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Covalent attachment of poly (acrylic acid) onto multiwalled carbon nanotubes functionalized with formaldehyde via electrophilic substitution reaction

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Abstract The functionalization with formaldehyde via an electrophilic substitution reaction and graft with poly (acrylic acid) (PAA) by "grafting from" technology have been carried out for multiwalled carbon nanotubes (MWNTs) and MWNTs-PAA composites have been formed. The IR and TEM results show presence of covalent band and so-called "core-shell" structures for MWNTs-PAA. The MWNTs-PAA exhibits excellent suspendability in water, which is significant to explore the potential application of carbon nanotube in biological and medical systems.

Introduction

Carbon nanotubes (CNTs) have attracted much attention in various disciplines such as physics, chemistry, biology, and material science [1–4] since their discovery in 1991 [5]. However, it is well known that CNTs are easy to agglomerate, bundle tighter, and entangle with one another [6] because of the strong Van der Waals force derived from the high polarizability of the electrons of graphite sheets. Thus, the dispersibility problem must be solved before CNTs are exploited fully. The functionalization of chemistry for CNTs is expected to play a vital role in improving the dispersibility. Among the various functionalized strategies, the attachment of small molecules as well as macromolecules has been demonstrated to improve solubility and cause exfoliation of large nanotubes bundles into individual solvate structures. Recently, extensive research focusing on surface modification of CNTs to enhance their chemical compatibility and dissolution properties has been reported [7–11]. A common approach to functionalization of CNTs requires harsh reaction condition in strong acid such as nitric acid and sulfuric acid or their mixtures at elevated temperatures. Nevertheless the molecular framework of CNTs such as sidewall, opening, and defect site is damaged remarkably resulting in that the excellent electronic and mechanical properties of CNTs cannot be retained [12, 13]. So creating an efficient chemical modification method without or with little damage to the framework of CNTs is significant to expand the utility of CNTs.

We have previously reported [14] the method that H_2SO_4/HNO_3-oxidated MWNTs (o-MWNTs) were reacted with formaldehyde in sodium hydroxide solution and attached into methylol groups (–CH_2OH). In this paper, we attempted to replace the o-MWNTs with the MWNTs purified by HCl (p-MWNTs) and carried out the electrophilic substitution reaction. We found that the novel approach of functionalization of MWNTs was very effective. The MWNTs functionlized with formaldehyde were reacted with poly (acrylic acid) (PAA) to form excellently hydrophilic nanotubes. The procedure is described as shown in Scheme 1. Because PAA is an excellent water-soluble polymer with outstanding performance, covalent attachment of PAA onto the surface of CNTs is expected to obtain perfectly hydrophilic CNTs, which have potential and versatile applications in biology and materials science. Some studies [15–17] have been previously reported on the

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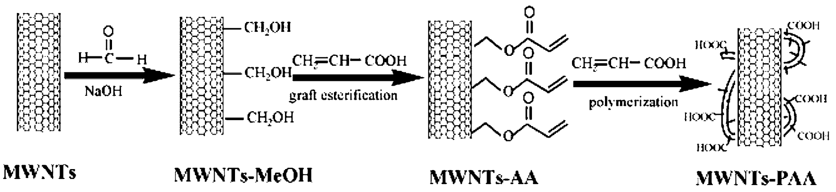


Scheme 1 The whole functionalization procedures of MWNTs

covalent functionalization of CNTs with PAA. Kong and co-workers [15, 16] reported that PAA and its copolymer polystyrene were grafted onto the surface of MWNTs by Atom Transfer Radical Polymerization technique. Recently, Wu and co-workers [17] investigated the preparation of PAA grafted MWNTs by a tow-step γ irradiation technique. Obviously, γ irradiation is harmful for operator as well as environment. Compared with these reports, one advantage of our strategy to modify MWNTs is to remain the inherent outstanding property of MWNTs due to little damage to molecular framework of MWNTs. It is another advantage of the present approach to provide a method for the functionalization of MWNTs which lowers the pollution to environment without harsh acid. It is further advantage that the experiment procedure is rather controllable and the raw materials are easy to acquire. To our knowledge, the novel strategy of functionalization with formaldehyde and covalent attachment with polymer for MWNTs has not been previously attempted. Significantly, the approach may open a new avenue for mass production of solubilized CNTs and exploring novel CNTs-based nanomaterials with tailormade structures and properties.

