Preparation of Poly(acrylic acid) Grafted Multiwalled Carbon Nanotubes by a Two-Step Irradiation Technique

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ABSTRACT: A facile strategy to prepare water-soluble multiwalled carbon nanotubes (MWNTs) by two steps of γ radiation is developed. First, MWNTs are irradiated in ethanol. The radiolysis of ethanol produces many active species such as $^{\bullet}CH_2CH_2OH$ and $^{\bullet}CH(CH_3)OH$ which react with C═C bonds on the surface of MWNTs. Afterward, poly(acrylic acid) (PAA) is covalently grafted to the surface of modified MWNTs by radiation in the presence of acrylic acid. FT-IR, ^{1}H NMR, and TGA results showed that PAA chains were successfully grafted onto the surface of MWNTs. The TEM images also provide direct evidence of the formation of a core−shell structure, and the external diameter of resultant MWNTs is increased remarkably. The PAA-*g*-MWNTs have very good solubility in water and other polar solvents. This two-step grafting approach may also be employed introducing other functional polymer chains onto MWNTs.

Introduction

Carbon nanotubes (CNTs) have attracted much attention among scientists in various disciplines since their discovery in 1991.[1] Both MWNTs and single-walled carbon nanotubes (SWNTs) possess tubular nanostructures with unique properties and are promising materials for engineering applications such as polymeric composites, electronic devices, field emission display and hydrogen storage, etc.[2] However, a number of challenges must be met before nanotubes can be exploited for most of these envisioned applications. These challenges include expanding synthetic approaches to large-scale production, searching for efficient purification methods, and developing chemical techniques for manipulating nanotubes.[3] Generally, SWNTs exhibit simpler structures and are more easily controllable compared with MWNTs. Hence, most of the previous academic research on CNTs including functionalization chemistry is focused on SWNTs. However, as of now, the high cost of SWNTs severely limits its commercial applications. Fortunately, MWNTs have been realized in industrial production recently.[4,5] Therefore, more attention will be paid to the application of MWNTs. On the other hand, like other bottlenecks, manipulation and processing of CNTs has been limited by their insolubility in most common solvents. Many approaches were employed to introduce functional groups noncovalently or covalently onto the surface of CNTs to solubilize these useful materials and facilitate their studies.[3,6−10] In our previous study, we also demonstrated that treating SWNTs with *sec*-butyllithium and subsequently with carbon dioxide leads to the SWNTs functionalized with both alkyl and carboxyl groups.[11] Among the various functionalized strategies, chemical modification of CNTs often alters their structure and electronic properties, and solubilization by noncovalent interactions is limited by stability. However, the grafting of polymer instead of low-molecular-weight compound onto CNTs by an appropriate method is a possible strategy for the preparation of tubes with little damage in structure and high solubility in solvent,[12] for which “grafting to” and “grafting from” approaches have been applied.[13−32] The “grafting to” method is self-limiting because the grafted chains hinder the approach of additional polymer chains to the surface; the “grafting from” method promises the polymer chains can be in situ grafted more densely from the surface of CNTs. Recently, intensive studies have been reported on various types of polymerization methods to introduce polymer chains onto CNTs accomplished by “grafting from” techniques, such as anionic polymerization,[13,14] electropolymerization,[15] ring-opening polymerization,[16,17] atom transfer radical polymerization (ATRP),[18−20] reversible addition−fragmentation chain transfer (RAFT),[21] and other radical polymerizations.[22−24] Among polymers selected to grafting onto CNTs, water-soluble polymers are very attractive because such materials have potential and versatile applications in biology and materials science.[33] Many water-soluble polymers such as polyamines,[34] poly(ethylene glycol),[35−37] poly(aminobenzenesulfonic acid),[31,38] poly(vinyl alcohol) and its copolymer poly(vinyl acetate-*co*-vinyl alcohol) (PVA−VA),[39,40] etc., have been successfully introduced onto CNTs by the “grafting to” method. Using the ATRP technique, poly(acrylic acid) and its copolymer polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA) were grafted onto the surface of CNTs by the “grafting from” approach, resulting in water-soluble CNTs.[41,42] However, so far most of the solubilized CNTs are obtained only on a milligram scale, which is far from the need of practical applications.

