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Tubular composite of doped polyaniline with multi-walled carbon nanotubes

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ABSTRACT We report on the synthesis of tubular composite of doped polyaniline (PANI) with carboxylic groups contained multi-walled carbon nanotube (MWNTs) by in situ polymerization. Based on the interaction between aniline monomers and c-MWNTs, aniline molecules were adsorbed and polymerized on the surface of c-MWNTs. The structural characterization showed that tubular composites are core (c-MWNTs)-shell (doped-PANI) structures with diameters of several tens of nanometers, and lengths of up to several hundreds of nanometers. The conductivities of these tubular composites are several times higher than that of PANI without MWNT, which will offer new application possibilities.

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1 Introduction

Since the first report on the preparation of carbon nanotube/ polymer composite by Ajayan et al. [1], many efforts have been made to design and fabricate nanotube-based composite and thus materials with superior properties, such as high mechanical strength, flexibility, and electric conductivity [2–5]. Among these carbon nanotube-based composites, many reports were focused on the combination of carbon nanotube and conducting polymers including carbon nanotubes composite with poly(p-phenylene vinylene) [6] or poly(3-octylthiophene) [7] for highly efficient photovoltaic cells, conjugated polymer/carbon nanotube composite LEDs with low current densities and good thermal stabilities [8], and aligned carbon nanotube/conducting polymer coaxial nanowires with high surface and interface areas [9]. Polyaniline (PANI), typically electronically conductive polymers (ECPs), is a promising candidate for the synthesis of such nanotube-based composites due to its environmental stability, high degree of processability, and interesting redox properties. Much new progress has been achieved in the designing and fabricating of PANI/nanotube composite. Examples include PANI/MWNT composites showing site-selective interaction between the quinoid ring of the polymer

and MWNT [10], doped PANI composite films fabricated by in situ polymerization [11, 12], and the fabrication of PANI/single-wall carbon nanotube composite [13]. Very recently, PANI nanostructures without protonic acid doping have been obtained by using sulfonated MWNTs as the self-assembled “template” [14].

Design, fabrication, and characterization, while important aspects of nanotube/polymer composites, are still complex and difficult. Previous studies have indicated that incorporation of CNTs into polymer matrices should lead to composites with unique properties [5, 6]. Several efficient methods were developed to prepare the polymer/nanotube composite, including dissolving polymer into the MWNT suspension of organic solvents [15], a melt mixing process [16], in situ polymerization [17], grafting the reaction of macromolecules to the CNT [12], and electrochemical process [18]. Among these methods, in situ polymerization was regarded as the best way to disperse the CNTs into polymer matrices because how to disperse the nanotubes individually and uniformly into the polymer matrices is a key to producing nanotube-based composites. Although the carbon nanotubes and polymer composites have been prepared either by physical mixing or by chemical bonding, it still remains a great challenge for scientists to fabricate CNT/polymer composites in a controlled way.

Herein we report, for the first time, the synthesis of a tubular composite of protonic acid doped polyaniline (PANI) with multi-wall carbon nanotubes (MWNTs). The as-prepared MWNTs were treated with a 4 : 1 mixture of concentrated H_2SO_4 : 30% aqueous H_2O_2 , which produced carboxylic acid groups at the defect sites and thus improved the solubility of the carboxylic groups contained MWNTs (c-MWNTs) in HCl solution. Based on the interaction between aniline monomers and c-MWNTs, tubular composite of doped-PANI with c-MWNTs can be synthesized by in situ chemical oxidation polymerization.

2 Experimental

Aniline monomer was distilled under reduced pressure. Ammonium persulfate (APS, oxidant), hydrochloric acid, and other organic solvents were used as received. The MWNTs used in this work were synthesized by ethylene CVD using Al_2O_3 supported Fe catalysts as described in a pre-

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vious study [19]. The purity of MWNTs was higher than 90% after purification. The as-prepared MWNTs were treated with a 4 : 1 mixture of concentrated H_2SO_4 and 30% aqueous H_2O_2 , which produced carboxylic acid groups at the defect sites and thus improved the solubility of the carboxylic groups contained MWNTs (c-MWNTs) in HCl solution. Figure 1 shows the IR spectrum of the c-MWNTs. The peak around 1570 cm^{-1} corresponds to the IR active phonon mode of MWNTs and the peak around 1720 cm^{-1} apparently corresponds to the stretch mode of carboxylic acid groups [20]. This indicated that carboxylic acid groups had formed at both the ends and sidewalls of the MWNTs. The high-resolution TEM image (inset in Fig. 1) clearly shows the multiple crystalline walls and hollow core of c-MWNT.

