Available online at www.sciencedirect.com

ScienceDirect

Materials Research Bulletin 43 (2008) 2818–2824

Materials Research Bulletin

www.elsevier.com/locate/matresbu

Short communication

Synthesis of Ru/multiwalled carbon nanotubes by microemulsion for electrochemical supercapacitor

Shancheng Yan, Peng Qu, Haitao Wang, Tian Tian, Zhongdang Xiao *

State Key Laboratory of Bioelectronics, School of Biological Science & Medical Engineering, Southeast University, Si Pai Lou 2#, Nanjing 210096, PR China

Received 22 June 2007; received in revised form 15 September 2007; accepted 18 October 2007
Available online 20 February 2008

Abstract

An efficient way to decorate multiwalled carbon nanotubes with Ru had been developed. In this method, Ru nanoparticles were prepared by water-in-oil reverse microemulsion, and the produced Ru anchored on MWCNTs. Transmission electron microscopy (TEM) result showed that RuO_2 nanoparticles had the uniform size distribution after electrochemical oxidation. Energy dispersive X-rays (EDX) spectra elucidated the presence of ruthenium oxide in the as-prepared composites after electrochemical oxidation. Cyclic voltammetry result demonstrated that a specific capacitance of deposited ruthenium oxide electrode was significantly greater than that of the pristine MWCNTs electrode in the same medium.

Keywords: B. Electrochemical properties; B. Chemical synthesis

1. Introduction

Supercapacitors are energy storage devices, which exhibit acceptable capacity, high power density and long cycle life [1]. According to energy storage mechanism, there are two types of supercapacitors, viz., double-layer and redox supercapacitors. In the former, energy storage arises mainly from the separation of electronic and ionic charges at the interface between the electrode materials and the electrolyte solution. In the latter, fast faradic reactions take place at the electrode materials [2]. Hence, it is obvious that the charge stored in redox supercapacitors should be higher than that in double-layer counterparts [3]. Electrode materials with electronic conductivity such as carbon black, carbon nanotubes, carbon fiber, etc. [4,5] are generally used as electronic conductors. Many transition metal oxides, such as Ru, Mn, Ni, etc. also have been used as electrode materials [6–8]. It is well known that hydrous RuO_2 is an excellent material with a remarkable high specific capacitance value [9]. Recently, the enhanced capacitance of multiwalled CNTs functionalized with ruthenium oxide has been widely researched.

In this work, the synthesis of Ru/MWCNTs nanocomposites through microemulsion method was reported. The resulting Ru/MWCNTs composites were characterized by energy dispersive X-rays (EDX) spectra and transmission electron microscopy (TEM). The electrochemical behavior of the composites electrodes was tested by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

* Corresponding author. Tel.: +86 25 83790820; fax: +86 25 83795635.
E-mail address: zdxiao@seu.edu.cn (Z. Xiao).

0025-5408/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.materresbull.2007.10.041

2. Experimental

The MWCNTs used in this work were synthesized in our laboratory. $RuCl_3 \cdot xH_2O$ used in this work was from Alfa Aesar (USA). All other chemicals were purchased from chemical reagent Co., Ltd. and used as received. Triple-distilled water of 18 M obtained from aqua MAX water system (ASW1-0501-U) was used to prepare all the solutions.

The preparation of Ru nanoparticles was by a two-emulsion technique. The microemulsion system used in this study consisted of TritonX-100 as a surfactant, isopropyl alcohol as a cosurfactant, cyclohexane as the continuous oil phase. The details were described by Zhang and Chan [10]. The prepared Ru nanoparticles and MWCNTs were dispersed in anhydrous ethanol by ultrasonic. A drop of this solution was coated on the polished surface of home-made carbon paste electrode (CPE) and dried under room temperature. A similar procedure was followed to prepare the MWCNTs electrode. The Ru nanoparticles in the composite were electrochemically oxidized by sweeping the voltage from open circuit potential to 0.75 V vs. Hg/Hg_2Cl_2 electrode and holding at 0.75 V for 2 h [11]. The morphologies and microstructures of the products were examined by means of TEM on a Tecnai G2 S-TWIN transmission electron microscope equipped with an EDX spectrometer using an accelerating voltage of 200 kV.

The electrochemical measurements were performed by means of an electrochemical analyzer system, CHI 660 C (CH Instruments). The impedance spectrum analyzer, IM6ex (ZAHNER) was employed to measure and analyze the AC-impedance spectra. The potential aptitude of AC was equal to 10 mV and its frequency ranged from 0.01 Hz to 100 kHz. All experiments were carried out in a three-compartment cell. A Hg/Hg_2Cl_2 electrode and a piece of platinum were employed as the reference and the counter electrode at room temperature, respectively.

3. Results and discussion

The effects of the initial mass ratio of Ru to MWCNTs on the composition of the prepared composites were investigated.

Fig. 1 shows the TEM image of MWCNTs. As seen in Fig. 1, multiwalled carbon nanotubes are entangled. The average diameter of MWCNTs is about 10–40 nm. A little amorphous carbon attaching on the MWCNTs can be found.

The typical TEM image of resulting Ru/MWCNTs composite is shown in Fig. 2. As seen in Fig. 2a, RuO_2 nanoparticles are anchored on the surface of MWCNTs. As seen in Fig. 2b, the RuO_2 nanoparticles are uniform in size.

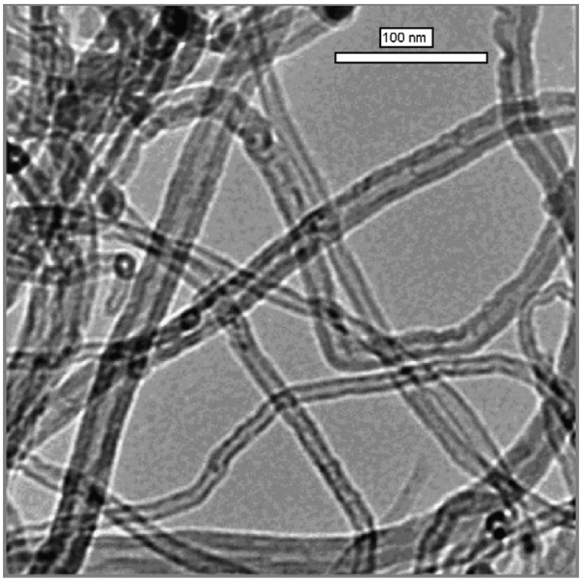

Fig. 1. Transmission electron microscopic image of MWCNTs.