Radiation-induced graft polymerization has been proposed for many years as a competitive methodology to develop new functional materials. The major advantages of radiation grafting are (a) the reaction is carried out at room temperature and more controllable than in chemical operation, (b) the grafting can be carried out in gaseous and liquid phase of the monomer, and (c) the modified material is free from residuals of initiator or catalyst. Radiation grafting is an effective and facile (including in engineering applications) method for contacting inorganic−organic materials interface and modifying surfaces of functional composites. However, to our knowledge, there is still no report in the literature about introducing polymer chains to CNTs by radiation-induced graft polymerization, despite the fact that the controlling of the length of grafted chains on the surface of

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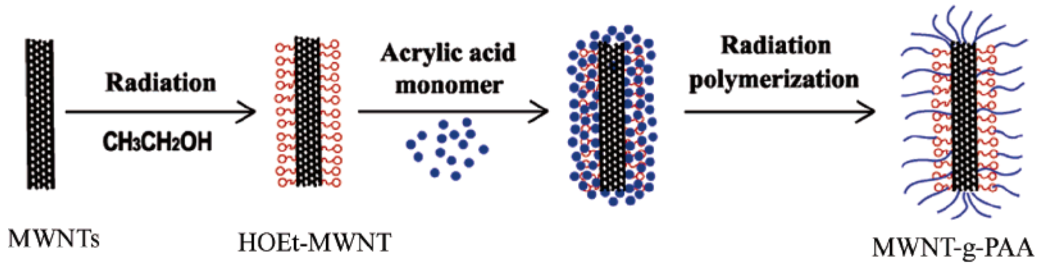
Scheme 1



CNTs by living polymerization is interesting and attractive. Rigorous and time-consuming procedures must be employed (for example, ATRP and anionic polymerization). One of the important breakthroughs in CNTs research may be mass production of solubilized CNTs to improve their manipulation for use in diverse technological fields. Here, we report a facile strategy to prepare water-soluble MWNTs by two steps of γ radiation on the laboratory scale, which also could be easily developed for the industrial manufacturing of solubilized CNTs. First, MWNTs were irradiated in ethanol; the radiolysis of ethanol produced many active species that react with C═C bonds on the surface of MWNTs. Afterward, adding acrylic acid (AA) monomer and radiation-induced graft polymerization under γ radiation, poly(acrylic acid) (PAA) can be covalently grafted to the surface of MWNTs, and the procedure is described as shown in Scheme 1.

Experimental Section

MWNTs were purchased from Shenzhen Nanotech Port Co., Ltd., synthesized by the chemical vapor deposition method (purity >95%, 20−35 nm diameter). The impurities were eliminated by refluxing the MWNTs in 2.6 M HNO_3 for 12 h and washed several times with deionized water and dried. Typically, 50 mg of purified MWNTs and 30 mL of ethanol were mixed together in a glass tube. The mixture was sonicated for 20 min before irradiation and then subjected to γ irradiation of ^{60}Co source for 48 h to a total dose of 50.0 kGy (dose rate: 17.4 Gy/min). After that, the mixture was filtered through 0.2 μm microporous poly(ether sulfone) membrane and dried under vacuum for 12 h at 60 °C. The product is hydroxyethylated MWNTs (HOEt-MWNT). Radiation-induced graft polymerization was carried out by mixing HOEt-MWNTs (40 mg), acrylic acid (5 mL), H_2O (25 mL), and $CuSO_4{\cdot}5H_2O$ (34.5 mg) in a glass ampule; after sonicating for 20 min and bubbling N_2 gas to remove the air, the mixture was exposed to a total dose of 20 kGy at a dose rate of 20.2 Gy/min under γ rays. After the irradiation, the mixture was filtered through 0.2 μm microporous poly(ether sulfone) membrane for 10 times. To ensure that no possible homopolymer and free reagents exist in the product, in each time, the filter mass was dispersed in deionized water, then filtered, and washed with water. The poly(acrylic acid) grafted MWNTs (MWNT-*g*-PAA, 32.4 mg) was obtained by filtration and drying overnight under vacuum. The yield of PAA-*g*-MWNT compared with the initial amounts of MWNT and acrylic acid was 72%.

