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Core/shell nanorods of MnO_2/carbon embedded with Ag nanoparticles as high-performance electrode materials for supercapacitors

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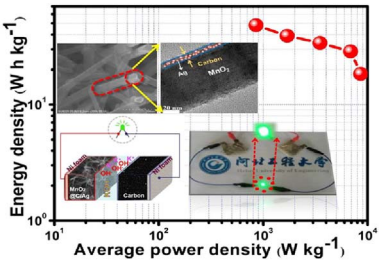
GRAPHICAL ABSTRACT



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ABSTRACT

Core/shell nanorods of MnO_2/carbon embedded with Ag nanoparticles (MCA) were successfully fabricated via a facile and effective hydrothermal and reduction method *in situ*. Typically, a MCA-1.5 sample (1.5 g·L^{-1} glucose reactant) exhibited the highest specific capacitance of 628 F·g^{-1} at the current density of 1 A·g^{-1} in three-electrode systems. Particularly, a fabricated asymmetric supercapacitor, using MCA-1.5 and active carbon as the positive and negative electrodes, respectively, delivered a maximum energy density of 48.3 W·h·kg^{-1} at power density of 851.7 W·kg^{-1} and exhibited a superior, long cycle life, showing ~98.5% specific capacitance retention after 2000 cycles. The practical energy-storage applicability of this device was demonstrated by the operation of an LED bulb when a duo of two such devices was charged. These results indicated that synthesized ternary nanocomposites have potential applications as supercapacitor electrodes in energy storage systems.

1. Introduction

The rapidly increasing adoption of electric and hybrid vehicles, portable electronics, forklifts, and many other applications has stimulated advancements in high-performance energy storage devices [1,2]. Supercapacitors (SCs) are considered one of the most advanced energy storage devices because of their high-power density, fast charge and discharge rates, long cycle life, and low cost [3–6]. Based on charge storage mechanisms, SCs can be divided into electrochemical double layer capacitors (EDLCs) and pseudocapacitors. Compared to EDLCs, which mainly use carbon materials as electrodes, pseudocapacitors are based on fast and reversible Faradic reactions of electroactive materials, which exhibit high energy density while maintaining high power density [7–10]. On the other hand, SCs store energy based on either ion adsorption or fast surface redox reactions and, thus, the electrode material's morphology, size, and porosity are an important determining factors for SC performance. Currently, owing to the advantages of high surface-to-volume ratios and short electron/ion diffusion distances in

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comparison with their bulk counterparts, one-dimensional (1D), nanostructured, metal oxide materials for electrochemical energy storage have appeared most attractive [11].

Manganese dioxide (MnO_2) is one of the most widely investigated materials for pseudocapacitor electrodes because of its abundance, good cycle stability, environmentally-friendly characteristics, and especially, remarkable theoretical capacity (1370 $F{\cdot}g^{-1}$) [12]. However, the poor electrical conductivity, cycling performance, and unfavorable ion transport efficiency of MnO_2 have blocked its practical utilization as advanced electrode materials [13]. Recently, it has been found that the electrical conductivity of silver (Ag) is 3–5 orders of magnitude higher than carbon materials, and various of Ag-decorated transition-metal oxides have been synthesized for high performance SC electrode materials [14–18]. Most recent studies have demonstrated that electrode materials decorated with Ag nanoparticles (AgNPs) could form electron transfer channels because of their excellent electrical conductivity and high surface activity. Thus, the addition of Ag maintains the low internal resistance of metal oxide electrodes and increases proton (H^+, Na^+, K^+, and Li^+) diffusion throughout the electrodes [16,19]. High SC values in Ag-metal oxide composites have not been possible because these composites have problems, such as having reduced surface area, being easily oxidized, and tendency for high agglomeration.

Based on the above considerations, core/shell nanorods of MnO_2/carbon (C) nanorod composites embedded with AgNPs were designed and constructed via a hydrothermal and reduction method *in situ* (Fig. 1). In this system, the C layer acted as the anchor for AgNP adherence with subsidence and was regarded as a protective layer that restrained agglomeration and Ag oxidation [20]. Meanwhile, the C layer assisted Ag in improving MnO_2's conductivity as well as to provide improved conduction channels and to efficiently shorten the transport path for both electrons and ions, leading to faster kinetics and higher utilization efficiency of these active materials. In addition, the existence of void spaces between the tribasic composite created material endurance against volume changes during long term cycling. As expected, these composites showed a maximum specific capacitance of 628 $F{\cdot}g^{-1}$ at a current density of 1 $A{\cdot}g^{-1}$. Moreover, an asymmetric SC (ASC) was constructed that possessed a maximum energy density of 48.3 $W{\cdot}h{\cdot}kg^{-1}$ at a power density of 851.7 $W{\cdot}kg^{-1}$ and showed a superior long cycle life, with ~98.5% specific capacitance retained after 2000 cycles.

