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Controllable synthesis of $NiC_2O_4 \cdot 2H_2O$ nanorods precursor and applications in the synthesis of nickel-based nanostructures

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Abstract

A controllable synthesis of $NiC_2O_4 \cdot 2H_2O$ nanorods precursor was obtained via the microemulsion-mediated solvothermal method and a further synthesis of β-$Ni(OH)_2$ nanorods, nickel oxide (NiO) sub-microtubes, Ni nanospheres and flower-like nickel complexes nanostructures by using the precursor. The morphologies and crystalline structures were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), and the X-ray powder diffraction (XRD). The morphologies and sizes of the precursors can be readily tuned by adjusting experimental parameters of the reverse microemulsion system. The synthesized β-$Ni(OH)_2$ nanorods composed of fine nanosheets shown excellent electrochemical performance as an electrode material in rechargeable battery systems.

Keywords: Microemulsion system; Solvothermal; Precursor; Specific capacity

1. Introduction

Low-dimensional nanomaterials of nickel and its compounds have been extensively studied owing to their widespread applications in catalysis [1,2], electronics [3], magnetics [4–8], etc. For instance, nickel hydroxide ($Ni(OH)_2$) has been applied in alkaline rechargeable batteries [9–11]. While nickel oxide (NiO) is a semiconductor and antiferromagnetic material and is also used in diverse fields, such as catalysis, gas sensors, electrochromic films, magnetic materials, active optical fibers, and fuel cell electrodes [12–15]. Recently, Taeghwan et al. [16] have demonstrated the synthesis of NiO-coated Ni nanoparticles and their successful application in the magnetic separation of His-tagged proteins. So far, many methods have been developed to fabricate nanostructured materials, among which using precursor is one of the successful methods. The precursor methods have been deeply developed to fabricate nickel nanostructures. Wang et al. [17] have reported the synthesis of NiO nanowires by oxygenating NiS nanoparticles. Qi et al. [18] have prepared Ag cage by reducing Ag_3PO_4 rhombododecahedral crystals. Li et al. [19] have synthesized $Ni(OH)_2$ coexistence of nanosheets and nanorods via bulk nickel oxalate NiC_2O_4 in NaOH solution at 160 °C for 12 h. Wang et al. [20] have successfully prepared NiO nanowires via the decomposition of NiC_2O_4 at high temperature. Therefore, how to prepare a suitable precursor becomes a crucial factor to obtain ideal building blocks for synthesizing different nanostructured materials. Among all the methods, the reverse micelles or microemulsion system have already been widely used to prepare different nanostructured materials. In our group, we have successfully prepared BaF_2 nanowhiskers [21], ultra-high-aspect-ratio $Ca_{10}(PO_4)_6(OH)_2$ nanofibers [22], MgF_2

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nanorods [23], $SrCO_3$ and $SrWO_4$ nanostructures with various morphologies [24,25] by the microemulsion-mediated solvothermal method.

In this article, we report a controllable synthesis of $NiC_2O_4 \cdot 2H_2O$ nanorods precursor via microemulsion-mediated solvothermal method. The morphologies and sizes of the precursor can be readily tuned by adjusting experimental parameters of the reverse microemulsion system, such as the molar ratio of H_2O to CTAB (defined w), the reaction temperature (T) and time (t). Furthermore, we have successfully demonstrated that β-$Ni(OH)_2$ nanorods composed of nanosheets, NiO sub-microtubes, Ni nanospheres and flower-like nickel complexes assembled by nanorods can be synthesized by using $NiC_2O_4 \cdot 2H_2O$ nanorods as precursor which has not been reported before. In addition, we have studied the electrochemical performance of β-$Ni(OH)_2$ electrode.

2. Experimental section

2.1. Materials

All chemicals, nickle sulfate ($NiSO_4 \cdot 6H_2O$, 99%), oxalic acid ($H_2C_2O_4 \cdot H_2O$, 99%), sodium hydroxide (NaOH), cetyltrimethylammonium bromide (CTAB), cyclohexane (C_6H_{12}), *n*-pentanol ($C_5H_{12}O$), and hydrazine hydrate ($NH_2NH_2 \cdot H_2O$, 50%) (Beijing Chemical Reagent, Co.) are analytical grade and were used without further purification distilled and deionized water was used in all of the studies.

