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Hydrothermal synthesis of $CoMoO_4/Co_{1-x}S$ hybrid on Ni foam for high-performance supercapacitors

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ABSTRACT

Cobalt molybdate/non-stoichiometric cobalt sulfide ($CoMoO_4/Co_{1-x}S$) hybrid was in situ grown on nickel foam by a simple two-step hydrothermal process. The as-prepared $CoMoO_4/Co_{1-x}S$ hybrid electrode possessed core-shell nanostructure, large surface area and high specific capacitance of 2250 F g^{-1} at a current density of 1 A g^{-1}. Using the hybrid as anode and activated carbon (AC) as cathode, an asymmetric supercapacitor of $CoMoO_4/Co_{1-x}S$//AC was fabricated. The optimized supercapacitor had large potential window of 1.6 V and high capacitance of 112 F g^{-1}, resulting in high power density of 804.5 W kg^{-1} and energy density of 39.8 Wh kg^{-1}. Furthermore, the supercapacitor exhibited an excellent long cycle life along with 86.4% specific capacitance retained after 5000 cycles. The superior performances and good stability of the asymmetric supercapacitor can be attributed to the unique structure of the two components in hybrid, and the positive synergistic effects of the hybrid electrodes. The facile preparation process and excellent performance presented here render the $CoMoO_4/Co_{1-x}S$ hybrid as a promising candidate for energy storage device.

1. Introduction

Nowadays, energy crisis has drawn greater attention due to the growing populations and the rapid social development. At the same time, better energy storage devices are urgently demanded. Developing environmental and high-efficiency energy storage is becoming crucial and necessary [1–3]. Supercapacitors have been considered as a promising solution for the problem of better energy storage because of their high power density, fast charge–discharge cycling processes and long cycle life [4,5]. According to the different energy storage mechanisms, supercapacitors are usually classified into three types: electrical double-layer capacitors (EDLCs), pseudocapacitors and hybrid capacitors [6–9]. Generally the mechanism of EDLCs is based on physical adsorption and desorption of ions on the electrode surface. Thus, the electrochemical performances of EDLCs depend on their electrical conductivity, porous structures and specific surface area. Meanwhile, the pseudocapacitors energy storage is decided by reversible and redox reactions. Hybrid capacitors are the combinations of an EDLC and a pseudocapacitor electrode in one supercapacitor [10,11]. Structurally, supercapacitors mainly consist of electrodes, an electrolyte, a separator and a current collector. During them, electrodes are generally considered to be critical on the electrochemical performance of supercapacitors, therefore electrodes are widely studied.

Transition metal sulfide materials, such as NiS_2, CoS_2, MoS_2, CuS_2, and WS_2, have been widely used for the electrode of supercapacitors [12–14]. The capacitances comparison of these sulfide materials are demonstrated in Table S1. Cobalt sulfide is a typical kind of transition metal chalcogenides, which includes binary sulfides of variety sorts. For instance, CoS_2, Co_3S_4 and Co_9S_8 are a small part of common sulfides [14–17]. Among the binary cobalt sulfides, $Co_{1-x}S$ has attracted high attention due to its complicated structure and excellent properties. $CoMoO_4$ has also aroused researchers' interests based on its advantages of abundant sources, low cost and good electrochemical properties [18–20]. Cobalt-based and nickel-based molybdate due to good electrochemical performance has been widely researched as supercapacitor electrode materials. Performance comparison of Co and Mo based asymmetric supercapacitors is listed in Table S2.

In this paper, a facile two-step hydrothermal method was used to synthesize $CoMoO_4/Co_{1-x}S$ hybrid nanorods on Ni foam [17,21,22]. In the first step of hydrothermal process, the precursor of $Co(CO_3)_{0.35}Cl_{0.20}(OH)_{1.10}\cdot 1.74H_2O$ was formed, in the second step the $CoMoO_4/Co_{1-x}S$ hybrid was obtained. The as-prepared hybrid

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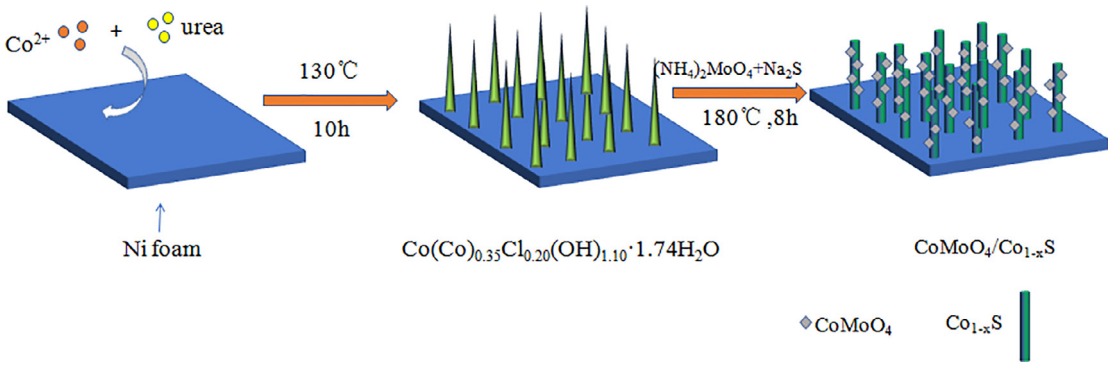

Fig. 1. Schematic diagram of the fabrication process of $CoMoO_4/Co_{1-x}S$ hybrid on the Ni foam.

combined the merits of both $CoMoO_4$ and $Co_{1-x}S$ and showed high electrode specific capacitance of 2250 F g^{-1}. Then, an asymmetric supercapacitor of $CoMoO_4/Co_{1-x}S$//AC was assembled. The potential window of the supercapacitor was widened to 1.6 V, accordingly providing high power density of 804.5 W kg^{-1} and energy density of 39.8 Wh kg^{-1}.

