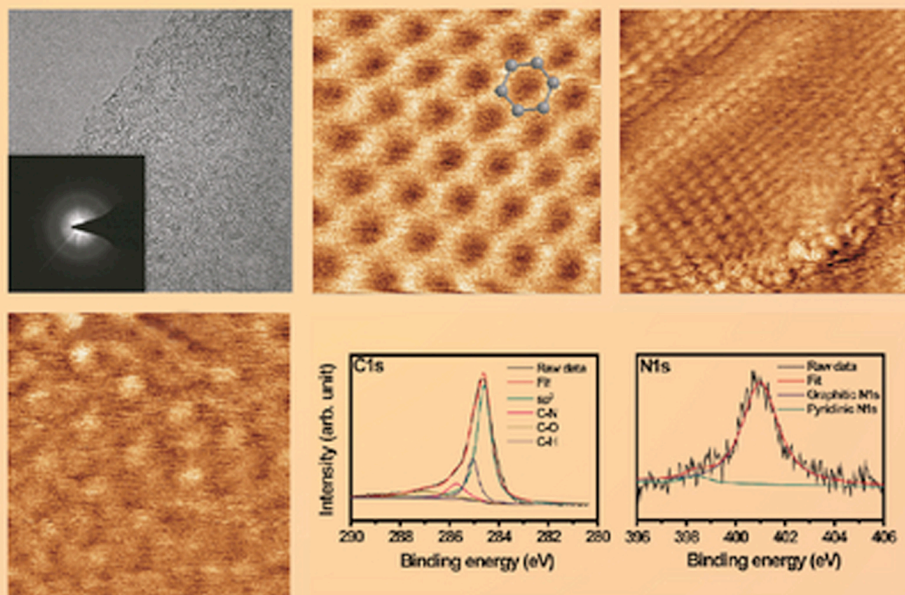


NANOMATERIALS, POLYMERS AND DEVICES

MATERIALS FUNCTIONALIZATION AND DEVICE FABRICATION



EDITED BY
ERIC S. W. KONG

WITH A FOREWORD BY
WOLFGANG KNOLL, *AUSTRIAN INSTITUTE OF TECHNOLOGY*

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**NANOMATERIALS, POLYMERS,
AND DEVICES**

NANOMATERIALS, POLYMERS, AND DEVICES

Materials Functionalization and Device Fabrication

Edited by

ERIC S. W. KONG

*Research Professor, Shanghai Jiao Tong University
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FOREWORD

For ages, the classical disciplines of physics, chemistry, biology, engineering, and the materials science developed and grew in a rather isolated mode, independently of each other, in separate silos. But with the advent of the nanosciences, we have seen a remarkable change in the scientific landscape. Originally, the new trend was identified as a separate and distinctly different subdiscipline of, for example, the physics of materials, where it was observed that the mere size of an object matters and largely defines the different properties of materials. Examples are the change of the optoelectronic properties of nanometer-sized semiconducting particles, the quantum dots. Whenever the dimensions of such an object reach the limit of intrinsic length scales, in this case the exciton radius of an electron–hole pair, fundamental properties like the energy bandgap begin to change and become size dependent. The consequence is well known: the emission wavelength of the recombination radiation after photoexcitation changes and quantum dots of different radii – although chemically identical – emit fluorescence light of different colors, a direct consequence of the quantum confinement.

Other examples are the size- and shape-dependent optical properties of nanoscopic metallic particles. In the bulk, the collective oscillation of the nearly free electron gas of the conduction band electron cloud leads to the well-defined plasma frequency of the material, characteristic for each metal. However, if the metallic particle, owing to its small dimensions in the nanometer range, “senses” the boundary to its dielectric surrounding specific resonances occur, observable as localized surface plasmon modes. Their frequency and polarization are strongly dependent on the size and the shape of the metallic nanoparticle.

A different yet also remarkable trend could be observed in recent years in chemistry of materials. Especially polymers for a long time were considered to be typical bulk materials. Even though it was known that many details of the properties and functions of structural bulk polymers could be understood only at the level of the molecular and supramolecular organization of individual chain molecules – their chemical nature, their linearity versus branching, their entanglement with other chains, the presence of soft and hard segments, etc. – those individual polymer molecules were only vaguely defined and typically characterized by rather fuzzy quantities like an average molecular mass and, at best, a molecular mass distribution, that is, their polydispersity. This changed dramatically with the appearance of certain novel polymeric molecular architectures, in particular, the dendrimers. These macromolecules could be synthesized in a strictly monodisperse fashion, all molecules with the absolutely same molecular mass of up to several hundred thousand Daltons. With some of them being also shape persistent all of a sudden, it became obvious that these molecules can be seen as well-defined objects, as building blocks for supramolecular architectures, and as individual units for the assembly of nanomaterials.

