can change environmental interactions.
    - Altered dimensionality or surface area and surface chemistry of NHs can influence adsorption of geo- and bio-macromolecules changing transformation.
    - Core-shell metallic or metal-graphitic NHs can show altered metal dissolution (Zn^{2+}, Ag^{+} ions), leading to changes in their toxic potential.
    - Hybridization can alter mechanical properties (e.g., stiffness of carbon nanotubes), which can change physical interactions with cellular microorganisms.
- Environmental risks of NHs will likely be more than the summation of the components.

8.1.3 Preparation and characterization of stable aqueous higher order fullerenes (Chapter 4)

- Increasing carbon numbers in HOFs lead to a linear increase in the binding energy between like fullerenes as demonstrated by MD simulation results.
- Calorimetric energy increase during sonication with increasing carbon numbers in HOFs

can successfully assist their aqueous solubilisation via solvent exchange process.

- Aqueous nHOF aggregates in deionized water remain stable over time within a narrow size distribution in the absence of electrolytes.
- Similar to nC_{60} aggregates, nHOFs also possess negative surface charge and are stabilized by electrostatic repulsion.

8.1.4 Preparation of non-aggregating aqueous fullerenes in highly saline solutions with a biocompatible non-ionic polymer (Chapter 5)

- Pluronic acid (PA) F-127, a biocompatible non-ionic triblock copolymer, can be used to prepare stable aqueous suspensions of nC_{60} and nC_{70} without the use of a toxic organic solvent.
- Increase in PA concentration (0.001-1% w/v) increases the concentrations of the fullerenes in the aqueous suspensions.
- Average hydrodynamic radii of the nC_{60}s and nC_{70}s decreases from 85-90 nm to 58-62 nm with the increase in PA concentrations from 0.001 to 0.1% and reaches a plateau.
- Size distributions of the clusters become narrower as the PA concentrations increase.
- Effective size control of nC_{60} and nC_{70} clusters is possible due to steric crowding of PA molecules around them.
- PA modified nC_{60} and nC_{70} clusters attain exceptional dispersion stability even in the presence highly saline solutions including 1M NaCl and biological cell culture media, e.g., Dulbecco's Modified Eagle Medium (DMEM), and Roswell Park Memorial Institute (RPMI) culture medium.
- Such exceptional colloidal stability and effective size control of PA modified fullerene clusters in highly saline solutions is attributed to steric repulsion produced by the

adsorbed non-ionic PA polymer.

8.1.5 Aggregation kinetics of higher order fullerenes in aquatic systems (Chapter 6)

- nC_{60} and nHOFs produced by solvent exchange method experience aggregation with increasing mono- (NaCl) and di-valent ($CaCl_2$) electrolyte concentrations.
- nHOFs possess higher aggregation propensity compared to nC_{60}.
- CCC values of nC_{60} and nHOFs linearly decreased with increasing carbon number. The relationship is more systematic for NaCl compared to $CaCl_2$.
- Net interaction energies between like-fullerene pairs in aqueous media (calculated by MD simulations) increases linearly with increasing carbon numbers in fullerene.
- Modified DLVO energy estimates show strong influence of vdW attraction energies with increasing carbon number, causing enhanced aggregation in cases of nHOFs.
- SRHA had a significant stabilization effect on nC_{60} and nHOFs reducing the aggregation rates by 80-95% even in presence of 100 mM NaCl.
- At low ionic strength of 10 mM all the nC_{60} and nHOFs were completely stabilized in the presence of SRHA.

8.1.6 Aggregation kinetics and antimicrobiality of TiO_2-multiwalled carbon nanotube nanohybrids (Chapter 7)

- OMWNT and sequentially synthesized NHs (OMWNT-TiO_2, OMWNT-$TiNbO_2$, OMWNT-TiO_2-Pt, and OMWNT-$TiNbO_2$-Pt) show DLVO type aggregation.
- Aggregation kinetics of the NHs is dictated by the type of the metal NPs present.
- OMWNT when hybridized with undoped TiO_2 showed higher aggregation with a lower CCC value.
- Nb-doping and Pt attachment makes OMWNT-TiO_2 NHs more stable and reaches CCC

values in the range of 170-270 mM NaCl.

- Electrostatic repulsion and vdW attraction both play significant roles in the aggregation behaviour of the NHs.
- OMWNT-TiO_2 NH showed higher inactivation of *P aeruginosa* in the presence of UV-irradiation when compared to OMWNT and TiO_2 component NPs.
- UV-irradiation mediated enhanced ROS generation is a likely mechanism for the increased antimicrobial capacity of OMWNT-TiO_2 NH (compared to OMWNT and TiO_2).

8.2 Environmental Implications of the Research

Hierarchical nanostructures, e.g., HOFs and nanohybrids (NHs) are becoming more attractive in for their ability to manifest multifunctionality and present emergent properties, thus increasing the environmental release and risk. Understanding the fate and toxicity of these novel HOFs and NHs is the key to understanding the associated hazard. This research is the first-of-its kind to layout strategies for studying EHS of NHs. The proposed definition of the NHs identifies a large set of materials that preset emergent properties leading to unique environmental interactions, hence necessitates systematic EHS assessment. This research also calls for new nano-EHS assessment strategies that goes beyond current practices to adequately assess emergent properties and expands into the forthcoming horizon nanomaterials.

This research developed two different methods for aqueous solubilization of HOFs – first with the solvent-exchange protocol and secondly using a non-ionic biocompatible polymer. These methods will enable environmental implication studies of HOFs (e.g., aggregation, transport, and toxicity) to be performed with greater control. Moreover, the method specific aggregation behavior implies to the importance of solvent/surfactant considerations for environmental implications of HOFs. For example, PA modified fullerenes may possess significantly higher mobility in the natural environment even at high ionic strength marine or estuarine environments when compared to the nC_{60} and nHOFs obtained through solvent exchange protocol.

This research systematically assessed aggregation behavior of HOFs (C_{70}, C_{76}, and C_{84}) in aquatic conditions. A strong linear correlation between CCC values with carbon number in fullerenes has been established. Carbon number can be used to predict CCC of HOFs in aquatic systems. The presence of electrolytes in natural waters likely will result in a high degree of aggregation for HOFs and will make them less mobile (compared to nC_{60}) in the aquatic systems. However, the presence of geo- and bio-macromolecules will likely stabilize the HOFs, even in presence of elevated electrolyte concentrations. Thus HOFs may become highly mobile in most aquatic environments with the presence of natural organic matter.

Aggregation behavior and toxicity of carbon-metallic NHs evaluated in this research identifies the uncertainty associated with environmental implications of this emerging class of nanomaterials. This is the first study to systematically study the effect of hybridization on the aggregation kinetics of conjugated nanostructures. Findings of this study indicate that the type of the metal nanoparticles attached on the surface of OMWNT will dictate their aggregation behavior. While, undoped TiO_2 upon conjugation with OMWNT decreases the CCC value below 100 mM NaCl (~70 mM NaCl), the colloidal stability increases significantly either by doping with Nb or by attachment of Pt NPs, leading to increase in CCC values up to 270 mM NaCl. Thus depending on the type of metal presence on the OMWNT surface, the aggregation propensity will vary in the natural environment. Furthermore, aggregation rates of OMWNT and

OMWNT-TiO_2 NHs are reduced by the presence of Suwannee River Humic Acid (SRHA), where Nb-doped TiO_2 and Pt attached NHs are completely stabilized by SRHA.

Hybridization enhanced UV-irradiated ROS generation and resulted in increased antimicrobial activity of the OMWNTs and TiO_2. Thus when exposed to sunlight in shallow surface water, these NHs may present increased toxicity to micro-organisms and other aquatic species. It is important to note that TiO_2 NPs typically are highly aggregating in aqueous environment and have CCC values in the range of 5-50 mM NaCl. However, OMWNT-TiO_2 NHs with higher CCC values (~75 mM NaCl) and enhanced phototoxicity can introduce elevated ecotoxicological concerns.

8.3 Recommendations for Future Research

The research presented in this dissertation is the first study on environmental implications of hierarchical nanostructures; i.e., HOFs (C_{70}, C_{76}, C_{84}, etc.) and multi-component NHs. Some of the future research needs are discussed in the following sections.

8.3.1 Transport, Transformation, and Toxicity of HOFs

This research assesses aqueous solubilisation and aggregation kinetics of HOFs for the first time. The key challenge identified in this study was to model the aggregation process of HOFs. The limitation is accurate estimation or measured values of van der Waals interaction energies. Determination of Hamaker constant values for the HOFs in aqueous media is necessary to better assess the mechanistic interfacial interaction of the HOFs. Also, the debate on origin of surface charge of aqueous nC_{60} and nHOFs need to be resolved. Furthermore, the higher mobility of HOFs in presence of natural organic matter necessitates systematic assessment of their environmental transformation and ecotoxicity.

Pluronic acid mediated size control can be effective in determining size specific environmental effects of C_{60}s and HOFs. The highly stable HOF clusters modified with biocompatible pluronic acid can result in careful assessment of size-specific eco- and nano-toxicity. Similarly, NOM stabilization and enhanced mobility of HOFs presented in this study highlights the considerations for geo- and bio-macromolecules in determining HOF fate and toxicity. However, this research only involved one type and concentration of organic matter (i.e., 2.5 mg TOC/L SRHA). Systematic investigation in presence of organic matter with a range of composition is necessary to better understand the fate and transport in aquatic systems.

8.3.2 Fate, Transformation, and Toxicity of NHs

This study delineating the aggregation kinetics and toxicity of carbon-metallic NH is the first of its kind to study EHS of hierarchical nanostructures. High degree of control over the conjugation process is desired. Novel characterization techniques of the conjugated materials are required to measure the emergent properties that the NHs may introduce. Moreover, control over the NH morphology, i.e., length, metal nanoparticle size and distribution, etc., need to be achievied in these nierarchical NM synthesis to further asseses their EHS. Further studies assessing aggregation and deposition of NHs and their components are necessitated. Accurate determination of Hamaker constant values is needed to model the aggregation process of these complex nanostructures. Similarly, the eco-toxicity studies with other gram-negative and gram-positive bacteria and higher species are desired. Mechanisms of toxicity need to be determined by studying the role of emergent properties with the known mechanisms. Furthermore, the role of ionic strength on toxicity behavior should be examined to determine the effect on NH aggregation in exposure media and subsequent microbial interaction.

Appendix A

Supplemental Information for Chapter 3
A Critical Review of Nanohybrids - Synthesis, Applications, and Environmental Implications

TABLE A-1. Annual production of articles in nanohybrid literature in the Web of Science, 1998-2012. The last column corresponds to a classification according to the definition offered by the authors.

Year	No. of Publications in NH Literature	NH of Env. Importance
1998	1	1
1999	3	2
2000	7	7
2001	9	9
2002	17	13
2003	14	12
2004	31	27
2005	36	30
2006	65	60
2007	58	53
2008	84	75
2009	106	88
2010	98	78
2011	147	113
2012	205	184
	881	752

TABLE A-2. Potential applications of nanohybrids.

Application	No. of Publications
Adsorption studies	8
Antimicrobial/antibacterial applications	8
Biomaterials	20
Catalytic/Photocatalytic/Electrocatalytic applications	65
Crystallography and polymer crystallization	31
Delivery Carriers, and Controlled Release of Drugs/Compounds	75
Dental research	0
Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	95
Fluorescence/luminescence/photoluminescence, light-energy harvesting	47
Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	39
Membrane research, gas removal, pollutant remediation	3
N/A*	129
Optical imaging and applications	47
Physical/electrical/mechanical properties (thermal, resistance, magnetic)	61
Semiconductors/superconductors/conductive materials	32
Sensors/biosensors/electrochemical sensors	65
Synthesis of new nanohybrids/materials	152
Transparent and conductive films	4
Total	881

*This category groups publications in which no NH could be identified or classified according to the definition of Environmentally Unique NH presented by the authors. It also includes articles in which the information could not be retrieved, was not available, or was not clear. Note: NH of environmental importance = 752.

TABLE A-3. Classification of publications from 1998 to 2012 using the Web of Science® search engine. Criteria: "nanohybrid" or "nano-hybrid". Literature was selected when it originated from scientific articles and referred specifically to the following combination of keywords, special character (*), and search field (Title): "Title=(nano-hybrid*) OR Title=(nanohybrid*)

#	Year	Title	Authors	Research Areas	Materials	Application	NH of Env Significance
1	1998	Superionic and superconducting nanohybrids with heterostructure, AgxIwBi2Sr2Can-1CunOy (0.76 <= x <= 1.17, n = 1, 2, and 3)	Choy, JH; Kim, YI; Hwang, SJ	Chemistry	AgxIwBi2ST2Can-1CunOy (n = 1, 2, and 3)	Semiconductors/superconductors/conductive materials	MMNH
2	1999	Intercalation route to nano-hybrids: inorganic/organic-high T-c cuprate hybrid materials	Choy, JH; Kwon, SJ; Hwang, SJ; et al.	Chemistry; Materials Science	M-X-Bi2Sr2Cam-1CumOy (M = Hg, Ag, Au; X = Br, I; m = 1-3), R2HgI4-Bi2Sr2Cam-1CumOy (R = organic cation)	Semiconductors/superconductors/conductive materials	OMCNH
3	1999	Intercalative nanohybrids of nucleoside monophosphates and DNA in layered metal hydroxide	Choy, JH; Kwak, SY; Park, JS; et al.	Chemistry	N/A	N/A	N/A
4	2000	Preparation of organic-inorganic nanohybrids by intercalation reactions	Fujita, K; Tagaya, H; Kadokawa, J	Polymer Science	Isonicotinic acid, Zn(OH)2	Synthesis of new nanohybrids/materials	OMCNH
5	2000	Novel synthetic route to superconducting-insulating nanohybrids	Choy, JH; Kwon, SJ; Jang, ES	Crystallography	Polymer, Cuprate, Cu	Semiconductors/superconductors/conductive materials	OMCNH
6	2000	Synthesis of TiO2-SiO2 nano-hybrid and its adsorption of polyelectrolyte	Hua, FJ; Sun, J; Gao, L; et al.	Chemistry	TiO2, SiO2	Adsorption studies	MMNH
7	2000	Intercalation route to novel superconducting nano-hybrids	Choy, JH; Lee, W; Jang, ES; et al.	Crystallography	M-X-Bi2Sr2Can-1CunOy (M = Ng, Ag, Au; X = Br, I; n = 1, 2, and 3), R2HgI4-Bi2Si2Can-1CunOy (R = organic cation)	Semiconductors/superconductors/conductive materials	OMCNH
8	2000	Nanohybrids of metal nanoparticles and block copolymers. Control of spatial distribution of the nanoparticles in microdomain space	Okumura, A; Tsutsumi, K; Hashimoto, T	Polymer Science	Pd, poly(2-vinylpyridine)-block-polyisoprene	Synthesis of new nanohybrids/materials	OMCNH
9	2000	HRTEM and micro-Raman studies on superconducting-superionic conducting nanohybrid, Ag1.17I1.54Bi2Sr2CaCu2Oy	Choy, JH; Kim, YI; Hwang, SJ; et al.	Chemistry	Ag1.17I1.54Bi2Sr2CaCu2Oy	Semiconductors/superconductors/conductive materials	MMNH
10	2001	Cellular uptake behavior of [gamma-P-32] labeled ATP-LDH nanohybrids	Choy, JH; Kwak, SY; Park, JS; et al.	Chemistry; Materials Science	Mg4Al2(OH)(12)(NO3)(2). mH(2)O, NO3-, biomolecules	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
11	2001	Nanohybrids of non-stoichiometric zinc ferrite in amorphous silica	Zhou, ZH; Wang, J; Xue, JM; et al.	Chemistry; Materials Science	Fe, Zn, Si	Crystallography and polymer crystallization	MMNH
12	2001	Structural modelling of Eu3+-based siloxane-poly(oxyethylene) nanohybrids	Dahmauche, K; Carlos, LD; Bermudez, VD; et al.	Chemistry; Materials Science	Polymer, Eu3+	Synthesis of new nanohybrids/materials	OMCNH
13	2001	Coordination of Eu3+ ions in siliceous nanohybrids containing short polyether chains and bridging urea cross-links	Bermudez, VD; Ferreira, RAS; Carlos, LD; et al.	Chemistry	Silica, Urea, Eu3+	Crystallography and polymer crystallization	MMNH
14	2001	Magnetic probing of tunable Eu3+ local site in organic-inorganic nanohybrids	Amaral, VS; Carlos, LD; Bermudez, VD	Engineering; Physics	Polymer, Urea, Eu3+	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
15	2001	Energy-transfer mechanisms and emission quantum yields in Eu3+-based siloxane-poly(oxyethylene) nanohybrids	Ferreira, RAS; Carlos, LD; Goncalves, RR; et al.	Chemistry; Materials Science	Polymer, Urea, Eu3+	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
16	2001	Cluster glass structure in nanohybrids of nonstoichiometric zinc ferrite in silica matrix	Zhou, ZH; Wang, J; Xue, JM; et al.	Physics	Fe, Zn, Si	Crystallography and polymer crystallization	MMNH

17	2002	A novel quantum dot pillared layered transition metal sulfide: CdS-MoS2 semiconductor-metal nanohybrid	Lee, JK; Lee, W; Yoon, TJ; et al.	Chemistry; Materials Science	CdS-MoS2	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
18	2002	Polyester layered silicate nanohybrids by controlled grafting polymerization	Lepoittevin, B; Pantoustier, N; Alexandre, M; et al.	Chemistry; Materials Science	Silica, caprolactone	Catalytic/Photocatalytic/Electrocatalytic applications	OMCNH
19	2002	Synthesis of layered organic-inorganic nanohybrid material: an organic dye, naphthol blue black in magnesium-aluminum layered double hydroxide inorganic lamella	bin Hussein, MZ; Zainal, Z; Yahaya, AH; et al.	Materials Science; Physics	Mg, Al, naphthol blue black (NBB)	Synthesis of new nanohybrids/materials	OMCNH
20	2002	A new nanohybrid photocatalyst between anatase (TiO2) and layered titanate	Lee, HC; Jung, H; Oh, JM; et al.	Chemistry	TiO2, titanate	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
21	2002	Exfoliation and restacking route to anatase-layered titanate nanohybrid with enhanced photocatalytic activity	Choy, JH; Lee, HC; Jung, H; et al.	Chemistry; Materials Science	TiO2, titanate, anatase	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
22	2002	Layered silicate/polyester nanohybrids by controlled ring-opening polymerization	Lepoittevin, B; Pantoustier, N; Alexandre, M; et al.	Polymer Science	Silicate, polyester	Synthesis of new nanohybrids/materials	OMCNH
23	2002	High temperature proton conducting organic-inorganic nanohybrids for polymer electrolyte membrane - Part II	Nakajima, H; Nomura, S; Sugimoto, T; et al.	Electrochemistry; Materials Science	N/A	N/A	N/A
24	2002	Layer-by-layer self-assembling of liposomal nanohybrid "cerasome" on substrates	Katagiri, K; Hamasaki, R; Ariga, K; et al.	Chemistry; Materials Science	Cerasome, Silicate	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
25	2002	Amphiphilic organic/inorganic nanohybrid macromolecules for intermediate-temperature proton conducting electrolyte membranes	Honma, I; Nakajima, H; Nishikawa, O; et al.	Electrochemistry; Materials Science	N/A	N/A	N/A
26	2002	Bio-LDH nanohybrid for gene therapy	Kwak, SY; Jeong, YJ; Park, JS; et al.	Chemistry; Physics	LDH, NO3-, biomolecules	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
27	2002	Intercalative route to heterostructured nanohybrids	Choy, JH; Paek, SM; Oh, JM; et al.	Materials Science; Physics	Titanate, MoS2, Cuprate	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
28	2002	Heterostructured high-T-c superconducting nanohybrid: (Me3S)(2)HgI4-Bi2Sr2CaCu2Oy	Kwon, SJ; Choy, JH; Jung, D; et al.	Physics	Cuprate, HgI2, organic cations	Semiconductors/superconductors/conductive materials	OMCNH
29	2003	Single-wall carbon nanotube-ferrocene nanohybrids: Observing intramolecular electron transfer in functionalized SWNTs	Guldi, DM; Marcaccio, M; Paolucci, D; et al.	Chemistry	SWNT, ferrocene	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
30	2003	Transparent nanohybrids of nanocrystalline TiO2 in PMMA with unique nonlinear optical behavior	Yuwono, AH; Xue, JM; Wang, J; et al.	Chemistry; Materials Science	TiO2, PMMA	Optical imaging and applications	OMCNH
31	2003	Sulfidation of single molecular sheets of MoO3 pillared by bipyridine in nanohybrid MoO3(4,4 '-bipyridyl)(0.5)	Wei, XM; Zeng, HC	Chemistry; Materials Science	N/A	N/A	N/A
32	2003	Nanohybrid scratch resistant coatings for teeth and bone viscoelasticity manifested in tribology	de la Isla, A; Brostow, W; Bujard, B; et al.	Materials Science	N/A	N/A	N/A
33	2003	The synthesis and morphology characteristic study of BAO-ODPA polyimide/TiO2 nano hybrid films	Chiang, PC; Whang, WT	Polymer Science	Polyimide, TiO2	Optical imaging and applications	OMCNH
34	2003	Effect of molecular weight of poly(epsilon-caprolactone) on interpenetrating network structure, apatite-forming ability, and degradability of poly(epsilon-caprolactone)/silica nano-hybrid	Rhee, SH	Engineering; Materials Science	Poly(epsilon-caprolactone), silica, calcium salt	Biomaterials	OMCNH

		materials					
35	2003	Magnetic properties of Fe-doped organic-inorganic nanohybrids	Silva, NJO; Amaral, VS; Carlos, LD; et al.	Physics	Siloxane (Si), urea, Fe	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
36	2003	Deposition of layer-by-layer inorganic-organic nano-hybrid Ultrathin films, electronics onto SBA-15	Ding, HM; Wang, LP; Shan, YK; et al.	Chemistry	TiO2, dye mcs, polymer, silicate	Synthesis of new nanohybrids/materials	OMCNH
37	2003	Structure of magnetic poly(oxyethylene)-siloxane nanohybrids doped with Fe-II and Fe-III	Silva, NJO; Dahmouche, K; Santilli, CV; et al.	Crystallography	Siloxane (Si), poly(oxyethylene), Fe	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
38	2003	Novel polyimide/silica nanohybrids from water glass	Wang, HT; Zhong, W; Du, QG; et al.	Polymer Science	Polyimide, SiO2	Crystallography and polymer crystallization	OMCNH
39	2003	Study on intercalative nanohybrid of cordycepin in layered double hydroxide	Ling, JY; Yang, J; Yang, QZ; et al.	Chemistry	Mg, Al, NO3-, biomolecules	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
40	2003	Synthesis of bioactive organic-inorganic nanohybrid for bone repair through sol-gel processing	Miyazaki, T; Ohtsuki, C; Tanihara, M	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Si, CaCl2, calcium acetate, Polymers	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
41	2004	Integrating single-wall carbon nanotubes into donor-acceptor nanohybrids	Guldi, DM; Rahman, GMA; Jux, N; et al.	Chemistry	SWNT, pyrene, zn porphyrin complex	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
42	2004	TEM characterization of sol-gel-processed alumina-silica and alumina-titanic nano-hybrid oxide catalysts	Wunderlich, W; Padmaja, P; Warrier, KGK	Materials Science	Alumina, Titania, Silica	Synthesis of new nanohybrids/materials	MMNH
43	2004	Construction of intermolecular communication system on "Cerasome" as an organic-inorganic nanohybrid	Sasaki, Y; Yamada, M; Terashima, T; et al.	Polymer Science	Cerasome, amino groups, pyridoxal 5'-phosphate, Cu	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
44	2004	Urethane cross-linked poly(oxyethylene)/siliceous nanohybrids doped with Eu3+ ions - Part 1. Coordinating ability of the host matrix	Bermudez, VD; Ostrovskii, D; Goncalves, MC; et al.	Chemistry; Physics	Silica, Urea, Eu3+	Crystallography and polymer crystallization	OMCNH
45	2004	Urethane cross-linked poly(oxyethylene)/siliceous nanohybrids doped with Eu3+ ions - Part 2. Ionic association	Bermudez, VD; Ostrovskii, D; Lavoryk, S; et al.	Chemistry; Physics	Silica, Urea, Eu3+	Crystallography and polymer crystallization	OMCNH
46	2004	Intercalative route to heterostructured nanohybrid	Choy, JH	Chemistry; Physics	Titanate, Cuprate, LDH, Pyridine, Biomolecules	Semiconductors/superconductors/conductive materials	OMCNH
47	2004	The synthesis and characteristic study of 6FDA-6FHP-NLO polyimide/SiO2 nanohybrid materials	Qiu, FX; Zhou, YM; Liu, JZ	Polymer Science	Polyimide, SiO2	Optical imaging and applications	OMCNH
48	2004	Nanohybrids from liquid crystalline extended amphiphilic dendrimers	Cho, BK; Jain, A; Mahajan, S; et al.	Chemistry	Poly(ethylene oxide), amphiphilic dendrimers, Silica, alumina	Synthesis of new nanohybrids/materials	OMCNH
49	2004	Photoluminescence and quantum yields of urea and urethane cross-linked nanohybrids derived from carboxylic acid solvolysis	Fu, LS; Ferreira, RAS; Silva, NJO; et al.	Chemistry; Materials Science	Urea, urethane	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
50	2004	Applications of telechelic polymers as compatibilizers and stabilizers in polymer blends and inorganic/organic nanohybrids	Kim, J; Kim, SS; Kim, KH; et al.	Polymer Science	N/A	N/A	N/A
51	2004	Synthesis and gas sensing properties of polypyrrole/MoO3-layered nanohybrids	Matsubara, I; Hosono, K; Murayama, N;	Chemistry	Polypyrrole, MoO3	Sensors/biosensors/electrochemical sensors	OMCNH

			et al.				
52	2004	Anatase crystal growth and photocatalytic characteristics of hot water-treated polyethylene oxide-titania nanohybrids	Sung, YM; Lee, YJ; Lee, SM	Crystallography; Materials Science; Physics	Polyethylene oxide, TiO2	Catalytic/Photocatalytic/Electrocatalytic applications	OMCNH
53	2004	Synthesis of organo-mineral nanohybrid material: indole-2-carboxylate in the lamella of Zn-Al-layered double hydroxide	bin Hussein, MZ; Long, CW	Materials Science	Zn, Al, Indole	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
54	2004	Optically functional Di-urethanesil nanohybrids containing Eu3+ ions	Goncalves, MC; Bermudez, VD; Ferreira, RAS; et al.	Chemistry; Materials Science	Poly(oxyethylene), siloxane, Eu	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
55	2004	Controlled morphology and crystalline phase of poly(ethylene oxide)-TiO2 nanohybrids	Sung, YM; Lee, JK	Chemistry; Crystallography; Materials Science	Poly(ethylene oxide), TiO2	Crystallography and polymer crystallization	OMCNH
56	2004	Cerasome as an organic-inorganic vesicular nanohybrid: Characterization of cerasome-forming lipids having a single or a dual trialkoxysilyl head	Hashizume, M; Inoue, H; Katagiri, K; et al.	Materials Science	Cerasome, siloxane	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
57	2004	Influence of host lattice on the chemical bonding nature of guest species in high-T-c superconducting I-Bi2Sr1.5-x,LaxCa1.5CU2Oy nanohybrids	Hwang, SJ; Park, DH; Choy, JH	Chemistry	I, Bi, Sr, La, Cu	Semiconductors/superconductors/conductive materials	MMNH
58	2004	Synthesis of kaolinite-organic nanohybrids with butanediols	Murakami, J; Itagaki, T; Kuroda, K	Chemistry; Physics	Kaolinite, methanol	Synthesis of new nanohybrids/materials	OMCNH
59	2004	Poly(N-isopropylacrylamide)-coated carbon nanotubes: Temperature-sensitive molecular nanohybrids in water	Kong, H; Li, WW; Gao, C; et al.	Polymer Science	MWNT, poly(N-isopropylacrylamide)	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
60	2004	Properties of polyimide/silica nanohybrids from silicic acid oligomer	Wang, HT; Zhong, W; Xu, P; et al.	Materials Science; Polymer Science	Polyimide, SiO2	Crystallography and polymer crystallization	OMCNH
61	2004	Surface roughness of nanofill and nanohybrid composite resin and ormocer-based tooth-colored restorative materials after several finishing and polishing procedures	Baseren, M	Engineering; Materials Science	N/A	N/A	N/A
62	2004	Synthesis and morphological characterization on PVP/ZnO nano hybrid films	Du, T; Ilegbusi, OJ	Materials Science	PVP, ZnO	Synthesis of new nanohybrids/materials	OMCNH
63	2004	Organic-inorganic polyamidoamine (PAMAM) dendrimer-polyhedral oligosilsesquioxane (POSS) nanohybrids	Dvornic, PR; Hartmann-Thompson, C; Keinath, SE; et al.	Polymer Science	Polyamidoamine dendrimer, polyhedral oligosilsesquioxane	Crystallography and polymer crystallization	OMCNH
64	2004	Controlling the crystallinity and nonlinear optical properties of transparent TiO2-PMMA nanohybrids	Yuwono, AH; Liu, BH; Xue, JM; et al.	Chemistry; Materials Science	Polymethyl methacrilate, TiO2	Optical imaging and applications	OMCNH
65	2004	Organic-inorganic nanohybrids obtained by sequential copolymerization of epsilon-caprolactone and L,L-lactide from activated clay surface	Pollet, E; Delcourt, C; Alexandre, M; et al.	Polymer Science	caprolactone, lactide, clay	Crystallography and polymer crystallization	OMCNH
66	2004	Preparation of the electrode for high temperature PEFCs using novel polymer electrolytes based on organic/inorganic nanohybrids	Nishikawa, O; Sugimoto, T; Nomura, S; et al.	Electrochemistry	N/A	N/A	N/A
67	2005	Evaluation of a chitosan nano-hybrid material containing silanol group and calcium salt as a bioactive bone graft	Rhee, SH; Lee, YK; Lim, BS	Materials Science	Chitosan, siloxane	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH

68	2005	A robust three-dimensional mesoporous Ag/TiO2 nanohybrid film	Wang, XC; Yu, JC; Ho, CM; et al.	Chemistry	Ag, TiO2	Synthesis of new nanohybrids/materials	OMCNH
69	2005	Polyimide/silica/titania nanohybrids via a novel non-hydrolytic sol-gel route	Wang, HT; Zhong, W; Xu, P; et al.	Engineering; Materials Science	Polyimide, SiO2, TiO2	Optical imaging and applications	OMCNH
70	2005	Immobilization of glucose oxidase using pyrrole-titania nanohybrids for electrochemical biosensor applications	Sung, YM; Park, KS; Lee, YJ; et al.	Electrochemistry; Materials Science	Pyrrole, TiO2	Sensors/biosensors/electrochemical sensors	OMCNH
71	2005	Influence of pH on the formation of Tyr/LDH nanohybrids	Li, SP; Zhao, G; Chen, HY	Chemistry	Tyrosine, LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
72	2005	Structuration of organo-minerals: nanohybrid materials resulting from the incorporation of alcohols in the tunnels of palygorskite	Kuang, W; Detellier, C	Chemistry; Materials Science	N/A	N/A	N/A
73	2005	Effect of surface stabilization of nanoparticles on luminescent characteristics in ZnO/poly(hydroxyethyl methacrylate) nanohybrid films	Hung, CH; Whang, WT	Chemistry; Materials Science	Poly(hydroxyethyl methacrylate), ZnO	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
74	2005	Effect of the polyimide structure and ZnO concentration on the morphology and characteristics of polyimide/ZnO nanohybrid films	Hsu, SC; Whang, WT; Hung, CH; et al.	Polymer Science	Polyimide, ZnO2	Crystallography and polymer crystallization	OMCNH
75	2005	Matrix assisted formation of ferrihydrite nanoparticles in a siloxane/poly(oxyethylene) nanohybrid	Silva, NJO; Amaral, VS; Bermudez, VD; et al.	Chemistry; Materials Science	Poly(oxyethylene), siloxane	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
76	2005	Optical characteristics of photo-curable methacryl-oligosiloxane nano hybrid thick films	Eo, YJ; Kim, JH; Ko, JH; et al.	Materials Science	N/A	N/A	N/A
77	2005	Soft-x-ray absorption spectroscopy of heterostructured high-T-c superconducting nanohybrids: X-Bi2Sr2CaCu2O8 [X=I, HgI2, and (Py-CH3)(2)HgI4]	Chen, JM; Chang, SC; Liu, RS; et al.	Physics	I, Hg, pyridine	Semiconductors/superconductors/conductive materials	MMNH
78	2005	Synthesis and molecular structure analysis of nano-sized methacryl-grafted polysiloxane resin for fabrication of nano hybrid materials	Eo, YJ; Lee, TH; Kim, SY; et al.	Polymer Science	N/A	N/A	N/A
79	2005	Inclusion of ferrocene in a cyclodextrin-functionalized layered metal hydroxide: A new organometallic-organic-LDH nanohybrid	Mohanambe, L; Vasudevan, S	Chemistry	Cyclodextrin, ferrocene	Synthesis of new nanohybrids/materials	OMCNH
80	2005	Multiwalled carbon nanotubes in donor-acceptor nanohybrids - towards long-lived electron transfer products	Guldi, DM; Rahman, GMA; Jux, N; et al.	Chemistry	MWNT, metalloporphyrin	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
81	2005	Dispersable carbon nanotube/gold nanohybrids: Evidence for strong electronic interactions	Rahman, GMA; Guldi, DM; Zambon, E; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	SWNT, MWNT, Au	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CMNH
82	2005	Nanohybrid Shish-kebabs: Periodically functionalized carbon nanotubes	Li, CY; Li, LY; Cai, WW; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	SWNT, MWNT, polyethylene and nylon	Synthesis of new nanohybrids/materials	OMCNH
83	2005	Interfacial interactions and structure of organic-inorganic nanohybrids	Zeng, QH; Yu, AB; Lu, GQ; et al.	Materials Science; Metallurgy & Metallurgical Engineering	dioctadecyldimethyl ammonium, clay	Synthesis of new nanohybrids/materials	OMCNH
84	2005	Transparent TiO2-PMMA	Yuwono, AH;	Optical; Physics	Polymethyl methacrilate,	Optical imaging and	OMCNH

		nanohybrids of high nanocrystallinity and enhanced nonlinear optical properties	Xue, JM; Wang, J; et al.		TiO2	applications	
85	2005	Synthesis beta-Sialon powder with rectorite/phenolic resin nano-hybrid precursor	Wang, ZF; Zhang, BG; Wang, XT; et al.	Materials Science; Metallurgy & Metallurgical Engineering	N/A	N/A	N/A
86	2005	An inorganic nanohybrid with high specific surface area: TiO2-pillared MoS2	Paek, SM; Jung, H; Park, M; et al.	Chemistry; Materials Science	TiO2, MoS2	Synthesis of new nanohybrids/materials	MMNH
87	2005	Organic-inorganic nanohybridization by block copolymer thin films	Kim, DH; Sun, ZC; Russell, TP; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Polystyrene, poly(ethylene oxide), TiO2	Sensors/biosensors/electrochemical sensors	OMCNH
88	2005	Synthetic model of a bioactive functionally graded nano-hybrid in silica-polydimethylsiloxane system	Lee, KY; Lee, YH; Kim, HM; et al.	Materials Science; Physics	Polydimethylsiloxane, SiO2	Synthesis of new nanohybrids/materials	OMCNH
89	2005	Thermomechanical properties and phase structure of epoxy/silica nano-hybrid materials constructed from a linear silicone oligomer	Ochi, M; Matsumura, T	Polymer Science	Epoxy, silicone oligomer	Crystallography and polymer crystallization	OMCNH
90	2005	Bioelectrochemically functional nanohybrids through co-assembling of proteins and surfactants onto carbon nanotubes: Facilitated electron transfer of assembled proteins with enhanced faradic response	Yan, YM; Zheng, W; Zhang, MN; et al.	Chemistry; Materials Science	SWNT, MWNT, Heme proteins	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
91	2005	Direct electron transfer and electrocatalysis of microperoxidase immobilized on nanohybrid film	Liu, Y; Wang, MK; Zhao, F; et al.	Chemistry; Electrochemistry	MWNT, Au, microperoxidase	Sensors/biosensors/electrochemical sensors	OMCNH
92	2005	Optical properties of self-assembled nano-hybrid materials	Kitazawa, N; Watanabe, Y	Materials Science; Physics	N/A	N/A	N/A
93	2005	Metallized organoclays as new intermediates for aqueous nanohybrid dispersions, nanohybrid catalysts and antimicrobial polymer hybrid nanocomposites	Weickmann, H; Tiller, JC; Thomann, R; et al.	Materials Science; Polymer Science	Sodium bentonite nanoplatelets, bentonite supported silver, palladium, copper	Synthesis of new nanohybrids/materials	OMCNH
94	2005	Studies of the preparation and photo-electric properties of nanohybrid LB films of 2,5-bis(ferrocenylethynyl)thiophene/tungstophosphoric heteropolyacids	Li, MX; Liu, L; Liu, SZ; et al.	Chemistry	2,5-bis(ferrocenylethynyl)thiophene (BFET)/dimethyldioctadecyl-ammonium. (DNMOA)/tungstophosphoric heteropolyacids	Synthesis of new nanohybrids/materials	OMCNH
95	2005	Influence of molar ratio of Zn/Al/Tyr on the formation of Tyr/Zn-Al-LDH nanohybrids	Li, SP; Xu, JJ; Zhao, G; et al.	Chemistry	Tyrosine, LDH, Zn, Al	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
96	2005	Preparation and characterization of organic-inorganic layered nanohybrid, Hydroxyl Double Salts (HDSs) - Isomer separation via preferential intercalation into layered framework	Tan, BH; Tagaya, H	Chemistry	Zn, Ni, hydroxyl double salts	Synthesis of new nanohybrids/materials	OMCNH
97	2005	Transparent polymer nanohybrid prepared by in situ synthesis of aluminosilicate nanofibers in poly(vinyl alcohol) solution	Yamamoto, K; Otsuka, H; Wada, SI; et al.	Chemistry; Materials Science; Physics; Polymer Science	Poly(vinyl alcohol), aluminosilicate	Crystallography and polymer crystallization	OMCNH
98	2005	Studies on the preparation and photo-electric properties of nanohybrid LB films of organometallic polymer/octadecylammium/heteropolyan ions	Liu, L; Zhang, GS; Liu, SZ; et al.	Chemistry	tungsto(molybdo)phosphoric heteropoly acids	Synthesis of new nanohybrids/materials	OMCNH
99	2006	Nanohybrids composed of quantum dots and cytochrome P450 as photocatalysts	Ipe, BI; Niemeyer, CM	Chemistry	CdS quantum dots, P450	Sensors/biosensors/electrochemical sensors	OMCNH
100	2006	In vitro bioactivity of Bi-structured nano-hybrids in the CaO-SiO2-	Koh, MY; Kim, HM;	Materials Science	poly(tetramethylene oxide), SiO2, CaO	Biomaterials	OMCNH

		PTMO system	Lee, HK; et al.				
101	2006	Sol-gel synthetic model of bi-structured bioactive nano-hybrids in TEOS-PDMS system	Lee, KY; Lee, YH; Kim, HM; et al.	Materials Science	tetraethoxysilane, polydimethylsiloxane, silicate	Biomaterials	OMCNH
102	2006	Osteogenic differentiation of human bone marrow stromal cells cultured on hydroxyl carbonate apatite layer preformed on poly(epsilon-caprolactone)-organosifoxane nano-hybrid materials	Yoo, JJ; Kim, HJ; Rhee, SH	Materials Science	poly(e-caprolactone)-organosiloxane, hydroxyl carbonate apatite layer	Biomaterials	OMCNH
103	2006	Layered titanate-zinc oxide nanohybrids with mesoporosity	Kim, TW; Hur, SG; Hwang, SJ; et al.	Chemistry	Titanate, ZnO	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	MMNH
104	2006	Characteristics of thin film of nano-hybrid synthesized from acrylic resin and colloidal silca-silane sol	Kang, DP; Park, HY; Kang, YT; et al.	Engineering; Materials Science	Acrylic, silane, silica	Synthesis of new nanohybrids/materials	OMCNH
105	2006	Proton conducting phosphated zirconia-sulfonated polyether sulfone nanohybrid electrolyte for low humidity, wide-temperature PEMFC operation	Anilkumar, GM; Nakazawa, S; Okubo, T; et al.	Electrochemistry	Zr, poly ether sulfone	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
106	2006	Electronically interacting single wall carbon nanotube-porphyrin nanohybrids	Rahman, GMA; Guldi, DM; Campidelli, S; et al.	Chemistry; Materials Science	SWNT, porphyrin	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
107	2006	Organo-mineral nanohybrids. Incorporation, coordination and structuration role of acetone molecules in the tunnels of sepiolite	Kuang, WX; Facey, GA; Detellier, C	Chemistry; Materials Science	Acetone, sepiolite	Crystallography and polymer crystallization	OMCNH
108	2006	Covalently porphyrin-functionalized single-walled carbon nanotubes: a novel photoactive and optical limiting donor-acceptor nanohybrid	Guo, Zhen; Du, Feng; Ren, Dongmei; et al.	Chemistry; Materials Science	SWNT, porphyrin	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
109	2006	Pulsed laser deposition and fabrication of CoO/ZnO and CoO/TiO2 nano-hybrid thin film	Van, LH; Hong, MH; Ding, J	Materials Science; Physics	CoO, ZnO, TiO2	Semiconductors/superconductors/conductive materials	MMNH
110	2006	Iron cytochrome C nanohybrids - Supramolecular electron transfer to an electron accepting fullerene	Guldi, Dirk M.; Zilbermann, Israel; Hatzimarinaki, Maria; et al.	Chemistry	Polyhedral oligosilsesquioxane (POSS), polymers	Crystallography and polymer crystallization	OMCNH
111	2006	Surfactant functionalization of carbon nanotubes (CNTs) for layer-by-layer assembling of CNT multi-layer films and fabrication of gold nanoparticle/CNT nanohybrid	Zhang, MN; Su, L; Mao, LQ	Chemistry; Materials Science	MWNT, Au	Sensors/biosensors/electrochemical sensors	CMNH
112	2006	Heterostructured nanohybrid of zinc oxide-montmorillonite clay	Hur, SG; Kim, TW; Hwang, SJ; et al.	Chemistry	ZnO, aluminosilicate	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
113	2006	Poly(triphenylamine) related copolymer noncovalently coated MWCNT nanohybrid: fabrication and observation of enhanced photoconductivity	Xu, WJ; Chen, HZ; Shi, MM; et al.	Science & Technology - Other Topics; Materials Science; Physics	MWNT, poly(triphenylamine)	Sensors/biosensors/electrochemical sensors	OMCNH
114	2006	Direct fabrication of anatase/activated carbon nano-hybrid materials by hydrothermal with ball milling method at low temperature	Sakamoto, N; Fujino, T; Watanabe, T; et al.	Materials Science	SWNT, MWNT, thioglycolic acid, CdTe	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and	CMNH

						Electronic Applications	
115	2006	Urea biosensor based on Zn3Al-urease layered double hydroxides nanohybrid coated on insulated silicon structures	Barhoumi, H; Maaref, A; Rammah, A; et al.	Materials Science	Urea, LDH, Zn, Al	Sensors/biosensors/electrochemical sensors	OMCNH
116	2006	Nanohybrid-layered double hydroxides/urease materials: Synthesis and application to urea biosensors	Vial, S; Forano, C; Shan, D; et al.	Materials Science	Urea, LDH, Zn, Al	Sensors/biosensors/electrochemical sensors	OMCNH
117	2006	Exfoliation and reassembling route to mesoporous titania nanohybrids	Paek, SM; Jung, H; Lee, YJ; et al.	Chemistry; Materials Science	Titanate, anatase	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
118	2006	Nano-hybrid luminescent dot: synthesis, characterization and optical properties	Xiao, Y; Liu, L; He, CB; et al.	Chemistry; Materials Science	polyhedral oligomeric silsesquioxanes, oligophenylene	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
119	2006	Noncovalent nanohybrid of ferrocene with single-walled carbon nanotubes and its enhanced electrochemical property	Yang, XY; Lu, YH; Ma, YF; et al.	Chemistry; Physics	SWNT, ferrocene	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
120	2006	Preparation and morphology of SiO2/PMMA nanohybrids by microemulsion polymerization	Xu, P; Wang, HT; Tong, R; et al.	Chemistry; Polymer Science	Polymethyl methacrylate, silica	Crystallography and polymer crystallization	OMCNH
121	2006	Preparation of well-defined PVOH/C60 nanohybrids by cobalt-mediated radical polymerization of vinyl acetate	Detrembleur, C; Stoilova, O; Bryaskova, R; et al.	Polymer Science	Poly(vinyl acetate), Co, C60	Optical imaging and applications	OMCNH
122	2006	Tin dioxide materials chemically modified with trialkynylorganotins: Functional nanohybrids for photovoltaic applications	Vilaca, G; Jousseaume, B; Mahieux, C; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Tin dioxide, trialkynylorganotins	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
123	2006	Photocatalytic degradation of flexible PVC/TiO2 nanohybrid as an eco-friendly alternative to the current waste landfill and dioxin-emitting incineration of post-use PVC	Kim, SH; Kwak, SY; Suzuki, T	Polymer Science	N/A	N/A	N/A
124	2006	Aluminosilicate nanohybrid materials. Intercalation of polystyrene in kaolinite	Elbokl, Tamer A.; Detellier, Christian	Chemistry; Physics	Polystyrene, kaolinite (aluminosilicate)	Catalytic/Photocatalytic/Electrocatalytic applications	OMCNH
125	2006	Exfoliation-restacking route to Au nanoparticle-clay nanohybrids	Paek, Seung-Min; Jang, Jae-Up; Hwang, Seong-Ju; et al.	Chemistry; Physics	kaolinite (aluminosilicate), Au	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
126	2006	Efficient delivery of anticancer drug MTX through MTX-LDH nanohybrid system	Oh, Jae-Min; Park, Man; Kim, Sang-Tae; et al.	Chemistry; Physics	Methotrexate, LDH(Mg, Al)	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
127	2006	A novel hetero structured RuS2-titanate nanohybrid	Jung, Hyun; Lee, Hyun-Chel; Paek, Seung-Min; et al.	Chemistry; Physics	RuS2 (ruthenium sulfide), titanate	Synthesis of new nanohybrids/materials	MMNH
128	2006	In situ formation of recombinant humanlike collagen-hydroxyapatite nanohybrid through bionic approach	Murugan, R; Ramakrishna, S	Physics	Collagen, hydroxyapatite	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
129	2006	Cytotoxicity evaluation of two different composites with/without fibers and one nanohybrid composite	Tuncel, Aykut; Oezdemir, Ali Kemal; Suemer,	Dentistry, Oral Surgery & Medicine; Materials Science	block copolymers, alkoxysilyl groups	Crystallography and polymer crystallization	OMCNH

