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Easy synthesis of carbon nanotubes with polypyrrole nanotubes as the carbon precursor

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ABSTRACT

An easy synthesis route for carbon nanotubes with polypyrrole nanotubes as a carbon precursor has been developed. Polypyrrole nanotubes were fabricated via a reactive self-degraded template method. Carbon nanotubes were further obtained by pyrolysis of the polypyrrole nanotube at 900 °C under a nitrogen atmosphere. The resultant carbon nanotube structure was found to be amorphous carbon on the basis of XRD, Raman spectra and high-resolution transmission electron microscopy (HRTEM) studies.

1. Introduction

Since the discovery of fullerenes and carbon nanotubes [1], synthesis of carbon nanostructures has attracted a great deal of attentions both for basic scientific research and for industrial applications. Although a rapid development has been made in carbon nanotube science, the diversification of fabrication methods of carbon nanotubes is still of great interest. The synthesis of well-defined carbon nanotubes with 50–100 nm diameters has been a long-standing goal of materials chemistry [2].

The preparation of carbon materials commonly involves pyrolysis of the carbon precursor (such as sucrose, furfuryl alcohol, acetylene, acenaphthene, or phenol resin). Aromatic polyimide film has aroused a great deal of interest as it is one of the attractive precursors for producing carbon and graphite films in recent years. Poly (acrylonitrile) (PAN) is another commonly used precursors [3,4]. Xia et al. reported a method of fabrication of carbon nanotubes by combining polyelectrolyte electrospinning with vapor deposition polymerization. The process is high-temperature carbonization of poly (acrylonitrile) nanotubes with poly (styrene sulfonate) sodium nanofibers as cores at 900 °C under a nitrogen flow [5]. Wu et al. prepared carbon nanospheres by the pyrolysis of nanospherical polyacrylonitrile (PAN) [6].

Polypyrrole (PPy) is a conducting polymer, which has been shown to be another good precursor to prepare graphitic carbon nanostructures [7]. Schuth et al. reported a route for template synthesis of ordered mesoporous carbons using PPy as a carbon precursor and ferric chloride ($FeCl_3$) as the oxidant [8]. Jang et al. reported on the facile synthesis of PPy nanotubes applying a template-mediated VDP and the conversion into carbon nanotubes through the carbonization process. They also produced the monodisperse PPy nanoparticles and fabricate the magnetic carbon nanoparticles with uniform size using PPy nanoparticles as a carbon precursor with the same method [9–13]. The doped transition metal was considered to promote the graphitization. Recently, they fabricated impregnated magnetic γ-Fe_2O_3–CNTs using PPy nanotubes as the carbon precursor [13]. Jones et al. produced carbon tubes by high-temperature (1000 °C) treatment under inert atmosphere PPy/PMMA coaxial fibers [14]. Therefore, it can be concluded that PPy is a new and effective carbon precursor to produce carbon materials.

In our previous study, we reported a new chemical approach, in which a fibrillar complex of the anionic azo dye MO (methyl orange), sodium 4-[4-(dimethyl-amino)-phenyldiazo] phenylsulfonate ($(CH_3)_2NC_6H_4N = NC_6H_4SO_3Na$) and the oxidant $FeCl_3$ was used as a reactive self-degradable seed template directing the growth of PPy on its surface and promoting the assembly into hollow nanotubular structures [15]. We have further developed the direct electrochemical synthesis of PPy nanotubes on a variety of electrodes in the presence of MO via a self-assembly process [16].

In this paper, we synthesize the carbon nanotubes successfully via the pyrolysis of the PPy nanotubes at 900 °C in nitrogen atmosphere. This synthesis method of the as-prepared carbon