Experimental section

Materials

MWNTs were prepared by catalytic decomposition of acetylene. The catalysts were synthesized [18] by concentrating $Ni(NO_3)_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and $Na_3C_6H_5O_7 \cdot 2H_2O$ solution to gelation and then grinding it to fine powder after sintering at 600 °C. MWNTs growth was obtained on the catalyst at 725 °C with a flow rate of acetylene 40 mL/min and nitrogen 400 mL/min. Sodium hydroxide, hydrochloric acid, formaldehyde, perchloric acid, acrylic acid, benzoperoxide and N,N′-diemethyformamide (DMF) were purchased from commercial source. DMF was distilled over sodium hydride before reaction.

Purification of MWNTs

One gram of raw MWNTs were suspended and refluxed in 2 M HCl solution for 4 h at 100 °C. After filtrating, the remaining solids were washed repeatedly with deionized water until neutral pH and then dried under vacuum.

Functionalizition of MWNTs with formaldehyde

The purified MWNTs (300 mg) (p-MWNTs) and NaOH (1 g) were dispersed in 100 mL of formaldehyde solution. Subsequently, the mixture was treated in an ultrasonic bath for 30 min and refluxed for 3 h at 50 °C. The solution was then filtered through a membrane filter with pore diameter of 800 nm and then washed several times with distilled water and ethanol, respectively. The resulting solids (MWNTs-MeOH) were dried in a vacuum at 100 °C.

Graft onto MWNTs with acrylic acid

MWNTs-MeOH (300 mg), acrylic acid (150 mL) and perchloric acid (10 mL) were blended and sonicated for 30 min. Then the suspension was refluxed for 2 h at 70 °C, separated by filtration through an 800 nm PTEF membrane, thoroughly washed with acetone and vacumm-dried for 24 h to yield 354 mg of MWNTs-AA.

PAA growing from MWNTs by “grafting from” technology

The polyreaction was performed according to the following procedures. First, MWNTs-AA (200 mg), acrylic acid (20 mL) and initiator (benzoperoxide) (50 mL) in 100 mL of DMF were sonicated 30 min. Second, the mixture was stirred for 6 h at 100 °C under nitrogen atmosphere. After cooling, the reactant was filtrated and washed with water and ethanol, respectively. 245 mg of MWNTs-AA was obtained after drying for 24 h.

Measurements

The infrared (IR) spectrum of the samples in KBr pellets were recorded on 300E Jasco Fourier transform infrared spectrometer (FTIR). X-ray diffraction (XRD) measurements were performed using Philips PW 1710 diffractometer with Cu $K_{\alpha 1}$ radiation. The powder resistivity of the dried sample in a cylinder (200 mm^2 in basal area) under 784 N was measured through GM-I automatic powder resistivity measurement system. The morphology and structure were determined on a JEM-3010 transmission electron microscope (TEM). The thermo gravimetric analysis (TGA) was carried out on a DT-40 Shimadzu thermal analyzer by heating from room temperature up to 750 °C at a heating rate of 10 °C/min under air flow.

Results and discussions

Transmission electron microscope was used to investigate the structure and morphology of the MWNTs before and after chemical modification. The TEM image of the p-MWNTs (Fig. 1a) shows that surfaces of nanotube are smooth and clean, with average outer diameter of 20–30 nm. Combined the XRD pattern of the p-MWNTs (Fig. 2b), it is confirmed that the catalyst particles are eliminated [18, 19]. To further verify whether or not to destroy the electronic properties during the process of purification, we measure powder resistivities of a series of MWNTs (Table 1). The results show the powder resistivity of MWNTs is little enhanced after purification with HCl, which may be due to mild reaction environment resulting in little damage to the framework of MWNTs. Comparing with conventional purification method [1], we conclude that the purification method with HCl, by which not only the catalyst particles are removed, but also the integrated properties of nanotubes are remained, is a very effective strategy.

Figure 1b–d indicate no obvious change of the surface structure of the nanotubes after functionalization with formaldehyde and esterification. Figure 1e displays the morphologies of MWNTs-PAA. Apparently, a dense covering layer around the surface of MWNTs is present, forming so-called "core-shell" structure. A TEM image with larger magnification (Fig. 1f) further confirms the structure. The non-crystalline PAA "shell" and the MWNTs "core" are clearly discerned. The polymer shell thickness is estimated to be 5–15 nm.

