UNIVERSITI PUTRA MALAYSIA

SYNTHESIS OF DIFFERENT TYPES OF CARBON NANOSTRUCTURE ON CARBON FIBER AND THEIR APPLICATION AS FILLERS IN POLYPROPYLENE COMPOSITE

FERIAL GHAEMI

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By

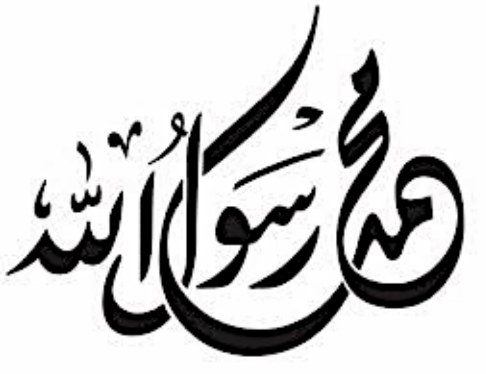
FERIAL GHAEMI

Thesis Submitted to the School of Graduate Studies,
Universiti Putra Malaysia, in fulfilment of the requirements for the Degree of
Doctor of Philosophy

July 2015

DEDICATIONS

To Prophet Mohammad (*salavato Allah alayh*)
and his respectable family



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

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By

FERIAL GHAEMI

July 2015

Chair: Professor Robiah Yunus, Ph.D.
Faculty: Institute of Advanced Technology

The potential application of carbon nanoparticles such as carbon nanotubes (CNT), carbon nanofibers (CNF) and graphene (G) flakes grown on carbon fiber (CF) surface as fillers in polypropylene composite is discussed. Carbon fiber surface must be modified before it can be used as fillers in composites. A one-step process using the chemical vapor deposition (CVD) method has been used to synthesize CNT, CNF and G and also G-CNF and G-CNT on the carbon fiber to modify its surfaces. In this study, CFs (Toho Tenax Co. Ltd.) was utilized as a substrate to grow carbon nanostructures and also as a filler in polypropylene pellets (PP 600G) polymer matrix. To the best of our knowledge, so far nobody has reported any work being widely carried out on synthesizing G layers on the CNF and CNT grown on CF by using a bimetallic catalyst (Ni/Cu) in a one-step CVD method in order to increase the CF surface area as well as to improve its properties. The synthesis of nanostructures on CF was accomplished using high purity acetylene (C_2H_2) as a carbon source, and nitrogen (Air Product, 99.9995) and hydrogen as carrier gases. Two types of catalysts namely copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) and nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) were utilized as bimetallic catalyst in the synthesis.

All the operating parameters of CVD process for growing the carbon nanostructures were optimized in order to obtain uniform and high quality carbon nanostructures. These parameters include catalyst concentration (from 50 mM to 150 mM), reaction temperature (different for each kind of carbon nanomaterial), reaction time (from 10 to 50 min) and carbon source flow rate (from 25 sccm to 100 sccm). Based on the SEM, TEM, TGA, BET surface area and Raman spectroscopy results, it was concluded that the optimum conditions are at 100mM catalyst concentration at 50sccm acetylene flow

rate for 30 min at 550ºC, 800 ºC and 1050 ºC for CNF, CNT and G growth, respectively.
The changes in the surface characteristics of CFs was studied with scanning electron microscopy (SEM), transmission electron microscope (TEM), Raman spectroscopy and BET surface area analyzer. By analyzing SEM and TEM images, the morphology, structure, size and diameter of the resulting carbon nanostructures were obtained. In Raman spectra, the I_D/I_G ratio of the samples decreases when graphene flakes are present. When the ratio of CF/catalyst was at the maximum value, the I_D/I_G ratio (≈1.13) coated with CNF, CNT and G, decreased to 0.94, 0.88, and 0.47 respectively. The I_D/I_G ratio of CF-CNF-G (0.85) and CF-CNT-G (0.81) indicates the effect of graphene growth on the crystallinity of the substrate.

Based on the results obtained from the surface modification of CF with various nanostructures, it is concluded that the carbon fiber coated with CNT-G (CF-CNT-G) with 80% yield and 46 m^2/g BET surface area is the best method for surface modification of CF. Other fillers such as CF-CNF produced 24% yield and 2.31 m^2/g surface area, CF-CNT with 46% yield and 5.22 m^2/g surface area, CF-CNF-G with 56% yield and 21 m^2/g surface area and, CF-G with 54% yield and 10.21 m^2/g surface area.

Polypropylene (PP) composites with different carbon-based fillers such as G on CF (G-CF), CNF on CF (CNF-CF), CNT on CF (CNT-CF) and also G-CNF-CF and G-CNT-CF were prepared by the melt mixed method and the effects of these nanoparticles on the mechanical and thermal behavior of the composites were analyzed. The mechanical behavior and thermal resistance of the produced composites were evaluated using the tensile test and thermal gravimetric analysis (TGA), respectively. The Raman images were then used to explain the observed mechanical behavior of the different types of fillers/PP composites. The tensile stress and young's modulus of neat PP are 28MPa and 1400MPa. The values increased when various nanostructures were grown on the CF, to about 8.9% and 14.5% for CF/PP, 21% and 30.5% for CF-CNF/PP, 30.7% and 50% for CF-CNF-G/PP, 58.9% and 58% for CF-CNT/PP, 98.2% and 114.2% for CF-CNT-G and finally 82.8% and 97% for CF-G. Based on the results, the PP composite reinforced with CF-CNT-G showed the highest improvement in tensile stress at 55.5 MPa, young's modulus at 2998.9 MPa and enhancement in thermal stability to 130ºC.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
Sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SINTESIS PELBAGAI JENIS KARBON BERSTRUKTUR NANO PADA SERAT KARBON DAN APLIKASI SEBAGAI PENGISI DALAM KOMPOSIT POLIPROPILENA

Oleh

FERIAL GHAEMI

Julai 2015

Pengerusi: Professor Robiah Yunus, Ph.D.
Fakulti: Institut Teknologi Maju

Potensi partikel nano karbon dalam aplikasi tiub nano karbon (CNT), serat nano karbon (CNF) dan serpihan grafin (G) yang dibina dan diperkembangkan di atas permukaan gentian karbon (CF), sebagai bahan pengukuh di dalam komposit polipropilena telah dibangunkan. Permukaan gentian karbon perlu diubah suai sebelum ia boleh digunakan sebagai bahan pengukuh di dalam bahan komposit. Proses satu langkah yang menggunakan kaedah pemendapan wap kimia (CVD) telah digunakan untuk mensintesis CNT, CNF dan G, berserta G-CNF dan G-CNT pada serat karbon untuk mengubah suai permukaannya. Dalam kajian ini, CF (Toho Tenax Co Ltd) telah digunakan sebagai substrat untuk menghasilkan struktur karbon nano dan juga sebagai bahan pengukuh di dalam matriks polimer bagi pelet polipropilena (PP 600g). Pada ketika ini, berdasarkan kajian yang telah dilakukan, masih tiada pihak yang melaporkan mengenai kerja-kerja mensintesis lapisan G di atas CNF dan CNT pada CF dengan menggunakan pemangkin dwi-logam (Ni/Cu) dengan hanya kaedah CVD satu langkah, bagi meningkatkan luas permukaan CF selain daripada menambah baik ciri-cirinya. Sintesis struktur nano pada CF telah berjaya dilaksanakan dengan menggunakan asetilena berketulenan tinggi (C_2H_2) sebagai sumber karbon, nitrogen (Air Product, 99,9995) dan hidrogen sebagai gas pembawa. Dua jenis pemangkin iaitu kuprum nitrat trihidrat (Cu $(NO_3)_2.3H_2O$) dan nikel nitrat heksahidrat (Ni $(NO_3)_2.6H_2O$) telah digunakan dalam sintesis tersebut.

Semua parameter yang terlibat dalam proses CVD untuk pembinaan struktur nano karbon dioptimumkan bagi mendapatkan struktur nano karbon yang berkualiti tinggi dan seragam. Parameter ini termasuk kepekatan pemangkin (dari 50mm hingga 150mm), suhu tindak balas (berbeza bagi setiap jenis bahan nano karbon), tempoh masa tindak balas (dari 10 hingga 50min) dan kadar aliran sumber karbon (dari 25sccm hingga 100sccm). Berdasarkan maklumat SEM, TEM, TGA, luas permukaan BET dan keputusan spektroskopi Raman, kesimpulan bagi keadaan optimum proses ini adalah pada kepekatan pemangkin 100mM, kadar aliran asetilena 50sccm selama 30 minit dengan suhu masing-masing 550ºC, 800ºC dan 1050ºC untuk pertumbuhan CNF, CNT dan G.

Perubahan pada ciri-ciri permukaan CF telah dikaji dengan menggunakan mikroskopi imbasan elektron (SEM), mikroskopi transmisi elektron (TEM), spektroskopi Raman dan analisis luas permukaan BET. Melalui dua analisa imej SEM dan TEM, morfologi, struktur, saiz dan diameter struktur karbon nano telah berjaya diperolehi. Spektrum Raman menunjukkan nisbah I_D/I_G sampel berkurangan dengan kehadiran serpihan grafin. Apabila nisbah CF/pemangkin berada pada nilai maksimum, nisbah I_D/I_G (≈1.13) yang disaluti dengan CNF, CNT dan G masing-masing menyusut kepada 0.94, 0.88, dan 0.4. Nisbah I_G/ I_D CF-CNF-G (0.85) dan CF-CNT-G (0.81) menunjukkan kesan pertumbuhan grafin pada hablur substrat.

Berdasarkan keputusan yang diperolehi daripada pengubahsuaian permukaan CF terhadap pelbagai struktur nano, kajian mendapati bahawa 80% serat karbon yang disaluti dengan CNT-G (CF-CNT-G) yang telah terhasil dengan luas permukaan BET 46 m^2/g adalah kaedah terbaik bagi pengubahsuaian permukaan CF. Bahan pengukuh lain seperti CF-CNF memberikan 24% hasil bahan dengan luas permukaan 2.31 m^2/g, CF-CNT dengan 46% hasil dan luas permukaan 5.22 m^2/g, CF-CNF-G dengan 56% hasil dan luas permukaan 21 m^2/g, dan akhir sekali, CF-G dengan 54% hasil dan luas permukaan 10.21 m^2/g.