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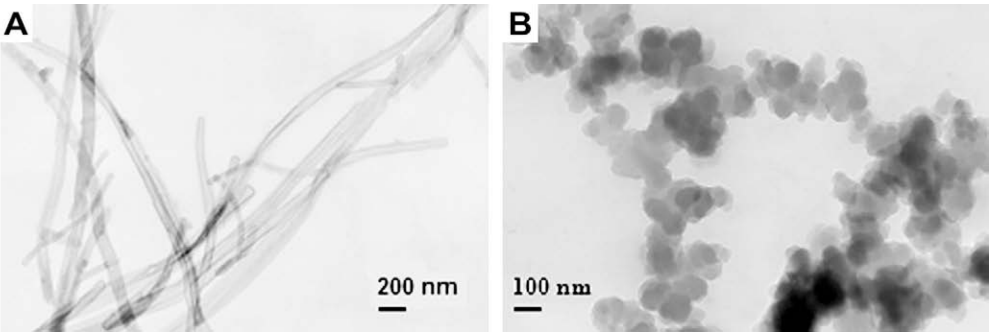

Fig. 1. The TEM images of the PPy nanotubes (A) and the PPy granules (B).

nanotubes is simple and would be an easy way to produce more nanotubes on a large scale.

The structure of the as-prepared carbon nanotubes was investigated by transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy and X-ray diffraction (XRD). Regarding the morphology of the nanotube, these as-prepared carbon nanotubes were found to be mostly amorphous in structure. It has been previously reported that, after thermal treatment at higher temperature (2200 °C), the amorphous carbons resulting from the carbonization (at 900 °C) could be transformed to highly ordered graphitic carbons [17].

2. Experimental section

2.1. Synthesis

0.243 g (1.5 mmol) of $FeCl_3$ was dissolved in the 30 mL of 5 mmol/l methyl orange deionized water solution (0.15 mmol). Then 105 μl (1.5 mmol) of pyrrole monomer (Aldrich) was added into the solution and the mixture was stirred at room temperature for 24 h. The formed PPy precipitate was washed with deionized water/ethanol several times until its filtrate was colorless and neutral, and finally dried under a vacuum atmosphere at 60 °C for 24 h. A kind of dry black powder is obtained which are the PPy nanotubes fabricated.

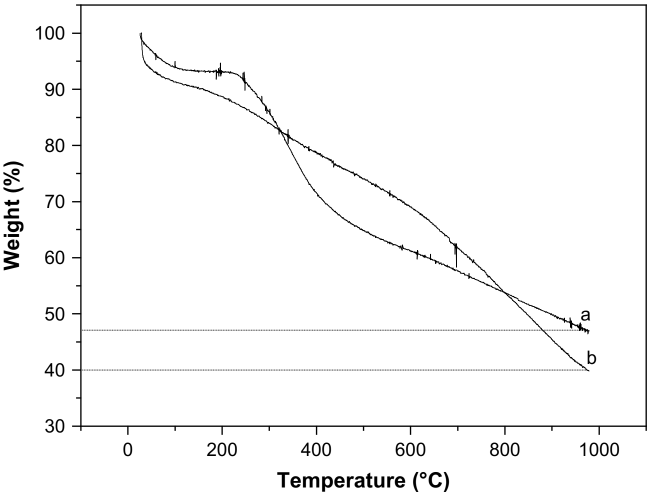

Fig. 2. The TGA curves of a: PPy nanotubes; b: PPy granules (under nitrogen atmosphere).

As a comparison, the PPy granules were fabricated by similar procedures of producing the PPy nanotube except methyl orange was not added.

The obtained PPy nanotubes were further carried out to carbonize to fabricate carbon nanotubes in a quartz tubular furnace under nitrogen atmosphere. The sample was gradually heated up to 900 °C at a heating rate of 3 °C min^{-1}, held 900 °C for 5 h and then cooled to room temperature. The carbon nanotubes were then successfully fabricated.

2.2. Characterization

A SDT 2960 thermogravimetric analyzer was used to investigate the thermal stability of the PPy nanotube with nitrogen as pure gas at a flow rate of 20 ml min^{-1}. The heating rate was 3 °C min^{-1}.

Table 1
The compositions of the PPy nanotubes and the carbon nanotubes.

