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# Mild and Nondestructive Chemical Modification of Carbon Nanotubes (CNTs): Direct Friedel-Crafts Acylation Reaction

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Additional information is available at the end of the chapter

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## 1. Introduction

Since Iijima's report on carbon nanotubes (CNTs) [1], which consist of graphene sheets rolled up into a cylindrical shape, many researchers have focused on CNTs due to their superior mechanical, electrical and thermal properties. Depending on the arrangement of aromatic rings along the cylindrical surface, specifically for single-walled carbon nanotubes (SWCNTs), CNTs can possess two distinguished properties such as metallic and semiconducting. In spite of many advantages, the practical applications of CNTs have been limited by their poor processability and dispersability in solvents, polymers, ceramics and metallic matrices. Indeed, the pristine CNTs are insoluble in any solvent, due to strong van der Waals interactions between CNTs and lack of chemical affinity to organic solvents. To overcome this limitation, many chemical (covalent) and physical (noncovalent) modification methods to functionalize CNTs have been developed during last decades for improved compatibilities with both liquid and solid matrices [2-3]. Among them, chemical approaches using various chemical reactions are considered to be the most promising protocol for enhancing dispersability and processability of CNTs. However, CNTs are chemically inert for efficient chemical modifications, and thus reactions have to be carried out in harsh conditions, causing significant structural damages to CNT frameworks. As a result, a sharp decrease in their intrinsic properties is inevitable [2-3]. In this regard, physical modifications of CNTs have been considered to be more favorable methods for electronic applications, because electronic structures can be largely preserved due to the noncovalent approaches for modified CNTs [4-6]. However, homogeneous dispersion using the physical method accom-

panied with sonication often damages CNTs due to the effects of dose time and strength. Furthermore, they also have some disadvantages such as limited utilization of materials and insufficient modification levels for practical applications. Thus, the development of nondestructive and efficient chemical modification of CNTs is highly desirable.

Since the pioneering work from Baek *et al.*, [7], direct Friedel-Crafts acylation reaction to inherent defective  $sp^2$ C-H sites on the surface of CNTs have been widely investigated [8-13], because it has several advantages such as nondestructive reaction nature, sufficient modification level, utilization of diverse materials and suitable for mass production. Furthermore, it can be expanded to all types of carbon-based nanomaterials such as fullerenes [14], carbon nanofibers [7, 15-17], nanodiamonds [18] and graphene [19-22]. Therefore, direct Friedel-Crafts acylation reactions could be one of ideal chemical modifications for carbon based materials, specifically CNTs. This chapter will focus on and discuss about the various aspects of direct Friedel-Crafts acylation reaction onto CNTs such as fundamental mechanisms, potential applications and perspectives. Of particular importance, this chapter is highly beneficial to general readers in research community of carbon based materials.

## 2. Direct Friedel-Crafts acylation of Carbon Nanotubes

### 2.1. Overview and mechanism

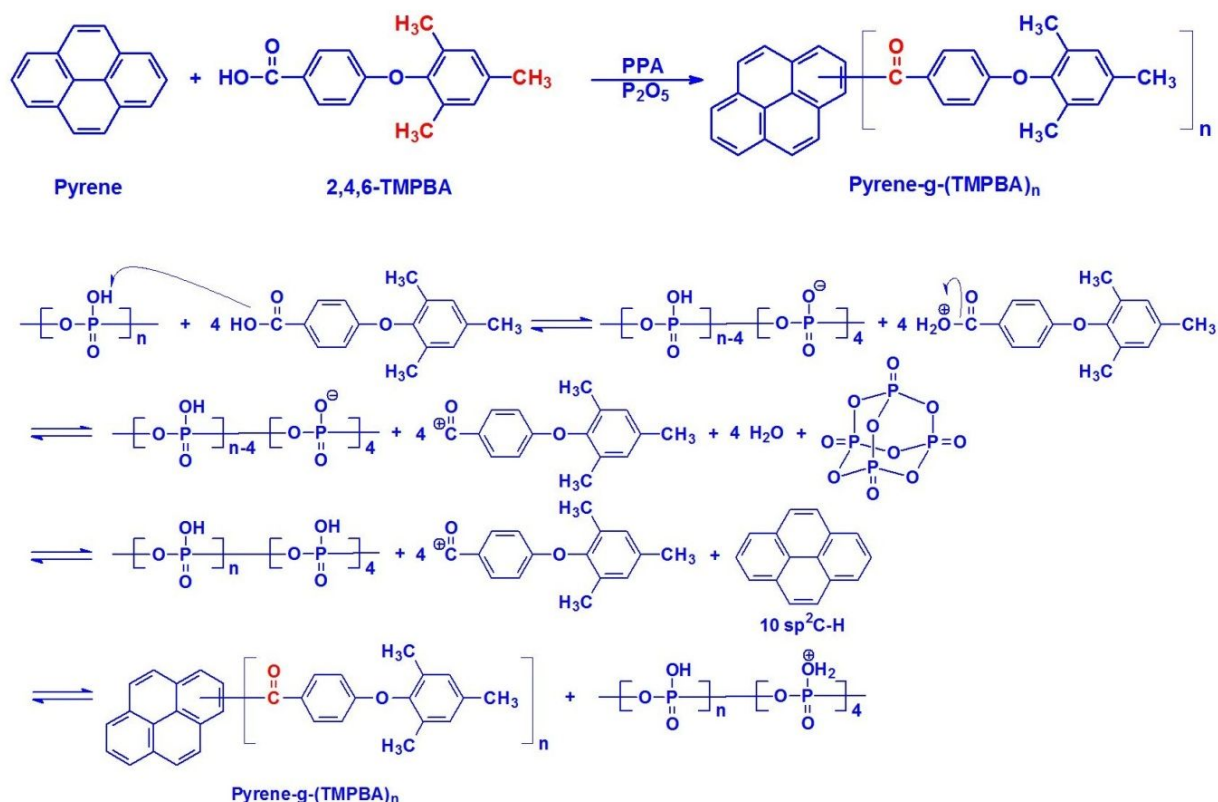
Although various chemical and physical modifications for enhancing the dispersability and processability of CNTs have been utilized for last decades, both methods have their own drawbacks depending on the platform as discussed earlier. The advantages and disadvantages of various modifications of CNTs are summarized in Table 1 [23].

Method	Principle	Possible damage to CNTs	Easy to use	Interaction with polymer matrix <sup>a</sup>	Re-agglomeration of CNTs in matrix	
Chemical Method	Side wall	Hybridization of C atoms from $sp^2$ to $sp^3$	√	×	S	√
	Defect	Defect transformation	√	√	S	√
	Polymer wrapping	van der Waals force, - stacking	×	√	V	×
Physical Method	Surfactant adsorption	Physical adsorption	×	√	W	×
	Endohedral Method	Capillary effect	×	×	W	√

<sup>a</sup> S: Strong; W:Weak; V: Variable according to the miscibility between matrix and polymer on CNT

**Table 1** Advantages and disadvantages of various modification methods of CNTs [23].

Additionally, the most chemical modifications are initiated by chemical oxidation of CNTs in strong acids [2-3]. Therefore, dramatic structural damages of CNTs can be easily happened during harsh oxidation reaction, which results in significant weakening of many useful intrinsic properties of CNTs. To overcome these problems, the development of alternative functionalization routes, which can not only introduce homogeneous surface functional groups with high density to enhance the compatibility of CNTs and various foreign matrixes, but also minimize the structural damages of CNTs during reactions to optimize their properties in various applications, are highly demanding.



**Figure 1.** A summary of reaction mechanism of direct Friedel-Crafts acylation reaction using pyrene as a model compound in poly(phosphoric acid)/phosphorous pentoxide medium [24].

