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# Green Intelligent Nanomaterials by Design (Using Nanoparticulate/2D-Materials Building Blocks) Current Developments and Future Trends

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Additional information is available at the end of the chapter

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## Abstract

Feasibility of designing and synthesizing ‘smart’ and ‘intelligent’ materials using nano-structured building blocks has been examined here based on the current status of the progress made in this context. The added advantages of using 2D layered/nonlayered materials along with phytosomal species derived from natural plants are highlighted with special reference to their better programmability along with minimum toxicity in biomedical applications. The current developments taking place in their upscaled productions are also included while assessing their upcoming industrial usages in diverse fields.

**Keywords:** materials by design, smart and intelligent materials, hybrid nanomaterials, targeted drug and gene deliveries, supramolecular complexes

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## 1. Introduction

The study of crystalline materials, initiated since the beginning of the twentieth century, took almost 6–7 decades to mature in the form of microelectronics and microsystems technologies creating a wealth of information in form of industrial know-how (FCM, 2009). Subsequently, the discovery of the nanomaterials followed by extensive R&D efforts put in during the last few decades resulting in simultaneous developments of production/application technologies enabled them to be integrated into the biological systems and is currently offering valuable supports to the activities in the area of nanobiotechnology – an interdisciplinary field [1].

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Finding inorganic/organic molecules biocompatible in hybrid nanomaterials syntheses, it was natural to explore mimicking the features of some simple living organisms in the pursuit of developing 'smart' and 'intelligent' materials responding to the environmental stimuli to start with. Consequently, attempts were made to identify the basic requirements of the materials to qualify for being 'smart' or 'intelligent.' Despite using these terms interchangeably earlier, some clarity started emerging particularly after several comprehensive deliberations held on this issue in different forums in form of two distinct levels of interactions between materials and the external stimuli. For instance, the materials that respond to the external stimuli by showing appreciable changes in their properties are termed as 'smart' leading to fabricate a variety of sensors and actuators. However, the material becomes 'intelligent' once it is endowed with the capability of reorganizing itself internally to take care of the changes due to external stimuli adaptively, and in such cases, a number of in-built features must be involved internally in a way similar to those in a conventional control system. For instance, the changes in material properties arising out of material-stimuli interactions must be communicated to a decision-making component of the material along with memory functions for taking decisions to initiate appropriate actions for countering the changes within a reasonable time period, which is an important parameter that may vary under different circumstances [2–5].

Coming back to the discussion of nanostructured materials, it may be noted that the modifications introduced into their physico-chemico-biological properties are considered as the result of the quantum confinement superimposed upon their bulk properties culminating into the morphology-specific features with enhanced activity arising from the exposure of the surface residing atomic species with sufficient unsaturated chemical bonds. These nanomaterials are subjected to still further modifications via their chemical conjugations involving strong/weak interactions in preparing the 1/2/3-dimensional nanobuilding blocks like nanowires, nanotubes, nanocoils, nanoropes, besides synthetic superlattices, and functional nanocomposites in addition to many other functional entities that are still being explored for their resultant structure-activity relationships (SAR) for developing newer materials. Further, the macromolecular species involving fullerenes, nanowires, nanotubes, and dendrimers prepared using different constituent materials are also being considered for new material discoveries owing to their chemical conjugations with a whole host of inorganic, organic, and biomolecular species [6–9].

The established links between the inorganic nanoparticles (NPs) and the biomolecular species using the biopolymeric compounds in different configurations possessing biocompatible, biodegradable, and low immunogenic features are currently being used in fabricating nanobiocarriers in drug/gene deliveries involving the polysaccharides, proteins, and nucleic acids to name a few [6]. For such applications, it is indeed imperative to control their morphology, surface charges, and the release profiles of the loaded therapeutic species. Subsequently, numerous bioactive nanomaterials were developed using silk proteins, collagen, gelatin, casein, albumin, protein-mimicking polypeptides, and polysaccharides like chitosan, alginate, pullulan, starch and heparin as typical examples. Protein engineered polymeric scaffolds, in addition, have been used in developing protein-polymer hybrids, where polymerization induces multifunctional properties leading to improved performances. Various kinds of supramolecular hydrogels with physicochemical properties for drug and gene deliveries owing to their features like good water-retention, better drug loading, biodegradability,

biocompatibility, stability combined with multiple functionalities including optoelectronic properties, bioactivity, self-healing, and shape-memory effects were consequently explored and put to use. In addition, their stimuli responding gel/sol transitions (reversible) due to their noncovalent cross-linkages-based interactions were considered as promising bioscaffolds in theranostics. Various SAR aspects of these hydrogels with particular reference to their applications in bioimaging/detection, therapeutic delivery, and tissue engineering were reviewed recently [6–8, 10–18].

The phenomenon of self-assembly with special reference to the supramolecular assemblies using noncovalent intra-/intermolecular interactions has been invoked in producing the micro-/nanostructures including micelles, membranes, vesicles, and liquid crystals in the framework of crystal engineering. Molecular recognition-based 'host-guest' complexes are currently finding increasing applications in the development of molecular sensors and catalysis. It is important to note that the enhanced reactivity associated with the nanostructured materials has always been useful in molecular recognition-based self-assemblies providing environment for the ensuing chemical reactions. Noncovalent bonds between the reactants and 'template' holding the reactants close to the reactive sites provide the required environment for chemistry. Mechanically interlocked molecular architectures of topologically connected molecules involving noncovalent bonds in catenanes, rotaxanes, molecular knots, molecular rings and ravel are known to mimic the biological systems in form of photo-electro-chemical systems, catalytic systems, protein designs, and self-replications. A template molecule surrounded by functional monomers starts attaching them via intergroup interactions that helps in forming an imprinted matrix after polymerization. Subsequent removal of the template forms complementary cavities offering selective binding sites for new material synthesis [19].

While developing these numerous types of nanomaterials, a new class of condensed state materials was discovered exhibiting properties that surpassed those of the bulk and conventional nanomaterials. The theoretical studies of these atomically thin two-dimensional (2D) nanomaterials have, in the mean time, uncovered a number of novel features particularly arising out of the electron confinement in the third dimension without interlayer interactions (monolayer) resulting in extreme mechanical flexibility and optical transparency well suited for the fabrication of highly flexible and transparent electronic/optoelectronic devices, and the large surface to volume ratio making them appropriate for surface active applications. This fascinating field of graphene-like 2D layered nanomaterials (GLNs) includes a number of already explored materials like graphene, hexagonal boron nitride (h-BN), transition metal dichalcogenides (TMDCs), graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>), layered metal oxides, layered double hydroxides (LDHs) besides materials belonging to metal-organic frameworks (MOFs), covalent organic frameworks (COFs), polymers, metals, black phosphorus (BP), silicene, and MXenes. Driven by their extraordinary characteristic properties assessed theoretically and validated partly in some cases, a large number of synthetic methods including mechanical/chemical exfoliations, ion-intercalation and exfoliation, anion-exchange and exfoliation, chemical vapor deposition (CVD), and wet-chemical syntheses have been developed for preparing them for numerous applications. These nanomaterials are showing high promises for a variety of applications in electronics, optoelectronics, catalysis, energy storage and conversion, biomedicine, sensors, and many more [20]. Their other physicochemical properties like strong

mechanical strength, unparalleled thermal conductivity, remarkable biocompatibility, and ease of surface functionalization make them highly useful in biochemical/medicinal applications particularly in biosensors, and nanomedicine comprising of electrochemical biosensors, optical biosensors, bioimaging, drug delivery and cancer therapy [21].

In particular, after the discovery of graphene, these 2D layered materials were exfoliated in the form of solvent dispersed crystalline few-/monolayers comprising the covalently bonded few atoms forming the crystalline stack, when bundled together with the van der Waals forces. For instance, heterostructures formed out of these monolayers of chalcogenides, graphene, and hBN are currently being examined as building blocks with tailored electronic band structures and associated physicochemical properties. Some of these predictions are yet to be realized experimentally as cited by many [22–38].

While studying the influence of structural features of these 2D material species, the characteristic features of the lamellar and 2D layered/nonlayered materials were found showing additional features worth use. It may particularly be noted that these 2D nanosheets not only exhibit novel optical and electronic properties due to the confinement of electron states along c-axis but also help in forming a variety of layered nano-/microsize entities involving differential stresses present in their bilayers to enforce numerous kinds of self-assemblies that are being explored in targeted deliveries. Based on these special features of 2D layered and nonlayered thin films along with the synthesis of lamellar nanoassemblies, an attempt has been made here in this chapter to highlight their syntheses along with their some novel applications already studied.