Komposit polipropilena (PP) dengan bahan pengukuh berasaskan karbon yang berbeza seperti G pada CF(G-CF), CNF pada CF (CNF-CF), CNT pada CF (CNT-CF) juga G-CNF-CF dan G-CNT -CF telah dihasilkan melalui kaedah peleburan campuran, seterusnya kesan partikel nano ini terhadap ciri-ciri mekanikal dan terma bagi komposit telah dianalisa. Ciri-ciri mekanikal dan rintangan haba bagi komposit yang dihasilkan, masing-masing telah dinilai dengan menggunakan ujian tegangan dan analisis gravimetri haba (TGA). Imej-imej Raman kemudiannya digunakan untuk menerangkan tingkah laku mekanikal yang diperhatikan daripada jenis pengukuh/komposit PP. Kekuatan tegangan dan modulus Young untuk bahan asas PP adalah 28MPa dan 1400MPa. Nilai tersebut meningkat apabila pelbagai struktur nano telah dibina pada kombinasi bahan yang berbeza atas di atas CF, kepada 8.9% dan 14.5% bagi CF/PP, 21% dan 30.5% bagi CF-CNF/PP, 30.7% dan 50% bagi CF-CNF-G/PP, 58.9% dan 58% bagi CF-CNT/PP, 98.2% dan 114.2% bagi CF-CNT-G dan juga 82.8% dan 97% bagi CF-G. Keputusan telah membuktikan bahawa komposit PP yang diperkukuhkan dengan CF-CNT-G menunjukkan peningkatan tertinggi dalam kekuatan tegangan pada 55.5 MPa, modulus Young pada 2998.9 MPa dan peningkatan dalam kestabilan terma sehingga mencapai 130ºC.

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I certify that a Thesis Examination Committee has met on 6 July 2015 to conduct the final examination of Ferial Ghaemi on his thesis entitled "Synthesis of Different Types of Carbon Nanostructure on Carbon Fiber and Their Application as Fillers in Polypropylene Composite" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

Members of the Thesis Examination Committee were as follows:

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Faculty of Science
Universiti Putra Malaysia
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Associate Professor
Faculty of Science
Universiti Putra Malaysia
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Thomas Choong Shean Yaw, PhD
Professor Ir.
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

Meng (Jim) Low, PhD
Professor
Curtin University
Australia
(External Examiner)

ZULKARNAIN ZAINAL, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 12 August 2015

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Robiah Yunus, Ph.D.
Professor
Institute of Advanced Technology
Universiti Putra Malaysia
(Chairman)

Mohamad Amran Mohd Salleh, Ph.D.
Senior Lecturer
Institute of Advanced Technology
Universiti Putra Malaysia
(Member)

Suraya Abdul Rashid, Ph.D.
Associate Professor
Institute of Advanced Technology
Universiti Putra Malaysia
(Member)

Hong Ngee Lim, Ph.D.
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

BUJANG KIM HUAT, Ph.D.
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LIST OF ABBREVIATIONS

BET: Brunauer-Emmett-Teller

CCCs: Carbon/Carbon composites

CCVD: Catalyst Chemical Vapor Deposition

CDE: Carbon Deposition Efficiency

CF: Carbon Fiber

CM: Carbon fiber Mass

CNF: Carbon Nanofiber

CNP: Carbon Nanoparticle

CNT: Carbon Nanotube

CVD: Chemical Vapor Deposition

EDX: Energy Dispersion X-ray

ESD: Electrostatic Discharge

FESEM: Field Emission Scanning Electron Microscopy

G: Graphene

IFSS: Interfacial Shear Strength

MM: Metal Mass

MWCNC: Multi-walled carbon nanocoils

MWCNT: Multi-walled carbon Nanotube

PECVD: Plasma Enhanced Chemical Vapor Deposition

PP: Polypropylene

PM: Product Mass

RBM: Radial Breathing Mode

S_A: Surface Area

Sccm: Standard Cubic Centimeter per minute

SEM: Scanning Electron Microscopy

SWCNT: Single-walled Carbon Nanotube

TEM: Transmission Electron Microscopy

TGA: Thermogravimetric Analysis

CHAPTER 1

INTRODUCTION

1.1 General background

1.1.1 Polypropylene

Polypropylene (PP) is one of the most widely used polymers in automobiles, housewares, packaging, and electronics because of several useful properties like high heat distortion temperature, transparency, flame resistance and dimensional stability (An et al., 2012_a). Since, PP has been used in many applications, it has been mixed with various nanofillers in order to improve its mechanical properties (Seo and Park, 2004).

1.1.2 Carbon Fiber

Carbon fiber is a material consisting of extremely thin fibers about 0.005–0.010 mm in diameter and composed mostly of carbon atoms. Carbon fiber (CF) has been widely used in various industry fields because of its high strength and low weight, and also its ability to be used as filler in polymer matrix to reinforce a composite (Zhang et al., 2009). A low portion of this filler in the polymer composite has revealed remarkable improvement of the thermal and mechanical properties (Rezaei et al., 2008; Aziz et al., 2014).

1.1.3 Polymer Composite

The area of hybrid fibre-reinforced polymeric composites has received considerable interest by the engineering community because of its unique structure and mechanical properties (Fu et al., 2009). CF reinforced polymeric composites have a wide range of unexplored potential applications in various technological areas such as aerospace, automobile, electronic and process industries due to their outstanding properties, such as high specific strength and stiffness, lower weight and flexible tailoring (Shazed et al., 2014).

1.1.4 Nanostructures and Polymer Nanocomposites

In addition, studies showed that when carbon nanostructure are grown on the carbon fiber surface, the mechanical interlocking between polymer matrix and carbon fiber was improved (Miranda et al., 2011). Recently, CF reinforced polymer composites incorporating carbon nanoparticles have attracted significant interest due to their extensive applications that conventional CF reinforced composites cannot offer (Yamamoto et al., 2009). Advanced polymer-based nanocomposites have been produced with improved properties such as electrical conductivity, mechanical, and thermal stability (Jia et al., 2011).

The properties of composite materials depend not only on the reinforcing fillers and polymer matrix but also on the interfacial adhesion between them. High interfacial adhesion provides the strong structure of composites with an effective load transfer from the polymer matrix to the fiber. Carbon nanomaterials, such as G and CNF, on CF have been shown to provide a robust network with a polymer matrix to enhance the interfacial properties of composites (Liang et al., 2013a). Today's, various types of carbon nanomaterials such as fullerenes, carbon nanotubes, carbon nanofibers, carbon nanospirals, carbon onions (multilayer fullerenes) and graphene have been applied as reinforcing materials. Polymeric composites based on carbon nanomaterials, such as carbon nanofiber (CNF), carbon nanotube (CNT) and graphene (G) have attracted tremendous attention due to their excellent physical and mechanical properties (Kattab et al., 2012; Coleman et al., 2006; Ghaemi et al., 2014).

The CNFs can act as rod-shaped fillers and enhance the polymer properties in the polymer composite (Novais et al., 2012). There is broad range of different carbon nanofibre types, depending on the size and orientation of the graphene layers within their structure. The graphene plates are grown at an angle to the fiber axis in the herringbone shape to form carbon nanofiber, and tubular graphene walls are parallel to the fiber axis in the carbon nanotube (Teo et al., 2003). However all types of nanofibres are used in scientific studies and commercially, with applications including fillers in composites.

CNTs are allotropes of carbon with exceptional mechanical, electrical and thermal properties. They are made by graphene sheets, where carbon atoms are arranged in hexagonal patterns. Since their discovery by Iijima in 1991 (Iijima, 1991), CNTs have become attractive candidates for fundamental engineering applications. Graphene with a two-dimensional structure and honeycomb lattice is the most stable carbon format standard conditions, which was discovered by Novoselov et al. (2004). This nanomaterial has the potential to be applied in both scientific research and industrial applications because of its remarkable characteristics in terms of the mechanical, thermal and electrical properties (Zhang et al., 2013b). Additionally, G is also known as outstanding reinforcing filler in a composite with good dispersion (Allen et al., 2009; Cai and Song, 2010; Kim et al., 2010; Kuilla et al., 2010; Sengupta et al., 2011;).

The incorporation of CNTs into polymer matrix was firstly reported by Ajayan and co-authors (1994). Since then, polymer composites of carbon nanoparticles have been studied in various composite research fields, mostly focusing on their mechanical applications (Coleman et al., 2006; Kumar et al., 2002; Shafer and Windle, 1999; Yu et al., 2006). Strong interaction between these carbon nanomaterials and the host polymer is the key for mechanical strength. The bulk mechanical strength and stiffness of such composites is directly dependent on the interface of polymer matrix with carbon nanoparticles. The elongated cylindrical forms of both CNTs and CNFs result in anomalously large interface area per particle (Yu et al., 2000,). In recent years, polymer/G nanocomposites have drawn more and more attention from both scientists and engineers due to their unique behaviors (Kim et al., 2010).

The advantages of hybrid systems include the combined nanomaterials properties of each component, more design choices, cost effectiveness, and superior performance (Kalaprasad et al., 2004). But the hybrid concept has rarely been considered for nanocomposites (Li et al., 2008a). By varying the reinforcement scale, it may be possible to tailor the mechanical and physical properties of the composites. The hybrids of CNFs and CNTs with graphene may avoid the aggregates of single nanofillers due to the high concentration (Sui et al., 2009).

1.1.5 Methods of carbon nanomaterials production

Although there are several methods to obtain carbon nanomaterials, such as arc-discharge (Iijima, 1991), laser ablation (Yudasaka et al., 1998), chemical vapor deposition (CVD) (Cao et al., 2003; Gu et al., 2010), self assembly (Wu et al., 2007), mechanical exfoliation and cleavage (Novoselov et al., 2004), chemical methods (Choucair et al., 2009) and unzipping CNT (Kosynkin et al., 2009) those based on chemical solution are stressed by its practical approach for scale up the production. To provide large-scale production with low dimension and high purity is an important issue in advanced nanomaterials research, the CVD technique has been investigated (Muñoz and Gómez-Aleixandre, 2013) and applied in the production of carbon nanoparticles.

CVD method is considered as the most effective method and has been applied to grow carbon nanoparticles by many researchers (Liu et al., 2010). Basically, the deposition of reactants on the surface of the catalyst involves a balance between diffusion of reactant molecules to the catalyst and the kinetics of deposition reaction**.** The deposition reaction, which takes place on the catalyst surface is composed of various steps, such as adsorption of the reactants on the active sites, chemical reaction on the active sites, and desorption of the products from the active sites. From a heat transfer point of view, the particles perform an extra function by carrying the heat, which is very important during carbon nanoparticles synthesis.