Recently, Baek *et al.*, [8-11, 13] have reported an efficient route to covalently functionalize CNTs *via* simple reaction called as direct Friedel-Crafts acylation. Interestingly, simple benzoic acid (-COOH) and benzamide (-CONH<sub>2</sub>) groups are directly used in this newly developed synthetic strategy instead of an expensive, inconvenient and corrosive carboxylic acid chloride (COCl), which is normally utilized in Friedel-Crafts acylation. The detailed reaction mechanism of this reaction using pyrene as a model compound is shown in Figure 1 [24]. The reaction normally takes place between benzoic acid derivatives and CNTs in a mild polyphosphoric acid (PPA)/phosphorous pentoxide (P<sub>2</sub>O<sub>5</sub>) medium. PPA used in this study is a viscous polymeric acid and expected to play two important roles. Its mild acidic nature (pK<sub>a</sub> ≈ 2.1) could still be enough to protonate the surface of CNTs for deaggregation without structural damage, which is frequently observed from the oxidation reaction of CNTs using

strong acids such as nitric acid ( $\text{pK}_a \approx -1.5$ ), sulfuric acid ( $\text{pK}_a \approx -3.0$ ) and their mixture. Thus, the outstanding properties of CNTs such as electrical, thermal and mechanical properties can be preserved. Additionally, viscous nature of PPA would help to impede reaggregation of CNTs after dispersion of CNTs with strong shear forces while mechanical stirring. Another component of reaction medium,  $\text{P}_2\text{O}_5$ , is used as a dehydrating agent to promote Friedel-Crafts reaction efficiently. In this reaction condition, defective  $\text{sp}^2\text{C-H}$  groups inherently presented on the surfaces or edges of CNTs are reactive sites for electrophilic substitution reaction with newly generated carbonium ions ( $\text{C}=\text{O}^+$ ) from benzoic acid and benzylamide derivatives in PPA/ $\text{P}_2\text{O}_5$  [25]. As a result, an efficient homogeneous introduction of various functional groups onto CNTs without structural damage has been obtained from the newly developed direct Friedel-Crafts acylation in PPA/ $\text{P}_2\text{O}_5$ . Furthermore, simple and scalable features of this approach could be regarded as additional advantages. In optimized reaction conditions, the fixed weight ratio of PPA/ $\text{P}_2\text{O}_5$  (4/1) has been used as a reaction medium and the reaction takes place using high-torque mechanical stirrer at 130 °C for 48 – 72 h under dry nitrogen purge. After reaction, the solid was transferred to an extraction thimble and extracted with water for 3 days and methanol for 3 days, and finally freeze-dried for 48 h to obtain final products.

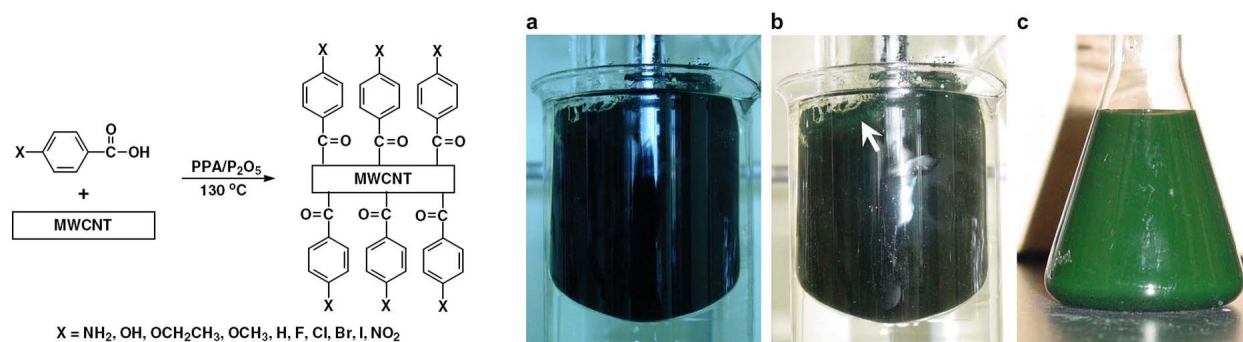
## 2.2. Applications

### 2.2.1. Functionalization of carbon nanotubes with small molecules

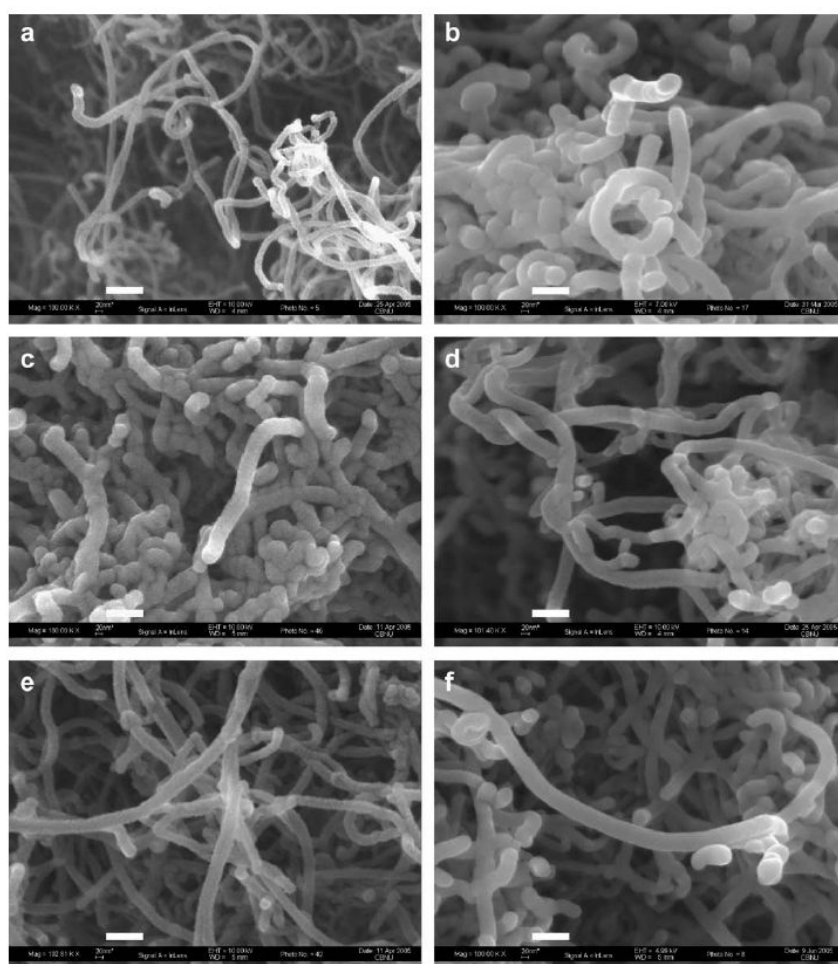
Recently, the functionalization of carbon nanotubes (CNTs) with small molecules containing benzoic acid [9, 13, 26] *via* direct Friedel-Crafts acylation reaction in PPA/ $\text{P}_2\text{O}_5$  have been successfully demonstrated by Baek *et al.* For providing a fundamental concept on the relationship between structure and reactivity, a reactivity hierarchy of 4-substituted benzoic acids with multi-walled carbon nanotubes (MWCNTs) in the reaction condition has been systematically investigated [9]. Accordingly, 10 different kinds of benzoic acids with various different functionalities to 4-position of benzoic acids such as amine, hydroxyl, ethoxy, methoxy, fluoro, chloro, bromo, iodo and nitro groups were selected for the functionalization (Figure 2-left). The functionalization of MWCNTs with all benzoic acid derivatives used in this study has been efficiently occurred *via* a simple direct Friedel-Crafts acylation reaction in PPA/ $\text{P}_2\text{O}_5$ . For examples, the photograph taken of the 4-ethoxybenzoic acid and MWCNTs reaction mixture without flashlight was shiny black as shown in Figure 2-right-a. When the mixture was illuminated by flashlight, the shiny-greenish-brown color became prominent (Figure 2-right-b). The precipitated in of the mixture after reaction in distilled water was deep green as it was in the reaction mixture under the flashlight (Figure 1-right-c). The green suspension might be due to the charge complex in acidic medium. The uniformly decorated 4-ethoxybenzoyl moiety on the surface of MWCNTs and the charge complexes formed on the ether linkage could possibly display green color. These photographs provided strong visual evidence that the MWCNTs could be effectively functionalized with 4-ethoxybenzoic acid moiety. After complete purification procedures, overall yields for all cases were in the range of 53-78%. As a result, the reactivity of compounds in direct Friedel-Crafts acylation reaction in PPA/ $\text{P}_2\text{O}_5$  could be greatly attributed to the 'elec-



tron-donating' and 'electron-accepting' natures of 4-substituted groups to the carboxylic acid [13]. The former displayed better reactivity than the latter.



**Figure 2.** (left) Functionalization of MWCNTs with various 4-substituted benzoic acids using direct Friedel-Crafts acylation reaction, (right) a - reaction mixture of 4-ethoxybenzoic acids and MWCNTs without flashlight, b - reaction mixture of 4-ethoxybenzoic acids and MWCNTs with flashlight and c - precipitation of reaction mixture of 4-ethoxybenzoic acids and MWCNTs in distilled water [13].

