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High Conductive Architecture: Bimetal Oxide with Metallic Properties @ Bimetal Hydroxide for High-performance Pseudocapacitor

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ABSTRACT

Poor electronic and ionic conductivities of electrode limit the development of pseudocapacitor. In this study, the $NiCo_2O_4$ nanowires array @ $NiCo(OH)_2$ nanosheets growth on Ni foam as a binary composite electrode is synthesized by hydrothermal and electrodeposition methods to improve the electrochemical performance of pseudocapacitor. In the composite electrode, the $NiCo_2O_4$ exhibits metallic properties, which is verified by the first principles calculation, and is responsible for the high conductivity of the composite electrode. Electrochemical measurements demonstrate the $NiCo_2O_4$ @ $NiCo(OH)_2$ electrode exhibits a high areal capacitance of 4.625 F cm^{-2} at 1 mA cm^{-2} (2890.6 F g^{-1} at 0.625 A g^{-1}) and an excellent cycling stability (maintaining 94.66% capacity after 5000 cycles at 10 mA cm^{-2}). Therefore, this work further extends the research on high conductive architecture electrode and shed some light on the design of applied materials for the future practical energy storage devices.

1. INTRODUCTION

Lately, a great lot of attentions have been dedicated to the improvement of next-generation energy stroage devices for solving the problems of environmental pollution and energy crisis [1–3]. A combination of fast charge/discharge rate, high power density and long durability, supercapacitors (SCs) play an improtant role in electrical and industrial fields [4–8]. Pseudocapacitors (PCs), a type of SCs, realize the charge storage by near-surface faradaic redox reaction, which have higher power density than that of electric double layer capacitors (EDLCs) [2,9–13]. However, most of pseudocapacitive electrodes suffer from poor electronic conductivity, which hinder the rate capability of pseudocapacitive materials and limit the development of PCs [14–18]. Therefore, it is necessary to promote the electronic conductivity of pseudocapacitive electrodes for improving the electrochemical preformance of PCs.

To address the aforementioned drawbacks of pseudocapacitive electrodes, an impactful method is derectly hybridizing the electroactive materials with high conductive materials to form a binder-free system for supercapacitors [19–25]. Gupta's group have done a series of works about Ni and Co-based hydroxide and oxide electrodes on conductive substrates for supercapacitors, and the as-prepaerd CoNi-LDH and $NiCo_2O_4$ growth on stainless-steel (SS) exhibited high specific capacitances of 2104 F g^{-1} and 580 F g^{-1}, respectively [26,27]. Meanwhile, Wang et al. demonstrated an electrode, ZnO @ Co_3O_4 composites growth on Ni foam, which revealed an outstanding electrochemical performance [28]. Furthermore, carbon materials and pseudocapacitive electrodes were hybirdized to enhance the electrochemical preformance for supercapacitors. For example, Wu et al. reported the alpha-Fe_2O_3 @ NiO composite growth on a carbon cloth, which achieved an areal capacitance of 557 mF cm^{-2} for high performance supercapacitor electrode [29]. Fisher and his co-workers reported a pseudocapacitive electrode Ni-Co hydroxide @ grephene petal foam for pseudocapacitors, which exhibited outstanding electrochemical preformance [30]. In another report, Shahrokhian et al. prepared an oriented pyrolytic graphite/$Ni(OH)_2$ composite electrode which exhibited a specific capacitance of 1665 F g^{-1} [31]. The above mentioned composites are applied to promote the resistance of whole electrodes and enhance the utilization rate of the electroactive materials. Thereinto, hybridizing pseudocapacitive electrodes with conductive materials to form composites could be supposed to improve the electrical conductivity of pseudocapacitive electrode and enhance the electrochemical performance of pseudocapacitor.

In this paper, the high conductive architecture $NiCo_2O_4$ nanowires array @ $NiCo(OH)_2$ nanosheets growth on Ni foam was successfully synthesized by hydrothermal and electrodeposition methods. In view of the high conductive architecture, the

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metallic $NiCo_2O_4$ improved the conductivity of the composite and promoted the electron transport in the electrode. The ultrathin $NiCo(OH)_2$ nanosheet shortened ion diffusion path and electron transport distance and enhanced the utilization of the composite. Hence, the $NiCo_2O_4$ nanowires array @ $NiCo(OH)_2$ nanosheets electrode exhibited the high areal capacitance of 4.625 F cm^{-2} at 1 mA cm^{-2} (2890.6 F g^{-1} at 0.625 A g^{-1}) and the durable cycling stability of 94.66% after 5000 cycles at 10 mA cm^{-2}.

2. EXPERIMENTAL SECTIONS

2.1. Pretreatment of Ni Foam

The Ni foam was pretreated in acetone and 6 mol L^{-1} HCl each for 10 minutes and cleaned in deionized water and absolute ethyl alcohol three times each for 10 minutes to guarantee a clean surface.

2.2. Preparation of $NiCo_2O_4$ Nanowires Array

$NiCo_2O_4$ nanowires array was gained through hydrothermal and annealed processes without any additional template. The experimental details were as follows: 4 mmol of $Ni(NO_3)_2{\cdot}6H_2O$, 8 mmol of $Co(NO_3)_2{\cdot}6H_2O$ and 48 mmol of urea were dissolved in 75 mL deionized water with constant stirring for 30 minutes. A piece of clean Ni foam was immersed into the above solution, and then transferred into 100 mL Teflon-linked stainless autoclave. The autoclave was sealed and maintained at 120 °C for 7 hours. After the reaction, the Ni foam substrate, covered with nanowires, was cleaned with deionized water and absolute ethyl alcohol, and was annealed at 350 °C in air for 3 hours to obtain the $NiCo_2O_4$ nanowires array.

