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# Functionalization of Carbon Nanotubes

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## 1. Introduction

Albeit initially reported by a Russian group and reported again by Oberlin and co-workers (Oberlin et al., 1976), carbon nanotubes (CNTs) were first brought to the attention of greater scientific community by Ijima in 1991. It was not until 1991 that CNTs came to limelight unfolding its exotic properties. Following this report, academic interest in this one-dimensional nanomaterial has grown remarkably and phenomenal number of research are being carried out worldwide. Its outstanding properties such as high mechanical strength, flexibility and impressive electrical and thermal conductivity make itself attractive and potential candidate for various applications. Despite CNTs's exceptional properties, there are two main limitations that hinder its use. The surface energy of CNTs is significantly different from that of matrices such as common organic solvents or polymers and CNTs may not have chemical affinity to the organic matrices and thus, the dispersion of CNTs into matrices is the biggest obstacle in practice (Song et al., 2005). In addition, the seamless surface of CNTs cannot provide physical interaction between CNTs and matrix (Ajayan et al., 2000). The modification of CNTs with other materials, makes it the most attractive and ultimate candidate for a plethora of applications which includes nanodevices, to organic electronics. In terms of the practical challenges that must be addressed to expand CNTs application scope in various potential fields of nanotechnology; many protocols have been proposed and considerable amount of research work is being focused on the interfacial molecular engineering of CNTs, aiming at improving their state of interaction with macromolecules, mainly to optimize the final properties of the hybrid nanomaterials. These protocols to prepare such hybrid composites have triggered burgeoning interest and to realize most of these applications practically, CNTs are most frequently functionalized with various kinds of technologically important polymers to improve the properties of the end material. Such assemblies have already suggested that the functionalization of polymers to CNTs draws equal importance in materials development for future applications in constructing optoelectronic devices. This chapter will focus and discuss the frequently used methods to functionalize CNTs namely; covalent and non-covalent strategies. Of particular importance, this chapter will also shed light on the 'pros and cons' of the frequent methods and alternative methods that have been developed in the recent past which can open the

path for their facile manipulation and processing in physiological environments and also to overcome difficulties in processing CNTs.

## 2. Carbon nanotubes

CNT is one of carbon allotropes such as diamond, graphite, graphene, fullerene and amorphous carbon. But, it is the one-dimensional carbon form which can have an aspect ratio greater than 1000 makes it interesting (Figure 1). The bonding in carbon nanotubes is  $sp^2$ , with each atom joined to three neighbours, as in graphite. CNTs are rolled-up graphene sheets (graphene is an individual graphite layer). This type of structural bonding, which is stronger than the  $sp^3$  bonds found in diamond, provides the molecules with their unique strength. Under high pressure, nanotubes can merge together, trading some  $sp^2$  bonds for  $sp^3$  bonds, giving the possibility of producing strong, unlimited length wires through high-pressure nanotube linking.



Fig. 1. Crystal structures of different allotropes of carbon. (Left to right) Three-dimensional diamond and graphite (3D); two-dimensional graphene (2D); one-dimensional nanotubes (1D); and zero-dimensional buckyballs (0D) (Mikhail & Katsnelson, 2007).

The properties of nanotubes depend on atomic arrangement (on how the sheets of graphite are 'rolled'), the diameter and length of the tubes, and morphology, or nano structure. Single walled nanotubes (SWNTs) consist of a single sheet of graphene rolled seamlessly to form a cylinder with diameter of order of 1 nm and length of up to centimeters (Bethune et al., 1993; Ijima et al., 1993). Multi-walled nanotubes (MWNTs) consist of an array of such cylinders formed concentrically and separated by 0.35 nm, similar to the basal plane separation in graphite (Ijima 1991). MWNTs can have diameters from 2 to 100 nm and lengths of tens of microns. Apart from these two main types, there was also the few-walled carbon nanotube (FWNTs) that was reported and found to have peculiar properties, often with much better structural integrity (Hutchinson et al. 2001).

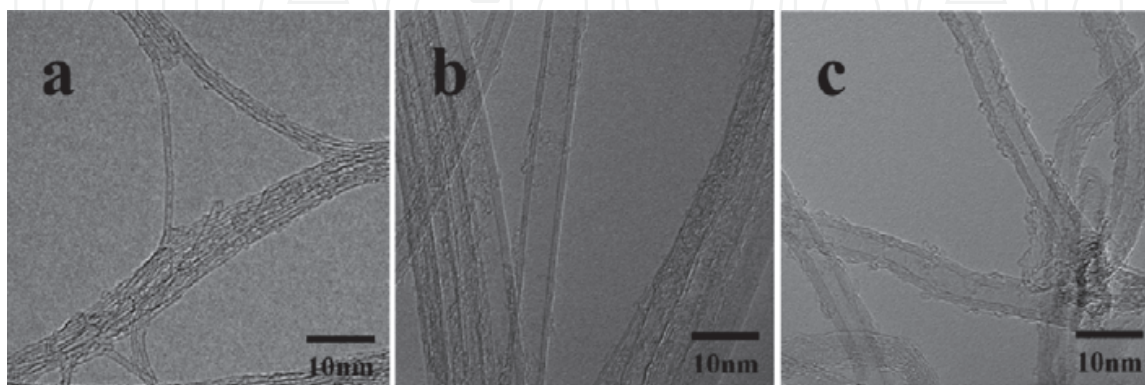


Fig. 2. TEM images of different types of CNTs: (a) single-walled carbon nanotubes; (b) few-walled carbon nanotubes; (c) multi-walled carbon nanotubes (Huo et al. 2009).

SWNTs are formed by rolling a sheet of graphene into a cylinder along an  $(m, n)$  lattice vector in the graphene (Figure 3). The  $(m, n)$  indices determine the diameter and chirality. Three types of SWNTs are revealed with these values: when  $n = m$ , the nanotube is called “armchair” type ( $= 0^\circ$ ); when  $m = 0$ , then it is of the “zigzag” type ( $= 30^\circ$ ). Otherwise, when  $n \neq m$ , it is a “chiral” tube and takes a value between  $0^\circ$  and  $30^\circ$ . The value of  $(m, n)$  determines the chirality of the nanotube and affects the optical, mechanical and electronic properties. For typical diameters, all armchair SWNTs and one-third of all zigzag nanotubes are metallic, the rest are semiconducting (Hamada et al.; 1992).

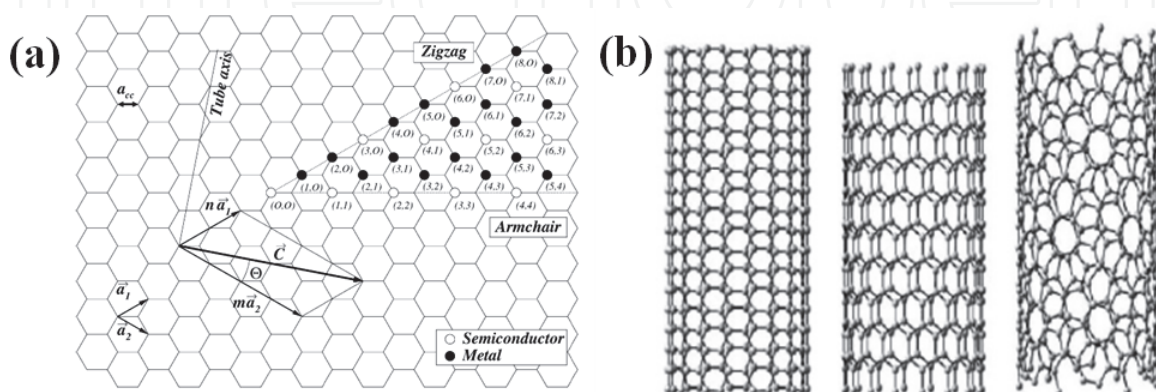


Fig. 3. (a) definition of the chiral vector describing the unit cell of a SWNT (Belin & Epron 2005); (b) CG images of armchair  $(n, n)$ , zigzag  $(n, 0)$ , and chiral nanotubes (Popov 2004).

It is clear that CNTs have many advantages over other materials in terms of mechanical, electrical and thermal properties although there is no consensus on the exact properties of CNTs (Table 1). Theoretical and experimental results have shown unusual mechanical properties with Young's modulus as high as 1.2 TPa and tensile strength of 50–200 GPa (Qian et al.; 2002). The relatively high values of modulus and strength values have been measured on high quality SWNT and arc discharge MWNT. However, CVD-MWNT was measured to have a modulus of 0.45 TPa and tensile strength of  $\sim 4$  GPa (Xie et al.; 2000). The much larger variation in modulus for CVD-MWNT compared to arc-MWNT strongly suggests that the modulus is very sensitive to defect concentration and type.

