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Review

Advanced technology for functionalization of carbon nanotubes

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Abstract

Functionalization of carbon nanotubes (CNTs) has attracted considerable interest in the fields of physics, chemistry, material science and biology. The functionalized CNTs exhibit improved properties enabling facile fabrication of novel nanomaterials and nanodevices. Most of the functionalization approaches developed at present could be categorized into the covalent attachment of functional groups and the non-covalent adsorption of various functional molecules onto the surface of CNTs. This review highlights recent development and our work in functionalization of carbon nanotubes, leading to bio-compatible CNTs, fluorescent CNTs and transition metal functionalized CNTs. These novel methods possess advantages such as simplified technical procedures and reduced cost of novel nanomaterials and nanodevices fabrication.

Keywords: Carbon nanotubes (CNTs); Functionalization; Bio-compatibility; Fluorescence; Transition metal

1. Introduction

Carbon nanotubes (CNTs), especially single-walled carbon nanotubes (SWNTs), have been the research focus in both academia and industry since their discovery in the 1990s [1–5]. Due to their remarkable and unique mechanical, electrical, optical and thermal properties, SWNTs have been one of the most popular nanomaterials after C_{60} (Fig. 1). However, SWNTs tend to form bundles and the solubility in common solvents is very limited. This has made them difficult to be manipulated and purified. A key challenge is how to break the cohesion of aggregated CNTs in order to obtain a fine dispersion in the selected solutions or matrices. Several methods have been developed, including covalent or non-covalent modifications. Depending on the methods used, functional groups can be introduced onto the surface of nanotubes. Meanwhile, it would endow CNTs with multifunctional applications by integrating other functional groups or materials onto their surface. A functionalized nanotube might have mechanical, optical or electrical properties that are different from those of the original nanotube. Therefore, it is an interesting area to functionalize CNTs for all kinds of applications.

2. Strategies for functionalization of CNTs

Functionalized CNTs have been intensively studied in the last few years [5–16]. In general, these methods could be summarized as two categories: covalent and non-covalent functionalizations.

Covalent functionalization is based on the formation of a covalent linkage between functional entities and the carbon skeleton of nanotubes. It could also be divided into direct covalent sidewall functionalization and indirect covalent functionalization with carboxylic groups on the surface of CNTs. Direct covalent sidewall functionalization is associated with a change in hybridization from sp^2 to sp^3 and a simultaneous loss of conjugation (e.g., fluorination

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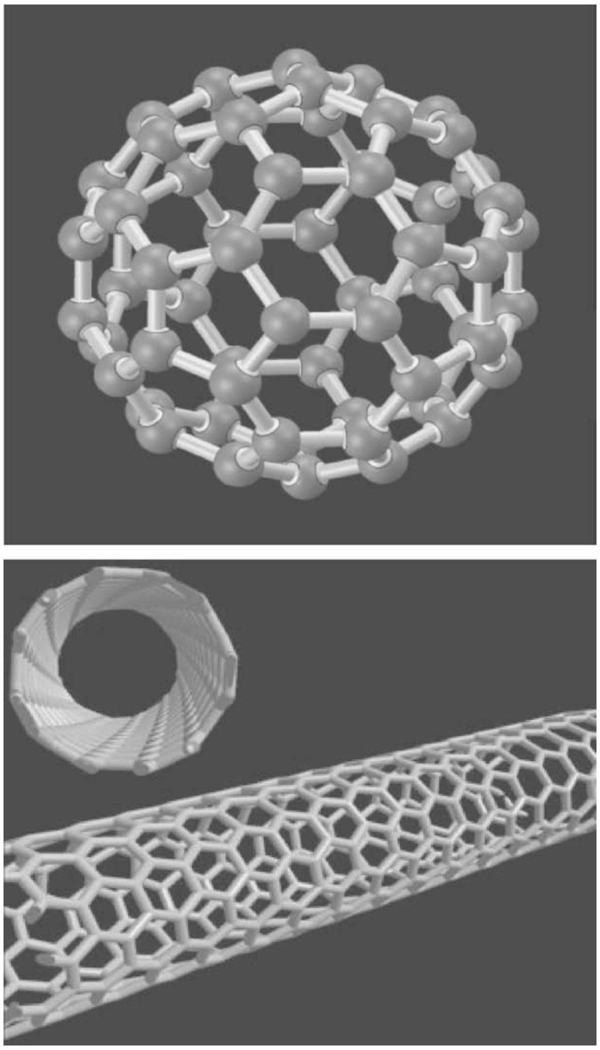

Fig. 1. C_{60} and SWNT.

of nanotubes [5,6]). Indirect covalent functionalization takes advantage of chemical transformations of carboxylic groups at the open ends and holes in the sidewalls. These carboxylic groups might have existed on the as-grown CNTs and also be further generated during oxidative purification. In order to increase the reactivity of CNTs, the carboxylic acid groups usually need to be converted into acid chloride and then undergo an esterification or amidation reaction [7,8]. The drawback of covalent functionalization is that the perfect structure of CNTs has to be destroyed, resulting in significant changes in their physical properties.