FT-IR spectra were recorded on a Nicolet Avater-360 spectrometer using KBr pellets. The ^1H NMR measurement was performed on a Bruker DMX500 spectrometer using TMS as an internal reference. TGA measurement was carried out using a Perkin-Elmer Pyris-1 series thermal analysis system under a flowing nitrogen atmosphere at a scan rate of 10 °C/min from 50 to 800 °C. Transmission electron microscopy (TEM) observations were performed with a Philips EM400 microscope at an accelerating voltage of 80 kV. High-resolution transmission electron microscopy (HR-TEM) images were taken with a JEOL JEM2011 electron microscope operating at 200 kV. The samples for TEM observation were prepared by depositing a drop of the nanotubes aqueous suspension on carbon-coated copper grids and then allowing them to dry in a desiccator.

Results and Discussion

Synthesis. It has been suggested that irradiation of carbon nanotubes with energetic particles can be successfully used for nanoengineering, e.g., for creating molecular junctions between the nanotubes, making nanotube-based quantum dots and composite materials with enhanced mechanical properties.[43,44] Skakalova et al.[45] used γ irradiation as a pretreatment for chemical functionalization of SWNTs with $SOCl_2$, and Wei et al.[46] applied γ radiation to cut MWNTs in the presence of dilute sulfuric acid. In our case, we first irradiated MWNTs in ethanol using γ rays. The tips and defects of MWNTs could be destroyed under γ radiation due to their high reactivity.[46] In the meantime, the radiolysis of ethanol produces many active species such as $^{\bullet}CH_2CH_2OH$ and $^{\bullet}CH(CH_3)OH$, which interact with the MWNTs and attach onto the surface of MWNTs. Herein we called these hydroxyethyl groups functionalized MWNTs as HOEt-MWNT for simplicity. The hydroxyethyl groups can not only help the HOEt-MWNTs suspend in aqueous acrylic acid solution but also improve the hydrophility of HOEt-MWNTs, leading to easier adsorption of acrylic acid monomer to the surface of HOEt-MWNTs (just like the function of surfactants), which is very important for the following radiation-induced graft polymerization of acrylic acid. On the other hand, same as other surface modification methods, to fulfill the modification of functional composites by radiation grafting, the surface of the materials is often required with active groups, such as hydroxyl, carbonyl, and carboxyl groups.[47] The radiation-induced graft polymerization is then initiated through these groups on the surface of the materials; the hydroxyethyl groups also act as the initiating sites of the polymerization of acrylic acid. That is to say, in our case the PAA polymer chains grafted not only directly to the skeleton of the tubes but also to the pregrafted hydroxyethyl groups. Furthermore, Cu^{2+} was added in order to suppress the homopolymerization of acrylic acid. In the control, we irradiated the raw MWNTs in aqueous acrylic acid solution in the presence of Cu^{2+}; the graft polymerization of acrylic acid onto the tubes did not occur effectively, since the as-treated MWNTs precipitated from water in a few hours after sonification and the TGA measurements showed no evidence of polymer grafted on the surface of nanotubes.

Characterization of Functionalized MWNTs by FT-IR and NMR. FTIR spectroscopy is a very informative measurement for studying the functional groups attached to side wall of MWNTs. Figure 1 shows the infrared spectra of MWNTs, HOEt-MWNT, and MWNT-*g*-PAA. The peaks in the 2805−3010 cm^{-1} region are characteristics of C−H stretchings, and their intensities are greatly enhanced after functionalization (in Figure 1b,c, compared with Figure 1a), which can be explained by the attachment of alkyl groups onto the surface of MWNTs and the increase of defects by irradiation. A broad peak at 1096

