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An extra-long-life supercapacitor based on $Co_3O_4/NiCo_2O_4/NiO/C\&S$ composite by decomposition of Co/Ni-based coordination complex

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Single-material electrodes do not satisfy the demands of high-performance supercapacitors. To exploit the advantages of both oxides and carbon-based materials, a tightly packed $Co_3O_4/NiCo_2O_4/NiO/C\&S$ nanocomposite is fabricated by sintering a Co/Ni-based coordination complex precursor at 400 °C. The composites and basic components are characterized using various techniques, namely, X-ray powder diffraction, scanning electron microscopy, transmission electron microscopy, Brunauer–Emmett–Teller specific surface area analysis, and elemental analysis. The electrochemical performance is analyzed by cyclic voltammetry, galvanostatic charge/discharge cycling, and electrochemical impedance spectrometry. A uniform nanocomposite was found to be formed of $NiCo_2O_4$, NiO, and Co_3O_4 nanoparticles, incompletely carbonized C, and incompletely vulcanized S. When used as supercapacitor electrodes, the synthesized composites show extra-long cycling stability (>20,000 cycles) during the charge/discharge process. This improvement in the cycle life of the composites is attributed to its highly stable structure. The roles of C and S in forming a stable structure are investigated. The results show that a supercapacitor with electrodes made from the as-prepared $Co_3O_4/NiCo_2O_4/NiO/C\&S$ composite will be promising for commercial applications.

1. Introduction

Recently, electrode materials for supercapacitors have been increasingly investigated in the field of energy materials [1–4]. Initially, carbon-based materials [5–13] were studied as electrode materials, followed by metal oxides [14–27], and more recently, conductive polymers [28–33]. However, the performance of these single-material electrodes still does not satisfy the demands of high-quality supercapacitors, such as good conductivity, high capacitance, long cycle life, environmental friendliness, and low cost [34,35].

Generally, carbon materials show excellent conductivity and a large specific area but poor supercapacitance. Metal oxides usually possess relatively high capacitance; however, their conductivity is commonly poor, and their specific surface area is low. Meanwhile, conductive polymers have a high capacitance and good conductivity, but their structures are unstable [5,14,28]. Therefore, as a frontier research topic, various composite materials are currently being studied for use as supercapacitor electrodes to compensate for the shortcomings of single materials. Many reports have demonstrated composite supercapacitors with superior properties to those of single materials [36–42]. However, most of these composite materials exhibit an unstable or short cycling life, making them difficult to apply in practice. Therefore, increasing the cycling life of supercapacitors remains an important challenge for their practical application.

NiO, $NiCo_2O_4$, and Co_3O_4 are p-type semiconductors with band gaps of 3.6 [43], 2.1 [44], and 2.2 eV [45], respectively. However, their practical application is hindered by their poor electrical conductivity, which results in a limited power density and poor cycling performance [46,47]. To address these issues, a common approach is to build tailored nanostructures that can promote their electronic and ionic transport abilities [48]. Compositing them with carbon-based materials is another effective strategy. Doping electrode materials with other semiconductors to introduce impurity band effects is a well-known strategy for increasing the electrical conductivity. For these reasons, tuning the microstructure of these oxide-based materials, doping them with other semiconductors, and compositing them with carbon-based materials are essential techniques to enable their application in electrochemical capacitors

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Herein, we present a method for fabricating a stable composite of Co_3O_4, $NiCo_2O_4$, $NiCo_2O_4$ with C and S (Co_3O_4/$NiCo_2O_4$/NiO/C&S) using o-mercaptobenzoic acid and Co/Ni salt in an alkaline ethanol solution to crystallize the particles. This coordination complex is then used as a precursor in a simple thermal treatment at temperatures under 400 °C to fabricate Co_3O_4/$NiCo_2O_4$/NiO/C&S composites. The as-prepared composite exhibits much longer cycle life than those of the individual $NiCo_2O_4$, NiO, and Co_3O_4 components, thus showing high performance as the electrode material for ECs. Therefore, these investigations open the door to commercializing transition metal oxides as advanced electrode materials.

2. Experimental section

2.1. Chemicals

The following chemicals were used directly as received from the suppliers without further purification: O-mercaptometh acid (Alfa Aisha; 98 at.%), sodium hydroxide (NaOH; Zhejiang Zhongxing; 99 at.%), anhydrous ethanol (CH_3CH_2OH; Anhui Ante; 96 at.%), nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$; Aladdin Shanghai; 99 at.%), and cobaltous chloride hexahydrate ($CoCl_2 \cdot 6H_2O$; Aladdin Shanghai; 99 at.%).

2.2. Preparation of Co_3O_4/$NiCo_2O_4$/NiO/C&S composites

We added 0.12 g (0.003 mol) of sodium hydroxide to 10 mL of anhydrous ethanol and placed the solution in an ultrasonic bath for ~30 min, until all sodium hydroxide was dissolved in the anhydrous ethanol. Next, o-mercaptobenzoic acid (0.003 mol, 0.4626 g) was added to the solution and stirred with a magnetic stirrer for 30 min at a constant temperature of 27 °C until complete dissolution. Next, $CoCl_2 \cdot 6H_2O$ (0.00075 mol, 0.1785 g) and $NiCl_2 \cdot 6H_2O$ (0.00075 mol, 0.1782 g) were completely dissolved in 5 mL of deionized water. This solution was slowly added dropwise into the ethanol solution and stirred for an additional 30 min. Then, the homogeneous solution was poured into a 50 mL Teflon-lined stainless-steel reactor, sealed, and allowed to react at 120 °C for 96 h in an electric blast oven. Then, the reactor was allowed to cool to 27 °C, and the resulting product was washed several times sequentially with deionized water and anhydrous ethanol and finally dried in an electric blast oven at 100 °C to obtain a black powder (yield of about 0.40 g, 48.5 wt % based on $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$ and o-mercaptobenzoic acid).