Non-covalent functionalization is mainly based on supramolecular complexation using various adsorption forces, such as Van der Waals force, hydrogen bonds, electrostatic force and π-stacking interactions [10–16]. Compared to the chemical functionalization, non-covalent functionalization has the advantages that it could be operated under relatively mild reaction conditions and the perfect graphitic structure of CNTs could be maintained.

In our group, utilizing non-covalent methods or developing new methods without obviously destroying the structure of CNTs to obtain various functionalized CNTs has been well investigated. Three types of functionalized CNTs were prepared including CNTs functionalized with bio-compatible amylose and cellulose [17,18], fluorescent ionic liquid (IL) [19] and zinc–bipyridine frameworks by the strategies of physical absorption, ion exchange and coordination chemistry, respectively.

3. Bio-compatible CNTs

Potential biological and biomedical applications of CNTs have been the focus since their discovery. The general bio-functionalization method is conjugating CNTs with DNA [20–23], proteins [24–26], or carbohydrates [27–37], which makes them possible to generate a new class of bioactive CNTs for the applications such as biosensors, scaffold materials and drug carriers. The modification of CNTs on a molecular level using biological molecules is essentially an example of the 'bottom-up' fabrication principle of bio-nanotechnology.

3.1. DNA functionalized CNTs

Zheng et al. [20,21] firstly reported that bundled SWNTs could be effectively dispersed in water by sonication in the presence of single-stranded DNA (ssDNA). They found that short oligonucleotides having repeating sequences of guanines and thymines (dGdT)n ($n = 10$–45), could wrap in a helical manner around a CNT with periodic pitch. This finding links one of the central molecules in biology to a technologically very important nanomaterial, and opens the door to CNTs-based applications in biotechnology. They also found that wrapping of CNTs by ssDNA was sequence-dependent. Poly(A) and poly(C) have lower dispersion efficiency than poly(T) because poly(A) and poly(C) are known to strongly self-stack in solution and impair the π-stacking with CNTs. They further integrated short double-stranded DNA and some RNA molecules onto the surface of SWNTs in aqueous solution to enhance their solubility. Molecular modelling suggests that DNAs are bound to SWNTs through π-stacking while exposing the sugar–phosphate groups to water, thus wrapped SWNTs are well soluble in water.

In the above work, the need for specific repeating sequences limits use to the man-made DNA that must be synthesized with optimal lengths of less than 150 bases. Gigliotti et al. [22] successfully utilized long genomic single-stranded DNA (>>100 base) with a completely random sequence of bases to disperse CNTs, these ssDNAs also formed tight helices around the CNTs with distinct periodic pitches. Although the helix pitch-to-pitch distances remain constant along the length of a single CNT, the distances are variable from one DNA–CNT to another.

In addition, Geckeler's group [23] prepared DNA-wrapped nanotubes of both multi-walled carbon nanotubes

(MWNTs) and SWNTs by a solid-state mechanochemical reaction. The nanotubes were cut into shorter lengths and were fully covered with DNA, where >90% of the multi-walled products were 500 nm to 3 μm and 80% of the single-walled products were 250 nm to 1 μm in length, respectively. These products are highly soluble in aqueous solution with a stability of more than 6 months.

3.2. Proteins and polypeptides functionalized CNTs

As a type of important biomaterials, proteins and polypeptides are often used to functionalize CNTs. Karajanagi et al. [24] used a variety of proteins with different size and structure to generate individual nanotube solutions by the non-covalent functionalization procedure. The wide variety of functional groups such as hydroxyl, sulfhydryl and amino existing on the adsorbed proteins may be used as orthogonal reactive handles for the further functionalization of CNTs.

Azamian et al. [25] found that two robust metalloproteins, cytochrome C and ferritin, could be easily adsorbed onto CNTs and the resulting complexes were pH- and ionic strength-independent (to at least 1 M KCl), indicating that electrostatic attraction was not the only driving force in the system. It is believed that weak physical interactions such as π-stacking interactions, Van der Waals forces and hydrophobic forces all contributed to absorption of proteins onto CNTs.

More recently, Dalton et al. [26] reported that the peptides could efficiently disperse individual SWNTs by folding into an amphiphilic α-helix. It was also demonstrated that the phenylalanine (Phe) residues on the hydrophobic face of the helix could interact via π-stacking with the aromatic surface of the SWNT. The ability of electron-donating (hydroxyl) and electron-withdrawing (nitro) groups on the phenyl ring of Phe affects the interactions between the peptide and SWNTs. That is, the ability of the peptides to disperse individual SWNTs increases with increasing electron density of the aromatic residue on the hydrophobic face.

3.3. Carbohydrates functionalized CNTs

In 2001, Stoddart et al. [27] firstly reported a starched SWNT. Although an aqueous solution of amylose could not dissolve SWNTs, pre-formed amylose/iodine complexes yielded more promising results. Based on these observations, they suggested a 'pea-shooting' mechanism where the carbon nanotube can enter the helical amylose/iodine complex by sequentially displacing the iodine inside the complex. Thus, it was concluded that the amylose/iodine complex had already prepared the way for SWNTs. They also put forward that pure SWNTs could be precipitated and obtained after adding amyloglucosidase into the aqueous solution of the starch-wrapped SWNTs. Thus it represents a practical method to purify SWNTs using the starch complexes.

