



Short communication

## Facile synthesis of activated carbon/carbon nanotubes compound for supercapacitor application

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### ABSTRACT

A large number of carbon nanotubes (CNTs) have been produced commingled in activated mesocarbon microbeads (AMCMBs) activated by potassium hydroxide in a stainless steel container at 900 °C, in which an especial buried-protection method with petroleum coke powders was used to protecting the product during activation. The CNTs were found to be about 50 nm in diameter and characteristic length more than 10 μm. In addition, the AMCMBs/CNTs compound when used for electrode material of electrochemical double-layer capacitors exhibited a specific capacitance of 243 F g<sup>-1</sup> in 6 M KOH aqueous solution.

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## 1. Introduction

The development of an effective and green technology in energy storage and conversion is becoming more and more essential due to the increasing world energy depletion and the worsening environmental issues. Electrochemical double-layer capacitors (EDLCs) or supercapacitor (SCs) is a promising energy storage technology for applications on account of its high power density and long-cycle life [1]. Activated carbons (ACs) have been played the leading role in SCs because of their high surface area, good electrical conductivity, low cost and environmental friendliness [2,3]. It was known that mesocarbon microbeads (MCMBs) extracted from the carbonized pitch can be used to fabricate high-performance carbon materials due to its particular properties of uniform sphere sizes and regular shapes [4,5]. Carbon nanotubes (CNTs) have attracted extensive research interest in many fields owing to their excellent physical and chemical properties since the landmark paper by Iijima in 1991 [6,7]. Recently, activated mesocarbon microbeads (AMCMBs), CNTs and ACs/CNTs compound have been studied as electrode materials for supercapacitor application [8–10].

In the present study, we have developed a novel procedure for preparation of AMCMBs/CNTs compound by chemically activating MCMB with potassium hydroxide (KOH). Different from the traditional preparation methods of ACs, a simple buried-protection

method with petroleum coke powders was used in our work. And a possible growth mechanism of the CNTs was proposed based on the results of experiment and related theories. Moreover, we have studied the electrochemical performances of the AMCMBs/CNTs compound used as supercapacitor electrode material in 6 mol L<sup>-1</sup> KOH electrolyte.

## 2. Experimental methods

The initial MCMB with a specific surface area of 32.6 m<sup>2</sup> g<sup>-1</sup> used in our experiments was supplied by Tianjin Tiecheng battery Co. Ltd., China. The typical preparation procedure of AMCMBs/CNTs compound is as follows: the MCMB was mixed with KOH (5:1, w/w) in deionized water to obtain homogeneous slurry, and then the slurry was placed in a stainless steel container (with a movable cap) before heated at 2 °C min<sup>-1</sup> up to 900 °C and held for 2 h in a muffle furnace (as presented in the schematic of Fig. 1), in which the sample was protected buried in petroleum coke powders (with particle size of ~100 μm). After cooling down, the produce AMCMB was washed with 10 wt% HNO<sub>3</sub> (remove the metallic impurities) and deionized water and then dried in vacuum.

Generally, the preparation of activated carbon by chemical activation was conducted in a horizontal cylindrical furnace under the protection of inert gas flow (N<sub>2</sub>, Ar or He) [11,12], in which the activated carbon produce could be protected against air oxidation at high temperature. However, both the high cost of inert gases and the complexity of activation equipment are unfavorable for the practical production. As for a well-known industrial

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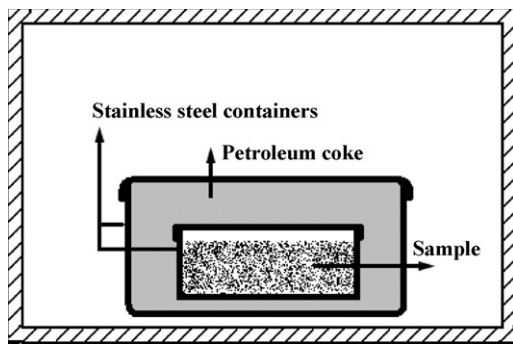


Fig. 1. Schematic of device for preparation of AMCMBs/CNTs compound.