			Zeynep; et al.				
130	2006	Redox behavior of nanohybrid material with defined morphology: Vanadium oxide nanotubes intercalated with polyaniline	Malta, Marcos; Louarn, Guy; Errien, Nicolas; et al.	Electrochemistry; Energy & Fuels	Vanadium oxide, polyaniline	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
131	2006	Abrasion properties of alkyd- and acrylic-based polymer-ceramic nano-hybrid coatings on wood surfaces	Rodriguez, Rogelio; Vargas, Susana; Rubio, Efrain; et al.	Materials Science	alkyd, acrylic polyurethane, silica	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
132	2006	Facile and large-scale synthesis and characterization of carbon nanotube/silver nanocrystal nanohybrids	Gao, C; Li, WW; Jin, YZ; et al.	Science & Technology - Other Topics; Materials Science; Physics	SWNT, MWNT, Ag	Synthesis of new nanohybrids/materials	CMNH
133	2006	Titania-PMMA nanohybrids of enhanced nanocrystallinity	Yuwono, Akhmad Herman; Xue, Junmin; Wang, John; et al.	Materials Science	Polyethylene glycol, 3-(triethoxysilyl)-propyl isocyanate, Zn	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
134	2006	Molecular assembly, luminescence and morphology of novel zinc/inorganic/organic nanohybrid material with covalent linkage	Yan, Bing; Yao, Run-Feng; Zhao, Li-Min	Materials Science	Poly(2-hydroxyethyl acrylate)-co-methyl methacrytalate, SiO2	Catalytic/Photocatalytic/Electrocatalytic applications	OMCNH
135	2006	A two-dimensional infrared correlation spectroscopic study on the thermal degradation of poly (2-hydroxyethyl acrylate)-co-methyl methacrylate/SiO2 nanohybrids	Xu, P; Wang, HT; Tong, R; et al.	Polymer Science	Zn, polyethylene glycol	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
136	2006	Room-temperature aqueous synthesis of highly luminescent BaWO4-polymer nanohybrids and their spontaneous conversion to hexagonal WO3 nanosheets	Oaki, Yuya; Imai, Hiroaki	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Ba, WO3 (tungsten trioxide), polyacrylic acid	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
137	2006	Preparation and characterization of nanohybrid LB films of tert-butylcalix[8]arene/molybdophosphoricheteropolyacids	Liu Li; Liu Shi-Zhong; Ai Wei-He; et al.	Chemistry	tert-butylcalix[8]arene, octadecylammonium, molybdophosphoricheteropolyacids	Synthesis of new nanohybrids/materials	OMCNH
138	2006	Bio-nanohybrids based on layered inorganic solids: Gelatin nanocomposites	Darder, Margarita; Isabel Ruiz, Ana; Aranda, Pilar; et al.	Biotechnology & Applied Microbiology; Science & Technology - Other Topics; Materials Science	N/A	N/A	N/A
139	2006	Bio-nanohybrids based on layered double hydroxide	Choy, Jin-Ho; Park, Man; Oh, Jae-Min	Biotechnology & Applied Microbiology; Science & Technology - Other Topics; Materials Science	N/A	N/A	N/A
140	2006	Nanohybrid enzymes - Layered double hydroxides: Potential applications	Forano, Claude; Vial, Stephanie; Mousty, Christine	Biotechnology & Applied Microbiology; Science & Technology - Other Topics; Materials Science	N/A	N/A	N/A
141	2006	Fabrication of UV-blocking nanohybrid coating via miniemulsion polymerization	Lu, Haifeng; Fei, Bin; Xin, John H.; et al.	Chemistry	Polystyrene, ZnO	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
142	2006	Functional nanohybrids constructed via complexation of multiwalled	Hwang, Seok-Ho;	Chemistry; Materials Science	MWNT, metallohexamers	Optical imaging and applications	CMNH

		carbon nanotubes with novel hexameric metallomacrocyles	Moorefield, Charles N.; Dai, Liming; et al.				
143	2006	Evidence of two-dimensional superconductivity in the single crystalline nanohybrid of organic-bismuth cuprate	Chung, Il-Won; Kwon, Soon-Jae; Kim, Seung-Joo; et al.	Chemistry	HgI2, pyridine, bismuth cuprate	Semiconductors/superconductors/conductive materials	MMNH
144	2006	Interactions in single wall carbon nanotubes/pyrene/porphyrin nanohybrids	Ehli, Christian; Aminur Rahman, G. M.; Jux, Norbert; et al.	Chemistry	SWNT, pyrene, porphyrin	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
145	2006	Lanthanide-based lamellar nanohybrids: Synthesis, structural characterization, and optical properties	Karmaoui, Mohamed; Ferreira, Rute A. Sa; Mane, Ankush T.; et al.	Chemistry; Materials Science	Ln(III) isopropoxides (Ln = Gd, Sm, Nd), Eu3+, Tb	Optical imaging and applications	MMNH
146	2006	Novel organic-inorganic poly (3,4-ethylenedioxythiophene) based nanohybrid materials for rechargeable lithium batteries and supercapacitors	Murugan, A. Vadivel	Electrochemistry; Energy & Fuels	N/A	N/A	N/A
147	2006	Xerogel from N,N '-bis(2-phosphonoethyl)-1,4,5,8-naphthalenediimide: a nanohybrid material displaying efficient tryptophan photooxidation	Rodrigues, Magali A.; Bemquerer, Marcelo P.; Mohallem, Nelcy D. S.; et al.	Chemistry; Materials Science	tetraethyl orthosilicate (TEOS), N,N'-bis(2-phosphonoethyl)-1,4,5,8-naphthalenediimide (DPN)	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	MMNH
148	2006	Optical properties of lanthanide-doped lamellar nanohybrids	Ferreira, Rute A. Sa; Karmaoui, Mohamed; Nobre, Sonia S.; et al.	Chemistry; Physics	Lanthanide doped lammellar nanohybrids, yttrium or gadolinium oxide crystalline layers, Tb3+, Eu3+, Nd3+	Optical imaging and applications	MMNH
149	2006	Synthesis and optical properties of nanohybrids in the system constituted by silica and lanthanide phosphoramide complexes	Khimich, N. N.; Zub, Yu. L.; Koptelova, L. A.; et al.	Chemistry	Silica, lanthanide phosphoramide	Synthesis of new nanohybrids/materials	MMNH
150	2006	The dynamic process in the formation of Tyr/LDH nanohybrids	Li, Shu-Ping	Chemistry	Tyrosine, LDH	Synthesis of new nanohybrids/materials	OMCNH
151	2006	Synthesis and characteristics of polyimide/titania nano hybrid films	Tsai, Mei-Hui; Liu, Shu-Jhuan; Chiang, Pei-Chun	Materials Science; Physics	Polyimide, TiO2	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
152	2006	Absorption and Raman study for POSS-oligophenylene nanohybrid molecules	Xiao, Yang; Tripathy, Sudhiranjan; Lin, Tingting; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Oligophenylene, Polyhedral Oligosilsesquioxane (POSS)	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
153	2006	Incorporation of lipid domains in Cerasome, a morphologically-stable organic-inorganic vesicular nanohybrid	Hashizume, Mineo; Saeki, Isamu; Otsuki, Masashi; et al.	Materials Science	Cerasome-forming lipid, a cationic synthetic lipid, and a zwitterionic phospholipid	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
154	2006	Diblock copolymer templated nanohybrid thin films of highly ordered TiO2 nanoparticle arrays in PMMA matrix	Yuwono, Akhmad Herman; Zhang, Yu; Wang, John; et al.	Chemistry; Materials Science	poly(methylmethacrylate)-b-polyethylene oxide diblock copolymer, TiO2	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
155	2006	Influence of temperature on the formation of Tyr/LDH nanohybrids	Li Shu-Ping	Chemistry	Tyrosine, LDH	Biomaterials	OMCNH
156	2007	Multifunctional magneto-polymeric nanohybrids for targeted detection and synergistic therapeutic effects on	Yang, Jaemoon; Lee, Choong-	Chemistry	QD, Block copolymers	Medicine (cancer research, biocompatibility,	OMCNH

		breast cancer	Hwan; Ko, Hyun-Ju; et al.			biomedical apps, bone regeneration/repair)	
157	2007	Functionalized nanohybrid materials obtained from the interlayer grafting of aminoalcohols on kaolinite	Letaief, Sadok; Detellier, Christian	Chemistry	Aminoalcohols, kaolinite	Synthesis of new nanohybrids/materials	OMCNH
158	2007	Preparation and characterization of a novel organic-inorganic nanohybrid "cerasome" formed with a liposomal membrane and silicate surface	Katagiri, Kiyofumi; Hashizume, Mineo; Ariga, Katsuhiko; et al.	Chemistry	organoalkoxysilanes, silicate cerosomes	Synthesis of new nanohybrids/materials	OMCNH
159	2007	Surface roughness of nanofill and nanohybrid resin composites after polishing and brushing	Senawongse, Pisol; Pongprueksa, Pong	Dentistry, Oral Surgery & Medicine	N/A	N/A	N/A
160	2007	Nanohybrid materials from the intercalation of imidazolium ionic liquids in kaolinite	Letaief, Sadok; Detellier, Christian	Chemistry; Materials Science	Kaolinite, imidazolium	Synthesis of new nanohybrids/materials	OMCNH
161	2007	Biocompatible protoporphyrin IX-containing nanohybrids with potential applications in photodynamic therapy	Kantonis, Giorgos; Trikeriotis, Markos; Ghanotakis, Demetrios F.	Chemistry	Protoporphyrin IX, Mg-Al LDH	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
162	2007	Organic - Inorganic Nano-Hybrid Materials	Chujo, Yoshiki	Engineering; Materials Science	N/A	N/A	N/A
163	2007	Hierarchical aqueous self-assembly of C60 nano-whiskers and C60-silver nano-hybrids under continuous flow	Iyer, K. Swaminathan; Raston, Colin L.; Saunders, Martin	Biochemistry & Molecular Biology; Chemistry; Science & Technology - Other Topics	Starch-iodine complex, C60, $AgNO_3$	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	CMNH
164	2007	Toxicity and biomedical imaging of layered nanohybrids in the mouse	Flesken-Nikitin, Andrea; Toshkov, Illia; Naskar, Jishnu; et al.	Pathology; Toxicology	Lucifer Yellow, Mg-Al LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
165	2007	Nondestructive formation of supramolecular nanohybrids of single-walled carbon nanotubes with flexible porphyrinic polypeptides	Saito, Kenji; Troiani, Vincent; Qiu, Hongjin; et al.	Chemistry; Science & Technology - Other Topics; Materials Science	SWNT, porphyrinic polypeptide	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
166	2007	Polypyrrole-Fe_2O_3 nanohybrid materials for electrochemical storage	Mallouki, M.; Tran-Van, F.; Sarrazin, C.; et al.	Electrochemistry	Polypyrrole, Fe_2O_3	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
167	2007	Poly(methyl acrylate) plus mesoporous silica nanohybrids: Mechanical and thermophysical properties	Perez, Leon D.; Giraldo, Luis F.; Brostow, Witold; et al.	Polymer Science	Poly(methyl acrylate), silica	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
168	2007	Nanohybrid polymer prepared by successive polymerization of methacrylate monomer containing silver nanoparticles in situ prepared under microwave irradiation	Wada, Yuji; Kobayashi, Taishi; Yamasaki, Hayahide; et al.	Polymer Science	Poly(methylmetacrylate), Ag	Optical imaging and applications	OMCNH
169	2007	Dynamics of stress bearing particle networks in poly(propylene)/alumina nanohybrids	Acierno, Domenico; Filippone, Giovanni; Romeo, Giovanni; et al.	Materials Science; Polymer Science	poly(propylene), alumina	Synthesis of new nanohybrids/materials	OMCNH
170	2007	Synthesis of biocompatible hydrophobic silica-gelatin nano-	Smitha, S.; Shajesh, P.;	Biophysics; Chemistry; Materials	SiO_2, methyltrimethoxysilane,	Optical imaging and applications	OMCNH

		hybrid by sol-gel process	Mukundan, P.; et al.	Science	gelatin		
171	2007	An organic-inorganic nanohybrid based on lunar soil simulant	Qiao, Yu; Chen, Jin; Han, Aijie	Materials Science	SWNT, porphyrin/Zn naphthalocyanine	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CMNH
172	2007	Nanohybrids for controlled antibiotic release in topical applications	Tammaro, L.; Costantino, U.; Bolognese, A.; et al.	Infectious Diseases; Microbiology; Pharmacology & Pharmacy	chloramphenicol succinate, Mg-Al LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
173	2007	Nanohybrid material of SWNTs covalently functionalized with porphyrin for light harvesting antenna: Synthesis and photophysical properties	Ren, Dongmei; Guo, Zhen; Du, Feng; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	SWNT, porphyrin	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
174	2007	New nanohybrids of poly(epsilon-caprolactone) and a modified Mg/Al hydrotalcite: Mechanical and thermal properties	Pucciariello, Rachele; Tammaro, Loredana; Villani, Vincenzo; et al.	Polymer Science	poly(epsilon-caprolactone), Mg-Al LDH	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
175	2007	Antiwetting silica-gelatin nanohybrid and transparent nano coatings synthesised through an aqueous sol-gel process	Smitha, S.; Shajesh, P.; Mukundan, P.; et al.	Materials Science	vinyltrimethoxysilane (gelatin), silica	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
176	2007	New inorganic-based drug delivery system of indole-3-acetic acid-layered metal hydroxide nanohybrids with controlled release rate	Yang, Jae-Hun; Han, Yang-Su; Park, Man; et al.	Chemistry; Materials Science	indole-3-acetic acid, Zn-Al, LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
177	2007	Donor-acceptor nanohybrids of zinc naphthalocyanine or zinc porphyrin noncovalently linked to single-wall carbon nanotubes for photoinduced electron transfer	Chitta, Raghu; Sandanayaka, Atula S. D.; Schumacher, Amy L.; et al.	Chemistry; Science & Technology - Other Topics; Materials Science	SWNT, porphyrin/Zn naphthalocyanine	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CMNH
178	2007	Nanohybrid TiO2/carbon black sensor for NO2 gas	Liou, Wei-Jen; Lin, Hong-Ming	Engineering; Materials Science	TiO2, carbon black	Sensors/biosensors/electrochemical sensors	CMNH
179	2007	Studies on microscopic structure of sol-gel derived nanohybrids containing heteropolyacid	Nakanishi, Takayuki; Norisuye, Tomohisa; Sato, Haruyoshi; et al.	Polymer Science	Heteropolyacid, 1,8-Bis(triethoxysilyl)octane (TES-Oct), (OC2H5)3-Si-(CH2)8-Si-(OC2H5)3, phosphotungstic acid (PWA), H3PW12O40	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
180	2007	Single-walled carbon nanotube gold nanohybrids: Application in highly effective transparent and conductive films	Kong, Byung-Seon; Jung, Dae-Hwan; Oh, Sang-Keun; et al.	Chemistry; Science & Technology - Other Topics; Materials Science	SWNT, Au	Transparent and conductive films	CMNH
181	2007	Au/titania composite nanoparticle arrays with controlled size and spacing by organic-inorganic nanohybridization in thin film block copolymer templates	Li, Xue; Fu, Jun; Steinhart, Martin; et al.	Chemistry	Au, TiO2, block copolymers (polystyrene-block-polyethylene oxide)	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
182	2007	Synthesis of osteoconductive organic-inorganic nanohybrids through modification of chitin with alkoxysilane and calcium chloride	Miyazaki, Toshiki; Ohtsuki, Chikara; Ashizukal, Masahiro	Engineering; Materials Science	Chitin, alkoxysilane, calcium chloride	Biomaterials	OMCNH
183	2007	Preparation of DNA - Silver nanohybrids in multilayer nanoreactors by in situ	Shang, Li; Wang, Yuling; Huang, Lijian;	Chemistry; Materials Science	Montmorillonite, polyimide	Synthesis of new nanohybrids/materials	OMCNH

		electrochemical reduction, characterization, and application	et al.				
184	2007	A simplified processing technique of organic-inorganic intercalation/exfoliation nanohybrid	Qiao, Yu; Chen, Jin; Han, Aijie; et al.	Materials Science	Carbon nanohorns, porphyrins	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
185	2007	Covalent functionalization of carbon nanohorns with porphyrins: Nanohybrid formation and photoinduced electron and energy transfer	Pagona, Georgia; Sandanayaka, Atula S. D.; Araki, Yasuyuki; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	DNA, Ag	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
186	2007	Femtosecond laser synthesized nanohybrid materials for bioapplications	Sajti, Cs. L.; Giorgio, S.; Khodorkovsky, V.; et al.	Chemistry; Materials Science; Physics	ZnO, Tetramethylrhodamine B isothiocyante, Rhodamine B	Biomaterials	OMCNH
187	2007	Quality of curing in relation to hardness, degree of cure and polymerization depth measured on a nano-hybrid composite	Ilie, Nicoleta; Hickel, Reinhard	Dentistry, Oral Surgery & Medicine	N/A	N/A	N/A
188	2007	Towards new drugs formulations: Gentamicin-anionic clay as nanohybrids	Caija, Gabriiela; Niiyama, Hiroo; CiobanU, Gabriela; et al.	Materials Science	Polymer, silicates	Synthesis of new nanohybrids/materials	OMCNH
189	2007	Lanthanide-based lamellar nanohybrids: The case of erbium	Karmaoui, Mohamed; Ferreira, Rute A. Sa; Carlos, Luis D.; et al.	Materials Science	Er2O3, benzoate	Optical imaging and applications	OMCNH
190	2007	Low-voltage-driven pentacene thin-film transistor with an organic-inorganic nanohybrid dielectric	Lee, Kwang H.; Choi, Jeong-M.; Im, Seongil; et al.	Physics	Aluminum oxide, indium-tin-oxide	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	MMNH
191	2007	New organic-inorganic nanohybrids via ring opening polymerization of (di)lactones initiated by functionalized polyhedral oligomeric silsesquioxane	Goffin, Anne-Lise; Duquesne, Emmanuel; Moins, Sebastien; et al.	Polymer Science	(di)lactones, polyhedral oligomeric silsesquioxane	Crystallography and polymer crystallization	OMCNH
192	2007	Comparative in vitro and in vivo studies using a bioactive poly(epsilon-caprolactone)-organosiloxane nanohybrid containing calcium salt	Yoo, Jeong Joon; Lee, Jong Eun; Kim, Hee Joong; et al.	Engineering; Materials Science	poly(epsilon-caprolactone), organosiloxane, calcium salts	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
193	2007	Preparation of nanohybrid solid-state electrolytes with liquidlike Mobilities by solidifying ionic liquids with silica particles	Shimano, Satoshi; Zhou, Haoshen; Honma, Itaru	Chemistry; Materials Science	Silica, 1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([BMIm][TFSI])	Semiconductors/superconductors/conductive materials	MMNH
194	2007	A nanohybrid membrane with lipid bilayer-like properties utilized as a conductimetric saccharin sensor	Chalkias, Nikolaos G.; Giannelis, Emmanuel P.	Biophysics; Biotechnology & Applied Microbiology; Chemistry; Electrochemistry; Science & Technology - Other Topics	N/A	N/A	N/A
195	2007	New nanohybrid materials for biophotonics	Sajti, C. L.; Giorgio, S.; Khodorkovsky, V.; et al.	Materials Science; Physics	ZnO, Tetramethylrhodamine B isothiocyante, Rhodamine B	Fluorescence/luminescence/photoluminescence, light-energy harvesting	MMNH

196	2007	Anticancer drug-inorganic nanohybrid and its cellular interaction	Kim, Ju Young; Choi, Soo-Jin; Oh, Jae-Min; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Methotrexate, LDH(Mg, Al)	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
197	2007	Nanohybrid material of bilateral switch based on diarylethene	Zou, Ying; Xiao, Shuzhang; Yi, Tao; et al.	Chemistry	photochromic cationic diarylethene, MnPS3	Optical imaging and applications	OMCNH
198	2007	Surface dyeability of cotton and nylon fabrics coated with a novel porous silk fibroin/silica nanohybrid	Li, Wenbin; Zou, Lingli; Zhou, Xingpin; et al.	Polymer Science	fibroin (porous silk fibrom), silica	Synthesis of new nanohybrids/materials	OMCNH
199	2007	Chromonic/Silica nanohybrids: Synthesis and macroscopic alignment	Hara, Mitsuo; Nagano, Shusaku; Mizoshita, Norihiro; et al.	Chemistry; Materials Science	chromonic lyotropic liquid crystals, silica	Optical imaging and applications	MMNH
200	2007	Effect of acidic degradation products of poly(lactic-co-glycolic)acid on the apatite-forming ability of poly(lactic-co-glycolic)acid-siloxane nanohybrid material	Rhee, Sang-Hoon; Lee, Seung Jin	Engineering; Materials Science	poly(lactic-co-glycolic) acid, siloxane	Synthesis of new nanohybrids/materials	OMCNH
201	2007	How can nanohybrids enhance polyester/sepiolite nanocomposite properties?	Duquesne, Emmanuel; Moins, Sebastien; Alexandre, Michael; et al.	Polymer Science	Sepiolite, poly(epsilon-caprolactone)	Crystallography and polymer crystallization	OMCNH
202	2007	Novel looped enzyme-polyamidoamine dendrimer nanohybrids used as biosensor matrix	Zeng, Yun-Long; Huang, Hao-Wen; Jiang, Jian-Hui; et al.	Chemistry	horseradish peroxidase, polyamidoamine	Sensors/biosensors/electrochemical sensors	OMCNH
203	2007	Structural evolution of self-assembling nanohybrid thin films from functionalized urea precursors	Karatchevtseva, Inna; Cassidy, David J.; Man, Michel Wong Chi; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	N/A	N/A	N/A
204	2007	Silica-based nanohybrids containing dipyridine, urethan, or urea derivatives	Cousinie, Sandra; Gressier, Marie; Alphonse, Pierre; et al.	Chemistry; Materials Science	organosilanes, silica	Catalytic/Photocatalytic/Electrocatalytic applications	OMCNH
205	2007	Nanohybrid kaolinite-based materials obtained from the interlayer grafting of 3-aminopropyltriethoxysilane and their potential use as electrochemical sensors	Tonle, Ignas K.; Diaco, Thomas; Ngameni, Emmanuel; et al.	Chemistry; Materials Science	kaolinite, 3-aminopropyltriethoxysilane	Sensors/biosensors/electrochemical sensors	OMCNH
206	2008	Nanohybrid carbon film for electrochemical detection of SNPs without hybridization or labeling	Kato, Dai; Sekioka, Naoyuki; Ueda, Akio; et al.	Chemistry	SWNT, porphyrin	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
207	2008	Layered inorganic/enzyme nanohybrids with selectivity and structural stability upon interacting with biomolecules	Chen, Guo-Jing; Yen, Ming-Cheng; Wang, Jen-Ming; et al.	Biochemistry & Molecular Biology; Chemistry	Montmorillonite, enzymes	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
208	2008	Spongy gel-like layered double hydroxide-alkaline phosphatase nanohybrid as a biosensing material	Geraud, Erwan; Prevot, Vanessa; Forano, Claude; et al.	Chemistry	Mg-Al LDH, alkaline phosphatase	Sensors/biosensors/electrochemical sensors	MMNH
209	2008	Elaboration of nanohybrid materials	Goubard,	Chemistry	poly(3,4-ethylene	Energy/Electron	OMCNH

		by photopolymerisation of 3,4-ethylenedioxythiophene on TiO2	Fabrice; Aubert, Pierre-Henri; Boukerma, Kada; et al.		dioxythiophene), TiO2	Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	
210	2008	Organic-inorganic nanohybrids through the direct tailoring of semiconductor nanocrystals with conjugated polymers	Lin, Zhiqun	Chemistry	Conjugated oligomers, conjugated polymers, nanocrystal	Semiconductors/superconductors/conductive materials	OMCNH
211	2008	Oligomeric alkoxysilanes with cagelike hybrids as cores: Designed precursors of nanohybrid materials	Kuge, Hideki; Hagiwara, Yoshiaki; Shimojima, Atsushi; et al.	Chemistry	SWNT, porphyrin, Poly[(vinylbenzyl)trimethylammonium chloride	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
212	2008	A novel soluble Tin(IV) porphyrin modified single-walled carbon nanotube nanohybrid with light harvesting properties	Ren, Dong-Mei; Guo, Zhen; Du, Feng; et al.	Chemistry	SWNT, Tin(IV) porphyrin	Fluorescence/luminescence/photoluminescence, light-energy harvesting	CMNH
213	2008	Characteristics of nanohybrid coating films synthesized from colloidal silica and organoalkoxysilanes by sol-gel process	Na, Moonkyong; Park, Hoyyul; Kang, Dongpil; et al.	Physics	Silica, Organoalkoxysilane	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
214	2008	Photoalignment and patterning of a chromonic-silica nanohybrid on photocrosslinkable polymer thin films	Hara, Mitsuo; Nagano, Shusaku; Kawatsuki, Nobuhiro; et al.	Chemistry; Materials Science	chromonic, silica	Synthesis of new nanohybrids/materials	MMNH
215	2008	Synthesis and characterisation of carboxylate-terminated silica nanohybrid powders and thin films	Arrachart, Guilhem; Karatchevtseva, Inna; Cassidy, David J.; et al.	Chemistry; Materials Science	carboxylate, silica	Synthesis of new nanohybrids/materials	OMCNH
216	2008	Nanohybrids via a polycation-based nanoemulsion method for dual-mode detection of human mesenchymal stem cells	Seo, Sung-Baek; Yang, Jaemoon; Lee, Eun-Sook; et al.	Chemistry; Materials Science	polycationic polyethylenimine, magnetic nanocrystals	Sensors/biosensors/electrochemical sensors	OMCNH
217	2008	Preparation and characterization of polyimide/fluorinated silicate nano-hybrid thin films with low refractive indices	Han, Yulai; Wakita, Junji; Kuroki, Shigeki; et al.	Polymer Science	magnesium organophyllosilicate clay	Biomaterials	OMCNH
218	2008	Fluorescent photoswitchable nanohybrids based on photochromism	Hu, Zhenkun; Zhang, Qing; Xue, Minzhao; et al.	Chemistry; Physics	diarylethene, 1,2-bis(2-methyl-1-benzo-thiophene-3-yl) perfluorocyclopentene (BTF6), perylenedicarboxylic acid bis(2-methylpropyl) ester (C.I. solvent green 5, SG5)	Optical imaging and applications	OMCNH
219	2008	Nano-Hybrid Material Formation on Polymer Materials by Versatile Inorganic Coatings and Its Biomaterial Function	Watanabe, Junji; Akashi, Mitsuru	Polymer Science	polyester, hydroxyapatite	Biomaterials	OMCNH
220	2008	Nano-hybrid polymers containing polyhedral oligosilsesquioxanes (POSS)	Janowski, Bartlomiej; Pielichowski, Krzysztof	Polymer Science	N/A	N/A	N/A
221	2008	Zr(HPO4)(2) based organic/inorganic nanohybrids as new proton conductors	Xu, Zhi Ping; Jin, Yonggang; da Costa, Joe C. Diniz; et al.	Chemistry; Physics	sulfanilic acid, alpha-Zr(HPO4)(2)	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
222	2008	Electrically stable low voltage ZnO transistors with organic/inorganic nanohybrid dielectrics	Cha, Sung Hoon; Oh, Min Suk; Lee, Kwang H.; et	Physics	ZnO, AlO, TiO, Polymer	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li	OMCNH

			al.			Batteries, and Electronic Applications	
223	2008	Preparation of layered organic-inorganic nanohybrid thin films of molybdenum trioxide with polyaniline derivatives for aldehyde gases sensors of several tens ppb level	Itoh, Toshio; Matsubara, Ichiro; Shin, Woosuck; et al.	Chemistry; Electrochemistry; Instruments & Instrumentation	molybdenum trioxide, polyaniline	Sensors/biosensors/electrochemical sensors	OMCNH
224	2008	Intermolecular interaction-induced hierarchical transformation in 1D nanohybrids: Analysis of conformational changes by 2D correlation Spectroscopy	Park, Ho Seok; Choi, Yeong Suk; Jung, Young Mee; et al.	Chemistry	N/A	N/A	N/A
225	2008	Estimation of phase separation behavior in nanohybrids by thermal and dielectric analyses	Min, Sung-Kyu; Park, Jae-Mann; Song, Ki-Tae; et al.	Chemistry	methyl trimethoxysilane (MTMS), bis(1,2-trimethoxysilyl)ethane (BTMSE)	Semiconductors/superconductors/conductive materials	OMCNH
226	2008	The effect of temperature on the viscoelastic properties of nano-hybrid composites	Papadogiannis, D. Y.; Lakes, R. S.; Papadogiannis, Y.; et al.	Dentistry, Oral Surgery & Medicine; Materials Science	N/A	N/A	N/A
227	2008	Influence of light energy and power density on the microhardness of two nanohybrid composites	Gritsch, Kerstin; Souvannasot, Sourasith; Schembri, Catherine; et al.	Dentistry, Oral Surgery & Medicine	N/A	N/A	N/A
228	2008	Noncovalently modified carbon nanotubes with carboxymethylated chitosan: A controllable donor-acceptor nanohybrid	Long, Dewu; Wu, Guozhong; Zhu, Guanglai	Chemistry	MWNT, carboxymethylated chitosan	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
229	2008	Design of nanohybrid and nanoporous materials through self-assembly of organosilane molecules	Shimojima, Atsushi	Materials Science	Siloxane, silica	Synthesis of new nanohybrids/materials	OMCNH
230	2008	Spirobenzopyran-based photochromic nanohybrids with photoswitchable fluorescence	Hu, Zhenkun; Zhang, Qing; Xue, Minzhao; et al.	Materials Science; Optical	Spirobenzopyran, chrome	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
231	2008	Laponite-based nanohybrid for enhanced solubility and controlled release of itraconazole	Jung, Hyun; Kim, Hyun-Mi; Bin Choy, Young; et al.	Pharmacology & Pharmacy	Laponite (layered aluminosilicate), itraconazole (drug)	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
232	2008	A triantennary dendritic galactoside-capped nanohybrid with a ZnS/CdSe nanoparticle core as a hydrophilic, fluorescent, multivalent probe for metastatic lung cancer cells	Chen, Chien-Tien; Munot, Yogesh S.; Salunke, Santosh B.; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	tri-antennary, galactoside-capped gallamide dendritic, CdSe, ZnS	Delivery Carriers, and Controlled Release of Drugs/Compounds	MMNH
233	2008	Structure and photoluminescence of di-amidosil nanohybrids incorporating europium triflate	Nunes, S. C.; Bermudez, V. de Zea; Cybinska, J.; et al.	Chemistry; Materials Science; Metallurgy & Metallurgical Engineering	di-amide cross-linked alkyl/siloxane, Eu3+	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
234	2008	Fabrication of alternate stacking MnO2/MoS2 layered nanohybrid by a sonochemistry technology	Su Zhi-Kui; Cui Yan-Hua; Tang Xiu-Hua; et al.	Chemistry	MnO2, MoS2	Synthesis of new nanohybrids/materials	MMNH
235	2008	Synthesis and photophysical properties of core-shell Eu(DBM)(3)phen/TiO2 nanohybrids	Qin, Weiping; Zhao, Dan; Zhang, Jisen; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	TiO2, tris(dibenzoylmethanato)phenanthroline	Fluorescence/luminescence/photoluminescence, light-energy harvesting	MMNH
236	2008	The synthesis of superparamagnetic Pt/Ni nanohybrids in direct micelles	Mirgorod, Yu. A.; Efimova,	Chemistry	lyotropic silica, chromonic	Synthesis of new nanohybrids/materials	MMNH

		of cationic surfactants	N. A.				
237	2008	Photoinduced formation of polythiophene/TiOP2 nanohybrid heterojunction films for Energy/Electron transfer, donor/acceptor, Solar/Fuel cells	Otsuka, Yasuhide; Okamoto, Yuko; Akiyama, Hitomi Y.; et al.	Chemistry; Science & Technology - Other Topics; Materials Science	polythiophene, TiO2	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
238	2008	Nanohybrid shish-kebabs: Supercritical CO2-induced PE epitaxy on carbon nanotubes	Zhang, Zhiwei; Xu, Qun; Chen, Zhimin; et al.	Polymer Science	SWNT, MWNT, supercritical CO2 antisolvent-induced polymer epitaxy	Synthesis of new nanohybrids/materials	OMCNH
239	2008	Synthesis of near-infrared responsive gold nanorod/PNIPAAm core/shell nanohybrids via surface initiated ATRP for smart drug delivery	Wei, Qingshan; Ji, Jian; Shen, Jiacong	Polymer Science	N-isopropylacrylamide (NIPAAm) on gold nanorods (Au NRs)	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
240	2008	Near infrared luminescence behavior of organic-inorganic nanohybrid films containing Er3+ doped YbPO4 nanoparticles	Lim, Mi Ae; Jana, Sunirmal; Il Seok, Sang; et al.	Materials Science; Physics	YbPO4, Er3+	Fluorescence/luminescence/photoluminescence, light-energy harvesting	MMNH
241	2008	Mechanical properties of alumina-zirconia-Nb micro-nano-hybrid composites	Bartolome, Jose F.; Gutierrez-Gonzalez, C. F.; Torrecillas, Ramon	Materials Science	Al2O3, ZrO, Nb	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	MMNH
242	2008	Anticancer drug-layered hydroxide nanohybrids as potent cancer chemotherapy agents	Choi, Soo-Jin; Oh, Jae-Min; Choy, Jin-Ho	Chemistry; Physics	Methotrexate (anticancer drug), LDH	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
243	2008	Nanohybrids of edible dyes intercalated in ZnAl layered double hydroxides	Choy, Jin-Ho; Kim, Yun-Kyung; Son, You-Hvvan; et al.	Chemistry; Physics	Edible dyes [Allura (R) Red AC (C18H14N2O8S22-), Sunset Yellow FCF (C16H10N2O7S22-), and Brilliant Blue FCF (C37H34N2O9S32-)], ZnAl LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
244	2008	Clay-chitosan-gold nanoparticle nanohybrid: Preparation and application for assembly and direct electrochemistry of myoglobin	Zhao, Xiaojuan; Mai, Zhibin; Kang, Xinhuang; et al.	Elecrochemistry	Clay, chitosan, Au	Biomaterials	MMNH
245	2008	Fluorescent magnetic nanohybrids as multimodal imaging agents for human epithelial cancer detection	Yang, Jaemoon; Lim, Eun-Kyung; Lee, Hong Jae; et al.	Engineering; Materials Science	MnFe2O4, pyrene	Optical imaging and applications	OMCNH
246	2008	A novel nanohybrid of daunomycin and single-walled carbon nanotubes: photophysical properties and enhanced electrochemical activity	Lu, Yanhong; Yang, Xiaoying; Ma, Yanfeng; et al.	Biotechnology & Applied Microbiology	SWNT, daunomycin	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
247	2008	Chlorinated polyethylene nanocomposites using PCL/clay nanohybrid masterbatches	Benali, Samira; Peeterbroeck, Sophie; Brocorens, Patrick; et al.	Polymer Science	poly(E-caprolactone), montmorillonite	Crystallography and polymer crystallization	OMCNH
248	2008	Sol-gel nanohybrid materials prepared via supramolecular organization	Katagiri, Kiyofumi	Materials Science	Organoalkoxysilanes, titania	Synthesis of new nanohybrids/materials	OMCNH
249	2008	Dielectric and conduction properties of polyimide/silica nano-hybrid films	Zhang, Ming-Yan; Zeng, Shu-Jin; Fan, Yong; et al.	Materials Science; Polymer Science	Polyimide, silica	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH

250	2008	In vitro sustained release of LMWH from MgAl-layered double hydroxide nanohybrids	Gu, Zi; Thomas, Anita C.; Xu, Zhi Ping; et al.	Chemistry; Materials Science	heparin, Mg-Al-Cl LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
251	2008	The polyurethane/SiO2 nano-hybrid membrane with temperature sensitivity for water vapor permeation	Zhou, Hu; Chen, Yi; Fan, Haojun; et al.	Engineering; Polymer Science	N/A	N/A	N/A
252	2008	Intensity-dependent enhancement of saturable absorption in PbS-Au(4) nanohybrid composites: Evidence for resonant energy transfer by Auger recombination	Elim, Hendry I.; Ji, Wei; Yang, Jian; et al.	Physics	$PbS–Au_4$	Semiconductors/superconductors/conductive materials	MMNH
253	2008	Supramolecular self-assembly of amphiphiles on carbon nanotubes: A versatile strategy for the construction of CNT/metal nanohybrids, application to electrocatalysis	Nicolas; Surendran, Geetarani; Remita, Hynd; et al.	Chemistry	MWNT, nitrilotriacetic acid, pyridinium, Pd	Catalytic/Photocatalytic/Electrocatalytic applications	CMNH
254	2008	CrAsH-quantum dot nanohybrids for smart targeting of proteins	Genin, Emilie; Carion, Olivier; Mahler, Benoit; et al.	Chemistry	CrAsH, Cys-tagged proteins, quantum dots	Delivery Carriers, and Controlled Release of Drugs/Compounds	MMNH
255	2008	Characterizations of interlayer organic-inorganic nanohybrid of molybdenum trioxide with polyaniline and poly(o-anisidine)	Itoh, Toshio; Matsubara, Ichiro; Shin, Woosuck; et al.	Materials Science	molybdenum trioxide, polyaniline, poly(o-anisidine)	Synthesis of new nanohybrids/materials	OMCNH
256	2008	Development of 3d micro-nano hybrid patterns using anodized aluminum and micro-indentation	Shin, Hong Gue; Kwon, Jong Tae; Seo, Young Ho; et al.	Materials Science; Physics	N/A	N/A	N/A
257	2008	Two-year clinical evaluation of ormocer, nanohybrid and nanofill composite restorative systems in posterior teeth	Mahmoud, Salah Hasab; El-Embaby, Abeer E.; AbdAllah, Asmaa Mohamed; et al.	Dentistry, Oral Surgery & Medicine	N/A	N/A	N/A
258	2008	Preparation and physical properties of transparent organic-inorganic nanohybrid materials based on urethane dimethacrylate	Daimatsu, Kazuki; Sugimoto, Hideki; Nakanishi, Eiji; et al.	Polymer Science	Silica, acrylic resin, urethane dimethacrylate	Synthesis of new nanohybrids/materials	OMCNH
259	2008	Direct electrochemistry and electrocatalysis of myoglobin immobilized on gold nanoparticles/carbon nanotubes nanohybrid film	Cao, Wei; Wei, Cuimei; Hu, Jingbo; et al.	Chemistry; Electrochemistry	MWNT, Au, myoglobin	Sensors/biosensors/electrochemical sensors	MMNH
260	2008	Characterisation of nanohybrids of porphyrins with metallic and semiconducting carbon nanotubes by EPR and optical spectroscopy	Cambre, Sofie; Wenseleers, Wim; Culin, Jelena; et al.	Chemistry; Physics	SWNT, porphyrin	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
261	2008	Mesoporous iron oxide-layered titanate nanohybrids: Soft-chemical synthesis, characterization, and photocatalyst application	Kim, Tae Woo; Ha, Hyung-Wook; Paek, Mi-Jeong; et al.	Chemistry; Science & Technology - Other Topics; Materials Science	FeO6, layered titanate	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
262	2008	ZnO-based low-voltage inverter with quantum-well-structured nanohybrid dielectric	Cha, Sung Hoon; Oh, Min Suk; Lee, Kwang H.; et al.	Engineering	AlOx/TiOx/AlOx layered, ZnO	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	MMNH

263	2008	Properties of nano-hybrid sol-gel coating films synthesized with colloidal silica and organoalkoxy silanes	Na, Moonkyong; Park, Hoyyul; Ahn, Myeongsang	Materials Science	organoalkoxy silanes, silica	Catalytic/Photocatalytic/Electrocatalytic applications	OMCNH
264	2008	Fe(3)O(4)@Polypyrrole Core-Shell Nanohybrid for Efficient DNA Retrieval	Park, Dae-Hwan; Oh, Jea-Min; Shul, Yong-Gun; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Fe(3)O(4), polypyrrole	Biomaterials	OMCNH
265	2008	Gadolinium (III) Diethylenetriamine Pentaacetic Acid/Layered Double Hydroxide Nanohybrid as Novel T(1)-Magnetic Resonant Nanoparticles	Kim, Su Yeon; Oh, Jae-Min; Lee, Jin Seong; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	gadolinium (III) diethylenetriamine pentaacetic acid, LDH	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
266	2008	Near infrared luminescence properties of nanohybrid film prepared from LaPO4:Er3+/LaPO4 core/shell nanoparticles and silica-based resin	Lim, Mi Ae; Il Seok, Sang; Chung, Woon Jin; et al.	Materials Science; Optical	LaPO4, Er3+	Fluorescence/luminescence/photoluminescence, light-energy harvesting	MMNH
267	2008	Organic-Inorganic Nanohybrids via Directly Grafting Gold Nanoparticles onto Conjugated Copolymers through the Diels-Alder Reaction	Liu, Xiaofeng; Zhu, Mei; Chen, Songhua; et al.	Chemistry; Materials Science	poly-p-phenyleneethynylene, Au	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
268	2008	Fabrication of surface-structure controlled photopatterns upon transparent silica-acryl nanohybrid films with enhanced thermal and mechanical properties	Kang, Dong Jun; Han, Dong Hee; Kang, Dong Pil; et al.	Optical	Silica, acryl	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
269	2008	Shear enhanced interfacial interaction between carbon nanotubes and polyethylene and formation of nanohybrid shish-kebabs	Liang, Si; Wang, Ke; Chen, Daiqiang; et al.	Polymer Science	MWNT, polyethylene	Synthesis of new nanohybrids/materials	OMCNH
270	2008	Controlled Release Compound Based on Metanilate-Layered Double Hydroxide Nanohybrid	Hussein, Mohd Zobir; Nasir, Norashikin Mat; Yahaya, Asmah H. J.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Metanilate, Zn-Al, Mg-Al, Ca-Al	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
271	2008	Novel Nanohybrids Derived from the Attachment of FePt Nanoparticles on Carbon Nanotubes	Tsoufis, Theodoros; Tomou, Aphrodite; Gournis, Dimitrios; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	MWNT, FePt	Synthesis of new nanohybrids/materials	CMNH
272	2008	Mechanism analysis of improved corona-resistant characteristic in polyimide/TiO(2) nanohybrid films	Zha, Jun-Wei; Song, Hong-Tao; Dang, Zhi-Min; et al.	Physics	Polyimide, TiO2	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
273	2008	Thermo(oxidative) stability of novel polyurethane/POSS nanohybrid elastomers	Janowski, Bartlomiej; Pielichowski, Krzysztof	Chemistry	N/A	N/A	N/A
274	2008	Nanohybrid materials from interlayer functionalization of kaolinite. Application to the electrochemical preconcentration of cyanide	Letaief, Sadok; Tonle, Ignas K.; Diaco, Thomas; et al.	Chemistry; Materials Science, Mineralogy	Polyimide, silica	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
275	2008	Nanohybrid PVA/ZrO(2) and PVA/Al(2)O(3) electrospun mats	Lamastra, F. R.; Bianco, A.; Meriggi, A.; et al.	Engineering	poly(vinyl alcohol), ZnO, AlO	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
276	2008	A Nano-Hybrid of Molybdenum Oxide Intercalated by Dithiocarbamate as an Oxidation Catalyst	Afsharpour, Maryam; Mahjoub, Alireza; Amini,	Polymer Science	Molybdenum Oxide, Dithiocarbamate	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH

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277	2008	SYNTHESIS AND ELECTRO-OPTIC PROPERTY OF INTERCALATION POLYIMIDE AND NANOHYBRID	Yang, D. Y.; Qiu, F. X.; Cao, G. R.	Optical; Physics	alkylsilane, Alumina, Titania	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	MMNH
278	2008	Monolayer-precision fabrication of mixed-organic-inorganic nanohybrid superlattices for flexible electronic devices	Lee, Byoung H.; Lee, Kwang H.; Im, Seongil; et al.	Materials Science; Physics	Kaolinite, dimethylsulfoxide	Sensors/biosensors/electrochemical sensors	OMCNH
279	2008	Electrochemical Synthesis and Photovoltaic Property of Cadmium Sulfide-Polybithiophene Interdigitated Nanohybrid Thin Films	Xi, Dongjuan; Zhang, Han; Furst, Stephen; et al.	Chemistry; Science & Technology - Other Topics; Materials Science	Cadmium Sulfide, Polybithiophene	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
280	2008	Structure of Organic-Inorganic Nanohybrids Incorporating Titanium(IV) Oxoalkoxyacylate Nanoclusters: A SANS Study	Karatchevtseva, Inna; Heinemann, Andre; Hartley, Veronica; et al.	Chemistry	Polymethyl methacrilate, TiO2	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
281	2009	Cell proliferation and controlled drug release studies of nanohybrids based on chitosan-g-lactic acid and montmorillonite	Depan, Dilip; Kumar, Annamalai Pratheep; Singh, Raj Pal	Engineering; Materials Science	chitosan-g-lactic acid, montmorillonite	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
282	2009	'Clicked' magnetic nanohybrids with a soft polymer interlayer	He, Hongkun; Zhang, Yu; Gao, Chao; et al.	Chemistry	MWNT, Fe3O4, Poly(acrylic acid), silica	Catalytic/Photocatalytic/Electrocatalytic applications	CMNH
283	2009	Efficient fluorescence resonance energy transfer in highly stable liposomal nanohybrid cerasome	Dai, Zhifei; Tian, Wenjie; Yue, Xiuli; et al.	Chemistry	cyanine dyes, silica, cerasome forming lipids	Biomaterials	OMCNH
284	2009	Sandwich nanohybrid of single-walled carbon nanohorns-TiO2-porphyrin for electrocatalysis and amperometric biosensing towards chloramphenicol	Tu, Wenwen; Lei, Jianping; Ding, Lin; et al.	Chemistry	SW nanohorns, TiO2, Porphyrin	Catalytic/Photocatalytic/Electrocatalytic applications	CMNH
285	2009	Carbon Nanotube-Acridine Nanohybrids: Spectroscopic Characterization of Photoinduced Electron Transfer	Mackiewicz, Nicolas; Delaire, Jacques A.; Rutherford, A. William; et al.	Chemistry	SWNT, 9-phenyl acridine, 10-methyl-9-phenyl acridinium	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
286	2009	Self-Assembly of Mn-Doped ZnS Quantum Dots/Octa(3-aminopropyl)octasilsequioxane Octahydrochloride Nanohybrids for Optosensing DNA	He, Yu; Wang, He-Fang; Yan, Xiu-Ping	Chemistry	Mn, ZnS Quantum Dots, Octa(3-aminopropyl)octasilsequioxane Octahydrochloride	Biomaterials	MMNH
287	2009	The Effect of Water Storage, Elapsed Time and Contaminants on the Bond Strength and Interfacial Polymerization of a Nanohybrid Composite	Perriard, Jean; Lorente, Maria Cattani; Scherrer, Susanne; et al.	Dentistry, Oral Surgery & Medicine	Cup-shaped nanocarbons, porphyrins	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
288	2009	Preparation and Theophylline Delivery Applications of Novel PMAA/MWCNT-COOH Nanohybrid Hydrogels	Zhang, Chang-Hu; Luo, Yan-Ling; Chen, Ya-Shao; et al.	Engineering; Materials Science; Polymer Science	MWNT, Theophylline, poly(methacrylic acid)	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
289	2009	Dynamic Mechanical Analysis of a Hybrid and a Nanohybrid Light-Cured Dental Resin Composite	Sideridou, Irini D.; Karabela, Maria M.; Spyroudi, Crysa S.	Engineering; Materials Science; Polymer Science	N/A	N/A	N/A
290	2009	Physical Properties of a Hybrid and a Nanohybrid Dental Light-Cured	Sideridou, Irini D.;	Engineering; Materials Science;	N/A	N/A	N/A

		Resin Composite	Karabela, Maria M.; Micheliou, Christina N.; et al.	Polymer Science			
291	2009	A novel core-shell structured magnetic organic-inorganic nanohybrid involving drug-intercalated layered double hydroxides coated on a magnesium ferrite core for magnetically controlled drug release	Zhang, Hui; Pan, Dengke; Zou, Kang; et al.	Chemistry; Materials Science	diclofenac, Mg-Al LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
292	2009	Nanohybrid materials from the grafting of imidazolium cations on the interlayer surfaces of kaolinite. Application as electrode modifier	Tonle, Ignas K.; Letaief, Sadok; Ngameni, Emmanuel; et al.	Chemistry; Materials Science	imidazolium, kaolinite	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
293	2009	Morphological modulation of optoelectronic properties of organic-inorganic nanohybrids prepared with a one-step co-fed chemical vapor deposition polymerization process	Hsiao, Chang-Tao; Lu, Shih-Yuan	Chemistry; Materials Science	poly(p-phenylene vinylene)-CdS	Optical imaging and applications	OMCNH
294	2009	Functional nanohybrids self-assembled from amphiphilic calix[6]biscrowns and noble metals	Guan, Bing; Liang, Qing; Zhu, Yuan; et al.	Chemistry; Materials Science	SWNT, AgNO3, HAuCl4, terminal amino calix[6]crowns	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
295	2009	Silver-Polymer Nanohybrids Prepared by Microemulsion Polymerization	Donescu, Dan; Nistor, Cristina Lavinia; Purcar, Violeta; et al.	Science & Technology - Other Topics; Materials Science; Physics	Ag, poly(styrene), poly(butyl acrylate), poly(methyl methacrylate)	Synthesis of new nanohybrids/materials	OMCNH
296	2009	Optical and Thermal Properties of Organo-silica/Polyimide Nano-hybrids Derived from Polysiloxazane Copolymers	Yorifuji, Daisuke; Matsumura, Akiko; Aoki, Tomoko; et al.	Polymer Science	silica, polyimide	Optical imaging and applications	OMCNH
297	2009	Photoinduced electron transfer of nanohybrids of carbon nanohorns with amino groups and tetrabenzoic acid porphyrin in aqueous media	Sandanayaka, Atula S. D.; Ito, Osamu; Tanaka, Takatsugu; et al.	Chemistry	Carbon nanohorns, tetrabenzoic acid porphyrin	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
298	2009	Photoluminescence of CdTe nanocrystals modulated by methylene blue and DNA. A label-free luminescent signaling nanohybrid platform	Shen, Jiang-Shan; Yu, Tao; Xie, Jian-Wei; et al.	Chemistry; Physics	Thioglycolic acid, CdTe, methylene blue	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
299	2009	Size effect of TiO2-SiO2 nano-hybrid particle	Ohno, Tomoya; Tagawa, Shouichiroh; Itoh, Hidenobu; et al.	Materials Science	TiO2, SiO2	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
300	2009	Synthesis and characterization of (zinc-layered-gallate) nanohybrid using structural memory effect	bin Hussein, Mohd Zobir; Ghotbi, Mohammad Yeganeh; Yahaya, Asmah Hj; et al.	Materials Science	calcined zinc hydroxide nitrate LDH, gallate	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
301	2009	Preparation of a new nano-layered materials and organic-inorganic nano-hybrid materials, Zn-Si LDH	Saber, Osama; Tagaya, Hideyuki	Chemistry; Materials Science	Organic acids, Zn-Si LDH	Synthesis of new nanohybrids/materials	OMCNH
302	2009	Origin of ultralow permittivity in polyimide/mesoporous silicate	Dang, Zhi-Min; Ma, Lan-	Physics	Mesoporous silicate, polyimide	Crystallography and polymer crystallization	OMCNH

		nanohybrid films with high resistivity and high breakdown strength	Jie; Zha, Jun-Wei; et al.				
303	2009	Two-dimensional nanohybridization of gold nanorods and polystyrene colloids	Yi, Dong Kee; Lee, Jin-Hyon; Rogers, John A.; et al.	Physics	Polystyrene, Au nanorods	Optical imaging and applications	OMCNH
304	2009	Incorporation of active nano-hybrids into poly(epsilon-caprolactone) for local controlled release: Antifibrinolytic drug	Tammaro, L.; Costantino, U.; Nocchetti, M.; et al.	Chemistry; Materials Science, Mineralogy	poly(epsilon-caprolactone), trans-4-(aminomethyl)cyclohexanecarboxylate, Mg-Al LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
305	2009	Controlled-release of Avermectin from Organically Modified Hydrotalcite-like Compound Nanohybrids	Qiu Depeng; Li Yonghai; Fu Xiying; et al.	Chemistry	sodium dodecyl sulfate, hydrotalcite, avermectin	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
306	2009	Fullerene nanohybrid metal oxide Ultrathin films, electronics	Yang, Do-Hyeon; Park, Chul Soon; Min, Ji Hye; et al.	Materials Science; Physics	Fullerene, metal alkoxide	Delivery Carriers, and Controlled Release of Drugs/Compounds	CMNH
307	2009	Controlled Release Formulation of Agrochemical Pesticide Based on 4-(2,4-dichlorophenoxy)butyrate Nanohybrid	Bin Hussein, Mohd Zobir; Hashim, Norhayati; Yahaya, Asmah Hj; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Zn-Al LDH, 4-(2,4-dichlorophenoxy)butyrate	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
308	2009	Preparation and characterisation of polyacrylamide/MWCNTs nanohybrid hydrogels with microporous structures	Luo, Y. L.; Zhang, C. H.; Chen, Y. S.; et al.	Materials Science	MWNT, polyacrylamide	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
309	2009	Time resolved emission studies of Ag-adenine-templated CdS (Ag/CdS) nanohybrids	Kumar, Anil; Chaudhary, Vidhi	Science & Technology - Other Topics; Materials Science; Physics	Ag, adenine, CdS	Optical imaging and applications	MMNH
310	2009	Transparent Photo-Stable Complementary Inverter with an Organic/Inorganic Nanohybrid Dielectric Layer	Oh, Min Suk; Lee, Kimoon; Lee, Kwang H.; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	ZnO, pentacene	Transparent and conductive films	OMCNH
311	2009	Smart Organic-Inorganic Nanohybrids Based on Amphiphilic Block Copolymer Micelles and Functional Silsesquioxane Nanoparticles	Schumacher, Manuela; Ruppel, Markus; Yuan, Jiayin; et al.	Chemistry; Materials Science	poly(n-butyl acrylate)-block-poly(acrylic acid) block copolymers, diglycidylaminopropyl-functional silsesquioxane	Biomaterials	OMCNH
312	2009	Synthesis and characterization of indole-3-butyric acid/hydrotalcite-like compound nanohybrids	Qiu, De-peng; Hou, Wan-guo	Chemistry	indole-3-butyric acid/hydrotalcite	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
313	2009	Sol-gel synthesis of compact nanohybrid structures based on silica gels	Khimich, N. N.; Zdravkov, A. V.; Koptelova, L. A.; et al.	Materials Science	N/A	N/A	N/A
314	2009	Amperometric hydrogen peroxide biosensor based on the immobilization of HRP on DNA-silver nanohybrids and PDDA-protected gold nanoparticles	Ma, Liping; Yuan, Ruo; Chai, Yaqin; et al.	Biochemistry & Molecular Biology; Chemistry	DNA-Ag, poly(diallyldimethlammonium chloride-Au	Sensors/biosensors/electrochemical sensors	OMCNH
315	2009	Fabrication of polymer micro/nano-hybrid lens array by microstructured anodic aluminum oxide (AAO) mold	Lee, Bong-Kee; Cha, Kyung Je; Kwon, Tai Hun	Engineering; Science & Technology - Other Topics; Optical; Physics	N/A	N/A	N/A
316	2009	Fabrication of PDMS micro/nano hybrid surface for increasing hydrophobicity	Kim, Dong Sung; Lee, Bong-Kee; Yeo, Jihoon; et al.	Engineering; Science & Technology - Other Topics; Optical; Physics	N/A	N/A	N/A
317	2009	Smart organic-inorganic nanohybrid stars based on star-shaped	Schumacher, Manuela;	Polymer Science	poly(acrylic acid) stars, N,N-di(2,3-dihydroxypropyl)3-	Biomaterials	OMCNH

		poly(acrylic acid) and functional silsesquioxane nanoparticles	Ruppel, Markus; Kohlbrecher, Joachim; et al.		aminopropyl functional silsesquioxane nanoparticles.		
318	2009	Synthesis and Characterization of Nano-Sized Epoxy Oligosiloxanes for Fabrication of Transparent Nano Hybrid Materials	Yang, Seungcheol; Kim, Jeong Hwan; Jin, Jung Ho; et al.	Polymer Science	N/A	N/A	N/A
319	2009	Performance simulation and analysis of a CMOS/nano hybrid nanoprocessor system	Cabe, Adam C.; Das, Shamik	Science & Technology - Other Topics; Materials Science; Physics	N/A	N/A	N/A
320	2009	Core-Shell Structures of Silica-Organic Pigment Nanohybrids Visualized by Electron Spectroscopic Imaging	Horiuchi, Shin; Horie, Shinji; Ichimura, Kunihiro	Science & Technology - Other Topics; Materials Science; Physics	N/A	N/A	N/A
321	2009	Highly Flexible Coaxial Nanohybrids Made from Porous TiO2 Nanotubes	Wang, Daoai; Liu, Ying; Wang, Chengwei; et al.	Chemistry; Science & Technology - Other Topics; Materials Science	Anatase TiO2, polypyrrole, poly(3-hexylthiophene), CdS, Ni, Au	Semiconductors/superconductors/conductive materials	MMNH
322	2009	Surface modification of P(EMA-co-HEA)/SiO2 nanohybrids for faster hydroxyapatite deposition in simulated body fluid?	Valles Lluch, A.; Gallego Ferrer, G.; Monleon Pradas, M.	Biophysics; Chemistry; Materials Science	Poly(ethyl methacrylate-co-hydroxyethyl acrylate), silica	Biomaterials	OMCNH
323	2009	Nanohybrids of Nylon 6 with Multi-Walled Carbon Nanotubes: Solvent-Free Polymerization of epsilon-Caprolactam Under Variable Experimental Conditions	Basiuk, Elena V.; Solis-Gonzalez, Obed A.; Alvarez-Zauco, Edgar; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	MWNT, E-caprolactam, nylon 6	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
324	2009	High-temperature chemical and microstructural transformations of an organic-inorganic nanohybrid captopril intercalated Mg-Al layered double hydroxide	Zhang, Hui; Guo, Shao-Huan; Zou, Kang; et al.	Materials Science	Captopril, Mg-Al LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
325	2009	Optical properties of zinc peroxide and zinc oxide multilayer nanohybrid films	Sebok, Daniel; Szabo, Tamas; Dekany, Imre	Chemistry; Materials Science; Physics	N/A	N/A	N/A
326	2009	Mineralization of surfactant functionalized multi-walled carbon nanotubes (MWNTs) to prepare hydroxyapatite/MWNTs nanohybrid	Tan, Qinggang; Zhang, Ke; Gu, Shuying; et al.	Chemistry; Materials Science; Physics	MWNT, hydroxyapatite	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	CMNH
327	2009	Nafion (R)/bio-functionalized montmorillonite nanohybrids as novel polyelectrolyte membranes for direct methanol fuel cells	Hasani-Sadrabadi, Mohammad Mahdi; Dashtimoghadam, Erfan; Majedi, Fatemeh S.; et al.	Electrochemistry; Energy & Fuels	Montmorillonite, nafion	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
328	2009	Molecular layer deposition of ZrO2-based organic-inorganic nanohybrid thin films for organic thin film transistors	Lee, Byoung H.; Im, Kyo K.; Lee, Kwang H.; et al.	Materials Science; Physics	ZrO2, alkylsilane	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
329	2009	Nanohybrid vs. fine hybrid composite in Class II cavities: Clinical results and margin analysis after four years	Kraemer, Norbert; Reinelt, Christian; Richter, Gert; et al.	Dentistry, Oral Surgery & Medicine; Materials Science	N/A	N/A	N/A