It is well known that the CVD reaction conversion depends on the extent of heat and mass transfer occurring within and between the gas-solid phases. Exothermic CVD reaction results in hot spots that frequently lead to catalyst deactivation and adverse changes in conversion and/or selectivity of the process. To achieve different structure and morphology, some critical parameters of CVD such as growth time, growth temperature, flow rate of carbon source gas and catalyst concentration can be varied (Thostenson et al., 2002; Zhu et al., 2003; Ghaemi et al., 2015). Synthesis of each carbon nanoparticle with CVD method needs to have different conditions. So for growing two 3D carbon nanoparticles (carbon nanofiber and carbon nanotubes and then graphene), different conditions are needed.

1.2 Problem statement

Carbon fiber (CF)-reinforced polymer composites have been extensively applied in the areas of aerospace, aircraft, rocket, sport and military industries due to the superior strength-to-weight, stiffness-to-weight ratio and high service temperature. One problem in these composites is that CF typically shows poor interfacial interactions with polymer matrix. Another critical drawback is the presence of matrix-rich and free-volume regions formed in the gaps between the interlaced fiber bundles. The interfacial and mechanical properties of a fiber-reinforced polymer composite are significantly influenced by interfacial characteristics between the reinforcing fibers and the polymer matrix. For improving the mechanical properties of composite material it is necessary to optimize the interface between the fiber and matrix using certain methods for modification of reinforcing fiber (Dobreva and Nenkova 2006).

Using carbon fibers as reinforcing filler, the surface area is an important factor that plays a contributing role in the interfacial behavior with the polymer matrix. The defective flow of the polymer matrix around neat carbon fiber causes decreased interfacial properties and easily pulls out of carbon fiber from the matrix. Appropriate surface-treatment may modify the fiber surface by increasing the surface area and/or by growing carbon nanoparticles on the CF surface that may provide high adhesion between the fibers and the polymer matrix (Miller et al., 2001). So one of the key points of their properties is the interface between the fibers and matrix, which can be modified by nanoparticles growth.

Recently it was suggested that carbon nanoparticles grafting onto carbon fibers might be a new method of improving the interface and increasing IFSS (Zhao et al., 2008). There are two main routes for adding carbon nano-filler into conventional fiber-reinforced polymeric materials. The first one is by dispersing carbon nano-fillers entirely throughout the polymeric matrix, which afterwards is layered with reinforcing fibers. The second route concerns the direct attachment of nano-fillers onto primary reinforcing fibers (Miranda et al., 2011). In this study, G with excellent properties was synthsized to not only modify the CF surface but also use as a filler to reinforce polymer composite. Besides, the potential of CNT, CNF and G flakes on carbon fiber and also the effects of the graphene growth in the CNF-G and CNT-G grown on carbon fiber (CF) surface as fillers in composite materials are explored and compared with together. In order to modify the CF surface, a one-step process using the chemical vapor deposition method, has been used to synthesize CNT, CNF and G and also G-CNF and G-CNT on carbon fibers surface.

The high cost of carbon nanoparticles (CNF, CNT and G) synthesis, which restricts its large-scale production, is the key factor to the development and commercialization of

CNF, CNT and G sheet related industrials. It is prudent to note that the carbon nanoparticles are currently produced with a relatively high quality but in limited quantities. Therefore, future use of this worthwhile material strongly depends on the development of the technology for its large-scale production. Accordingly, large-scale syntheses of CNF, CNT and G have been the subject of intensive researches, and many attempts have been explored to optimize and control the carbon nanoparticles growth.

Chemical vapor deposition (CVD) provides a large contact area among the reactant and particle catalyst. The catalyst solution has a critical role to synthesize the CNT, CNF and the G layers on CF. Besides; to synthesize high quality graphene flakes on CNF or CNT, which were grown on CF, in one step, selecting a proper catalyst is important part of the CVD method. The selected catalyst should have the potential to grow CNF, CNF and G on CF and also G flakes on CF-CNF or CF-CNT in a large-area and a few-layer garphene. Among the different catalysts, Fe, Ni and Co are found suitable to synthesize CNF and CNT by CVD. On the other hand, for graphene growth Ni, Co and Cu have been used as the effective catalysts. Therefore, it is particularly important to develop a scalable synthesis method such as CVD method that could effectively control the size of fibers and tubes of CNF and CNT as well as the size and number of graphene layers, to enable large-scale production of the carbon nanoparticles (Liu et al., 2013). Consequently, to synthesis two layers of the carbon nanoparticles on the CF surface, using proper catalyst (bimetallic) with optimum amount should be found.

1.3 Objectives

In this study four objectives have been identified as follows:

1. To optimize the condition for CF surface modification by growing different carbon nanomaterials (CNF, CNT and G) in the vertical fixed bed CVD reactor

2. To develop one-step method by use of bimetallic catalyst to synthesis two layers of carbon nanomaterials (CNF-G and CNT-G) on CF surface.

3. To prepare polymer nanocomposite by mixing different fillers with polypropylene matrix and analysis the mechanical and thermal properties.

1.4 Thesis Scope

In this thesis work, we studied the synthesis and compared different kind of carbon nanoparticles grown on CF in order to increase the surface area of the CF as well as improve its properties. To synthesize high quality graphene, CVD on Cu catalyst is considered as one of the most promising methods because of its fabrication in a large-area and a single-layer graphene. However, Ni is one of the most widely studied catalysts for the synthesis of carbon nanaofibers and also graphene because a strong

Ni–C interaction causes a repulsive interaction within the C–C interaction and causes the dissolution at the edge of a graphene. However, limited research has been devoted to the usage of a bimetallic catalyst (Ni/Cu) to synthesize CNF, CNT and G. The Cu/Ni alloy is an excellent bimetallic system to control carbon solubility by tuning the atomic fraction of Ni in Cu in order to synthesis two layers of carbon nanostructures (CNF-G and CNT-G) in one-step production. To grow small size of CNF/CNT and few layer of graphene with high quality, the parameters of CVD method including catalyst concentration, reaction temperature, reaction time and acetylene flow rate should be optimized. These parameters include temperature, run time, catalyst amount and ratio of Ni/Cu, and flow rate of carbon source.

For growing carbon nanofiber on the CF, the operating parameters varied were as follows: Temperature, 550-650ºC, time: 10-60 min, catalyst amount: 50mM-150mM, catalyst ratio of Ni/Cu: 0/100, 30/70. 50/50, 70/30, 100/0 and carbon source flow rate: 25-150sccm. For growing carbon nanotubes the parameters varied were as follows: Temperature: 700-850ºC, time: 10-60 min, catalyst amount: 50mM-150mM, catalyst ratio of Ni/Cu: 0/100, 30/70. 50/50, 70/30, 100/0 and carbon source flow rate: 25-150sccm. For growing graphene the operating parameters varied were as follows: Temperature: 900-1050ºC, time: 10-60 min, catalyst amount: 50mM-150mM, catalyst ratio of Ni/Cu: 0/100, 30/70. 50/50, 70/30, 100/0 and carbon source flow rate: 25-150sccm.

Finally, the produced CNF, CNT, G, CNF-G and CNT-G, on CF surface, were incorporated into a polypropylene to fabricate the different composites. Furthermore, the effects of the carbon nanoparticles as coated phases on the CF surface were investigated in terms of the mechanical and thermal properties of the PP composite. Therefore, a tensile test as well as thermal gravimetric analysis (TGA) was applied. The surface morphology and structural characterization of the samples were analyzed through scanning electron microscopy (SEM), transmission electron microscope (TEM) and Raman spectroscopy.

1.5 Thesis Layout

This thesis is organized into five chapters. Following this chapter, chapter two begins with an extensive literature review. Firstly, it begins with the introduction of the carbon fiber and carbon nanoparticles. This chapter also provides description of some common characterization techniques for different carbon nanoparticles employed in this research. Secondly, the chapter covers the CVD process that is commonly used for CNF, CNT and G synthesis on CF. The growth mechanisms of each carbon nanoparticles are presented, including descriptions of the roles of the all effected parameters namely temperature, time, carbon amount and ratio and flow rate of carbon source gas. Then discussion is shifted towards synthesis of CNF-G and CNT-G on CF including principles and achievements obtained hitherto.

The last part of the literature review section is dedicated to a brief description and explanation of the carbon nanoparticles potential application polymer matrix and evaluate the mechanical and thermal properties. The considered polymer in this research is polypropylene, which was the preferred reinforcing polymer since it is a member of the group of commodity thermoplastics synthesized in large quantities and not very responsive to chemical stress cracking. This part presents related information about PP and its properties, mechanical reinforcement as well as thermal resistance. Moreover, the result of researchers who work with PP and add nanofiller in its matrix was studied.

After a comprehensive literature review with respect to the dissertation topic, in Chapter 2, research methodology and obtained results and discussions are presented in the following Chapters, 3 and 4. Research methodology was designed and conducted according to the objectives of this dissertation. Chapter 4 begins with results from synthesis of Carbon nanofibers on CF and optimize the catalyst concentration, growth time and temperature and also hydrocarbon flow rate. After that, CNT and G synthesis and optimize their growth parameters. Besides, the CNF-G and the CNT-G on CF are produced and analyzed their structures and characterizations. Moreover, the resulting nanoparticles are used as fillers in polymer matrix and analysis the thermal and mechanical behavior of the different composites. Finally, chapter 5 conducts with conclusion and recommendation.

REFERENCES

Aghababazadeh, R., Mirhabibi, A. R., Ghanbari, H., Chizari, K., Brydson, R. M. and Brown, A. P. (2006). Synthesis of carbon nanotubes on alumina-based supports with different gas flow rates by CCVD method. *Journal of Physics: Conference Series*, 26 (1): 135-138

Ajayan, P. M., Stephan, O., Colliex, C. and Trauth, D. (1994). Aligned carbon nanotube arrays formed by cutting a polymer resin—nanotube composite. *Science*, *265*(5176): 1212-1214.

Allen, M. J., Tung, V. C. and Kaner, R. B. (2009). Honeycomb carbon: a review of graphene. *Chemical reviews*, *110*(1): 132-145.

Alvarez, W.E., Kitiyana, B., Borgn, A. and Resasc, D.E. (2001). Synergism of Co and Mo in the catalytic production of single-wall carbon nanotubes by decomposition of CO. Carbon, 39(4): 547-58.

