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THE FUNCTIONALIZATION OF CARBON NANOTUBES AND NANO-ONIONS

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1.1 FUNCTIONALIZATION OF CARBON NANOTUBES

The unique structure and morphology of carbon nanotubes have kept attracting researchers to explore their novel properties and applications since their discovery by Iijima in 1991 (1). Carbon nanotube (CNT) is a tubular structure made of carbon atoms and denoted as single-walled or multiwalled CNTs, having diameter of nanometer scale but length in micrometers. As in graphite, the carbon atoms in CNTs are in sp^2 hybridization and these sp^2 carbon sets give a great mechanical strength to CNTs. Single-walled carbon nanotubes (SWCNTs) are narrow and possess the simplest geometry and have been observed with diameters ranging from 0.4 to 3 nm. Multiwalled carbon nanotubes (MWCNTs) possess diameters of up to 100 nm. In general, pure CNTs have all carbons bonded in a hexagonal pattern except at their ends, and other defects in the sidewalls and the formation of various patterns resulting from the mass production generally humiliate desired properties.

Starting from diamond and fullerene to related nanostructures (Fig. 1.1) (2), CNTs have progressive properties, and during the past decade, CNTs had fascinated much attention for their electronic and mechanical properties. One of the main challenges in implementing serious applications of CNTs is functionalizing them. The lack of solubility and the difficult processing of CNTs in solvents impose great limitations to the practical applications of CNTs. Therefore, surface functionalization of CNTs has become the focus of research in recent years in order to improve their compatibility with matrices. Several methods, such as covalent or noncovalent functionalization, have been developed to achieve effective dispersion and bonding without the loss of properties of CNTs. The scope of applicability of CNTs has been expanded by extensive research particularly on tuning structural and electronic properties. According to the reports in recent times, CNTs have been used for many purposes and still implementation has been done day to day. Among those diverse applications, CNTs alone find some limitations in thermal, electrical, and mechanical properties, and this can be improved by combining them with certain polymers. Grafting polymers on CNTs is likely to improve the thermal and electrical properties (3, 4). Nanotube reinforcement into the polymer matrix has been considered as the primary need in order to obtain strongly enough composites (5). In general, CNTs have hollow structure and a very high aspect ratio (length-to-diameter ratio) which help them to form a network of conductive tubes. The surface properties of CNT-grafted polymers have been reported early by Downs and Baker (6) and Thostenson et al. (7). In particular, surface area tends to increase by the growth of nanofibers when compared to conventional process as predicted by Downs et al. It was observed that the surface area increased around 300 times and the interfacial shear strength by 4.75 times. From then, the feasibility of grafting CNT-polymers has been investigated to a larger extent and the nanotube composites have been designed according to the requirement of specific applications. The development of polymer-CNT composite methodology is based on improving the dispersion and controlling the orientation of CNTs in the polymer matrix (8). In general, high resistance at the nanotube-matrix interface limits thermal transfer along percolating networks of CNTs. However, viscoelasticity of the nanocomposites has been greatly enhanced by the nanotube network interpenetrating the polymer template. The small cross-sectional dimensions and extreme length of the CNTs allow bending to a large extent to have good intertube interactions under processing conditions. It has been clearly explained that the CNTs not only influence the electrical or thermal properties but they also eliminate the die swell, a problem faced during polymer processing (9).

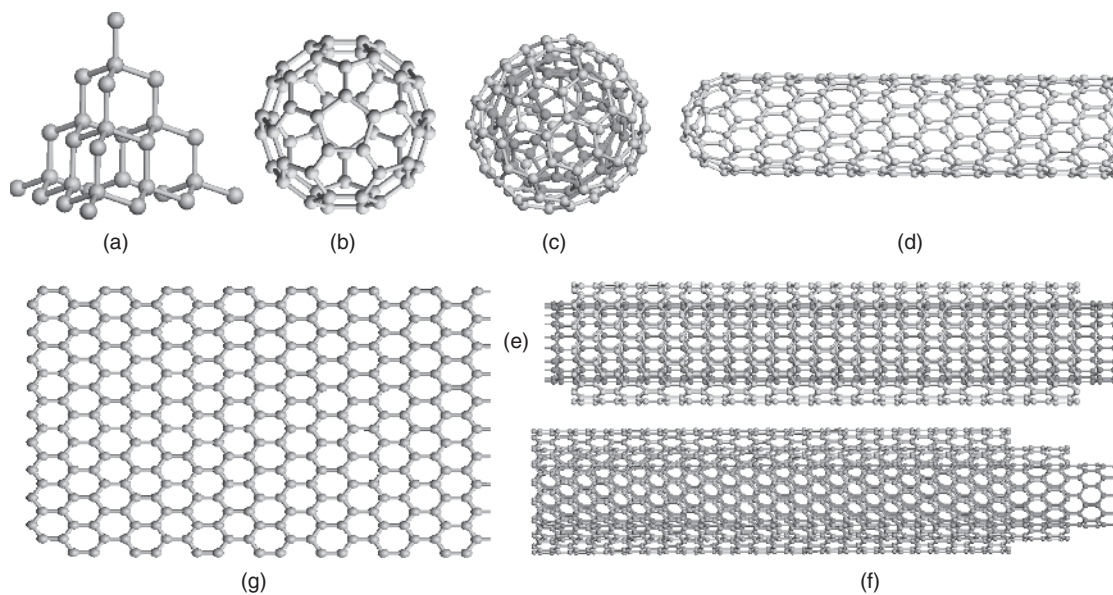


Figure 1.1 Model structures of carbon: (a) diamond, (b) fullerene, (c) multilayer fullerene, (d) single-walled carbon nanotubes, (e) double-walled carbon nanotubes, (f) multiwalled carbon nanotubes, and (g) graphene. (Source: Reproduced with permission from Reference 2).

1.1.1 Surface Chemistry of CNTs (Small Molecules)

After the CNTs came into existence, the structure, surface properties, and formation mechanism took the prime place to prove one or the other. Surface modification of pristine CNTs with no damage to CNT sidewalls is indispensable in current materials world when concerned with the mass production. Much of the applications involve the interaction of the CNT with the surrounding medium, and in particular, for example, molecules encapsulated or bonded/grafted in or to the CNTs. In these systems, the hydrophobic–hydrophilic behavior of the CNT is considered to be important to achieve well-designed surface-modified CNT materials. In general, CNTs line up into bundle of ropes held together by van der Waals (VDW) forces, more distinctively, pi-stacking. Ruoff et al. suggested that adjacent nanotubes which are present within the multiple cylindrical layers could be deformed by VDW forces, thereby destroying cylindrical symmetry (10). It is also important to note that the interaction between a CNT and the environment mainly consists of VDW forces (either attractive or repulsive force). It is these forces that are strong enough to insert molecules inside the CNT channel. The next step of explanation could be well understood in a simple CNT–molecule–water system. The molecule remains encapsulated inside the CNT channels, and based on the energy change during this process, it was proposed that the largest energy is contributed by the creation of cavities in the water to contain the nanotubes (11). In this section, it is more confined to polymer-grafted CNTs and thereafter will be discussed briefly about various grafting methods, type of polymerization, properties, and applications. Grafting of polymers to CNTs is of much interest since the first polymer-grafted MWCNTs were reported by Jin et al. (12). The solubility of polymers/CNT composites in organic solvents is considerably good, and various methods were proposed with the aim of dispersing both CNTs and polymer-grafted CNTs (13, 14).

Studies on inner surface of CNTs and nanoporosity processes have been reported by Chamberlain et al. (15). The convex surface is reactive and the inner concave surface is inert and can hold or encapsulate the molecules in it. But metal particles (Re complex) could deform the sidewalls at atomic scale as stated by this work. This sidewall tube opening would be similar to the nanobud-like structure. Such a negative curvature, a characteristic of nanobuds, is considered important in electronic properties of CNTs (15). Synthesis, properties, and commercial applications of CNTs make them a great deal to be considered in future (16, 17).

1.1.2 Linear Polymer-Grafted CNTs

Highly soluble linear polymers were used for grafting them as covalently attached moieties to solubilize CNTs by Riggs et al. (18). The resulted linear polymer-grafted CNTs were found to be strongly luminescent, showing a new opening for the grafted CNTs served as electron acceptors. The functionalized nanotubes were synthesized to contain both short and long nanotubes and mixed with poly-(propionylethylenimine-*co*-ethylenimine) (MW 200 000, EI mole fraction 15%). Luminescence of the polymer-bound MWCNTs and SWCNTs were in the same order of magnitude, although the long SWCNTs bound to the polymer displayed less luminescence. Starting from this report, many researchers reported the covalently grafted CNTs associated with good optical and photoluminescence properties.

Apart from MWCNTs, SWCNTs are also grafted and the possibility of dissolving them in various solvents took priority. In such a way, a variety of linear polymers such as polyvinyl pyrrolidone (PVP) and polystyrene sulfonate (PSS) have been chosen for grafting to SWCNTs by Smalley et al. (19). A general phenomenon called wrapping has been employed for grafting water-soluble polymers onto SWCNTs to

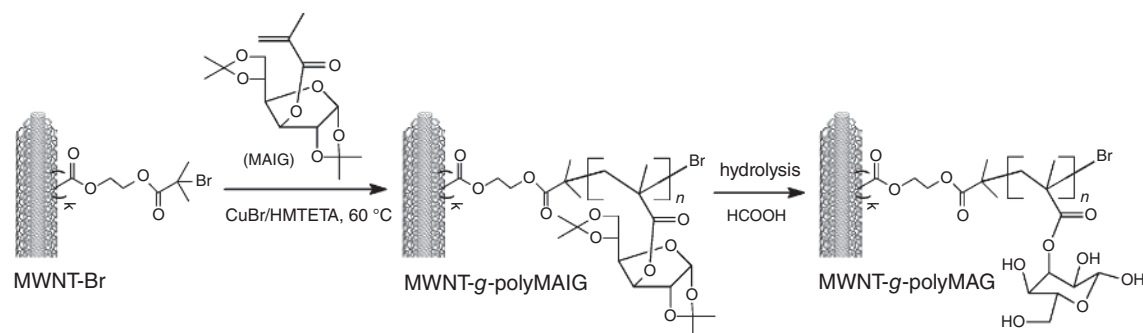


Figure 1.2 Synthetic strategy for grafting linear glycopolymer from surfaces of MWNTs by ATRP. (Source: Reproduced with permission from Reference 23).

avoid hydrophobic interface between CNTs and aqueous medium depending on thermodynamic factors. The stability of the polymer–CNT materials obtained by this method endured high ionic strength as they open up an idea for biological applications. Also, a simple method was introduced by Iijima et al. to chemically react the linear polymer poly(methyl methacrylate) (PMMA) with SWCNTs by ultrasonication (20). The aforementioned method originated while purifying the CNTs by ultrasonic irradiation and the functionalization mainly depended on frequency and duration of sonication. The organic molecules/polymer PMMA with SWCNTs could be synthesized by controlling ultrasonic irradiation, where the polymer molecules get dissociated at the hot spots produced by waves and also CNTs sidewalls get damaged to form bonding with the polymer. In another early work, SWNTs and MWNTs have been functionalized with polyvinyl alcohol (PVA) and PVA–CNT composite thin films were prepared (21). The thin films were achieved due to the highly soluble nature in polar solvents such as DMSO and water. The linear polymer PVA is considerably a good hosting polymer matrix for providing composites with high optical properties. Homogeneous dispersion of CNTs in the solvent and high optical quality of the CNT–PVA displays the effective functionalization by this method.

An *in situ* polycondensation approach has been introduced by Gao et al. to bond linear polyurea and polyurethane on amino-functionalized MWNTs. Polyurea-grafted MWNTs presented self-assembly behaviors, forming flat- or flowerlike morphologies in the solid state. Moreover, Raman spectra indicated that the signals of polymer-functionalized CNTs are dependent on the polymer species involved and not on the content of the polymer. Structure and morphology of the MWNT/polyurea molecular nanocomposites were studied by TEM and SEM. The grafted polymers onto the tubes were uniform, and it was determined that the higher the quantity of the grafted polymer, the thicker is the polymer shell. Covalent linkage between the core and the shell referred to as molecular nanocomposites could well explain the difference between grafted NTs and crude CNTs as the surface remains smooth in the latter. The main objective involved the synthesis of various flowerlike structures which would pave the way for its scope in supramolecular chemistry (22).

