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One-pot synthesis of nickel-cobalt hydroxyfluorides nanowires with ultrahigh energy density for an asymmetric supercapacitor

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ABSTRACT

A novel and unique nickel-cobalt hydroxyfluorides (NiCo-HF) nanowires material is fabricated by one-pot solvothermal synthesis method for asymmetric supercapacitor. The synthesis mechanism and factors that influence the formation of the NiCo-HF nanowires have been further discussed. The as-prepared NiCo-HF electrode exhibits a high specific capacitance of 3,372.6 F g^{-1}, and the capacitance retention of 94.3% can be achieved at a high current density of 20 A g^{-1} after 10,000 cycles. The outstanding electrochemical performance of the electrode can be attributed to the synergistic effect of the nanowires morphology and complicated redox process of active material. Furthermore, an asymmetric supercapacitor assembled with NiCo-HF nanowires as positive electrode and activated carbon as the negative electrode shows an ultrahigh energy density of 83.6 Wh kg^{-1} at a power density of 379.4 W kg^{-1} and an excellent cycling stability with 86.3% capacitance retention after 10,000 cycles, indicating that this novel material has great promise for potential application in energy storage device.

1. Introduction

With the rapidly increasing of global warming and environmental pollution, it is extremely urgent to look for renewable energy sources to replace the traditional fossil energy [1,2]. Supercapacitors, as a novel efficient energy storage devices, have attracted considerable research interest due to their fast charge-discharge ability, high power density and long cycling life [3,4]. However, construction of high-performance supercapacitor with high energy density, as well as high power density is still a challenging work. Therefore, the continuous exploration of high energy density materials has been a major target for the development of supercapacitors [5–7]. It is known that the energy density can be enhanced by increasing the specific capacitance of the electrode or the operation potential window [8]. Recently, asymmetric supercapacitors, which combine a capacitor-type electrode and battery-type Faradic electrode, have become very promising energy storage devices due to the increased operation potential window and thus the energy density [9,10].

Generally, transition metal hydroxides or oxides have been widely applied in gas sensor, solar cell, Li-ion batteries, as well as supercapacitor owing to their fast redox reaction between the multiple oxidation states [11–16]. Among various transition metal hydroxides or oxides, $Co(OH)_2$ and $Ni(OH)_2$ have received wide attention in asymmetric supercapacitors due to their layered structures and characteristic redox reaction [17,18]. However, owing to the poor electrical conductivity, the low rate capability and cycling life limit their practical application. Recently, instead of single transition metal hydroxides or oxides, the mixed hydroxides or oxides materials have been employed to make materials more stable and durable for long-term use. In particular, Ni-Co double hydroxide nanostructure materials have been most investigated because of their high electrical conductivity and high specific capacitance. For example, Yan et al. [19] demonstrated Ni-Co double hydroxide microspheres offered an excellent supercapacitor performance with the specific capacitance of 2,275.5 F g^{-1} at current density of 1 A g^{-1}. Chen et al. [20] reported the Ni-Co layered double hydroxide hybrid film displayed an enhanced specific capacitance of 2,682 F g^{-1} at current density of 3 A g^{-1}. The

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asymmetric supercapacitor based on the Ni-Co layered double hydroxide hybrid film achieved an ultrahigh energy density of 188 Wh kg^{-1} at an average power density of 1,499 W kg^{-1}. Cheng et al. [21] synthesized layered Co-Ni double hydroxide/graphene composites at first and then assembled them into films by integrating with carbon nanotubes. The hybrid Co-Ni double hydroxide/graphene/carbon nanotube (CNT) self-standing electrode exhibited the maximum specific capacitance of 2,360 F g^{-1} at current density of 0.5 A g^{-1} and still kept value of 2,030 F g^{-1} at current density of 20 A g^{-1}.

Except for the mixing the single transition metal hydroxides or oxides with other transition metal cations, the supercapacitor performance also can be improved by introduction of anions into transition metal hydroxides or oxides materials. Up to now, some nanostructured transition metal sulphides [22,23], phosphates [24], fluorides [25], and carbonate-hydroxides [26] have been developed for applying in supercapacitor. Among them, metal carbonate hydroxides with divalent metal ions have been attracted extensive research attention in application for supercapacitor, which the hydrophilic CO_3^{2-} ion can sufficiently increase the wettability of electrode surface [27,28]. For instance, Zhao et al. [29] synthesized single-layered binary Ni-Co hydroxyl carbonate through hydrothermal method, which exhibited a maximum specific capacitance of 2,266 F g^{-1} at 0.5 A g^{-1}, and the relevant asymmetric supercapacitor showed high energy density of 50 Wh kg^{-1} at 78 W kg^{-1}. Recent research on Ni-Co hydroxyfluorides (NiCo-HF) is limited, however, their application on the lithium-ion batteries enlighten us to explore their potential application in supercapacitors [30,31]. Inspired by the excellent performance of Ni-Co fluorides and carbonate hydroxides, NiCo-HF should become an outstanding electrode materials for supercapacitors because they offer much more redox reactions than the single components, which is similar way as layered double hydroxides compared with the single component hydroxides [32].

