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An investigation of ultrathin nickel-iron layered double hydroxide nanosheets grown on nickel foam for high-performance supercapacitor electrodes

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ABSTRACT

Layered double hydroxide materials with sheet-like morphologies (i.e., LDH nanosheets) have been proposed to use in supercapacitors. However, the practical application of LDH nanosheets has been inhibited by the notorious inter-particle aggregation and poor charge transport between active materials and current collectors. In this work, 3D nickel-iron layered double hydroxide (NiFe-LDH) nanosheet films with porous nanostructures were synthesized using a hydrothermal method. The ultrathin nanosheets are homogeneously and vertically aligned on the surface of Ni foam. The pseudocapacitors assembled using NiFe-LDH nanosheets exhibit a superior specific capacitance of 2708 F g^{-1} at 5 A g^{-1}, higher than the previously reported LDHs. The effect of growth concentration and Ni/Fe mole ratio on the electrochemical properties was also investigated. Asymmetric supercapacitors with the NiFe-LDH nanosheets film as the positive electrode and active carbon as the negative electrode display a high energy density of 52 Wh kg^{-1} at an average power density of 800 W kg^{-1}. When two aqueous asymmetric supercapacitors were assembled in series and charged for only 1 min, the stored energy was capable of powering two green light-emitting-diodes for more than 5 min, indicating the great potential of these 3D NiFe-LDH nanosheets for high-performance energy storage.

1. Introduction

With the daunting challenges of global warming and depletion of fossil fuels, a great deal of efforts have been focused on sustainable energy sources, including designing high-performance energy storage systems and developing earth abundant energy resources [1]. Recently, the fabrication of high performance energy storage devices, such as solar cells, fuel cells, lithium battery and supercapacitor, has become a crucial research field [2]. Owing to their larger capacity in store energy than conventional capacitors, and higher specific power and longer cycle-life than batteries, supercapacitors have drawn great interest [1-3]. Most of the commercial supercapacitors are based on electrical double layer capacitor and mainly consist of carbon-based materials, such as carbon nanotubes [3], graphene [4], and active carbon (AC) [5]. They usually possess good cycle lifetime and high power density, but fail to meet the requirements of high specific capacitance and energy density as peak-power assistance in electric vehicles [6,7]. In contrast, pseudocapacitive materials (e.g., RuO_2, MnO_2, NiO, Co_3O_4, $Ni(OH)_2$, $Co(OH)_2$ and their composites), which are dominated by reversible fast surface faradaic redox reactions, can deliver

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much higher specific capacitance than carbon-based materials [8,9]. Among these materials, RuO_2 possesses a specific capacitance as large as 720 F/g, but due to its high cost, the application of this material was limited [8]. Thus, researchers have focused on the development of novel materials for pseudocapacitor applications.

High-performance supercapacitor electrodes should possess characteristics such as high utilization efficiency and high transport rate for both electrolyte ions and electrons [5]. Thus, it is of significance to improve the electron transport in active materials, and the electric contacts between active materials and current collectors by designing nanoscale electrode materials with large surface areas and stable porous nanostructures [10-13]. Layered double hydroxides (LDHs) with a general formula of $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[A^{n-}_{x/n}\cdot mH_2O]^{x-}$ (M^{II} and M^{III} denote the layers of divalent and trivalent metallic ions, respectively; A^{n-} is an interlayer anion), have attracted increasing attention because of their relatively low cost, high redox activity, large specific surface area, laminated structure and environmentally friendly nature [14]. Specially, LDHs containing transition metals, such as Ni, Co, Mn, Fe, and Al, are deemed as promising candidates [15]. For example, Guo et al. prepared NiMn-LDH nanosheets through a one-step wet-method and found the specific capacitance of the NiMn-LDH can reach 1511 F g^{-1} at 2.5 A g^{-1} [16]. Li et al. reported that a novel structure of CoFe-LDH nanoplatelets shell supported on a copper wire produced by an electrosynthesis method delivered a high specific capacitance of 755 mF cm^{-2} at the discharge current density of 2.5 mA cm^{-2} [17].

In recent years, NiFe-based composites with different morphologies (such as nanoparticles, nanowires, nanorods, nanotubes, and flowerlike) have been introduced as electrode materials in electrochemical energy conversion and storage [1,18]. The analysis of density of states and partial density of states of NiFe-LDH and $Ni(OH)_2$ showed that NiFe-LDH has a stronger capability for electron transportation and higher activity than $Ni(OH)_2$ [19]. However, NiFe-LDHs synthesized via co-precipitation and hydrothermal methods are usually powders, and thus polymer binders, e.g., Nafion, are usually required to form compact electrodes, leading to low conductivity with current collectors and poor mechanical stability [20,21]. To overcome these limitations, increasing interest was paid on the growth of hierarchical nanostructured materials directly on the Ni foam, which has large surface area, high porosity and enhanced conductivity to improve supercapacitance performance. Chen et al. fabricated NiCo-LDH nanosheets on Ni foam via a hydrothermal co-deposition process, and the LDH showed very high capacitance (2682 F g-1 at 3 A g-1) [22]. However, to the best of our knowledge, NiFe-LDH grown on Ni foam for supercapacitor has not been reported.