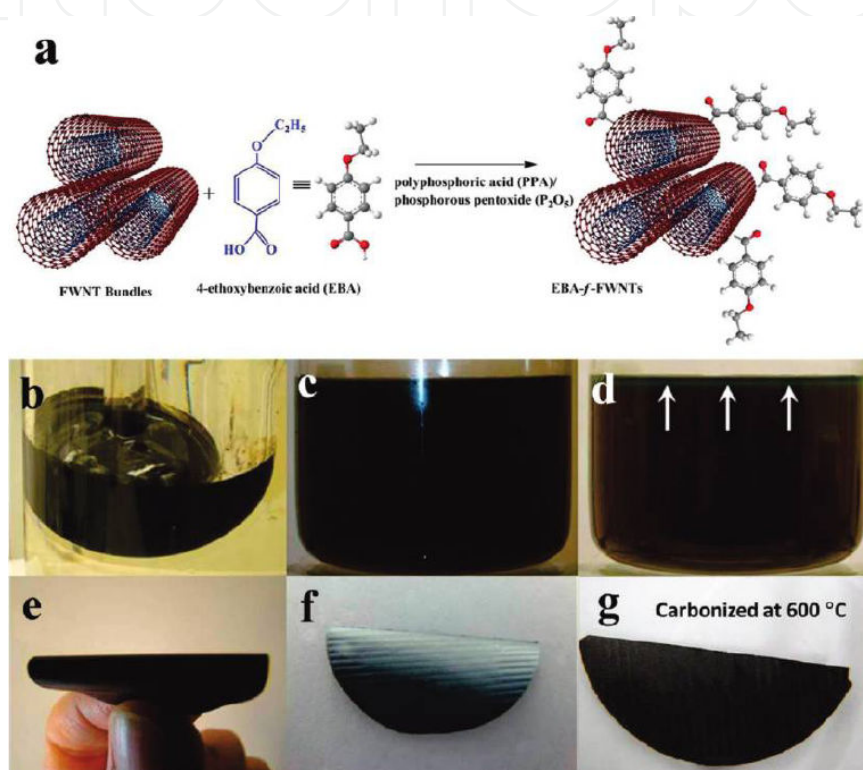


**Figure 3.** SEM images of MWCNTs: (a) pristine MWCNTs, (b) 4-aminobenzoic, (c) 4-ethoxybenzoic, (d) 4-hydroxybenzoic, (e) 4-bromobenzoic and (f) 4-nitrobenzoic acid functionalized MWCNTs. Scale bars are 100 nm [13].

The dispersability of MWCNTs was greatly enhanced by functionalization and debundling of MWCNTs with small molecules *via* direct Friedel-Crafts acylation reaction in PPA/P<sub>2</sub>O<sub>5</sub>, but the surface properties of functionalized MWCNTs could be altered significantly due to different functional groups were introduced [13]. For examples, the polar 4-hydroxybenzoyl substituted MWCNTs displayed the best solubility and they were easily dispersed in polar solvents such as tetrahydrofuran (THF), dichloromethane and *N,N*-dimethylacetamide (DMF). However, 4-bromobenzoyl functionalized MWCNTs were proved to be insoluble in all tested solvents. In addition to dispersability, the polarity of surface group on MWCNTs has also great influence on their size and morphology. The pristine MWCNTs show the clean and smooth surface with an average diameter of 10-20 nm (Figure 3a), while the surfaces of functionalized MWCNTs with 4-substituted benzoic acids reveal structurally intact with a larger diameter in the range of 40-70 nm (Figure 2b-f). Assuming the length of 4-substituted benzoyl units to be approximately 1 nm, the diameters of functionalized MWCNTs should be within the range of 12-22 nm. However, all functionalized MWCNTs showed larger diameters, at least twice that of pristine MWCNTs. This implies that they were in the bundled state. The size of bundles was closely related to the polarity of the surface groups and the degree of functionalization. When there is enough lateral interaction among tubes to overcome axial rigidity, the larger number of tubes are aggregated to form bundle, and thus the diameters are increased. The SEM images in Figure 3 show that the average diameters of samples with polar surface groups such as amino, hydroxyl and nitro benzoic acids were larger than those of samples with non-polar surface groups such as ethoxy and bromo. Furthermore, the surface morphologies of functionalized MWCNTs with non-polar surface groups appeared to be soft and puffy (Figure 3c and d), while functionalized MWCNTs with polar surface groups showed shiny and rigidly smooth morphologies (Figure 3b, d and f).

Furthermore, this unique synthetic strategy can be applied to different types of CNTs like single- [10], few- [27-28] and multi-walled CNTs [8-13]. Recently, it has been reported that few-walled carbon nanotubes (FWCNTs), defined as nanotubes with sidewalls typically of 2 to 6 layers, diameters ranging from 3 to 8 nm, have particularly distinguished from other types of CNTs [29]. Therefore, the functionalization of FWCNTs without structural damages to generate nanocomposites hybrid materials or even thin film has attracted great attentions for their various potentials in device applications. In this purpose, Baek *et al.*, demonstrated that the functionalization of FWCNTs with two different surface groups using a direct Friedel-Crafts acylation reaction in a nondestructive PPA/P<sub>2</sub>O<sub>5</sub> medium [27]. The less polar 4-ethylbenzoic acid and more polar 4-(aminomethyl)benzoic acid have been used for the surface modification of FWCNTs. Interestingly, 4-ethylbenzoic acid functionalized FWCNTs can absorb water more than 28 times its own weight, indicating that the nature of surface functional groups was significantly attributed to the sponge behavior of functionalized FWCNTs. In addition the electrical capacitance of functionalized FWCNTs was also significantly affected by the nature of surface groups [27]. Furthermore, it has been also reported that an efficient route to prepare highly conducting and flexible FWCNTs thin film by Baek *et al.*, (Figure 4) [28]. The free standing thin films were fabricated by functionalizing FWCNTs with 4-ethoxybenzoic acid *via* a direct Friedel-Crafts acylation reaction in a similar condition. The resulting 4-ethoxybenzoic acid functionalized FWCNTs (EBA-f-FWCNTs)

were readily dispersed in water and the films were simply casted from the filtration of the dispersed solution. Room temperature electrical conductivity of the thin flexible film of EBA-f-FWCNTs shows a value as high as  $29,400 \text{ S/cm}^{-1}$ , while the tensile strength and modulus of it were found to be about 80 MPa and 15 Gpa, respectively. In addition cyclic voltamogram reveals a rectangular shape with superior capacitance of 133 F/g for the thin film [28]. This study demonstrated the simple and efficient preparation methods to produce highly flexible and conductive thin film of FWCNTs using a direct Friedel-Crafts acylation reaction in a mild reaction condition.

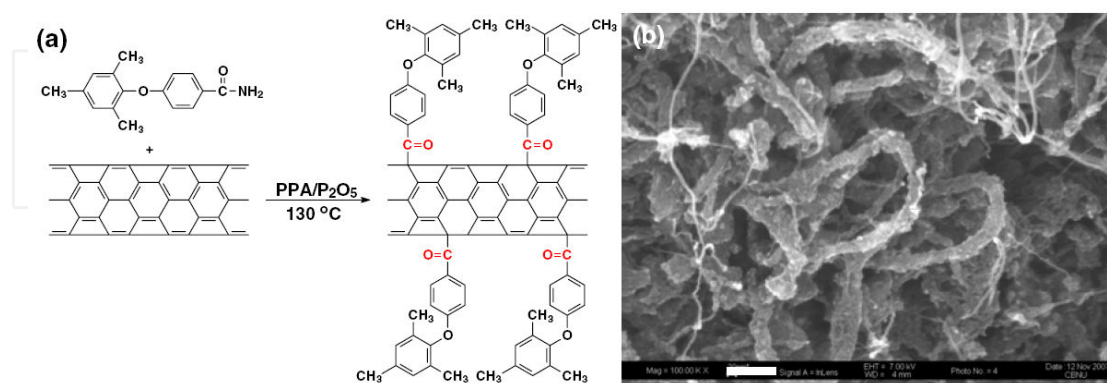


**Figure 4.** (a) Schematic cartoon depicting the functionalization of FWCNTs with 4-ethoxybenzoic acid. Digital photographs of (b) reaction flask, (c) EBA-f-FWCNTs dispersed in water without light, (d) EBA-f-FWCNTs dispersed in water light, (e) thin film made of EBA-f-FWCNTs (f) 180 °C folded thin film and (g) carbonized EBA-f-FWCNTs thin film at 600 °C for 2h [28].