An, J. E., Jeon, G. W. and Jeong, Y. G. (2012a). Preparation and properties of polypropylene nanocomposites reinforced with exfoliated graphene. *Fibers and Polymers*, *13*(4): 507-514.

An, F., Lu, C., Li, Y., Guo, J., Lu, X., Lu, H. and Yang, Y. (2012b). Preparation and characterization of carbon nanotube-hybridized carbon fiber to reinforce epoxy composite. *Materials & Design*, *33*: 197-202.

Arshad, S. N., Naraghi, M. and Chasiotis, I. (2011). Strong carbon nanofibers from electrospun polyacrylonitrile. *Carbon*, *49*(5): 1710-1719.

Aziz, S., Rashid, S. A., Rahmanian, S. and Salleh, M. A. (2014). Experimental evaluation of the interfacial properties of carbon nanotube coated carbon fiber reinforced hybrid composites. *Polymer Composites*. doi: 10.1002/pc.23103.

Balandin, A. A. (2011). Thermal properties of graphene and nanostructured carbon materials. *Nature materials*, *10*(8): 569-581.

Batzill, M. (2012). The surface science of graphene: Metal interfaces, CVD synthesis, nanoribbons, chemical modifications, and defects. *Surface Science Reports*, *67*(3): 83-115.

Bijwe, J. and Sharma, M. (2011). Carbon Fabric‐ Reinforced Polymer Composites and Parameters Controlling Tribological Performance. *Wear of Advanced Materials*, 1-60. doi: 10.1002/9781118562093.ch1.

Biris, A. R., Lazar, M. D., Pruneanu, S., Neamtu, C., Watanabe, F., Kannarpady, G. K. and Biris, A. S. (2013). Catalytic one-step synthesis of Pt-decorated few-layer graphenes. *RSC Advances*, *3*(48): 26391-26402.

Brukh, R. and Mitra, S. (2006). Mechanism of carbon nanotube growth by CVD. *Chemical physics letters*, *424*(1): 126-132.

Cançado, L. G., Jorio, A., Ferreira, E. M., Stavale, F., Achete, C. A., Capaz, R. B. and Ferrari, A. C. (2011). Quantifying defects in graphene via Raman spectroscopy at different excitation energies. *Nano letters*, *11*(8): 3190-3196.

Cao, Z. L., Wang, J. N., Ding, D. Y., Dai, J. H. and Yu, F. (2003). Fast growth of well-aligned carbon nanotubes by chemical vapor deposition on plain glass. *New carbon materials*, *18*(1): 48-52.

Callister, W. D. J. and Rethwisch, D. G. (2007). Materials Science and Engineering: an Introduction, Vol. 7. New York: Wiley.

Cassell, A. M., Ye, Q., Cruden, B. A., Li, J., Sarrazin, P. C., Ng, H. T. and Meyyappan, M. (2004). Combinatorial chips for optimizing the growth and integration of carbon nanofibre based devices. *Nanotechnology*, *15*(1), 9-15.

Castranova, V., Schulte, P. A. and Zumwalde, R. D. (2012). Occupational nanosafety considerations for carbon nanotubes and carbon nanofibers. *Accounts of chemical research*, *46*(3): 642-649.

Chandrasekaran, S., Faiella, G., Prado, L. A. S. A., Tölle, F., Mülhaupt, R. and Schulte, K. (2013). Thermally reduced graphene oxide acting as a trap for multiwall carbon nanotubes in bi-filler epoxy composites. *Composites Part A: Applied Science and Manufacturing*, *49*: 51-57.

Chen, C. M., Dai, Y. M., Huang, J. G. and Jehng, J. M. (2006). Intermetallic catalyst for carbon nanotubes (CNTs) growth by thermal chemical vapor deposition method. *Carbon*, *44*(9): 1808-1820.

Cheng, Q., Wang, B., Zhang, C. and Liang, Z. (2010). Functionalized Carbon‐ Nanotube Sheet/Bismaleimide Nanocomposites: Mechanical and Electrical Performance Beyond Carbon‐ Fiber Composites. *Small*, *6*(6): 763-767.

Chhowalla, M., Teo, K. B. K., Ducati, C., Rupesinghe, N. L., Amaratunga, G. A. J., Ferrari, A. C. and Milne, W. I. (2001). Growth process conditions of vertically aligned carbon nanotubes using plasma enhanced chemical vapor deposition. *Journal of Applied Physics*, *90*(10): 5308-5317.

Choucair, M., Thordarson, P. and Stride, J. A. (2009). Gram-scale production of graphene based on solvothermal synthesis and sonication. *Nature Nanotechnology*, *4*(1): 30-33.

Coleman, J. N., Khan, U., Blau, W. J. and Gun'ko, Y. K. (2006). Small but strong: a review of the mechanical properties of carbon nanotube–polymer composites. *Carbon*, *44*(9): 1624-1652.

Coville, N. J., Mhlanga, S. D., Nxumalo, E. N. and Shaikjee, A. (2011). A review of shaped carbon nanomaterials. *South African Journal of Science*, *107*(3-4): 1-15.

Dai, G. P., Wu, M. H., Taylor, D. K., Brennaman, M. K. and Vinodgopal, K. (2012). Hybrid 3D graphene and aligned carbon nanofiber array architectures. *RSC Advances*, *2*(24): 8965-8968.

De Greef, N., Zhang, L., Magrez, A., Forró, L., Locquet, J. P., Verpoest, I. and Seo, J. W. (2015). Direct growth of carbon nanotubes on carbon fibers: Effect of the CVD parameters on the degradation of mechanical properties of carbon fibers. *Diamond and Related Materials*, *51*: 39-48.

Ding, F., Larsson, P., Larsson, J. A., Ahuja, R., Duan, H., Rosén, A. and Bolton, K. (2008). The importance of strong carbon-metal adhesion for catalytic nucleation of single-walled carbon nanotubes. *Nano letters*, *8*(2): 463-468.

Dobreva, D. and Nenkova, S. (2006). Investigation of the microstructure of polypropylene composites filled with wood flour modified with monochloracetic acid. In *Functional Properties of Nanostructured Materials* (pp. 177-180). Netherlands: Springer.

Dong, Q., Wang, G., Hu, H., Yang, J., Qian, B., Ling, Z. and Qiu, J. (2013). Ultrasound-assisted preparation of electrospun carbon nanofiber/graphene composite electrode for supercapacitors. *Journal of Power Sources*, *243*: 350-353.

Dong, X., Li, B., Wei, A., Cao, X., Chan-Park, M. B., Zhang, H. and Chen, P. (2011). One-step growth of graphene–carbon nanotube hybrid materials by chemical vapor deposition. *Carbon*, *49*(9): 2944-2949.

Du, X., Skachko, I., Barker, A. and Andrei, E. Y. (2008). Approaching ballistic transport in suspended graphene. *Nature nanotechnology*, *3*(8): 491-495.

Dvir, H., Jopp, J. and Gottlieb, M. (2006). Estimation of polymer–surface interfacial interaction strength by a contact AFM technique. *Journal of colloid and interface science*, *304*(1): 58-66.

Edie, D.D. and McHugh, J.J. (1999). High performance carbon fibers. In: Carbon materials for advanced technologies, (pp. 119–138). Oxford: Elsevier.

Endo, M., Nishimura, K., Kim, Y. A., Hakamada, K., Matushita, T., Dresselhaus, M. S. and Dresselhaus, G. (1999). Raman spectroscopic characterization of submicron vapor-grown carbon fibers and carbon nanofibers obtained by pyrolyzing hydrocarbons. *Journal of materials research*, *14*(12): 4474-4477.

Endo, M., Kim, Y. A., Hayashi, T., Fukai, Y., Oshida, K., Terrones, M. and Dresselhaus, M. S. (2002). Structural characterization of cup-stacked-type nanofibers with an entirely hollow core. *Applied Physics Letters*, *80*(7): 1267-1269.

Endo, M., Kim, Y. A., Hayashi, T., Nishimura, K., Matusita, T., Miyashita, K. and Dresselhaus, M. S. (2001). Vapor-grown carbon fibers (VGCFs): basic properties and their battery applications. *Carbon*, *39*(9): 1287-1297.

Eom, D., Prezzi, D., Rim, K. T., Zhou, H., Lefenfeld, M., Xiao, S. and Flynn, G. W. (2009). Structure and electronic properties of graphene nanoislands on Co (0001). *Nano letters*, *9*(8): 2844-2848.

Fedorov, A. V., Varykhalov, A. Y., Dobrotvorskii, A. M., Chikina, A. G., Adamchuk, V. K. and Usachov, D. Y. (2011). Structure of graphene on the Ni (110) surface. *Physics of the Solid State*, *53*(9): 1952-1956.

Ferrari, A. C. and Robertson, J. (2004). Raman spectroscopy of amorphous, nanostructured, diamond–like carbon, and nanodiamond. *Philosophical Transactions of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences*, *362*(1824): 2477-2512.

Ferrari, A. C. and Basko, D. M. (2013). Raman spectroscopy as a versatile tool for studying the properties of graphene. *Nature nanotechnology*, *8*(4): 235-246.

Frank, O., Vejpravova, J., Holy, V., Kavan, L. and Kalbac, M. (2014). Interaction between graphene and copper substrate: The role of lattice orientation. *Carbon*, *68*: 440-451.

Fu, S. Y., Lauke, B. and Mai, Y. W. (2009). *Science and engineering of short fibre reinforced polymer composites*. Cambridge: Elsevier.

Gallego, M. M., Bernal, M. M., Hernandez, M., Verdejo, R. and Lopez-Manchado, M. A. (2013). Comparison of filler percolation and mechanical properties in graphene and carbon nanotubes filled epoxy nanocomposites. *European Polymer Journal*, *49*(6): 1347-1353.

Geim, A. K. and Grigorieva, I. V. (2013). Van der Waals heterostructures. *Nature*, *499*(7459): 419-425.

Ghaemi, F., Amiri, A. and Yunus, R. (2014). Methods for coating solid-phase microextraction fibers with carbon nanotubes. *TrAC Trends in Analytical Chemistry*, *59*: 133-143.

Ghaemi, F., Yunus, R., Mohd Salleh, M. A., Lim, H. N. and Rashid, S. A. (2015). Bulk production of high-purity carbon nanosphere by combination of chemical vapor deposition methods. *Fullerenes, Nanotubes and Carbon Nanostructures*, *23*(8): 669-675.

