PREPARATION OF THIN-WALLED CARBON NANOTUBES WITH LARGER INNER DIAMETER BY ACID TREATMENT

Liu Yunfang, Chi Weidong, Liu Bo, Pan Yan, Shen Zengmin

Key Laboratory of Carbon Fiber and Functional Polymers of Ministry of Education, Institute of Carbon Fibers and Composites, Beijing University of Chemical Technology, Beijing 100029, P. R. China

Introduction

Since their special inner hollow structure, carbon nanotubes (CNTs) have wide applications, such as nanoreactor, template for nanowire production, nanochannel, nanoinjector, nanocontainer and energy storage materials, etc. CNTs with large inner diameter were usually needed in some fields, so how to get CNTs wtih large inner diameter is important. Some progress has been achieved. The template method has been widely used to get CNT with large inner diameter [1-3]. And the diameter of CNTs could be controlled by adjusting the reaction parameters [4, 5]. Adding sodium carbonate to the catalyst in CVD procedure shows the obvious effect on the inner diameter of CNT [4]. The inner diameter of the CNTs is enlarged from 3-7 nm to 40-60 nm. CNTs with large inner diameter and thin tube wall could be obtained by using the Y zeolite support with large secondary pores [5]. The HNO_3 oxidation method has been widely used to purify and modify CNTs [6-9]. HNO_3 molecule usually removes the tip and external carbon and decrease the outer diameter, while has few effect on the inner diameter. In this research, we used a special kind of multi-walled CNTs (MWCNTs) for HNO_3 oxidation to get thin-walled CNTs (TWCNTs) with large inner diameter. And the electrochemical properties of CNTs etched at different conditions were investigated.

Experimental

The original MWCNTs were produced by catalytical pyrolysis method using a vertical furnace. Benzene was used as carbon source, and ferrocene (0.5 g/ml) was used as catalyst with thiophene (0.12 ml/ml) as auxiliary catalyst. The reaction temperature was kept at about 1160 ^oC. The flow rates of N_2 and H_2 were 1 L/min and 5.4 L/min, respectively. The MWCNTs (1 g) were dispersed in concentrated HNO_3 (100 ml) by ultrasonic treatment (30 min) and treated at 110 ^oC for different time (2 ~ 24 h). After that, the acid-treated MWCNTs were filtered and washed.

Transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) were employed to analyze the microstructure of CNTs. The change of crystal structures was characterized by X-ray diffractionmeter with Cu Kα radiation (Rigaku B/max-2400). The electrochemical properties of CNTs were investigated in two-electrode test cells. In order to prepare the working electrodes, a slurry consisting of CNTs (80 wt.%), acetylene black (10 wt.%) and polyvinylidene fluorine (10 wt.%) was spread on a nickel mesh current collector. The electrode was dried at 120 ^oC for 2 h. The diameter of the disc working electrode was 14 mm for galvanostatic experiment. The electrolyte was 6M KOH aqueous solution.

Results and Discussion

Fig. 1 shows the TEM and HRTEM images of as-prepared MWCNTs. As showed in Fig. 1a, MWCNTs have smooth surface and closed tip. The outer diameters of most CNTs are in the range of 30 ~ 100 nm, and the inner diameter is less than 10 nm. The wall thickness of MWCNTs is about 30 ~ 90 nm. Fig. 1b shows that the wall of MWCNT consists of two parts: inner regular graphite structure and outer irregular pyrolytic carbon layer. The inner graphene planes are orientated at an angle with respect to the axial direction of MWCNT, which is similar to fishbone structure [10, 11]. The outer carbon layer consists of discontinued graphite structure.

Fig. 2 is the TEM images of MWCNTs that were treated in concentrated HNO_3 with different time. As we can see, the inner diameters of MWCNTs have been enlarged obviously by the acid oxidation, which is about 20 ~ 80 nm. The closed tip was opened, and the wall thickness decreases to about 4 ~ 10 nm. Thick-walled CNTs were changed to thin-walled CNTs. CNTs became shorter and thinner with the increase of the oxidation time.

Fig. 3 shows the SEM images of the acid-treated CNTs. The closed tip of CNT was removed. The smooth outer surface becomes coarse, especially for the samples treated at 16 h. From the broken tip of CNTs showed in Fig. 3b, we can see that the inner surface is also coarse. Both sides of CNTs were oxidated.

Fig. 4 is the XRD patterns of CNTs etched with different time. The (002) peak of the pristine CNTs is relatively sharp and regular, and the value of d_{002} is 0.3386 nm. The peaks of the acid treated CNTs become a little wider. The d_{002} values of the samples etched at 10 and 16 h increase to 0.3424 and 0.3461 nm, respectively. Those results suggest that the crystal structures of CNTs were destroyed by the HNO_3 treatment.