Also, linear glycopolymer-grafted MWNTs by surface-initiated atom transfer radical polymerization (ATRP) were reported by Gao et al. (Fig. 1.2) (23). In this work, linear biocompatible and water-soluble polymers were grafted from the surface of MWCNTs with 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-D-glucopyranose (MAIG). The structural elucidation of the resulting grafted MWNT-g-polyMAIG was predicted by NMR and FTIR. MWNT-g-polyMAIG was deprotected in 80% formic acid to get multihydroxy MWNT-g-polyMAIG. The solubility of deprotected MWNT-g-polyMAIG was studied, and the material was highly soluble in polar solvents such as water, methanol, DMSO, and DMF. SEM, TEM, and SFM observations on the morphology and nanostructures of the resulting grafted MWNTs showed that a nanowire-like morphology could be observed and the space among nanowires becomes smaller for MWNT-g-polyMAIG. A diffused nanowire-like morphology was observed for the lower polymer content which results from the cleavage of the protected units. From the TEM images, for the sample obtained after 10.5 h, the core–shell structure of polymer-grafted CNTs can be distinctly observed under high magnification. On deprotecting the material, as obtained after 29 h, a core–shell structure (4–6 nm) of polymer shell was observed which evidenced grafting of polymer on nanotube surface. The grafting method of linear glycopolymers is biocompatible as the deprotected glycopolymers with hydroxyl groups are water soluble, leading to effective grafting over CNTs. These grafting techniques would pave the way for their focus on bionanotechnology in the future.

Wu et al. reported the grafting of bromo-ended polystyrene (Br–PS–Br and PS–Br) to MWNTs over CuBr/bipy catalytic system (24). ATRP technique was used to prepare the linear polymer grafting with distinct optical limiting effect. Also, solubility of the linear polymer PS/MWNTs was observed to be good in DCB, THF, and CHCl_3 . The PS-modified MWCNTs were found to bond together as polymer chains were covalently connected to the convex walls of nanotubes. Optical limiting properties was tested for the PS-MWCNTs and found to be preserved by the covalent attachment of PS to CNTs. The optical limiting results from the open-aperture z-scan of MWCNT-PS and MWCNTs in chloroform showed a reduction in the transmittance. In general, the mechanism of the optical performance of the linear polymer–CNT solution could be regarded to both nonlinear scattering and nonlinear absorption, one or the other and the proof are under progress. Solvation of CNTs and functionalizing them remain a challenge till now that has to be boosted up to be available for biology and medicine where the solubility factor is much more critical. To abide this, water solubility of CNTs has been improved via noncovalent interactions in poly(ethylene glycol) (PEG)-based ABA linear copolymers as reported by Adeli's group (25). The water-soluble CNT nanoparticles were obtained by the

grafting method using linear-dendritic copolymer, as the method finds better observations than that observed for other methods. The hybrid materials were found to be a good system for loading the drugs and deliver to kill cancer cells.

Recently, CNTs modified with phenylacetylene groups were found to enhance the reaction of porphyrin monomers with CuAAC to give rise to linear polymers on the CNT surfaces (26). These novel nanotube–porphyrin polymer hybrids are photoactive and found to possess good optical and electrochemical properties. It was attributed that covalent bonding of the polymer to the CNT surface enhances the stability of CNTs, and moreover, the attached polymer shields a large area of the CNT surface from VDW attraction to the neighbor CNT. This was supported by previous work by Qin et al. when a linear polymer, poly(sodium 4-styrenesulfonate) (PSS), was grafted onto SWCNTs in aqueous solution by *in situ* method (27). The method was applicable to functionalize, solubilize, and purify the pristine SWCNTs in lab scale.

1.1.2.1 “Grafting to” Approach The “grafting to” technique comprises a method of attachment of as-prepared or preformed end-functionalized polymer on to the CNT reactive surface groups. In general “grafting to” method involves the generation of carboxylic acid groups on the surface of CNTs and then covalently linking the polymers with these carboxylic acid groups. Also, the polymers should possess functional groups for grafting with CNTs in this approach. A controlled synthesis and comprehensible characterization of polymer structure can be offered prior to the grafting process by this technique. In particular, the method provides synthesis path of definite polymer structures and also enables the prepared polymers to attach consequently to the CNT surface (28).

Initially, the functionalization of CNTs by “grafting to” method was reported by Fu et al. This study involves the preparation of CNTs with functional COOH groups and then converting them to acyl chlorides by refluxing with thionyl chloride. The resulting CNTs with acyl chloride moieties were further treated with the hydroxyl groups of the dendritic polymer (29). Qin et al. used “grafting to” approach for functionalizing SWNTs with polystyrene. The azide end-functional polystyrene (PS–N₃) was synthesized by ATRP of styrene through end-group transformation and then grafted to SWCNTs via cycloaddition reaction. In this case, it was suggested that the grafting density was not high due to the low reactivity and high steric hindrance of the macromolecules (30). Thus, this method has some limitations as the grafted polymer chains will not allow a further high extent of grafting. To overcome these limitations, existing methods need to be modified and implemented to achieve higher degree of polymer grafting. As an alternative to “grafting to” technique, Lou et al. (31) reported the direct covalent bonding of polymeric radicals, released by thermolysis of 2,6,6-tetramethylpiperidyl-1-oxyl-(TEMPO)-end-capped polymers to pristine nanotubes. The resulted polymer-modified MWCNTs were observed to be good in dispersion in various solvents. A hydrophobic polymer, poly2VP, which is soluble in apolar solvents and also is polyelectrolyte in water at low pH, was chosen to graft CNTs. The end-capped poly2VP type of polymer forms a shell-like layer over the CNTs, which help CNTs to dissolve in organic solvents and in acid solution. More clearly, poly2VP with positive charge plays an important role in depositing CNTs over oppositely charged layers.

1.1.2.2 “Grafting from” Approach Until now, several strategies have been proposed based on the noncovalent and covalent bonding of organic molecules to the surface of CNTs. Grafting of polymer chain on CNTs can be carried out by either “grafting from” or “grafting to” technique (28, 32). In order to obtain specific functionalities over CNTs, polymer molecules in different solvents has been preformed for grafting CNTs by grafting from technique and the grafted material as a whole is found to possess good dispersibility. “Grafting from” approach relies on the immobilization of initiators at the surface of CNTs, followed by *in situ* surface-initiated polymerization to generate tethered polymer chains. Polymer molecules grafted on the surface of CNTs in the presence of active functional groups (–COOH, –NH₂, –OH) seemed to be an effective method for nanocomposites. “Grafting from” approach was first used for the fabrication of CNT–polymer composites by an *in situ* radical polymerization process (33). The “grafting from” approach is based on the initial immobilization of initiators onto the nanotube surface, followed by *in situ* polymerization with the formation of polymer molecules attached to CNTs. The double bonds of the CNTs were opened by the monomer molecules and more exactly, the surface of the nanotube was considered to be important for this method of grafting. Early works were more focused on this phenomena and PSS was first grafted on the surface of CNTs through this method by Ajayan et al. (34). Guldi et al. reported the use of grafting from method for the grafting of PSS from the CNT surface with positively charged porphyrin, and in the following work, CNT–porphyrin hybrids were incorporated onto indium tin oxide (ITO) electrodes, which find importance in high efficient energy conversion devices (35, 36). The advantage of this approach is that polymer-functionalized nanotubes with high grafting density can be prepared. However, this process needs a strict control on the amounts of initiator and substrate.

1.1.2.3 In Situ Polymerization Approach *In situ* polymerization is a common method that has been widely explored for the synthesis of polymer-grafted nanotubes and other polymer processing techniques. In this method, polymer macromolecules can be grafted onto the walls of CNTs and more suitable for the preparation of insoluble and thermally unstable polymers, which cannot be processed by melt or solution processing. Also, this processing technique enables high nanotube loading and high miscibility with the polymer molecules. It has been practically shown that *in situ* polymerization provided stable dispersion of CNTs even after thermal processing. Moreover, CNTs can induce the local ordering of certain polymers during *in situ* polymerization. Mechanical properties of the composites can be improved due to ordered polymer packing on the CNTs that enhance stress transfer from the polymer to CNTs across the interface (37, 38).

To design novel nanomaterials like CNTs with progressive properties, *in situ* method provides an easy way to graft CNTs with polymer by various strategies depending on the interaction between the polymer and CNTs (Fig. 1.3).

The first *in situ* radical polymerization was introduced by Jia et al. in 1999 to graft CNTs to produce homogeneous composites. The method includes the use of PMMA grafted to high content of CNTs (33). In order to attach the carbon network of CNTs, initiator and monomer were mixed via *in situ* method to get the longer polymer chains grafted to CNTs. Following this, “*in situ*” bulk polymerization provided an easy way to predict the synthesis and dispersion characteristics of MWCNT composites with polymers. Owing to the grafting nature of PMMA, a uniform dispersion of MWCNTs in PMMA matrix could be achieved better than that prepared from composites by post mixing methods (40).

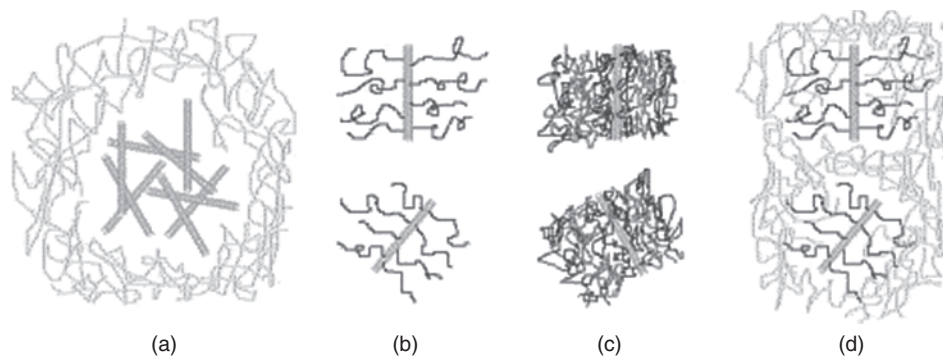


Figure 1.3 Schematic illustration of (a) CNTs dispersed mechanically in polymer matrix, (b) polymer-bonded CNTs, (c) polymer-coated CNTs by layer-by-layer self-assembly approach, and (d) polymer-functionalized CNTs dispersed in free polymer matrix. (Source: Reproduced with permission from Reference 39).

TABLE 1.1 Young's Modulus and Elongation at Break of MWNTs/PA1010 Composites Made by *In Situ* Polymerization and Melt-Mixing

Sample ^a	MWNTs Content (wt%) ^b	Young's Modulus (MPa)	Increment (%) ^c	Increment (%) ^d	Elongation at Break (%)
LPA1010	0	1021	-	-	37
NTPA-1	1	1301	27.4	8.1	35
NTPA-2	2.5	1302	27.5	8.2	31
NTPA-5	5	1449	41.9	20.4	23
NTPA-10	10	1748	71.2	45.3	17
NTPA-20	20	1813	77.6	50.7	9
NTPA-30	30	1912	87.3	58.9	5
NTPA-5B	5	1226	20.1	1.9	27
NTPA-10B	10	1694	65.9	40.8	19
NTPA-30B	30	1769	73.3	47.0	8

Source: Reproduced with permission from Reference 39.

^aSamples of NTPA-1 to NTPA-30 were made by the *in situ* polymerization method, and samples of NTPA-5B to NTPA-30B were made by the melt-mixing method.

^bThe content represents the feed weight percentage.

^cIncrement with LPA1010 as the reference, calculated by the equation: Young's modulus of (composites-LPA1010)/Young's modulus of LPA1010.

^dIncrement with CPA1010 as the reference, calculated by the equation: Young's modulus of (composites-CPA1010)/Young's modulus of CPA1010.

As a suitable method to graft polymers over CNTs, *in situ* method was used along with other techniques to achieve a strong interfacial adhesion between the CNTs and the polymer matrix. Other early works (41–43) continued the interest for *in situ* method, and now most composites involve a combination along with “*in situ*” polymerization technique. Kong et al. employed a novel *in situ* ATRP “grafting from” approach to functionalize MWCNTs and provided a new idea for extending it further to copolymerization systems to synthesize nanocomposites based on CNTs (44).

Homogeneous surface coating of long carbon nanotubes (MWCNTs) has been performed by *in situ* polymerization of ethylene to achieve high-performance polyolefinic nanocomposites. The method used here is a form of polymerization filling technique (PFT) and applied to polymerize ethylene directly onto the CNT surface. Higher tensile properties with nanofiller loading of 1 wt% were observed which is attributed to the pre-break-up of the MWCNT bundles by the PFT (45). Mostly, epoxy nanocomposites have been prepared by using *in situ* polymerization method. Polyamide 6 (PA6)/CNT composites have been prepared using pristine and carboxylated MWNT via *in situ* polymerization. In this study, the tensile strength and storage modulus of PA6/CNT composites were found to be improved and also the addition of small amount of CNTs had an effect on the crystallization and glass transition properties (46). The MWNT-reinforced PA1010 composites prepared by Zeng et al. by *in situ* polymerization method were found to possess excellent mechanical properties. Young's modulus increases with the addition of MWNTs, for example, 30 wt% MWNT improved Young's modulus of PA1010 by 87.3% (Table 1.1) (39).

