Materials Chemistry and Physics 143 (2014) 1344–1351

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

High-yield synthesis of carbon nanotube–porous nickel oxide nanosheet hybrid and its electrochemical capacitance performance

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HIGHLIGHTS

- CNT–NiO hybrid nanocomposites were large-scale fabricated.
- CNT–NiO presented a high specific capacitance of 759 F g^{-1}.
- The obtained CNT–NiO exhibit excellent cycling performance.

ARTICLE INFO

Article history:
Received 29 March 2013
Received in revised form
12 October 2013
Accepted 24 November 2013

Keywords:
Nanostructures
Chemical synthesis
Electrochemical techniques
Electrochemical properties

ABSTRACT

This study reports an easy chemical conversion route toward large-scale fabrication of carbon nanotube (CNT)–porous nickel oxide (NiO) hybrid nanocomposites as supercapacitor electrode materials. The electrocapacitive performance of CNT–porous NiO hybrids is evaluated by cyclic voltammetry and galvanostatic charge–discharge measurements. The synthesized CNT–NiO hybrid nanocomposite electrode presents a high specific capacitance of 759 F g^{-1} at 0.5 A g^{-1} in 6 M KOH aqueous electrolyte, which is almost twice that of pure NiO nanoparticle (388 F g^{-1}) electrodes and nine times of that of commercial NiO particle (88.4 F g^{-1}) electrodes. Furthermore, good capacitance retention is achieved after 1000 cycles of galvanostatic charge–discharge. The synergistic effects from the pseudocapacitance of porous NiO particles, good electrical conductivity, and open tip CNTs attribute to the high capacitance performance.

1. Introduction

An ideal electrochemical electrode material for practical applications should have high electrochemical capacity and cyclic stability [1], large-scale processible material form (powder or slurry) for device fabrication [2], low cost, and environment friendly [3,4]. Nickel oxide (NiO) has been widely used as a battery electrode material because of its low cost [5], abundant natural resources, theoretical ultrahigh specific capacitance of 2584 F g^{-1}, and low environmental toxicity [6,7]. Similar to other metal oxide electrode materials, large specific volume change commonly occurs in the NiO host matrix during the cycling of the charging–discharging processes. This characteristic leads to the pulverization of the NiO electrode and rapid capacity decay. Moreover, the poor electrical conductivity of NiO reduces its bulk electrode charging speed and full utilization of its capacitance [8–10]. Thus, persistent involvement has been attempted in the recent years to resolve these problems. Several studies have shown that NiO nanoparticles (NPs) with an increased specific surface area are favorable to ion exchange with electrolyte environments, consequently increasing its specific capacitance [11–13]. Furthermore, compositing NiO with conductive fillers, such as carbon nanotube (CNT) and graphene, can effectively improve its cyclic stability and partially improve the specific capacitance of NiO composite electrodes to as high as 525 F g^{-1} because of the high electron transfer rate of build in conducting network during faradaic charge transfer reactions [14–17]. In addition, an appropriate approach toward large-scale fabrication of nanostructured NiO-based composite is still a great challenge for practical applications.

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http://dx.doi.org/10.1016/j.matchemphys.2013.11.045

In the current study, a hard template technique was developed to prepare CNT–porous NiO hybrid nanocomposites. The formation processes of the composite is illustrated in Fig. 1. The activated CNT acts as a template for polyethylene glycol (PEG) and ammonia to direct the nucleation and growth of $Ni(OH)_2$. The as-obtained CNT–$Ni(OH)_2$ hybrid was further calcined in a furnace to dehydrate $Ni(OH)_2$ into NiO and decompose PEG. This treatment led to the formation of porous NiO nanoplates uniformly dispersed in the conducting CNT network. The nanostructured electrodes with CNT–NiO hybrid materials exhibited a 759 F g^{-1} high specific capacitance because of the enhanced interfacial faradaic process and effective charge accession. Meanwhile, the CNT build in the network largely reinforced the reversibility of the electrochemical performance. The cyclic charge–discharge process can preserve more than 95% of the initial specific capacitance over 1000 cycles. Furthermore, the present CNT–NiO nanocomposites can be synthesized in the level of tens of grams, which are critical for practical applications as electrode materials.

2. Experimental

2.1. Chemicals

CNTs were purchased from Shenzhen Nano Tech Port Co., Ltd. Other A.R. grade chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. and were used as received without further purification.

2.2. Treatment of CNTs

The raw materials were treated as previously reported [18]. CNTs were refluxed in 68 wt% HNO_3 at 180 °C for 12 h. The mixture was then washed several times with deionized water on a sintered glass filter. Finally, the CNTs were dried in an oven at 100 °C for 5 h.

