Available online at www.sciencedirect.com

ScienceDirect

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

Hierarchical porous cobalt monoxide nanosheet@ultrathin manganese dioxide nanosheet core-shell arrays for high-performance asymmetric supercapacitor

Xuezhao Wang [a], *Yuanhua Xiao* [b,*], *Dangcheng Su* [b], *Shengang Xu* [a], *Liming Zhou* [b], *Shide Wu* [b], *Lifeng Han* [a,b], *Shaoming Fang* [b,**], *Shaokui Cao* [a,***]

[a] *School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450052, PR China*
[b] *State Laboratory of Surface and Interface Science and Technology, Zhengzhou University of Light Industry, Zhengzhou 450002, PR China*

ARTICLE INFO

Article history:
Received 12 February 2016
Received in revised form
12 June 2016
Accepted 14 June 2016
Available online 5 July 2016

Keywords:
CoO
MnO_2
Nanoarray
Core-shell
Asymmetric supercapacitors

ABSTRACT

Hierarchical hybrid electrodes CoO@MnO_2 nanosheet@nanosheet arrays (NNAs) for high-performance supercapacitors are designed and grown on a 3D nickel foam by a simple two step solution method combined with a post annealing treatment in Ar gas. The MnO_2 nanosheets can grow directly on the CoO precursor nanosheet arrays without any pre-treatment, and its thickness on the CoO NAs can also be tailored by adjusting the hydrothermal time. The NNAs with the elegant synergy between CoO and MnO_2 lead to a highly enhanced areal capacitance (2.40 F cm^{-2} at 2.0 mA cm^{-2}, with a wide potential window of 0.8 V). We further fabricated asymmetric supercapacitor device based on the CoO@MnO_2 NNAs and active carbon, which achieved a high-energy density of 1.4 mWh cm^{-3} at a power density of 9.6 mW cm^{-3}, a high power density of 192.3 mW cm^{-3} at 0.7 mWh cm^{-3} and good cyclic stability.

Introduction

The ever-growing environmental issues and energy crisis have greatly stimulated substantial effort to exploit alternative clean energy [1]. Pseudocapacitor as a new type of energy storage device, is gaining increasing interest in the field of energy storage because of its fast charge–discharge process, excellent cycling stability, high power density, and so on [2]. Among various pseudocapacitive materials, transition metal oxide generally exhibits a higher specific capacitance compared with carbon-based materials and a longer cycle stability compared with conductive polymer materials. In particular, MnO_2 has been considered to be one of the most

* *Corresponding author*. Tel./fax: +86 371 6355 6510.
** *Corresponding author*. Tel./fax: +86 371 6355 6510.
*** *Corresponding author*. Tel./fax: +86 371 6355 6510.
E-mail addresses: yuanhua_xiao@163.com (Y. Xiao), mingfang@zzuli.edu.cn (S. Fang), caoshaokui@zzu.edu.cn (S. Cao).
http://dx.doi.org/10.1016/j.ijhydene.2016.06.133
0360-3199/

promising electrode materials for supercapacitor because of its high theoretical specific capacitance (1370 F g^{-1}), wide electrochemical window, low cost, environmental friendliness, and natural abundance [3]. However, the low electrical conductivity of MnO_2 (10^{-5}~10^{-6} S/cm), remains a significant challenge and restricts its high rate capability performance, thus the most of reported specific capacitance values for MnO_2 is substantially less than its theoretical value [4].

Recently, abundant efforts have been devoted to designing and constructing three-dimensional (3D) hybrid nanoarchitectures for improved supercapacitor performance [5,6]. Especially the 3D hierarchical core-shell nanoarrays on the conductive substrate, which can avoid extra contact resistance and "dead surface" owing to the introduction of conductive agent and polymer binder, and can significantly increase the utilization rate of electrode materials even at high rates [7]. For example, various configurations of core-shell hybrid structures, such as Co_3O_4@$NiCo_2O_4$ [8], ZnO@-Co_3O_4 [9], Co_3O_4@Au@MnO_2 [10], Co_3O_4@Pt@MnO_2 [11], NiC-o_2O_4@MnO_2 [12], $ZnCo_2O_4$@$Ni(OH)_2$ [13], Pt@MnO_2 [14] and so on, have been developed with improved electrochemical performance.

In order to further optimize the design and configuration of core-shell nanoarray, the core structures grown directly on a conductive substrate should possess a good electronic conductivity and high capacitance and hence serve as an effective current collector and capacity provider.

