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Facile synthesis of Co_3O_4 nanoflowers grown on Ni foam with superior electrochemical performance

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ABSTRACT

Novel large-scale Co_3O_4 nanoflower (NF) structures on Ni foam are prepared for the first time via a general two-step synthesis. Through a controllable solvothermal process and hereafter with a post-calcination process in air, the NFs have been grown firmly on Ni foam, which is convenient for the construction of supercapacitors without any extra electrode preparation process. The pore sizes and the amount of Co_3O_4 NFs can be tuned through different post-calcination and solvothermal conditions, respectively. The electrochemical properties of the NFs are tested by cyclic voltammetry, galvanostatic charge–discharge in 6.0 M KOH solution. The results show that the NFs can have a specific capacitance of 1936.7 F g^{-1} at a current density of 0.2 A g^{-1} and a capacity retention of 78.2% after 1000 cycles at a current density of 3 A g^{-1} (1309.4 F g^{-1}). The Co_3O_4 NFs grown on Ni foam with large area and superior electrochemical performance have great potential application in supercapacitors.

1. Introduction

Supercapacitors, an important energy storage device, offer ideally high power density, excellent reversibility and long cycle life for time-dependent power needs of modern electronics and power systems [1–4]. Cobalt oxide, because of its favorable capacitive characteristics and environmental friendliness, is generally considered as promising electrode materials for supercapacitors [5–8]. The theoretical specific capacitance for Co_3O_4 is 3560 F g^{-1} [5,8]. Recently, self-supported nanostructures directly grown on current-collectors represent an attractive architecture for supercapacitors [5–9]. Deng et al. prepared a Co_3O_4 electrode on Ni–Cu alloy film with a specific capacitance of 2200 F g^{-1} using an entirely electrochemical process [8]. Gao et al. prepared Co_3O_4 nanowire arrays on Ni foam with a capacitance of 746 F g^{-1} via template-free growth followed by thermal treatment [5]. These nanostructures grown on current-collectors displayed much higher capacitance than that of the conventional Co_3O_4 powders [5–9]. Therefore the structure of the active electrode materials has significant effects on their capacitive performance. Each nanostructure has its own electric contact with the substrate and thus can ensure all nanostructures participate in the electrochemical reaction, which enhances the utilization of active materials and saves the tedious process of mixing active materials with ancillary materials such as carbon black and polymer [5,10]. The open space between neighboring nanostructures facilitates the diffusion of electrolyte into the inner region of the electrode, particularly helpful for reducing internal resistance and improving high-power performance [5,10,12].

There have been some reports on the synthesis of one-dimensional (such as nanowires, nanotubes [5,9–14]) and two-dimensional (such as nanoflakes [7,15]) cobalt oxide on substrates. However, there are very few reports on the fabrication of three-dimensional (3D) Co_3O_4 nanostructures on substrates, except the Co_3O_4 bowl-like nanostructures on Ni–Cu alloy film using an electrochemical method [8]. To the best of our knowledge, there are no reports on the synthesis of Co_3O_4 3D nanoflower (NF) structures on substrates.

In this paper, novel large-scale Co_3O_4 NFs on Ni foam are prepared for the first time by a simple solvothermal-thermal decomposition method. The extraordinary redox activity of the NFs is demonstrated in terms of pseudocapacitive performance.

2. Experimental

2.1. Materials preparation

All reagents used in this experiment were of analytical grade without further purification. 0.5–2 g $Co(NO_3)_2{\cdot}6H_2O$, 1 g Hexadecyl trimethyl ammonium Bromide (CTAB) and 0.5–4 ml water were dissolved in 23.5–20 ml absolute methanol to form a red solution. The resulting solution was then transferred into a 30 ml Teflon-lined stainless steel autoclave. A piece of Ni foam (420 g m^{-2}) was

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rinsed with water, subjected to an ultrasonic in ethanol and dried, then immersed in the growing solution for 24 h at 150–180 °C to allow growth of NFs. The Ni foam covered with products was washed with H_2O and ethanol, dried in a vacuum at 120 °C for 8 h, and the final products were denoted as sample A-as-prepared. In another experiment, another 1 g CTAB were added to the above solution, the following processes were similar to the former one, and the final products were denoted as sample B-as-prepared.

The samples A-as-prepared were then calcined at 250 °C for 4 h, 250 °C for 14 h, 300 °C for 4 h, and the final products were denoted as samples A-250-4, A-250-14, and A-300-4, respectively. The sample B-as-prepared was calcined at 300 °C for 4 h, and the final product was denoted as sample B-300-4. The deposit weight of Co_3O_4 was accurately measured by weighing the Ni foam before hydrothermal process and the Ni foam coated with Co_3O_4 after calcination with an analytical balance (model AY 220, max. 220 g, 0.1 mg of resolution, Shimadzu, Kyoto, Japan).

2.2. Materials characterizations

Phase identifications of the synthesized products were conducted by a MXPAHF X-ray diffractometer from 20° to 80° with a Cu Kα of 1.54056 Å. The morphology was examined by scanning electron microscope (SEM, JSM-6360), field-emission scanning electron microscope (FESEM, Nova Nona230). The structural details of the NFs were characterized with the high-resolution transmission electron microscope (HRTEM, GEOL-2010).

2.3. Electrochemical characterization

Electrochemical measurements were made in a conventional three-electrode cell, in which the Co_3O_4 NFs on Ni foam acted as the working electrode, a platinum plate acted as the counter electrode and a saturated calomel electrode (SCE) served as the reference electrode. 6.0 M KOH solution was used as the electrolyte. Cyclic voltammetry (CV) and galvanostatic charge/discharge tests were performed on a CHI660B electrochemical workstation (Shanghai, China).

