Journal of Colloid and Interface Science 534 (2019) 322–331

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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

Regular Article

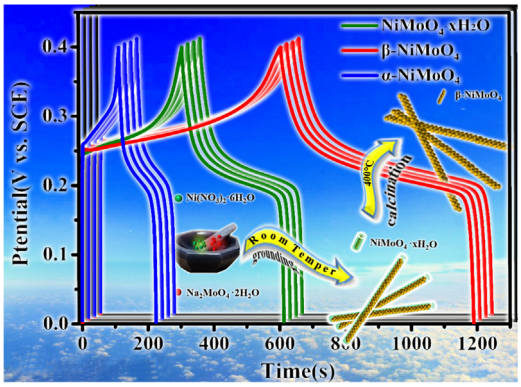
Solid-state chemical fabrication of one-dimensional mesoporous β-nickel molybdate nanorods as remarkable electrode material for supercapacitors

Xiaoyan Lu, Wei Jia, Hui Chai, Jindou Hu, Shiqiang Wang, Yali Cao *

Key Laboratory of Energy Material, Ministry of Education, Key Laboratory of Advanced Functional Materials, Autonomous Region, Institute of Applied Chemistry, Xinjiang University, Urumqi 830046, Xinjiang, PR China

GRAPHICAL ABSTRACT

The β-$NiMoO_4$ nanomrods were successfully fabricated by a green solid-state chemical approach and exhibit high electrochemical performance for supercapacitors.



ARTICLE INFO

Article history:
Received 28 May 2018
Revised 9 September 2018
Accepted 12 September 2018
Available online 12 September 2018

Keywords:
Solid-state synthesis
β-$NiMoO_4$
Nanostructures
Supercapacitors

ABSTRACT

Simple solid-state chemical reaction was adopted to synthesize $NiMoO_4$ nanomaterials with different crystal phase without the use of organic solvent or templating agent. The as-prepared $NiMoO_4{\cdot}xH_2O$, α-$NiMoO_4$ and β-$NiMoO_4$ nanostructures were investigated as the electrode materials for supercapacitors. The β-$NiMoO_4$ nanorods were composed of the nanoparticles, which exhibited relatively high specific capacitances about 1415 F g^{-1} at a charge density of 1 A g^{-1}, 80.2% of the initial reversible capacity was maintained after 1000 cycles. The β-$NiMoO_4$//rGO asymmetric supercapacitor (ASC) system was assembled in serials, which displayed high specific energy density of 29.3 Wh kg^{-1} at a high power density of 187 W kg^{-1}. This ASC system can drive the light-emitting diode (LED) effectively and give out light about 40 min, even easily light two LEDs in serials for 20 min. The remarkable electrochemical performances make the as-prepared $NiMoO_4$ nanostructures an excellent candidate as electrode materials for advanced supercapacitors.

* Corresponding author.
E-mail address: caoyali523@163.com (Y. Cao).

https://doi.org/10.1016/j.jcis.2018.09.042
0021-9797/

1. Introduction

Development of high efficiency and renewable energy has become an imperious demand for us to retard global warming and fossil fuel excessive depletion [1,2]. Meanwhile, the increasing need for electric vehicles, portable electronic devices and smart grids has stimulated the rapid development of energy reserve systems with higher energy density and larger power density. Electrochemical supercapacitors are currently identified with prospective candidates for energy storage applications with high power density than batteries and high energy density than conventional dielectric capacitors [3–5].

As the core of supercapacitors, the electrode materials are critical to the overall performance of the energy storage device. Transition-metal oxides have been extensively explored as the cheap electrode materials for supercapacitors. Among them, metal molybdate has attached great interest as a novel electrode material in supercapacitor owning to its low cost, environmental friendliness and natural abundance in recent years. Wang et al. reported 3D α-$MnMoO_4$ hierarchical architectures synthesized by liquid synthetic method, which displayed high specific capacitance of 562 F g^{-1} at a charging density of 1 A g^{-1} and outstanding cycling stability with 99.8% of specific capacitance retention rate after 1000 cycles [6]. Xu et al. successfully prepared one-dimensional $CoMoO_4{\cdot}0.9H_2O$/rGO nanocomposites through a refluxing method under mild conditions, which displayed a specific capacitance of 802.2 F g^{-1} at the current density of 1 A g^{-1} [7]. Cai et al. fabricated $NiMoO_4$ nanospheres that showed special specific capacitance of 631.8 F g^{-1} at a charging density of 5 A g^{-1} [8]. Especially, one-dimensional nanoscale electrode materials possessed a large contact area and short diffusion distance, thus exhibited excellent electrochemical performance, which have prospect of application in the field of energy storage [9,10]. Molybdate electrode materials have been synthesized by some approach, such as hydrothermal or solvothermal synthesis, sol-gel process, chemical vaporous deposition and microwave technology [9,11–14]. However, these approaches involved redundant template-removal treatments and selection of solvents, which are usually synthesized by tedious multistep process even under harsh condition [15–18]. Therefore, it is necessary to develop a simple and mild synthetic method for molybdate electrode materials.