Depending on the relationship between this axial direction and the unit vectors describing the hexagonal lattice, CNTs can either be metallic or semi-metallic. Semi-metallic nanotubes have band gaps that scale inversely with diameter, ranging from approximately 1.8 eV for very small diameter nanotubes to 0.18 eV for the widest possible stable SWNT (Elliot et al.; 2004). In addition, carrier mobility as high as  $105 \text{ cm}^2/\text{Vs}$  have been observed in semi-conducting nanotubes (Kim et al.; 2004). Superconductivity has also been observed in SWNTs at the transition temperatures of 5 K (Tang et al.; 2001). CNTs are also very conductive for phonons. Theory predicts a room temperature thermal conductivity of up to  $6000 \text{ W/m} \cdot \text{K}$  (Che et al.; 2000 & Osman et al.; 2001) but, the values around  $200 \text{ W/m} \cdot \text{K}$  have been measured (Hone et al.; 2002). These properties offer CNTs great potential for wide applications in field emission, conducting plastics, thermal conductors, energy storage, conductive adhesives, thermal interface materials, structural materials, fibers, catalyst supports, biological applications, air and water filtration, ceramics to name a few (Thostenson et al. 2001; Ajayan et al.; 2003; Coleman et al.; 2006).

|                      |                                                                                                                                                                                 |                                                                                              |
|----------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------|
| Property             | Carbon nanotubes                                                                                                                                                                | Graphite                                                                                     |
| Lattice structure    | (Cylindrical) hexagonal lattice helicity<br>Nanotubes: ropes, tubes arranged in triangular lattice with lattice parameters of $a = 1.7 \text{ nm}$ , tube-tube distance = 0.314 | Planar hexagonal, plane-to-plane distance $c = 0.335$                                        |
| Specific gravity     | 0.8-1.8 $\text{gcc}^{-1}$ (theoretical)                                                                                                                                         | 2.26 $\text{gcc}^{-1}$                                                                       |
| Elastic modulus      | $\sim 1 \text{ TPa}$ for SWNT<br>$\sim 0.3\text{-}1 \text{ TPa}$ for MWNT                                                                                                       | 1 TPa (in-plane)                                                                             |
| Strength             | 50-500 GPa for SWNT<br>10-50 GPa for MWNT                                                                                                                                       |                                                                                              |
| Resistivity          | $\sim 5\text{-}50 \text{ micro-ohm cm}$                                                                                                                                         | 50 (in-plane)                                                                                |
| Thermal conductivity | 3000 $\text{W m}^{-1}\text{K}^{-1}$ (theoretical)                                                                                                                               | 3000 $\text{W m}^{-1}\text{K}^{-1}$ (in-plane)<br>6 $\text{W m}^{-1}\text{K}^{-1}$ (c axis)  |
| Thermal expansion    | Negligible (theoretical)                                                                                                                                                        | $-1 \times 10^{-6} \text{ K}^{-1}$ (in-plane)<br>$29 \times 10^{-6} \text{ K}^{-1}$ (c axis) |
| Oxidation in air     | $>700 \text{ }^{\circ}\text{C}$                                                                                                                                                 | 450-650 $^{\circ}\text{C}$                                                                   |

Table 1. Theoretical and experimentally measured properties of carbon nanotubes (Schadler 2004).

The synthesis methods for CNTs include arc-discharge (Journet et al. 1997), laser ablation (Rinzler et al. 1998), gas-phase catalytic growth from carbon monoxide (Nikolaev et al. 1999) and chemical vapor deposition (CVD) from hydrocarbons (Ren et al 1999 & 2007). The arc-discharge and laser ablation are well established in producing high-quality and nearly perfect nanotube structures. But, due to their scale-up limitations the production cost is too high hence limiting its access. During the synthesis process, impurities in the form of catalyst particles, amorphous carbon and non-tubular fullerenes are also produced. Thus, subsequent purification steps are required to separate the tubes. The gas-phase catalytic growth with carbon monoxide as the carbon source yielded in quantity high-purity single walled nanotubes at the highest accessible temperature and pressure (1200  $^{\circ}\text{C}$ , 10 atm). However, this method is not economically practical due to high temperature and pressure of the synthesis conditions. The CVD process tended to tend nanotubes with fewer impurities and was more amenable to large-scale processing. Therefore, the CVD method has the highest potential to produce a large quantity and high purity of CNTs.

| method                | arc discharge                                                                                       | laser ablation                                                                    | chemical vapor deposition                                                |
|-----------------------|-----------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|--------------------------------------------------------------------------|
| description           | arc evaporation of graphite in the presence of inert gas; CNT formed on electrodes during quenching | vaporization of graphite target by laser; CNT formed on receiver during quenching | decomposition of hydrocarbons over transition metal catalyst to form CNT |
| operating temperature | $\approx 3000 \text{ }^{\circ}\text{C}$                                                             | $\approx 3000 \text{ }^{\circ}\text{C}$                                           | $<1200 \text{ }^{\circ}\text{C}$                                         |
| operating pressure    | 50-7600 Torr generally under vacuum                                                                 | 200-750 Torr generally under vacuum                                               | 760-7000 Torr                                                            |
| advantages            | good quality CNTs                                                                                   | good quality CNTs; single conformation SWNT formed (10, 10)                       | easy scale up; synthesis on templates possible                           |
| disadvantages         | difficult to scale up                                                                               | difficult to scale up; expensive                                                  | quality of CNT not as good                                               |

Table 2. Comparison of the established techniques for CNT synthesis (See et al. 2007).

### 3. Functionalization of carbon nanotubes

The main problem with the majority of popular synthetic methods is that they produce samples yielding a mixture of various diameters and chiralities of nanotubes that are normally contaminated with metallic and amorphous impurities. Thus, post-synthesis chemical processing protocols (Strano et al.; 2004 & Li et al.; 2002) that purify tubes that can also separate individual tubes according to diameter and chirality by taking advantage of their differential reactivities are often the only viable routes to rational and predictable manipulation of the favorable electronic and mechanical properties of these materials (Niyogi et al.; 2002 & Tasis et al.; 2003).

The full potential of CNTs as reinforcements has been severely limited due to poor interfacial interaction, van der Waals interaction, between CNTs and polymer matrix. The nature of dispersion problem for CNTs is rather different from other conventional fillers, such as spherical particles and carbon fibers, because CNTs are characteristic of small diameter in nanometer scale with high aspect ratio ( $>1000$ ) and thus possessing large surface area. In addition, the commercialized CNTs are supplied in the form of heavily entangled bundles, resulting in inherent difficulties in dispersion.

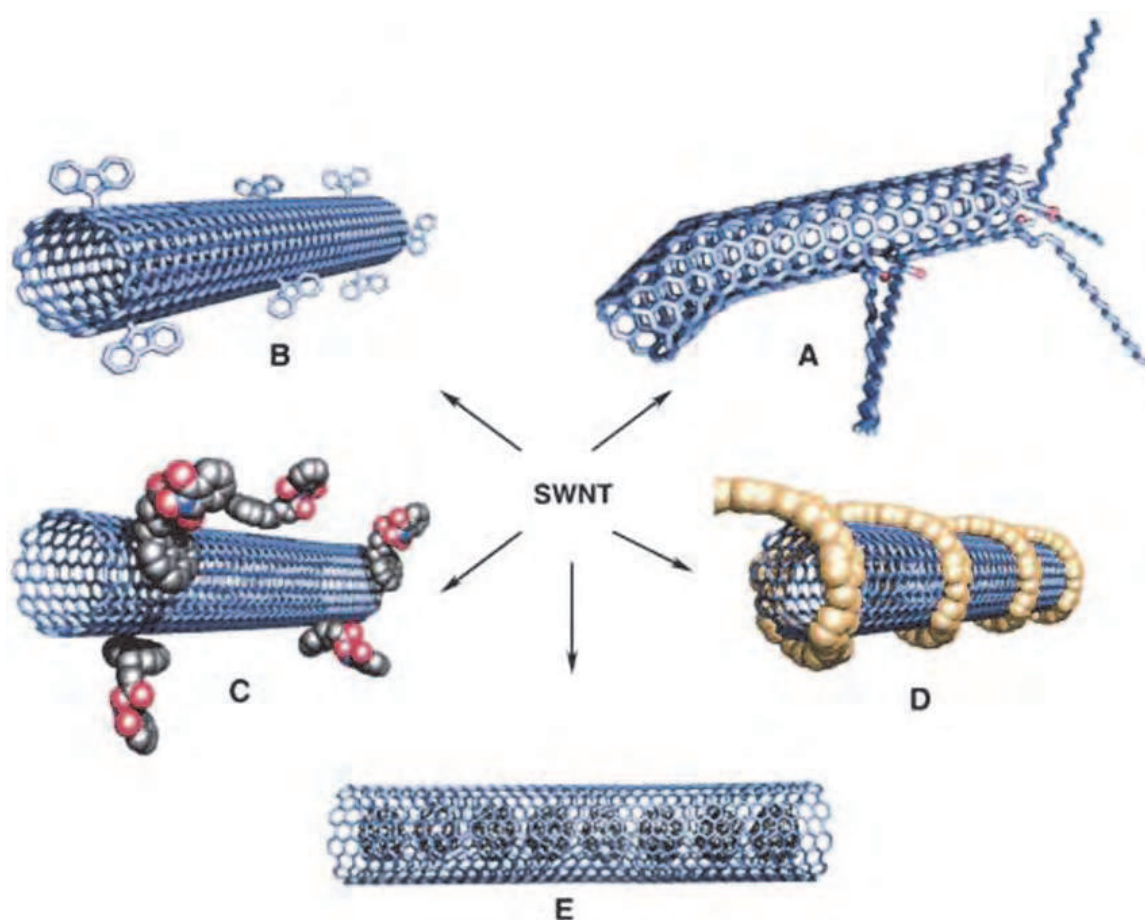


Fig. 4. Functionalization possibilities for SWNTs: a) defect-group functionalization, b) covalent sidewall functionalization, c) non-covalent exohedral functionalization with surfactants, d) non-covalent exohedral functionalization with polymers, and e) endohedral functionalization with, for example,  $C_{60}$ . For methods B-E, the tubes are drawn in idealized fashion, but defects are found in real situations (Hirsch 2002).

To resolve those problems, it has been directed towards developing methods to modify surface properties of CNTs. These approaches can be simply divided into chemical (covalent) and physical (noncovalent) functionalization as interactions between active materials and CNTs. The characterization corresponding to these methods are summarized in Figure 4.

### 3.1 Covalent functionalization

The end caps of nanotubes tend to be composed of highly curved fullerene-like hemispheres, which are therefore highly reactive, as compared with the side walls (Hirsch 2002 & Sinnott 2002). The sidewalls themselves contain defect sites such as pentagon-heptagon pairs called Stone-Walls defects,  $sp^3$ -hybridized defects, and vacancies in the nanotube lattice (Figure 5) (Hirsch 2002).