In the context of examining the usability of biopolymeric species in nanomedicines, the self-assembled liposomes were found offering special features that are quite useful in the targeted deliveries, where the hydrophilic/hydrophobic contents embedded in nano-/microsize double-layer enclosed spherical volumes with very effective protections from the enzymes, alkaline solutions, digestive juices, bile, and intestinal flora inside human body as well as free radicals. Accordingly, the liposomes are not only noted to check the oxidation and degradation of the embedded cores but also retain their double-layer barrier intact until the contents are delivered to the desired site. Discovered in the 1960s, liposomes are known to possess versatile features owing to their compositional variability and structural properties leading to a number of pharmaceutical, nutraceutical, and cosmeceutical applications, wherein, even the herbal extracts like flavonoids, glycosides, and terpenoids have been enclosed and transported from the hydrophilic to the lipophilic part of the membrane showing better bioavailability/efficacy, as noted in case of ginkgo biloba, grape seed, green tea, milk thistle, ginseng, and many other herbal families already explored for their applications in therapeutic formulations and dietary supplements [6, 7, 11, 18]. Liposomes are currently used in the pharmaceutical applications showing promises as intracellular delivery systems for antisense molecules, ribosomes, proteins/peptides, and DNA. Liposomes with enhanced drug delivery and long circulation times are finally getting clinically accepted as the liposomal drugs exhibiting reduced toxicities while retaining enhanced efficacy compared to their free complements [39–41].

Before putting these synthetic materials species to use in the form of nanomedicines, their toxicity features must be rigorously evaluated following the recommended standard procedures. Somehow, the data available in this context are inadequate as the associated toxicity

is a complex function of the surface modification causing highly variable solubility of the inorganic nanomaterials. Accordingly, the associated toxicity scare is so strong that the regulatory authorities permit no relaxation in allowing for their human trials. Because of the mostly unknown nanotoxicological properties of these newer kinds of synthetic nanomaterials, even their nonbiological applications are presumably not considered safe, which, to a certain extent, has been creating hurdles in developing their further applications [42].

A relatively safer approach of mitigating these toxicity issues could be to use the benign nanomaterials particularly derived from the plants as phytochemicals. Such nanobuilding blocks of natural origin, already studied extensively in the recent past, are not only found adequately safe but are also compatible with numerous biomolecular species ensuring more benign interactions in contrast to those derived from purely synthetic materials of inorganic/organic origins. This approach is certainly green in nature while meeting various requirements of hybrid nanostructured materials species put to use in form of novel applications. A large variety of biomimetic designs are thus becoming feasible to invoke once green phytosomal building blocks are put to use in synthesizing new kinds of materials [11].

The recent developments in the field of liposomal encapsulations involving single/multiple bilayer nanosize enclosures and graphene-like few-/monolayered nanosheets, introduced above in very brief, do indicate toward the suitability of using these nanosize thin films as building blocks capable of imparting novel features for their applications that will be appreciated with wider impacts in the times to come. Keeping in view the importance of this growing field of nanosize thin film materials, an effort has been made here in this review by assessing the current status before attempting to foresee the trends from the angle of developing intelligent materials in due course of time by employing them in new materials discoveries.

## 2. Programmable physicochemical properties

The phenomenon of quantum confinement involved in preparing 1-, 2-, and 3D nanomaterials has already been validated experimentally before using them in newer applications while considering the electrons and the photons together in the form of diverse material building blocks designs as highlighted in the following.

### 2.1. Metal and semiconductor NPs

The plasmon resonance excited in metal NPs in the presence of a dielectric as a function of morphology and the metal used, and falling in the visible/IR region, have been exploited in electromagnetic enhancement resulting in Raman, fluorescence, and infrared absorption spectroscopies for single molecule detection; tip enhanced Raman spectroscopy, optical circuits, high efficiency LEDs, chemical/biochemical sensors, and efficient solar cells due to better light confinement in the photoactive material, or achieving resonant internal light scattering. In one of the highest efficiency organic solar cells, for instance (P3HT: PCBM bulk HJ), the efficiency limitations due to lower cutoff wavelength ( $\sim 650$  nm/ $E_g \sim 2.1$  eV) was taken care of by enhancing optical absorption as reported [43–55].

Semiconducting NPs, also called quantum dots (QDs), behave like quasi-atoms with electrons/holes possessing discrete energy levels, and exhibiting size-specific absorption and luminescence spectra characterized by the material used. QDs are very efficient light emitters with photoluminescence quantum efficiency  $\sim 80\%$  and size-dependent emission characteristics. For instance, varying the size of CdSe QDs from 3 to 6.5 nm changed the emission from 470 to 630 nm. A number of optoelectronic devices using QDs are reported including biological tags, white LEDs, OLEDs, and photovoltaic solar cells (PVSCs) with efficiencies exceeding Shockley-Queisser limit [56–61].

## 2.2. Polymeric NPs

A variety of polymeric NPs involving either dispersion of preformed polymers or the polymerization of monomers have been reported using techniques like solvent evaporation, salting-out, dialysis, supercritical fluid technology, microemulsion, miniemulsion, surfactant-free emulsion, and interfacial polymerization, where the actual choice depends on a number of factors like particle size, size distribution, and the area of applications as discussed in a recent review [62].

Investigations have already correlated the physicochemical properties of the polymeric NPs with their biological responses, in which the morphology and surface charges on biodegradable entities were explored in designing various formulations in a recent review highlighting the challenges involved with *in vivo* trials [63]. Polymeric NPs are known to offer not only protection from environmental stimuli but also providing site-specific deliveries, particularly in case of charged NPs that are well protected. Parameters like uptake, bioavailability, and long-term therapeutic efficacies are possible to optimize by controlling their electrostatic interactions as mentioned below [64].

The study of drug release characteristics of diazepam loaded PLGA NPs confirmed that the parameters like sonication time, polymer content, surfactant, ratio of organic to aqueous phase, and the amount of drug—all influenced their sustained release [65]. Similarly, surface modifications of poly (ethylene glycol)-*b*-poly ( $\epsilon$ -caprolactone) (PEG-*b*-PCL) NPs by 1, 4 and 8-residue-long oligoarginines caused substantial increase in cellular uptake highlighting the influence of surface functionalization of polymeric NPs in subcellular targeting [66]. In yet another study, core-shell type NPs, loaded with doxorubicin (DOX), were assessed for their *in vitro* cytotoxicity against breast cancer and human fibroblast cell lines in which AgNPs, Ag/PVA and Ag/PVP NPs were found more cytotoxic to MCF-7 cells than normal fibroblasts, as well as DOX-Ag, DOX-Ag/PVA, DOX-Ag/PEG and DOX-Ag/PVP nanocarriers exhibiting enhanced cytotoxicity to breast cancer cells [67]. The inorganic NPs embedded polymer matrix showed enhanced performance as discussed in a recent review dealing with preparation and characterization of cytocompatible multifunctional polymeric NPs by analyzing their fluorescence efficiency, the nature of the artificial cell-membrane structure, and their performance as *in-cell* devices [68]. In enzyme replacement therapy of lysosomal storage disorders (LSDs), using PLGA NPs modified with 7-aminoacid glycopeptide (g7) NPs along with high MW drug (FITC-albumin) improved the barrier crossing of albumin while delivering the drug to the brain [69].

### 2.3. Supramolecular systems

Molecular self-assembly is exploited in supramolecular formulations for preparing molecular assemblies through noncovalent intra-/intermolecular interactions resulting in the formations of micelles, membranes, vesicles, and liquid crystals. Molecular recognition-based host-guest complexes are now being exploited in molecular sensors and catalysis. It is noteworthy that reactive species are found essential for participating in such molecular-recognition-based self-assemblies providing environment for chemical reactions. Noncovalent bonds between the reactants and template holding the reactants near the reactive sites provide the environment for chemistry. Mechanically interlocked molecular architectures are formed consisting of topologically linked molecules involving noncovalent bonds in molecular architectures like catenanes, rotaxanes, molecular knots, rings and ravel. There are a number of these systems that mimic the biological processes through photo-electro-chemical/catalytic systems, protein designs, and self-replications. In another process of molecular imprinting, a host is constructed out of suitable molecules as a template that is subsequently removed leaving the guests stabilized through steric interactions besides incorporating hydrogen bonding and other interactions.