In recent times, the unique properties of CNTs and Nylon-6 were combined to obtain nanocomposites through *in situ* polymerization. In this study, the plasma-polymerized CNTs and raw CNTs were added to *in situ* polymerization of ϵ -caprolactam catalyzed by 6-aminocaproic acid to obtain nanocomposites with 2 and 4 wt% of nanotubes. The electrical conductivity of nanocomposites with 4 wt% reached a maximum of

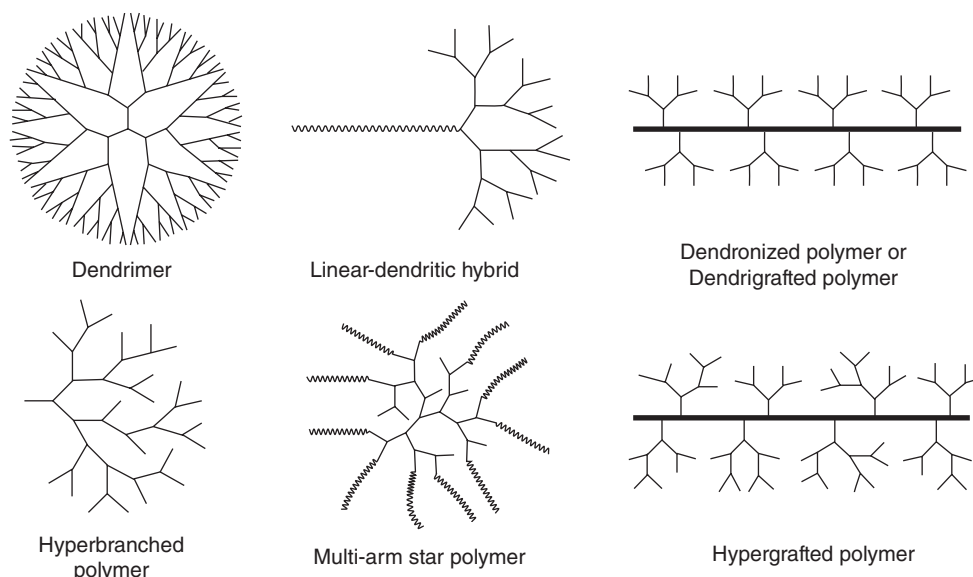


Figure 1.4 Schematic description of dendritic polymers. (Source: Reproduced with permission from Reference 51).

10^{-4} S/cm, suggesting a semiconductive material. The method used in this work was effective for the dispersion of CNTs which can be used to form nanocomposites with improved properties compared with pure Nylon-6 (47). At present, *in situ* method finds its use in many processing techniques including the production of strong nanocomposites and fibers. Hu et al. successfully prepared poly(*p*-phenylene benzobisoxazole) (PBO)–CNT fibers that are still stronger by *in situ* polymerization method. Solubility, dispersivity, reactivity, and interfacial adhesion of CNTs in polymer matrix have been greatly enhanced by this method. Dry-jet wet-spinning technique was used to fabricate continuous CNT–PBO copolymer fibers and the observations concluded that (PBO–CNT) copolymers had the high tensile modulus (89.4 ± 6.6 GPa), tensile strength (2.17 ± 0.19 GPa), and thermal stability (11% higher) compared to the PBO fibers (48). Furthermore, covalently functionalized unzipped CNTs (uCNTs) with PMMA (uCNTs-P) via *in situ* free radical polymerization has been studied recently by Wang et al., in which the mechanical reinforcement of uCNTs-P was higher than uCNTs and functionalized MWNTs (MWNTs-P) (49). Also, a combination of *in situ* polymerization and electrospinning processes has been tried to prepare CNT/polyaniline (PANI) thermoelectric composite nanofibers. Highly ordered structure of PANI backbone chains also increases the effective degree of electron delocalization in addition to reducing the π – π conjugated defects in the polymer backbone that helps in improving the thermoelectric properties (50).

1.1.3 Dendritic Polymer-Grafted CNTs

Dendrimers have prospective applications in a broad range of fields from drug delivery to material/metal coatings due to their high soluble nature, low melting viscosity, and profusion of functional groups. In general, dendrons and dendrimers possess high regularity and controlled molecular weight, and their synthesis involves step-by-step convergent and divergent approaches. Appropriately, a dendronized polymer is referred to as a linear polymer connected with side dendrons. Dendronized polymer can be obtained by direct polymerization of dendritic monomers or by linking linear polymeric core and dendrons. A review by Gao et al. reported the synthesis and applications of various polymers including the dendrimers under hyperbranched polymers in which the formation mechanism has been extensively explained (Fig. 1.4) (51).

Fu et al. introduced the dendritic polyethylene glycol with its hydroxyl group bound with the functionalized CNTs by “grafting to” method. The dendron-functionalized CNTs were hydrolyzed by trifluoroacetic acid (TFA) to defunctionalize them to get soluble CNTs. The defunctionalization of dendron-f-CNTs showed a decrease in UV/vis absorption, which leads to estimate the average absorptivities of the CNT species in solution. The observed average absorptivity for SWNTs at 500 nm is 97 ± 31 (mg/ml)/cm, a higher value obtained than that for fullerene (C₆₀) (29). Various dendrons (52) and dendrimers (53) were synthesized and grafted onto CNTs by different methods. A different type of star-shaped nanostructures was observed resulting from the reaction of the outer surface of a multifunctional dendrimer with nanotubes. Lipophilic and hydrophilic dendron species were used to functionalize CNTs under amidation and esterification reaction conditions by Sun et al. (52). The dendrons were terminated with long alkyl chains and oligomeric PEG moieties before grafting on to CNTs. Defunctionalization of the grafted materials proved an evidence for the presence of ester linkages between the dendron functionalities and CNTs. The lipophilic dendron-functionalized materials were soluble in weakly polar solvents and oligomeric PEG functionalized CNTs were soluble in organic solvents and water. These results are helpful for exploring the solubility nature of nanotubes that in turn is considered to be important to study their optical properties.

Multihydroxyl dendritic polymers were grown on the convex surfaces of MWCNTs by *in situ* ring-opening polymerization (ROP) method by “grafting from” approach to produce one-dimensional nanocomposites by our group (54). High functionalization and possibility of

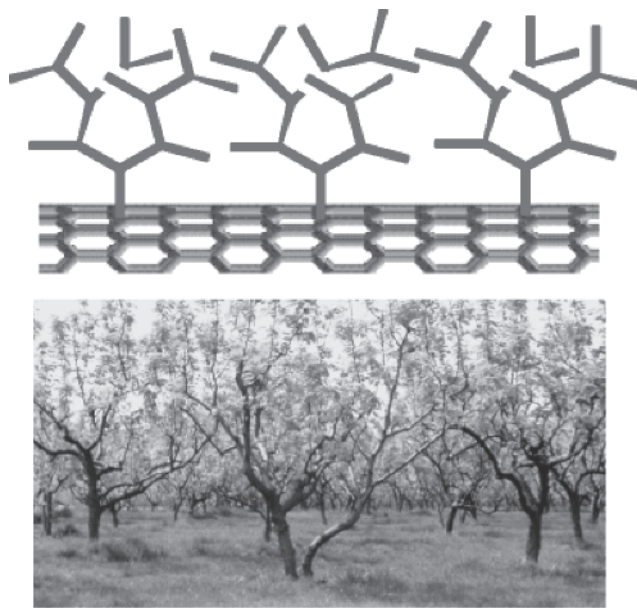


Figure 1.5 HP-grafted CNTs – branched-like trees. Graphical representation of a section of MWNTHP nano hybrids presented in this chapter (top) and a photograph of the trees grown on a hillside (bottom). (Source: Reproduced with permission from Reference 54).

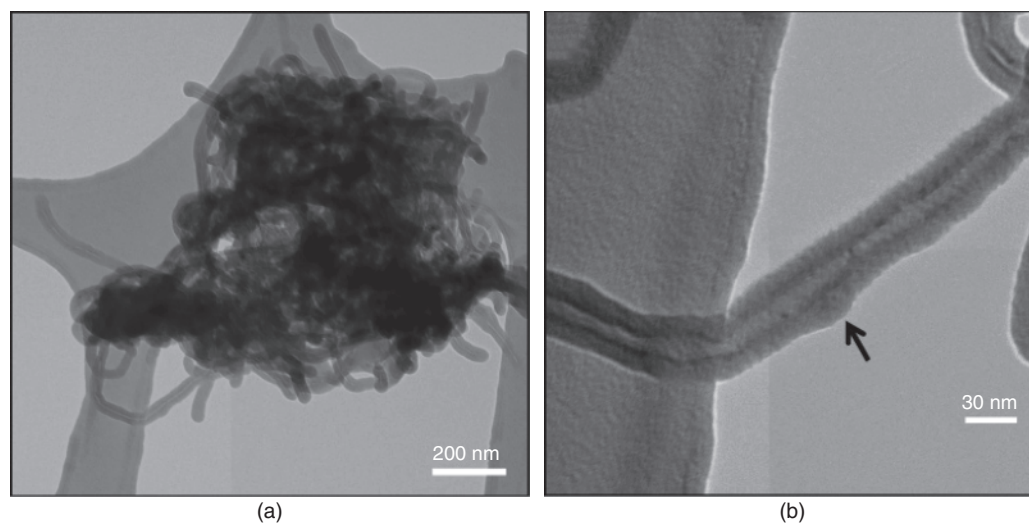


Figure 1.6 TEM images of MWNT-HP5 at (a) low magnification and (b) high magnification. (Source: Reproduced with permission from Reference 54).

extending functionalization at the ends of the tubes to build more complex nano hybrids with polymers (Fig. 1.5) were considered to provide interesting applications in designing nanomaterials and nanodevices. The dispersibility of the functionalized CNTs was good in polar solvents and the increase in the content of the grafted polymer relatively increased the dispersibility. Also, M_n of the grafted hyperbranched polymer (HP) was found to be greater than that of free HPs. The grafting seemed to have been well enough bonded with the MWNTs as there was considered to be no chance of termination than that would be in polymer solution alone. The reason for the high molecular weight remains as it could suggest another factor that MWNT-OH groups were activated initially by the catalyst before the monomer addition. Moreover, the topology of hyperbranched polymers depends on molecular weight (MW), degree of branching (DB), and unit density. Core-shell structures of HP-grafted MWNTs were observed from TEM images as shown in the figure and the thickness of the shell ranges from ~12 to 18, ~6 to 8, and ~7 to 10 nm, respectively. Polymers grown on the nanotube surface can be seen as in the TEM images (Fig. 1.6).

In order to avoid the rigid structure of the hyperbranched polymer, to make it flexible, dendrons of AB_2 type were prepared prior to the grafting to CNTs by Feng et al. The AB_2 monomer was initially synthesized from trimellitic anhydride and 1,6-diaminohexane and the resulted

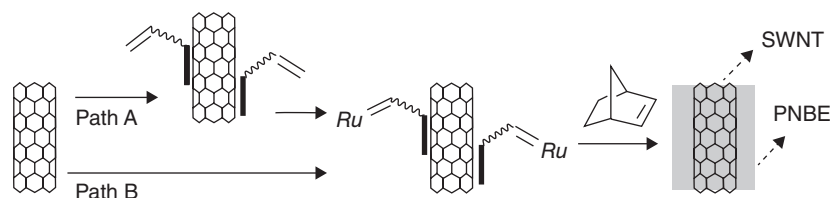


Figure 1.7 Complete functionalization strategy of ROP. (Source: Reproduced with permission from Reference 60).

products contained phenyl rings and aliphatic chains. Then, thermal polymerization of the AB_2 monomer yielded the PAI hyperbranched polymer. Following this, the HP polymer was grafted to MWCNT-COCl. To investigate the grafting nature and the interaction between the CNTs and polymer, the polymer-grafted functionalized CNTs were adsorbed on NH_2 -Si substrate. It was observed that there is a strong absorption of CNTs over the Si substrate, which confirmed the strong grafting of polymer to CNTs (55). Pan et al. reported the growth of multiamine terminated poly(amidoamine) dendrimers on the surface of CNTs. Covalent sidewall derivatization of nanotubes was confirmed by thermal degradation studies and the weight of the dendrimer increased with M_n , linearly from 2.0 to 5.0. Finally, from the observations, the amount of polymer that was grafted to CNTs could be controlled to about 10–50 wt% (56).