330	2009	Magnetorheological Characteristics of Polymer Coated Magnetite Particle Composites With Carbon Nanotube Nanohybrid	Ko, Seung Woo; Hong, Min Ki; Choi, Hyoung Jin; et al.	Engineering; Physics	MWNT, Fe3O4	Optical imaging and applications	CMNH
331	2009	LDH-intercalated D-gluconate: Generation of a new food additive-inorganic nanohybrid compound	Ghotbi, Mohammad Yeganeh; bin Hussein, Mohd Zobir; Yahaya, Asmah Hj; et al.	Chemistry; Physics	D-gluconate, Zn-Al LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
332	2009	Evaluations of Bioactive Poly(epsilon-Caprolactone)-Organosiloxane Nano-Hybrid as a Material for Bone Repair	Yoo, Jeong Joon; Rhee, Sang-Hoon; Lee, Jae Il; et al.	Cell Biology; Engineering	Poly(epsilon-Caprolactone) Organosiloxane	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
333	2009	pH-Driven synthesis of collagen-silica nanohybrids	Garcia-Valdes, C. J.; Hernandez-Padron, G.; Garcia-Garduno, M. V.; et al.	Polymer Science	Silica, collagen	Synthesis of new nanohybrids/materials	OMCNH
334	2009	Synthesis, Characterization, and Magnetically Controlled Release Behavior of Novel Core-Shell Structural Magnetic Ibuprofen-Intercalated LDH Nanohybrids	Zhang, Hui; Pan, Dengke; Duan, Xue	Chemistry; Science & Technology - Other Topics; Materials Science	ibuprofen (IBU)-intercalated Mg-Al-LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
335	2009	Formation of polymer/carbon nanotubes nano-hybrid shish-kebab via non-isothermal crystallization	Zhang, Ling; Tao, Tao; Li, Chunzhong	Polymer Science	MWNT, polyethylene	Crystallography and polymer crystallization	OMCNH
336	2009	Refractive Index Control and Rayleigh Scattering Properties of Transparent TiO2 Nanohybrid Polymer	Elim, Hendry I.; Cai, Bin; Kurata, Yu; et al.	Chemistry	TiO2, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane	Optical imaging and applications	OMCNH
337	2009	Preparation and Structural Characterization of Novel Nanohybrids by Cationic 3D Silica Nanoparticles Sandwiched between 2D Anionic Montmorillonite Clay through Electrostatic Attraction	Tseng, Tzu-Fan; Wu, Jeng-Yue	Chemistry; Science & Technology - Other Topics; Materials Science	Silica, montmorillonita	Synthesis of new nanohybrids/materials	MMNH
338	2009	Photoinduced Electron Storage in WO3/TiO2 Nanohybrid Material in the Presence of Oxygen and Postirradiated Reduction of Heavy Metal Ions	Zhao, Dan; Chen, Chuncheng; Yu, Cailan; et al.	Chemistry; Science & Technology - Other Topics; Materials Science	WO3, TiO2	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	MMNH
339	2009	A Study of Asynchronous Design Methodology for Robust CMOS-Nano Hybrid System Design	Chakraborty, Rajat Subhra; Bhunia, Swarup	Computer Science; Engineering; Science & Technology - Other Topics	N/A	N/A	N/A
340	2009	Nanohybrid composite vs. fine hybrid composite in extended Class II cavities: Clinical and microscopic results after 2 years	Kraemer, Norbert; Reinelt, Christian; Garcia-Godoy, Franklin; et al.	Dentistry, Oral Surgery & Medicine	N/A	N/A	N/A
341	2009	Functionalization of silica nanoparticles with 4-isocyanato-4 '-(3,3 '-dimethyl-2,4-dioxo-azetidino)diphenyl methane, surface chemical reactivity and nanohybrid preparation	Liu, Ying-Ling; Wu, Yen-Hsing; Jeng, Ru-Jong; et al.	Chemistry	4-isocyanato-4 '-(3,3 '-dimethyl-2,4-dioxo-azetidino)diphenyl methane, silica	Synthesis of new nanohybrids/materials	OMCNH
342	2009	Preparation and Supramolecular Self-Assembly of Amphiphilic Dendron-POSS Nanohybrids	Chang, Gung-Pei; Jeng, Ru-Jong; Dai, Shenghong A.;	Chemistry; Science & Technology - Other Topics; Materials Science;	urea malonamide dendron, POSS	Synthesis of new nanohybrids/materials	OMCNH

			et al.	Physics			
343	2009	Genotoxic Properties of Nylon-6/MWNTs Nanohybrid	Ochoa-Olmos, Omar E.; Montero-Montoya, Regina; Serrano-Garcia, Luis; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	MWNT, nylon 6	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
344	2009	Electrospun poly(epsilon-caprolactone)/Ca-deficient hydroxyapatite nanohybrids: Microstructure, mechanical properties and cell response by murine embryonic stem cells	Bianco, Alessandra; Di Federico, Erica; Moscatelli, Ilana; et al.	Materials Science	poly(epsilon-caprolactone), Ca-deficient hydroxyapatite	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
345	2009	Ionic-Liquid-Assisted Sonochemical Synthesis of Carbon-Nanotube-Based Nanohybrids: Control in the Structures and Interfacial Characteristics	Park, Ho Seok; Choi, Bong Gill; Yang, Seong Ho; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	MWNT, Pt, Pd, Au, Ag, SnOx, FeOx, ZnOx	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CMNH
346	2009	Synthesis of Molybdenum Oxide Nanohybrids as Efficient Catalysts in Oxidation of Alcohols	Afsharpour, Maryam; Mahjoub, Alireza; Amini, Mostafa M.	Polymer Science	N/A	N/A	N/A
347	2009	Nanohybrid Resin Composites: Nanofiller Loaded Materials or Traditional Microhybrid Resins?	Moraes, R. R.; Goncalves, L. S.; Lancellotti, A. C.; et al.	Dentistry, Oral Surgery & Medicine	N/A	N/A	N/A
348	2009	Synthesis and Characterization of Photoluminescent Eu(III) Coordination Halloysite Nanotube-Based Nanohybrids	Wan, Chaoying; Li, Ming; Bai, Xin; et al.	Chemistry; Science & Technology - Other Topics; Materials Science	methyl methacrylate (MMA), hydroxyethyl methacrylate (HEMA), Eu^{3+},	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
349	2009	Emulsions Stabilized by Carbon Nanotube-Silica Nanohybrids	Shen, Min; Resasco, Daniel E.	Chemistry; Materials Science	SWNT, silica	Catalytic/Photocatalytic/Electrocatalytic applications	CMNH
350	2009	Direct Formation of Nanohybrid Shish-Kebab in the Injection Molded Bar of Polyethylene/Multiwalled Carbon Nanotubes Composite	Yang, Jinghui; Wang, Chaoyu; Wang, Ke; et al.	Polymer Science	MWNT, polyethylene	Crystallography and polymer crystallization	OMCNH
351	2009	Correlation of Ultrastructure with Mechanical Properties of Nano-Hybrid Dental Composites	Schmitt, Lena; Lurtz, Claudia; Sternberg, Katrin; et al.	Materials Science	N/A	N/A	N/A
352	2009	The disruption of bacterial membrane integrity through ROS generation induced by nanohybrids of silver and clay	Su, Hong-Lin; Chou, Chih-Cheng; Hung, Da-Jen; et al.	Engineering; Materials Science	Ag, silicate	Antimicrobial/antibacterial applications	MMNH
353	2009	Synthesis and third-order nonlinear optical properties of a multiwalled carbon nanotube-organically modified silicate nanohybrid gel glass	Zheng, Chan; Feng, Miao; Du, Yuhong; et al.	Chemistry; Materials Science	MWNT, silicate	Optical imaging and applications	OMCNH
354	2009	Synthesis and Characterization of Imidacloprid/Hydrotalcite-like Compound Nanohybrids	Qiu Depeng; Hou Wanguo; Xu Jie; et al.	Chemistry	Hydrotalcite, dodecyl sulfate, imidacloprid	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
355	2009	Scratch resistance of a polycarbonate plus organoclay nanohybrid	Arribas, A.; Bermudez, M.-D.; Brostow, W.; et al.	Polymer Science	Polycarbonate, montmorillonite	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
356	2009	Shell-Controlled Photoluminescence in CdSe/CNT Nanohybrids	Si, Hua-Yan; Liu, Cai-Hong; Xu, Hua; et al.	Science & Technology - Other Topics; Materials Science; Physics	CNT, CdSe quantum dots	Fluorescence/luminescence/photoluminescence, light-energy harvesting	CMNH
357	2009	Development of Urease/Layered	Baccar, Z. M.;	Chemistry;	Urease, Mg-Al LDH, Zn-Al	Catalytic/Photocatalyti	OMCNH

		Double Hydroxides Nanohybrid Materials for the Urea Detection: Synthesis, Analytical and Catalytic Characterizations	Caballero, D.; Zine, N.; et al.	Electrochemistry; Instruments & Instrumentation; Physics	LHD	c/Electrocatalytic applications	
358	2009	Resistance of nanofill and nanohybrid resin composites to toothbrush abrasion with calcium carbonate slurry	Suzuki, Toshimitsu; Kyoizumi, Hideaki; Finger, Werner J.; et al.	Dentistry, Oral Surgery & Medicine; Materials Science	N/A	N/A	N/A
359	2009	Structural and photoluminescence properties of laser processed ZnO/carbon nanotube nanohybrids	Aissa, Brahim; Fauteux, Christian; El Khakani, My Ali; et al.	Materials Science	MWNT, ZnO, Co, Ni, SiO2,	Fluorescence/luminescence/photoluminescence, light-energy harvesting	CMNH
360	2009	Observation of a Type II Heterojunction in a Highly Ordered Polymer-Carbon Nanotube Nanohybrid Structure	Schuettfort, Torben; Nish, Adrian; Nicholas, Robin J.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	SWNT, regioregular poly(3-hexylthiophene)	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
361	2009	The Effect of Single, Binary and Ternary Anions of Chloride, Carbonate and Phosphate on the Release of 2,4-Dichlorophenoxyacetate Intercalated into the Zn-Al-layered Double Hydroxide Nanohybrid	Hussein, Mohd Zobir; Jaafar, Adila Mohamad; Yahaya, Asmah Hj.; et al.	Science & Technology - Other Topics; Materials Science; Physics	2,4-Dichlorophenoxyacetate, Zn-Al LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
362	2009	In-Vitro Release Kinetics and Stability of Anticardiovascular Drugs-Intercalated Layered Double Hydroxide Nanohybrids	Panda, H. S.; Srivastava, R.; Bahadur, D.	Chemistry	pravastatin, fluvastatin, Mg-Al LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
363	2009	Characterization of nanohybrid membranes for direct methanol fuel cell applications	Hasani-Sadrabadi, Mohammad Mahdi; Ghaffarian, Seyed Reza; Mokarram-Dorri, Nassir; et al.	Chemistry; Physics	N/A	N/A	N/A
364	2009	A novel method for fabricating polyelectrolyte complex/inorganic nanohybrid membranes with high isopropanol dehydration performance	Zhao, Qiang; Qian, Jinwen; Zhu, Chenxiao; et al.	Engineering; Polymer Science	N/A	N/A	N/A
365	2009	Thermal decomposition pathway of undoped and doped zinc layered gallate nanohybrid with Fe3+, Co2+ and Ni2+ to produce mesoporous and high pore volume carbon material	Ghotbi, Mohammad Yeganeh; bin Hussein, Mohd Zobir; Yahaya, Asmah Hj; et al.	Chemistry; Physics	Zinc layered gallate, Fe3+, Co2+, Ni2+	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
366	2009	Synthesis and Characterization of Floxuridine-Layered Double Hydroxide Nanohybrids	Li Yan-Hong; Xu Jie; Zhang Shao-Jie; et al.	Chemistry	Floxuridine, LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
367	2009	A novel nonenzymatic hydrogen peroxide sensor based on multi-wall carbon nanotube/silver nanoparticle nanohybrids modified gold electrode	Zhao, Wei; Wang, Huicai; Qin, Xia; et al.	Chemistry	MWNT, Ag, Au	Sensors/biosensors/electrochemical sensors	CMNH
368	2009	Relationship between Electrode Performance and Chemical Bonding Nature in Mesoporous Metal Oxide-Layered Titanate Nanohybrids	Ha, Hyung-Wook; Kim, Tae Woo; Choy, Jin-Ho; et al.	Chemistry; Science & Technology - Other Topics; Materials Science	FeO, NiO, titanate, Li	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	MMNH
369	2010	Innovative Inorganic-Organic	Schulz-Drost,	Chemistry	SWNT, Quantum dots, pyrene	Energy/Electron	CMNH

		Nanohybrid Materials: Coupling Quantum Dots to Carbon Nanotubes	Christian; Sgobba, Vito; Gerhards, Christina; et al.			Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	
370	2010	Stabilized liposomal nanohybrid cerasomes for drug delivery applications	Cao, Zhong; Ma, Yan; Yue, Xiuli; et al.	Chemistry	Paclitaxel, cerasomes	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
371	2010	Novel high-performance nanohybrid polyelectrolyte membranes based on bio-functionalized montmorillonite for fuel cell applications	Hasani-Sadrabadi, Mohammad Mahdi; Dashtimoghadam, Erfan; Majedi, Fatemeh S.; et al.	Chemistry	N/A	N/A	N/A
372	2010	A DNA-templated catalyst: the preparation of metal-DNA nanohybrids and their application in organic reactions	Wang, Ye; Ouyang, Guanghui; Zhang, Jintang; et al.	Chemistry	Pd, Au, Ag, Pt, DNA	Catalytic/Photocatalytic/Electrocatalytic applications	OMCNH
373	2010	Superior SWNT dispersion by amino acid based amphiphiles: designing biocompatible cationic nanohybrids	Brahmachari, Sayanti; Das, Dibyendu; Das, Prasanta Kumar	Chemistry	SWNT, amino acid based amphiphiles	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
374	2010	Diameter dependent electron transfer in supramolecular nanohybrids of (6,5)- or (7,6)-enriched semiconducting SWCNT as donors and fullerene as acceptor	Sandanayaka, Atula S. D.; Maligaspe, Eranda; Hasobe, Taku; et al.	Chemistry	SWNT, pyrene, fullerene	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CCNH
375	2010	Synthesis of Poly(vinyl alcohol)/C-60 and Poly(N-vinylpyrrolidone)/C-60 Nanohybrids as Potential Photodynamic Cancer Therapy Agents	Hurtgen, Marie; Debuigne, Antoine; Mouithys-Mickalad, Ange; et al.	Chemistry	Fullerene, poly(vinyl alcohol), poly(N-vinylpyrrolidone)	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
376	2010	Fabrication of polypyrrole/ZnCoO nanohybrid systems for solar cell applications	Kumar, G. Mohan; Raman, V.; Kawakita, Jin; et al.	Chemistry	Polypyrrole, ZnCoO	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
377	2010	Nanohybrid Structures Formed by Carbon Nanotubes with Long Polynucleotide	Karachevtsev, V. A.; Karachevtsev, M. V.; Leontiev, V. S.; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	SWNT, polyribonucleotides	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
378	2010	Preparation and Characterization of PMAA/MWCNTs Nanohybrid Hydrogels With Improved Mechanical Properties	Luo, Yan-Ling; Xu, Feng; Feng, Qiang-Suo; et al.	Engineering; Materials Science	MWNT, poly(methacrylic acid)	Biomaterials	OMCNH
379	2010	Immediate repair bond strengths of microhybrid, nanohybrid and nanofilled composites after different surface treatments	Rinastiti, Margareta; Oezcan, Mutlu; Siswomihardjo, Widowati; et al.	Dentistry, Oral Surgery & Medicine	N/A	N/A	N/A
380	2010	Inorganic-based phytohormone delivery vector of 2-chloroethylphosphonate nanohybrid: a new stimulating compound with controlled release property to	Hussein, Mohd Zobir; Jaafar, Adila Mohamad; Yahaya,	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Ethephon, Zn-Al LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH

		increase latex production	Asmah Hj.; et al.				
381	2010	Synthesis of an herbicides-inorganic nanohybrid compound by ion exchange-intercalation of 3(2-chlorophenoxy)propionate into layered double hydroxide	Hussein, M. Z.; Hashim, N.; Yahaya, A. H.; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	3(2-chlorophenoxy)propionate, Zn-Al LHD	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
382	2010	Fabrication and dielectric properties of advanced high permittivity polyaniline/poly(vinylidene fluoride) nanohybrid films with high energy storage density	Yuan, Jin-Kai; Dang, Zhi-Min; Yao, Sheng-Hong; et al.	Chemistry; Materials Science	N/A	N/A	N/A
383	2010	Interlayer modification of a layered H-octosilicate (H-RUB-18) with methanol: formation of a highly ordered organosilicate nanohybrid	Kiba, Shosuke; Itagaki, Tetsuro; Nakato, Teruyuki; et al.	Chemistry; Materials Science	Silicate, polysilic acid, methanol	Synthesis of new nanohybrids/materials	OMCNH
384	2010	Carbon nanotube-based magnetic-fluorescent nanohybrids as highly efficient contrast agents for multimodal cellular imaging	Chen, Bingdi; Zhang, Hui; Zhai, Chuanxin; et al.	Chemistry; Materials Science	MWNT, CdTe quantum dots, FeO	Fluorescence/luminescence/photoluminescence, light-energy harvesting	CMNH
385	2010	Silica xerogel-chitosan nano-hybrids for use as drug eluting bone replacement	Lee, Eun-Jung; Jun, Shin-Hee; Kim, Hyoun-Ee; et al.	Engineering; Materials Science	Silica xerogel, chitosan	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
386	2010	Nanohybrids of Ultrathin Titania Nanosheets and Zinc Oxide Nanoparticles by an Electrostatic Interaction	Kim, Sunmi; Paek, Seungwoo; Lee, Seonghoon	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Titania, ZnO	Synthesis of new nanohybrids/materials	MMNH
387	2010	Preparation of Soluble Polyimide/MgO Nanohybrid Films by In situ Hybridization Method and Evaluation of Their Thermal Conductivity	Murakami, Kimiya; Yamada, Kazuhiko; Deguchi, Kenzo; et al.	Polymer Science	Polyimide, MgO	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
388	2010	Preparation and Characterization of Polyimide/ZnO Nano-hybrid Films Exhibiting High Refractive Indices	Suzuki, Atsuhisa; Ando, Shinji	Polymer Science	Polyimide, ZnO	Optical imaging and applications	OMCNH
389	2010	Pentacene thin-film on organic/inorganic nanohybrid dielectrics for ZnO charge injection memory transistor	Cha, Sung Hoon; Park, Aaron; Lee, Kwang H.; et al.	Materials Science; Physics	N/A	N/A	N/A
390	2010	Spectroscopical properties of organic/metal nanohybrids	Dellepiane, Giovanna; Cuniberti, Carla; Alloisio, Marina; et al.	Chemistry; Physics	polydiacetylenes, Au	Sensors/biosensors/electrochemical sensors	OMCNH
391	2010	Nano-hybrid self-crosslinked PDMA/silica hydrogels	Carlsson, Linn; Rose, Severine; Hourdet, Dominique; et al.	Chemistry; Materials Science; Physics; Polymer Science	poly(N,N-dimethylacrylamide), silica	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
392	2010	Fabrication of Micro-Nano Hybrid Patterns on a Solid Surface	Liu, Peng; Ding, Jiandong	Chemistry; Materials Science	N/A	N/A	N/A
393	2010	Electrocatalytic oxidation and determination of ascorbic acid in the presence of dopamine at multiwalled carbon nanotube-silica network-gold nanoparticles based nanohybrid modified electrode	Ragupathy, Dhanusuraman; Gopalan, Anantha Iyengar; Lee, Kwang-Pill	Chemistry; Electrochemistry; Instruments & Instrumentation	MWNT, silica, Au	Catalytic/Photocatalytic/Electrocatalytic applications	CMNH

394	2010	Synthesis and spectroscopic characterization of solution processable highly ordered polythiophene-carbon nanotube nanohybrid structures	Schuettfort, T.; Snaith, H. J.; Nish, A.; et al.	Science & Technology - Other Topics; Materials Science; Physics	SWNT, regio-regular poly(3-hexylthiophene)	Crystallography and polymer crystallization	OMCNH
395	2010	Organization of Molybdenum Oxide Nanohybrids by Intercalation of Aminohydroxy Ligands into Layered Molybdic Acid: Efficient Catalysts in Oxidation of Alcohols	Afsharpour, M.; Mahjoub, A. R.; Amini, M. M.; et al.	Biotechnology & Applied Microbiology; Science & Technology - Other Topics; Materials Science	N/A	N/A	N/A
396	2010	Random lasing action from ZnO-silica nanohybrids	Stassinopoulos, Andreas; Das, Rabindra N.; Anastasiadis, Spiros H.; et al.	Optical	ZnO, silica	Fluorescence/luminescence/photoluminescence, light-energy harvesting	MMNH
397	2010	Hierarchical structure of injection-molded bars of HDPE/MWCNTs composites with novel nanohybrid shish-kebab	Yang, Jinghui; Wang, Ke; Deng, Hua; et al.	Polymer Science	MWNT, polyethylene	Crystallography and polymer crystallization	OMCNH
398	2010	Hierarchically Constrained Dynamics and Emergence of Complex Behavior in Nanohybrids	Carlos, L. D.; Pacheco, J. M.; Ferreira, R. A. S.; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	N/A	N/A	N/A
399	2010	Ordered luminescent nanohybrid thin films of Eu(BA)(3)Phen nanoparticle in polystyrene matrix from diblock copolymer self-assembly	Wang, Chao; Zhang, Yaoming; Pei, Xianqiang; et al.	Chemistry; Materials Science; Physics	polystyrene-block-poly(ethylene oxide), Eu(BA)3	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
400	2010	Surface texture and roughness of polished nanofill and nanohybrid resin composites	Endo, Tatsuo; Finger, Werner J.; Kanehira, Masafumi; et al.	Dentistry, Oral Surgery & Medicine; Materials Science	N/A	N/A	N/A
401	2010	Nano-hybrids incorporation into poly(epsilon-caprolactone) for multifunctional applications: Mechanical and barrier properties	Bugatti, Valeria; Costantino, Umberto; Gorrasi, Giuliana; et al.	Polymer Science	Benzoate (Bz), 2,4-dichlorobenzoate (BzDC), para-hydroxybenzoate (p-BzOH) and ortho-hydroxybenzoate (o-BzOH), Zn-Al LDH	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
402	2010	Antimalarial evaluation of copper(II) nanohybrid solids: inhibition of plasmepsin II, a hemoglobin-degrading malarial aspartic protease from Plasmodium falciparum	Mohapatra, Subash Chandra; Tiwari, Hemandra Kumar; Singla, Manisha; et al.	Biochemistry & Molecular Biology; Chemistry	LCu(CH(3)COO)(2), LCuCl(2), L = diamide	Antimicrobial/antibacterial applications	OMCNH
403	2010	Visible photoluminescence of MWCNT/CdS nanohybrid structure synthesized by a simple chemical process	Paul, Rima; Kumbhakar, P.; Mitra, A. K.	Materials Science; Physics	MWNT, CdS	Fluorescence/luminescence/photoluminescence, light-energy harvesting	CMNH
404	2010	In-Situ Template Synthesis of a Polymer/Semiconductor Nanohybrid Using Amphiphilic Conducting Block Copolymers	Lee, Yi-Huan; Chang, Chun-Jie; Kao, Chi-Jen; et al.	Chemistry; Materials Science	CdS, polyphenylene-b-poly(2-vinyl pyridine)	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
405	2010	Synthesis of Phenoxyherbicides-Intercalated Layered Double Hydroxide Nanohybrids and Their Controlled Release Property	Sarijo, Siti Halimah; bin Hussein, Mohd Zobir; Yahaya, Asmah Hj; et	Biotechnology & Applied Microbiology; Science & Technology - Other Topics; Materials	2-chloro-(2CPA) and 2,4,5trichlorophenoxy acetates (TCPA), LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH

			al.	Science			
406	2010	Selective cell affinity of biomimetic micro-nano-hybrid structured TiO2 overcomes the biological dilemma of osteoblasts	Hori, Norio; Iwasa, Fuminori; Ueno, Takeshi; et al.	Dentistry, Oral Surgery & Medicine; Materials Science	N/A	N/A	N/A
407	2010	High flux composite PTMSP-silica nanohybrid membranes for the pervaporation of ethanol/water mixtures	Claes, S.; Vandezande, P.; Mullens, S.; et al.	Engineering; Polymer Science	N/A	N/A	N/A
408	2010	Tuning the Charge-Transfer Property of PbS-Quantum Dot/TiO2-Nanobelt Nanohybrids via Quantum Confinement	Wang, Defa; Zhao, Haiguang; Wu, Nianqiang; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	PbS quantum dots, titania	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	MMNH
409	2010	Self-assembly and characterization of Ca-Al-LDH nanohybrids containing casein proteins as guest anions	Yu, Bin; Bian, Hang; Plank, Johann	Chemistry; Physics	Ca-Al LDH, casein	Synthesis of new nanohybrids/materials	OMCNH
410	2010	P-coumaric acid-zinc basic salt nanohybrid for controlled release and sustained antioxidant activity	Biswick, Timothy; Park, Dae-Hwan; Shul, Yong-Gun; et al.	Chemistry; Physics	P-coumaric acid, Zn basic salt	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
411	2010	Synthesis and characterization of the SnO2-pillared layered titanate nanohybrid	Ko, Ji Eun; Kwon, Bob Jin; Jung, Hyun	Chemistry; Physics	SnO2, titanate	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	MMNH
412	2010	Encapsulation of Conjugated Oligomers in Single-Walled Carbon Nanotubes: Towards Nanohybrids for Photonic Devices	Loi, Maria Antonietta; Gao, Jia; Cordella, Fabrizio; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	SWNT, conjugated oligomers	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CCNH
413	2010	Nanohybrids of Magnetic Iron-Oxide Particles in Hydrophobic Organoclays for Oil Recovery	Hsu, Ru-Siou; Chang, Wen-Hsin; Lin, Jiang-Jen	Science & Technology - Other Topics; Materials Science	Magnetic FeO, silicate clay (montmorillonite)	Membrane research, gas removal, pollutant remediation	MMNH
414	2010	Solution Chemistry of Self-Assembled Graphene Nanohybrids for High-Performance Flexible Biosensors	Choi, Bong Gill; Park, HoSeok; Park, Tae Jung; et al.	Chemistry; Science & Technology - Other Topics; Materials Science	Graphene, nafion	Sensors/biosensors/electrochemical sensors	OMCNH
415	2010	Efficient epoxidation over cyanocobalamine containing SBA-15 organic-inorganic nanohybrids	Karimi, Z.; Mahjoub, A. R.	Chemistry; Materials Science; Physics	SBA-15 mesoporous silica, triblock copolymer P123, aminopropyl, thiol, ammonium and sulfonic acid	Catalytic/Photocatalytic/Electrocatalytic applications	OMCNH
416	2010	Exploring Cellular Adhesion and Differentiation in a Micro-/Nano-Hybrid Polymer Scaffold	Cheng, Ke; Kisaalita, William S.	Biotechnology & Applied Microbiology; Food Science & Technology	N/A	N/A	N/A
417	2010	Synthesis and characterization of [4-(2,4-dichlorophenoxybutyrate)-zinc layered hydroxide] nanohybrid	Hussein, Mohd Zobir; Hashim, Norhayati; Yahaya, Asmah Hj.; et al.	Chemistry; Physics	4-(2,4-dichlorophenoxy)butyrate (agrochemical), Zn layered hydroxide	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
418	2010	Glucose-Responsive Bioinorganic Nanohybrid Membrane for Self-Regulated Insulin Release	Gordijo, Claudia R.; Shuhendler, Adam J.; Wu, Xiao Yu	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	N/A	N/A	N/A
419	2010	Prediction of first matrix cracking in micro/nanohybrid brittle matrix	Pavia, F.; Letertre, A.;	Materials Science	N/A	N/A	N/A

		composites	Curtin, W. A.				
420	2010	Development of a Glucose Biosensor Using Advanced Electrode Modified by Nanohybrid Composing Chemically Modified Graphene and Ionic Liquid	Yang, Min Ho; Choi, Bong Gill; Park, HoSeok; et al.	Chemistry; Electrochemistry	Graphene, ionic liquid	Sensors/biosensors/electrochemical sensors	OMCNH
421	2010	Synthesis and Characterization of Functionalized Silica-Based Nanohybrid Materials for Oxyanions Adsorption	Karatchevtseva, Inna; Astoux, Marion; Cassidy, David J.; et al.	Chemistry; Materials Science	Silica, amino-functionalized alkyltrialkoxysilanes and tetraalkoxysilanes, aromatic carbosylic acid.	Adsorption studies	OMCNH
422	2010	Thermal degradation studies of polyurethane/POSS nanohybrid elastomers	Lewicki, James P.; Pielichowski, Krzysztof; De la Croix, Pauline Tremblot; et al.	Polymer Science	N/A	N/A	N/A
423	2010	Noble Metal-Organic Nanohybrids for Chemical Sensing: Synthesis and Characterization	Alloisio, Marina; Demartini, Anna; Cuniberti, Carla; et al.	Chemistry; Electrochemistry; Instruments & Instrumentation; Physics	10,12-pentacosadiynoic acid, Ag, Au	Synthesis of new nanohybrids/materials	OMCNH
424	2010	Optical, structural and adsorption properties of zinc peroxide/hydrogel nanohybrid films	Sebok, Daniel; Janovak, Laszlo; Dekany, Imre	Chemistry; Materials Science; Physics	zinc-peroxide, poly(acrylamide)	Optical imaging and applications	OMCNH
425	2010	Transparent acryl-clay nanohybrid films with low thermal expansion coefficient	Sugimoto, Hideki; Nunome, Kazunori; Daimatsu, Kazuki; et al.	Chemistry; Polymer Science	N/A	N/A	N/A
426	2010	Synthesis and characterization of poly(EMA-co-HEA)/SiO2 nanohybrids	Valles-Lluch, A.; Rodriguez-Hernandez, J. C.; Gallego Ferrer, G.; et al.	Polymer Science	poly(ethyl methacrylate (EMA)-co-hydroxyethyl acrylate(HEA)), SiO2	Synthesis of new nanohybrids/materials	OMCNH
427	2010	Synthesis and Characterization of Hippurate-Layered Double Hydroxide Nanohybrid and Investigation of its Release Property	Hussein, M. Z.; Bahar, F. A.; Yahaya, A. Hj	Chemistry	hippurate, Zn-Al LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
428	2010	Microgel/clay nanohybrids as responsive scavenger systems	Berger, Sebastian; Singh, Rekha; Sudha, Janardhanannair D.; et al.	Polymer Science	Silicon, phosphorous, sulfur	Synthesis of new nanohybrids/materials	OMCNH
429	2010	Molybdenum Peroxo Nanohybrid Compounds in Different Structures and Catalytic Properties	Afsharpour, Maryam; Mahjoub, Alireza; Amini, Mostafa M.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	N/A	N/A	N/A
430	2010	Solid state dye sensitized solar cells based on supersonic beam deposition of organic, inorganic cluster assembled, and nanohybrid materials	Coppede, N.; Nardi, M.; Toccoli, T.; et al.	Energy & Fuels	TiO2, CuPc	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	MMNH
431	2010	Tensile properties, cell adhesion, and drug release behavior of chitosan-silver-gelatin nanohybrid films and scaffolds	Rana, V. K.; Kushwaha, Omkar S.; Singh, RajPal; et al.	Polymer Science	Chitosan, Ag, gelatin	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH

432	2010	Chitosan-mediated synthesis of carbon nanotube-gold nanohybrids	Gravel, Edmond; Foillard, Stephanie; Zhang HongBin; et al.	Chemistry	Carbon nanotube, Au, chitosan	Synthesis of new nanohybrids/materials	CMNH
433	2010	Mimicking Natural Dentin Using Bioactive Nanohybrid Scaffolds for Dentinal Tissue Engineering	Valles-Lluch, Ana; Novella-Maestre, Edurne; Sancho-Tello, Maria; et al.	Cell Biology; Biotechnology & Applied Microbiology	N/A	N/A	N/A
434	2010	Synthesis and Characterization of Poly(vinyl alcohol)/Water Glass (SiO2) Nano-Hybrids via Sol-Gel Process	Tenkayala, Sobha Rani; Subha, Marata Chinna Subbarao; Gorla, Venkata Reddy; et al.	Polymer Science	Poly(vinyl alcohol), Water Glass (SiO2)	Synthesis of new nanohybrids/materials	OMCNH
435	2010	Hierarchically-Ordered Electroactive Silica-Polyaniline Nanohybrid: A Novel Material with Versatile Properties	Manian, Manesh Kalayil; Iyengar, Gopalan Anantha; Lee, Kwang-Pill; et al.	Polymer Science	Poly(trimethoxy silylpropylaniline), silica	Synthesis of new nanohybrids/materials	OMCNH
436	2010	Design of a Multifunctional Nanohybrid System of the Phytohormone Gibberellic Acid Using an Inorganic Layered Double-Hydroxide Material	Hafez, Inas H.; Berber, Mohamed R.; Minagawa, Keiji; et al.	Agriculture; Chemistry; Food Science & Technology	phytohormone gibberellic acid, Mg-Al LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
437	2010	Intercalated heterostructured nanohybrids of the semiconductor-nematic configuration: Preparation, properties, and applications	Ivashchishin, F. O.; Grygorchak, I. I.	Physics	N/A	N/A	N/A
438	2010	Raman Spectroscopy and Theoretical Characterization of Nanohybrids of Porphyrins with Carbon Nanotubes	Karachevtsev, Victor A.; Zarudnev, Evgen S.; Stepanian, Stepan G.; et al.	Chemistry; Science & Technology - Other Topics; Materials Science	SWNT, meso-5,10,15,20-tetrakis(N-methyl-4-pyridyl)porphyrin (TMPyP4) and meso-5,10,15,20-tetraphenylporphyrin (TPP)	Synthesis of new nanohybrids/materials	OMCNH
439	2010	Effect of incoming and outgoing exchangeable anions on the release kinetics of phenoxyherbicides nanohybrids	Sarijo, Siti Halimah; Hussein, Mohd Zobir; Yahaya, Asmah H. J.; et al.	Engineering; Environmental Sciences & Ecology	2-chloro- (2CPA), 4-chloro and 2,4,5-trichloro (TCPA) phenoxyacetates, Zn-Al LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
440	2010	Bio-inspired fabrication of composite membranes with ultrathin polymer-silica nanohybrid skin layer	Pan, Fusheng; Jia, Huiping; Cheng, Qinglai; et al.	Engineering; Polymer Science	poly(vinyl alcohol), protamine	Biomaterials	OMCNH
441	2010	One-pot sonochemical synthesis of dendron-stabilized gold nanoparticles as promising nano-hybrid with potential impact in biological application	Leonard, Kwati; Kawashima, Masatake; Okamura, Hiroaki; et al.	Materials Science; Physics	Dihydroxy fatty acid-based dendron, Au	Biomaterials	OMCNH
442	2010	Fabrication and application of a novel plant hormone sensor for the determination of methyl jasmonate based on self-assembling of phosphotungstic acid-graphene oxide nanohybrid on graphite electrode	Gan, Tian; Hu, Chengguo; Chen, Zilin; et al.	Chemistry; Electrochemistry; Instruments & Instrumentation	Poly(ethylene terephthalate), polyhedral oligomeric silsesquioxane	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	MMNH
443	2010	Characterization and biocompatibility	Chen, Jingdi;	Biophysics;	Hydroxyapatite, chitosan	Medicine (cancer	OMCNH

		of nanohybrid scaffold prepared via in situ crystallization of hydroxyapatite in chitosan matrix	Nan, Kaihui; Yin, Shiheng; et al.	Chemistry; Materials Science		research, biocompatibility, biomedical apps, bone regeneration/repair)	
444	2010	Li4Ti5O12/reduced graphite oxide nano-hybrid material for high rate lithium-ion batteries	Kim, Hyun-Kyung; Bak, Seong-Min; Kim, Kwang-Bum	Electrochemistry	Li4Ti5O12, graphite oxide	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CMNH
445	2010	Effect Aging Conditions on the Repair Bond Strength of a Microhybrid and a Nanohybrid Resin Composite	Ozcan, Mutlu; Cura, Cenk; Brendeke, Johannes	Dentistry, Oral Surgery & Medicine	N/A	N/A	N/A
446	2010	Inorganic-polymer nanohybrid carrier for delivery of a poorly-soluble drug, ursodeoxycholic acid	Choi, Goeun; Lee, Ji-Hee; Oh, Yeon-Ji; et al.	Pharmacology & Pharmacy	ursodeoxycholic acid (pooorly-soluble drug), Mg-Al LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
447	2011	Electrochemical detection of extracellular hydrogen peroxide released from RAW 264.7 murine macrophage cells based on horseradish peroxidase-hydroxyapatite nanohybrids	Li, Chunyun; Zhang, Hui; Wu, Ping; et al.	Chemistry	horseradish peroxidase, hydroxyapatite	Sensors/biosensors/electrochemical sensors	OMCNH
448	2011	TiO2-decorated graphene nanohybrids for fabricating an amperometric acetylcholinesterase biosensor	Wang, Kun; Li, He-Nan; Wu, Jun; et al.	Chemistry	Graphene, TiO2	Sensors/biosensors/electrochemical sensors	CMNH
449	2011	Nanohybridization of Polyoxometalate Clusters and Single-Wall Carbon Nanotubes: Applications in Molecular Cluster Batteries	Kawasaki, Naoya; Wang, Heng; Nakanishi, Ryo; et al.	Chemistry	SWNT, polyoxometalate	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
450	2011	Catalytic Oxidation of Silanes by Carbon Nanotube-Gold Nanohybrids	John, Jubi; Gravel, Edmond; Hagege, Agnes; et al.	Chemistry	MWNT, Au	Catalytic/Photocatalytic/Electrocatalytic applications	CMNH
451	2011	Conjugation of Porphyrin to Nanohybrid Cerasomes for Photodynamic Diagnosis and Therapy of Cancer	Liang, Xiaolong; Li, Xiaoda; Yue, Xiuli; et al.	Chemistry	Porphyrin, Cerasomes	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
452	2011	Platinum Nanoparticles Encapsulated by Aminopeptidase: A Multifunctional Bioinorganic Nanohybrid Catalyst	San, Boi Hoa; Kim, Sungsu; Moh, Sang Hyun; et al.	Chemistry	Pt, aminopeptidase	Catalytic/Photocatalytic/Electrocatalytic applications	OMCNH
453	2011	Photoresponsive liposomal nanohybrid cerasomes	Liang, Xiaolong; Yue, Xiuli; Dai, Zhifei; et al.	Chemistry	Indium tin oxide, Ag	Optical imaging and applications	MMNH
454	2011	Nanohybridization of ferrocene clusters and reduced graphene oxides with enhanced lithium storage capability	Zhu, Jixin; Sun, Kuo; Sim, Daohao; et al.	Chemistry	Graphene oxide, ferrocene	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CMNH
455	2011	One-Step and Self-Assembly Based Fabrication of Pt/TiO2 Nanohybrid Photocatalysts with Programmed Nanopatterns	Jang, Yu Jin; Kim, Dong Ha	Chemistry	Pt, TiO2	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
456	2011	Nanohybrid Materials as Transducer Surfaces for Electrochemical Sensing Applications	Pereira da Silva Neves, Marta Maria; Gonzalez Garcia, Maria Begona;	Chemistry; Electrochemistry	N/A	N/A	N/A

			Delerue-Matos, Cristina; et al.				
457	2011	Visible-light active nanohybrid TiO2/carbon photocatalysts with programmed morphology by direct carbonization of block copolymer templates	Kochuveedu, Saji Thomas; Jang, Yu Jin; Jang, Yoon Hee; et al.	Chemistry	Carbon nanodots, TiO2	Catalytic/Photocatalytic/Electrocatalytic applications	CMNH
458	2011	TiO2 micro-nano-hybrid surface to alleviate biological aging of UV-photofunctionalized titanium	Iwasa, Fuminori; Tsukimura, Naoki; Sugita, Yoshihiko; et al.	Science & Technology - Other Topics; Pharmacology & Pharmacy	N/A	N/A	N/A
459	2011	Development of antiproliferative nanohybrid compound with controlled release property using ellagic acid as the active agent	Hussein, Mohd Zobir; Al Ali, Samer Hasan; Zainal, Zulkarnain; et al.	Science & Technology - Other Topics; Pharmacology & Pharmacy	ellagic acid, Zn layered hydroxide	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
460	2011	Preparation of hippurate-zinc layered hydroxide nanohybrid and its synergistic effect with tamoxifen on HepG2 cell lines	Al Ali, Samer Hasan Hussein; Al-Qubaisi, Mothanna; Hussein, Mohd Zobir; et al.	Science & Technology - Other Topics; Pharmacology & Pharmacy	hippurate, Zn layered hydroxide	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
461	2011	30-Month randomised clinical trial to evaluate the clinical performance of a nanofill and a nanohybrid composite	Maciel de Andrade, Ana Karina; Duarte, Rosangela Marques; Sales Cunha Medeiros e Silva, Fabia Danielle; et al.	Dentistry, Oral Surgery & Medicine	N/A	N/A	N/A
462	2011	Four-year clinical evaluation of Class II nano-hybrid resin composite restorations bonded with a one-step self-etch and a two-step etch-and-rinse adhesive	van Dijken, Jan W. V.; Pallesen, Ulla	Dentistry, Oral Surgery & Medicine	N/A	N/A	N/A
463	2011	Optical, photophysical and magnetic behavior of GMP-templated binary (beta-Fe2O3/CdS) and ternary (beta-Fe2O3/Ag/CdS) nanohybrids	Kumar, Anil; Singhal, Aditi	Chemistry; Materials Science	beta-Fe2O3/CdS, beta-Fe2O3/Ag/CdS	Optical imaging and applications	MMNH
464	2011	Self-assembled Fe3O4-layered double hydroxide colloidal nanohybrids with excellent performance for treatment of organic dyes in water	Chen, Chunping; Gunawan, Poernomo; Xu, Rong	Chemistry; Materials Science	Fe3O4, Mg-Al LDH	Optical imaging and applications	MMNH
465	2011	Silica nanohybrids integrated with CuInS2/ZnS quantum dots and magnetite nanocrystals: multifunctional agents for dual-modality imaging and drug delivery	Hsu, Jen-Chieh; Huang, Chih-Ching; Ou, Keng-Liang; et al.	Chemistry; Materials Science	SiO2 nanohybrids are composed of CuInS2/ZnS quantum dots and magnetite nanocrystals	Delivery Carriers, and Controlled Release of Drugs/Compounds	MMNH
466	2011	UV Screening of Ferulic Acid-Zinc Basic Salt Nanohybrid with Controlled Release Rate	Biswick, Timothy; Park, Dae-Hwan; Shul, Yong-Gun; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Ferulic acid, Zn basic salt	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
467	2011	Nanohybrid Versus Nanofill Composite in Class I Cavities: Margin Analysis After 12 Months	Maciel de Andrade, Ana Karina; Duarte, Rosangela Marques;	Anatomy & Morphology; Life Sciences & Biomedicine - Other Topics; Microscopy	N/A	N/A	N/A

			Guedes Lima, Severino Jackson; et al.				
468	2011	Making silica nanoparticle-covered graphene oxide nanohybrids as general building blocks for large-area superhydrophilic coatings	Kou, Liang; Gao, Chao	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Silica, graphene oxide	Synthesis of new nanohybrids/materials	MMNH
469	2011	A facile synthetic route for the preparation of gold nanostars with magnetic cores and their reusable nanohybrid catalytic properties	Miao, Xiumin; Wang, Tingting; Chai, Fang; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Au nanostars, Fe3)4	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
470	2011	Polyethylenimine-carbon nanotube nanohybrids for siRNA-mediated gene silencing at cellular level	Foillard, Stephanie; Zuber, Guy; Doris, Eric	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Polyethylenimine, carbon nanotube?	Sensors/biosensors/electrochemical sensors	OMCNH
471	2011	A general procedure to synthesize highly crystalline metal oxide and mixed oxide nanocrystals in aqueous medium and photocatalytic activity of metal/oxide nanohybrids	Thanh-Dinh Nguyen; Cao-Thang Dinh; Trong-On Do	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	In2O3, Y2O3, ZrO2, TiO2, CeO2, tungstate, vanadate, molybdate, Ag, Au	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
472	2011	Experimental investigation of the thermal transport properties of a carbon nanohybrid dispersed nanofluid	Baby, Tessy Theres; Ramaprabhu, Sundara	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Graphene, MWNT	Semiconductors/superconductors/conductive materials	CCNH
473	2011	Synthesis of multi-walled carbon nanotube/polyhedral oligomeric silsesquioxane nanohybrid by utilizing click chemistry	Yadav, Santosh Kumar; Mahapatra, Sibdas Singha; Yoo, Hye Jin; et al.	Science & Technology - Other Topics; Materials Science; Physics	MWNT, polyhedral oligomeric silsesquioxane	Synthesis of new nanohybrids/materials	OMCNH
474	2011	Operator Variability Using Different Polishing Methods and Surface Geometry of a Nanohybrid Composite	Zimmerli, B.; Lussi, A.; Flury, S.	Dentistry, Oral Surgery & Medicine	N/A	N/A	N/A
475	2011	Rayleigh scattering study and particle density determination of a high refractive index TiO2 nanohybrid polymer	Elim, Hendry I.; Cai, Bin; Sugihara, Okihiro; et al.	Chemistry; Physics	TiO2, polymer	Transparent and conductive films	OMCNH
476	2011	Novel 1-D biophotonic nanohybrids: protein nanofibers meet quantum dots	Wei, Gang; Keller, Thomas F.; Zhang, Jiantao; et al.	Chemistry; Materials Science; Physics; Polymer Science	N-hydroxysulfosuccinimide modified CdSe-ZnS core-shell quantum dots, fibronectin nanofibers	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
477	2011	Preparation of ITO/Ag nanohybrid particles by a reverse micellar layer-by-layer coating	Fan, Jin-Wei; Tseng, Tzu-Tsung; Chen, Chun-Nan; et al.	Materials Science	Ag,ITO DNA	Synthesis of new nanohybrids/materials	MMNH
478	2011	The effect of nanohybrid materials on the pour-point and viscosity depressing of waxy crude oil	Wang Feng; Zhang DongMin; Ding YanFen; et al.	Materials Science	N/A	N/A	N/A
479	2011	Corrosion Resistance Nano-hybrid Sol-Gel Coating on Steel Sheet	Guin, Akshya Kumar; Nayak, Suryakanta; Rout, Tapan Kumar; et al.	Metallurgy & Metallurgical Engineering	N/A	N/A	N/A
480	2011	Electrochemical Synthesis of M:DNA Nanohybrids	Jayaraman, Shrisudersan; Tang, Wei; Yongsunthon, Ruchirej	Electrochemistry; Materials Science	N/A	N/A	N/A