Hitherto, a various aspects of direct Friedel-Crafts acylation reaction in PPA/ $\text{P}_2\text{O}_5$  between 4-substituted benzoic acids and CNTs have been discussed. Interestingly, this strategy can be expanded to 4-substituted benzamides instead of 4-substituted carboxylic acids. The benzamide could also be directly attached to the surface of CNTs. As a model compound, 4-(2,4,6-trimethylphenoxy)benzamide (TMPBA) was reacted with single-walled carbon nanotubes (SWCNTs) in PPA/ $\text{P}_2\text{O}_5$  as a mild direct Friedel-Crafts acylation reaction condition to afford TMPBA functionalized SWCNTs (Figure 5a) [10]. The covalent attachment of TMPBA onto the surface of SWCNTs was proved by elemental analysis (EA), Fourier-transform infrared spectroscopy (FT-IR), Raman spectroscopy and thermogravimetric analysis (TGA). In addition, the SEM image of TMPBA-g-SWCNT shows that the surface of SWCNTs is apparently



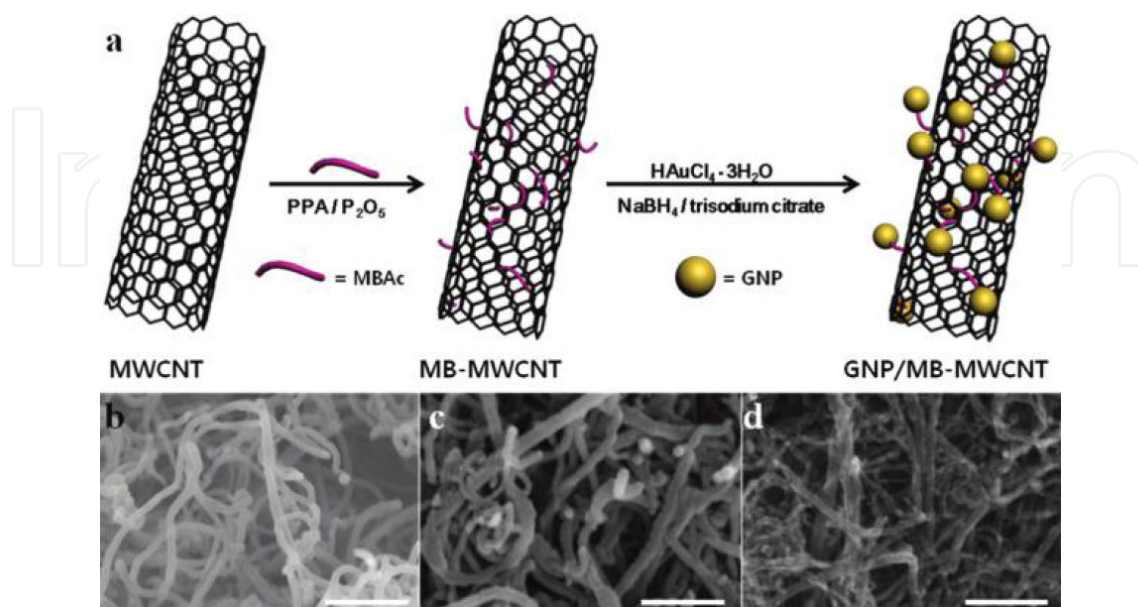
decorated with covalently bonded moieties (Figure 5b). From the results, direct Friedel-Crafts acylation reaction in PPA/P<sub>2</sub>O<sub>5</sub> could be one of powerful tools for the covalent modification of CNTs with small molecules containing various functional moieties.



**Figure 5.** (a) Functionalization of SWCNTs with 4-(2,4,6-trimethylphenoxy)benzamide (TMPBA) and (b) SEM image of TMPBA-g-SWCNTs. Scale bar is 100 nm [10].

Due to the efficient modification of CNTs with a covalent attachment of small molecules with various functionalities, the functionalized CNTs are very useful for the preparation of composites *via* both solution and melt processes. For examples, 4-ethoxybenzoic acid modified MWCNTs could be homogeneously dispersed in ethylene glycol (EG) and *in situ* polymerized with terephthalic acid. The pilot scale preparation of polyethyleneterephthalate (PET)/4-ethoxybenzoyl modified MWCNTs composited was successfully demonstrated [30]. Various systems such as polycarbonate/4-hydroxybenzoyl modified MWCNTs, polyester thermoplastic elastomer/4-chlorobenzoyl modified MWCNTs [31], epoxy (EPON 828)/4-aminobenzoyl modified MWCNTs [32], poly(3-hexylthiophene)/4-hydroxybenzoyl modified MWCNTs [33] and Nylon 610/4-chlorobenzoyl modified MWCNTs composites were prepared *via* either *in situ* or interfacial polymerizations [26]. Furthermore, various conducting polymers such as polyaniline [11, 34-35] and polypyrrole [36] have also been successfully grafted onto 4-aminobenzoyl modified MWCNTs as an anchoring sites *via in situ* polymerization. These composite materials with conducting polymers grafted to MWCNTs show the enhanced conductivity and unique electrocatalytic activities. In addition to polymers, inorganic materials such as gold nanoparticles (GNPs) can also be immobilized onto the surface 4-mercaptobenzoyl functionalized MWCNTs as a platform (Figure 6) [37]. Firstly, the functionalization of MWCNTs with 4-mercaptobenzoic acid by a direct Friedel-Crafts acylation reaction to afford MWCNTs containing thiol groups was carried out in a nondestructive condition. Then, the separately prepared citrate stabilized GNPs were mixed with MWCNTs containing thiol moieties. Due to the strong interactions between thiol and GNPs, they can be stably immobilized onto the surface of MWCNTs covered by thiol groups without agglomeration. These hybrid inorganic-CNTs composites exhibit high electrocatalytic activity and electrochemical stability [37]. These numerous findings of CNTs based composite materials using functionalized CNTs prepared by a simple direct Friedel-Crafts

acylation reaction in a mild reaction medium reveal various utilizations of them for application-specific purposes.

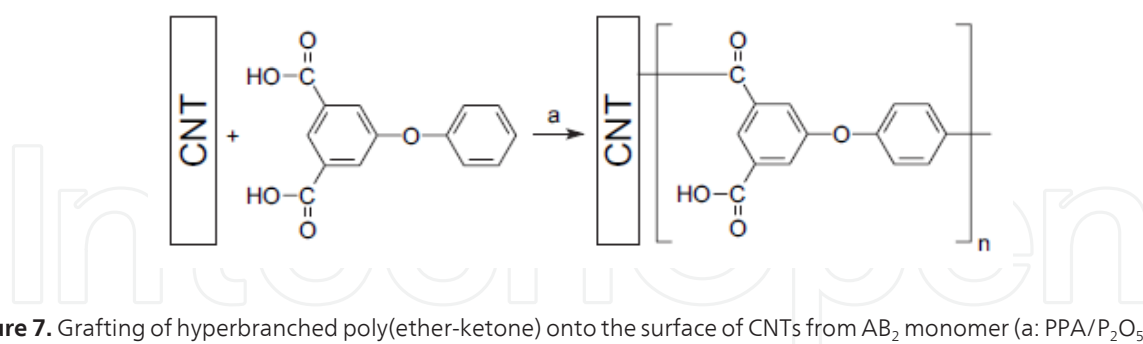


**Figure 6.** (a) Functionalization of MWCNTs with 4-mercaptobenzoic acid and preparation of hybrid composites with gold nanoparticles (TMPBA) and SEM images of (b) pristine MWCNTs, (c) 4-mercaptobenzoic acid modified MWCNTs and (d) their hybrid composites with gold nanoparticles. Scale bar is 200 nm [37].

### 2.2.2. *In situ* grafting of linear or hyperbranched polymers onto carbon nanotubes

Due to the unique features of CNTs, they have been actively investigated for uses as reinforcing components to deliver outstanding properties to various matrixes such as polymers [38-39], ceramics [40] and low melting metals [41]. The resultant nanocomposites are expected to display enhanced properties providing various potential applications for light-weight and multifunctional materials. Unfortunately, CNTs usually exist in ropes and bundles due to strong lateral interactions between the tubes, causing difficulty in homogeneous dispersing them in a multi-component system. Therefore, various physical and chemical modifications to afford homogeneous dispersion of CNTs are required for the effective transfer of their outstanding properties to the matrix materials. However, chemical approach using strong acids and physical approach with sonication treatment can easily cause significant damages such as sidewall opening and tube breakage on their structures. In addition to dispersion, the strong interfacial adhesion between CNTs and matrix is also one of crucial factors in nanocomposites. It is also well known that noncovalent interactions between CNTs and matrix in nanocomposites are not expected to have any synergic effect even after homogeneous dispersions of CNTs could be achieved. Thus, it is highly desirable to covalently link desired polymers to the surface of CNTs. As a result, the development of efficient covalent polymer grafting to the surface of CNTs without structural damages is highly demanding to meet the above mentioned two important requirements for nanocomposites, *i.e.*, homogeneous dispersion and strong adhesion interaction with matrix. In this context, the

