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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

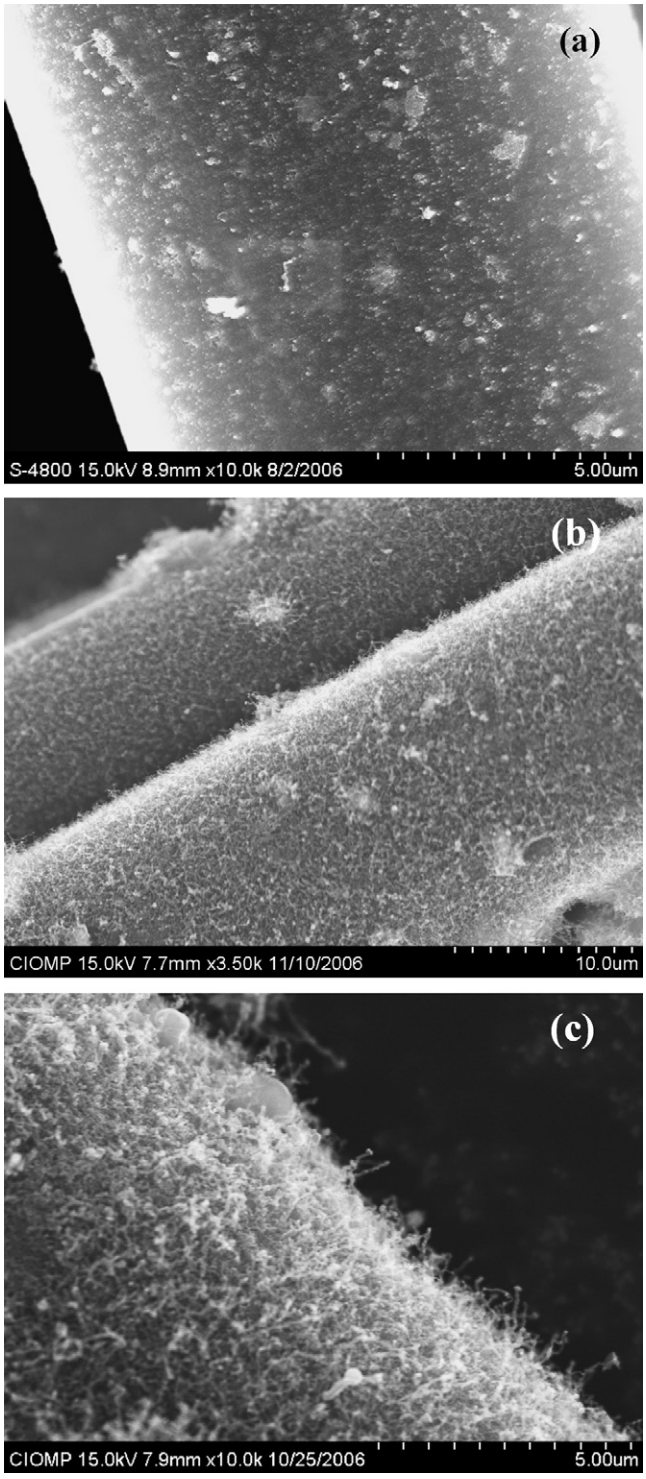
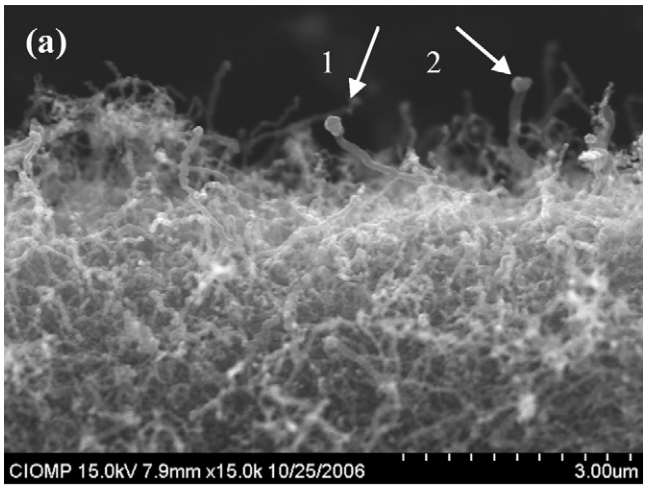



Fig. 1. FESEM images of CNTs on CMFs [(a) on untreated CMFs; (b) and (c) on treated CMFs].



