Energy 123 (2017) 296–304

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Morphology controlled preparation of $ZnCo_2O_4$ nanostructures for asymmetric supercapacitor with ultrahigh energy density

Le Xu [a, 1], Yan Zhao [b, ***, 1], Jiabiao Lian [b], Yuanguo Xu [a], Jian Bao [b], Jingxia Qiu [b], Li Xu [b], Hui Xu [a, b], Mingqing Hua [a, **], Huaming Li [a, b, *]

[a] School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, 212013, PR China
[b] Institute for Energy Research, Jiangsu University, Zhenjiang, 212013, PR China

ARTICLE INFO

Article history:
Received 10 June 2016
Received in revised form
9 January 2017
Accepted 3 February 2017
Available online 6 February 2017

Keywords:
Asymmetric supercapacitor
$ZnCo_2O_4$
Freeze-dried RGO
Tunable morphologies
High energy density

ABSTRACT

Porous $ZnCo_2O_4$ nanostructures with hexamethylenetetramine (HMT) as adscititious alkali are fabricated *via* a facile hydrothermal route and heat treatment process. The morphology of the materials can be easily tuned from nanowires to nanobelts by simple varying the hydrothermal temperature. Due to the superiority of the porous nanostructure and the convenient ion transport, the obtained $ZnCo_2O_4$ nanostructures are further applied as electrode materials for supercapacitors and exhibit noticeable pseudocapacitive performance with high specific capacitance of 776.2 F g^{-1} at 1 A g^{-1} and good cycle stability (84.3% capacity retention at 3 A g^{-1}). Moreover, a high-voltage asymmetric supercapacitor using the $ZnCo_2O_4$ as the anode assembled with the freeze-dried reduced graphene oxide (F-RGO) cathode displays superior electrochemical performance with an ultrahigh energy density (84.48 Wh kg^{-1} at 0.4 kW kg^{-1}), which reveals a great promise for practical application in electrochemical devices.

1. Introduction

Supercapacitors (SCs), also called electrochemical capacitors, have attracted extensive research interest due to the release of great breakthroughs in terms of higher power densities, lower costs, faster charge–discharge rates and longer cycle stabilities than conventional built-in batteries [1–5]. However, the unsatisfactory energy density of supercapacitors greatly limits their further practical applications. According to the equation of $E = 1/2\ C_sV^2$, the cell potential (V) and capacitance (C_s) have a great impact on the energy density (E) of supercapacitors [6,7]. The specific capacitance can be improved with development of well-designed electrode materials [8]. Moreover, the operating potential window can be broaden by using an asymmetric supercapacitors device, which is combined of a capacitive electrode (as power source) and a battery-like electrode (as energy source) [9]. Hence, it can be urgent to seek high performance electrode materials with facile preparation strategy and careful select the cathode and anode materials with proper operating potential window.

Usually, carbon materials (such as carbon micro/nanospheres, activated carbon, graphene etc.) can be used as a capacitive electrode, and nanostructured pseudocapacitors materials can be used as a Faradic electrode. Carbon-based materials have been widely investigated as electrodes due to their inexpensive price, high surface area, good electrical conductivity, and excellent stability [10–12]. Graphene or reduced graphene oxides (RGO) are good candidates for the capacitive electrodes as energy source since they may supply a high approachable surface area for fast transport of aquated ions in order to obtain high electrical double layer capacitance (EDLC) [13,14]. However, the agglomeration of RGO sheets often hinders its applications [15]. To resolve this problem, a simple freeze-drying method was used to prevent the agglomeration of RGO sheets [16]. In addition, pseudocapacitors, for example, transition metal oxides and conducting polymers can provide much higher specific capacitance than EDLCs. Nevertheless, they generally suffer from poor electron conductivity, toxicity or low operating voltage [17–19]. Recently, the binary metal oxides (such as $NiCo_2O_4$ and $ZnCo_2O_4$) have attracted more and more attention in our day-to-day life. Among all the factors that account for this phenomenon, the following are worth mentioning. First and

* Corresponding author. School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, 212013, PR China.
** Corresponding author.
*** Corresponding author.
E-mail addresses: yanzhao@ujs.edu.cn (Y. Zhao), huamq840710@163.com (M. Hua), lhm@ujs.edu.cn (H. Li).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.energy.2017.02.018
0360-5442/

foremost, they can increase the electrochemical performances synergistically in terms of reversible capacity, structural stability, and electrical conductivity [20,21]. For instance, binary zinc cobalt oxide ($ZnCo_2O_4$) has shown better electrical conductivity and higher electrochemical activity than unitary zinc oxide (ZnO) and cobalt oxide (Co_3O_4) [22]. Furthermore, the different nanostructures morphology exerted a certain influence on the electrochemical properties [23]. With environmental friendliness, inexpensive and rich in natural resources, $ZnCo_2O_4$ possesses a normal spinel structure with the bivalent Zn-ions occupying the tetrahedral sites and the trivalent Co-ions occupying the octahedral sites (Fig. 1a). Due to the superior supercapacitive properties and better electroactivity than those of pure cobalt oxides, $ZnCo_2O_4$ can be regarded as promising electrode materials for supercapacitors [24,25]. In spite of various $ZnCo_2O_4$ nanostructures based electrodes have been reported for supercapacitors, including nanorods, nanospheres and nanosheets, which displayed excellent electrochemical properties [26–28]. The low specific capacitance and tedious preparation process made it troublesome to satisfy the needs of practical application [29,30]. Moreover, the asymmetric supercapacitors based on the $ZnCo_2O_4$ nanostructures and the freeze dried RGO (F-RGO) nanosheets have never been reported in the open literature to the best of our knowledge. In addition, the facile fabrication of temperature-controlled $ZnCo_2O_4$ nanostructures and systematic investigation of the possible formation mechanism are still difficult tasks.

