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Materials Research Bulletin 41 (2006) 620–627

Materials Research Bulletin

www.elsevier.com/locate/matresbu

Preparation of urchinlike NiO nanostructures and their electrochemical capacitive behaviors

Xian-Ming Liu [a,b], Xiao-Gang Zhang [c], Shao-Yun Fu [a,*]

[a] *Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100080, PR China*
[b] *Graduate School, Chinese Academy of Sciences, Beijing 100039, PR China*
[c] *College of Material Science & Engineering, Nanjin University of Aeronautics and Astronautics, Nanjin 210016, PR China*

Received 14 June 2005; received in revised form 22 August 2005; accepted 2 September 2005
Available online 26 September 2005

Abstract

Urchinlike NiO nanostructures were prepared by thermal decomposition of the precursor obtained via a hydrothermal process using urea as a hydrolysis-controlling agent and polyethylene glycol (PEG) as a surfactant. The structure and morphology of the samples were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM) and infrared absorption spectra (IR). Structure characterizations indicated urchinlike nanostructures for the nickel oxide samples with high purity. Electrochemical properties of urchinlike NiO were examined by cyclic voltammetry and galvanostatic charge–discharge measurements. The results showed that NiO calcined at 300 °C had a higher specific capacitance and better capacitive behavior than NiO calcined at 500 °C. The specific capacitance of about 290 and 170 F g^{-1}, respectively, could be achieved with NiO calcined at 300 and 500 °C in the voltage range of 0.0–0.5 V. The calculated capacitances decreased with the increase of cycle number of the NiO sample. The specific capacitance of NiO calcined at 300 °C decreased to 217 F g^{-1} after 500 cycles. It revealed that the NiO materials exhibited good cycling performance. NiO calcined at 300 °C possessed the high capacitance because it had the high surface redox reactivity due to its special nanostructures.

Keywords: A. Nanostructures; A. Oxides; C. Electrochemical measurements; D. Electrochemical properties; D. Energy storage

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1. Introduction

Electrochemical capacitors (ECs) have greater power density than common batteries and can be deeply discharged without any deleterious effect on lifetime. Compared to dielectric capacitors, electrochemical capacitors have greater energy density. Thus, ECs are becoming attractive energy storage systems particularly for applications involving high power requirements. ECs are also attractive for other applications such as power sources for camera flash equipment, lasers, pulsed light generators and as backup power source for computer memory [1–3]. Energy storage mechanisms of electrochemical capacitors are classed into two areas: (1) double-layer capacitance arising from the charge separation at the electrode/electrolyte interface and (2) pseudocapacitance arising from fast, reversible Faradaic reactions occurring at or near a solid electrode surface. Carbon materials with high surface area are widely used for double-layer capacitors [4]. On the other hand, transition metal oxides like RuO_2 and IrO_2 exhibit Faradaic pseudocapacitance with capacitance reported to be as large as 760 F g^{-1} [5]. But the high cost of these materials limits their commercialization.

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[*] Corresponding author. Tel.: +86 10 62659040; fax: +86 10 62564049/62659040.
E-mail address: syfu@cl.cryo.ac.cn (S.-Y. Fu).

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doi:10.1016/j.materresbull.2005.09.006

Then, other metal oxides such as nickel oxides [6–14], cobalt oxides [15] and manganese oxides [16–19] are studied because they are inexpensive and exhibit pseudocapacitance behavior similar to that of RuO_2 and IrO_2.

Nickel oxide is being considered as one of the promising potential electrode materials for electrochemical capacitors as well as for many other applications such as catalyst, electrochromic films, fuel cell electrodes and gas sensors. Nickel oxide films for the electrochemical capacitors can be prepared by electrochemical route [7–9,11,12], sol–gel method [6] and electrostatic spray deposition technique [10]. In the case of nickel oxide films, the specific capacitance for a single electrode was observed to be from 200 to 278 F g^{-1} [7–9,11,12], but those synthesis conditions were rigid and the deposition quantity was restricted of the dimension of the electrode. Other nanostructured nickel oxide can be prepared by simple preparation method and exhibits high specific capacitance comparable to nickel oxide films. It was reported that NiO crystalline synthesized by a simple liquid method displayed a specific capacitance of approximately 300 F g^{-1} in the range of 0.0–0.5 V, and mesoporous NiO with a controlled pore structure can exhibit a high specific capacitance and good capacitive behavior [13,14]. In our previous work [20], since the conductivity of NiO nanocrystals are very low and pseudocapacitors fabricated by NiO electrodes have low power and energy density, the low capacitance and energy density of NiO can be improved by introduction of RuO_2 into NiO-based composite electrode by co-precipitation method.

Recently, nanostructured electrode materials have attracted great interests since the nanostructured electrodes show better rate capabilities than conventional electrodes composed of the same materials. To the best of our knowledge, there has been no report on selectively controlled 3D morphologies (such as urchinlike nanostructures) for NiO under mild conditions. Herein, we demonstrate a selected-control hydrothermal method to synthesize highly pure uniform urchinlike NiO nanostructures via the reaction between $Ni(NO_3)_2$ and urea when the polymers (PEG-10,000) were introduced into this system. The structure, morphology and electrochemical capacitive behavior of the urchinlike NiO are discussed.

2. Experimental

2.1. Preparation of urchinlike NiO

All the chemicals used in this study were analytical grade and used without further purification. Deionized water was used throughout. Nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$), urea ($CO(NH_2)_2$) and polyethylene glycol (PEG, MW = 10,000) were all supplied by Beijing Chemical Reagent Company. In a typical procedure, $Ni(NO_3)_2{\cdot}6H_2O$ (0.004 mol), $CO(NH_2)_2$ (0.016 mol) and PEG (0.4 g) were placed in a conical flask with 40 mL deionized water, stirred with a magnetic stirrer at room temperature until a transparent solution was obtained. The mixed solution was then transferred into a Teflon-lined stainless steel autoclave, sealed and maintained at 100 °C for 24 h. After the reaction was complete, the resulting light green solid product was filtered off, washed with distilled water and absolute ethanol several times, respectively, to remove the possible absorbed ions, and then dried at 80 °C in vacuum. The precursor of NiO were calcined in air at 300 and 500 °C, respectively, for 2 h to obtain NiO powders which color is absolutely dark. The calcined products were then collected for analysis.

2.2. Structure characterization

The as-obtained products were characterized by X-ray power diffraction (XRD) using a M18XCE X-ray power diffractometer equipped with graphite-monochromated Cu Kα radiation ($\lambda = 1.54178$ Å), employing a scanning rate $0.02^\circ\ s^{-1}$ in the 2θ ranging from 10° to 80°. The scanning electron microscopy (SEM) images were obtained using a HITACHI S-4300 microscope. The infrared (IR) spectra were recorded on a BRUKER EQUINOX-55 IR spectrometer on samples palletized with KBr powders.

2.3. Electrochemical tests

Electrodes for electrochemical capacitors were prepared by mixing the prepared powders with 25 wt.% carbon black and 5 wt.% PTFE binder of the total electrode mass. A small amount of water was then added to those composites to make more homogeneous mixtures, which were pressed on nickel grid (1.2×10^7 Pa) to get an approximate thickness of 0.2 mm. The loading density of the electroactive materials was 20 mg cm^{-2}. All