



Synthesis of three-dimensionally ordered macroporous manganese dioxide–carbon nanocomposites for supercapacitors



Zhi Liu^{*}, Xiuli Tan, Xin Gao, Lihong Song

Institute of Chemistry for Functionalized Materials, Faculty of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian 116029, PR China

HIGHLIGHTS

- Three-dimensionally ordered macroporous MnO₂–carbon nanocomposites (3DOM MCNs) are prepared.
- The 3DOM MCNs possess hierarchical pore structure with highly dispersed MnO₂ nanoparticles.
- The 3DOM MCNs are promising for supercapacitor applications.

ARTICLE INFO

Article history:

Received 11 March 2014

Received in revised form

12 May 2014

Accepted 3 June 2014

Available online 11 June 2014

Keywords:

Manganese dioxide

Carbon

Three-dimensionally ordered macropore

Nanocomposite

Supercapacitor

ABSTRACT

In this article, we report a composite of MnO₂ nanoparticles supported by three-dimensionally ordered macroporous carbon (MnO₂/3DOM carbon nanocomposites) fabricated by means of a simple multi-component infiltration of three-dimensional templates. MnO₂ nanoparticles of 2 nm–6 nm are observed to be highly dispersed on the 3DOM carbon scaffolds. Cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy techniques are employed to assess the properties of these nanocomposites for use in supercapacitors. The results demonstrate that MnO₂ can be effectively utilized with assistance of the 3DOM carbon in the electrode. The specific capacitance of the nanocomposite electrode can reach as high as 347 F g⁻¹ at a current density of 0.5 A g⁻¹. Moreover, the electrode exhibit excellent charge/discharge rate and good cycling stability, retaining over 92% of its initial charge after 5500 cycles at a current density of 2.5 A g⁻¹. Such MnO₂/3DOM carbon nanocomposite represents a promising exploring direction for enhancing the device performance of metal oxide-based electrochemical supercapacitors.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Recently, the interest in the design and fabrication of MnO₂–carbon nanocomposites (MCNs) with various architectures as supercapacitors is growing rapidly owing to their remarkably enhanced capacitive performance compared to the single MnO₂ or carbon counterpart [1,2]. The combination of MnO₂ with carbon not only in principle retains the high theoretical specific capacitance of MnO₂ (1370 F g⁻¹) with significantly improved conductivity, but it also fully utilizes the structural versatility of carbon materials (one, two, or three-dimension) with rich porosities and high accessible surface areas to well disperse the MnO₂ phase. Up to date, various forms of MCNs, such as MnO₂ associating with activated carbon [3,4], carbon nanotubes [5–8], graphene or reduced graphene oxide [9–11], graphite [12,13], carbon cloth [14], ordered mesoporous carbon [15–17], carbon aerogels and nanofoams [18,19], have been

synthesized by different approaches including chemical or electrochemical deposition, redox reaction, sonochemical or microwave-assisted synthesis, and layer by layer assembly. Although desired capacitive enhancements are achieved to some degree, these fabrication techniques are often costly, experimentally fussy with multistep synthesis procedures, time/energy-consuming, and hard to produce in large-scale. Moreover, they uncontrollably either come into being a random distribution of constitutive MnO₂ and carbon phases, or result in the preferential formation of MnO₂ layers located on the exterior of the carbon substrates, which inevitably blocks inwards diffusion of MnO₂ and consequently leads to a low MnO₂ utilization at a high loading content. Even worse, the formed MnO₂ probably decreases pore accessibility of ions and electron conductivity of the MCNs. Therefore, designing a scalable strategy for fabricating a new MCN with a uniform framework composition, the highest possible dispersion of MnO₂ nanostructure with regular pore texture for easy transport of ions as well as good electron conductivity ability,

^{*} Corresponding author. Tel.: +86 411 82156989; fax: +86 411 82156858.
E-mail address: zhiliu@lnnu.edu.cn (Z. Liu).

is highly desired and attractive for ensuring a satisfactory capacitance performance.

Over the past years, three-dimensionally ordered macroporous (3DOM) materials, with uniform pore size and well-defined periodic structure, have stimulated much more attention due to their potential applications in electrochemistry, catalysis, separation and photonic crystals, etc [20–22]. Particularly in electrochemistry used as supercapacitors, in addition to their 3D network paths, uniform pore sizes, interconnected macropores providing a fast ion transportation pathway for the electrolyte to reach the surface of the active material, and contribution electrical double-layer capacitance (EDLC) to the overall energy storage, the 3DOM materials with a hierarchical porous texture can generate large specific surface area to increase effective interfacial area between the active phase and the electrolyte, thus maximizing the capacitance. As a continuous network of electrode materials, 3DOM materials are monolithic which have smoother electron conductivity than loosely aggregated nanocrystalline materials. Furthermore, the free space within porous 3D electrodes can act as buffer for the drastically volume variation of the entire electrode during the consecutive charge/discharge process [23–31]. Conventionally, the colloidal crystal templating strategy (CCTS) is employed to prepare 3DOM materials [32]. Briefly, uniform monodispersed microspheres, such as polymethyl methacrylate (PMMA), polystyrene or silica spheres, can assemble into ordered three-dimensional array in densified packing. These ordered arrays offer a 3D scaffold in which a variety of precursors can be infiltrated. After subsequent solidification of the precursors and removal of the colloidal microspheres, periodic 3D framework structures are obtained. To the best of our knowledge, there are scarce reports to date concerning a 3DOM MCN possessing a hierarchical pore structure with a uniform composition of MnO_2 and carbon used as supercapacitors. Aroused by this interest, we for the first time report the synthesis of a novel 3DOM material composed of MnO_2 and carbon by means of a multi-component (manganous nitrate, phenol–formaldehyde resol, and triblock copolymer F127) infiltration of 3D templates. F127 was selected as a structure-directing agent to create mesopores in 3DOM skeletons and increase surface area for charge storage. The resulting MCNs exhibit highly ordered 3D macroporous structures. The MnO_2 content in the MCNs can be continuously tuned from 6.5 to 21.3 wt.%, and MnO_2 nanoparticles are highly distributed on the macropore walls of the 3DOM carbon scaffold. When tested as supercapacitor electrodes, the MCN with a MnO_2 content of 21.3 wt.% exhibits the best capacitive performance with a total specific capacitance of 347 F g^{-1} and a MnO_2 specific capacitance of 1178 F g^{-1} at a current density of 0.5 A g^{-1} .

