



Solvent influence on the morphology and supercapacitor performance of the nickel oxide



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ABSTRACT

NiO with different morphologies were fabricated via hydrothermal method in different kinds of solvent. The morphology of the obtained NiO samples varied from nanoflakes to nanoparticles with the different volume ratios of water to ethanol. The electrochemical results showed that the specific capacitance of NiO-S5 obtained in ethanol was up to 1337.5 F g^{-1} at a current density of 0.62 A g^{-1} , which was greatly higher than that of the other samples. These results indicated that NiO-S5 had the superior electrochemical behavior which may be due to its small-size effect.

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1. Introduction

Recently, the energy crisis is increasingly serious so that developing alternative energy storage system is urgent and challenging [1,2]. As a potential electrochemical power source, supercapacitors have attracted much interest because of its high power density, preferable cycling stability and low maintenance cost [3,4]. According to the energy storage mechanism [5,6], supercapacitors can be classified as electrochemical double layer capacitors (EDLCs) and pseudocapacitors. Generally, carbon materials are electrode materials used in EDLCs, while electrode materials in pseudocapacitors are transition metal oxides, such as MnO_2 [7], Co_3O_4 [8], NiCo_2O_4 [9] and NiO [10–12]. Among them, NiO has been paid much attention as a promising electrode material due to its outstanding theoretical specific capacitance (3750 F g^{-1}), high chemical stability, rich natural abundance and environmental benignity [5,10–13]. At present, various NiO nanostructures have been synthesized via hydrothermal process which is effective to prepare nanomaterials [5,13,14]. However, rarely reports have concerned with the influence of solvent on the NiO morphology and its supercapacitive performance using hydrothermal and solvothermal method. Herein, NiO nanomaterials with different morphologies are prepared via hydrothermal and solvothermal method in different solvents by means of adjusting the volume ratio of water to ethanol. The electrochemical results show that the obtained NiO nanomaterials in different conditions exhibit great difference in pseudocapacitive performance.

2. Experimental

2.1. Materials synthesis

The synthesis process is as follows. 1.188 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.200 g NaOH were dissolved in 30 ml ethanol. Then the obtained solution was transferred to a Teflon-lined stainless steel autoclave and maintained at 120°C for 24 h. After cooling down to room temperature, the precipitate was filtrated and washed with ethanol. Then the obtained precipitate was dried at 60°C and calcined at 300°C for 2 h. In order to investigate the influence of the solvent on the morphology and electrochemical performance, the product was fabricated under different volume ratios of the deionized water to ethanol: 30:0 (S1), 20:10 (S2), 15:15 (S3), 10:20 (S4), 0:30 (S5) (V/V). The corresponding samples were marked as NiO-S1, NiO-S2, NiO-S3, NiO-S4 and NiO-S5, respectively.

2.2. Characterization

The obtained samples were characterized by X-ray powder diffraction (XRD) with a Rigaku D/Max-3B diffractometer using $\text{Cu-K}\alpha$ radiation. The morphology was observed by field emission scanning electron microscopy (FESEM, JEOL JSM-6701 F).

2.3. Electrochemical measurements

All the electrochemical measurements were carried out in a three-electrode test cell in a 6 M KOH aqueous solution. The working electrode was fabricated by mixing the electroactive material, carbon black and poly(tetrafluoroethylene) at a weight

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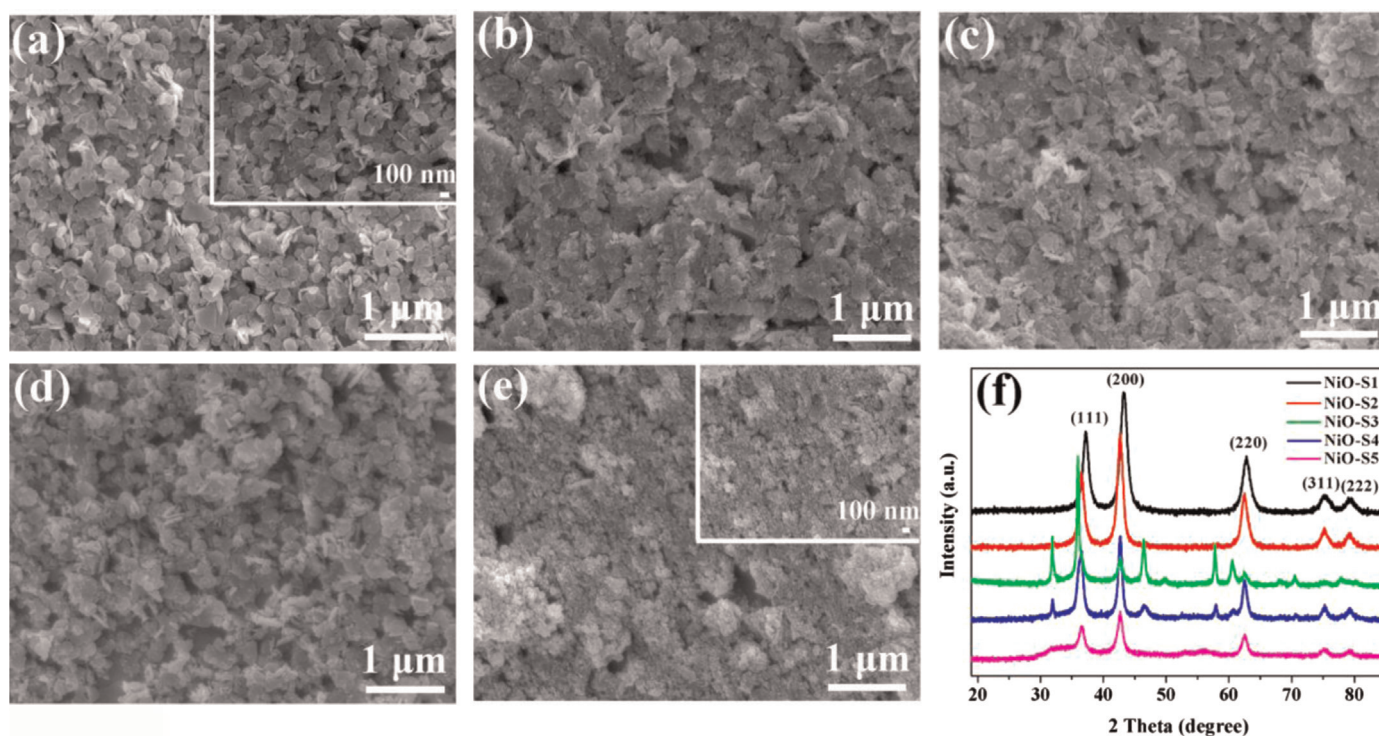


