Preparation of water-soluble multi-walled carbon nanotubes by Ce(IV)-induced redox radical polymerization

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Abstract

Poly(acrylic acid), poly(*N*-isopropylacrylamide) and polyacrylamide functionalized MWNTs were prepared by Ce(IV)-induced redox radical polymerization. The reaction can be conducted in aqueous media at room temperature, and the polymer graft ratio increased with the increase of monomer feed ratio. MWNTs anchored with PAA on the surface are pH sensitive and exhibit a reversible assembly–deassembly response in aqueous solution, whereas those coated with PNIPAM are thermally sensitive. All the polymer-functionalized MWNTs are highly soluble in water to give robust stable black solutions. Such water-soluble MWNTs are promising for biological and biomedical applications.

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1. Introduction

Carbon nanotubes (CNTs) have raised widespread concerns due to their unique physical and chemical properties [1–4]. CNTs show an even greater importance in nanoscience and nanotechnology, and they are considered ideal materials for several applications, such as ultra-strong fibers [5], sensors [6] and field emission displays [7]. Recently, CNTs have generated great interest in biological and biomedical applications, where suitably modified CNTs can serve as protein transporters or drug carriers [8–11]. For biological and biomedical applications, the poor solubility of CNTs in aqueous media has been a major obstacle. Chemical functionalization is an effective way to solubilize and disperse CNTs in water.

So far, many strategies of chemical functionalization, grafting hydrophilic sections to CNTs through 'graft to' or 'graft from' methods, have been used to prepare water-soluble CNTs [12–15]. Chen et al. [16] have prepared poly(acrylic acid) (PAA)-grafted multi-walled carbon nanotubes (MWNTs) via a two-step irradiation technique. Lin et al. [17,18] have successfully prepared poly(vinyl alcohol) (PVA)-functionalized MWNTs by the esterification reaction of polymer-bound hydroxyl groups with acid oxidative treated MWNTs (MWNT-COOH). Kong et al. [19] have prepared poly(*N*-isopropylacrylamide)-grafted MWNTs by *in situ* atom transfer radical polymerization (ATRP). Using a similar method, PAA-grafted MWNTs have also been prepared [20]. However, most of the methods mentioned above involve multi-step treatments and a high reaction temperature and organic solvents are often required. It is very necessary and yet challenging work to explore a facile platform, which can prepare water-soluble CNTs at a lower temperature and in aqueous media.

In our previous work, we have prepared hydroxyl groups directly modified MWNTs (MWNTols) via an alkaline-mediated hydrothermal treatment [21] on a large

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scale. Herein, we reported that using the hydroxyl groups on the surface of MWNTols, upon reaction with Ce(IV), forms redox centers to initiate polymerization of acrylic acid, N-isopropylacrylamide and acrylamide in aqueous solution. The processes are described in Fig. 1. The main advantage of our protocol is that it can react in aqueous media and at room temperature.

2. Experimental

2.1. Materials

Pristine MWNTs (purity > 95%) were purchased from Shenzhen Nanotech Port Co. Ltd. Sodium hydroxide (purity > 96%), acrylic acid (AA, purity > 98%) and acrylamide (AM, purity > 98%) were purchased from Shanghai Chemical Reagent Corporation. N-Isopropylacrylamide (NIPAM, purity > 97%) and cerium(IV) ammonium nitrate (CAN, purity > 99.99%) were purchased from Sigma–Aldrich. All the reagents were used as received. MWNTols were prepared according to our previous work, and the mole percentage of hydroxyl groups evaluated by X-ray photoelectron spectroscopy (XPS) is 5% [21].

