

Original article

Ni–Al composite hydroxides fabricated by cation–anion double hydrolysis method for high-performance supercapacitor

Shuang-Shuang Yang^{a,b}, Ming-Jiang Xie^b, Yu Shen^b, Yong-Zheng Wang^b,
Xue-Feng Guo^{b,*}, Bin Shen^{a,*}^aSchool of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China^bKey Lab of Mesoscopic Chemistry MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

ARTICLE INFO

Article history:

Received 30 December 2015

Received in revised form 15 January 2016

Accepted 21 January 2016

Available online 11 February 2016

Keywords:

Nanocomposites
Porous materials
Double hydrolysis
Doped Ni(OH)₂
Energy storage

ABSTRACT

Chemical doping of nickel hydroxide with other cations (e.g. Al³⁺) is an efficient way to enhance its electrochemical capacitive performances. Herein, a simple cation–anion (Ni²⁺ and AlO₂⁻) double hydrolysis method was developed toward the synthesis of nickel–aluminum (Ni–Al) composite hydroxides. The obtained composite hydroxides possesses a porous structure, large surface area (121 m²/g) and homogeneous element distribution. The electrochemical test shows that the obtained composite hydroxides exhibits a superior supercapacitive performances (specific capacitance of 1670 F/g and rate capability of 87% from 0.5 A/g to 20 A/g) to doping-free nickel hydroxide (specific capacitance of 1227 F/g and rate capability of 47% from 0.5 A/g to 20 A/g). Moreover, the galvanostatic charge/discharge test displays that after 2000 cycles at large current density of 10 A/g, the composite hydroxides achieves a high capacitance retention of 98%, indicative of an excellent electrochemical cycleability.

© 2016 Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences. Published by Elsevier B.V. All rights reserved.

1. Introduction

Electrochemical capacitors (EC) [1–3], also named supercapacitor, have attracted increasing attentions because of their higher power density and longer cycling life than secondary batteries. To develop an advanced EC device, an active electrode material with high capacity and rate capability performances is indispensable. Among various electrode materials, Ni(OH)₂ has been considered as a potential candidate [4–6] for EC due to its high theoretic capacity, excellent redox behavior, ease of synthesis, abundant sources, low cost, environmentally friendly and *etc.* To date, various approaches [7–12] have been explored to fabricate nanostructured nickel hydroxide, however, the actual rate capability reported for most nanostructures remains unsatisfactory, which mainly caused by the poor electrode conductivity. As a result, in recent years, extensive research has been carried out to improve the electrode conductivity through chemical doping or morphology control of active materials on the nanoscale [13,14]. It

is reported that the electrode conductivity can be improved by chemical doping with other cations such as cobalt (Co) [15,16], aluminum (Al) [17], and zinc (Zn) [18].

Herein, a simple cation–anion (Ni²⁺ and AlO₂⁻) double hydrolysis, *i.e.* Ni²⁺ (aq.) + 2AlO₂⁻ (aq.) + 4H₂O → Ni(OH)₂ (s) + 2Al(OH)₃ (s) method was developed for the synthesis of nickel–aluminum (Ni–Al) composite hydroxides. Unlike previous synthesis methods of Ni(OH)₂-based materials, it needs neither any adscititious alkali [19,20] sources nor heat treatment (hydrothermal or microwave irradiation) for producing OH⁻ ions due to the described double hydrolysis is a spontaneous reaction. The obtained composite hydroxides possesses a porous structure, large surface area (121 m²/g), and a homogeneous element distribution. Moreover, the final composite nickel hydroxide exhibits a superior supercapacitive performances (specific capacitance of 1670 F/g and rate capability of 87% from 0.5 A/g to 20 A/g) to doping-free nickel hydroxide (specific capacitance of 1227 F/g and rate capability of 47% from 0.5 A/g to 20 A/g).

2. Experimental

Synthesis: Typically, 2.91 g (0.01 mol) Ni(NO₃)₂·6H₂O were dissolved in 500 mL distilled water to obtain the precursor

* Corresponding authors.

