

Synthesis of Ni-riched NiO-Co₃O₄ sheet-like nanocomposites and their application in supercapacitors

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In this reported work Ni-riched NiO-Co₃O₄ sheet-like nanocomposites (SNCs) were obtained through a facile solvothermal method in a mixed solvent and subsequently calcinated in air. Galvanostatic charge-discharge measurement revealed that the Ni-riched NiO-Co₃O₄ SNCs electrode has an impressive specific capacitance as high as 836 F g⁻¹ at 4 A g⁻¹ in 3 M KOH solution. The as-obtained Ni-riched NiO-Co₃O₄ SNCs product showed a weak cycling stability, but the higher capacitance (424 F g⁻¹) was retained after 1000 cycles at 4 A g⁻¹.

1. Introduction: In recent years, ever-growing energy consumption demands highly efficient and advanced energy conversion and storage devices, such as rechargeable batteries and capacitors which can store electrical energy in the form of chemical energy [1–6]. Therefore, supercapacitors (SCs), namely electrochemical capacitors as power supply devices have attracted much attention because of their low cost, high power density and long cycle life [7]. In the past decade, transition metal oxides and their composites have been applied in the field of SCs because of their good capacitive properties and environmental friendliness. Among them, the ternary nickel cobaltite (AB₂O₄) with different morphologies has been conceived as a promising SC electrode material [8–19]. A simple template-free solution method combined with a post-annealing treatment has been successfully developed to grow interconnected NiCo₂O₄ materials on various conductive substrates (such as Ni foam, Ti foil, stainless-steel foil, flexible graphite paper or carbon fabric and carbon fibre) with robust adhesion as a binder- and conductive-agent-free electrode for SCs [8–19]. It is well-known that the chemistry and physics properties of materials are very dependent on size, shape and composition. In previous reports, more of the works focused on the synthesis of Co-riched ternary nickel cobaltite SC electrode materials, but the study of Ni-riched nickel-cobalt oxides SC electrode materials is very limited.

In this Letter, we present a simple solvothermal method in a mixed solvent and subsequent annealing process for preparing Ni-riched NiO-Co₃O₄ nanocomposites with sheet-like structures. The SC property of Ni-riched NiO-Co₃O₄ sheet-like nanocomposites (SNCs) was investigated. As-obtained Ni-riched NiO-Co₃O₄ SNCs exhibited excellent electrochemical characteristics and high cycling stability with a potential range of 0–0.45 V in KOH solution (3 M).

2. Experimental

2.1. Synthesis of Ni-riched NiO-Co₃O₄ SNCs: All the chemicals were of analytical grade and used as received without further purification. For Ni-riched NiO-Co₃O₄ SNCs, a typical synthesis process was as follows: 1 mmol of NiCl₂·6H₂O, 0.5 mmol of CoCl₂·6H₂O and 1.5 mmol of urea were dissolved in a mixed solvent (20 mL H₂O and 20 mL ethylene glycol) under stirring at room temperature. After stirring for 30 min, a transparent solution was obtained, and then transferred into a 50 mL Teflon-lined stainless steel autoclave. The autoclave was kept in an electric

oven at 140°C for 10 h. After the solution was cooled to room temperature, the solid products were collected by centrifugation, and washed with distilled water and ethanol several times, and then dried in a vacuum oven at 70°C for 6 h. Finally, the precursor was calcinated at 300°C for 3 h in air to obtain Ni-riched NiO-Co₃O₄ SNCs.

2.2. Characterisation: The structure, composition and morphology of the samples were characterised by X-ray diffraction (XRD, Shimadzu XRD-6000), scanning electron microscopy (SEM, Hitachi S-4800) and energy dispersive X-ray (EDX, INCAx-Sight OXFORD) spectrometry attached to a scanning electron microscope, respectively.

2.3. Electrochemical tests: Electrochemical measurements were performed in a solution of 3 M KOH aqueous electrolyte in a three-electrode system. A standard calomel electrode (SCE) and platinum foil were used as the reference and counter electrodes, respectively. The working electrode consisted of Ni-riched NiO-Co₃O₄ SNCs, acetylene black and polyvinylidene fluoride binder with a weight ratio of 80:10:10 onto a piece of Ni foam and dried under vacuum at 110°C for 6 h to remove the NMP. Cyclic voltammetry (CV) was performed within a potential range of 0–0.45 V at scan rates from 10 to 100 mV s⁻¹. Galvanostatic charge-discharge was tested at current densities from 4 to 20 A g⁻¹. All of the electrochemical measurements were conducted using a CHI 660C electrochemical workstation (ChenHua Corp., Shanghai, China).

