1
Carbon Nanotubes Surface Modifications: An Overview

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1.1
Introduction

Carbon nanotubes are allotropes of carbon and are regarded as the ultimate carbon fibers [1–3]. The credit for realizing the nanotubes in an arc discharge apparatus is given generally to Iijima who successfully proved the existence of first multiwalled carbon nanotubes (MWCNTs) mixed with other forms of carbon [4], though the existence of these materials was realized earlier also, for example, by Endo in 1976 [5]. Subsequently, single-walled carbon nanocomposites (SWCNTs) were discovered and a significant research effort followed thereafter [6–9]. Carbon nanotubes have unique mechanical, electrical, magnetic, optical, and thermal properties [10]. Although the organic–inorganic nanocomposites can conventionally contain inorganic fillers which differ by the virtue of their primary particle dimensions [11–16], nanotubes containing composites generate much high-end application potential thus signifying the importance of nanotubes. The synthesis methods for the generation of nanotubes include high-temperature evaporation using arc-discharge [17–19], laser ablation [20], chemical vapor deposition, etc. [21–26].

Owing to their inert nature, the nanotubes tend to form bundles with each other and thus do not disperse well in the organic matrices in their pristine state. Suitable enhancement of the surface of the nanotubes is thus required in order to optimize their dispersion in the organic matrices. Out of various possible ways to achieve the surface functionalization, noncovalent means of surface modification are quite common. In this methodology, polymer chains are wrapped around the nanotubes or various surfactant molecules are adsorbed on the surface of nanotubes. In this case, the modification molecules are only physically bound to the surface. In the covalent means of surface modification, polymer chains can be grafted to or from the surface of the nanotubes. Controlled living polymerization methods have also been used to control the architecture of these grafts. These methods generate surface modifications which are chemically bound to the surface of the tubes, but such chemical means of modifications also disturb the structural homogeneity of the tubes, thereby decreasing the mechanical properties. Thus different surface functionalization methods have their own benefits

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and limitations, and the choice of these methods is dictated by the applications required from the generated nanocomposite materials. Pi–pi stacking is also one of the means to organophilize the nanotubes. The surface modification of the nanotubes forms a critical phase in the nanocomposite synthesis as the interactions of the surface modification molecules with the polymer chains dictate if the nanotubes can be homogenously dispersed in the organic phase or not. Therefore, various methods of surface modification of nanotubes are required to be reviewed in detail in order to tune the nanocomposite morphology and subsequent properties.

1.2
Noncovalent Functionalization of Nanotubes

Noncovalent mode of nanotube functionalization has received a lot of academic interest owing to the noninvasive mode of surface functionalization, which keeps the original nanotube properties intact. However, for some load-bearing applications, the presence of physically bound modifier molecules on the surface can also be a concern. The following studies detail the noncovalent functionalization of nanotubes for eventual dispersion in polymer matrices.

Zhu *et al.* reported the noncovalent functionalization of nanotubes based on the colloid stabilization principles [27]. In this approach, charged inorganic ZrO_2 nanoparticles were used as stabilizing media as shown in Figure 1.1. HiPco SWNTs were first purified following a two-step procedure in which the nanotubes were heated in an O_2 atmosphere at 300 °C and subsequent removal of metal catalysts in HCl at 60 °C for 2 h. The purified SWCNTs were then mixed with ZrO_2 nanoparticle aqueous solutions and were sonicated. The suspensions were allowed to stand for few hours to few days to remove the unstable large bundles of nanotubes. After this gravity-driven sedimentation of the uncoated nanotubes, the suspensions of nanotubes with nanoparticles were observed to be very stable for long periods of time and the suspensions were transparent. The microscopic investigations by AFM also confirmed the existence of single nanotubes in the dispersed mode. It was suggested that charge repulsion originating from ZrO_2 particles can be the most plausible phenomena and there was no direct evidence of nanoparticle haloing of ZrO_2 around SWNTs. The external stimuli were observed to self-assemble the dispersed nanotubes into macroscopic materials in solution indicating that the functionalization of the nanotubes with the nanoparticles was very efficient in tuning the surface properties.

Proteins (like streptavidin) adsorb spontaneously on the surface of the nanotubes [28]. Nonspecific binding of the proteins has also been proven microscopically on nanotubes after exposure of the nanotubes with solution of streptavidin. A number of polymer systems have been used for the prevention of nonspecific binding of proteins on the surfaces by forming coatings and self-assembled monolayers. In an interesting study on the interactions of proteins with nanotubes (Figure 1.2), it was demonstrated that by noncovalent functionalization of nano-

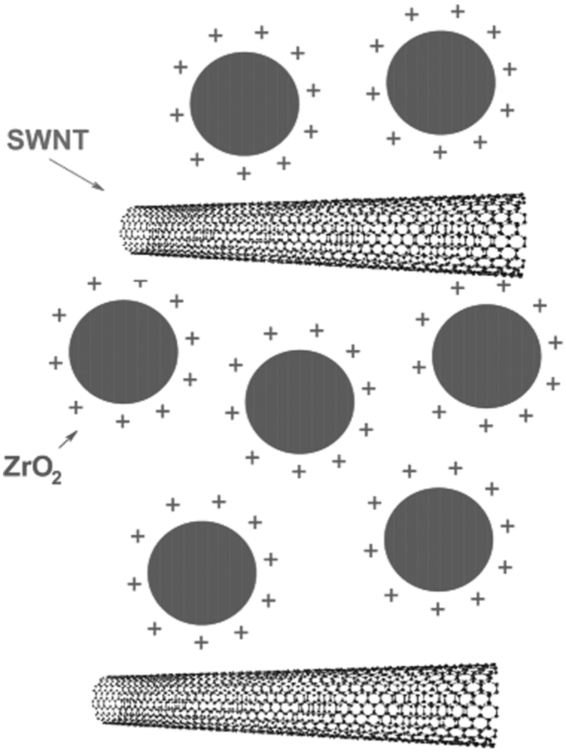

Figure 1.1 Schematic representation of dispersion of nanotubes in water by using inorganic nanoparticles. Reproduced from Ref. [27] with permission from American Chemical Society.

tubes, nonspecific binding of the proteins on the nanotube surface could be eliminated and specific binding of proteins after surface functionalization could be achieved [29]. Poly(ethylene glycol) is the most commonly used polymer to eliminate the nonspecific binding of the proteins on the surface [30–32]. However, it was observed by the authors that the poly(ethylene glycol) though irreversibly adsorbed on the nanotube surface, but appreciable adsorption of streptavidin was still observed indicating that the coverage of nanotube with the polymer was not optimum. The authors suggested that surfactant can be used for improving the coverage of the surface with poly(ethylene glycol). Triton-X surfactant containing an aliphatic chain and a short hydrophilic poly(ethylene glycol) unit was used to bind to the nanotube surface by hydrophobic interactions. Its adsorption alone on the surface was observed to resist the nonspecific binding of the proteins on the surface and after the adsorption of poly(ethylene glycol) on the surface, no streptavidin adsorption was observed. The authors also suggested means to specifically bind proteins on the surface by following the similar noncovalent functionalization of nanotubes. Biotin moiety was attached to the poly(ethylene glycol) chains by using amine-functionalized poly(ethylene glycol) and covalently linking it with

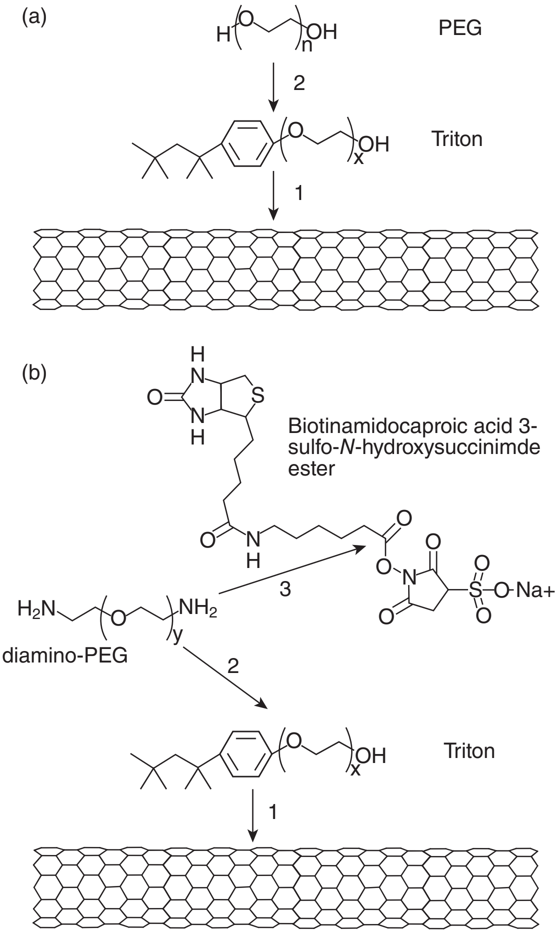

Figure 1.2 (a) Functionalization of SWNTs for preventing nonspecific binding of protein and (b) strategy for introducing selective binding of streptavidin with prevention of nonspecific binding. Reproduced from Ref. [29] with permission from American Chemical Society.

an amine reactive biotin reagent. As streptavidin demonstrates high affinity to biotin, the triton-PEG-biotin functionalized nanotubes were ideal substrates for the very specific adsorption of streptavidin on them.