Numerous molecular systems that have been studied recently include mechanically interlocked systems employing  $\pi/\pi$  charge-transfer interactions of bipyridinium with dioxyarenes and diaminoarenes, crown ether binding with metal/ammonium cations, formations of carboxylic acid dimers and other hydrogen bonding interactions, bi/tri-pyridines combinations with ruthenium, silver, and other metal ions, and complexation of porphyrins and phthalocyanines around metal ions used by Nature in abundance. Similarly, there are macrocycles providing cavities surrounding guest species during chemical modifications for fine-tuning of their features, cyclodextrins, calixerenes, cucurbiturils, and crown ethers; cyclophanes, and cryptands; metallocycles with metal ions in the ring formed from angular and linear modules including triangles, squares, and pentagons, each bearing functional groups that connect the pieces via self-assembly; and metallo-macrocycles generated from fused chelate-rings that have been studied for their several possible applications. Further, for introducing suitable spacing and conformations relative to each other, a number of structural units have been employed including spacers, connecting groups out of polyether chains, bi/tri-phenyls, and simple alkyl chains; NPs, NRs, fullerenes, dendrimers offering nanometer-sized structure and encapsulation units, scaffolds on surfaces for interfacing electrochemical systems with electrodes. In addition, photochromic and photoisomerizable groups with ability to change their shapes and properties upon light exposure, TTF, and quinones capable of being switched with redox chemistry or electrochemistry, usage of benzidine derivatives, viologens groups and fullerenes in supramolecular electrochemical devices [70–80].

### 3. Nanomaterial synthesis

Knowing well about the advantages associated with quantum confinement in 1/2/3 dimensions in nanostructured material species during their preliminary investigations, it became



imperative to explore the possibility of synthesizing them in quantity with controlled properties in stable form. Some of these aspects of nanostructured material species are examined here from the point of view of their industrial applications.

### 3.1. Synthesis of nanoparticulate materials

The basic scheme of chemical synthesis of metal NPs employs a suitable stabilizing agent added to a mixture of metal salt precursor and reducing agent chosen out of several including sodium citrate, sodium borohydride, and alcohols to convert metal ions into metal atoms that ultimately form NPs [81–83]. Silver colloidal solution prepared using citrate reduction reported in 1982 did contain 20–600 nm NPs, in which pH affected the morphology by changing from triangular to spherical/cylindrical shapes after changing the pH from 5.7 to 11.1 [84–87]. Similarly, polyol-based synthesis of Ag NPs was reported producing a wide range of NPs using precursor along with capping agent [88–91]. Using propylene, and 1,2-propylene glycols or 1,5-pentanediol as reducing agents and controlling temperature and precursor concentration was also found to influence the morphology of the final product [92].

Alternately, in a different route of photochemical synthesis, light irradiations helped in synthesizing metal NPs as seen in laser irradiated aqueous solution of metal salt + surfactant producing metal NPs besides using laser melting of metal nanospheres to produce nanoplates [93–100]. In contrast, green syntheses of metal NPs were reported from metallic electrodes and spray pyrolysis-based synthesis of 10 and 100 nm (average PS) Ag NPs, respectively [101, 102].

Seed crystals-mediated synthesis reported lately in 2010 produced Ag nanocubes from spherical/cubic single crystal seeds with the edges ranging from 30 to 200 nm [92, 103–105]. In another, very old process of silver mirror reaction, discovered way back in 1835 for depositing Ag metal on solid surfaces using  $\text{Ag}(\text{NH}_3)_2\text{OH}$  reduction by sugar or any aldehyde containing compound, has been used for Ag NP synthesis [106].

Precisely controlled morphologies of metal NPs have been realized successfully using template-assisted synthesis already known to depend to follow the template features, in which the surfactant molecules behaved as soft templates in contrast to porous anodic aluminum oxide (AAO) membranes as hard templates [107, 108]. Soft template-assisted synthesis has been found producing metal nanowires, nanorods, hollow spheres, and nanoplates by exploiting a variety of surfactant compounds including ionic surfactants like cetyltrimethyl ammonium bromide, octadecyltrimethylammonium chloride, disodium (2-ethylhexyl) sulfosuccinate, and sodium dodecylsulfate; non ionic surfactants like oleic acid, oleylamine, trioctylphosphine and trioctylphosphine oxide; and polymer surfactants involving poly (vinyl pyrrolidone), poly(vinyl alcohol), and poly(ethylene oxide) as reported extensively [109–141]. Template-assisted synthesis is known to produce well-dispersed forms due to reduced particle aggregation along with mild reaction conditions [142–144].

Unlike above-mentioned chemical syntheses, lithographic patterning and deposition-based nanofabrication processes involving optical, e-beam, scanning probe, and multiphoton lithographies are known to produce precisely controlled nanostructured materials not limited to metal species alone [145–147].

Nanoparticulate material species are well-known building blocks to assist self-assembly processes forming micron size nanosheets and other structures. DNA-assisted self-assembly of metal NPs is another route explored for synthesizing plasmonic NPs into chain, triangular shape, 3D lattices, and Janus nanoclusters, in which the interaction of NPs in solutions involving attractive and repulsive forces comprising of hydrophobic, electrostatic, hydrogen bonding and biospecific interactions impacts the self-assembly to a large extent [148–161].

High-temperature hydrothermal synthesis of triangular shaped Ru nanoplates (~3 nm thick) was reported using  $\text{RuCl}_3 \cdot \text{H}_2\text{O} + \text{HCHO} + \text{PVP}$  @ 160°C, which changed to irregular shaped but with reduced thickness of 1.5nm subsequently by changing the concentration of Ru salt and PVP. In case of silver salt, it produced triangular Ag nanoplates with sharp and curved corners [162–164].

Recently, the potentials of living microorganisms including bacteria, fungi and plants have been examined for the synthesis of NPs like CdS, Ti/Ni, titanate, zirconia, Au, and Ag [165–171]. It is very important to note that using microorganisms is environmental friendly and benign synthesis route providing good control over size distribution of nanostructures. For example, Ag nanoparticulates were synthesized using bacteria with size less than 200 nm.

### 3.2. Physical and chemical syntheses

The physical/chemical methods of preparing NPs include lithography, laser ablation, high-energy irradiation, chemical reduction, electrochemistry, and photochemical reduction [172–179].

A number of process parameters that are important to consider in NP synthesis include temperature, concentrations, process kinetics describing interactions between metal ion precursors and the reducing agent, and adsorption kinetics involving the stabilizing agent and the NPs. Consequently, the current emphasis is on designing processes capable of ensuring adequately precise control of the size, shape, stability, and physicochemical properties of the NPs [180–183].

The conventional methods of NP syntheses, however, are known to involve chemical/physical processes that often use toxic materials like organic solvents, reducing agents, and stabilizers causing ultimately substantial environmental pollutions, cytotoxicity, and carcinogenicity in addition to the toxicity of some of the NPs due to their compositions, size, shape, and surface chemistry [184]. However, all these hazardous factors associated with NP syntheses are possible to mitigate using biologically mediated production schedules. There is a strong emerging interest in developing clean, reliable, biologically compatible, benign, and environment-friendly green processes to synthesize NPs for their numerous applications [185].

### 3.3. Green synthesis

Green synthesis of NPs involving microorganisms and plants is noted to be safe, inexpensive, and environment-friendly as they absorb and accumulate inorganic metal ions from their surroundings leading to an unexplored field of useful research [186–189]. A number

of biotechnological applications including bioremediation and bioleaching are possible to implement by exploiting the efficacy of the microorganisms to interact with the environment via their lipid-based amphipathic membranes enabling a variety of oxidation-reduction mechanisms occurring and promoting these biochemical conversions [190–194]. It has been shown that unicellular/multicellular organisms are capable of synthesizing (extra/intracellular) inorganic micro-/nano-sized particulate materials in particular environment of their culture promoting coupled oxidation and reduction reactions that needs further investigations to understand the processes of nucleation, and subsequent NP growth kinetics and the interaction of these processes with metabolic processes of the microorganisms involved [192, 193, 195–198].

A similar situation is met in case of plants based synthesis of NPs with the advantage of plants over other eco-friendly biologically based systems such as bacteria and fungi that avoid using culture preparations and isolation techniques that are involved and expensive. Conversely, biosynthesis of NPs using plants/plant-based extracts is safe with relatively short production times, and having a lower cultivation cost compared to other biological systems [199].

Various methods explored in biologically synthesizing metal NPs include actinomycetes, algae, bacteria, fungus, plants, viruses, and yeast, where each entity has varying degrees of biochemical processing capabilities for preparing metallic or metal oxide NPs. Generally, biological entities with a potential to accumulate heavy metals offer better chance of synthesizing metal NPs [200]. In case of microorganisms, optimization of parameters like nutrients, light, pH, temperature, mixing speed, and buffer strength used in their culture could significantly enhance the enzyme activity [188, 201, 202].

