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Binary transition metal oxides (BTMO) (Co-Zn, Co-Cu) synthesis and high supercapacitor performance

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ABSTRACT

Binary transition metal oxides (BTMO) (Co-Zn, Co-Cu) on Ni foam are fabricated through a facile and cost efficient hydrothermal method. In the three-electrode system testing, CoO@ZnO shows the highest specific capacitance of 2.394 F/cm^2 at a current density of 5 mA/cm^2 as well as excellent cycling stability which remains 76.5% of initial capacitance after 1000 cycles. This study provides an important method for the synthesis of high performance BTMO for supercapacitors.

1. Introduction

Recently, the energy crisis is increasingly serious so that developing alternative energy storage system is urgent and challenging [1,2]. As a potential electrochemical power source, supercapacitors have attracted much interest because of its high power density, preferable cycling stability and low maintenance cost [3,4]. Supercapacitors, also called electrochemical capacitors, according to the energy storage mechanism are usually grouped into two categories: electrical double-layer capacitors (EDLCs) and pseudocapacitors [5]. Carbonaceous materials are typical electrode materials for EDLCs. In general, the supercapacitor with double-layer active material has good ratio and circulation performance, but the energy density is relatively low [6]. Transition metal oxides are typical electrode materials for pseudocapacitors. Importantly, the pseudocapacitive material can provide considerable energy output, which has higher capacity than that of the double-layer material.

To prepare high energy density supercapacitors, the researchers focus on the pseudocapacitive materials. RuO_2 has shown ideal pseudocapacitive behavior with a capacitance higher than 800 F/g [7]. However, the high cost of Ru has limited its commercial acceptance as an electrode material in electrochemical capacitors. In this condition, the study of cheaper electrode materials is an effective measure to solve this problem.

It has been found that the abundant transition metal oxides, such as NiO [8], ZnO [9], Co_3O_4 [10] and Fe_2O_3 [11] have excellent redox activity, such as high theoretical specific capacity, and can be used as electrode materials instead of RuO_2. Although transition metal oxides have many commonalities, there are some differences between the crystal structure and the redox behavior of each other. Meanwhile, the valence state of the reaction can be limited. BTMO composed of at least one transition metal ion and electrochemically active ions has many advantages over single metal oxides for supercapacitor. Zeng et al. prepared flower-like cobalt-nickel binary oxide (Co_3O_4-NiO), showing its specific capacitance (687.5 F/g) is higher than Co_3O_4 (235 F/g) or NiO (267 F/g) at the same current density of 0.5 A/g [12]. Bi et al. synthesized NiO/MnO_2 composite grown on the surface of graphite as a high performance electrode material. Moreover, NiO/MnO_2@graphite had greater performance than that of NiO@graphite [13]. As expected, BTMO can enhance the comprehensive electrochemical properties of materials by synergy of different components, making these materials have better electrical conductivity and more active sites.

Among various pseudocapacitive materials, cobalt oxide has been considered as one of promising electrode materials because of its high theoretical capacitance, environment friendly, low cost, reversibility and good pseudocapacitive performance [14,15]. However, poor rate capability and cyclability are the main weakness of Co-based materials.

Zinc oxide (ZnO), an attractive multifunctional material, has been extensively studied in many fields, such as piezotronics, electronics devices, surface switches, strain sensors and

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photocatalysis. The wide application of this amphoteric oxide depends on its good electric conduction and special optoelectronic properties, as well as the excellent chemical and thermal stabilities [16,17]. At present, ZnO has also been used as a pseudocapacitive electrode material for supercapacitors. Li et al. reported ZnO@MoO_3 nanocables, which exhibited much enhanced specific capacitance than that of MoO_3 nanoparticles [18]. Cai et al. reported ZnO@Co_3O_4 electrode exhibits high specific capacitance of 1.72 F/cm^2, which is higher than that of the Co_3O_4 electrode (0.956 F/cm^2) at a current density of 2 mA/cm^2 [19].

In this article, we report a cost-effective and simple strategy to design and fabricate novel nanostructures CoO@Cu_4O_3, CoO, CoO@ZnO, which grow on Ni foam as a binder free electrode for high-performance electrochemical energy storage application. To the best of our knowledge, the proposed synthesis method has never been explored for BTMO materials. The electrochemical properties of the three kinds of electrode materials based supercapacitors were measured.