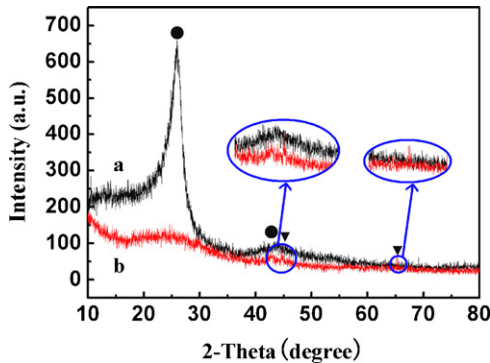


Fig. 2. XRD patterns of the (a) initial MCMB and (b) AMCMBs/CNTs compound.

raw material, petroleum coke has been widely used in preparation of a variety of engineering materials, based on its abundance and low cost [13–15]. In this study, replacing the expensive inert gases, petroleum coke was used acting as an air-insulating surrounding in the preparation of AMCMB. It is believed that petroleum coke could participate in the reaction with  $O_2$  in air at high temperature to form  $CO_2$  [13], which play an important role in protection of AMCMB produce against oxidation at the high temperature of  $900^\circ C$  during the activation process.

The surface area of AMCMBs/CNTs compound was investigated using physical adsorption of nitrogen at the liquid-nitrogen temperature (77 K) on an automatic volumetric sorption analyzer. The crystal structure of the sample was analyzed by X-ray diffraction (XRD). The morphology and microstructure of sample were observed using field-emission scanning electron microscope (FE-SEM) and transmission electron microscopy (TEM) techniques. In addition, an energy dispersion spectrometry (EDS) instrument was used to analyze the elements and their contents of the sample.

In order to study the electrochemical performances, the as-prepared AMCMBs/CNTs compound was prepared into electrodes and assembled into supercapacitor cells as follows: Firstly, the active substance was mixed with acetylene black and polytetrafluoroethylene (90:5:5, w/w/w) in ethanol to form a sticky slurry, then the slurry was rolled into a film ( $80\ \mu m$  in thickness) before cut into disk electrodes with diameter of 10 mm. Subsequently, fastener-type symmetric supercapacitor cells were assembled with a pair of disk electrodes divided by a piece of microporous separator. Cyclic voltammetry (CV) performed on an electrochemical workstation and the charge–discharge conducted with a Battery Tester is applied to measure the capacitive performances of the as-prepared supercapacitors.

### 3. Results and discussion

XRD patterns of the initial MCMB and as-prepared AMCMBs/CNTs compound are shown in Fig. 2. The pattern of MCMB before activation shows a strong peak at 24.8 and a weak peak at 43.9, corresponding to (002) and (101) diffraction peaks (marked in ●) of crystalline graphite, respectively. However, for the AMCMBs/CNTs compound, the peak at 24.8 decreases sharply and peak at 43.9 is also very weak, suggesting that both the AMCMBs and CNTs are amorphous structures. In addition, there are two diffraction peak at 44.5 and 65.2 (marked in ▼) corresponding to iron (Fe) and chromium (Cr), which were mainly derived from the reaction vessel.

Fig. 3(a) and (b) is the FE-SEM images of the initial MCMB and AMCMBs/CNTs compound in low magnification. As seen in Fig. 3(a), the MCMBs are of very good sphericities. From Fig. 3(b), it can be seen that the AMCMB was broken with a crack in the middle of sphere (marked in arrow) and there are many special structures in the sample (marked in circles). It was proved that these special structures were mostly composed of CNTs, by application of high-resolution FE-SEM, TEM and EDS techniques later. The specific surface area of the activated carbon was  $2462\ m^2\ g^{-1}$  determined from Brunauer–Emmett–Teller (BET) method.

Fig. 4 shows the microstructure of AMCMBs/CNTs compound by high-resolution FE-SEM and TEM techniques. As shown in Fig. 4(a), we can see the special structures separated from AMCMB (marked in rectangle) and on its surface (marked in circle), obvious nanofilm structure or fibriform structure were observed from the higher magnification images in Fig. 4(b) (marked in arrows). TEM analysis (Fig. 4(c) and (d)) combined with EDS analysis (Fig. 5) confirms that the nanofilms and fibriforms are carbon nanofilms and CNTs, respectively. Obviously, a large number of CNTs (more than  $10\ \mu m$  in length with curved or tangled shapes) can be observed in the AMCMB sample from Fig. 4(e) and (f). It was well known that CNTs