To further confirm the changes on the surfaces of MWNTs after chemical modification, the IR spectrum

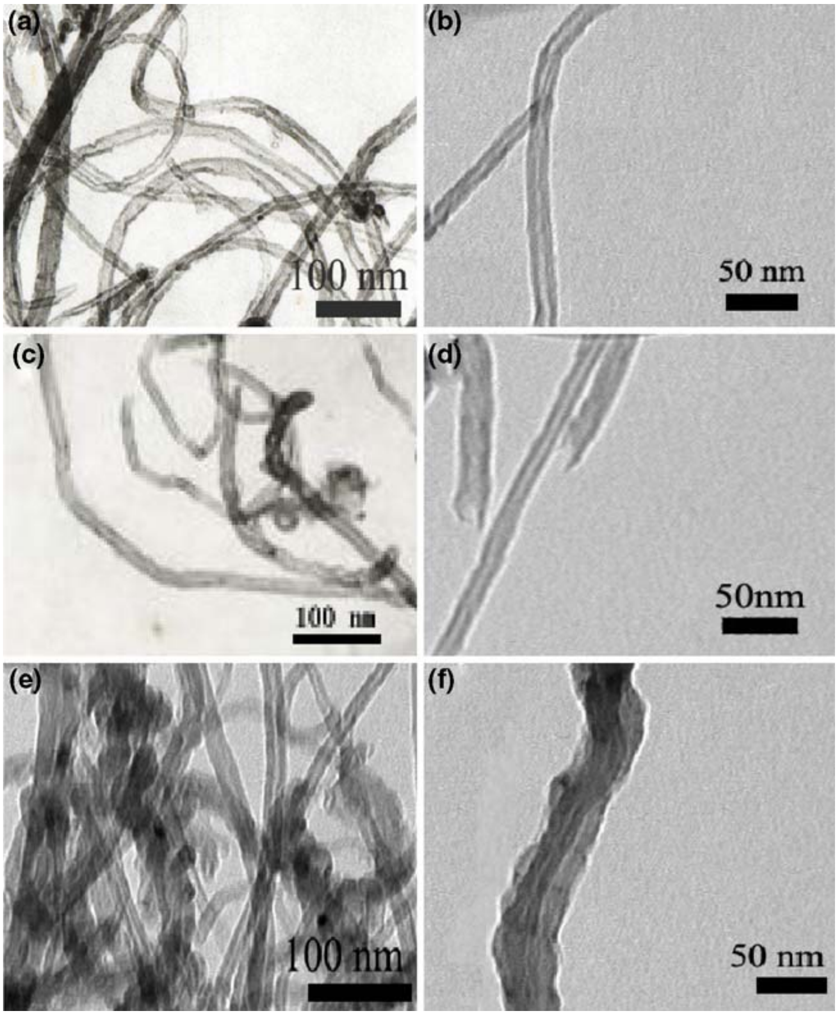


Fig. 1 TEM image of: p-MWNTs (**a**), individual MWNTs-MeOH (**b**), MWNTs-AA (**c**), individual MWNTs-AA (**d**), MWNTs-PAA (**e**), individual MWNTs-PAA (**f**)

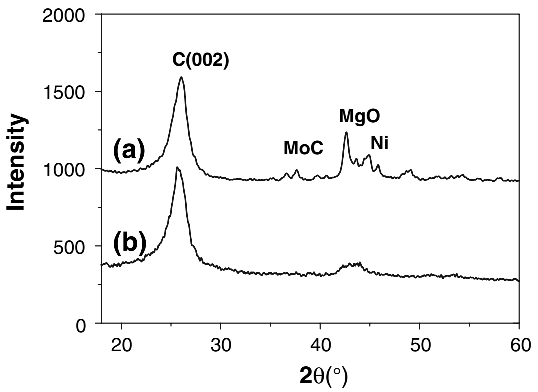


Fig. 2 XRD patterns for raw MWNTs (**a**) and p-MWNTs (**b**)

Table 1 The power resistivity of MWNTs

	Power resistivity (Ω·m)
The raw MWNTs	1,345
The purified MWNTs with H_2SO_4 and HNO_3 (V/V 3:1) for 2 h	2,651
The purified MWNTs with H_2SO_4 and HNO_3 (V/V 3:1) for 6 h	2,761
The purified MWNTs with HCl for 2 h	1,405
The purified MWNTs with HCl for 6 h	1,431