In our work, we reported simple synthesis of one-dimensional $NiMoO_4$ nanostructure through a template-free and eco-friendly solid-state chemical route. It is found that the phases of nanoarchitectures can be easily regulated to be the $NiMoO_4{\cdot}xH_2O$, β-$NiMoO_4$ and α-$NiMoO_4$ by turning the treating temperature. Furthermore, diverse phase $NiMoO_4$ nanostructures can show different electrochemical performance in overall kinetics and long-term stability. It is worth mentioned that one-dimensional β-$NiMoO_4$ nanostructures exhibit high specific capacitance and good cycling stability, which have great application prospects as an excellent electrode material for supercapacitor.

2. Experimental

2.1. Synthesis of $NiMoO_4{\cdot}xH_2O$, α-$NiMoO_4$ and β-$NiMoO_4$

$NiMoO_4$ nanostructures were prepared by a facile and low-cost solid-state chemical method without the use of any structure-induced agents and liquid solvent. In their synthesis process, all the chemicals are analytically pure from commercial sources and without any further purification. Typical synthesis for $NiMoO_4$ nanostructures were as follows. Nickel nitrate hexahdrate ($Ni(NO_3)_2{\cdot}6H_2O$, AR, >99%) and sodium molybdate dehydrate ($Na_2MoO_4{\cdot}2H_2O$, AR, >99%) were mixed with a molar ratio of 1:1 by continuous grinding in an agate mortar at room temperature. Simultaneously, it was clearly observed that the color of the mixture gradually changed from green to yellow green after grinding for 1 h. The mixture was washed several times by distilled water, then $NiMoO_4{\cdot}xH_2O$ was obtained. The as-fabricated $NiMoO_4{\cdot}xH_2O$ was calcined at 400 °C and 700 °C for 2 h, respectively (the heating rate: 2 °C min^{-1}). After naturally cooling at room temperature, the β-$NiMoO_4$ and α-$NiMoO_4$ were fabricated. The fabrication route of samples is shown in Scheme 1. The chemical reaction equations were showed as follows [19]:

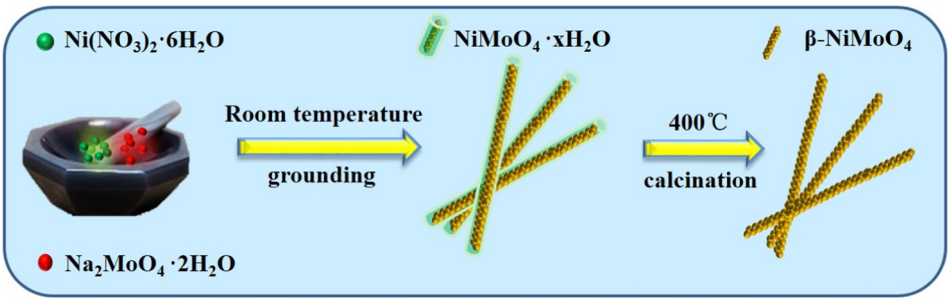
$$Ni(NO_3)_2{\cdot}6H_2O + Na_2MoO_4{\cdot}2H_2O \rightarrow NiMoO_4{\cdot}xH_2O + 2NaNO_3 \quad (1)$$

$$NiMoO_4\hat{A}\cdot xH_2O \xrightarrow{400\hat{A}^{\circ}C} \beta - NiMoO_4 + xH_2O \quad (2)$$

$$NiMoO_4\hat{A}\cdot xH_2O \xrightarrow{700\hat{A}^{\circ}C} \alpha - NiMoO_4 + xH_2O \quad (3)$$

2.2. Characterization

The phase of as-fabricatd $NiMoO_4$ nanomaterials was investigated by powder X-ray diffractometer (XRD, Bruker D8) equipped with (Cu-Kα) radiation (λ = 1.5406 Å) source and a Ni filter in a 2θ range of 5–80°. The element component was obtained on energy dispersive X-ray spectroscopy (EDS). X-ray photoelectron spectra signals were detected by ESCALAB 250 Xi system. The morphologies of as-synthesized nanomaterials were investigated on field-emission scanning electron microscope (FESEM, Hitachi S-4800) at 15 kV and high resolution transmission electron microscope (HRTEM, JEOL JEM-2010F) with an accelerating voltage of 200 kV. According to the Brunauer-Emmett-Teller (BET) theory and the Barrett-Joyner-Halenda (BJH) model of surface area and porosity, the N_2 absorption-desorption isotherm was measured on a Quant-



Scheme 1. Schematic for the formation process of $NiMoO_4$ nanostrctures.