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Hierarchical structures of nickel, cobalt-based nanosheets and iron oxyhydroxide nanorods arrays for electrochemical capacitors

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ABSTRACT

Dimensionality and rational design of electrode architectures play a crucial role in determining materials' fundamental properties and the electrochemical performance of supercapacitor. For a proof-of-concept, Ni–Co layered double hydroxides (LDH), $NiCo_2O_4$ and $NiCo_2S_4$ nanosheets supported on carbon fiber paper (CFP) substrate are prepared by simple hydrothermal methods in this work. When tested as the pseudo-capacitor positive electrode, the self-support nanosheets on CFP demonstrate good performance and rate capability as well as excellent cycling life, which contributes to the unique hierarchical nanosheets structure supported on 3D conductive CFP substrate with open permeable channels, facilitating electrolyte penetration and ensuring more efficient ion diffusion and faster electron transport. The asymmetric supercapacitor based on pseudocapacitance of both electrodes is further first realized by using $NiCo_2S_4$ nanosheets and FeOOH nanorods as positive and negative materials, respectively. The obtained device can deliver a maximum power density of 8.6 kW kg^{-1} and energy density of 45.9 Wh kg^{-1} and even after 10000 reversible cycles at a cell voltage of 1.6 V in aqueous electrolyte, there still retained 86.4% of its initial capacitance.

1. Introduction

Electrochemical capacitors (ECs) have triggered significant researches for their potential applications in portable electronics, electric or hybrid electric vehicles, and other high power energy sources owing to their large power density, fast charging/discharging process, long cycling life and high reliability [1–3]. Up to now, various nanostructured materials have been investigated as electrodes for ECs and their morphologies are versatile, such as zero dimensional (0D) nanoparticles [4], 1D nanowires/tubes/rods/belts [5–8], 2D nanosheets/plates [9,10] and 3D porous frameworks/networks [11–13]. Importantly, recent researches have shown that, in addition to the composition and arrangement of atoms in materials, dimensionality plays a crucial role in determining materials' fundamental properties, which has been most strikingly highlighted with 2D graphene over the past few years [14,15] and this has led to the exploration of other 2D materials, such as boron nitride [16], layered transition metal hydroxides/oxides, transition metal dichalcogenides [17–25] and so on. Among which, layered transition metal hydroxides/oxides and transition metal dichalcogenides have been widely investigated as active materials for ECs because of their multiple oxidation states for pseudocapacitance, which can provide higher energy density than electrical double layer capacitance delivered by carbon-based active materials [6,11,26]. In addition, superior to single-phase metal hydroxides/oxides/dichalcogenides, binary metal (Mn, Fe, Co, Ni, Zn, etc.) hydroxides/oxides/dichalcogenides can synergistically improve the electrochemical performance due to their feasible oxidation states and high electrical conductivity [27]. For example, nickel and cobalt binary hydroxides/oxides/dichalcogenides [6,9,28] have emerged as a promising class of active materials due to their excellent redox reversibility and relatively high capacity. Specifically, it has been reported that there is a morphology-dependent relationship in electrochemical energy storage performance. Compared with nanorods/nanowires, ultrathin nanosheets morphology can exhibit better cycling performance, because it is advantageous for efficient ion and electron transport and can better accommodate the volume change during

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the electrochemical reaction [29–31]. However, there are still few reports about the nickel and cobalt binary dichalcogenides with nanosheets morphology.

In addition, for a supercapacitor device, the energy density is usually limited to the operating voltage (V) and capacitance (C), according to the equation $E = 1/2CV^2$. To design a better electrochemical capacitor with high energy density, an effective strategy is to construct an asymmetric supercapacitors (ACSs) to extent the operating voltage, which typically consists of a battery-type Faradic electrode (positive electrode) as the energy source and a capacitor-type electrode (negative electrode) as the power source. Even though carbon-based nano-materials, such as activated carbon (AC), graphene and carbon nanotubes have been widely used as negative electrodes for ASCs because of their large surface area, excellent electrical conductivity, and outstanding electrochemical stability, however, carbon materials often suffer low specific capacitance which falls short of the demand for SCs with high energy density. On the contrary, the redox-active materials may provide a pronounced improvement in energy density by giving higher specific capacitance. And in this work, we focused on enhancing the capacitance and energy density of ASCs based on pseudocapacitance in both electrodes. Despite rarely reports about iron oxyhydroxide, it has the advantage of low cost and low toxicity as negative electrode materials for ECs, however, its low electrical conductivity and low ion diffusion constant can result in a low specific capacitance and poor rate capability, which is a major drawback for their application in ECs [32]. However, it can be partly remedied by growing iron oxyhydroxide nanostructure directly on a current collector substrate to enhance the conductivity of the electrode.

