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Three-dimensional $ZnFe_2O_4@MnO_2$ hierarchical core/shell nanosheet arrays as high-performance battery-type electrode materials

Chang Liu [a, b], Tao Peng [a, b], Chunlei Wang [a, b], Yang Lu [a, b], Hailong Yan [a, b], Yongsong Luo [a, b, *]

[a] School of Physics and Electronic Engineering, Xinyang Normal University, Xinyang 464000, PR China
[b] Key Laboratory of Advanced Micro/Nano Functional Materials, Xinyang Normal University, Xinyang 464000, PR China

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ABSTRACT

In this paper, a highly ordered three-dimensional $ZnFe_2O_4@MnO_2$ core/shell nanosheet arrays ($ZnFe_2O_4@MnO_2$ NSAs) on three-dimensional (3D) Nickel foam (Ni foam) have been prepared via a facile, stepwise hydrothermal approach and further investigated as a battery-type electrode material. It is found that the honeycomb-like $ZnFe_2O_4@MnO_2$ NSAs have outstanding electrochemical performances using cyclic voltammetry (CV), galvanostatic charge-discharge (CD), and electrochemical impedance spectroscopy (EIS) in a three-electrode system. Based on the unique nanostructure, the $ZnFe_2O_4@MnO_2$ NSAs exhibit an exceptional capacity of 1084 C g^{-1} at current density of 2 A g^{-1} and long-term capacity retention of 96.1% after 5000 cycles at current density of 4 A g^{-1}. Moreover, the $ZnFe_2O_4$ nanosheet arrays ($ZnFe_2O_4$ NSAs) also have 714 C g^{-1} at a current density of 2 A g^{-1} exhilaratingly and the capacity value is proven to be the highest when compared with other structures of $ZnFe_2O_4$ taken from the other literatures. Some synergistic effects are identified to be responsible for the observations: Firstly, high crystalline quality of the $ZnFe_2O_4$ NSAs core which is directly grown on 3D Nickel foam (a conductive current collector), allowing fast electron transport; secondly, the unique structure of honeycomb-like MnO_2 shell that has an ultralarge surface area for electrochemical reaction; thirdly, smart combination of $ZnFe_2O_4$ and MnO_2 effectively utilizes their different virtues and also compensate their defects; finally, highly conductive 3D Ni foam substrate, which fully eliminate conductive additives and binders.

1. Introduction

With the ever-increasing energy and power demand in the applications of portable electronics to electric vehicles (EVs), there is a constantly technological progress in lithium-ion batteries, supercapacitors and other storage devices during the past few decades. Therefore, the worldwide scientists are searching for renewable energy sources to substitute the traditional fossil fuels and decrease the pressure from the continuously degrading environment. Rapid developing sector of EVs is claiming the better energy-storage devices to supplement their intrinsically sluggish kinetics [1–6]. A variety of battery-type materials that include hydroxides, transition metal oxides (TMOs) (such as $Ni(OH)_2$ [5,6], Co_3O_4 [3,4] etc.) and their binary systems are drawing extensive attentions to identify electrodes of high electrochemical performance . In general, electrochemical charge-storage electrodes can be typically classified into three types based on the type of charge-storage mechanism: (I) Electric double layer (EDL) electrodes; (II) Pseudo capacitive electrodes; (III) Battery—type electrodes. The detailed classification is given in Table 1. The electrochemical reaction of battery-type electrodes, although, can't be considerable to be capacitive, they are commonly coupled with EDL electrodes in the “so-called” asymmetric device to compromise the characteristics of batteries (high energy density) and supercapacitors (high power density) [7–13].

Recently, as a special metal conductor with excellent electrochemical properties, spinel transition metal oxides (AB_2O_4) containing two metal elements have gained great attention as promising electrode materials. Particularly, among the spinel metal ferrites (MFe_2O_4), $ZnFe_2O_4$ is the most promising due to its low toxicity, high specific surface area, good chemical performance and ultralow-cost, environmental benignity and rich abundance . To the

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* Corresponding author. School of Physics and Electronic Engineering, Xinyang Normal University, Xinyang 464000, PR China.
E-mail address: ysluo@xynu.edu.cn (Y. Luo).

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Table 1
The classification of electrochemical charge-storage electrode and typical materials correspondingly.

Electrode types	EDL electrodes	Pseudocapacitive electrodes	Battery-type electrodes
Typical Materials	activated carbon [41]	RuO_2 [45]	Co_3O_4 [49]
	reduced graphene oxide [42]	Nb_2O_5 [46]	NiO [50]
	carbon aerogels [43]	MnO_2 [47]	$NiCo_2O_4$ [51]
	carbon nanotube [44]	Polyaniline [48]	Fe_2O_3 [52]

best of our knowledge, the sole $ZnFe_2O_4$ suffers from poor retention of cyclic capacity and rate capacity, and this is a general obstacle on the application [14–20]. However, $ZnFe_2O_4$ have a good capacity and possess ultrahigh conductivity. In contrast, MnO_2 has low conductivity (10^{-5}-10^{-6} S cm^{-1}), which greatly hinder their practical application with sole institute, and the capacity of MnO2 is also unsatisfactory. But we all know MnO_2 has a perfect cyclic performance and rate-performance. To address facing problems, the key is designing a smart composite, which can utilize their various merits entirely by combining two or more different materials. Therefore, we are auspicious to prepare a smart integration of $ZnFe_2O_4$@MnO_2 nanostructure [21–23].