chemical modification methods of CNTs with various linear and hyperbranched polymers using less destructive direct Friedel-Crafts acylation reaction in a mild PPA/P<sub>2</sub>O<sub>5</sub> medium have been demonstrated by Baek, *et al.*, [8, 12, 25, 42-43]. *In situ* covalent attachments of linear and/or hyperbranched poly(ether-ketone) onto the surface of CNTs were successfully performed in a mild reaction medium. AB and AB<sub>2</sub> types of monomers was used for the grafting of linear and hyperbranched polymers, respectively, to the surface of CNTs. The linear poly(ether-ketone) grafted CNTs show the dramatic increase in solution viscosity due to the formation of giant molecules during polymerization and the polymer chains are uniformly coated on the surface of CNTs. The resulting nanocomposites were easily fabricated using a simple compression molding technique and the possibility of aligning the CNTs in their nanocomposites *via* solution spinning to significantly enhance the anisotropic tensile properties along the fiber axial direction was also demonstrated [42]. Compared to linear counterpart, the unique highly branched structures and available surface functionalities of hyperbranched polymers offer unusual properties such as low viscosity and enhanced solubility [44-45]. After covalent attachment of three-dimensional globular hyperbranched polymer molecules to the surface of CNTs (Figure 7) [43], the resultant hyperbranched polymer grafted (HBP-g-CNTs) nanocomposites are expected to display both enhanced dispersion and interfacial interaction. The former would be originated from impeding the lateral interaction between CNTs when hyperbranched polymers grafted to the surface of them and the latter is enhanced by the topological roughness contributed from the broad size distribution of the hyperbranched macromolecules. Furthermore, the numerous periphery surface groups and fractal molecular architecture of rigid hyperbranched polymers could provide additional chemical interactions and mechanical interlocking between HBP-g-CNTs nanocomposites and supporting matrix.

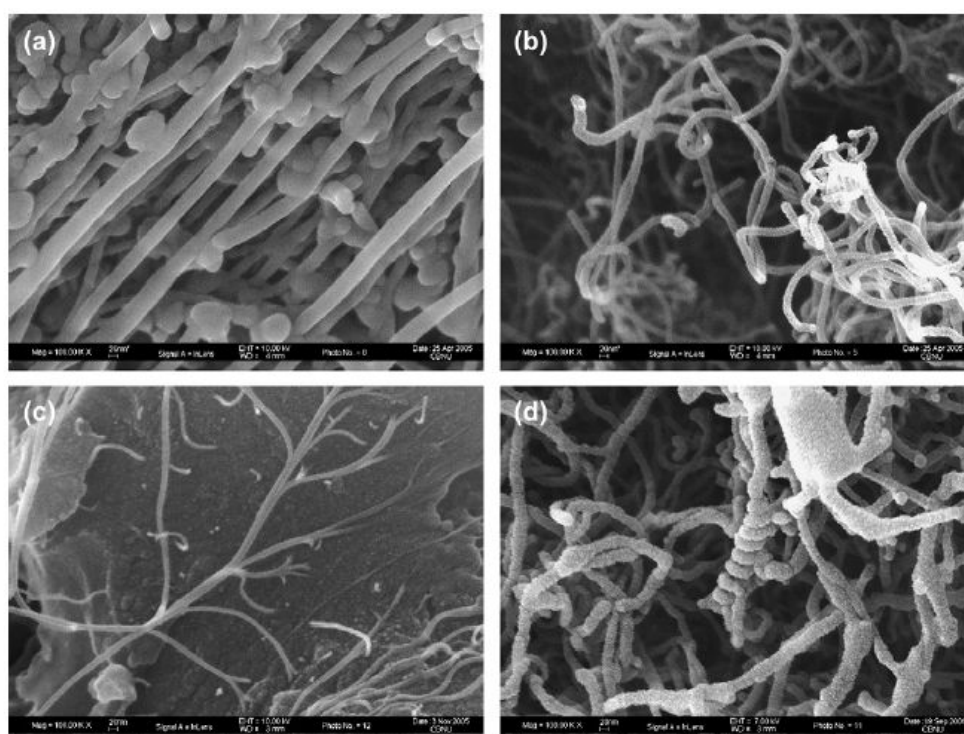


**Figure 7.** Grafting of hyperbranched poly(ether-ketone) onto the surface of CNTs from AB<sub>2</sub> monomer (a: PPA/P<sub>2</sub>O<sub>5</sub>) [43].

The hyperbranched poly(ether-ketone) has been attached onto the surface of both SWCNTs and MWCNTs [43]. The diameter range of pristine SWCNTs bundles is 40-60 nm (Figure 8a), while hyperbranched polymer grafted SWCNTs (HBP-g-SWCNTs) bundles show much smaller diameter range of 5-25 nm than that of pristine SWCNTs (Figure 8c). In addition, the shape of them resembles fractal structures. Some HBP-g-SWCNTs fibrils are stemmed out like tree branches and imbedded into hyperbranched matrix. The overall state of dispersion is homogeneous. Therefore, it could be hypothesized that once split is occurred at the edge of SWCNTs bundle when mechanical stirring shear force is applied, viscous polymeric reac-



tion medium containing AB<sub>2</sub> monomer, which is readily react, is penetrated in between split and finally wedged by hyperbranched poly(ether-ketone). As a result, the splits are started from the tips of SWCNTs bundles and propagated further into the bundles (Figure 6c). In case of MWCNTs, the pristine MWCNTs show the seamless and smooth surfaces (Figure 8b). However, heavy amount of hyperbranched poly(ether-ketone) attached to MWCNTs could be clearly seen from the SEM images after grafting of hyperbranched poly(ether-ketone) (Figure 8d). The resultant hyperbranched polymer grafted MWCNTs (HBP-g-MWCNTs) have the diameter range of 40-150 nm, which is strong indication that the covalent attachment of hyperbranched poly(ether-ketone) to the surface of MWCNTs. Furthermore, the surfaces of nanocomposites are appeared to be puppy and bumpy compared to pristine MWCNTs.

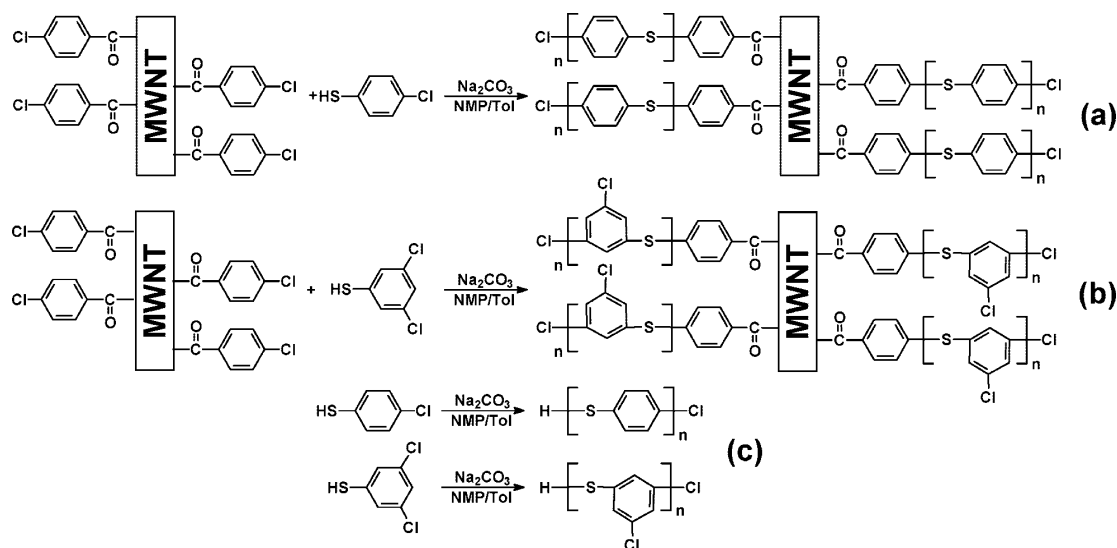


**Figure 8.** SEM image of (a) SWCNTs, (b) MWCNTs, (c) HBP-g-SWCNTs and (d) HBP-g-MWCNTs. All images are captured under the same magnification (100,000 $\times$ ) [43].