Ghazinejad, M., Guo, S., Wang, W., Ozkan, M. and Ozkan, C. S. (2013). Synchronous chemical vapor deposition of large-area hybrid graphene–carbon nanotube architectures. *Journal of Materials Research*, *28*(7): 958-968.

Gu, J. Y., Li, K. X., Wang, J. and He, H. W. (2010). Control growth of carbon nanofibers on Ni/activated carbon in a fluidized bed reactor. *Microporous and Mesoporous Materials*, *131*(1): 393-400.

He, D. and Bai, J. (2011). Acetylene‐ Enhanced Growth of Carbon Nanotubes on Ceramic Microparticles for Multi‐ Scale Hybrid Structures. *Chemical Vapor Deposition*, *17*(4‐ 6): 98-106.

Hofmann, S., Csanyi, G., Ferrari, A. C., Payne, M. C. and Robertson, J. (2005). Surface diffusion: the low activation energy path for nanotube growth. *Physical review letters*, *95*(3): 036101-036104.

Hood, A. R., Saurakhiya, N., Deva, D., Sharma, A. and Verma, N. (2013). Development of bimetal-grown multi-scale carbon micro-nanofibers as an immobilizing matrix for enzymes in biosensor applications. *Materials Science and Engineering: C*, *33*(7): 4313-4322.

Hoyos-Palacio, L. M., García, A. G., Pérez-Robles, J. F., González, J. and Martínez-Tejada, H. V. (2014). Catalytic effect of Fe, Ni, Co and Mo on the CNTs production. *IOP Conference Series: Materials Science and Engineering* 59(1): 012005-0120012.

Hsieh, Y. P., Hofmann, M. and Kong, J. (2014). Promoter-assisted chemical vapor deposition of graphene. *Carbon*, *67*: 417-423.

Hu, K., Kulkarni, D. D., Choi, I. and Tsukruk, V. V. (2014). Graphene-polymer nanocomposites for structural and functional applications. *Progress in Polymer Science*, *39*(11): 1934-1972.

Huang, G., Wang, S., Song, P. A., Wu, C., Chen, S. and Wang, X. (2014). Combination effect of carbon nanotubes with graphene on intumescent flame-retardant polypropylene nanocomposites. *Composites Part A: Applied Science and Manufacturing*, *59*: 18-25.

Hwang, J. Y., Kuo, C. C., Chen, L. C. and Chen, K. H. (2010). Correlating defect density with carrier mobility in large-scaled graphene films: Raman spectral signatures for the estimation of defect density. *Nanotechnology*, *21*(46): 465705.

Hwang, Y., Kim, M. and Kim, J. (2013). Improvement of the mechanical properties and thermal conductivity of poly (ether-ether-ketone) with the addition of graphene oxide-carbon nanotube hybrid fillers. *Composites Part A: Applied Science and Manufacturing*, *55*: 195-202.

Ibrahim, I., Bachmatiuk, A., Warner, J. H., Büchner, B., Cuniberti, G. and Rümmeli, M. H. (2012). CVD‐ Grown Horizontally Aligned Single‐ Walled Carbon Nanotubes: Synthesis Routes and Growth Mechanisms. *Small*, *8*(13): 1973-1992.

Iijima, S. (1991). Helical microtubules of graphitic carbon. *nature*, *354*(6348): 56-58.

Ismach, A., Segev, L., Wachtel, E. and Joselevich, E. (2004). Atomic‐ Step‐ Templated Formation of Single Wall Carbon Nanotube Patterns. *Angewandte Chemie*, *116*(45): 6266-6269.

Jang, B. Z. and Zhamu, A. (2008). Processing of nanographene platelets (NGPs) and NGP nanocomposites: a review. *Journal of Materials Science*, *43*(15): 5092-5101.

Jen, M. H. R., Chang, C. K., Chen, J. G. and Lin, B. C. (2012). Fatigue Response of Ti/APC-2 Nanocomposite Laminate Prosthesis. *Life Science Journal*, *9*(2):178-184.

Jia, Y., Peng, K., Gong, X. L. and Zhang, Z. (2011). Creep and recovery of polypropylene/carbon nanotube composites. *International Journal of Plasticity*, *27*(8): 1239-1251.

Jiang, X., Cao, Y., Li, P., Wei, J., Wang, K., Wu, D. and Zhu, H. (2015). Polyaniline/graphene/carbon fiber ternary composites as supercapacitor electrodes. *Materials Letters*, *140*: 43-47.

Jin, Z., Chu, H., Wang, J., Hong, J., Tan, W. and Li, Y. (2007). Ultralow feeding gas flow guiding growth of large-scale horizontally aligned single-walled carbon nanotube arrays. *Nano letters*, *7*(7): 2073-2079.

Joseph, P. V., Rabello, M. S., Mattoso, L. H. C., Joseph, K. and Thomas, S. (2002). Environmental effects on the degradation behaviour of sisal fibre reinforced polypropylene composites. *Composites Science and Technology*, *62*(10): 1357-1372.

Kalaprasad, G., Francis, B., Thomas, S., Kumar, C. R., Pavithran, C., Groeninckx, G. and Thomas, S. (2004). Effect of fibre length and chemical modifications on the tensile properties of intimately mixed short sisal/glass hybrid fibre reinforced low density polyethylene composites. *Polymer international*, *53*(11): 1624-1638.

Kamada, K., Ikuno, T., Takahashi, S., Oyama, T., Yamamoto, T., Kamizono, M. and Oura, K. (2003). Surface morphology and field emission characteristics of carbon nanofiber films grown by chemical vapor deposition on alloy catalyst. *Applied surface science*, *212*: 383-387.

Kichambare, P. D., Qian, D., Dickey, E. C. and Grimes, C. A. (2002). Thin film metallic catalyst coatings for the growth of multiwalled carbon nanotubes by pyrolysis of xylene. *Carbon*, *40*(11): 1903-1909.

Kim, D. H., Jang, H. S., Kim, C. D., Cho, D. S., Kang, H. D., Jee, J. G. and Lee, H. R. (2003). In situ monitoring of carbon nanotube growth. *Carbon*, *41*(3): 583-585.

Kim, H., Abdala, A. A. and Macosko, C. W. (2010). Graphene/polymer nanocomposites. *Macromolecules*, *43*(16): 6515-6530.

Kim, K. S., Zhao, Y., Jang, H., Lee, S. Y., Kim, J. M., Kim, K. S. and Hong, B. H. (2009). Large-scale pattern growth of graphene films for stretchable transparent electrodes. *Nature*, *457*(7230): 706-710.

Kimmari, E., Podgursky, V., Simunin, M., Adoberg, E., Surženkov, A., Viljus, M. and Kulu, P. (2013). Tribological behavior of carbon nanofibers deposited on hard nanocomposite (nc-Ti1−xAlxN)/(a-Si3N4) coating. *Surface and Coatings Technology*, *225*: 21-25.

Kitiyanan, B., Alvarez, W. E., Harwell, J. H. and Resasco, D. E. (2000). Controlled production of single-wall carbon nanotubes by catalytic decomposition of CO on bimetallic Co–Mo catalysts. *Chemical Physics Letters*, *317*(3): 497-503.

Klein, K. L., Melechko, A. V., Rack, P. D., Fowlkes, J. D., Meyer, H. M. and Simpson, M. L. (2005). Cu–Ni composition gradient for the catalytic synthesis of vertically aligned carbon nanofibers. *Carbon*, *43*(9): 1857-1863.

Koh, A. T., Foong, Y. M. and Chua, D. H. (2012). Comparison of the mechanism of low defect few-layer graphene fabricated on different metals by pulsed laser deposition. *Diamond and Related Materials*, *25*: 98-102.

Kosynkin, D. V., Higginbotham, A. L., Sinitskii, A., Lomeda, J. R., Dimiev, A., Price, B. K. and Tour, J. M. (2009). Longitudinal unzipping of carbon nanotubes to form graphene nanoribbons. *Nature*, *458*(7240): 872-876.

Kouravelou, K. B. and Sotirchos, S. V. (2005). Dynamic study of carbon nanotubes production by chemical vapor deposition of alcohols. *Reviews on Advanced Materials Science*, *10*(3): 243-248.

Kovtyukhova, N. I., Martin, B. R., Mbindyo, J. K., Smith, P. A., Razavi, B., Mayer, T. S. and Mallouk, T. E. (2001). Layer-by-layer assembly of rectifying junctions in and on metal nanowires. *The Journal of Physical Chemistry B*, *105*(37): 8762-8769.

Kuilla, T., Bhadra, S., Yao, D., Kim, N. H., Bose, S. and Lee, J. H. (2010). Recent advances in graphene based polymer composites. *Progress in polymer science*, *35*(11): 1350-1375.

Kukovitsky, E. F., L'vov, S. G., Sainov, N. A., Shustov, V. A. Chernozatonskii, L. A. (2002). Correlation between metal catalyst particle size and carbon nanotube growth. *Chemical Physics Letters*, *355*(5): 497-503.

Kumar, M. and Ando, Y. (2010). Chemical vapor deposition of carbon nanotubes: a review on growth mechanism and mass production. *Journal of nanoscience and nanotechnology*, *10*(6): 3739-3758.

Kumar, S., Dang, T. D., Arnold, F. E., Bhattacharyya, A. R., Min, B. G., Zhang, X. and Willis, P. A. (2002). Synthesis, Structure, and Properties of PBO/SWNT Composites&. *Macromolecules*, *35*(24): 9039-9043.

Lahiri, J., Miller, T., Adamska, L., Oleynik, I. I. and Batzill, M. (2010). Graphene growth on Ni (111) by transformation of a surface carbide. *Nano letters*, *11*(2): 518-522.

Lakshminarayanan, P. V., Toghiani, H. and Pittman, C. U. (2004). Nitric acid oxidation of vapor grown carbon nanofibers. *Carbon*, *42*(12): 2433-2442.

Lamouroux, E., Serp, P., Kihn, Y. and Kalck, P. (2007). Identification of key parameters for the selective growth of single or double wall carbon nanotubes on FeMo/Al 2 O 3 CVD catalysts. *Applied Catalysis A: General*, *323*: 162-173.

Li, C., Li, Z., Zhu, H., Wang, K., Wei, J., Li, X. and Wu, D. (2010a). Graphene nano-“patches” on a carbon nanotube network for highly transparent/conductive thin film applications. *The Journal of Physical Chemistry C*, *114*(33): 14008-14012.

