Electrochimica Acta 252 (2017) 470–481

Contents lists available at ScienceDirect

Electrochimica Acta

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

Research paper

Hydrothermal Synthesis of $CoMoO_4/Co_9S_8$ Nanorod Arrays on Nickel Foam for High-Performance Asymmetric Supercapacitors with High Energy Density

Rui Xu, Jianming Lin*, Jihuai Wu*, Miaoliang Huang, Leqing Fan, Xin He, Yiting Wang, Zedong Xu

Engineering Research Center of Environment-Friendly Functional Materials, Ministry of Education, College of Materials Science and Engineering, Institute of Materials Physical Chemistry, Huaqiao University, Xiamen, China

ARTICLE INFO

Article history:
Received 17 July 2017
Received in revised form 10 August 2017
Accepted 26 August 2017
Available online 2 September 2017

Keywords:
Asymmetric supercapacitor
Cobalt molybdate
Nanorod arrays
Hydrothermal route

ABSTRACT

$CoMoO_4/Co_9S_8$ nanorod arrays supported on nickel foam are successfully assembled via a facile two-step hydrothermal route. Due to the unique nanorod array structure, the $CoMoO_4/Co_9S_8$, as the electrode, possesses a high capacity 1.54 mA h·cm^{-2} (343.21 mA h·g^{-1}) and a large capacitance 9.17 F cm^{-2} (2059.26 F g^{-1}) at a current density of 20 mA·cm^{-2} (4.44 A·g^{-1}), and an excellent cycling stability (8.6% degradation after 3000 cycles). The asymmetric supercapacitor based on the $CoMoO_4/Co_9S_8$ nanorod arrays as a positive electrode and porous active carbon as a negative electrode in an alkaline KOH aqueous electrolyte is fabricated. Owing to the synergetic effect between $CoMoO_4/Co_9S_8$ and active carbon, $CoMoO_4/Co_9S_8$//active carbon asymmetric supercapacitor exhibits an outstanding energy density of 42 Wh·kg^{-1} and an excellent cycling stability with 89.5% specific capacitance retained after 5000 cycles in an operating voltage of 1.6 V. The facile synthesis route and remarkable supercapacitive performance of the $CoMoO_4/Co_9S_8$ nanorod arrays is promising as a positive electrode materials for high-performance asymmetric supercapacitors.

1. Introduction

In the 21 st century, the ever-growing energy requirement, depletion of fossil-fuel resources, and environmental issues have led to an increase in demand for the investigation and development of an environmentally friendly, low-cost, and sustainable energy-storage systems [1,2]. Compared with other energy storage devices such as batteries and fuel cells, flexible and lightweight supercapacitors (SCs), also called electrochemical capacitors (ECs) or ultracapacitors, as the emerging energy-storage devices, have attracted the extensive research and practical application due to their high power density, fast charge/discharge process, long cycle life, low maintenance cost, as well as the environmental friendliness [3–6]. According to intrinsic energy-storage mechanisms of SCs, they can be grouped into two types: electric double layer capacitors (EDLCs) which is utilizing diffusion and accumulation of the electrostatic charge at the interfaces between carbon-based electrode and electrolyte and pseudocapacitors which deliver higher capacitance values than EDLCs because of the unique energy-storage mechanism via a typical faradaic redox reactions at the electrode materials [7–11]. In addition, developing and fabricating asymmetric supercapacitors (ASCs, also called hybrid devices) is also an efficient approach to significantly improve energy density, which can take full advantage of the two electrodes (faradaic electrode and an electrochemical double layer electrode) and provide the two different operating voltage in the same electrolyte [7,12]. Although great efforts have been made in the fabrication of high-energy-density hybrid devices, the low capacitance of electrode materials still severely limits their future practical applications, which cannot meet the demand for SCs with the high energy/power density.