Tubular composite of protonic acid doped polyaniline (PANI) with c-MWNT was synthesized by in situ chemical oxidation polymerization. In a typical synthesis experiment, 53.3 mg c-MWNTs were dissolved in 150 ml 1.0 M HCl solutions and sonicated over an hour, then transferred into a 500 ml four-neck flask with an ice-bath. Aniline monomer (0.8 ml) in 100 ml of 1.0 M HCl solution was added to the above c-MWNTs suspension. A 50 ml 1.0 M HCl solution containing 1.96 g APS was slowly added dropwise into the suspension with constant mechanical stirring at a reaction temperature of $0\text{--}5\text{ }^\circ\text{C}$. The reaction mixture was stirred for an additional 8 h at $0\text{--}5\text{ }^\circ\text{C}$, and then the product was filtered and rinsed several times with distilled water and methanol. The black powder obtained was dried under a vacuum at room temperature for 24 h.

The UV-vis spectroscopy, Raman spectroscopy, and X-ray diffraction were used to characterize the composite. UV-vis spectra were performed on a JASCO V550 with scanning speed 200 nm/min and bandwidth 0.1 nm . Raman spectra were recorded under a Renishaw system 1000 using a 50 mW He-Ne laser operating at 632.8 nm with a CCD detector. The final spectrum presented is an average of 15 spectra recorded at different regions over the entire range of the sample. X-ray powder diffraction was carried out on a RINT2000 Wilder-angle goniometer using a $\text{Cu } K_\alpha$ radiating, Rigaku rotating

anode X-ray source. SEM was conducted at 25 kV using an XL30S-FEG field-emission instrument, and TEM was performed on a JEM200CX at 200 kV . High-resolution transmission electron microscope (HRTEM) and selected area electronic diffraction (SAED) images were recorded on a Tecnai F30 at 300 kV . The conductivity at room temperature was measured by a Keithley 196 SYSTEM DM digital multimeter system.

3 Results and discussion

Based on the interaction between aniline monomers and c-MWNTs, aniline molecules were adsorbed on the surface of c-MWNTs. The tubular composite of doped-PANI/c-MWNTs can then be synthesized successfully on a large-scale by in situ chemical oxidation polymerization. Typical SEM and TEM images of the tubular composite are shown in Fig. 2. It can be clearly observed that the dimensions of the tubular composite are highly uniform with a diameter in the range of several tens of nanometers and a length up to several hundreds of nanometers (Fig. 2a). Compared with the original c-MWNTs, the diameter of the tubular composite becomes larger after in situ polymerization. This tendency can be more clearly seen from the histograms of the diameter distribution by measuring hundreds of SEM images at different sample locations. The diameter distribution of the c-MWNTs in Fig. 3a illustrates a peak centered at 16 nm . While after in situ polymerization, a new peak centered at 40 nm emerged in the diameter distribution plot of the tubular composite (Fig. 3b). Closer inspection of higher magnification SEM and TEM images (Fig. 2b,c) revealed that the surface of the tubular composite is smooth. From Fig. 3a and b, we can determine the average thickness of the PANI layer to be about 12 nm . The SAED image indicates that this tubular composite has a polycrystal structure (Fig. 2d). HRTEM images clearly shows us that the hollow structure between the two sides of the multiple crystalline walls, and the polyaniline macromolecules encapsulated at the surface of the c-MWNT (Fig. 2e). This tubular composite is the typical core-shell structure, MWNT serves as the core and is dispersed individually into the PANI matrices. The aniline monomer is uniformly polymerized on the surface of the MWNT and forms a shell of tubular composite. In addition, we can see in Fig. 2e that there is an amorphous layer in the interface between the PANI polycrystal layer and c-MWNT, which demonstrates that the aniline monomers were firstly adsorbed and polymerized to form the amorphous layer on the surface of the c-MWNT at random. They tend to form a regular structure on the surface of the amorphous layer. The formation of the amorphous layer can probably be attributed to the irregular distribution of COOH groups at the surface of MWNTs and to the interaction between the quinoid ring of the polymer and c-MWNT discussed in the following section.