481	2011	A general strategy to prepare graphene-metal/metal oxide nanohybrids	Ji, Junyi; Zhang, Guanghui; Chen, Hongyu; et al.	Chemistry; Materials Science	poly(3,4-ethylene dioxythiophene), TiO2	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CMNH
482	2011	Crystal engineering and SERS properties of Ag-Fe3O4 nanohybrids: from heterodimer to core-shell nanostructures	Huang, Jianmei; Sun, Yanhui; Huang, Shoushuang; et al.	Chemistry; Materials Science	Ag, Fe3O4	Sensors/biosensors/electrochemical sensors	MMNH
483	2011	Facile route to prepare film of poly(3,4-ethylene dioxythiophene)-TiO2 nanohybrid for solar cell application	Dehaudt, J.; Beouch, L.; Peralta, S.; et al.	Materials Science; Physics	poly(3,4-ethylenedioxythiophene), TiO2	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
484	2011	High dielectric permittivity and low percolation threshold in polymer composites based on SiC-carbon nanotubes micro/nano hybrid	Yuan, Jin-Kai; Li, Wei-Long; Yao, Sheng-Hong; et al.	Physics	N/A	N/A	N/A
485	2011	High performance n-type organic-inorganic nanohybrid semiconductors for flexible electronic devices	Park, Yerok; Han, Kyu S.; Lee, Byoung H.; et al.	Materials Science; Physics	N/A	N/A	N/A
486	2011	Study on the Structural and Photocatalytic Properties for Pore Size Tailored SnO2-Pillared Layered Titanate Nanohybrids	Ko, Ji Eun; Kim, In Young; Hwang, Seong-Ju; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	mesoporous SnO2-pillared layered titanate	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
487	2011	In Vitro Biocompatibility of PLGA-HA Nano-Hybrid Scaffold	Seo, Na Mi; Ko, Jae Hoon; Park, Young Hwan; et al.	Cell Biology; Engineering	N/A	N/A	N/A
488	2011	Zinc-stearate-layered hydroxide nanohybrid material as a precursor to produce carbon nanoparticles	Ghotbi, Mohammad Yeganeh; Bagheri, Narjes; Sadrnezhaad, S. K.	Chemistry; Materials Science; Metallurgy & Metallurgical Engineering	Zinc-stearate-layered hydroxide	Synthesis of new nanohybrids/materials	OMCNH
489	2011	Fe-phthalocyanine oligomer/Fe3O4 nano-hybrid particles and their effect on the properties of polyarylene ether nitriles magnetic nanocomposites	Meng, Fanbin; Zhao, Rui; Xu, Mingzhen; et al.	Chemistry	Fe phthalocyanine oligomer/Fe3O4	Synthesis of new nanohybrids/materials	OMCNH
490	2011	Nano-hybrid shish-kebab: Isotactic polypropylene epitaxial growth on electrospun polyamide 66 nanofibers via isothermal crystallization	Liang, Yanyan; Zheng, Guoqiang; Han, Wenjuan; et al.	Materials Science; Physics	Polyamide 66, isotactic polypropylene	Crystallography and polymer crystallization	OMCNH
491	2011	Giant Rabi splitting in metal/semiconductor nanohybrids	Bellessa, Joel; Symonds, Clementine; Vynck, Kevin; et al.	Physics	N/A	N/A	N/A
492	2011	Microleakage of repaired class V silorane and nano-hybrid composite restorations after preparation with erbium:yttrium-aluminum-garnet laser and diamond bur	Yaman, Batu Can; Efes, Begum Guray; Dorter, Can; et al.	Engineering; Surgery	N/A	N/A	N/A
493	2011	Photophysics and photoelectrochemical properties of nanohybrids consisting of fullerene-encapsulated single-walled carbon nanotubes and poly(3-	Tezuka, Noriyasu; Umeyama, Tomokazu; Matano,	Chemistry; Energy & Fuels; Engineering; Environmental Sciences & Ecology	single-walled carbon nanotubes (SWNTs) encapsulating C-60 or C-70 with poly(3-hexylthiophene) (P3HT)	Semiconductors/superconductors/conductive materials	CCNH

		hexylthiophene)	Yoshihiro; et al.				
494	2011	Kinetically Controlled Cellular Interactions of Polymer-Polymer and Polymer-Liposome Nanohybrid Systems	Sunoqrot, Suhair; Bae, Jin Woo; Jin, Su-Eon; et al.	Biochemistry & Molecular Biology; Chemistry	N/A	N/A	N/A
495	2011	Effects of External Electric Field on Film Growth, Morphology, and Nanostructure of Polyelectrolyte and Nanohybrid Multilayers onto Insulating Substrates	Zhang, Guojun; Dai, Limin; Zhang, Lei; et al.	Chemistry; Materials Science	Poly(sodium styrene sulfonate), poly(diallyldimethyl ammonium chloride), ZrO2	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
496	2011	Porous zirconium complex-layered titanate nanohybrids with gas adsorption and photocatalytic activity	Kim, In Young; Lee, Kang Yoon; Kim, Tae Woo; et al.	Materials Science; Physics	Zr, titanate	Adsorption studies	MMNH
497	2011	Monomer elution from nanohybrid and ormocer-based composites cured with different light sources	Manojlovic, Dragica; Radisic, Marina; Vasiljevic, Tatjana; et al.	Dentistry, Oral Surgery & Medicine; Materials Science	N/A	N/A	N/A
498	2011	Thermomechanical and Surface Properties of Novel Poly(ether urethane)/Polyhedral Oligomeric Silsesquioxane Nanohybrid Elastomers	Tan, Juanjuan; Jia, Zhiyuan; Sheng, Dekun; et al.	Engineering; Polymer Science	Poly(ether urethane)/Polyhedral Oligomeric Silsesquioxane	Synthesis of new nanohybrids/materials	OMCNH
499	2011	Micro-nano hybrid structures with manipulated wettability using a two-step silicon etching on a large area	Kim, Beom Seok; Shin, Sangwoo; Shin, Seung Jae; et al.	Science & Technology - Other Topics; Materials Science; Physics	N/A	N/A	N/A
500	2011	Synthesis and characterization of a lamellar hydroxyapatite/DNA nanohybrid	Zuo, Guifu; Wan, Yizao; Meng, Xianguang; et al.	Materials Science	lamellar hydroxyapatite, DNA	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
501	2011	In situ synthesis of palladium nanoparticle-graphene nanohybrids and their application in nonenzymatic glucose biosensors	Lu, Li-Min; Li, Hong-Bo; Qu, Fengli; et al.	Biophysics; Biotechnology & Applied Microbiology; Chemistry; Electrochemistry; Science & Technology - Other Topics	Graphene, Pd	Sensors/biosensors/electrochemical sensors	CMNH
502	2011	Novel electrocatalytic system for the oxidation of methyl jasmonate based on layer-by-layer assembling of montmorillonite and phosphotungstic acid nanohybrid on graphite electrode	Gan, Tian; Hu, Chengguo; Chen, Zilin; et al.	Electrochemistry	Montmorillonite, phosphotungstic acid	Catalytic/Photocatalytic/Electrocatalytic applications	OMCNH
503	2011	Nanohybrid vs. fine hybrid composite in extended Class II cavities after six years	Kraemer, Norbert; Garcia-Godoy, Franklin; Reinelt, Christian; et al.	Dentistry, Oral Surgery & Medicine; Materials Science	Ag, coumarin, rhodamine	Sensors/biosensors/electrochemical sensors	MMNH
504	2011	Organic-Inorganic Nanohybrids as Novel Thermoelectric Materials: Hybrids of Polyaniline and Bismuth(III) Telluride Nanoparticles	Toshima, Naoki; Imai, Masahiro; Ichikawa, Shoko	Electrochemistry; Materials Science; Physics	polyaniline, polypyrrole, and polyphenylenevinylene, bismuth (III) telluride	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
505	2011	Glucose biosensor based on nanohybrid material of gold nanoparticles and glucose oxidase on a bioplatform	Zhang, Yan; Jia, Wenjuan; Cui, Miao; et al.	Biochemistry & Molecular Biology; Biotechnology & Applied Microbiology	Titania, Hyperbranched polyglycidol	Catalytic/Photocatalytic/Electrocatalytic applications	OMCNH
506	2011	Facile synthesis of	Li, Haiqing;	Chemistry; Science	N/A	N/A	N/A

		titania/hyperbranched polyglycidol nanohybrids with controllable morphologies: from solid spheres, capsules to tubes	Zhang, Lin; Jo, Jung Kyu; et al.	& Technology - Other Topics; Materials Science			
507	2011	Plasmonic Nanohybrid with Ultrasmall Ag Nanoparticies and Fluorescent Dyes	Raino, Gabriele; Stoeferle, Thilo; Park, Chanhee; et al.	Chemistry; Science & Technology - Other Topics; Materials Science	silver nanocrystals in a block copolymer micelle	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
508	2011	Fabrication and Interfacial Electronic Structure Studies on Polypyrrole/TiO(2) Nano Hybrid Systems for Photovoltaic Aspects	Kumar, Ganesan Mohan; Kawakita, Jin; Jayavel, Ramasamy	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Polypyrrole, TiO2	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
509	2011	Special susceptive aqueous ammonia chemi-sensor: Extended applications of novel UV-curable polyurethane-clay nanohybrid	Khan, Sher Bahadar; Rahman, Mohammed M.; Jang, Eui Soung; et al.	Chemistry	N/A	N/A	N/A
510	2011	Carboxymethyl tamarind gum-silica nanohybrids for effective immobilization of amylase	Singh, Vandana; Kumar, Pramendra	Biochemistry & Molecular Biology; Chemistry	Carboxymethyl tamarind gum, tetramethoxysilane	Biomaterials	OMCNH
511	2011	Indigo-sepiolite nanohybrids: Temperature-dependent synthesis of two complexes and comparison with indigo-palygorskite systems	Ovarlez, Sonia; Giulieri, Francoise; Delamare, Francois; et al.	Chemistry; Science & Technology - Other Topics; Materials Science	Indigo, sepiolite	Synthesis of new nanohybrids/materials	OMCNH
512	2011	Physical properties of current dental nanohybrid and nanofill light-cured resin composites	Sideridou, Irini D.; Karabela, Maria M.; Vouvoudi, Evangelia Ch.	Dentistry, Oral Surgery & Medicine; Materials Science	N/A	N/A	N/A
513	2011	Preparation and nonlinear optical response of novel palladium-containing micellar nanohybrids	Iliopoulos, Konstantinos; Chatzikyriakos, George; Demetriou, Maria; et al.	Materials Science; Optical	Pd, poly(lauryl methacrylate)-block-poly(2-(aceto-acetoxy)ethyl methacrylate)	Optical imaging and applications	OMCNH
514	2011	Application of thermal analysis for the characterisation of intercalated and grafted organo-kaolinite nanohybrid materials	Letaief, Sadok; Detellier, Christian	Chemistry	dimethyl sulfoxide, kaolinite	Synthesis of new nanohybrids/materials	OMCNH
515	2011	Enhanced Fibroblasts Functions in a New Family of Hierarchically Organized Nanohybrid Elastomers	Shah, Jinesh; Girase, Bhupendra; Misra, R. Devesh K.	Materials Science	titania with a bi-functional agent, acrylic acid	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
516	2011	Nanohybridization of Silica-Coated Au Nanorods and Silica Nanoballs	Yi, Dong Kee	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Silica, Au	Synthesis of new nanohybrids/materials	MMNH
517	2011	In situ Formation of TiO2 in Electrospun Poly(methyl methacrylate) Nanohybrids	Zhang, Junhua; Maurer, Frans H. J.; Yang, Mingshu	Chemistry; Science & Technology - Other Topics; Materials Science	TiO2, poly(methyl methacrylate)	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
518	2011	Tunable Electronic and Magnetic Properties in BxNyCz Nanohybrids: Effect of Domain Segregation	Manna, Arun K.; Pati, Swapan K.	Chemistry; Science & Technology - Other Topics; Materials Science	Boron, Nitride, Carbon	Synthesis of new nanohybrids/materials	MMNH
519	2011	Electrochemical measurement of the flux of hydrogen peroxide releasing	Wu, Ping; Cai, Zhewei; Chen,	Biophysics; Biotechnology &	enzyme-attapulgite clay	Sensors/biosensors/electrochemical sensors	OMCNH

		from RAW 264.7 macrophage cells based on enzyme-attapulgite clay nanohybrids	Jing; et al.	Applied Microbiology; Chemistry; Electrochemistry; Science & Technology - Other Topics			
520	2011	Protein-Promoted Synthesis of Pt Nanoparticles on Carbon Nanotubes for Electrocatalytic Nanohybrids with Enhanced Glucose Sensing	Wei, Gang; Xu, Fugang; Li, Zhuang; et al.	Chemistry; Science & Technology - Other Topics; Materials Science	Carbon nanotube, Pt	Catalytic/Photocatalytic/Electrocatalytic applications	CMNH
521	2011	Novel Nanohybrids of Silver Particles on Clay Platelets for Inhibiting Silver-Resistant Bacteria	Su, Hong-Lin; Lin, Siou-Hong; Wei, Jiun-Chiou; et al.	Life Sciences & Biomedicine - Other Topics	Ag, silica	Antimicrobial/antibacterial applications	MMNH
522	2011	Preparation and Toroid Formation of Multiblock Polystyrene/C-60 Nanohybrids	Peng, Kang-Jen; Liu, Ying-Ling	Polymer Science	Fullerene, polystyrene	Synthesis of new nanohybrids/materials	OMCNH
523	2011	Tailoring of physical properties in highly filled experimental nanohybrid resin composites	Pick, Barbara; Pelka, Matthias; Belli, Renan; et al.	Dentistry, Oral Surgery & Medicine; Materials Science	N/A	N/A	N/A
524	2011	Synergistic effects of UV photofunctionalization and micro-nano hybrid topography on the biological properties of titanium	Tsukimura, Naoki; Yamada, Masahiro; Iwasa, Fuminori; et al.	Engineering; Materials Science	N/A	N/A	N/A
525	2011	Study on the Release Behavior and Mechanism by Monitoring the Morphology Changes of the Large-Sized Drug-LDH Nanohybrids	Huang, Wei; Zhang, Hui; Pan, Dengke	Engineering	Ibuprofen, Mg-Al LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
526	2011	Transmission Electron Microscopy as a Tool to Image Bioinorganic Nanohybrids: The Case of Phage-Gold Nanocomposites	Cao, Binrui; Xu, Hong; Mao, Chuanbin	Anatomy & Morphology; Life Sciences & Biomedicine - Other Topics; Microscopy	N/A	N/A	N/A
527	2011	Silica Nanohybrid Membranes with High CO2 Affinity for Green Hydrogen Purification	Lau, Cher Hon; Liu, Songlin; Paul, Donald R.; et al.	Chemistry; Energy & Fuels; Materials Science; Physics	N/A	N/A	N/A
528	2011	Synthesis and luminescence properties of cinnamide based nanohybrid materials containing Eu (II) ions	Kumar, A. B. V. Kiran; Jayasimhadri, M.; Cha, Hyeongrae; et al.	Crystallography; Materials Science; Physics	N-(3-(triethoxysilyl)propyl)cinnamide, Eu(II)	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
529	2011	Multifunctional Polydiacetylene-Graphene Nanohybrids for Biosensor Application	Yun, Ji Sun; Yang, Kwang Suk; Kim, Do Hyun	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Polydiacetylene-Graphene	Sensors/biosensors/electrochemical sensors	OMCNH
530	2011	Highly conducting gold nanoparticles-graphene nanohybrid films for ultrasensitive detection of carcinoembryonic antigen	Han, Jing; Zhuo, Ying; Chai, Ya-Qin; et al.	Chemistry	Au, graphene	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	CMNH
531	2011	Polyethylene/carbon nanotube nano hybrid shish-kebab obtained by solvent evaporation and thin-film crystallization	Li, Lingyu; Wang, Wenda; Laird, Eric D.; et al.	Polymer Science	SWNT, polyethylene	Crystallography and polymer crystallization	OMCNH
532	2011	Effect of TiO2 Formation on the Free Volume Properties of Electrospun PMMA Nanohybrids	Zhang, Junhua; Yang, Mingshu; Maurer, Frans	Polymer Science	Poly(methyl methacrylate), TiO2	Crystallography and polymer crystallization	OMCNH

			H. J.				
533	2011	Electrochemical sensors for hemoglobin and myoglobin detection based on methylene blue-multiwalled carbon nanotubes nanohybrid-modified glassy carbon electrode	Pakapongpan, Saithip; Palangsuntikul, Rungtiva; Surareungchai, Werasak	Electrochemistry	MWNT, methylene blue	Sensors/biosensors/electrochemical sensors	OMCNH
534	2011	Nano-Hybrid Surface Coatings on Uncoated Papers from Softwood Fibers and Woodfree Fibers and Printability	Cengiz, Candan	Chemistry	N/A	N/A	N/A
535	2011	Mn-doped ZnS quantum dots/methyl violet nanohybrids for room temperature phosphorescence sensing of DNA	He Yu; Yan XiuPing	Chemistry	ZnS quantum dots/methyl violet, Mn	Sensors/biosensors/electrochemical sensors	MMNH
536	2011	"Nanohybrids" Based on pH-Responsive Hydrogels and Inorganic Nanoparticles for Drug Delivery and Sensor Applications	Riedinger, Andreas; Leal, Manuel Pernia; Deka, Smriti R.; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	CdS Quantum Dot-Polyoxotungstate	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
537	2011	Enhancement of Interfacial Polymer Crystallinity Using Chromism in Single Inorganic Nanowire-Polymer Nanohybrids for Photovoltaic Applications	Rodd, Christopher M.; Agarwal, Ritesh	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	poly(3-hexIthiophene-2,5-diyl), CdS	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
538	2011	Synthesis of Dichlorprop-Zn/Al-hydrotalcite Nanohybrid and its Controlled Release Property	Hussein, Mohd Zobir; Hashim, Norhayati; Yahaya, Asmah Hj; et al.	Science & Technology - Other Topics	dichlorprop[2(2,4-dichlorophenoxy)propionate], -Zn-Al LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
539	2011	Self-Assembly of Nanosized 0D Clusters: CdS Quantum Dot-Polyoxotungstate Nanohybrids with Strongly Coupled Electronic Structures and Visible-Light-Active Photofunctions	Kim, Hyo Na; Kim, Tae Woo; Choi, Kyong-Hoon; et al.	Chemistry	CdS Quantum Dot-Polyoxotungstate Nanohybrid	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
540	2011	Synthesis and Characterization of PU-Si Nanohybrid: Influence of Silica on Properties of UV-curable Polyurethane Acrylate	Jang, Eui Sung; Khan, Sher Bahadar; Choi, Joonsuk; et al.	Chemistry	polyurethane acrylate-silica	Synthesis of new nanohybrids/materials	OMCNH
541	2011	Effects of Si-O-Si Agglomerations on CO2 Transport and Separation Properties of Sol-Derived Nanohybrid Membranes	Lau, Cher Hon; Chung, Tai-Shung	Polymer Science	N/A	N/A	N/A
542	2011	Single-Walled Carbon Nanotube/Pyrenecyclodextrin Nanohybrids for Ultrahighly Sensitive and Selective Detection of p-Nitrophenol	Wei, Yan; Kong, Ling-Tao; Yang, Ran; et al.	Chemistry; Materials Science	SWNT, Pyrenecyclodextrin	Sensors/biosensors/electrochemical sensors	OMCNH
543	2011	Excitonic Resonance in Semiconductor-Metal Nanohybrids	Climente, Juan I.; Movilla, Jose L.; Goldoni, Guido; et al.	Chemistry; Science & Technology - Other Topics; Materials Science	CdS	Semiconductors/superconductors/conductive materials	MMNH
544	2011	Novel nanohybrid materials based on L-leucine on hydrotalcite clays: Asymmetric epoxidation reaction of chalcona	Miranda, Ronald-Alexander; Llorca, Jordi; Finocchio, Elisabetta; et al.	Chemistry; Engineering	L-leucine on hydrotalcite clays	Catalytic/Photocatalytic/Electrocatalytic applications	OMCNH
545	2011	A Novel Preparation of High-Refractive-Index and Highly Transparent Polymer Nanohybrid	Cai, Bin; Sugihara, Okihiro; Elim,	Physics	N/A	N/A	N/A

		Composites	Hendry I.; et al.				
546	2011	Phase Transfer Mediated Self-Assembly of CdTe-Polymer Nanohybrids for Uniform Fluorescent Films	Shen, Fu-Chun; Yang, Jian; Wang, Cai-Feng; et al.	Polymer Science	poly(methylmethacrylate-co-dimethyl diallyl ammonium chloride), CdTe	Optical imaging and applications	OMCNH
547	2011	Formation and photoinduced properties of zinc porphyrin-SWCNT and zinc phthalocyanine-SWCNT nanohybrids using diameter sorted nanotubes assembled via metal-ligand coordination and pi-pi stacking	Das, Sushanta K.; Subbaiyan, Navaneetha K.; D'Souza, Francis; et al.	Chemistry	Zn, porphyrin, SWCNT	Synthesis of new nanohybrids/materials	CMNH
548	2011	Molecular Aggregation State and Electrical Properties of Terthiophenes/Imogolite Nanohybrids	Yah, Weng On; Irie, Atsushi; Jiravanichanun, Nattha; et al.	Chemistry	terthiophenes and imogolite	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
549	2011	Mesoporous Layer-by-Layer Ordered Nanohybrids of Layered Double Hydroxide and Layered Metal Oxide: Highly Active Visible Light Photocatalysts with Improved Chemical Stability	Gunjakar, Jayavant L.; Kim, Tae Woo; Kim, Hyo Na; et al.	Chemistry	Zn-Cr LDH, TiO2	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
550	2011	Nanohybrids investigation by waveguide SNOM illumination mode	El-Kork, Nayla; Moretti, Paul; Jacquier, Bernard	Optical	N/A	N/A	N/A
551	2011	Synthesis and morphology of new functional polyimide/titania nano hybrid materials	Seyedjamali, Hojjat; Pirisedigh, Azadeh	Materials Science	Polyimide, TiO2	Synthesis of new nanohybrids/materials	OMCNH
552	2011	Large pore volume mesoporous copper particles and scaffold microporous carbon material obtained from an inorganic-organic nanohybrid material, copper-succinate-layered hydroxide	Ghotbi, Mohammad Yeganeh; Bagheri, Narjes; Sadrnezhaad, S. K.	Chemistry	Copper-succinate layered hydroxide,	Semiconductors/superconductors/conductive materials	OMCNH
553	2011	Preparation of hollow platinum nanospheres/carbon nanotubes nanohybrids and their improved stability for electro-oxidation of methanol	Kuang, Y. J.; Wu, B. H.; Cui, Y.; et al.	Electrochemistry	Carbon nanotube, Pt	Catalytic/Photocatalytic/Electrocatalytic applications	CMNH
554	2011	Effects of surface conditioning on repair bond strengths of non-aged and aged microhybrid, nanohybrid, and nanofilled composite resins	Rinastiti, Margareta; Oezcan, Mutlu; Siswomihardjo, Widowati; et al.	Dentistry, Oral Surgery & Medicine	N/A	N/A	N/A
555	2011	A Nano-hybrid Silver Colloidal Suspension Preparation	Zhao, Jian; Xie, Xuan; Zhou, Xiaodong	Polymer Science	tri-block copolymer polystyrene-b-poly(acrylic acid)-b-poly(gamma-methacryloxypropyltrimethoxysilane), Ag	Catalytic/Photocatalytic/Electrocatalytic applications	OMCNH
556	2011	Facile synthesis and characterization of carbon nanotubes/silver nanohybrids coated with polyaniline	Van Hoa Nguyen; Shim, Jae-Jin	Materials Science; Physics; Polymer Science	MWNT, Ag	Synthesis of new nanohybrids/materials	CMNH
557	2011	Facile fabrication of flexible magnetic nanohybrid membrane with amphiphobic surface based on bacterial cellulose	Zhang, Wen; Chen, Shiyan; Hu, Weili; et al.	Chemistry; Polymer Science	N/A	N/A	N/A
558	2011	Synthesis and characterization of heterostructured nanohybrid of MgO-TiO2-Al2O3/montmorillonite	Dou, Binlin; Chen, Haisheng;	Materials Science	MgO-TiO2-Al2O3/montmorillonite	Synthesis of new nanohybrids/materials	MMNH

			Song, Yongchen; et al.				
559	2011	Efficient Charge Separation in Multidimensional Nanohybrids	Peng, Xiaohui; Misewich, James A.; Wong, Stanislaus S.; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	DWNT, CdSe QDs	Fluorescence/luminescence/photoluminescence, light-energy harvesting	CMNH
560	2011	Superparamagnetic Plasmonic Nanohybrids: Shape-Controlled Synthesis, TEM-Induced Structure Evolution, and Efficient Sunlight-Driven Inactivation of Bacteria	Zhai, Yueming; Han, Lei; Wang, Ping; et al.	Chemistry; Science & Technology - Other Topics; Materials Science	Fe(3)O(4), Ag	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
561	2011	An Integrated Optimization Approach for Nanohybrid Circuit Cell Mapping	Xia, Yinshui; Chu, Zhufei; Hung, William N. N.; et al.	Engineering; Science & Technology - Other Topics; Materials Science; Physics	N/A	N/A	N/A
562	2011	Influence of Magnetic Field and Lighting during the Creation Process of Nanohybrid Semiconductor-Nematic Structures on Their Impedance and Photo Response	Ivashchyshyn, Fedir; Grygorchak, Ivan; Sudakova, Olena; et al.	Materials Science; Metallurgy & Metallurgical Engineering	N/A	N/A	N/A
563	2011	Nanoporous Graphene Oxide Thin Films from Nanohybrid Multilayers	Hong, Jinkee; Kang, Sang Wook	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	reduced graphene oxide, Au	Synthesis of new nanohybrids/materials	CMNH
564	2011	SiO2-Fe2O3-pillared Clay Nanohybrid with an Enhanced Gas Removal Property	Yang, Jae-Hun; Lee, Hee-Suk; Paek, Seung-Min; et al.	Chemistry	SiO2-Fe2O3, montmorillonite	Membrane research, gas removal, pollutant remediation	MMNH
565	2011	Preparation and properties of PVC/PMMA-g-imogolite nanohybrid via surface-initiated radical polymerization	Ma, Wei; Otsuka, Hideyuki; Takahara, Atsushi	Polymer Science	Poly(methyl methacrylate), imogolite clay	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
566	2011	Novel Nanohybrid Structured Regioregular Polyhexylthiophene Blend Films for Photoelectrochemical Energy Applications	Ram, Manoj K.; Gomez, Humberto; Alvi, Farah; et al.	Chemistry; Science & Technology - Other Topics; Materials Science	regioregular polyhexylthiophene, nanodiamond particles	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
567	2011	Chelating agent free-solid phase extraction (CAF-SPE) of Co(II), Cu(II) and Cd(II) by new nano hybrid material (ZrO2/B2O3)	Yalcinkaya, Ozcan; Kalfa, Orhan Murat; Turker, Ali Rehber	Engineering; Environmental Sciences & Ecology	ZrO2, B2O3, Co(II), Cu(II), Cd(II)	Sensors/biosensors/electrochemical sensors	MMNH
568	2011	Facile Preparation of PbTiO3 Nanodot Arrays: Combining Nanohybridization with Vapor Phase Reaction Sputtering	Kim, Jiyoon; Hong, Jongin; Park, Moonkyu; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	PbTiO3, PbO, TiO2	Synthesis of new nanohybrids/materials	MMNH
569	2011	Organo/layered double hydroxide nanohybrids used to remove non ionic pesticides	Chaara, D.; Bruna, F.; Ulibarri, M. A.; et al.	Engineering; Environmental Sciences & Ecology	Alachlor, metochlor, Mg-Al LDH	Adsorption studies	OMCNH
570	2011	Selective antileukemia effect of stabilized nanohybrid vesicles based on cholesteryl succinyl silane	Ma, Yan; Dai, Zhifei; Zha, Zhengbao; et al.	Engineering; Materials Science	cholesteryl succinyl silane	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
571	2011	Liposomal architecture boosts biocompatibility of nanohybrid cerasomes	Ma, Yan; Dai, Zhifei; Gao, Yanguang; et al.	Science & Technology - Other Topics; Toxicology	Cerasome, silica	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
572	2011	Silver-clay nanohybrid structure for	Girase, B.;	Materials Science	Ag, nanocor (clay),	Antimicrobial/antibacte	MMNH

		effective and diffusion-controlled antimicrobial activity	Depan, D.; Shah, J. S.; et al.			rial applications	
573	2011	Metal Nitride/Graphene Nanohybrids: General Synthesis and Multifunctional Titanium Nitride/Graphene Electrocatalyst	Wen, Zhenhai; Cui, Shumao; Pu, Haihui; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Graphene, titanium nitride	Catalytic/Photocatalytic/Electrocatalytic applications	CMNH
574	2011	Optical properties of thin nanohybrid films based on polyvinylcarbazole (PVK) and CdSe/ZnS quantum dots of core-shell type	Tugai, O. O.; Savvin, Yu. N.; Kryzhanovskaya, A. S.; et al.	Science & Technology - Other Topics; Physics	polyvinylcarbazole, CdSe ZnS QDs	Optical imaging and applications	MMNH
575	2011	Photosensitized Hydrogen Evolution from Water Using a Single-Walled Carbon Nanotube/Fullerodendron/SiO2 Coaxial Nanohybrid	Tajima, Tomoyuki; Sakata, Wakako; Wada, Takaaki; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	SWNT, fullerodendron, SiO2	Catalytic/Photocatalytic/Electrocatalytic applications	CMNH
576	2011	Thermally Stable, Dye-Bridged Nanohybrid-Based White Light-Emitting Diodes	Kwak, Seung-Yeon; Yang, SeungCheol; Kim, Na Ree; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	N/A	N/A	N/A
577	2012	Nonorganic semiconductor - Conductive polymer intercalate nanohybrids: Fabrication, properties, application	Ivashchyshyn, F.; Grygorchak, I.; Stakhira, P.; et al.	Materials Science; Physics	InSe, poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)	Semiconductors/superconductors/conductive materials	OMCNH
578	2012	Porous SnO2/layered titanate nanohybrid with enhanced electrochemical performance for reversible lithium storage	Kang, Joo-Hee; Paek, Seung-Min; Choy, Jin-Ho	Chemistry	SnO2, titanate	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	MMNH
579	2012	Engineering of a novel pluronic F127/graphene nanohybrid for pH responsive drug delivery	Hu, Haiqing; Yu, Jinhai; Li, Yongyong; et al.	Engineering; Materials Science	Graphene, pluronic F127	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
580	2012	Nanoparticle induced piezoelectric, super toughened, radiation resistant, multi-functional nanohybrids	Tiwari, Vimal K.; Shripathi, T.; Lalla, N. P.; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	poly(vinylidene fluoride-co-chlorotrifluoroethylene), silicate	Crystallography and polymer crystallization	OMCNH
581	2012	Improvement of optical properties and thermal stability of poly vinyl alcohol using salicylic acid confined in nanohybrid material	Saber, O.	Polymer Science	poly vinyl alcohol , Zn-Al LDH	Optical imaging and applications	OMCNH
582	2012	Synthesis of well-dispersed polyimide/TiO2 nanohybrid films using a pyridine-containing aromatic diamine	Seyedjamali, Hojjat; Pirisedigh, Azadeh	Polymer Science	polyimide, TiO2	Synthesis of new nanohybrids/materials	OMCNH
583	2012	Facile synthesis of Ag/GNS-g-PAA nanohybrids for antimicrobial applications	Tai, Zhixin; Ma, Haibin; Liu, Bin; et al.	Biophysics; Chemistry; Materials Science	Graphene, Ag	Antimicrobial/antibacterial applications	CMNH
584	2012	Photocatalytic oxidation of water by polymeric carbon nitride nanohybrids made of sustainable elements	Zhang, Jinshui; Grzelczak, Marek; Hou, Yidong; et al.	Chemistry	Co3O4, Polymeric Carbon Nitride	Catalytic/Photocatalytic/Electrocatalytic applications	OMCNH
585	2012	Thermodynamic interaction and mechanical characteristics of Nylon 6 and polyhedral oligomeric silsesquioxane nanohybrids	Lim, Sang-Kyun; Hong, Eun-Pyo; Song, Yu-Hyun; et al.	Materials Science	Nylon 6, polyhedral oligomeric silsesquioxane	Synthesis of new nanohybrids/materials	OMCNH
586	2012	Synthesis of a Layered Organic-Inorganic Nanohybrid of 4-Chlorophenoxyacetate-zinc-Layered Hydroxide with Sustained Release	Hussein, Mohd Zobir; Nazarudin, Nor Farhana	Science & Technology - Other Topics; Materials Science	Zn layered hydroxide, 4-chlorophenoxy acetate	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH

		Properties	Binti; Sarijo, Siti Halimah; et al.				
587	2012	Fabrication of dumbbell-like CdTe/Au nanohybrids	Ma, Hongchao; Bai, Xiangtao; Zheng, Liqiang	Materials Science; Physics	CdTe quantum dots, Au	Synthesis of new nanohybrids/materials	MMNH
588	2012	Novel mesoporous NiO/HTiNbO5 nanohybrids with high visible-light photocatalytic activity and good biocompatibility	Zhai, Zheng; Yang, Xiaoyan; Xu, Lin; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	NiO, HTiNbO5	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
589	2012	ZnO/Ag nanohybrid: synthesis, characterization, synergistic antibacterial activity and its mechanism	Ghosh, Somnath; Goudar, V. S.; Padmalekha, K. G.; et al.	Chemistry	ZnO, Ag	Antimicrobial/antibacterial applications	MMNH
590	2012	Physical properties of a molecular conductor (BEDT-TTF)(2)I-3 nanohybridized with silica nanoparticles by dry grinding	Funabiki, Akira; Sugiyama, Hiroki; Mochida, Tomoyuki; et al.	Chemistry	bis(ethylenedithio) tetrathiafulvalene, silica	Synthesis of new nanohybrids/materials	OMCNH
591	2012	Facile fabrication of PtNP/MWCNT nanohybrid films for flexible counter electrode in dye-sensitized solar cells	Chang, Ling-Yu; Lee, Chuan-Pei; Huang, Kuan-Chieh; et al.	Chemistry; Materials Science	MWNT, Pt	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CMNH
592	2012	Biocompatible Magnetite/Gold Nanohybrid Contrast Agents via Green Chemistry for MRI and CT Bioimaging	Narayanan, Sreeja; Sathy, Binulal N.; Mony, Ullas; et al.	Science & Technology - Other Topics; Materials Science	Fe3O4, Au	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	MMNH
593	2012	Photoinduced charge separation in three-layer supramolecular nanohybrids: fullerene-porphyrin-SWCNT	D'Souza, Francis; Das, Sushanta K.; Sandanayaka, Atula S. D.; et al.	Chemistry; Physics	Fullerene, porphyrin, SWCNT	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CCNH
594	2012	Design of a Polymer-Carbon Nanohybrid Junction by Interface Modeling for Efficient Printed Transistors	Kim, Do Hwan; Shin, Hyeon-Jin; Lee, Hyo Sug; et al.	Chemistry; Science & Technology - Other Topics; Materials Science	SWNT, polymer semiconductors	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
595	2012	Corrosion behavior of nanohybrid titania silica composite coating on phosphated steel sheet	Guin, A. K.; Nayak, S. K.; Rout, T. K.; et al.	Chemistry; Materials Science	Titania, silica	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	MMNH
596	2012	Indigo/sepiolite nanohybrids: stability of natural pigments inspired by Maya blue	Giulieri, Francoise; Ovarlez, Sonia; Chaze, Anne-Marie	Science & Technology - Other Topics; Materials Science	Indigo, palygorskite, sepiolite	Synthesis of new nanohybrids/materials	MMNH
597	2012	A general green strategy for fabricating metal nanoparticles/polyoxometalate/graphene tri-component nanohybrids: enhanced electrocatalytic properties	Liu, Rongji; Li, Shiwen; Yu, Xuelian; et al.	Chemistry; Materials Science	Graphene, polyoxometalate, Pt, Pd	Catalytic/Photocatalytic/Electrocatalytic applications	CMNH
598	2012	Remarkable fluorescence enhancement in YVO4:Eu3+@Ag nano-hybrids induced by interface effect	Xu, Wen; Bai, Xue; Xu, Sai; et al.	Chemistry	YVO4, Eu3, Ag	Fluorescence/luminescence/photoluminescence, light-energy harvesting	MMNH
599	2012	Plasmonic Molecular Nanohybrids-Spectral Dependence of Fluorescence Quenching	Olejnik, Maria; Bujak, Lukasz;	Chemistry	Au, organic dyes	Fluorescence/luminescence/photoluminescence, light-energy	OMCNH

			Mackowski, Sebastian			harvesting	
600	2012	Cell Mapping for Nanohybrid Circuit Architecture Using Genetic Algorithm	Chu, Zhu-Fei; Xia, Yin-Shui; Wang, Lun-Yao	Computer Science	N/A	N/A	N/A
601	2012	Synthesis and Study of Optical and Electrical Characteristics of Single-wall Carbon Nanotube/Gold Nanohybrid	Paul, Rima; Mitra, Apurba Krishna	Science & Technology - Other Topics; Materials Science; Physics	SWNT, Au	Optical imaging and applications	CMNH
602	2012	Intensification of electrochemiluminescence of luminol on TiO2 supported Au atomic cluster nano-hybrid modified electrode	Yu, Zhimin; Wei, Xiuhua; Yan, Jilin; et al.	Chemistry	TiO2, Au	Fluorescence/luminescence/photoluminescence, light-energy harvesting	MMNH
603	2012	Plasmonic Ag/AgBr nanohybrid: synergistic effect of SPR with photographic sensitivity for enhanced photocatalytic activity and stability	Wang, Zhichao; Liu, Jinghai; Chen, Wei	Chemistry	Plasmonic Ag, AgBr	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
604	2012	Zeolite-Y encapsulated nanohybrid materials: synthesis, spectroscopic characterization, and catalytic significance	Modi, C. K.; Trivedi, Parthiv M.	Chemistry	Zeolite-Y, Mn(II), Co(II), Ni(II), Cu(II), vanillin thiophene-2-carboxylic hydrazone, vanillin furoic-2-carboxylic hydrazone)	Catalytic/Photocatalytic/Electrocatalytic applications	OMCNH
605	2012	Polydiacetylene Single-Walled Carbon Nanotubes Nano-Hybrid for Cellular Imaging Applications	Yang, Kwang Suk; Yun, Ji Sun; Kim, Jin Chul; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	SWNT, Polydiacetylene	Optical imaging and applications	OMCNH
606	2012	Green and controlled synthesis of Cu2O-graphene hierarchical nanohybrids as high-performance anode materials for lithium-ion batteries via an ultrasound assisted approach	Zhang, Yu; Wang, Xiao; Zeng, Liang; et al.	Chemistry	Graphene, Cu2O	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CMNH
607	2012	A nanohybrid system for taste masking of sildenafil	Lee, Ji-Hee; Choi, Goeun; Oh, Yeon-Ji; et al.	Science & Technology - Other Topics; Pharmacology & Pharmacy	Montmorillonite, sildenafil	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
608	2012	Facile Low-Temperature Synthesis of Carbon Nanotube/TiO2 Nanohybrids with Enhanced Visible-Light-Driven Photocatalytic Activity	Xie, Yunlong; Qian, Huanhuan; Zhong, Yijun; et al.	Chemistry; Energy & Fuels; Optical; Physics	Carbon nanotube, TiO2	Fluorescence/luminescence/photoluminescence, light-energy harvesting	CMNH
609	2012	Fluorescent nanohybrids: quantum dots coupled to polymer recombinant protein conjugates for the recognition of biological hazards	Mansur, Herman Sander; Piscitelli Mansur, Alexandra Ancelmo	Chemistry; Materials Science	carboxylic functionalized poly(vinyl alcohol), semiconductors QDs	Sensors/biosensors/electrochemical sensors	OMCNH
610	2012	Well-defined hydroxyapatite-polycation nanohybrids via surface-initiated atom transfer radical polymerization for biomedical applications	Cai, Q.; Zhu, Y.; He, J. Q.; et al.	Chemistry; Materials Science	Hydroxyapatite, (2-dimethyl amino) ethyl methacrylate	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
611	2012	Free-standing liposomal nanohybrid cerasomes as ideal materials for sensing of cupric ions	Yue, Xiuli; Guo, Caixin; Jing, Yuanmiao; et al.	Chemistry	cerasomes with inorganic polyorganosiloxane	Sensors/biosensors/electrochemical sensors	OMCNH
612	2012	Thermoresponsive silver/polymer nanohybrids with switchable metal enhanced fluorescence	Liu, Jingquan; Li, Aihua; Tang, Jianguo; et al.	Chemistry	Ag, Poly(N-isopropylamide), polyacrylic acid	Sensors/biosensors/electrochemical sensors	OMCNH
613	2012	DNA-templated silver nanoclusters-graphene oxide nanohybrid materials: a platform for label-free and sensitive fluorescence turn-on detection of	Tao, Yu; Lin, Youhui; Huang, Zhenzhen; et	Chemistry	Graphene oxide, DNA, Ag	Sensors/biosensors/electrochemical sensors	CMNH

		multiple nucleic acid targets	al.				
614	2012	Efficacy and safety of nanohybrids comprising silver nanoparticles and silicate clay for controlling Salmonella infection	Chiao, Shu-Her; Lin, Siou-Hong; Shen, Ching-I; et al.	Science & Technology - Other Topics; Pharmacology & Pharmacy	Ag, silicate clay	Antimicrobial/antibacterial applications	MMNH
615	2012	A nanohybrid of graphene oxide-fluorescein derived silyl ether for photocurrent generation triggered by F- ions	Cheng, Lan-Ya; Zhou, Ji; Zou, Qi; et al.	Chemistry	Graphene oxide, fluorescein	Optical imaging and applications	CMNH
616	2012	Application of imogolite clay nanotubes in organic-inorganic nanohybrid materials	Ma, Wei; Yah, Weng On; Otsuka, Hideyuki; et al.	Chemistry; Materials Science	N/A	N/A	N/A
617	2012	Synthesis and characterisation of nanohybrids of olsalazine-intercalated Al-Mg layered double hydroxide	Nejati, Kamellia; Rezvani, Zolfaghar	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	olsalazine, Al-Mg LDH	Synthesis of new nanohybrids/materials	OMCNH
618	2012	Carbon-Dot-Based Dual-Emission Nanohybrid Produces a Ratiometric Fluorescent Sensor for In Vivo Imaging of Cellular Copper Ions	Zhu, Anwei; Qu, Qiang; Shao, Xiangling; et al.	Chemistry	CdSe/ZnS	Sensors/biosensors/electrochemical sensors	MMNH
619	2012	ZnO-Au nanohybrids by rapid microwave-assisted synthesis for CO oxidation	Kundu, Paromita; Singhania, Nisha; Madras, Giridhar; et al.	Chemistry	ZnO, Au	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
620	2012	Preparation and evaluation of well-defined hemocompatible layered double hydroxide-poly(sulfobetaine) nanohybrids	Hu, H.; Wang, X. B.; Xu, S. L.; et al.	Chemistry; Materials Science	zwitterionic 3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate, LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
621	2012	Pt-NP-MWNT nanohybrid as a robust and low-cost counter electrode material for dye-sensitized solar cells	Dao, Van-Duong; Ko, Seung Hyeon; Choi, Ho-Suk; et al.	Chemistry; Materials Science	MWNT, Pt	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CMNH
622	2012	Heterogeneous photocatalytic removal and reaction kinetics of Rhodamine-B dye with Au loaded TiO2 nanohybrid catalysts	Zhang, Dongfang	Chemistry; Engineering	Au, TiO2	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
623	2012	Semiconducting carbon nanotube and covalent organic polyhedron-C-60 nanohybrids for light harvesting	Lohrman, Jessica; Zhang, Chenxi; Zhang, Wei; et al.	Chemistry	Fullerene, SWNT dicarbazolylacetylene	Fluorescence/luminescence/photoluminescence, light-energy harvesting	CCNH
624	2012	Nanostructure controlled anti-cancer drug delivery using poly(epsilon-caprolactone) based nanohybrids	Singh, Narendra K.; Singh, Sunil K.; Dash, Debabrata; et al.	Chemistry; Materials Science	Poly(epsilon-caprolactone), montmorillonite, dexamethasone (anticancer drug)	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
625	2012	Molecular cluster batteries of nano-hybrid materials between Keggin POMs and SWNTs	Wang, Heng; Kawasaki, Naoya; Yokoyama, Toshihiko; et al.	Chemistry	SWNT, polyoxometalates	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
626	2012	Biomimetic graphene-FePt nanohybrids with high solubility, ferromagnetism, fluorescence, and enhanced electrocatalytic activity	Wei, Gang; Zhang, Yue; Steckbeck, Sascha; et al.	Chemistry; Materials Science	Graphene, FePt	Catalytic/Photocatalytic/Electrocatalytic applications	CMNH
627	2012	Three-dimensional nanohybrids of Mn3O4/ordered mesoporous carbons	Li, Zhaoqiang; Liu, Ningning;	Chemistry; Materials Science	N/A	N/A	N/A

		for high performance anode materials for lithium-ion batteries	Wang, Xuekun; Wang, Changbin; Qi, Yongxin; Yin, Longwei				
628	2012	Organic-inorganic nanohybrid nonvolatile memory transistors for flexible electronics	Han, Kyu Seok; Park, Yerok; Han, Gibok; Lee, Byoung Hoon; Lee, Kwang Hyun; Son, Dong Hee; Im, Seongil; Sung, Myung Mo	Chemistry; Materials Science	N/A	N/A	N/A
629	2012	Nitrogen-doped mesoporous nanohybrids of TiO2 nanoparticles and HTiNbO5 nanosheets with a high visible-light photocatalytic activity and a good biocompatibility	Zhai, Zheng; Hu, Chenhui; Yang, Xiaoyan; Zhang, Lihong; Liu, Chao; Fan, Yining; Hou, Wenhua	Chemistry; Materials Science	TiO2, HTiNbO5 nanosheets	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	MMNH
630	2012	Bioadhesion-inspired polymer-inorganic nanohybrid membranes with enhanced CO2 capture properties	Li, Yifan; Wang, Shaofei; Wu, Hong; Wang, Jingtao; Jiang, Zhongyi	Chemistry; Materials Science	N/A	N/A	N/A
631	2012	Kaolinite-ionic liquid nanohybrid materials as electrochemical sensors for size-selective detection anions	Dedzo, Gustave Kenne; Letaief, Sadok; Detellier, Christian	Chemistry; Materials Science	Grafting ionic liquids (trihydroxyethylmethylammonium iodide (AE1), 1-(2-hydroxyethyl)-3-methylimidazolium chloride (AE2) and 1-benzyl-3-(2-hydroxyethyl) imidazolium chloride (AE3) , kaolinite	Sensors/biosensors/electrochemical sensors	OMCNH
632	2012	Oxazine-1 J-aggregates in polymer nanohybrids	Giovanella, Umberto; Leone, Giuseppe; Ricci, Giovanni; Virgili, Tersilla; Lopez, Inma Suarez; Rajendran, Sai Kiran; Botta, Chiara	Chemistry; Physics	poly(norbornene)/oxazine-1	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
633	2012	The synergistic behavior of polyoxometalates and metal nanoparticles: from synthetic approaches to functional nanohybrid materials	Mitchell, Scott G.; de la Fuente, Jesus M.	Chemistry; Materials Science	N/A	N/A	N/A
634	2012	Silica-coated flexible liposomes as a nanohybrid delivery system for enhanced oral bioavailability of curcumin	Li, Chong; Zhang, Yan; Su, Tingting; Feng, Lianlian; Long, Yingying; Chen, Zhangbao	Science & Technology - Other Topics; Pharmacology & Pharmacy	silica-coated flexible liposomes loaded with curcumin	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
635	2012	Visible-light plasmonic photocatalyst anchored on titanate nanotubes: a novel nanohybrid with synergistic	Tang, Yuxin; Jiang, Zhelong; Tay,	Chemistry	Ag, Cl, Br, I, titanate nanotubes	Adsorption studies	MMNH

		effects of adsorption and degradation	Qiuling; Deng, Jiyang; Lai, Yuekun; Gong, Dangguo; Dong, Zhili; Chen, Zhong				
636	2012	Preparation of organic-inorganic (SWCNT/TWEEN-TEOS) nano hybrids and their NO gas sensing properties	Yu, Ming-Ru; Suyambrakasam, Gobalakrishnan; Wu, Ren-Jang; et al.	Chemistry; Electrochemistry; Instruments & Instrumentation	SWNT, polyoxyethylene (20) sorbitan monooleate, tetraethoxy orthosilicate	Sensors/biosensors/electrochemical sensors	OMCNH
637	2012	Celiac disease detection using a transglutaminase electrochemical immunosensor fabricated on nanohybrid screen-printed carbon electrodes	Neves, Marta M. P. S.; Gonzalez-Garcia, Maria Begona; Nouws, Henri P. A.; et al.	Biophysics; Biotechnology & Applied Microbiology; Chemistry; Electrochemistry; Science & Technology - Other Topics	Carbon nanotubes and gold nanoparticles	Sensors/biosensors/electrochemical sensors	CMNH
638	2012	Ultrasensitive indicator-free and enhanced self-signal nanohybrid DNA sensing platform based on electrochemically grown poly-xanthurenic acid/Fe2O3 membranes	Zhang, Wei; Yang, Tao; Jiao, Kui	Biophysics; Biotechnology & Applied Microbiology; Chemistry; Electrochemistry; Science & Technology - Other Topics	poly-xanthurenic acid/Fe2O3	Sensors/biosensors/electrochemical sensors	OMCNH
639	2012	Graphene Oxide-Based Supramolecular Hydrogels for Making Nanohybrid Systems with Au Nanoparticles	Adhikari, Bimalendu; Biswas, Abbijit; Banerjee, Arindam	Chemistry; Materials Science	Graphene oxide, au	Synthesis of new nanohybrids/materials	CMNH
640	2012	Nanohybrid systems of non-ionic surfactant inserting liposomes loading paclitaxel for reversal of multidrug resistance	Ji, Xiufeng; Gao, Yu; Chen, Lingli; et al.	Pharmacology & Pharmacy	non-ionic surfactant (Solutol (R) HS 15 (HS-15), pluronic F68 (PF-68) and cremophor EL (CrEL)) inserting liposomes loading paclitaxel	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
641	2012	Molecular design of nanohybrid gas separation membranes for optimal CO2 separation	Lau, Cher Hon; Paul, Donald R.; Chung, Tai Shung	Polymer Science	N/A	N/A	N/A
642	2012	Nanohybrid and microfilled hybrid versus conventional hybrid composite restorations: 5-year clinical wear performance	Palaniappan, Senthamaraiselvi; Elsen, Liesbeth; Lijnen, Inge; et al.	Dentistry, Oral Surgery & Medicine	N/A	N/A	N/A
643	2012	Fibrous membrane of nano-hybrid poly-L-lactic acid/silica xerogel for guided bone regeneration	Jang, Tae-Sik; Lee, Eun-Jung; Jo, Ji-Hoon; et al.	Engineering; Materials Science	poly-L-lactic acid, silica	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
644	2012	The mechanical stability of nano-hybrid composites with new methacrylate monomers for matrix compositions	Schmidt, Christine; Ilie, Nicoleta	Dentistry, Oral Surgery & Medicine; Materials Science	N/A	N/A	N/A
645	2012	Magnetic-fluorescent nanohybrids of carbon nanotubes coated with Eu, Gd Co-doped LaF3 as a multimodal imaging probe	Chen, Bingdi; Zhang, Hui; Du, Ning; et al.	Chemistry	MWNT, Eu, Gd, LaF3	Fluorescence/luminescence/photoluminescence, light-energy harvesting	CMNH
646	2012	Crystallisation of nanohybrids of poly(epsilon-caprolactone) and hydrotalcites containing	Pucciariello, R.; Villani, V.; Giammarino,	Materials Science; Polymer Science	poly(epsilon-caprolactone) and hydrotalcites	Antimicrobial/antibacterial applications	OMCNH

		antimicrobial species	G.				
647	2012	Scanning transmission X-ray microscopy, X-ray photoelectron spectroscopy, and cyclic voltammetry study on the enhanced visible photocatalytic mechanism of carbon-TiO2 nanohybrids	Ming, Hai; Zhang, Hengchao; Ma, Zheng; et al.	Chemistry; Materials Science; Physics	Carbon, TiO2	Catalytic/Photocatalytic/Electrocatalytic applications	CMNH
648	2012	Charge transfer and retention in directly coupled Au-CdSe nanohybrids	Gao, Bo; Lin, Yue; Wei, Sijie; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Au-CdSe	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	MMNH
649	2012	Silica encapsulation of luminescent silicon nanoparticles: stable and biocompatible nanohybrids	Maurice, Vincent; Rivolta, Ilaria; Vincent, Julien; et al.	Chemistry; Science & Technology - Other Topics; Materials Science	Silica nanoparticles and nanocrystals	Fluorescence/luminescence/photoluminescence, light-energy harvesting	MMNH
650	2012	Morphology study of layered silicate/chitosan nanohybrids	Potarniche, C. G.; Vuluga, Z.; Donescu, D.; et al.	Chemistry	Chitosan, montmorillonite	Synthesis of new nanohybrids/materials	OMCNH
651	2012	Integrating Water-Soluble Graphene into Porphyrin Nanohybrids	Malig, J.; Romero-Nieto, C.; Jux, N.; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Graphene, porphyrin	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
652	2012	Superhydrophobic Graphene/Nafion Nanohybrid Films with Hierarchical Roughness	Choi, Bong Gill; Park, Ho Seok	Chemistry; Science & Technology - Other Topics; Materials Science	Graphene, nafion	Optical imaging and applications	OMCNH
653	2012	The synthesis and properties of ZnO-graphene nano hybrid for photodegradation of organic pollutant in water	Fu, Dongying; Han, Gaoyi; Chang, Yunzhen; et al.	Materials Science	Graphene, ZnO	Catalytic/Photocatalytic/Electrocatalytic applications	CMNH
654	2012	Thermal properties of biodegradable poly(PHB/PCL-PEG-PCL) urethanes nanocomposites using clay/poly(epsilon-caprolactone) nanohybrid based masterbatch	Naguib, Hala F.; Aziz, Mohamed S. Abdel; Sherif, Sherif M.; et al.	Chemistry; Materials Science; Mineralogy	clay/poly(epsilon-caprolactone)	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
655	2012	Silver nanoparticle (AgNPs) doped gum acacia-gelatin-silica nanohybrid: An effective support for diastase immobilization	Singh, Vandana; Ahmed, Shakeel	Biochemistry & Molecular Biology	gum acacia-gelatin-silica	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
656	2012	Study of the preparation, properties and kinetics of anion release in drug intercalated magnetic nanohybrids	Panda, H. S.; Bahadur, D.	Materials Science	Fe3O4, LDH, fluvastatin	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
657	2012	Condensation/Hydrogenation of Biomass-Derived Oxygenates in Water/Oil Emulsions Stabilized by Nanohybrid Catalysts	Zapata, Paula A.; Faria, Jimmy; Ruiz, M. Pilar; et al.	Chemistry	SWNT, MWNT, MgO	Catalytic/Photocatalytic/Electrocatalytic applications	CMNH
658	2012	Optimized CVD Production of CNT-Based Nanohybrids by Taguchi Robust Design	Santangelo, S.; Lanza, M.; Piperopoulos, E.; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	CNTs and alumina, magnesia or sodium-exchanged montmorillonite	Synthesis of new nanohybrids/materials	CMNH
659	2012	Tribological Properties of Polymer Nanohybrids Containing Gold Nanoparticles Obtained by Laser Ablation	Olea-Mejia, Oscar; Brostow, Witold; Escobar-Alarcon, Luis; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Polystyrene, Au	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
660	2012	Nanohybrids based on polymeric ionic liquid prepared from	Katsigiannopoulos,	Polymer Science	MWNT, poly(4-vinylpyridine)	Synthesis of new nanohybrids/materials	OMCNH

		functionalized MWCNTs by modification of anionically synthesized poly(4-vinylpyridine)	Dimitrios; Grana, Eftychia; Avgeropoulos, Apostolos; et al.				
661	2012	Electropolymerized surface ion imprinting films on a gold nanoparticles/single-wall carbon nanotube nanohybrids modified glassy carbon electrode for electrochemical detection of trace mercury(II) in water	Fu, Xu-Cheng; Wu, Ju; Nie, Li; et al.	Chemistry	SWNT, Au	Sensors/biosensors/electrochemical sensors	CMNH
662	2012	A highly sensitive non-enzymatic glucose sensor based on nickel and multi-walled carbon nanotubes nanohybrid films fabricated by one-step co-electrodeposition in ionic liquids	Sun, Aili; Zheng, Jianbin; Sheng, Qinglin	Electrochemistry	MWNT, Ni	Sensors/biosensors/electrochemical sensors	CMNH
663	2012	Collagen-silica xerogel nanohybrid membrane for guided bone regeneration	Lee, Eun-Jung; Jun, Shin-Hee; Kim, Hyoun-Ee; et al.	Engineering; Materials Science	Collagen, silica	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
664	2012	beta-Cyclodextrin-Platinum Nanoparticles/Graphene Nanohybrids: Enhanced Sensitivity for Electrochemical Detection of Naphthol Isomers	Zhu, Gangbing; Gai, Pengbo; Wu, Liang; et al.	Chemistry	graphene, beta-Cyclodextrin, Pt	Sensors/biosensors/electrochemical sensors	CMNH
665	2012	Use of nanohybrid materials as electrochemical transducers for mercury sensors	Martin-Yerga, Daniel; Begona Gonzalez-Garcia, Maria; Costa-Garcia, Agustin	Chemistry; Electrochemistry; Instruments & Instrumentation	Carbon nanotube, Au	Sensors/biosensors/electrochemical sensors	CMNH
666	2012	Synthesis of a monophasic nanohybrid for a controlled release formulation of two active agents simultaneously	Hussein, Mohd Zobir; Rahman, Nor Shazlirah Shazlyn Abdul; Sarijo, Siti Halimah; et al.	Chemistry; Materials Science; Mineralogy	4-(2,4-dichlorophenoxy)butyrate (DPBA), 2-(3-chlorophenoxy)propionate	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
667	2012	Organic/Metallic Nanohybrids Based on Amphiphilic Dumbbell-Shaped Dendrimers	Shau, Shi-Min; Chang, Chia-Cheng; Lo, Chia-Hao; et al.	Science & Technology - Other Topics; Materials Science	poly(oxyalkylene), 4-isocyanate-4'-(3,3-dimethyl-2,4-dioxo-azetidine)-diphenylmethane	Synthesis of new nanohybrids/materials	OMCNH
668	2012	Amphiphilic Nanohybrid Catalysts for Reactions at the Water/Oil Interface in Subsurface Reservoirs	Drexler, Santiago; Faria, Jimmy; Ruiz, M. Pilar; et al.	Energy & Fuels; Engineering	SWCNT/silica	Catalytic/Photocatalytic/Electrocatalytic applications	CMNH
669	2012	Dispersion and STM Characterization of Au-CdSe Nanohybrids on Au(111)	Gao, Bo; Kuang, Yan-min; Liao, Yuan; et al.	Physics	Au, CdSe	Fluorescence/luminescence/photoluminescence, light-energy harvesting	MMNH
670	2012	Voltammetric and amperometric determination of hydrogen peroxide using a carbon-ceramic electrode modified with a nanohybrid composite made from single-walled carbon nanotubes and silver nanoparticles	Habibi, Biuck; Jahanbakhshi, Mojtaba; Pournaghi-Azar, Mohammad Hossein	Chemistry	SWNT, Ag	Catalytic/Photocatalytic/Electrocatalytic applications	CMNH
671	2012	Self-assembly of novel architectural nanohybrid multilayers and their selective separation of solvent-water mixtures	Zhang, Guojun; Li, Jie; Ji, Shulan	Engineering	poly(sodium styrene sulfonate), ZrO_2	Membrane research, gas removal, pollutant remediation	OMCNH

