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Controllable morphologies and electrochemical properties of graphitizing MCMB-based hybrids with nanostructure via a simple chemical vapor deposition method

Youliang Cheng [a], Qingling Zhang [a], Changqing Fang [a, *], Jing Chen [a], Shaohua Guo [b], Xinchuan Che [b]

[a] Faculty of Printing, Packaging Engineering and Digital Media Technology, Xi'an University of Technology, Xi'an 710048, PR China
[b] Institute of Materials Science and Engineering, Xi'an University of Technology, Xi'an 710048, PR China

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ABSTRACT

The graphitizing mesocarbon microbeads (g-MCMB) based nanostructure hybrids are prepared by a simple chemical vapor deposition method. The growth temperature and the flow ratio of H_2 to C_2H_2 (r) are the key parameters of controlling the morphologies of the hybrids. When r is 4, many CNTs mixed with carbon fibers grow on g-MCMB surfaces at 700 °C. However, there are almost no CNTs to be observed at 750 °C and 800 °C. In addition, the specific surface area of as-prepared hybrids is a little higher than that of g-MCMB, and the specific capacitance is much higher than the latter. The sample of g-MCMB-NS-4-700 exhibits the highest specific capacitance (303 $F \cdot g^{-1}$ at the current density of 0.5 $A\ g^{-1}$), which is approximately 1.46 folds of g-MCMB. Moreover, the prepared hybrids have an excellent cycling stability and the specific capacitance retention is above 90% after 500 cycles.

1. Introduction

Due to the high bulk density, excellent electrolyte compatibility and particular spherical shapes, the applications of mesocarbon microbeads (MCMB) in lithium-ion batteries have attracted many attentions of the researchers [1–6]. However, the low specific surface area and nonporous structure limit the application of MCMB in supercapacitors. Some researchers have reported that activated MCMB exhibit high specific surface area and pore volume and can be used as the electrode materials for supercapacitor [7–9]. Thus, MCMB after properly treated can be used as the electrodes of supercapacitors. In addition, the specific capacitance and charge-discharge rate of supercapacitors are related to the specific surface area and electrical conductivity of electrode materials. Therefore, the key parameters to improve the specific capacitance are using the high specific surface area and electrical conducting electrode materials [10]. Recently, porous carbons are widely used as the active electrode materials for supercapacitors, including activated carbons (such as activated carbon powders, activated carbon films and monoliths and activated carbon fibers) [11–13], holey graphene [14,15] and carbon nanotubes (CNTs) [10].

In recent years, CNTs-based composites are wildly used as the electrode of supercapacitor due to the excellent electrochemical properties, high external surfaces and outstanding electrical conductivity [16,17]. However, it is difficult to grow CNTs on the nonporous substrates using by chemical vapor deposition (CVD) method. There are many parameters to control the growth of CNTs, such as growth temperature, the ratio of gas flow and catalyst species. These parameters have important effects on the morphologies of the products [18]. Recent researches have reported that carbon nanostructures can grow on substrate surfaces (except MCMB surface) by using CVD method [19–21]. It can be found that the growth conditions can change the morphologies of grown carbon nanostructures (such as CNTs, carbon fibers, carbon particles, carbon filaments and carbon sheets) and then the products exhibit different electrochemical properties.

In this paper, we investigate the influences of growth temperature and the ratio of gas flow on the growth of nanostructures on g-MCMB surfaces. The different parameters cause the carbon nanostructures to have various morphologies, which have great impact on electrochemical properties of products. Thus, we study the electrochemical properties of the as-prepared hybrids by using

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* Corresponding author.
E-mail address: fcqxaut@163.com (C. Fang).

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cyclic voltammetry (CV), electrochemical impedance spectroscope (EIS) and galvanostatic charge-discharge (GCD).

2. Experimental

2.1. Materials

Commercial graphitizing MCMB (denoted as g-MCMB) with diameter of 5–13 μm (Nanjing Jones New Energy Science and Technology Co. Ltd.) and Iron nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$, analytical purity, Tianjin Tianli Chemical Reagents Co. Ltd.) are used in this paper.

2.2. Preparation of samples

The g-MCMB were dipped in 0.1 M catalyst solution ($Fe(NO_3)_3{\cdot}9H_2O$ in ethanol) for 2 h and dried in an oven at 100 °C. After that, above mixture on a ceramic thin chip were placed in a quartz tube furnace and Ar was used as the carrier gas for eliminating the air. CVD process can be divided into two stages: first, the furnace temperature increased to 450 °C from room temperature with a heating rate of 20 $°C{\cdot}min^{-1}$, subsequently H_2 was introduced to the furnace maintaining for 1 h. Next, the furnace temperature continued to increase to 750 °C from 450 °C with a heating rate of 10 $°C{\cdot}min^{-1}$, then C_2H_2 was introduced to the tube holding for 30 min. After the growth ended, the C_2H_2 and H_2 supply were stopped immediately while the Ar flow was maintained. When the temperature of the furnace cooled to the room temperature, the products were taken out. During the growth, the flow of H_2 was maintained at 160 sccm, the flow ratio of H_2 to C_2H_2 (r) was set as 4 and 8, and the growth temperature was set as 700 °C, 750 °C and 800 °C, respectively. These samples were denoted as g-MCMB-x-y ($x = 4{,}8$, $y = 700, 750, 800$), respectively.