Element	C (%)	N (%)	O (%)	S (%)	Cl (%)	Fe (%)
PPy nanotubes	77.00	11.76	5.48	3.86	1.80	0.10
Carbon nanotubes	88.77	4.59	4.38	1.74	0	0.52

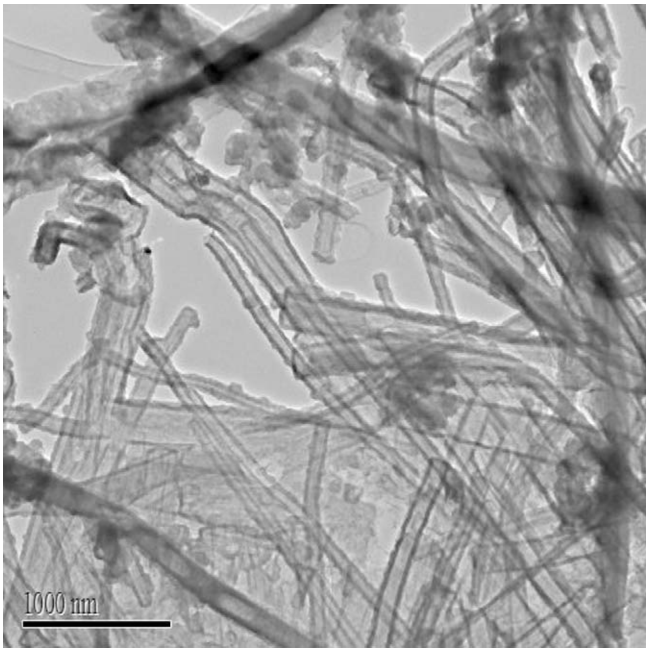

Fig. 3. The TEM images of the carbon nanotubes.

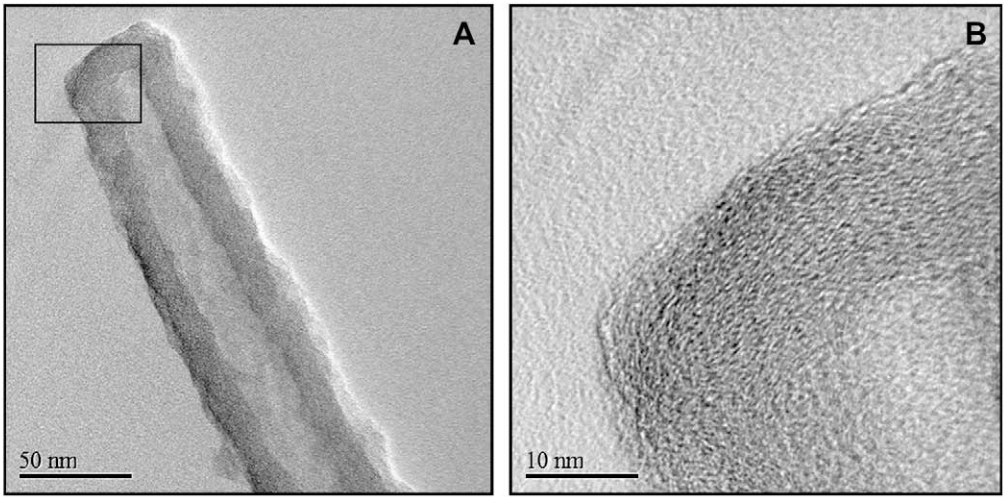

Fig. 4. (A) The TEM image of one carbon nanotube; (B) the HRTEM image of circled part of (A).

The morphologies of the samples were examined by TEM (JEM-2000CX) and HRTEM (JEOL-2010) operated at accelerating voltage of 100 and 200 kV, respectively. A few drops of the solvent extracts were placed onto the copper mesh covered with a per-coated carbon film and allowed to evaporate.

XRD patterns were obtained on PHILIPS PW 3710 diffractometer in the reflection mode using Cu Kα radiation at room temperature.

Raman spectra was recorded in the range of 0–3500 cm^{-1} at ambient temperature with a labRAM HR 800 (France, Jobin Yvon) using 532 nm laser as the excitation source.

3. Results and discussions

The TEM images of the PPy nanotubes (A) and the PPy granules (B) are observed and showed in Fig. 1.

The Fig. 1(A) shows that the PPy nanotubes are hollow, and that their outer and inner diameters are determined as about 70 and 50 nm respectively. Therefore, their wall thicknesses are about 20 nm [15].