3. Results and discussion

3.1. Structures

The XRD patterns of the samples A-as-prepared, A-250-4, A-250-14, A-300-4 and B-300-4 are shown in Fig. 1. A mixture of β-$Co(OH)_2$ (JCPDS 30-0443), cobalt carbonate nitrate hydroxide hydrate (JCPDS 50-1891) and Ni foam can be identified from the XRD pattern of the precursor, sample A-as-prepared. By comparing samples A-as-prepared and A-250-4, we find that (0 0 9) of cobalt carbonate nitrate hydroxide hydrate phase and (1 0 1) of $Co(OH)_2$ one are still present in sample A-250-4, indicating that $Co(OH)_2$ and $Co(OH)_{1.81}(NO_3)_{0.11}(CO_3)_{0.04}{\cdot}0.6H_2O$ phases are still exist after calcined the precursor A-as-prepared at 250 °C for 4 h. Except for the reflections from the Ni foam, only spinel Co_3O_4 with face centered cubic (FCC) structure (JCPDS 80-1544) can be observed in the XRD patterns of A-250-14, A-300-4 and B-300-4, indicating that phase pure Co_3O_4 is obtained. By increasing the post-calcination duration from 4 h to 14 h at 250 °C or improving post-calcination temperature from 250 to 300 °C for 4 h, these residual phases in sample A-250-4 can be removed.

3.2. Morphologies

The photographs of the Ni foam (left), samples A-as-prepared (middle) and A-250-4 (right) are shown in Fig. 2. The Ni foam turns

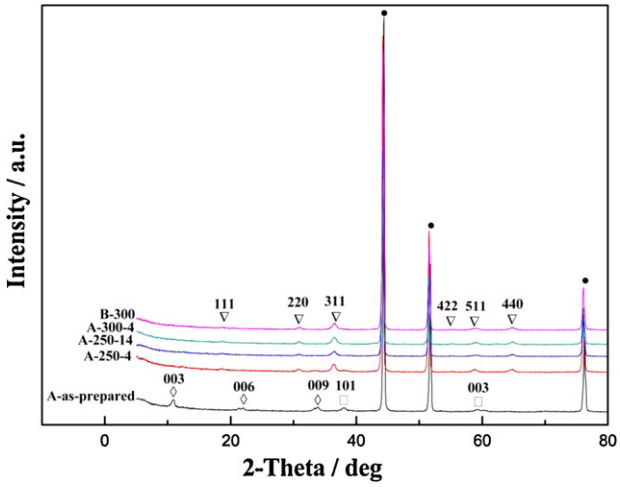

Fig. 1. The XRD patterns of the samples A-as-prepared, A-250-4, A-250-14, A-300-4 and B-300-4. □ denotes diffraction peaks from the β-$Co(OH)_2$. ♦ denotes diffraction peaks from the cobalt carbonate nitrate hydroxide hydrate in the precursor. ▲ denotes diffraction peaks from the Co_3O_4, and ● denotes diffraction peaks from the Ni substrate.

to a green color after solvothermal reaction, suggesting the formation of cobalt carbonate nitrate hydroxide hydrate on the Ni foam. The red color of β-$Co(OH)_2$ can not be seen, which may be due to the amount of β-$Co(OH)_2$ is very small. When annealed at 250 °C for 4 h, the green Ni foam turns to a black color, suggesting the formation of Co_3O_4.

Low- and high- magnification SEM images of sample A-as-prepared are shown Fig. 3a and b respectively. Fig. 3b shows the high-magnified FESEM image of a single NF. It is clear that the individual NF is constructed by many nanosheets with jagged edges. The mean diameter of NFs is about 2–5 μm. The typical size of the nanosheets is in the range of 60–110 nm in thickness, 0.2–2.5 μm in width, and 0.2–2.5 μm in length. The surface of the nanosheets is very smooth and well faceted. It can also be seen that the nanosheets are grown at various angles in high density over the entire surface of Ni foam, so the NFs can provide an efficient electron transport channel when used as electrodes for suercapacitors. It is well known that the shape of crystals can be controlled by adding chemical capping reagents as shape controllers into the solution. The CTAB probably acts as the adsorbing species on such faces and thus changes the habits of crystallization, and therefore promotes the growth of NFs.

SEM images of sample A-250-4 are presented in Fig. 3c and d. As shown in Fig. 3c and d, the flower-like morphology of precur-

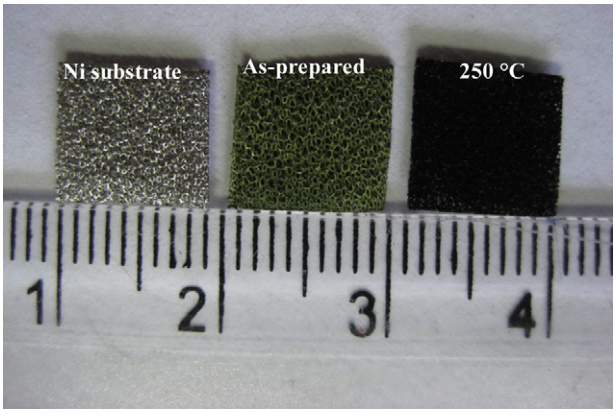

Fig. 2. Photographs of the Ni foam (left), samples A-as-prepared (middle) and A-250-4 (right).