2. Experimental details

2.1. Materials synthesis

2.1.1. Synthesis of CoO

All of the reagents were of analytical purity grade and used without further purification. Before a facile hydrothermal process, Ni foam (2 × 2 cm^2) was pretreated with 5% HCl solution to remove the oxide layer on its surface, and then it was ultrasonically washed with acetone, ethanol and deionized water (DI), with each step sustained for 15 min. Subsequently, 2 mmol $Co(NO_3)_2 \cdot 6H_2O$, 0.5 mmol $Zn(NO_3)_2 \cdot 6H_2O$, 35 mmol urea and 5 mmol NH_4F were dissolved in 50 mL DI, with continuous stirring for 60 min to form a solution. Then the solution was transferred into a 100 mL Teflon-lined stainless steel autoclave with a piece of pretreated Ni foam immersed into it and sealed and hydrothermally treated at 363 K for 12 h. After that, the Ni foam loaded with precursor was washed three times with DI and was placed in a solution of 5 M (mol/L) of sodium hydroxide for 15 h. Next, the sample was washed several times with DI and dried at 333 K in the oven. Finally, the Ni foam with CoO was obtained by annealing the precursor at 573 K for 3 h in air. Schematic diagram of synthesis process for CoO was shown in Fig. 1.

2.1.2. Synthesis of CoO@ZnO

For a comparison, the CoO@ZnO on nickel foam was synthesized at the same condition except for no placed in a solution of 5 M (mol/L) of sodium hydroxide for 15 h.

2.1.3. Synthesis of CoO@Cu_4O_3

For a comparison, ZnO@Cu_4O_3 on nickel foam was synthesized at the same condition except for no placed in a solution of 5 M (mol/L) of sodium hydroxide for 15 h, and 0.5 mmol $Zn(NO_3)_2 \cdot 6H_2O$ was replaced by 0.5 mmol $Cu(NO_3)_2 \cdot 3H_2O$.

2.2. Material characterizations

X-ray diffraction (XRD) data of the as-obtained samples were recorded on a Rigaku D/max D8 ADVANCE diffractometer with Cu Ka radiation ($\lambda = 0.15418$ nm) at a scan rate of 4°/min. X-ray photoelectron spectroscopy (XPS) was performed on an ESCA-LAB Mk II (Vacuum Generators) spectrometer with unmonochromatized Al Ka X-rays (240 W). Cycles of XPS measurements were conducted in a high-vacuum chamber with a base pressure of 1.33×10^{-6} Pa. Morphologies of the as-prepared samples were investigated on the S-4800 field emission scanning electron microscope (FESEM).

2.3. Electrochemical measurements

For electrochemical performance, cyclic voltammograms (CV), galvanostatic charge-discharge (GCD) curves and electrochemical impedance spectroscopy (EIS) measurements were carried out at room temperature, using a conventional three-electrode system on an CHI 660E electrochemical station (Chenhua instrument Co. Shanghai, China) in 6 M KOH. The as-synthesized products as the working electrodes, a platinum foil (2 cm × 2 cm) and a saturated calomel electrode were used as the counter and the reference electrode, respectively.

3. Results and discussion

To investigate the crystal structure and phase composition, the XRD patterns of the as-prepared CoO@Cu_4O_3, CoO, CoO@ZnO on Ni foam are shown in Fig. 2, respectively. Obviously, the three intensive peaks can be indexed to the (111), (200) and (220) planes of Ni foam in all samples, respectively [20]. For the CoO@ Cu_4O_3 shown in Fig. 2(a), the diffraction peaks located at 30.5°, 59.0°, and 64.4°can be indexed to the (200), (224), and (026) planes of the Cu_4O_3 [21]. The diffraction peaks located at 36.7° and 43.1°can be indexed to the (101) and (002) planes of the CoO [22]. XRD pattern of CoO is

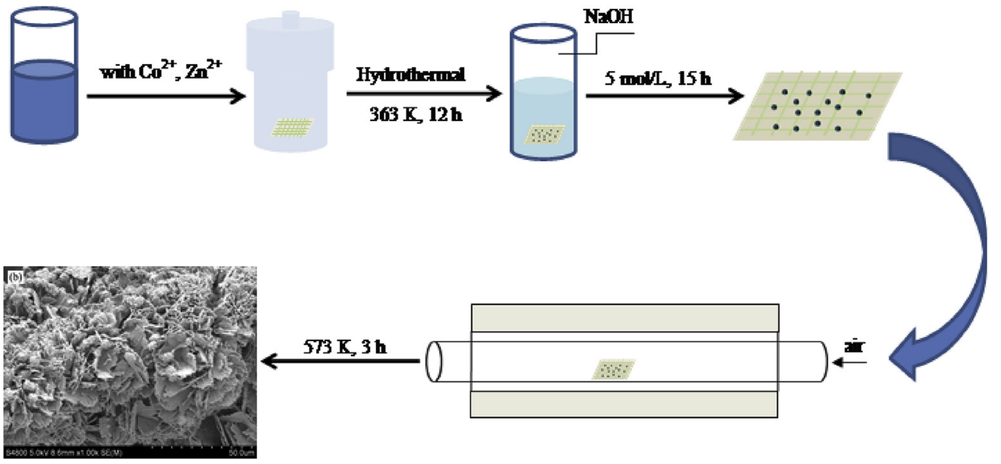

Fig. 1. Schematic diagram of synthesis process for CoO sample.