Polymer wrapping method was reported by O'Connell *et al.* for the noncovalent functionalization of polymer nanotubes [33]. The SWCNTs were dispersed in 1% sodium dodecyl sulfate (SDS) in water by using shear mixer and ultrasonication followed by the addition of aqueous solution of poly(vinyl pyrrolidone) (PVP). Excess amount of the polymer was used for wrapping process, and the excess of SDS and PVP were subsequently removed by ultracentrifugation. The AFM images shown in Figure 1.3 confirm that most of the nanotubes existed as single

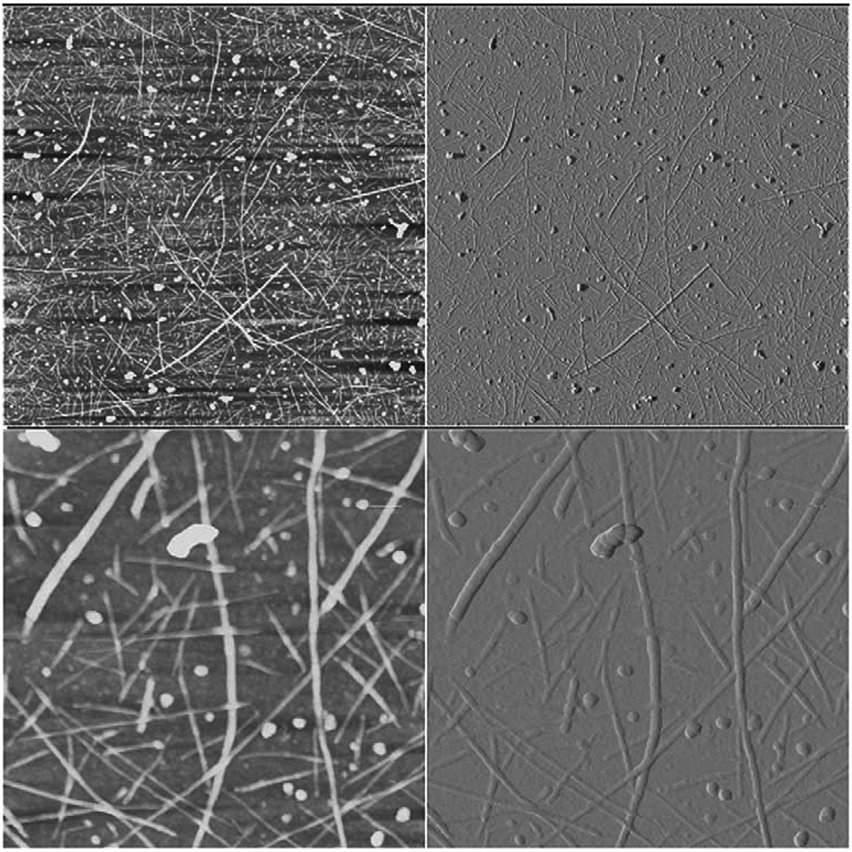

Figure 1.3 AFM images of PVP–SWNT system adsorbed on a functionalized substrate. Top two images correspond to 5 μm height and amplitude images, respectively, whereas bottom two images correspond to 1 μm counterparts. Reproduced from Ref. [33] with permission from Elsevier.

tubes associated with at most a single layer of polymer and only a smaller number of aggregates consisting of more than one nanotube. The suspensions were observed to be stable for months and once dried, the nanotubes were reported to disperse in water with minimal ultrasonication. Nonwrapped nanotubes were observed to assemble into mats of tangled and seemingly endless ropes, whereas it was not the case in the polymer-wrapped nanotubes. The modified nanotubes were also tested for the strength of bonding between the polymer and the nanotubes. The modified tubes were subjected to a cross flow in the channel of field-flow fractionation device and there was no effect on the nature of the nanotubes. The authors suggested that the nanotube wrapping is driven largely by the thermodynamic drive to eliminate the hydrophobic interface between the tubes and

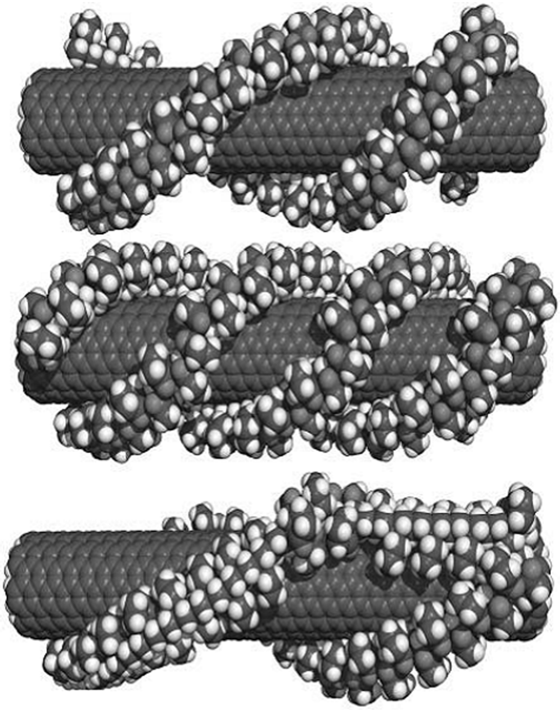

Figure 1.4 Possible arrangements of the polymer wrapping around the nanotubes. Top image corresponds to a double helix, the middle scheme is a triple helix, whereas the bottom arrangement shows switch backs, which allow multiple parallel wrapping strands to come from the same polymer chain owing to the backbone bond rotations. Reproduced from Ref. [33] with permission from Elsevier.

the dispersion medium. The molecular level image of the nanotubes wrapped with polymer chains is also demonstrated in Figure 1.4. The authors suggested that the helical wrapping of the chains around the nanotubes takes place due to the free rotation about the backbone bonds. However, single tight coil was suggested to generate significant bond angle strain in the polymer backbone. Therefore polymer coverage by multihelical wrapping was suggested. This mode of wrapping provides high extents of surface coverage with low backbone strain and locally multiple strands of polymer coil around the nanotube close to their nascent backbone curvature.

Apart from polymer layer medications, the coverage of the nanotube surfaces with an inorganic silica layer has also been reported and the generated silica layer was bound noncovalently to the nanotubes [34]. Functionalizing the sidewalls of carbon nanotubes with a layer of SiO_2 also opens the possibilities of further modification of the nanotube surfaces by utilizing the surface reactions available for silica surfaces. The process of nanotube functionalization is demonstrated in

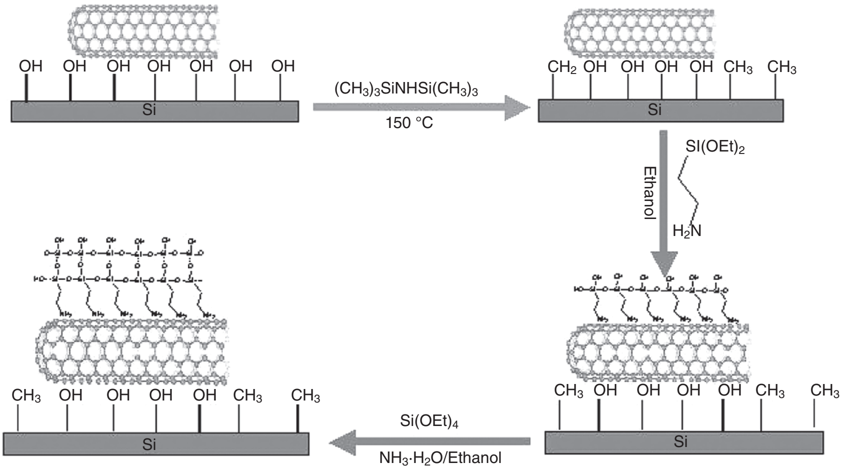

Figure 1.5 Growth of thin SiO_2 films on the walls of single-walled carbon nanotubes by using 3-APTES as promoter. Reproduced from Ref. [34] with permission from American Chemical Society.

Figure 1.5. A promoter, 3-aminopropyltriethanoxysilane (APTES), was absorbed on the sidewalls of the nanotubes by the interaction of sidewalls of nanotubes with the amine groups followed by the polymerization of the molecule by heat treatment. This, thus, generates an irreversible coating on the nanotube surfaces. As a next step, thin shell of SiO_2 of thickness roughly 1 nm was generated around the nanotubes by using tetraethyl orthosilicate as the precursor. The thickness of the coating can be adjusted by controlling the reaction time and the concentration of tetraethyl orthosilicate. This, thus, generates two advantages: first, the thin silica layer is bound noncovalently to the surface; and second, this can then further allow using the SiO_2 functionalization chemistries to generate different functionalities on the SiO_2 surface. The nanotubes were grown by chemical vapor deposition method in this study, and the authors also opined that the similar inorganic surface modifications can also be extended to other oxide materials. Similarly, norbornene polymerization was achieved on the nanotube surface via noncovalently bound ring-opening metathesis initiator [35].