2.2. Preparation of water-soluble polymer-functionalized MWNTs (MWNT-PAA, MWNT-PNIPAM and MWNT-PAM)

In a typical reaction, to a de-ionized aqueous solution (45 mL) of MWNTols (30 mg) in a flask (100 mL) upon sonication for 10 min was added 1.0 g of monomer (AA, NIPAM or AM). After stirring for 15 min, the mixture was purged with nitrogen. A de-ionized aqueous solution (5.0 mL) containing CAN (0.1 g) was injected into the above-mentioned solution and the mixture was stirred at room temperature (25 °C) for 5 h. Then, the mixture was filtered through a 0.45 μm PVDF membrane. The black solid filtered out was dispersed in de-ionized water (50 mL); after sonication for 15 min, the solution was filtered through a 0.45 μm PVDF membrane again. This procedure was repeated five times. At last, the black solid was dried overnight in vacuum at 40 °C.

2.3. Instruments and measurements

FT-IR spectroscopy was carried out on a Nicolet Magna 550 spectrometer using KBr pallets. TGA measurement was carried out on a Perkin-Elmer Pyris-1 series thermal analysis system under nitrogen atmosphere at a scan rate of 20 °C/min. Transmission electron microscopy (TEM) images were obtained on a JEOL-1230 transmission electron microscope. Samples for TEM measurements were prepared by casting a methanol solution of samples on a carbon-coated copper grid.

3. Results and discussion

It is well known that the Ce(IV)-alcohol redox pair is an effective initiator for radical polymerization of a variety of vinyl monomers [22]. The hydroxyl groups on the surface of MWNTols, in conjunction with Ce(IV), can form a redox-active surface for synthesizing polymer-functionalized MWNTs. In fact, we found that such redox pairs can initiate polymerization of water-soluble vinyl monomers such as AA, NIPAM and AM on the exterior surface of MWNTols. A series of MWNT-Polymer were synthesized by Ce(IV)-induced redox radical polymerization, and the data are summarized in Table 1.
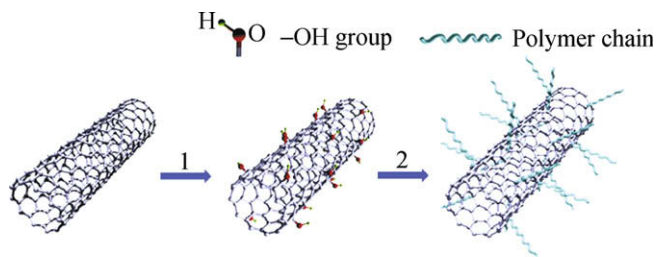
3.1. Preparation and characterization of MWNT-PAA

MWNTols, in the presence of cerium(IV) ammonium nitrate (CAN), are highly active in initiating polymerization of AA in aqueous solution at room temperature (25 °C) to give a homogeneous solution after 5 h. Simple after-treatment upon filtration of the polymerization mixture with a 0.45 μm PVDF membrane followed by washing with water gave a black solid. In comparison with MWNTs and MWNTols, the black solid (MWNT-PAA-2) shows very intense IR peaks (Fig. 2(a)), with C–H vibrational bands at 2930, 2860, and 1366 cm^{-1}, a C=O vibrational band at 1740 cm^{-1}, and an O–H vibrational band at 3440 cm^{-1}, respectively. These results indicate a successful polymerization of AA on the exterior surface of MWNTols. As seen in Fig. 2(b), the TGA curves of

H·O –OH group ∿∿∿ Polymer chain

1: Alkaline-mediated hydrothermal treatment
2: Ce(IV) ions initiate redox polymerization

Fig. 1. Schematic synthetic route of polymer grafting MWNTs.

Table 1
Polymerization of AA, NIPAM, and AM on MWNTols in the presence of Ce(IV) in aqueous solution at room temperature.

