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Sculpturing the Core towards Mesoporous Manganese Dioxides Nanosheets-Built Nanotubes for Pseudocapacitance

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ABSTRACT

Ultrathin MnO_2 nanosheets-built nanotubes have been fabricated via a large-scale chemical etching method. The diameter and thickness of MnO_2 nanotubes can be controlled by fine-tuning the concentration of $KMnO_4$ solution, and the relationship between electrochemical properties and different wall thickness is notably investigated. Besides, the MnO_2 nanotubes possess a high surface area of 179.5 $m^2 g^{-1}$ and lots of mesopores. Such unique features are beneficial for providing easy access of the electrolyte to the structure and shortening the diffusion distance of ions. More significantly, recyclable copper ions after etching can be used to synthesize Cu nanowires again. The MnO_2 nanotubes in a three-electrode system display much high specific capacitance (377.5 $F g^{-1}$ at current density of 0.25 $A g^{-1}$), good rate performance. Moreover, an asymmetric supercapacitor on the basis of MnO_2 nanotubes as the positive electrode and activated graphenes (AG) as the negative electrode produced an energy density of 22.68 Wh kg^{-1} and a maximum power density of 4.5 kW kg^{-1}. These attractive discoveries suggest that it can be an aussichtsreich candidate as an efficient supercapacitive electrode.

1. Introduction

Electrochemical capacitors (ECs) have captured increasing attention due to high power density, fast charge-discharge properties, long cycling lifetime and environmentally benign nature [1–5]. The performances of ECs are directly determined by the electrochemical properties of electrode materials. Recently, a series of various electrode materials have been extensively studied for supercapacitors, such as carbon materials [6,7], conducting polymer [8] and transition-metal oxide [9,10]. In these electrode materials, manganese dioxide (MnO_2) has drawn tremendous notice on account of abundant resources, wide potential window, high theoretical capacity (~1370 $F g^{-1}$) and non-toxicity for supercapacitors electrodes [11–14].

The electrochemical properties of manganese dioxide are closely related with their morphologies, structures and crystallinity. To date, MnO_2 with diverse morphologies and structures has been synthesized and investigated successfully [15–17]. However, most MnO_2 materials usually suffer from austere aggregation, resulting in a low surface area and deficient utilization of the active materials. Consequently, the rational structural design and synthesis of MnO_2 could be beneficial to improve the issue. Among these structures, MnO_2 nanotubes have been of tremendous favours by reason of offering high surface area, short ion diffusion length and fast kinetics. The synthetic methods of the MnO_2 nanotubes are extremely plentiful. Grote et al. [18] prepared the free-standing MnO_2 nanotube arrays by three-step template assisted synthesizing process, which was somewhat complicated and needed post processing. Huang et al. [19] fabricated CuO@MnO_2 core-shell nanotubes via hydrothermal method, which owned a low surface area (only involves outer surfaces, without inner surface of MnO_2 nanosheets-built shells around copper or CuO) and diminutive hollow channel. The synthesis of MnO_2 nanosheets-built nanotubes is rarely reported by specific chemical etching method, enjoying high surface area (outer and inner surface of MnO_2 shell) and controllable wall thickness. Based on the previous data, we successfully sculptured the core "CuO" via sulfuric acid, and MnO_2 nanotubes with different wall thickness were perfectly obtained on a large scale. Naturally, MnO_2 nanotubes with large hollow channel can own high surface area and improve the effective interaction on the surface and inside of the nanotubes between the electrode and electrolyte.

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In this work, we have fabricated porous MnO_2 nanotubes by a facile and effective two-step approach including hydrothermal synthesis and chemical etching method. The diameter and thickness of MnO_2 nanotubes can be controlled by adjusting the concentration of $KMnO_4$ solution. The wall thickness increases along with fortifying of the concentration of $KMnO_4$ solution, which is linked closely with electrochemical properties. More significantly, recyclable copper ions after etching can be used to synthesize Cu nanowires again. Moreover, an asymmetric supercapacitor on the basis of MnO_2 nanotubes as the positive electrode and activated graphenes (AG) as the negative electrode achieves 22.68 Wh kg^{-1} and a maximum power density of 4.5 kW kg^{-1}.

2. Experimental

2.1. Synthesis of the CuO@MnO_2 nanocomposites

All the chemical reagents were of analytical grade and used without any further purification. Cu nanowires were prepared by minor modified method [20]. First, the Cu NWs (10∼15 mg) were dispersed in different $KMnO_4$ solution (30 ml; 0.01 M, 0.02 M and 0.03 M) and sonicated for 10 min to form a homogeneous solution. Then the mixtures were put into Teflon-lined stainless steel autoclaves maintained at 160 °C for 24 h. Finally, the samples were collected and washed with distilled water and ethanol for several times, and dried at 60 °C for 12 h to obtain the CuO@MnO_2 powders.

2.2. Preparation of the MnO_2 nanotubes

In a typical synthesis, 30 mg CuO@MnO_2 were dispersed in H_2SO_4 solution (30 ml, 1 M) to form a homogeneous precursor. The mixture was put in a water bath at 30 °C for 24 h, and then the solid products were washed with distilled water and ethanol (till the pH of the suspension was neutral). In the end, the samples were dried at 60 °C for 12 h.