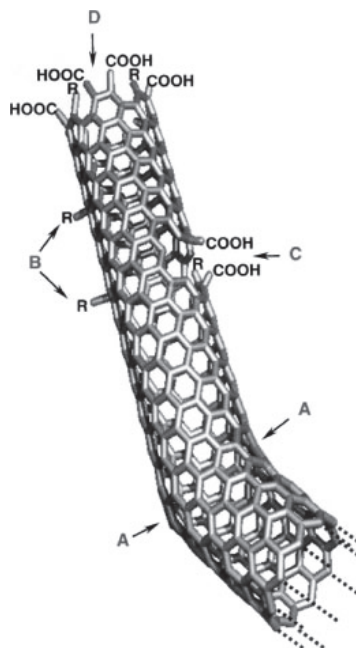


Fig. 5. Typical defects in a SWNT. a) five-or seven-membered rings in the carbon framework, instead of the normal six-membered ring, leads to a bend in the tube. b)  $sp^3$ -hybridized defects ( $R=H$  and  $OH$ ). c) carbon framework damaged by oxidative conditions, which leaves a hole lined with  $-COOH$  groups. d) open end of the SWNT, terminated with  $COOH$  groups. Besides carboxyl termini, the existence of which has been unambiguously demonstrated, other terminal groups such as  $-NO_2$ ,  $-OH$ ,  $-H$ , and  $=O$  are possible (Hirsch 2002).

Chemical functionalization is based on the covalent bond of functional groups onto carbon form of CNTs. It can be performed at the end caps of nanotubes or at their sidewalls which have many defects. Direct covalent sidewall functionalization is associated with a change of hybridization from  $sp^2$  to  $sp^3$  and a simultaneous loss of  $p$ -conjugation system on graphene layer (Figure 6). This process can be made by reaction with some molecules of a high chemical reactivity. In the first approach, fluorination of CNTs has become popular for initial investigation of the covalent functionalization because the CNTs sidewalls are expected to be inert (Bianco et al.; 2008 & Mickelson et al.; 1998). The fluorinated CNTs have C-F bonds that are weaker than those in alkyl fluorides (Kelly et al. 1993) and thus

providing substitution sites for additional functionalization (Touhara et al.; 2002). Successful replacements of the fluorine atoms by amino, alkyl and hydroxyl groups have been achieved (Stevens et al.; 2003). Other methods, including cycloaddition, such as Diels-Alder reaction, carbene and nitrene addition (Hu et al. 2003), chlorination, bromination (Unger et al. 2002), hydrogenation (Kim et al.; 2002), azomethineylides (Tagmatarchis 2004) have also been successfully employed.

Another method is defect functionalization of CNTs. These intrinsic defects are supplemented by oxidative damage to the nanotube framework by strong acids which leave holes functionalized with oxygenated functional groups (Chen et al.; 1998). In particular, treatment of CNTs with strong acid such as  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  or a mixture of them (Esumi et al.; 1996 & Liu et al.; 1998), or with strong oxidants such as  $\text{KMnO}_4$  (Yu et al.; 1998), ozone (Sham et al.; 2006), reactive plasma (Wang et al.; 2009) tend to open these tubes and to subsequently generate oxygenated functional groups such as carboxylic acid, ketone, alcohol and ester groups, that serve to tether many different types of chemical moieties onto the ends and defect sites of these tubes. These functional groups have rich chemistry and the CNTs can be used as precursors for further chemical reactions, such as silanation (Ma et al.; 2006), polymer grafting Sano et al. 2001 & Kong et al. 2003), esterification (Hamno et al. 2002), thiolation (Liu et al.; Science 1998), and even some biomolecules (Coleman et al.; 2006). The CNTs functionalized by the covalent methods has good advantage which that was soluble in various organic solvents because the CNTs possess many functional groups such as polar or non-polar groups.

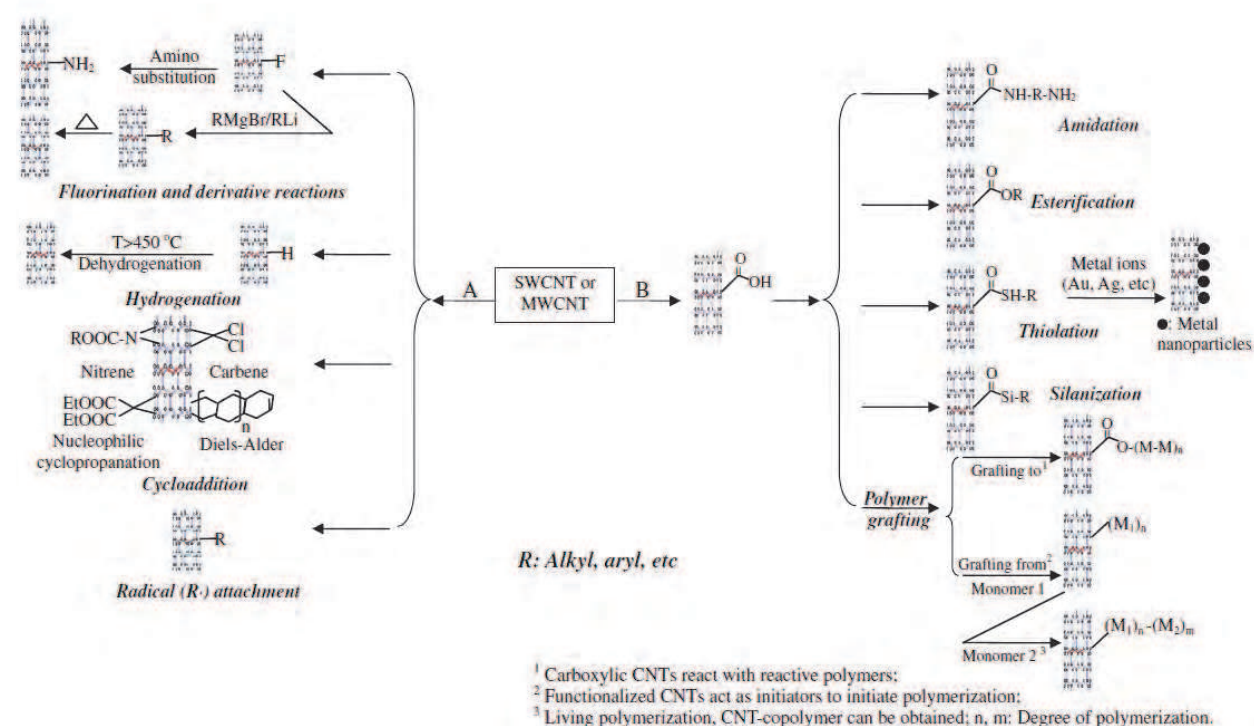


Fig. 6. Strategies for covalent functionalization of CNTs (A: direct sidewall functionalization; B: defect functionalization) (Ma et al.; 2010).

However these methods have two major drawbacks. First, during the functionalization reaction, especially along with damaging ultrasonication process (Figure 7), a large number

of defects are inevitably created on the CNT sidewalls, and in some extreme cases, CNTs are fragmented into smaller pieces (Figure 8). Namely, the carbon hybridization of CNTs was changed from  $sp^2$  to  $sp^3$ . These damaging effects result in severe degradation in mechanical properties of CNTs as well as disruption of  $\pi$  electron system in nanotubes. The disruption of  $\pi$  electrons is detrimental to transport properties of CNTs because defect sites scatter electrons and phonons that are responsible for the electrical and thermal conductions of CNTs, respectively. Secondly, concentrated acids or strong oxidants are often used for CNT functionalization, which are environmentally unfriendly. Therefore, many efforts have been put forward to developing methods that are convenient to use, of low cost and less damage to CNT structure.

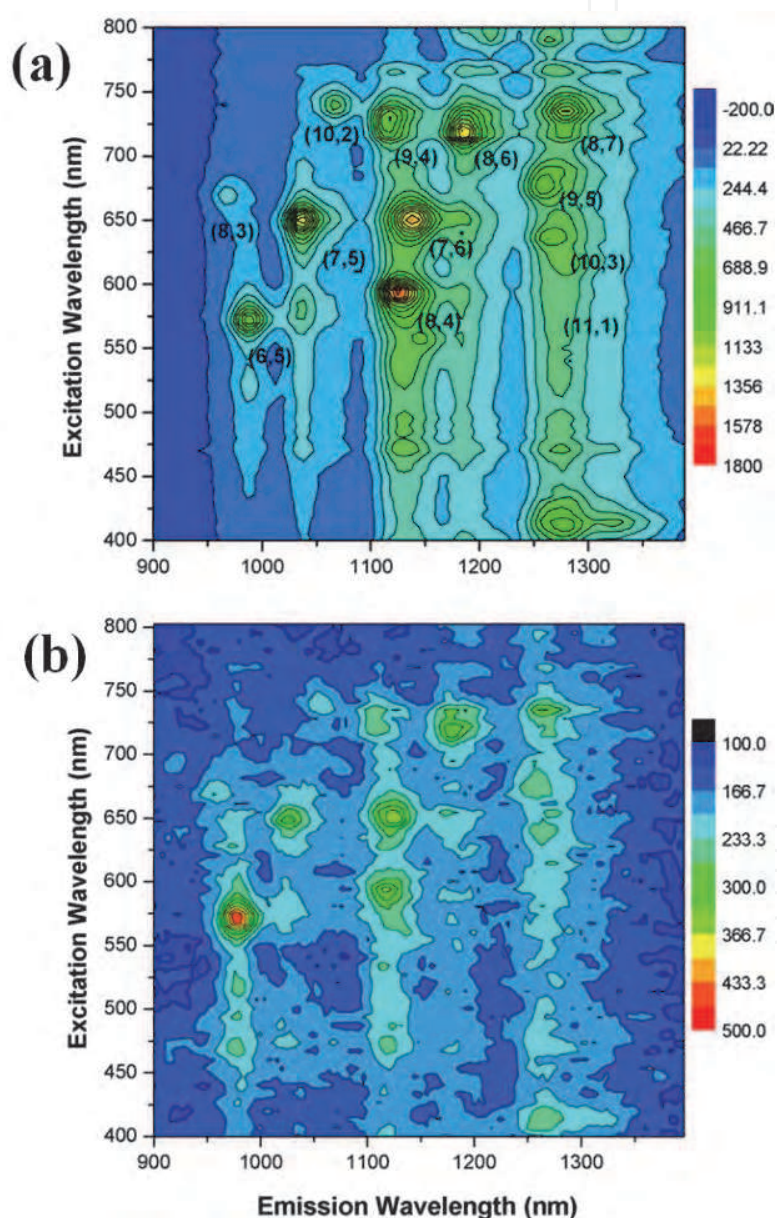


Fig. 7. (a) fluorescence excitation profile of sodium cholate-suspended SWNT in water, (b) profile of the same SWNT after 10min of probe-tip sonication conducted without controlling temperature (Heller et al.; 2005).