Sample code	Monomer weight (g)[a]	Content of polymer attached to MWNTs (wt%)
MWNT-PAA-1	1.0	27.1
MWNT-PAA-2	2.0	68.2
MWNT-PNIPAM-1	1.0	13.1
MWNT-PNIPAM-2	2.0	27.7
MWNT-PNIPAM-3	3.0	46.6
MWNT-PAM	1.0	10.3

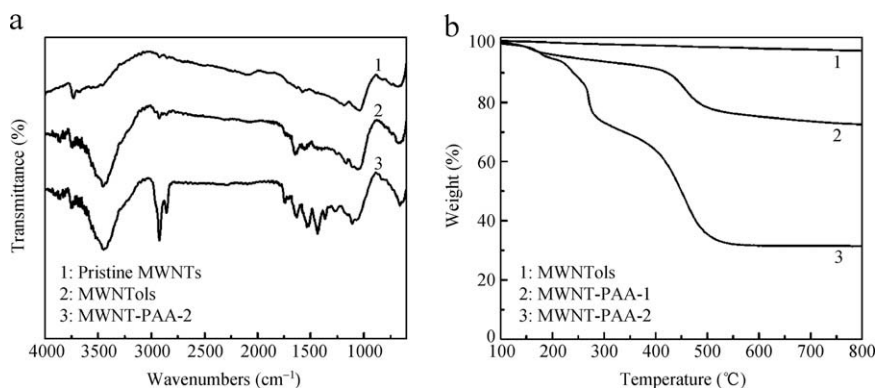[a] Through all the polymerizations, MWNTols/CAN/H_2O is kept at 30 mg/0.1 g/50 g.

Fig. 2. (a) FT-IR spectral profile of pristine MWNTs, MWNTols, and MWNT-PAA-2 and (b) TGA curves of MWNTols, MWNT-PAA-1, and MWNT-PAA-2.

MWNT-PAA-1 and MWNT-PAA-2 show two weight-loss steps at 150–300 °C and 400–500 °C, due to the thermal decomposition of carboxyl groups and polymer main chains, respectively. The content of PAA was estimated to be 27.2 and 68.1 wt% for MWNT-PAA-1 and MWNT-PAA-2, respectively, from their corresponding TGA curves. In comparison with MWNTs and MWNTols, TEM images of MWNT-PAA-2 (Fig. 3(c) and (d)) show that the morphology and length of MWNTs are well retained, indicating that the redox polymerization reaction does not affect the tubular structure of MWNTs. The MWNTs were wrapped by a PAA shell with a thickness of about 8–12 nm.

The MWNT-PAA-2 (5 mg) in aqueous solution (15 mL) gives a homogeneous stable solution upon standing for even months. When an aqueous HCl solution (2 mol L^{-1}) was added to the above solution, the resulting mixture (pH 3) becomes phase separated, which proceeds smoothly and finally leaves a precipitate of MWNT-PAA-2 after several minutes, as shown in Fig. 4. On the other hand, when the pH value increased to 5.0 or higher, upon addition of NaOH or ammonia solution, the black precipitate dissolved to give a homogeneous solution. The high critical soluble pH value for MWNT-PAA-2 was evaluated to be 5.0, upon examination of a series of solutions at different pH values. The pH-driven aggregation and dissolution of
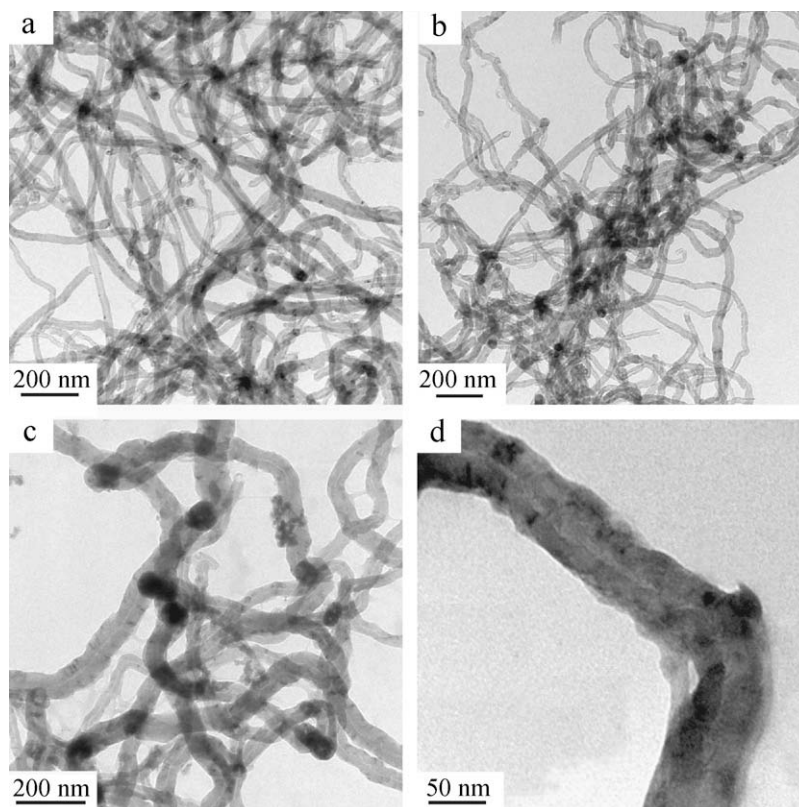

