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The precipitant influence on the electrochemical performance of $NiCoO_2$ nanostructure

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ABSTRACT

Different precipitants are employed to fabricate $NiCoO_2$ with various morphologies. X-ray powder diffraction characterization demonstrates that the $NiCoO_2$ products obtained using different precipitants display the same crystallization. The electrochemical performance display that the specific capacitance of the $NiCoO_2$ nanostructure obtained using urea is up to 328.5 $F\ g^{-1}$ at a current density of 0.62 $A\ g^{-1}$ in 2 M KOH aqueous electrolyte. The obvious redox peaks on the cyclic voltammetry curves show that the $NiCoO_2$ displays pseudocapacitor performance. The cycling stability reveals that the specific capacitance retains 95.2% after 1500 cycles at different current densities, indicating superior rate capability of the $NiCoO_2$-urea electrode. These results indicate a promising potential application of $NiCoO_2$ for using as an effective electrode material in supercapacitors.

1. Introduction

Electrochemical capacitors (ECs), a new energy storage system, have attracted more interest because of their high power capability, excellent cycling stability and high energy density compared with common batteries [1–3]. According to the energy storage mechanism, ECs can be classified into electrochemical double layer capacitors and pseudocapacitors [4–6]. Transition metal oxides are frequently used as the electrodes in pseudocapacitors and have been extensively studied. Among them, Co_3O_4 has been extensively studied as a promising alternative electrode material in supercapacitors because of its natural abundance and high theoretical specific capacitance [7–9]. However, the disadvantages of Co_3O_4, such as toxicity, valuableness and low electronic conductivity, have hindered its development. Replacing Co_3O_4 partially by co-friendly and cheaper alternative metals is an efficient approach to solve the above issue. At present, nickel cobalt oxide ($NiCoO_2$) has been deemed to a potential cost effective and scalable alternate for ECs owing to its inherent advantages, including low cost, abundant resources and environmental benignity [10,11]. Moreover, as a binary metal oxide, $NiCoO_2$ possesses better electrical conductivity and higher electrochemical activity than individual nickel oxide or cobalt oxide [12]. Otherwise, the synergistic effect of the binary $NiCoO_2$ is also beneficial to its electrochemical performance.

Recently, nickel cobalt oxides with different nanostructures, including nanosheets, nanotubes and the formation of nanocomposites with other materials have been synthesized [13–15]. It is well known that the precipitant has a significant effect on the $NiCoO_2$ nanostructure and the electrochemical performance. In this study, $NiCoO_2$ with various morphologies is fabricated via solvothermal method using urea, NaOH and CH_3COONa as precipitants. The electrochemical results of the corresponding samples exhibit that the $NiCoO_2$ obtained using urea display superior pseudocapacitive performance than the other two samples obtained using NaOH and CH_3COONa, respectively. This result provides theoretical foundation for nickel and cobalt based electrode materials in electrochemical energy-storage devices.

2. Experimental section

2.1. Material synthesis

In a typical process, $NiCl_2$ $6H_2O$ (5 mmol), $CoCl_2$ $6H_2O$ (5 mmol) and precipitant were dissolved in 30 ml anhydrous ethanol. After magnetically stirring for 30 min, the uniform and clear solution was transferred into a Teflon-lined stainless steel autoclave and maintained at 120 °C for 24 h in an electric oven. After cooled to room temperature naturally, the product was centrifuged and washed with deionized water and anhydrous alcohol for several times. The obtained precipitate was dried at 60 °C for 8 h in an electric oven and subsequently calcined at 400 °C for 3 h in air at the rate of 2 °C min^{-1} to obtain the final product. The products obtained using different precipitants were marked as $NiCoO_2$-urea, $NiCoO_2$-NaOH and $NiCoO_2$-CH_3COONa, respectively.

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2.2. Materials characterization

The characterization analysis of the obtained $NiCoO_2$ nanostructures was performed by X-ray powder diffraction (XRD) on a Rigaku diffractometer. The field-emission scanning electron microscopy (FESEM) and transmission electron microscope (TEM) were used to investigate the morphologies.

2.3. Electrochemical measurements

Electrochemical tests were performed with a three-electrode test cell on a CHI660E electrochemical working station in 2 M KOH electrolyte. The working electrode was fabricated by mixing the active material, acetylene black and polytetrafluoroethylene with a mass ratio of 80:10:10 to form homogeneous slurry (The total mass of the electrode is 10 mg) which was pressed onto the nickel foam as the working electrode and then was dried at 80 °C. The platinum sheet and Ag/AgCl were used as the counter and reference electrodes, respectively. Cyclic voltammograms (CV) were tested within the potential window of 0–0.8 V. Galvanostatic charge-discharge (GCD) curves were performed in the potential range of 0–0.5 V at different current densities. Electrochemical impedance spectroscopy (EIS) were measured in the frequency range of 10^{-2}–10^{5} Hz.