In this work, we propose a one-step hydrothermal method to directly synthesis ultrathin NiFe-LDH nanosheets on 3D Ni foams. The morphologies and electrochemical properties of NiFe-LDHs with different Ni/Fe molar ratios were explored. The as-synthesized NiFe-LDH electrode exhibits outstanding performance. We fabricated an aqueous asymmetric supercapacitor using the NiFe-LDH film as the positive electrode and active carbon as the negative electrode. In addition, the asymmetric supercapacitor was used in powering green light-emitting-diode. Our results suggest that the NiFe-LDH nanosheet arrays can act as high-performance electrode materials for supercapacitor applications.

2. Experimental section

2.1. Synthesis of NiFe-LDH nanosheets on Ni foam

All chemical reagents were used as received without further purification. The film electrode material was prepared by a simple one-step process as illustrated in Scheme 1: Firstly, Ni foam (10 mm × 20 mm × 1.7 mm, 380 g m^{-2}, 110 ppi) was pretreated successively with 3 M HCl solution, deionized water, and absolute ethanol in an ultrasound bath for 10 min each in order to remove NiO layer and residual organics on the surface. Then, an aqueous solution containing $Ni(NO_3)_2\cdot 6H_2O$, $Fe(NO_3)_3\cdot 9H_2O$, urea, H_2O (36 mL) was stirred thoroughly to form a clear solution. After drying, the Ni foam was immersed in a 50 ml Teflon-lined autoclave containing above homogeneous solution. The autoclave was sealed, maintained at 120 °C for 12 h, and then cooled to room temperature naturally. The final product was thoroughly washed with H_2O and ethanol and vacuum dried at 60 °C for 8 h. For the sake of comparison, nanosheets with different feeding contents of total metal ion ($Ni^{2+}$and Fe^{3+}) before reaction and different feeding mole ratio of Ni^{2+}/Fe^{3+} were also synthesized by the same process (see Table S1). The mole ratio of urea/feeding metal ion is 5. The mass of the nanosheets on Ni foam was determined by subtracting the weight before deposition from the weight after deposition. The average loading densities of active materials were about 1 mg cm^{-2} for all electrodes.

2.2. Fabrication of asymmetric supercapacitor

To construct an asymmetric supercapacitor, the NiFe-LDH nanosheet arrays on Ni foam were used as the positive electrode and active carbon as the negative electrode (Scheme 1). The negative electrode was prepared by mixing activated carbon, acetylene black, and poly(vinylidene fluoride) with a mass ratio of 8:1:1, which pressed on Ni foam and dried at 80 °C for 12 h. The asymmetric supercapacitor was separated by a separator, and a 1 M KOH aqueous solution was used as the electrolyte.

2.3. Material characterization

The morphological investigations of the samples were received by scanning electron microscopy (SEM, JEOL JSM-7800F), and energy dispersive spectrometer (EDS) attached to the SEM was employed to characterize distribution of elements of samples. Transmission electron microscope (TEM) images were obtained on a HITACHI HT7700 field emission microscope. X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance diffractometer using a Cu Kα source. The functional groups were analyzed by fourier transform infrared spectroscopy (FT-IR, Nicolet iS50). Kratos Axis Ultra X-ray photoelectron spectroscope (XPS, Al Kα source) was used to investigate the surface properties.

2.4. Electrochemical measurements

Electrochemical performances of all as-prepared LDH nanosheets electrodes were evaluated using a three-electrode setup. The Ni foam supported NiFe-LDH nanosheets acted as the working electrode (10 mm × 10 mm × 1.7 mm), which were soaked in a 1 M KOH solution. A large-area platinum foil and a saturated calomel electrode (SCE) served as the counter electrode and the reference electrode, respectively. The electrochemical properties of asymmetric supercapacitor were investigated under a two-electrode cell configuration in 1 M KOH electrolyte solution. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) measurements were conducted on a CHI760E electrochemical workstation (Chenhua, Shanghai). The specific capacitance, Cs (F g^{-1}), of nanosheets film electrodes were calculated from GCD curves as follows: $C_s = I \times \Delta t/(\Delta V \times m)$, where I (A) is the discharge current, ΔV (V) refers to the potential change during the discharge time Δt (s), and m (g) represents the mass of the active material in the electrode. The C_s of asymmetric