E-mail addresses: guoxf@nju.edu.cn (X.-F. Guo), binshen2000@hotmail.com (B. Shen).

solution. Then, 1.63 g NaAlO_2 (0.02 mol) was added to the precursor solution under magnetic stirring for 24 h to undergo a cation–anion double hydrolysis reaction. After double hydrolysis reaction, the obtained precipitate was filtered, washed and dried. The final obtained product was denoted as D- $\text{Ni}(\text{OH})_2$ (D: doping). As comparison, a doping-free $\text{Ni}(\text{OH})_2$ was prepared by a reported solvothermal method with anhydrous ethanol as solvent, nickel nitrate as precursor. Typically, 0.145 g nickel nitrate was firstly dissolved in 50 mL anhydrous ethanol and then transferred to an autoclave to undergo a solvothermal treatment at 120 °C for 24 h. After solvothermal treatment, the obtained precipitate was filtered, washed and dried. The final obtained product by solvothermal method was denoted as DF- $\text{Ni}(\text{OH})_2$ (DF: doping-free).

Characterization: X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert X-ray diffractometer with a $\text{Cu K}\alpha$ radiation (40 kV, 40 mA). Transmission electron micrograph (TEM) and element mapping images were obtained with a JEOL 2100 microscope operated at 200 kV. N_2 sorption isotherms were measured using a Micromeritics ASAP2020 analyzer at -196 °C. Before measurements, all samples were degassed at 200 °C for 6 h. The specific surface area is calculated by Brunauer–Emmett–Teller (BET) theory and the pore size distribution is determined by adsorption branch via Barrett–Joyner–Halenda (BJH) method. X-ray photoelectron spectrum (XPS) were recorded on a Thermo ESCALAB 250 by using $\text{Al K}\alpha$ radiation (15 kV, 150 W). All binding energies were referenced to the $\text{C}1\text{s}$ peak at 284.6 eV. The composition of the product is examined by inductively coupled plasma atomic emission spectroscopy (ICP) on Optima 5300DV.

Electrochemical test: Electrochemical measurements were carried out in a 6.0 mol/L KOH aqueous electrolyte at room temperature, using a three-electrode cell with an Hg/HgO reference electrode and a platinum coil counter electrode. The testing electrode was prepared by mixing the obtained product powder, carbon black and polytetrafluorethylene (PTFE) together at a mass ratio of 7:2:1, and dipping the resulting mixture into nickel foam (1 cm \times 2 cm, current collector) before being pressed

together at 10.0 MPa. The electrochemical performances of samples were determined by cyclic voltammetry (CV) and galvanostatic charge/discharge curves. The mass specific capacitance was calculated by the discharge curve according to the formula of $C = (I\Delta t/m\Delta V)(F/g)$, where I is the current density (A), Δt is the discharge time (s), m is the weight of active material, ΔV is the potential window of discharging (V).

3. Results and discussion

The structure and the composition of the obtained nickel hydroxides were characterized by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), respectively. For DF- $\text{Ni}(\text{OH})_2$, the XRD pattern (Fig. 1a—red) shows six well-defined diffraction peaks that can be indexed to (0 0 3), (0 0 6), (1 0 1), (0 1 5), (1 0 2) and (1 1 0) diffractions of $\text{Ni}(\text{OH})_2$ (JCPDS: 00-001-1047). As to D- $\text{Ni}(\text{OH})_2$, the diffraction pattern (Fig. 1a—black) shows seven diffraction peaks that can be indexed to the mixed phase of $\text{Al}(\text{OH})_3$ and $\text{Ni}(\text{OH})_2$, indicative of the feasibility of the presented double hydrolysis method toward the fabrication of Ni–Al composite hydroxides. The XPS survey spectrum (Fig. 1b) reveals that the obtained D- $\text{Ni}(\text{OH})_2$ is composed of three elements of Ni, Al and O. The high-resolution XPS spectra of $\text{Al}2\text{p}$ (Fig. 1c) show that the elements of Al in D- $\text{Ni}(\text{OH})_2$ exist in the form of $\text{Al}(\text{OH})_3$. The high-resolution XPS spectra of $\text{Ni}2\text{p}$ of the two hydroxides (Fig. 1d) both show four peaks around 855, 860, 873 and 878 eV that can be indexed to $\text{Ni}2\text{p}_{3/2}$, $\text{Ni}2\text{p}_{3/2}$ satellite, $\text{Ni}2\text{p}_{1/2}$ and $\text{Ni}2\text{p}_{1/2}$ satellite signals of $\text{Ni}(\text{OH})_2$, which further confirms the successful preparation of Ni–Al composite hydroxides by the presented double hydrolysis method. The actual elemental composition was confirmed by ICP and the measured molar ratio of Ni/Al in the final composite hydroxides is 1:1.86.