### 3.4. Microemulsions synthesis

The most popular approach of synthesizing NPs from microemulsions uses a mix of two or more separate microemulsions of the required constituents that participate in nucleations on the micellar edges due to supersaturation of the reactants inside causing growth around the nucleation sites with the arrival of more reactants from intermicellar exchange. Examination of the process details clarified the NP growth starts at the interface, and subsequently moves on to the micellar cores with a intermicellar exchange specific rate limiting phenomenon occurring over a time duration longer than the times involved in reagents diffusions inside the polar domains causing large variation in reaction completion times compared to those observed in native aqueous solutions. Controlling this process by modifying the interfacial characteristics of the surfactant membrane was exploited subsequently as noted in case of  $\text{BaTiO}_3$  using three separate microemulsions [10, 203–206]. NPs were also prepared from single microemulsion with stabilized reactant inside the reverse micelles after adding the reducing agent to produce the metal NPs. Recently, silver halide and cuprous oxide NPs were synthesized using direct reaction of solubilized silver metal with dioctyldimethylammonium halide counter-ion in reverse micelles, and gamma irradiation of copper nitrate micellar solution, respectively, using faster rate of reaction with morphological control in a single microemulsion. Despite its versatile nature, limitations were pointed out, for example, during synthesizing either ZnTe or incorporating Mn into either ZnTe or CdTe [207–210]. The

parameters that influence the size and polydispersion of the synthesized NPs include—type of the solvent employed, surfactant/cosurfactants used, electrolyte, concentration of reagents and, molar ratio of water and surfactant as discussed in detail elsewhere [211].

A simple surfactant/water/oil system was found producing many types of self-assembled structures—by changing composition, one could have spheres (reverse micelles or micelles), cylinders, interconnected cylinders, and planes called lamellar phases, which could reorganize into onion-type structures [212, 213]. Numerous studies were conducted involving a variety of surfactants and system compositions (surfactant/water concentrations) in connection with investigating the growth of different NC structures [214]. However, the idea that different shapes of synthesized NCs could be due to template effect was found invalid as different shapes could be synthesized without changing the template shape, and even no template was involved in some cases at all [215, 216]. Most recently, a method was proposed for controlling the NP shapes by considering the influence of stacking faults in certain plane as observed during the synthesis of silver nanodisks with varying size characterized by HRTEM/SAED showing the presence of forbidden  $1/3\{422\}$  reflections that were proposed to be promoted by the stacking faults in [110] plane [217]. From these observations, it could be concluded that defect engineering could possibly be used in influencing the shape of NPs as confirmed in case of copper system, yielding similar results [129].

Stabilized microemulsions are possible in a supercritical fluid (SCF) by using appropriate surfactant leading to smooth transition in solvent quality by pressure and temperature control required in nanoparticulate material syntheses [218, 219]. Relevantly, the advantage of using SCF-CO<sub>2</sub> process was demonstrated after having stabilized the microemulsion (water/P104/xylene) at higher pressure causing formations of Au NPs via KBH<sub>4</sub>-based reduction of HAuCl<sub>4</sub>, which was not feasible at ambient pressure due to inadequacy of xylene as solvent. These gold NPs were recovered by reducing the pressure to release the solvent by precipitation. In another variant, known as RESOLV (rapid expansion of a supercritical solution into a liquid solvent), a stable microemulsion of silver cations was expanded through a nozzle into solvent containing reducing agent to produce controlled morphology silver NPs [220]. Finally, water-in-SCF microemulsions were successfully used in water-in-oil microemulsions in synthesizing compounds for industrial applications.

The process involves preparing a stable dispersion using appropriate surfactant. In case of water-in-oil (w/o) microemulsions, the surfactant AOT supplemented with fluorinated cosurfactants like PFPE-PO<sub>4</sub> (perfluoropolyether-phosphate), PFPE-NH<sub>4</sub> (ammonium perfluoropolyether) and F-pentanol are employed in stabilizing the dispersions in most of the liquid/supercritical alkanes applied [129, 218, 221–230].

While searching for hydrocarbon-based surfactants or polymers capable of stabilizing w/sc-CO<sub>2</sub> microemulsions primarily due to economic and environmental benefits, iso-steric acid was found useful in a SCF-CO<sub>2</sub> with <10 V/V% hexane solubilizing the reactants inside reverse micelles [231]. These microemulsions are formulated in a pressure cell to which the second reactant is added using a high-pressure syringe pump. Hence, the NP reactions that take place are similar to those occurring in normal liquid w/o microemulsions as noted in microemulsions-based synthesis of Ag NPs where NP recovery by CO<sub>2</sub> venting and rapid expansion method is possible [220, 227, 229, 230, 232].

### 3.5. Pharmacosomes (liposomes)

Besides regular inorganic/ organic NPs, there is another class of nanostructured materials involving biomolecules that have been explored well for drug/gene delivery applications, and termed as pharmacosomes derived from two terms namely—‘pharmakon = drug’ and ‘soma = carrier’ representing vesicles (drugs and carrier attached together). These are neutral particles with positive and negative charges imparting hydrophilic and hydrophobic features (involving polyphenol and phospholipids), in which the drugs are dispersed via lipid interactions (i.e., electron pair sharing, electrostatic forces, and hydrogen bonds) forming colloids, nanomicelles, vesicles and hydrogen bonded hexagonal assemblies. The carboxylic group or functional hydrogen atoms in the amino, and hydroxyl radicals of the drug molecules are converted into esters with the help of the hydroxyl moiety of the lipid forming prodrugs causing reduction in interfacial tension with larger area contacts, and improving bioavailability in addition to helping transport across the cell membrane, wall, and tissues. These prodrugs assemble into single/multiple layers, when in contact with water, forming pharmacosomes [233, 234].

The liposomes are formed by dispersing phospholipids in aqueous media followed by exposure to high shear rates using microfluidization or colloid mill in addition to mechanical dispersion involving sonication, pressure cell or membrane extrusions, freeze thawing, film hydration, microemulsion, and dried reconstituted vesicles—all initiating hydrophilic-hydrophobic interactions between phospholipids and water molecules. Liposomes are characterized by their mean particle size, zeta potential, lamellarity, encapsulation efficiency, in vitro drug release, and vesicle stability. Spherical bilayer membranes are the manifestations of the favored self-assembly features of phospholipids, which is although not limited to bilayer formations alone but also produce colloidal particles from self-aggregation of the polar lipids. Liposomes efficiently entrap even highly unstable compounds including antimicrobials, antioxidants, flavors and bioactive elements by shielding their functionality [235]. Liposomes are the latest additions to the targeted deliveries carrying hydrophilic/hydrophobic contents in nano/microsize double-layer covered spherical volumes providing effective protection from the enzymes, alkaline solutions, digestive juices, bile, and intestinal flora inside human body as well as free radicals. Liposomes not only check oxidation and degradation but also retain the double-layer barrier undamaged until the contents are delivered to the desired site.

Liposomes, discovered in the 1960s, are versatile nanocarriers owing to their compositional variability and structural properties leading to numerous applications in pharmaceutical, nutraceutical, and cosmetics sectors, wherein the herbal extracts like flavonoids, glycosides, and terpenoids are enclosed and transported from the hydrophilic to the lipophilic part of the membrane showing better bioavailability/efficacy, as noted in case of ginkgo biloba, grape seed, green tea, milk thistle, ginseng, and many other herbs already explored in therapeutic applications and dietary supplements. Liposomes are currently being used in a broad range of pharmaceutical applications showing better promises as intracellular delivery systems for antisense molecules, ribosomes, proteins/peptides, and DNA. Liposomes with enhanced drug delivery and long circulation times are currently getting clinically accepted. Liposomal drugs are known to exhibit reduced toxicities while retaining enhanced efficacy compared

to the free complements [39–41]. The phospholipid liposomes were reported mimicking red blood cells by optimizing concentrations of phosphatidylserine, di-stearylphosphatidylcholine, and dipalmitoylphosphatidylcholine for a fixed concentration of lecithin and Tween® 80 using response surface methodology resulting in 112–196 nm particle size with lower efficiency encapsulation at lower levels of insulin but increasing at higher levels fulfilling the requirement for intravenous drug delivery having biodegradable and biocompatible features [236].