2. Experimental

2.1. Preparation of MnO_2 and MnO_2/C nanorods

MnO_2 nanorods were prepared using a simple method. Briefly, 0.1264 g of $KMnO_4$, 0.4 mL of HCl, and 1 mL of H_2O_2 (3% by vol) were dissolved sequentially in 20 mL of deionized water. The solution was magnetically stirred for 5 min, sealed into a 25 mL of Teflon-lined, and treated at 433 K for 12 h. Finally, the sample was centrifuged and the sediment rinsed several times with water and then dried at 333 K for 4 h, yielding MnO_2 nanorods. To prepare MnO_2/C nanorods, MnO_2 nanorods (15 mg) and 20 mL glucose solution (1.5 $g{\cdot}L^{-1}$) were autoclaved, with heating to 160 °C at the rate of 10 °C·min^{-1}, held at temperature for 4 h, and cooled down to room temperature. Finally, the precipitate was centrifuged, washed sequentially three times with ethanol and deionized water until there were no other possible impurities in the product. The resulting product was then dried at 60 °C for 2 h, yielding MnO_2/C nanorods, which were denoted as MC-1.5. By this method, samples MC-0.5, MC-1, MC-1.5, MC-2, and MC-3 were prepared, using starting glucose solutions of 0.5, 1, 1.5, 2 and 3 $g{\cdot}L^{-1}$, respectively, for further tests.

2.2. Preparation of MnO_2/C/Ag nanorod composites

MnO_2/C/Ag nanorod composites were fabricated by a simple reduction method *in situ*. In the detailed synthesis, 10 mg of MnO_2/C nanorods were put into 20.0 mL of a solution containing of 0.01 g of $SnCl_2$ and 5 mL HCl, the suspension stirred for 6 h, and then rinsed with water three times. After activation with Sn^{2+}, the nanorods were transferred into a $[Ag(NH_3)_2]OH$ solution (20 mL, 5×10^{-5} M), stirred for 2 h, filtered from the solution, and washed with distilled water to dislodge free ions. The resulting MnO_2/C/Ag nanorod composites were denoted as MCA-0.5, MCA-1, MCA-1.5, MCA-2 and MCA-3, respectively.

2.3. Materials characterization

Scanning electron microscope (SEM) investigations were carried out on a FEI Quanta FEG 250 field-emission SEM system (FEI Co., Hillsboro, OR, USA). Transmission electron microscopy (TEM) imaging was obtained using a JEM 2100F (accelerating voltage, 200 kV; JEOL Ltd., Tokyo, Japan). Powder X-ray diffraction (XRD) patterns were used for detection of sample crystal structures, with Cu-Kα radiation from 10 to 70°. The samples' chemical states were analyzed by X-ray photoelectron spectroscopy (XPS; VG Scientific ESCALAB LK II spectrometer; Thermo Fisher Scientific Inc., Waltham, MA, USA). Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 449 C thermoanalyzer in air atmosphere.

2.4. Fabrication of an ASC

An ASC was fabricated using MCA-1.5 as the positive electrode and active carbon (AC) as the negative electrode. The loading mass ratio of active materials (MCA-1.5/AC) was determined by the charge balance relationship of $q^+ = q^-$, where q^+ and q^- are the positive and negative electrode charges, respectively. To satisfy $q^+ = q^-$, the mass balance was expressed using the following relationships [21]:

$$q = m \times C \times \Delta V \quad (1)$$

$$m^+/m^- = (C^- \times \Delta V^-)/(C^+ \times \Delta V^+) \quad (2)$$

where C ($F{\cdot}g^{-1}$) is the electrode specific capacitance, m (g) the electrode active material mass, and ΔV (V) the potential window.

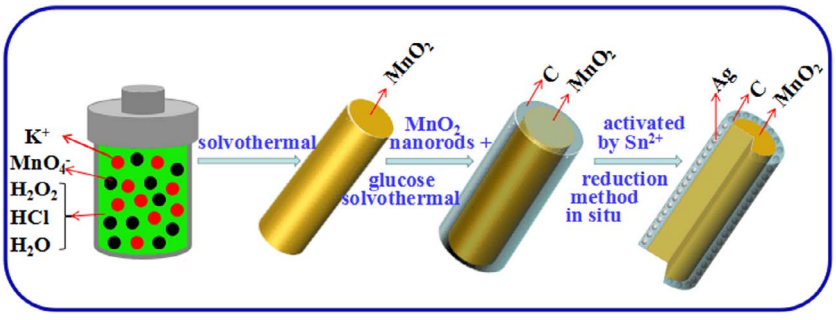

Fig. 1. The schematic illustration of preparation process for the MnO_2/C/Ag nanorod composites.