2. Experimental

2.1. Chemicals and materials

All chemical reagents were A. R. grade and commercially purchased without any further purification. Urea (purity ≥ 99.0%), potassium hydroxide (KOH, purity ≥ 99%) was purchased from Aladding. Sodium sulfide nonahydrate ($Na_2S{\cdot}9H_2O$, purity ≥ 98%), cobalt chloride hexahydrate ($CoCl_2{\cdot}6H_2O$, purity ≥ 99%), ammonium molybdate tetrahydrate [$(NH_4)_2MoO_4{\cdot}4H_2O$, purity of 99.99%] were purchased from Alfa Aesar.

The Ni foam (NF) was purchased and treated with dilute hydrochloric acid solution to remove oxides on the surface. Then, it was cut into small pieces about 1 × 1 cm^2. Acetone, DI water and absolute ethanol were used in turn to wash the Ni foam for 15 min with the assistance of ultrasonic cleaning, which was finally dried in an oven at 60 °C for 24 h and standby.

2.2. Synthesis of $CoMoO_4/Co_{1-x}S$ hybrid

The $CoMoO_4/Co_{1-x}S$ hybrids were synthesized by a two-step hydrothermal method [21,22]. The schematic diagram of the fabrication process is shown in Fig. 1. In a typical synthesis, the first step was applied to prepare a precursor of $Co(CO)_{0.35}Cl_{0.20}(OH)_{1.10}{\cdot}1.74H_2O$ nanorods. A 60 mL mixing solution contained 2.5 mmol of $CoCl_2{\cdot}6H_2O$ and 10 mmol of urea [$CO(NH_2)_2$] and cleaned NF (1 cm^2) were transferred to a 100 mL of Teflon-lined autoclave. The autoclave was programmed heated at 130 °C for 10 h. After hydrothermal reaction, the resulting product was collected by centrifugation, washed with distilled water and absolute ethanol for several times and dried at 60 °C overnight to obtain the precursor.

Followed by a sulfuration reaction, a 60 mL mixing solution contained 0.18 g (0.67 mmol) $(NH_4)_2MoO_4{\cdot}4H_2O$ and 0.12 g (0.5 mmol) $Na_2S{\cdot}9H_2O$ and the as-synthesized precursors were transferred to a 100 mL of Teflon-lined autoclave. The system was heated at 180 °C for 8 h. The resultant was collected by centrifugation, washed with distilled water and absolute ethanol for several times and dried at 60 °C for 24 h to obtain $CoMoO_4/Co_{1-x}S$ hybrids. The mass loading of $CoMoO_4/Co_{1-x}S$ was weighed and calculated as about 2.25 mg (1 cm^2).

For comparison, a bare $Co_{1-x}S$ was synthesized using the same route without adding $(NH_4)_2MoO_4$. The pure $CoMoO_4$ was synthesized using the same route without adding $(NH_4)_2MoO_4{\cdot}4H_2O$.

2.3. Fabrication of supercapacitor

To prepare AC electrodes, 8:1:1 (in mass ratio) of activated carbon (AC), acetylene black and PEFT aqueous solution was weighted and dispersed in a right amount of anhydrous ethanol, stirred with a glass rod and ultrasonic to form a homogeneous black paste. Under the pressure of 10 MPa, the slurry was pressed into thin flakes using a double-stick tablet machine. Then the thin flakes were pressed onto adequate sizes of clean stainless steel wire mesh. After being dried at 60 °C for 24 h, AC electrodes were prepared and used as the cathode. $CoMoO_4/Co_{1-x}S$ electrodes were prepared by the above mentioned two-step hydrothermal method on Ni foam directly used as the anode. A supercapacitor of $CoMoO_4/Co_{1-x}S$//AC thus was fabricated. The measurement was operated in 3 mol L^{-1} KOH aqueous solution.

2.4. Characterizations and measurements

Crystal structures of the as-prepared $CoMoO_4$, $Co_{1-x}S$ and $CoMoO_4/Co_{1-x}S$ were observed by X-ray diffraction (XRD, Rigaku, Japan, Cu-$K\alpha$ radiation) at 10° min^{-1} over 2θ range from 10° to 80°. The surface morphologies were obtained by field emission scanning electron microscopy (FESEM) (SU8000, HITACHI, 3 kV) and high transmission electron microscopy (HRTEM) (JEM2100, 200 kV). Cyclic voltammetry curves (CV), galvanostatic charge/discharge (GCD) curves and electrochemical impedance spectroscopy (EIS) were tested with an electrochemical working station CHI760E. The scan rates of CV curves were tested from 5 mV s^{-1} to 50 mV s^{-1}. GCD test was carried out at different current densities with a 0 to 0.52 V potential window. EIS measurements were performed in the frequency range between high (10^6 Hz) and low-frequency region (10^{-2} Hz) at room temperature with an amplitude of 5 mV.

A three-electrode system, the as-prepared $CoMoO_4/Co_{1-x}S$ on Ni foam as the working electrode, Hg/HgO as the reference electrode, and platinum wire as the counter electrode was conducted to study the electrochemical properties of the single $CoMoO_4/Co_{1-x}S$ electrode. A double electrode system, the as-prepared $CoMoO_4/Co_{1-x}S$ on Ni foam as the anode, AC electrode as the cathode was assembled to research the practical properties of the supercapacitor. The specific capacitance of a single electrode (C_S, F g^{-1}) in a three electrode system and the specific capacitance of supercapacitor (C_T, F g^{-1}) in a double electrode system can be calculated from GCD curves system according to the fol-

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