672	2012	Preparation and biocompatibility of nanohybrid scaffolds by in situ homogeneous formation of nano hydroxyapatite from biopolymer polyelectrolyte complex for bone repair applications	Chen, Jingdi; Yu, Qifeng; Zhang, Guodong; et al.	Biophysics; Chemistry; Materials Science	hydroxyapatite, polyelectrolyte	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
673	2012	Self-assembled quantum dots-polyhedral oligomeric silsesquioxane nanohybrids with enhanced photoluminescence	Li, Qi; Dong, Lijie; Wang, Xiang; et al.	Science & Technology - Other Topics; Materials Science; Metallurgy & Metallurgical Engineering	polyhedral oligomeric silsesquioxane-modified quantum dots	Fluorescence/luminescence/photoluminescence, light-energy harvesting	OMCNH
674	2012	Plasma Functionalization of Multiwalled Carbon Nanotubes and Their Use in the Preparation of Nylon 6-Based Nanohybrids	Scaffaro, Roberto; Maio, Andrea; Agnello, Simonpietro; et al.	Physics; Polymer Science	MWNT, polyamide 6	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
675	2012	Novel and Sensitive Ethanol Chemi-Sensor Based on Nanohybrid Materials	Khan, Sher Bahadar; Rahman, Mohammed M.; Akhtar, Kalsoom; et al.	Electrochemistry	poly propylene carbonate, silica	Sensors/biosensors/electrochemical sensors	OMCNH
676	2012	Surface modification of gold-carbon nanotube nanohybrids under the influence of near-infrared laser exposure	Schrand, Amanda M.; Stacy, Bradley M.; Hussain, Saber M.; et al.	Engineering; Science & Technology - Other Topics; Physics	SWNT, Au	Synthesis of new nanohybrids/materials	CMNH
677	2012	Facile Synthesis of Au-Nanoparticle/Polyoxometalate/Graphene Tricomponent Nanohybrids: An Enzyme-Free Electrochemical Biosensor for Hydrogen Peroxide	Liu, Rongji; Li, Shiwen; Yu, Xuelian; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	Graphene, Au, Polyoxometalate	Sensors/biosensors/electrochemical sensors	CMNH
678	2012	Magnetically Responsive Inorganic/Polydiacetylene Nanohybrids	Lee, Joosub; Yoon, Bora; Ham, Dae-Young; et al.	Polymer Science	polydiacetylene, magnetite	Sensors/biosensors/electrochemical sensors	OMCNH
679	2012	Synthesis and characterization of one-dimensional magnetic photocatalytic CNTs/Fe3O4-ZnO nanohybrids	Sui, Jiehe; Li, Jing; Li, Zhiguo; et al.	Materials Science	Carbon nanotubes, Fe3O4, ZnO	Catalytic/Photocatalytic/Electrocatalytic applications	CMNH
680	2012	Highly Transparent and Multifunctional Polymer Nanohybrid Film with Superhigh ZnO Content Synthesized by a Bulk Polymerization Method	Liu, Hai-Tao; Zeng, Xiao-Fei; Zhao, Hong; et al.	Engineering	ZnO, poly(n-butyl methacrylate)	Transparent and conductive films	OMCNH
681	2012	Synthesis and Characterization of a Noble Metal Enhanced Optical Nanohybrid (NEON): A High Brightness Detection Platform Based on a Dye-Doped Silica Nanoparticle	Roy, Shibsekhar; Dixit, Chandra K.; Woolley, Robert; et al.	Chemistry; Materials Science	Au, dye-doped silica	Optical imaging and applications	MMNH
682	2012	Adsorption of arsenic on multiwall carbon nanotube-zirconia nanohybrid for potential drinking water purification	Ntim, Susana Addo; Mitra, Somenath	Chemistry	MWNT, zirconia	Adsorption studies	CMNH
683	2012	Formation of a nanohybrid composite between mesostructured cellular silica foam and microporous copper trimesate	Seo, You-Kyong; Yoon, Ji Woong; Lee, U-Hwang; et al.	Chemistry; Science & Technology - Other Topics; Materials Science	N/A	N/A	N/A
684	2012	Zeolite-Y based nanohybrid materials: Synthesis, characterization and catalytic aspects	Modi, Chetan K.; Trivedi, Parthiv M.	Chemistry; Science & Technology - Other Topics; Materials Science	salicylaldehyde thiophene-2-carboxylic hydrazone, salicylaldehyde furoic-2-carboxylic hydrazone, Ru(III), Fe(III)	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
685	2012	Mannosylated Polyethyleneimine-	Mahor, Sunil;	Biochemistry &	Mannosylated	Delivery Carriers, and	OMCNH

		Hyaluronan Nanohybrids for Targeted Gene Delivery to Macrophage-Like Cell Lines	Dash, Biraja C.; O'Connor, Stephen; et al.	Molecular Biology; Chemistry	Polyethyleneimine, Hyaluronan	Controlled Release of Drugs/Compounds	
686	2012	COIMMOBILIZATION OF ACETYLCHOLINESTERASE AND CHOLINE OXIDASE ON NEW NANOHYBRID MEMBRANES OBTAINED BY SOL GEL TECHNOLOGY	Yotova, Lyubov; Medhat, Nourelhoda	Biotechnology & Applied Microbiology	Acetylcholinesterase, choline oxidase, SiO2	Sensors/biosensors/electrochemical sensors	OMCNH
687	2012	ZnO/Liquid Crystalline Nanohybrids: From Properties in Solution to Anisotropic Growth	Saliba, Sarmenio; Coppel, Yannick; Mingotaud, Christophe; et al.	Chemistry	ZnO, liquid crystals	Synthesis of new nanohybrids/materials	MMNH
688	2012	Immediate vs Delayed Repair Bond Strength of a Nanohybrid Resin Composite	El-Askary, Farid S.; El-Banna, Ahmed H.; van Noort, Richard	Dentistry, Oral Surgery & Medicine	N/A	N/A	N/A
689	2012	Herbicide-Intercalated Zinc Layered Hydroxide Nanohybrid for a Dual-Guest Controlled Release Formulation	Hussein, Mohd Zobir; Rahman, Nor Shazlirah Shazlyn Abdul; Sarijo, Siti H.; et al.	Chemistry	4-(2,4-dichlorophenoxy) butyrate, 2-(3-chlorophenoxy) propionate, Zinc LH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
690	2012	Nanohybrids of Silver Particles Immobilized on Silicate Platelet for Infected Wound Healing	Chu, Chia-Yu; Peng, Fu-Chuo; Chiu, Ying-Fang; et al.	Life Sciences & Biomedicine - Other Topics	Ag, silica plateletes	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	MMNH
691	2012	Pyrene-POSS nanohybrid as a dispersant for carbon nanotubes in solvents of various polarities: its synthesis and application in the preparation of a composite membrane	Majeed, Shahid; Filiz, Volkan; Shishatskiy, Sergey; et al.	Science & Technology - Other Topics; Materials Science; Physics	pyrene, polyhedral oligomeric silsesquioxanes, MWNT	Semiconductors/superconductors/conductive materials	OMCNH
692	2012	Nano-hybrid carboxymethyl-hexanoyl chitosan modified with (3-aminopropyl)triethoxysilane for camptothecin delivery	Hsiao, Meng-Hsuan; Tung, Tsan-Hua; Hsiao, Chi-Sheng; et al.	Chemistry; Polymer Science	carboxymethyl, hexanoyl chitosan, (3-aminopropyl)triethoxysilane	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
693	2012	Ketoprofen-LDH Nanohybrid for Transdermal Drug Delivery System	Park, Myung-Chul; Kim, Hark; Park, Dae-Hwan; et al.	Chemistry	Ketoprofen, LDH	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
694	2012	Photophysical properties of fluorescent PMMA/SiO2 nanohybrids for solar energy applications	El-Bashir, S. M.	Optical	poly(methylmethacrylate), SiO2	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
695	2012	Synthesis, amine functionalization and dye removal ability of titania/silica nano-hybrid	Mahmoodi, Niyaz Mohammad; Najafi, Farhood	Chemistry; Science & Technology - Other Topics; Materials Science	Titania, silica	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	MMNH
696	2012	Hydroxyapatite-poly(L-lactide) nanohybrids via surface-initiated ATRP for improving bone-like apatite-formation abilities	He, Jiqing; Yang, Xiaoping; Mao, Jiaofu; et al.	Chemistry; Materials Science; Physics	Hydroxyapatite-poly(L-lactide)	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
697	2012	Heterostructured zero valent iron-montmorillonite nanohybrid and their catalytic efficacy	Son, You-Hwan; Lee, Jung-Kun; Soong, Yee; et	Chemistry; Materials Science; Mineralogy	Fe, montmorillonite	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH

			al.				
698	2012	Glycolic acid-g-chitosan-Pt-Fe3O4 nanoparticles nanohybrid scaffold for tissue engineering and drug delivery	Kumari, Sangeeta; Singh, Raj Pal	Biochemistry & Molecular Biology	Glycolic acid-g-chitosan-Pt-Fe3O4	Delivery Carriers, and Controlled Release of Drugs/Compounds	OMCNH
699	2012	Environmentally Friendly Photocatalytic Synthesis of Porphyrin/Ag Nanoparticles/Reduced Graphene Oxide Ternary Nanohybrids Having Superior Catalytic Activity	Li, Haiyan; Zhang, Yingwei; Chang, Guohui; et al.	Chemistry	Reduced graphene oxide, Ag, porphyrin	Catalytic/Photocatalytic/Electrocatalytic applications	OMCNH
700	2012	NANOHYBRID POLYURETHANE/FUNCTIONALIZED SILSESQUIOXANE SYSTEMS. Part I. STRUCTURAL INVESTIGATIONS USING FT-IR AND NMR METHODS	Janowski, Bartlomiej; Pielichowski, Krzysztof	Polymer Science	polyurethane, functionalized silsesquioxane	Synthesis of new nanohybrids/materials	OMCNH
701	2012	Pt Nanoparticle-Reduced Graphene Oxide Nanohybrid for Proton Exchange Membrane Fuel Cells	Park, Dae-Hwan; Jeon, Yukwon; Ok, Jinhee; et al.	Chemistry, Multidisciplinary; Chemistry, Physical; Nanoscience & Nanotechnology; Materials Science, Multidisciplinary; Physics, Applied; Physics, Condensed Matter	Carbon Nanotube, Pt	Catalytic/Photocatalytic/Electrocatalytic applications	CMNH
702	2012	Transparent Anti-Stain Coatings with Good Thermal and Mechanical Properties Based on Polyimide-Silica Nanohybrids	Choi, Myeon-Cheon; Sung, Giju; Nagappan, Saravanan; et al.	Chemistry, Multidisciplinary; Chemistry, Physical; Nanoscience & Nanotechnology; Materials Science, Multidisciplinary; Physics, Applied; Physics, Condensed Matter	Pt, reduced graphene oxide	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CMNH
703	2012	A Hydrophobic Dye-Encapsulated Nano-Hybrid as an Efficient Fluorescent Probe for Living Cell Imaging	Chang, Shu; Wu, Xumeng; Li, Yongsheng; et al.	Materials Science	Polyimide, SiO2	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
704	2012	Highly Catalytic Carbon Nanotube/Pt Nanohybrid-Based Transparent Counter Electrode for Efficient Dye-Sensitized Solar Cells	Chen, Hong-Yan; Liao, Jin-Yun; Lei, Bing-Xin; et al.	Chemistry	CNT, Pt	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CMNH
705	2012	Plasmon-controlled narrower and blue-shifted fluorescence emission in (Au@SiO2)SiC nanohybrids	Sui, Ning; Monnier, Virginie; Zakharko, Yuriy; et al.	Chemistry; Science & Technology - Other Topics; Materials Science	Au, SiO2	Fluorescence/luminescence/photoluminescence, light-energy harvesting	MMNH
706	2012	C/TiO2 nanohybrids co-doped by N and their enhanced photocatalytic ability	Ming, Hai; Huang, Hui; Pan, Keming; et al.	Chemistry	carbon, TiO2	Catalytic/Photocatalytic/Electrocatalytic applications	CMNH
707	2012	Ultrafast Photoinduced Charge Separation in Metal-Semiconductor Nanohybrids	Mongin, D; Shaviv, E; Maioli, P; Crut, A; Banin, U; Del Fatti, N; Vallee, F	Chemistry; Science & Technology - Other Topics; Materials Science	Au, CdS	Semiconductors/superconductors/conductive materials	MMNH
708	2012	A General Approach to One-Pot Fabrication of Crumpled Graphene-Based Nanohybrids for Energy Applications	Mao, S; Wen, ZH; Kim, H; Lu, GH; Hurley, P; Chen, JH	Chemistry; Science & Technology - Other Topics; Materials Science	Graphene oxide, graphene	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CCNH

709	2012	Clinical Evaluation of a Nanohybrid and a Flowable Resin Composite in Non-carious Cervical Lesions: 24-Month Results	Karaman, E; Yazici, AR; Ozgunaltay, G; Dayangac, B	Dentistry, Oral Surgery & Medicine	N/A	N/A	N/A
710	2012	Injectable and Biodegradable Nanohybrid Polymers with Simultaneously Enhanced Stiffness and Toughness for Bone Repair	Cai, Lei; Chen, Jihua; Rondinone, Adam J.; et al.	Chemistry; Science & Technology - Other Topics; Materials Science; Physics	poly(propylene fumarate)-co-polyhedral oligomeric silsesquioxane	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
711	2012	Dual-emission of a fluorescent graphene oxide-quantum dot nanohybrid for sensitive and selective visual sensor applications based on ratiometric fluorescence	Zhu, Houjuan; Zhang, Wen; Zhang, Kui; et al.	Science & Technology - Other Topics; Materials Science; Physics	Graphene, CdTe QDs	Sensors/biosensors/electrochemical sensors	CMNH
712	2012	Synthesis and characterization of model silica-gold core-shell nanohybrid systems to demonstrate plasmonic enhancement of fluorescence	Roy, S; Dixit, CK; Woolley, R; O'Kennedy, R; McDonagh, C	Nanoscience & Nanotechnology; Materials Science, Multidisciplinary; Physics, Applied	Au, silica	Fluorescence/luminescence/photoluminescence, light-energy harvesting	MMNH
713	2012	Amperometric sensor for nitrite using a glassy carbon electrode modified with thionine functionalized MWCNTs/Au nanorods/SDS nanohybrids	Zhang, Yu; Yuan, Ruo; Chai, Yaqin; et al.	Chemistry	MWNT, Au, sodium dodecyl sulfate	Sensors/biosensors/electrochemical sensors	CMNH
714	2012	CSA doped polyaniline/CdS organic-inorganic nanohybrid: Physical and gas sensing properties	Raut, B. T.; Chougule, M. A.; Nalage, S. R.; et al.	Materials Science	polyaniline, CdS	Sensors/biosensors/electrochemical sensors	OMCNH
715	2012	Functionalization of polyhedral oligomeric silsesquioxanes with bis(hydroxyethyl) ester and preparation of the corresponding degradable nanohybrids	Wang, Bing Tao; Zhang, Yan; Zhang, Ping; et al.	Chemistry	polyhedral oligomeric silsesquioxanes, bis(hydroxyethyl) ester	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
716	2012	Formation of aggregates in nanohybrid material of dye molecules-titanate nanosheets	Tsurumachi, Noriaki; Okamoto, Hiroki; Ishii, Kenta; et al.	Chemistry	titanate, rhodamine 6g, pseudoisocyanine	Optical imaging and applications	OMCNH
717	2012	Carbon nanotube-polyaniline nanohybrids: Influence of the carbon nanotube characteristics on the morphological, spectroscopic, electrical and thermoelectric properties	King, Roch Chan Yu; Roussel, Frederick; Brun, Jean-Francois; et al.	Materials Science; Physics; Polymer Science	Carbon nanotube-polyaniline	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
718	2012	Enhanced Electrochemical Sensing for Persistent Organic Pollutants by Nanohybrids of Graphene Nanosheets that are Noncovalently Functionalized with Cyclodextrin	Zhu, GB; Zhang, XH; Gai, PB; Chen, JH	Chemistry, Multidisciplinary	Graphene, cyclodextrin	Sensors/biosensors/electrochemical sensors	OMCNH
719	2012	The effect of titania content on the physical properties of polyimide/titania nanohybrid films	Kizilkaya, Canan; Dumludag, Fatih; Karatas, Sevim; et al.	Polymer Science	polyimide, titania	Synthesis of new nanohybrids/materials	OMCNH
720	2012	Facilitating the formation of nanohybrid shish kebab structure in helical polymer systems by using carbon nanotube bundles	Ning, NY; Zhang, W; Zhao, YS; Tang, CY; Yang, MB; Fu, Q	Polymer Science	SWNT, helical polymer	Crystallography and polymer crystallization	OMCNH
721	2012	Preparation, characterization, and properties of novel biodegradable aliphatic-aromatic copolyester nanohybrids with polyhedral oligomeric silsesquioxanes moieties	Wang, Bing-Tao; Zhang, Yan; Zhang, Ping; et al.	Polymer Science	aliphatic, aromatic copolyester, polyhedral oligomeric silsesquioxanes	Synthesis of new nanohybrids/materials	OMCNH
722	2012	Depth of cure and mechanical properties of nano-hybrid resin-based composites with novel and	Frauscher, KE; Ilie, N	Dentistry, Oral Surgery & Medicine	N/A	N/A	N/A

		conventional matrix formulation					
723	2012	Ultrasensitive photoelectrochemical sensing of nicotinamide adenine dinucleotide based on graphene-TiO2 nanohybrids under visible irradiation	Wang, K; Wu, J; Liu, Q; Jin, YC; Yan, JJ; Cai, JR	Chemistry, Analytical	Graphene, TiO2	Sensors/biosensors/electrochemical sensors	CMNH
724	2012	Layer-by-layer assembled nanohybrid multilayer membranes for pervaporation dehydration of acetone-water mixtures	Li, J; Zhang, GJ; Ji, SL; Wang, NX; An, W	Engineering, Chemical; Polymer Science	N/A	N/A	N/A
725	2012	Facile Synthesis of an Ag2O-ZnO Nanohybrid and Its High Photocatalytic Activity	Wu, M; Yan, JM; Zhao, M; Jiang, Q	Chemistry, Multidisciplinary	Ag2O, ZnO	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
726	2012	Preparation of a Responsive Carbohydrate-Coated Biointerface Based on Graphene/Azido-Terminated Tetrathiafulvalene Nanohybrid Material	Kaminska, I; Barras, A; Coffinier, Y; Lisowski, W; Roy, S; Niedziolka-Jonsson, J; Woisel, P; Lyskawa, J; Opallo, M; Siriwardena, A; Boukherroub, R; Szunerits, S	Nanoscience & Nanotechnology; Materials Science, Multidisciplinary	Graphene, azido-terminated tetrathiafulvalene	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
727	2012	Low-Temperature Fabrication of Au-Co Cluster Mixed Nanohybrids With High Magnetic Moment of Co	Zhang, DF; Zhang, Q; Huang, WF; Guo, L; Chen, WM; Chu, WS; Chen, CP; Wu, ZY	Nanoscience & Nanotechnology; Materials Science, Multidisciplinary	Au, Co	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
728	2012	Synthesis, structural analysis and in situ transmission electron microscopy mechanical tests on individual aluminum matrix/boron nitride nanotube nanohybrids	Yamaguchi, M; Tang, DM; Zhi, CY; Bando, Y; Shtansky, D; Golberg, D	Materials Science, Multidisciplinary; Metallurgy & Metallurgical Engineering	Boron nitride, alumina	Synthesis of new nanohybrids/materials	MMNH
729	2012	Ultrasonic synthesis of CoO/graphene nanohybrids as high performance anode materials for lithium-ion batteries	Chen, BD; Peng, CX; Cui, Z	Metallurgy & Metallurgical Engineering	Graphene, CoO	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CMNH
730	2012	Morphological, Dielectric and Electrical Conductivity Characteristics of Clay-Containing Nanohybrids of Poly(N-Vinyl Carbazole) and Polypyrrole	Haldar, I; Biswas, M; Nayak, A; Ray, SS	Chemistry; Science & Technology - Other Topics; Materials Science	Poly(N-vinyl carbazole) (PNVC) and polypyrrole (PPY)-montmorillonite (MMT)	Semiconductors/superconductors/conductive materials	OMCNH
731	2012	High performance PA6/CNTs nanohybrid fibers prepared in the melt	Scaffaro, R; Maio, A; Tito, AC	Materials Science, Composites	MWNT, polyamide 6	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
732	2012	DNA Oligonucleotide Templated Nanohybrids Using Electronic Type Sorted Carbon Nanotubes for Light Harvesting	Zhang, HY; Baker, BA; Cha, TG; Sauffer, MD; Wu, YJ; Hinkson, N; Bork, MA; McShane, CM; Choi, KS; McMillin, DR; Choi, JH	Chemistry, Multidisciplinary; Chemistry, Physical; Nanoscience & Nanotechnology; Materials Science, Multidisciplinary; Physics, Applied; Physics, Condensed Matter	SWNT, oligonucleotide DNA	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
733	2012	Polymer-gold nanohybrids with potential use in bimodal MRI/CT: enhancing the relaxometric properties of Gd(III) complexes	Beija, M; Li, Y; Duong, HT; Laurent, S; Vander	Chemistry, Physical; Materials Science, Multidisciplinary	Au, gadolinium, polymer	Optical imaging and applications	OMCNH

			Elst, L; Muller, RN; Lowe, AB; Davis, TP; Boyer, C				
734	2012	Correlation of the degree of conversion with the amount of elutable substances in nano-hybrid dental composites	Durner, J; Obermaier, J; Draenert, M; Ilie, N	Dentistry, Oral Surgery & Medicine; Materials Science, Biomaterials	N/A	N/A	N/A
735	2012	Second generation 'nanohybrid supercapacitor': Evolution of capacitive energy storage devices	Naoi, K; Ishimoto, S; Miyamoto, J; Naoi, W	Chemistry, Multidisciplinary; Energy & Fuels; Engineering, Chemical; Environmental Sciences	Li4Ti5O12, Carbon nanofibers	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CMNH
736	2012	Preparation and Characterization of Novel Polyimide/SiO2 Nano-hybrid Films by In Situ Polymerization	Babanzadeh, S; Mehdipour-Ataei, S; Mahjoub, AR	Polymer Science	Polyimide, SiO2	Synthesis of new nanohybrids/materials	OMCNH
737	2012	Nanohybrid shish kebab structure and its effect on mechanical properties in poly(L-lactide)/carbon nanotube nanocomposite fibers	Ning, NY; Zhang, W; Zhao, YS; Luo, F; Fu, Q	Polymer Science	DWNT, poly(L-lactide)	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	OMCNH
738	2012	Effect of surface "groove" structure of carbon nanotube bundles on the formation of nanohybrid shish kebab	Ning, NY; Zhang, W; Yan, JJ; Xu, F; Tang, CY; Fu, Q	Materials Science, Multidisciplinary	DWNT, MWNT, Polyethylene	Crystallography and polymer crystallization	OMCNH
739	2012	Lipid-Based Bio-Nanohybrids for Functional Stabilisation of Influenza Vaccines	Wicklein, B; del Burgo, MAM; Yuste, M; Darder, M; Llavata, CE; Aranda, P; Ortin, J; del Real, G; Ruiz-Hitzky, E	Chemistry	Sepiolite, Mg/Al LDH, Lipid	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	OMCNH
740	2012	Development of Pt/TiO2 nanohybrids-modified SWCNT electrode for sensitive hydrogen peroxide detection	Han, KN; Li, CA; Bui, MPN; Pham, XH; Kim, BS; Choa, YH; Seong, GH	Chemistry; Electrochemistry; Instruments & Instrumentation	Pt, TiO2, SWNT	Sensors/biosensors/electrochemical sensors	CMNH
741	2012	New POSS/magnesium silicate nano-hybrids obtained by chemical or mechanical methods	Ambrozewicz, D; Marciniec, B; Jesionowski, T	Engineering	Magnesium silicate; Polyhedral oligomeric silsesquioxane	Sensors/biosensors/electrochemical sensors	OMCNH
742	2012	Copper Oxide Based Polymer Nanohybrid for Chemical Sensor Applications	Khan, SB; Rahman, MM; Akhtar, K; Asiri, AM; Alamry, KA; Seo, J; Han, H	Electrochemistry	CuO, Poly propylene carbonate	Sensors/biosensors/electrochemical sensors	OMCNH
743	2012	Electrical and thermal properties of polyamideimide-colloid silica nanohybrid for magnetic enameled wire	Han, SW; Kang, DP	Materials Science	Polyamidimide, colloidal silica	Semiconductors/superconductors/conductive materials	OMCNH
744	2012	Organic/inorganic hybrid electrochromic devices based on photoelectrochemically formed polypyrrole/TiO2 nanohybrid films	Takagi, S; Makuta, S; Veamatahau, A; Otsuka, Y; Tachibana, Y	Chemistry; Materials Science	Polypyrrole, TiO2	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	OMCNH
745	2012	Indium(III) and Gallium(III) phthalocyanines-based nanohybrid materials for optical limiting	Gu, HL; Li, S; Wang, J; Blau, WJ; Chen, Y	Materials Science	In(III), Ga(III) phthalocyanines, Poly(methylmethacrylate) PMMA	Optical imaging and applications	MMNH
746	2012	Incubating non-prefabricated	Huang, CY;	Chemistry	TiO2, TiO2 nanotubes	Energy/Electron	MMNH

		nanocrystals in anodized nanotubes for TiO2 nano-hybrids	Tao, JC; Sun, Y; Zhang, RJ; Wu, YZ; Chen, X; Dai, N			Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	
747	2012	Electro-catalytic activity of multiwall carbon nanotube-metal (Pt or Pd) nanohybrid materials synthesized using microwave-induced reactions and their possible use in fuel cells	Kumar, LV; Ntim, SA; Sae-Khow, O; Janardhana, C; Lakshminarayanan, V; Mitra, S	Electrochemistry	MWNT, Pt, Pd	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CMNH
748	2012	Effect of grafting architecture on the surfactant-like behavior of clay-poly(NiPAAm) nanohybrids	Lin, HC; Hsieh, BZ; Lin, YL; Sheng, YJ; Lin, JJ	Chemistry	Poly(N-isopropylacrylamide) (PNiPAAm), silicate platelets	Synthesis of new nanohybrids/materials	OMCNH
749	2012	CeO2-layered aluminosilicate nanohybrids for UV screening	Kamada, K; Kang, JH; Paek, SM; Choy, JH	Chemistry; Physics	CeO2, aluminosilicate clay	Optical imaging and applications	MMNH
750	2012	Polyepoxide-based nanohybrid films with self-assembled linear assemblies of nanodiamonds	Cho, HB; Nguyen, ST; Nakayama, T; Suematsu, H; Suzuki, T; Jiang, WH; Tanaka, S; Kim, BS; Niihara, K	Materials Science, Multidisciplinary; Metallurgy & Metallurgical Engineering	Polyepoxide, nanodiamonds	Synthesis of new nanohybrids/materials	OMCNH
751	2012	Self-assembly of graphene oxide and polyelectrolyte complex nanohybrid membranes for nanofiltration and pervaporation	Wang, NX; Ji, SL; Zhang, GJ; Li, J; Wang, L	Engineering	N/A	N/A	N/A
752	2012	Preparation of cytocompatible luminescent and magnetic nanohybrids based on ZnO, Zn0.95Ni0.05O and core@shell ZnO@Fe2O3 polymer grafted nanoparticles for biomedical imaging	Balti, I; Barrere, A; Gueguen, V; Poussard, L; Pavon-Djavid, G; Meddahi-Pelle, A; Rabu, P; Smiri, LS; Jouini, N; Chaubet, F	Chemistry; Science & Technology - Other Topics; Materials Science	ZnO, Fe2O3	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	MMNH
753	2012	Hematoporphyrin-ZnO Nanohybrids: Twin Applications in Efficient Visible-Light Photocatalysis and Dye-Sensitized Solar Cells	Sarkar, S; Makhal, A; Bora, T; Lakhsman, K; Singha, A; Dutta, J; Pal, SK	Science & Technology - Other Topics; Materials Science	Hematoporphyrin, ZnO	Catalytic/Photocatalytic/Electrocatalytic applications	OMCNH
754	2012	Facilely constructing robust nanohybrids comprising high dispersion of platinum-ruthenium nanoparticles on carbon nanotubes and their enhanced electrocatalytic performance	Cui, Y; Wu, BH; Mao, LQ; Yin, DL	Materials Science; Physics	CNT, dodecylamine(DA), PtRu	Semiconductors/superconductors/conductive materials	CMNH
755	2012	Visible-light photocatalytic activity of mesoporous nanohybrid assembled by tantalotungstate nanosheets and manganese ions	Lin, BZ; He, LW; Zhu, BL; Chen, YL; Gao, BF	Chemistry	Mn, tatalotungstates nanosheets	Catalytic/Photocatalytic/Electrocatalytic applications	MMNH
756	2012	Pulsed Laser Ablation based Direct Synthesis of Single-Wall Carbon Nanotube/PbS Quantum Dot Nanohybrids Exhibiting Strong, Spectrally Wide and Fast Photoresponse	Ka, I; Le Borgne, V; Ma, D; El Khakani, MA	Chemistry; Science & Technology - Other Topics; Materials Science	SWNT, PbS	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CMNH
757	2012	Injectable Nanohybrid Scaffold for	Tan, HP;	Polymer Science	N/A	N/A	N/A

		Biopharmaceuticals Delivery and Soft Tissue Engineering	Shen, Q; Jia, XJ; Yuan, ZP; Xiong, DS				
758	2012	Double-templated electrodeposition: Simple fabrication of micro-nano hybrid structure by electrodeposition for efficient boiling heat transfer	Shin, S; Kim, BS; Choi, G; Lee, H; Cho, HH	Physics	N/A	N/A	N/A
		Selected Nanohorn Publications					
759	2004	Carbon nanohorns hybridized with a metal-included nanocapsule	Sano, N; Kikuchi, T; Wang, HL; Chhowalla, M; Amaratunga, GAJ	Chemistry, Physical; Materials Science, Multidisciplinary	Nanohorn	Synthesis of new nanohybrids/materials	CCNH
760	2006	Preparing a magnetically responsive single-wall carbon nanohorn colloid by anchoring magnetite nanoparticles	Utsumi, S; Urita, K; Kanoh, H; Yudasaka, M; Suenaga, K; Iijima, S; Kaneko, K	Chemistry, Physical	Nanohorn	Synthesis of new nanohybrids/materials	CCNH
761	2007	Formation of single-wall carbon nanohorn aggregates hybridized with carbon nanocapsules by laser vaporization	Kobayashi, K; Shimazu, T; Yamada, Y; Koshio, A; Takahashi, Y; Kokai, F	Materials Science, Multidisciplinary; Physics, Applied	Nanohorn	Synthesis of new nanohybrids/materials	CCNH
762	2007	Theoretical study in donor-acceptor carbon nanohorn-based hybrids	Petsalakis, ID; Pagona, G; Tagmatarchis, N; Theodorakopoulos, G	Chemistry, Physical; Physics, Atomic, Molecular & Chemical	Nanohorn	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CCNH
763	2009	Properties, applications and functionalisation of carbon nanohorns	Pagona, G; Mountrichas, G; Rotas, G; Karousis, N; Pispas, S; Tagmatarchis, N	Nanoscience & Nanotechnology; Materials Science, Multidisciplinary	Nanohorn	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
764	2009	Solvent-free microwave-assisted Bingel reaction in carbon nanohorns	Economopoulos, SP; Pagona, G; Yudasaka, M; Iijima, S; Tagmatarchis, N	Chemistry, Physical; Materials Science, Multidisciplinary	Nanohorn	Synthesis of new nanohybrids/materials	CCNH
765	2009	Single wall carbon nanohorns coated with anatase titanium oxide	Battiston, S; Bolzan, M; Fiameni, S; Gerbasi, R; Meneghetti, M; Miorin, E; Mortalo, C; Pagura, C	Chemistry, Physical; Materials Science, Multidisciplinary	Nanohorn	Synthesis of new nanohybrids/materials	CCNH
766	2009	Solubilization of Carbon Nanohorns by Block Polyelectrolyte Wrapping and Templated Formation of Gold Nanoparticles	Mountrichas, G; Ichihashi, T; Pispas, S; Yudasaka, M; Iijima, S; Tagmatarchis, N	Chemistry, Physical; Nanoscience & Nanotechnology; Materials Science, Multidisciplinary	Nanohorn	Synthesis of new nanohybrids/materials	CCNH
767	2009	Structural characterization of single-wall carbon nanohorn aggregates hybridized with carbon nanocapsules and their formation mechanism	Kokai, F; Tachi, N; Kobayashi, K; Koshio, A	Chemistry, Physical; Materials Science, Coatings & Films; Physics, Applied; Physics, Condensed Matter	Nanohorn	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
768	2009	Decoration of Carbon Nanohorns	Karousis, N;	Chemistry,	Nanohorn	Synthesis of new	CCNH

		with Palladium and Platinum Nanoparticles	Ichihashi, T; Yudasaka, M; Lijima, S; Tagmatarchis, N	Multidisciplinary; Nanoscience & Nanotechnology; Materials Science, Multidisciplinary; Physics, Applied; Physics, Condensed Matter		nanohybrids/materials	
769	2009	Simultaneous electrochemical determination of uric acid, dopamine, and ascorbic acid at single-walled carbon nanohorn modified glassy carbon electrode	Zhu, SY; Li, HJ; Niu, WX; Xu, GB	Biophysics; Biotechnology & Applied Microbiology; Chemistry, Analytical; Electrochemistry; Nanoscience & Nanotechnology	Nanohorn	Sensors/biosensors/electrochemical sensors	CCNH
770	2010	A Carbon Nanohorn-Porphyrin Supramolecular Assembly for Photoinduced Electron-Transfer Processes	Vizuete, M; Gomez-Escalonilla, MJ; Fierro, JLG; Sandanayaka, ASD; Hasobe, T; Yudasaka, M; Iijima, S; Ito, O; Langa, F	Chemistry, Multidisciplinary	Nanohorn	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CCNH
771	2010	Imidazolium modified carbon nanohorns: switchable solubility and stabilization of metal nanoparticles	Karousis, N; Ichihashi, T; Chen, S; Shinohara, H; Yudasaka, M; Iijima, S; Tagmatarchis, N	Chemistry, Physical; Materials Science, Multidisciplinary	Nanohorn	Synthesis of new nanohybrids/materials	CCNH
772	2010	Template-free electrochemical nanofabrication of polyaniline nanobrush and hybrid polyaniline with carbon nanohorns for supercapacitors	Wei, D; Wang, HL; Hiralal, P; Andrew, P; Ryhanen, T; Hayashi, Y; Amaratunga, GAJ	Nanoscience & Nanotechnology; Materials Science, Multidisciplinary; Physics, Applied	Nanohorn	Semiconductors/superconductors/conductive materials	CCNH
773	2010	Highly Efficient Field Emission from Carbon Nanotube-Nanohorn Hybrids Prepared by Chemical Vapor Deposition	Yuge, R; Miyawaki, J; Ichihashi, T; Kuroshima, S; Yoshitake, T; Ohkawa, T; Aoki, Y; Iijima, S; Yudasaka, M	Chemistry, Multidisciplinary; Chemistry, Physical; Nanoscience & Nanotechnology; Materials Science, Multidisciplinary	Nanohorn	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CCNH
774	2011	Microwave-assisted functionalization of carbon nanohorns via [2+1] nitrenes cycloaddition	Karousis, N; Ichihashi, T; Yudasaka, M; Iijima, S; Tagmatarchis, N	Chemistry, Multidisciplinary	Nanohorn	Synthesis of new nanohybrids/materials	CCNH
775	2011	Nucleic acid detection using single-walled carbon nanohorns as a fluorescent sensing platform	Zhu, SY; Liu, ZY; Zhang, W; Han, S; Hu, LZ; Xu, GB	Chemistry, Multidisciplinary	Nanohorn	Sensors/biosensors/electrochemical sensors	CCNH
776	2011	A soluble hybrid material combining carbon nanohorns and C-60	Vizuete, M; Gomez-Escalonilla, MJ; Fierro, JLG;	Chemistry, Multidisciplinary	Nanohorn	Synthesis of new nanohybrids/materials	CCNH

			Yudasaka, M; Iijima, S; Vartanian, M; Iehl, J; Nierengarten, JF; Langa, F				
777	2011	Enhanced supercapacitors from hierarchical carbon nanotube and nanohorn architectures	Hiralal, P; Wang, HL; Unalan, HE; Liu, YL; Rouvala, M; Wei, D; Andrew, P; Amaratunga, GAJ	Chemistry, Physical; Materials Science, Multidisciplinary	Nanohorn	Semiconductors/superconductors/conductive materials	CCNH
778	2011	Single-step synthesis and characterization of single-walled carbon nanohorns hybridized with Pd nanoparticles using N-2 gas-injected arc-in-water method	Poonjarernsilp, C; Sano, N; Charinpanitkul, T; Mori, H; Kikuchi, T; Tamon, H	Chemistry, Physical; Materials Science, Multidisciplinary	Nanohorn	Synthesis of new nanohybrids/materials	CCNH
779	2011	Synthesis, characterization, and photophysical properties of a carbon nanohorn-coumarin hybrid material	Pagona, G; Katerinopoulos, HE; Tagmatarchis, N	Chemistry, Physical; Physics, Atomic, Molecular & Chemical	Nanohorn	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
780	2012	Amperometric detection of hypoxanthine and xanthine by enzymatic amplification using a gold nanoparticles-carbon nanohorn hybrid as the carrier	Zhang, L; Lei, JP; Zhang, J; Ding, L; Ju, HX	Chemistry, Analytical	Nanohorn	Sensors/biosensors/electrochemical sensors	CCNH
781	2012	Carbon Nanohorn-Porphyrin Dimer Hybrid Material for Enhancing Light-Energy Conversion	Pagona, G; Zervaki, GE; Sandanayaka, ASD; Ito, O; Charalambidis, G; Hasobe, T; Coutsoleos, AG; Tagmatarchis, N	Chemistry, Physical; Nanoscience & Nanotechnology; Materials Science, Multidisciplinary	Nanohorn	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CCNH
782	2012	Carbon nanohorns functionalized with polyamidoamine dendrimers as efficient biocarrier materials for gene therapy	Guerra, J; Herrero, MA; Carrion, B; Perez-Martinez, FC; Lucio, M; Rubio, N; Meneghetti, M; Prato, M; Cena, V; Vazquez, E	Chemistry, Physical; Materials Science, Multidisciplinary	Nanohorn	Delivery Carriers, and Controlled Release of Drugs/Compounds	CCNH
783	2012	Direct evidence for covalent functionalization of carbon nanohorns by high-resolution electron microscopy imaging of C-60 conjugated onto their skeleton	Karousis, N; Sato, Y; Suenaga, K; Tagmatarchis, N	Chemistry, Physical; Materials Science, Multidisciplinary	Nanohorn	Synthesis of new nanohybrids/materials	CCNH
784	2012	Enhanced docetaxel-mediated cytotoxicity in human prostate cancer cells through knockdown of cofilin-1 by carbon nanohorn delivered siRNA	Perez-Martinez, FC; Carrion, B; Lucio, MI; Rubio, N; Herrero, MA; Vazquez, E; Cena, V	Engineering, Biomedical; Materials Science, Biomaterials	Nanohorn	Delivery Carriers, and Controlled Release of Drugs/Compounds	CCNH
785	2012	Electrochemical sensing platform based on Schiff-base cobalt(II)/single-walled carbon nanohorns complexes system	Lu, BP; Zhang, Z; Hao, JH; Xu, GB; Zhang,	Chemistry, Analytical; Food Science & Technology;	Nanohorn	Sensors/biosensors/electrochemical sensors	CCNH

			BL; Tang, JL	Spectroscopy			
Selected Nanobud Publications							
786	2007	Investigations of NanoBud formation	Nasibulin, AG; Anisimov, AS; Pikhitsa, PV; Jiang, H; Brown, DP; Choi, M; Kauppinen, EI	Chemistry, Physical; Physics, Atomic, Molecular & Chemical	Nanobud	Synthesis of new nanohybrids/materials	CCNH
787	2008	WS2 nanobuds as a new hybrid nanomaterial	Remskar, M; Virsek, M; Jesih, A	Chemistry, Multidisciplinary; Chemistry, Physical; Nanoscience & Nanotechnology; Materials Science, Multidisciplinary; Physics, Applied; Physics, Condensed Matter	Nanobud	Synthesis of new nanohybrids/materials	CCNH
788	2008	Combined Raman spectroscopy and transmission electron microscopy studies of a NanoBud structure	Tian, Y; Chassaing, D; Nasibulin, AG; Ayala, P; Jiang, H; Anisimov, AS; Kauppinen, EI	Chemistry, Multidisciplinary	Nanobud	Synthesis of new nanohybrids/materials	CCNH
789	2008	First-principles study of a carbon nanobud	Wu, XJ; Zeng, XC	Chemistry, Multidisciplinary; Chemistry, Physical; Nanoscience & Nanotechnology; Materials Science, Multidisciplinary	Nanobud	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
790	2008	The local study of a nanoBud structure	Tian, Y; Chassaing, D; Nasibulin, AG; Ayala, P; Jiang, H; Anisimov, AS; Hassanien, A; Kauppinen, EI	Physics, Condensed Matter	Nanobud	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
791	2009	Periodic Graphene Nanobuds	Wu, XJ; Zeng, XC	Chemistry, Multidisciplinary; Chemistry, Physical; Nanoscience & Nanotechnology; Materials Science, Multidisciplinary; Physics, Applied; Physics, Condensed Matter	Nanobud	Synthesis of new nanohybrids/materials	CCNH
792	2009	Magnetism in hybrid carbon nanostructures: Nanobuds	Zhu, X; Su, HB	Physics, Condensed Matter	Nanobud	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
793	2009	Detection of Neural Signals with Vertically Grown Single Platinum Nanowire-Nanobud	Choi, DS; Fung, AO; Moon, H; Villareal, G; Chen, Y; Ho, D; Presser, N; Stupian, G; Leung, M	Chemistry, Multidisciplinary; Nanoscience & Nanotechnology; Materials Science, Multidisciplinary; Physics, Applied; Physics, Condensed Matter	Nanobud	Sensors/biosensors/electrochemical sensors	CCNH
794	2009	Electronic Structures and Raman Features of a Carbon Nanobud	He, HY; Pan, BC	Chemistry, Physical; Nanoscience & Nanotechnology; Materials Science,	Nanobud	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li	CCNH

				Multidisciplinary		Batteries, and Electronic Applications	
795	2009	Interaction between nanobuds and hydrogen molecules: A first-principles study	Wang, XX; Ma, CG; Chen, K; Li, HNA; Wang, P	Physics, Multidisciplinary	Nanobud	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
796	2010	Discrete and Continuous Approximations for Nanobuds	Baowan, D; Cox, BJ; Hill, JM	Chemistry, Physical; Nanoscience & Nanotechnology; Materials Science, Multidisciplinary; Physics, Atomic, Molecular & Chemical	N/A	N/A	N/A
797	2010	First-principles study of the electronic transport properties of the carbon nanobuds	Zhao, P; Wang, PJ; Zhang, Z; Ren, MJ; Liu, DS	Physics, Condensed Matter	Nanobud	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
798	2010	Selective Covalent Functionalization of Carbon Nanobuds	Raula, J; Makowska, M; Lahtinen, J; Sillanpaa, A; Runeberg, N; Tarus, J; Heino, M; Seppala, ET; Jiang, H; Kauppinen, EI	Chemistry, Physical; Materials Science, Multidisciplinary	Nanobud	Synthesis of new nanohybrids/materials	CCNH
799	2010	Temperature Dependent Raman Spectra of Carbon Nanobuds	He, MS; Rikkinen, E; Zhu, Z; Tian, Y; Anisimov, AS; Jiang, H; Nasibulin, AG; Kauppinen, EI; Niemela, M; Krause, AOI	Chemistry, Physical; Nanoscience & Nanotechnology; Materials Science, Multidisciplinary	Nanobud	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
800	2010	A comparative study of field emission from NanoBuds, nanographite and pure or N-doped single-wall carbon nanotubes	Kleshch, VI; Susi, T; Nasibulin, AG; Obraztsova, ED; Obraztsov, AN; Kauppinen, EI	Physics, Condensed Matter	Nanobud	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CCNH
801	2011	Magnetic properties of all-carbon graphene-fullerene nanobuds	Wang, M; Li, CM	Chemistry, Physical; Physics, Atomic, Molecular & Chemical	Nanobud	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
802	2011	A DFT study of carbon nanobuds	Seif, A; Zahedi, E; Ahmadi, TS	Physics, Condensed Matter	N/A	N/A	N/A
803	2012	Fabrication of Highly Rough Ag Nanobud Substrates and Surface-Enhanced Raman Scattering of lambda-DNA Molecules	Deng, CY; Ma, WY; Sun, JL	Nanoscience & Nanotechnology; Materials Science, Multidisciplinary	Nanobud	Synthesis of new nanohybrids/materials	CCNH
804	2012	Mechanical Properties of Graphene Nanobuds: A Molecular Dynamics Study	Zheng, YP; Xu, LQ; Fan, ZY; Wei, N; Lu, Y; Huang, ZG	Biotechnology & Applied Microbiology; Nanoscience & Nanotechnology; Materials Science, Multidisciplinary	Nanobud	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
805	2012	Effects of chemical functionalization	Havu, P;	Physics, Condensed	Nanobud	Energy/Electron	CCNH

		on electronic transport in carbon nanobuds	Sillanpaa, A; Runeberg, N; Tarus, J; Seppala, ET; Nieminen, RM	Matter		Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	
806	2012	Selective chemical functionalization of carbon nanobuds	Anoshkin, IV; Nasibulin, AG; Mudimela, PR; Raula, J; Ermolou, V; Kauppinen, EI	Chemistry, Physical; Materials Science, Multidisciplinary	Nanobud	Synthesis of new nanohybrids/materials	CCNH
Selected Peapod Publications							
807	2002	Mapping the one-dimensional electronic states of nanotube peapod structures	Hornbaker, DJ; Kahng, SJ; Misra, S; Smith, BW; Johnson, AT; Mele, EJ; Luzzi, DE; Yazdani, A	Multidisciplinary Sciences	Peapod	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CCNH
808	2002	Theory of scanning tunneling spectroscopy of fullerene peapods	Kane, CL; Mele, EJ; Johnson, AT; Luzzi, DE; Smith, BW; Hornbaker, DJ; Yazdani, A	Physics, Condensed Matter	N/A	N/A	N/A
809	2003	Quantum conductance of carbon nanotube peapods	Yoon, YG; Mazzoni, MSC; Louie, SG	Physics, Applied	Peapod	Semiconductors/superconductors/conductive materials	CCNH
810	2004	Electronic properties of potassium-intercalated C-60 peapods	Liu, X; Pichler, T; Knupfer, M; Fink, J; Kataura, H	Physics, Condensed Matter	Peapod	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CCNH
811	2004	Density functional calculations for C-60 peapods	Dubay, O; Kresse, G	Physics, Condensed Matter	N/A	N/A	N/A
812	2005	Energetics and electronic structures of potassium-intercalated C-60 peapods	Okada, S	Physics, Condensed Matter	N/A	N/A	N/A
813	2005	Influence of the C-60 filling on the nature of the metallic ground state in intercalated peapods	Rauf, H; Shiozawa, H; Pichler, T; Knupfer, M; Buchner, B; Kataura, H	Physics, Condensed Matter	Peapod	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
814	2006	Novel carbon nanotube peapods encapsulating Au-32 golden fullerene	Zhao, JJ; Wen, B; Zhou, Z; Li, TJ; Chen, ZF; Schleyer, PV; Xie, JRH	Chemistry, Multidisciplinary; Nanoscience & Nanotechnology; Materials Science, Multidisciplinary; Physics, Applied; Physics, Condensed Matter	Peapod	Synthesis of new nanohybrids/materials	CCNH
815	2006	Enhancement of inner tube formation from peapods in de-pressurized inert gas environment	Fujita, Y; Niwa, N; Bandow, S; Iijima, S	Materials Science, Multidisciplinary; Physics, Applied	Peapod	Synthesis of new nanohybrids/materials	CCNH
816	2008	Modeling spin interactions in carbon peapods using a hybrid density functional theory	Ge, L; Montanari, B; Jefferson, JH; Pettifor, DG; Harrison, NM; Briggs, GAD	Physics, Condensed Matter	N/A	N/A	N/A

