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Synthesis and characterization of carbon nanotubes on carbon microfibers by floating catalyst method

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Abstract

In this paper, carbon nanotubes were synthesized on carbon microfibers by floating catalyst method with the pretreatment of carbon microfibers at the temperature of 1023 K, using C_2H_2 as carbon source and N_2 as carrier gas. The morphology and microstructure of carbon nanotubes were characterized by field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). The composition of carbon nanotubes was determined by energy dispersive X-ray spectroscopy (EDX). The results showed that the surface of treated carbon microfibers was thickly covered by carbon nanotubes with diameters of about 50 nm. EDX image indicated that the composition of carbon nanotubes was carbon. In comparison with the sample grown on untreated carbon microfibers surface, it was found that after carbon microfibers were boiled in the solution of sulfur acid and nitric acid ($V_{H_2SO_4}$:V_{HNO_3} = 1:3) and immersed in the solution of iron nitrate and xylene, carbon nanotubes with uniform density can be grown on carbon microfibers surface. Based on the results, we concluded that the pretreatment of carbon microfibers had great effect on the growth of carbon nanotubes by floating catalyst method.

Keywords: Carbon nanotubes; Carbon microfibers; Floating catalyst

1. Introduction

Since their discovery in 1991 [1], carbon nanotubes (CNTs) have attracted considerable attention and interest owing to unique physical and chemical properties [2–4], and CNTs also have been synthesized on different substrates [5–9]. However, some problems were present about the growth of CNTs on carbon microfibers (CMFs) substrate: catalyst was easily diffused into CMFs substrate and other carbonaceous byproducts were also easily brought [10,11]. The two factors limited the synthesis of CNTs on CMFs substrate. Therefore, by far, only few studies were reported about the synthesis of CNTs on CMFs substrate [12–17]. CNTs and CMFs are both carbon-based materials with the structure of graphite, and both of them have superior properties. Moreover, synthesizing CNTs on conductive and chemical stable CMFs substrate will further improve the properties and applications of CNTs/CMFs composite materials. For example, CNTs/CMFs composite materials may be good candidates for capacitor, battery, field emission electron source materials, electrode materials, absorption-wave materials and so on. Therefore, it is very important of searching a simple and effective method for the synthesis of CNTs on CMFs substrate.

In our study, CNTs with uniform distribution were synthesized on CMFs by floating catalyst method with the pretreatment of CMFs before the experiment, which is different from others [12–17]. Then the morphology and microstructure of CNTs were respectively characterized by FESEM, TEM and HRTEM, and the composition of CNTs was determined by EDX. Finally, the effect of the pretreatment of CMFs on the growth of CNTs was also discussed.

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2. Experiment

2.1. Pretreatment of carbon microfibers

The treating approach of carbon microfibers was as follows:

(1) CMFs were ultrasonically cleaned in acetone and ethanol respectively for 10 min, then were dried at room temperature.
(2) CMFs obtained from (1) were boiled in the solution of sulfur acid and nitric acid ($V_{H_2SO_4}$:V_{HNO_3} = 1:3) for 30 min to activate the surface of CMFs, then were rinsed with deionised water for three times and dried at room temperature.
(3) Preparation of the solution of iron nitrate and xylene. 0.1 g $Fe(NO_3)_3$ was dissolved in 100 ml xylene. The solution was magnetically stirred for 30 min to dissolve adequately. Then the CMFs obtained from (2) were immersed into the solution. After about 12 h, the CMFs were taken out and dried at room temperature.

2.2. Synthesis of carbon nanotubes

The growth of CNTs was carried out in a tubular furnace with a horizontal quartz tube at atmospheric pressure by floating catalyst method. First CMFs setted in a quartz boat were pushed into the center of the quartz tube. Then the quartz tube was heated in N_2 ambient with a flow rate of 50 sccm to ensure no oxygen in it, when the temperature was increased to 1023 K, C_2H_2/ferrocene mixtures were introduced, the flow rate of C_2H_2 was 30 sccm and simultaneously the flow rate of N_2 was 150 sccm, after about 30 min, C_2H_2 gas and power supply were shut. Finally, the quartz tube was cooled down to room temperature in N_2 ambient with a flow rate of 50 sccm. The purities of C_2H_2 and N_2 employed in the experiment are both higher than 99.5%.