To further confirm the structure of this tubular composite, X-ray power diffraction of c-MWNT, PANI, and MWNT@PANI were investigated and the spectra are shown in Fig. 4. For c-MWNTs, the peaks at $2\theta = 25.9^\circ$ and 43° were observed in the spectrum, corresponding to graphite like diffraction and small amounts of catalytic particles encapsulated inside the walls of carbon nanotubes, respectively [21].

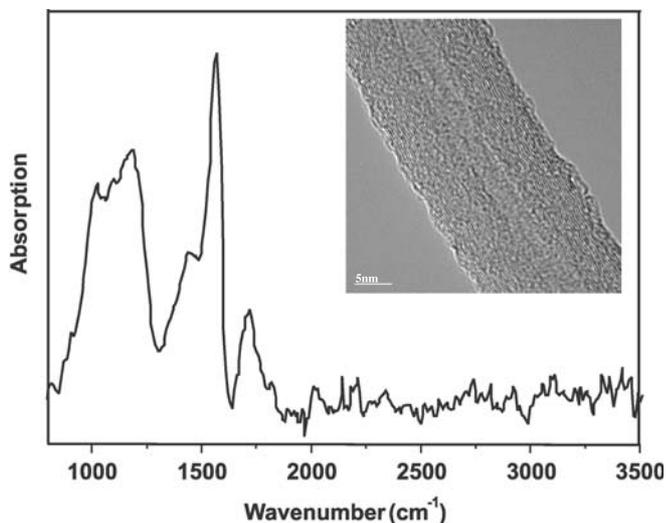


FIGURE 1 Infrared spectrum of c-MWNT (Inset: HRTEM image of c-MWNT)

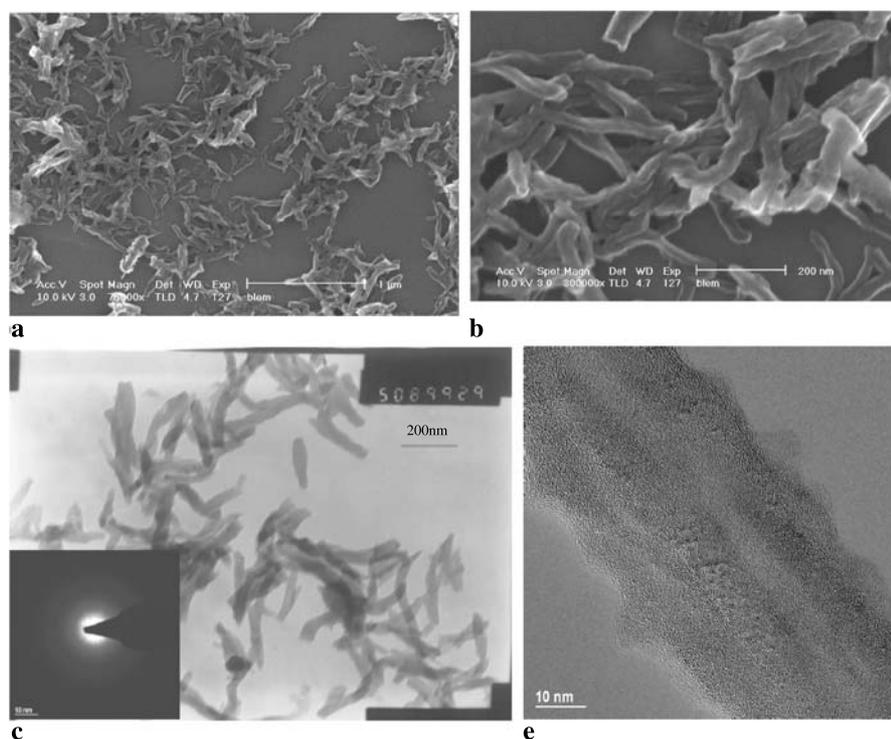


FIGURE 2 SEM and TEM images of tubular composite of MWNT@PANI: **a** SEM image with large scale; **b** SEM image with small scale; **c** TEM image; **d** SEAD image and **e** HRTEM image