Kim's group [28], however, studied the interaction between amylose and SWNTs in aqueous DMSO solution in the absence of iodine. In this reaction medium, amylose is only loosely coiled, in contrast to the case when iodine is present. They discovered that amylose can host a large guest molecule with a diameter of more than 1 nm forming a loosely twisted A/S-C structure of approximately 30 nm in diameter. This process requires two important conditions, presonication of CNTs in water and subsequent treatment of the fine CNT dispersion with amylose in a specified DMSO–H_2O mixture (ca. 10–20% DMSO), followed by a postsonication. The former step disaggregates the CNT bundles, and the latter step maximizes cooperative interactions between CNTs and amylose, leading to immediate and complete solubilisation.

Besides experimental investigations, a theoretical basis for the preparation of carbohydrates/CNTs complexes has also been studied. Soh et al. [29] studied the mode of interaction between the initially separated amylose and SWNT fragments by molecular dynamics (MD) simulations. It was found that the Van der Waals force was dominant and it always played an important role in promoting non-covalent association. Thus, amylose molecules could be used to bind with nanotubes and the sizes of nanotubes have an obvious influence during the non-covalent functionalization of CNTs.

Single-chain schizophyllan and curdlan (s-SPG and s-curdlan, respectively) were also used to dissolve SWNTs in aqueous solution by Numata et al. [30]. Interestingly, s-SPG or s-curdlan could wrap SWNTs resulting in a twined helical structure. It was clearly seen from the high-resolution TEM images that the two s-SPG chains twined one SWNT and the helical motif was right-handed. The functional groups on polysaccharides make it possible to further functionalize CNTs. Furthermore, the presence of the periodical structure on the composite surface implies that one can combine the present system with the concept of supramolecular or self-assembly chemistry. In the subsequent research [31], they attached lactoside onto the active positions of SPG, the thus obtained SWNTs showed excellent water solubility and specific lectin-affinity with the p-conjugate system of CNTs being maintained. Since various SPG-derivatives are easily accessible through reductive amination, it was suggested that this non-covalent strategy could be applied not only to many biochemical purposes but also to various photo- and electrochemical materials.

In addition, gum Arabic and cyclodextrins are often used to functionalize CNTs [32–37]. There are three main types of cyclodextrins, however, only γ-cyclodextrin has an inner cavity diameter of 0.75–0.83 nm and has the ability to accommodate a guest molecule into its inner cavity and forms inclusion complexes. For example, a simple grinding procedure to coat SWNTs with γ-cyclodextrin was proposed [36], and the 'Two-stage' modification strategy could also be further carried out by taking advantage of the active position on these carbohydrates.

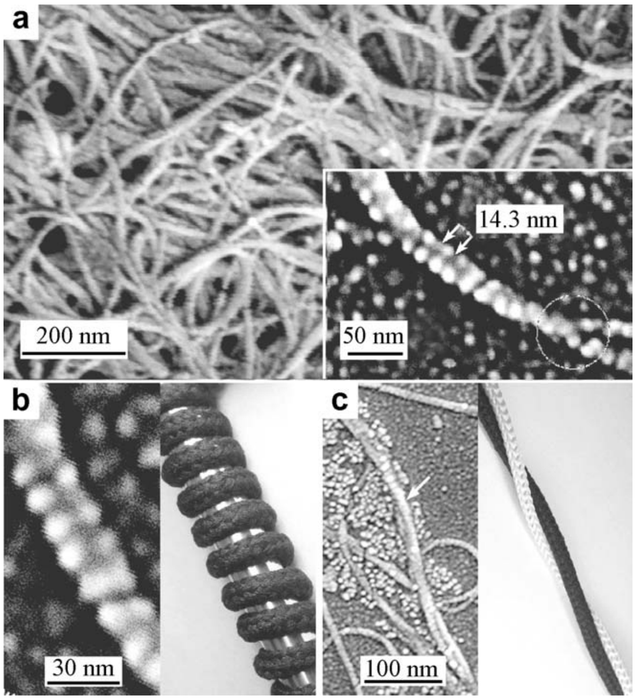

Fig. 2. FE-SEM images of A/S-C. (a) FE-SEM image of the A/S-C in a large vision field, the insert image represents a magnified picture; (b) wrapped A/S-C and its cartoon scheme; (c) twisted A/S-C bundles and their cartoon scheme.

Based on the previous literatures, our group has prepared a bio-compatible amylose/SWNTs complex (A/S-C) using the non-covalent functionalization method. The complex has a regular helical morphology and the pitch is estimated to be 14.3 nm (Fig. 2) [17]. It could be concluded from variable-temperature ^{1}H NMR and Raman spectra that, besides the hydrophobic interaction, the hydrogen bonding also plays a certain role as the driving force in the self-assembly process. In combination with other measurements such as HR-TEM, FE-SEM and AFM, a 'hierarchical self-assembly' model, including the wrapping of amylose chains around SWNT and the hierarchical self-assembly of wrapped-SWNTs into the superstructural A/S-C, was put forward to explain the formation process of the helical A/S-C [18]. The rationality of this model was confirmed by an experiment of destroying hydrogen bonds. The model will be helpful to study the formation of other polysaccharides/SWNTs complexes. Subsequently, the tests of WST-1 and AO/EB staining revealed that A/S-C had much better biocompatibility than pure SWNTs (Fig. 3).