Li, D. C., Dai, L., Huang, S., Mau, A. W. and Wang, Z. L. (2000). Structure and growth of aligned carbon nanotube films by pyrolysis. *Chemical Physics Letters*, *316*(5): 349-355.

Li, D., Müller, M. B., Gilje, S., Kaner, R. B. and Wallace, G. G. (2008a). Processable aqueous dispersions of graphene nanosheets. *Nature nanotechnology*, *3*(2): 101-105.

Li, H., He, D., Li, T., Genestoux, M. and Bai, J. (2010b). Chemical kinetics of catalytic chemical vapor deposition of an acetylene/xylene mixture for improved carbon nanotube production. *Carbon*, *48*(15): 4330-4342.

Li, J., Wong, P. S. and Kim, J. K. (2008b). Hybrid nanocomposites containing carbon nanotubes and graphite nanoplatelets. *Materials Science and Engineering: A*, *483-484*: 660-663.

Li, K., Eres, G., Howe, J., Chuang, Y. J., Li, X., Gu, Z. and Pan, Z. 2013. Self-assembly of graphene on carbon nanotube surfaces. *Scientific reports*, *3*. 2353, DOI:10.1038/srep02353.

Li, Q., Yan, H., Zhang, J. and Liu, Z. (2004). Effect of hydrocarbons precursors on the formation of carbon nanotubes in chemical vapor deposition. *Carbon*, *42*(4): 829-835.

Li, W. Z., Wen, J. G. and Ren, Z. F. (2001a). Straight carbon nanotube Y junctions. *Applied Physics Letters*, *79*(12): 1879-1881.

Li, X., Cai, W., Colombo, L. and Ruoff, R. S. (2009). Evolution of graphene growth on Ni and Cu by carbon isotope labeling. *Nano letters*, *9*(12): 4268-4272.

Li, Y., Liu, J., Wang, Y. and Wang, Z. L. (2001b). Preparation of monodispersed Fe-Mo nanoparticles as the catalyst for CVD synthesis of carbon nanotubes. *Chemistry of Materials*, *13*(3): 1008-1014.

Liang, H. W., Liu, J. W., Qian, H. S. and Yu, S. H. (2013a). Multiplex templating process in one-dimensional nanoscale: controllable synthesis, macroscopic assemblies, and applications. *Accounts of chemical research*, *46*(7): 1450-1461.

Liang, J., Saha, M. C. and Altan, M. C. (2013b). Effect of carbon nanofibers on thermal conductivity of carbon fiber reinforced composites. *Procedia Engineering*, *56*: 814-820.

Lim, S. L., Suda, Y., Takimoto, K., Ishii, Y., Maruyama, K., Tanoue, H. and Umeda, Y. (2013). Optimization of Chemical Vapor Deposition Process for Reducing the Fiber Diameter and Number of Graphene Layers in Multi Walled Carbon Nanocoils. *Japanese Journal of Applied Physics*, *52*(11S), 11NL04.

Liu, Y. and Kumar, S. (2012). Recent progress in fabrication, structure, and properties of carbon fibers. *Polymer Reviews*, *52*(3): 234-258.

Liu, W., Kraemer, S., Sarkar, D., Li, H., Ajayan, P. M. and Banerjee, K. (2013). Controllable and rapid synthesis of high-quality and large-area Bernal stacked bilayer graphene using chemical vapor deposition. *Chemistry of Materials*, *26*(2): 907-915.

Loginova, E., Bartelt, N. C., Feibelman, P. J. and McCarty, K. F. 2009. Factors influencing graphene growth on metal surfaces. *New Journal of Physics*, *11*(6): 063046.

Losurdo, M., Giangregorio, M. M., Capezzuto, P. and Bruno, G. (2011). Graphene CVD growth on copper and nickel: role of hydrogen in kinetics and structure. *Physical Chemistry Chemical Physics*, *13*(46): 20836-20843.

Lozano, K. and Barrera, E. V. (2001). Nanofiber‐ reinforced thermoplastic composites. I. Thermoanalytical and mechanical analyses. *Journal of Applied Polymer Science*, *79*(1), 125-133.

Maruyama, S., Kojima, R., Miyauchi, Y., Chiashi, S. and Kohno, M. (2002). Low-temperature synthesis of high-purity single-walled carbon nanotubes from alcohol. *Chemical physics letters*, *360*(3): 229-234.

Méhn, D., Fonseca, A., Bister, G. and Nagy, J. B. (2004). A comparison of different preparation methods of Fe/Mo/Al2O3 sol–gel catalyst for synthesis of single wall carbon nanotubes. *Chemical physics letters*, *393*(4): 378-384.

Melechko, A. V., Merkulov, V. I., McKnight, T. E., Guillorn, M. A., Klein, K. L., Lowndes, D. H. and Simpson, M. L. (2005). Vertically aligned carbon nanofibers and related structures: controlled synthesis and directed assembly. *Journal of applied physics*, *97*(4): 041301.

Meng, L. Y., Moon, C. W., Im, S. S., Lee, K. H., Byun, J. H. and Park, S. J. (2011). Effect of Ni catalyst dispersion on the growth of carbon nanofibers onto carbon fibers. *Microporous and Mesoporous Materials*, *142*(1): 26-31.

Mi, W., Lin, J. Y., Mao, Q., Li, Y. and Zhang, B. (2005). A Study on the Effects of Carrier Gases on the Structure and Morphology of Carbon Nanotubes Prepared by Pyrolysis of Ferrocene and C~ 2H~ 2 Mixture. *Journal of Natural Gas Chemistry*, *14*(3): 151-155.

Mičušík, M., Omastová, M., Krupa, I., Prokeš, J., Pissis, P., Logakis, E. and Pionteck, J. (2009). A comparative study on the electrical and mechanical behaviour of multi‐ walled carbon nanotube composites prepared by diluting a masterbatch with various types of polypropylenes. *Journal of Applied Polymer Science*, *113*(4): 2536-2551.

Miller, T.C., Chajes, M.J., Mertz, D.R. and Hastings, J.N. (2001). Strengthening of a steel bridge girder using CFRP plates, *J. Bridge* Eng. 6(6): 514–522.

Miranda, A.N.D., Pardini, L.C., Santos, C.A.M.D. and Vieira, R. (2011). Evaluation of carbon fiber composites modified by in situ incorporation of carbon nanofibers. Materials Research, 14(4): 560-563.

Mittal, G., Dhand, V., Rhee, K. Y., Park, S. J. and Lee, W. R. (2015). A review on carbon nanotubes and graphene as fillers in reinforced polymer nanocomposites. *Journal of Industrial and Engineering Chemistry*, *21*: 11-25.

Mohiuddin, T.M.G., Lombardo, A., Nair, R.R., Bonetti, A., Savini, G., Jalil, R. and Ferrari, A.C. (2009). Uniaxial strain in graphene by Raman spectroscopy: G peak splitting, Grüneisen parameters, and sample orientation. *Physical Review B*, *79*(20): 205433.

Morgan, P. (2005). *Carbon fibers and their composites*, Boca Raton: Taylor& Francis.

Morgan, S. and Mokaya, R. (2008). Aligned bundles of carbon nanotubes are easily grown on as-synthesized mesoporous silicate substrates. *The Journal of Physical Chemistry C*, *112*(39): 15157-15162.

Morjan, R. E., Nerushev, O. A., Sveningsson, M., Rohmund, F., Falk, L. K. L. and Campbell, E. E. B. (2004). Growth of carbon nanotubes from C60. *Applied Physics A*, *78*(3): 253-261.

Muñoz, R. and Gómez‐ Aleixandre, C. (2013). Review of CVD synthesis of graphene. *Chemical Vapor Deposition*, *19*(10-11-12): 297-322.

Ng, H. T., Chen, B., Koehne, J. E., Cassell, A. M., Li, J., Han, J. and Meyyappan, M. (2003). Growth of carbon nanotubes: a combinatorial method to study the effects of catalysts and underlayers. *The Journal of Physical Chemistry B*, *107*(33): 8484-8489.

Novais, R. M., Covas, J. A. and Paiva, M. C. (2012). The effect of flow type and chemical functionalization on the dispersion of carbon nanofiber agglomerates in polypropylene. *Composites Part A: Applied Science and Manufacturing*, *43*(6): 833-841.

Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V. and Firsov, A. A. (2004). Electric field effect in atomically thin carbon films. *science*, *306*(5696): 666-669.

Ouyang, Y., Cong, L.M., Chen, L., Liu, Q.X. and Fang, Y. (2008). Raman Study on Single-Walled Carbon Nanotubes and Multi-Walled Carbon Nanotubes with Different Laser Excitation Energies, Physica E, 40(7): 2386–2389.

Paiva, J. M. F., Santos, A.N. and Rezende, M.C. (2009). Mechanical and morphological characterizations of carbon fiber fabric reinforced epoxy composites used in aeronautical field. *Mater Res,* 12(3): 367–74.

Paiva, M. C., Bernardo, C.A. and Nardin, M. (2000). Mechanical, surface and interfacial characterisation of pitch and PAN-based carbon fibres. *Carbon,* 38(9): 1323–37.

Paredes, J. I., Martınez-Alonso, A. and Tascon, J. M. D. (2002). Oxygen plasma modification of submicron vapor grown carbon fibers as studied by scanning tunneling microscopy. *Carbon, 40*(7): 1101-1108.

Park, S. J. and Kim, B. J. (2005). Roles of acidic functional groups of carbon fiber surfaces in enhancing interfacial adhesion behavior. *Materials Science and Engineering: A*, *408*(1): 269-273.

Paul, D. R. and Robeson, L. M. (2008). Polymer nanotechnology: nanocomposites. *Polymer*, *49*(15): 3187-3204.

Pedroni, L. G., Soto‐ Oviedo, M. A., Rosolen, J. M., Felisberti, M. I. and Nogueira, A. F. (2009). Conductivity and mechanical properties of composites based on MWCNTs and styrene‐ butadiene‐ styrene block™ copolymers. *Journal of applied polymer science*, *112*(6): 3241-3248.

Pelsoci, T. M. and Bond, P. J. (2004). Composites Manufacturing Technologies: Applications in Automotive, Petroleum: Gaithersburg, USA.