2.3. Materials characterization

The compositions of as-prepared products were established by powder X-ray diffraction (XRD, D/max 2500, Cu Kα). The morphology and structure of as-prepared samples were observed by focused ion beam scanning electron microscopy (ZEISS AURIGA FIB/SEM) equipped with an energy dispersive X-ray spectrometer (EDS) and transmission electron microscopy (TEM, ZEISS LIBRA 200). Nitrogen adsorption and desorption isotherms were measured by a micrometrics ASAP 2020 sorptometer.

2.4. Electrochemical measurements

All the electrochemical measurements were carried out by an electrochemical workstation (CHI 660E) in 1 M Na_2SO_4 solution using a three electrode system. The working electrode was prepared by mixing active materials, carbon black, and polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) with proportion of 7:2:1, and the slurry was spread onto a foam nickel (1×1 cm^2). The electrode was kept at 120 °C for 12 h under 10 MPa. The saturated calomel (SCE) and the platinum plate electrodes were worked as the reference and counter electrodes, respectively. The working electrode contained ∼2 mg of MnO_2 nanotubes alone. The electrochemical impedance spectroscopy (EIS) was conducted with a perturbation amplitude of 5 mV in the frequency range between 100 kHz and 0.01 Hz.

The electrochemical performance of asymmetric supercapacitor was measured with a two- electrode system. In the two-electrode, MnO_2 nanotubes were as the positive electrode and activated graphenes (AG) were as the negative electrode, respectively. All the operating current densities were calculated on the basis of the total weight of MnO_2 NTs and AG.

3. Results and discussion

Fig. 1a shows the XRD patterns of the CuO@MnO_2 composites and the MnO_2 nanotubes. Obviously, the diffraction peaks of the CuO@MnO_2 composites of 32.5°, 35.5°, 38.7°, 48.7°, 61.5°, 67.8° and 75° are in accord with the XRD pattern of the CuO (JCPDS NO. 80-1916) [21]. On the other hand, the (006) peak of CuO@MnO_2 nanocomposites is not extra clear, indicating the nanocrystalline nature of the synthesized MnO_2. Meanwhile, it could be observed that the diffraction peaks of the MnO_2 nanotubes at about 12.3°, 24.8°, 36.6°, 42.2°, 65.5° and 78° are well in line with the standard XRD pattern of birnessite-type MnO_2 (JCPDS NO. 86-0666) [22]. No other peaks can be observed, manifesting high purity of the MnO_2 NTs obtained after etching. The typical SEM image and corresponding EDS mapping of the MnO_2 NTs are revealed in Fig. 1b and c, the mapping results demonstrate that K, Mn and O elements are well distributed. The as-prepared sample is K-birnessite type MnO_2, K^+ was introduced to the interlayer of MnO_2 during the hydrothermal reaction. These consequences make clear that

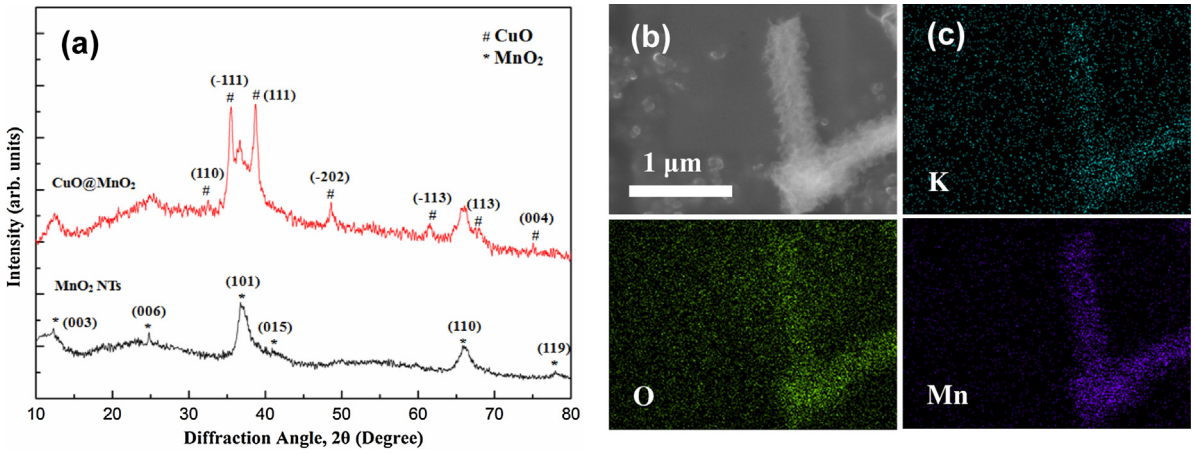

Fig. 1. (a) XRD patterns of CuO@MnO_2 composites and MnO_2 nanotubes;(b-c) Typical SEM image and the corresponding EDS mapping of MnO_2 nanotubes.