To solve these problems, it is essential for the devices to choose a highly conductive and capacitance electrode materials, many electrode materials have been studied, such as carbon-based materials (reduced grapheme oxide [13], ultrathin porous carbon shell [14], continuous carbon nitride polyhedron assembly [15], alkynyl carbon materials [16]), metal-organic framework (MOF)-based materials (Co/Ni-MOF//CNTs-COOH [17], conductive MOF

---

* Corresponding authors.
E-mail addresses: 863453918@qq.com (R. Xu), jmlin@hqu.edu.cn (J. Lin), jhwu@hqu.edu.cn (J. Wu), huangml@hqu.edu.cn (M. Huang), lqfan@hqu.edu.cn (L. Fan), 467924213@qq.com (X. He), 2296813995@qq.com (Y. Wang), 1752542026@qq.com (Z. Xu).

http://dx.doi.org/10.1016/j.electacta.2017.08.148
0013-4686/© 2017 Elsevier Ltd. All rights reserved.

nanowire arrays [18], hierarchical porous Zr-MOFs [19]), polymer-based materials (PPy nanowires [20], dendritic conducting polymers [21], core/shell conducting polymer nanowires/manganese dioxide nanoflakes [22], hybrid multiwalled carbon nanotubes/polyaniline electrodes [23]), and metal materials (Mn_3O_4-rGO hybrid materials [24], $NiCo_2O_4$@rGO hybrid nanostructures [25], $CoMoO_4$ nanoplate arrays [26]). Among various electrode materials, binary molybdenum-containing oxides (denoted as $MMoO_4$: M = Co, Ni, Mn . . .) have received extensively research interests due to a low cost, a unique set of physical and chemical properties, and an enhanced electrochemical performance/activity [4,6,26,27–30]. In particular, $CoMoO_4$ shows excellent electrochemical performances because of the unique crystallographic structure, n-type semiconductivity, various valence states, and the reversibility of small ions storage [30]. For example, Chi et al. synthesize Ni/GF/H-$CoMoO_4$ electrode which exhibits the area capacitance of 5.36 $F \cdot cm^{-2}$ (1472 $F \cdot g^{-1}$) at a current density of 1 $mA \cdot cm^{-2}$ with a higher rate capability [31]. Another recent work on $CoMoO_4$@MnO_2 core-shell nanosheet by Zhang et al. displays the area capacitance of 2.27 $F \cdot cm^{-2}$ at 3 $mA \cdot cm^{-2}$ with the desirable cycling stability [26]. Despite many advantages of transition metal oxides/sulfides, a number of limitations still severely restrict the performances and preparation of SCs, such as the low electronic conductivity and high reaction temperature [32].

Intrigued by these results, the $CoMoO_4/Co_9S_8$ nanorods are designed and prepared by a facile two-step hydrothermal method which can avoid the annealing process and resultant effect on the size and morphology. Meanwhile, using the 3D nickel foam (Ni foam) with the unique three dimensional nanostructures as the conductive pathway and backbone for electrode materials can remarkably improve the electronic conductivity and provide a large surface area for the samples growth. Furthermore, the $CoMoO_4/Co_9S_8$ nanorods/nickel foam can be directly used as an electrode for supercapacitors without any conductive additives and polymer binder [33]. For its superiority, the prepared nickel foam supported $CoMoO_4/Co_9S_8$ electrode with outstanding conductivity, remarkable mechanical strength, and a relatively high active material loading displays superior supercapacitor performances. Furthermore, the $CoMoO_4/Co_9S_8$//activated carbon (AC) asymmetric supercapacitor also combines the advantage of a high energy density and a good capacity retention. The unique $CoMoO_4/Co_9S_8$ nanorod arrays as a future energy storage material maybe has a direct impact on increasing energy density of not only the supercapacitors but also other energy storage devices.

2. Experimental section

2.1. Materials

The Cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, 99.99%, AR), sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$, 99.99%, AR), and urea ($CO(NH_2)_2$, 99%, AR) used in the experiments were purchased from Sigma-Aldrich, India. The ammonium molybdate ($(NH_4)_2MoO_4$, 99.99%, GR) was obtained from Alfa Aesar, U.S.A. All the reagents were directly used without further purification.