A graft copolymer polystyrene-*g*-(glycidyl methacrylate-*co*-styrene) (PS-*g*-(GMA-*co*-St)) was reported to noncovalently modify the surface of nanotubes [36]. The graft copolymer was synthesized by free radical melt grafting of GMA on PS chains. The PS chains owing to their affinity of the surface of the MWNTs led to the noncovalent modification of the nanotubes. The MWNTs, which were produced by catalytic pyrolysis of propylene in this study, were dispersed in THF by mixing with excess of copolymer. The surface modification allowed the nanotubes to be dispersed in a variety of polar and nonpolar solvents. Also, when the acid-treated MWNTs were used, the presence of GMA in the copolymer provided the

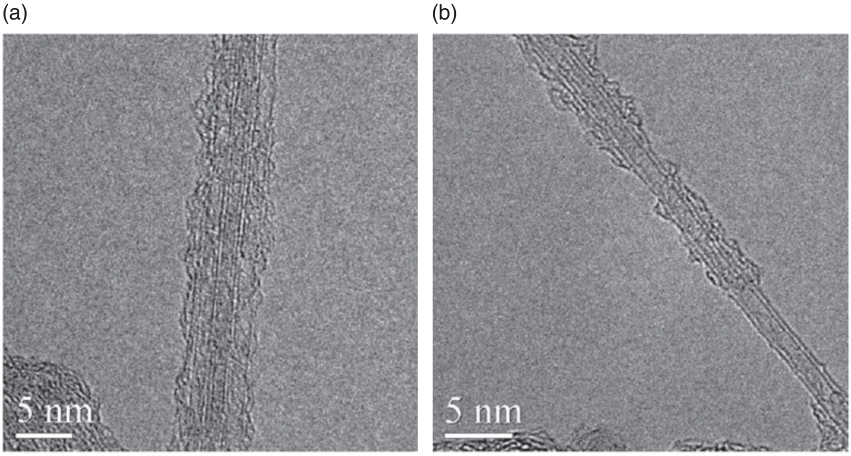

Figure 1.6 High-resolution TEM images of nanotubes modified by the polymer (a) noncovalently and (b) covalently. Reproduced from Ref. [36] with permission from Elsevier.

epoxy functional groups to which the acidic groups present on the surface of nanotubes could covalently attach to form esters. Figure 1.6 shows the nanotubes functionalized by the copolymer by following both the above-mentioned functionalization approaches. The nanotubes, which had only noncovalent functionalization, were observed to be uniformly modified on the surface by the polymer layer. However, in the nanotubes, which were acid-treated and hence had a covalent binding of the polymer chains, the polymer was bound to the surface only at sites where the carboxyl groups were present. Different modification mechanisms were also observed to significantly affect the solubility characteristics of the nanotubes. The noncovalently modified nanotubes were observed to swell well in different polar and nonpolar solvents, whereas the covalently functionalized nanotubes were swollen in solvents in which polystyrene is soluble. In the case of noncovalently functionalized nanotubes, the polystyrene component of the copolymer was attached to the nanotubes surface, thus leaving the chains containing gylcidyl methacrylate dangling away from the nanotube surface. As glycidyl methacrylate is readily soluble in many solvents, the swelling of noncovalently functionalized nanotubes was improved significantly. However, in the case of covalently functionalized nanotubes, the polystyrene chains formed the external "capsules" owing to the chemical reaction of the GMA block of the copolymer with the surface of nanotubes. Thus, the swellability of nanotubes was dictated by the swelling or solubility characteristics of polystyrene chains.

In another study, the authors stressed the need of noncovalent functionalization of nanotubes to retain their attractive electronic and mechanical properties. To achieve this, the authors used an approach for the functionalization of nanotubes by using polymer multilayers [37]. The formation of polymer electrolyte layers has been reported in the literature as a promising strategy to functionalizing the surfaces [38–45]. The thickness of the layers depends on the nature of the polymer used for adsorption as well as pH tuning and the ionic strength of the solution used for adsorption. In this study, hydrolyzed-poly(styrene-*alt*-maleic anhydride) (h-PSMA) was adsorbed noncovalently onto nanotubes surface via hydrophobic interactions. As the copolymer contained carboxylic acid groups, these groups could be used to further attach a second layer of polyethyleneimine covalently forming a cross-linked polymer bilayer. The same process was followed to attach second layer of h-PSMA and subsequently a second layer of polyethyleneimine. In the end, a layer of polyacrylic acid was generated on the surface of the nanotubes. The functionalization of the surfaces by the polymer multilayers was confirmed by using polarized infrared (IR) internal reflectance spectroscopy. Gold nanoparticles could also be immobilized on the surface by generating a third layer of polyethyleneimine. As gold particles were negatively charged, they could bind to the positive charges in the polyethyleneimine layer by electrostatic interactions. A control sample which was untreated substrates was also immersed in aqueous suspension of gold nanoparticles. A negligible amount of gold nanoparticles was observed to attach to this sample, thus confirming the tuning of the surface properties by using polymer multilayers approach. Figure 1.7 shows the functionalization of nanotubes by the polymer multilayers approach. Thus, this noncovalent mode of surface functionalization retains the properties of nanotubes as well as generates reactive functional groups on the surface to tune the properties of nanotubes accordingly.

Chen *et al.* reported the pi-stacking approach to immobilize biomolecules on carbon nanotubes [46]. Noncovalent functionalization of the sidewalls of SWCNTs was achieved, subsequent immobilization of various biological molecules was observed, and the process was reported to be controllable and site-specific.

For the noncovalent functionalization of nanotubes, a bifunctional molecule, 1-pyrenebutanoic acid, succinimidyl ester was irreversibly adsorbed onto the inherently hydrophobic surfaces of SWNTs in dimethylformamide or methanol. The pyrenyl group is highly aromatic in nature and, therefore, is known to interact strongly with the basal plane of graphite via pi-stacking [46, 47]. The authors also observed the similar interaction of the pyrenyl group with the nanotubes surface. It was also observed that the ester molecule was irreversibly adsorbed on the surface and resisted desorption in aqueous solutions.

Succinimidyl ester groups are highly reactive to nucleophilic substitution by primary and secondary amines present in excess on the surface of most proteins; therefore the functionalization of nanotubes with these groups opens the possibilities for nanotubes to generate specific interactions with the biomolecules. Figure 1.8 demonstrates these functionalization processes. The authors suggested that the proteins immobilization on nanotubes involves the nucleophilic substitution of *N*-hydroxysuccinimide by an amine group on the protein, resulting in the formation of an amide bond. Successful immobilization of both ferritin and streptavidin proteins could be achieved by this method, thus indicating the versatility of this functionalization approach to make the surfaces of nanotubes more usable. Apart from proteins, any other chemical molecules can also be reacted on the