The resulting black powder was heated to 400 °C at a heating rate of $2\,^{\circ}C \cdot min^{-1}$ and heat-treated for 1 h in ambient air to obtain the final electrode material.

2.3. Characterization

X-ray powder diffraction (XRD) measurements were performed using a Bruker D8 ADVANCE diffractometer at 40 kV and 40 mA with Cu Kα ($\lambda = 1.5406$ Å) radiation, with a θ step size of 0.01° and a scan speed of $0.1\ s \cdot step^{-1}$. Thermogravimetric analysis (TGA) was performed under N_2 at a heating rate of $5\,^{\circ}C \cdot min^{-1}$ using a TA-Q600 system (TA Instruments, USA). The thermal stability of the as-synthesized complex precursor was investigated from room temperature to 800 °C. Scanning electron microscopy (SEM) was performed using a Multimode Nanoscope IIIa SEM instrument. Transmission electron microscopy (TEM) images were recorded using a Tecnai G2 F30 high-resolution TEM instrument. Elemental analyses (C, H, N, and S) were carried out using a Heraeus CHN-O-S RaPid Elemental Analyzer. The distributions of Ni, Co, S, and C were determined by energy dispersive X-ray (EDX). Elemental mapping was performed using a Hitachi S-4800 field-emission SEM. The pore properties were investigated by nitrogen adsorption/desorption experiments (ASAP, 2020) and analyzed using the Brunauer–Emmett–Teller (BET) method.

2.4. Electrochemical measurements

The obtained electrode material Co_3O_4/$NiCo_2O_4$/NiO/C&S composite, acetylene black, and polytetrafluoroethylene (PTFE) were combined in a mortar at a ratio of 8:1:1 with a small amount of absolute ethanol; the mixture was ground with a pestle until it was completely mixed and uniformly pulverized. The electrode material paste was then applied to a Ni foam collector cut in a certain shape. Specifically, around 2–5 mg of the active substance (electrode paste) was applied over an area of around 1 cm^2, and the assembly was then dried in an electric blast oven at 90 °C. Finally, a powder tablet was pressed at 10 MPa to form an electrode, which was immersed in a newly prepared 6 $mol\ L^{-1}$ potassium hydroxide solution for 10 h before performing electrochemical tests.

A software-controlled three-electrode cell (Electrochemical Workstation CHI650E) was used for all electrochemical measurements of the as-prepared supercapacitor electrodes. The cell consisted of the as-prepared samples as the working electrode, Hg/HgO electrode as the reference electrode, Pt wire as the counter electrode, and 6 M KOH solution as the electrolyte. All measurements were performed at 27 °C. Cyclic voltammetry (CV) was performed at different scan rates from 5 to 100 $mV\ s^{-1}$. Galvanostatic (GV) charge/discharge measurements were conducted at various current densities from 0.5 to 10 $A\ g^{-1}$ to evaluate the specific capacitance, specific power, and specific energy. A potential window from 0 to 0.6 V was used for all CV and GV measurements. Electrochemical impedance spectroscopy (EIS) was carried out to investigate the capacitive performance at open circuit potential in a 6 M KOH electrolyte within a frequency range of 0.01–100,000 Hz. The constant current charge/discharge method was employed to test the long-term cycle capability of the electrode materials. The long-term cycle stability of the electrodes was also tested using the galvanostatic charge/discharge method over 20,000 cycles at a current density of 3 $A\ g^{-1}$.

The specific capacitance of the electrode at different specific current can be calculated using $C = It/\Delta Vm$ [49], where, C ($F \cdot g^{-1}$) is the specific capacitance, I (A) is the discharge current, t (s) is the total discharge time, ΔV (V) is the potential drop during discharge, and m (g) is the mass of active material.

3. Results and discussion

3.1. Structural characterization

Although perfect single crystals (supported through subsequent analyses) of the precursor complex could not be obtained to determine the structure, TGA was performed to support the existence of organic ligands because they can carbonize with residues such as C and S. TGA was also used to further determine suitable conditions for the thermal decomposition of the complex precursor. Generally, the sample decomposed in two main stages from 0 °C to 400 °C (Fig. 1). During the first stage, the weight of the complex sample slowly decreased from 28 °C to 110.191 °C, representing a weight decrease of about 4.9%, which was mainly due to the release of small molecules coordinating with Co^{2+}/Ni^{2+}, such as H_2O and ethanol, from the structure, as observed previously [50]. During the second stage, from 299.031 °C to 407.224 °C, the fast decrease in the sample weight (~39.5%) indicates the decomposition of the organic ligands, suggesting the rapid collapse of the structure. Co and Ni were oxidized, and the structure collapsed into