817	2008	Photoemission study of electronic structures of fullerene and metallofullerene peapods	Nakayama, Y; Fujiki, S; Hirado, Y; Shiozawa, H; Ishii, H; Miyahara, T; Maniwa, Y; Kodama, T; Achiba, Y; Kataura, H; Kubozono, Y; Nakatake, M; Saitoh, T	Physics, Condensed Matter	Peapod	Fluorescence/luminescence/photoluminescence, light-energy harvesting	CCNH
818	2009	Effects of Doping on Electronic Structure and Correlations in Carbon Peapods	Ge, L; Jefferson, JH; Montanari, B; Harrison, NM; Pettifor, DG; Briggs, GAD	Chemistry, Multidisciplinary; Chemistry, Physical; Nanoscience & Nanotechnology; Materials Science, Multidisciplinary	Peapod	Synthesis of new nanohybrids/materials	CCNH
819	2010	Host-guest interactions in azafullerene (C59N)-single-wall carbon nanotube (SWCNT) peapod hybrid structures	Iizumi, Y; Okazaki, T; Liu, Z; Suenaga, K; Nakanishi, T; Iijima, S; Rotas, G; Tagmatarchis, N	Chemistry, Multidisciplinary	Peapod	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
820	2010	Transport via coupled states in a C-60 peapod quantum dot	Eliasen, A; Paaske, J; Flensberg, K; Smerat, S; Leijnse, M; Wegewijs, MR; Jorgensen, HI; Monthioux, M; Nygard, J	Physics, Condensed Matter	Peapod	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
821	2012	Predicting the electronic structure of weakly interacting hybrid systems: The example of nanosized peapod structures	Milko, M; Puschnig, P; Draxl, C	Physics, Condensed Matter	N/A	N/A	N/A
			Selected Nanoonion Publications				
822	1999	Optical properties of Si-Ge semiconductor nano-onions	Hill, NA; Pokrant, S; Hill, AJ	Chemistry, Physical	Nanoonion	Optical imaging and applications	CCNH
823	2000	Phenomenological magnetic modeling of Au : Fe : Au nano-onions	Wiggins, J; Carpenter, EE; O'Connor, CJ	Physics, Applied	Nanoonion	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
824	2001	Growth of fullerene-like carbon nitride thin solid films consisting of cross-linked nano-onions	Czigany, Z; Brunell, IF; Neidhardt, J; Hultman, L; Suenaga, K	Physics, Applied	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
825	2001	Cross-linked nano-onions of carbon nitride in the solid phase: Existence of a novel C48N12 aza-fullerene	Hultman, L; Stafstrom, S; Czigany, Z; Neidhardt, J; Hellgren, N; Brunell, IF; Suenaga, K; Colliex, C	Physics, Multidisciplinary	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
826	2002	Stability of carbon nanoonion C-20@C-60@C-240: Molecular dynamics simulations	Erkoc, S	Chemistry, Multidisciplinary; Chemistry, Physical; Nanoscience & Nanotechnology;	N/A	N/A	N/A

				Materials Science, Multidisciplinary; Physics, Applied; Physics, Condensed Matter			
827	2002	Magneto-optical effects calculated for granular composites with magnetized nano-onions dispersed in matrixes	Abe, M; Kuroda, J	Physics, Applied	Nanoonion	Optical imaging and applications	CCNH
828	2002	Templating effect of hydrogen-passivated silicon nanowires in the production of hydrocarbon nanotubes and nanoonions via sonochemical reactions with common organic solvents under ambient conditions	Sun, XH; Li, CP; Wong, NB; Lee, CS; Lee, ST; Teo, BK	Chemistry, Multidisciplinary	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
829	2003	Characterisation of carbon nano-onions using Raman spectroscopy	Roy, D; Chhowalla, M; Wang, H; Sano, N; Alexandrou, I; Clyne, TW; Amaratunga, GAJ	Chemistry, Physical; Physics, Atomic, Molecular & Chemical	Nanoonion	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
830	2004	Evaluation of the tribological behavior of nano-onions in Krytox 143AB	Street, KW; Marchetti, M; Vander Wal, RL; Tomasek, AJ	Engineering, Chemical; Engineering, Mechanical	Nanoonion	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
831	2004	The preparation of nano-onion-like fullerencs by arc discharge	Zhang, HX; Wang, XM; Wang, HY; Liu, XG; Xu, BS	Materials Science, Multidisciplinary	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
832	2005	Magneto-optical enhancement by surface plasmon resonance in magnetic "nano-onions" with multicore-shell structures	Abe, M; Takeshi, S	Physics, Applied	Nanoonion	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
833	2005	Molecular characterization of the cytotoxic mechanism of multiwall carbon nanotubes and nano-onions on human skin fibroblast	Ding, LH; Stilwell, J; Zhang, TT; Elboudwarej, O; Jiang, HJ; Selegue, JP; Cooke, PA; Gray, JW; Chen, FQF	Chemistry, Multidisciplinary; Chemistry, Physical; Nanoscience & Nanotechnology; Materials Science, Multidisciplinary; Physics, Applied; Physics, Condensed Matter	Nanoonion	Medicine (cancer research, biocompatibility, biomedical apps, bone regeneration/repair)	CCNH
834	2006	Preparation and functionalization of multilayer fullerenes (carbon nano-onions)	Rettenbacher, AS; Elliott, B; Hudson, JS; Amirkhanian, A; Echegoyen, L	Chemistry, Multidisciplinary	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
835	2006	Study on electromagnetic property of nano onion-like fullerenes	Ge, AY; Xu, BS; Wang, XM; Li, TB; Han, PD; Liu, XG	Chemistry, Physical	Nanoonion	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
836	2006	Production of carbon nanoonions and nanotubes using an intermittent arc discharge in water	Imasaka, K; Kanatake, Y; Ohshiro, Y; Suehiro, J; Hara, M	Materials Science, Multidisciplinary; Materials Science, Coatings & Films; Physics, Applied; Physics, Condensed Matter	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
837	2006	Strain distributions in nano-onions with uniform and non-uniform compositions	Duan, HL; Karihaloo, BL; Wang, J;	Nanoscience & Nanotechnology; Materials Science,	Nanoonion	Semiconductors/superconductors/conductive materials	CCNH

			Yi, X	Multidisciplinary; Physics, Applied			
838	2006	Semiconductor "nano-onions" with multifold alternating CdS/CdSe or CdSe/CdS structure	Pan, DC; Wang, Q; Pang, JB; Jiang, SC; Ji, XL; An, LJ	Chemistry, Physical; Materials Science, Multidisciplinary	Nanoonion	Semiconductors/superconductors/conductive materials	CCNH
839	2007	Reactivity differences between carbon nano onions (CNOs) prepared by different methods	Palkar, A; Melin, F; Cardona, CM; Elliott, B; Naskar, AK; Edie, DD; Kumbhar, A; Echegoyen, L	Chemistry, Multidisciplinary	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
840	2007	Functionalization of carbon nano-onions by direct fluorination	Liu, Y; Vander Wal, RL; Khabashesku, VN	Chemistry, Physical; Materials Science, Multidisciplinary	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
841	2007	Radical addition of a conjugated polymer to multilayer fullerenes (carbon nano-onions)	Rettenbacher, AS; Perpall, MW; Echegoyen, L; Hudson, J; Smith, DW	Chemistry, Physical; Materials Science, Multidisciplinary	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
842	2007	Plasma characterization and room temperature growth of carbon nanotubes and nano-onions by excimer laser ablation	Radhakrishnan, G; Adams, PM; Bernstein, LS	Chemistry, Physical; Materials Science, Coatings & Films; Physics, Applied; Physics, Condensed Matter	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
843	2007	Carbon nano-onions prepared by arc-discharge in water	Jiang, P; Yao, KF	Materials Science, Multidisciplinary	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
844	2008	Pyridyl-functionalized and water-soluble carbon nano onions: First supramolecular complexes of carbon nano onions	Palkar, A; Kumbhar, A; Athans, AJ; Echegoyen, L	Chemistry, Physical; Materials Science, Multidisciplinary	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
845	2008	Anti-wear and friction reducing mechanisms of carbon nano-onions as lubricant additives	Joly-Pottuz, L; Vacher, B; Ohmae, N; Martin, JM; Epicier, T	Engineering, Chemical; Engineering, Mechanical	Nanoonion	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CCNH
846	2008	Fe-encapsulating carbon nano onionlike fullerenes from heavy oil residue	Yang, Y; Liu, X; Xu, B	Materials Science, Multidisciplinary	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
847	2009	Facile Functionalization of Multilayer Fullerenes (Carbon Nano-Onions) by Nitrene Chemistry and "Grafting from" Strategy	Zhou, L; Gao, C; Zhu, D; Xu, W; Chen, FF; Palkar, A; Echegoyen, L; Kong, ESW	Chemistry, Multidisciplinary	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
848	2009	A Carbon Nano-Onion-Ferrocene Donor-Acceptor System: Synthesis, Characterization and Properties	Cioffi, CT; Palkar, A; Melin, F; Kumbhar, A; Echegoyen, L; Melle-Franco, M; Zerbetto, F; Rahman, GMA; Ehli, C; Sgobba, V; Guldi, DM; Prato, M	Chemistry, Multidisciplinary	Nanoonion	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CCNH
849	2009	Synthesis of nano onion-like fullerenes by using Fe/Al2O3 as catalyst by chemical vapor deposition	Liu, XG; Wang, CJ; Yang, YZ; Guo, XM;	Multidisciplinary Sciences	Nanoonion	Synthesis of new nanohybrids/materials	CCNH

			Wen, HR; Xu, BS				
850	2009	High-yield synthesis of carbon nano-onions in counterflow diffusion flames	Hou, SS; Chung, DH; Lin, TH	Chemistry, Physical; Materials Science, Multidisciplinary	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
851	2009	The mechanism of growth and decay of carbon nano-onions formed by ordering of amorphous particles	Szerencsi, M; Radnoczi, G	Materials Science, Multidisciplinary; Physics, Applied	Nanoonion	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
852	2010	Small Noncytotoxic Carbon Nano-Onions: First Covalent Functionalization with Biomolecules	Luszczyn, J; Plonska-Brzezinska, ME; Palkar, A; Dubis, AT; Simionescu, A; Simionescu, DT; Kalska-Szostko, B; Winkler, K; Echegoyen, L	Chemistry, Multidisciplinary	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
853	2010	Electrochemical Properties of Small Carbon Nano-Onion Films	Plonska-Brzezinska, ME; Palkar, A; Winkler, K; Echegoyen, L	Electrochemistry; Materials Science, Multidisciplinary	Nanoonion	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
854	2010	Electrochemical properties of composites containing small carbon nano-onions and solid polyelectrolytes	Breczko, J; Winkler, K; Plonska-Brzezinska, ME; Villalta-Cerdas, A; Echegoyen, L	Chemistry, Physical; Materials Science, Multidisciplinary	Nanoonion	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
855	2010	Friction Properties of Carbon Nano-Onions from Experiment and Computer Simulations	Joly-Pottuz, L; Bucholz, EW; Matsumoto, N; Phillpot, SR; Sinnott, SB; Ohmae, N; Martin, JM	Engineering, Chemical; Engineering, Mechanical	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
856	2010	Functionalization of Multilayer Fullerenes (Carbon Nano-Onions) using Diazonium Compounds and "Click" Chemistry	Flavin, K; Chaur, MN; Echegoyen, L; Giordani, S	Chemistry, Organic	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
857	2010	Observation of Hybrid Carbon Nanostructures as Intermediates in the Transformation from Hydrocarbon Nanotubes and Nano-onions to Carbon Nanotubes and Nano-onions via Sonolysis on Silicon Nanowires and Nanodots, Respectively	Teo, BK; Sun, XH; Li, CP; Wong, NB; Lee, ST	Chemistry, Physical; Materials Science, Multidisciplinary	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
858	2010	Solubilization of carbon nanoparticles, nanotubes, nano-onions, and nanodiamonds through covalent functionalization with sucrose	Kuznetsov, OV; Pulikkathara, MX; Lobo, RFM; Khabashesku, VN	Chemistry, Multidisciplinary	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
859	2010	Edge-Mediated Dislocation Processes in Multishell Carbon Nano-Onions?	Akatyeva, E; Huang, JY; Dumitrica, T	Physics, Multidisciplinary	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
860	2010	Flame synthesis of carbon nano-onions enhanced by acoustic modulation	Chung, DH; Lin, TH; Hou, SS	Nanoscience & Nanotechnology; Materials Science, Multidisciplinary; Physics, Applied	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
861	2011	Effect of high pressures and	Dubitsky, GA;	Chemistry,	Nanoonion	Physical/electrical/mec	CCNH

		temperatures on carbon nano-onion structures: comparison with C-60	Serebryanaya, NR; Blank, VD; Skryleva, EA; Kulnitsky, BA; Mavrin, BN; Aksenenkov, VV; Bagramov, RK; Denisov, VN; Perezhogin, IA	Multidisciplinary		hanical properties (thermal, resistance, magnetic)	
862	2011	The efficient synthesis of carbon nano-onions using chemical vapor deposition on an unsupported Ni-Fe alloy catalyst	Zhang, CG; Li, JJ; Shi, CS; Liu, EZ; Du, XW; Feng, W; Zhao, NQ	Chemistry, Physical; Materials Science, Multidisciplinary	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
863	2011	Resonant excitation of precursor molecules in improving the particle crystallinity, growth rate and optical limiting performance of carbon nano-onions	Gao, Y; Zhou, YS; Park, JB; Wang, H; He, XN; Luo, HF; Jiang, L; Lu, YF	Nanoscience & Nanotechnology; Materials Science, Multidisciplinary; Physics, Applied	Nanoonion	Optical imaging and applications	CCNH
864	2011	Synthesis of nano onion-like fullerenes by chemical vapor deposition using an iron catalyst supported on sodium chloride	Yang, YZ; Liu, XG; Guo, XM; Wen, HR; Xu, BS	Chemistry, Multidisciplinary; Nanoscience & Nanotechnology; Materials Science, Multidisciplinary	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
865	2011	Preparation of Carbon Nano-Onions and Their Application as Anode Materials for Rechargeable Lithium-Ion Batteries	Han, FD; Yao, B; Bai, YJ	Chemistry, Physical; Nanoscience & Nanotechnology; Materials Science, Multidisciplinary	Nanoonion	Energy/Electron Transfer, Donor/Acceptor, Solar/Fuel Cells/Ion-Li Batteries, and Electronic Applications	CCNH
866	2011	Electrochemical Properties of Oxidized Carbon Nano-Onions: DRIFTS-FTIR and Raman Spectroscopic Analyses	Plonska-Brzezinska, ME; Dubis, AT; Lapinski, A; Villalta-Cerdas, A; Echegoyen, L	Chemistry, Physical; Physics, Atomic, Molecular & Chemical	Nanoonion	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
867	2011	Transformation of nano-diamonds to carbon nano-onions studied by X-ray diffraction and molecular dynamics	Hawelek, L; Brodka, A; Tomita, S; Dore, JC; Honkimaki, V; Burian, A	Materials Science, Multidisciplinary	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
868	2011	Carbon Nano-onions for Imaging the Life Cycle of Drosophila Melanogaster	Ghosh, M; Sonkar, SK; Saxena, M; Sarkar, S	Chemistry, Multidisciplinary; Chemistry, Physical; Nanoscience & Nanotechnology; Materials Science, Multidisciplinary; Physics, Applied; Physics, Condensed Matter	Nanoonion	Optical imaging and applications	CCNH
869	2011	The synthesis and characterization of carbon nano-onions produced by solution ozonolysis	Plonska-Brzezinska, ME; Lapinski, A; Wilczewska, AZ; Dubis, AT; Villalta-Cerdas, A;	Chemistry, Physical; Materials Science, Multidisciplinary	Nanoonion	Synthesis of new nanohybrids/materials	CCNH

			Winkler, K; Echegoyen, L				
870	2012	Microfluidic size selective growth of palladium nano-particles on carbon nano-onions	Yasin, FM; Boulos, RA; Hong, BY; Cornejo, A; Iyer, KS; Gao, LZ; Chua, HT; Raston, CL	Chemistry, Multidisciplinary	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
871	2012	Water soluble carbon nano-onions from wood wool as growth promoters for gram plants	Sonkar, SK; Roy, M; Babar, DG; Sarkar, S	Chemistry, Multidisciplinary; Nanoscience & Nanotechnology; Materials Science, Multidisciplinary; Physics, Applied	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
872	2012	Preparation and Characterization of Composites that Contain Small Carbon Nano-Onions and Conducting Polyaniline	Plonska-Brzezinska, ME; Mazurczyk, J; Palys, B; Breczko, J; Lapinski, A; Dubis, AT; Echegoyen, L	Chemistry, Multidisciplinary	Nanoonion	Physical/electrical/mechanical properties (thermal, resistance, magnetic)	CCNH
873	2012	Molecular dynamics investigation of the lubrication mechanism of carbon nano-onions	Bucholz, EW; Phillpot, SR; Sinnott, SB	Materials Science, Multidisciplinary	N/A	N/A	N/A
874	2012	Carbon Nano-Onions as Nontoxic and High-Fluorescence Bioimaging Agent in Food Chain-An In Vivo Study from Unicellular E. coli to Multicellular C-elegans	Sonkar, SK; Ghosh, M; Roy, M; Begum, A; Sarkar, S	Nanoscience & Nanotechnology; Materials Science, Multidisciplinary	Nanoonion	Optical imaging and applications	CCNH
875	2012	Dynamics of Phenanthrenequinone on Carbon Nano-Onion Surfaces Probed by Quasielastic Neutron Scattering	Chathoth, SM; Anjos, DM; Mamontov, E; Brown, GM; Overbury, SH	Chemistry, Physical	N/A	N/A	N/A
876	2012	Electrochemical oxidation and determination of dopamine in the presence of uric and ascorbic acids using a carbon nano-onion and poly(diallyldimethylammonium chloride) composite	Breczko, J; Plonska-Brzezinska, ME; Echegoyen, L	Electrochemistry	Nanoonion	Sensors/biosensors/electrochemical sensors	CCNH
877	2012	Electrochemical Study of Functionalized Carbon Nano-Onions for High-Performance Supercapacitor Electrodes	Borgohain, R; Li, JC; Selegue, JP; Cheng, YT	Chemistry, Physical; Nanoscience & Nanotechnology; Materials Science, Multidisciplinary	Nanoonion	Semiconductors/superconductors/conductive materials	CCNH
878	2012	Synthesis of hollow carbon nano-onions and their use for electrochemical hydrogen storage	Zhang, CG; Li, JJ; Liu, EZ; He, CN; Shi, CS; Du, XW; Hauge, RH; Zhao, NQ	Chemistry, Physical; Materials Science, Multidisciplinary	Nanoonion	Synthesis of new nanohybrids/materials	CCNH
879	2012	Characterization of carbon nano-onions for heavy metal ion remediation	Seymour, MB; Su, CM; Gao, Y; Lu, YF; Li, YS	Chemistry, Multidisciplinary; Nanoscience & Nanotechnology; Materials Science, Multidisciplinary	Nanoonion	Adsorption studies	CCNH
880	2012	Platinum Electrodeposition on Unsupported Carbon Nano-Onions	Santiago, D; Rodriguez-Calero, GG; Palkar, A; Barraza-Jimenez, D; Galvan, DH; Casillas, G;	Chemistry, Multidisciplinary; Chemistry, Physical; Materials Science, Multidisciplinary	Nanoonion	Adsorption studies	CCNH

			Mayoral, A; Jose-Yacaman, M; Echegoyen, L; Cabrera, CR				
881	2012	Preparation and Characterization of Carbon Nano-Onion/PEDOT:PSS Composites	Plonska-Brzezinska, ME; Lewandowski, M; Blaszyk, M; Molina-Ontoria, A; Lucinski, T; Echegoyen, L	Chemistry, Physical; Physics, Atomic, Molecular & Chemical	Nanoonion	Synthesis of new nanohybrids/materials	CCNH

TABLE A-4. Specific examples of nanohybrid class, specific type of nanohybrid, and synthesis process used.

NH Class	Specific Types	Synthesis process used	Citations
CCNH	Fullerene-CNT peapods	Thermal annealing of SWNTs	Smith, B. W.; Monthioux, M.; Luzzi, D. E., Encapsulated C-60 in carbon nanotubes. *Nature* **1998,** *396*, (6709), 323-324
		Refluxing mixture of fullerenes and SWNTs in n-hexane solvent	Simon, F.; Kuzmany, H.; Rauf, H.; Pichler, T.; Bernardi, J.; Peterlik, H.; Korecz, L.; Fülöp, F.; Jánossy, A., Low temperature fullerene encapsulation in single wall carbon nanotubes: synthesis of N@C60@SWCNT. *Chemical Physics Letters* **2004,** *383*, (3–4), 362-367.
	Graphene-CNT peapods	In-situ growth from vapor-based deposition reactions	Lv, R.; Cui, T.; Jun, M.-S.; Zhang, Q.; Cao, A.; Su, D. S.; Zhang, Z.; Yoon, S.-H.; Miyawaki, J.; Mochida, I.; Kang, F., Open-Ended, N-Doped Carbon Nanotube-Graphene Hybrid Nanostructures as High-Performance Catalyst Support. *Adv. Funct. Mater.* **2011,** *21*, (5), 999-1006.
	Carbon nano-onions	Water assisted arc discharge	Imasaka, K.; Kanatake, Y.; Ohshiro, Y.; Suehiro, J.; Hara, M., Production of carbon nanoonions and nanotubes using an intermittent arc discharge in water. *Thin Solid Films* **2006,** *506*, 250-254.
		Chemical vapor depositon: Catalytic deposition decomposition of acetylene using Fe/Al_2O_3 as catalyst	Liu, X.; Wang, C.; Yang, Y.; Guo, X.; Wen, H.; Xu, B., Synthesis of nano onion-like fullerenes by using Fe/Al_2O_3 as catalyst by chemical vapor deposition. *Chinese Science Bulletin* **2009,** *54*, (1), 137-141.
		Water and thermal annealing of fullerenes	Palkar, A.; Melin, F.; Cardona, C. M.; Elliott, B.; Naskar, A. K.; Edie, D. D.; Kumbhar, A.; Echegoyen, L., Reactivity differences between carbon nano onions (CNOs) prepared by different methods. *Chem.-Asian J.* **2007,** *2*, (5), 625-633
		Arc discharge	Zhang, H. X.; Wang, X. M.; Wang, H. Y.; Liu, X. G.; Xu, B. S., The preparation of nano-onion-like fullerencs by arc discharge. *New Carbon Materials* **2004,** *19*, (1), 61-64.
	CNT-graphene exohedral hybrid	In-situ growth of SWNTs from the graphene (Co-valent structure)	Zhu, Y.; Li, L.; Zhang, C. G.; Casillas, G.; Sun, Z. Z.; Yan, Z.; Ruan, G. D.; Peng, Z. W.; Raji, A. R. O.; Kittrell, C.; Hauge, R. H.; Tour, J. M., A seamless three-dimensional carbon nanotube graphene hybrid material. *Nat. Commun.* **2012,** *3*.
		Ultrasonic mixing of graphene oxide and CNT colloidal suspensions (Non-covalent)	Chen, S.; Yeoh, W.; Liu, Q.; Wang, G., Chemical-free synthesis of graphene–carbon nanotube hybrid materials for reversible lithium storage in lithium-ion batteries. *Carbon* **2012,** *50*, (12), 4557-4565
		Layer-by-layer assemblies by dipping substate alternately in solutions of functionalized CNTs and polymer-graphene suspension	Yu, D.; Dai, L., Self-Assembled Graphene/Carbon Nanotube Hybrid Films for Supercapacitors. *The Journal of Physical Chemistry Letters* **2009,** *1*, (2), 467-470
	Fullerene-grpahene hybrid	Non-covalent functionalization using pyrene as linker	Qu, S.; Li, M.; Xie, L.; Huang, X.; Yang, J.; Wang, N.; Yang, S., Noncovalent Functionalization of Graphene Attaching 6,6 -Phenyl-C61-butyric Acid Methyl Ester (PCBM) and Application as Electron Extraction Layer of Polymer Solar Cells. *ACS nano* **2013,** *7*, (5), 4070-81
		Layer-by-layer assemblies of functionalized graphene with polymer-fullerene by spin-casting	Wang, J.; Wang, Y.; He, D.; Wu, H.; Wang, H.; Zhou, P.; Fu, M., Influence of Polymer/Fullerene-Graphene Structure on Organic Polymer Solar Devices. *Integrated Ferroelectrics* **2012,** *137*, (1), 1-9.
	CNT-fullerene exohendral hybrid	Covalent functionalization of CNTs by fullerene derivatives	Wu, W.; Zhu, H. R.; Fan, L. Z.; Yang, S. H., Synthesis and characterization of a grapevine nanostructure consisting of single-walled carbon nanotubes with covalently attached 60 fullerene balls. *Chem.-Eur. J.* **2008,** *14*, (19), 5981-5987.
		Catalytic vapor decomposition on iron catalyst for Nano-bud formation	Nasibulin, A. G.; Pikhitsa, P. V.; Jiang, H.; Brown, D. P.; Krasheninnikov, A. V.; Anisimov, A. S.; Queipo, P.; Moisala, A.; Gonzalez, D.; Lientschnig, G.; Hassanien, A.; Shandakov, S. D.; Lolli, G.; Resasco, D. E.; Choi, M.; Tomanek, D.; Kauppinen, E. I., A novel hybrid carbon material. *Nat Nano* **2007,** *2*, (3), 156-161
CMNH	Metal inside fullerenes	Vapor deposition using ferrocene pyrolysis	Watts, P. C. P.; Hsu, W. K.; Randall, D. P.; Kotzeva, V.; Chen, G. Z., Fe-filled carbon nanotubes: Nano-electromagnetic inductors.

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		Heating SWNT with molten metal	Thamavaranukup, N.; Hoppe, H. A.; Ruiz-Gonzalez, L.; Costa, P.; Sloan, J.; Kirkland, A.; Green, M. L. H., Single-walled carbon nanotubes filled with M OH (M = K, Cs) and then washed and refilled with clusters and molecules. *Chemical Communications* **2004**, (15), 1686-1687
		Thermal annealing of SWNTs	Chancolon, J.; Archaimbault, F.; Pineau, A.; Bonnamy, S., Filling of carbon nanotubes with selenium by vapor phase process. *J. Nanosci. Nanotechnol.* **2006,** *6*, (1), 82-86 Kim, B. M.; Qian, S.; Bau, H. H., Filling carbon nanotubes with particles. *Nano Lett.* **2005,** *5*, (5), 873-878
		Wet capillary approach	Dujardin, e.; ebbesen, t. W.; hiura, h.; tanigaki, k., Capillarity and wetting of carbon nanotubes. *Science* **1994,** *265*, (5180), 1850-1852
	Endohedral metallofullerenes	Chemical vapor deposition	Shinohara, H., Endohedral metallofullerenes. *Reports on Progress in Physics* **2000,** *63*, (6), 843-892
		Arc discharge	Shinohara, H.; Takata, M.; Sakata, M.; Hashizume, T.; Sakurai, T., Metallofullerenes: Their formation and characterization. In *Cluster Assembled Materials*, Sattler, K., Ed. 1996; Vol. 232, pp 207-232
	MNP-CNM conjugation via linkers	Noncovalent conjugation of SWNT and Zinc via pyrene or naphthalocyanine	Chitta, R.; Sandanayaka, A. S. D.; Schumacher, A. L.; D'Souza, L.; Araki, Y.; Ito, O.; D'Souza, F., Donor-acceptor nanohybrids of zinc naphthalocyanine or zinc porphyrin noncovalently linked to single-wall carbon nanotubes for photoinduced electron transfer. *J. Phys. Chem. C* **2007,** *111*, (19), 6947-6955.
		Noncovalent conjugation of graphene and AuNP using DNA as linker	Liu, J. B.; Li, Y. L.; Li, Y. M.; Li, J. H.; Deng, Z. X., Noncovalent DNA decorations of graphene oxide and reduced graphene oxide toward water-soluble metal-carbon hybrid nanostructures via self-assembly. *J. Mater. Chem.* **2010,** *20*, (5), 900-906
		TiO_2 porphyrin dentate binding onto carboxyl functionalized carbon nanohorns	Tu, W.; Lei, J.; Ding, L.; Ju, H., Sandwich nanohybrid of single-walled carbon nanohorns-TiO2-porphyrin for electrocatalysis and amperometric biosensing towards chloramphenicol. *Chemical Communications* **2009,** *0*, (28), 4227-4229
	MNP direct deposition onto CNMs	Sol-gel	Ning, J. W.; Zhang, J. J.; Pan, Y. B.; Guo, J. K., Surfactants assisted processing of carbon nanotube-reinforced SiO2 matrix composites. *Ceram. Int.* **2004,** *30*, (1), 63-67
		Sol-gel plus plasma treatment	Li, H. Q.; Ha, C. S.; Kim, I., Fabrication of Carbon Nanotube/SiO2 and Carbon Nanotube/SiO2/Ag Nanoparticles Hybrids by Using Plasma Treatment. *Nanoscale Res. Lett.* **2009,** *4*, (11), 1384-1388
		Hydrothermal	Ding, S. J.; Luan, D. Y.; Boey, F. Y. C.; Chen, J. S.; Lou, X. W., SnO2 nanosheets grown on graphene sheets with enhanced lithium storage properties. *Chemical Communications* **2011,** *47*, (25), 7155-7157
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		Microemulsion	Moriguchi, I.; Hidaka, R.; Yamada, H.; Kudo, T.; Murakami, H.; Nakashima, N., A Mesoporous Nanocomposite of TiO_2 and Carbon Nanotubes as a High-Rate Li-Intercalation Electrode Material. *Advanced Materials* **2006,** *18*, (1), 69-73
		Magnetron sputtering	Wei-De, Z., Growth of ZnO nanowires on modified well-aligned carbon nanotube arrays. *Nanotechnology* **2006,** *17*, (4), 1036
		Pulsed laser deposition	Ikuno, T.; Yasuda, T.; Honda, S. I.; Oura, K.; Katayama, M.; Lee, J. G.; Mori, H., Coating carbon nanotubes with inorganic materials by pulsed laser deposition. *J. Appl. Phys.* **2005,** *98*, (11)
		Chemical vapor deposition	Kuang, Q.; Li, S.-F.; Xie, Z.-X.; Lin, S.-C.; Zhang, X.-H.; Xie, S.-Y.; Huang, R.-B.; Zheng, L.-S., Controllable fabrication of SnO2-coated multiwalled carbon nanotubes by chemical vapor deposition. *Carbon* **2006,** *44*, (7), 1166-1172
		Atomic layer deposition	Gomathi, A.; Vivekchand, S. R. C.; Govindaraj, A.; Rao, C. N. R., Chemically Bonded Ceramic Oxide Coatings on Carbon Nanotubes and Inorganic Nanowires. *Advanced Materials* **2005,** *17*, (22), 2757-2761

		Chemical redox	Sivakkumar, S. R.; Ko, J. M.; Kim, D. Y.; Kim, B. C.; Wallace, G. G., Performance evaluation of CNT/polypyrrole/MnO2 composite electrodes for electrochemical capacitors. *Electrochimica Acta* **2007,** *52*, (25), 7377-7385
		Electrodeposition	Lee, C. Y.; Tsai, H. M.; Chuang, H. J.; Li, S. Y.; Lin, P.; Tseng, T. Y., Characteristics and electrochemical performance of supercapacitors with manganese oxide-carbon nanotube nanocomposite electrodes. *Journal of the Electrochemical Society* **2005,** *152*, (4), A716-A720
		Electroless deposition	Qu, L.; Dai, L., Substrate-Enhanced Electroless Deposition of Metal Nanoparticles on Carbon Nanotubes. *J. Am. Chem. Soc.* **2005,** *127*, (31), 10806-10807
MMNH	Bimetallic core-shell or alloy-like NHs	Microwave-polyol (sequential reduction)	Tsuji, M.; Miyamae, N.; Lim, S.; Kimura, K.; Zhang, X.; Hikino, S.; Nishio, M., Crystal Structures and Growth Mechanisms of Au@Ag Core−Shell Nanoparticles Prepared by the Microwave−Polyol Method. *Crystal Growth & Design* **2006,** *6*, (8), 1801-1807
		Photo-chemical deposition	Wang, C.-y.; Liu, C.-y.; Zheng, X.; Chen, J.; Shen, T., The surface chemistry of hybrid nanometer-sized particles I. Photochemical deposition of gold on ultrafine TiO2 particles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **1998,** *131*, (1–3), 271-280
		Electroless plating	Kim, S.-D.; Choe, W.-G.; Jeong, J.-R., Environmentally friendly electroless plating for Ag/TiO2-coated core–shell magnetic particles using ultrasonic treatment. *Ultrasonics Sonochemistry* **2013,** *20*, (6), 1456-1462
		Solvothermal	Sun, M.; Fu, W.; Yang, H.; Sui, Y.; Zhao, B.; Yin, G.; Li, Q.; Zhao, H.; Zou, G., One-step synthesis of coaxial Ag/TiO2 nanowire arrays on transparent conducting substrates: Enhanced electron collection in dye-sensitized solar cells. *Electrochemistry Communications* **2011,** *13*, (12), 1324-1327
		Hydrothermal	Muduli, S.; Game, O.; Dhas, V.; Vijayamohanan, K.; Bogle, K. A.; Valanoor, N.; Ogale, S. B., TiO2-Au plasmonic nanocomposite for enhanced dye-sensitized solar cell (DSSC) performance. *Solar Energy* **2012,** *86*, (5), 1428-1434
		Sol-gel	Ohno, T.; Tagawa, S.; Itoh, H.; Suzuki, H.; Matsuda, T., Size effect of TiO2-SiO2 nano-hybrid particle. *Mater. Chem. Phys.* **2009,** *113*, (1), 119-123
		Ion implantation within polymer matrix	Peña, O.; Pal, U.; Rodríguez-Fernández, L.; Silva-Pereyra, H. c. G.; Rodríguez-Iglesias, V.; Cheang-Wong, J. C.; Arenas-Alatorre, J. s.; Oliver, A., Formation of Au−Ag Core−Shell Nanostructures in Silica Matrix by Sequential Ion Implantation. *The Journal of Physical Chemistry C* **2009,** *113*, (6), 2296-2300
		Epitaxial growth	Sánchez-Iglesias, A.; Carbó-Argibay, E.; Glaria, A.; Rodríguez-González, B.; Pérez-Juste, J.; Pastoriza-Santos, I.; Liz-Marzán, L. M., Rapid Epitaxial Growth of Ag on Au Nanoparticles: From Au Nanorods to Core–Shell Au@Ag Octahedrons. *Chemistry – A European Journal* **2010,** *16*, (19), 5558-5563
		Flame-aerosol	Johannessen, T.; Jenson, J. R.; Mosleh, M.; Johansen, J.; Quaade, U.; Livbjerg, H., Flame synthesis of nanoparticles - Applications in catalysis and product/process engineering. *Chemical Engineering Research & Design* **2004,** *82*, (A11), 1444-1452
		Plasma assisted deposition	Kim, S. H.; Jung, C.-H.; Sahu, N.; Park, D.; Yun, J. Y.; Ha, H.; Park, J. Y., Catalytic activity of Au/TiO2 and Pt/TiO2 nanocatalysts prepared with arc plasma deposition under CO oxidation. *Applied Catalysis A: General* **2013,** *454*, (0), 53-58
		Sonochemical co-reduction of metal salts	Anandan, S.; Grieser, F.; Ashokkumar, M., Sonochemical Synthesis of Au−Ag Core−Shell Bimetallic Nanoparticles. *The Journal of Physical Chemistry C* **2008,** *112*, (39), 15102-15105
		Optical lithography for patterned growth	Liu, F.-K.; Huang, P.-W.; Chang, Y.-C.; Ko, F.-H.; Chu, T.-C., Combining Optical Lithography with Rapid Microwave Heating for the Selective Growth of Au/Ag Bimetallic Core/Shell Structures on Patterned Silicon Wafers. *Langmuir* **2005,** *21*, (6),

			2519-2525
		Template-based growth processes can be used to obtain hollow spherical, porous, or tubular structures	(1) Zhang, J.; Zhan, P.; Liu, H.; Wang, Z.; Ming, N., A facile colloidal templating method to monodisperse hollow Ag and Ag/Au submicrometer spheres. *Mater. Lett.* **2006,** *60*, (2), 280-283. (2) Wang, X.; Mitchell, D. R. G.; Prince, K.; Atanacio, A. J.; Caruso, R. A., Gold Nanoparticle Incorporation into Porous Titania Networks Using an Agarose Gel Templating Technique for Photocatalytic Applications. *Chemistry of Materials* **2008,** *20*, (12), 3917-3926. (3) Chueh, Y. L.; Chou, L. J.; Wang, Z. L., SiO2/Ta2O5 core-shell nanowires and nanotubes. *Angew. Chem.-Int. Edit.* **2006,** *45*, (46), 7773-7778.
		Water-in-oil microemulsion	Wu, M.-L.; Lai, L.-B., Synthesis of Pt/Ag bimetallic nanoparticles in water-in-oil microemulsions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2004,** *244*, (1–3), 149-157
		Nano-emulsion	Liu, H.; Wu, J.; Min, J. H.; Zhang, X.; Kim, Y. K., Tunable synthesis and multifunctionalities of Fe3O4–ZnO hybrid core-shell nanocrystals. *Materials Research Bulletin* **2013,** *48*, (2), 551-558
		Layer-by-layer reverse micellization	Fan, J. W.; Tseng, T. T.; Chen, C. N.; Wei, M. H.; Tseng, W. J., Preparation of ITO/Ag nanohybrid particles by a reverse micellar layer-by-layer coating. *Ceram. Int.* **2011,** *37*, (1), 43-47
		Physisorption of MNPs on polymer modified MNPs	Zhai, Y.; Zhai, J.; Wang, Y.; Guo, S.; Ren, W.; Dong, S., Fabrication of Iron Oxide Core/Gold Shell Submicrometer Spheres with Nanoscale Surface Roughness for Efficient Surface-Enhanced Raman Scattering. *The Journal of Physical Chemistry C* **2009,** *113*, (17), 7009-7014
		Biogenic process using natural extracts as solvent or reducing agents	Shankar, S. S.; Rai, A.; Ahmad, A.; Sastry, M., Rapid synthesis of Au, Ag, and bimetallic Au core–Ag shell nanoparticles using Neem (Azadirachta indica) leaf broth. *Journal of Colloid and Interface Science* **2004,** *275*, (2), 496-502
OMCNH		NM surface functionalization with organic molecules	D'Souza, F.; Ito, O., Supramolecular donor-acceptor hybrids of porphyrins/phthalocyanines with fullerenes/carbon nanotubes: electron transfer, sensing, switching, and catalytic applications. *Chemical Communications* **2009**, (33), 4913-4928

		electrochemical immobilization of biomolecules	Xue, M. H.; Xu, Q.; Zhou, M.; Zhu, J. J., In situ immobilization of glucose oxidase in chitosan-gold nanoparticle hybrid film on Prussian Blue modified electrode for high-sensitivity glucose detection. *Electrochemistry Communications* **2006,** *8*, (9), 1468-1474
		Polymer grafting from or grafted to NM surfaces	(1) Achilleos, D. S.; Vamvakaki, M., End-Grafted Polymer Chains onto Inorganic Nano-Objects. *Materials* **2010,** *3*, (3), 1981-2026. (2) Wu, W. T.; Shen, J.; Banerjee, P.; Zhou, S. Q., Core-shell hybrid nanogels for integration of optical temperature-sensing, targeted tumor cell imaging, and combined chemo-photothermal treatment. *Biomaterials* **2010,** *31*, (29), 7555-7566 (3) Tagliazucchi, M.; Blaber, M. G.; Schatz, G. C.; Weiss, E. A.; Szleifert, I., Optical Properties of Responsive Hybrid Au@Polymer Nanoparticles. *ACS nano* **2012,** *6*, (9), 8397-8406.
		Emulsification	Tian, J.; Jin, J.; Zheng, F.; Zhao, H. Y., Self-Assembly of Gold Nanoparticles and Polystyrene: A Highly Versatile Approach to the Preparation of Colloidal Particles with Polystyrene Cores and Gold Nanoparticle Coronae. *Langmuir* **2010,** *26*, (11), 8762-8768
		Ion-exchange	Qiu, L. H.; Peng, Y. J.; Liu, B. Q.; Lin, B. C.; Peng, Y.; Malik, M. J.; Yan, F., Polypyrrole nanotube-supported gold nanoparticles: An efficient electrocatalyst for oxygen reduction and catalytic reduction of 4-nitrophenol. *Applied Catalysis a-General* **2012,** *413*, 230-237

TABLE A-5. Specific examples of class, specific type, and potential application of nanohybrids.

NH Class	Specific Types	Applications	Citations
CCNH	Fullerene-CNT peapods	Field effect transistors	Shimada, T.; Ohno, Y.; Okazaki, T.; Sugai, T.; Suenaga, K.; Kishimoto, S.; Mizutani, T.; Inoue, T.; Taniguchi, R.; Fukui, N.; Okubo, H.; Shinohara, H., Transport properties of C-78, C-90 and Dy@C-82 fullerenes-nanopeapods by field effect transistors. *Physica E* **2004,** *21*, (2-4), 1089-1092. Li, Y.; Kaneko, T.; Hatakeyama, R. In *Photoresponse of fullerene and azafullerene peapod field effect transistors*, Nanotechnology, 2009. IEEE-NANO 2009. 9th IEEE Conference on, 26-30 July 2009, 2009; 2009; pp 86-89 Li, Y. F.; Kaneko, T.; Hatakeyama, R., Electrical transport properties of fullerene peapods interacting with light. *Nanotechnology* **2008,** *19*, (41), 415201 Shimada, T.; Ohno, Y.; Okazaki, T.; Sugai, T.; Suenaga, K.; Kishimoto, S.; Mizutani, T.; Inoue, T.; Taniguchi, R.; Fukui, N.; Okubo, H.; Shinohara, H., Transport properties of C-78, C-90 and Dy@C-82 fullerenes-nanopeapods by field effect transistors. *Physica E* **2004,** *21*, (2-4), 1089-1092
		Lithium ion storage	Kawasaki, S.; Iwai, Y.; Hirose, M., Electrochemical lithium ion storage property of C60 encapsulated single-walled carbon nanotubes. *Materials Research Bulletin* **2009,** *44*, (2), 415-417
	Graphene-CNT peapods	Catalyst support	Lv, R.; Cui, T.; Jun, M.-S.; Zhang, Q.; Cao, A.; Su, D. S.; Zhang, Z.; Yoon, S.-H.; Miyawaki, J.; Mochida, I.; Kang, F., Open-Ended, N-Doped Carbon Nanotube-Graphene Hybrid Nanostructures as High-Performance Catalyst Support. *Adv. Funct. Mater.* **2011,** *21*, (5), 999-1006.
		Energy storage	Wu, C.; Huang, X. Y.; Wu, X. F.; Xie, L. Y.; Yang, K.; Jiang, P. K., Graphene oxide-encapsulated carbon nanotube hybrids for high dielectric performance nanocomposites with enhanced energy storage density. *Nanoscale* **2013,** *5*, (9), 3847-3855
	Carbon nano-onions	Lithium ion batteries	Han, F. D.; Yao, B.; Bai, Y. J., Preparation of Carbon Nano-Onions and Their Application as Anode Materials for Rechargeable Lithium-Ion Batteries. *J. Phys. Chem. C* **2011,** *115*, (18), 8923-8927.
		Bioimaging	Sonkar, S. K.; Ghosh, M.; Roy, M.; Begum, A.; Sarkar, S., Carbon Nano-Onions as Nontoxic and High-Fluorescence Bioimaging Agent in Food Chain-An In Vivo Study from Unicellular E. coli to Multicellular C-elegans. *Materials Express* **2012,** *2*, (2), 105-114
		Heavy metal ion removal	Seymour, M. B.; Su, C.; Gao, Y.; Lu, Y.; Li, Y., Characterization of carbon nano-onions for heavy metal ion remediation. *Journal of Nanoparticle Research* **2012,** *14*, (9)
		Lubricant additives	Joly-Pottuz, L.; Vacher, B.; Ohmae, N.; Martin, J. M.; Epicier, T., Anti-wear and friction reducing mechanisms of carbon nano-onions as lubricant additives. *Tribology Letters* **2008,** *30*, (1), 69-80.
	CNT-graphene exohedral hybrid	Transparent conductive films	Hong, T.-K.; Lee, D. W.; Choi, H. J.; Shin, H. S.; Kim, B.-S., Transparent, Flexible Conducting Hybrid Multilayer Thin Films of Multiwalled Carbon Nanotubes with Graphene Nanosheets. *ACS nano* **2010,** *4*, (7), 3861-3868 Tung, V. C.; Chen, L. M.; Allen, M. J.; Wassei, J. K.; Nelson, K.; Kaner, R. B.; Yang, Y., Low-Temperature Solution Processing of Graphene-Carbon Nanotube Hybrid Materials for High-Performance Transparent Conductors. *Nano Lett.* **2009,** *9*, (5), 1949-1955
		Supercapacitors	Yu, D.; Dai, L., Self-Assembled Graphene/Carbon Nanotube Hybrid Films for Supercapacitors. *The Journal of Physical Chemistry Letters* **2009,** *1*, (2), 467-470
		Fuel cell	Jha, N.; Jafri, R. I.; Rajalakshmi, N.; Ramaprabhu, S., Graphene-multi walled carbon nanotube hybrid electrocatalyst support material for direct methanol fuel cell. *International Journal of Hydrogen Energy* **2011,** *36*, (12), 7284-7290.
		Lithium ion storage	Jha, N.; Jafri, R. I.; Rajalakshmi, N.; Ramaprabhu, S., Graphene-multi walled carbon nanotube hybrid electrocatalyst support material for direct methanol fuel cell. *International Journal of Hydrogen Energy* **2011,** *36*, (12), 7284-7290.