2. Experimental

2.1. Chemical agents

Pluronic F127 ($\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$) was supplied by Sigma–Aldrich and has an average molecular weight of 12,600. Methyl methacrylate (MMA), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), $\text{Mn}(\text{NO}_3)_2$ (50 wt.%) solution and sodium hydroxide (NaOH) were purchased from Tianjin Kermel Chemical Reagent Co. Ltd. Phenol, formaldehyde (37 wt.%), hydrochloric acid (37 wt.%) (HCl), and ethanol were purchased from Shenyang Chemical Preparation Corp. All the chemicals were used as received without further purification. Deionized water was used in all experiments.

2.2. Synthesis of PMMA template

The PMMA colloidal crystal templates for the creation of 3DOM MCN were synthesized via a soap-free-emulsion polymerization

according to a modified procedure based on Ref. [33]. In a typical synthesis, a desired amount of monomer MMA was washed three times with a NaOH solution (10 wt.%) and di-distilled water respectively to remove any traces of the inhibitor. Then, 11.3 g of the washed MMA and 150 g of di-distilled water were added to a 500 mL round bottom flask and stirred for a while. Then, 12 mL (0.0005 g mL^{-1}) $\text{K}_2\text{S}_2\text{O}_8$ was added to the solution and the mixture was constantly reacted at 70°C for 7 h under a nitrogen atmosphere with mild stirring until a milky solution appeared. After filtering the milky solution to remove large agglomerates, the monodispersed PMMA microspheres were obtained. Finally, the as-synthesized monodispersed PMMA microspheres were packed into PMMA colloidal crystal template by evaporating the water solvent at 70°C for 24 h.

2.3. Preparation of precursors

The phenol–formaldehyde (P–F) resol precursor was prepared according to Ref. [34]. Briefly, 6.0 g of phenol was mixed with 1.0 g of 20 wt.% NaOH aqueous solution under stirring, and 10.0 g of formaldehyde solution was then added. The resulting transparent solution was stirred at 75°C for 1 h, cooled to room temperature, and the pH was then adjusted to about 7.0 by 2.0 mol L^{-1} HCl. After water was removed by distillation, the mixture was redispersed in a required amount of ethanol. The NaCl precipitate was removed by filtration, and the filtrate, the P–F resol precursor with a concentration of 50 wt.% in ethanol, was collected for further use. For a typical synthesis of manganese precursor (MP), a required amount of $\text{Mn}(\text{NO}_3)_2$ was dissolved in 11.0 g of ethanol under stirring for 30 min. Next, 1.0 g of P–F resol was added to the solution and stirred for another 1 h. To the above resulting solution was added 0.11 g of F127 and then stirring overnight. By varying the amount of $\text{Mn}(\text{NO}_3)_2$, the MPs with different content of manganese were prepared and denoted as MP-B, MP-C, and MP-D, respectively. In addition, a blank manganese precursor (denoted as MP-A) was also prepared under the same conditions as those for the MPs, but without the adding of $\text{Mn}(\text{NO}_3)_2$. The detailed preparation conditions and the corresponding sample I.D. are summarized in Table 1.

2.4. Preparation of 3DOM MCNs

The hierarchical pore structured 3DOM MCN was prepared by employing the CCTS with the different MPs. Typically, the PMMA template was firstly soaked in the MP for 30 min. Care was taken to keep the solution level below the top of the PMMA template. After wiping off the excess solution, the infiltrated template was dried at 100°C for 2 h. Then, the soaking–drying steps were repeated for three times to ensure a complete filling of the void spaces between the PMMA microspheres. Finally, the resultant was pyrolyzed under flowing N_2 at 450°C for 2 h and then at 800°C for another 3 h with a heating rate of 1°C min^{-1} . The as-synthesized products were denoted as A, B, C and D.

2.5. Electrode preparation and electrochemical measurements

The fabrication of working electrodes was carried out as follows. Briefly, the active material (the as-prepared samples A–D), carbon

Table 1
Synthesis conditions of manganese precursor.

MCN sample I.D.	Manganese precursor	$\text{Mn}(\text{NO}_3)_2$ (50 wt.%) (g)	Ethanol (g)	P–F resol (g)	F127 (g)
A	MP-A	0.0	11.0	1.0	0.11
B	MP-B	0.15	11.0	1.0	0.11
C	MP-C	0.31	11.0	1.0	0.11
D	MP-D	0.54	11.0	1.0	0.11

Download English Version:

<https://daneshyari.com/en/article/1286658>

Download Persian Version:

<https://daneshyari.com/article/1286658>

[Daneshyari.com](https://daneshyari.com)