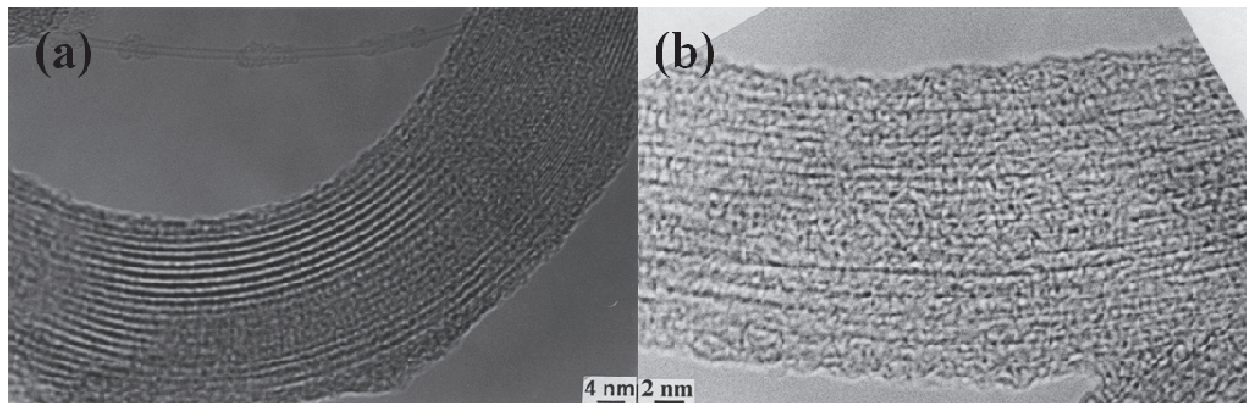


Fig. 8. TEM images: (a) as prepared SWNTs rope; (b) acid treated SWNTs rope (Monthieux et al.; 2001).

### 3.2 Non-covalent functionalization

The advantage of non-covalent functionalization is that it does not destroy the conjugated system of the CNTs sidewalls, and therefore it does not affect the final structural properties of the material. The non-covalent functionalization is an alternative method for tuning the interfacial properties of nanotubes. The CNTs are functionalized non-covalently by aromatic compounds, surfactants, and polymers, employing  $\pi$ - $\pi$  stacking or hydrophobic interactions for the most part. In these approaches, the non-covalent modifications of CNTs can do much to preserve their desired properties, while improving their solubilities quite remarkably. It will summarize as followed: aromatic small molecule absorption, polymer wrapping, surfactants, biopolymers and endohedral method.

Aromatic molecules, such as pyrene, porphyrin, and their derivatives, can and do interact with the sidewalls of CNTs by means of  $\pi$ - $\pi$  stacking interactions, thus opening up the way for the non-covalent functionalization of CNTs (Figure 9). Dai and co-workers have reported a general and attractive approach to the non-covalent functionalization of CNTs sidewalls and the subsequent immobilization of biological molecules onto CNTs with a high degree of control and specificity (Dai et al.; 2001). Hecht et al. fabricated CNTs/FET devices functionalized non-covalently with a zinc porphyrin derivative, was used to detect directly a photo induced electron transferring within the zinc porphyrin derivative-CNTs system (Hecht et al.; 2006). (Hu et al.; 2008) prepared CdSe-CNTs hybrids by self-assembling the pyrene-functionalized CdSe (pyrene/CdSe) nanoparticles onto the surfaces of the CNTs.

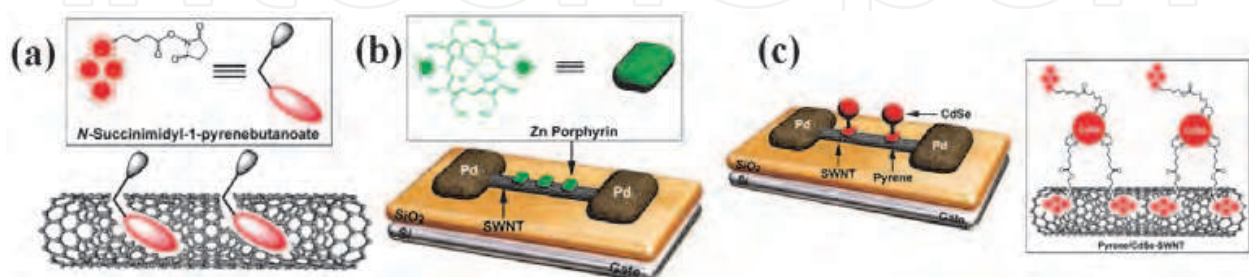


Fig. 9. Aromatic small-molecule based non-covalent functionalization: (a) *N*-succinimidyl-1-pyrenebutanoate coated CNTs; (b) zinc porphyrin-coated CNTs; (c) pyrene/CdSe coated CNTs (Zhao et al. 2009).

Polymers, especially conjugated polymers, have been shown to serve as excellent wrapping materials for the non-covalent functionalization of CNTs as a result of  $\pi$ - $\pi$  stacking and van der Waals interactions between the conjugated polymer chains containing aromatic rings and the surfaces of CNTs (Figure 10) (Star et al.; 2001, 2002, 2003 Cheng et al.; 2006 & Yi et al.; 2008). Those has reported some organic-soluble conjugated poly(*m*-phenylenevinylene)-co-(2,5-dioctoxy-*p*-phenylene) vinylene (PmPV) (Star et al.; 2001) poly(2,6-pyridinlenevinylene)- co-(2,5-dioctoxy-*p*-phenylene)vinylene (PPyPV) (Steuerman et al.; 2002), poly-(5-alkoxy-*m*-phenylenevinylene)-co-(2,5-dioctoxy-*p*-phenylene)- vinylene (PAmPV) (Star et al.; 2003), and stilbene-like dendrimers(Star et al.; 2002), to investigate their non-covalent functionalization for CNTs.

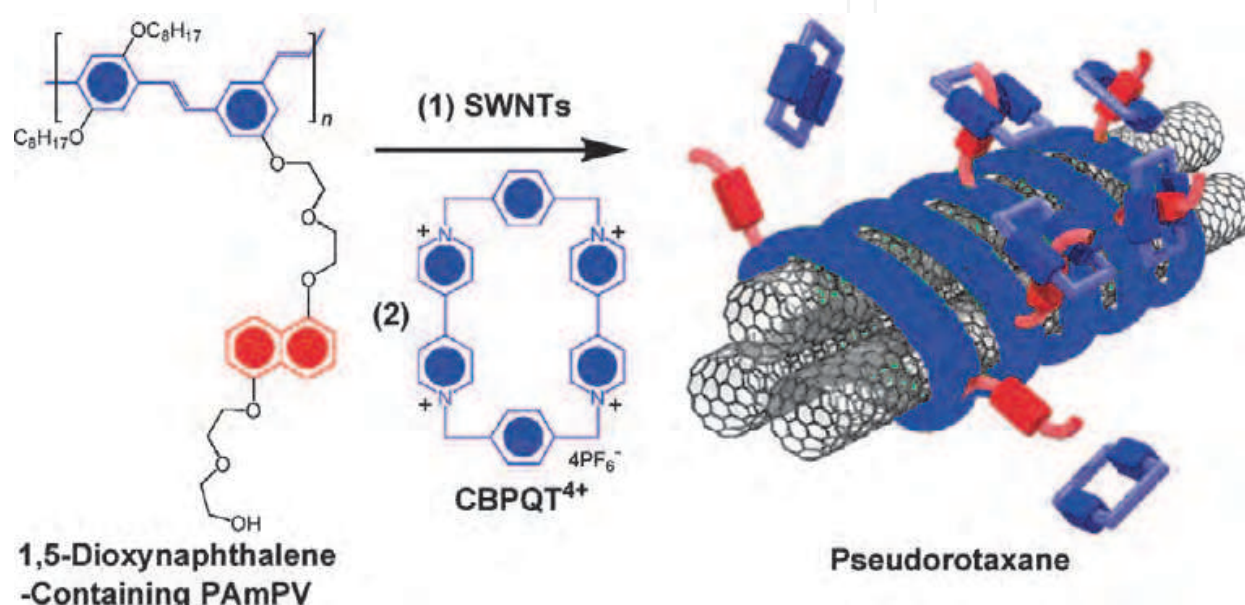


Fig. 10. The side arms of the 1,5-dioxynaphthalene containing PAmPV-decorated CNTs hybrids associate with cyclobis(paraquat-*p*-phenylene) (CBPQT<sup>4+</sup>) rings (Zhao et al.; 2006).