Of course, materials scientists saw the enormous potential for the buildup of nanomaterials in a truly bottom-up approach by assembling materials, object by object, using building blocks of different materials. This paradigm shift offered fascinating novel strategies for the fabrication of synthetic materials that were never made or observed before because their structures and properties were completely defined by the man-made protocol of how to assemble them into 2D or 3D architectures.

This brought physics and chemistry again much closer to each other: the mutual interest of understanding the properties of nanoscopic objects from classical materials like metals and semiconductors and the novel synthetic efforts in generating organic and/or polymeric objects with property profiles that were defined – almost at will – by the chemical nature of the building blocks containing chromophores, redox centers, charges, etc., resulted in a convergence of the classical scientific disciplines that was not observed for the past decades.

In passing, we note that naturally, almost inevitably, objects of biological origin came into the game, too. Whether these were (large) proteins, micellar or vesicular structures from lipid molecules, or simple or highly complex supramolecular assemblies from DNA molecules – their use as building blocks in nanomaterials widened the spectrum of properties that could be tailored into these materials by another dimension.

As a result of this merging of ideas and concepts from different classical research areas in materials science, we see a very exciting cross-disciplinary effort in designing and fabricating nanoscopic materials with tailor-made properties and functionalities. Of course, this new horizon in materials properties triggered the phantasy of those engineers that design new functional devices. Their approach was governed for a long time by a top-down strategy, increasing the functionality and the integration density of sensors, logic gates, storage devices, etc., by making the individual functional unit smaller and smaller. Looking at Moore's law, for example, in microelectronics, this concept has been remarkably successful for a remarkably long time. However, the limit of this scaling down concept is now more serious than ever: if structural features in a single transistor reach 22 nm, if the current that switches the gate from on to off is carried by a few electrons only (and if the costs for the development of the next generation of storage device cannot be borne by a single player anymore ...), new strategies are needed urgently.

The bottom-up approach that the nanosciences offer, using nanomaterials that have never been available, designed by multidisciplinary concepts, using the principle of self-organization of the individual building blocks, for the construction of hierarchical systems, following examples from nature – all this has inspired the imagination of materials scientists and is currently in the center of the interest of materials science and engineering groups around the world.

Many of them have contributed to this book describing in numerous chapters the fabrication, the assembly, and the structural characterization of nanomaterials and refer to their functional potential that they offer for the device engineers. Most of them focus, for good reasons, on the currently most promising forms of nanocarbon, that is, single- or multiwalled carbon nanotubes and graphene, the monomolecular thin layer of graphite. Awarded with Nobel Prizes, both novel nanomaterials are currently the most widely studied nanomaterials worldwide. The set of articles assembled in this book represent a unique snapshot of where the field is and where it is heading toward. This book starts off with the first five chapters on the synthesis and functionalization of nanomaterials. The second part of this book covers various devices, with emphasis on nanofabrication. Light-emitting diodes are discussed in Chapters 6 and 7. Nanophotonics and nano-optics are covered between Chapters 8 and 9. Between Chapters 12 and 14, photovoltaic devices are discussed in depth. In the last section of the book, between Chapters 15 and 19, nanoelectronic devices are covered in detail. Enjoy this unique journey into the world of nanomaterials, polymers, and the devices made from them.

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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).