A different methodology was adopted for the SWCNTs grafting with poly(amidoamine) dendrimers by Campidelli et al. (57). Grafting involved two steps: in the first step, SWNTs were reacted with amino acid and paraformaldehyde, through a typical 1,3-dipolar cycloaddition reaction in DMF, to yield pyrrolidine ring functionalized with *N*-tert-butoxycarbonyl (Boc)-protected amine group, which was grafted to nanotubes in the second step. From thermogravimetric analysis (TGA) results, a weight loss of 62% was observed for SWNT nanoconjugates which revealed that unreacted amine groups must have been involved to suggest an approximate average of two porphyrins on each dendrimer. By this method more functionality can be loaded over CNTs without any deterioration of electronic properties of CNTs. MWCNT-PAMAM-PEG-PAMAM linear-dendritic copolymer composite was reported by Adeli et al. (58). Most importantly, the interaction between CNT and water has been considered to obtain better grafted CNTs with polymer molecules. In this regard, recent work on dispersing the CNTs in water by a two-step process was employed by Sohn et al. Here, poly(ether-ketone) (HPEK), a dendritic hyperbranched polymer, was grafted onto the surface of the MWCNT to avoid oxidative damages of CNTs by introducing copious reactive sites. On sulfonation of the resulting HPEK-grafted MWCNT, a zeta potential value of -57.8 mV was observed and the effect of the presence of sulfonic acids on the grafted CNTs makes them hydrophilic to get the oxygen being absorbed frequently (59).

1.1.3.1 In Situ Ring-Opening Approach Among various approaches in grafting polymer to CNTs, *in situ* ring-opening approach is another strategy that has been used to grow specific polymers from CNTs. Noncovalent functionalization of SWNTs with polymer by ROP has been carried out by Gomez et al., who proposed a selective coating of CNTs with organic polymer. Such a method was believed to be a new opening to modify the CNT structure without any destruction (Fig. 1.7) (60).

The method involves the functionalization of SWNTs with ruthenium alkydienes through cross-metathesis reactions over the walls of the CNTs and treated with norbornene (NBE). This technique was followed by two routes: (i) initially, organic precursors being adsorbed on the CNTs and in turn with a ruthenium alkydine with cross-metathesis, and (ii) pyrene-substituted ruthenium alkydine adsorbed over CNTs. AFM results showed that an ideal nonfunctionalized nanotube has the diameter of 1.4 nm and the diameter of polynorbornene (PNB)-grafted SWNT was found to be 9.1 nm, and in addition, a high selectivity of functionalization was achieved by this method. Moreover, the thickness of the PNB layer on nanotube was found to increase with the amount of monomer used and the time experienced no remarkable change during the polymerization. Also, the solubility of the polymer was good as the polymer growth seems to be longer.

Although the aforementioned method finds a novel pathway, it needs some modifications to avoid the polymer desorbed from the nanotubes. This case in general is considered to be more concerned when the polymers with high molecular weight are used for coating on CNTs. Following this, Liu et al. reported the grafting of high-molecular-weight polymers to the CNT surface by *in situ* ROP. Their experiments involve the covalent attachment of ring-opening metathesis polymerization (ROMP) catalysts to the CNTs and controlled polymerization of norbornene. Raman spectra, TEM, and AFM studies revealed the consistent properties and characteristics associated with grafted CNTs. In order to predict the effect of time over molecular weight during polymerization, polymer-grafted CNTs were treated with KOH/18 crown 6 in THF, resulting in the cleavage of the ester linkages, leaving the polymer in the solution. A linear increase in molecular weight with time was observed for 5–180 min. Also, glass transition temperature was found to be 27 °C obtained after cleavage, which was obvious with the literature values for polynorbornene (61).

In situ cationic ROP was used to grow multihydroxyl hyperbranched polymers from CNTs by using 3-ethyl-3-(hydroxymethyl) oxetane (EHOX) by Gao et al. (Fig. 1.8). Highly functionalized CNTs could be obtained by hyperbranched polymers on grafting CNTs with retaining the end-group functionalization, which can be surface modified further. Good compatibility of CNT with hyperbranched polymer matrix helps to extend the idea to achieve additional functionalization in the form of producing molecular nanoforests (discussed previously in dendritic polymer-grafted CNTs) (54).

Subsequently, poly(*ε*-caprolactone) (PCL) was employed by Gao's group by "grafting from" approach based on *in situ* ROP (Fig. 1.9) (62). CNTs as the "hard" core and the hairy polymer layer as the "soft" shell constitute the core-shell structures in the presence of grafted polymer chains in high density. CNT-grafted-PCL was further investigated for its biodegradability, which often required for a modified nanomaterial.

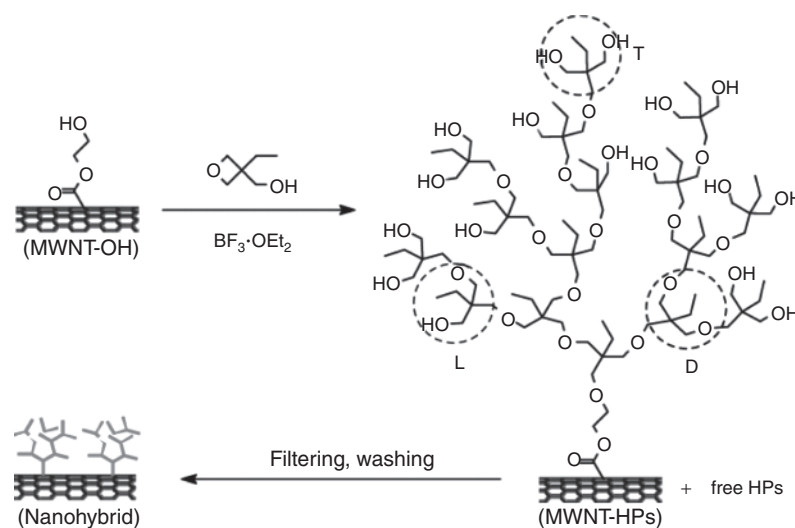


Figure 1.8 Synthesis of dendritic HP-MWNT nano hybrid through *in situ* ROP. (Source: Reproduced with permission from Reference 54).

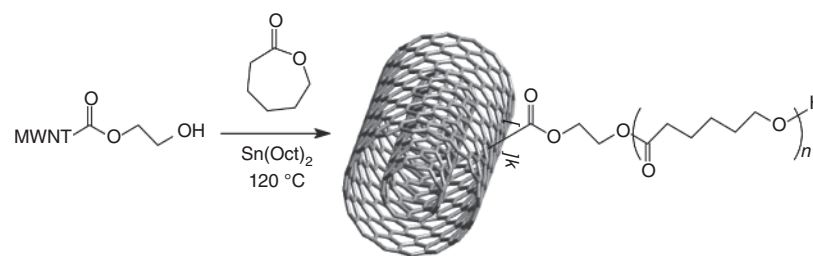


Figure 1.9 Grafting of PCL onto MWNTs. (Source: Reproduced with permission from Reference 62).

The results from the Raman spectra were interesting and showed the presence of two peaks of G band for PCL-functionalized MWNTs, implying that a large amount of polymer is grafted on to the CNTs and the additional peak corresponds to the degree of disorder in CNTs. Biodegradation nature of MWNT-g-PCL materials was tested by a bioactive enzyme catalyst, pseudomonas (PS) lipase. In the experiment, the samples were collected at regular intervals and analyzed by SEM and TEM. The results proved that there was no significant degradation for MWNT-g-PCL in the absence of the enzyme. At this stage, the CNTs were found to be thick with diameters of ~ 90.3 and 85.5 nm, respectively. Degradation occurred in the presence of PS lipase and resulted in thinner tubes than before, ~ 83.3 and 75.7 nm, respectively). For 48 h, the tubes were still thinner and after 96 h of degradation, residual polymer lies on the surfaces of MWNTs while the nanotubes were found with diameters of ~ 20 – 30 nm, which is more or less equal to that of the purified tubes. Covalently grafted biodegradable PCL onto CNT surfaces retains the biodegradability of conventional PCL, which suggests that it could be completely biodegraded by PS lipase within 4 days. It is evident that grafted CNTs could support cell growth without any damage of the enzyme.

Other works involved the use of ROP to build uniform and efficient grafting to CNTs and find specific applications depending upon the properties of polymer and CNTs. Grafting of poly(L-lactide) (PLLA) on CNTs by surface-initiated polymerization was carried out by Chen et al. (63). Purified MWNTs were acid functionalized and then hydroxyl functionalized with SOCl_2 to yield MWNT-OH. PLLA-grafted CNTs were obtained by the addition of L-lactide to MWNTs-OH with tin(II) 2-ethylhexanoate at various temperatures under nitrogen atmosphere. The materials were found to have good solubility in organic solvents such as chloroform and DMF due to the higher PLLA content. The measured weight of the PLLA-grafted CNTs increased after polymerization, which confirms the effective grafting. Raman spectroscopy revealed that I_D/I_G ratio for the grafted CNTs was 0.69, higher than that of the pristine MWNT (0.61), which is attributed to the grafting of PLLA. The work suggests that the Raman studies still needed further evidences to understand the interaction between CNTs and the polymer onto it. In another method adopted by Feng et al., PLLA brushes were grafted on MWNTs and the grafted polymers were found to possess superparamagnetic properties. A uniform layered grafting was achieved by this method and the layer depends on the feed ratio of the initial monomer to CNTs (64).

Gao et al. reported the functionalization of CNTs with hyperbranched polyglycerol (HPG) by anionic ROP (Fig. 1.10). Water-soluble and biocompatible HPG as a polymer with multihydroxyl groups was assumed to be more suitably prepared by anionic ROP technique. More particularly, a stable macroinitiator was prepared in the presence of anions by one-step [2+1] cycloaddition of nitrenes to the MWNTs.

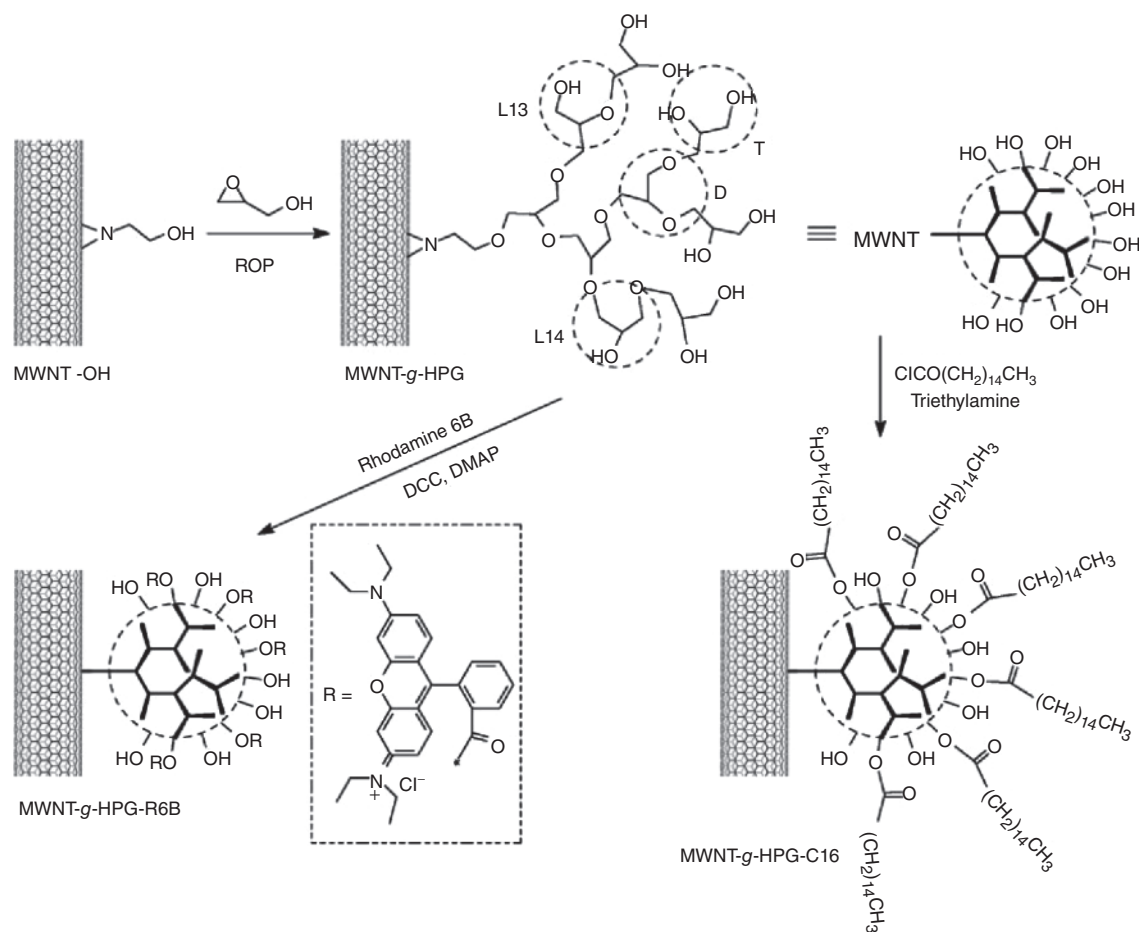


Figure 1.10 Functionalization of multiwalled carbon nanotubes (MWCNTs) with hyperbranched polyglycerol (HPG) by anionic ring-opening polymerization (ROP) and modification of the grafted HPG. (Source: Reproduced with permission from Reference 65).