In addition, surfactants polymers have also been employed to functionalize CNTs (Figure 11). The physical adsorption of surfactant on the CNTs surface lowered the surface tension of CNTs that effectively prevented the aggregation of CNTs. Furthermore, the surfactant-treated CNTs overcame the van der Waals attraction by electrostatic/steric repulsive forces. The efficiency of this method depended strongly on the properties of surfactants, medium chemistry and polymer matrix. The relation between surfactants and CNTs studied previously as followed: (i) non-ionic surfactants, such as polyoxyethylene 8 lauryl or C<sub>12</sub>EO<sub>8</sub> (Gong et al.; 2000), polyoxyethylene octylphenylether (Triton X-100) (Vaisman et al.; 2006), (ii) anionic surfactants, such as sodium dodecylsulfate (SDS), sodium dodecylbenzenesulfonate (NaDDBS), poly(styrene sulfate) (PSS) (Islam et al.; 2003 & Yu et al.; 2007) (iii) cationic surfactants, such as dodecyl tri-methyl ammoniumbromide (DTAB) (Whitsitt et al.; 2003), cetyltrimethylammounium 4-vinylbenzoate (Kim et al.; 2007). Although surfactants may be efficient in the solubilization of CNTs, they are known to be permeable plasma membranes. They are toxic for biological applications. Therefore, the use of surfactant-stabilized CNTs complexes is potentially limited for biomedical applications (Klumpp et al.; 2006).

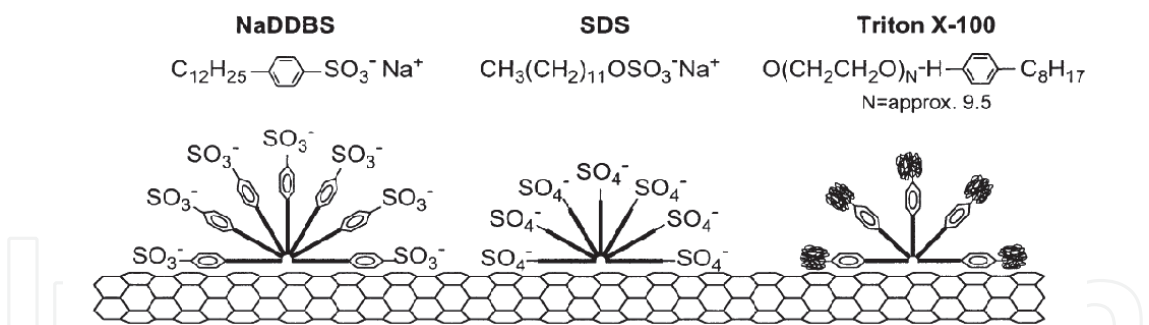


Fig. 11. The schematic representation of how surfactants may adsorb onto the CNTs surface (Islam et al 2003).

The solubilization of CNTs with biological components is certainly more appropriate towards integration of this new type of material with living systems (Figure 12). The biomacromolecules for non-covalent functionalization of CNTs has included simple saccharides and polysaccharides (Barone et al.; 2006; Star et al.; 2002; Chambers et al.; 2003 &

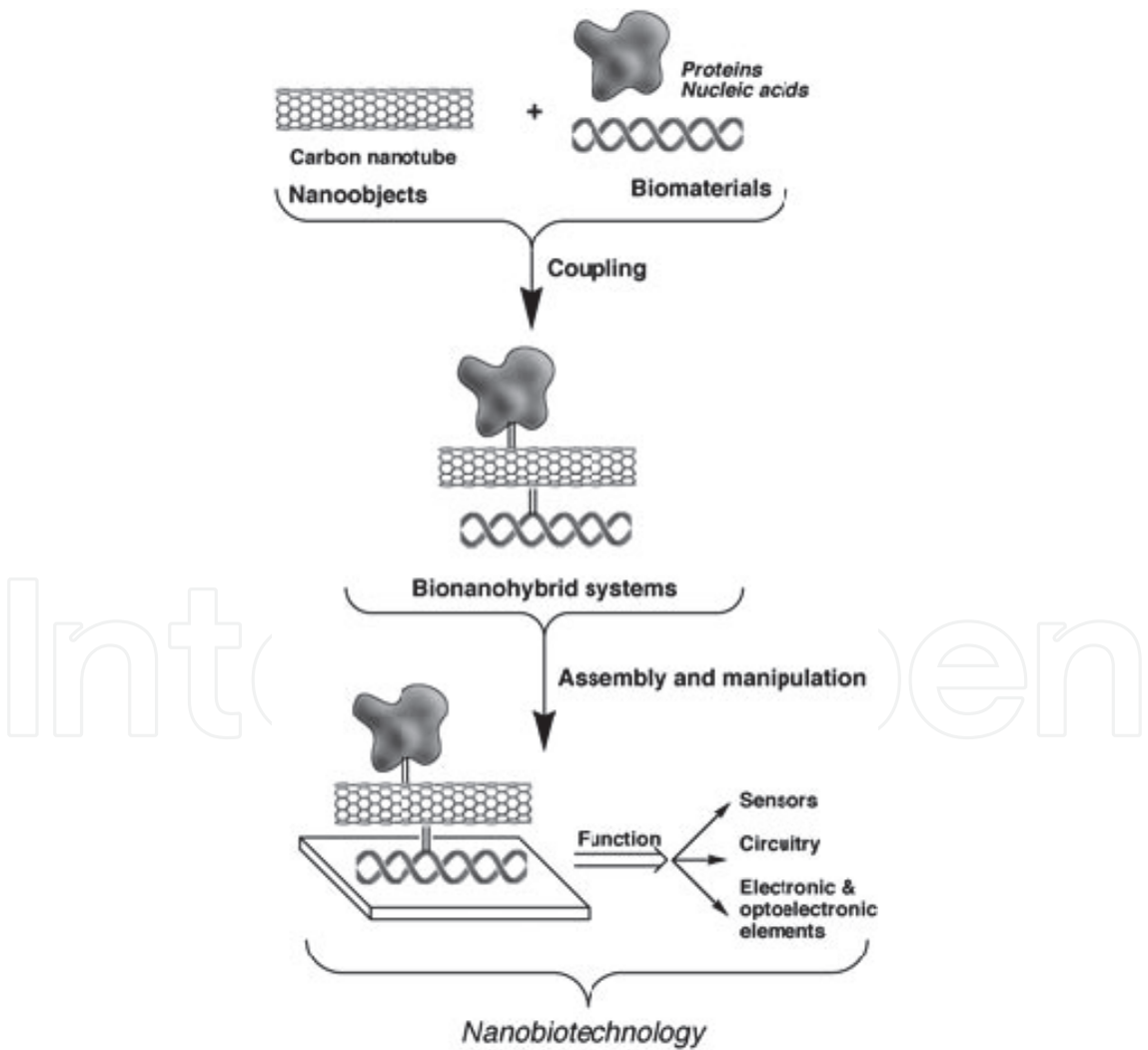


Fig. 12. The conceptual generation of biomolecules-CNTs conjugates and their assembly to yield functional devices.

Ikedada et al.; 2007), proteins (Chen et al.; 2001), enzymes, DNA, etc. Various biomaterials such as *n*-decyl- $\beta$ -Dmaltoside (Ishibashi et al.; 2006),  $\gamma$ -cyclodextrin (Chambers et al.; 2003),  $\eta$ -cyclodextrin (Dodzuik et al.; 2003), chitosan (Yan et al.; 2008), pullulan (Kim et al.; 2003) and phospholipid-dextran (Goodwin et al.; 2009) have been used for the non-covalent functionalization of CNTs. They have been aided due to the fact that such saccharides and polysaccharides have almost no light absorption in UV-vis wavelength region, so that the CNTs hybrids can be characterized by photochemical experiments and also the saccharide- and polysaccharide-coated CNTs hybrids are usually biocompatible and may be applicable for many medicinal purposes.

3.3 Alternative routes for the functionalization of carbon nanotubes

Though various methods for enhancing the interaction between CNTs and polymers were adopted in the recent past, the two main routes; namely covalent and non-covalent functionalization generally provided. As discussed earlier, both methods had their own merits depending on the platform. Additionally, the traditional covalent functionalization strategy of CNT is most frequently initiated by chemical acid oxidation acid treatment. However, dramatic amounts of induced defects during functionalization hinder the intrinsic mobility of carriers along CNTs, which is not preferred in any case. This method not only functionalizes the nanotube surfaces with carboxylic acid groups but leaves behind detrimental structures, hence hampering their potential for practical applications and can also compromise the mechanical properties of the nanotubes. Therefore, as a common rule, and a now widespread approach to alleviate these problems is to find alternative routes such as an effective functionalization method that can not only introduce high density and homogenous surface functional groups, which enhance the compatibility between CNTs and the foreign matrix, but allow direct grafting and has little or no structural damage to the CNTs, thus, optimizing their properties for various applications.

| 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 <sup>2</sup> to sp <sup>3</sup> | ✓                       | ✗           | S                                            | ✓                                  |
|                 | Defect                | Defect transformation                                            | ✓                       | ✓           | S                                            | ✓                                  |
| Physical method | Polymer wrapping      | Van der Waals force, $\pi$ - $\pi$ stacking                      | ✗                       | ✓           | V                                            | ✗                                  |
|                 | 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 3. Advantage and disadvantage of various CNT functionalization methods (Ma et al.; 2010).