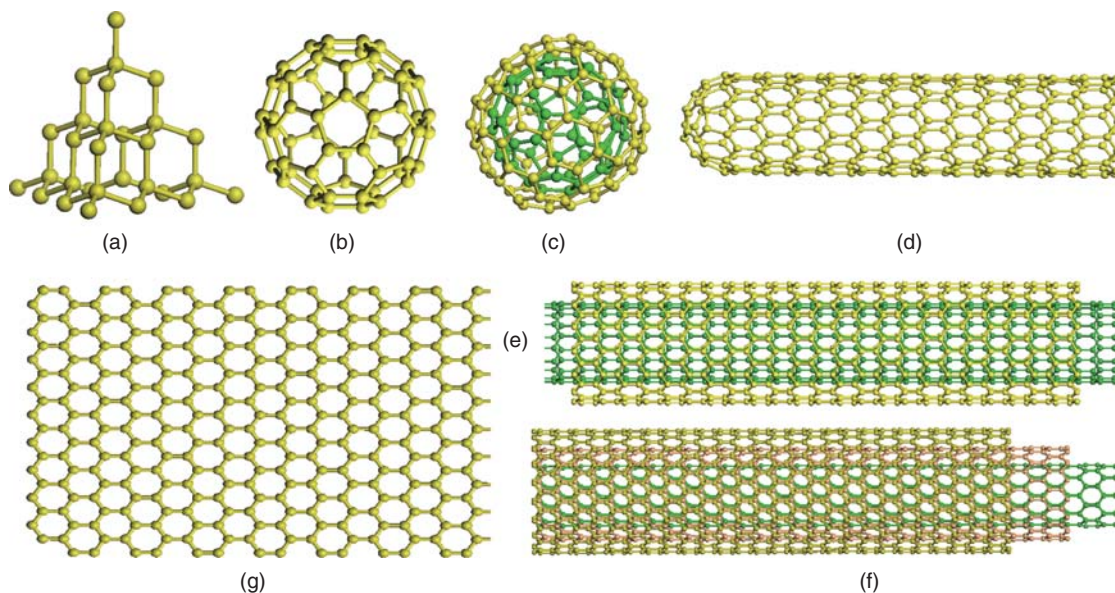


Figure 1.1 Model structures of carbon: (a) diamond, (b) fullerene, (c) multilayer fullerene, (d) single-walled carbon nanotubes, (e) double-walled carbon nanotubes, (f) multiwalled carbon nanotubes, and (g) graphene. (Source: Reproduced with permission from Reference 2).

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 nanoprotrusion 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

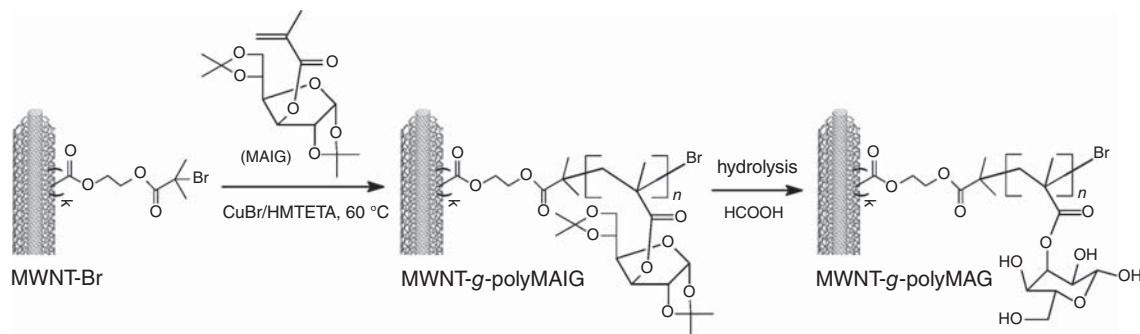


Figure 1.2 Synthetic strategy for grafting linear glycopolymer from surfaces of MWNTs by ATRP. (Source: Reproduced with permission from Reference 23).

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 CHCl₃. 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-tetramethylpiperidiny-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).

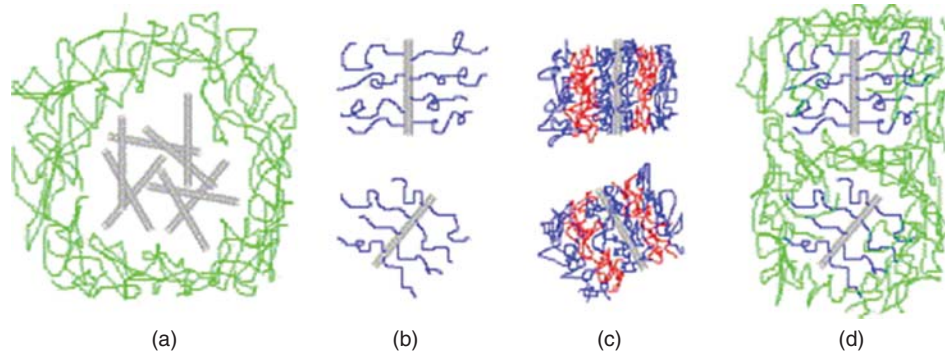


Figure 1.3 Schematic illustration of (a) CNTs dispersed mechanically in polymer matrix, (b) polymer-bonded CNTs, (c) polymer-coated CNTs by layer-by-layer self-assembly approach, and (d) polymer-functionalized CNTs dispersed in free polymer matrix. (Source: Reproduced with permission from Reference 39).