The presence of hydroxyl groups in the MWNT-grafted HPGs contributes to the better formation of multifunctional nanohybrids. This was better understood by synthesizing the amphiphilic hyperbranched polymer-grafted MWNTs, on the addition of palmitoyl chloride with MWNT-g-HPGs in triethylamine. The selected results of HPG-grafted MWNTs (MWNT-g-HPG4) are shown in Table 1.2. It was observed that the grafted polymer content increases from ~ 22.8 to 90.8 wt% for the weight feed ratio (R_{wt}) rising from $\sim 5.75:1$ to $103.5:1$. This is attributed to the fact that the weight fraction of grafted polymer (f_{wt}) could be well adjusted in a wide range by R_{wt} with the grafting efficiency up to 90.8 wt%. The efficiency was high when compared to that observed for other methods to obtain dendritic polymer-grafted CNTs. Also, the solubility was found to be good in weakly polar or nonpolar solvents such as THF, chloroform, and dichloromethane than that observed in polar solvents. Such MWNT-g-HPG hybrids synthesized by ROP method with tunable properties proposed a resourceful platform for bionanotechnology (65).

Moreover, MWNT-g-PCL was synthesized by ROP and compared for the demonstration of the reactivity and functions of the immobilized organic moieties with various CNT-polymer substrates (66).

Functional groups have been covalently anchored to the MWNTs. However, it is not clear in some aspects like, since the surface functionalities could not be distinguished even by HR-TEM, to predict whether the functional groups are anchored on the MWNTs uniformly or uneven or around the tips. Second, whether the chemical reactivity of functional groups would be retained and finally is that possible to graft polymer directly from the tube surfaces to propose a simple and cost-effective method. In order to clarify these doubts, various chemical reactions were performed on the f-MWNTs, as shown in Figure 1.11.

In situ ROP of ϵ -caprolactone has been reviewed by Han and Gao and the review presents the highlights of functionalization of CNTs by azide chemistry (2). An *in situ* ring-opening copolymerization of L-lactide (LA) and ϵ -caprolactone (CL) was reported by Chakoli et al. using stannous octanoate and hydroxylated MWCNTs (MWCNT-OHs) as the initiators (67). Although there is an increase in the mechanical strength of the polymers due to the presence of MWCNTs, the elongation properties of the resulting material were found to decrease. Apart from compatibility between CNTs and polymer matrix, the fabrication of CNTs with appropriate functional groups associated with controlled thickness is extremely a subtle task. Recently, Wua et al. reported the feasibility of ring-opening approach for grafting

TABLE 1.2 Reaction Conditions and Selected Results for Grafting HPG from MWNT Surface

Sample	R_{wt}^a	R_{mole}^a	f_{wt}^c	$M_{n,GPC}^d$ g/mol	PDI ^d	$M_{n,TGA}^e$ g/mol	m_{nongra}/m_{gra}^f
MWNT-g-HPG1	5.75/1	56/1	22.8	1,300	1.37	1,230	11.6
MWNT-g-HPG2	13.8/1	134/1	39.2	8,300	1.79	4,640	7.2
MWNT-g-HPG3	34.5/1	335/1	49.6	21,100	1.74	7,080	4.8
MWNT-g-HPG4	63.25/1	614/1	66.1	57,600	1.54	14,200	5.1
MWNT-g-HPG5	74.75/1	726/1	74.5	81,300	1.69	21,020	4.5
MWNT-g-HPG6	103.5/1	1005/1	90.8	100,600	1.58	71,000	4.2

Source: Reproduced with permission from Reference 65.

^aWeight feed ratio of glycidol to MWNT-OH.

^bMole feed ratio of glycidol to hydroxyl groups of the MWNT-OH.

^cWeight fraction of grafted polymer in the product of MWNT-g-HPG calculated from corresponding TGA data between 200 and 500 °C.

^dNumber-average molecular weight (M_n) and polydispersity index (PDI) of the free polymer collected from the centrifugated solution, measured by GPC with DMF as the eluent and PS as the calibration.

^eAverage molecular weight of the grafted HPG calculated from TGA data is $M_{n,TGA} = m_{gra}/n_{gra} = f_{wt}/[(1 - f_{wt}) \cdot 1.39 \times 10^{-3}]$, where 1.39 represents the concentration of initiating sites per gram of MWNTs (mmol g^{-3}), m_{gra} and n_{gra} represent the mass and molar amount of the grafted HPG, respectively. $M_{n,TGA}$ for MWNT-g-HPG1 is the molar mass of neat HPG units excluding the weight fraction of organic moieties attached onto MWNT-OH, because of the great influence of such weight fraction on the calculation for such a low R_{mole} .

^fMass ratio of nongrafted polyglycerol to grafted amount.

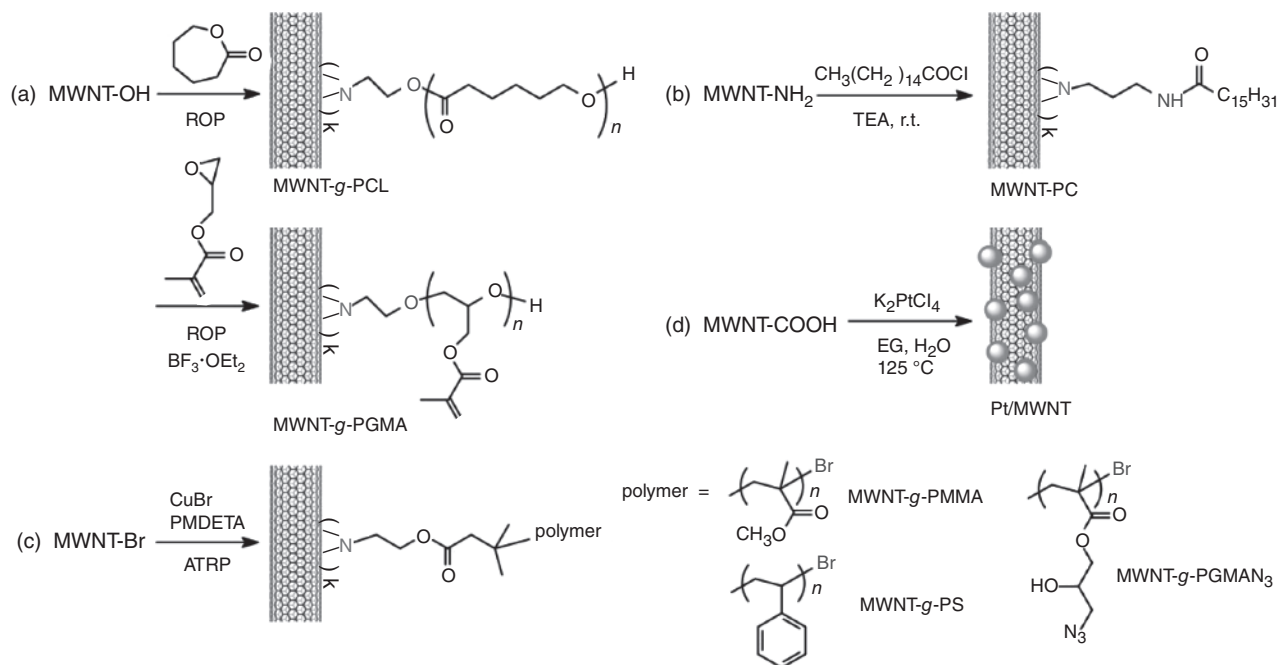


Figure 1.11 Chemical reactions on f-MWNTs. (Source: Reproduced with permission from Reference 66).

polybutylene terephthalate on MWNTs by using cyclic butylene terephthalate oligomers (68). Adeli et al. successfully modified MWCNTs using highly branched polyglycerol (PG) through *in situ* ROP of glycidol onto their surface (69). High biocompatibility and water solubility of MWCNT-g-PG hybrid materials was used in biological systems to test the level of toxicity of CNTs. *In vitro* cytotoxicity tests and hemolysis assay results showed no adverse effects on the HT1080 cell and red blood cells up to 1 mg/ml concentration. Polyglycerol functionalized CNTs found to decrease *in vitro* cytotoxicity of CNT.

1.1.3.2 Self-Condensing Vinyl Polymerization Approach Self-condensing vinyl polymerization (SCVP) has found to be very useful process since its discovery by Frechet et al. (70). The process involves the polymerization of double bonds initiated by the active center of the functional group B* and A being the double bond, where AB* is an inimer. Later, the kinetic and mechanism for the SCVP was proposed by Muller et al. (71). A clear review on SCVP method involving its origin, its mechanism, and its uses has been reported by Gao and

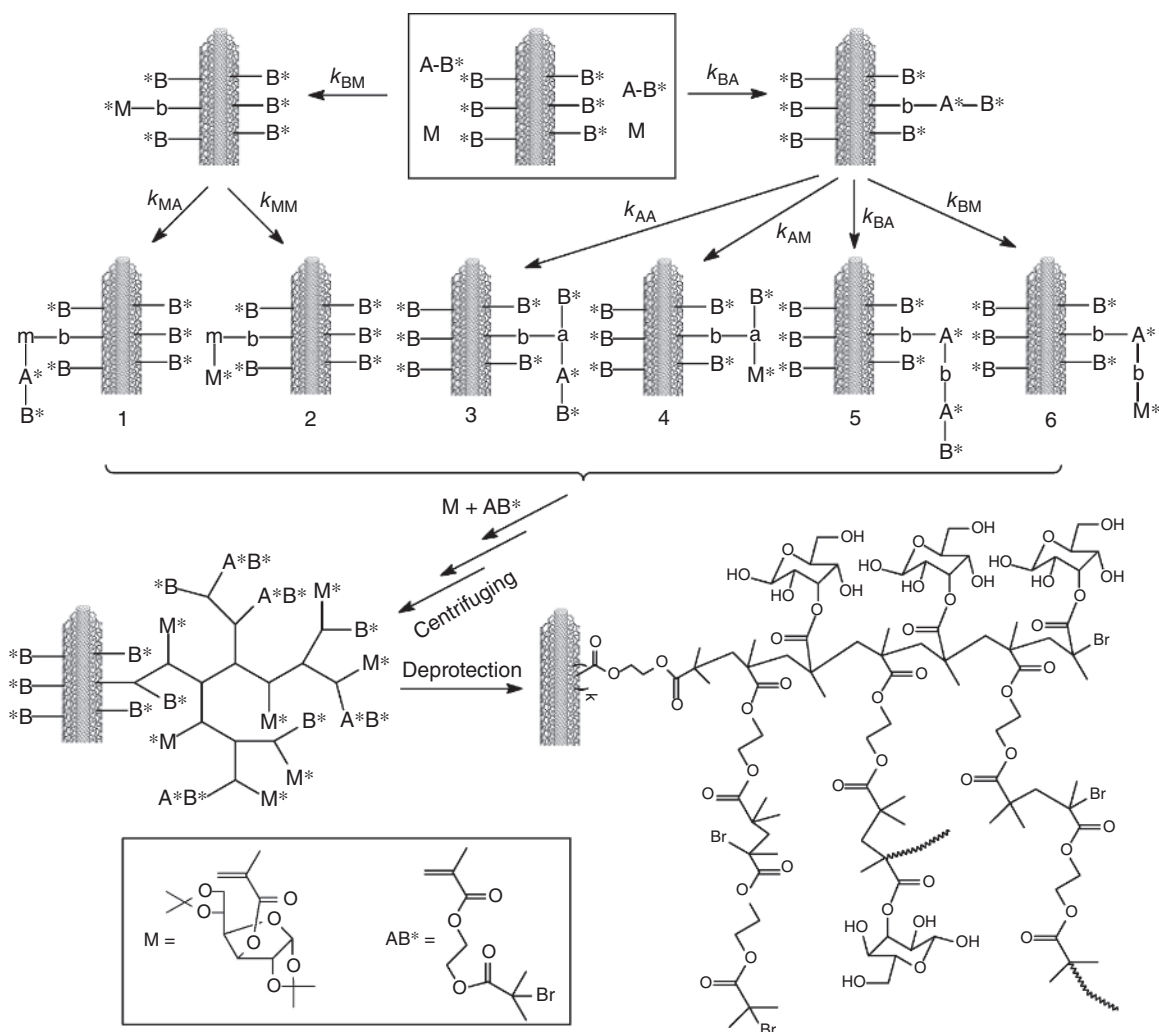


Figure 1.12 Synthetic strategy for grafting hyperbranched glycopolymer from surfaces of MWNTs by self-condensing vinyl copolymerization (SCVCP) of inimer (AB^*) and monomer (M) via ATRP. (Source: Reproduced with permission from Reference 23).