Similarly, the grafting of hyperbranched poly(ether-ketone) to the surface of MWCNTs could be realized in alternative way using unique self-controlled polycondensation methodology directly from the mixture of commercially available A<sub>3</sub> and B<sub>2</sub> monomers in the same reaction medium of PPA/P<sub>2</sub>O<sub>5</sub> without gelation problem [8]. In addition, linear and hyperbranched poly(ether-ketone) containing flexible oxymethylene spacers grafted MWCNTs were also prepared by a direct Friedel-Crafts acylation reaction [25]. The resultant nanocomposites are soluble in most strong acids such as trifluoroacetic acid, methanesulfonic acid and sulfuric acid, and they are expected to display enhanced melt processability due to the flexible spacers in structural unit. It is worth to note that the semimetallic nanocomposites,



linear or hyperbranched poly(phenylene sulfide) (PPS) grafted MWCNTs, could be successfully prepared by two-step reaction sequences [12]. Firstly, MWCNTs were functionalized with 4-chlorobenzoyl acid using a direct Friedel-Crafts acylation reaction in PPA/P<sub>2</sub>O<sub>5</sub> to afford 4-chlorobenzoyl functionalized MWCNTs (CB-MWCNTs). A subsequent nucleophilic substitution reaction between CB-MWCNTs and 4-chlorobenzenethiol as an AB monomer or 3,5-dichlorobenzenethiol as an AB<sub>2</sub> monomer was conducted to graft the linear PPS (LPPS) or hyperbranched PPS (HPPS) in NMP/toluene in the presence of sodium carbonate to afford LPPS grafted MWCNTs (LPPS-g-MWCNTs) or HPPS grafted MWCNTs (HPPS-g-MWCNTs), respectively (Figure 9). The covalent attachment of corresponding polymers onto the surface of MWCNTs was indirectly confirmed by a model study without MWCNTs.

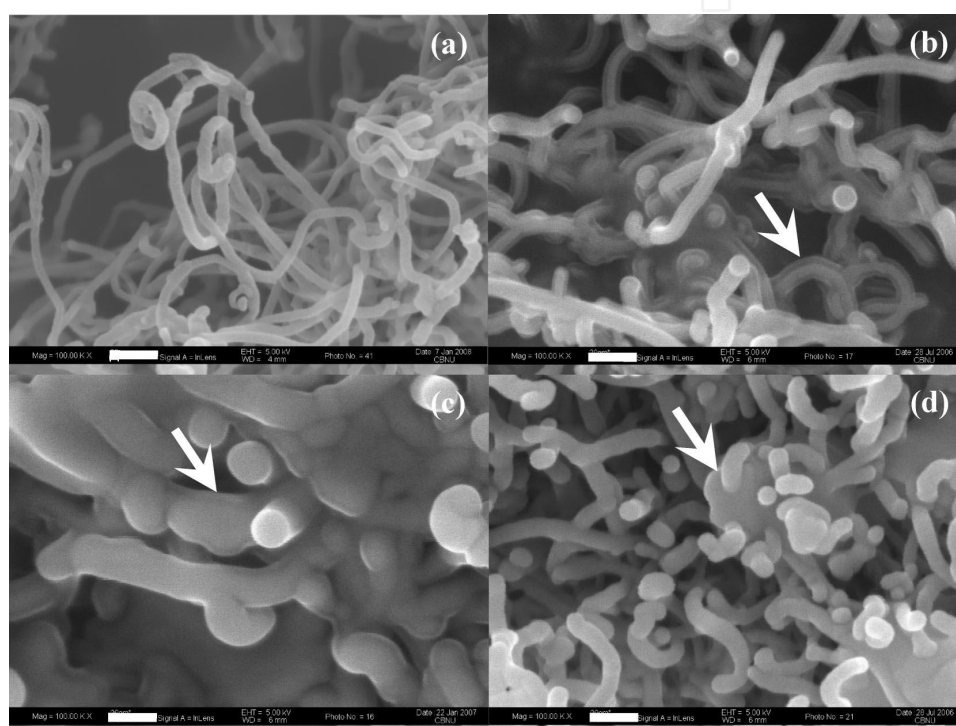


**Figure 9.** Grafting of (a) LPPS and (b) HPPS onto CB-g-MWCNTs, (c) Synthesis of LPPS and HPPS [12].

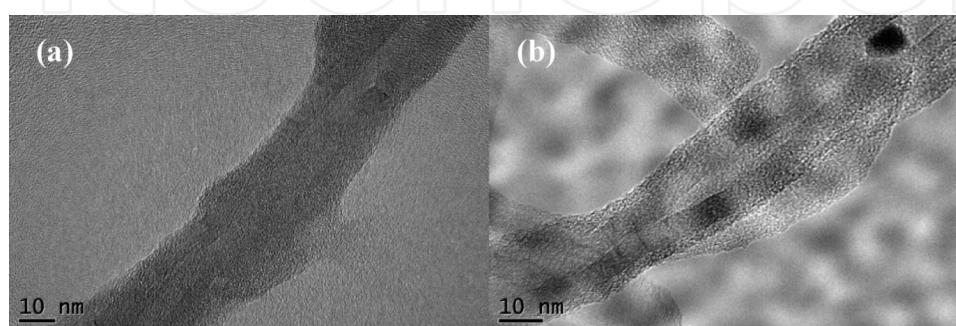
The SEM image of pristine MWCNTs shows that the tubes have seamless and smooth surfaces with an average diameter of 10-20 nm (Figure 10a). However, the average diameter of CB-MWCNTs is approximately 40 nm, which is 2-4 times thicker than that of pristine MWCNTs (Figure 10b). Interestingly, the shape of tube could be discerned by two parts. Opaque inner-hard core is covered by translucent outer-shadow-like part. The diameter of inner part in a range of 10-20nm agrees well with that of the parent MWCNTs. Out-shadow-like part could be due to the 4-chlorobenzoyl moieties that have uniformly covered the surface of CB-MWCNTs. The SEM images of LPPS-g-MWCNTs reveal that the diameter approximately 100 nm, which is much larger than that of pristine MWCNTs and CB-MWCNTs (Figure 10c). Therefore, it is estimated that LPPS is heavily grafted to the CB-MWCNTs. In case of HPPS-g-MWCNTs, although the diameter dimension is close to that of CB-g-MWCNTs, the original outer-shadow-like part of CB-MWCNTs appears to be completely covered with newly attached HPPS (Figure 10d).

For the verification of structural integrity of MWCNTs during reaction sequences and the covalent attachment of the relevant polymers, transmission electron microscopic (TEM)

analysis was conducted. The TEM images of LPPS-g-MWCNTs and HPPS-g-MWCNTs show that the tubes are heavily decorated with polymers (Figure 11). Furthermore, the clear wall-to-wall stripes of MWCNTs framework with its structural integrity suggest that the structural stability of MWCNTs under the two-step reaction sequence. The resultant nanocomposites show the enhanced dispersability and melt-processability, and they could be easily compression molded. Due to the synergetic effect originated from two components of MWCNTs and PPS, even without chemical doping, the surface conductivities of LPPS-g-MWCNTs and HPPS-g-MWCNTs molded samples could be reached to the semimetallic transport region at 11.76 and 3.56 S/cm, respectively [12].



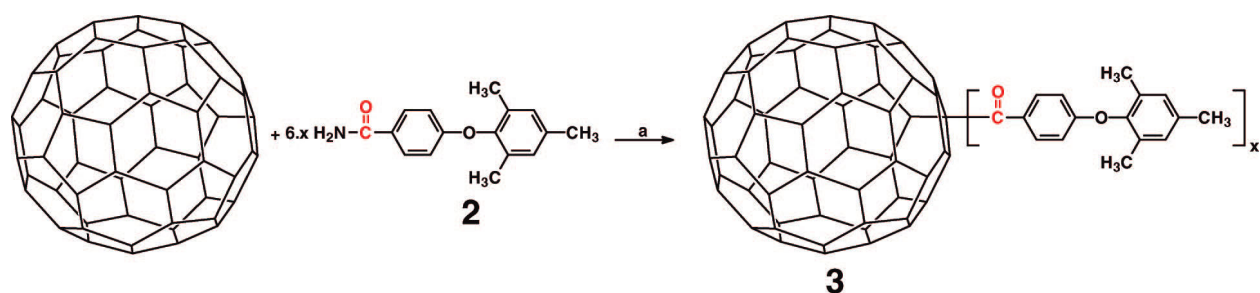
**Figure 10.** SEM image of (a) pristine MWCNTs, (b) CB-g-MWCNTs, (c) LPPS-g-MWCNTs and (d) HPPS-g-MWCNTs. All images are captured under the same magnification (100,000x) [12].



