Journal of Colloid and Interface Science 483 (2016) 17–25

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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

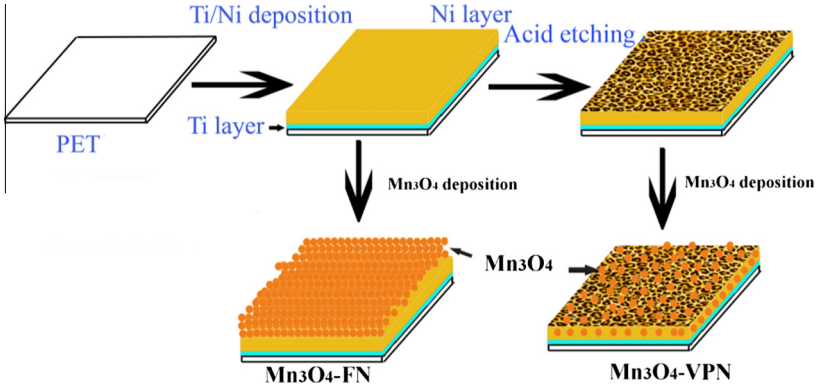
Regular Article

# Vertically porous nickel thin film supported $Mn_3O_4$ for enhanced energy storage performance

Xiao-Jun Li [a,b], Zhi-wei Song [b], Yong Zhao [c], Yue Wang [b], Xiu-Chen Zhao [a,*], Minghui Liang [b,*], Wei-Guo Chu [b,*], Peng Jiang [b,*], Ying Liu [a]

[a] School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, China
[b] CAS Center for Excellence in Nanoscience, Key Laboratory of Nanosystem and Hierarchical Fabrication, National Center for Nanoscience and Technology (NCNST), Beijing 100190, China
[c] ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, Innovation Campus, University of Wollongong, NSW 2522, Australia

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 14 June 2016
Revised 31 July 2016
Accepted 2 August 2016
Available online 3 August 2016

*Keywords:*
Supercapacitor
Microsupercapacitor
Lithography
Micro/nanofabrication
Vertically porous electrode
$Mn_3O_4$

## ABSTRACT

Three-dimensionally porous metal materials are often used as the current collectors and support for the active materials of supercapacitors. However, the applications of vertically porous metal materials in supercapacitors are rarely reported, and the effect of vertically porous metal materials on the energy storage performance of supported metal oxides is not explored. To this end, the $Mn_3O_4$-vertically porous nickel (VPN) electrodes are fabricated via a template-free method. The $Mn_3O_4$-VPN electrode shows much higher volumetric specific capacitances than that of flat nickel film supported $Mn_3O_4$ with the same loading under the same measurement conditions. The volumetric specific capacitance of the vertically porous nickel supported $Mn_3O_4$ electrode can reach 533 F $cm^{-3}$ at the scan rate of 2 mV $s^{-1}$. The fabricated flexible all-solid microsupercapacitor based on the interdigital $Mn_3O_4$-VPN electrode has a volumetric specific capacitance of 110 F $cm^{-3}$ at the current density of 20 μA $cm^{-2}$. The capacitance retention rate of this microsupercapacitor reaches 95% after 5000 cycles under the current density of 20 μA $cm^{-2}$. The vertical pores in the nickel electrode not only fit the micro/nanofabrication process of the $Mn_3O_4$-VPN electrode, but also play an important role in enhancing the capacitive performances of supported $Mn_3O_4$ particles.



* Corresponding authors.
*E-mail addresses:* zhaoxiuchen@bit.edu.cn (X.-C. Zhao), liangmh@nanoctr.cn (M. Liang), wgchu@nanoctr.cn (W.-G. Chu), pjiang@nanoctr.cn (P. Jiang).

http://dx.doi.org/10.1016/j.jcis.2016.08.006
0021-9797/

## 1. Introduction

To develop thin film energy storage technology is of significance for meeting the energy demand of microelectronic devices, micro-electro-mechanical system (MEMS) and wearable electronic devices [1–7]. Supercapacitors are one kind of important energy storage devices having the properties of high power density, fast charge-discharge rate, long lifespan, low cost, and environmental friendliness [8–13]. Metal oxides, such as $RuO_2$, $MnO_2$ and NiO, have higher theoretical mass specific capacitance than that of carbon materials, such as active carbon, graphene and carbon nanotubes, so metal oxides-based supercapacitors (pseudocapacitors) are promising for the practical application [14–20]. However, most of the metal oxides suffer from the bad conductivity, which often show much lower specific capacitance than the theoretical value [21–25]. To improve the conductivity of metal oxides-based electrode materials, carbon materials and conducting polymers have been used to combine with metal oxides, and the capacitance performance of metal oxides can be enhanced [26–31]. Another kind of conductive material, metal electrode, particularly nickel foam, can act as both current collectors and support for metal oxides. However, presently used nickel foams are of three-dimensionally macroporous structure, which may cause that the difficulty in the effectively direct support of the metal oxides on nickel foam. On the other hand, the vertical pores in the porous nickel may facilitate the transport of electrolyte during the charge-discharge process of supercapacitors. Therefore, it is necessary to explore the effect of vertical pores on the energy storage performance of metal oxides, which is not reported to our knowledge.