Yan (51), including the first attempt to synthesize hybrid nanoparticles with hyperbranched polymer shells with the use of SCVP by Muller et al. (71).

Earlier work by Yan et al. initiated the use of SCVP via ROP to graft hyperbranched polymer on MWNTs. It was suggested that the ATRP would be helpful for the syntheses of hyperbranched polymers by SCVP (54). The grafting of HPs to CNTs finds some difficulties when inimer is employed in the polymerization as free polymer. An attempt to grow polymers on the CNTs without removing the monomer from the solution was carried out by Hong et al. (72). This process involves the preparation of bromoisobutyryl fragment-immobilized MWNTs to get MWNT-Br (ATRP surface initiator) and was further used to attach a hyperbranched polymer shell to obtain a polyfunctional initiator (B^*f) in the SCVP to generate hyperbranched macromolecule functionalized MWNTs. By slow addition of AB^* inimer, immobilization of B^* on the surface of MWNTs helps in initiating SCVP. Also, hyperbranched polymer-grafted MWNTs were found to be dispersed in solvents even without observing sedimentation for a long period of time.

Gao et al. reported the grafting of linear and hyperbranched glycopolymers from the surface of MWCNTs by self-condensing vinyl copolymerization of 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-*D*-glucofuranose (MAIG) and AB^* inimer, 2-(2-bromoisobutyryloxy)ethyl methacrylate (BIEM) (Fig. 1.12) (23). The kinetic study of SCVP showed that the molecular weight and polydispersity index (PDI) increased with conversion for lower γ (0.5 and 1) and for higher γ (2.5 and 5). After maximum conversion ($\sim 90\%$), the molecular weight reached a stand point and then multihydroxy hyperbranched glycopolymer-grafted MWNTs were obtained by deprotection. PDI was observed to be broader as after 45–50% conversion, which might be due to the polymer coupling in the reaction system.

The grafted polymer content and other results are shown in Table 1.3. DB of the hyperbranched glycopolymers is an important factor and was determined for the polymer-grafted CNTs by 1H NMR. It can be seen that the DB decreases from 0.49 to 0.21 with increase in γ from 0.5 to 5, which is well in agreement with the theory. It was concluded that the kinetics observed for sacrificial initiator (first-order time

TABLE 1.3 Reaction Conditions and Results for the Self-Condensing Vinyl Copolymerization (SCVCP) of MAIG and BIEM in the Presence of MWNT-Br

γ^a	Time, h ^b	Convsn, % ^c	$M_{n,app}^d$	PDI ^d	$f_{wt}, \%^e$	MW _{TGA} ^f	DB _{NMR}	DB _{theo}
0	4.5	~95.0	4000	1.88	0.38	1165		0.465
0.5	21.5	73.8	3660	1.77	0.40	1270	0.49	0.50
1	4.5	~95.7	5630	2.03	0.42	1380	0.43	0.49
2.5	22.0	~93.0	4200	1.86	0.46	1680	0.34	0.40
5	29.5	~90.0	4370	1.81	0.53	2140	0.21	0.24

Source: Reproduced with permission from Reference 23.

^aThe feed mole ratio of MAIG to BIEM.

^bA sample is taken from the reaction system after a given time to determine the conversion by NMR. The final reaction time set is dependent on the conversion of vinyl groups and the viscosity of the reaction system. In the case of either quite high viscosity (so it is difficult to take a sample by the syringe from the reaction system) or the small conversion difference after a relatively long reaction time, the reaction would be stopped. The initial feed ratio of BIEM to ethyl acetate is approximately 1/2 ($\gamma = 0$), 1/5 ($\gamma = 0.5$), 1/2 ($\gamma = 1$), 1/2.5 ($\gamma = 2.5$), and 1/5 ($\gamma = 5$) g/ml.

^cThe conversion of vinyl groups determined by ¹H NMR.

^dThe apparent number-average molecular weight (M_n) and polydispersity index (PDI) of soluble polymer measured by GPC.

^eThe polymer content grafted on MWNTs, determined by TGA.

^fThe average molecular weight evaluated from TGA.

conversion plot) is comparable with the ATRP of MAIG initiated by MWNT-Br. These observations on polymer-CNT nanohybrids could be well enough expected to open new ventures in bionanotechnology.

1.2 FUNCTIONALIZATION OF CARBON NANO-ONIONS

Among the fullerene family, onion-like carbons consisting of multiple concentric graphitic shells to form encapsulated structures called as carbon nano-onions (CNOs) have been found by Ugarte in 1992 (73). Also, multishelled fullerenes or CNOs were discovered by Iijima and Ichihashi in 1993, at the same time they invented CNTs (74). Like CNTs, CNOs possess interesting properties such as high surface area, density, and multilayer morphology (75), and their rich attributes led to applications in different fields including catalysis, fuel cells, optical limiting, electromagnetic shielding, energy storage, tribology, tumor therapy, and supercapacitors (76–90). Till now, CNOs have not been explored as only few reports exist. It is considered that CNOs find importance for tribological applications due to their spherical shape (91). In particular, NASA has shown much interest on CNOs for their specific aerospace applications (84).

Ozawa et al. suggested the formation of spiroid-to-onion transformation, but the formation mechanism of CNOs has been left unproved till now (92). The transformation takes place through interlayer valence isomerization in which the delocalized radical centers propagate radially in a zipper-like fashion. The structure resembles a sphere with regular shells, which are the primary particles of carbon black. In recent times, CNOs has been found to exhibit dislocation dynamics in a different manner apart from bulk crystalline phase (93). The observed spherical topology results in an asymmetry that would have been attributed to an unexpected attraction of dislocations toward the core. The dislocation is mainly considered to be important for mechanical properties. The isolation and purification of CNOs are difficult and thus the clear mechanism has not been proved yet. The production of extremely pure CNOs in high yields by annealing carbon nanodiamond particles at temperatures above 1200 °C was reported by Kuznetsov et al. (94). The production of nano-onions to high yield have also been employed by Sano et al. in water by arcing between two graphite electrodes which involves without vacuum (95). The nonvacuum method involves the use of carbon arc sustained in deionized water by initiating arc discharge by contacting a pure graphite anode (tip diameter, 5 mm) with the carbon cathode (tip diameter, 12 mm) and the discharge voltage and current were 16–17 V and 30 A, respectively (Fig. 1.13). The nano-onions were collected on the water surface with high purity. In this study, they were able to produce 3 mg/min with average diameter of 25–30 nm (range 5–40 nm), a useful size range for many lubrication applications. Similarly to CNTs, CNOs are surface functionalized to make it more appropriate to be available for various applications.

Functionalization of carbon materials by diazonium-based compounds has been used for CNTs before and the same method was followed to functionalize CNOs by Flavin et al. (96). Pristine CNOs in DMF were dispersed and aniline derivative and isoamyl nitrite were added under inert nitrogen atmosphere and stirred at 60 °C overnight. The functionalized CNOs were obtained by centrifuging finally. Degree of derivatization of the f-CNOs was predicted by TGA and the observations were useful in differentiating the graphitic structure of CNOs. In addition, Raman spectra presented the D-band at 1354 cm⁻¹, which relates to the conversion of sp² to sp³ carbon.

Ontoria et al. reported the covalent functionalization of CNOs with hexadecyl chains (Fig. 1.14) (97). The functionalization was achieved by reducing CNOs with Na/K alloy in a solvent under vacuum followed by nucleophilic substitution by using 1-bromohexadecane. The covalent functionalization was evidenced primarily by TGA and Raman spectroscopy. It was observed from the Raman studies that the pristine CNOs presents a varying ratio of $I(D)/I(G)$ with respect to the particle size. $I(D)/I(G)$ of 0.8 and 1.4 were observed for large CNOs prepared by arc discharge of graphite under water and that obtained by annealing method of nanodiamond particles to produce small CNOs.

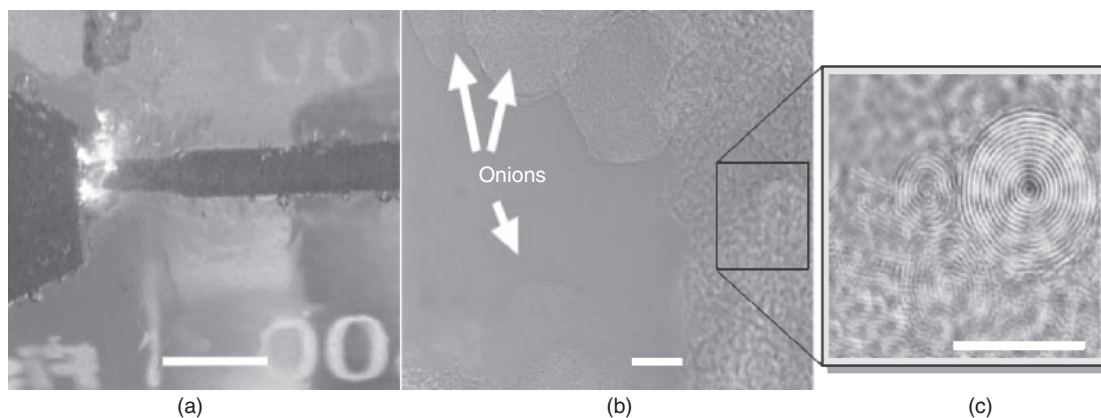


Figure 1.13 Carbon nano-“onions” created by arc discharge in water. (a) Image of a carbon arc discharge in water. Scale bar, 12 mm. (b, c) Low- and high-magnification electron micrographs of carbon nano-onions floating on the water surface after their production. Scale bars, 10 nm. (Source: Reproduced with permission from Reference 95).

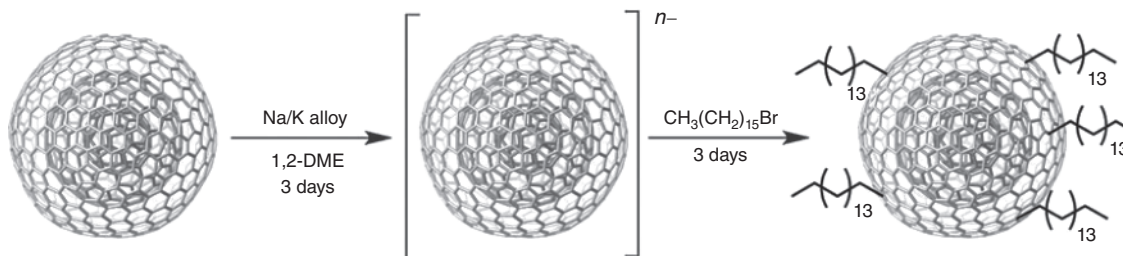


Figure 1.14 Reductive treatment of CNOs by a Na–K alloy in 1,2-DME and subsequent alkylation using 1-bromohexadecane. (Source: Reproduced with permission from Reference 97).

Functionalization of the CNOs with 1-bromohexadecane helps homogeneous dispersion and also the structure obtained with more consistent porous morphology and definite channels.

A different functionalization of CNOs was attempted by modifying CNOs with varying concentrations of RuO₂ by a controlled chemical method by Borgohain et al. (98). The f-CNOs was used as electrodes and found to enhance the specific capacitance, high power, and high energy density. The method proposed the synthesis of CNOs with 5–7 nm diameter in a graphitization furnace by annealing nanodiamond (Dynalene NB50) at 1650 °C for 1 h under helium. Then the CNOs were functionalized with RuO₂ in the presence of glycolic acid. CNOs and chemically modified CNOs have good electrical conductivity, ideal mesoporosity for ion transport, and high electrochemical and thermal stability. It was suggested that sp² carbon in CNOs could enhance the charge-transfer processes in metal oxide redox based supercapacitors. This method displays a relatively high specific capacitance of 334 F/g for 67.5 wt% RuO₂ loading which in turn can deliver an energy density of 11.6 W h/kg. In another work, porosity on CNOs was introduced by KOH activation, thereby improving remarkable changes in structure, surface area, and pore size (99). In this process CNOs were synthesized by combustion in air on laser resonant excitation of ethylene. Highly concentric pristine CNOs obtained at a laser wavelength of 10.5321 μm were used for further activation and tested for electrochemical performance. The activated CNOs demonstrate high charge/discharge rates at scan rates up to 5000 mV/s and the high capacitance retention ratio of about 71% was observed for an increase in the current density from 0.75 to 25 A/g. The considerable improvement of capacitance is ascribed to the high surface area, porosity, and hydrophilic surface upon KOH activation. It was concluded that the activated CNOs may find its objective in capacitor field which have a high knee frequency (825 Hz) and a smaller relaxation time constant (82.5 ms). Research on CNOs is still to be explored and the mechanism is far from the accomplishment to explain from the origin to different intermediates. However, there is an urge to this type of nanostructures in applying them in different fields, more particularly, as emerging lubricants up-to-date.