2.2. Preparation of $CoMoO_4/Co_9S_8$ nanorod arrays on nickel foam

Nickel foam (1×1 cm^2) was cleaned with acetone, isopropanol, ethanol, and deionized water in an ultrasound bath for 30 min, consecutively, followed by soaking the nickel foam in 6 M HCl solution for 15 min, and in the last washed with deionized water in order to remove the HCl solution from the surface.

The precursor was synthesized via a facile hydrothermal method. $CoCl_2 \cdot 6H_2O$ (3 mmol) and $CO(NH_2)_2$ (10 mmol) were slowly dropped into the deionized water (60 ml) under magnetic stirring for 30 min to form a homogeneous pink solution. Then, a piece of nickel foam and the clear solution were transferred to a Teflon-lined stainless steel autoclave (100 ml) and maintained at 130 °C for 4 h. After cooling to room temperature, the precursor/Ni foam was dried at 60 °C for 6 h.

$(NH_4)_2MoO_4$ (0.024 $mol \cdot L^{-1}$) and $Na_2S \cdot 9H_2O$ (0.006 $mol \cdot L^{-1}$) were dissolved in 60 mL of deionized water under stirred conditions to form a clear yellow solution. To investigate the influence of the different ratios of the molar concentrations (C_{MoO4}/C_S), the precursor was researched with the ratios of 0: 10, 7:3, 8:2, 9:1, and 10: 0. After that, the precursor and resultant mixture were transferred into a 100 ml Teflon-lined stainless steel autoclave. Following hydrothermal treatment at 140 °C for 4 h, the sample was cooled to room temperature and dried at 60 °C for 6 h. All the mass loadings of all the as-prepared samples were 4.5 $mg \cdot cm^{-2}$.

2.3. Characterization

The crystal structural, phase purity, and chemical bonding of the powder samples were characterized using X-ray diffraction (XRD, Rigaku SmartLab Cu Kα, λ = 1.5418 Å, 3 kW, Japan) and X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB250Xi, U.S.A), and the chemical elements were obtained by the energy dispersive X-ray spectroscopy (EDS, INCA Energy, OXFORD, UK). In order to analyze the surface morphologies and microstructures of the powder samples, the field-emission scanning electron microscopy (FESEM, SU8000, Hitachi, Japan) and the high resolution transmission electron microscopy (HRTEM, JEM2100, JEOL, Japan) were used.

2.4. Electrochemical measurements

The electrochemical impedance spectroscopy (EIS), galvanostatic charge/discharge (GCD) tests and cyclic voltammetry (CV) measurements were conducted on an electrochemical workstation (CHI660E, Chenhua Co. Ltd, Shanghi), and the cycle stability was carried out on a LAND battery program-controlled test system (CT2001A, LANHE Co. Ltd, Wuhan). The electrochemical measurements were performed in a three-electrode electrochemical cell, with the 3 M potassium hydroxide (KOH) aqueous solution as the electrolyte, platinum wire as the counter electrode, Hg/HgO as the reference electrode, and the samples/nickel foam as the working electrode.

2.5. Fabrication of asymmetric supercapacitors

The asymmetric supercapacitor device is fabricated using the $CoMoO_4/Co_9S_8$ nanorod arrays/Ni foam as the positive electrode, the AC as the negative electrode, and 3 M KOH as the electrolyte. The mass specific capacity and area specific capacity can be calculated from the GCD curves according to Equations (1) and (2) [6,7,17]:

$$C_m = Q/M = I\Delta t/3600M \tag{1}$$

$$C_a = Q/A = I\Delta t/3600A \tag{2}$$

where C_m ($mA\,h \cdot g^{-1}$), C_a ($mA\,h \cdot cm^{-2}$), M (g), A (cm^2), Q, I (mA), and Δt (s) are the mass specific capacity, area specific capacity, mass of the active materials, area, the quantity of charge, the constant discharge current, and the discharge duration of the active