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Shape-controlled synthesis of ternary nickel cobaltite and their application in supercapacitors

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ABSTRACT

A facile hydrothermal method and subsequent annealing approach have been successfully developed to synthesize ternary nickel cobaltite hexapods, hexagonal prisms and nanowires. The products were investigated in detail by means of XRD, FESEM, TEM, HRTEM, BET, TGA and XPS. The hexapods have six clusters, and every cluster has many typical nanorods with diameter of about 10 nm and length of 1.2 μm. The nanowires are uniform in size, with diameters of about 10 nm. The hexagonal prisms with average size of about 120 nm have the highest BET specific surface area of 74.66 $m^2 g^{-1}$ and a pore volume of 0.1874 $cm^3 g^{-1}$, which exhibited superior specific capacitance of 663 F g^{-1} at a current density of 1 A g^{-1}. It has impressive cycling stability with 88.4% initial capacitance retained after 5000 cycles at 4 A g^{-1}, revealing the excellent stability of the electrode.

1. Introduction

In recent years, in order to solve the problems of environmental pollution and energy insufficiency, many kinds of energy storage devices and technologies have been developed [1]. Among the various technologies, the electrochemical capacitors have attracted numerous attentions due to their high power density and energy density, excellent reversibility, high capacity, long cycle life, and so forth [2–5].

Electrochemical capacitors are also known as supercapacitors, their primary potential applications are uninterruptible power supplies, hybrid electrical vehicle systems and renewable energies [6,7]. In general, supercapacitors can be divided into two different types based on the charge-storage mechanism: electrical double-layer capacitors (EDLCs) and pseudocapacitors (also called redox electrochemical capacitors) [4,8]. Carbon-based materials, such as activated carbons [9], carbon nanotubes [10], carbon spheres [11] and microporous carbons [12] are used for EDLCs. However, it usually suffers from a low capacitance of 100–200 F g^{-1} [8]. In contrast, the pseudocapacitors usually provide much higher specific capacitance, and energy density of pseudocapacitors is usually many times greater than EDLCs [13]. For pseudocapacitors, the charge-storage mechanism involved in faradic processes with charge transfer between electrode and electrolyte [14]. Metal oxides and conducting polymers are usually used as pseudocapacitors electrode materials [15–19].

Among many metal oxides, ternary nickel cobaltite ($NiCo_2O_4$) has been conceived as a promising material since it offers many advantages such as low cost and environmental friendliness [20,21]. Ternary nickel cobaltite with the general formula A_2BO_4 is a pure spinel structure in which nickel occupies the octahedral sites and cobalt distributes over both octahedral and tetrahedral sites [22]. Previous reports show that $NiCo_2O_4$ has a better electronic conductivity and a better electrochemical activity than that of NiO and Co_3O_4 [23,24]. In particular, $NiCo_2O_4$ as a promising material of pseudocapacitor shows a high specific capacitance [25]. In the past decade, as a supercapacitors electrode material, much effort has been devoted to the synthesis of various $NiCo_2O_4$ nanostructures for the sake of improving their capacitance and cycling stability. So far, there are lots of $NiCo_2O_4$ structures with different morphologies have been synthesized, including nanoparticles [26], nanoflowers [27], nanoflakes [28], nanoneedle arrays [29], urchin-like nanostructures [30], and mesoporous microspheres [31].

In this work, without the use of any template, we present a facile hydrothermal method and subsequent annealing approach for preparing three kinds of ternary nickel cobaltite with distinct structures: hexapods, hexagonal prisms and nanowires. We further investigate the properties of three as-obtained $NiCo_2O_4$ samples for supercapacitors. As-synthesized three $NiCo_2O_4$ nanostructures exhibited excellent electrochemical characteristics and high cycling stability with a potential window of 0–0.45 V in 3 M KOH solution.

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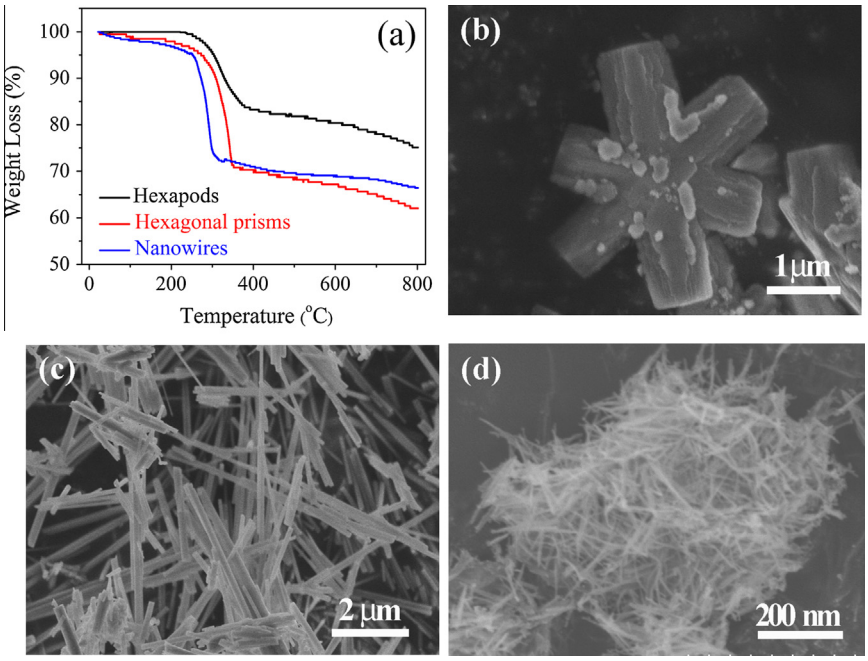

