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Letter to the editor

Preparation of activated carbon nanotubes

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Since carbon nanotubes (CNTs) were first found by Iijima in 1991 [1], they have become one of the most interesting materials for their novel structure characters: nanometre hollow tubes, high surface area with a narrow pore distribution size, excellent conductivity and high stability. They are considered as a promising candidate for many materials, such as composite material, catalyst material, field emission material, hydrogen storage material [2–4] and electrochemical supercapacitor electrode material [5,6]. Especially, their high surface area with a narrow pore distribution size is very important to applications such as hydrogen storage material and electrochemical supercapacitor electrode material, because materials with larger specific surface area can store more hydrogen and more electric energy. Multi-walled CNTs can be obtained easily, however, their specific surface area is low, normally a few hundred square metres per gram. This disadvantage has limited their applications. In this communication, we report a method to enlarge the specific surface area of CNTs with KOH activation. The activated CNTs have not changed their nanometre hollow tube structure. At the same time, their specific surface area is greatly increased. We call the CNTs being activated, the activated CNTs and the CNTs without activation the non-activated CNTs.

The non-activated CNTs were prepared by catalytic pyrolysis of CH_4 using La_2NiO_4 as the catalyst [7]. Nitric acid treatment was employed to remove the catalyst particles. After the treatment, the CNTs were examined by transmission electron microscopy (TEM) and their image is shown in Fig. 1a. We can see that the non-activated CNTs are multi-walled CNTs, randomly entangled and a good interior-empty structure. They are about 20 nm in diameter and very long.

As we know, KOH is an excellent activating agent for the preparation of activated carbon [8]. In our experiments, KOH was also used to activate the non-activated CNTs. The non-activated CNTs and KOH were dried sufficiently before activation. They were mixed very well in an agate mortar at 4:1 (m_{KOH}:m_{CNTs}), loaded in a ceramic boat and

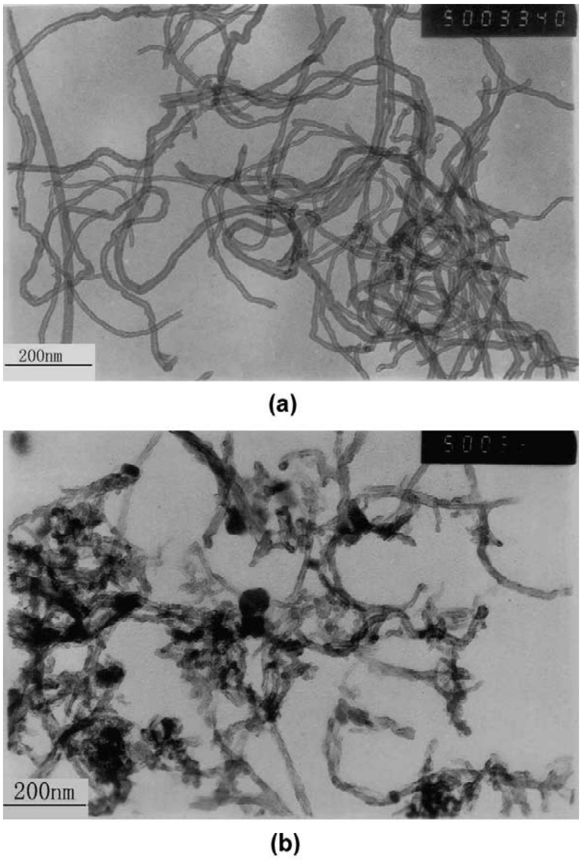

Fig. 1. TEM images of the carbon nanotubes: (a) non-activated and (b) activated.

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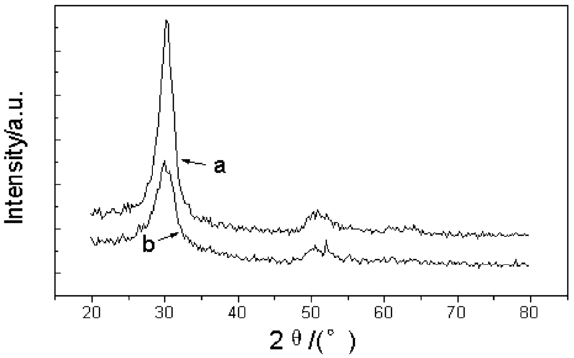

Fig. 2. TEM image of the activated carbon nanotubes. The XRD patterns of the non-activated CNTs (a) and activated CNTs (b).