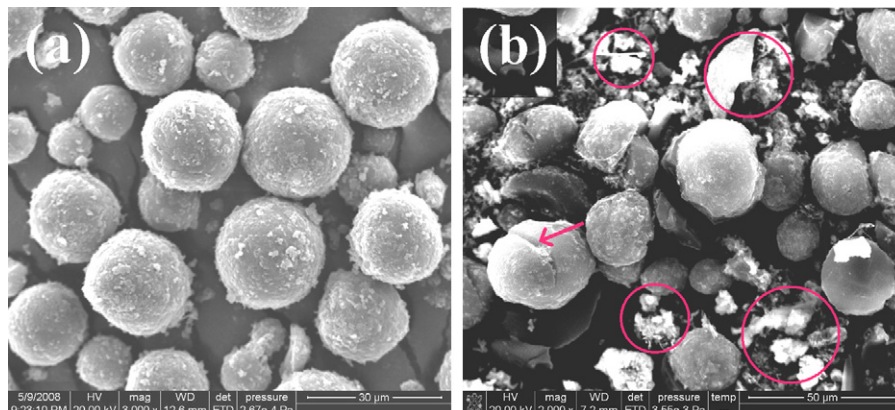
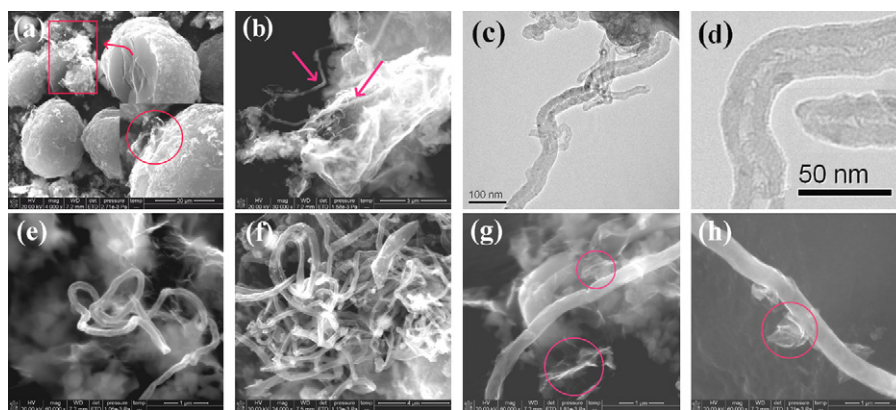


Fig. 3. FE-SEM images of (a) initial MCMB and (b) AMCMBs/CNTs compound in low magnification.



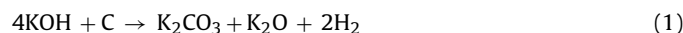
**Fig. 4.** Microstructure of AMCMBs/CNTs compound by high-resolution FE-SEM (a) and (b), (e)–(h) and TEM (c) and (d).

can be visualized as hexagonal net work of carbon atoms (graphite nanosheets) that was rolled up into a hollow cylinder [16,17]. From Fig. 4 (g) and (h), some carbon nanofilm fragments surrounding a CNT or attaching on its surface (marked in circles) can be seen clearly, which suggests that some of the CNTs have been unfolded

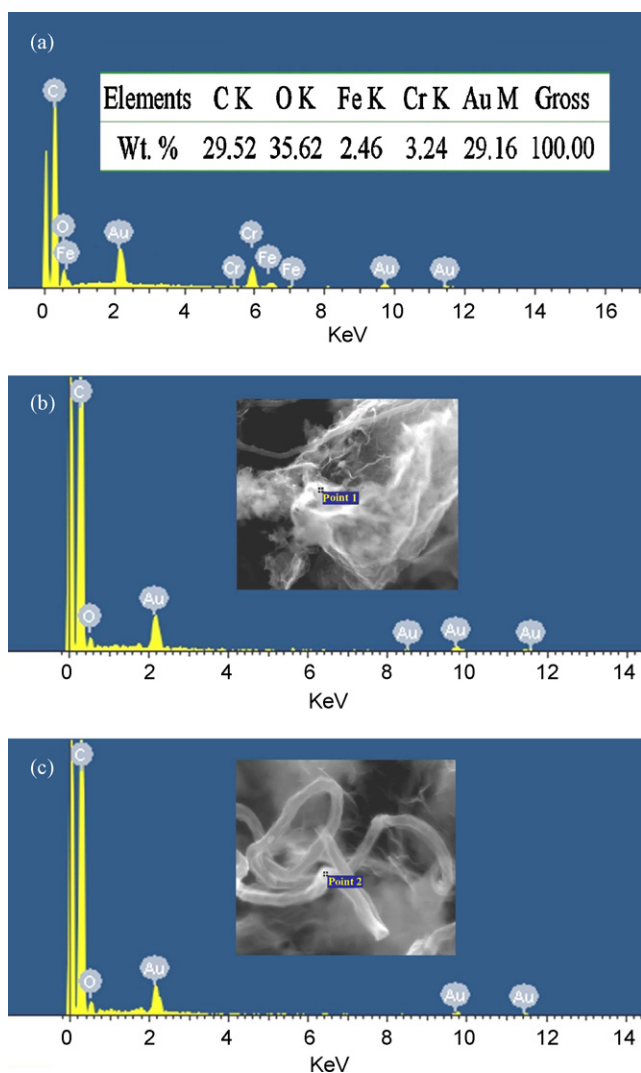
and transformed into amorphous carbon nanofilm in the late activation. Thus, it should be considered that a higher surface area of the AMCMBs/CNTs compound may originated from both the activated CNTs and amorphous AMCMB.