### 3.6. Phytosomal nanoparticulate materials

Phytosomes contain herbal drugs and the lipids in stoichiometric ratio in a solvent, wherein, the polar functional groups of the substrate and phosphate and ammonium groups of the polar heads of the phospholipids form the hydrogen bonds while getting attached to the phospholipid polar head and merging with the membrane. For instance, in a phosphatidylcholine and catechin complex, hydrogen bonds are established between hydroxyl groups in the phenols of the flavones and phosphate groups of the phosphatidylcholines without any change in their fatty acid chains suggesting the protected enclosure of the active components into the long aliphatic chains. These interactions form lipophilic envelope shielding the polar phospholipid as well as the constituent. The pharmacokinetic studies and the animal/human trials have confirmed the enhanced bioavailability and absorption of the lipophilic herbal extracts forming micellar constructs in water [237, 238]. Some typical examples are taken here to highlight their applications in nanomedicines.

Optimized icaritin phytosomes, prepared by solvent evaporation of icaritin in ethanol (icaritin: phospholipid = 1:3, reaction time ~1 h @50°C) showed enhanced solubility by 1.6 and 5.9 times in *n*-octyl alcohol enabling icaritin and the coprecipitate of icaritin phytosomes in PVP to dissolve in vitro better [239]. Curcumin-phytosome-loaded chitosan microspheres (Cur-PS-CMs) were reported involving curcumin-phytosomes (Cur-PSs) in chitosan microspheres via gelation (PS =  $23.21 \pm 6.72$   $\mu\text{m}$ , loading efficiency ~2.67%). In vitro curcumin release from Cur-PS-CMs was slower than that from curcumin-loaded chitosan microspheres (Cur-CMs) in pH 1.0, 4.0, 6.8, and 7.4 showing 1.67 and 1.07-fold increase in absorption of curcumin compared with Cur-PSs and Cur-CMs, respectively. The half-life of orally administered Cur-PS-CMs was longer than those of Cur-PSs and Cur-CMs by ~2 and 1.5-times, respectively, confirming oral absorption with prolonged retention time for sustained delivery of lipophilic compounds [240]. The MMC-soybean phosphatidylcholine complex-loaded PEG-lipid-PLA hybrid NPs were reported with Folate functionalization (FA-PEG-PE-PLA NPs@MMC-SPC) for targeted drug delivery and dual-controlled drug release involving hydrophobic core (PLA) loaded with MMC-SPC, an amphiphilic lipid interface layer (PE), a hydrophilic shell (PEG), and a targeting ligand (FA) on the surface, with a spherical shape, and high encapsulation efficiency (95%). In vitro cytotoxicity and hemolysis assays demonstrated the associated cyto-/hemocompatibility along with significantly prolonged blood circulation time compared to that of the free MMC with enhanced cell uptake/cytotoxicity in vitro and superior tumor accumulation and therapeutic efficacy in vivo while reducing the systemic toxicity showing a promising design of the water-soluble drug-phospholipid complex-based targeted drug

delivery [241]. *Calendula officinalis* extract-based encapsulation of Au-NPs was examined with high efficiency encapsulation of chlorogenic acid and quercetin exhibiting significant antioxidant and wound-healing properties as anticipated [242]. Mitomycin C (MMC)-loaded polymer-lipid hybrid NPs were reported using single-step assembly of MMC-soybean phosphatidylcholine (SPC) complex and biodegradable PLA for intravenous delivery ensuring enhanced efficacy with safety in controlled release of MMC showing a significant accumulation of MMC in the nuclei with significantly higher anticancer effect compared to PLA-NP/MMC or free MMC injection *in vitro* and *in vivo* [243]. Curcumin phytosomes were reported (solvent evaporation based) to have free flowing powder to enhance curcumin content in different soft gel formulations employing castor oil/oleic acid, PEG 400, Miglyol 812 along with Cremophor EL and KLS P 124 surfactants revealing good stability and spherical curcumin phytosomes [244]. Self-assembled  $152.5 \pm 3.2$  nm NPs of methotrexate (MTX)-phospholipid (PC) complex (MTX-PC NPs) were reported having drug-loading efficiency  $\sim 20.7 \pm 2.4\%$ , and sustained release behavior compared to free MTX and MTX-loaded liposomes with better promises for cancer therapy compared to traditional drug delivery systems [245]. The active lactone form of 10-hydroxycamptothecin (CPT)-soybean phosphatidylcholine (SPC) self-assembled NPs (CPT-SPC NPs) was reported showing efficient complexation between active lactone and SPC (complexation rate  $\sim 98\%$ ;  $210.7 \pm 6.1$  nm diameter, ZP  $\sim -24.9 \pm 3.1$  mV, and a high drug-loading content of  $16.3 \pm 0.5\%$ ) comprising of biphasic delivery (initial burst followed by sustained release). Animal imaging results indicated excellent tumor targeting in HeLa tumor-bearing nude mice [246].

The phytosomes with bioactive plant-based molecular species are poorly soluble in flavanones and terpenes. Features like biocompatibility, nontoxicity, easy to administer, reduced dosage and enhanced retention time of the liposomes and the phytosomes make potent vehicles for drug delivery as discussed [247].

Different flavones like naringin, neoeriocitrin and neohesperidin known for their antioxidant activity and phenolic content were encapsulated in phospholipid vesicles (glycerosomes, hyalurosomes and glycerol containing hyalurosomes) using a high ratio of extract/phospholipid counteracting the oxidative stress in skin cells. The glycerol containing hyalurosomes prevented the oxidative damages and death of both keratinocytes and fibroblasts by promoting their viability [248]. Berberine (BER)—a natural alternative to synthetic antidiabetic drugs, has poor gastrointestinal absorption, and low oral bioavailability limiting its clinical applications was loaded in phytosomes as berberine-phospholipid complex (P-BER) by solvent evaporation method followed by a self-assembly showing nanosize particles with negative surface charge, and excellent drug entrapment efficiency ( $<85\%$ ) and threefold enhanced bioavailability causing significant reductions in fasting glucose levels and improving the ability of systematic hyperlipidemia metabolism of diabetic mice [249]. The solubility and permeability study of Standardized Bacopa Extract (SBE) were reported showing improved aqueous solubility compared to the pure SBE (20-fold), or the physical mixture of SBE and the phospholipid (13-fold). Similarly, *in vitro* dissolution studies confirmed higher SBE release efficiency ( $>97\%$ ) in comparison with the pure SCE ( $\sim 42\%$ ), or the physical mixture ( $\sim 47\%$ ). The *ex vivo* studies confirmed improved permeation of SBE ( $>90\%$ ), compared to the pure SBE ( $\sim 21\%$ ), or the physical mixture ( $\sim 24\%$ ). This kind of drug-phospholipid complexation could be used for solubility enhancement of bioactive phytoconstituents [250].

### 3.7. Nonlayered 2D material synthesis

Besides exploring the novel features of 2D layered materials as mentioned earlier, a number of nonlayered 2D nanomaterials were also reported recently using 2D nanomaterial templates. Some of these include the examples of 2.4-nm-thick square hexagonal-close packed (hcp) gold nanosheets (hcp AuSSs) onto GO template followed by secondary growth for even thicker layers, Ag onto hcp AuSSs resulting in (100) f-oriented fcc core-shell or (110) h/(101) f-oriented hcp/fcc square nanosheets (Au@Ag); and Pt/Pd onto AuSSs inducing transformation from hcp to fcc forming core-shell Au@Pt or Au@Pd nanoplates, to name a few cases already explored. Coatings of Pt or Pd onto hcp AuSSs led to fcc Au@Pt or Au@Pd rhombic nanoplates, in which the large lattice mismatch between Pt or Pd and Au compared with Ag was believed responsible for the (101) f-oriented core-shell nanoplates. In phase transformations from hcp to fcc, the role of ligand exchange was found responsible as noted in case of transformation into (100) f-oriented fcc AuSSs by replacing oleylamine capping with thiol molecules. In another study, 0.55–0.59 nm thick and  $\sim 1$  mm square freestanding  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanosheets were synthesized using CuO nanoplate-templates. Further, a number of 2D nanostructures including ternary/quaternary chalcogenides like CuInS<sub>2</sub>, CuIn<sub>x</sub>Ga<sub>1-x</sub>S<sub>2</sub>, Cu<sub>2</sub>ZnSnS<sub>4</sub>, Cu<sub>2-x</sub>Se and Cu<sub>1.97</sub>S were prepared via the cation exchange on CuSe/CuS templates or phase transformations resulting in uniform size, shape and thickness. In addition, NiO nanosheets were reported from layered  $\alpha$ -Ni(OH)<sub>2</sub> nanosheets through a simple annealing treatment as discussed in cited references [251–260].