To overcome this challenge, Baek et al. (2005; 2004; 2006; 2007; 2010) have reported an efficient route to covalently functionalize CNTs via direct Friedel-Crafts acylation technique (Figure 13). This kind of covalent grafting of the nanotubes is a promising strategy to not only improve nanotube dispersion but also provide a means for creating microscopic interlinks. On the whole, this kind of surface functionalization not only enhances the reactivity, but also improves the specificity and provides an avenue for further chemical modification of CNTs. Considerable achievements have been made in enhancing the various functionalities of CNT-polymer nanocomposites, generally not achievable for each of the components individually. The approach is conceptualized on the basis of our foray into the

CNT chemistry using 'direct' Friedel-Crafts acylation technique which has superior operational simplicity. Not only a mild and an alternative route to functionalize CNTs, this strategy was previously shown to be a less-destructive and/or nondestructive reaction condition for the efficient dispersion and functionalization of carbon nanomaterials. As a result, CNT damage from severe chemical treatments including oxidation and sonication can be avoided to a larger extent. Thus, maximum enhanced properties can be expected from improved dispersion stability as well as chemical affinity with matrices.

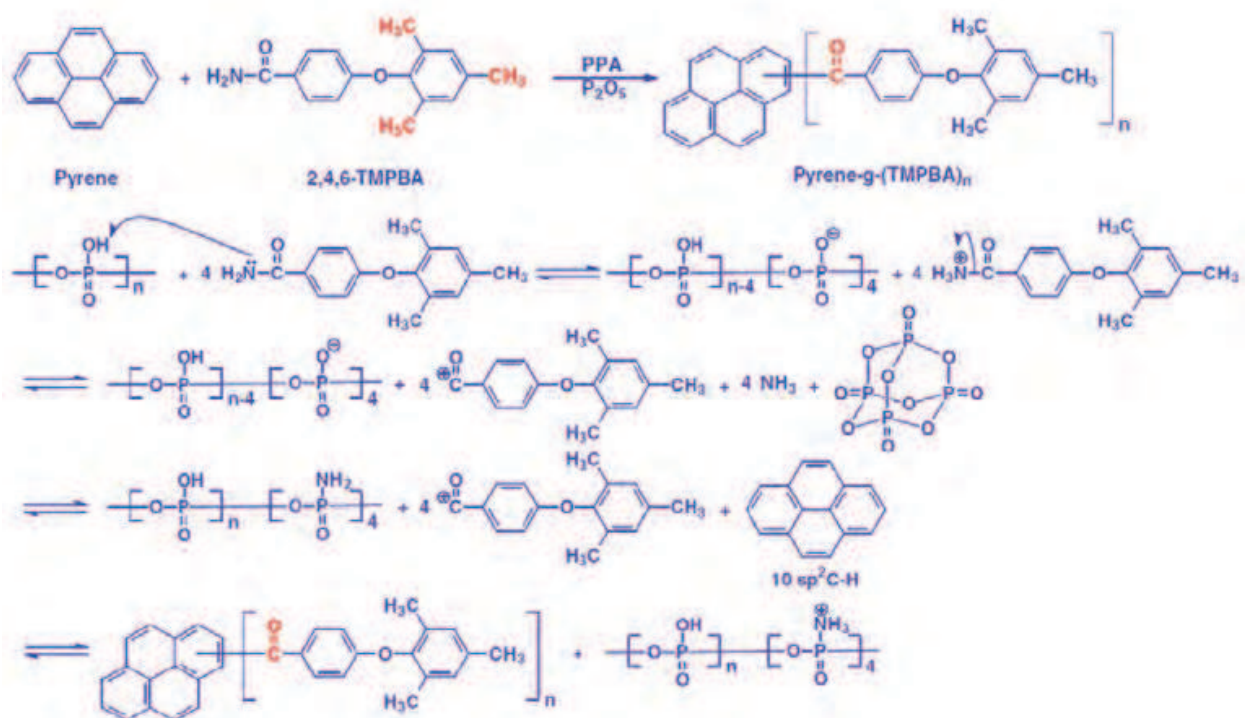


Fig. 13. Friedel-Crafts acylation reaction of pyrene as a miniature graphene and organic material in poly(phosphoric acid)/phosphorous pentoxide medium (Jeon et al.; 2010).

#### 4. Conclusion and outlook

In light of the continuous progress of nanotechnology and material science over the last two decades, CNT based materials have opened new pathways for developing novel functional materials. In summary, CNTs were always been regarded as new and interesting type of materials, especially for energy and electronic applications. All types of CNTs are being investigated with equal importance. While few strategies have been developed so that the handling and manipulation of CNTs be relatively easier, on the whole there is much room for investigations in areas such as supercapacitors. Very recent reports show CNT based supercapacitor devices with better capacitor performance. Precisely, the combination of CNTs with particular macromolecules that offer to enhance the conductivity of the material is one interesting research. Particularly, the large electrochemical window and the environmental stability draw critical importance on such materials. Furthermore, the extension of these functional methods to the 2D forms of carbon namely graphene based materials are also now a fast growing area. While the quest for new materials are always on,

the research on CNT based materials in special fields such as doping are still open for investigations and discussion.

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## 6. References

- Radushkevich O.L.V. & Lukyanovich V.M. (1952). *Zurn. Fisic. Chim.* 28, 88- 95.
- Oberlin A.; Endo M.; & Koyama T. (1976). Filamentous growth of carbon through benzene decomposition. *J. Cryst. Growth* 32, 335-349.
- Iijima, S. (1991). Helical microtubules of graphitic carbon. *Nature* 354, 56-58.
- Song, Y. S. & Youn, J. R. (2005). Influence of dispersion states of carbon nanotubes on physical properties of epoxy nanocomposites. *Carbon* 43, 1378-1385.
- Ajayan, P.M.; Schadler, L.S.; Giannaris, C. & Rubio, A. (2000). Single-Walled Carbon Nanotube-Polymer Composites: Strength and Weakness. *Adv. Mater.* 12, 750-753.
- Mikhail, I. Katsnelson. (2007). Graphene: carbon in two dimensions. *Materials Today* 10, 20-27.
- Bethune, D.S.; Kiang, C.H.; Devries, M.S.; Gorman, G.; Savoy, R.; Vazquez J, et al. (1993). Cobalt-catalyzed growth of carbon nanotubes with singleatomic-layerwalls. *Nature* 363 (6430), 605-607.
- Iijima, S. & Ichihashi T. (1993). Single-shell carbon nanotubes of 1-nm diameter. *Nature* 363, (6430), 603-605.
- Hutchison, J.L.; Kiselev, N.A.; Krinichnaya, E.P.; Krestinin, A.V.; Loutfy, R.O.; Morawsky, A.P.; Muradyan, V.E.; Obraztsova, E.D.; Sloan, J.; Terekhov, S.V. & Zakharov, D.N. (2001). Double-walled carbon nanotubes fabricated by a hydrogen arc discharge method. *Carbon* 39, 761-770.
- Hou, Y.; Tang, J.; Zhang, H.; Qian, C.; Feng, Y. & Liu, J. (2009). Functionalized Few-Walled Carbon Nanotubes for Mechanical Reinforcement of Polymeric Composites. *ACS Nano* 3, 1057-1062.
- Hamada, N., Sawada, S. & Oshiyama, A. (1992). New one-dimensional conductors: Graphitic microtubules *Phys. Rev. Lett.* 68, 1579-1581.
- Belin, T. & Epron, F. (2005). Characterization methods of carbon nanotubes: A review. *Mater. Sci. Eng., B* 119, (2), 105-118.
- Popov, V.N. (2004). Carbon nanotubes: Properties and application. *Mater. Sci. Eng., R* 43 (3), 61-102.
- Qian, D.; Wagner, G.J.; Liu, W.K.; Yu, M.F. & Ruoff R.S. (2002). Mechanics of carbon nanotubes. *Appl. Mech. Rev.* 55, 495-533.
- Xie, S.; Li, W.; Pan, Z.; Chang, B. & Sun, L. (2000). Mechanical and physical properties on carbon nanotube. *J. Phys. Chem. Solids* 61, (7), 1153-1158.

- Schadler, L.S. (2004). Polymer-Based and Polymer-Filled Nanocomposites, in Nanocomposite Science and Technology (eds P. M. Ajayan, L. S. Schadler and P. V. Braun), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
- Elliott, J.A.; Sandler, J.K.W.; Windle, A.H.; Young, R.J. & Shaffer, M.S.P. (2004) Collapse of single-wall carbon nanotubes is diameter dependent. *Phys. Rev. Lett.* 92(9), 1–4.
- Kim, B.M. & Fuhrer, A.M.S. (2004). Properties and applications of high-mobility semiconducting nanotubes. *J. Phys: Condens. Matter* 16(18) R553–R580.
- Tang, Z.K.; Zhang, L.Y.; Wang, N.; Zhang, X.X.; Wen, G.H.; Li, G.D.; et al. (2001). Superconductivity in 4 Angstrom single-walled carbon nanotubes. *Science* 292, (5526), 2462–2465.
- Che, J.W.; Cagin, T. & Goddard, W.A. (2000). Thermal conductivity of carbon nanotubes. *Nanotechnology* 11, (2), 65–69.
- Osman, M.A. & Srivastava, D. (2001) Temperature dependence of the thermal conductivity of single-wall carbon nanotubes. *Nanotechnology* 12, (1), 21–24.
- Hone, J.; Llaguno, M.C.; Biercuk, M.J.; Johnson, A.T.; Batlogg, B.; Benes, Z.; et al. (2002) Thermal properties of carbon nanotubes and nanotube-based materials. *Appl. Phys. A – Mater. Sci. Process* 74, (3), 339–343.
- Thostenson, E.T. Ren, Z.F. & Chou, T.W. (2001). Advances in the science and technology of CNTs and their composites: a review. *Compos. Sci. Technol.* 61, 1899–1912.
- Ajayan, P.M.; Schadler, L.S. & Braun, P.V. Nanocomposite science and technology. Weinheim: Wiley-VCH; 2003. p. 77–80.
- Coleman, J.N.; Khan, U. & Gunko, Y.K. (2006). Mechanical reinforcement of polymers using carbon nanotubes. *Adv. Mater.* 18, 689–706.
- Journet, C.; Maser, W.K.; Bernier, P.; Loiseau, A.; de la Chapelle M.L.; Lefrant, S.; et al. (1997). Large-scale production of single-walled carbon nanotubes by the electric-arc technique *Nature* 388, 756–758.
- Rinzler, A.G.; Liu, J.; Dai, H.; Nikolaev, P.; Huffman, C.B.; Rodriguez Macias, F.J. et al. (1998). Large-scale purification of single-wall carbon nanotubes: process, product, and characterization. *Appl. Phys. A* 1998, 67, 29–37.
- Nikolaev, P.; Bronikowski, M.J.; Bradley, R.K.; Fohmud, F.; Colbert, D.T.; Smith K.A.; et al. (1999). Gas-phase catalytic growth of single-walled carbon nanotubes from carbon monoxide. *Chem. Phys. Lett.* 313, 91–97.
- Ren, Z.F.; Huang, Z.P.; Xu, J.W.; Wang, D.Z.; Wen, J.G.; Wang, J.H.; et al. (1999). Growth of a single freestanding multiwall carbon nanotube on each nanonickel dot. *Appl. Phys. Lett.* 75, 1086–1088.
- Ren, Z.F.; Huang, Z.P.; Xu, J.W.; Wang, J.H.; Bush, P.; Siegal, M.P.; et al. (1998). Synthesis of Large Arrays of Well-Aligned Carbon Nanotubes on Glass. *Science*. 282, 1105–1107.
- See, C.H. & Harris, A.T. (2007). A Review of Carbon Nanotube Synthesis via Fluidized-Bed Chemical Vapor Deposition. *Ing. Eng. Chem. Res.* 46, 997–1012.
- Strano, M.S.; Kyke, C.A.; Usrey, M.L.; Barone, P.W.; Allen, M.J.; Shan, H.; Kittrell, C.; Hauge, R.H.; Tour, J.M. & Smalley, R.E. (2003). Electronic Structure Control of Single-Walled Carbon Nanotube Functionalization *Science* 301, 1519–1522.