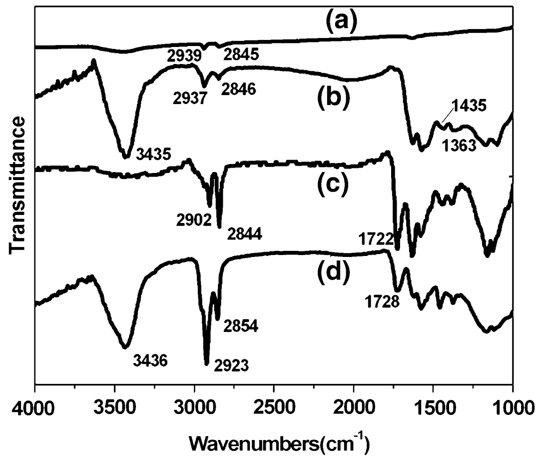


Fig. 3 FTIR spectra for p-MWNTs (**a**), MWNTs-MeOH (**b**), MWNTs-AA (**c**), and MWNTs-PAA (**d**)

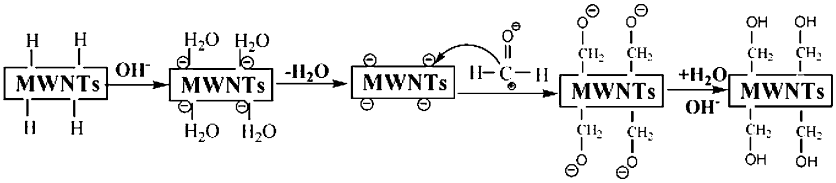
measurements were performed. Figure 3a shows the IR of p-MWNTs. Two peaks in 2,939 and 2,845 cm^{-1} are characteristics of sp^{3}C–H and sp^{2}C–H stretching vibration on the surface of MWNTs, since hydrocarbon is used as the major component in the feedstock for their productions. The configuration such as C–H is very useful because further substitution can be accomplished. On the basis of the principle, we attempt to functionalize the MWNTs with formaldehyde via an electrophilic substitution reaction.

Figure 3b presents the IR of MWNTs-MeOH. Bands at 2,937 and 2,846 cm^{-1} attributing to C–H stretching vibrations, and at 1,435 and 1,363 cm^{-1} corresponding to $–CH_2–$ bending vibrations are obviously observed. Their intensities are greatly enhanced after functionalization compared with Fig. 3a. These confirm that the methylene ($–CH_2–$) groups have been attached onto the surfaces of MWNTs. Moreover, the appearance of the peak at 1,095 cm^{-1} attributing to C–O stretching vibrations on primary alcohol indicates the presence of hydroxyl groups in the MWNTs-MeOH. Combined these analytic results, it is confirmed the methylol groups ($–CH_2OH$) are covalently attached onto the surface of MWNTs after functionalization with formaldehyde. The reaction mechanism is described as shown in Scheme 2. Since hydroxyl groups are hydrophilic, which not only improve the MWNTs-MeOH suspendability in acrylic acid solution but also lead to easier esterification linkage of acrylic acid molecule to the surfaces of the MWNTs-MeOH. We think the functionalization process is vital for livelong grafted polymerization of acrylic acid.

The IR spectra of MWNTs-AA is shown in Fig. 3c, where the characteristic peak of O–H stretching vibrations disappears and a new peak at 1,722 cm^{-1} corresponding to C=O (in ester) stretching vibrations is observed. These confirm the covalent linkage between the –OH on MWNTs-MeOH and the –COOH on acrylic acid by esterification reaction.

The obvious change is observed for MWNTs after graft with PAA (Fig. 3d). Two new peaks at 1,728 and 3,436 cm^{-1} attributing to C=O and O–H stretching vibrations, respectively, are observed, and the intensity of C–H stretching vibrations (at 2,854 and 2,923 cm^{-1}) is enhanced. Combined these conclusions, it is concluded the PAA are covalently grafted onto the surfaces of MWNTs.

Since MWNTs is thermally stable below 600 °C as shown in Fig. 4a, the weight loss before MWNTs decomposition can be used to estimate the quantity of various groups attached to nanotube by TGA [20] Fig. 4 shows TGA curves of p-MWNTs, MWNTs-MeOH, MWNTs-AA, MWNTs-PAA, and pure PAA in air atmosphere at a heating rate of 10 °C/min. Compared with the TGA curve of p-MWNTs, MWNTs-MeOH shows a new weight-loss region from 100 °C to 200 °C, which may be attributed to decomposition of methylene and hydroxyl groups on MWNTs-MeOH. A similar weight-loss region (100–350 °C) is also observed in Fig. 4c, corresponding to decomposition of various groups attached to MWNTs-AA. The TGA curve of MWNTs-PAA (Fig. 4d) presents two weight-loss regions. The first region (150–280 °C) may be corresponded to decomposition of carbonyl groups on the



Scheme 2 The electrophilic substitution reaction mechanism of functionalization of MWNTs with formaldehyde