3. Results and discussion

FESEM micrographs vividly depict the morphology of $NiCoO_2$ products prepared using different precipitants. From Fig. 1, the nanostructure of $NiCoO_2$-NaOH is hollow structure gathered by the $NiCoO_2$ nanoparticles, which is different from $NiCoO_2$-urea and $NiCoO_2$-CH_3COONa. However, the TEM image (shown in Fig. S1) exhibits that the $NiCoO_2$-urea displays micropores morphology which may be due to the gas emission from decomposition of $NiCoO_2$-urea in the annealing procedure. The X-ray powder diffraction patterns of the $NiCoO_2$ nanostructures prepared using different precipitants are shown in Fig. 1d. All the diffraction peaks for the $NiCoO_2$-urea, $NiCoO_2$-NaOH and $NiCoO_2$-CH_3COONa are similar. The diffraction peaks at 23.4°, 31.2°, 37.3°, 43.2° and 62.8° can be indexed to the (111), (220), (311), (400) and (440) crystal planes of cubic $NiCoO_2$ (JCPDS card No. 20–0718). It is clearly seen that the (400) and (440) peaks in the XRD pattern of the $NiCoO_2$-urea are more sharp than the corresponding peaks of $NiCoO_2$-NaOH and $NiCoO_2$-CH_3COONa, indicating the better crystallinity of the $NiCoO_2$-urea sample.

CV is carried out to explore the electrochemical behavior of the three $NiCoO_2$ electrodes. From Fig. 2a, the current density-potential (CDP) curves of the three electrodes tested at a scan rate of 5 mV s^{-1} show a pair of obvious redox peaks, indicating the presence of pseudocapacitive effect. Significantly, a obvious difference can be observed in the CDP curve area among the three electrodes, and the current density at the same potential for the $NiCoO_2$-urea nanostructure is higher than that of the other two electrodes, which implys its higher specific capacitance. In order to further investigate the rate capability of the $NiCoO_2$-urea electrode, the CV curves at various scan rates are collected. From Fig. 2b, the shapes of these CV curves do not significantly change as the scan rate increase from 1 to 40 mV s^{-1}, which reveals the ideal rate capability and good charge-collection ability of the $NiCoO_2$-urea nanostructure. Additionally, with the scan rate increased, the potential and the current at the redox peaks shifted

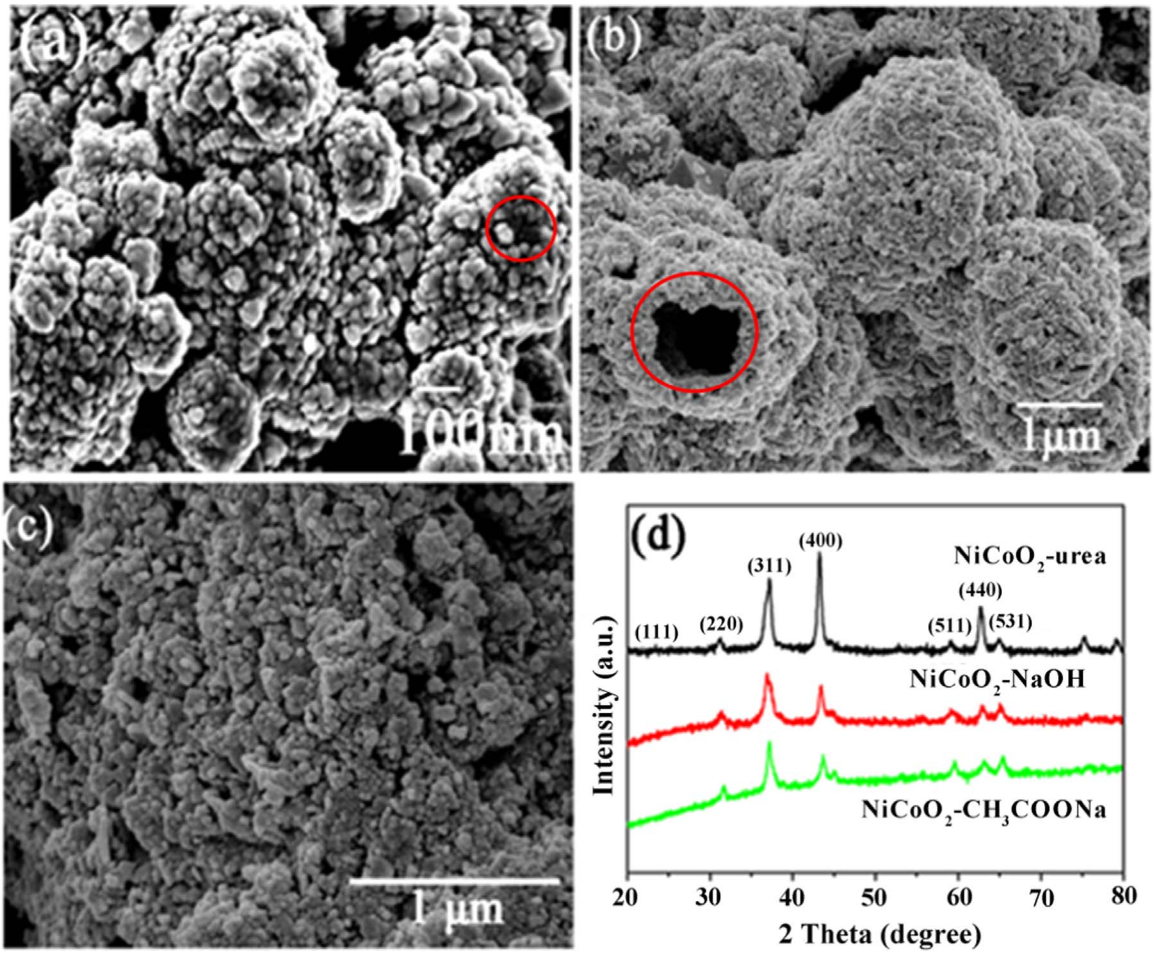

Fig. 1. FESEM images of (a) $NiCoO_2$-urea, (b) $NiCoO_2$-NaOH and (c) $NiCoO_2$-CH_3COONa, (d) XRD patterns of the three electrodes.