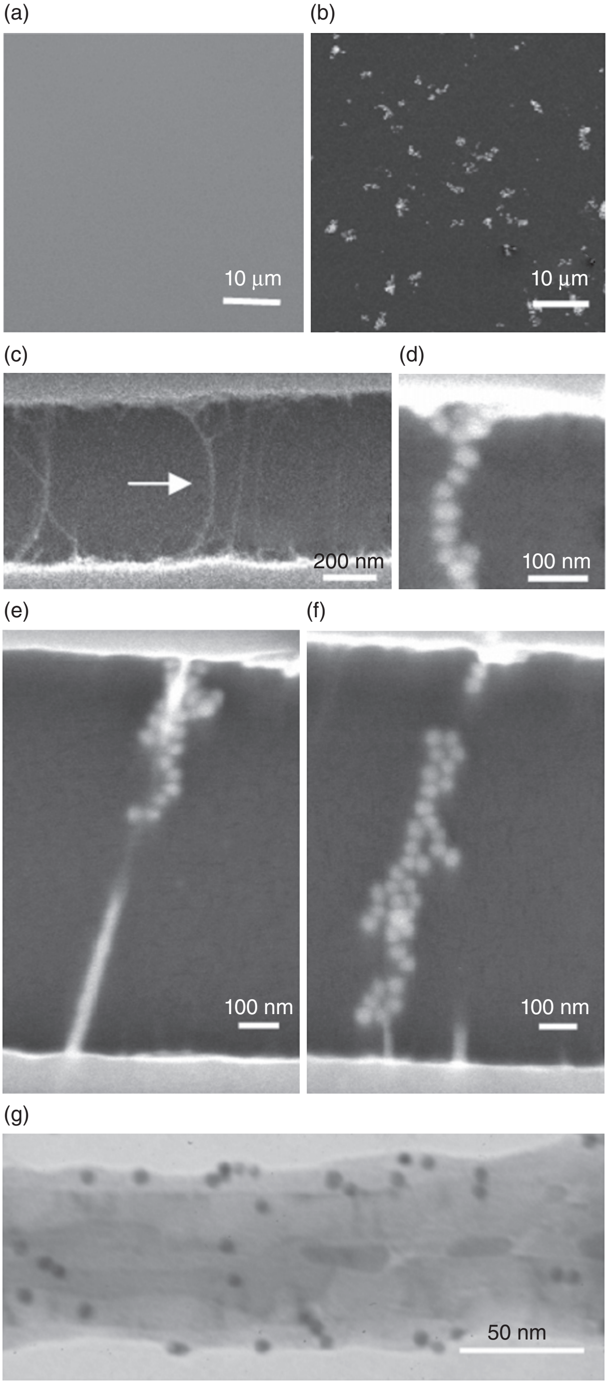

Figure 1.7 Functionalization of graphite and nanotube surfaces: (a) fluorescence micrograph of polymer-coated graphite, (b) SEM image of gold nanoparticles immobilized on polymer-coated graphite, (c) SEM image of substrate-grown SWNTs, (d)–(f) SEM images of gold nanoparticles immobilized on polymer-coated SWNTs, and (g) TEM image of gold nanoparticles immobilized on polymer-coated MWNTs. Reproduced from Ref. [37] with permission from American Chemical Society.

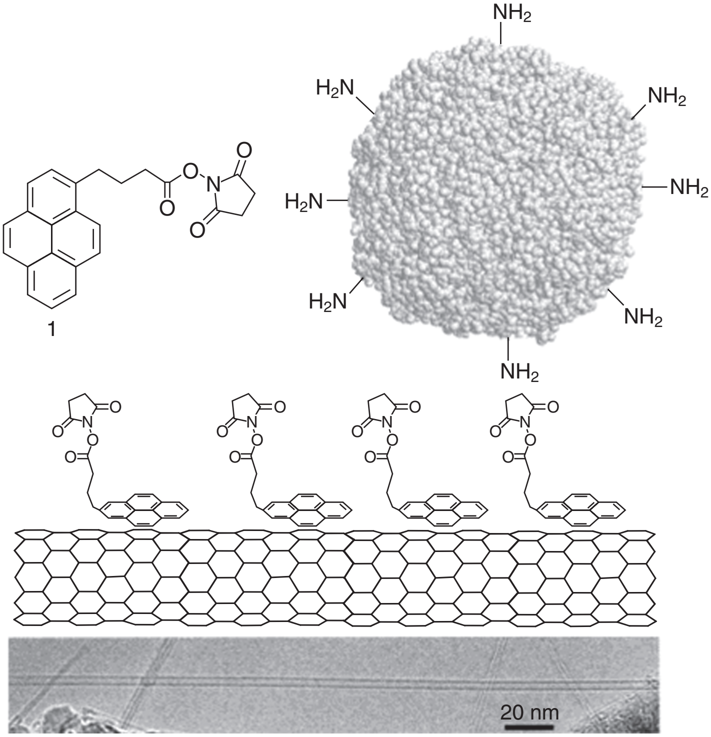

Figure 1.8 Irreversible adsorption of 1-pyrenebutanoic acid, succinimidyl ester on the side walls of nanotubes. Reproduced from Ref. [46] with permission from American Chemical Society.

surfaces treated with ester and thus the surface properties can be tuned or controlled according to the requirement.

Kang *et al.* [48] reported an interesting approach of encapsulating polymer nanotubes within cross-linked, amphiphilic copolymer micelles, similarly reported by other researchers [49, 50]. The modified nanotubes could be dispersed in a variety of polar and nonpolar solvents and polymer matrices. The authors used an amphiphilic poly(styrene)-block-poly(acrylic acid) copolymer, which was dissolved in dimethylformamide (DMF), a solvent in which both the blocks of the copolymer are soluble and do not form micelles. The nanotubes were subsequently suspended in the copolymer solution by ultrasonication. Micellization of the copolymer was achieved by the gradual addition of water to the suspension, leading to the encapsulated nanotubes inside these micelles. The poly(acrylic acid) blocks were subsequently cross-linked by the addition of diamine linker and carbodiimide activator. The nanotubes were observed to remain dispersed throughout the cross-linking process. It was also observed that full cross-linking of poly(acrylic acid) blocks was not necessary to achieve stabilization; conversion of 25% acid groups to amides was enough to bring about the stability of nanotube suspension. The

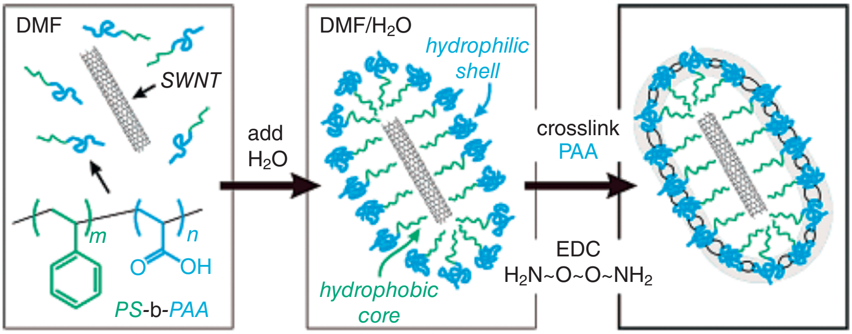

Figure 1.9 Encapsulation of nanotubes by using poly(styrene)-block-poly(acrylic acid) copolymer. Reproduced from Ref. [48] with permission from American Chemical Society.

treated nanotubes were washed off the excess reagents and empty micelles, and the encapsulated nanotubes could be successfully redispersed in different solvents. Apart from that, these suspensions were stable over long period of time as neither the visible absorbance nor the scattered light intensity of the suspensions changed as a function of time. It was hypothesized that high solubility of these encapsulated nanotubes resulted because of solvation of at least one block of the encapsulating copolymer in the solvents used. The authors reported in some cases the solvation of even both the blocks of the copolymer in the solvent. The solvents were also analyzed and it was confirmed that no polymer was desorbed from the surface of nanotubes. Figure 1.9 shows the schematic of the encapsulation process.

Many other studies have been reported for the noncovalent functionalization of nanotubes. Conjugated luminescent polymer poly(metaphenylenevinylene) (PmPv) could be coated on to the nanotubes surface [51]. Water-soluble polyvinyl alcohol was coated around the nanotubes, thus allowing the dispersion of nanotubes in water [52]. Carbon nanotubes were also wrapped with starch to generate starched nanotubes [53]. Long-chain polymers like Gum Arabic were also physically adsorbed to disperse the nanotubes individually in solvents [54]. Aromatic polyimides were also used as functionalizing polymer to achieve noncovalent functionalization of carbon nanotubes [55].

1.3
Covalent Modifications of Carbon Nanotubes

Covalent functionalization of nanotubes though may produce defects in the wall structure of the nanotubes, this mode of surface functionalization is required when the load-transfer properties are concerned. Thus, the choice of the modifications on the nanotubes surface may be a direct result of the properties required from them. Following paragraphs explain the various methodologies reported in the literature in order to achieve covalent functionalization of nanotubes.

Velasco-Santos *et al.* reported the advantages of chemical functionalization of nanotubes in improving the composite properties [56]. In the study, *in situ* polymerization of methyl methacrylate (MMA) was achieved both in the presence of unfunctionalized and acid-functionalized nanotubes. Interesting phenomena regarding the mode of polymerization and resulting composite properties were reported. Some studies have earlier reported that the unfunctionalized nanotubes can have chemical interactions with the polymer through opening of the pi bonds in the nanotube structure and subsequently nanotube can take part in polymerization reaction, thus grafting the polymer chains covalently bound to the clay surface [57, 58]. The authors also observed in this study that the position of vibration bands in the IR spectra was observed to increase, indicating that the pi bonds in the nanotubes could have been opened. However, it was suggested that the covalent functionalization provides much more attractive route as the generated reactive groups on the tips and surface of nanotubes can be much more useful in binding the nanotubes to the polymer chains during the course of polymerization. Composites generated using functionalized nanotubes were confirmed through IR spectroscopic characterization to have a chemical connection between the formed polymer and nanotubes. It was concluded that covalent surface functionalization in the presence of *in situ* polymerization to attach the polymer chains covalently to the surface of nanotubes is the best method for generating nanotube nanocomposites.

