



Morphology-controllable synthesis of 3D CoNiO₂ nano-networks as a high-performance positive electrode material for supercapacitors



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ABSTRACT

Here, we report a novel three-dimensional (3D) assembly of CoNiO₂ nanowire networks using a facile and scalable hydrothermal method followed by an annealing process for supercapacitor applications. The X-ray diffraction (XRD) results revealed the formation of highly-crystalline CoNiO₂ nano-networks. Scanning electron microscope (SEM) analysis showed the formation of a 3D interconnected network of CoNiO₂ nanowires during the synthesis. In addition, a formation mechanism for 3D CoNiO₂ nano-networks was proposed. Electrochemical analysis showed a typical pseudocapacitive behavior for the CoNiO₂ nanowire networks. The as-prepared CoNiO₂ electrode exhibited a high specific capacitance of 1462 F g⁻¹ (45.32 F cm⁻²) at a current density of 1 A g⁻¹ (31 mA cm⁻²) and an excellent rate capability of 1000 F g⁻¹ (31 F cm⁻²) at 32 A g⁻¹ (992 mA cm⁻²). Moreover, a good cycle stability was achieved at 4 A g⁻¹ with no degradation over 800 cycles, indicating the stable 3D structure of CoNiO₂ after the redox reactions. The high rate capability and the good cycle stability indicated that the as-prepared 3D CoNiO₂ electrode could satisfy the needs of supercapacitors with both high power and energy densities.

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1. Introduction

The gradual depletion of fossil fuels and the environmental issues have pushed human beings to find renewable and sustainable energy to meet the increasing demands of energy consumption. In recent years human beings have achieved a great progress in the field of renewable and sustainable energy [1–3]. Therefore, there is an urgent need to develop cost-effective energy storage technologies to ensure a safe, efficient and reliable energy supply for the future. As one of the most promising energy storage technologies, supercapacitors have attracted considerable attention because of their rapid charging and discharging, high power density, and long cycle life [4–8].

It is well-known that the performance of supercapacitors relies mostly on the intrinsic properties of the electrode materials [9–11]. In order to improve its energy density, transition metal oxides or hydroxides are commonly used as electrode materials for pseudocapacitors. There has been a growing interest in the development of

high-performance pseudocapacitor electrode materials such as RuO₂ [12,13], MnO₂ [14–16], Mn₃O₄ [17], Co₃O₄ [18–20], NiO [21], and V₂O₅ [22], Ni(OH)₂ [23], Co(OH)₂ [24] etc. However, there have been some challenges in the mass production of electrode materials for practical use such as the high cost of the active materials, the slow redox reaction, and the poor conductivity [25,26]. Binary transition metal oxides can effectively improve the redox reaction speed and drastically increase the conductivity of electrode materials [27,28], thereby enhancing the electrode performance. Nickel cobalt oxides (mainly NiCo₂O₄) have been widely investigated as promising electrode materials for supercapacitors [29–32] in recent years because of their better electrical conductivity, environmental friendliness, low cost, higher electrochemical activity, and high theoretical specific capacitance compared to individual nickel oxide (NiO) and cobalt oxide (Co₃O₄). Controlling the assembly of nickel cobalt oxide nanostructures with different morphologies is a very effective way to increase the electrochemical activity and improve the carrier transport properties [33]. Thus, NiCo₂O₄ nanostructures were successfully fabricated in a broad range of morphologies, including one-dimensional nanorods [34], porous nanotubes [35], two-dimensional nanosheets [36], nano-flowers [37], three-dimensional urchin-like [38], and microspheres [39]. Although NiCo₂O₄-based active materials have been

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extensively investigated, to further expand its performance has been very limited and other nickel cobalt oxides have rarely been researched as active materials for supercapacitors. Zheng et al. [40] synthesized CoNiO₂ nanowires on the surface of a TiN-TiN_xO_y thin film fabricated on a Ni foam using a hydrothermal method along with a post annealing treatment, which demonstrated extremely high areal capacitances of 3181 and 2763 F g⁻¹ at current densities of 2 and 10 mA cm⁻², respectively. In this case, the TiN-TiN_xO_y thin film improved the carrier transport between the electrode and the electrolyte because of its high conductivity. While this approach can achieve high capacitance, it is not easy to provide an industrial mass production.

It has been shown that the design of material architecture is very important to improve the supercapacitors performance [41,42]. The 3D nanostructure exhibits interconnected porous structure, high electrical conductivity and fast redox reactions with rapid kinetics because of the short and direct diffusion path for electrons and ions [43,44]. The electrolyte can easily soak into the inside of the materials with 3D nanostructure. The 3D nanostructure is not only beneficial to the electrolyte diffusion which can accelerate ion transportation but also to ensure high utilization of the electrode material [45]. However, there have been very few reports on 3D CoNiO₂ due to the lack of feasible fabrication methods without the use of poisonous and noxious reagents to realize mass production [46,47]. Therefore, facile and scalable synthesis methods for CoNiO₂ should be investigated to achieve various structure designs of CoNiO₂ nanomaterials with different morphologies for practical applications [48].