Besides, the supercapacitor performance can be further improved by controlled the nanostructure of the electrode to raise the specific surface area, which contribute to fast redox reactions and ion/electron transport at the electrode/electrolyte interface. Active materials with nanowire structures can provide high specific surface area and accelerate the ion diffusion and electron transport, which lead to the high specific capacitance. Herein, we report a simple, one-pot solvothermal method to synthesize NiCo-HF nanowires used as the electrode for supercapacitor. The novel NiCo-HF nanowires exhibit a high specific capacitance of 3,372.6 F g^{-1} at a current density of 1 A g^{-1} and maintain the specific capacitance of 2,505.7 F g^{-1} at a current density of 20 A g^{-1}. Moreover, about 94.3% of the initial specific capacitance is maintained at 20 A g^{-1} after 10,000 cycles. In addition, the as-assembled NiCo-HF//activated carbon (AC) asymmetric supercapacitor shows high energy density (86.3 Wh kg^{-1} at 379.4 W kg^{-1}) with high power density (7,490 W kg^{-1} at 65.4 Wh kg^{-1}) and cycling retention of 86.3% after 10,000 charge-discharge cycles.

2. Materials and methods

2.1. Synthesis of NiCo-HF nanowires

All materials and reagents were of analytical grade and were used without further purification. In the typical synthesis process, 2 mmol $Ni(CH_3COO)_2{\cdot}4H_2O$, 2 mmol $Co(CH_3COO)_2{\cdot}4H_2O$, 4 mmol NH_4F and 10 mmol urea were dissolved in 40 mL isopropyl alcohol-water mixture solution (volume ratio is 1:1). After ultrasonic for 30 min, the resulting solution was sealed in a 50 mL Teflon-lined autoclave and heated to 140 °C for 10 h, then cooled to room temperature naturally. The NiCo-HF nanowires were collected by filtration and washed with absolute ethanol and deionized water several times, and then dried at 60 °C overnight. The Ni-HF and Co-HF were obtained by adding $Ni(CH_3COO)_2{\cdot}4H_2O$ (4 mmol) and $Co(CH_3COO)_2{\cdot}4H_2O$ (4 mmol) respectively in the starting materials, while keeping the other experimental conditions unchanged. Moreover, in order to gain the growth mechanism of NiCo-HF nanowires, the reaction temperatures at different stages (120, 140, 160 and 180 °C) were carefully carried out, at the same time the other experimental conditions were kept unchanged.

2.2. Characterization

The morphologies of Ni-HF, Co-HF and NiCo-HF samples were characterized using an SU8020 field-emission scanning electron microscopy (FESEM, Hitachi, Japan), respectively. The chemical composition and distribution of as-prepared samples were recorded by energy dispersive X-ray spectroscopy (EDS). The structures and crystalline phases were investigated by X-ray powder diffraction (XRD, Rigaku, Japan). High resolution transmission electron microscopy (HRTEM) images were observed using a JEM-2100F (JEOL, Japan) operating at 200 kV. X-ray photoelectron spectroscopy (XPS) spectra were recorded on ESCALAB250 (Thermo, USA) using a monochromatic Al Kα X-ray beam. The specific surface area and pore size distribution of samples were examined by the Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) model (SA3100 Surface Area Analyzer).

2.3. Fabrication of NiCo-HF//AC asymmetric supercapacitors

The working electrodes were prepared by mixing the as-prepared samples, acetylene black and polyvinylidone fluoride (PVDF) at a weight ratio of 8:1:1 in 1-methyl-2-pyrrolidinone solvent to form the slurry and coating on the nickel foam uniformly. Prior to prepare the electrode, Ni foam was pretreated with 5% HCl solution to remove the surface oxide layer and ultrasonically washed with acetone, ethanol and deionized water, respectively. The mass loading density of the electrode material on the nickel foam was about 5 mg cm^{-2}. The asymmetric supercapacitor was assembled by combining the NiCo-HF nanowires positive electrode and the commercial AC negative electrode face-to-face with poly (vinyl alcohol) (PVA)-KOH gel electrolyte and dried at 60 °C until the gel electrolyte was solidified with the evaporation of water. The PVA-KOH gel electrolyte was prepared as follows: 3 g of PVA powder was dissolved in 30 mL deionized water under vigorous stirring at 90 °C until PVA dissolved completely, and then 3.4 g KOH powder was slowly added into the viscous solution with sufficient stirring until the solution became clear. The mass ratio of the positive electrode and negative electrode was calculated according to the following Eq. (1) [33]:

$$\frac{m_+}{m_-} = \frac{C_{s-} \times \Delta V_-}{C_{s+} \times \Delta V_+} \quad (1)$$

where m, C_s and ΔV are the mass, the specific capacitance and the potential window for positive (+) and negative (−) electrodes, respectively. The optimal mass ratio of NiCo-HF to AC can be calculated to be $m_+/m_- = 0.74$.

2.4. Electrochemical measurements

The electrochemical measurements of the as-fabricated electrodes were carried out in three-electrode cell with 2 mol L^{-1} KOH aqueous solution as the electrolyte at room temperature. The as-fabricated electrode was used as the working electrode, while the Ag/AgCl electrode and Pt wire electrode were used as the reference and counter electrode, respectively. All the electrochemical performances were tested on a CHI760E electrochemical

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