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Three-Dimensional Nickel Oxide@Carbon Hollow Hybrid Networks with Enhanced Performance for Electrochemical Energy Storage

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ABSTRACT

In this paper, the novel nickel oxide@carbon (NiO@C) hollow hybrid networks (HHNs) consisted of nanotubes with interconnected branches are designed and fabricated via template-assisted electrodeposition method. Electrochemical measurements demonstrate that the NiO@C HHNs electrodes exhibit high specific capacitance (C_{sp}) (572.5 F/g) at current density of 2.5 A/g, which is more than twice as that of NiO hollow networks (HNs) electrode (259.6 F/g). The NiO@C HHNs electrodes show high flexibility and excellent cycle performance (almost no capacitance loss after 2000 cycles) and exhibit superior rate capability (~14% C_{sp} decay with scan rate increasing from 5 to 100 mV/s). The assembled asymmetric supercapacitors (ASCs) based on NiO@C HHNs as positive electrodes and 3D active carbon (AC) as negative electrodes also shows high specific capacitance, excellent cycle performance, and high energy and power densities. Two ASC device units connected in series could drive a red light-emitting diode (LED, 2.0 V) well for more than 60 s after charging at 28 A/g for 10 s. The above results indicate that the NiO@C HHNs own promising potential for electrochemical energy storage.

1. Introduction

Along with the deterioration of ecological environment and energy depletion, scientists are devoting to research and develop the advanced energy storage and conversion systems [1–8]. The supercapacitors (SCs), also known as electrochemical capacitors, have received considerable attention as the promising energy storage devices, owing to their higher power density, safer and longer life cycle compared with batteries, and higher energy density, wider working temperature than the conventional dielectric capacitors [9–18]. Because of the above advantages, the SCs show huge potential applications in electric vehicles, power sources, portable electronics and aerospace fields [19–25]. However, to become the primary devices for power supply, the SCs must be further developed to improve their abilities to deliver, simultaneously, high energy and power densities [26–33].

To realize this objective, the electrodes with high performance have been investigated from a variety of different functional materials [34–43]. Among the various electrode materials for SCs, nickel oxide (NiO) has been considered to be one of the most attractive materials because of its low cost, high abundance,high theoretical specific capacitance (C_{sp}), and environmental friendliness [44–47]. However, the poor conductivity of NiO remains a major challenge and limits rate capability for high power performance and utilization for thick electrodes, thus hindering its wide applications in energy storage systems [48–51]. Based on these considerations, the goal of the present work is to build the advanced NiO supercapacitor electrodes using a simple and scalable fabrication technique and to optimize electrode performance using the controlled functional materials and well-defined hollow hybrid networks (HHNs) with large surface area and minimum resistivity. Here we designed and synthesized novel NiO@C HHNs consisted of nanotubes with inter connected branches via template-assisted electrodeposition technique. The carbon layers are uniformly coated on the surface of NiO and show a great potential for the conductivity enhancement of NiO because of the high conductivity of carbon material. The results in this study prove that the fabricated NiO@C HHNs exhibit high C_{sp}, superior rate capability, high energy/power densities and excellent long-term cycle stability and are promising electrode materials for electrochemical energy storage.

2. Experimental section

2.1. Synthesis of 3D NiO@C HHNs

All chemical reagents used in this study were analytical (AR) grade. Electrodeposition was carried out in a simple three-electrode