The HNO_3 oxidation has become an ordinary way to purify and functionalize CNTs [6-9]. But few reports discussed the effect on the inner diameter of CNTs. For the ordinary CNTs, the inner graphene layers are parallel to the axial direction of CNTs. It is more difficult for the HNO_3 molecular to oxidate the inner regular graphite structure. In our experiments, the HNO_3 molecular enter into the inner channel of CNTs after the tip was opened. The active terminal of the inner graphite layers will directly expose to HNO_3 and be etched, so the inner diameter was enlarged.

Table 1 lists the specific capacitances of CNTs treated by HNO_3 with different time. As we can see, the specific capacitance of CNTs was improved after the acid treatment. The capacitance of the pristine CNTs is only 7.2 F/g, while that of CNTs treated with 10 h reaches 49.4 F/g. The reason for the capacitance improvement of CNTs is that the close tip was opened and mesopore was formed in the wall after the acid treatment. When the treatment time was prolonged

further, the specific capacitance of CNTs decreases. It is possible that the wall of CNTs was thinned and the pore structure in the wall was changed.

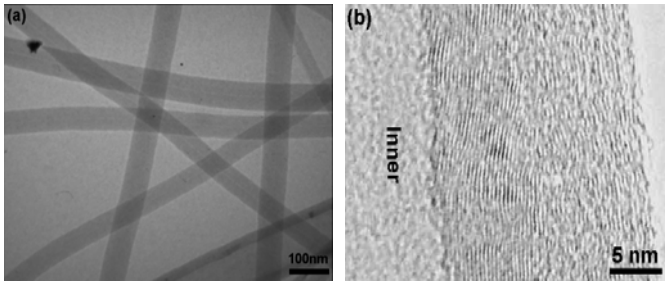

Fig. 1 Images of as-prepared MWCNTs (a) TEM (b) HRTEM

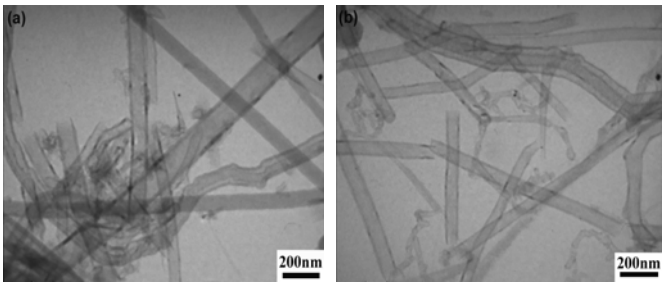

Fig. 2 TEM images of CNTs etched by HNO_3 with different time (a) 10 h (b) 16 h

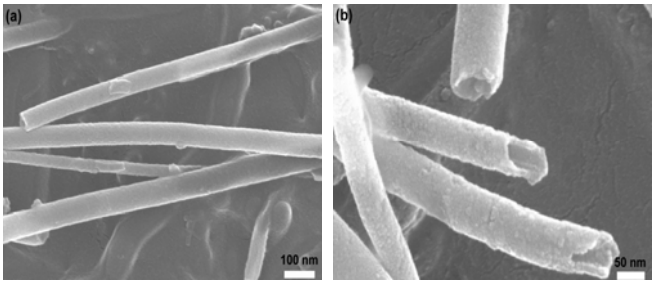

Fig. 3 SEM images of CNTs etched by HNO_3 with different time (a) 10 h (b) 16 h

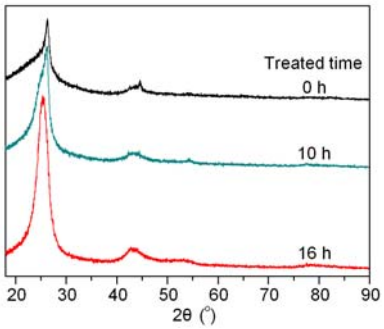

Fig. 4 XRD patterns of CNTs etched by HNO_3 with different time

Table 1 Specific capacitance of CNTs treated by HNO_3 with different time

Time (h)	0	6	10	16	20
Specific capacitance (F/g)	7.2	38.2	49.4	29.4	25.3

Conclusions

Thin-walled CNTs with large inner diameter were prepared by the acid treatment of thick-walled CNTs. The inner diameters of the acid-treated CNTs are larger than 20 nm, while that of the original CNTs are less than 10 nm. After the acid treatment, the wall thickness of CNTs decreased obviously, and the surface becomes very rough. The specific capacitance of CNTs treated with 16 h reaches 49.4 F/g, which is as about 7 times as that of the original CNTs.

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