2.3. Synthesis of CNT–porous NiO hybrid nanocomposites

Approximately 6.5 g of $NiCl_2 \cdot 6H_2O$, 8 g of PEG6000, and 50 mL of ethanol were dissolved in 100 mL H_2O. In addition, 2 g of treated CNTs were initially immersed in a mixed solution, and stirred at 60 °C for 0.5 h. Approximately 1 L of 1% ammonium hydroxide was then dropped into the suspension. After filtering the suspension with deionized water and drying at 100 °C for 3 h, the precursor of CNT–$Ni(OH)_2$ composites was obtained. The precursor was finally calcined at 380 °C for 2 h to obtain CNT–porous NiO hybrid nanocomposites. NiO NPs were prepared via the aforementioned method without CNTs. All experiments were carried out under normal atmospheric environments.

2.4. Characterization

X-ray diffraction (XRD) analysis of phases was carried out using a Rigaku D/MAX 24000 diffractometer with Cu Kα radiation ($\lambda = 1.54056\text{Å}$) and a scanning speed of 0.02° s^{-1}. The accelerating voltage and emission current were 40 kV and 40 mA, respectively. The sample morphology was checked using a scanning electron microscopy (SEM, JSM-6700F) at an accelerating voltage of 30 kV equipped with an Inca energy dispersive spectrometer (EDS). The fine structure of the CNT–NiO hybrid nanocomposites was further investigated on a Tecnai G2 F20 S-Twin high resolution transmission electron microscope (HRTEM) with an accelerating voltage of 200 kV. The thermal decomposition behavior of the precursor was analyzed using thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) analysis on a Netzsch–STA 409 thermal analysis device. TG-DSC determination was carried out in an air flow with a 10 °C min^{-1} temperature increasing rate from room temperature to 1000 °C. Core level analysis was conducted on an X-ray photoelectron spectrum (XPS) using a Kratos AXIS Ultra DLD X-ray photoelectron spectrometer at room temperature with 1486.6 eV X-ray from the Al Kα line.

2.5. Electrochemical measurements

All electrochemical experiments were carried out using a three-electrode system at room temperature. Fabricating the working electrodes required mixing 80 wt% active materials with 15 wt% graphite and 5 wt% polyvinylidene difluoride (PVDF) binder. Afterward, the mixture was diluted with a small amount of deionized water to form homogeneous mixture slurry. After a short period of drying by evaporation, the resulting paste was pressed into a pretreated nickel grid under a pressure of 1.2×10^7 Pa. The electrode was then dried for 12 h at room temperature under ambient atmosphere. Each electrode has a geometric surface area of 10 mm × 10 mm. Electrochemical measurements were carried out using 6 M KOH aqueous solution as electrolyte. Before the tests, the electrodes were soaked overnight in 6 M KOH aqueous solution. A platinum foil and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. All cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge–discharge processes were performed on a CHI 660D workstation. The galvanostatic charge–discharge process was carried out with current densities ranging from 0.5 A g^{-1} to 5.0 A g^{-1}. The specific capacitance (C [F g^{-1}]) of the electrode

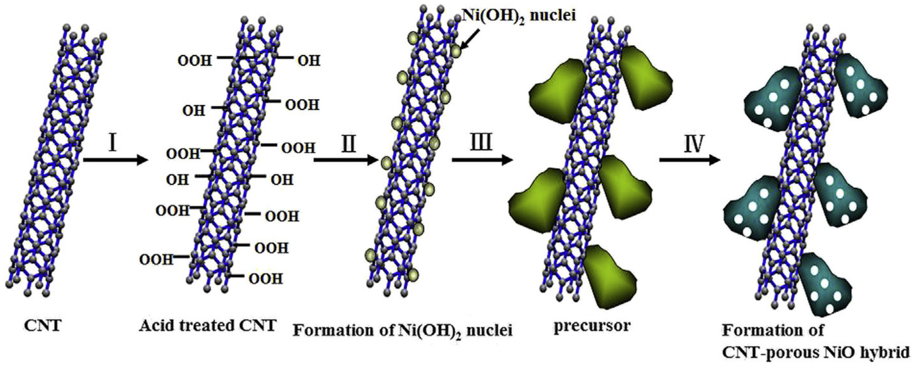

Fig. 1. Schematics for the formation of CNT–porous NiO hybrid nanocomposites: (I) acid treatment; (II) formation of nuclei; (III) growth of $Ni(OH)_2$; and (IV) calcination to CNT–porous NiO hybrid nanocomposites.