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

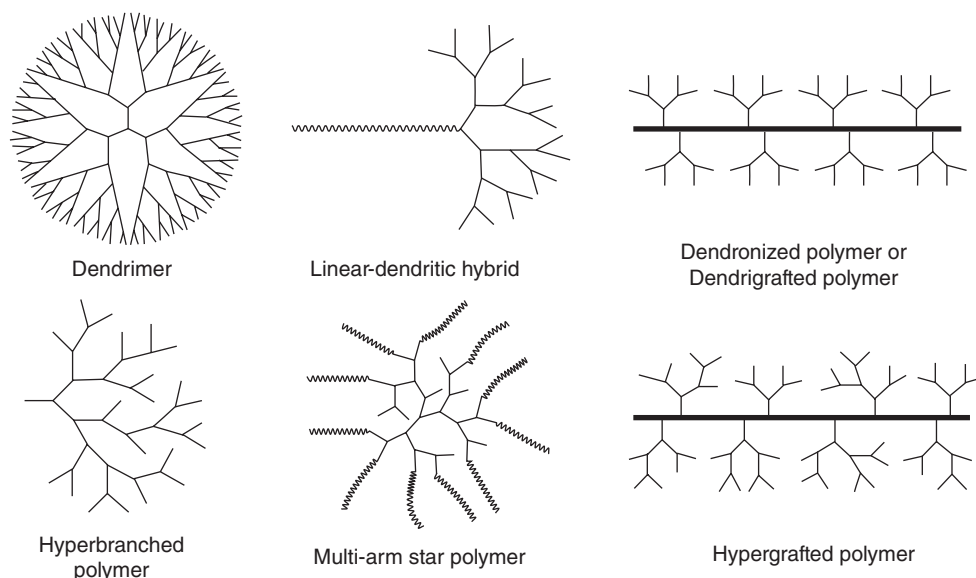


Figure 1.4 Schematic description of dendritic polymers. (Source: Reproduced with permission from Reference 51).

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

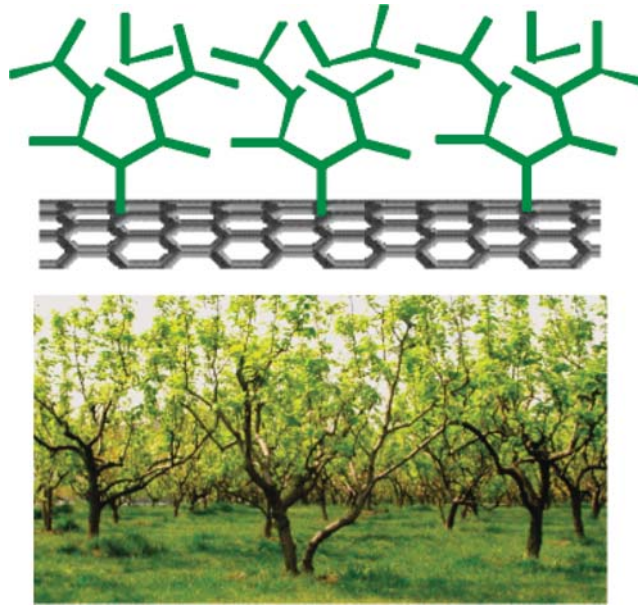


Figure 1.5 HP-grafted CNTs – branched-like trees. Graphical representation of a section of MWNTHP nano hybrids presented in this chapter (top) and a photograph of the trees grown on a hillside (bottom). (Source: Reproduced with permission from Reference 54).