2.3. Characterization

The morphology and microstructure of CNTs were characterized by Hitachi S-4800 SEM (with EDX accessory), Tecnai F30 TEM and HRTEM, respectively. The composition of CNTs was determined by EDX. The fabrication method of TEM and HRTEM sample was that a few CNTs were scratched from CMFs surface. The CNTs were dispersed in the ethanol by ultrasound to form a suspension. After about 20 min, one or two droplets were dropped onto a carbon-coated copper grids.

3. Results and discussion

Fig. 1 shows SEM images of CNTs grown on untreated and treated CMFs substrates. In Fig. 1(a), we can see that hardly any CNT is grown on untreated CMFs surface other than some carbon particles. In contrast, on treated CMFs surface, many CNTs thickly cover the surface of CMFs. Moreover, the density of CNTs on CMFs surface is comparatively well-proportioned, as shown in Fig. 1(b) and (c). The length of CNTs is below 5 μm, and many CNTs are interlaced one another. The small length and uniform distribution of CNTs on CMFs surface are advantageous for the application of CNTs in field emission. In order to obtain well field emission result, the density of emitters must be appropriate and uniform. The density distribution of CNTs in our sample can ensure the emission density of emitters, and simultaneously can avoid the electric field

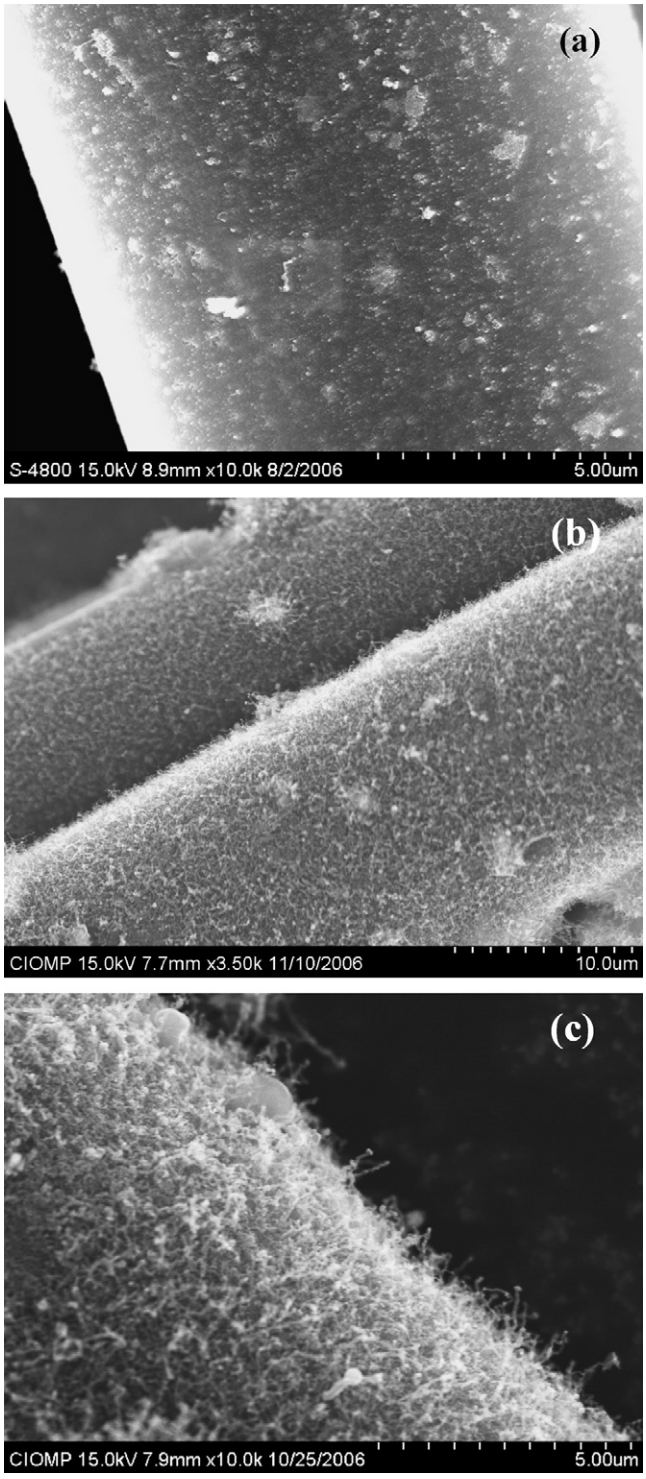

Fig. 1. FESEM images of CNTs on CMFs [(a) on untreated CMFs; (b) and (c) on treated CMFs].