Fig. 3. TEM images of (a) pristine MWNTs; (b) MWNTols; (c) and (d) MWNT-PAA-2 at different magnifications.
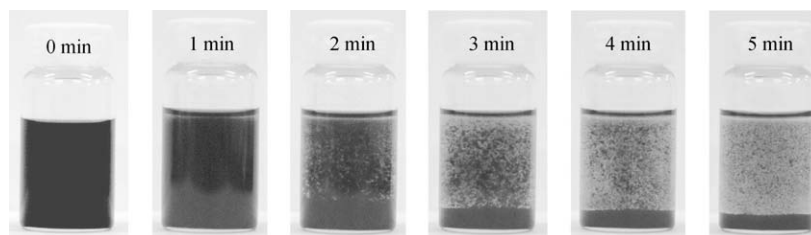
Fig. 4. Photograph of an aqueous solution of MWNT-PAA-2 upon standing for 5 min after addition of HCl (pH of the resulting solution = 3) at 25 °C.

MWNT-PAAs is reversible and can be repeated several times. In sharp contrast, a simple mixture of MWNTols and PAA does not show any clear aggregation–dissolution response, irrespective of the pH values. Therefore, PAA chains capable of a protonation–deprotonation cycle, while anchored on the exterior surface of MWNT-PAAs, make it possible for the carbon nanotubes to respond quickly and reversibly to the change of the pH value.

3.2. Preparation and characterization of MWNT-PNIPAM

Polymerization of NIPAM was carried out under the same condition as that for AA. The FT-IR spectrum of MWNT-PNIPAM-3 (Fig. 5(a)) shows typical PNIPAM peaks with characteristic bands at 2970, 1450, and 1366 cm^{-1} due to the C–H bond, at 1650 cm^{-1} due to the C=O group, and at 3300 and 1550 cm^{-1} due to N–H moiety, respectively. The MWNT-PNIPAMs bearing PNIPAM chains on the exterior surface display obvious weight loss at 300–450 °C in TGA curves (Fig. 5(b)), as a result of thermal decomposition of the PNIPAM segment. The content of PNIPAM in MWNT-PNIPAM-1, MWNT-PNIPAM-2, and MWNT-PNIPAM-3 was thus evaluated to be as high as 13.1, 27.7, and 46.6 wt%, respectively, from their corresponding TGA curves, which is in good agreement with the fact that the amount of NIPAM utilized in the polymerization was increased from 1 to 2 and 3 g.

The TEM images of MWNT-PNIPAM-3 (Fig. 6) reveal that MWNTs are covered by a PNIPAM shell with a thickness of about 5–10 nm. Since PNIPAM is a thermally responsive polymer and exhibits an assembly–deassembly cycle as a result of hydrogen bonding-driven conformational
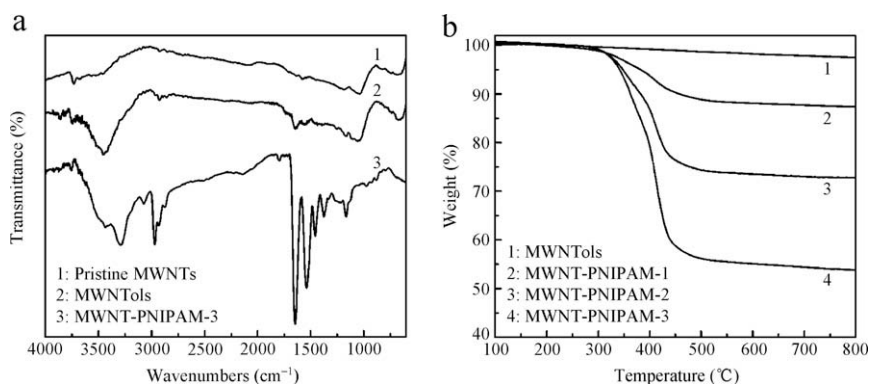

Fig. 5. (a) FT-IR spectral profile of pristine MWNTs, MWNTols, and MWNT-PNIPAM-3; (b) TGA curves of MWNTols, MWNT-PNIPAM-1, MWNT-PNIPAM-2, and MWNT-PNIPAM-3.
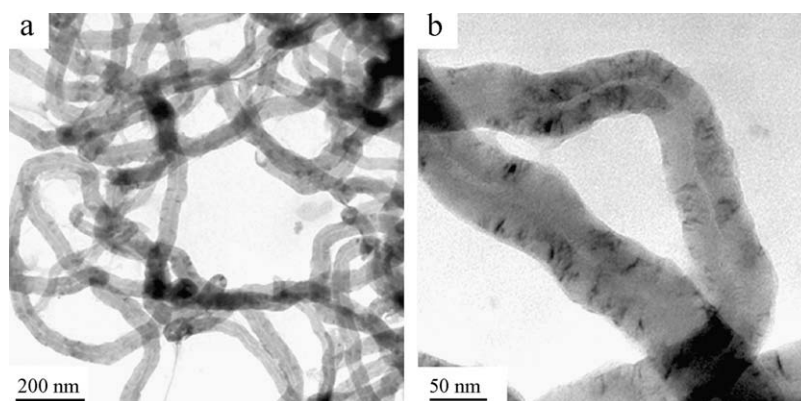

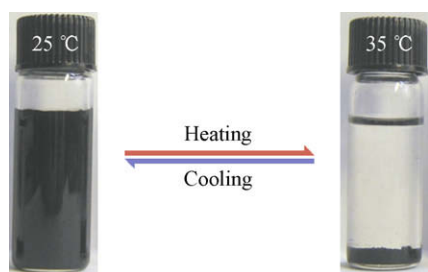Fig. 6. TEM images of MWNT-PNIPAM-3 at different magnifications.

Fig. 7. Photograph of an aqueous solution of MWNT-PNIPAM-3 at 25 and 35 °C.

changes, we investigated the thermal behavior of MWNT-PNIPAM-3 in an aqueous solution. In a typical experiment, 1 mg of MWNT-PNIPAM-3 was added to 5 mL of water at 25 °C, and the resulting solution was heated up to 35 °C and then cooled down to 25 °C. We found that MWNT-PNIPAM-3 at 25 °C forms a stable homogenous black solution. Of interest, when the solution was heated at 35 °C, MWNT-PNIPAM-3 starts to aggregate quickly to afford large black bundles and precipitates completely from the solution in a few minutes. When the mixture was cooled at 25 °C, a homogenous black solution was recovered again, which can be seen from Fig. 7. In sharp

contrast, a simple mixture of MWNTols and PNIPAM does not show any thermally induced precipitation–dissolution responses at all. By virtue of the PNIPAM segments covalently anchored on the shell, the thermal responsibility of MWNT-PNIPAM-3 is totally reversible and can be repeated several times without any deterioration.