Pérez-Cabero, M., Monzón, A., Rodrıguez-Ramos, I. and Guerrero-Ruíz, A. (2004). Syntheses of CNTs over several iron-supported catalysts: influence of the metallic precursors. *Catalysis today*, *93-95*: 681-687.

Pesin, L.A. (2002). Review—Structure and Properties of Glass-Like Carbon, J. Mater. Sci., 37(1): 1–28.

Piedigrosso, P., Konya, Z., Colomer, J. F., Fonseca, A., Van Tendeloo, G. and Nagy, J. B. (2000). Production of differently shaped multi-wall carbon nanotubes using various cobalt supported catalysts. *Physical Chemistry Chemical Physics*, *2*(1): 163-170.

Pukánszky, B. (2005). Interfaces and interphases in multicomponent materials: past, present, future. *European Polymer Journal*, *41*(4): 645-662.

Qi, J. L., Zheng, W. T., Zheng, X. H., Wang, X. and Tian, H. W. (2011). Relatively low temperature synthesis of graphene by radio frequency plasma enhanced chemical vapor deposition. *Applied Surface Science*, *257*(15): 6531-6534.

Qian, W., Liu, T., Wei, F., Wang, Z. and Li, Y. (2004). Enhanced production of carbon nanotubes: combination of catalyst reduction and methane decomposition. *Applied Catalysis A: General*, *258*(1): 121-124.

Qiu, J., Li, Q., Wang, Z., Sun, Y. and Zhang, H. (2006). CVD synthesis of coal-gas-derived carbon nanotubes and nanocapsules containing magnetic iron carbide and oxide. *Carbon*, *44*(12): 2565-2568.

Rahmanian, S., Suraya, A. R., Zahari, R. and Zainudin, E. S. (2013). Synthesis of vertically aligned carbon nanotubes on carbon fiber. *Applied Surface Science*, *271*: 424-428.

Reina, A., Hofmann, M., Zhu, D. and Kong, J. (2007). Growth mechanism of long and horizontally aligned carbon nanotubes by chemical vapor deposition. *The Journal of Physical Chemistry C*, *111*(20): 7292-7297.

Reina, A., Jia, X., Ho, J., Nezich, D., Son, H., Bulovic, V. and Kong, J. (2008). Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition. *Nano letters*, *9*(1): 30-35.

Reina, A. and Kong, J. (2012). Graphene growth by CVD methods. In *Graphene Nanoelectronics* (pp. 167-203). Atlanta: Springer.

Rezaei, F., Yunus, R., Ibrahim, N. A. and Mahdi, E. S. (2008). Development of short-carbon-fiber-reinforced polypropylene composite for car bonnet. *Polymer-Plastics Technology and Engineering*, *47*(4): 351-357.

Robinson, Z. R., Tyagi, P., Murray, T. M., Ventrice Jr, C. A., Chen, S., Munson, A. and Ruoff, R. S. (2012). Substrate grain size and orientation of Cu and Cu–Ni foils used for the growth of graphene films. *Journal of Vacuum Science & Technology A*, *30*(1): 011401.

Rümmeli, M. H., Kramberger, C., Grüneis, A., Ayala, P., Gemming, T., Büchner, B. and Pichler, T. (2007). On the graphitization nature of oxides for the formation of carbon nanostructures. *Chemistry of materials*, *19*(17): 4105-4107.

Sager, R. J., Klein, P. J., Lagoudas, D. C., Zhang, Q., Liu, J., Dai, L. and Baur, J. W. (2009). Effect of carbon nanotubes on the interfacial shear strength of T650 carbon fiber in an epoxy matrix. *Composites Science and Technology*, *69*(7), 898-904.

Sahoo, N. G., Rana, S., Cho, J. W., Li, L. and Chan, S. H. (2010). Polymer nanocomposites based on functionalized carbon nanotubes. *Progress in polymer science*, *35*(7): 837-867.

Sahoo, R. K., Jeyapandiarajan, P., Chandrasekhar, K. D., Daniel, B. S. S., Venimadhav, A., Sant, S. B. and Jacob, C. (2014). Single-step synthesis of graphene-carbon nanofiber hybrid material and its synergistic magnetic behaviour. *Journal of Alloys and Compounds*, *615*: 348-354.

Seah, C. M., Chai, S. P. and Mohamed, A. R. (2014). Mechanisms of graphene growth by chemical vapour deposition on transition metals. *Carbon*, *70*: 1-21.

Sengupta, R., Bhattacharya, M., Bandyopadhyay, S. and Bhowmick, A. K. (2011). A review on the mechanical and electrical properties of graphite and modified graphite reinforced polymer composites. *Progress in polymer science*, *36*(5): 638-670.

Seo, M. K. and Park, S. J. (2004). Electrical resistivity and rheological behaviors of carbon nanotubes-filled polypropylene composites. *Chemical Physics Letters*, *395*(1): 44-48.

Serp, P., Corrias, M. and Kalck, P. (2003). Carbon nanotubes and nanofibers in catalysis. *Applied Catalysis A: General*, *253*(2): 337-358.

Sharma, R., Rez, P., Treacy, M. M. and Stuart, S. J. (2005). In situ observation of the growth mechanisms of carbon nanotubes under diverse reaction conditions. *Journal of electron microscopy*, *54*(3): 231-237.

Sharma, S. P. and Lakkad, S. C. (2009). Morphology study of carbon nanospecies grown on carbon fibers by thermal CVD technique. *Surface and Coatings Technology*, *203*(10): 1329-1335.

Shazed, M. A., Suraya, A. R., Rahmanian, S. and Salleh, M. M. (2014). Effect of fibre coating and geometry on the tensile properties of hybrid carbon nanotube coated carbon fibre reinforced composite. *Materials & Design*, *54*: 660-669.

Shu, H., Chen, X., Tao, X. and Ding, F. (2012). Edge structural stability and kinetics of graphene chemical vapor deposition growth. *Acs Nano*, *6*(4): 3243-3250.

Shubhra, Q. T., Alam, A. K. M. M. and Quaiyyum, M. A. (2011). Mechanical properties of polypropylene composites: A review. *Journal of Thermoplastic Composite Materials*, 0892705711428659.

Sohn, J. I., Lee, S., Song, Y. H., Choi, S. Y., Cho, K. I. and Nam, K. S. (2001). Patterned selective growth of carbon nanotubes and large field emission from vertically well-aligned carbon nanotube field emitter arrays. *Applied physics letters*, *78*(7): 901-903.

Song, W. L., Wang, J., Fan, L. Z., Li, Y., Wang, C. Y. and Cao, M. S. (2014). Interfacial Engineering of Carbon Nanofiber–Graphene–Carbon Nanofiber Heterojunctions in Flexible Lightweight Electromagnetic Shielding Networks. *ACS applied materials & interfaces*, *6*(13): 10516-10523.

Somani, P. R., Somani, S. P. and Umeno, M. (2006). Planer nano-graphenes from camphor by CVD. *Chemical Physics Letters*, *430*(1): 56-59.

Somani, R. H., Yang, L., Sics, I., Hsiao, B. S., Pogodina, N., Winter, H. H. and Tsou, A. (2002). Orientation-induced crystallization in isotactic polypropylene melt by step-shear deformation. MACROMOLECULAR SYMPOSIA, 185: 105-117.

Son, S. Y., Lee, Y., Won, S., Lee, D. H., Kim, S. D. and Sung, S. W. (2008). High-quality multiwalled carbon nanotubes from catalytic decomposition of carboneous materials in gas-solid fluidized beds. *Industrial & Engineering Chemistry Research*, *47*(7): 2166-2175.

Su, M., Li, Y., Maynor, B., Buldum, A., Lu, J. P. and Liu, J. (2000). Lattice-oriented growth of single-walled carbon nanotubes. *The Journal of Physical Chemistry B*, *104*(28): 6505-6508.

Sui, G., Zhong, W. H., Liu, M. C. and Wu, P. H. (2009). Enhancing mechanical properties of an epoxy resin using "liquid nano-reinforcements". *Materials Science and Engineering: A*, *512*(1): 139-142.

Sun, X., Sun, H., Li, H. and Peng, H. (2013). Developing polymer composite materials: carbon nanotubes or graphene?. *Advanced Materials*, *25*(37): 5153-5176.

Tang, N., Zhong, W., Gedanken, A. and Du, Y. (2006). High magnetization helical carbon nanofibers produced by nanoparticle catalysis. *The Journal of Physical Chemistry B*, *110*(24): 11772-11774.

Tedesco, J. L., Jernigan, G. G., Culbertson, J. C., Hite, J. K., Yang, Y., Daniels, K. M. and Gaskill, D. K. (2010). Morphology characterization of argon-mediated epitaxial graphene on C-face SiC. *Applied Physics Letters*, *96*(22): 222103–222105.

Teo, K. B., Singh, C., Chhowalla, M. and Milne, W. I. (2003). Catalytic synthesis of carbon nanotubes and nanofibers. *Encyclopedia of nanoscience and nanotechnology*, *10*(1): 1-22.

Thostenson, E. T., Li, W. Z., Wang, D. Z., Ren, Z. F. and Chou, T. W. (2002). Carbon nanotube/carbon fiber hybrid multiscale composites. *Journal of Applied physics*, *91*(9): 6034-6037.

Tibbetts, G. G., Lake, M. L., Strong, K. L. and Rice, B. P. (2007). A review of the fabrication and properties of vapor-grown carbon nanofiber/polymer composites. *Composites Science and Technology*, *67*(7): 1709-1718.

Tiwari, S., Bijwe, J. and Panier, S. (2012). Enhancing the adhesive wear performance of polyetherimide composites through nano-particle treatment of the carbon fabric. *Journal of Materials Science*, *47*(6): 2891-2898.

Tkalya, E. E., Ghislandi, M., de With, G. and Koning, C. E. (2012). The use of surfactants for dispersing carbon nanotubes and graphene to make conductive nanocomposites. *Current Opinion in Colloid & Interface Science*, *17*(4): 225-232.

Tzeng, S. S., Hung, K. H. and Ko, T. H. (2006). Growth of carbon nanofibers on activated carbon fiber fabrics. *Carbon*, *44*(5): 859-865.

Vlassiouk, I., Regmi, M., Fulvio, P., Dai, S., Datskos, P., Eres, G. and Smirnov, S. (2011). Role of hydrogen in chemical vapor deposition growth of large single-crystal graphene. *Acs Nano*, *5*(7): 6069-6076.