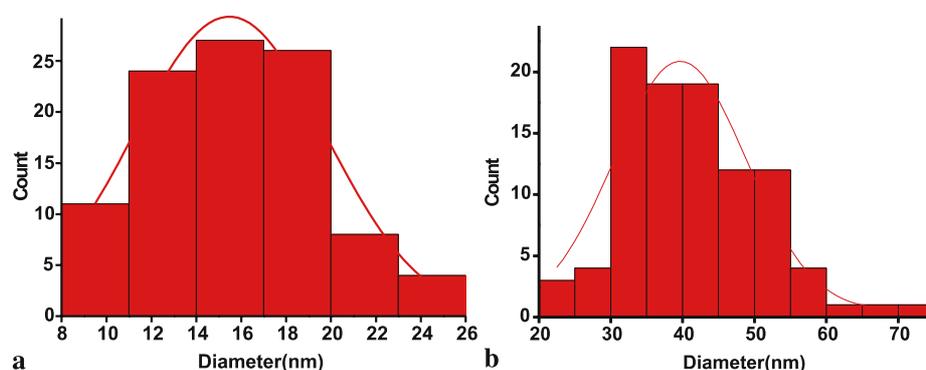


FIGURE 3 Diameter and its distribution for **a** c-MWNT and **b** tubular composite of MWNT@PANI

While in the case of PANI samples, crystalline peaks appeared around $2\theta = 15^\circ$ and 25.2° , and an amorphous peak appeared at about $2\theta = 20^\circ$ [22]. The crystalline peak is more prominent than the amorphous peak indicating that protonic acid doped PANI is not fully amorphous. When the tubular composite was formed, the peaks at $2\theta = 15^\circ$, 20° and 25.2° were also observed which clearly showed us that from a structural point of view, no additional order has been introduced. In addition, the intensity ratio of the crystalline peaks at 15° and 25.2° to the amorphous peaks at 20° is higher than that for PANI. Due to the small mass fraction, the graphite like diffraction peaks of c-MWNT for tubular composite can hardly be detected. So the relative increase of the intensity of crystalline peaks comes from the occurrence of c-MWNT in the tubular composite. In other words, although there is a very thin amorphous layer on the surface of the c-MWNT, the c-MWNT easily orders the PANI macromolecule along the axis of the c-MWNT, and thus the percentage crystallinity of the outer layer of the tubular composite increases.

In order to characterize the molecular structures of the tubular composite, Raman spectroscopy was used. Figure 5 shows

Raman spectra of c-MWNT, PANI, and MWNT@PANI. For c-MWNT, two strong peaks at 1580 cm^{-1} and 1326 cm^{-1} were observed in the spectrum, attributable to stretching of the *D* mode and *G* mode [3]. While in the case of PANI and MWNT@PANI, C–H bending of the quinoid/benzene ring at 1161 cm^{-1} , C–C in-plane deformation of the quinoid ring at 1486 cm^{-1} , and C–C stretching of the benzene ring at 1586 cm^{-1} were observed, indicating the presence of the doped PANI structures [4]. Clearly, there are almost no differences in Raman spectra of PANI and MWNT@PANI, demonstrating again that MWNT serves as the core of the tubular composite.

UV-vis spectroscopy was used to characterize the interfacial interaction between polymer and c-MWNT. As shown in Fig. 6, no absorption peak is observed for the c-MWNT sample over 300–850 nm, as for the sample of protonic acid doped PANI in *N,N*-dimethyl formamide, two peaks at 323 and 628 nm are observed, and are assigned to the excitation of the benzenoid and quinoid segments on the polyemeraldine chain, respectively. It indicates that PANI has not been fully doped [5]. When the tubular composite of