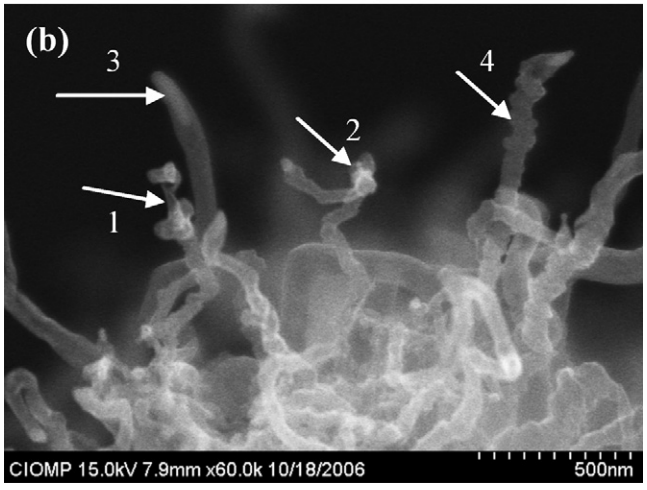




Fig. 2. Magnification SEM images of CNTs on treated CMFs [(a) 15 000× and (b) 60 000×].

shielding effect between adjacent CNTs brought by the supersaturation of CNTs density.

Fig. 2(a) and (b) are the magnification images of CNTs. It can be found that the diameters of CNTs are mostly 50 nm, only several are more than 50 nm. Moreover, the majority of CNTs are not straight, they are either curving (arrows 1 and 2 in Fig. 2(b)) or herringbone (arrow 4 in Fig. 2(b)). Arrows 3 and 4 in Fig. 2(b) indicate closed nanotubes, and the top of them are thinner than the diameter of CNTs. But arrows 1 and 2 in Fig. 2(b) point at a different geometry where an overlapping of nanostructures could be supposed. Furthermore, arrows 1 and 2 in Fig. 2(a) indicate that a carbon spherical structure seems to be present on the top of CNTs.

Fig. 3 shows EDX image of CNTs grown on CMFs substrate. It can be found that the composition of CNTs is carbon. On the one hand, Fe and O come from catalyst and its oxidation. In the process of floating catalyst, Fe nanoparticles were brought by the pyrolysis of ferrocene. When the sample was placed in the air, O was also brought. On the other hand, Fe and O may come from the immersion of CMFs in the solution of iron nitrate and xylene.

Further, the microstructure of CNTs is characterized by TEM and HRTEM in Fig. 4. It can be clearly seen that in

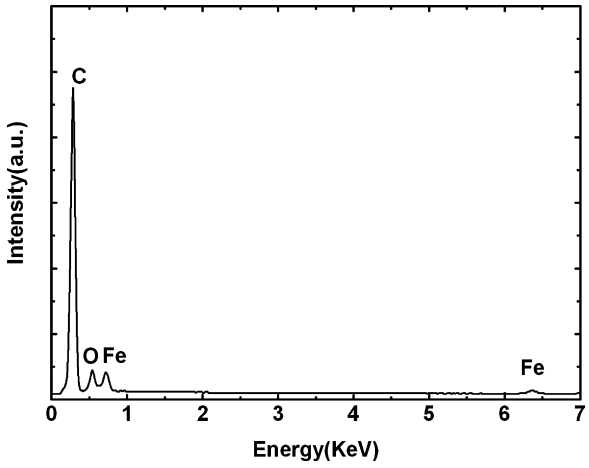
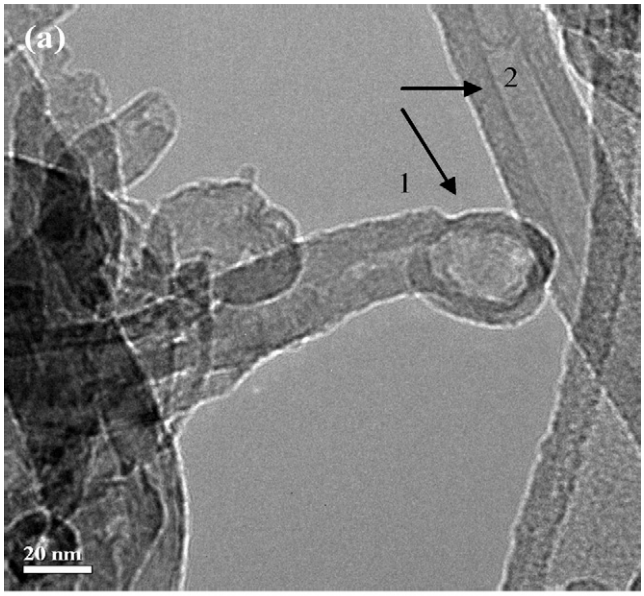



Fig. 3. EDX image of CNTs on treated CMFs.



