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Facile synthesis of a nano-structured nickel oxide electrode with outstanding pseudocapacitive properties

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ABSTRACT

A superior electrode for high-performance supercapacitors has been designed by growing homogeneous NiO nanoparticles on conductive Ni foam substrate through a facile two-step method. The preparation strategy involves the electrodeposition of nickel hydroxide precursor on Ni foam and subsequent low-temperature annealing process. These NiO nanoparticles are interconnected with each other, forming a loose network with a highly open and porous structure. This unique 3D NiO–Ni foam electrode manifests the electrolyte penetration and ion migration as well as large electroactive surface area. As a result, outstanding pseudocapacitive performance is achieved with a high specific capacitance ($2558\,\mathrm{F\,g^{-1}}$ at $2\,\mathrm{A\,g^{-1}}$ in a potential window of 0.5 V) and excellent rate capability (70% capacity retention at $40\,\mathrm{A\,g^{-1}}$), which shows great potential in the development of high-performance energy-storage systems.

1. Introduction

Supercapacitors, as a new class of energy storage devices, have raised considerable attention over the past decade because of higher power delivery and better cycling lifespan over batteries [1–3]. The fast charge and discharge capability make supercapacitors favorable for applications in hybrid vehicles, portable electronics, and backup energy systems [4]. It is noted that these supercapacitor performance is mainly determined by electrode materials in terms of the morphology, size, porosity and so forth. Of all the metal oxides investigated as electrode materials for pseudocapacitor, hydrated ruthenium oxide is considered to be the most advantageous one, which has a high capacitance, reversible charge–discharge features, and good electrical conductivity [5]. However, commercial application of ruthenium oxide is impeded due to its high cost, low porosity and toxic nature. Therefore, it is imperative to develop alternative electrode materials/structures with superior electrochemical performance but at a low cost for the development of high-performance supercapacitors.

Nickel oxide, known to be cheap and environment friendly, is a promising electrode material for pseudocapacitors. The theoretical capacitances of NiO in a potential window of 0.5 V is up to $2583\,\mathrm{F\,g^{-1}}$ [6,7]. To date, there have been a variety of reports of the synthesis of different NiO nanostructures including nano/microspheres [8,9], nanoflowers [10], nanosheets [11], nanofibers [12], nanowires [13],

and nano-films with open pores [14,15]. Different morphologies and microstructures show substantial differences in electrochemical performance due to dissimilarities in the electrode/electrolyte interface properties and ion transfer rates during the charge storage processes. In addition, the pseudocapacitive performance of nickel oxide is dependent on microwave heating [16], intercalating anions [17], and the ionic nature of the surfactant during synthesis [18]. Despite significant progress, the observed specific capacitances in most cases are much less than the theoretical value, especially at high rates, as the active NiO materials are typically too insulating to support fast electron transport.

To achieve high energy and power density simultaneously, an emerging new concept is to develop various NiO/Ni electrodes for supercapacitors. This electrode architecture has several particular merits. On the one hand, the conductive network of Ni cores can minimize the lattice mismatch with the active NiO surface layer so that good adhesion could be obtained. On another, this design renders other auxiliary components like conductive agents and binders completely unnecessary and further optimizes the electrode performance using a well-defined electrode network with minimum resistivity. For instance, Xiao et al. reported a high specific capacitance of $900\,\mathrm{F\,g^{-1}}$ for monolithic NiO/Ni electrode with high-energy ($60\,\mathrm{Wh\,kg^{-1}}$) and high-power ($10\,\mathrm{kW\,kg^{-1}}$) densities [19]. In addition, the Ni–NiO core–shell inverse opal electrode [20], which was fabricated by the polystyrene template, demonstrated increased supercapacitor performance. Zhu et al. prepared the coaxial NiO/Ni nanowire arrays with the aid of an AAO template and a specific capacitance of 140–$179\,\mathrm{F\,g^{-1}}$ is achieved at a scan rate of $10\,\mathrm{mV\,s^{-1}}$ [21]. Although a wide variety of NiO/Ni have been synthesized and

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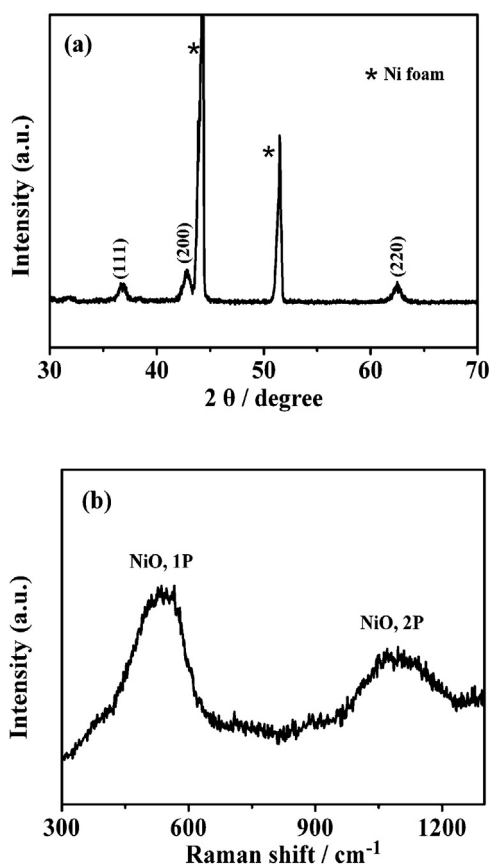 *E-mail addresses:* xfwang@tongji.edu.cn, tungstenbeauty@gmail.com (X. Wang).