Hydro/solvo-thermal syntheses were found useful in preparing a number of nonlayered 2D materials as briefly summarized here. A facile solvothermal synthesis of poly (vinylpyrrolidone) (PVP)-supported single-layer rhodium (Rh) nanosheets (0.4 nm thick with 500–600 nm edge length) was reported recently followed by a generalized method of synthesizing a number of metal oxide nanosheets, including TiO<sub>2</sub>, ZnO, Co<sub>3</sub>O<sub>4</sub>, WO<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> and MnO<sub>2</sub>. In addition, hydro/solvothermal methods were found useful in synthesizing several nonlayer 2D nanosheets including ZnSe, ZnS, CeO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, Co<sub>9</sub>Se<sub>8</sub> and Co<sub>9</sub>S<sub>8</sub>-oleylamine hybrid. The synthesis of ZnSe and ZnS nanosheets was reported by preparing lamellar organic-inorganic intermediates [(Zn<sub>2</sub>Se<sub>2</sub>)(n-propylamine) and (Zn<sub>2</sub>S<sub>2</sub>)(n-propylamine)], followed by their sonicated exfoliation to have freestanding 0.9 and  $\sim 500$  nm lateral dimensions of ultrathin nanosheets followed by synthesis of CdS nanosheets (300–800 nm lateral dimension and  $\sim 4$  nm thick) using diethylenetriamine (DETA) as the surfactant. In another study, atomically thin CeO<sub>2</sub> sheets with surface pits and ultrathin In<sub>2</sub>O<sub>3</sub> porous sheets with rich oxygen vacancies were reported using hydrothermal methods followed by subsequent thermal annealing as reported in many publications [260–268].

## 4. Looking ahead

The novel features of 2D layered/nonlayered materials already explored in micron size samples during their preliminary studies are certainly expected to be translated into production processes with better yield, reproducibility, and process reliability once the process details are fully understood and steps optimized accordingly. The progress made in this context is possible to assess as highlighted below.



#### 4.1. Large-scale synthesis

While examining the basic science of the nanomaterials, efforts have been made in parallel to develop the related technologies as well to support the needs of the growing industries led by innovative exploitations. In this context, it is imperative to have an idea about the market size, growth trends and support extended by the State Agencies.

With the growing trend *vis-à-vis* the market size of US\$ 1.34 billion of gold NPs in 2014, it is expected to touch US\$ 8 billion by 2022, primarily driven by the innovations supported by higher R&D spending, along with growing applications in healthcare and diagnostics. The emerging gold NPs market size, particularly in China and India, seems to reach US\$ 2.9 billion by 2022 [269].

The emerging demands of nanoparticulate materials (NPMs) in growing industrial applications is further evidenced by the initiatives taken by the European Commission in allocating funds for the private-public partnership programs in manufacturing to meet the industrial requirements from various sectors (e.g., FP6/FP7 Projects—€240,000,000; HORIZON 2020 Program—over €1 billion) that are expected to provide scaled-up production of nanostructured materials (~100 kg/day) at lower costs [270].

A brief description of various methods that are already explored for volume production of NPMs is included here in brief to highlight the limitations that are faced in the industry despite fast rising demands from different sectors in general. Those emerging processes that have shown potentials for production after further developments of their technologies in near future are also included in the discussion.

#### 4.2. Production technologies

NPMs (i.e., molecular sizes to 100  $\mu\text{m}$  in diameter) have been produced by flame involving precursors that are sprayed either onto a heated surface or in a hot environment. Oxford University developed an electrospray process for semiconductor/metal NPs, and spray gun deposited catalysts for CNT growth that are simple and economical examples [271–275].

Alternate technique of producing metal vapors through arc discharge has been exploited equally effectively for producing metal, metal-oxides, and other compounds based NPMs in inert/oxygen/reactive gas environment. For taking care of the process reproducibility issues arising from the high temperature arcs generating high evaporation rates leading to the formation of larger size particles from vaporized metal rich carrier gas, the European project (BUONAPART-E) funded a program of upscaling and optimization of NPMs manufacture by flame pyrolysis showing preliminary achievement in form of a versatile and reliable unit capable of producing 0.1–10 g/h throughput in this context [276–278].

Another production process of metallic NPMs involving gas-phase condensation, reported way back in 1930, uses a vacuum evaporation unit attached to a separate collection chamber filled with inert/reactive gas for powder collection ensuring particle formation during rapid cooling of the arriving stream of metal atoms initiating nucleation and particle formation resulting in broad distribution of PSs as their agglomeration is quite random [275].

In a combination of ultrasonic irradiation-assisted chemical reactions followed by precipitation known as sonochemical synthesis, the molecular species are subjected to chemical reactions via energetic acoustic cavitation including formation, growth and collapse of microbubbles inside the irradiated liquid medium. This method efficiently produces the NPMs facilitating preparation of smaller PSs of different shapes at lower costs [279–281].

Milling-based production of NPMs is known since 1970 with many variants developed for preparing nanopowders of crystalline/crystalline or crystalline/amorphous, and atomic bonding-based metal/metal, metal/semiconductor, metal/ceramic, and their combinations with the advantage of low temperature working. There are two different routes of mechanical milling namely—single-phase powder milling by controlling the competing processes of fracturing and cold-welding, where particles larger than 100 nm are not cold welded, and consequently, a reduction in the average PS from 50–100  $\mu\text{m}$  up to 2–20 nm is feasible. A severe plastic deformation caused by mechanical attrition at elevated temperature of 100–200°C gives rise to refinements in internal structures of the particles to produce nm size particles. The environmental sensitivity of the milling process is put to use by controlling the ambient conditions accordingly for chemical reactions to occur between the environment and the milled powders leading to a novel, cost-effective method of producing a variety of nanopowders. Mechanochemical processing (MCP) is another variant of milling used as a low temperature chemical reactor, wherein the ball mill accelerates the reaction kinetics in the powder mixture as a result of the intimate mixing and refinement of the grain structure to nm scale. For this reason, it is useful to employ a proper reactive gas environment of  $\text{O}_2$ ,  $\text{N}_2$ , atmospheric air, or precursor. Oxide and nitride of Ti, Fe, V, Zr, W, Hf, Ta and Mo could, thus, be converted into NPMs in reactive milling. Similarly, in wet milling, an organic fluid is used for transforming the metal powders into nanocrystalline metal-ceramic composites comprising of individual single nanometer sized grains dispersed in a matrix. Of course, it is necessary to go for further heat treatment for ascertaining that the reaction is complete. The reduction of the process cost and the industrialization of products are achieved by using a variety of precursors for producing a large variety of NPMs in the form of oxides, carbonates, sulfates, chlorides, fluorides, hydroxides, and others. Different kinds of ball mills including tumbler mills, attrition, shaker mills, vibratory mills, planetary mills, and other variants are commercially available for mechanical attrition. A common method in all these mills is to place the material powder in a sealed container with the balls of hardened steel or tungsten carbide, while mass ratio for the ball to the powder is kept around 5:10 in case of a typical 50  $\mu\text{m}$  powder. Kinetic energy of balls is a function of their mass and velocity, and as a result, steel and tungsten that are high-density materials are preferred as means of milling [282–286].

Recently developed room temperature ionic liquids (RTILs) are being used as reaction media for inorganic NPMs mainly by using their preorganized structures to template porous inorganic nanomaterials and their intrinsic high charges and polarizability in affecting electrostatic and steric stabilization. For example, IL templates are used for fabricating mesoporous/super-microporous silica, and in synthesizing transition metal NPs including Ir, Au, Ag, Pt, and Pd, where the IL acts as a solvent, template, reducing agent and stabilizer.  $\text{TiO}_2$ -based NCs and microspheres, and Te- and CoPt-based nanorods, have also been fabricated using ILs [287–295].

Nanolithographic techniques involving e-beam/focused ion-beam writing, proximal probe patterning, X-ray lithography, along with dry/wet etching are found useful in fabricating a variety of nanostructured materials. By nanolithography, nanostructures and their arrays are possible to fabricate by a directed or constrained growth from one to few nm with the advantage of producing large quantities of 1D nanostructures using a wide variety of the available materials [296–300].

One of the most popular and maybe the most economical methods of nanolithography is template fabrication based suitable for growing nanowires (NWs) using electrodeposition, sol-gel or by vapor-phase followed by independently controlled NWs after removing from the templates. In this process, the ordered nanopore templates are made before filling them with the chosen materials, using one of the methods referred before. Electrodeposition of metals inside the nanopores is performed in acidic or basic baths that contain metal salts, and the metal is deposited on the cathode (working electrode), and for this reason, one end of the porous membrane is metallized with Ti and Au or Ag by sputtering or evaporation, and the anode is normally graphite or Pt with calomel or Ag/AgCl as reference electrode. The deposition conditions (DC or pulsed) affect the polycrystallinity of the nanowires.