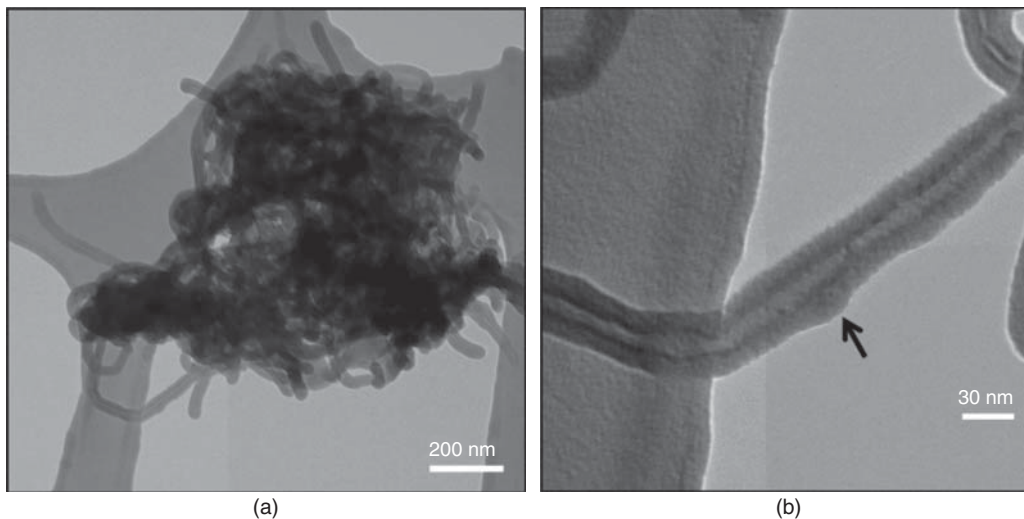


Figure 1.6 TEM images of MWNT-HP5 at (a) low magnification and (b) high magnification. (Source: Reproduced with permission from Reference 54).

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 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 range 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 was 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

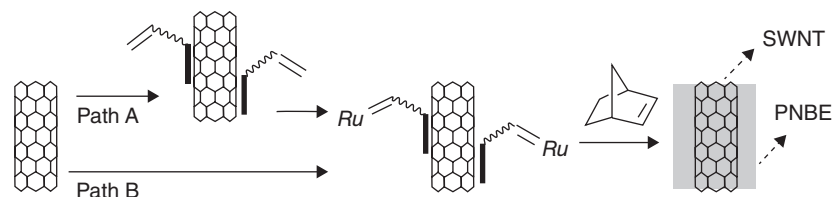


Figure 1.7 Complete functionalization strategy of ROP. (Source: Reproduced with permission from Reference 60).

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 alkylidenes 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 to the CNTs and in turn with a ruthenium alkylidene with cross-metathesis, and (ii) pyrene-substituted ruthenium alkylidene 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.

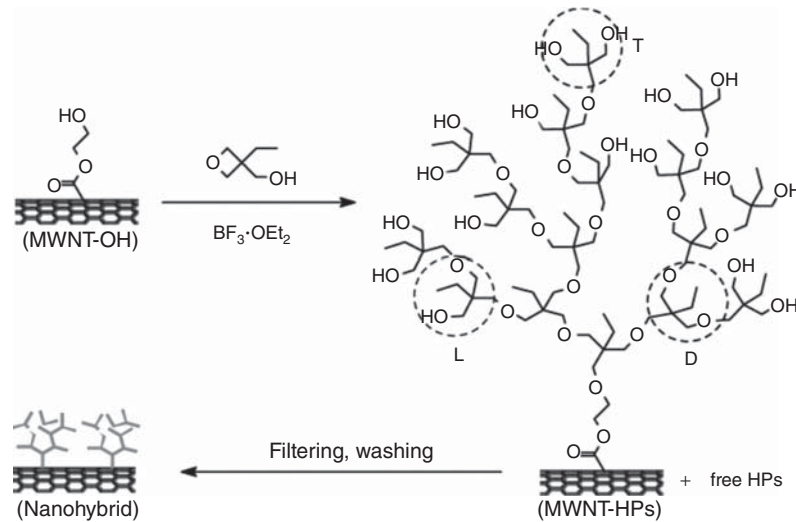


Figure 1.8 Synthesis of dendritic HP-MWNT nano hybrid through *in situ* ROP. (Source: Reproduced with permission from Reference 54).

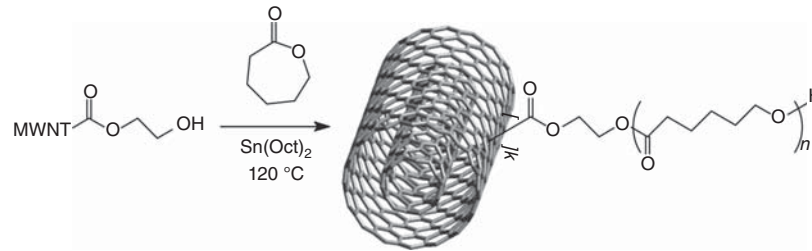


Figure 1.9 Grafting of PCL onto MWNTs. (Source: Reproduced with permission from Reference 62).

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.

