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Facile *in-situ* redox synthesis of hierarchical porous activated carbon@MnO_2 core/shell nanocomposite for supercapacitors

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Abstract

In this paper, hierarchical porous activated carbon@manganese dioxide (AC@MnO_2) core-shell nanocomposite for supercapacitors have been synthesized by a facile *in-situ* chemical redox reaction. The microstructures of as-prepared materials have been characterized by Fourier transform-infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and nitrogen sorption isotherm measurements. Electrochemical properties of as-prepared samples were studied by cyclic voltammetry (CV), galvanostatic charging–discharging (GCD) and electrochemical impedance spectroscopy (EIS) tests in 6 mol L^{-1} KOH aqueous electrolytes based on their two-electrode symmetric capacitors. Thanks to the advanced hierarchical porous core/shell nanostructures, the AC@MnO_2 composite exhibit a larger specific surface area (658.1 $m^2\ g^{-1}$) compared with either AC (557.9 $m^2\ g^{-1}$) or MnO_2 (113.6 $m^2\ g^{-1}$) and show a lower charge transfer resistance (0.74 Ω) and Warburg resistance (0.16 S $sec^{0.5}$) than those of AC (0.96 Ω, 0.11 S $sec^{0.5}$) and MnO_2 (0.82 Ω, 0.054 S $sec^{0.5}$), which all contribute to the improved electron/ion transport processes and the superior capacitive performance. The results show that AC@MnO_2 composite exhibit enhanced specific capacitance (193 F g^{-1}, 0.2 A g^{-1}), rate performance (154 F g^{-1}, 2 A g^{-1}) and cycling stability (77.8% retention after 1500 cycles at 0.8 A g^{-1}) than those of AC (181 F g^{-1}, 0.2 A g^{-1}; 129 F g^{-1}, 2 A g^{-1}; 50% retention after 1500 cycles) and MnO_2 (64 F g^{-1}, 0.2 A g^{-1}; 10 F g^{-1}, 2 A g^{-1}; 11.3% retention after 1500 cycles). The superior capacitive behavior and the facile preparation method indicate a good candidate of the hierarchical porous AC@MnO_2 core/shell nanocomposite for supercapacitors.

Keywords: Activated carbon@MnO_2 nanocomposite; Supercapacitors; Core/shell; Hierarchical porous; *In-situ* redox reaction

1. Introduction

Currently there has been an ever-increasing demand for environment friendly and sustainable energy storage systems owing to the large proliferation of portable electronic products. Supercapacitors (SCs), one of the most promising electrochemical energy storage devices, have attracted tremendous attention as they possess high power capability, excellent cycle stability and reversibility, *etc.* [1–4]. They not only fill the gap between batteries and conventional solid state and electrolytic capacitors, but also offer a versatile solution to various emerging energy applications [5–9]. Supercapacitors can be categorized as electrochemical double layer capacitors (EDLCs) and pseudo-capacitors (PCs) according to the charge storage mechanism [10–12]: EDLCs store charges by electrostatic charge separation at the electrode/electrolyte interface, while PCs are based on highly reversible faradaic electrochemical redox surface processes. For supercapacitors, one of the great challenges being faced mainly lies in the low-cost, environmentally and high performance electrode materials.

To date, much effort has been dedicated to the electrode materials for supercapacitors. Generally, three types of materials including carbonaceous materials, transition metal oxides and conducting polymers have been considered as alternative candidates [1]. Among them, manganese dioxide (MnO_2) is

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considered to be the most outstanding one for its superior characteristics benefiting from its low-cost, environmental benignity, natural abundance and large theoretical specific capacitance (1370 F g^{-1}) [13–16]. Despite of the advantages, yet the poor electrical conductivity and low specific surface area of MnO_2 materials are also largely prevents their widespread practical applications. To overcome these limitations, carbon materials such as mesoporous carbon [17–20], carbon nanotubes [21–24] and graphene [3,13,15,16,25,26] have been widely used. Studies have shown that the combination of MnO_2 and carbonaceous materials can successfully improve the specific capacitance of supercapacitor devices. However, up to now, few studies have focused on porous activated carbon (AC) nanospheres.