Fig. 1. FESEM images of (a) NiO-S1, (b) NiO-S2, (c) NiO-S3, (d) NiO-S4 and (e) NiO-S5, (f) XRD patterns of the five samples. (The insets are the high resolution images.).

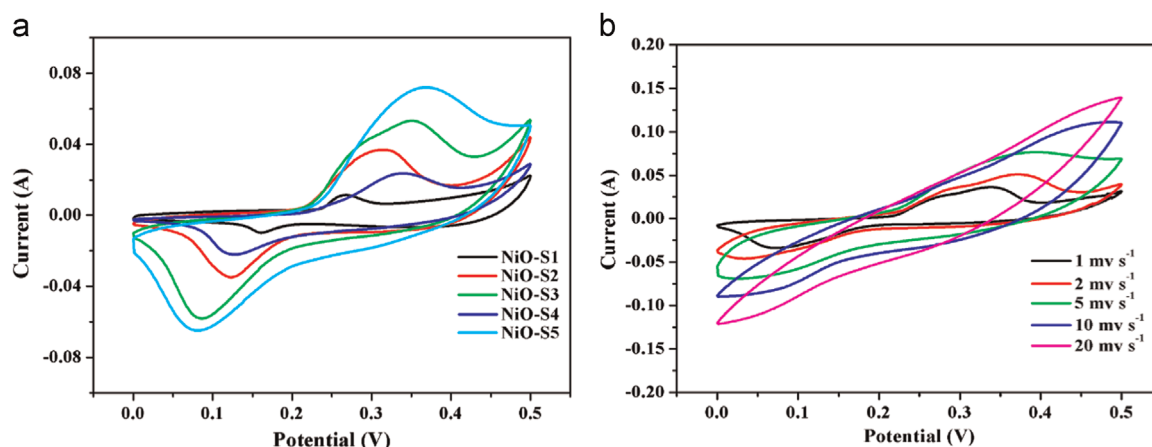


Fig. 2. (a) CV curves of NiO-S1, NiO-S2, NiO-S3, NiO-S4 and NiO-S5 at a scan rate of 5 mV s^{-1} , (b) CV curves of NiO-S5 at different scan rates.

ratio of 80:10:10 to form a homogeneous slurry which was coated onto the nickel foam and was dried at 80°C for 12 h. A platinum sheet and Ag/AgCl were used as the counter and reference electrodes, respectively. Cyclic voltammograms were recorded at different scan rates from 1 to 20 mV s^{-1} in the potential range of 0–0.5 V. Galvanostatic charge–discharge curves were performed at different current densities within the potential window from 0 to 0.4 V.

3. Results and discussion

Fig. 1 shows the morphologies of the NiO nanomaterials prepared under different conditions. It can be clearly seen that the morphology of NiO obtained in pure water is nanoflakes with the thickness of 20–30 nm. When the volume of ethanol increases gradually, NiO nanoflakes are fragmented (shown in Fig. 1b, c and d). In Fig. 1e, NiO nanoparticles are obtained in absolute ethanol.

Consequently, the volume ratio of the deionized water to absolute ethanol has most significant influence on the morphology of NiO nanomaterials.

Fig. 1f shows the XRD patterns of NiO-S1, NiO-S2, NiO-S3, NiO-S4 and NiO-S5. All the diffraction peaks at 37.2° , 43.3° , 62.9° , 75.4° and 79.4° can be indexed as (111), (200), (220), (311) and (222) crystal planes of a cubic NiO phase (JCPDS card No. 47–1049). The extra peaks in the XRD patterns of NiO-S3 and NiO-S4 correspond to the NiCl_2 (JCPDS card No. 22–0747) which comes from the raw material. The XRD pattern for the NiO-S5 sample clearly shows that all the diffraction peaks can be attributed to NiO and there are no other diffraction peaks about impurity.

The cyclic voltammetry (CV) curves for the obtained NiO samples at a scan rate of 5 mV s^{-1} are presented in Fig. 2a. It can be clearly seen that there are a couple of redox peaks in the CV curves of these five samples, representing the corresponding faradic oxidation/reduction reactions. The oxidation peak is the reaction of NiO converted to NiOOH, whereas the reduction peak is

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