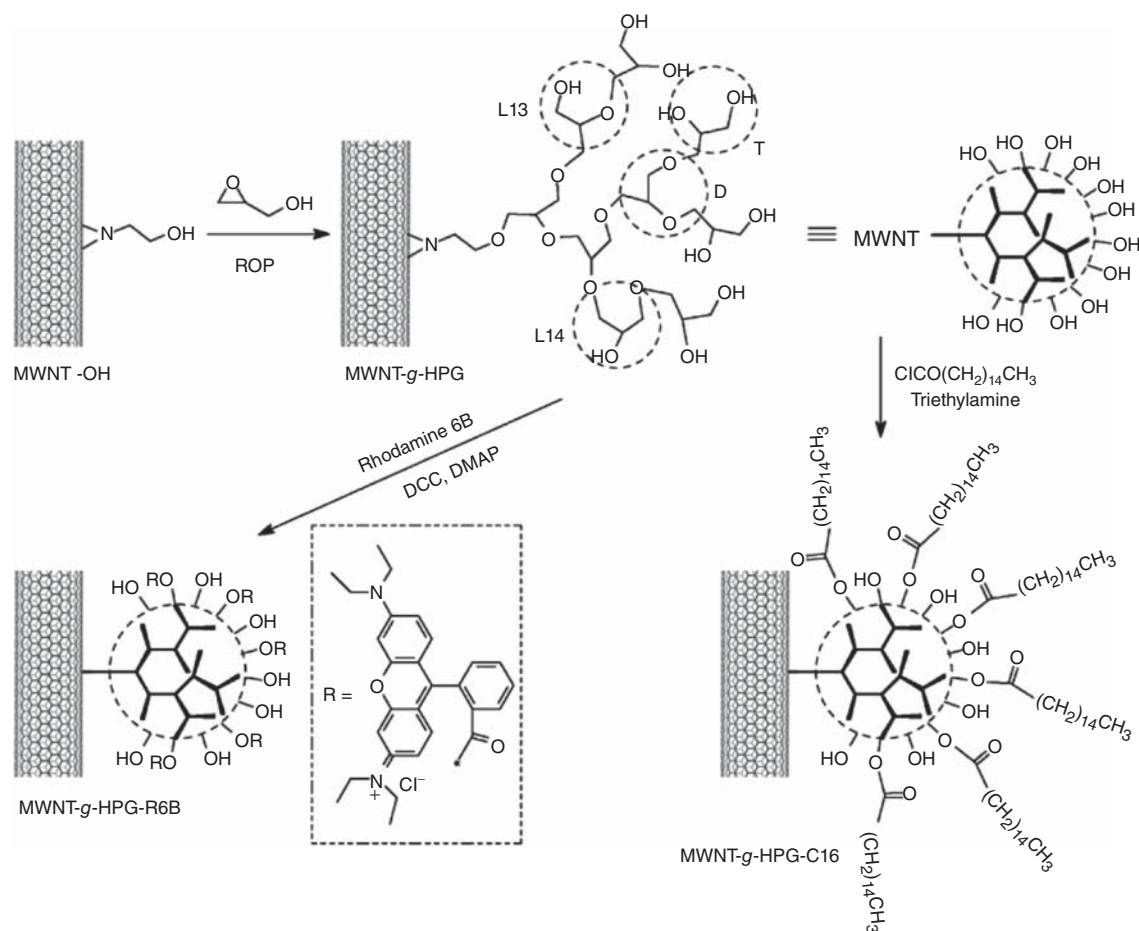


Figure 1.10 Functionalization of multiwalled carbon nanotubes (MWCNTs) with hyperbranched polyglycerol (HPG) by anionic ring-opening polymerization (ROP) and modification of the grafted HPG. (Source: Reproduced with permission from Reference 65).

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.