Herein, porous $ZnCo_2O_4$ nanostructures with tunable morphologies are reported *via* a simple hydrothermal method and a subsequent calcination process. The possible formation mechanism of $ZnCo_2O_4$ nanostructures has also been discussed. Moreover, the obtained $ZnCo_2O_4$ nanostructures based electrodes exhibited an excellent specific capacitance, great structure stability and good cycle stability. Moreover, an asymmetric supercapacitor using the $ZnCo_2O_4$ nanostructures as the anode and the F-RGO as the cathode showed ultrahigh energy density (84.48 Wh kg^{-1} at 0.4 kW kg^{-1}). The excellent properties may be ascribed to the superior energy contribution of the smart designed porous $ZnCo_2O_4$ nanostructures and F-RGO electrodes, as well as the expanding potential window of the supercapacitor.

2. Experimental

2.1. Materials

Zinc chloride ($ZnCl_2$), ammonium fluoride (NH_4F), Cobalt chloride ($CoCl_2 \cdot 6H_2O$, 99%), Hexmethylene tetramine (HMT, $C_6H_{12}N_4$, 99%), potassium hydroxide (KOH), hydrochloric acid (HCl) and acetone were commercially available from Aladdin Chemical Co. All materials were used without further purification.

2.2. Synthesis of $ZnCo_2O_4$ nanowires or nanobelts

The $ZnCo_2O_4$ nanowires or nanobelts were firstly fabricated *via* a facile hydrothermal method and calcination treatment. In brief, 2 mmol of $CoCl_2 \cdot 6H_2O$, 1 mmol of $ZnCl_2$, 5 mmol of NH_4F and 6 mmol of HMT were dissolved together into 80 mL H_2O. The resulting suspension was magnetically stirred to form a uniform pink transparent solution at room temperature. Afterwards, the mixed solution were poured into a 100 mL of polytetrafluoroethylene substrate autoclave, heated in an oven at various reaction temperatures (100 °C, 120 °C, 140 °C and 160 °C for 6 h, respectively) and then cool down to room temperature naturally. The as-prepared products were collected and rinsed with a copious amount of ethanol and deionized water for several times, followed by vacuum drying at 100 °C for 4 h. Finally, the as-obtained products were annealed at 400° centigrade in air for 2 h with a ramping rate of 2 °C min^{-1}.

2.3. Preparation of $ZnCo_2O_4$ electrodes

To prepare working electrode, the active material (70 wt%), acetylene black (20 wt%) and polytetrafluoro-ethylene (PTFE) binder (10 wt%) were mixed to obtain a viscous slurry. The slurry was coated on a piece of nickel foam (1.0 cm × 2.0 cm), and dried under vacuum at 100 °C for 4 h. Nickel foam was precleaned by sonication in 2 M HCl, acetone, deionized water and ethanol for 10 min each in order to remove the organics and the oxide layer.

2.4. Fabrication of F-RGO electrodes

The fabrication of Free-dried reduced graphene oxide (F-RGO) was reported before [7,31]. Typically, the mass ratios of F-RGO: acetylene black: polytetrafluoroethylene is 7:2:1. Afterwards, a litter bit of ethanol was mixed with the aforementioned materials to form the homogeneous paste. Finally, this paste was coated onto the current-collector to produce F-RGO electrode [16].

2.5. Assemble of asymmetric supercapacitor

The F-RGO electrodes and $ZnCo_2O_4$ electrodes were immersed in a 2 M KOH aqueous solution to measure the electrochemical properties. Three full cells were encapsulated as an example to prove their practical application by flexible plastic film with the above mentioned electrodes and the separator based on one piece of cellulose paper.

2.6. Materials characterization

The X-ray diffraction (XRD) patterns of samples were collected

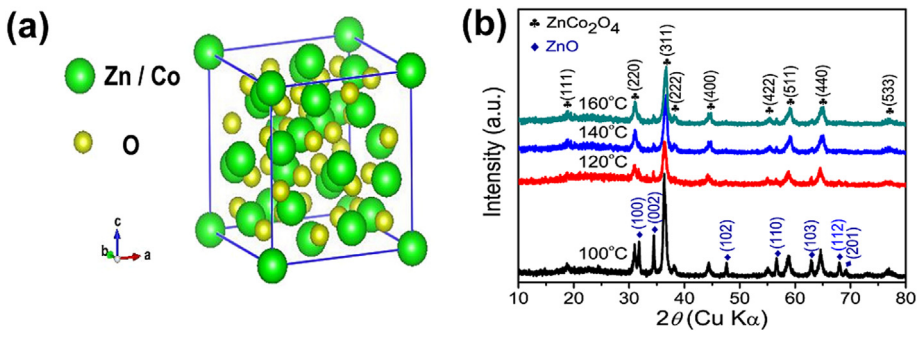

Fig. 1. Crystallographic structure (a) and the XRD pattern (b) of the as-prepared porous $ZnCo_2O_4$ nanostructures.