**Figure 11.** TEM images of (a) LPPS-g-MWCNTs and (b) HPPS-g-MWCNTs.

### 2.3. Other carbon-based nanomaterials: fullerene ( $C_{60}$ ), carbon nanofiber, and graphene

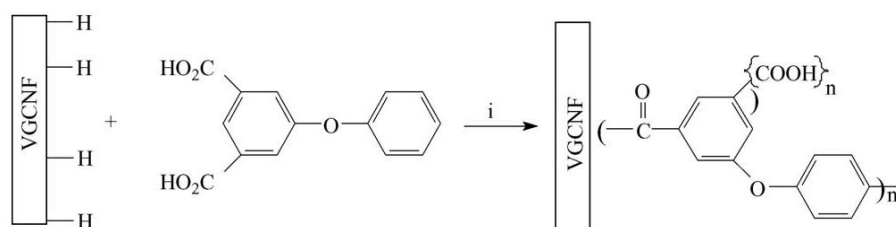
In addition to CNTs, the covalent modification method of direct Friedel-Crafts acylation reaction in a mild PPA/ $P_2O_5$  medium can be expanded to other carbon-based nanomaterials such as fullerene ( $C_{60}$ ) [14], carbon nanofiber [7, 15-17] and graphene [19-22]. Buckminster fullerene,  $C_{60}$ , which is of the most abundant carbon sphere, is generally considered as a stable electron deficient material. Due to the electron affinity,  $C_{60}$  is considered as to be more susceptible to nucleophilic reaction than to electrophilic one. However, Baek *et al.*, firstly reported the covalent electrophilic functionalization of  $C_{60}$  *via* direct Friedel-Crafts acylation reaction in a mild PPA/ $P_2O_5$  medium using 4-(2,4,6-trimethylphenoxy)benzamide (TMPBA) as a substituent (Figure 12) [14]. After careful characterizations, it is suggested to that multiple destructive covalent attachments of TMPBAs onto  $C_{60}$  has successfully occurred and an average of 6.4 carbons was regioselectively detached from  $C_{60}$  framework to give  $C_{53.6}(TMPBA)_6$ .



**Figure 12.** Synthesis of 4-(2,4,6-trimethylphenoxy) benzoyl functionalized fullerene. (a: PPA/ $P_2O_5$ ) [14].

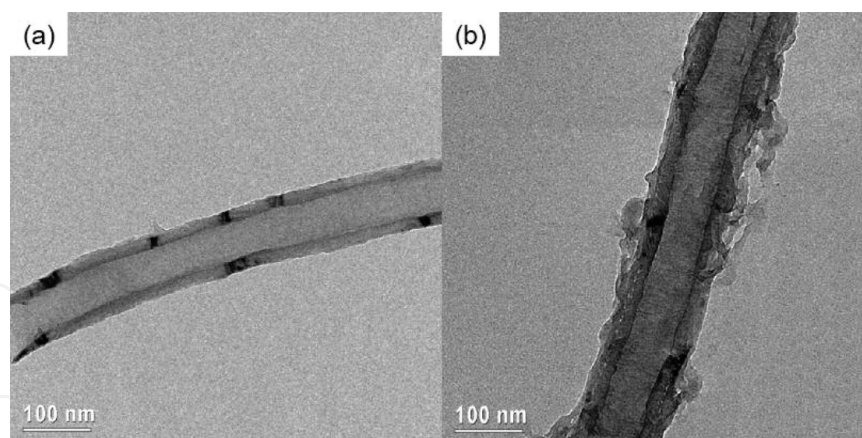
In comparison to CNTs, vapor-grown carbon nanofibers (VGCNFs), which are structurally hollow and multi-walled but several orders of magnitude larger in diameter and length than those of CNTs, are more attractive from a standpoint of practicality in terms of their relatively low cost and availability in larger quantities as a result of their more advanced stage in commercial production. These carbon nanofibers (CNFs) are typically produced by a vapor-phase catalyst process in which a carbon-containing feedstock (e.g.  $CH_4$ ,  $C_2H_4$ , etc.) is pyrolyzed in the presence of small metal catalyst (e.g. ferrocene,  $Fe(CO)_5$ , etc.) and have an outer diameter of 60-200 nm, a hollow core of 30-90 nm, and length in the order of 50-100  $\mu m$  [15-16]. Furthermore, VGCNFs have been widely used for tailoring properties in their polymer composites via cost-effective way, because of their inherent electrical and mechanical properties. To enhance compatibility and dispersability of VGCNF in polymeric matrix, various covalent grafting methods including ring-opening, atom-transfer radical and self-condensing polymerizations have been developed [17]. However, these approaches generally require multi-step synthetic procedures and limited species of materials can be utilized. To overcome these problems, Baek *et al.*, developed efficient functionalization and grafting methods onto the surface of VGCNF in a mild PPA/ $P_2O_5$  medium, called as a direct Friedel-Crafts acylation reaction (Figure 13) [15-17]. As a result, the dispersion, interfacial adhesion and solution processability of VGCNF have been greatly improved, which is quite beneficial for the development of high performance polymer-based nanocomposites.





**Figure 13.** Synthesis of 3,5-diphenoxybenzoic acid functionalized VGCNF. (i: PPA/P<sub>2</sub>O<sub>5</sub>) [16].

Similarly to CNTs, the functionalization of VGCNF *via* direct Friedel-Crafts acylation reaction in PPA/P<sub>2</sub>O<sub>5</sub> with various materials such as small molecules [7, 32], linear [15] and hyperbranched poly(ether-ketone) [16-17] have been successfully demonstrated. Specifically, the covalent attachment of hyperbranched poly(ether-ketone) onto the surface of VGCNF has been clearly verified by TEM analysis. The TEM image of pristine VGCNF shows a smooth surface (Figure 14a). However, the nanofiber surfaces of VGCNF containing 20 wt % of grafted hyperbranched poly(ether-ketone) polymers show a rough and fuzzy surface (Figure 14b). Furthermore, there is an obvious increase in the diameter due to the heavy coating by the attached hyperbranched poly(ether-ketone) with a thickness range of 10-20 nm [17]. Due to intrinsic nature of hyperbranched polymers such as a reduced viscosity, for example, the hyperbranched poly(ether-ketone) grafted VGCNF would be amenable to applications where speed and large-area coverage are required, such as spraying and painting techniques.

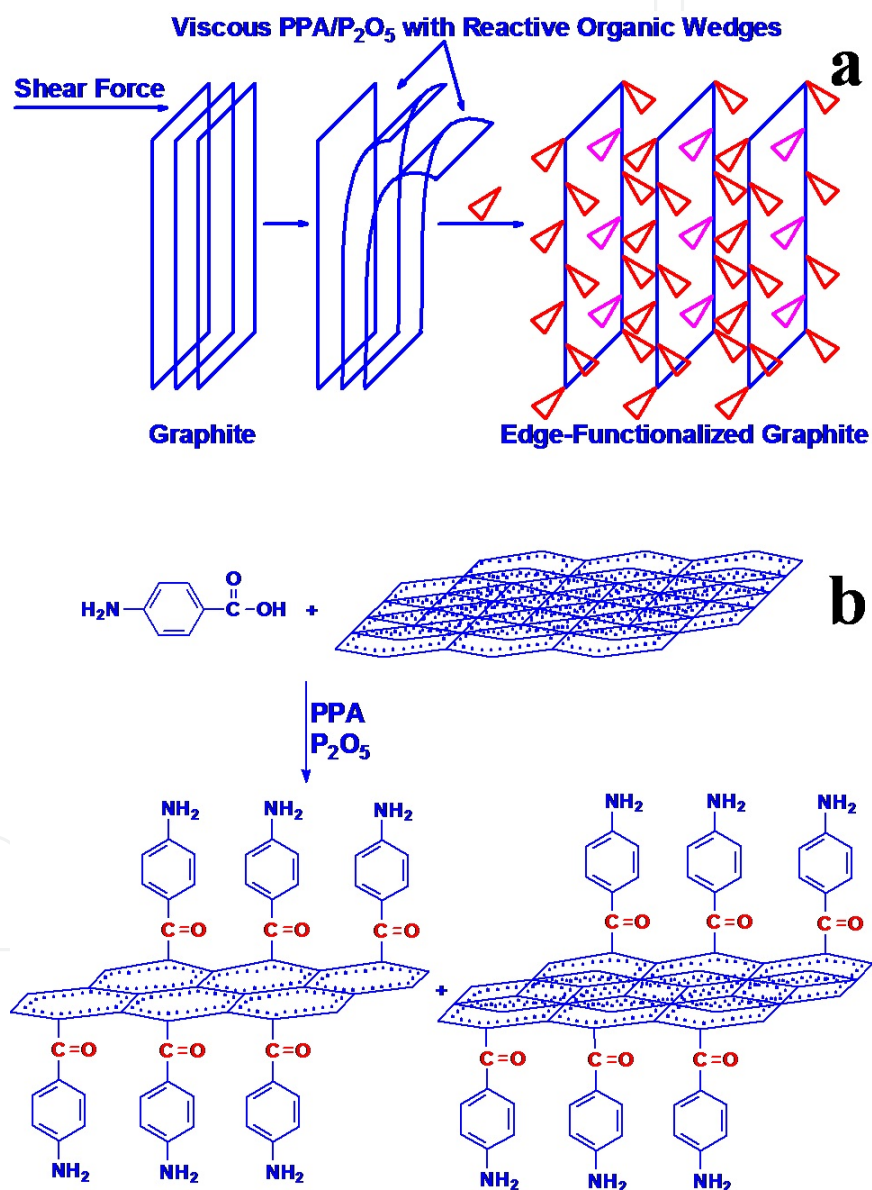


**Figure 14.** TEM images of (a) pristine VGCNF and (b) hyperbranched poly(ether-ketone) polymer grafted VGCNF [17].

Graphene as a one of carbon-based nanomaterials, is currently the focal point for research into condensed matter due to its promising properties such as exceptional mechanical strength ( $\sim 1100$  GPa), high thermal conductivity ( $\sim 5000$  Wm<sup>-1</sup>K<sup>-1</sup>), large specific surface area ( $\sim 2630$  m<sup>2</sup>g<sup>-1</sup>) and ultra high electron transport properties (200,000 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>) [46]. There are two major approaches used in the preparation of graphene. The first method is the exfoliation of pristine graphite into graphene, which involves physical and chemical methods