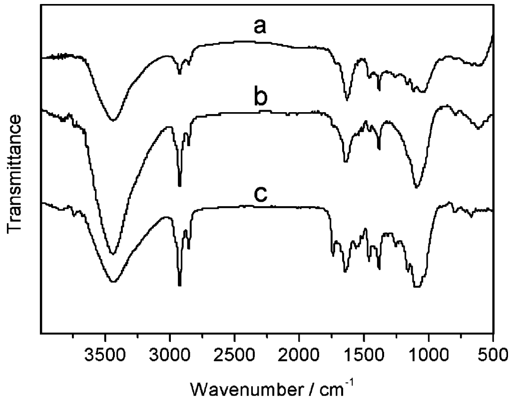


Figure 1. FT-IR spectra of: the pristine MWNTs (a), HOEt-MWNTs (b), and MWNT-*g*-PAA (c).

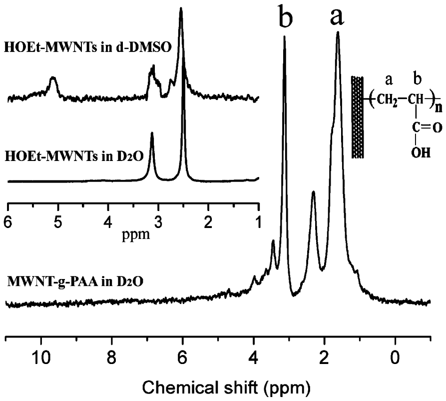


Figure 2. ^{1}H NMR spectra of HOEt-MWNT and MWNT-*g*-PAA.

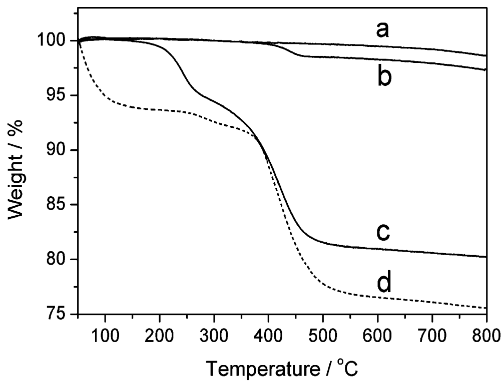


Figure 3. TGA curves of the pristine MWNTs (a), h-MWNTs (b), MWNT-*g*-PAA (c), and a mixture of PAA with MWNTs (d) in N_2 (10 °C/min).

cm^{-1} in Figure 1b is identified as the C−O stretching mode, indicating the presence of hydroxyl groups in the HOEt-MWNT. The peak at 1736 cm^{-1} in Figure 1c can be clearly assigned to the stretching mode of carbonyl groups, indicating the presence of PAA chains in MWNT-*g*-PAA. In addition, a broad shoulder band in the 3100−3600 cm^{-1} region is attributed not only to the presence of hydroxyethyl groups and PAA chains containing OH moieties but also to traces of water in the KBr pellet used for the analysis which is inaccessible to be fully removed.[18,48]

The chemical structures of HOEt-MWNT and MWNT-*g*-PAA were further characterized by ^{1}H NMR (Figure 2). The broader signals in the spectrum may be due to poor solubility, local field effects due to MWNTs itself, or slow tumbling of the very large polymer brush in solution.[19,49,50] An effective method for confirming the existence of OH groups on a substrate is to measure the ^{1}H NMR in D_2O and another deuterated solvent. As shown in Figure 2, the spectrum of HOEt-MWNTs in d-DMSO shows the signal of OH group at 5.11 ppm; however, this signal disappears in D_2O due to the chemical exchange of diplogen. Signals at 2.5 and 3.1 ppm observed both in d-DMSO and D_2O belong to the aliphatic protons of the hydroxyethyl groups. The integral area ratio of aliphatic protons at the two positions of the spectra is 2.2/1 (neither 2/2 nor 3/1). This agrees well with our mechanism mentioned above: the radiolysis of ethanol produces many active species such as $^{\bullet}CH_2CH_2OH$ and $^{\bullet}CH(CH_3)OH$ which react with C=C bonds on the surface of MWNTs. Therefore, the resultant HOEt-MWNTs contains two types of hydroxyethyl groups. ^{1}H NMR spectra of MWNT-*g*-PAA are also presented in Figure 2. The inherent peaks of PAA such as those of methylene ($-CH_2-$) and tertiary carbon hydrogen (−CH−) on the backbone of the polymer chains clearly appear in the spectra at 1.16−2.05 and 2.87−3.34 ppm, respectively. The signal of the hydrogen in carboxyl groups cannot be detected because of chemical exchange. All the evidence confirmed the existence of PAA polymer chains on the sample MWNT-*g*-PAA.