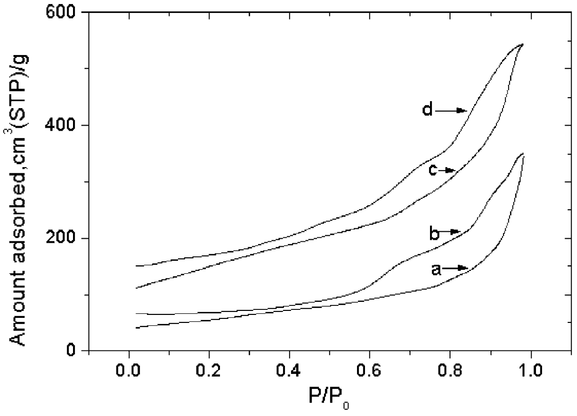

Fig. 3. The isotherms of the non-activated CNTs (a, adsorption curve; b, desorption curve) and activated CNTs (c, adsorption curve; d, desorption curve).

put in the tube of a horizontal-chamber furnace. The temperature was ramped at 10 °C/min up to 850 °C and held for 1 h, then naturally cooled to ambient temperature. All of the activating process was performed under a nitrogen flow (240 ml/min).

The obtained activated products were mixed with distilled water, then stirred for 2 h and filtered. They were dried in air for 12 h at 110 °C and weighed. Fig. 1b is the TEM image of the activated CNTs, from which we can see the activated CNTs are about 20 nm in diameter and 1000 nm in length. Comparing Fig. 1a with Fig. 1b, we can see the activated CNTs are clearly shorter than the non-activated CNTs.

X-ray diffraction (XRD) experiments were performed and the XRD profiles of the non-activated CNTs and activated CNTs are shown in Fig. 2. It is clearly shown that the activated CNTs also have the same graphite structure as that of the non-activated CNTs. But the crystalline size of the activated CNTs is smaller than that of the non-activated CNTs as shown by the X-ray peak half-width of the activated CNTs which is larger, which indicates the activated CNTs have smaller crystal grain and more structure defects, which gives the activated CNTs a higher specific surface area.

The measurements of specific surface area, pore volume, pore size and pore distribution were performed with an AUTOSORP ZXF-4 using nitrogen as adsorption gas at 77 K. The specific surface area was calculated by the BET equation, the mesopore and micropore volumes were calculated by the *t*-plot, the pore size and pore distribution were calculated by the BJH method. The total pore volumes (sum of micropore and mesopore volumes) were estimated to be the liquid volume of nitrogen at a relative pressure of about 0.999. All the results are listed in Table 1 from which we can see that the BET specific surface area of non-activated CNTs is 194.1 m^2/g and that of activated CNTs is 510 m^2/g, about three times higher. The total pore volume of the non-activated CNTs is 0.66 cm^3/g and that of activated CNTs is 0.91 cm^3/g, about 1.5 times higher. The mesopore and micropore volumes of the activated CNTs are both increased. The mean pore diameter is decreased from 14.64 nm to 8.16 nm.

The nitrogen adsorption and desorption isotherms at 77 K of the non-activated CNTs and activated CNTs are shown in Fig. 3. The isotherms of the activated CNTs are obviously higher than those of the non-activated CNTs, which indicates that the activated CNTs can adsorb more nitrogen than the non-activated CNTs. Therefore, we can deduce that the activated CNTs may have larger specific surface area and total pore volume than the non-activated CNTs. Moreover, from the shapes of the isotherms, we can know that the pores are mainly mesopores.

Fig. 4 shows the pore distribution of the non-activated CNTs and the activated CNTs, from which we can see that the pore distribution of the non-activated CNTs ranges from 3.0 to 40.0 nm, mainly from 10.0 to 40.0 nm. And

Table 1
The characteristics of the non-activated and activated CNTs

CNTs	Yield (%)	S_{BET} (m^2/g)	V_{tot} (cm^3/g)	V_{mi} (cm^3/g)	V_{me} (cm^3/g)	D_{mean} (nm)
Non-activated	–	194.1	0.66	0.016	0.644	14.64
Activated	85	510.5	0.91	0.139	0.771	8.16

S_{BET}, BET surface area; V_{tot}, total volume; V_{mi}, micropore volume; V_{me}, mesopore volume; D_{mean}, mean pore diameter.

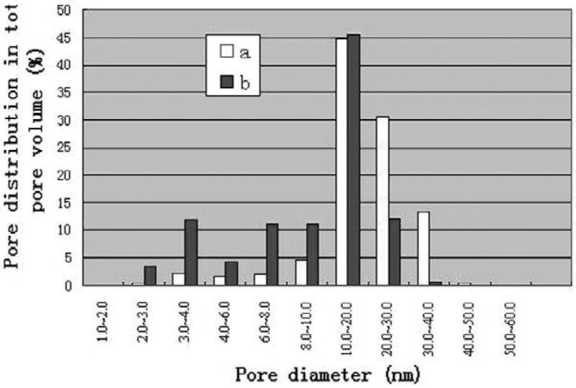

Fig. 4. The pore diameter distributions of (a) non-activated CNTs and (b) activated CNTs.

the pore distribution of the activated CNTs ranges from 2.0 to 30.0 nm, mainly from 3.0 to 30.0 nm.

In conclusion, the specific surface area and the total pore volume of CNTs can be greatly improved by activation operation, which can also make some changes to the pore distribution. Most of the pores are found to be mesopores, which is very important if the CNTs are to be applied as electrochemical supercapacitor electrode material [9].

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