The thermogravimetric (TGA) curves in Fig. 2 show the weight losses of the PPy nanotubes (a) and the PPy granules (b). Both the TGA curves of the PPy nanotubes and the PPy granules show a two-step weight loss during the heating processes. The weight loss (about 5%) that occurred in the first step below 100 °C could be attributed to the loss of residual moisture. In the second step starting around 260 °C, the weight loss could correspond to the degradation of PPy and decomposition of dopants. The weight loss of the PPy nanotubes appeared smaller than that of the PPy granules. About 47% of the original weight was left for PPy nanotubes while only 40% for the PPy granules.

The PPy nanotubes were then carbonized at 900 °C in a quartz tubular furnace under a nitrogen atmosphere for 5 h. The carbon nanotubes were successfully fabricated since they are stable even under the extremely high temperature. The chemical compositions of the as-prepared carbon nanotubes and the PPy nanotubes were evaluated by EDS (Energy Dispersive Spectrometer) analysis. The data were summarized in Table 1.

It was evident that the content of carbon was increased after calcinations. During the carbonization process for PPy nanotubes,

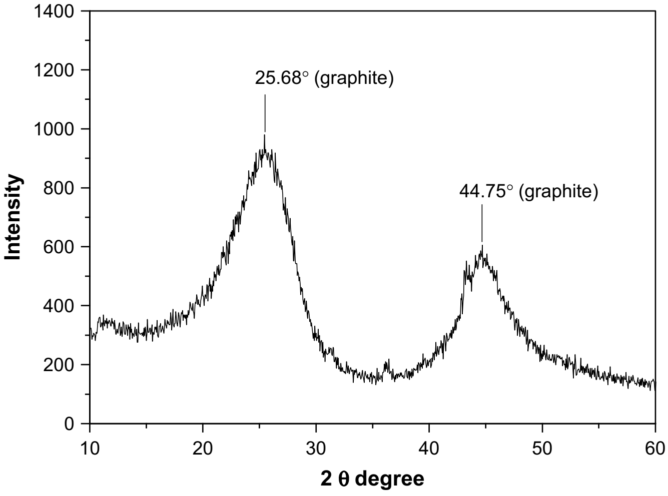

Fig. 5. XRD pattern of carbon nanotubes.

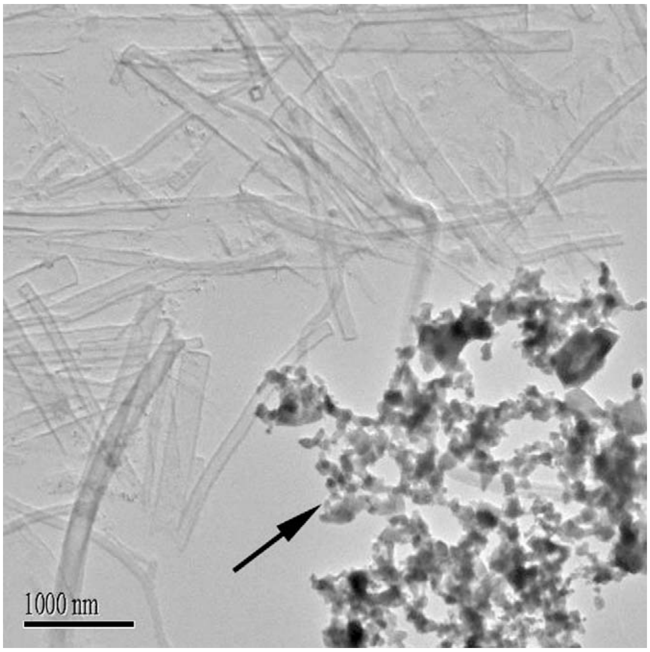

Fig. 6. The TEM images of the carbon nanotubes and iron.