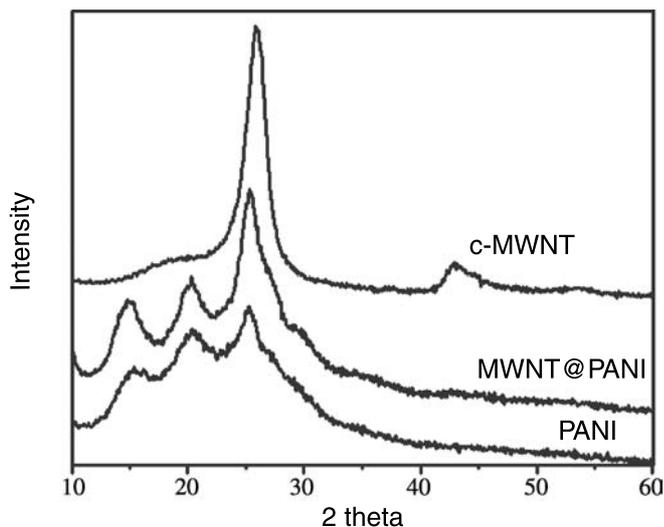


FIGURE 4 XRD spectra for c-MWNT, PANI, and tubular composite of MWNT@PANI

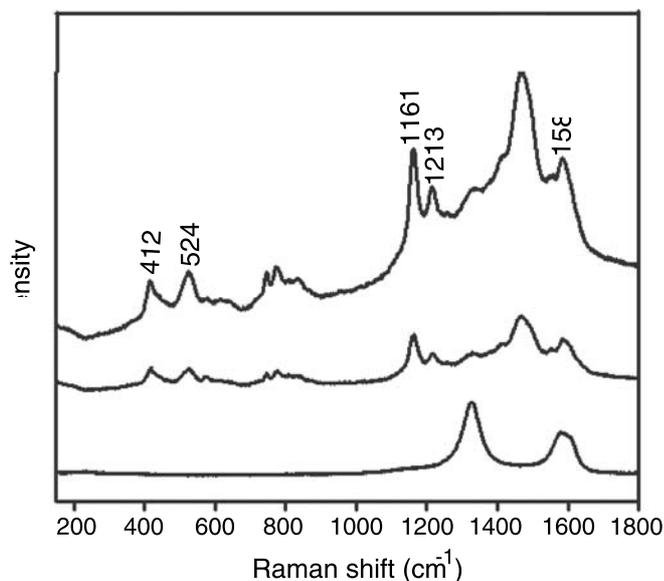


FIGURE 5 Raman spectra for c-MWNT, PANI, and tubular composite of MWNT@PANI

c-MWNT@PANI was formed, two peaks assigned to the excitation of the benzenoid and quinoid segments were shifted to 322.5 and 624.5 nm, respectively, revealing the interaction between PANI and c-MWNT, and especially, the site-selective interaction between the quinoid ring of the polymer and c-MWNT [10].

The formation mechanism of tubular composite is believed to arise from the strong interaction between aniline monomer and MWNT. The interaction possibly comes from two parts: one is the π - π electron interaction between MWNT and the aniline monomer [26]; another is the hydrogen bond interaction between the carboxyl groups of c-MWNT and amino (or imino) groups of aniline monomers (or oligomers). Such strong interaction ensures aniline monomer adsorbed on the surface of MWNT during the formation of tubular composite. MWNTs therefore serves as the template and the core during the formation of the tubular composites. Although there are carboxylic groups on the defect sites of MWNTs to in-