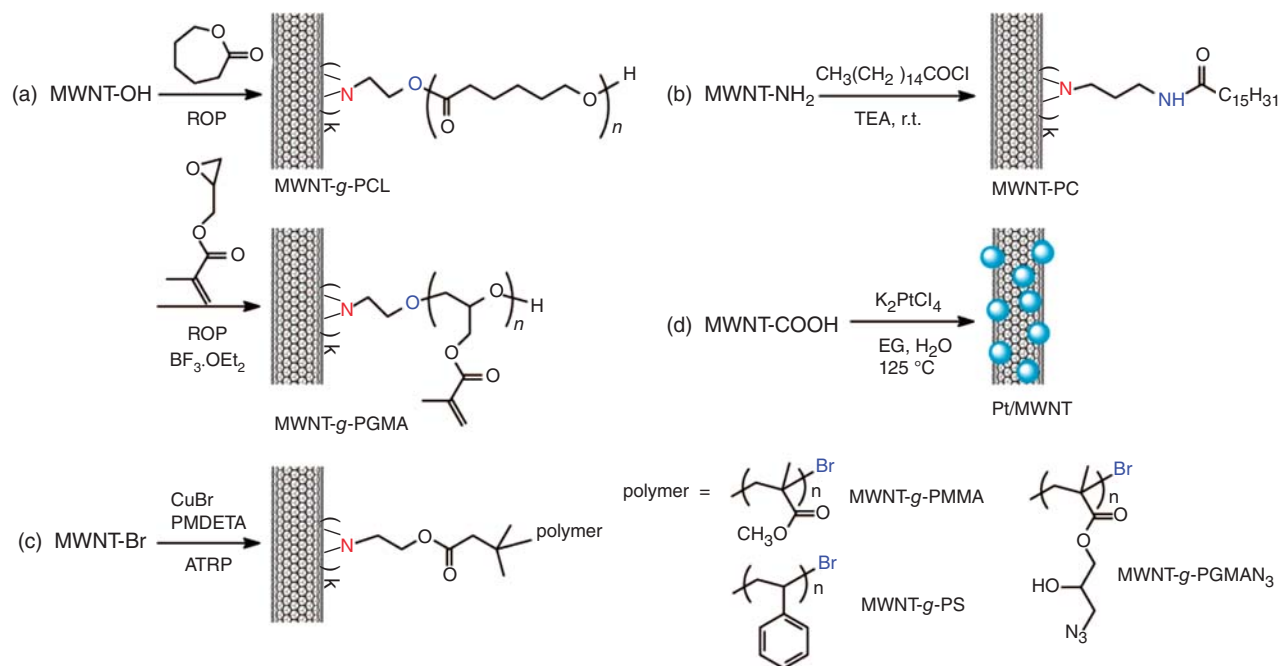


Figure 1.11 Chemical reactions on f-MWNTs. (Source: Reproduced with permission from Reference 66).