2.3. Preparation of $NiCo_2O_4$ Nanowires Array @ $NiCo(OH)_2$ Nanosheets

The $NiCo(OH)_2$ nanosheets were prepared by an explicit cathodic electrodeposition method, and then electrodeposited on $NiCo_2O_4$ nanowires array which grew on Ni foam. The electrodeposition process was carried out in a standard three-electrode configuration at room temperature, the $NiCo_2O_4$ nanowires array grown on Ni foam as the working electrode and a bare Ni foam for contrast experiment, platinum mesh as the counter and Ag/AgCl as the reference electrode, respectively. The Ni foam, covered with $NiCo_2O_4$ nanowires, was immersed into the electrolyte (0.1 mol L^{-1} metal ion solution with $Ni(NO_3)_2{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$). The sample was placed in the solution by the voltage static method at −1.0 V for 420 seconds to deposit $NiCo(OH)_2$ nanosheets (The electrodeposition process of $NiCo(OH)_2$ nanosheets was described in Supporting Information Experiments Section). Then, the as-obtained electrode was washed in deionized water and absolute ethyl alcohol three times each for 5 minutes, and dried in a vacuum oven at 80 °C for 10 hours to obtain the $NiCo_2O_4$ nanowires array @ $NiCo(OH)_2$ nanosheets composite. The mass loading densities of the $NiCo_2O_4$, $NiCo(OH)_2$ and $NiCo_2O_4$ @ $NiCo(OH)_2$ composites were 2.3, 2.1 and 3.2 mg cm^{-2}, respectively.

2.4. Structural Characterization

X-ray diffraction (XRD) patterns were collected on a Bruker D8-Advance using CuKα radiation (λ = 1.5406 Å). The morphology of the as-obtained products could be observed by scanning electron microscope (SEM, S-4300, Hitachi) with an accelerating voltage of 20 kV. Transmission electron microscopy (TEM, HRTEM) images were investigated using JEOL EM-2100F with an accelerating voltage of 200 kV. The surface chemical composition of the $NiCo_2O_4$ @ $NiCo(OH)_2$ composite was investigated by X-ray photo-electron spectroscopy (XPS, Kratos Amicus, Kratos Group PLC) through X-radiation Mg Kα with an accelerating voltage of 12 kV, 180 W. Raman spectrums were performed using a Renishaw InVia Microscope Raman with a laser excitation of 532 nm. Fourier transform infrared spectra (FT-IR) were measured on Spectrum Two (PerkinElmer). Composition of elements was examined by energy dispersive spectroscopy mapping (EDS Mapping) with S-3400 (Hitachi).

2.5. Electrochemical Measurements

The electrochemical measurements of the as-prepared electrodes were carried out in a standard three-electrode configuration in 6.0 mol L^{-1} KOH solution. A platinum mesh was used as the counter electrode, an Ag/AgCl was used as the reference electrode and the as-obtained products were pressed at 10 MPa for 60 seconds and then used as the working electrode. The above three electrodes were immersed into 6.0 mol L^{-1} KOH solution for 30 minutes to improve the wetness degree between the working electrode and the electrolyte. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out in CHI 760E electrochemical workstation (Chenhua, Shanghai) at room temperature. EIS tests were conducted under a frequency range of $0.01–10^5$ Hz at amplitude of 5 mV at the open circuit potential. The galvanostatic charge–discharge (CD) tests were performed on a LAND battery program-control test system.

3. RESULTS AND DISCUSSION

3.1. First-principles electronic structure calculations of $NiCo_2O_4$

Fig. 1(a) shows the cubic lattice of Fd3 m space group of the $NiCo_2O_4$ spinel structure [32,33]. Thereinto, Ni and Co atoms occupied the tetrahedral sites and octahedral sites, respectively. In a unit cell, only one-eighth of the Ni sites were occupied by Ni^{2+} and half of the Co sites were occupied by Co^{3+} [34]. The first principles calculation was used to identify the metallic properties of the spinel structure $NiCo_2O_4$. The crystal structure optimized lattice constant was 8.178 Å, which was in good agreement with the theoretical value of 8.11 Å of cubic lattice of $NiCo_2O_4$ spinel structure (JCPDS Card No. 20-0781). According to the calculation results, the nonspin polarization was shown in Fig. 1(b), the hybridization intensively existed between the Ni and Co d states and O p states near the Fermi level (0 eV), and electronic bands were crossing the Fermi level, all of which verified the metallic properties of $NiCo_2O_4$.

3.2. Synthesis and Characterization

The fabrication procedures of the composite were schematically showed in Fig. 2(a). Initially, $NiCo_2O_4$ nanowires array grew on Ni foam through hydrothermal method. Afterwards, $NiCo(OH)_2$ nanosheets were electrodeposited onto the as-obtained $NiCo_2O_4$ nanowires array surface, from which formed the $NiCo_2O_4$ nanowires array @ $NiCo(OH)_2$ nanosheets composite. Fig. 2(b)–(d) are SEM images of synthesis process of the $NiCo_2O_4$ nanowires array @ $NiCo(OH)_2$ nanosheets. The SEM image of $NiCo_2O_4$ nanowires array growth on Ni foam with lower-magnification was shown in Fig. S1. The bare Ni foam was homogeneously covered by $NiCo_2O_4$ nanowires array after the hydrothermal process. The formation of $NiCo_2O_4$ nanowires array resulted from heterogeneous nucleation and growth by hydrolysis of urea in aqueous solution, which reduced the interfacial nucleation energy on the Ni foam [35]. Furthermore, the $NiCo_2O_4$ nanowires were separated and the bottoms of which were interconnected, and then formed a