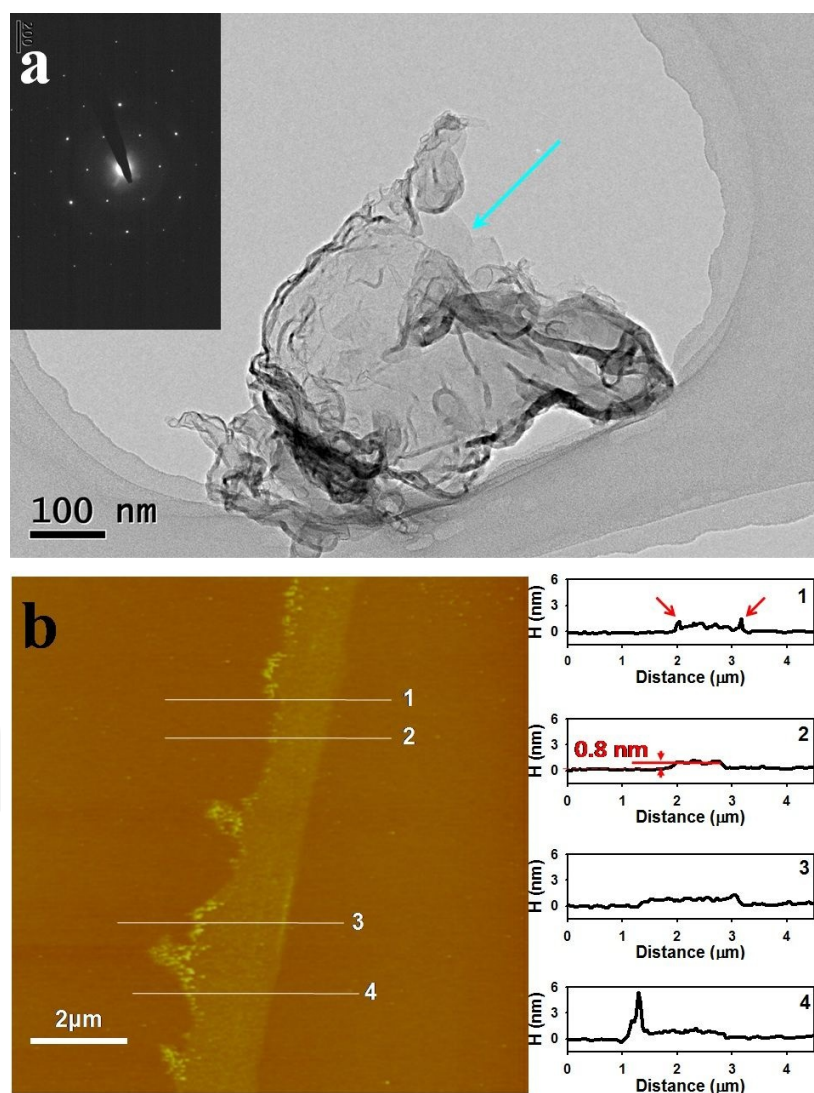


[47-48]. The second method is where graphene can be directly grown using chemical vapor deposition (CVD) on a metal substrate [49] or from single crystal carbide [50]. For mass production, the chemical methods belong to the first approach is more preferred, but they still need to be optimized. In this regard, graphene oxide (GO) are widely investigated for the various applications of graphene, however GO has larger structural damages during the harsh preparation methods using strong acids and requires reduction, which has a limited conversion to reduced graphene oxide (rGO). Hence, the original graphitic structures cannot be efficiently restored in final graphitic structure, when GO is used as a starting material.



**Figure 15.** (a) Schematic presentation of graphite exfoliation mechanism and (b) schematic representation of the reaction between graphite and 4-aminobenzoic acid as amolecular wedge via Friedel-Crafts acylation in PPA/P<sub>2</sub>O<sub>5</sub> medium [20].

Therefore, the development of less destructive and highly efficient method to exfoliate graphite into two-dimensional graphene and/or graphene-like sheets is highly required for the graphene research community. To meet this strong demand, Baek *et al.*, developed a new approach to chemical exfoliation of graphite by grafting organic molecular wedges to the defect sites (mostly  $sp^2C-H$ ) located mainly on the edges of graphite *via* a direct Friedel-Crafts acylation reaction in a mild PPA/ $P_2O_5$  medium [19-22]. The reaction condition has been previously optimized for the functionalization of carbon-based nanomaterials such as fullerene [14], CNTs [8-13] and VGCNF [7, 15-17]. This method is the first attempt at large-scale direct chemical exfoliation of graphite not involving strong acid and sonication that are known to damage graphitic carbon framework. The schematic presentation of graphite exfoliation mechanism and the reaction between graphite and 4-aminobenzoic acid as a molecular wedge *via* direct Friedel-Crafts acylation are shown in Figure 15 [20].



**Figure 16.** (a) TEM images with electron diffraction pattern (inset) of EFG and (b) AFM image with topological height profiles [20].

The resultant edge-selectively functionalized graphene (EFG) becomes dispersible without damaging the inner crystalline graphitic structure. The TEM image for EFG dispersion in NMP and dip-coated on an aperture carbon-grid, along with the corresponding selected-area electron diffraction (SAED) pattern is shown in Figure 16a. The graphene sheet is wrinkled due to its flexibility, and its surface is clean without noticeable flaws. Most of EFG consists of less than five graphene sheets. AFM images obtained from EFG on a silicon wafer clearly show EFG with approximately  $\sim 2 \mu\text{m}$  width and a few micron lengths (Figure 16b). Many bright spots on the edges of graphene are seen due to the covalent attachment of organic wedges. The thickness of graphene is 0.8 nm, whose value indicates single layer graphene. All topological height profiles clearly show that the interior (basal plane) are lower than the edges, implying that edge-functionalization is exclusively occurred at edges, where presumably  $\text{sp}^2\text{C-H}$  defects are located [20]. Thus the efficient exfoliation of graphite and edge-selective functionalization of graphene for improving dispersability and processability have been successfully achieved by simple one-pot reaction using a direct Friedel-Crafts acylation reaction in a mild PPA/ $\text{P}_2\text{O}_5$  medium. In addition to small molecular wedges, various macromolecular wedges using linear [51] or hyperbranched [21] polymer have also been introduced to graphene. Due to the enhanced dispersability and compatibility without structural damages, the resultant EFG has huge potentials in various applications such as polymer nanocomposites [51-52], fuel cells [22] and optoelectronic devices [19].

### 3. Conclusion

“Direct” Friedel-Crafts acylation reaction of electron-deficient CNTs in a mild PPA/ $\text{P}_2\text{O}_5$  medium is a simple but less destructive functionalization method. Numerous results envision that various functional materials such as small molecules, linear and hyperbranched polymers could be covalently attached to the surface of CNTs without or with minimal damages to their carbon framework. The dispersability and compatibility of the functionalized CNTs have been greatly improve keeping their intrinsic properties, which could be regarded as a feasible approach to hybridization of CNTs and organic materials such as polymers. Furthermore, this nondestructive synthetic strategy can be expanded to other carbon-based nanomaterials such as fullerene, carbon nanofiber and graphene. Therefore, a direct Friedel-Crafts acylation reaction in a mild PPA/ $\text{P}_2\text{O}_5$  medium possesses indeed significant potentials for the development of functional materials in various fields from all types of carbon-based nanomaterials.

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