- Li, H.; Zhou, B.; Lin, Y.; Gu, L.; Wang, W.; Fernando K.A.S.; Kumar, S.; Allard, L.F. & Sun, Y.-P. (2004). Selective Interactions of Porphyrins with Semiconducting Single-Walled Carbon Nanotube. *J. Am. Chem. Soc.* 126, 1014-1015.
- Niyogi, S.; Hamon, M.A.; Hu, H.; Zhao, B.; Bhowmik, P.; Sen, R.; Itkis, M.E. & Haddon, R.C. (2002) Chemistry of Single-Walled Carbon Nanotubes. *Acc. Chem. Res.* 35, (12), 1105-1113.
- Tasis, D.; Tagmatarchis, N.; Georgakilas, V. & Prato, M. (2003). Soluble Carbon Nanotubes. *Chem. Eur. J.* 9, (17), 4000-4008.
- Hirsch, A. (2002). Functionalization of Single-Walled Carbon Nanotubes. *Angew, Chem, Int. Ed.* 41, (11), 1853-1859.
- Sinnott, S.B. (2002). Chemical Functionalization of Carbon Nanotubes. *Journal of Nanoscience and Nanotechnology J. Nanosc. Nanotechnol.* 2, 113-123.
- Bianco, A.; Prato, M.; Kostarelos, K. & Bianco, A. (2008). Functionalized Carbon Nanotubes in Drug Design and Discovery. *Acc. Chem. Res.* 41, (1), 60-68.
- Mickelson, E.T.; Huffman, C.B.; Rinzler, A.G.; Smalley, R.E.; Hauge, R.H. & Margrave, J.L. (1998) Fluorination of single-wall carbon nanotubes. *Chem. Phys. Lett.* 296, (1-2), 188-194.
- Kelly, K.F.; Chiang, I.W.; Mickelson, E.T., et al. (1993). Insight into the mechanism of sidewall functionalization of single-walled nanotubes: an STM study. *Chem. Phys. Lett.* 313, 445-450
- Touhara. H.; Inahara, J.; Mizuno T.; et al. (2002). Fluorination of cup-stacked carbon nanotubes, structure and properties. *Fluorine Chem.* 114, 181-188.
- Stevens, J.L.; Huang, A.Y.; Peng, H.; et al. (2003). Sidewall amino-functionalization of SWNTs through fluorination and subsequent reactions with terminal diamines. *Nano Lett.* 3, 331-336.
- Hu, H.; Zhao, B.; Hamon, M.A.; et al. (2003). Sidewall functionalization of single-walled carbon nanotubes by addition of dichlorocarbene. *J. Am. Chem. Soc.* 125, 14893-14900.
- Unger, E.; Graham, A.; Kreupl, F.; Liebau, M.; Hoenlein, W., (2002). Electrochemical functionalization of multi-walled carbon nanotubes for solvation and purification. *Curr. Appl. Phys.* 2, 107-111.
- Kim, K.S.; Bae, D.J.; Kim, J.R.; Park, K.A.; Lim, S.C.; Kim, J.J.; Choi, W.B.; Park, C.Y. & Lee, Y.H. (2002). Modification of Electronic Structures of a Carbon Nanotube by Hydrogen Functionalization. *Adv. Mater.* 14, (24), 1818-1821
- Tagmatarchis, N. & Prato, M.J. (2004). Functionalization of carbon nanotubes via 1,3-dipolar cycloadditions. *J. Mater. Chem.* 14, 437-439.
- Chen, J.; Hamon, M.A.; Hu, H.; Chen, Y.; Rao, A.M.; Eklund, P.C.; Haddon, R.C. (1998). Solution Properties of Single-Walled Carbon Nanotubes. *Science* 282, (5386), 95-98.
- Esumi, K.; Ishigami, M.; Nakajima, A.; Sawada, K. & Honda, H. (1996). Chemical treatment of carbon nanotubes. *Carbon* 34, 279-281.
- Liu, J.; Rinzler, A.G.; Dai, H.; Hafner, J.H.; Bradley, R.K.; Boul, P.J.; et al. (1998). Fullerene Pipes. *Science* 280, 1253-1256.

- Yu, R.; Chen, L.; Liu, Q.; Lin, J.; Tan, K.-L.; Ng, S.C.; Chan, H S.O.; Xu, G.-Q. & Hor, T.S.A. (1998). Platinum Deposition on Carbon Nanotubes via Chemical Modification. *Chem. Mater.* 10, 718-722.
- Sham, M.-L. & Kim, J.-K., (2006). Surface functionalities of multi-wall carbon nanotubes after UV/Ozone and TETA treatments. *Carbon* 44, (4), 768-777.
- Wang, S.C.; Chang, K.S. & Yuan, C.J. (2009). Enhancement of electrochemical properties of screen-printed carbon electrodes by oxygen plasma treatment. *Electrochimica Acta* 54, (21), 4937-4943.
- Ma, P.C.; Kim, J.K. & Tang, B.Z. (2006). Functionalization of carbon nanotubes using a silane coupling agent. *Carbon* 44, 3232-3238.
- Sano, M.; Kamino, A.; Okamura, J. & Shinkai, S. (2001). Self-Organization of PEO-graft-Single-Walled Carbon Nanotubes in Solutions and Langmuir-Blodgett Films. *Langmuir* 17, (17), 5125-5128.
- Kong, H.; Gao, C. & Yan, D. (2003). Controlled Functionalization of Multiwalled Carbon Nanotubes by in Situ Atom Transfer Radical Polymerization. *J. Am. Chem. Soc.* 126, 412-413.
- Hamon, M.A.; Hui, H. & Bhowmik P. (2002). Ester-functionalized soluble single-walled carbon nanotubes. *Appl. Phys. A* 74, 333-338.
- Coleman, J.N.; Khan, U. & Gun'ko, Y.K. (2006). Mechanical Reinforcement of Polymers Using Carbon Nanotubes. *Adv. Mater.* 18, 689-706.
- Ma, P.-C.; Siddiqui, N.A.; Marom, G. & Kim, J.-K. (2010). Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: A review. *Composites: Part A* 41, 1345-1364.
- Heller D.A., Barone, P.W., Strano, M.S. (2004). Sonication-induced changes in chiral distribution: A complication in the use of single-walled carbon nanotube fluorescence for determining species distribution. *Carbon* 43, 651-673.
- Monthieux M., Smith B.W., Burtiaux B., Claye A., Fischer, J.E. & Luzzi, D.E. (2001). Sensitivity of single-wall carbon nanotubes to chemical processing: an electron microscopy investigation. *Carbon* 39, (8), 1251-1272.
- Chen, R. J.; Zhang, Y.; Wang, D. & Dai, H. (2001). Noncovalent Sidewall Functionalization of Single-walled carbon nanotubes for protein immobilization. *J. Am. Chem. Soc.* 123, 3838-3839.
- Hecht, D.S.; Ramirez, R.J.A.; Briman, M.; Artukovic, E.; Chichak, K.S.; Stoddart, J.F. & Gruner, G. (2006). Bioinspired detection of light using a porphyrin-sensitized singlewall nanotube field effect transistor. *Nano Lett.* 6, 2031-2036.
- Hu, L.; Zhao, Y.-L.; Ryu, K.; Zhou, C.; Stoddart, J.F.; Gruner, G. Light-induced charge transfer in pyrene/CdSe-SWNT hybrids. *Adv. Mater.* 2008, 20, 939-946.
- Zhao, Y.-L. & Stoddart, J.F. (2009). Noncovalent Functionalization of Single-Walled Carbon Nanotubes. *Acc. Chem. Res.* 42, (8), 1161-1171
- Star, A.; Stoddart, J.F.; Steuerman, D.; Diehl, M.; Boukai, A.; Wong, E.W.; Yang, X.; Chung, S.-W.; Choi, H. & Heath, J.R. (2001). Preparation and Properties of Polymer-Wrapped Single-Walled Carbon Nanotubes. *Angew. Chem., Int. Ed.* 2001, 40, 1721-1725.

