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Flower-like NiFe layered double hydroxides coated MnO_2 for high-performance flexible supercapacitors

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ABSTRACT

The flower-like NiFe layered double hydroxides loaded on Ni foam (NF/NiFe LDHs) are synthesized via one-pot hydrothermal method and the synthesized NF/NiFe LDHs are further coated with MnO_2 nanosheets (MnO_2@NF/NiFe LDHs) through an extra hydrothermal process. The excellent supercapacitor performance of MnO_2@NF/NiFe LDH has been observed with a high capacitance of 4274.4 mF cm^{-2} at 5 mA cm^{-2} and a capacitance retention of 95.6% after 1000 cycles from a traditional three-electrode system. A low-cost flexible asymmetric supercapacitor has also been designed and fabricated using MnO_2@NF/NiFe LDH as anode and active graphene as cathode. The working voltage window of this asymmetric supercapacitor is up to 1.4 V and the asymmetric supercapacitor delivered an energy density of 24.6 mWh cm^{-2} at 350 mW cm^{-2}. These outstanding supercapacitor performances of the synthesized composite MnO_2@NF/NiFe LDHs are attributed to the combination of unique NiFe layered double hydroxides structure and higher conductivity of MnO_2 nanosheets.

1. Introduction

There is a rapid increasing consumption of energy nowadays, which may cause serious energy crisis and environmental problems as the majority of it comes from the combustion of fossil fuels [1,2]. It is very urgent to find new and clean energy sources and promote the efficiency of energy storage and conversion. Among possible candidates, the development of supercapacitors is highly attractive derived from the high power output, fast-rate capability and long cycling life [3–6]. In general, supercapacitors include electrical double-layer capacitors (EDLCs) and pseudocapacitors based on the working principles. The energies in EDLCs are stored in the electric double-layer via electrostatic accumulation of charges while pseudocapacitors mainly utilize reversible Faradaic reactions to keep the energies, providing higher mass and/or volumetric specific capacitance [7–10]. Normally, metal oxides (such as CoO_x, MnO_2, and Fe_2O_3) [11–13] and conducting polymers (PPy, PANI. and PEDOT) are widely utilized pseudocapacitive electrode materials. However, these materials suffer from serious limitations, such as the relatively low operating voltage windows of NiO_x, CoO_x, MnO_2, conducting polymers, and high cost of RuO_2 [14–16]. On the other hand, metal nitrides also attract much attention due to their unique properties, but their insufficient stability is not avoidable [17–19]. Thus, much effort has been paid to design and prepare excellent electrode materials with precisely controlled compositions and structures in order to achieve high-performance supercapacitors.

Layered double hydroxides (LDHs), which also named as anionic clays or hydrotalcite-like multifunctional materials, are potential electrochemical capacitor electrode materials. The compositions of LDHs are tunable and can be described as $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[A^{n-}]_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are metal cations and A^{n-} is anion which balances the positive charges on the layers [20–24]. Wu et al. synthesized CoNi-LDHs nanosheets electrode using chemical vapor deposition (CVD) method together with electrochemical deposition for high-performance supercapacitors and obtained 1.62 F cm^{-2} at 1 mA cm^{-2} [25]. Ma et al. prepared the Co-Fe LDHs onto carbon fiber cloth through hydrothermal process and achieved 774 F g^{-1} at 1 A g^{-1} [26]. Li

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et al. fabricated Ni-Mn LDH via co-precipitation method, which delivered 1635 F g^{-1} at 1 A g^{-1} [27]. Nevertheless, the low electrical conductivity of LDHs hinders the potential electrochemical capacitor application though their high specific capacitances are well presented. Constructing 3D architecture of LDHs onto metallic substrates can improve the conductivity, resulting in enhanced electrochemical performance of LDH materials [28,29]. Among them, Nickel foam (NF) is a promising candidate in LDH-based supercapacitors due to the combination of macro-porous structure, acceptable surface area, and strong physical strength [10]. Furthermore, flexible devices are highly desirable due to their great potentials in many fields such as wearable power sources [19,30,31].

Herein, the flower-like NiFe layered double hydroxides has been synthesized using Ni foam as conductive support. The hierarchical MnO_2@NF/NiFe LDHs are prepared through an additional hydrothermal process. The obtained MnO_2@NF/NiFe LDHs have been tested as supercapacitor electrode materials, possessing a higher surface area, showing 4274.4 mF cm^{-2} at 5 mA cm^{-2}, and displaying an excellent cycling stability. Moreover, a flexible asymmetric supercapacitor has also been made using MnO_2@NF/NiFe LDHs as the cathode and active graphene coated on NF as the anode, demonstrating 24.6 mWh cm^{-2} at 350 mW cm^{-2}.

2. Experimental

2.1. Materials and reagents

All the chemicals used in this article were ordered from Alfa Aesar and in analytical purity.