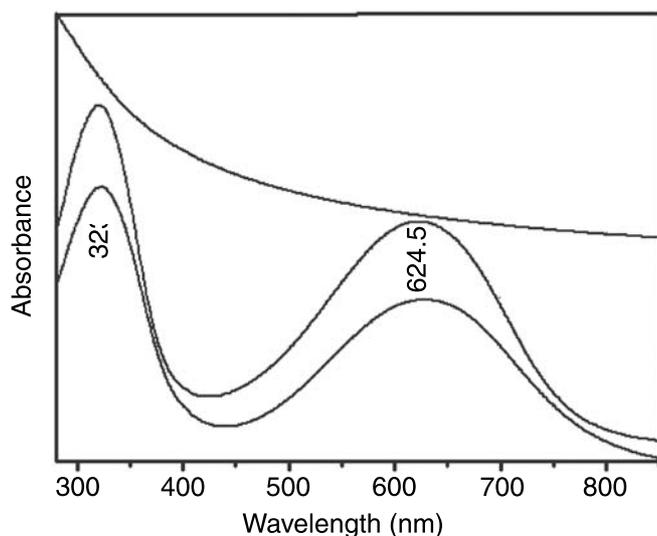


FIGURE 6 UV-vis spectra for c-MWNT, PANI, and tubular composite of MWNT@PANI

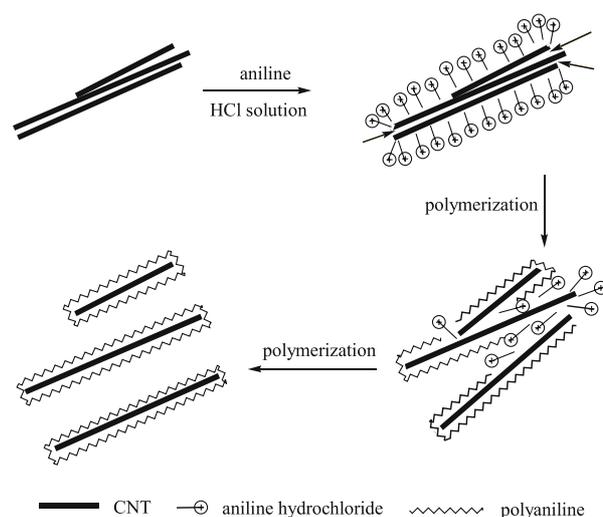


FIGURE 7 Schematic diagram of the formation mechanism for tubular composites of MWNT@PANI

crease the solubility of MWNTs in HCl solution, c-MWNT bundles are still in existence. Due to the random formation of MWNT bundles, there are some “special gaps” (Fig. 7) between individual c-MWNTs. Aniline molecules were wedged into such “special gaps” because of the strong interaction between c-MWNTs and aniline monomers, and then in situ polymerized. As polymerization proceeds, the growing PANI macromolecules would break down the CNT bundles into individuals, and thus c-MWNTs can be dispersed into PANI matrices uniformly and individually. Owing to the site-selective interaction between the quinoid ring of the polymer and c-MWNT [10], PANI macromolecules were also adsorbed at the surface of the c-MWNT and formed the shell of tubular composites.

Accordingly, the standard Van Der Pauwe dc four-probe method [27] was used to measure the conductivities of PANI and the tubular composite of MWNT@PANI. The room-temperature conductivities for protonic acid doped PANI

and its tubular composite were 0.17 and 0.63 S/cm, respectively. While that for dedoped tubular composite was 1.9×10^{-5} S/cm. However, for dedoped PANI it was too small to be detected. The low room temperature conductivity of PANI was ascribed to its low protonic acid doping degree, which was confirmed by UV-vis spectra in the previous section. The reason for the relative low doping degree probably comes from the relative dilute aniline concentration in our synthesis than that in the conventional process. Compared to PANI without MWNT, the room-temperature conductivities for PANI with c-MWNT (namely tubular composite MWNT@PANI) are several times higher in the doped state and at least an order of magnitude higher in the dedoped state, respectively. This shows that MWNT can enhance the conductivities of PANI several times and such tubular composites possess synergistic effects, which will offer new possibilities for its application, such as rechargeable batteries, chemical sensors, ion-selecting electrodes, electronic circuits, etc.

4 Conclusions

Carboxylic acid groups contained MWNTs were used as a "template" for the formation of a tubular composite of doped PANI with MWNT. Based on the interaction between aniline monomers and c-MWNTs, aniline molecules were adsorbed and then polymerized on surfaces of c-MWNTs. Employing this strategy, tubular composites of c-MWNTs (core) and doped-PANI (shell) structures with a diameter of several tens of nanometers, and a length up to several hundreds of nanometers, were successfully obtained. Property tests show that the conductivities for this tubular composite are several times higher than that for PANI without c-MWNT at the same doping conditions indicating that a good synergistic effect occurs between PANI and c-MWNT, which will offer new potential applications.

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