TGA Measurements. It is known that the defunctionalization of carbon nanotubes can be realized by thermal decomposition. In the present study, we used thermal gravity analysis (TGA) to determine the relative amount of grafted polymer of MWNT-*g*-PAA. Figure 3 shows the TGA traces of MWNTs, HOEt-MWNT, and MWNT-*g*-PAA under nitrogen. The weight loss corresponding to the pristine purified MWNTs and HOEt-MWNT at 800 °C under nitrogen is 1.3 and 2.7 wt %, respectively. All of the functional groups and grafted PAA chains are assumed to be lost at 800 °C;[51] that is to say, almost all of the weight loss during fragmentation is due to the pyrolysis of side-chain groups. For the sample of MWNT-*g*-PAA, two main weight-loss regions are found. The first weight-loss region (∼150−270 °C) may be assigned to the decomposition of carboxyl groups of PAA on the surface of MWNT, and the significant weight reduction in the second region (∼270−500 °C) is likely due to the decomposition of the polymer backbone and hydroxyethyl groups.[51,52] In addition, to compare with the thermal stability of MWNT-*g*-PAA, the pure PAA (22.4 wt %) was mechanically blended with MWNTs, and the TGA curve of this mixture was added in Figure 3d. Two weight-loss regions are also found for this mixed sample. However, the decomposition of carboxyl groups is lower by about 100 °C than that of MWNT-*g*-PAA. A similar phenomenon has been reported before.[20]

Microscopy Analysis and Solubility. The TEM images of the pristine and functionalized MWNTs are shown in Figure 4. The average internal and external diameters of the MWNTs are about 5−10 and 20−35 nm, respectively. The length of the MWNT is approximately several micrometers (Figure 4a). For the sample of HOEt-MWNTs, some of shortened tubes can be found after a dose of 50 kGy in ethanol (Figure 4b). A possible explanation is that the collision of active species with carbon atoms in MWNTs may result in displacement of atoms. Therefore, some defects are formed under γ radiation, and further reaction between active species and defects finally leads to the cutting of the MWNTs.[44,46] The TEM image of MWNTs showed that the MWNTs were piled up to form large bundles and ropes, but the MWNT-*g*-PAA was dispersed individually (as shown in Figure 4c), indicating that original MWNTs can be separated into individual tubes by radiation-induced polymerization of acrylic acid. At the same time, the external diameters of MWNTs-*g*-PAA are about 50−65 nm, which increased remarkably when compared with the MWNTs or HOEt-