1.3 CONCLUSIONS AND FUTURE SCOPE

CNTs have been considered to be one of the ideal forms of carbon materials for various applications due to its extremely high electrical conductivity, and strong mechanical strength. Grafting of polymer on the surface of CNTs has been in practice to enhance mechanical and electrical properties; however, massive efforts are still needed to implement effective functionalization methodologies. The most

essential problem lies in how to prepare homogeneous composition of CNT-grafted polymers and maintain control over molecular weight, polymerization time, grafting density, and molecular weight distribution. High molecular weight and the high grafting density of the CNT-grafted polymers make a subtle task in controlling them to achieve grafted materials with average molecular weight. Functionalization of CNTs and related nanostructures like CNOs have already emerged as an important aspect in applying hybrid materials in various applications from energy field to medicine. Future directions of research on modifying and developing novel functionalization strategies would pave the way for such nanomaterials to be used in various fields.

REFERENCES

1. Iijima S. Helical microtubules of graphitic carbon. *Nature* 1991;354(6348):56–58.
2. Han J, Gao C. Functionalization of carbon nanotubes and other nanocarbons by azide chemistry. *Nano-Micro Lett* 2010;2(3):213–226.
3. Baughman RH, Zakhidov AA, de Heer WA. Carbon nanotubes--the route toward applications. *Science* 2002;297(5582):787–792.
4. Huxtable ST, Cahill DG, Shenogin S, Xue L, Ozisik R, Barone P, Keblinski P. Interfacial heat flow in carbon nanotube suspensions. *Nat Mater* 2003;2(11):731–734.
5. Calvert P. Nanotube composites: a recipe for strength. *Nature* 1999;399(6733):210–211.
6. Down WB, Baker RTK. Modification of the surface properties of carbon fibers via the catalytic growth of carbon nanofibers. *J Mater Res* 1995;10(03):625–633.
7. Thostenson ET, Li WZ, Wang DZ, Ren ZF, Chou TW. Carbon nanotube/carbon fiber hybrid multiscale composites. *J Appl Phys* 2002;91(9):6034–6037.
8. Spitalsky Z, Tasis D, Papagelis K, Galiotis C. Carbon nanotube–polymer composites: chemistry, processing, mechanical and electrical properties. *Prog Polym Sci* 2010;35(3):357–401.
9. Pasquali M. Polymer composites: Swell properties and swift processing. *Nat Mater* 2004;3(8):509–510.
10. Ruoff RS, Tersoff J, Lorents DC, Subramoney S, Chan B. Radial deformation of carbon nanotubes by van der Waals forces. *Nature* 1993;364(6437):514–516.
11. Walther JH, Jaffe R, Halicioglu T, Koumoutsakos P. Carbon nanotubes in water: structural characteristics and energetics. *J Phys Chem B* 2001;105(41):9980–9987.
12. Jin Z, Sun X, Xu G, Goh SH, Ji W. Nonlinear optical properties of some polymer/multi-walled carbon nanotube composites. *Chem Phys Lett* 2000;318(6):505–510.
13. Curran SA, Ajayan PM, Blau WJ, Carroll DL, Coleman JN, Dalton AB, Davey AP, Drury A, McCarthy B, Maier S, Strevens A. A composite from poly (m-phenylenevinylene-co-2, 5-dioctoxy-p-phenylenevinylene) and carbon nanotubes: A novel material for molecular optoelectronics. *Adv Mater* 1998;10(14):1091–1093.
14. Coleman JN, Curran S, Dalton AB, Davey AP, McCarthy B, Blau W, Barklie RC. Percolation-dominated conductivity in a conjugated-polymer-carbon-nanotube composite. *Phys Rev B* 1998;58(12):R7492.
15. Chamberlain TW, Meyer JC, Biskupek J, Leschner J, Santana A, Besley NA, Bichoutskaia E, Kaiser U, Khlobystov AN. Reactions of the inner surface of carbon nanotubes and nanoprotusion processes imaged at the atomic scale. *Nat Chem* 2011;3(9):732–737.
16. Dai H. Carbon nanotubes: synthesis, integration, and properties. *Acc Chem Res* 2002;35(12):1035–1044.
17. De Volder MF, Tawfick SH, Baughman RH, Hart AJ. Carbon nanotubes: present and future commercial applications. *Science* 2013;339(6119):535–539.
18. Riggs JE, Guo Z, Carroll DL, Sun YP. Strong luminescence of solubilized carbon nanotubes. *J Am Chem Soc* 2000;122(24):5879–5880.
19. O’Connell MJ, Boul P, Ericson LM, Huffman C, Wang Y, Haroz E, Kuper C, Tour J, Ausman KD, Smalley RE. Reversible water-solubilization of single-walled carbon nanotubes by polymer wrapping. *Chem Phys Lett* 2001;342(3):265–271.
20. Koshio A, Yudasaka M, Zhang M, Iijima S. A simple way to chemically react single-wall carbon nanotubes with organic materials using ultrasonication. *Nano Lett* 2001;1(7):361–363.
21. Lin Y, Zhou B, Shiral Fernando KA, Liu P, Allard LF, Sun YP. Polymeric carbon nanocomposites from carbon nanotubes functionalized with matrix polymer. *Macromolecules* 2003;36(19):7199–7204.
22. Gao C, Jin YZ, Kong H, Whitby RL, Acquah SF, Chen GY, Qian H, Hartschuh A, Silva SRP, Henley S, Fearon P, Kroto HW, Walton DR. Polyurea-functionalized multiwalled carbon nanotubes: synthesis, morphology, and Raman spectroscopy. *J Phys Chem B* 2005;109(24):11925–11932.
23. Gao C, Muthukrishnan S, Li W, Yuan J, Xu Y, Müller AH. Linear and hyperbranched glycopolymer-functionalized carbon nanotubes: synthesis, kinetics, and characterization. *Macromolecules* 2007;40(6):1803–1815.
24. Wu HX, Tong R, Qiu XQ, Yang HF, Lin YH, Cai RF, Qian SX. Functionalization of multiwalled carbon nanotubes with polystyrene under atom transfer radical polymerization conditions. *Carbon* 2007;45(1):152–159.
25. Adeli M, Hakimpoor F, Ashiri M, Kabiri R, Bavadi M. Anticancer drug delivery systems based on noncovalent interactions between carbon nanotubes and linear–dendritic copolymers. *Soft Matter* 2011;7(8):4062–4070.
26. Hijazi I, Joussetme B, Jégou P, Filoramo A, Campidelli S. Formation of linear and hyperbranched porphyrin polymers on carbon nanotubes via a CuAAC “grafting from” approach. *J Mater Chem* 2012;22(39):20936–20942.

27. Qin S, Qin D, Ford WT, Herrera JE, Resasco DE, Bachilo SM, Weisman RB. Solubilization and purification of single-wall carbon nanotubes in water by in situ radical polymerization of sodium 4-styrenesulfonate. *Macromolecules* 2004;37(11):3965–3967.
28. Liu Y, Yao Z, Adronov A. Functionalization of single-walled carbon nanotubes with well-defined polymers by radical coupling. *Macromolecules* 2005;38(4):1172–1179.
29. Fu K, Huang W, Lin Y, Riddle LA, Carroll DL, Sun YP. Defunctionalization of functionalized carbon nanotubes. *Nano Lett* 2001;1(8):439–441.
30. Qin S, Qin D, Ford WT, Resasco DE, Herrera JE. Functionalization of single-walled carbon nanotubes with polystyrene via grafting to and grafting from methods. *Macromolecules* 2004;37(3):752–757.
31. (a) Lou X, Detrembleur C, Sciannamea V, Pagnouille C, Jérôme R. Grafting of alkoxyamine end-capped (co) polymers onto multi-walled carbon nanotubes. *Polymer* 2004;45(18):6097–6102. (b) Lou XD, Detrembleur C, Pagnouille C, Jérôme R, Bocharova V, Kiriy A. Surface modification of multiwalled carbon nanotubes by poly (2-vinylpyridine): Dispersion, selective deposition, and decoration of the nanotubes. *Adv Mater* 2004;16(23–24):2123–2127.
32. Coleman JN, Dalton AB, Curran S, Rubio A, Davey AP, Drury A, McCarthy B, Lahr B, Ajayan PM, Roth S, Barklie RC, Blau WJ. Phase separation of carbon nanotubes and turbostratic graphite using a functional organic polymer. *Adv Mater* 2000;12(3):213–216.
33. Jia Z, Wang Z, Xu C, Liang J, Wei B, Wu D, Zhu S. Study on poly (methyl methacrylate)/carbon nanotube composites. *Mater Sci Eng, A* 1999;271(1):395–400.
34. Viswanathan G, Chakrapani N, Yang H, Wei B, Chung H, Cho K, Ryu Y, Ajayan PM. Single-step in situ synthesis of polymer-grafted single-wall nanotube composites. *J Am Chem Soc* 2003;125(31):9258–9259.
35. Guldi DM, Rahman GNA, Ramey J, Marcaccio M, Paolucci D, Paolucci F, Qin S, Ford WT, Balbinot D, Jux N, Tagmatarchis N, Prato M. Donor–acceptor nanoensembles of soluble carbon nanotubes. *Chem Commun* 2004;18:2034–2035.
36. Guldi DM, Rahman GMA, Prato M, Jux N, Qin S, Ford W. Single-Wall Carbon Nanotubes as Integrative Building Blocks for Solar-Energy Conversion. *Angew Chem Int Ed* 2005;44:2015–2018.
37. Coleman JN, Cadek M, Blake R, Nicolosi V, Ryan KP, Belton C, Fonseca A, Nagy JB, Gun'ko YK, Blau WJ. High performance nanotube-reinforced plastics: understanding the mechanism of strength increase. *Adv Funct Mater* 2004;14(8):791–798.
38. Coleman JN, Cadek M, Ryan KP, Fonseca A, Nagy JB, Blau WJ, Ferreira MS. Reinforcement of polymers with carbon nanotubes. The role of an ordered polymer interfacial region. *Experiment and modeling. Polymer* 2006;47(26):8556–8561.
39. Zeng H, Gao C, Wang Y, Watts PC, Kong H, Cui X, Yan D. In situ polymerization approach to multiwalled carbon nanotubes-reinforced nylon 1010 composites: mechanical properties and crystallization behavior. *Polymer* 2006;47(1):113–122.
40. Park SJ, Cho MS, Lim ST, Choi HJ, Jhon MS. Synthesis and Dispersion Characteristics of Multi-Walled Carbon Nanotube Composites with Poly (methyl methacrylate) Prepared by In-Situ Bulk Polymerization. *Macromol Rapid Commun* 2003;24(18):1070–1073.
41. Fan J, Wan M, Zhu D, Chang B, Pan Z, Xie S. Synthesis, characterizations, and physical properties of carbon nanotubes coated by conducting polypyrrole. *J Appl Polym Sci* 1999;74(11):2605–2610.
42. Tang BZ, Xu H. Preparation, alignment, and optical properties of soluble poly (phenylacetylene)-wrapped carbon nanotubes. *Macromolecules* 1999;32(8):2569–2576.
43. Velasco-Santos C, Martinez-Hernandez AL, Lozada-Cassou M, Alvarez-Castillo A, Castano VM. Chemical functionalization of carbon nanotubes through an organosilane. *Nanotechnology* 2002;13(4):495–498.
44. Kong H, Gao C, Yan D. Controlled functionalization of multiwalled carbon nanotubes by in situ atom transfer radical polymerization. *J Am Chem Soc* 2004;126(2):412–413.
45. Bonduel D, Mainil M, Alexandre M, Monteverde F, Dubois P. Supported coordination polymerization: a unique way to potent polyolefin carbon nanotube nanocomposites. *Chem Commun* 2005;6:781–783.
46. Zhao C, Hu G, Justice R, Schaefer DW, Zhang S, Yang M, Han CC. Synthesis and characterization of multi-walled carbon nanotubes reinforced polyamide 6 via in situ polymerization. *Polymer* 2005;46(14):5125–5132.
47. Cruz-Delgado VJ, España-Sánchez BL, Avila-Orta CA, Medellín-Rodríguez FJ. Nanocomposites based on plasma-polymerized carbon nanotubes and Nylon-6. *Polym J* 2012;44(9):952–958.
48. Hu Z, Li J, Tang P, Li D, Song Y, Li Y, Zhao L, Li C, Huang Y. One-pot preparation and continuous spinning of carbon nanotube/poly (p-phenylene benzobisoxazole) copolymer fibers. *J Mater Chem* 2012;22(37):19863–19871.
49. Wang J, Shi Z, Ge Y, Wang Y, Fan J, Yin J. Functionalization of unzipped carbon nanotube via in situ polymerization for mechanical reinforcement of polymer. *J Mater Chem* 2012;22(34):17663–17670.
50. Wang Q, Yao Q, Chang J, Chen L. Enhanced thermoelectric properties of CNT/PANI composite nanofibers by highly orienting the arrangement of polymer chains. *J Mater Chem* 2012;22(34):17612–17618.
51. Gao C, Yan D. Hyperbranched polymers: from synthesis to applications. *Prog Polym Sci* 2004;29(3):183–275.
52. Sun YP, Huang W, Lin Y, Fu K, Kitaygorodskiy A, Riddle LA, Yu YJ, Carroll DL. Soluble Dendron-Functionalized Carbon Nanotubes: Preparation, Characterization, and Properties. *Chem Mater* 2001;13(9):2864–2869.
53. Sano M, Kamino A, Shinkai S. Construction of carbon nanotube “stars” with dendrimers. *Angew Chem* 2001;113(24):4797–4799.
54. Xu Y, Gao C, Kong H, Yan D, Jin YZ, Watts PC. Growing multihydroxyl hyperbranched polymers on the surfaces of carbon nanotubes by in situ ring-opening polymerization. *Macromolecules* 2004;37(24):8846–8853.