Wang, S., Qiao, L., Zhao, C., Zhang, X., Chen, J., Tian, H. and Han, Z. (2013). A growth mechanism for graphene deposited on polycrystalline Co film by plasma enhanced chemical vapor deposition. *New Journal of Chemistry*, *37*(5): 1616-1622.

Wei, C. and Srivastava, D. (2004). Nanomechanics of carbon nanofibers: Structural and elastic properties. *Applied physics letters*, *85*(12): 2208-2210.

Weisenberger, M. C., Grulke, E. A., Jacques, D., Rantell, A. T. and Andrewsa, R. (2003). Enhanced mechanical properties of polyacrylonitrile/multiwall carbon nanotube composite fibers. *Journal of nanoscience and nanotechnology*, *3*(6): 535-539.

Wen, Q., Qian, W., Nie, J., Cao, A., Ning, G., Wang, Y. and Wei, F. (2010). 100 mm Long, Semiconducting Triple‐ Walled Carbon Nanotubes. *Advanced Materials*, *22*(16): 1867-1871.

Wirth, C. T., Hofmann, S. and Robertson, J. (2009). State of the catalyst during carbon nanotube growth. *Diamond and Related Materials*, *18*(5): 940-945.

Wu, B., Geng, D., Xu, Z., Guo, Y., Huang, L., Xue, Y. and Liu, Y. (2013). Self-organized graphene crystal patterns. *NPG Asia Materials*, *5*(2):e36. DOI:10.1038/am.2012.68.

Wu, D., Zhang, F., Liang, H. and Feng, X. (2012). Nanocomposites and macroscopic materials: assembly of chemically modified graphene sheets. *Chemical Society Reviews*, *41*(18): 6160-6177.

Wu, D., Zhi, L., Bodwell, G. J., Cui, G., Tsao, N. and Müllen, K. (2007). Self-Assembly of Positively Charged Discotic PAHs: From Nanofibers to Nanotubes. *Angewandte Chemie International Edition*, *46*(28): 5417-5420.

Xiong, G. Y., Suda, Y., Wang, D. Z., Huang, J. Y. and Ren, Z. F. (2005). Effect of temperature, pressure, and gas ratio of methane to hydrogen on the synthesis of double-walled carbon nanotubes by chemical vapour deposition. *Nanotechnology*, *16*(4): 532-235.

Xu, Z., Huang, Y., Zhang, C. and Chen, G. (2007). Influence of rare earth treatment on interfacial properties of carbon fiber/epoxy composites. *Materials Science and Engineering: A*, *444*(1): 170-177.

Xu, Z., Sun, H., Zhao, X. and Gao, C. (2013). Ultrastrong fibers assembled from giant graphene oxide sheets. *Advanced Materials*, *25*(2): 188-193.

Yamamoto, N., Hart, A. J., Garcia, E. J., Wicks, S. S., Duong, H. M., Slocum, A. H. and Wardle, B. L. (2009). High-yield growth and morphology control of aligned carbon nanotubes on ceramic fibers for multifunctional enhancement of structural composites. *Carbon*, *47*(3): 551-560.

Yang, M., Hou, Y. and Kotov, N. A. (2012). Graphene-based multilayers: Critical evaluation of materials assembly techniques. *Nano Today*, *7*(5): 430-447.

Yang, S., Lozano, K., Lomeli, A., Foltz, H. D. and Jones, R. (2005). Electromagnetic interference shielding effectiveness of carbon nanofiber/LCP composites. *Composites Part A: applied science and manufacturing*, *36*(5): 691-697.

Yang, X., Wang, Z., Xu, M., Zhao, R. and Liu, X. (2013). Dramatic mechanical and thermal increments of thermoplastic composites by multi-scale synergetic reinforcement: carbon fiber and graphene nanoplatelet. *Materials & Design*, *44*: 74-80.

Yao, Y., Dai, X., Liu, R., Zhang, J. and Liu, Z. (2009). Tuning the diameter of single-walled carbon nanotubes by temperature-mediated chemical vapor deposition. *The Journal of Physical Chemistry C*, *113*(30): 13051-13059

Yazdani-Pedram, M., Menzel, C., Toro, P., Quijada, R., May-Pat, A. and Avilés, F. (2013). Mechanical and thermal properties of multiwalled carbon nanotube/polypropylene composites using itaconic acid as compatibilizer and coupling agent. *Macromolecular Research*, *21*(2): 153-160.

Yazyev, O. V. and Pasquarello, A. (2008). Effect of metal elements in catalytic growth of carbon nanotubes. *Physical review letters*, *100*(15): 156102.

Yen, Y. W., Huang, M. D. and Lin, F. J. (2008). Synthesize carbon nanotubes by a novel method using chemical vapor deposition-fluidized bed reactor from solid-stated polymers. *Diamond and Related Materials*, *17*(4): 567-570.

Yi, J., Lee, J. M. and Park, W. I. (2011). Vertically aligned ZnO nanorods and graphene hybrid architectures for high-sensitive flexible gas sensors. *Sensors and Actuators B: Chemical*, *155*(1): 264-269.

Young, R. J., Kinloch, I. A., Gong, L. and Novoselov, K. S. (2012). The mechanics of graphene nanocomposites: a review. *Composites Science and Technology*, *72*(12): 1459-1476.

Yu, A., Hu, H., Bekyarova, E., Itkis, M. E., Gao, J., Zhao, B. and Haddon, R. C. (2006). Incorporation of highly dispersed single-walled carbon nanotubes in a polyimide matrix. *Composites science and technology*, *66*(9): 1190-1197.

Yu, D. and Dai, L. (2009). Self-assembled graphene/carbon nanotube hybrid films for supercapacitors. *The Journal of Physical Chemistry Letters*, *1*(2): 467-470.

Yu, Q., Lian, J., Siriponglert, S., Li, H., Chen, Y. P. and Pei, S. S. (2008). Graphene segregated on Ni surfaces and transferred to insulators. *Applied Physics Letters*, *93*(11): 113103.

Yu, Q., Qin, G., Li, H., Xia, Z., Nian, Y. and Pei, S. S. (2006). Mechanism of horizontally aligned growth of single-wall carbon nanotubes on R-plane sapphire. *The Journal of Physical Chemistry B*, *110*(45): 22676-22680.

Yu, M. F., Lourie, O., Dyer, M. J., Moloni, K., Kelly, T. F. and Ruoff, R. S. (2000). Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load. *Science*, *287*(5453): 637-640.

Yu, S., Jiang, Y. and Wang, C. (2013). A polymer composite consists of electrochemical reduced graphene oxide/polyimide/chemical reduced graphene oxide for effective preparation of SnSe by electrochemical atomic layer deposition method with enhanced electrochemical performance and surface area. *Electrochimica Acta, 114*: 430-438.

Yuan, G. D., Zhang, W. J., Yang, Y., Tang, Y. B., Li, Y. Q., Wang, J. X. and Lee, S. T. (2009). Graphene sheets via microwave chemical vapor deposition. *Chemical Physics Letters, 467*(4): 361-364.

Yudasaka, M., Komatsu, T., Ichihashi, T., Achiba, Y. and Iijima, S. (1998). Pressure dependence of the structures of carbonaceous deposits formed by laser ablation on targets composed of carbon, nickel, and cobalt. *The Journal of Physical Chemistry B, 102*(25): 4892-4896.

Zaginaichenko, S. Y., Schur, D. V. and Matysina, Z. A. (2003). The peculiarities of carbon interaction with catalysts during the synthesis of carbon nanomaterials. *Carbon*, *41*(7): 1349-1355.

Zhang, H., Zhang, Z. (2007). Impact behaviour of polypropylene filled with multi walled carbon nanotubes, European Polymer journal. 43(8): 3197-3207.

Zhang, J., Xu, Z., Shan, M., Zhou, B., Li, Y., Li, B. and Qian, X. (2013). Synergetic effects of oxidized carbon nanotubes and graphene oxide on fouling control and anti-fouling mechanism of polyvinylidene fluoride ultrafiltration membranes. *Journal of Membrane Science, 448*: 81-92.

Zhang, Q., Liu, J., Sager, R., Dai, L. and Baur, J. (2009). Hierarchical composites of carbon nanotubes on carbon fiber: influence of growth condition on fiber tensile properties. *Composites Science and Technology*, *69*(5): 594-601.

Zhang, S., Yin, S., Rong, C., Huo, P., Jiang, Z. and Wang, G. (2013a). Synergistic effects of functionalized graphene and functionalized multi-walled carbon nanotubes on the electrical and mechanical properties of poly (ether sulfone) composites. *European Polymer Journal*, *49*(10): 3125-3134.

Zhang, X., Ning, J., Li, X., Wang, B., Hao, L., Liang, M. and Zhi, L. (2013b). Hydrogen-induced effects on the CVD growth of high-quality graphene structures. *Nanoscale, 5*(18): 8363-8366.

Zhang, Y., Zhang, L. and Zhou, C. (2013c). Review of chemical vapor deposition of graphene and related applications. *Accounts of chemical research*, *46*(10): 2329-2339.

Zhao, J., Liu, L., Guo, Q., Shi, J., Zhai, G., Song, J. and Liu, Z. (2008). Growth of carbon nanotubes on the surface of carbon fibers. *Carbon*, *46*(2): 380-383.

Zheng, L., Liao, X. and Zhu, Y. T. (2006). Parametric study of carbon nanotube growth via cobalt-catalyzed ethanol decomposition. *Materials Letters*, *60*(16): 1968-1972.

Zheng, Z., Wang, Z., Feng, Q., Du, Y. and Wang, C. (2013). Preparation of surface-silvered graphene-CNTs/polyimide hybrid films: Processing, morphology and properties. *Materials Chemistry and Physics*, *138*(1): 350-357.

Zhou, Z. and Wu, X. F. (2013). Graphene-beaded carbon nanofibers for use in supercapacitor electrodes: synthesis and electrochemical characterization. *Journal of Power Sources*, *222*: 410-416.

Zhu, S., Su, C. H., Lehoczky, S. L., Muntele, I. and Ila, D. (2003). Carbon nanotube growth on carbon fibers. *Diamond and Related Materials*, *12*(10): 1825-1828.

Zhu Y, Murali S, Stoller MD, Ganesh K, Cai W, Ferreira PJ,Pirkle A, Wallace RM, Cychosz KA, Thommes M (2011). Carbon-basedsupercapacitors produced by activation of graphene. Science, 332(6037):1537–1541.