Though the natural materials such as DNA, proteins, amylose, SPG and cyclodextrins have been widely investigated to functionalize CNTs, they are costly and not readily available, which limits their extensive use. Thus, we tried to use cellulose to modify CNTs. Cellulose is the most abundant renewable material in the biosphere and much cheaper than other natural polymers. However, cellulose consists of linear polymeric D-glucose units, cross-linked by 1,4-glucoside bonds, which form hydrogen-bonded supramolecular structures and is insoluble in most common solvents. Thus, we dissolved cellulose in ionic liquids, then functionalized it onto SWNTs. The obtained C/S-C is water-dissolved and can be stored at room temperature for more than one year without precipitation. Furthermore, C/S-C has been confirmed to possess good biocompatibility via a test of Hela cell viability and AO/EB double staining (Fig. 4). Thus, it is a relatively facile and cheap method to obtain bio-compatible CNTs.

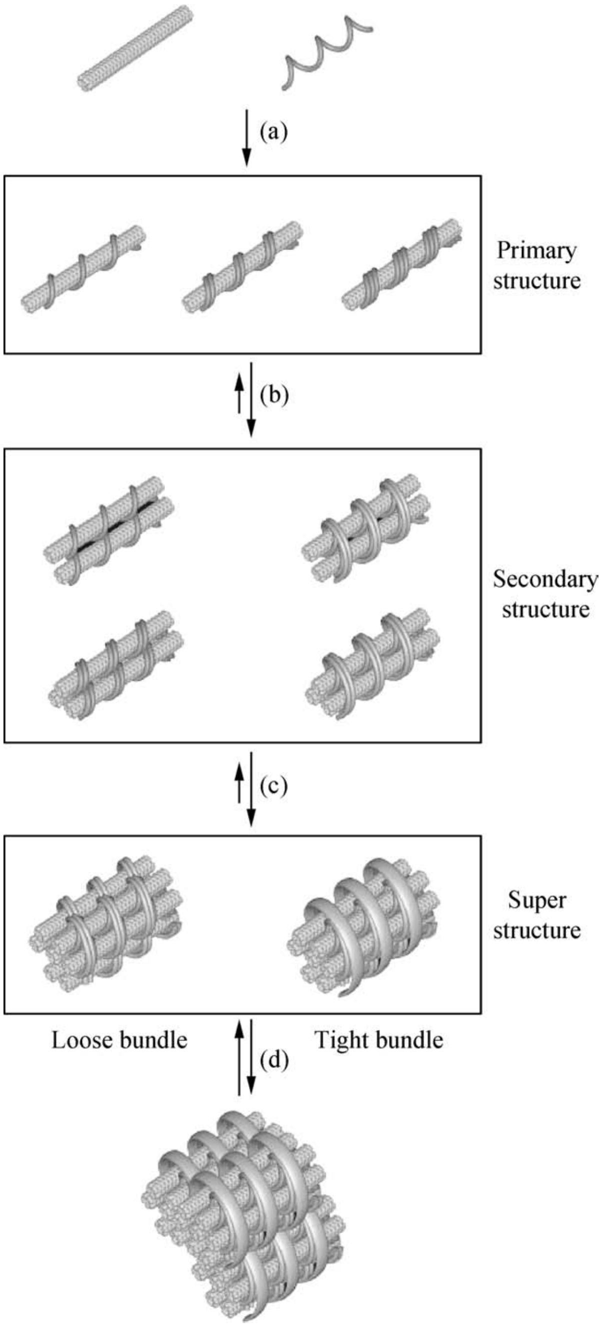

Fig. 3. Formation mechanism of A/S-C. (a) The driving force for the formation of primary A/S-C, including hydrophobic interaction, hydrogen bond interaction or their synergism. (b–d) The driving force for the subsequent process – hydrogen bond interaction.

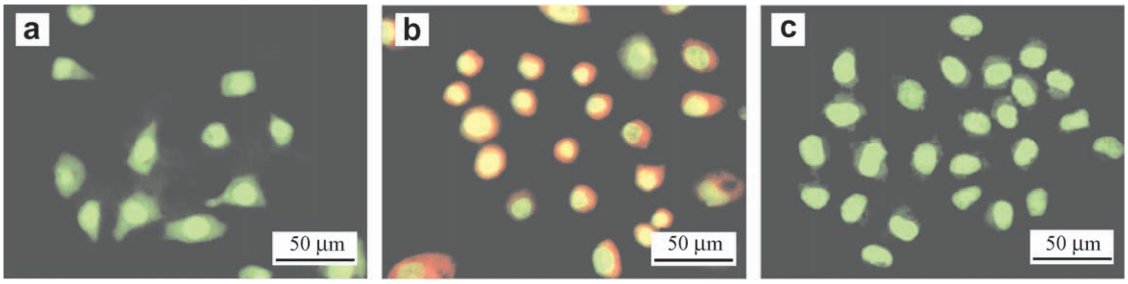

Fig. 4. Fluorescence microscopy images of HeLa cells cultured for 24 h on (a) glass slide, (b) SWNTs, (c) C/S-C. The cells were stained by AO and EB (healthy cells have green nuclei and uniform chromatin while the cells undergoing apoptosis have orange nuclei and condensed chromatin).