3. Results and discussion

3.1. Structure and morphology studies of Ni-riched NiO-Co₃O₄ SNCs: Considering the previous reports [20–22], we know that the carbonate hydroxide is always formed for Co²⁺ and Ni²⁺ under the hydrothermal environment in the presence of urea. Herein, the Ni, Co-based precursor was firstly prepared by a facile hydrothermal process in a mixed solvent. The XRD pattern (Fig. 1a) of the precursor shows nearly the same pattern as that of Ni_{0.75}Co_{0.25}(CO₃)_{0.125}(OH)₂ (JCPDS No. 40-0216), except all the diffraction peaks slightly shift to the low diffraction direction, which is similar to the previous report [22]. As shown in Fig. 1b, precursor with a sheet-like structure is obtained. Subsequently, by a simple precursor transformation method, we successfully prepared

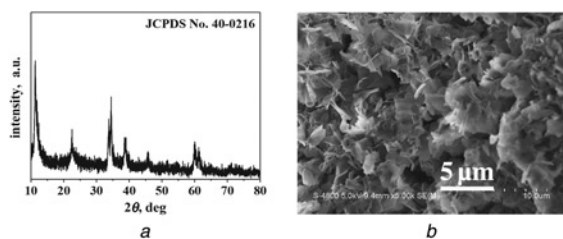


Figure 1 Characterisation of Ni-rich precursor
a XRD pattern
b SEM image

the Ni-rich NiO-Co₃O₄ SNCs. Fig. 2a shows the XRD pattern of Ni-rich NiO-Co₃O₄ SNCs, all the peaks with high intensity indicate good crystallisation of the product. The diffraction peaks correspond to the cubic phase NiO (JCPDS No. 04-0835) and Co₃O₄ (JCPDS No. 42-1467) structures. Fig. 2b shows the SEM image of the Ni-rich NiO-Co₃O₄ sample, which confirms that the as-obtained sample kept the sheet-like morphology unchanged by calcination in air at 300 K. The EDX spectrometry (Fig. 2c) shows the element ratio of Ni to Co is 35.8:17.3, which is very close to the initial ratio of Ni²⁺ to Co²⁺ which is 2:1.

3.2. Supercapacitive property of Ni-rich NiO-Co₃O₄ SNCs: The capacitance of the Ni-rich NiO-Co₃O₄ SNCs samples was characterised in a three-electrode electrochemical cell by CV, galvanostatic charging-discharging and electrochemical impedance response (EIS) measurements in 3 M KOH solution, respectively. As shown in Fig. 3a, typical cyclic voltammograms (CVs) were obtained in 3 M KOH aqueous electrolyte at various scan rates ranging from 10 to 100 mV s⁻¹. Apparently, the CV curves of the Ni-rich NiO-Co₃O₄ SNCs electrode suggest typical pseudocapacitive characteristics of the active material. With an increasing of the scan rate, the height of the peak currents varies and a higher potential was observed. To further evaluate the capacitance performances of the as-synthesised Ni-rich NiO-Co₃O₄ SNCs product, the galvanostatic charge-discharge measurements were conducted in 3 M KOH solution with a potential window of 0 to 0.45 V (against the SCE reference electrode) at various current densities ranging from 4 to

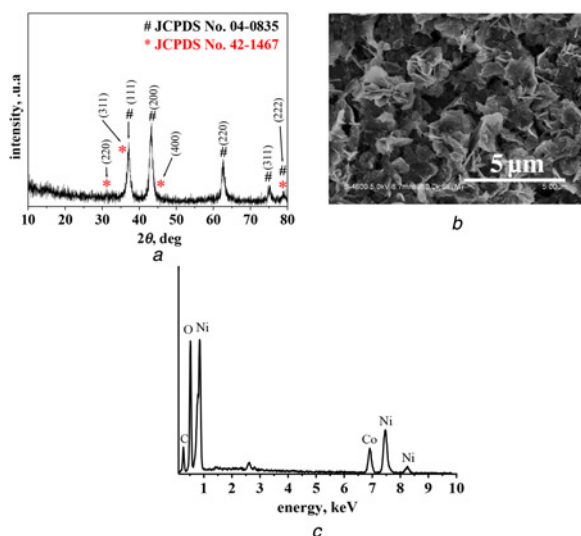


Figure 2 Characterisation of Ni-rich NiO-Co₃O₄ SNCs
a XRD pattern (is marks as NiO and * marks Co₃O₄)
b SEM image
c EDX spectrometry