As one-dimensional materials have strong potential as building blocks in electronics, nanohybrid materials from CNTs and nanoparticles were reported in which the nanoparticles were covalently immobilized on the nanotubes surface [59–61]. To achieve theses functionalizations, the nanotubes were treated with nitric acid followed by thionyl chloride to generate COCl groups on the surface. Magnetite colloid solution was prepared in ethanol solution, to which 3-aminopropyltrimethoxysilane (APTS) was added with rapid stirring. APTS-coated magnetite nanoparticles were dried under vacuum at room temperature, which resulted in amine-terminated magnetite nanoparticles. These particles were reacted with COCl-treated nanotubes at room temperature using ultrasonification as explained in Figure 1.10. Transmission electron microscopy observations also revealed that the magnetite nanoparticles were deposited and homogenously distributed on the surface of the carbon nanotubes. It also demonstrated the effectiveness of the pretreatment of nanotubes in generating active sites on the carbon nanotubes. The resulting nanohybrids were also easily dispersible in aqueous solvents and were observed to be stable for more than 2 months; no precipitation of the inorganic material was observed. It should be noted that noncovalent immobilization of nanoparticles on the nanotubes surface has also been reported, but the covalent functionalization was reported to be more efficient and stronger in interactions between the components.

Covalent functionalization method was reported for the modification of SWCNTs with enzymes and amines [62]. In a typical experiment, SWNTs were refluxed in 4 M HNO_3 for 24 h and were exposed to 1 M HCl. The carboxylated SWNTs were then filtered and washed with water followed by drying in air.

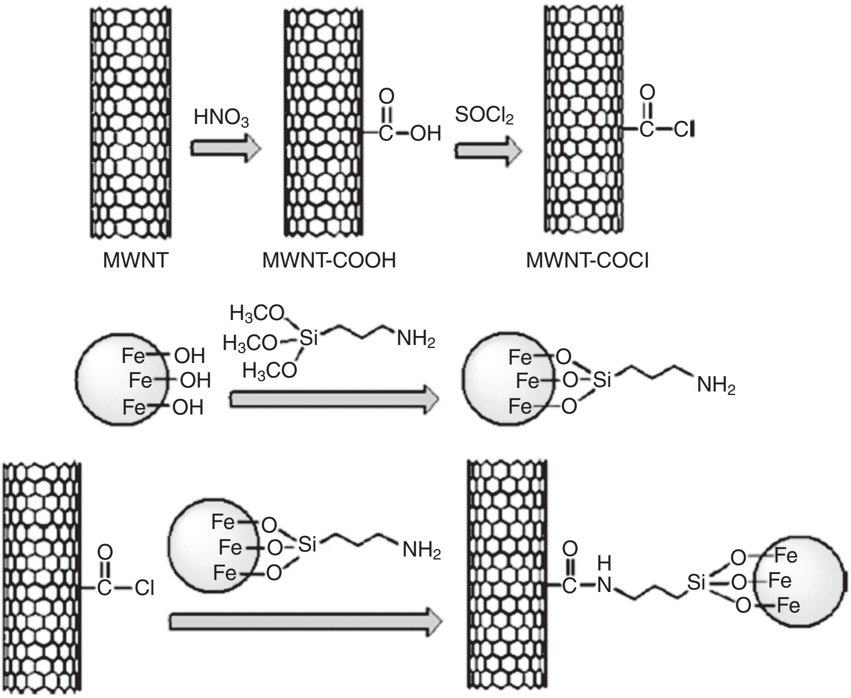

Figure 1.10 Covalent attachment of magnetite nanoparticles on the carbon nanotube surface. Reproduced from Ref. [61] with permission from Elsevier.

Acylation reactions with the acid-treated nanotubes were carried out by stirring the nanotubes in a 20 : 1 mixture of thionyl chloride and DMF at 70 °C for 24 h. The nanotubes were then filtered, washed with anhydrous THF, and dried under vacuum at room temperature. The so-obtained nanotubes were then reacted with desired amines using DMF as solvent, at 110 °C. The amines were used in excess, which after the reaction was washed first with DMF, followed by anhydrous THF. In the case of the enzymes, the reactions were carried out at low temperatures. Successful reactions of the following molecules with the surface groups on nanotubes could be achieved: porcine pancrease lipase (PPL), amino lipase (AK), *cis*-myrtanylamine, 2,4-dinitroaniline, 2,6-dinitroaniline, *N*-decyl-2,4,6-trinitroaniline, and *N*-(3-morpholinopropyl)-2,4,6-trinitroaniline). It was observed that the generated defects and covalent binding of amines on the surface after functionalization caused the reduction in electrical conductivity in the functionalized nanotubes. It was also observed that both the single nanotubes as well as bundles could be grafted, indicating that initial homogenous dispersion of nanotubes during functionalization is immensely important. Successful immobilization of a variety of amine as well as biological entities on the surface confirmed the potential as well as robustness of the functionalization

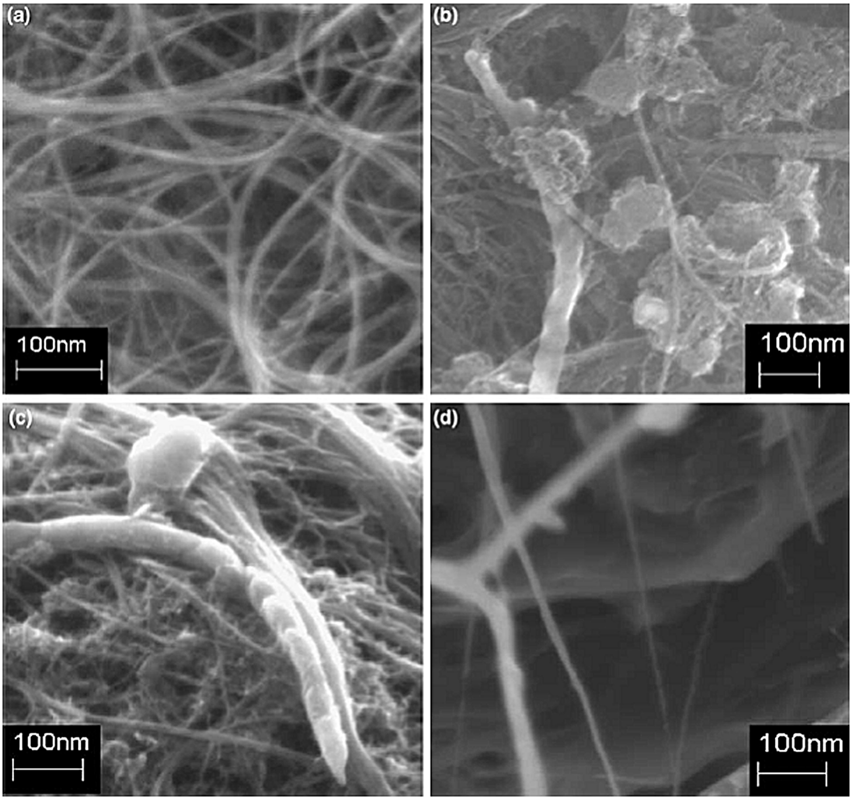

Figure 1.11 SEM images of (a) pristine SWNTs, (b) *cis*-myrtanylamine functionalized SWNTs, (c) AK functionalized SWNTs, and (d) PPL functionalized SWNTs. Reproduced from Ref. [62] with permission from Elsevier.

method. Figure 1.11 shows the SEM images of the untreated and treated nanotubes [62].

Grafting from the surface methods has been studied widely in detail and can also be directly applied on the nanotubes [63–68]. Qin *et al*. reported the polymerization of *n*-butyl methacrylate from the surface of nanotubes by using controlled living polymerization method [69]. To achieve such surface grafting, nanotubes were first refluxed in nitric acid, which generates acid functional groups on the sidewalls of the tubes. These acid groups were subsequently reacted with thionyl chloride to convert them into acyl chloride groups. An atom transfer radical polymerization agent 2-hydroxyethyl-2-bromopropionate (HEBP) was synthesized by the reaction of ethylene glycol and 2-bromopropionlybromide. The acyl chloride groups on the surface of nanotubes were then reacted with the ATRP initiator. After the ATRP ignition moiety was bound to the surface of nanotubes, these nanotubes could then be used to graft brushes of poly(*n*-butyl methacrylate) in the presence of CuCl and BiPy. Figure 1.12 shows the schematic of the functionalization process. The grafted brushes had significant effect on the solubility properties of nanotubes. This process also offers many other advantages: the amount of ATRP initiator on the surface can be controlled, the chain length of the grafts can also be tuned according to requirement, and a large number of monomers can be polymerized to graft brushes of various functionalities from the surface of nanotubes. Gao *et al.* also followed the similar grafting from the surface approach and polymerized MMA on the surface by using atom transfer radical polymerization [70]. Figure 1.13 shows the images of the pristine nanotubes as well as treated nanotubes where reaction conditions have been altered to change the grafting characteristics. Polymer thicknesses from 3.8 to 14 nm were grafted by changing the feed ratios, and the nanotubes after functionalization with poly(methyl methacrylate) could also be further reacted to form another layer of hydroxyethyl methacrylate (HEMA).