Herein, in this work, among various strategies including co-precipitation, electrodeposition and solvothermal, a facile and simple hydrothermal method and subsequent thermal decomposition and sulfuration process route was employed to fabricate nickel and cobalt binary dichalcogenides nanosheets. We obtained 3D hierarchical structure containing self-assembly 2D $NiCo_2S_4$ nanosheets supported on carbon fiber paper (CFP). In order to prove the versatile and feasibility of this concept as well as to compare the electrochemistry performances of its corresponding hydroxides and oxides, Ni–Co layered double hydroxides (LDH) and $NiCo_2O_4$ were also prepared. The electrochemical tests showed that the areal capacitance of Ni–Co LDH, $NiCo_2O_4$ and $NiCo_2S_4$ is 402, 292 and 531 mF cm^{-2} at current density of 8 mA cm^{-2}, respectively. And this kind of structure proves to have excellent cycling stability as well as good rate capability. Moreover, 3D structure consisting of FeOOH nanorods supported on CFP is also prepared, and it exhibits an areal capacitance of 341 mF cm^{-2} at the current density of 4 mA cm^{-2}. Hence, to design a better electrochemical capacitor with high energy density, a novel ASC device composed of the as-prepared $NiCo_2S_4$ (positive electrode) and FeOOH nanorods (negative electrode) was demonstrated for the first time. The cell voltage can reach 1.6 V in an aqueous electrolyte, delivering high energy density (45.9 Wh kg^{-1}) and high power density (8.6 kW kg^{-1}) as well as outstanding cycling stability.

2. Experimental

2.1. Preparation of Ni–Co LDH/$NiCo_2O_4$/$NiCo_2S_4$ nanosheets

Typically, 0.015 M $Ni(NO_3)_2{\cdot}6H_2O$, 0.03 M $Co(NO_3)_2{\cdot}6H_2O$ and 0.135 M HMT were dissolved in 30 ml distilled water. Then the solution was transferred to a Teflon-lined stainless-steel autoclave of 50 mL capacity and a piece of clean carbon fiber paper was immersed into the precursor. After 5 h growth at 120 °C, the autoclave was cooled down to the room temperature naturally and Ni–Co LDH nanosheets were obtained. The hydroxides were further annealed at 300 °C for 2 h in air to form $NiCo_2O_4$ nanosheets. Then, the $NiCo_2S_4$ were fabricated by placing $NiCo_2O_4$ nanosheets arrays in a Teflon-lined stainless-steel autoclave at 100 °C for 12 h containing 0.05 M Na_2S aqueous solution and the final product was rinsed with distilled water and dried in vacuum at 60 °C for 2 h. The load weigh of $NiCo_2S_4$ was about 0.6 mg cm^{-2}.

2.2. Preparation of FeOOH nanorods

FeOOH nanorods were fabricated on carbon fiber paper by hydrothermal method. A clean carbon fiber paper substrate was

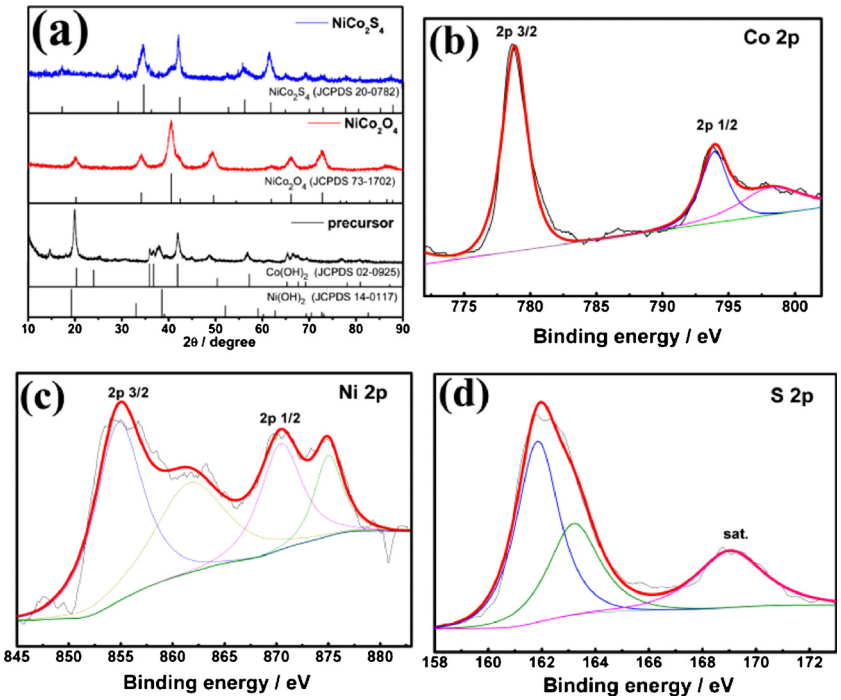

Fig. 1. (a) XRD patterns of Ni–Co LDH, $NiCo_2O_4$ and $NiCo_2S_4$ nanosheets and (b) XPS spectra of (b) Co 2p, (c) Ni 2p and (d) S 2p for $NiCo_2S_4$ nanosheets.