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Ternary Ni-Co-Mo oxy-hydroxide nanoflakes grown on carbon cloth for excellent supercapacitor electrodes

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ABSTRACT

Ternary Ni-Co-Mo oxy-hydroxide nanoflakes grown on carbon cloth was successfully fabricated based on a facile hydrothermal method. This composite product consists of three components: Ni-Co double hydroxide and Mo oxide. As a novel electrode material for pseudocapacitors, the Ni-Co-Mo oxy-hydroxide nanoflakes on carbon cloth exhibit excellent electrochemical properties, with a specific capacitance of 2562 F g^{-1} at 1 A g^{-1}, and a good cycling stability. The excellent electrochemical performance can be attributed to the large specific surface area and the enhanced conductivity achieved through incorporating of Mo. By virtue of simple fabrication procedures and enhanced electrochemical performance, such ternary oxy-hydroxide nanoflakes have highly promising potential for energy storage devices.

1. Introduction

As one of the promising advanced energy storage devices, supercapacitor has attracted considerable attention because of its fast charge-discharge capability, high power density, long cycle life and environmental friendliness [1,2]. Supercapacitor has shown wide potential applications in the fields of hybrid electric vehicles, portable electronics and the backup power for electric utilities [3,4]. Based on the energy storage mechanism, supercapacitors can be classified into electrical double-layer capacitors and pseudocapacitors [5]. Among them, pseudocapacitors exhibit higher capacitance but weaker charge–discharge cycling stability. For pseudocapacitors, transition metal oxides/hydroxides and intrinsically conductive polymers have been intensively reported in the literature [6–8].

Recently, Ni-Co oxide/hydroxide based nanostructures become attractive electroactive materials due to their versatile properties of low cost, good redox activity, and high theoretical specific capacitance [9–11]. Particularly, Ni-Co oxide/hydroxide nanoflakes offer superior electro-chemical properties over other nanostructures due to the interconnected arrangement and high specific surface area. However, their cycle stability is a serious challenge [12]. Although some hydroxides such as $Al(OH)_3$ and $Cu(OH)_2$ [13,14] have been introduced to improve the capacitive performances of Ni-Co hydroxides, the challenges for being high-efficient energy storage systems are still there. In this paper, a facile hydrothermal method to synthesize ternary Ni-Co-Mo oxy-hydroxide nanoflakes on carbon cloth is developed, which show high capacity properties with a specific capacitance of 2562 F g^{-1} at 1 A g^{-1}, and a good cycling stability.

2. Experimental section

All the reagents used in the experiment were of analytical grade and were used without further purification. Prior to the synthesis, commercial carbon cloth (3 cm × 3 cm) was cleaned by sonication sequentially in acetone, ethanol, and deionized water for 10 min each. In a typical synthesis of Ni-Co-Mo oxy-hydroxide nanoflakes, 0.44 g of $Ni(NO_3)_2{\cdot}6H_2O$, 1.31 g of $Co(NO_3)_2{\cdot}6H_2O$, 0.64 g of $Na_2MoO_4{\cdot}2H_2O$, 0.21 g of methenamine, and 0.18 g of urea were dissolved in 30 mL of deionized water by constant intense stirring. The solution was then transferred into a Teflon-lined stainless autoclave and the pre-treated carbon cloth was placed in the autoclave that was then sealed and maintained at 120 °C for 3 h. After it was cooled down to room temperature, the product was washed by deionized water and ethanol several times.

The as-synthesized products were characterized by scanning electron microscopy (SEM, FEI Quanta 450 FEG), X-ray diffraction (XRD, D8 Advance), X-ray photoelectron spectroscopy (XPS, Thermo scientific ESCALAB250) and transmission electron microscope (TEM, JEM 2010) equipped with a selected area electron diffraction (SAED) pattern and energy dispersive X-ray (EDX) spectrum. Electrochemical measurements were carried out on CHI 660E electrochemical analyzer (CH Instruments, China) with a three-electrode system, the tailored product (1 cm × 1 cm) as

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working electrode, an Ag/AgCl electrode as the reference electrode and a platinum electrode as the counter electrode.