The results of element analysis of the AMCMBs/CNTs compound by EDS technique were presented in Fig. 5. From Fig. 5(a), it can be seen that the sample contains elements of C, O, Fe, Cr and Au, in which Au came from preparation process of test. The content of Fe and Cr in the sample is found to be about 2.46 wt% and 3.24 wt%, respectively. It is worth noting that both the carbon nanofilm and CNT in the sample are free of Fe and Cr contamination from Fig. 5(b) and (c), which shows that the nanocarbon prepared in this work is of relatively good purity.

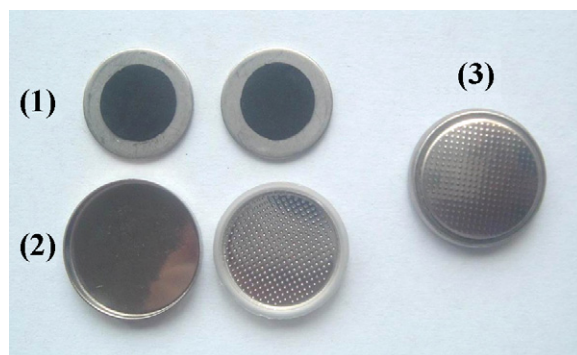
It is believed that, during activation of carbonaceous materials with KOH, a series of chemical reactions and K intercalation play an important role in their high surface area (up to  $3000\text{ m}^2\text{ g}^{-1}$ ). The generally accepted reactions for the KOH activation are as follows [18–20], where carbon monoxide (CO) is the exclusive final product derived from carbonaceous materials.



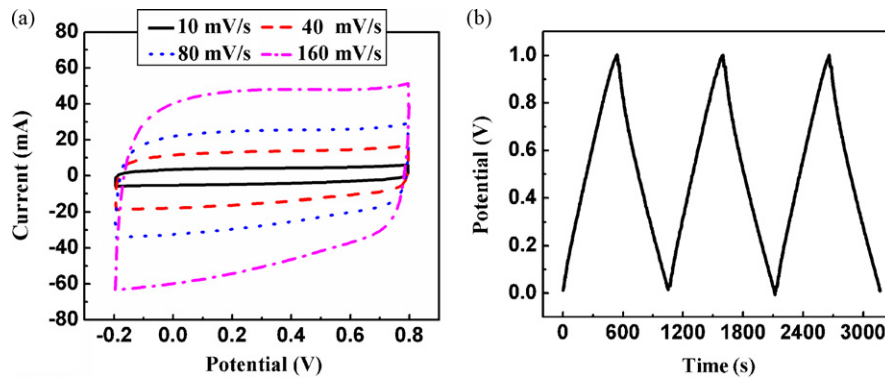
On the other hand, it is well-established that CNTs can be grown transformed from CO at a high temperature ( $>700^\circ\text{C}$ ) and a certain pressure (1–10 MPa) via CO disproportionation with Fe catalysis [21–24], which is one of the most effective synthesis routes for preparation of CNTs currently (so called high-pressure carbon monoxide (HiPCO) method).



**Fig. 5.** EDS spectrogram of sample: (a) mapping element analysis of AMCMBs/CNTs compound based on Fig. 3(b), (b) pointing element analysis of carbon nanofilm and (c) pointing element analysis of CNT.



**Fig. 6.** Picture of the supercapacitor cell assembled: (1) disk electrodes (2) electrode shells (3) fastener-type supercapacitor cell.



**Fig. 7.** (a) Cyclic voltammetry curves of the supercapacitor cell at different scan rates ( $10 \text{ mV s}^{-1}$ ,  $40 \text{ mV s}^{-1}$ ,  $80 \text{ mV s}^{-1}$  and  $160 \text{ mV s}^{-1}$ ); (b) galvanostatic charge/discharge curve of the supercapacitor cell at the constant specific current of  $0.5 \text{ A g}^{-1}$ .