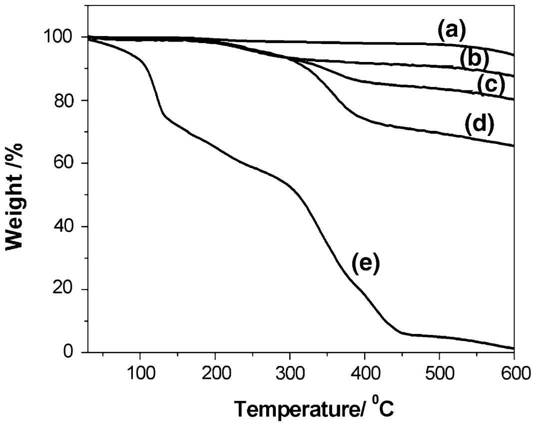


Fig. 4 Thermogravimetric analysis cures for p-MWNTs (**a**), MWNTs-MeOH (**b**), MWNTs-AA (**c**), MWNTs-PAA (**d**), and pure PAA (**e**)

surface of MWNTs-PAA, and the second region (280–400 °C) should be due to decomposition of fundamental chain of PAA. To determine more accurately the amount of grafted PAA in MWCNTs-PAA, the TGA analysis of pure PAA (Fig. 4e) has been performed. The total weight loss of 96.4% is observed within 450 °C for the pure PAA. On the basis of these TGA data, we estimate the amount of PAA attached to the surface of MWNTs-PAA is approximately 30 wt%.

In order to assess the suspendability of MWNTs before and after chemical modification, 5 mg of samples such as p-MWNTs, MWNTs-MeOH, MWNTs-AA and MWNTs-PAA, are ultrasonically dispersed in 50 mL water for 30 min, respectively. Figure 5 shows the optical photos for samples suspendability. Obviously, the p-MWNTs are very difficult to be dispersed in water as indicated in Fig. 5a. This is possibly attributed to little hydrophilic groups on nanotubes and inherent property of MWNTs. The sample of MWNTs-MeOH can form a homogeneous suspension in water within 1 h (Fig. 5b), and then the sedimentation appears after 12 h (Fig. 5c). The improvement of suspendability should be attributed to the hydrophilic groups (–OH) on the MWNTs-MeOH. When the surfaces of the nanotubes are covalently grafted by PAA, no sedimentation is observed (Fig. 5e) even after 7 days. Combining the TEM results, we conclude that the great improvement of solubility is due to covalently coating or wrapping with PAA on the surface of MWNTs resulting in appearance of abundant carboxyl groups (–COOH) on the PAA attached to the MWNTs-PAA.

Conclusion

The purified MWNTs without harsh acid process were functionalized with formaldehyde via an electrophilic substitution reaction and subsequently attached to the methylol groups. The PAA was covalently attached onto the surface of MWNTs by "grafting from" technology and the PAA-wrapped MWNTs were obtained. The PAA wrapped around the MWNTs improves greatly the hydrophilicity of MWNTs, which is significant to explore the potential application of CNTs in biological and medical systems. We believe the novel strategy to modify MWNTs can be extended and employed in other fields for functionalization and application of CNTs.

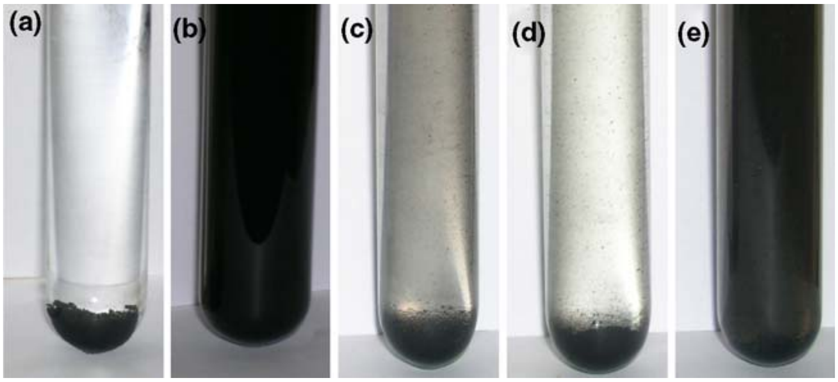


Fig. 5 Dissolution water-solubility of: (**a**) p-MWNTs (t = 1 h), (**b**) MWNTs-MeOH (t = 1 h), (**c**) MWNTs-MeOH (t = 12 h), (**d**) MWNTs-AA (t = 2 h), (**e**) MWNTs-PAA (t = 7 days)

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