Ge *et al.* reported the chemical grafting of polyetherimides on the surface of nanotubes [71]. A polyetherimide (BisADA-DCB) was synthesized via the condensation polymerization of 4,4′-bis(4,4′-isopropylidene diphenoxy)-bis(phthalic anhydride) (BisADA) and 2,2′-dichloro-4,4′-biphenyldiamine (DCB) in *m*-cresol with isoquinonline at elevated temperatures via one-step imidization. The resulting BisADA-DCB containing diamine endgroups was observed to be soluble in many solvents such as chloroform, methylene chloride, THF, and cyclopentanone. The carboxylic acid functionalized MWNTs were reacted with polyetherimide and new characteristic bands were detected in the attenuated total reflection Fourier trans-

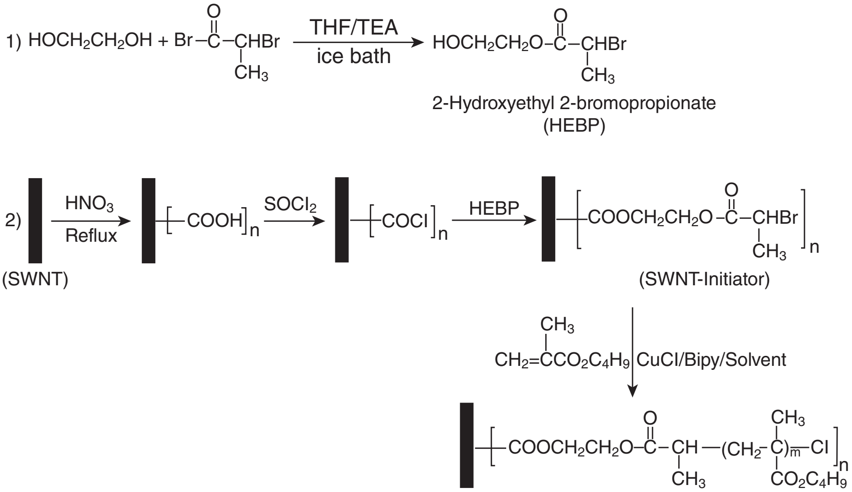

Figure 1.12 Atom transfer radical polymerization method from the grafting of poly(*n*-butyl acrylate) chains from the surface of nanotubes. Reproduced from Ref. [69] with permission from American Chemical Society.

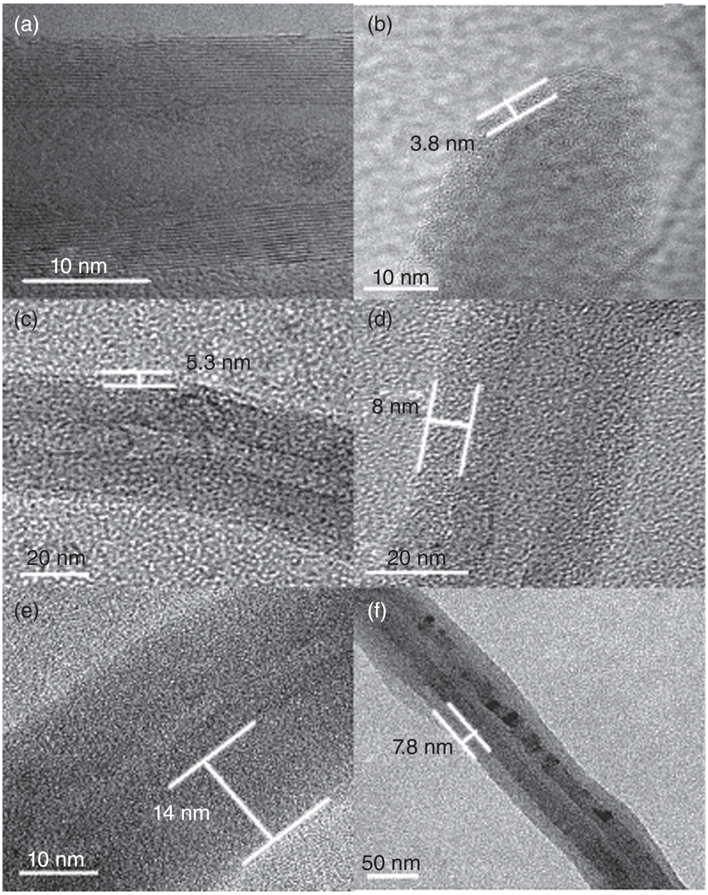

Figure 1.13 (a) Pristine nanotubes and (b–f) nanotubes modified with varying thicknesses of polymer film grafted from the surface. Reproduced from Ref. [70] with permission from American Chemical Society.

form IR spectroscopy. Transmission electron microscopy was also used to investigate the MWNTs before and after chemical grafting. A large population of MWNTs was coated by BisADA-DCB. A thin layer of BisADA-DCB with a thickness of 5–20 nm was observed. Figure 1.14 shows the schematic of functionalization process.

Attachment of diglycidyl ether of bisphenol A on the nanotubes surfaces was studied [72] to covalently functionalize the nanotubes. MWCNTs with acidic groups on the surface were reacted with epoxide-terminated molecule as shown in Figure 1.15. As the molecule had epoxy groups in both the ends, both the groups

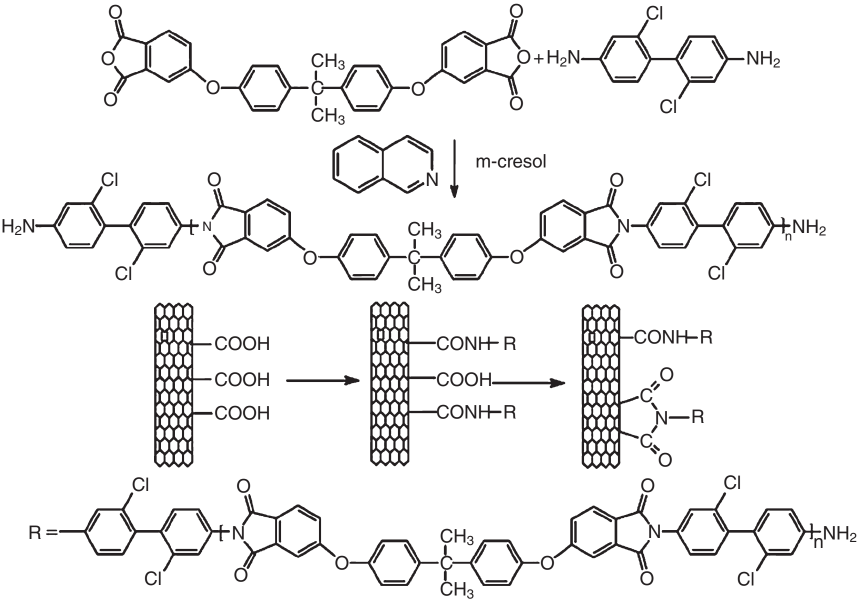

Figure 1.14 Functionalization of MWNT with polyetherimide. Reproduced from Ref. [71] with permission from American Chemical Society.

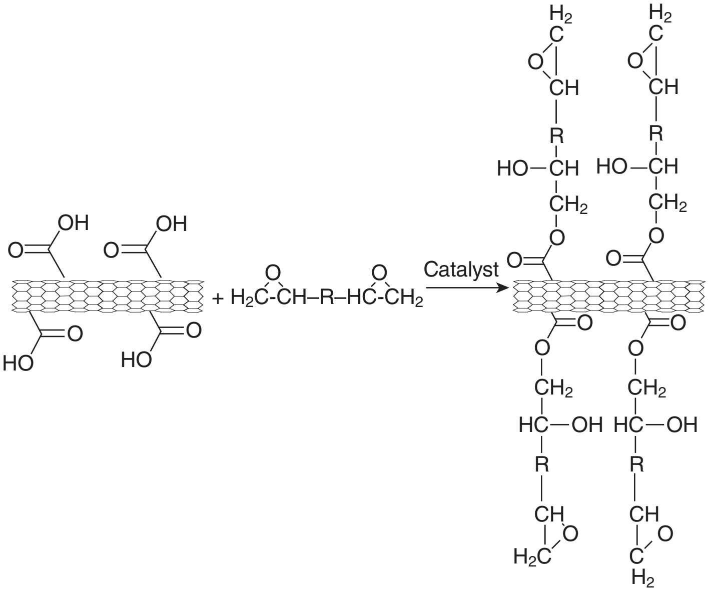

Figure 1.15 Epoxy functionalization of the nanotubes. Reproduced from Ref. [72] with permission from American Chemical Society.

could take part in the functionalization reactions, which was also confirmed with IR spectrometry. It was observed that the epoxide groups reacted either by the epoxide–epoxide reactions followed by the reaction of the epoxide ring with the carboxylic acid group on the nanotube, or both the epoxide groups can react with the acid groups present on the nanotube surface.