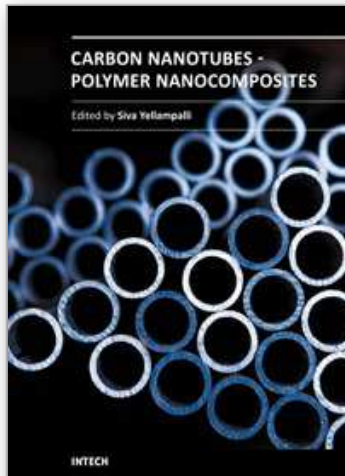
- Steuerman, D.W.; Star, A.; Narizaano, R.; Choi, H.; Ries, R.S.; Nicolini, C.; Stoddart, J.F. & Heath, J.R. (2002). Interactions between conjugated polymers and singlewalled carbon nanotubes. *J. Phys. Chem. B* 106, 3124–3130.
- Star, A.; Liu, Y.; Grant, K.; Ridvan, L.; Stoddart, J.F.; Steuerman, D.W.; Diehl, M.R.; Boukai, A. & Heath, J.R. (2003). Noncovalent side-wall functionalization of singlewalled carbon nanotubes. *Macromolecules* 36, 553–560.
- Star, A. & Stoddart, J.F. (2002). Dispersion and solubilization of single-walled carbon nanotubes with a hyperbranched polymer. *Macromolecules* 35, 7516–7520.
- Cheng, F.; & Adronov, A. (2006). Noncovalent functionalization and solubilization of carbon nanotubes by using a conjugated Zn-porphyrin polymer. *Chem. Eur. J.* 12, 5053–5059.
- Yi, W.; Malkovskiy, A.; Chu, Q.; Sokolov, A. P.; Colon, M.L.; Meador, M. & Pang, Y. (2008). Wrapping of single-walled carbon nanotubes by a  $\pi$ -conjugated polymer: The role of polymer conformation-controlled size selectivity. *J. Phys. Chem. B* 112, 12263–12269.
- Gong, X.; Liu, J.; Baskaran, S.; Voise, R.D. & Young, J.S. (2000). Surfactant-Assisted Processing of Carbon Nanotube/Polymer Composites. *Chem. Mater.* 12 (4), 1049–1052.
- Vaisman, L.; Marom, G. & Wagner, H.D. (2006). Dispersions of Surface-Modified Carbon Nanotubes in Water-Soluble and Water-Insoluble Polymers. *Adv. Funct. Mater.* 16 (3), 357–363
- Islam, M.F.; Rojas, E.; Bergey, D.M.; Johnson, A.T.; Yodh, A.G. (2003). High Weight Fraction Surfactant Solubilization of Single-Wall Carbon Nanotubes in Water. *Nano Lett.* 3 (2), 269–273
- Yu, J.; Grossiord, N.; Koning, C.E. & Loos, J. (2007). Controlling the dispersion of multi-wall carbon nanotubes in aqueous surfactant solution. *Carbon* 45 (3), 618–623.
- Whitsitt, E.A. & Barron, A.R., (2003). Silica Coated Single Walled Carbon Nanotubes. *Nano Lett.* 3, (6), 775–778.
- Kim, T.H.; Doe, C.; Kline, S.R. & Choi, S.M. (2007). Water-Redispersible Isolated Single-Walled Carbon Nanotubes Fabricated by In Situ Polymerization of Micelles. *Adv. Mater.* 19, (7), 929–933.
- Klumpp, C.; Kostarelos, K.; Prato, M.; & Bianco, A. (2006). Functionalized carbon nanotubes as emerging nanovectors for the delivery of therapeutics. *Biochim. Biophys. Acta, (BBA) - Biomembranes* 1758, (3), 404–412.
- Barone, P.W.; & Strano, M.S. (2006). Reversible Control of Carbon Nanotube Aggregation for a Glucose Affinity Sensor. *Angew. Chem., Int. Ed.* 45, 8138–8141.
- Star, A.; Steuerman, D.W.; Heath, J.R. & Stoddart, J.F. (2002) Starched carbon nanotubes. *Angew. Chem., Int. Ed.* 41, 2508–2512.
- Chambers, G.; Carroll, C.; Farrell, G.F.; Dalton, A.B.; McNamara, M.; in het Panhuis, M.; & Byrne, H.J. (2003). Characterization of the interaction of gamma cyclodextrin with single-walled carbon nanotubes. *Nano Lett.* 3, 843–846.
- Ikeda, M.; Hasegawa, T.; Numata, M.; Sugikawa, K.; Sakurai, K.; Fujiki, M. & Shinkai, S. (2007). Instantaneous inclusion of a polynucleotide and hydrophobic guest

- molecules into a helical core of cationic 1,3-glucan polysaccharide. *J. Am. Chem. Soc.* 129, 3979–3988.
- Chen, R.J.; Zhang, Y.; Wang, D. & Dai, H. (2001). Single-walled carbon nanotubes for protein immobilization. *J. Am. Chem. Soc.* 123, 3838–3839.
- Ishibashi, A. & Nakashima, N. (2006). Individual dissolution of single-walled carbon nanotubes in aqueous solution of steroid or sugar compounds and their Raman and Near-IR spectral properties. *Chem. Eur. J.* 12, 7595–7602.
- Dodziuk, H.; Ejchart, A.; Anczewski, W.; Ueda, H.; Krinichnaya, E.; Dolgonos, G. & Kutner, W. (2003). Water solubilization, determination of the number of different types of single-wall carbon nanotubes and their partial separation with respect to diameters by complexation with  $\eta$ -cyclodextrin. *Chem. Commun.* 986–987.
- Yan, L.Y.; Poon, Y.F.; Chan-Park, M.B.; Chen, Y.; Zhang, Q. (2008). Individually dispersing single-walled carbon nanotubes with novel neutral pH water-soluble chitosan derivatives. *J. Phys. Chem. C* 112, 7579–7587.
- Kim, O.-K.; Je, J.; Baldwin, J.W.; Kooi, S.; Pehrsson, P.E.; & Buckley, L.J. (2003). Solubilization of single-walled carbon nanotubes by supramolecular encapsulation of helical amylase. *J. Am. Chem. Soc.* 125, 4426–4427.
- Goodwin, A.P.; Tabakman, S.M.; Welsher, K.; Sherlock, S.P.; Prencipe, G. & Dai, H. (2009). Phospholipid-dextran with a single coupling point: A useful amphiphile for functionalization of nanomaterials. *J. Am. Chem. Soc.* 131, 289–296.
- Baek, J.-B.; Lyons, C.B.; & Tan, L.-S. (2004). Covalent modification of vapour-grown carbon nanofibers via direct Friedel-Crafts acylation in polyphosphoric acid. *J. Mater. Chem.* 14 (13), 2052–2056.
- Baek, J.-B.; Lyons, C.B. & Tan, L.-S. (2004). Grafting of Vapor-Grown Carbon Nanofibers via in-Situ Polycondensation of 3-Phenoxybenzoic Acid in Poly(phosphoric acid). *Macromolecules* 37 (22), 8278–8285.
- Lee, H.-J.; Oh, S.-J.; Choi, J.-Y.; Kim, J.W.; Han, J.; Tan, L.-S. & Baek, J.-B. (2005). In Situ Synthesis of Poly(ethylene terephthalate) (PET) in Ethylene Glycol Containing Terephthalic Acid and Functionalized Multiwalled Carbon Nanotubes (MWNTs) as an Approach to MWNT/PET Nanocomposites. *Chem. Mater.* 17, (20), 5057–5064.
- Oh, S.-J.; Lee, H.-J.; Keum, D.-K.; Lee, S.-W.; Wang, D. H.; Park, S.-Y.; Tan, L.-S. & Baek, J.-B. (2006). Multiwalled carbon nanotubes and nanofibers grafted with polyetherketones in mild and viscous polymeric acid. *Polymer* 47, (4), 1132–1140.
- Choi, J.-Y.; Oh, S.-J.; Lee, H.-J.; Wang, D. H.; Tan, L.-S. & Baek, J.-B. (2007). In-Situ Grafting of Hyperbranched Poly(ether ketone)s onto Multiwalled Carbon Nanotubes via the A3 + B2 Approach. *Macromolecules* 40, (13), 4474–4480.
- Choi, J.-Y.; Han, S.-W.; Huh, W.-S.; Tan, L.-S. & Baek, J.-B. (2007). In situ grafting of carboxylic acid-terminated hyperbranched poly(ether-ketone) to the surface of carbon nanotubes. *Polymer* 48, (14), 4034–4040.
- Wang, D.H.; Arlen, M.J.; Baek, J.-B. & Tan, L.-S. (2007). Nanocomposites Derived from a Low-Color Aromatic Polyimide (CP2) and Amine-Functionalized Vapor-Grown Carbon Nanofibers: In Situ Polymerization and Characterization. *Macromolecules* 40, (17), 6100–6111.

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## **Carbon Nanotubes - Polymer Nanocomposites**

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Polymer nanocomposites are a class of material with a great deal of promise for potential applications in various industries ranging from construction to aerospace. The main difference between polymeric nanocomposites and conventional composites is the filler that is being used for reinforcement. In the nanocomposites the reinforcement is on the order of nanometer that leads to a very different final macroscopic property. Due to this unique feature polymeric nanocomposites have been studied exclusively in the last decade using various nanofillers such as minerals, sheets or fibers. This book focuses on the preparation and property analysis of polymer nanocomposites with CNTs (fibers) as nano fillers. The book has been divided into three sections. The first section deals with fabrication and property analysis of new carbon nanotube structures. The second section deals with preparation and characterization of polymer composites with CNTs followed by the various applications of polymers with CNTs in the third section.

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