High-temperature anneal (500–600°C) of low temperature sol-gel processed complex oxide NWs was found necessary for the required stoichiometric phase. For instance, taking out the alumina template after dipping into sol for some time, it was necessary to dry before anneal to produce the proper phase. CVD/PVD methods were also explored for growing semiconducting nanotubes, including ordered arrays of CNTs. Plasma-assisted CVD has shown adequate promises to grow aligned nanotubes of complex semiconductor or oxides in alumina templates, and in future, this technique will certainly find more applications [301].

Scanning probe microscopy (SPM)-based lithography has already been established for creating nm size patterns on metallic and semiconducting surfaces using lithography masks either via chemical route called dip-pen lithography (DPN) or SPM route based on anodic oxidation where water meniscus formation from the atmospheric moisture capillary condensation between the substrate and the tip plays an important role.

The presence of water meniscus enables the molecules to interact with the substrate for forming chemical bonds via controlled molecular transport across the region between the tip and the substrate. Another variant employs the meniscus as an electrochemical cell where the applied bias produces the metal/semiconductor nanostructures promoting nanostructures on the surface for directed assembly of nanoparticles [302–304]. Likewise, in anodic oxidation, the water meniscus forms an electrochemical cell, where moisture provides 'nanoreaction vessel' like environment for anodic oxidation after applying a negative bias to the tip with respect to the substrate, wherein the applied electric field helps in accelerating the OH<sup>-</sup> ions to the substrate causing a self-limiting type oxidation that terminates automatically at fields below 10<sup>7</sup> V/cm. The geometrical features of the oxidized pattern depend on the applied bias and the radius of curvature of the tip that is micromachined for reproducible sizes, shapes and aspect ratios. By controlling all these parameters, reproducible lithography of known resolutions is performed as an advantage of this technique [305].

### 4.3. 2D materials production

With the emerging applications of graphene possessing novel features, systematic efforts were made in developing production methods with higher yield and improved quality of graphene and other 2D materials nanosheets. For example, the exfoliation efficiency of graphene nanosheets was improved (e.g., yield >85%;  $\leq 3$  layers; lateral size  $\sim 44 \mu\text{m}$ ) using aqueous solutions of  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{K}_2\text{SO}_4$  and exhibiting hole mobility  $\sim 310 \text{ cm}^2/\text{Vs}$ . Highly conducting films were brush coated on paper from a graphene ink for fabricating all-solid-state flexible supercapacitors delivering a high area capacitance of  $11.3 \text{ mF}/\text{cm}^2$  [306]. A green production of graphene was reported using saccharin in aqueous solution showing that the number of graphene layers decreased with increase in the intercalation potential, while yield improved with increase in the exfoliation potential. The defect density in the exfoliated graphene layer was sensitive to the exfoliation potential as it initially increased with exfoliation potential and then eventually decreased [307]. Improved performance of exfoliation arising out melamine additive during graphite electroexfoliation was assigned to the hydrophilic force from the basal plane promoting exfoliation besides providing protection against further oxidation, leading to high-yield production of graphene of larger crystallite size. This process exhibited better performance in terms of higher uniformity (>80% in <3 layered graphene), lower oxidation density (C/O ratio of 26.17), lower defect level ( $I_D/I_G < 0.45$ ), and low sheet resistance of  $13.5 \text{ k}\Omega/\text{Y}$  (95% transmittance). A graphene nanocomposite with polyvinyl butyral (PVB) exhibited an electrical conductivity of  $3.3 \times 10^{-3} \text{ S}/\text{m}$  for the graphene-loading fraction of 0.46vol%. The continuous process for producing graphene was demonstrated, with a yield rate of 1.5 g/h [308]. The influence of a number of reducing agents (such as 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), ascorbic acid, and sodium borohydride) was investigated to eliminate  $\text{HO}\cdot$  radical generated out of water electrolysis responsible for defect formation on graphene during electroexfoliation in aqueous ammonium sulfate. TEMPO-assisted exfoliation could produce large graphene sheets ( $\sim 5\text{--}10 \mu\text{m}$  average), exhibiting hole mobilities  $< 405 \text{ cm}^2/\text{Vs}$ , very low Raman  $I_D/I_G$  ratios ( $< 0.1$ ), and extremely high carbon to oxygen (C/O) ratios ( $< 25.3$ ). High concentration graphene ink in dimethylformamide exhibited (6 mg/mL) was found useful in transparent conductive films and flexible supercapacitors [21]. Low defect concentration few-layer graphene (FLG) sheets were fabricated by a two-step electrochemical intercalation exfoliation, including a graphite foil pretreatment in sodium hydroxide solution and a subsequent further exfoliation in sulfuric acid solution. During this process, the pretreatment resulted in the expansion of the graphite foil and in turn facilitated the final exfoliation in sulfuric acid solution showing  $I_D/I_G$  of the FLG sheets as low as 0.29 while maintaining relatively high yield (>56%). In addition, the oxygen content in the FLG sheets is 8.32% with the C/O ratio of 11.02 [309]. Using *in situ* optical and electrical measurements, it was found that that solvent intercalation is the required first step and the degree of intercalation controls the thickness of the exfoliated graphene. Electrochemical decomposition of water into gas bubbles causes the expansion of graphite controlling the functionalization and lateral size of the exfoliated graphene. Both process steps proceed at different time scales and can be individually addressed through application of pulsed voltages. The potential of the presented approach was demonstrated by improving the performance of graphene-based transparent conductors by 30 times [310].

In a more recent study, graphene production was reported using  $\text{HNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$ -based exfoliation in sodium dodecylbenzene sulfonate as a surfactant [311]. Studying the influence of varying parameters like anodic bias (1–10 V), and shear field (400–74,400/s) concluded that thicker and more fragmented graphene sheets were formed at higher biases, while at potentials as low as 1 V, shear force could cause pronounced exfoliation. This process under optimum condition could produce large graphene flakes ( $\sim 10 \mu\text{m}$ ) with a high proportion of single, bilayer, and trilayer graphene and small  $I_D/I_G$  ratio (0.21–0.32) with only a small contribution from carbon-oxygen species [312]. Biomolecules are also attracting attentions as dispersants for 2D materials providing a number of advantages over more conventional, synthetic surfactants particularly in case of biomolecules including proteins and peptides, nucleotides and nucleic acids (RNA, DNA), polysaccharides, plant extracts and bile salts as colloidal dispersants as discussed in a recent review [313].

Graphene quantum dots (GQDs) were examined in terms of their size-dependent energy storage efficiency and optical behavior while functioning as an active material in rechargeable lithium ion batteries (LIBs). Considering three different SOC's (<05, <50 and <95%), reversible changes were noticed in the UV-VIS absorption spectra that could be explained by the mechanism of charging-discharging involving the influx/out flux of Li-ions. Some of these results could be used for understanding the energetics of Li-ion intercalation and deintercalation in multilayer graphene and related composites [314]. Single-step synthesis of halogen-functionalized graphenes (HGs) was reported using electroexfoliation of graphite in aqueous potassium halide solutions confirming the variation in the degree of halogenation between 2.32 and 0.26 atom% in fluorinated graphene (FG) and iodinated graphene (IG), respectively, which were attributed to the difference in reactivity of the halogen species generated during the exfoliation process. Among all HGs, FG has shown the superior electrocatalytic behavior for  $2\text{Br}^-/\text{Br}_2$  redox reaction. The anodic (11.2  $\text{mA}/\text{cm}^2$ ) and cathodic (10.7  $\text{mA}/\text{cm}^2$ ) peak current densities were higher for FG than that of other halogenated graphenes. ZBB flow cell fabricated with FG as bromine electrode exhibited enhanced electrochemical performance in terms of efficiency (81% of voltaic efficiency and 72% energy efficiency) and durability up to 350 cycles [315].

Comparison of the two routes of liquid phase exfoliation (LPE) and electrochemical exfoliation (ECE) made it clear the LPE took about 13 days against 3 min for ECE process [316]. A simple and fast method of electroexfoliating graphite into graphene oxide (GO) and then its rapid reduction to graphene nanosheets (GNs) was reported using microwaves. This electroexfoliation combined with microwaves reduction offered a low-cost and efficient route to produce high-quality graphene with high yield [317].