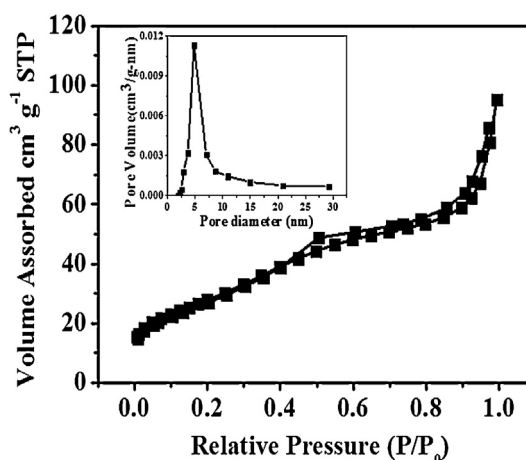Fig. 1. (a) XRD pattern and (b) Raman spectrum of the NiO–Ni foam.

Fig. 2. Nitrogen adsorption and desorption isotherms measured at 77 K for the NiO sample. The inset shows the corresponding BJH pore size distribution.

tested, it still represents a great challenge to identify the most promising structure that dramatically enhance the supercapacitor performance relative to the high theoretical specific capacitance of nickel oxide.

In this paper, we develop a NiO–Ni foam through a facile two-step strategy and the hybrid structure is then directly used as an electrode for electrochemical evaluation in a three-electrode system at room temperature. The synthesis involves the electrodeposition of the nickel hydroxide precursor on Ni foam and subsequent thermal transformation to ultrafine NiO particles in the absence of any templates. Remarkably, the as-prepared 3D hybrid structure of NiO–Ni foam, manifests ultrahigh capacitance and excellent rate capability, making it a promising electrode for high performance supercapacitors.

2. Experimental

2.1. Synthesis of the NiO–Ni foam

All the chemicals were of analytical grade and were used without further purification. Ni foam (approximately 1 cm × 3 cm, Changsha Lyrun New Material Co. Ltd., Changsha, PR China) was carefully cleaned with 6 M HCl solution in an ultrasound bath for 30 min in order to remove the NiO layer on the surface, and then rinsed with de-ionized water and absolute ethanol. The electrodeposition was performed in a standard three-electrode glass cell consisting of the clean Ni foam working electrode, a platinum plate counter electrode and a saturated calomel reference electrode (SCE) at room temperature. The nickel hydroxide precursor was electrodeposited upon Ni foam in a 6 mM $Ni(NO_3)_2 \cdot 6H_2O$ aqueous electrolyte using on a CHI660D electrochemical working station.

The electrodeposition potential is −1.0 V (vs. SCE). After electrodeposition for 2 min, the green Ni foam was carefully rinsed several times with deionized water and absolute ethanol with the assistance of ultrasonication, and finally dried in air. Then, the sample was put in a quartz tube and calcined at 250 °C in air atmosphere for 2 h with a ramping rate of 2 °C min^{-1} to transform into ultrafine NiO nanoparticles. In average, 0.85 mg of NiO is grown on Ni foam (1 cm^2), carefully weighted after calcination.

2.2. Materials characterization

The morphology and microstructure of the NiO–Ni foam were characterized by field emission scanning electron microscopy (FESEM; JSM-6701F, Japan), transmission electron microscope (TEM; JEOL, JEM-2100, Japan) and X-ray diffraction (XRD; Philips PC-APD with Cu Kα radiation). The NiO powder was scratched from Ni foam. Samples for TEM observation were suspended in ethanol and supported on a carbon-coated copper grid. Raman spectrum was collected using a 514 nm laser with RM100 under ambient conditions, with a laser spot size of about 1 mm.

2.3. Electrochemical measurement

The NiO–Ni foam directly acted as the working electrode for the following electrochemical tests by cyclic voltammetry (CV), galvanostatic charge–discharge and electrochemical impedance spectroscopy (EIS) performed with a CHI660D electrochemical working station. All measurements were carried out in a three-electrode cell with a working electrode, a platinum plate counter electrode and a saturated calomel electrode (SCE) as the reference electrode at room temperature. The electrolyte was a 1 M KOH aqueous solution. Before electrochemical measurement, the NiO–Ni foam electrode was electrochemically activated at 10 mV s^{-1} for 10 CV cycles in a stable potential window of −0.08 and 0.42 V, which was similar to previous work [22].

3. Results and discussion

The preparation process of the NiO–Ni foam mainly includes two steps. In the first step, a green nickel precursor is electrodeposited onto the Ni foam. When the electrical current passes the electrolyte containing $Ni(NO_3)_2$, nitrate ions can be reduced on the cathodic surface to produce hydroxide ions. The generation of OH$^-$ at the