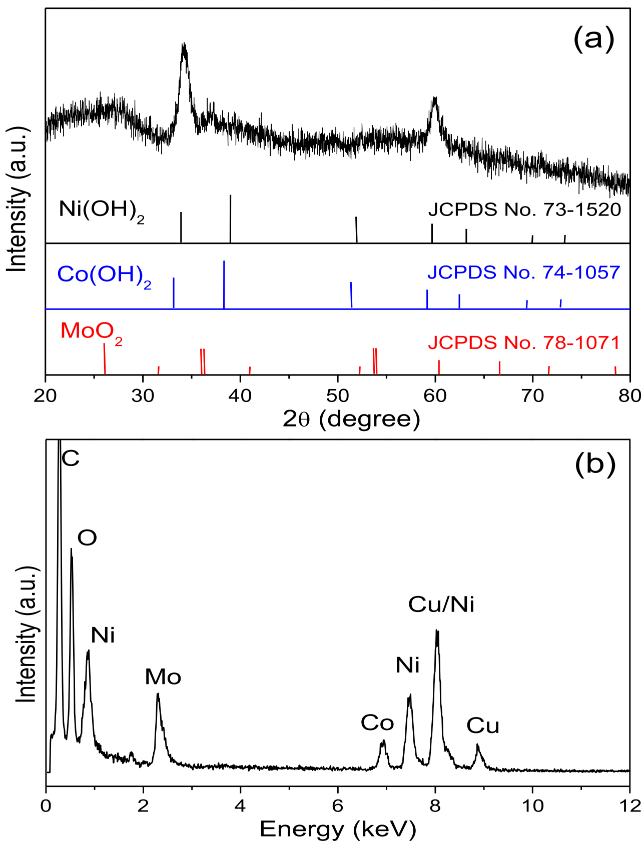

Fig. 1. (a) XRD pattern and (b) EDX spectra of the Ni-Co-Mo oxy-hydroxide nanoflakes.

3. Results and discussion

The phase composition of the prepared product was characterized by XRD and the pattern is depicted in Fig. 1a. Although these peaks are all weak, they still can be identified. It indicates that the product consists of three compounds: Ni–Co double hydroxide and some MoO_2. This speculation can be confirmed by the corresponding EDX analysis. The typical EDX spectrum shown in Fig. 1b indicates the existence of Ni, Co, Mo, and O. Further quantitative analysis indicates that the average atom ratio of Ni, Co and Mo given by EDX system was 9:3:7. Surely, the Cu signals come from the carbon-supported Cu grid. The chemical composition of the product was also analyzed by the XPS technique and the data can be seen in Supplementary Material. The corresponding results further demonstrate that our product is composed of Ni–Co double hydroxide and Mo oxide.

An overview SEM image of the products is presented in Fig. 2a. Highly uniform and dense nanoflakes are distributed on the carbon cloth. A magnified SEM image illustrates that the product has a flake-like morphology (Fig. 2b) with lateral size range from 100 to 200 nm and a few nanometers in thickness. These small flakes are interlaced with each other, creating a highly porous 3D network in a large scale on the substrate, which offers large specific surface area. Fig. 2c shows the general characteristic of the nanoflake in TEM imaging. The flake-like nanostructures can be clearly seen. The corresponding SAED pattern (inset of Fig. 2c) indicates that the nanoflake appears to be polycrystalline. A close TEM examination at high magnification (Fig. 2d) reveals that the ultrathin nanoflakes are highly porous, composed of interconnected nanocrystallites and numerous mesopores ranging from 2 to 5 nm in size. This structure could provide large surface area and short diffusion path for both electrons and ions, which could result in superior electrochemical reaction activity [15].

To evaluate the electrochemical performance of our product as supercapacitor electrode, cyclic voltammetry (CV) and galvanostatic charge-discharge curves were recorded in 2 mol L^{-1} KOH

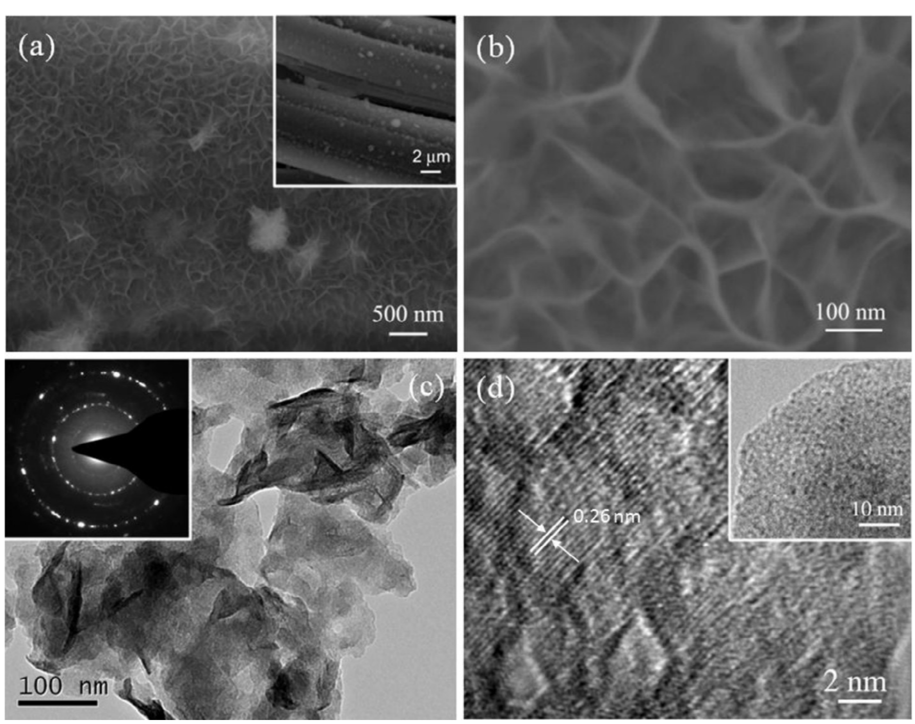

Fig. 2. (a) SEM image of the Ni-Co-Mo oxy-hydroxide nanoflakes, (b) the high-magnification SEM image, (c) TEM image of our product, Inset: corresponding SAED pattern, (d) the high-magnification TEM image.

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