A rapid electroexfoliation of natural  $\text{Bi}_2\text{Se}_3$  and  $\text{Bi}_2\text{Te}_3$  crystals in aqueous media was reported to prepare single-/few-layer nanosheets representing a simple, reagent-free, and scalable method for the fabrication of single-/few-layer nanosheets of these materials [318]. 2D TMDCs with relatively lower toxicity, higher stability in aqueous environments, and adhering well to the biological materials such as proteins are currently being considered promising for biosensing, cell imaging, diagnostics, and therapeutics. Preparation and exfoliation of 2D TMDCs showing heavily dependent features on the number of layers and lateral size were described using their liquid exfoliation from their bulk materials along with the protocols for functionalizing or

modifying them [319]. Group-VI TMDCs including  $\text{MoS}_2$  and  $\text{WSe}_2$  being semiconductors with sizable energy band gaps offer themselves as building blocks for new generation optoelectronics particularly involving their specificity and tunability of their band gaps based on strong light-matter interactions between TMDC crystal and specific photons triggering complex phenomena like photoscattering, photoexcitation, photodestruction, photophysical modification, photochemical reaction, and photooxidation. Subsequently, photoelectric conversion devices enabled by laser excitation and the functionality extension and performance improvement in the TMDs materials via laser modification were comprehensively reviewed [320]. A green and cost-effective production process of 2D  $\text{MoS}_2$  was reported using sonication milling (CUM) to exfoliate natural molybdenite powders to achieve few-layer  $\text{MoS}_2$  (FL- $\text{MoS}_2$ ) nanosheets in *N*-methyl-2-pyrrolidone (NMP) with polyvinylpyrrolidone (PVP) molecules with the synergistic effect of sonication and sand milling enhancing the exfoliation efficiency, and the precursor of natural molybdenite powders minimizing the cost. The influence of various factors on exfoliation was studied by varying initial concentration of natural molybdenite powder (15–55 g/L), ultrasonic power (200–350 W), rotation speed of sand mill (1500–2250 rpm), exfoliation time (0.5–6 h), and the molar ratio of PVP unit to  $\text{MoS}_2$  (0–1). Under the optimal condition, the yield and exfoliation rate reached as high as 21.6% (in 6 h) and 1.42 g/Lh, respectively. This process could, thus, be considered as a low-cost, green, and efficient method of producing FL- $\text{MoS}_2$  nanosheets from natural molybdenite powders [321].

#### 4.4. Future perspectives

From the exceptionally faster developments taking place in the domain of 2D nanomaterials, one can easily assess about the future R&D activities in synthesizing and using still more varied combinations of ultrathin 2D nanomaterials in times to come as highlighted below.

For example, noble metals/alloys that are known as robust industrial catalyst are expected to perform better once converted into single-/few-layer forms. Similarly, the metal organic frameworks (MOFs) materials, currently found useful in gas storage, separations, and catalysis due to their tunable structures/functions, larger surface areas, and highly ordered pores, are, though, not used in electronic devices owing to their poor electrical conductivity and difficult film-forming ability, but once these shortcomings are taken care of, their device integration would open newer avenues [20].

2D TMDCs including ternary and quaternary compounds besides already known binaries like  $\text{MoS}_2$ ,  $\text{WS}_2$ ,  $\text{MoSe}_2$ , and  $\text{WSe}_2$  are expected to offer novel applications in electronics, optoelectronics, electrocatalysis, and energy storage, even though, some of them are yet to be synthesized.

Reversible conversion from one crystal phase into the other in 2D materials is another area of potential uses offered by the phase-engineered nanomaterials. For instance, some TMDCs including  $\text{MoS}_2$  and  $\text{WS}_2$  exist in either of the two main crystal phases namely—2H and 1T. It is interesting to note that  $\text{MoS}_2$  is semiconducting and metallic in 2H and 1T phase, respectively, with phase reversal caused by butyl lithium intercalation. The metallic phases of  $\text{MoS}_2$  and  $\text{WS}_2$  have better conductivity, whereas 2H phases exhibit enhanced electrocatalytic

actions in hydrogen evolution and supercapacitors [322–325]. Similar features are anticipated in case of noble metals prepared in different crystal phases. For example, Au crystallizing in face-centered cubic (fcc) phase was also synthesized in hexagonal 2H and 4H-phases that were transformed back to fcc and thus could be used for tuning its optical, catalytic, and plasmonic properties accordingly [341].

Practical implementations of H-termination along with van der Waals epitaxy in adjusting not only the band gaps, and stability, but also other properties of germanane are currently being considered as additional scope in future. For instance, germanane is converted into germoxanene after replacing H by OH-group and attaching different ligands to polysiloxene shifting the photoluminescence features along with band gap positions. Germanane is possible to restack with other materials using different intercalation techniques like electrochemical (alkali metals insertions between few layers), organic, and similar other zero-valent metal intercalation resulting in novel properties. Highly anisotropic properties caused due to electron-hole localization in transverse direction of germanane monolayer combined with their direct band gaps make them usable in a number of electronic applications including transistors, solar cells, and cooling layers. Additionally, combined use of topotactic deintercalation with exfoliations has been found better options of synthesis, though implemented only in limited number of Zintl phase compounds. Such layered materials include polygermanane, polysilanes, siloxenes, and spinels along with others like  $\text{CaSi}_2$ ,  $\text{CaGaSi}$ ,  $\text{CaZn}_2\text{Sb}_2$ , and  $\text{Ca}_{11}\text{GaSb}_9$ , that are expected to exhibit new and better material features in the form of 2D-hydrogenated/oxygenated semiconductors with precisely tuned electronic properties. These newer families of 2D materials, when used in heterostacks comprising of layers with different physical characteristics and further modified by restacking, are expected to offer newer engineered architectures for specific applications. The process of synthesizing flat materials endowed with exceptionally high charge carrier mobility transport established at molecular scales is expected to introduce significant changes in the electron device designs employing ‘atom by atom’ or ‘group by group’ substitutional alterations in realizing p-n junctions at the desired locations in near future providing better options of touch screens, supercapacitors, batteries, fuel cells, sensors, high frequency circuits, and flexible electronics [26, 326–332].

Using 2D exfoliated nanosheets appears better suited for realizing the five types of heterointerfaces for their device applications. For instance, layer-after-layer deposition of two different nanomaterials in a vertical heterostructure is an example of type I heterointerface already demonstrated in TMDCs, h-BN, or topological insulators on graphene or in situ epitaxial growth of vertical  $\text{CuS}/\text{TiS}_2$  type heterostructures [260, 333–336]. Similarly, type II heterointerface was reported in case of combinations of  $\text{WSe}_2/\text{WS}_2$ ,  $\text{MoSe}_2/\text{MoS}_2$ , and  $\text{MoSe}_2/\text{WSe}_2$ , wherein the growth of one type of nanosheet was made to start from the edge of the other forming an in-plane 2D heterojunction [268, 337–339]. Type III is similarly realized using a vertical growth of aligned ultrathin 2D nanosheet arrays on another ultrathin 2D nanomaterial substrate to form hierarchical heterostructures. Unlike these three afore-mentioned heterointerfaces, it is also feasible using the crystal-phase concept of heterointerfaces representing another kind using the same chemical compound but with different crystal phases. Type IV heterointerface may thus be prepared using a partially converted crystal phase in a  $\text{MoS}_2$  nanosheet by changing a part of it from its 2H phase into 1T phase resulting in an

in-plane 2H-1T heterointerface. Further, type V heterointerface involving superlattices is also conceivable using binary, ternary, or multiple phase patterns in ultrathin 2D noble metal nanostructures. The phase engineered Au-nanosheets in fcc, 2H, and 4H phases, already synthesized using wet-chemical methods and validated, are good candidates for crystal-phase superlattices with the help of self-assembly or lithography. Besides binary phase heterostructures, ternary phase comprising of 2H-fcc-4H might also be explored for similar applications using ultrathin 2D Au nanostructures having promising applications in catalysis, waveguide, surface enhanced Raman spectroscopy, and many others [256–259, 340, 341].

## 5. Conclusions

Adding 2D materials species with the nanoparticulate inorganic, organic, and biomolecular species and invoking different aspects of molecular recognition-based self-assemblies and self-organized formations of supramolecular hierarchical complexes seems to be a feasible way of improving the smart features of a large variety of nanomaterials in addition to paving the way for introducing the intelligent features in them in due course of time. Appropriate combinations of biomolecular species endowed already with the intelligent features are going to make this transition from 'smart' to 'intelligent' materials faster and easier as they possess the basic traits required for their participation in the functioning of living organisms. Other inorganic and organic building blocks once conjugated appropriately would certainly help in accelerating various components of intelligence discussed earlier. Further, the phytosomal building blocks when combined with 2D materials would certainly provide more insight into controlling the physico-chemico-biological properties of the resultant nanomaterial species with additional assurance of their green nature as compared to other species especially in the domain of applications involving human health care.

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