2.2. Synthesis of NF/NiFe LDH

Firstly, $Ni(NO_3)_2{\cdot}6H_2O$ (0.3 mmol), $Fe(NO_3)_3{\cdot}9H_2O$ (0.3 mmol) and $CO(NH_2)_2$ (3 mmol) were dissolved in 35 mL DI H_2O and dispersed under ultrasonication to obtain a homogeneous solution. One piece of Ni foam (1.5 × 4 cm^2) was dipped into the prepared solution and then transferred into a 50 mL Teflon-lined stainless-steel autoclave, which was sealed, maintained at 120 °C. A brown thin film was observed on the Ni foam substrate and the film and metal substrate were rinsed with DI H_2O and ethanol several times, and dried at 60 °C for 6 h. It is still challenge to measure the exact mass loading of the NiFe LDH on the Ni foam because some of the Ni substrate would be oxidized by the Fe^{3+} ion and dissolved in the solution. The NiFe LDHs prepared for 6 h and 12 h were designated as S_0 and S_1, respectively.

2.3. Synthesis of MnO_2@NF/NiFe LDH

The MnO_2@NF/NiFe LDH was obtained using the hydrothermal method. Typically, S_1 was immersed into the 50 mL Teflon-lined stainless-steel autoclave containing $KMnO_4$ solution (40 mL, 0.02 M), which was subsequently maintained at 140 °C for 4 h. The synthesized MnO_2@NF/NiFe LDH denoted as S_2 was washed with DI H_2O and ethanol several times, and dried at 60 °C for 6 h.

2.4. Characterization methods

The crystal structures of the samples were recorded on powder X-ray diffraction (XRD, Rigaku D/max 2500, Cu Kα). The morphology and structure of as-prepared nanostructures was characterized by focused ion beam scanning electron microscopy (Zeiss Auriga FIB/SEM), equipped with an energy dispersive X-ray spectrometry (EDS).

2.5. Electrochemical measurements

All the electrochemical measurements were recorded on an electrochemical workstation (CHI 660E) in a traditional three-electrode cell with 2 M KOH aqueous solution as the electrolyte. The counter electrode and reference electrode were platinum foil and a saturated calomel electrode (SCE), respectively. At the same time, the Ni-foam-supported nanocomposites (1 × 1 cm^2) were utilized directly in the testing. The cyclic voltammetry (CV) curves were conducted in range from 0 V to 0.4 V with scan rates between 10 and 100 mV s^{-1}. Galvanostatic charge-discharge (CC) curves were performed at current densities from 5 to 20 mA cm^{-2}. The electrochemical impedance spectroscopy (EIS) was obtained in the frequency range from 100 kHz to 0.01 Hz. The durability tests were performed via repeating 1000 charge-discharge cycles at 15 mA cm^{-2}.

2.6. Fabrication of an asymmetric supercapacitor

To fabricate the asymmetric supercapacitor, the S_3 (1.5 × 1.5 cm^2) was applied as cathode, the active graphene (AG) also deposited on Ni foam as anode (AG: carbon black: PVDF = 7:2:1), and a filter paper as separator. The built up device was soaked into 2 M KOH solution for 20 min before being packed between two PET films.

The energy density and power density of the asymmetric supercapacitor were calculated as follows:

$$C = \frac{I \times \Delta t}{m \times \Delta V} \quad (1)$$

$$E = \frac{C \times \Delta V^2}{2} \quad (2)$$

$$P = \frac{E}{\Delta t} \quad (3)$$

where C (mF cm^{-2}) is the capacitance of the asymmetric supercapacitor; I (mA) is discharge current; ΔV (V) is the applied voltage; Δt (s) is the discharge time; m is the total weight of the asymmetric supercapacitor; E and P are the corresponding energy density and power density, respectively.

3. Results and discussion

Flower-like NF/NiFe LDH and MnO_2@NF/NiFe LDH were obtained through hydrothermal processes, as schematically displayed in Fig. 1. To begin with, metal salts (including Ni^{2+} and Fe^{3+} ions) and urea were dissolved in DI H_2O, followed by the immerse of Ni foam. Metal ions M^{n+} were adsorbed onto the surface of Ni foam through the electrostatic force between the cations and the metal surface negative charges [32]. Under the hydrothermal condition of 120 °C for 12 h, OH^- which from the decomposition of urea induced the formation of NiFe LDH seeds on the NF surface. Interestingly, LDH seeds firstly grew to nanowires (S_0) when the process lasted for 6 h, and then the nanowires gradually grew to nanosheets with the time increasing to 12 h (S_1). At the second stage, MnO_2 was coated onto the LDH via the decomposition of $KMnO_4$ as described in the experimental section and MnO_2@NF/NiFe LDH was obtained. In the synthesis, NF provides room for the nucleation of NiFe LDHs and anchoring sites for LDH sheet growth. On the other hand, NF is a good electrical conductor, which would promote the conductivity of LDH films.

XRD (Fig. 2) was employed to check the phase and composition of the as-prepared samples. Four peaks in the low angle of XRD