		Electrochemical sensor	Chen, X.; Zhu, J.; Xi, Q.; Yang, W., A high performance electrochemical sensor for acetaminophen based on single-walled carbon nanotube-graphene nanosheet hybrid films. *Sensors and Actuators B-Chemical* **2012,** *161*, (1), 648-654.
		Biosensors	Mani, V.; Devadas, B.; Chen, S. M., Direct electrochemistry of glucose oxidase at electrochemically reduced graphene oxide-multiwalled carbon nanotubes hybrid material modified electrode for glucose biosensor. *Biosens. Bioelectron.* **2013,** *41*, 309-315
		Contaminant removal	Ai, L.; Jiang, J., Removal of methylene blue from aqueous solution with self-assembled cylindrical graphene-carbon nanotube hybrid. *Chemical Engineering Journal* **2012,** *192*, 156-163.
		Heat transfer application	Aravind, S. S. J.; Ramaprabhu, S., Graphene wrapped multiwalled carbon nanotubes dispersed nanofluids for heat transfer applications. *J. Appl. Phys.* **2012,** *112*, (12)
		Structural health monitoring in construction industry	Li, W. K.; Dichiara, A.; Bai, J. B., Carbon nanotube-graphene nanoplatelet hybrids as high-performance multifunctional reinforcements in epoxy composites. *Compos. Sci. Technol.* **2013,** *74*, 221-227 Hwang, S. H.; Park, H. W.; Park, Y. B., Piezoresistive behavior and multi-directional strain sensing ability of carbon nanotube-graphene nanoplatelet hybrid sheets. *Smart Mater. Struct.* **2013,** *22*, (1)
	Fullerene-graphene hybrid	Organic photovoltaics	(1) Qu, S.; Li, M.; Xie, L.; Huang, X.; Yang, J.; Wang, N.; Yang, S., Noncovalent Functionalization of Graphene Attaching 6,6 -Phenyl-C61-butyric Acid Methyl Ester (PCBM) and Application as Electron Extraction Layer of Polymer Solar Cells. *ACS nano* **2013,** *7*, (5), 4070-81. (2) Wang, J.; Wang, Y.; He, D.; Wu, H.; Wang, H.; Zhou, P.; Fu, M., Influence of Polymer/Fullerene-Graphene Structure on Organic Polymer Solar Devices. *Integrated Ferroelectrics* **2012,** *137*, (1), 1-9. (3) Yang, J.; Heo, M.; Lee, H. J.; Park, S. M.; Kim, J. Y.; Shin, H. S., Reduced Graphene Oxide (rGO)-Wrapped Fullerene (C-60) Wires. *ACS nano* **2011,** *5*, (10), 8365-8371
		Optical limiting devices	Liu, Z. B.; Xu, Y. F.; Zhang, X. Y.; Zhang, X. L.; Chen, Y. S.; Tian, J. G., Porphyrin and Fullerene Covalently Functionalized Graphene Hybrid Materials with Large Nonlinear Optical Properties. *J. Phys. Chem. B* **2009,** *113*, (29), 9681-9686.
	CNT-fullerene exohendral hybrid	Organic photovoltaics	Wu, W.; Zhu, H. R.; Fan, L. Z.; Yang, S. H., Synthesis and characterization of a grapevine nanostructure consisting of single-walled carbon nanotubes with covalently attached 60 fullerene balls. *Chem.-Eur. J.* **2008,** *14*, (19), 5981-5987.
	CNT-fullerene-graphene hybrid	Organic optoelectronics	Tung, V. C.; Huang, J. H.; Tevis, I.; Kim, F.; Kim, J.; Chu, C. W.; Stupp, S. I.; Huang, J. X., Surfactant-Free Water-Processable Photoconductive All-Carbon Composite. *J. Am. Chem. Soc.* **2011,** *133*, (13), 4940-4947
CMNH	Exohedral hybrids	Photovoltaics and solar cells	Kim, H.-i.; Moon, G.-h.; Monllor-Satoca, D.; Park, Y.; Choi, W., Solar Photoconversion Using Graphene/TiO2 Composites: Nanographene Shell on TiO2 Core versus TiO2 Nanoparticles on Graphene Sheet. *J. Phys. Chem. C* **2012,** *116*, (1), 1535-1543 Yin, Z.; Wu, S.; Zhou, X.; Huang, X.; Zhang, Q.; Boey, F.; Zhang, H., Electrochemical Deposition of ZnO Nanorods on Transparent Reduced Graphene Oxide Electrodes for Hybrid Solar Cells. *Small* **2010,** *6*, (2), 307-312.
		Optical limiting devices	Zhu, Y. W.; Elim, H. I.; Foo, Y. L.; Yu, T.; Liu, Y. J.; Ji, W.; Lee, J. Y.; Shen, Z. X.; Wee, A. T. S.; Thong, J. T. L.; Sow, C. H., Multiwalled carbon nanotubes beaded with ZnO nanoparticles for ultrafast nonlinear optical switching. *Advanced Materials* **2006,** *18*, (5), 587-+
		Supercapacitors	Raymundo-Pinero, E.; Khomenko, V.; Frackowiak, E.; Beguin, F., Performance of manganese oxide/CNTs composites as electrode materials for electrochemical capacitors. *Journal of the Electrochemical Society* **2005,** *152*, (1), A229-A235 Chen, P.; Chen, H.; Qiu, J.; Zhou, C., Inkjet Printing of Single-Walled Carbon Nanotube/RuO_2 Nanowire Supercapacitors on Cloth Fabrics and Flexible Substrates. *Nano Research* **2010,** *3*, (8), 594-603

		Lithium storage	Ding, S.; Chen, J. S.; Luan, D.; Boey, F. Y. C.; Madhavi, S.; Lou, X. W., Graphene-supported anatase TiO2 nanosheets for fast lithium storage. *Chemical Communications* **2011,** *47*, (20), 5780-5782
		Catalysis	Karousis, N.; Tsotsou, G.-E.; Evangelista, F.; Rudolf, P.; Ragoussis, N.; Tagmatarchis, N., Carbon nanotubes decorated with palladium nanoparticles: Synthesis, characterization, and catalytic activity. *J. Phys. Chem. C* **2008,** *112*, (35), 13463-13469 Li, Y.; Fan, X.; Qi, J.; Ji, J.; Wang, S.; Zhang, G.; Zhang, F., Gold nanoparticles-graphene hybrids as active catalysts for Suzuki reaction. *Materials Research Bulletin* **2010,** *45*, (10), 1413-1418
		Electrochemical sensing	Guo, S.; Wen, D.; Zhai, Y.; Dong, S.; Wang, E., Platinum Nanoparticle Ensemble-on-Graphene Hybrid Nanosheet: One-Pot, Rapid Synthesis, and Used as New Electrode Material for Electrochemical Sensing. *ACS nano* **2010,** *4*, (7), 3959-3968
		Bio-imaging and drug delivery	Chen, M.-L.; He, Y.-J.; Chen, X.-W.; Wang, J.-H., Quantum Dots Conjugated with Fe_3O_4-Filled Carbon Nanotubes for Cancer-Targeted Imaging and Magnetically Guided Drug Delivery. *Langmuir* **2012,** *28*, (47), 16469-16476 Li, W. W.; Gao, C.; Qian, H. F.; Ren, J. C.; Yan, D. Y., Multiamino-functionalized carbon nanotubes and their applications in loading quantum dots and magnetic nanoparticles. *J. Mater. Chem.* **2006,** *16*, (19), 1852-1859
		Fuel cell	Li, Y.; Gao, W.; Ci, L.; Wang, C.; Ajayan, P. M., Catalytic performance of Pt nanoparticles on reduced graphene oxide for methanol electro-oxidation. *Carbon* **2010,** *48*, (4), 1124-1130 Wen, Z. H.; Ci, S. Q.; Mao, S.; Cui, S. M.; Lu, G. H.; Yu, K. H.; Luo, S. L.; He, Z.; Chen, J. H., TiO2 nanoparticles-decorated carbon nanotubes for significantly improved bioelectricity generation in microbial fuel cells. *Journal of Power Sources* **2013,** *234*, 100-106
		Contaminant degradation	Zhao, D.; Yang, X.; Chen, C.; Wang, X., Enhanced photocatalytic degradation of methylene blue on multiwalled carbon nanotubes–TiO2. *Journal of Colloid and Interface Science* **2013,** *398*, (0), 234-239 Lv, T.; Pan, L. K.; Liu, X. J.; Lu, T.; Zhu, G.; Sun, Z., Enhanced photocatalytic degradation of methylene blue by ZnO-reduced graphene oxide composite synthesized via microwave-assisted reaction. *Journal of Alloys and Compounds* **2011,** *509*, (41), 10086-10091 Liu, X. J.; Pan, L. K.; Lv, T.; Zhu, G.; Lu, T.; Sun, Z.; Sun, C. Q., Microwave-assisted synthesis of TiO2-reduced graphene oxide composites for the photocatalytic reduction of Cr(VI). *RSC Adv.* **2011,** *1*, (7), 1245-1249
		Antimicrobial	Kavitha, T.; Gopalan, A. I.; Lee, K.-P.; Park, S.-Y., Glucose sensing, photocatalytic and antibacterial properties of graphene–ZnO nanoparticle hybrids. *Carbon* **2012,** *50*, (8), 2994-3000 Das, M. R.; Sarma, R. K.; Saikia, R.; Kale, V. S.; Shelke, M. V.; Sengupta, P., Synthesis of silver nanoparticles in an aqueous suspension of graphene oxide sheets and its antimicrobial activity. *Colloids and Surfaces B: Biointerfaces* **2011,** *83*, (1), 16-22
	Endohedral metallofullerenes	MRI agent	Bolskar, R. D., Gadofullerene MRI contrast agents. *Nanomedicine* **2008,** *3*, (2), 201-213. Toth, E.; Bolskar, R. D.; Borel, A.; Gonzalez, G.; Helm, L.; Merbach, A. E.; Sitharaman, B.; Wilson, L. J., Water-soluble gadofullerenes: Toward high-relaxivity, pH-responsive MRI contrast agents. *J. Am. Chem. Soc.* **2005,** *127*, (2), 799-805
MMNH		Optical limiting devices	Tom, R. T.; Nair, A. S.; Singh, N.; Aslam, M.; Nagendra, C. L.; Philip, R.; Vijayamohanan, K.; Pradeep, T., Freely Dispersible $Au@TiO_2$, $Au@ZrO_2$, $Ag@TiO_2$, and $Ag@ZrO_2$ Core−Shell

			Nanoparticles: One-Step Synthesis, Characterization, Spectroscopy, and Optical Limiting Properties. *Langmuir* **2003,** *19*, (8), 3439-3445
		Photovoltaics and solar cell	Sun, M.; Fu, W.; Yang, H.; Sui, Y.; Zhao, B.; Yin, G.; Li, Q.; Zhao, H.; Zou, G., One-step synthesis of coaxial Ag/TiO2 nanowire arrays on transparent conducting substrates: Enhanced electron collection in dye-sensitized solar cells. *Electrochemistry Communications* **2011,** *13*, (12), 1324-1327
		Lithium ion battery	Ahmad, M.; Shi, Y. Y.; Nisar, A.; Sun, H. Y.; Shen, W. C.; Wei, M.; Zhu, J., Synthesis of hierarchical flower-like ZnO nanostructures and their functionalization by Au nanoparticles for improved photocatalytic and high performance Li-ion battery anodes. *J. Mater. Chem.* **2011,** *21*, (21), 7723-7729
		Catalysis	Shinde, V. M.; Madras, G., Low temperature CO oxidation and water gas shift reaction over Pt/Pd substituted in Fe/TiO_2 catalysts. *International Journal of Hydrogen Energy* **2012,** *37*, (24), 18798-18814
		Bioimaging and cancer therapy	Timothy, A. L.; James, B.; Jesse, A.; Konstantin, S., Hybrid plasmonic magnetic nanoparticles as molecular specific agents for MRI/optical imaging and photothermal therapy of cancer cells. *Nanotechnology* **2007,** *18*, (32), 325101 Fan, Z.; Shelton, M.; Singh, A. K.; Senapati, D.; Khan, S. A.; Ray, P. C., Multifunctional Plasmonic Shell–Magnetic Core Nanoparticles for Targeted Diagnostics, Isolation, and Photothermal Destruction of Tumor Cells. *ACS nano* **2012,** *6*, (2), 1065-1073.
		Pathogen detection and destruction	Wang, C.; Irudayaraj, J., Multifunctional Magnetic–Optical Nanoparticle Probes for Simultaneous Detection, Separation, and Thermal Ablation of Multiple Pathogens. *Small* **2010,** *6*, (2), 283-289
		Catalysis	Yang, Y.-F.; Sangeetha, P.; Chen, Y.-W., Au/TiO2 catalysts prepared by photo-deposition method for selective CO oxidation in H2 stream. *International Journal of Hydrogen Energy* **2009,** *34*, (21), 8912-8920
		Contaminant sensor	Liu, J. M.; Wang, X. X.; Cui, M. L.; Lin, L. P.; Jiang, S. L.; Jiao, L.; Zhang, L. H., A promising non-aggregation colorimetric sensor of AuNRs-Ag+ for determination of dopamine. *Sensors and Actuators B-Chemical* **2013,** *176*, 97-102
		Contaminant degradation	Costi, R.; Saunders, A. E.; Elmalem, E.; Salant, A.; Banin, U., Visible light-induced charge retention and photocatalysis with hybrid CdSe-Au nanodumbbells. *Nano Lett.* **2008,** *8*, (2), 637-641 Wang, X.; Mitchell, D. R. G.; Prince, K.; Atanacio, A. J.; Caruso, R. A., Gold Nanoparticle Incorporation into Porous Titania Networks Using an Agarose Gel Templating Technique for Photocatalytic Applications. *Chemistry of Materials* **2008,** *20*, (12), 3917-3926 Veres, A.; Rica, T.; Janovak, L.; Domok, M.; Buzas, N.; Zollmer, V.; Seemann, T.; Richardt, A.; Dekany, I., Silver and gold modified plasmonic TiO2 hybrid films for photocatalytic decomposition of ethanol under visible light. *Catalysis Today* **2012,** *181*, (1), 156-162 Yu, H.; Ming, H.; Zhang, H.; Li, H.; Pan, K.; Liu, Y.; Wang, F.; Gong, J.; Kang, Z., Au/ZnO nanocomposites: Facile fabrication and enhanced photocatalytic activity for degradation of benzene. *Mater. Chem. Phys.* **2012,** *137*, (1), 113-117
		Bio-sensor	Zhao, G. H.; Lei, Y. Z.; Zhang, Y. G.; Li, H. X.; Liu, M. C., Growth and favorable bioelectrocatalysis of multishaped nanocrystal Au in vertically aligned TiO2 nanotubes for hemoprotein. *J. Phys. Chem. C* **2008,** *112*, (38), 14786-14795
		Antimicrobial	Li, M.; Noriega-Trevino, M. E.; Nino-Martinez, N.; Marambio-Jones, C.; Wang, J.; Damoiseaux, R.; Ruiz, F.; Hoek, E. M. V., Synergistic Bactericidal Activity of Ag-TiO2 Nanoparticles in Both Light and Dark Conditions. *Environ. Sci. Technol.* **2011,** *45*, (20), 8989-8995 Valodkar, M.; Modi, S.; Pal, A.; Thakore, S., Synthesis and anti-bacterial activity of Cu, Ag and Cu-Ag alloy nanoparticles: A green approach. *Materials Research Bulletin* **2011,** *46*, (3), 384-389 Zhai, Y. M.; Han, L.; Wang, P.; Li, G. P.; Ren, W.; Liu, L.; Wang,

			E. K.; Dong, S. J., Superparamagnetic Plasmonic Nanohybrids: Shape-Controlled Synthesis, TEM-Induced Structure Evolution, and Efficient Sunlight-Driven Inactivation of Bacteria. *ACS nano* **2011,** *5*, (11), 8562-8570
OMCNH		Photovoltaics	D'Souza, F.; Ito, O., Supramolecular donor-acceptor hybrids of porphyrins/phthalocyanines with fullerenes/carbon nanotubes: electron transfer, sensing, switching, and catalytic applications. *Chemical Communications* **2009**, (33), 4913-4928
		Optical limiting devices	Guo, Z.; Du, F.; Ren, D. M.; Chen, Y. S.; Zheng, J. Y.; Liu, Z. B.; Tian, J. G., Covalently porphyrin-functionalized single-walled carbon nanotubes: a novel photoactive and optical limiting donor-acceptor nanohybrid. *J. Mater. Chem.* **2006,** *16*, (29), 3021-3030
		Chemical and bio-sensing	Ovádeková, R.; Jantová, S.; Letašiová, S.; Štepánek, I.; Labuda, J., Nanostructured electrochemical DNA biosensors for detection of the effect of berberine on DNA from cancer cells. *Analytical and Bioanalytical Chemistry* **2006,** *386*, (7-8), 2055-2062. Qian, L.; Yang, X., Composite film of carbon nanotubes and chitosan for preparation of amperometric hydrogen peroxide biosensor. *Talanta* **2006,** *68*, (3), 721-727
		Bioimaging	Dubertret, B.; Calame, M.; Libchaber, A. J., Single-mismatch detection using gold-quenched fluorescent oligonucleotides. *Nature Biotechnology* **2001,** *19*, (4), 365-370.
		Drug delivery	Gibson, J. D.; Khanal, B. P.; Zubarev, E. R., Paclitaxel-functionalized gold nanoparticles. *J. Am. Chem. Soc.* **2007,** *129*, (37), 11653-11661 Hu, Y.; Chen, Q.; Ding, Y.; Li, R. T.; Jiang, X. Q.; Liu, B. R., Entering and Lighting Up Nuclei Using Hollow Chitosan-Gold Hybrid Nanospheres. *Advanced Materials* **2009,** *21*, (36), 3639-+

Appendix B

Supplemental Information for Chapter 4
Preparation and Characterization of Stable Aqueous Higher Order Fullerenes

B-1. Details of the Input System Energy Estimation. A graduated cylinder was filled with 60 mL of deionized water (Barnstead). An ultrasonic dismembrator S-4000 (Misonix, Inc. Farmingdale, NY) was used to sonicate this water for 15 min at amplitude of 50 and power of 25 W. The water temperature increase with time was monitored every 0.5 min using a mercury thermometer. The procedure was repeated twice and temperature profiles were obtained as presented in Figure S2(a-b). The temperature increase was linear until about 7 min of continuous sonication. From 7 min onwards, the water sample was beginning to reaching its specific heat capacity and thereby the profile started to deviate from linearity. Average linear slope of temperature profile is estimated as $\left(\frac{dT}{dt}\right) = 4.33 \pm 0.15\ \mathrm{K/min}$. The slope thus obtained was used in equation S1 to estimate input wattage.

$$W_I = m \times C_p \times \left(\frac{dT}{dt}\right) \qquad \text{(S1)}$$

Where,

W_I= estimated input wattage (W)

m= mass of water, (g)

C_p= specific heat of water = 4.2 J/gK

The amount of sonication time for each synthesis was then incorporated into equation S2 to estimate the cumulative input energy for the duration of the synthesis process.

$$E_I = m \times C_p \times \left(\frac{dT}{dt}\right) \times \Delta t \qquad \text{(S2)}$$

Where,

E_I=estimated cumulative input energy, (J)

Δt=total time of sonication, (min)

For a volume V (mL) of water, system input energy per mL of water is $\frac{E_I}{V}$ (J/mL) or $\frac{E_I}{V \times 1000}$ (kJ/mL). This energy is then divided by the molar concentration of fullerenes in the water, which then gives the energy input per mol of fullerenes.

Table B-1. Experimental details of the synthesis process (solvent volume, sonication time, and energy input to the system).

<table>
<tr><th rowspan="2">Fullerene</th><th rowspan="2" colspan="2">Water (mL)</th><th colspan="2">Sonication time (min)</th><th colspan="2">Calorimetric-energy-input per mL water (kJ/mL water)</th><th rowspan="2">Average Calorimetric-energy input (MJ/mol)</th></tr>
<tr><th>Batch 1</th><th>Batch 2</th><th>Batch 1</th><th>Batch 2</th></tr>
<tr><td>C_{60}</td><td colspan="2">60</td><td>180</td><td>210</td><td>3.27</td><td>3.81</td><td>38232</td></tr>
<tr><td>C_{70}</td><td colspan="2">60</td><td>330</td><td>360</td><td>5.99</td><td>6.54</td><td>79002</td></tr>
<tr><td>C_{76}</td><td>30</td><td>45</td><td>450</td><td>510</td><td>8.18</td><td>9.26</td><td>103455</td></tr>
<tr><td>C_{84}</td><td colspan="2">60</td><td>780</td><td>750</td><td>14.16</td><td>13.6</td><td>210168</td></tr>
</table>

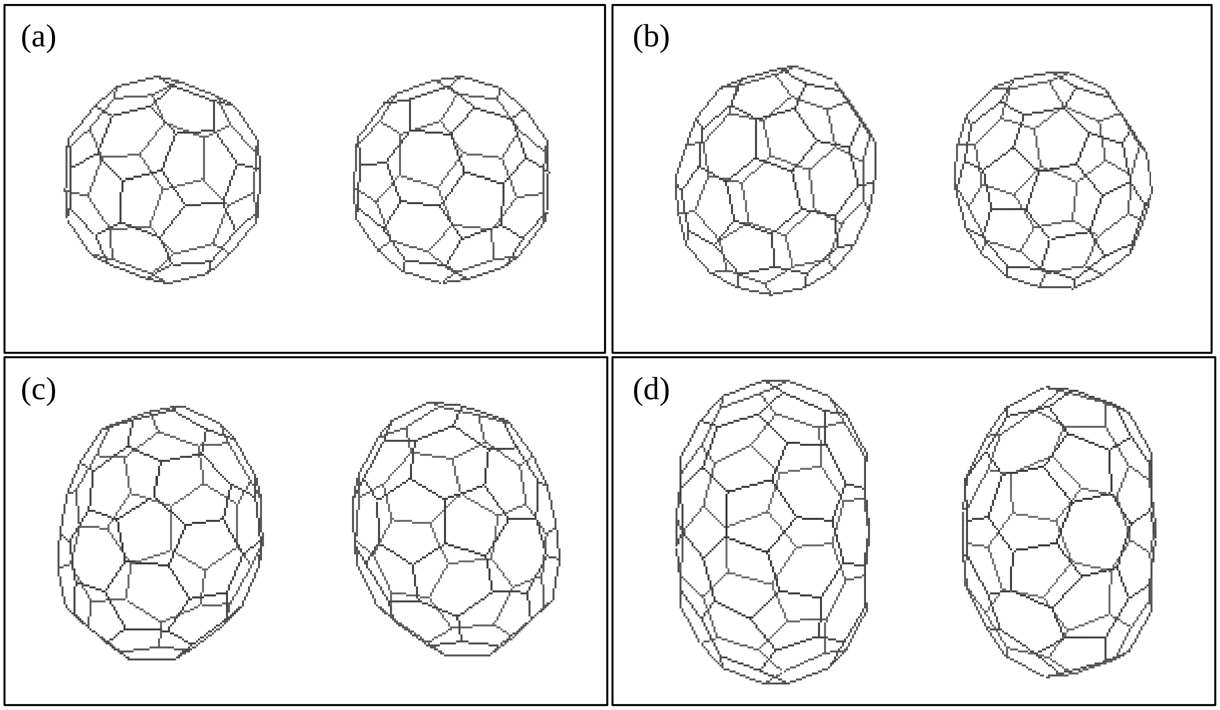


FIGURE B-1. Optimized geometries at the DFT-D/BLYP/6-31+G(d) level for (a) nC_{60}, (b) nC_{70}, (c) nC_{76}, and (d) nC_{84} fullerene pairs. The optimum center to center distances between the fullerene pairs are computed as 9.99, 10.1, 9.75, and 9.17 Å, respectively.

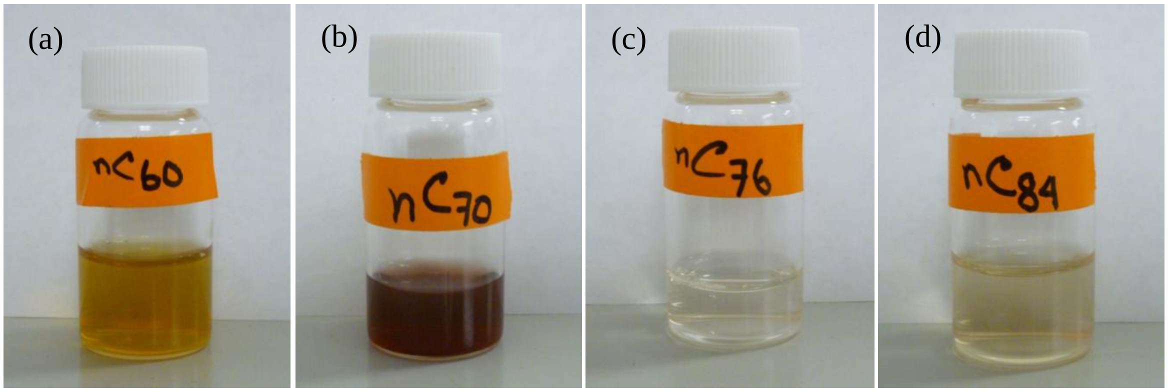


FIGURE B-2. Aqueous suspensions of (a) nC_{60}, (b) nC_{70}, (c) nC_{76}, and (d) nC_{84} fullerenes, immediately after synthesis.

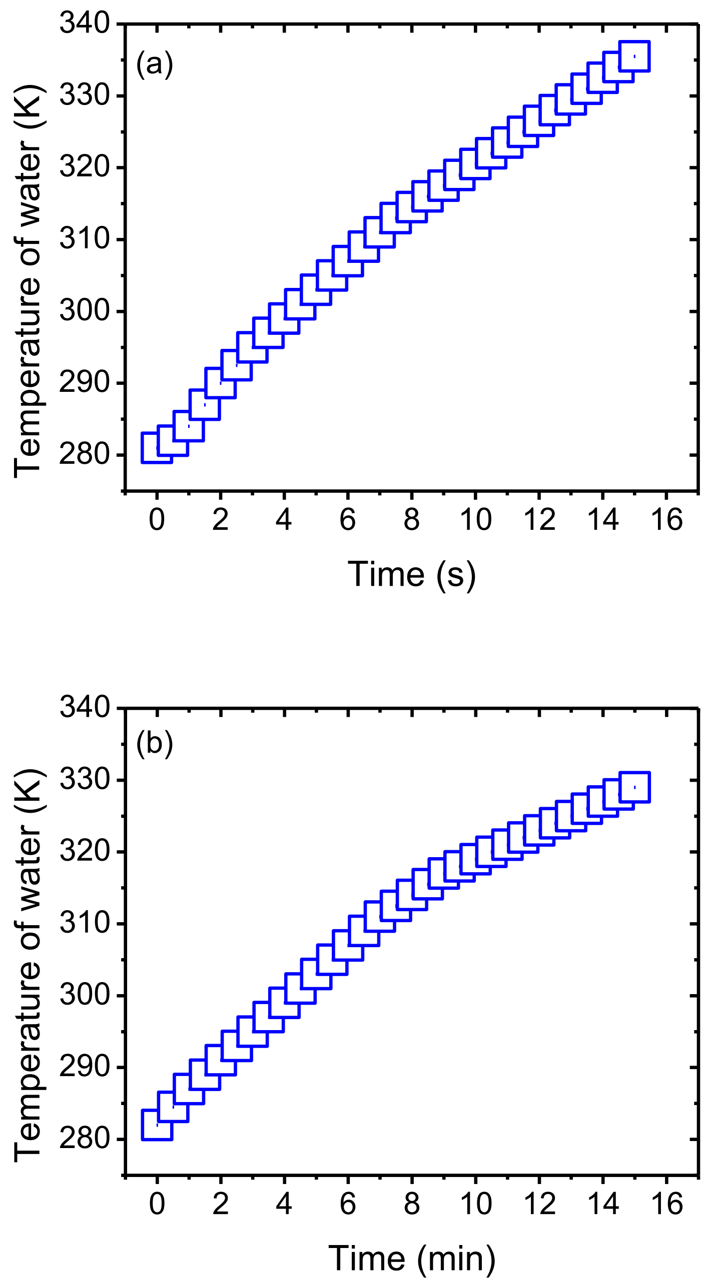


FIGURE B-3. Temperature profile for the ultrasonic dismembrator assembly used to synthesize aqueous fullerene suspensions. The temperatures for each trial is presented here in (a-b) with the linear slope for (a) $\left(\frac{dT}{dt}\right)_1 = 4.43$ K/min and (b) $\left(\frac{dT}{dt}\right)_1 = 4.22$ K/min.

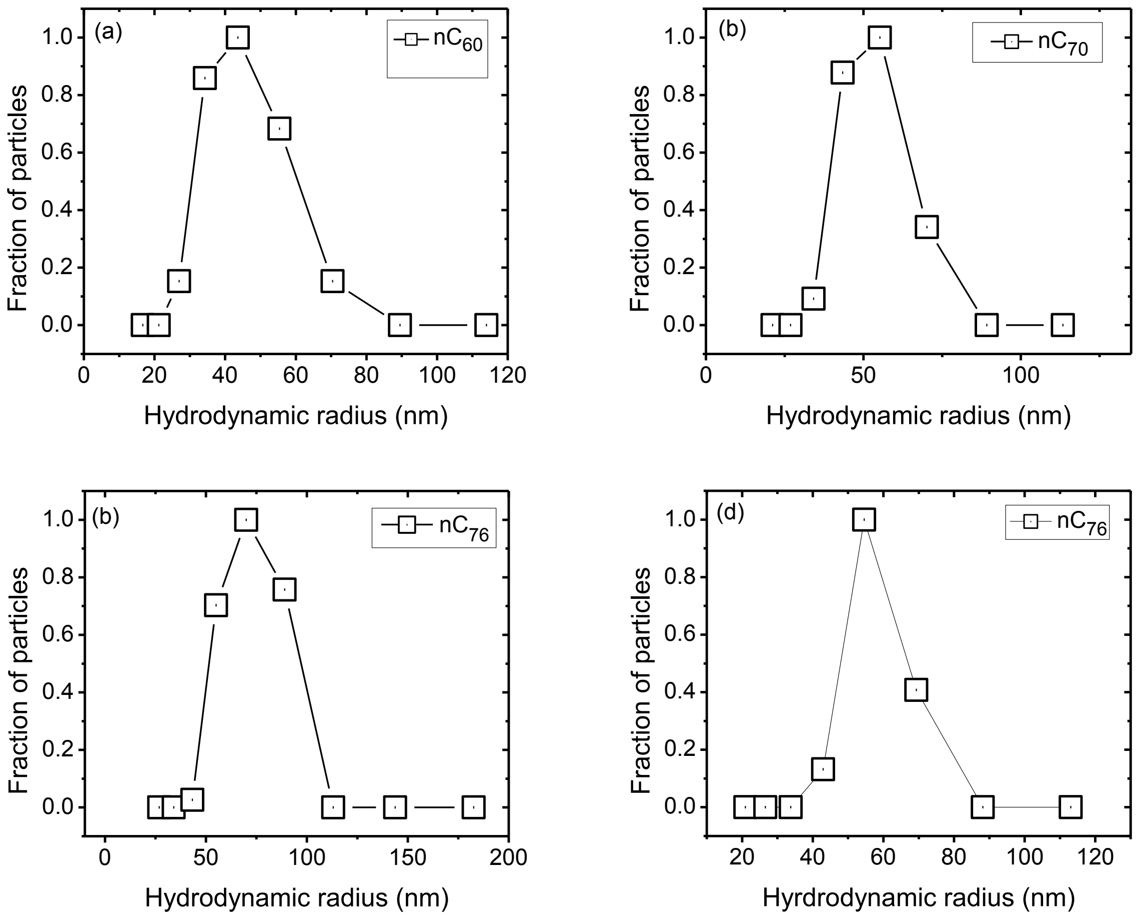


FIGURE B-4. Particle size distribution of (a) nC_{60}, (b) nC_{70}, (c) nC_{76}, and (d) nC_{84} fullerenes immediately after synthesis. This size distribution is generated from DLS measurements using built-in ‘cumulant algorithm’ of the ALV software.

Appendix C

Supplemental Information for Chapter 5
Preparation of Non-Aggregating Aqueous Fullerenes in Highly Saline Solutions with A Biocompatible Non-Ionic Polymer

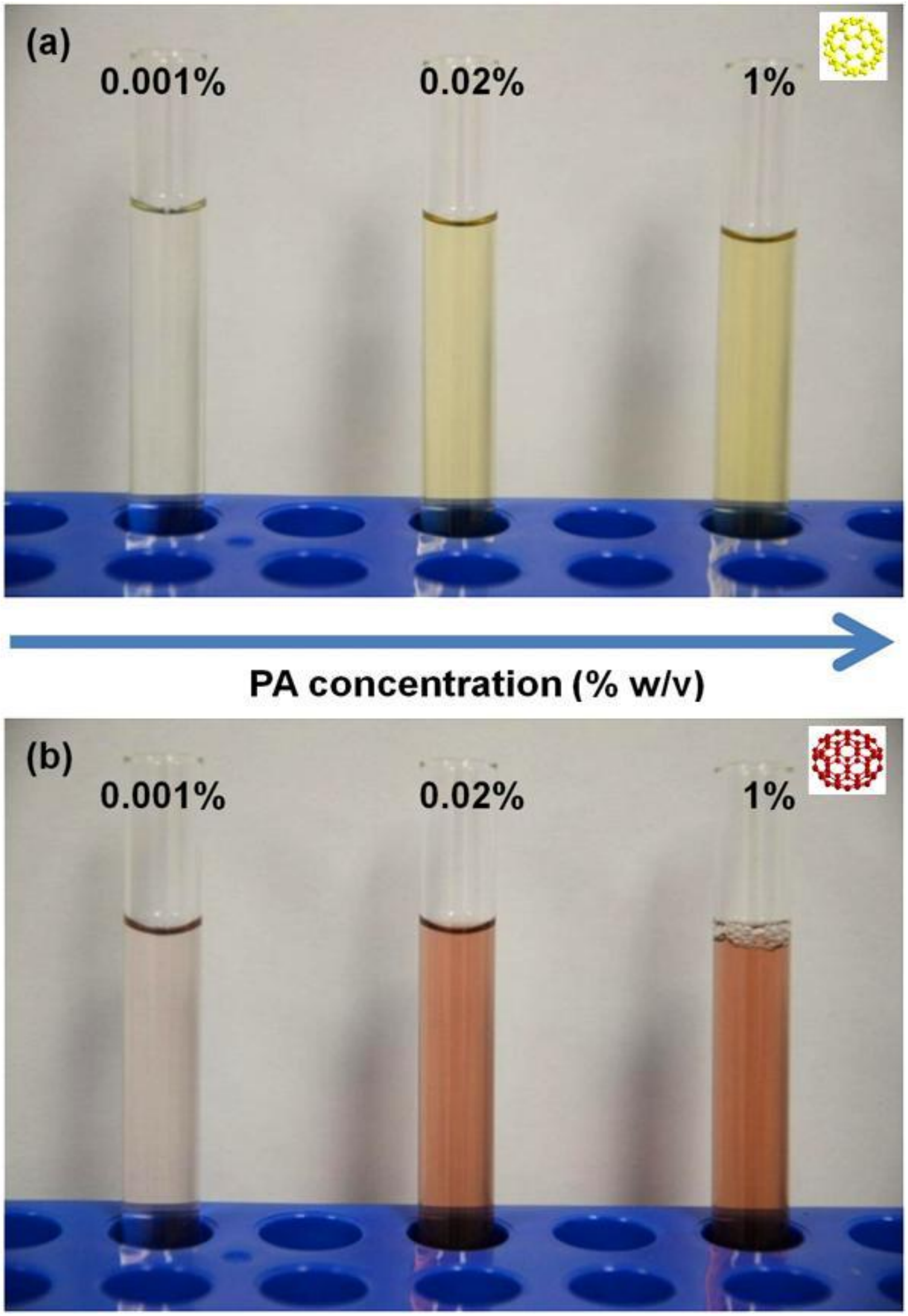
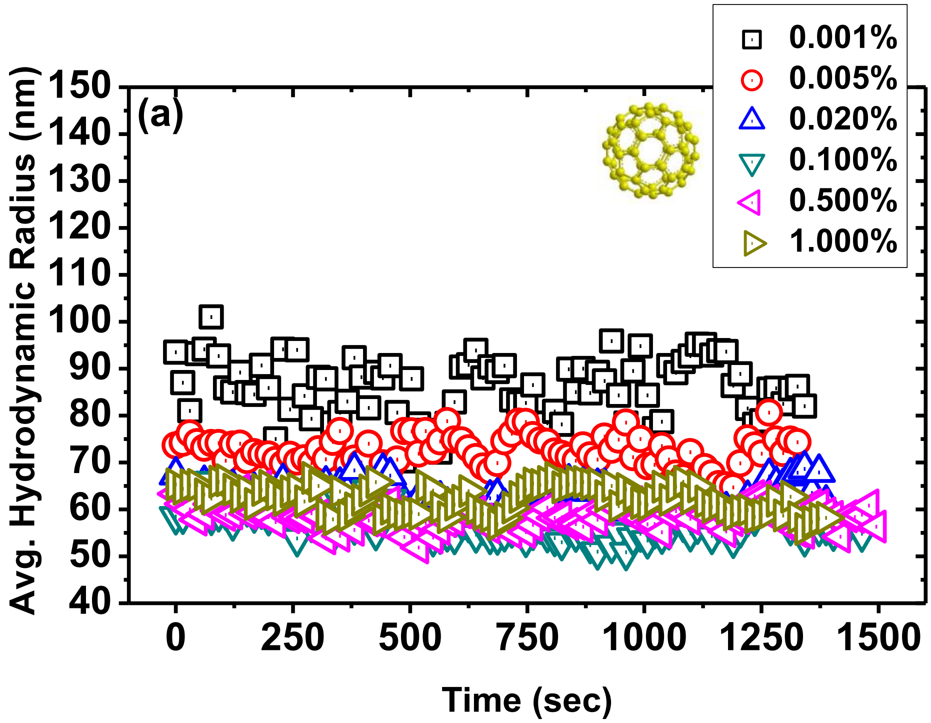


FIGURE C-1. PA solubilized colloidal (a) nC_{60} and (b) nC_{70} suspensions. The vials (from left to right) show increasing concentration of solubilized fullerenes with gradual increase in PA concentrations.

TABLE C-1. Polydispersity index (PDI) of nC_{60} and nC_{70} at different PA concentrations

PA conc. (% w/v)	**nC_{60}**	**nC_{70}**
	PDI	PDI
0.001	0.245±0.03	0.18±0.03
0.005	0.161±0.02	0.133±0.03
0.020	0.13±0.05	0.142±0.03
0.100	0.06±0.02	0.09±0.02
0.500	0.159±0.02	0.142±0.043
1.000	0.158±0.03	0.133±0.04



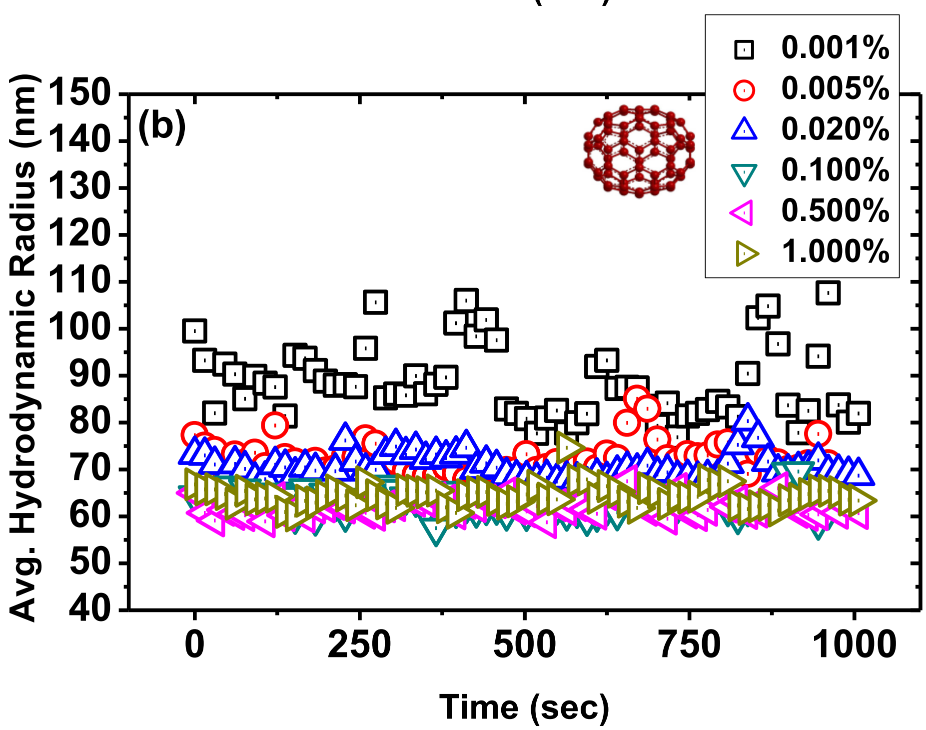


FIGURE C-2. Time dependent hydrodynamic radii profiles of aqueous (a) nC_{60} and (b) nC_{70} for a range of PA concentrations. Multiple stability runs were carried out at 22±0.5 °C.

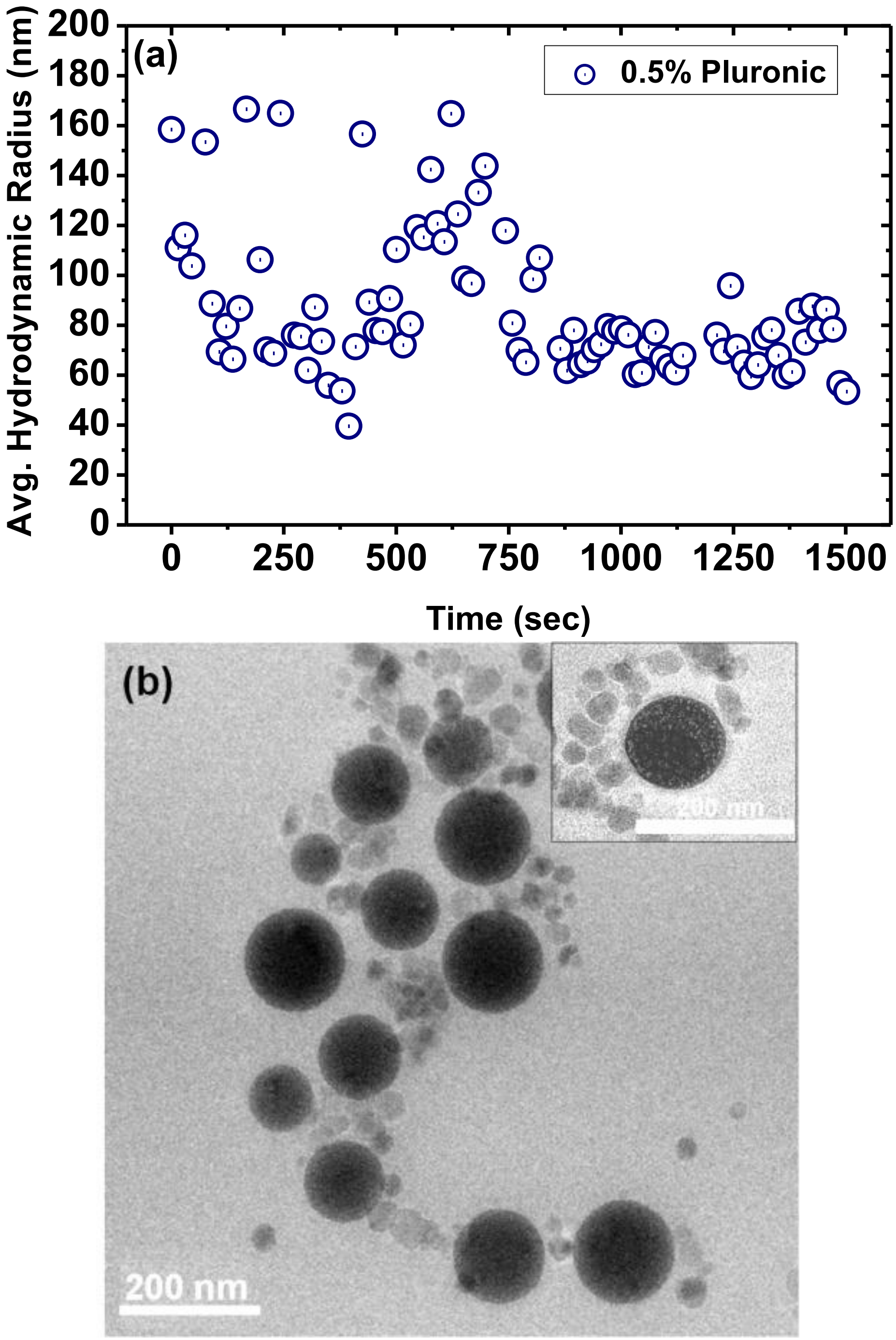
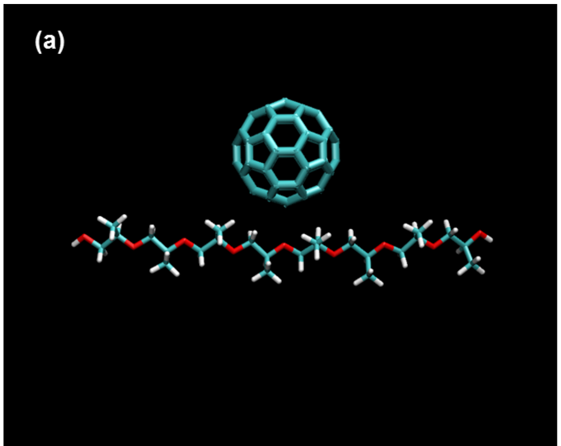
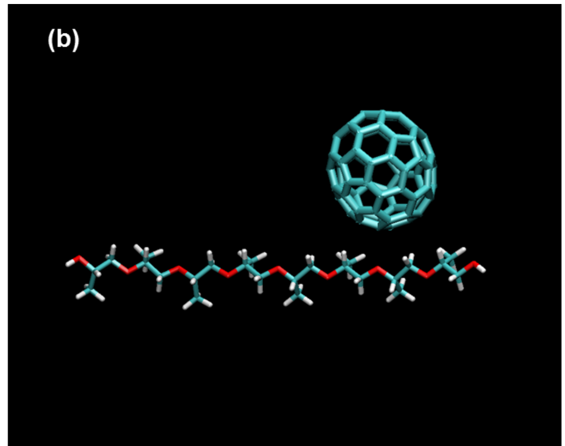


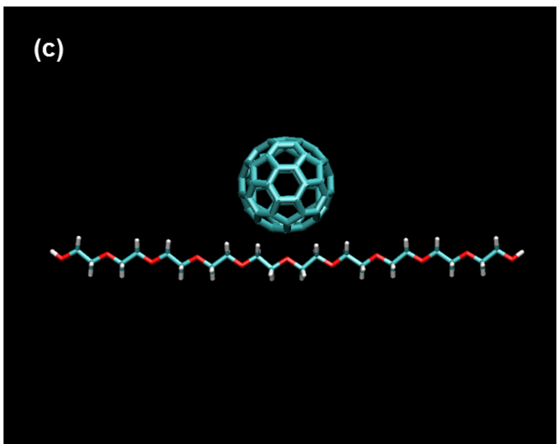
FIGURE C-3. (a) Hydrodynamic radii profile of PA micelles at 0.5 %w/v PA; and (b) TEM image of the 0.50 %w/v PA concentration, showing spherical PA micelles. Inset of (b) shows internal miceller features.



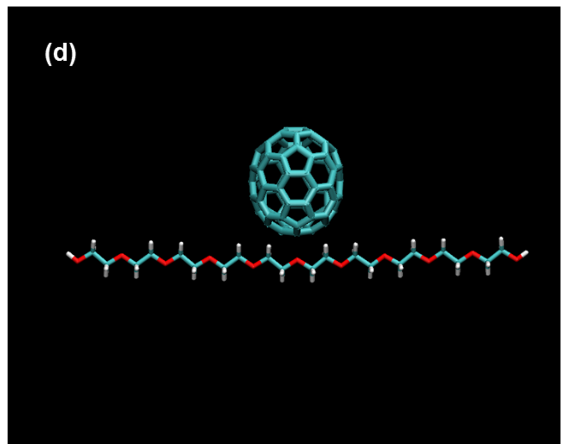
C_{60}-PA-center: –8.2 kcal mol^{-1}



C_{70}-PA-center: –8.5 kcal mol^{-1}



C_{60}-PA-edge: –9.4 kcal mol^{-1}



C_{70}-PA-edge: –8.6 kcal mol^{-1}

FIGURE C-4. BLYP-D3/6-31++G(d,p) optimized geometries of the individual fullerenes with the sections of the PA polymer and the corresponding interaction energies.

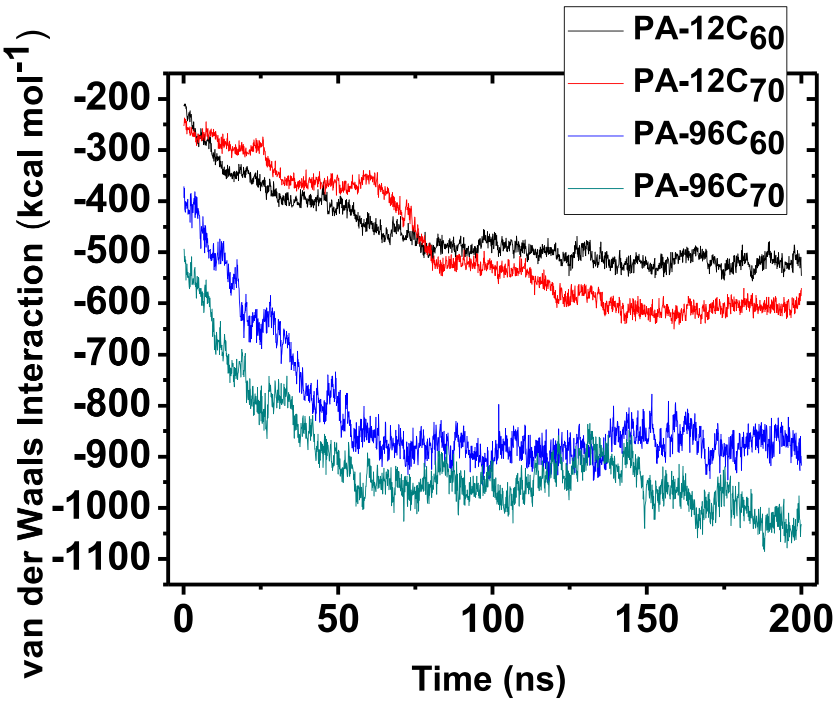


FIGURE C-5. Van der Waals interactions in PA-12C_{60}, PA-12C_{70}, PA-96C_{60}, and PA-96C_{70} complexes as found with time dependent MD simulation.

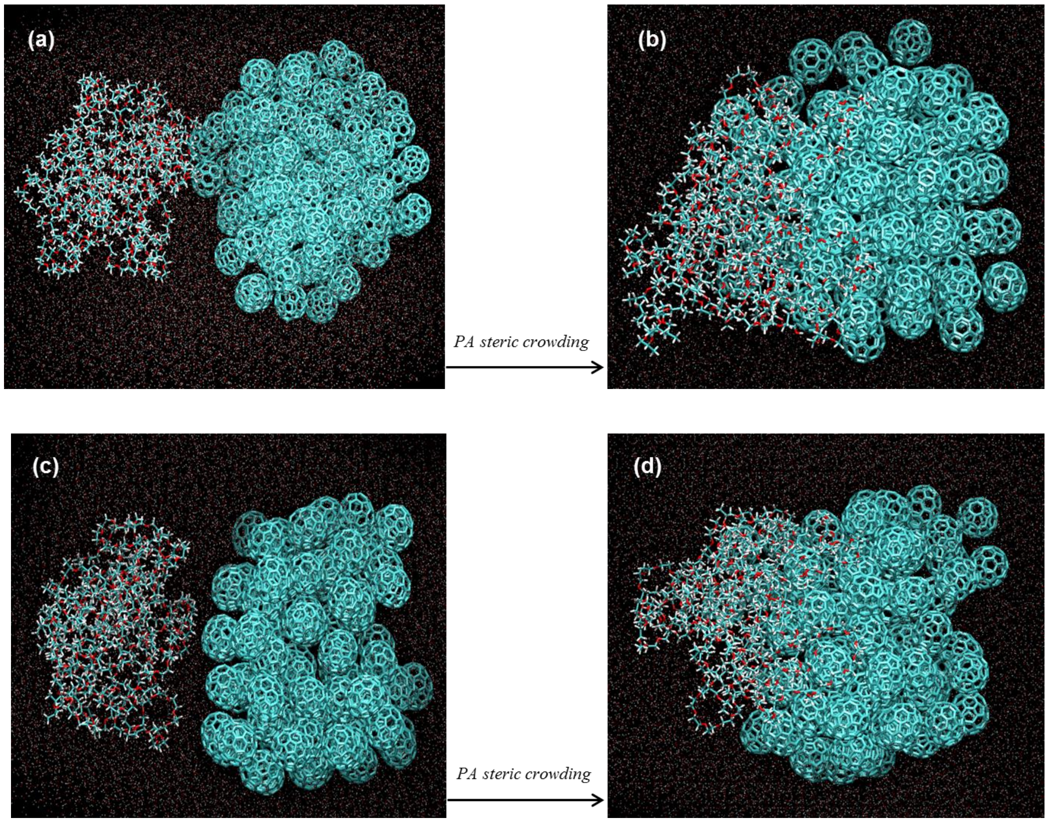


FIGURE C-6. Representative MD snapshot of (a) PA-96C_{60} starting configuration (b) PA-96C_{60} configuration after 200 ns simulation (c) PA-96C_{70} starting configuration (d) PA-96C_{70} configuration after 200 ns simulation.