Cobalt monoxide (CoO) as the simplest cobalt oxide with a high conductivity, often be used as conductive agent to decrease the inner resistance of the Ni-H battery in KOH electrolyte and improve the performance of nickel hydroxide electrode [15,16]. In addition, CoO also possess a higher theoretical specific capacitance 4292 F g^{-1} than Co_3O_4 (3560 F g^{-1}) [17]. Furthermore, when the CoO added to Co_3O_4, the specific capacitance of composite CoO/Co_3O_4, also can be remarkably enhanced [17]. However, up to now, the CoO was rarely researched on its electrochemical property and only as the rock salt monoxide was extensively used as an additive to create blue-colored in the ceramics industry [18].

In this work, we report the design and synthesis of a novel and a facile two step solution method combined with a post annealing treatment in Ar gas to construct a hierarchical CoO@MnO_2 nanosheets@nanosheets arrays (NNAs), as shown in Fig. 1. In the first step, the ultrathin Co-precursor nanosheet arrays were grown on the nickel foam by using a solvothermal method, then Co-precursor NAs without any treatments were directly added into the $KMnO_4$ solution for hydrothermal reaction. Next, MnO_2 nanosheets can be produced on the surface of the nanosheet arrays. Finally, the CoO@MnO_2 core-shell hybrid composite obtained was annealed at the temperature of 350 °C. The materials exhibit enhanced areal capacitance to 2.4 F cm^{-2} in a relatively wide potential window of 0.8 V, which outperforming most reported Co_3O_4 based core-shell nanoarray. Moreover, a new ASC system based on the CoO@MnO_2 NNAs and active carbon (AC), which demonstrated an ultrahigh energy density of 1.4 mWh cm^{-3} at a power density of 9.6 mW cm^{-3} and a high power density of 192.3 mW cm^{-3} at 0.7 mWh cm^{-3}, as well as long-term stability. Thus, the CoO@MnO_2 NNAs arrays will be one of the highly promising materials for high performance supercapacitors.

Experimental section

Reagents and materials

All chemicals used in this study were of analytical (AR) grade and purchased from Shanghai Analytical Chemicals Company. Before the experiment, the Ni foam (2 × 1 × 0.1 cm) was firstly treated with a 3 M HCl solution and then cleaned by sonication in ethanol, and deionized (DI) water in sequence for 5 min each.

Synthesis of CoO precursor nanosheet array (NAs)

In a typical synthesis, 2.5 mmol of $Co(NO_3)_2 \cdot 6H_2O$ and 4 mmol of urea were dissolved into a mixed solution composed of 5 mL DI water and 35 mL ethylene glycol with a magnetic stirring. After 15 min, the above solution and a piece of Ni foam were then transferred to a Teflon-lined autoclave (50 mL), heated to 160 °C and kept for 20 h. After the reaction, the autoclave was allowed to cool to room temperature. The array sample was collected and rinsed with distilled water and ethanol for three times, respectively, and finally dried at 60 °C for 24 h to obtain CoO precursor products.

For comparison, CoO nanosheet array was prepared with an annealing method at 350 °C in Ar for 2 h.

Synthesis of CoO@MnO_2 NNAs

In a similar synthesis, 1 piece of Ni foam with CoO precursor nanosheet array was immersed in a 40 mL of 0.05 M $KMnO_4$ solution then transferred to a 50 mL Teflon-lined stainless steel autoclave, and maintained at 160 °C for 5 h.

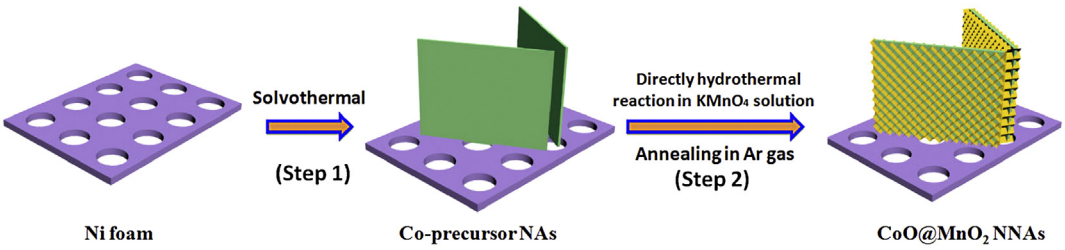

Fig. 1 – Schematic illustration of the formation process of CoO@MnO_2 nanosheet@nanosheet arrays.