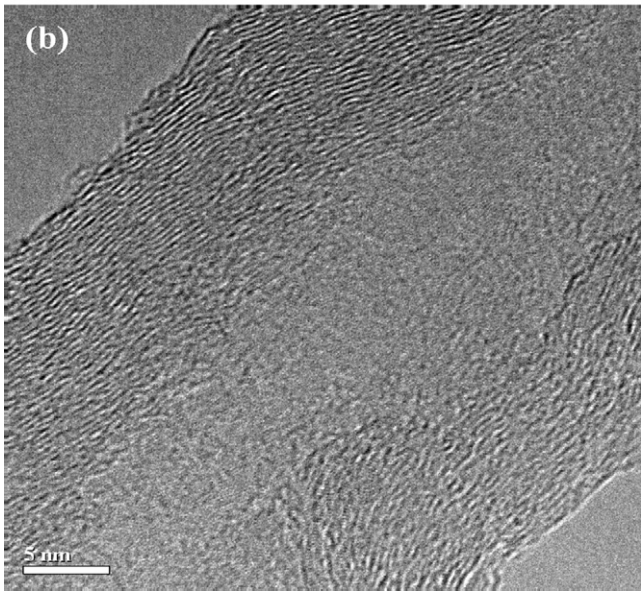




Fig. 4. TEM and HRTEM images of CNTs [(a) TEM and (b) HRTEM].

Fig. 4(a), a closed carbon spherical structure lies on the top of the CNT, and the diameter of spherical structure is larger than the middle of CNT (arrow 1 in Fig. 4(a)), which is also in accordance with the observation in Fig. 2(a). It can be observed that the wall of CNT is smooth and uniform (arrow 2 in Fig. 4(a)). In Fig. 4(b), the diameter of CNTs is about 50 nm, and the distinct samdwich of graphite consisted of more than 30 layers can also be observed.

The method used in our paper is different from that of [12], in which CNTs were synthesized on CMFs by thermal chemical vapor deposition method with the immersion of CMFs in ferrofluide solution diluted by acetone at 1023 K. It is also different from the growth of CNTs by only floating catalyst method [13]. Above results show that the density of CNTs synthesized in our paper is comparatively large and well-proportioned. It illuminates that floating catalyst method with the pretreatment of CMFs is a simple and effective method, in which the predeposition of catalyst was avoided, and simultaneously the density distribution of CNTs was uniform and ordered. In the process of floating catalyst, the contact time between catalyst and CMFs was decreased, which made the diffusion of catalyst into CMFs be decreased. By comparing the results of untreated and treated CMFs, we find that the effect of the pretreatment of CMFs on the growth of CNTs is great. On treated CMFs subtrate, hardly any carbon particle was grown other than CNTs, which was distinctly different from that of untreated CMFs substrate. On the one hand, after CMFs were boiled in the solution of sulfur/nitric acid, the surface of CMFs was activated. The defects of surface were formed and the amorphous carbon on CMFs surface was also taken away. The activated surface and defects of surface may provide the growth sites of CNTs. On the other hand, the immersion of CMFs in the solution of iron nitrate/xylene should be the key for the growth of CNTs. In the process of immersion, some ferric ions were absorbed on the CMFs surface and others were diffused into CMFs. Ferric ions probably had the effect of saturation diffusion for CMFs substrate. Therefore, when catalyst and carbon source were introduced, ferric ions absorbed on CMFs surface decreased the diffusion of catalyst into CMFs, which made it possible for the growth of CNTs on CMFs surface.

Before the growth of CNTs by floating catalyst method with the pretreatment of carbon fibers, the growth experiment of CNTs on treated CMFs substrate without floating catalyst also had been done, but the result was similar to that of experiment with only floating catalyst. Therefore, the pretreatment of CMFs is not a predeposition process of catalyst, but rather a key approach to the growth of CNTs by floating catalyst method.

Based on above results, we consider that CNTs/CMFs should have important application in field emission displays field. For example, the uniform and ordered distribution of CNTs on CMFs can ensure the consistency of CNTs emitters, and simultaneously can also effectively avoid the electric field shielding effect between adjacent emitters. Therefore, CNTs/CMFs composite materials should be good candidates for field emission electron source materials.

## 4. Conclusions

In our paper, using floating catalyst method with the pretreatment of CMFs, CNTs were synthesized on CMFs substrate. The results showed that the surface of treated CMFs was thickly covered by CNTs, and the density distribution of CNTs on CMFs surface was uniform. After CMFs were boiled in the solution of sulfur/nitric acid and were immersed in the solution of iron nitrate/xylene, the surface of CMFs was activated and the defects of surface were also formed, which provided the growth sites of CNTs. Moreover, the ferric ions absorbed on CMFs surface decreased the diffusion of catalyst into CMFs. The two factors were the base of growing uniform CNTs on CMFs substrate. Therefore, in the process of floating catalyst, the pretreatment of CMFs substrate was the key for the growth of CNTs.

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