Contents lists available at ScienceDirect

Electrochimica Acta

Construction of Porous Hierarchical Manganese Dioxide on Exfoliated Titanium Dioxide Nanosheets as a Novel Electrode for Supercapacitors

Huimin Zhu[a], Qi Liu[b,**], Jingyuan Liu[a], Rumin Li[a], Hongsen Zhang[a], Songxia Hu[b], Zhanshuang Li[a,*]

[a] Key Laboratory of Superlight Material and Surface Technology, Ministry of Education, Harbin Engineering University, 150001, PR China
[b] Institute of Advanced Marine Materials, Harbin Engineering University, 150001, PR China

A B S T R A C T

A facile composite of tremella-on-sheet manganese dioxide (MnO_2)/titanium dioxide (TiO_2) has been fabricated successfully as the electrode material for supercapacitors. The results of scanning electron microscopy and transmission electron microscopy reveal that hierarchical tremella-like MnO_2 grows onto the exfoliated two-dimensional (2D) TiO_2 nanosheets. The uniquely structured composite covers a large specific surface area with typical mesoporous characteristics for achieving high pseudocapacitance performance. The composite exhibits higher specific capacitance ($286.69\,F\,g^{-1}$ at a current of $1\,A\,g^{-1}$) and has 81.1% retained specific capacitance after 1000 cycles in three-electrode system. The high performance of the electrode is attributed to a unique structure, 3D hierarchical morphology, particular conductive substrate, and low contact resistance.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

With increasing pollution of the environment and depletion of fossil energy, more advanced energy storage devices with higher capacity and conversion devices are intensively demands [1–3]. Representing a class of energy storage devices, supercapacitors (or electrochemical capacitors), are of great interest nowadays owing to their high power density and long life cycle [4–6]. The choice of electrode material directly impacts the performance of the supercapacitor [7]. There are three general categories of electrode materials: carbon materials, conducting polymers and transition metal oxides. Research has focused on further improvement of the performance of the transition metal oxides because they possess multiple oxidation states to enable augmented redox reactions.

Of the metal oxides, manganese dioxide is considered as a potential pseudocapacitive material due to its low cost, wide potential window, low toxicity, natural abundance, and environmentally friendly nature [8–10]. The specific capacitance of MnO_2 is estimated to be as high as $1370\,F\,g^{-1}$ from a theoretical viewpoint of redox reactions involving one electron-transfer per manganese atom [11,12]. However, the densely packed structure, low surface area and poor electronic conductivity of MnO_2 severely limit practical capacitance (less than $200\,F\,g^{-1}$) [13–15]. There are two major approaches to overcome these problems. The first approach is to develop the microstructured of electrodes with large surface area [16]. The second approach is to increase the electrical conductivity of electrodes [17]. Thus, various substrates are developed to enhance electrical conductivity, morphological properties, porosity and surface area.

In comparison to various substrates, titanium dioxide nanosheets are attractive for supercapacitor applications because of their high surface area, chemical stability, ease of fabrication, and excellent control ability [18–21]. Moreover, TiO_2 has higher electronic conductivity (10^{-5}–$10^{-2}\,S\,cm^{-1}$) than MnO_2 (10^{-6}–$10^{-5}\,S\,cm^{-1}$) [22]. He Zhou et al. reported that the TiO_2 nanotube arrays substrate compound with MnO_2 improved the electrode stability and enhanced the ion/charge transport properties between the MnO_2 electrode and the electrolyte interface [23]. However, few articles have reported on the combination TiO_2 nanosheets as substrate with MnO_2 in supercapacitors. It is possible to prepare 2D TiO_2 nanosheet materials from a layered structure by an exfoliation route. The exfoliated TiO_2 nanosheets provide high surface area for the growth of MnO_2 and improve the utilization efficiency of MnO_2 materials by shortening the diffusion path for electron transfer [24].

In this work, we report on the well-designed hierarchical tremella-on-sheet MnO_2/TiO_2 as the electrode material for supercapacitors. In the synthetic procedure, high crystallinity and well-organized layered titanate is exfoliated to 2D ultrathin TiO_2 nanosheets using tetrabutylammonium hydroxide (TBAOH)

---

* Corresponding author. Tel.: +86 0451 8251 9303; fax: +86 0451 8251 9303.
** Corresponding author.
  E-mail addresses: qiliu@hrbeu.edu.cn (Q. Liu), lzs@hrbeu.edu.cn (Z. Li).

solution by the intercalating macromolecular method, and then tremella-like hierarchical manganese dioxide are formed in situ on the surface of the titanium dioxide nanosheets. The uniform structure offers excellent charge transportation and gives rise to a large specific surface area of $81.4\,m^2\,g^{-1}$ by 24 h growth. Furthermore, the MnO_2/TiO_2 composite by 24 h growth exhibits high specific capacitance and excellent capacitive retention.

2. Experimental

2.1. Synthesis

Preparation and exfoliation of TiO_2. All chemical reagents were of analytical grade. 1 g of anatase TiO_2 and 0.75 g of Cs_2CO_3 were mixed and calcined sufficiently at 800 °C in a crucible at muffle for 20 h. The as-prepared sample was removed, milled and annealed again as above. Then the product was ion-exchanged with 1 M HCl with vigorous stirring for 4 days. The acid was replaced with a fresh one every 24 h. After treatment, the sample was collected by centrifugation, washed with deionized water, and dried at 60°C. The protonated product was dispersed in 50 mL TBAOH and shaken at a speed of 160 rpm in a thermostatic shaker at room temperature for 3 days. And the acquired white suspension was centrifugation and washed several times until the supernatant solution became neutral.