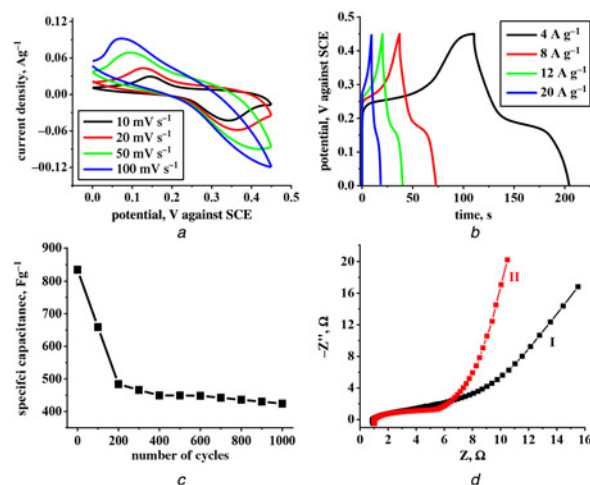


Figure 3 Electrochemical characterisation of the Ni-rich NiO-Co₃O₄ SNCs electrode

a CV curves at different scan rates ranging from 10 to 100 mV s⁻¹
b Galvanostatic charge-discharge curves at various current densities ranging from 4 to 20 A g⁻¹
c The capacitance against current density of 4 A g⁻¹
d EIS measured before (I, black line) and after 1000 charge-discharge cycles (II, red line)

20 A g⁻¹. Consistent with the CV results, the plateaus in the charge/discharge curves indicate the existence of Faradaic processes. Fig. 3b is the representative plots of the charge-discharge curves with various current densities of 4, 8, 12 and 20 A g⁻¹, and the specific capacitances can be calculated to be 836 F g⁻¹ for 4 A g⁻¹, 640 F g⁻¹ for 8 A g⁻¹, 539 F g⁻¹ for 12 A g⁻¹ and 409 F g⁻¹ for 20 A g⁻¹, respectively. The reduction of specific capacitance at high rate can be attributed to the low diffusion of the electrolyte ion [22–24]. As shown in Fig. 3c, the cycling stability was also evaluated by the repeated charging-discharging measurements at progressively increasing current densities and subsequently at a constant current density of 4 A g⁻¹. Although only 50.7% capacitance is retained after 1000 cycles, this is higher than that of numerous NiO or Co₃O₄, such as nanocrystalline NiO [25], mesoporous NiO [26] or Co₃O₄ [27], ultralayered Co₃O₄ [28] and mesoporous CuO–NiO micropolyhedrons [6] reported previously. Moreover, the capacitance of Ni-rich NiO-Co₃O₄ SNCs after 1000 cycles is close to the urchin-like Co₃O₄ microspherical hierarchical superstructures [29]. The as-obtained Ni-rich NiO-Co₃O₄ SNCs product shows weak cycling stability, but the higher capacitance is retained after 1000 cycles. To demonstrate the evolution of the electrochemical behaviour of the Ni-rich NiO-Co₃O₄ SNCs electrode, EIS was performed before and after 1000 charge-discharge cycles, as shown in Fig. 3d. The small semi-circle in the high frequency domain almost perpendicular to the straight line in the low frequency portion of the spectrum shows that the materials have charge transfer resistance. The semi-circle became larger after 1000 cycles. These results also reveal the enhancement of the charge-transfer resistance in the electrode reaction [13].

4. Conclusion: In summary, Ni-rich NiO-Co₃O₄ SNCs were successfully prepared by a hydrothermal method and subsequent calcination in air. The property of the SC was studied. The Ni-rich NiO-Co₃O₄ SNCs display an excellent specific capacitance of 836 F g⁻¹ at 4 A g⁻¹ and 409 F g⁻¹ at 20 A g⁻¹, respectively. The high capacitance is kept at 424 F g⁻¹ after 1000 cycles. Therefore, the good electrochemical performance of the Ni-rich NiO-Co₃O₄ SNCs will make them attractive for potential application in the field of SCs.

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