4. Fluorescent CNTs

Recently, with the development of CNT science in biology, electronics and other fields, fluorescent CNTs have attracted increasing attention due to their promising applications in nanoscale photoactive materials, biological probes and fluorescent nanosensors. Fluorescent CNT complexes can be prepared by conjugating CNTs with fluorescent materials such as quantum dots (QDs), dyes and chromophore-containing polymers.

4.1. Preparation of fluorescent CNTs by non-covalent functionalization

It was found that fluorescein, a widely used fluorophore, can be strongly adsorbed onto the sidewall of SWNTs, likely via π-stacking and hydrophilic force [14]. They used fluorescein-polyethylene glycol (Fluor-PEG) to non-covalently functionalize SWNTs. For the obtained conjugates (Fluor-PEG/SWNT), PEG chains impart high aqueous solubility and simultaneously fluorescein affords fluorescent labels to nanotubes. Fluorescein molecules bound to SWNTs exhibit interesting pH-dependent optical absorbance and fluorescence properties. Fluorescence emission from fluorescein adsorbed on SWNT is quenched by ~67%, but remains sufficient and useful as a fluorescent label. In addition, the fluorescent SWNTs can be further functionalized by using the carboxyl group on PEG.

Kobuke's group [38] prepared two kinds of stable porphyrin/SWNT composites by condensation of tetraformylporphyrins and diaminopyrenes on SWNTs. The degree of interaction between SWNTs and porphyrin was evaluated by UV–vis and fluorescence spectra. In the composites, the Soret and Q-bands of porphyrin moieties were significantly broadened and their fluorescence was almost quenched.

Murray et al. [39] found that anthracene and their derivatives could be strongly adsorbed onto SWNTs. The adsorption coverage of anthracene molecules on SWNTs varied with the aromatic ring substituents. The observed red shifts of emission peaks of the absorptive adduct appear to depend on the energy level of the lowest unoccupied molecular orbital (LUMO) of the adsorbate. This phenomenon is consistent with the adsorption by a charge-transfer interaction, in which the SWNT is the electron donor and anthracene is the acceptor.

Tang and his co-workers [40] synthesized a series of pyrene-containing poly(phenylacetylene)s (PPAs). Then, they mixed the polymers and CNTs in an appropriate solvent affording the polymer/MWNT hybrids, which are soluble in common organic solvents such as chloroform and THF. The hybrids are electronically more conjugated and emit blue-green light more efficiently than their parent polymers upon photo-excitation. The surface photovoltaic cell fabricated from the hybrids is bipolar, suggesting an efficient photo-induced charge-transfer between the two components.

Smalley's group [41] focused on the development of CNTs' optical devices and probes for biomedical research. They obtained a fluorescently labeled polymer poly(vinylpyrrolidone) (PVP-1300) by attaching fluorescent molecules onto PVP, then fluorescent PVP-1300 forms a monomolecular ~2.5 nm thick layer coiling around individual SWNTs or nanotube bundles. This causes individual SWNTs to be observed by a fluorescent microscope. The spare polymer strands left over after wrapping around the relatively shorter nanotubes form junctions between SWNTs, tying them together into new configurations, primarily 'Y-' and 'ψ-' type junctions. The ability to use a single fluorescent polymer strand to fasten nanotubes together is useful in the assembly of nanotube-made devices.

In summary, non-covalent modifications involve weak physical interactions such as π-stacking, Van der Waals forces and hydrophobic forces between fluorescent materials and SWNTs. They have the advantages of facile operation and mild reaction conditions. However, the fluorescence of the molecules adsorbed onto SWNTs tends to be badly quenched due to the effective energy and electron transfer between the two units.

4.2. Preparation of fluorescent CNTs by covalent functionalization

Li et al. [42] synthesized porphyrin-decorated SWNT samples in which the nanotubes were covalently tethered with derivatized porphyrin molecules. Results from steady-state and time-resolved fluorescence investigations showed that the excited-state energy transfer quenching of porphyrin fluorescence depended on the length of the linker between the porphyrin moiety and the nanotube. There was no fluorescence quenching in the sample with a shorter linker because the shorter linker inhibited the porphyrin ring to take a position facing SWNT and thus suppressed their energy and electron transfer.

Zhu et al. [8] prepared soluble, chromophore-functionalized SWNTs (SWNT-NA) via covalent bonding with minimal alteration to the characteristic one-dimensional electronic states of SWNTs. Significant fluorescence quenching was observed for the naphthalimide chromophore bonded to the SWNT backbone, which showed the existence of electronic interactions between the chromophores and SWNTs in their ground and/or excited states. They also found that the absorption and luminescence (steady-state and transient) spectra were dependent upon the length of the linkers between chromophores and SWNTs, thus the electronic interaction can be controlled by designing the structure of the linkers.