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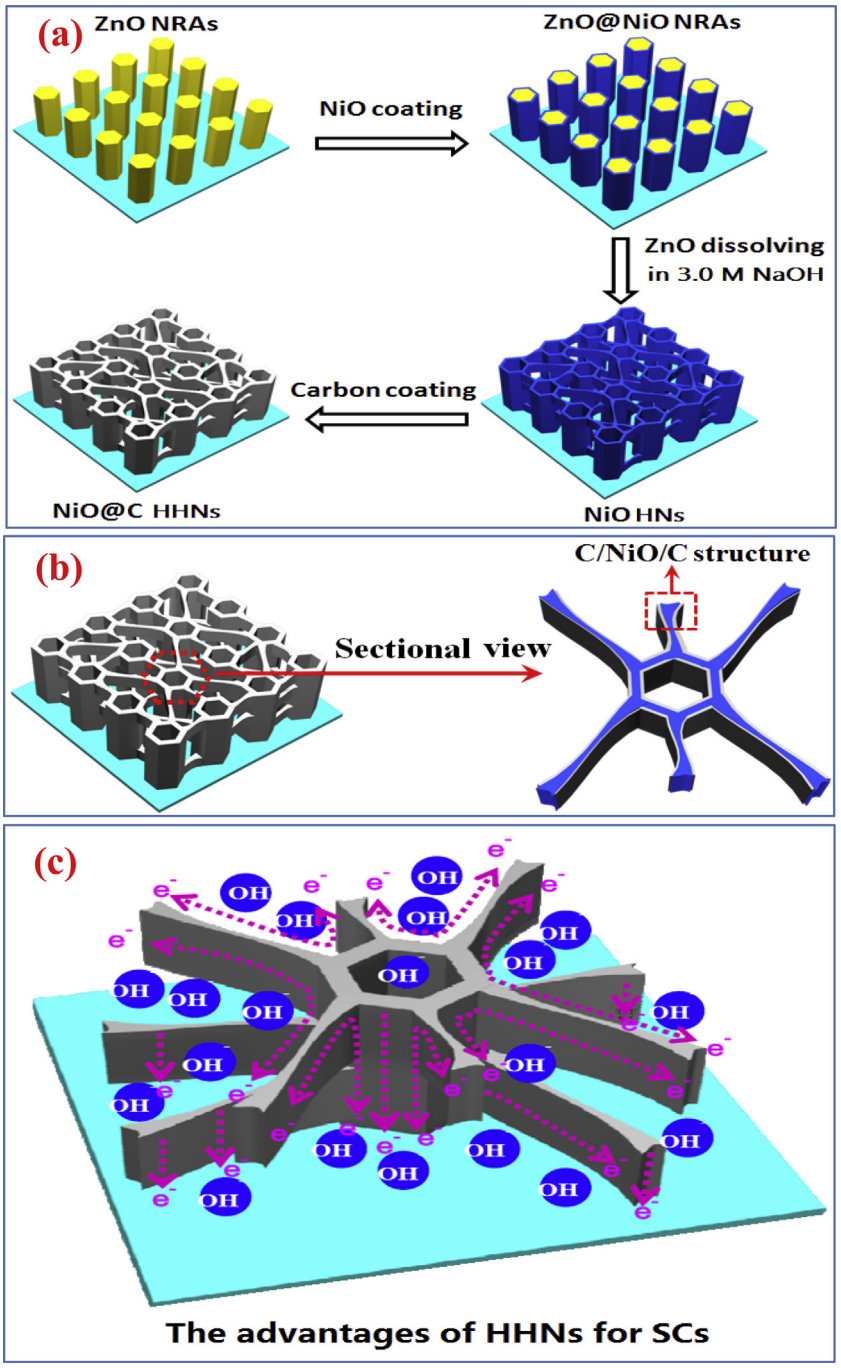
cell via galvanostatic electrolysis, and the graphite electrode was utilized as a counterelectrode (spectral grade, 1.8 cm^2). The 3D NiO@C HHNs were fabricated via following procedures:

i) ZnO nanorod arrays (NRAs) template was electrodeposited in solution of 0.01 M $Zn(NO_3)_2$ + 0.05 M NH_4NO_3 with current density of 0.5 mA/cm^2 at 70 °C for 90 min. Ti thin plates (99.99%, 2.5 cm^2) were used as the conductive substrates for electrodeposition, and they were prepared complying the following steps before each experiment: firstly polished by SiC abrasive paper from 300 to 800 grits, then dipped in HCl solution (5%) for 10 min and rinsed with acetone in ultrasonic bath for 5 min, and finally washed by distilled water.

ii) ZnO@NiO core-shell NRAs were prepared by the electrodeposition of NiO onto the surfaces of ZnO NRAs in solution of 0.1 M $Ni_2SO_4 \cdot 6H_2O$ + 0.006 M citric acid trisodium ($C_6H_5Na_3O_7 \cdot 2H_2O$) + 0.05 M H_3BO_3 at 0.25 mA/cm^2 at 30 °C for 40 min.

iii) NiO hollow networks (HNs) were fabricated by dissolving ZnO templates in 3.0 M NaOH solution for 30 min.

iv) NiO@C HHNs were fabricated via following procedures: the NiO HNs were firstly immersed in 0.1 M β-cyclodextrin solution for 2 h at 70 °C. Then the samples were dried at 60 °C in the oven. Finally the samples were calcined in tube furnace in N_2 atmosphere via following programme: temperature was increased from room temperature to 200 °C and was kept at 200 °C for 2 h,



Scheme 1. (a) Schematic illustration of the fabrication process of NiO@C HHNs; (b) Sectional view of NiO@C HHNs; (c) The advantages of NiO@C HHNs for SCs: large surface area and fast transports of ions and electrons.