The MnO_2/TiO_2 composite was synthesized via a crystallization in situ growth technique. Briefly, in a typically synthesis, 37.5 mg as-obtained TiO_2 was ultrasonic dispersed in $KMnO_4$ solution (60 mL, 0.01 M) for 10 min. The mixed solution was then transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 140°C for 8 h, 16 h, 24 h, 36 h, 48 h in an electric oven (the products prepared for 8 h, 16 h, 24 h, 36 h and 48 h were expressed as sample MT-8 h, MT-16 h, MT-24 h, MT-36 h and MT-48 h respectively). After cooling to room temperature, the black resultants were collected by centrifugation and dried at 60°C for 12 h in a vacuum oven.

2.2. Characterization methods

The morphologies of the prepared samples were characterized by scanning electron microscope (SEM, JEOL, JSM-6480) and transmission electron microscope (TEM, FEI Teccai G2S-Twin, Philips). The crystallographic structures of the materials were measured on a powder X-ray diffraction (XRD) system (Rigaku TTR-III) with Cu Kα radiation (λ = 0.15406 nm). The X-ray source was operated at 40 kV and 150 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI 5700 ESCA spectrometer with Al KR radiation (h_v = 1486.6 eV). All of the XPS spectra were corrected by the C 1s line at 284.5 eV. Nitrogen adsorption-desorption isotherms were measured at liquid nitrogen temperature using a micromeritics ASAP 2010 instrument to assess surface area and porosity.

2.3. Preparation of the electrodes and electrochemical characterization

The electrochemical properties of the as-obtained products were tested under a three-electrode electrochemical system. The working electrodes were prepared by a previously reported procedure [25]. Briefly, 80wt% as-prepared materials, 15wt% acetylene black, and 5wt% polytetrafluoroethylene (PTFE) were mixed and dispersed in ethanol to produce a homogeneous paste. Then the resulting mixture was coated onto the nickel foam current collector (1.0cm × 1.5 cm, projected area of 1.0cm × 1.0 cm). The obtained electrodes were dried at 60 °C for 8 h. The mass of TiO_2, MT-8 h, MT-16 h, MT-24 h, MT-36 h and MT-48 h are 3.2, 2.8, 2.5, 2.7, 3.2 and 3.1 mg cm^{-2} on the Ni foam, respectively. Platinum foil (1 cm^2) was served as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. In addition, the electrochemical measurements were carried out in 1 M Na_2SO_4 aqueous electrolyte. A CHI 660D electrochemical workstation was employed to perform cyclic voltammetry, galvanostatic charge–discharge tests, and electrochemical impedance spectroscopy.
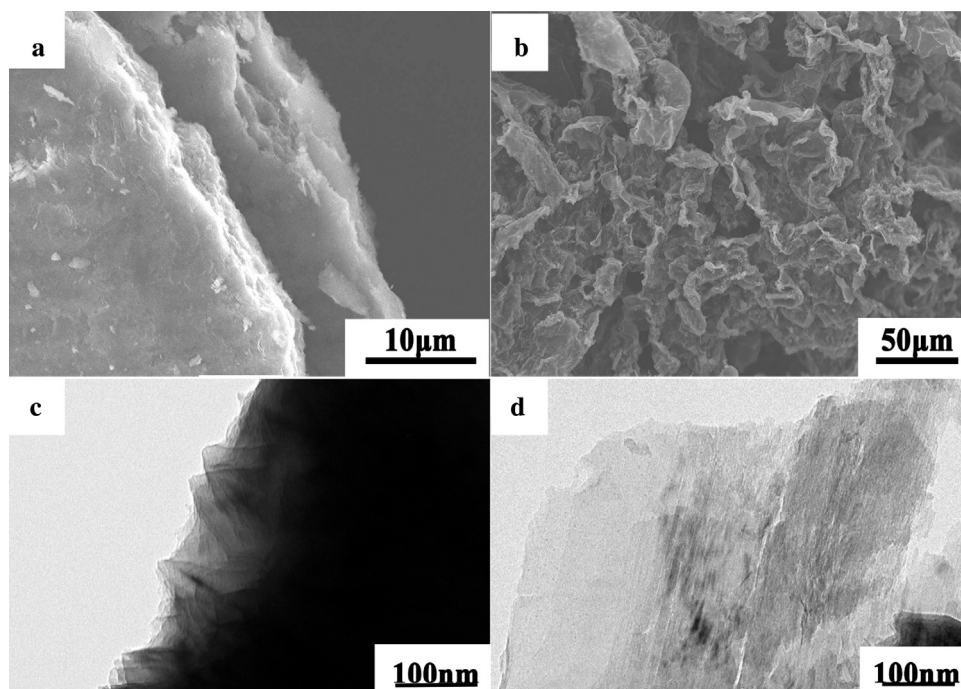

Fig. 1. The SEM and TEM images of the TiO_2 before (a, c) and after (b, d) exfoliation.