Herein, we report a simple and cost-effective method to design three-dimensional core/shell arrays of the composite of MnO_2/$ZnFe_2O_4$ as a bind-free for battery–type electrode materials. In the core/shell structure, the mesoporous $ZnFe_2O_4$ NSAs work as a “core” and honeycomb-like MnO_2 layer acting as a “shell” layer composed by numerous edge to edge MnO_2 nanoflakes. MnO_2 was chosen as the “shell” for its low cost, low-toxicity and natural abundance [23]. This design has several advantages: (i) The virtues of $ZnFe_2O_4$ (a fresh material for storage devices) and MnO_2 (a typical material with good cyclic performance and rate performance) were combined skillfully; (ii) $ZnFe_2O_4$ NSAs with well-defined single-crystalline nanostructure serves both the backbone and conductive connection for MnO_2 materials, and porous feature can enlarge the specific surface area; (iii) the honey-comb like MnO_2 layer can offer a considerable region for electrochemical reaction and also provide a giant room for ion transfer; (iv) Ni foam substrates of smart three-dimensional network structure afford an ideal electron pathway as a bind-free electrode; (v) the core materials of vertical $ZnFe_2O_4$ NSAs directly grow on the Ni foam and this make the hierarchical nanostructure to be very stable. We will discuss the morphologies and electrochemical properties below with respect to honeycomb-like $ZnFe_2O_4$@MnO_2 NSAs in detail.

2. Experimental section

2.1. Chemicals

The chemical reagents include, Iron nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$), Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), Ammonium fluoride (NH_4F), Urea, Glucose and Potassium permanganate ($KMnO_4$). All the purchased chemicals were analytical grade and used directly.

2.2. Synthesis of three-dimensional mesoporous $ZnFe_2O_4$ NSAs on Ni foam

In a typical experiment, 0.1486 g of $Zn(NO_3)_2 \cdot 6H_2O$ and 0.404 g $Fe(NO_3)_3 \cdot 9H_2O$ were initially dissolved into 80 mL of deionized water (DI water) to form a transparent solution at room temperature, then 0.148 of NH_4F and 0.72 g of Urea were added into solution respectively. A piece of Ni foam (a rectangular shape of 1.5 cm × 3.0 cm area) was immersed in a 5 M HCL solution in an ultrasound bath for 20 min to remove the possible surface oxide layer, and then rinsed with DI water and absolute ethanol several times subsequently. After that, the above prepared aqueous solution and the pre-treated Ni foam were transferred into a 100 mL Teflon-lined stainless-steel autoclave, which was heated up to 140 °C in 2 h and then kept for 4 h in an electric oven. Finally, after the oven cooled down to a room temperature naturally, the product was taken out, washed with DI water in an ultrasound bath for 2 min, vacuum dried and then thermally treated at 400 °C in air for 2 h to get crystallized $ZnFe_2O_4$ nanosheet arrays on Ni foam.

2.3. Synthesis of honeycomb-like hierarchical $ZnFe_2O_4$@MnO_2 NSAs on Ni foam

$ZnFe_2O_4$@MnO_2 hierarchical structures were prepared by growing MnO_2 nanoflakes directly onto the $ZnFe_2O_4$ nanostructure backbones after a carbon-assisted reaction process. Initially, self-supported $ZnFe_2O_4$ nanosheet arrays were coated by a thin layer of carbon. In a typical process: a piece of Ni foam grown $ZnFe_2O_4$ nanostructure was immersed into a 0.04 M aqueous glucose solution for 36 h, followed by carbonization at 450 °C in Ar gas for 4 h. After that, the carbon coated Ni foam of $ZnFe_2O_4$ was put into a Teflon-lined stainless steel autoclave containing a 0.05 M $KMnO_4$ solution, which was subsequently maintained at 180 °C for 3–6 h. Finally, the product was taken out, washed with DI water and ethanol, then dried at 60 °C to obtain a honeycomb-like hierarchical $ZnFe_2O_4$@MnO_2 nanosheet arrays.

2.4. Materials characterizations

The material including Ni foam was directly evaluated by X-ray diffraction (XRD) using a D8 Advance (Bruker) system with Cu-Ka radiation ($l = 1.5418$ Å) at 40 kV and 40 mA in a 2 range from 10° to 80°at room temperature and Raman spectroscopy was carried out using WITEC CRM2000 Raman system equipped with a 532 nm laser source and 100• objective lens. The crystalline structure of the materials was scraped from the Ni foam and the structure and morphology of the materials was monitored on a field emission scanning electron microscope (FESEM, JEOL S-4800) and a transmission electron microscope (TEM, JEOL JEM-2010).

2.5. Electrochemical evaluation

The electrochemical measurements were performed on an electrochemical workstation (CHI 660D, CH Instruments Inc., Shanghai) by using a three-electrode mode in 2 M KOH aqueous solution within the potential window of approximately 0–0.5 V. The neat $ZnFe_2O_4$ NSAs ($m_{ZnFe2O4} = 1.2$ mg) and $ZnFe_2O_4$@MnO_2 NSAs ($m_{ZnFe2O4@MnO2} = 1.7$ mg) were directly used as the working electrode. A Pt plate (1×1 cm^2) as the counter electrode and the calomel electrode was adopted as the reference electrode. The electrochemical impedance spectra (EIS) was obtained by the electrochemical workstation in the frequency range from 0.01 Hz to 100 KHz. The specific capacity (C_s in C g^{-1}) was calculated using the equation: