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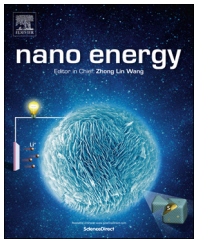

RAPID COMMUNICATION

Highly porous honeycomb manganese oxide@carbon fibers core–shell nanocables for flexible supercapacitors

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Abstract
Core–shell electrodes composed of highly porous honeycomb manganese oxide@carbon fibers (HMO@CFs) are synthesized by a facile hydrothermal approach involving an *in situ* redox replacement reaction between potassium permanganate ($KMnO_4$) and carbon fibers. In this reaction, the carbon fibers serve as not only a sacrificial reductant, but also the substrate. The porous HMO@CFs core–shell nanocables deliver remarkable electrochemical performance with a high capacitance (295.24 F g^{-1} at 100 mA g^{-1}), high good rate capability, and superior cycling stability (about 96.4% specific capacitance retained after 3000 cycles). The maximum energy density of 22.2 W h kg^{-1} (at a power density of 400 W kg^{-1}) and power density of 12,000 W kg^{-1} (at an energy density of 10 W h kg^{-1}) can be achieved at an operating voltage of 1.6 V. The fabrication method is simple, cost-effective, and readily scalable thereby having large commercial potential.

Introduction

With increasing demand for clean and renewable energy, a great deal of research is being targeted towards developing renewable clean energy [1-7]. In particular, on the heels of

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the fast development of light and flexible portable electronic devices, research on efficient flexible energy storage and conversion devices is becoming very important [8-13]. Electrochemical storage devices such as supercapacitors (SCs) are one of the major players in energy storage and conversion due to their outstanding properties such as high power density, good safety, long cycle life, use of economical and abundant raw materials, and cost-effective synthesis [14-22]. SCs store energy using either ion adsorption (electrochemical double layer capacitors, EDLCs) [1,23] or fast surface redox reactions (pseudo-capacitors, PCs) [24,25]. Generally, EDLCs use carbon-active materials as the electrodes and PCs use redox-active materials. Previous studies have shown that the performance of SCs depends mainly on the type and structure of the electrode materials. Although carbon continues to be the dominant electrode materials in commercial SCs, the devices fail to meet the stringent requirements for future large-scale applications [1,26-28]. Therefore, electrode materials with better performance are needed. In this respect, nanostructured electrodes offer many unique properties, for instance, increased active surface areas, short ion transport pathways, better accommodation of strain, enhanced rate capability (or power density), and cycling stability [29-32]. The nanostructured materials that have attracted attention include transition metal oxides, conducting polymers, and hybrid composites which are aimed at replacing or complementing carbon materials to attain higher specific capacitance and better cycle performance [4,33-35]. Among them, metal oxides with high capacity and low cost are especially attractive for advanced electrode materials. MnO_2 has been investigated due to its high specific capacitance (theoretical specific capacitance $\approx 1370\ F\ g^{-1}$), environmental compatibility, and cost effectiveness [36,37]. One of the key issues for Mn-based oxides is the extremely low conductivity (10^{-5}-10^{-6} S/cm) thus hindering electrochemical reactions [38-40]. It is thus desirable to synthesize composites by integrating high capacity MnO_2 with more conductive materials such as carbon nanotubes [41], graphene [42], carbon fibers [37], or other forms of carbon materials [43]. For example, Liu et al. [43] have prepared manganese dioxide (MnO_2)-graphene foam by solution casting and electrochemical methods. The electrodes exhibit high specific capacitance and rate capability. The specific capacitance of MnO_2-graphene calculated at $1\ A\ g^{-1}$ is $422.5\ F\ g^{-1}$. About 54.2% of specific capacitance has been retained when the current density increased from 1 to $10\ A\ g^{-1}$. By using polymer gel electrolytes, the maximum energy density of $31.8\ W\ h\ kg^{-1}$ (at a power density of $453.6\ W\ kg^{-1}$) and power density of $9188.1\ W\ kg^{-1}$ (at an energy density of $18.2\ W\ h\ kg^{-1}$) can be achieved at an operating voltage of 1.8 V. Luo et al. [37] have fabricated ordered whisker-like manganese dioxide (MnO_2) arrays on carbon fibers which deliver high-capacitance performance with specific capacitance up to $274.1\ F\ g^{-1}$ and excellent long cycle-life property with 95% of its specific capacitance retained after 5000 cycles at a current density of $0.1\ A\ g^{-1}$. Wang et al. [44] have fabricated carbon nanoparticles/MnO_2 nanorods flexible solid-state supercapacitors. The device has good electrochemical performance with an energy density of $4.8\ W\ h\ kg^{-1}$ at a power density of $14\ kW\ kg^{-1}$. However, in spite of recent progress so far, to our best of knowledge, highly porous honeycomb MnO_2@carbon fibers core-shell nanocable electrodes have not been reported.