Guo's group [43] synthesized covalently porphyrin-functionalized SWNTs by the reaction of SWNTs with *in situ* generated porphyrin diazonium compounds. The electronic properties of the modified tubes were mostly retained, without damaging their one-dimensional electronic properties. The fluorescence from the porphyrin moiety was almost completely quenched by SWNTs, indicating that the unique direct linkage mode facilitated the effective energy and electron transfer between the excited porphyrin moiety and the extended π-system of SWNTs. This nanohybrid material also exhibited superior optical limiting effects for nanosecond laser pulses, significantly better than SWNTs and C_{60}, thus could be used for optical limiting and solar-energy conversion.

Tang and coworkers [44] designed and synthesized several azido-functionalized polyacetylenes. By utilization of the cyclization reaction of the azido group with the strained double bonds, the polyacetylene chains were attached to the sidewall of SWNTs. The molecular functionalization approach enables the combination of the advantageous properties of the two components in one hybrid system: the polymer makes the addend light emitting, while the nanotube renders it optical limiting. The author suggested that the jacket effect of the alkyl pendants might allow one to introduce other useful functional properties such as liquid crystallinity to the nanotube hybrid system, which might in turn enable the addend to be aligned or oriented by convenient external stimuli such as electric field and mechanical shearing.

Common covalent modification methods mainly include the esterification or amidation of carboxylic acid groups on the surface of SWNTs. Under proper reaction conditions, fluorescent SWNT with high quantum yields can be obtained. However, in order to increase the reactivity of SWNTs, the carboxylic acid groups usually need to be converted into acid chloride in this procedure, which requires stringent conditions and long reaction time, typically several days.

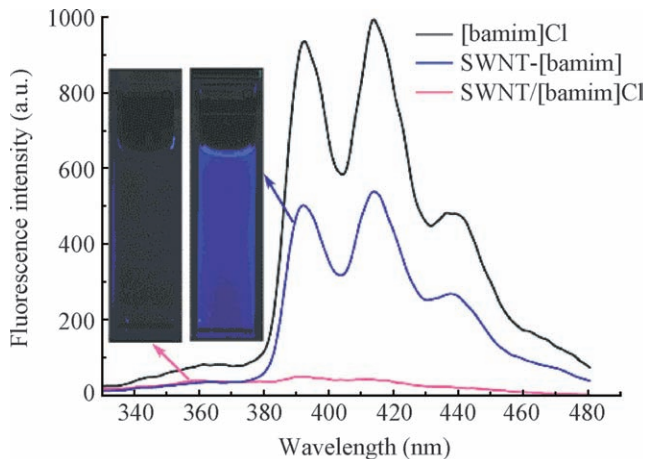

Fig. 5. Fluorescence emission spectra of SWNT-[bamim], SWNT/[bamim]Cl and [bamim]Cl in ethanol excited at 254 nm (~1.5×10^{-4} M $[\text{bamim}]^+$ in all samples). Inset: the fluorescence images of SWNT-[bamim] and SWNT/[bamim]Cl.

4.3. *Preparation of fluorescent CNTs by ion exchange*

Both covalent modifications and non-covalent modifications have their shortcomings, thus our group firstly developed a facile ion exchange method to prepare fluorescent CNTs [19]: the fluorescent imidazolium salt 1,3-bis (9-anthracenylmethyl)imidazolium chloride, [bamim]Cl, was designed and synthesized. Subsequently, *via* ion exchange, $[\text{bamim}]^+$ was attached to SWNTs to produce SWNT-[bamim], which can emit a blue light at 392, 414 and 438 nm excited at 254 nm (Fig. 5). The ion exchange strategy offers specific advantages including that (1) the reaction can take place in mild condition, (2) the resulting product retains a high fluorescence QY (0.40), (3) the fluorescent SWNTs retain one-dimensional electronic states of SWNTs. We also functionalized SWNTs with a series of other imidazolium salts. The successful formation of these SWNT–ILs systems indicates that ion exchange could be used as a universal strategy to functionalize nanotubes.

5. Transition metal functionalized CNTs

The research on transition metal functionalized CNTs was initiated by Ajayan in 1994 [45]. They prepared Ru/nanotubes catalyst, in which Ru nanoparticles were loaded on SWNTs with a uniform distribution of sizes. The Ru/nanotubes catalyst contains 0.2% Ru and can be used in hydrogenation of cinnamic aldehyde. It is noteworthy that the high selectivity for cinnamyl alcohol (up to 92%) is maintained to 80% conversion of cinnamic aldehyde. Under the same conditions, they found a cinnamyl alcohol selectivity of only 20–30% on Ru/Al_2O_3 catalysts with similar-sized Ru particles.

After that, a great quantity of work about transition-metal/CNTs hybrids was reported. The main methods can be divided into three categories: (1) *in situ* reduction of metal precursors onto CNTs, (2) non-covalent functionalization of CNTs with metal nanoparticles and (3) covalent functionalization of CNTs with metal nanoparticles.