In this study, we successfully developed a facile and scalable hydrothermal method combined with a post-annealing process for large-scale synthesis of three-dimensional networks of CoNiO₂ nanowires, in which sodium-p-styrenesulfonate (PSS) played a key role in forming the three-dimensional nanostructured network. This 3D CoNiO₂ cathode material exhibited a high electrochemical performance and a long cycle life. Interestingly, the same method can also be used to fabricate CoNiO₂-based nanostructures with different morphologies by simply controlling the addition of PSS during synthesis.

2. Experimental section

2.1. Reagents and materials synthesis

All reagents were of analytical grade and were used without any further purification. In a typical procedure, 150 mmol of Ni(NO₃)₂·6H₂O and 150 mmol Co(NO₃)₂·6H₂O were dissolved in 900 mL of deionized water under constant magnetic stirring. After the formation of a transparent solution, 3000 mL of PSS solution at a concentration of 4 g L⁻¹ was added, followed by 1350 mmol of urea. The resultant clear solution was transferred to a 5000 mL of stainless steel autoclave. The autoclave was heated at 90 °C for 9 h under mechanical stirring. The reaction products were ultrasonically cleaned in separate baths of deionized water and ethanol several times. The cleaned products were then filtered and dried at 60 °C for 12 h to form the CoNiO₂ precursor. The final CoNiO₂ products were obtained by annealing the precursor in air at 300 °C for 2 h at a heating rate of 5 °C min⁻¹.

2.2. Materials characterization

The crystal structure of the as-prepared samples was characterized using an X-ray diffractometer (PANalytical X'Pert Pro XRD, CuKα λ = 0.15405 nm) at a scan rate of 5° min⁻¹. The samples were ground into powder for the XRD measurements. The morphology of the samples was observed using a field emission scanning electron

microscope (FESEM, Inspect F, FEI) at an accelerating voltage of 20 kV.

2.3. Electrochemical measurements

Electrochemical test was performed in a three-electrode electrochemical system with a KOH electrolyte solution (6 M). Platinum foil and SCE electrode were used as the counter and reference electrodes, respectively. To prepare a positive electrode, a mixture of the active material, the conductive material (super-p), and the adhesive (tetrafluoroethylene) with a mass ratio of 80:15:5 in ethanol was used to form a homogeneous slurry. Then, the slurry was spread onto a nickel foam and pressed into a positive electrode sheet with a roller press after drying at 100 °C in air. The effective area of the working electrodes was approximately 1 cm², and the mass loading of the positive electrode was approximately 31 mg cm⁻². The electrochemical measurements were performed using a RST5200F electrochemical workstation (Suzhou Risetest Electronic Co., Ltd., Suzhou, China). All electrochemical tests were conducted at room temperature. The specific capacitance of the working electrodes was calculated using the galvanostatic charge/discharge curves according to the following Equation (1):

$$C = I\Delta t/m\Delta V \quad (1)$$

where C, m, I, ΔV, and Δt, are the specific capacitance (F/g) of the active material, the weight of the active material (g), the discharge current (A), the potential range during discharge (V), and the discharge time (s), respectively. Electrochemical impedance spectroscopy (EIS) measurements were performed by applying an AC voltage of 5 mV amplitude in the 0.01 Hz - 10 kHz frequency range at the open circuit potential.

3. Results and discussion

3.1. Characteristics of the as-prepared CoNiO₂

The crystal structures of the CoNiO₂ precursor and the post-annealed CoNiO₂ product were studied using XRD. As shown in Fig. 1a, it is hard to find any clear reflection peaks to index the XRD pattern of the CoNiO₂ precursor. However, after the CoNiO₂ precursor was annealed at 300 °C for 2 h in air, the characteristic CoNiO₂ peaks were observed at 36.84°, 42.90°, 61.81°, 74.02°, and 78.00° corresponding to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) planes of CoNiO₂, respectively (JCPDS 100188) (Fig. 1a). Therefore, it can be concluded that the precursor annealing at 300 °C led to the successful formation of the highly-crystalline CoNiO₂ nano-networks in the final product.

SEM images of the as-prepared CoNiO₂ precursor and the post-annealed CoNiO₂ product are presented in Fig. 1b and c, respectively. The nanomorphologies found in the CoNiO₂ precursor were very similar to those in the post-annealed CoNiO₂ product, in which both samples showed many interconnected nanowires forming a 3D network as seen in Fig. 1b and c. The diameter and length of the nanowires were approximately 50 nm and 500 nm, respectively. The similarities between the SEM images of the CoNiO₂ precursor and the post-annealed CoNiO₂ product indicated that the annealing process only improved the crystallinity without inducing any visible morphological change. The formation mechanism of the CoNiO₂ precursor is presented in Fig. 1d–f. First, the sulfonic groups in PSS react with nickel and cobalt ions to form stable complexes due to the attraction between the charged species. With complexation, the nascent crystallites are formed on the PSS chains as shown in Fig. 1d. Then, the nascent crystallites gradually grow into the CoNiO₂ nanowires, which are interconnected within the

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