Fig. 1. (a) Thermogravimetric analysis (TGA) curves of three samples; (b–d) FESEM images of the three precursors of hexapods, hexagonal prisms and nanowires before calcination.

2. Experimental

2.1. Material preparation

Cobalt chloride hexahydrate ($CoCl_2{\cdot}6H_2O$), cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$), urea ($CO(NH_2)_2$), ammonium fluoride (NH_4F), N,N-Dimethylformamide (DMF), polyvinylpyrrolidone (PVP, K-30), acetylene black, polyvinylidene fluoride (PVDF), potassium hydroide (KOH), N-methyl-2-pyrrolidone (NMP), ammonium chloride (NH_4Cl), all these reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. with analytical grade. Deionized (DI) water was used throughout.

2.2. Synthesis of $NiCo_2O_4$ hexapods and hexagonal prisms

For hexapods, in a typical synthesis, 0.6 mmol of $CoCl_2{\cdot}6H_2O$, 0.3 mmol of $NiCl_2{\cdot}6H_2O$ and 2 mmol of $CO(NH_2)_2$ were dissolved in 30 mL DI water under stirring at room temperature. After a few minutes, 5 mmol NH_4F was added into the reaction medium. After stirring for 15 min, a pink transparent solution was obtained, which was then transferred into a 40 mL Teflon-lined stainless steel autoclave. The autoclave was kept in an electric oven at 120 °C for 12 h. After cooling down to room temperature naturally, the as-obtained precursor was collected by filtration, washed with deionized water and ethanol for several times each, and then dried at 60 °C for 2 h. Finally, the precursor was calcinated at 350 °C for 2 h in air to get $NiCo_2O_4$ hexapods.

In the case of the preparation for $NiCo_2O_4$ hexagonal prisms, all procedures were similar to that of hexapods except that NH_4Cl was used instead of NH_4F.

2.3. Synthesis of $NiCo_2O_4$ nanowires

In a typical synthesis, 2 mmol of $Co(NO_3)_2{\cdot}6H_2O$, 1 mmol of $Ni(NO_3)_2{\cdot}6H_2O$ and 0.1 g of polyvinylpyrrolidone (PVP, K-30) were dissolved in 30 mL N,N-Dimethylformamide (DMF) under stirring for 1 h at room temperature. Then the mixture was transferred into a 40 mL Teflon-lined stainless steel autoclave, which was treated at 200 °C for 12 h. After cooling down to room temperature naturally, the as-prepared precursor was collected, washed and calcinated as that described in step 2.2.

2.4. Characterization

Thermogravimetric analysis (TGA) were performed using a Shimadzu DTG-60A thermal analyzer under the protection of argon gas with a ramping rate of 10 °C min^{-1}. X-ray powder diffraction (XRD) patterns were obtained on a Rigaku Max-2200 with Cu Kα radiation. X-ray photoelectron spectra (XPS) were recordered on an ESCALab MKII X-ray photoelectron spectrometer with nonmonochromatized Mg Kα X-ray as the excitation source. The binding energies in XPS analysis were corrected by referencing C1s to 284.60 eV. The field emission scanning electron microscopy (FESEM) images were taken with a Hitachi S-4800 scanning electron microscope. N_2 adsorption measurements were performed on a Micromeritics ASAP 2020 M + C volumetric adsorption equipment at 77 K using Barrett–Emmett–Teller (BET) calculations for surface area. Transmission electron microscopy (TEM) images and high-resolution transmission electron microscopy (HRTEM)

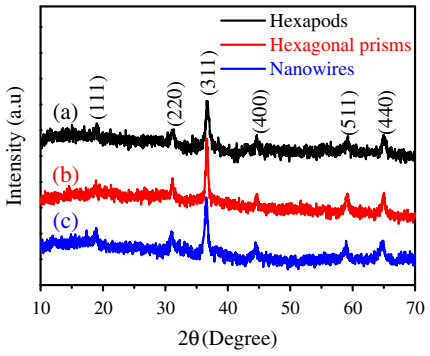

Fig. 2. XRD patterns of three samples after calcination at 350 °C in air.