2.3. Characterizations

The surface morphologies of g-MCMB/CNTs hybrids were investigated by using a scanning electron microscope (SEM Hitachi SU8000) at 1.0 KV and a transmission electron microscope (TEM JEOL JEM-3010) under the voltage of 200 kV. Raman spectroscopy was performed on a Raman spectrometer (Horiba JOBIN YVON HR800) using 633 nm argon-ion laser (spot size of 0.3 μm) under the ambient conditions. X-Ray diffractions (XRD) were carried out on an X-Ray diffractometer (XRD SHIMADZU LIMITED XRD-700) with a Cu Ka radiation source ($\lambda \approx 1.54$ Å). The nitrogen sorption experiments were measured on an adsorption instrument (PM2-0648) for the determination of specific surface area and total pore volume. Prior to analysis, all of the samples were degassed at 200 °C for 10 h. The surface area was calculated using the Brunauer–Emmett–Teller (BET) equation and the total pore volume was estimated at a relative pressure of 0.99.

2.4. Electrochemical measurements

The electrochemical properties of the g-MCMB/CNTs samples were measured by a CHI650D electrochemical workstation using two-electrode method. The working electrodes were fabricated by mixing the prepared powders with acetylene black and polytetrafluoroethylene (PTFE) binder, and the mass ratio was 8:1:1. The appropriate amount of ethanol was added to the mixture to form a paste. Subsequently, the mixture was pressed onto nickel foam and dried at 100 °C for 10 h. The active area of the electrode was around 1 cm^2, and 1.5 M Na_2SO_4 solution was used as the electrolyte. The mass loading of active materials is about 5 mg. The potential for CV was 0–1 V at the scan rates of 0.01–0.4 VS^{-1}. The frequency for EIS ranged from 1 Hz to 100 K Hz. The GCD measurements were performed on a NEW WARE battery workstation with a two-electrode symmetric cell (CT-4008-5V 20 mA-S4) from 0.1 to 1 A g^{-1}, and the potential was 0–1 V.

3. Results and discussions

3.1. The morphologies and structures of samples

Fig. 1 shows SEM and TEM photographs of g-MCMB-NS-4-750, g-MCMB-NS-8-750, g-MCMB-NS-4-700 and g-MCMB-NS-4-800 (The SEM image of graphitizing MCMB as shown in Fig. S1). As shown in Fig. 1(a), there are a few nanostructures on the surface of

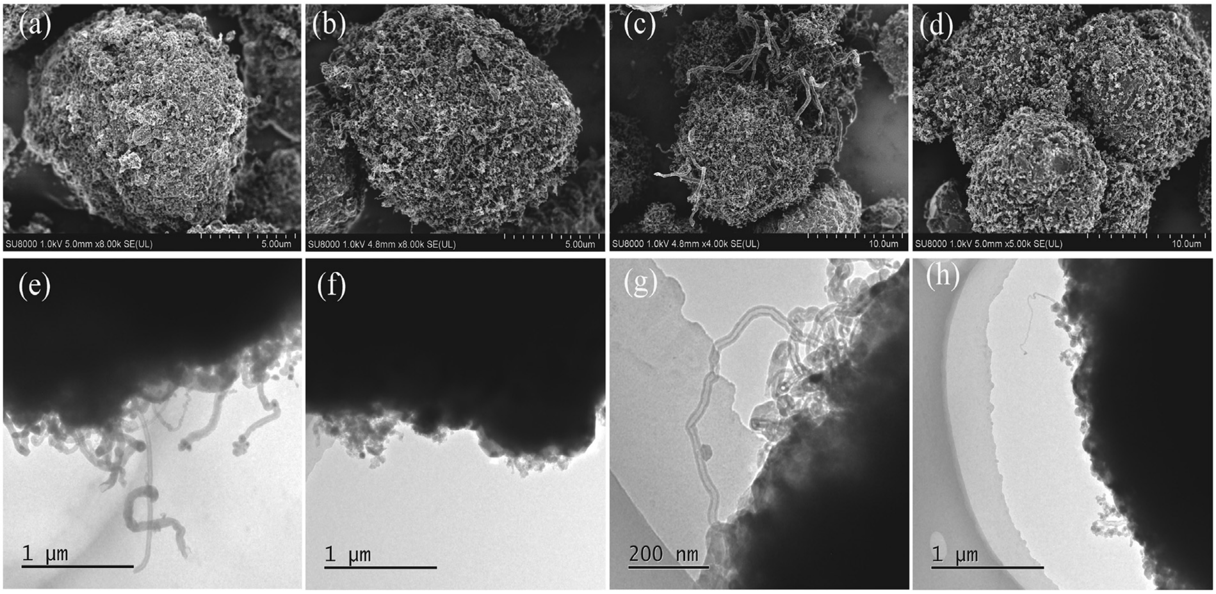

Fig. 1. SEM images of (a) g-MCMB-NS-4-750, (b) g-MCMB-NS-8-750, (c) g-MCMB-NS-4-700, (d) g-MCMB-NS-4-800 and TEM images of (e) g-MCMB-NS-4-750, (f) g-MCMB-NS-8-750, (g) g-MCMB-NS-4-700, (h) g-MCMB-NS-4-800.