5.1. In situ reduction of metal precursors onto CNTs

Noble or rare metal nanoparticles such as Pt, Au, Pd, Ag, Rh, Ru and Ni can be directly deposited onto the surface of CNTs by Van der Waals force when their salts were reduced in the presence of CNTs.

Hersam [46] reported a novel method for non-covalent functionalization of SWNTs with Pt nanoparticles: *cis*-platin and potassium tetrachloroplatinate were firstly bound to DNA that encapsulates SWNTs in aqueous solution, the bound platinum salt could then be reduced to decorate the DNA-encapsulated SWNTs with platinum nanoparticles. The platinum-coated SWNTs possess a unique combination of catalytic activity of nanoscale platinum, biological functionality of DNA and optoelectronic properties of SWNTs, representing an advanced material with potential applications in fuel cells, catalysts, biosensors and electrochemical devices.

Li et al. [47] developed a modified polyol synthesis method to prepare Pt catalysts supported on MWNTs. Pt metal loading was about 10% for all Pt/MWNTs samples and the particle size of the Pt catalyst supported on MWNTs could be controlled by adjusting the ratio of H_2O to ethylene glycol in the preparation process. The MWNTs-supported homogeneous Pt particles also showed an optimum O reduction reaction activity when used as cathode catalysts in DMFCs. Xing et al. used a facile sonochemical method to prepare highly dispersed, high-loading Pt nanoparticles on CNTs as fuel cell catalysts [48]. The Pt metal loading reached even about 30%.

Raghuveer's group [49] combined microwave radiation with polyol reduction of a metal salt to obtain CNTs with Au nanoparticles in a single processing step. Exposing CNTs to microwaves resulted in defect creation and formation of functional groups on the CNT surface. The functional groups served as preferred nucleation points for reducing metal ions from solution by a microwave-assisted reduction reaction, yielding CNTs that were uniformly decorated with gold nanoparticles.

Wang et al. reduced metal ions in ethylene glycol (EG) [50] by the addition of a salt such as sodium dodecyl sulfate (SDS) and p-$CH_3C_6H_4SO_3Na$, resulting in high dispersions and high loadings of platinum nanoparticles on CNTs without aggregation. By exploiting the salt effect, homogeneous nucleation was effectively depressed, leading to selective heterogeneous metal nucleation and growth, even on unmodified CNTs.

5.2. Non-covalent functionalization of CNTs with metal nanoparticles

Rahman's group reported on dispersible samples of CNTs which were accomplished through immobilizing gold nanoparticles-S-$(CH_2)_{11}$-CH_3 on the CNTs surface [51]. These complexes were easy to dissolve in water due to the presence of the thiols. The dispersed samples gave rise to strong electronic coupling, in which the Au nanoparticles function as an electron acceptor, receiving additional electron density from CNTs.

Han et al. [52] prepared the nanoparticles-coated CNTs composites, which involved molecularly mediated assembly of monolayer-capped nanoparticles on MWNTs via a combination of hydrophobic and hydrogen-bonding interactions between the capping/mediating shell and the CNT surface. The advantage of this route is that it does not require tedious surface modification of CNTs. The composite nanomaterials could be dispersed in organic solvent, and the capping/linking shells could be removed by thermal treatment to produce controllable nanocrystals on the CNT surfaces.

Aromatic compounds with conjugate macrocycle such as pyrene, anthracene and their derivatives could be tightly adsorbed onto CNTs by π-stacking interactions. Therefore, they were used as linkage to bind metal nanoparticles to CNTs. Liu et al. [53] and Yang et al. [54] reported similar gold nanoparticles/CNTs composites, respectively. Gold nanoparticles were self-assembled onto the surface of soluble carbon nanotubes through an interlinker of bi-functionalized molecule terminated with pyrenyl unit at one end and thiol group at the other end. Thiol groups can easily interact with gold while pyrene is attached on the surface of CNTs by π-stacking. However, the fluorescence is almost totally quenched by the binding of gold nanoparticles. The enhancement of the Raman responses of nanotubes by the gold nanoparticles was also observed, indicating the charge-transfer interactions between nanotubes and gold nanoparticles. The phenomenon of charge-transfer was also observed by Guldi [55,56] in SWNTs/zinc/porphyrin composites. Georgakilas et al. [57] used a similar method to combine magnetic nanoparticles with CNTs by the interlinker of a carboxylic derivative of pyrene. The increased organophilic character of the capped nanoparticles induced high solubility in organic media for the modified carbon nanotubes.

The method of layer-by-layer self-assembly was also used to prepare metal nanoparticles-functionalized CNTs by Kim and Sigmund [58]. The zeta potential of oxidative MWNTs changed from negative charge to positive charge when cationic polyelectrolytes were self-assembled on their surface. With addition of anionic polyelectrolytes, cationic polyelectrolyte-coated MWNTs showed the expected charge reversal as expected for multilayer self-assembly. Complex formation of positively charged gold nanoparticles and negatively charged MWNTs could be achieved with and without polyelectrolyte coatings by electrostatic interaction. It suggested that positively charged gold nanoparticles could be used to detect negatively charged defect sites on CNTs.