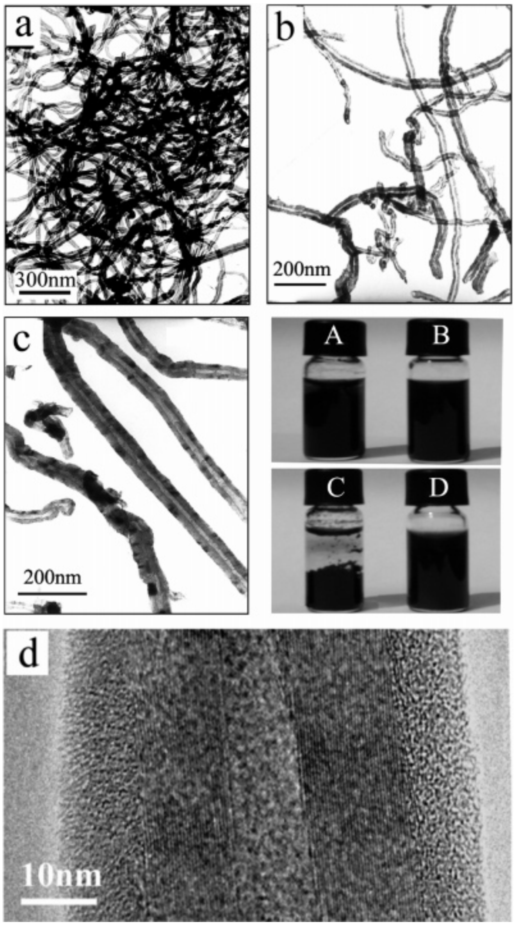


Figure 4. TEM images of the pristine MWNTs (a), HOEt-MWNTs (b), MWNT-*g*-PAA (c), and the HRTEM image of MWNT-*g*-PAA (d). The inset photographs show the stability in water (after sonication for 30 min) of HOEt-MWNTs ($t = 0$) (A), MWNT-*g*-PAA ($t = 0$) (B), HOEt-MWNTs ($t = 2$ days) (C), and MWNT-*g*-PAA ($t = 30$ days) (D). The concentration of either the HOEt-MWNTs or the MWNT-*g*-PAA in the bottles is 3 mg/mL.

MWNTs, indicating that the MWNTs-*g*-PAA has a core−shell structure in which the tubes are clothed with a polymer layer. This is further confirmed by the observation with HRTEM. As shown in Figure 4d, the polymer shell and the MWNTs graphite sheet structure are clearly observed in the HRTEM image; even the thickness of the polymer shell can be discerned. It should be mentioned that the polymer layer is not uniform. From the analysis of HRTEM, the thickness of the grafted PAA layer was found to be 3−10 nm. In addition, although the content of PAA grafted on MWNTs is only around 20 wt %, as seen from the HRTEM image, the number of graphite layers of the MWNT used in this study is over 20. We tend to consider that the content of 20 wt % PAA is enough to coat the tube surface completely.

The pristine MWNTs cannot dissolve in any solvents we tested. After irradiation in ethanol, the resulting HOEt-MWNTs exhibited a small (relatively) solubility in water, but much sedimentation was found at the bottom of bottle after 2 days (the inset of Figure 4). However, when the PAA chains were attached to the wall of the nanotubes, the MWNT-*g*-PAA showed a very good solubility in tested solvents such as water, methanol, and *N*,*N*-dimethylformamide (DMF); the behavior is almost similar to that of pure PAA. As shown in Figure 4, the aqueous solution of MWNT-*g*-PAA at the concentration 3 mg/mL keep stable for more than 2 months,[53] whereas most of the HOEt-MWNTs will precipitate in 2 days (the inset of Figure 4). We also attempted to disperse MWNTs into solvents with pure PAA present, but it is shown that PAA is a poor dispersant for MWNTs. All of this evidence supports the solubilization of the MWNTs by covalently bound PAA polymer chains on the surface of MWNTs.

Conclusions

The functionalization of MWNTs with PAA via in situ radiation-induced polymerization by two steps of irradiation under γ rays is demonstrated for the first time. After the hydroxyethyl groups attached onto the surface of MWNTs by irradiation of MWNTs in ethanol, the adsorption of acrylic acid monomer to MWNTs becomes easier and the polymerization takes place on the surface of the tubes, forming the PAA-coated MWNTs that exhibits very good solubility in water and some polar solvents. The PAA functionalized MWNTs was confirmed by FT-IR, ^{1}H NMR, TGA, and TEM. This simple but effective method may be extended to the grafting of various functional polymers on the tubes. We believe that this methodology will pave the way for mass production of solubilized CNTs to improve their manipulation for use in diverse biological and technological fields.

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References and Notes

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(53) The exact solubility of MWNT-*g*-PAA in water was determined as follows: A saturated solution of the MWNT-*g*-PAA was prepared by the sonication of 100 mg of material in 10 mL of deionized water for 1 h. The resulting suspension was allowed to stand 3 days at room temperature. 2 mL of solution of the upper layer was carefully extracted with a syringe and placed in an oven to remove the water. Subsequently, it was dried overnight under vacuum at 60 °C, obtaining MWNT-*g*-PAA (10.8 mg), giving solubility values of 5.4 mg/mL.

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