3.3. Preparation and characterization of MWNT-PAM

Polymerization of AM was carried out under the same condition as that for AA and NIPAM. The FT-IR spectrum of MWNT-PAM (Fig. 8(a)) shows typical PAM peaks with characteristic bands at 2860 and 2930 cm^{-1} due to C–H stretch vibration, at 1655 cm^{-1} due to the C=O group, and at 3440 and 1560 cm^{-1} due to N–H moiety, respectively, which indicate a successful polymerization of AM on the exterior surface of MWNTols. As seen from the TGA curves in Fig. 8(b), MWNT-PAM shows an obvious weight loss at 300–450 °C, due to the thermal decomposition of grafted PAM. The graft ratio of PAM was 10.3 wt%. The surface of MWNT-PAM was much rougher than MWNTols (Fig. 9) due to the grafted PAM covering. Because the graft ratio is only approximately 10 wt%, it is hard to observe the PAM shell.
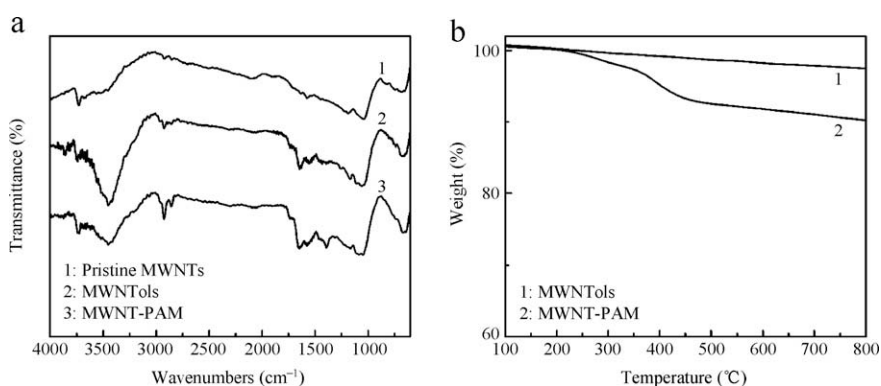

Fig. 8. (a) FT-IR spectral profile of pristine MWNTs, MWNTols, and MWNT-PAM and (b) TGA curves of MWNTols and MWNT-PAM.
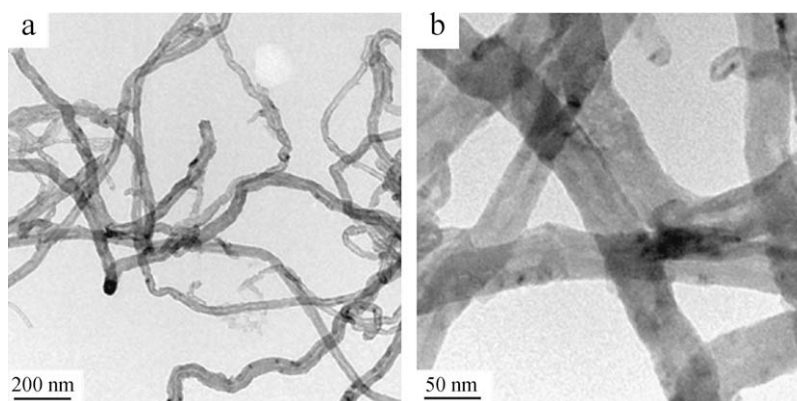

Fig. 9. TEM images of MWNT-PAM at different magnifications.

4. Conclusions

In summary, we reported a facile approach that enables the preparation of water-soluble MWNTs by taking advantage of Ce(IV)-induced redox radical polymerization. The prepared water-soluble MWNTs, such as MWNT-PAAs, MWNT-PNIPAMs and MWNT-PAM, are highly soluble in water. One important characteristic of the present synthetic method is that the reaction can be conducted in aqueous media and at room temperature. By virtue of the stimuli-responsibility of the polymer shell, MWNT-PAAs and MWNT-PNIPAMs exhibit a quick and reversible response to pH and thermal stimulus, respectively. Such water-soluble MWNTs possess great potential in biological and biomedical applications.

Acknowledgements

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