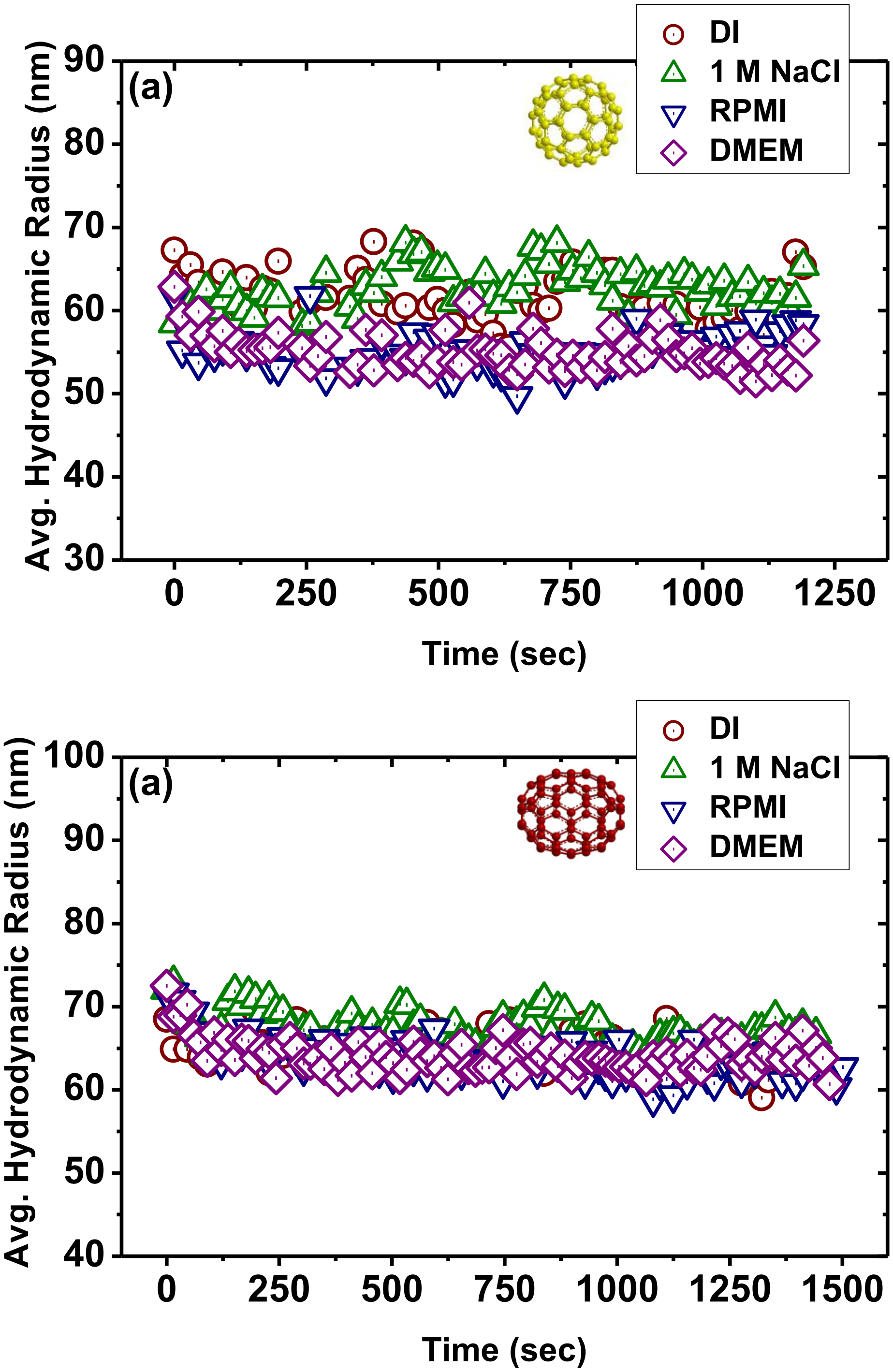


FIGURE C-7. Time-dependent hydrodynamic radii profiles of aqueous (a) nC_{60} and (b) nC_{70}, prepared with 0.020 %w/v PA in different media conditions. These experiments were carried out at 22±0.5 °C.

Appendix D

Supplemental Information for Chapter 6
Aggregation Kinetics of Higher Order Fullerenes in Aquatic Systems

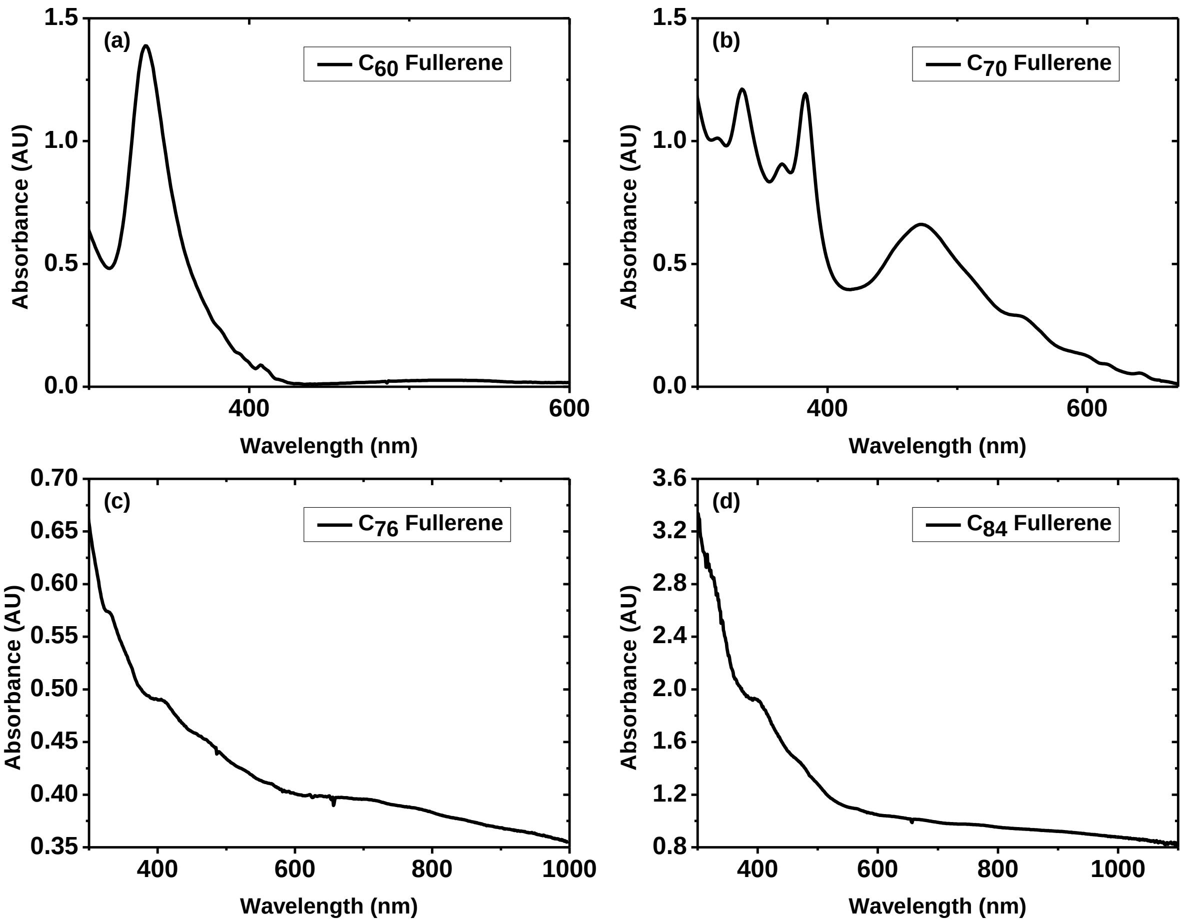


FIGURE D-1. UV-VIS spectra of (a) nC_{60}, (b) nC_{70}, (c) nC_{76}, and (d) nC_{84} in toluene. All measurements are performed at 21±0.5 °C.

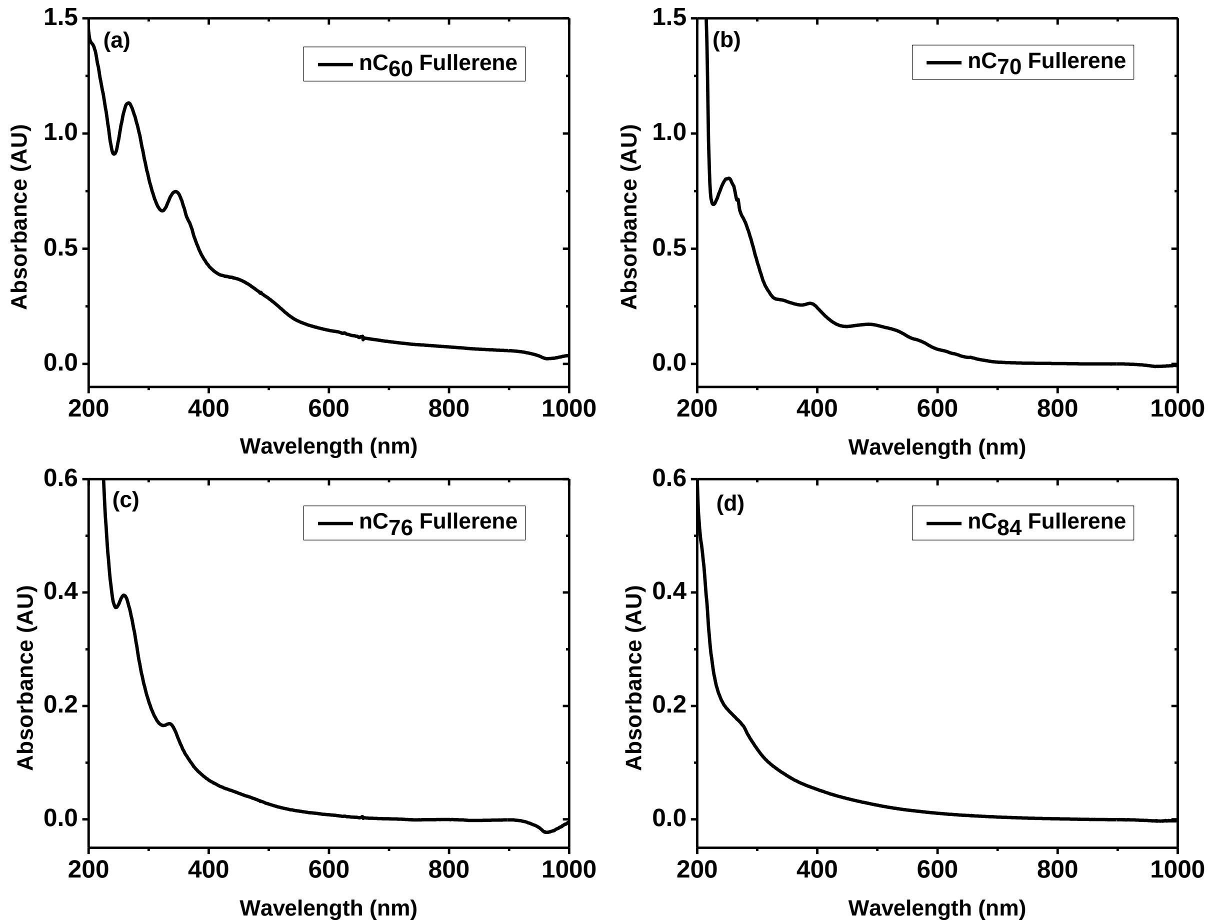
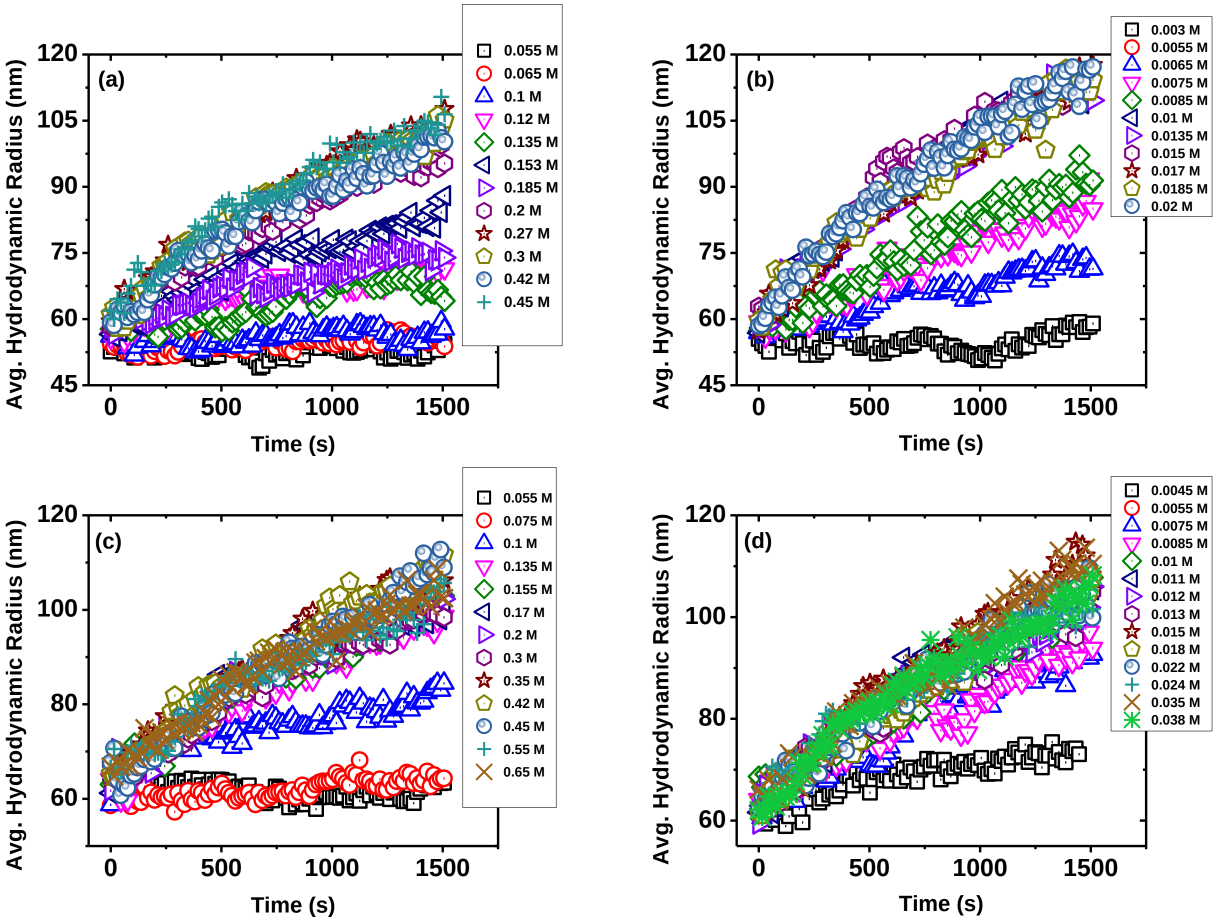


FIGURE D-2. UV-VIS spectra of (a) nC_{60}, (b) nC_{70}, (c) nC_{76}, and (d) nC_{84} in water. All measurements are performed at 21±0.5 °C.



(a)
Avg. Hydrodynamic Radius (nm)
Time (s)
0.055 M
0.065 M
0.1 M
0.12 M
0.135 M
0.153 M
0.185 M
0.2 M
0.27 M
0.3 M
0.42 M
0.45 M
(b)
Avg. Hydrodynamic Radius (nm)
Time (s)
0.003 M
0.0055 M
0.0065 M
0.0075 M
0.0085 M
0.01 M
0.0135 M
0.015 M
0.017 M
0.0185 M
0.02 M
(c)
Avg. Hydrodynamic Radius (nm)
Time (s)
0.055 M
0.075 M
0.1 M
0.135 M
0.155 M
0.17 M
0.2 M
0.3 M
0.35 M
0.42 M
0.45 M
0.55 M
0.65 M
(d)
Avg. Hydrodynamic Radius (nm)
Time (s)
0.0045 M
0.0055 M
0.0075 M
0.0085 M
0.01 M
0.011 M
0.012 M
0.013 M
0.015 M
0.018 M
0.022 M
0.024 M
0.035 M
0.038 M

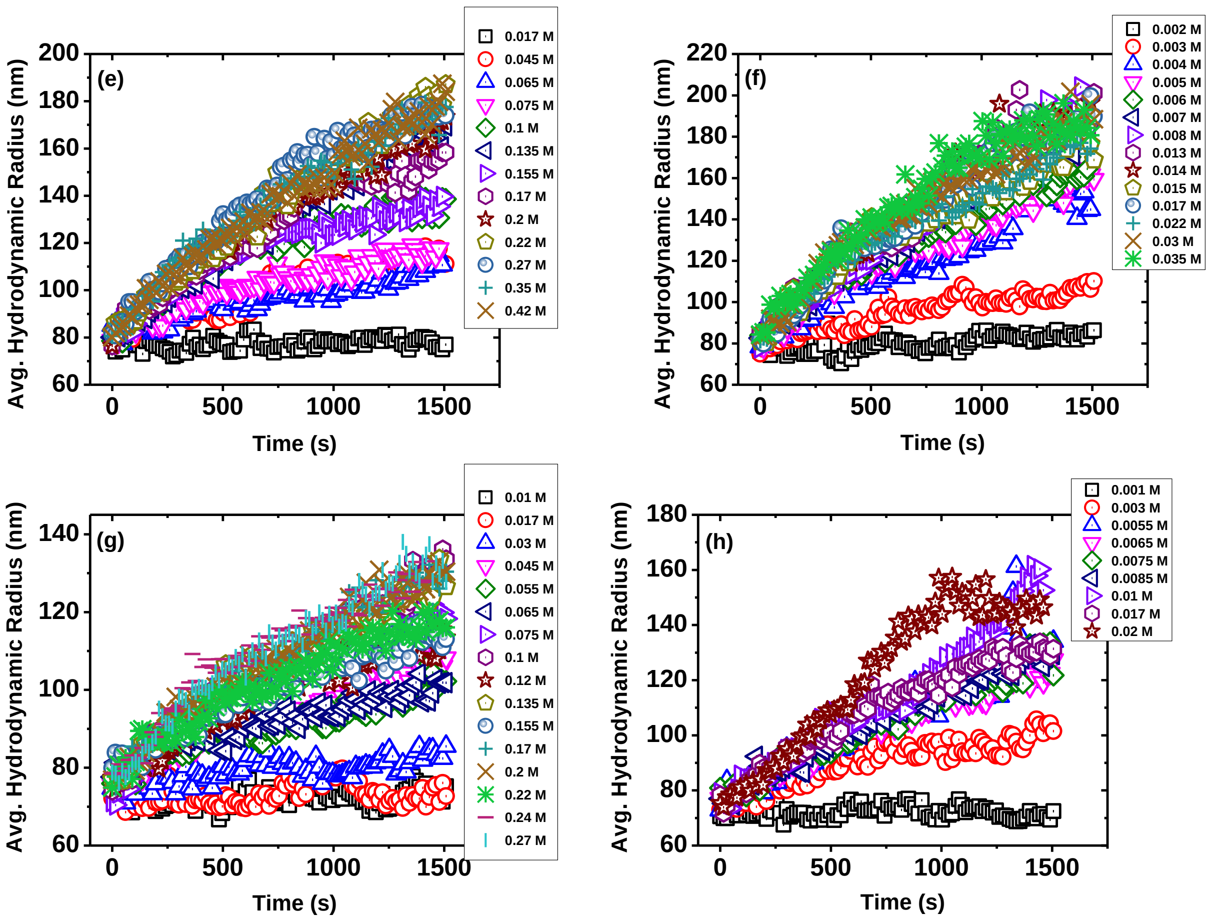


FIGURE D-3. Aggregation history of aqueous (a-b) nC_{60}, (c-d) nC_{70}, (e-f) nC_{76}, and (g-h) nC_{84} fullerenes in the presence of mono-valent NaCl (a, c, e, g) and di-valent $CaCl_2$ (b, d, f, h) electrolytes. All measurements are performed at 21±0.5 °C and at pH of 5.5-5.8 with no added buffer.

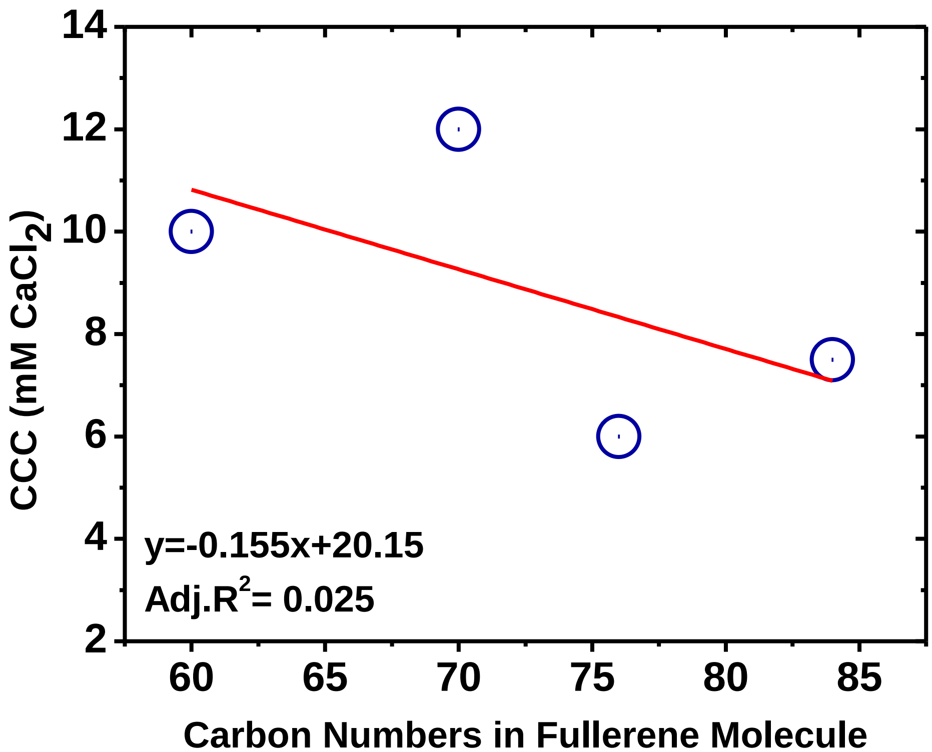


FIGURE D-4. Linear regression of CCC values with carbon numbers in fullerene molecules for di-valent $CaCl_2$ electrolyte.

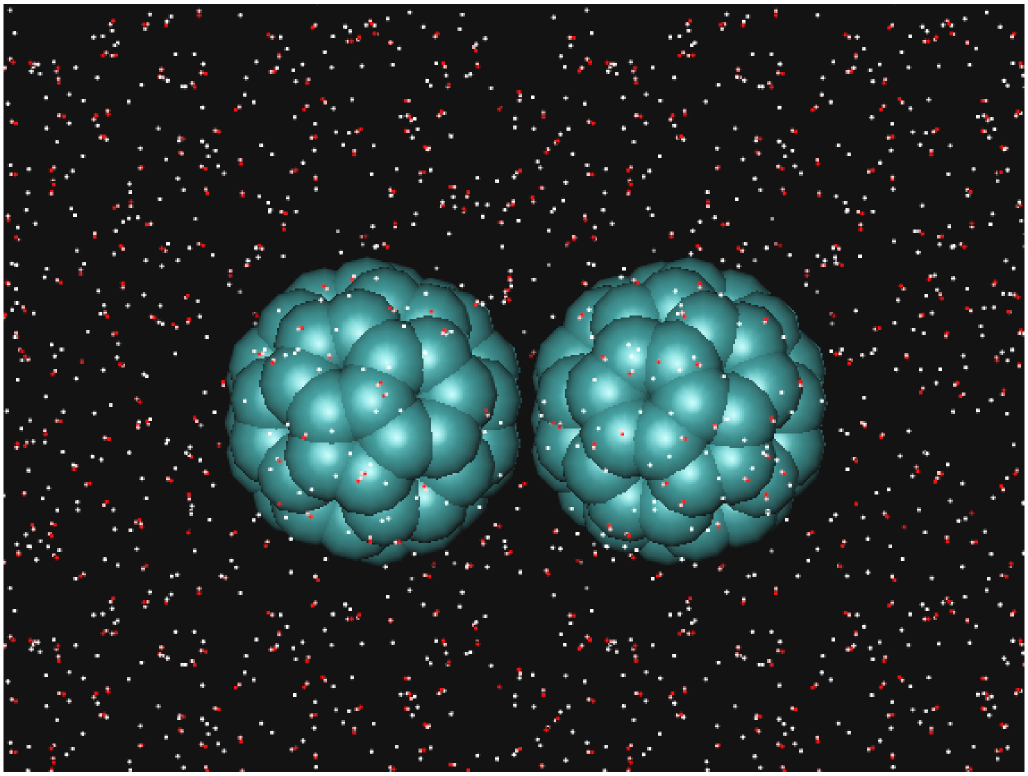


FIGURE D-5. Representative MD snapshot of C_{60}-C_{60} fullerene pair surrounded by an envelope of water molecules.

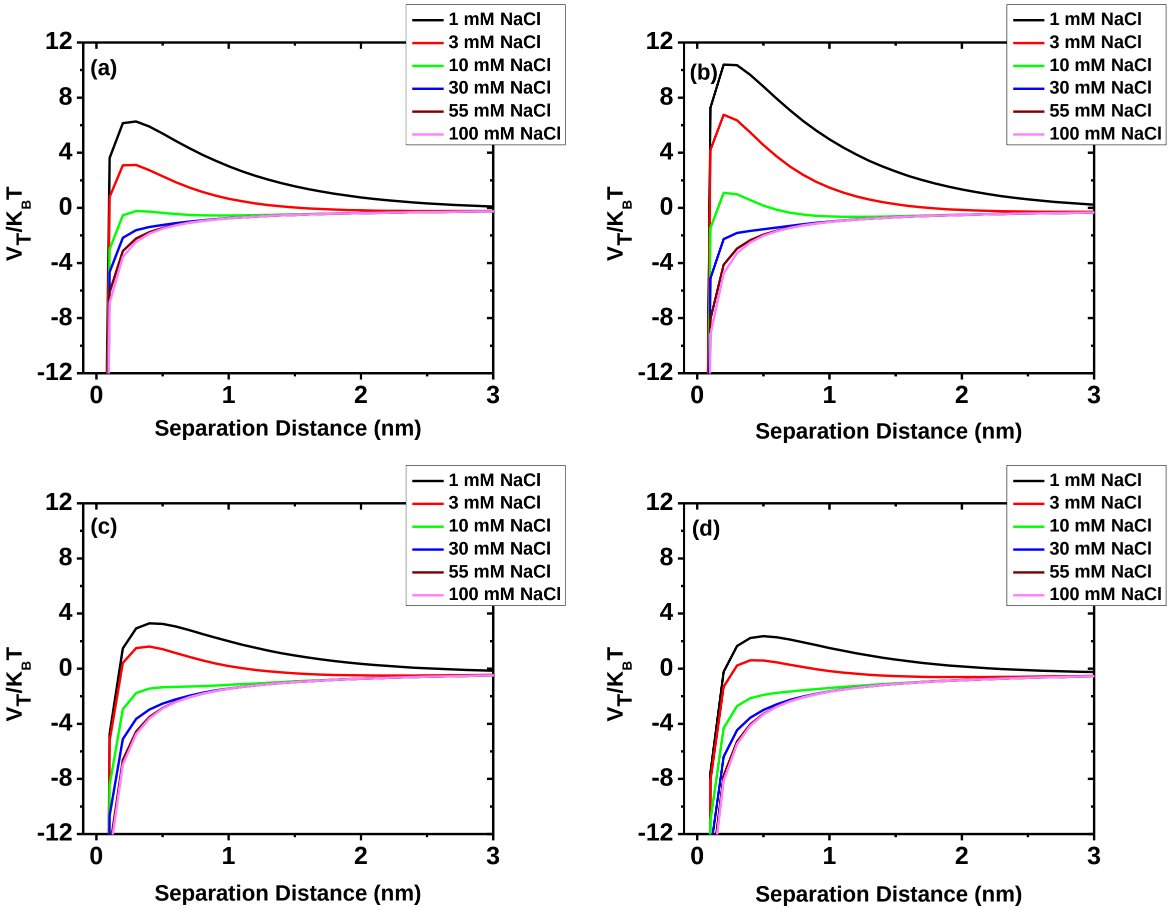


FIGURE D-6. Estimated total interaction energy (V_T/K_BT) with separation distance using modified DLVO theory for aqueous (a) nC_{60}, (b) nC_{70}, (c) nC_{76}, and (d) nC_{84} at different NaCl concentrations.

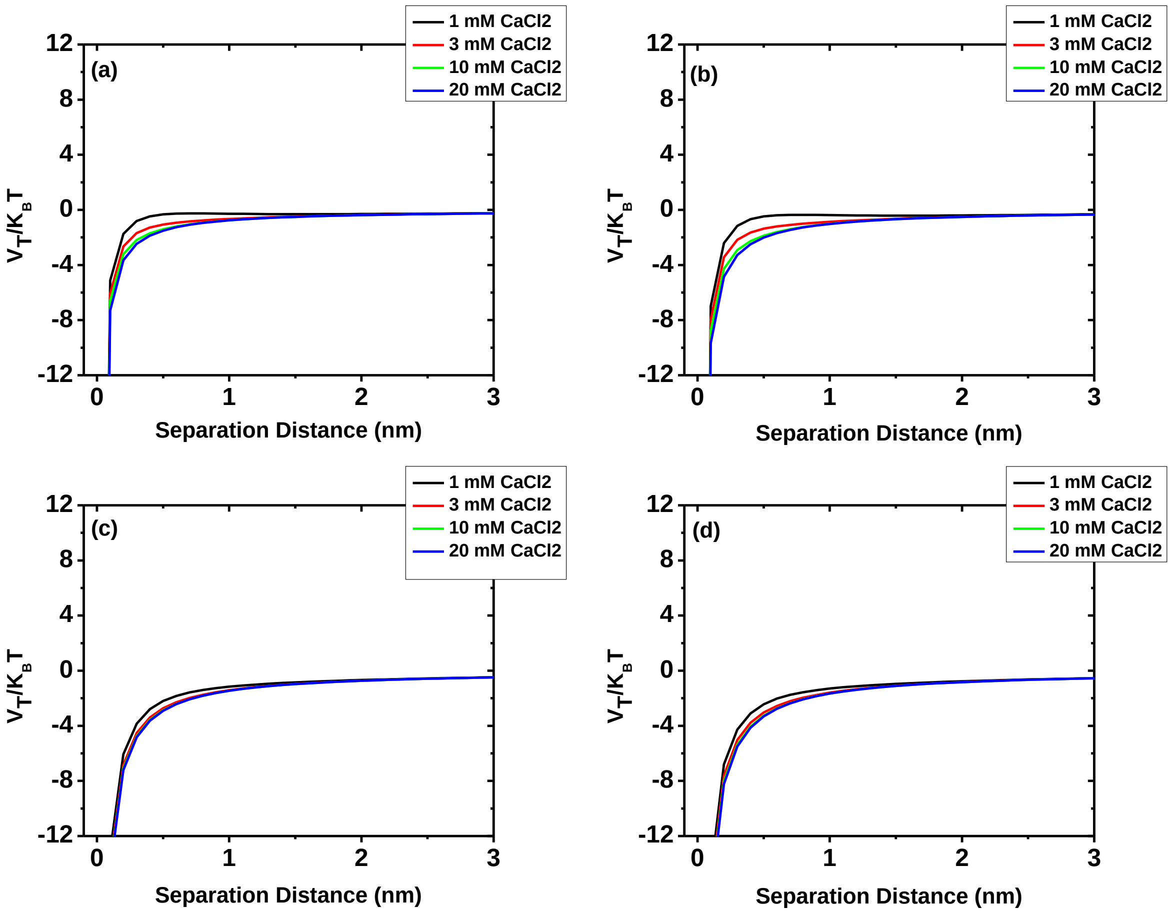


FIGURE D-7. Estimated total interaction energy (V_T/K_BT) with separation distance using modified DLVO theory for aqueous (a) nC_{60}, (b) nC_{70}, (c) nC_{76}, and (d) nC_{84} at different $CaCl_2$ concentrations.

Appendix E

Supplemental Information for Chapter 7
Aggregation Kinetics and Antimicrobiality of TiO_2-Multiwalled Carbon Nanotube Nanohybrids

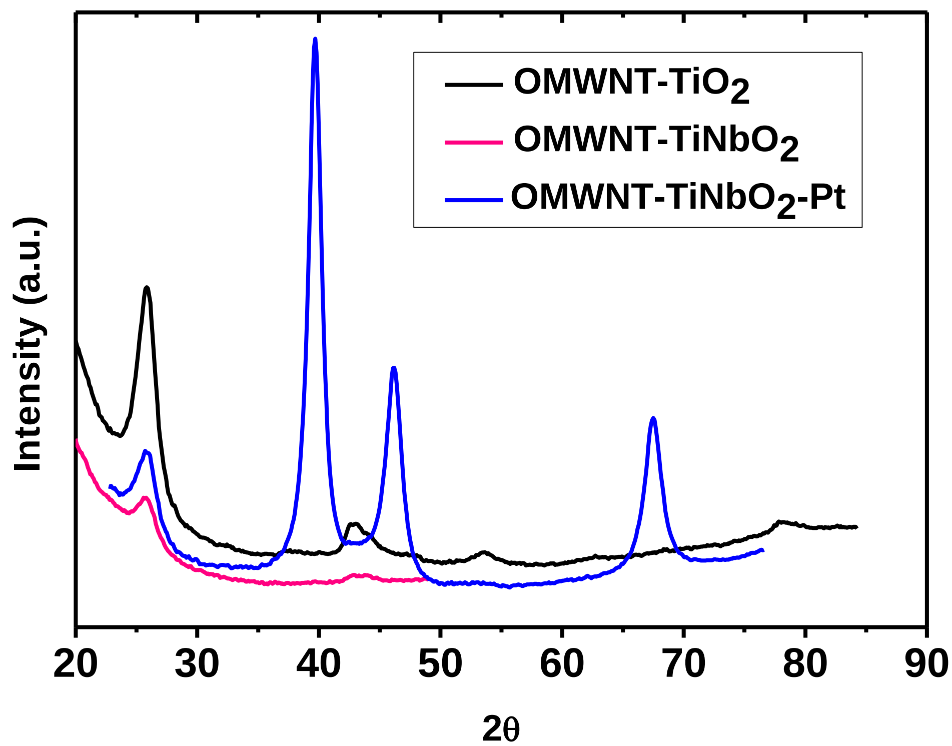


FIGURE E-1. XRD spectra of OMWNT-TiO_2, OMWNT-$TiNbO_2$ and OMWNT-$TiNbO_2$-Pt NH.

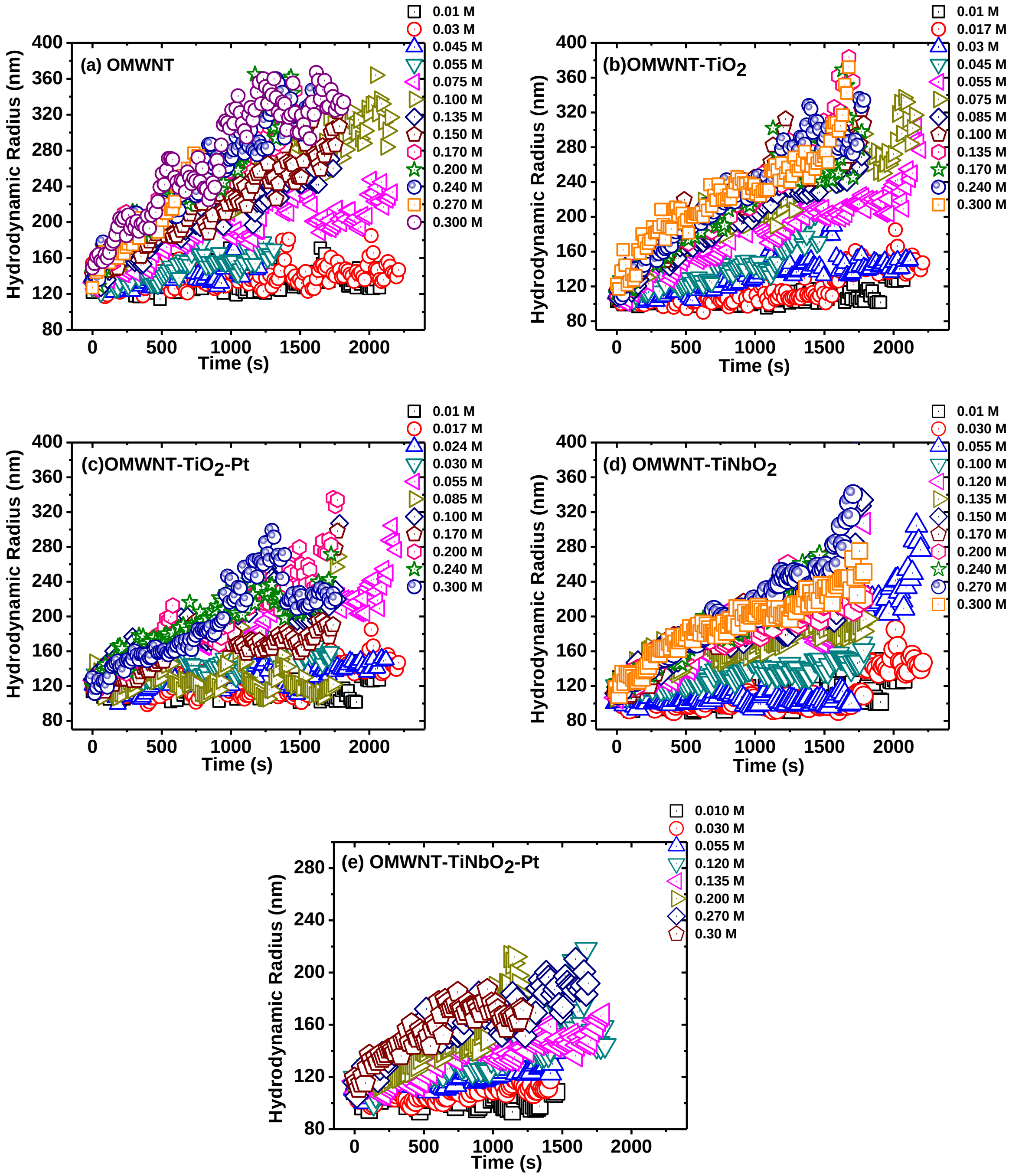


FIGURE E-2. Aggregation history profiles of (a) OMWNT, (b) OMWNT-TiO_2, (c) OMWNT-TiO_2-Pt, (d) OMWNT-$TiNbO_2$, and (e) OMWNT-$TiNbO_2$-Pt in the presence of different NaCl salt concentrations.

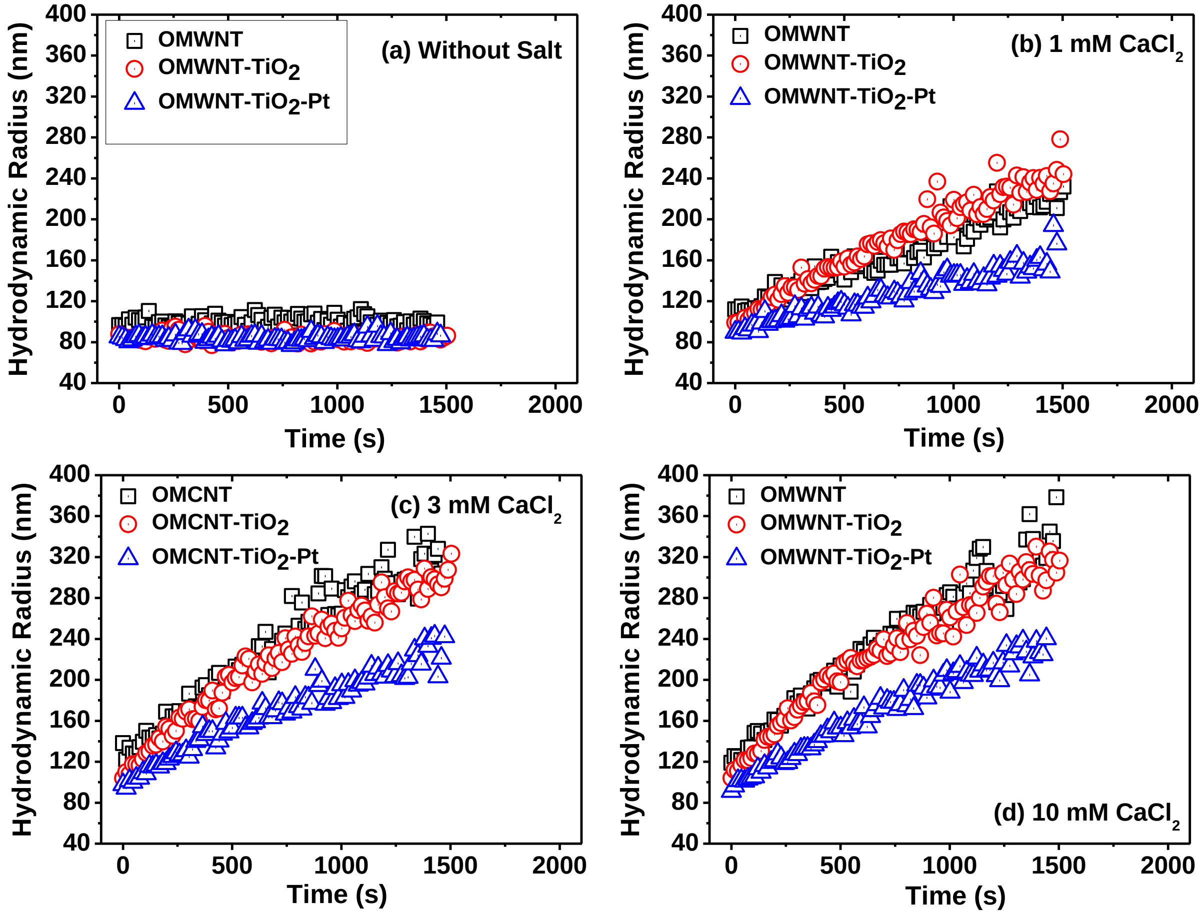


FIGURE E-3. Aggregation history profiles of OMWNT, OMWNT-TiO_2, and OMWNT-TiO_2-Pt in the absence (a) and presence (b-d) of $CaCl_2$.

Appendix F

Scholarly Contributions

E-1: Peer Reviewed Journal Articles **(**first author: 8**)**

(1) **Aich, N.;** Rigdon, W.A.; Das, D.; Plazas-Tuttle, J.; Huang, X.; Saleh, N. B., Aggregation kinetics and antimicrobiality of Tio_2-multiwalled carbon nanotube nanohybrids. (In Preparation).

(2) **Aich, N.;** Boateng, L. K.; Sabaraya, I. V.; Das, D.; Flora, J. R. V.; Saleh, N. B., Aggregation kinetics of higher order fullerenes in aquatic systems. *Environ. Sci. Technol.* 2015. (In Review)

(3) **Aich, N.,** Plazas-Tuttle, J., Lead, J.R., Saleh, N.B., "A Critical review of nanohybrids: synthesis, applications, and environmental implications", *Environ Chem*, 2014, 11, 609-623. (Cover Article)

(4) **Aich, N.*,** Kim, E.*, El-Batanouny, M., Plazas-Tuttle, J., Yang, J.K., Saleh, N.B., Ziehl, P., "Detection of crack formation and stress distribution for carbon fiber reinforced polymer specimens through triboluminescent-based imaging", *Journal of Intelligent Material Systems and Structures*, 2014, DOI: 10.1177/1045389x14535017.

(5) **Aich, N**, Boateng, L., Flora, J.R.V., Saleh, N.B., "Preparation of non-aggregating aqueous fullerenes in highly saline solutions with a biocompatible non-ionic polymer", *Nanotechnology*, **2013**, 24, (39), 395602.

(6) **Aich, N.,** Apalla, A., Saleh, N.B., Ziehl, P., "Triboluminescence for distributed damage assessment in cement based materials". *Journal of Intelligent Material Systems and Structures",* **2013,** 24, (14), 1714-1721.

(7) **Aich, N.,** Zohhadi, N., Khan, I.A., Matta, F., Ziehl, P., Saleh, N.B., "Applied TEM approach for micro/nanostructural characterization of carbon nanotube reinforced cementitious composites", *J Res Updates Poly Sci*, **2012**, 1, (1), 14-23.

(8) **Aich, N.**, Flora, J.R.V., Saleh, N.B., "Preparation and characterization of stable aqueous higher order fullerenes", *Nanotechnology*, **2012**, 23, (5), 1-7.

E-2: Peer Reviewed Journal Articles **(**co-author: 7**)**

(1) Saleh, N.B., Milliron, D., **Aich, N.,** Katz, L.E., Liljestrand, H.M., Kirisits, M.J., "Doping, dopant distribution, and nano-scale defects will affect electronic band structure: Implications for reactive oxygen species", *Sci Tot Envr*, (In Review)

(2) Saleh, N.B., Chambers, B.*, **Aich, N.*,** Plazas-Tuttle, J., Kirisits, M.J., "Mechanistic lessons learned from metallic nanomaterials' antimicrobial studies: Implications for nano-biofilm interactions", *Special Issue for Frontiers in Microbiology,* **2015,** 6.

(3) Khan, I.A, Afrooz, A.R.M.N., **Aich, N.,** Schierz, P.A., Flora, J.R.V., Ferguson, P.L., Sabo-Attwood, T., Saleh, N.B., "Change in chirality of semiconducting single-walled carbon nanotubes can overcome anionic surfactant stabilization: A systematic study of aggregation kinetics", *Environ Chem,* **2015**, (Online)

(4) Saleh, N.B., **Aich, N.**, Plazas-Tuttle, J., Lead, J.R., Lowry, G.V., "Research strategy to determine when novel nanohybrids pose unique environmental risks", *Environ Sci: Nano,* **2015,** 2, 11-18. (Cover Article)

(5) Saleh, N.B., Afrooz, A.R.M.N., Bisesi, J.H.Jr., **Aich, N.**, Plazas-Tuttle, J., Sabo-Attwood, T., "Emergent properties and toxicological considerations for nanohybrid materials in aquatic systems", *Nanomaterials,* **2014,** *4,* (2), 372-407. (Featured Article in 2014)

(6) Chambers, B.A., Afrooz, A.R.M.N., Bae, S., **Aich, N.,** Katz, L., Saleh, N.B., Kirisits, M.J., "Effects of chloride and ionic strength on physical morphology, dissolution, and bacterial toxicity of silver nanoparticles", *Environ Sci Technol,* **2014**, 48, 761-769.

(7) Khan, I.A., **Aich, N.,** Afrooz, A.R.M.N., Flora, J.R.V., Ferguson, P.L., Sabo-Attwood, T., Saleh, N.B., "Fractal structures of single-walled carbon nanotubes in biologically relevant conditions: Role of chirality vs. media conditions", *Chemosphere,* **2013**, *93*, (9), 1997-2003.

E-3: Book Chapters (first-author:1)

(1) **Aich, N.;** Saleh, N. B.; Plazas-Tutle, J., Fullerenes, higher fullerenes, and their hybrids: Synthesis, characterization, and environmental considerations. In *Carbon Nanomaterials for Advanced Energy Systems*, Lu, W.; Baek, J. B.; Dai, L. M., Eds. John Wiley and Sons, Inc.: Hoboken, NJ, 2014; pp 3-45.

E-4: Book Chapters (co-author:3)

(1) Saleh, N.B., Afrooz, A.R.M.N., **Aich, N.,** Plazas-Tuttle, J., "Aggregation kinetics and fractal structure of nanomaterials in environmental systems" in *Engineered Nanoparticles and the Environment: Biophysicochemical Processes and Biotoxicity*, 2014. *(In Press)*

(2) Zohhadi, N.; **Aich, N.;** Matta, F.; Saleh, N. B.; Ziehl, P., "Graphene Nanoreinforcement for Cement Composites" in *Nanotechnology in Construction*, Sobolev, K. and Shah, S.P. (Eds.), Springer New York: 2015; pp 265-270.

(3) Saleh, N. B.; Lead, J. R.; **Aich, N.;** Das, D.; Khan, I. A., "Environmental Interactions of Geo-and Bio-Macromolecules with Nanomaterials" in *Bio-Inspired Nanotechnology-From*

Surface Analysis to Applications, Knecht, M., Walsh, T (Eds.), Springer New York: 2014; pp 257-290.

E-5: Conference Proceedings (first Author: 6)

(1) **Aich, N.,** Rigdon, W.A., Das, D., Plazas-Tutle, J., Huang, X., Saleh, N.B., "Hybridization with titania changes aggregation kinetics of carbon nanotubes", 247th ACS National Meeting, March 16-20, 2014, Dallas, TX.

(2) **Aich, N.,** Das, D., Saleh, N.B., "Extent of tin doping influences nano indium tin oxide's aggregation behavior in aqueous systems", Second Sustainable Nanotechnology Organization Conference, November 3-5, 2013, Santa Barbara, CA.

(3) **Aich, N.,** Flora, J. R. V., Boatang, L., Saleh, N.B. "Size tuned aqueous nC_{60}s and nC_{70}s stabilized with biocompatible surface coatings", 245th ACS National Meeting, April 7-11, 2013, New Orleans, LA.

(4) **Aich, N.,** Saleh, N.B., "Aggregation kinetics of endohedral metallofullerene-single-walled carbon nanohorn and nanotube peapods", 241st ACS National Meeting, Mar 27-31, 2011, Anaheim, CA.

(5) **Aich, N.,** Saleh, N.B., "Aggregation kinetics of higher order fullerenes in aquatic environment", 241st ACS National Meeting, Mar 27-31, 2011, Anaheim, CA.

(6) **Aich, N.,** Saleh, N.B., "Aggregation Kinetics of Fullerene-Single-walled Carbon Nanotube Hybrids", 240th ACS National Meeting, Aug 22-26, 2010, Boston, MA.

E-6: Conference Proceedings (co-author: 10)

(1) Saleh, N.B., **Aich, N.,** Das, D., Kirisits, M.J., Sabo-Attwood, T., "Microbial interactions of carbon nanotube-titania-platinum nanohybrid electrocatalyst", 250th ACS National Meeting, August 16-20, 2015, Boston, MA.

(2) Das, D., Sabaraya, I.V., **Aich, N.,** Saleh, N.B., "Aggregation kinetics of carbon nanotube and metal or metal oxide nanohybrids in aquatic environment", 250th ACS National Meeting, August 16-20, 2015, Boston, MA.

(3) Bisesi, J.H.Jr., Ngo, T., **Aich, N.,** Rigdon, W., Huang, X., Saleh, N.B., Sabo-Attwood, T., "Analysis of the contributions of component materials to the toxicity of hybrid nanomaterials", 9th International Conference on the Environmental Effects of Nanoparticles and Nanomaterials (ICEENN), September 7-11, 2014, Columbia, SC.

(4) Saleh, N.B., **Aich, N.**, Chambers, B.A., Afrooz, A.R.M.N., Kirisits, M.J., “Influence of tin doping on environmental interactions of nano indium oxides in aqueous systems”, 247th ACS National Meeting, March 16-20, 2014, Dallas, TX.

(5) Saleh, N.B., **Aich, N.,** Rowles, L.S., “Synthesis and characterization of carbonaceous nanomaterial-mutimetallic hybrids for simultaneous removal of radioactive and organic contaminants: A case study on navajo nation”, 247th ACS National Meeting, March 16-20, 2014, Dallas, TX.

(6) Das, D., **Aich, N.,** Irin, F., Green, M.J., Saleh, N.B., “Surface coating dependent aggregation kinetics of graphene suspensions”, 247th ACS National Meeting, March 16-20, 2014, Dallas, TX.

(7) Saleh, N.B., **Aich, N.,** Plazas-Tutle, J. Lead, J.R., Rigdon, W., Huang, X., “Are nanohybrid environmental implication studies overdue?”, Second Sustainable Nanotechnology Organization Conference, November 3-5, 2013, Santa Barbara, CA.

(8) Daniels, K.M., **Aich, N.,** Miller, K.P., Andrews, J., Shetu, S., Daas, B.K., Sudarshan, T.S., Saleh, N.B., Decho, A.W., Chandrashekhar, M.V.S., “Real-time sensing of *E. coli* biofilm growth using epitaxial graphene”, 2013 IEEE Sensors, November 3–6, 2013, Baltimore, Maryland.

(9) Saleh, N.B., Afrooz, A.R.M.N., **Aich, N.,** Khan, I.A., “Filtration of anisotropic and hybrid nanomaterials”, 240th ACS National Meeting, Aug 22-26, 2010, Boston, MA.

(10) Saleh, N.B., Afrooz, A.R.M.N., **Aich, N.,** Khan, I.A., "Saturated porous media transport of anisotropic and hybrid nanomaterials", Environmental Effects of Nanoparticles and Nanomaterials, SETAC-Clemson University, Aug 22-26, 2010, Clemson, SC.

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Chapter 4

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