Herein, we present a facile preparation of hierarchical porous AC@MnO_2 core/shell nanocomposite as the electrode materials for supercapacitors. Among them, the AC nanospheres cores are produced with a green, simple and inexpensive method including the aromatization, carbonization and activation of β-cyclodextrin with hydrothermal treatment. Subsequently the MnO_2 nanoshells can be *in-situ* anchored on the surfaces of AC nanospheres through a facile redox reaction under basic conditions, where H_2O_2 serves as the oxidant and $MnSO_4$ acts as the reductant. The fact proved that the fabricated core/shell nanocomposite can display the merits of superior specific surface area and fast electron/ion transport rates which would be very beneficial to achieve higher electrochemical performance for supercapacitors. The AC@MnO_2 composite show a high capacitance of 193 F g^{-1} at 0.2 A g^{-1}, reasonable rate performance of 154 F g^{-1} at 2 A g^{-1}and good cycle stability with 77.8% retention after 1500 cycles at 0.8 A g^{-1}. These results imply that the hierarchical porous AC@MnO_2 core/shell nanocomposite have a good potential value in the application of high-performance supercapacitors.

2. Experimental

2.1. Preparation of activated carbon (AC) nanospheres

All the reagents used in the experiment were of analytical grade and used without further purification. Briefly, the AC nanospheres were synthesized by a facile hydrothermal process and followed by a two-step heat treatment. Typically, 8.0 g β-cyclodextrin aqueous solution was placed in to 80 mL Teflon-sealed autoclave and maintained at 200 °C for 12 h. After a natural cooling process, the precursors were collected and washed with distilled water several times and followed by vacuum-drying at 80 °C for 12 h. Then, the collected precursors were calcined at 800 °C for 2 h in an argon atmosphere for carbonization, afterwards, the obtained products were further annealed at 400 °C for 1.5 h in air for an activation [27–29].

2.2. Synthesis of hierarchical porous AC@MnO_2 core/shell nanocomposite

In a typical process, 0.326 g of AC nanospheres was firstly dispersed in 50 mL of $MnSO_4$ aqueous solution under magnetic stirring for 24 h (with a MnO_2/AC feeding ratio of 4:6). Subsequently, 20 mL of the diluted 30% of H_2O_2 were added into the above solution slowly with magnetic stirring for 8 h. The resulted products were then washed with distilled water several times and finally dried in a vacuum oven at 60 °C for 24 h to obtain the hierarchical porous AC@MnO_2 core/shell nanocomposite. For comparison, the pure MnO_2 is also obtained according to the way mentioned above.

2.3. Structural characterizations

Fourier transform-infrared spectroscopy (FT-IR) spectra were recorded in the range 400–4000 cm^{-1} on a Nicolet 6700 type spectrophotometer with KBr pellets. Scanning electron microscopy (SEM) observations were carried out using a JEOL JEM-3010SEM microscope., Transmission electron microscopy (TEM) images were obtained using a JEOL 2010 microscope (200 kV), X-ray diffraction (XRD) patterns were obtained on a D/MAX-3C diffractiometer using Cu Kα radiation (λ=1.5406 Å). The specific surface area and pore structures of as-prepared samples were estimated from the isotherms of nitrogen adsorption-desorption at 77 K (NOVA-2200, Quantachrome) by using the Brunauer-Emmett-Teller (BET) equation and Barrett-Joyner-Halenda (BJH) method.

2.4. Electrode/capacitor fabrications and electrochemical measurements

The electrodes were prepared by first mixing 80 wt% as-prepared samples (AC@MnO_2, AC, MnO_2), 10 wt% polivinylidene fluoride (PVDF) and 10 wt% acetylene black (AB) with N-methyl pyrrolidone NMP under vigorous stirring conditions to form a homogenous slurry, and the slurry were then coated onto stainless steel meshes (diameter, 10 mm) and dried in a vacuum oven at 100 °C overnight. The typical mass loading of the active materials in each electrode thin film is about 3 mg. Sandwich-type capacitors were set up with two symmetric electrodes separated by a nylon septum with aqueous electrolytes of 6 mol L^{-1} KOH.

Electrochemical experiments were carried out in a two-electrode symmetric capacitor by means of a CHI 660 A electrochemical workstation (CHI Inc., USA) under ambient conditions. Cyclic voltammetry (CV) experiments were measured at the scan rate of 2 mV s^{-1}, galvanostatic charging–discharging (GCD) were conducted at current densities ranging from 0.2 to 2 A g^{-1}, and electrochemical impedance spectroscopy (EIS) measurements were performed at opening circuit potential (OCV) by sweeping frequencies from 100 kHz to 10 mHz with an amplitude of 5 mV. The mass specific capacitance (C, F g^{-1}) of the electrode is calculated according to the following equation:

$$C = 2\frac{I \times \Delta t}{\Delta V \times m} \tag{1}$$

Here, I (A) is the discharging current, m (g) is the average mass of active materials in the two working electrodes, Δt (s) is the discharging time, ΔV (V) represents the voltage window during the corresponding discharging time.