The morphology of the obtained Ni–Al composite hydroxides was characterized by transmission electron micrograph (TEM) shown in Fig. 2. The TEM image (Fig. 2a) reveals that the final obtained D- $\text{Ni}(\text{OH})_2$ possesses a disordered porous structure. Fig. 2b–d shows the element maps of Ni, Al and O, which are all

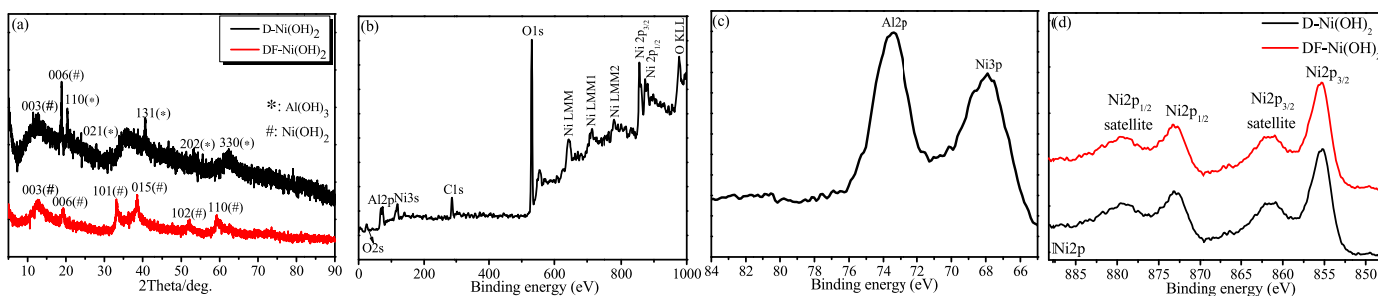


Fig. 1. X-ray diffraction patterns (XRD) and X-ray photoelectron spectroscopy (XPS) analyses. (a) XRD patterns of D- $\text{Ni}(\text{OH})_2$ and DF- $\text{Ni}(\text{OH})_2$; (b) XPS survey spectrum of D- $\text{Ni}(\text{OH})_2$; (c) $\text{Al}2\text{p}$ XPS spectrum of D- $\text{Ni}(\text{OH})_2$; (d) $\text{Ni}2\text{p}$ XPS spectrum of D- $\text{Ni}(\text{OH})_2$ and DF- $\text{Ni}(\text{OH})_2$.

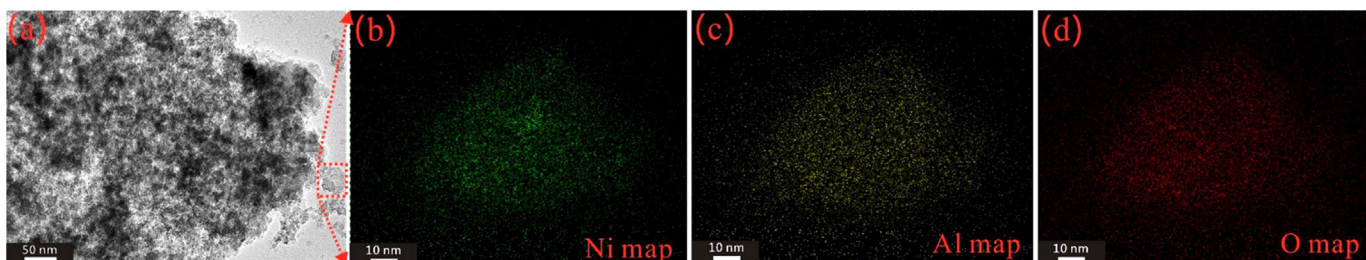


Fig. 2. TEM image of D- $\text{Ni}(\text{OH})_2$ and corresponding element maps of Ni, Al and O.

Download English Version:

<https://daneshyari.com/en/article/1256904>

Download Persian Version:

<https://daneshyari.com/article/1256904>

[Daneshyari.com](https://daneshyari.com)