A novel approach to *in situ* surface functionalization of the nanotubes by the attachment of polystyrene chains to SWCNTs based on anionic polymerization scheme was reported by Viswanathan *et al.* [73] as shown in Figure 1.16. As produced nanotubes without any purification or surface treatment were used for the functionalization process, these procedures were suspected to introduce functionalities that hinder carbanion formation. To achieve the grafting, SWCNTs were dispersed by sonication in purified cyclohexane to which a slight excess of butyl lithium was added. This introduced carbanions on the SWCNT surface, which help to exfoliate the nanotube bundles because of the repulsion between the negatively charged nanotubes and also provided initiating sites for the polymerization of styrene. The small diameters of nanotubes offer high reactivities for the carbanion addition reactions owing to their high curvatures. Raman spectroscopy was used to confirm the evidence of formation of carbanions and subsequent attachment of polymer chains. On addition of styrene, both free butyl lithium and the nanotube carbanions were observed to initiate polymerization, resulting in an intimately mixed composite system. The polymerization could efficiently be terminated by the addition of degassed *n*-butanol.

Low-molecular-weight chitosan, a natural and green polymer, was covalently bound to the sidewalls of MWCNTs by a nucleophilic substitution reaction on the surface of nanotubes [74]. Amino and primary hydroxyl groups of chitosan were reported to contribute mainly to the formation of MWNT–chitosan structures. These groups reacted with COCl groups generated on the nanotube surfaces by

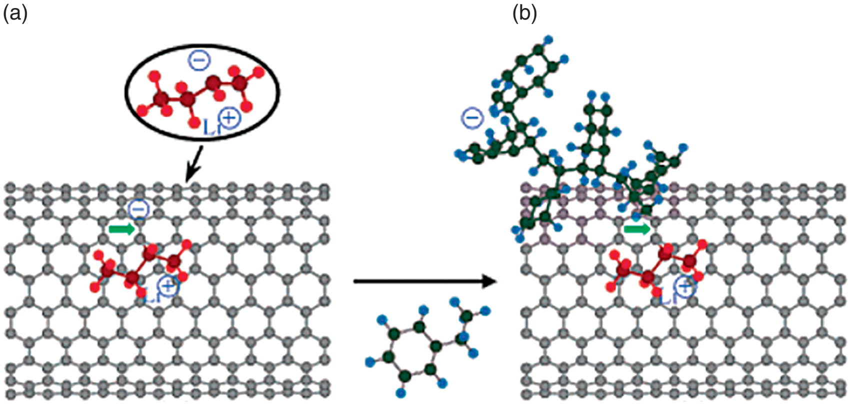

Figure 1.16 Covalent functionalization of nanotubes by anionic polymerization approach. Reproduced from Ref. [73] with permission from American Chemical Society.

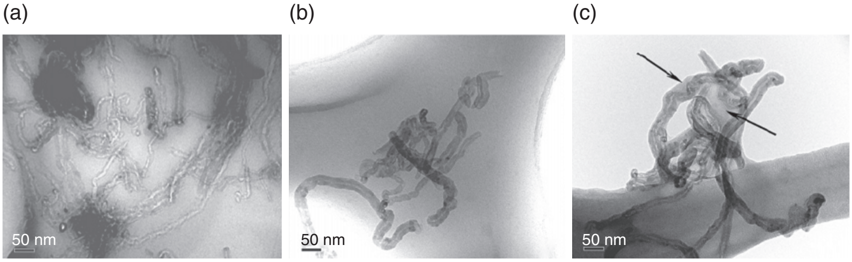

Figure 1.17 TEM images of (a) raw MWNTs, (b) cut and purified MWNTs, and (c) the MWNT-modified with chitosan. Arrows indicate the typical features of the attached polymer. Reproduced from Ref. [74] with permission from American Chemical Society.

acid treatment. By thermogravimerty, the extent of chitosan in the organically modified nanotubes was approximately 58 wt%, indicating a significant amount of chitosan grafting to the surface. It was observed from XPS data that a nitrogen-to-carbon ratio of 0.091 was present in the modified nanotubes, which was used to estimate the average degree of functionalization in the nanotubes. On the basis of this information, it is calculated that approximately four molecular chains of the LMCS were attached to 1000 carbon atoms of the nanotube sidewalls. The functionalized nanotubes were soluble in a variety of solvents like dimethylformamide, dimethyl acetamide, dimethylsulfoxide, and acetic acid aqueous solution. Figure 1.17 also shows the TEM images of the nanotubes before and after the modification of the tubes with chitosan.

Microwave irradiation for the acid functionalization of both single and MWCNTs was also reported, which caused the generation of significant amount of hydrophilic functional groups on the surface [75]. Immobilization of DNA on the nanotubes was reported by covalent functionalization of nanotubes with polyethylenimine (PEI) [76]. Plasma deposition of polymers as thin films on the surface of nanotubes has also been reported [77, 78]. Fluorinated SWCNTs have also been reported to demonstrate higher potential for further derivatization due to higher reactivity than the unfunctionalized nanotubes [79–81].

References

1 Ajayan, P.M. and Ebbesen, T.W. (1997) *Rep. Prog. Phys.*, **60**, 1025.

2 Dresselhaus, M.S., Dresselhaus, G., and Eklund, P.C. (1996) *Science of Fullerenes and Carbon Nanotube*, Academic Press, New York.

3 Dai, H. (2002) *Acc. Chem. Res.*, **35**, 1035.

4 Iijima, S. (1991) *Nature*, **354**, 56.

5 Endo, M. (1978) (In Japanese), PhD Thesis, Nagoya University, Japan.

6 Harris, P.J.F. (2001) *Carbon Nanotubes and Related Structures, New Materials for the Twenty-First Century*, Cambridge University Press, Cambridge.

7 O'Connell, M.J. (2006) *Carbon Nanotubes Properties and Applications*, CRC Taylor & Francis, Boca Raton, FL.

8 Harris, P.J.F. (2001) *Carbon Nanotubes and Related Structures*, Cambridge University Press, Cambridge.

9 Ajayan, P.M. (1999) *Chem. Rev.*, **99**, 1787.

10 Xie, X.-L., Mai, U.-W., and Zhou, X.-P. (2005) *Mater. Sci. Eng. R*, **49**, 89.

11 Pavlidoua, S. and Papaspyrides, C. (2008) *Prog. Polym. Sci.*, **33**, 1119.

12 Mark, J.E. (1996) *Polym. Eng. Sci.*, **36**, 2905.

13 Reynaud, E., Gauthier, C., and Perez, J. (1999) *Rev. Metall./Cah. Inf. Tech.*, **96**, 169.

14 Calvert, P. (1997) *Carbon Nanotubes* (ed. T.W. Ebbesen), CRC Press, Boca Raton, FL.

15 Favier, V., Canova, G.R., Shrivastava, S.C., and Cavaille, J.Y. (1997) *Polym. Eng. Sci.*, **37**, 1732.

16 Mittal, V. (2006) Organic modifications of clay and polymer surfaces for specialty applications, PhD Thesis, ETH Zurich.

17 Journet, C., Master, W.K., Bernier, P., Loiseau, A., Lamy de la Chapelle, M., Lefrant, S., Deniard, P., Lee, R., and Fischer, J.E. (1997) *Nature*, **388**, 756.

18 Ebbesen, T.W. and Ajayan, P.M. (1992) *Nature*, **358**, 220.

19 Colbert, D.T., Zhang, J., McClure, S.M., Nikolaev, P., Chen, Z., Hafner, J.H., Owens, D.W., Kotula, P.G., Carter, C.B., Weaver, J.H., Rinzler, A.G., and Smalley, R.E. (1994) *Science*, **266**, 1218.

20 Thess, A., Lee, R., Nikolaev, P., Dai, H., Petit, P., Robert, J., Xu, C., Lee, Y.H., Kim, S.G., Rinzler, A.G., Colbert, D.T., Scuseria, G.E., Tomanek, D., Fischer, J.E., and Smalley, R.E. (1996) *Science*, **273**, 483.

21 Cheng, H.M., Li, F., Su, G., Pan, H.Y., He, L.L., Sun, X., and Dresselhaus, M. (1998) *Appl. Phys. Lett.*, **72**, 3282.

22 Rao, C.N.R., Govindaraj, A., Sen, R., and Satishkumar, B. (1998) *Mater. Res. Innov.*, **2**, 128.

23 Andrews, R., Jacques, D., Rao, A.M., Derbyshire, F., Qian, D., Fan, X., Dickey, E.C., and Chen, J. (1999) *Chem. Phys. Lett.*, **303**, 467.

24 Ren, Z.F., Huang, Z.P., Xu, J.W., Wang, J.H., Bush, P., Siegel, M.P., and Provenico, P.N. (1998) *Science*, **282**, 1105.

25 Singh, C., Shaffer, M.S.P., Kinloch, I.A., and Windle, A.H. (2002) *Physica B*, **323**, 339.

26 Kuzmany, H., Kukovecz, A., Simon, F., Holzweber, M., Kramberger, C., and Pichler, T. (2004) *Synth. Metals*, **141**, 113.

27 Zhu, J., Yudasaka, M., Zhang, M., and Ijima, S. (2004) *J. Phys. Chem. B*, **108**, 11317.

28 Balvlavoine, F., Schultz, P., Richard, C., Mallouh, V., Ebbeson, T.W., and Mioskowski, C. (1999) *Angew. Chem. Int. Eng. Ed.*, **38**, 1912.