As a result, it can be inferred that, the growth of CNTs from MCMB in present study is most likely based on above formation mechanism. The probable process could be described as follows: Firstly, CO was produced in according to reactions (1)–(3) during activation of MCMB with KOH [18]. Secondly, the resulting CO was transformed to CNTs at  $900^\circ\text{C}$  in reactions (4) catalyzed by Fe that was impregnated into sample from reaction vessel in activation process.

It is known that, based on different synthesis methods, the formation of CNTs in general needs to meet three conditions [25]: an effective carbon source (a variety of materials with high-carbon content, graphite, carbon black, methane, ethene, CO, etc.), a certain reaction temperature ( $500\text{--}3000^\circ\text{C}$ ) and an effective catalysts (Fe, Co, Ni, Cr, Mo, etc.). In fact, some studies have shown that synergy between the catalyst, carbon source, and growth conditions such as temperature and pressure is vital to obtain a high yield of CNTs [20,26]. Recently, it was reported that a small quantity of CNTs (about 200 nm in diameter) were found in activation of MCMB/Co composites with KOH at  $900^\circ\text{C}$  while none in the graphitized MCMB/Co even at a high temperature of  $2500^\circ\text{C}$  without KOH [27], which indicates that the KOH does play an important role (a motivity for CO generation) in the CNT growth besides Co catalysis. Therefore, it is reasonable to propose such a deduction: the effective carbon source may be CO derived from MCMB rather than MCMB itself for the grown of CNTs in activation of MCMB with KOH. Furthermore, the activation process reported in the above literature was carried out in  $\text{N}_2$  flow protection, which indicates that most of the CO produced in activation was taken away by the  $\text{N}_2$  flow. However, a special buried-protection method with petroleum coke powders was used differently in present work. So, it is expected that here the closely sealed-protection method could be inclined to form a higher-pressure reaction system due to increment of CO in the reaction vessel with settled cubage (as showed in schematic of Fig. 1), which is constructive to the transformation of CO into CNTs in small diameter during HiPCO process (Fe as the effective catalyst) [21,24,28]. Based on these discussions, this novel buried-protection method with petroleum coke powders in activation most likely accounts for the small diameter (50 nm presented by TEM) and obvious amount of CNTs prepared in our work.

The pictures of the supercapacitor cells based on AMCMBs/CNTs compound electrodes are shown in Fig. 6. The results of electrochemical measurements of the as-prepared supercapacitors in 6 M KOH aqueous solution are presented in Fig. 7. Fig. 7(a) depicted the CV curves of the AMCMBs/CNTs compound electrode at different rates ( $10 \text{ mV s}^{-1}$ ,  $40 \text{ mV s}^{-1}$ ,  $80 \text{ mV s}^{-1}$  and  $160 \text{ mV s}^{-1}$ ). Obviously, all the curves have good rectangular shapes at potential region of  $-0.2 \text{ V}$  to  $0.8 \text{ V}$ , indicating good capacitive performances of the supercapacitors [29]. Fig. 7(b) shows the charge/discharge curves of AMCMBs/CNTs compound electrode at a current density of  $0.5 \text{ A g}^{-1}$ . It can be seen that the shape of the curve is closely lin-

ear and show typical triangle symmetrical distribution at potential region of  $0.0\text{--}1.0 \text{ V}$ , which also indicates good capacitive properties of the supercapacitors. The specific capacitance ( $C_s$ ) of single electrode was  $243 \text{ F g}^{-1}$  calculated from the discharging plots with the following formula [30]:

$$C_T = \frac{I \Delta t}{\Delta V} \frac{1}{C_T} = \frac{1}{m_1 C_s} + \frac{1}{m_2 C_s}$$

where  $C_T$  is total series capacitance of the two electrodes in supercapacitor (F),  $I$  is the current (A),  $\Delta t$  is the discharging time (s),  $\Delta V$  is the voltage difference of discharge (V),  $C_s$  is the specific capacitance of a single electrode ( $\text{F g}^{-1}$ ),  $m_1$  and  $m_2$  are the active mass of the two electrodes, respectively.

#### 4. Conclusions

A simple buried-protection method with petroleum coke powders in activation of MCMB with KOH was applied in this study, and a large number of CNTs are produced during the activation process. We consider that the final product CO derived from MCMB and Fe released from reaction vessel play significant roles in acting the effective carbon source and effective catalyst, respectively, for the grown of CNTs in the present study. Electrochemical measurements showed that the AMCMBs/CNTs compound electrode is of high specific capacitance of  $243 \text{ F g}^{-1}$ , which persuade us to propose this compound as a promising electrode material for supercapacitor application.

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