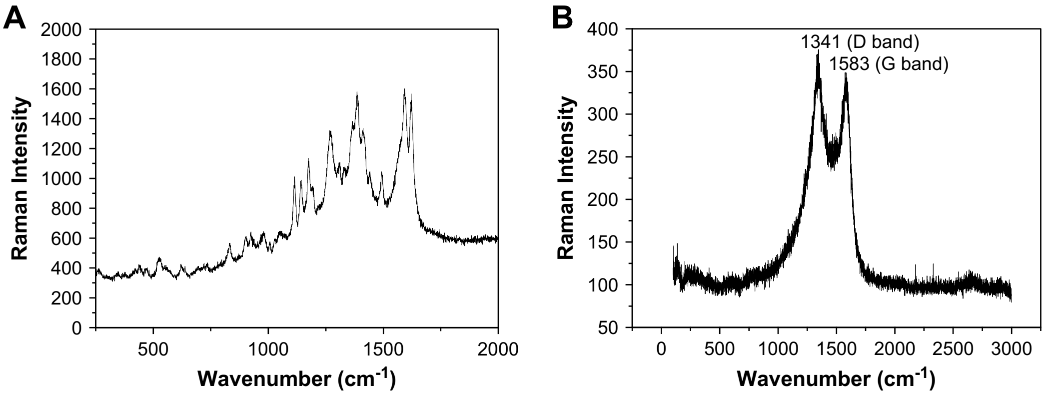

Fig. 7. The Raman spectrums of (A) the PPy nanotubes and (B) carbon nanotubes.

carbonization reactions such as dehydrogenation and denitrogenation occur and produce more compact polycondensed graphitic species [18,19].

In order to investigate the structure of the as-prepared carbon nanotubes, their TEM image is shown in Fig. 3.

From Fig. 3, it was evident that the tubular structures were obtained after pyrolysis at 900 °C. The wall thickness of the carbon nanotube is about 15 nm, which is thinner than that of the original PPy nanotubes (20 nm). The size reduction originates from the weight loss and the formation of more compact structure in the carbonization process.

The HRTEM image (Fig. 4(B)) of the as-prepared carbon nanotubes shows some ordered graphitic layers on the wall of the carbon nanotube. Regarding the morphology of the nanotube, these carbon nanotubes were found to be mostly amorphous in structure. The main activity that occurred at this temperature (900 °C) can be best described as carbonization but not graphitization. Graphitization may occur at higher temperature such as 2200 °C [17].

The XRD pattern of the as-prepared carbon nanotubes is shown in Fig. 5. The wide-angle XRD of the carbonized PPy-nanotubes contain two broad signals at 25.68°and 44.75°, corresponding to (002) and a superposition of the (101) reflections of the graphite structure. The XRD peak with a maximum at $2\theta = 25.68°$, which is equivalent to the d spacing of about 3.432 Å. In addition to the strong (002) peak, the same XRD pattern also showed peaks at 44.75°, which may be ascribed to the diffraction peak of (101) plane of graphite. This confirmed that the structure of as-prepared carbon nanotubes is between the disordered amorphous carbon phase and highly ordered graphitic phase [20].

After the formation of PPy nanotubes, some residual iron salts ($FeCl_2$) were left inside the PPy nanotubes because the redox polymerization of pyrrole was conducted by using $FeCl_3$ as an oxidizing agent. In addition, the chemical oxidation polymerization led to the incorporation of iron-based species like $FeCl_4^-$ anions, which can be coordinated to the polymer backbone [21]. The iron complexes break away from the PPy nanotubes and form iron when they expose to 900 °C under nitrogen [22]. The darker part of Fig. 6 is the cluster of iron that breaks away from the PPy nanotubes (arrow in Fig. 6).

The structure of the as-prepared carbon nanotubes can also be observed by the Raman spectra as displayed in Fig. 7, which were very similar to those reported in the literature for carbon fibers [23], with a characteristic strong, relatively narrow band around 1583 cm^{-1}, corresponding to a graphitic species (G-band) and a band at 1341 cm^{-1}, corresponding to an sp^3 carbon species (D-band) [24]. The bands at 1583 cm^{-1} and 1341 cm^{-1} may be ascribed to the graphite-like and disordered structure of carbons, respectively [25]. The D-band showed increased intensity relative to that of the G-band. The results also indicated that the as-prepared carbon nanotubes were the disordered amorphous carbon phase.

4. Conclusions

Carbon nanotubes were successfully fabricated by carbonization of the PPy nanotubes as its carbon precursor at mild carbonization temperature, i.e. at 900 °C. The results of this research indicate that this synthesis method is simple, feasible and practical, which would become an easy way to produce carbon nanotubes on a large scale.

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