Microsupercapacitors (MSCs) as a type of important supercapacitors can be readily integrated into the micro-circuits because of their planar property and micron-scale size. Due to the limited space in the microelectronic devices, it is highly desirable to obtain the MSCs with high volumetric specific capacitance, high flexibility, and long cycling lifetime. The volumetric specific capacitance of MSCs depends on the mass specific capacitance and the density of the active materials for energy storage. As far as the fabrication techniques for MSCs are concerned, the micro/nanofabrication technology can be used to fabricate MSCs with desired patterns, which is compatible for the fabrication of microelectronic devices and MEMS [32–34]. For the loading of active materials on support, the e-beam evaporation method is a kind of reliable method, and more importantly, this method can be coupled with micro/nanofabrication technology [35,36]. To deposit metal oxides on vertical pores with e-beam evaporation method not only can facilitate the application of MSCs, but also is worth trying for improving the energy storage performance of supported metal oxides.

Herein, we report a $Mn_3O_4$-vertically porous nickel ($Mn_3O_4$-VPN) electrode for flexible supercapacitors fabricated with a template-free method. The $Mn_3O_4$-VPN electrode had higher volumetric specific capacitance than that of $Mn_3O_4$ supported on flat nickel electrode. The interdigital $Mn_3O_4$-VPN electrodes for MSCs can be prepared via a lithography route, and the properties of the enhanced capacitances, high flexibility and long lifetime for the fabricated MSC can be reached.

## 2. Experimental

### 2.1. Materials and methods

Titanic and nickel target were of high purity of 99.995% (General Research Institute for Nonferrous Metals, China); $Mn_3O_4$ powder (99.99%) was also supplied by General Research Institute for Nonferrous Metals; Other reagents were of analytical grade without any further purification. Polyethylene terephthalate (PET) thin film was washed by acetone and dried at 75 °C for 30 min, and then it was treated by oxygen plasma at 200 W for 2 min (partial pressure of oxygen was 2 Pa). The 10 nm thick titanic layer as the sticker layer was deposited on PET using magnetron sputtering system with the power of 150 W under the pressure of 5 mtorr at room temperature for 10 min; then 300 nm nickel layer on titanic layer was deposited for 1 h at the same condition using Ni target. The nickel film on PET was statically soaked in hydrochloride (2.5 mol $l^{-1}$) for about 9 min, and then the obtained porous nickel film was washed by deionized water (18 Mohm) and dried at 80 °C for 2 h. $Mn_3O_4$ film was deposited on the vertically porous nickel film with electron beam evaporation, and the $Mn_3O_4$-vertically porous nickel ($Mn_3O_4$-VPN) electrode with nano-hierarchical structure was obtained. For the preparation of patterned electrodes for microsupercapacitors, the photoresist layer with raster-type pattern was prepared with lithography process first (Süss, MA6, Germany), and the following procedure was same as above, at last the photoresist layer was removed with lift-off process, and the patterned $Mn_3O_4$-VPN composite electrode can be obtained. For the microsupercapacitor with five couples of interdigital electrodes, the width of electrode was 100 μm, and the distance between electrodes was 200 μm, and the length of the electrode was 5 mm.

### 2.2. Characterizations

The sputtering process was performed on Lab 18 (Kurt J. Lesker Company, USA); the electron beam evaporation of $Mn_3O_4$ was executed on BOC 500 (Edwards, UK), and the lithography process was carried out on MA6 (Süss, Germany); the samples was observed on scanning electron microscopy (SEM, NOVA NanoSEM430, FEI Company, USA), transmission electron microscopy (TEM, F20, FEI Company, USA) and other characterizations of the samples were performed on X-ray diffraction (XRD, Smartlab, Rigaku corp., Japan), and X-ray photoelectron spectroscopy (XPS, ESCA Lab 250).

### 2.3. Electrochemical measurements

The electrochemical performances measurements of the samples were carried out on VMP3 Potentiostat Galvanostat (EG&G, Princeton Applied Research). A three electrodes system was employed for verifying the electrochemical properties of $Mn_3O_4$-based composite electrodes; the composite materials on PET served as working electrode in 1 M $Na_2SO_4$ aqueous solution at room temperature, a Pt foil and a saturated calomel electrode (SCE) serving as the counter and reference electrode, respectively. The $Mn_3O_4$-VPN based microsupercapacitor was fabricated by coating the polyvinyl alcohol (PVA)-LiCl (mass ratio = 1:2) gel on interdigital electrodes; the all solid flexible and transparent supercapacitor was assembled by attaching two pieces of transparent $Mn_3O_4$-VPN electrodes with PVA-LiCl (mass ratio = 1:2) being used as solid electrolyte and the whole device was sealed by polydimethylsiloxane (PDMS). Electrochemical impedance spectra (EIS) were measured with a sinusoidal wave of 5 mV amplitude at the open circuit potential with frequencies spanned from 0.01 Hz to 100 MHz. The mass, areal, and volumetric specific capacitances of the electrode were calculated from the galvanostatic charge/discharge (GCD) curves according to the following two equations, respectively:

$$C_m = i/[-(\Delta U/\Delta t)m_e] \quad (1)$$

$$C_a = i/[-(\Delta U/\Delta t)A_e] \quad (2)$$

$$C_v = i/[-(\Delta U/\Delta t)V_e] \quad (3)$$