29 Shim, M., Kam, N.W.S., Chen, R.J., Li, Y., and Dai, H. (2002) *Nano Lett.*, **2**, 285.

30 Harris, J.M., and Zalipsky, S. (1997) *Poly(Ethylene Glycol): Chemistry and Biological Application*, American Chemical Society, Washington, DC.

31 Szycher, M. (ed.) (1983) *Biocompatible Polymers, Metals and Composites*, Technomic, Lancaster, PA.

32 Ostuni, E., Chapman, R.G., Holmlin, R.E., Takayama, S., and Whitesides, G.M. (2001) *Langmuir*, **17**, 5605.

33 O'Connell, M.J., Boul, P., Ericson, L.M., Huffman, C., Wang, Y., Haroz, E., Kuper, C., Tour, J., Ausman, K.D., and Smalley, R.E. (2001) *Chem. Phys. Lett.*, **342**, 265.

34 Fu, Q., Lu, C., and Liu, J. (2002) *Nano Lett.*, **2**, 329.

35 Gomez, F.J., Chen, R.J., Wang, D., Waymouth, R.M., and Dai, H. (2003) *Chem. Commun.*, 190.

36 Liu, Y.-T., Zhao, W., Huang, Z.-Y., Gao, Y.-F., Xie, X.-M., Wang, X.-H., and Ye, X.-Y. (2006) *Carbon*, **44**, 1613.

37 Carillo, A., Swartz, J.A., Gambe, J.M., Kane, R.S., Chakrapani, N., Wei, B., and Ajayan, P. (2003) *Nano Lett.*, **3**, 1437.

38 Decher, G., Lvov, Y., and Schmitt, J. (1994) *Thin Solid Films*, **244**, 772.

39 Stroock, A.D., Kane, R.S., Weck, M., Metallo, S.J., and Whitesides, G.M. (2003) *Langmuir*, **10**, 2466.

40 Korneev, D., Lvov, Y., Decher, G., Schmitt, J., and Yaradaikin, S. (2005) *Physica B*, **213-214**, 954.

41 Hammond, P.T. (1999) *Curr. Opin. Colloid Interface Sci.*, **4**, 430.

42 Schmitt, J., Grünewald, T., Decher, G., Pershan, P.S., Kjaer, K., and Lösche, M. (1993) *Macromolecules*, **26**, 7058.

43 Wang, T.C., Chen, B., Rubner, M.F., and Cohen, R.E. (2001) *Langmuir*, **17**, 6610.

44 Caruso, F., Caruso, R.A., and Mohwald, H. (1998) *Science*, **282**, 1111.

45 Chapman, R.G., Ostuni, E., Liang, M.N., Meluleni, G., Kim, E., Yan, L., Pier, G., Warren, H.S., and Whitesides, G.M. (2001) *Langmuir*, **17**, 1225.

46 Chen, R.J., Zhang, Y., Wang, D., and Dai, H. (2001) *J. Am. Chem. Soc.*, **123**, 3838.

47 Katz, E. (1994) *J. Electroanal. Chem.*, **365**, 157.

48 Kang, Y., and Taton, T.A. (2003) *J. Am. Chem. Soc.*, **125**, 5650.

49 Huang, H.Y., Kowalewski, T., Remsen, E.E., Gertzmann, R., and Wooley, K. (1997) *J. Am. Chem. Soc.*, **119**, 11653.

50 Zhang, L., Shen, H., and Eisenberg, A. (1997) *Macromolecules*, **30**, 1001.

51 Star, A., Stoddart, J.F., Steuerman, D., Diehl, M., Boukai, A., Wong, E.W., Yang, X., Chung, S.-W., Choi, H., and Heath, J. (2001) *Angew. Chem. Int. Ed.*, **40**, 1721.

52 Vedala, H., Choi, Y.C., Kim, G., Lee, E., and Choi, W.B. (2004). Proceedings of 2nd International Latin American and Caribbean Conference for Engineering and Technology, Florida, USA.

53 Star, A., Steurmann, D.W., Heath, J.R., and Stoddart, J.F. (2002) *Angew. Chem. Int. Ed.*, **41**, 2508.

54 Bandyopadhyaya, R., Nativ-Roth, E., Regev, O., and Yerushalmi-Rozen, R. (2002) *Nano Lett.*, **2**, 25.

55 Yang, Z., Chen, X., Chen, C., Li, W., Zhang, H., Xu, L., and Yi, B. (2007) *Polym. Compos.*, doi: 10.1002/pc.20254.

56 Velasco-Santos, C., Martinez-Hernandez, A.L., Fischer, F.T., Ruoff, R., and Castano, V. (2003) *Chem. Mater.*, **15**, 4470.

57 Jia, Z., Wang, Z., Xu, C., Liang, J., Wei, B., Wu, D., and Zhu, S. (1999) *Mater. Sci. Eng.*, **A271**, 395.

58 Geng, H.Z., Rosen, R., Zheng, B., Shimoda, H., Fleming, L., Liu, J., and Zhou, O. (2002) *Adv. Mater.*, **14**, 1387.

59 Pan, B., Gao, F., and Gu, H. (2005) *J. Colloid Interface Sci.*, **284**, 1.

60 Xu, Y., Gao, C., Kong, H., Yan, D., Jin, Y.Z., and Watts, P.C.P. (2004) *Macromolecules*, **37**, 8846.

61 Xu, P., Cui, D., Pan, B., Gao, F., He, R., Li, Q., Huang, T., Bao, C., and Yang, H. (2008) *Appl. Surf. Sci.*, **254**, 5236.

62 Wang, Y., Iqbal, Z., and Malhotra, S. (2005) *Chem. Phys. Lett.*, **402**, 96.

63 Matyjaszewski, K., Miller, P.J., Shukla, N., Immaraporn, B., Gelman, A., Luokala, B.B., Siclovan, T.M., Kickelbick, G., Vallant, T., Hoffmann, H., and Pakula, T. (1999) *Macromolecules*, **32**, 8716.

64 Vestal, C.R. and Zhang, Z.J.J. (2002) *J. Am. Chem. Soc.*, **124**, 14312.

65 Jordan, R. and Ulman, A. (1998) *J. Am. Chem. Soc.*, **120**, 243.

66 Jordan, R., Ulman, A., Kang, J.F., Rafailovich, M.H., and Sokolov, J. (1999) *J. Am. Chem. Soc.*, **121**, 1016.

67 Weck, M., Jackiw, J.J., Rossi, R.R., Weiss, P.S., and Grubbs, R.H. (1999) *J. Am. Chem. Soc.*, **121**, 4088.

68 Mittal, V. (2007) *J. Colloid Interface Sci.*, **314**, 141.

69 Qin, S., Qin, D., Ford, W.T., Resasco, D.E., and Herrera, J.E. (2004) *J. Am. Chem. Soc.*, **126**, 170.

70 Kong, H., Gao, C., and Yan, D. (2004) *J. Am. Chem. Soc.*, **126**, 412.

71 Ge, J.J., Zhang, D., Li, Q., Hou, H., Graham, M.J., Dai, L., Harris, F.W., and Cheng, S.Z.D. (2005) *J. Am. Chem. Soc.*, **127**, 9984.

72 Eitan, A., Jiang, K., Dukes, D., Andrews, R., and Schadler, L. (2003) *Chem. Mater.*, **15**, 3198.

73 Viswanathan, G., Chakrapani, N., Yang, H., Wei, B., Chung, H., Cho, K., Ryu, C.Y., and Ajayan, P.M. (2003) *J. Am. Chem. Soc.*, **125**, 9258.

74 Ke, G., Guan, W., Tang, C., Guan, W., Zeng, D., and Deng, F. (2007) *Biomacromolecules*, **8**, 322.

75 Kakade, B.A. and Pillai, V.K. (2008) *Appl. Surf. Sci.*, **254**, 4936.

76 Liu, Y., Wu, D.-C., Zhang, Y.-D., Jiang, X., He, C.-B., Chung, T.S., Goh, S.H., and Leong, K.W. (2005) *Angew. Chem. Int. Ed.*, **44**, 4782.

77 Shi, D., Lian, J., He, P., Wang, L.M., van Ooij, W.J., Schulz, M., Liu, Y., and Mast, D. (2002) *Appl. Phys. Lett.*, **81**, 5216.

78 Tseng, C.-H., Wang, C.-C., and Chen, C.-Y. (2007) *Chem. Mater.*, **19**, 308.

79 Khabashesku, V.N., Billups, W.E., and Margrave, J.L. (2002) *Acc. Chem. Res.*, **35**, 1087.

80 Khabashesku, V.N. and Margrave, J.L. (2004) *Encyclopedia of Nanoscience and Nanotechnology* (ed. H.S. Nalwa), American Scientific Publishers, Stevenson Ranch, CA.

81 Pulikkathara, M.X., Kuznetsov, O.V., and Khabashesku, V.N. (2008) *Chem. Mater.*, **20**, 2685.