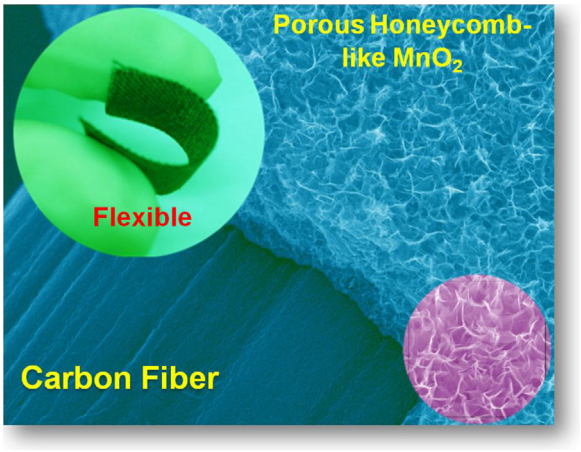

Figure 1 Highly porous honeycomb manganese oxide@carbon fibers core-shell nanocables for flexible supercapacitors.

Herein, highly porous honeycomb MnO_2@carbon fibers core-shell (HMO@CFs) nanocables serving as binder-free electrochemical energy storage materials are synthesized hydrothermally using an *in situ* redox replacement reaction between potassium permanganate ($KMnO_4$) and CFs. As shown in Figure 1, the CFs are the "core" and HMO the "shell" layer. This smart electrode design offer several advantages. Firstly, the CFs core is flexible and light thus permitting the fabrication of collapsible and portable devices. Secondly, the one-dimensional (1D) carbon fibers serve as both the backbone and ideal electron pathway for HMO. Thirdly, the porous honeycomb feature facilitates fast diffusion of ions the surface to the inside of the MnO_2 thereby making full use of the active materials. These desirable features contribute to the improved capacity and cycle life of the supercapacitor.

Experimental section

Synthesis of porous honeycomb-like MnO_2 on carbon fibers (HMO@CFs)

All the reagents were analytical grade and used directly without further purification. Prior to deposition, rectangular carbon fiber cloth ($1.5 \times 4\ cm^2$) was cleaned ultrasonically in acetone, deionized water, and ethanol sequentially for 15 min each, dried, and stored. In the typical synthesis, 0.059 g of $KMnO_4$ was dissolved in 75 mL of deionized water under vigorous stirring for 30 min at room temperature to form a homogeneous amaranth $KMnO_4$ solution (5 mM). The mixture was transferred to a 100 mL Teflon-lined stainless autoclave. The cleaned carbon fibers were immersed in the mixture and the autoclave was kept at 160 °C for 3 h. After natural cooling to ambient temperature, the product was taken out, washed, and vacuum dried at 60 °C to obtain the HMO@CFs. For comparison, the reaction was conducted for 1 and 5 h.

Characterization

The crystal structure and phase of the products were determined by X-ray diffraction (XRD) on a D8 Advance