55. Feng QP, Xie XM, Liu YT, Zhao W, Gao YF. Synthesis of hyperbranched aromatic polyamide-imide and its grafting onto multiwalled carbon nanotubes. *J Appl Polym Sci* 2007;106(4):2413–2421.
56. Pan B, Cui D, Gao F, He R. Growth of multi-amine terminated poly (amidoamine) dendrimers on the surface of carbon nanotubes. *Nanotechnology* 2006;17(10):2483.
57. Campidelli S, Soombar C, Lozano Diz E, Ehli C, Guldi DM, Prato M. Dendrimer-functionalized single-wall carbon nanotubes: synthesis, characterization, and photoinduced electron transfer. *J Am Chem Soc* 2006;128(38):12544–12552.
58. Adeli M, Beyranvand S, Kabiri R. Preparation of hybrid nanomaterials by supramolecular interactions between dendritic polymers and carbon nanotubes. *Polym Chem* 2013;4(3):669–674.
59. Sohn GJ, Choi HJ, Jeon IY, Chang DW, Dai L, Baek JB. Water-dispersible, sulfonated hyperbranched poly (ether-ketone) grafted multiwalled carbon nanotubes as oxygen reduction catalysts. *ACS Nano* 2012;6(7):6345–6355.
60. Gómez FJ, Chen RJ, Wang D, Waymouth RM, Dai H. Ring opening metathesis polymerization on non-covalently functionalized single-walled carbon nanotubes. *Chem Commun* 2003;(2):190–191.
61. Liu Y, Adronov A. Preparation and utilization of catalyst-functionalized single-walled carbon nanotubes for ring-opening metathesis polymerization. *Macromolecules* 2004;37(13):4755–4760.
62. Zeng HL, Gao C, Yan DY. Poly (ϵ -caprolactone)-Functionalized Carbon Nanotubes and Their Biodegradation Properties. *Adv Funct Mater* 2006;16(6):812–818.
63. Chen GX, Kim HS, Park BH, Yoon JS. Synthesis of Poly (L-lactide)-Functionalized Multiwalled Carbon Nanotubes by Ring-Opening Polymerization. *Macromol Chem Phys* 2007;208(4):389–398.
64. Feng J, Cai W, Sui J, Li Z, Wan J, Chakoli AN. Poly (L-lactide) brushes on magnetic multiwalled carbon nanotubes by in-situ ring-opening polymerization. *Polymer* 2008;49(23):4989–4994.
65. Zhou L, Gao C, Xu W. Efficient Grafting of Hyperbranched Polyglycerol from Hydroxyl-Functionalized Multiwalled Carbon Nanotubes by Surface-Initiated Anionic Ring-Opening Polymerization. *Macromol Chem Phys* 2009;210(12):1011–1018.
66. Gao C, He H, Zhou L, Zheng X, Zhang Y. Scalable functional group engineering of carbon nanotubes by improved one-step nitrene chemistry. *Chem Mater* 2008;21(2):360–370.
67. Chakoli AN, Wan J, Feng JT, Amirian M, Sui JH, Cai W. Functionalization of multiwalled carbon nanotubes for reinforcing of poly (l-lactide-co- ϵ -caprolactone) biodegradable copolymers. *Appl Surf Sci* 2009;256(1):170–177.
68. Wu F, Yang G. Poly (butylene terephthalate)-functionalized MWNTs by in situ ring-opening polymerization of cyclic butylene terephthalate oligomers. *Polym Adv Technol* 2011;22(10):1466–1470.
69. Adeli M, Mirab N, Alavidjeh MS, Sobhani Z, Atyabi F. Carbon nanotubes-graft-polyglycerol: Biocompatible hybrid materials for nanomedicine. *Polymer* 2009;50(15):3528–3536.
70. Frechet JM, Henmi M, Gitsov I, Aoshima S, Leduc MR, Grubbs RB. Self-condensing vinyl polymerization: an approach to dendritic materials. *Science* 1995:1080.
71. Mori H, Seng DC, Zhang M, Müller AH. Hybrid nanoparticles with hyperbranched polymer shells via self-condensing atom transfer radical polymerization from silica surfaces. *Langmuir* 2002;18(9):3682–3693.
72. Hong CY, You YZ, Wu D, Liu Y, Pan CY. Multiwalled carbon nanotubes grafted with hyperbranched polymer shell via SCVP. *Macromolecules* 2005;38(7):2606–2611.
73. Ugarte D. Curling and closure of graphitic networks under electron-beam irradiation. *Nature* 1992;359(6397):707–709.
74. Iijima S, Ichihashi T. Single-shell carbon nanotubes of 1-nm diameter. *Nature* 1993;363:603–605.
75. Cioffi CT, Palkar A, Melin F, Kumbhar A, Echegoyen L, Melle-Franco M, Zerbetto F, Rahman GMA, Ehli C, Sgobba V, Guldi DM, Prato M. A Carbon Nano-Onion-Ferrocene Donor-Acceptor System: Synthesis, Characterization and Properties. *Chem A Eur J* 2009;15(17):4419–4427.
76. Keller N, Maksimova NI, Roddatis VV, Schur M, Mestl G, Butenko YV, Kuznetsov VL, Schlögl R. The Catalytic Use of Onion-Like Carbon Materials for Styrene Synthesis by Oxidative Dehydrogenation of Ethylbenzene. *Angew Chem Int Ed* 2002;41(11):1885–1888.
77. Langlet R, Lambin P, Mayer A, Kuzhir PP, Maksimenko SA. Dipole polarizability of onion-like carbons and electromagnetic properties of their composites. *Nanotechnology* 2008;19(11):115706.
78. Sano N, Wang H, Alexandrou I, Chhowalla M, Teo KBK, Amaratunga GAJ, Iimura K. Properties of carbon onions produced by an arc discharge in water. *J Appl Phys* 2002;92(5):2783–2788.
79. Hirata Y, Mataga N. Photoionization of aromatic diamines in electron-accepting solvents: formation of short-lived ion pairs. *J Phys Chem* 1984;88(14):3091–3095.
80. Joly-Pottuz L, Vacher B, Ohmae N, Martin JM, Epicier T. Anti-wear and friction reducing mechanisms of carbon nano-onions as lubricant additives. *Tribol Lett* 2008;30(1):69–80.
81. Joly-Pottuz L, Buchholz EW, Matsumoto N, Phillpot SR, Sinnott SB, Ohmae N, Martin JM. Friction properties of carbon nano-onions from experiment and computer simulations. *Tribol Lett* 2010;37(1):75–81.
82. Ding L, Stilwell J, Zhang T, Elboudwarej O, Jiang H, Selegue JP, Cooke PA, Gray JW, Chen FF. Molecular characterization of the cytotoxic mechanism of multiwall carbon nanotubes and nano-onions on human skin fibroblast. *Nano Lett* 2005;5(12):2448–2464.

83. Pech D, Brunet M, Durou H, Huang P, Mochalin V, Gogotsi Y, Taberna PL, Simon P. Ultrahigh-power micrometre-sized supercapacitors based on onion-like carbon. *Nat Nanotechnol* 2010;5(9):651–654.
84. Street KW, Marchetti M, Vander Wal RL, Tomasek AJ. Evaluation of the tribological behavior of nano-onions in Krytox 143AB. *Tribol Lett* 2004;16(1–2):143–149.
85. Zhang C, Li J, Liu E, He C, Shi C, Du X, Hauge RH, Zhao N. Synthesis of hollow carbon nano-onions and their use for electrochemical hydrogen storage. *Carbon* 2012;50(10):3513–3521.
86. Rettenbacher AS, Elliott B, Hudson JS, Amirkhanian A, Echegoyen L. Preparation and Functionalization of Multilayer Fullerenes (Carbon Nano-Onions). *Chem A Eur J* 2006;12(2):376–387.
87. Rettenbacher AS, Perpall MW, Echegoyen L, Hudson J, Smith DW. Radical addition of a conjugated polymer to multilayer fullerenes (carbon nano-onions). *Chem Mater* 2007;19(6):1411–1417.
88. Matsumoto N, Joly-Pottuz L, Kinoshita H, Ohmae N. Application of onion-like carbon to micro and nanotribology. *Diamond Relat Mater* 2007;16(4):1227–1230.
89. Joly-Pottuz L, Matsumoto N, Kinoshita H, Vacher B, Belin M, Montagnac G, Martin JM, Ohmae N. Diamond-derived carbon onions as lubricant additives. *Tribol Int* 2008;41(2):69–78.
90. Joly-Pottuz L, Ohmae N. Carbon-based nanolubricants. In: Martin JM, Ohmae N, editors. *Nanolubricants*. Chichester, UK: John Wiley & Sons; 2008. p 93–147.
91. Hirata A, Igarashi M, Kaito T. Study on solid lubricant properties of carbon onions produced by heat treatment of diamond clusters or particles. *Tribol Int* 2004;37(11):899–905.
92. Ozawa M, Goto H, Kusunoki M, Osawa E. Continuously growing spiral carbon nanoparticles as the intermediates in the formation of fullerenes and nanooxions. *J Phys Chem B* 2002;106(29):7135–7138.
93. Akatyeva E, Huang JY, Dumitrică T. Edge-mediated dislocation processes in multishell carbon nano-onions? *Phys Rev Lett* 2010;105(10):106102.
94. Kuznetsov VL, Chuvilin AL, Butenko YV, Mal'kov IY, Titov VM. Onion-like carbon from ultra-disperse diamond. *Chem Phys Lett* 1994;222(4):343–348.
95. Sano N, Wang H, Chhowalla M, Alexandrou I, Amaratunga GAJ. Nanotechnology: Synthesis of carbon 'onions' in water. *Nature* 2001;414(6863):506–507.
96. Flavin K, Chaur MN, Echegoyen L, Giordani S. Functionalization of Multilayer Fullerenes (Carbon Nano-Onions) using Diazonium Compounds and "Click" Chemistry. *Org Lett* 2010;12(4):840–843.
97. Molina-Ontoria A, Chaur MN, Plonska-Brzezinska ME, Echegoyen L. Preparation and characterization of soluble carbon nano-onions by covalent functionalization, employing a Na–K alloy. *Chem Commun* 2013;49(24):2406–2408.
98. Borgohain R, Li J, Selegue JP, Cheng YT. Electrochemical study of functionalized carbon nano-onions for high-performance supercapacitor electrodes. *J Phys Chem C* 2012;116(28):15068–15075.
99. Gao Y, Zhou YS, Qian M, He XN, Redepenning J, Goodman P, Li HM, Jiang L, Lu YF. Chemical activation of carbon nano-onions for high-rate supercapacitor electrodes. *Carbon* 2013;51:52–58.