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

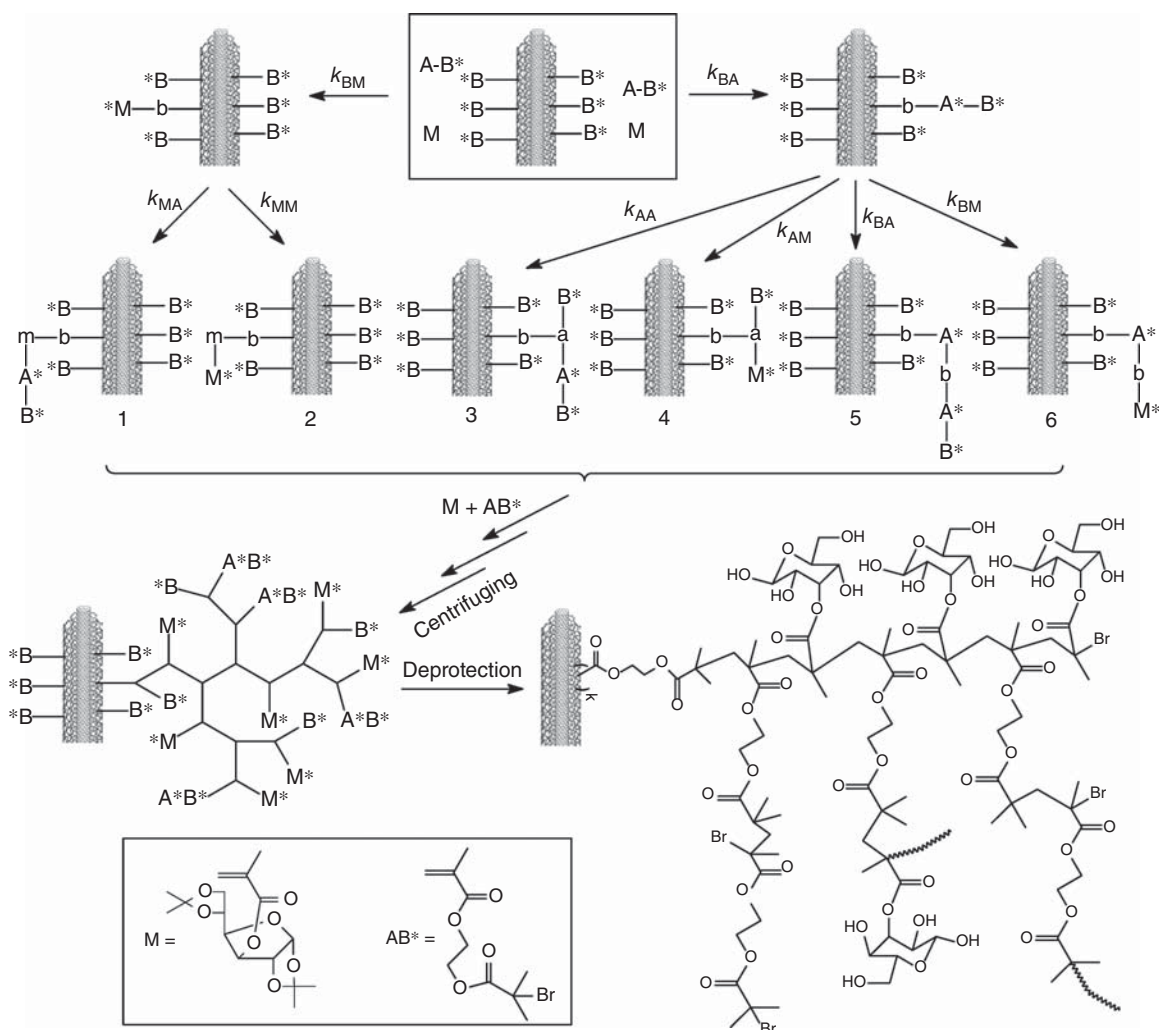


Figure 1.12 Synthetic strategy for grafting hyperbranched glycopolymer from surfaces of MWNTs by self-condensing vinyl copolymerization (SCVP) of inimer (AB*) and monomer (M) via ATRP. (Source: Reproduced with permission from Reference 23).

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.

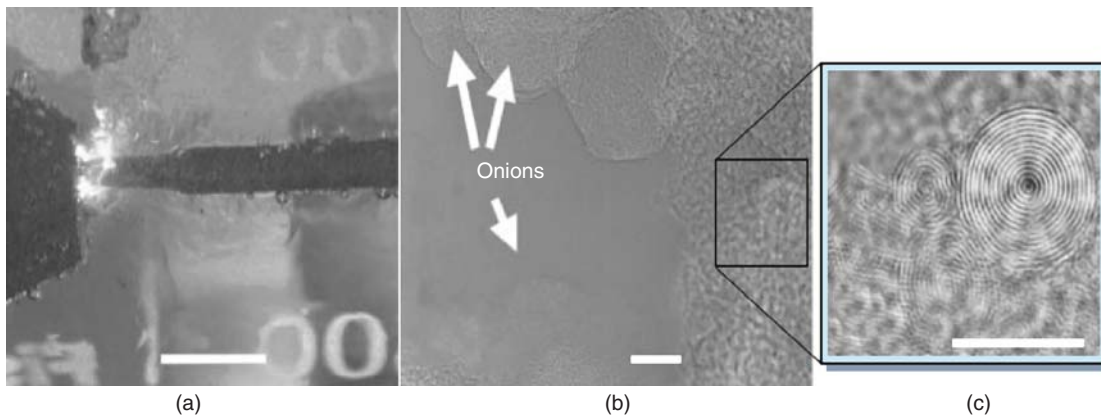


Figure 1.13 Carbon nano-“onions” created by arc discharge in water. (a) Image of a carbon arc discharge in water. Scale bar, 12 mm. (b, c) Low- and high-magnification electron micrographs of carbon nano-onions floating on the water surface after their production. Scale bars, 10 nm. (Source: Reproduced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

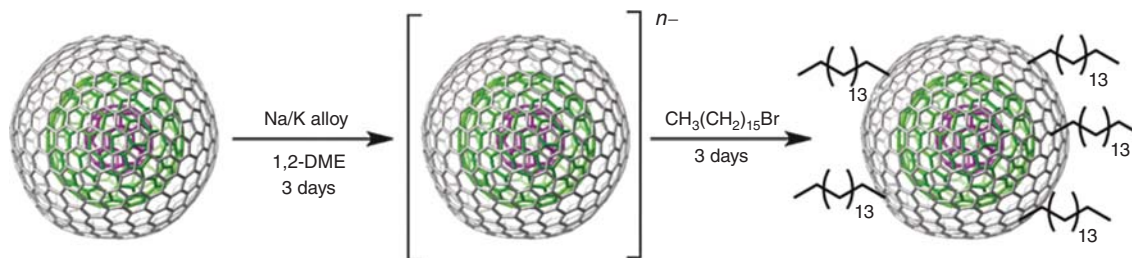


Figure 1.14 Reductive treatment of CNOs by a Na–K alloy in 1,2-DME and subsequent alkylation using 1-bromohexadecane. (Source: Reproduced with permission from Reference 97).

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 RuO_2 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 RuO_2 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 sp^2 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% RuO_2 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.

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