2.2. Preparation of $NiC_2O_4 \cdot 2H_2O$ nanorods precursor

First, two same quaternary micromulsion systems, CTAB/water/cyclohexane/*n*-pentanol, were prepared by dissolving 5 mmol CTAB in 30 mL of cyclohexane and 1.5 mL of *n*-pentanol. The mixing solution was stirring for 30 min until it became transparent. And then, $NiSO_4$ and $H_2C_2O_4$ aqueous solutions of identical concentration and volume were added to the above microemulsion solutions, respectively. After substantial stirring, the two optically transparent microemulsion solutions were mixed together and stirred for another 10 min. The resulting microemulsion solution was then transferred into an 80 mL stainless Teflon-lined autoclave and heated at 120 °C for 12 h. After the reaction was completed, the resulting suspension was naturally cooled to the room temperature, and the precipitates were collected by centrifuging, washed for several times with absolute ethanol and distilled water, and dried in atmosphere at the room temperature.

2.3. Synthesis of β-Ni(OH)$_2$ nanorods, NiO submicortubes, Ni nanospheres and flower-like nickel complexes

In a typical synthesis process, 2 mmol of the $NiC_2O_4 \cdot 2H_2O$ nanorods precursor and 4 mL 1 M NaOH were dispersed in 50 ml distilled water successively. The suspension was heated up to boil for 30 min by vigorously stirring under atmosphere condition. Then the resultant green precipitates were naturally cooled to the room temperature. The precipitates were collected by centrifuging and washed with absolute ethanol and distilled water for several times, and then dried in atmosphere at the room temperature.

Meanwhile the NiO sub-microtubes were obtained by calcination of the as-prepared $NiC_2O_4 \cdot 2H_2O$ nanorods at 400 °C for 2 h in a Muffle furnace.

The Ni nanospheres were prepared by reducing $NiC_2O_4 \cdot 2H_2O$ nanorods precursor with $NH_2NH_2 \cdot H_2O$. Firstly, 0.5 mmol of the precursor $NiC_2O_4 \cdot 2H_2O$ nanorods was dispersed in 50 mL distilled water, then added 1 mL 1 M NaOH and 10 mL $NH_2NH_2 \cdot H_2O$ orderly. The resulting suspension was then transferred into an 80 mL stainless Teflon-lined autoclave and heated at 120 °C for 12 h. The resultant black precipitates were naturally cooled to the room temperature, then collected, washed with ethanol and water for several times, and dried in vacuum. However, when we changed the hydrothermal treatment to an ultrasonic treatment at 70 °C for 6 h and kept the other condition invariable, we finally obtained the violet mixture of flower-like nickel complexes assembled by nanorods.

2.4. Characterizations

The overall crystallinity and purity of the as-synthesized samples were analyzed by X-ray powder diffractometer (XRD) equipped with graphite monochromatized Cu$K\alpha$ radiation ($\lambda = 1.54060$ Å) by a SHIMADZU XRD-6000 operated at 40 kV voltage and 50 mA current. XRD patterns were recorded in the 2θ range of 10–80° with a scanning step of 0.02°. The thermogravimetric analysis (TGA) of $NiC_2O_4 \cdot 2H_2O$ was carried out on Perkin Elmer Diamond TG-DTA/DSC apparatus (Germany) with a heating rate of 10 °C min^{-1} in flowing air from 80 to 900 °C. The morphology patterns, size distribution and selected area electron diffraction (SAED) of the as-prepared products were observed using Hitachi model H-800 transmission electron microscope (TEM), and S-4800 scanning electron microscope (SEM) at the accelerating voltage of 200 kV and 15 kV, respectively. The specimens for TEM images and SAED studies were prepared by suspending the solid samples in ethanol. About 1 mg of sample was added into 5 mL ethanol in a small glass container that was then placed in an ultrasonic water bath and sonicated for 15 min. A drop of this well-dispersed suspension was placed on a carbon-coated 200-mesh copper grid, followed by drying the sample under ambient condition before it was placed in the sample holder of the microscope.

2.5. Preparation of the β-Ni(OH)$_2$ electrode

The active material paste containing β-$Ni(OH)_2$ and nickel powder was inserted into a 1 cm × 1 cm nickel foam