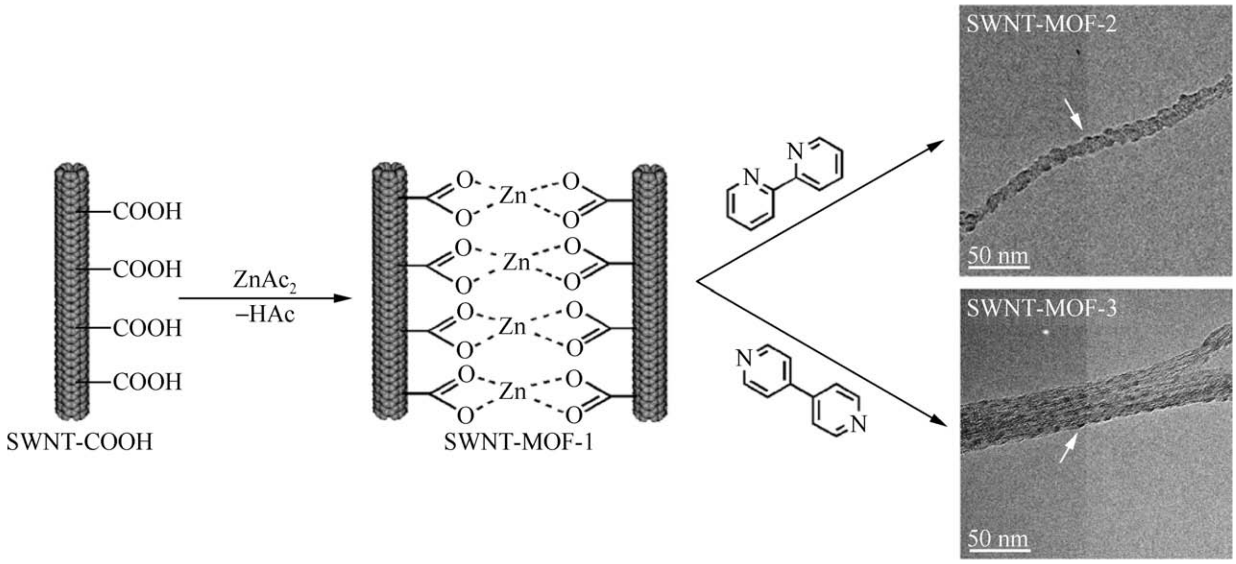

Fig. 6. Synthesis of SWNT–MOFs from oxidative SWNTs.

5.3. Covalent functionalization of CNTs with metal nanoparticles

To the best of our knowledge, relatively less research has been carried out on the covalent functionalization of CNTs with metal nanoparticles because of the complicated process. Nakamura et al. [59] photolyzed cyclic disulfides with SWNTs leading to a sidewall modification of the surfaces to introduce sulfur-containing functional groups. A subsequent treatment of sulfur-containing substituents-modified SWNTs with gold nanoparticles gave an attachment of gold on the surface of SWNTs through thioalkylthiol linkage. In addition, Coleman et al. [60] introduced thiol groups onto the surface of SWNTs under Bingel reaction conditions, then ~5 nm gold colloids were grafted onto SWNTs by exploiting the gold sulfur binding interaction.

5.4. Printing metal-organic frameworks on CNTs

Metal-organic frameworks (MOFs) with highly interesting topologies have potential applications in hydrogen storage, DNA sensing and many other areas, thus attracting the increasing interest of researchers. We firstly prepared MOFs based on the coordination chemistry of zinc, combined with SWNTs, which provides an alternative type of template (Fig. 6). The synthetic route to the SWNT–MOFs is relatively facile and inexpensive. Using this approach a wide range of transition metals could be incorporated into SWNT systems and new types of supramolecular architectures could be developed. By using different linkers (additional ligands), the properties of the SWNT–MOFs might be easily tuned. This approach may eventually lead to new SWNT-based materials that could have diverse applications including gas transport and storage, and catalysis.

6. Conclusions

This article reviewed the recent development of bio-compatible CNTs, fluorescent CNTs and transition metal functionalized CNTs. The work reported by us on SWNTs functionalized with bio-compatible amylose and cellulose, fluorescent ionic liquid (IL) and zinc–bipyridine frameworks was introduced as well. These novel methods are of significance to reduce cost and to simplify technology, thus might promote the practical applications of CNTs in many fields. However, compared to the traditional aromatic systems, the functionalization of CNTs is in its infancy and largely unexplored. It is still an attractive field in the future and the following directions will be the popular topics.

(1) The current functionalization methods could not meet all the application demands due to their disadvantages. New functionalization methods, such as ion exchange, coordination chemistry and ring-opening polymerization, are expected to obtain functionalized CNTs with improved performance.
(2) Following the guidance of ‘Task-specific’, novel CNTs composites or nano-devices could be constructed via grafting the multifunctional monomers or polymers onto the surface of CNTs. The different functional groups or materials could be conjugated with CNTs via both one-step reaction and ‘two-stage’ modification strategy.
(3) Parallel to the experimental studies, theoretical studies of CNTs have also been conducted during the past decades. However, the applications in commercial scale are still limited due to the high cost, complicated preparation process and difficulties in scaling up. More efforts to solve these problems are required for their application in commercialization in the future.

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