Materials Research Bulletin 48 (2013) 747–751

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

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

Synthesis and characterization of a novel tube-in-tube nanostructured PPy/MnO_2/CNTs composite for supercapacitor

Juan Li [a,b,*], Tingli Que [a], Jianbin Huang [a,b,**]

[a] College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830046, PR China
[b] Beijing National Laboratory for Molecular Sciences (BNLMS), State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China

ARTICLE INFO

Article history:
Received 9 November 2011
Received in revised form 17 September 2012
Accepted 6 November 2012
Available online 15 November 2012

Keywords:
Nanostructures
Composites
Electrochemical properties
One dimension assemblies

ABSTRACT

Ternary organic–inorganic complex of polypyrrole/manganese dioxide/carbon nanotubes (PPy/MnO_2/CNTs) composite was prepared by in situ chemical oxidation polymerization of pyrrole in the host of inorganic matrix of MnO_2 and CNTs, using complex of methyl orange (MO)/$FeCl_3$ was used as a reactive self-degraded soft-template. The morphological structures of the composite were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopic (HRTEM), Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD), respectively. All the results indicate that the PPy/MnO_2/CNTs composite possesses the typical tube-in-tube nanostructures: the inner tubules are CNTs and the outer tubules are template-synthesized PPy. MnO_2 nanoparticles may either sandwich the space between the inner and outer tubules or directly latch onto the wall of the PPy tubes. The composite yields a good electrochemical reversibility through 1000 cycles' cyclic voltammogram (CV) test in the potential range of −0.6 to 0.4 V and its specific capacitance was up to 402.7 F g^{-1} at a current density of 1 A g^{-1} in galvanostatic charge–discharge experiment.

1. Introduction

Conducting polymers/inorganic components based on composite materials have attracted tremendous attentions owing to their outstanding optical properties, high flexibility, excellent toughness, easy processing methods and anti-corrosion ability. They are supposed to be used in many fields such as molecular electronics, electrochemical display devices, catalysis, electro-magnetic shields, microwave-absorbing materials, supercapacitor, batteries and so on [1–4]. A large number of conducting polymers have been widely engaged in synthesizing composites with inorganic nanoparticles [5–7]. Among them, PPy is the favorite specie because of its good environmental stability, low toxicity, high conductivity, and excellent redox property [8,9]. Various nanocomposites of PPy coupled inorganic nanoparticles have been synthesized and investigated [10–15]. MnO_2, a semiconductor material, is known as remarkable characteristics due to its low cost, environmentally friendly nature, and ideal electrochemical performance [16,17]. It had been widely used in various battery electrodes for more than 150 years and is now thought to be a very promising electrode material for the supercapacitor [18]. Up to now, there are several reports on synthesizing the PPy/MnO_2 composite [6,12], and their results show that this composite material is an ideal option for the optimized supercapacitor.

Although PPy/MnO_2 composite has a potential application in electrochemical capacitor, its stability still can be improved by further efforts. Considering the outstanding properties of carbon nanotubes (CNTs) such as a narrow distribution size, highly accessible surface area, low resistivity, and high stability [19,20], PPy/MnO_2/CNTs ternary composite are therefore regarded as one of the best options for construct materials for supercapacitor. S.R. Sivakkumar et al. [21] reported a ternary composite of CNT/polypyrrole/hydrous MnO_2 by using $KMnO_4$ as oxidant and the composite with granular morphology has presented good electrochemical stability for electrochemical capacitors. It was already demonstrated that nanostructure indeed can significantly affect the electrochemical properties of the active electrodes materials. The overall electrochemical properties not only depend on the structural factors but also the size and morphology of the active electrodes materials. Compared with the bulk phase materials, one-dimensional nanostructure is far easier to achieve transmission of the ions and/or charges. Hence, we focus our interesting on one-dimensional tube-in-tube nanostructured PPy/MnO_2/CNTs composite. It was synthesized by a simple technique in neutral

* Corresponding author. Tel.: +86 0991 8582887; fax: +86 0991 8580032.
** Corresponding author at: College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830046, PR China.
E-mail addresses: lj-panpan@163.com (J. Li), JBhuang@pku.edu.cn (J. Huang).

0025-5408/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.materresbull.2012.11.014

medium at low temperature, using complex of methyl orange (MO)/$FeCl_3$ as a reactive self-degraded soft-template and oxidant. As we expected, further investigation demonstrated that the material has excellent electrochemical properties.

2. Experimental

All of the chemical reagents used were A.R. grade. Pyrrole monomer was distilled under reduced pressure before being used. CNTs (Shenzhen Nanoport Corporation of China) with an outer diameter between 20 and 40 nm were treated by refluxing in 6 M HNO_3 previous to synthesizing of composite.

2.1. Treatment of MnO_2/CNTs composite

The MnO_2/CNTs composite was prepared under hydrothermal condition. The typical synthesis process was carried out as follows: Firstly, $KMnO_4$ and $MnSO_4{\cdot}H_2O$ (the molar ratio was 2:3) were co-dissolved in appropriate amount of distilled water and stirred strongly for ten minutes to form a homogeneous solution. Secondly, metrological amount of CNTs (the molar ratio to $KMnO_4$ was 5:9) was added to the solution and ultrasonically stirred for better dispersion. Later on, the complex was loaded into a Teflon-lined stainless-steel autoclave. The autoclave was heated to 140 °C and kept at this temperature for 10 h, and then was naturally cooled to room temperature. After that, the precursors were washed with distilled water and anhydrous alcohol several times. And finally, the recovered product was dried at 60 °C in a vacuum oven for 24 h.

2.2. Preparation of PPy/MnO_2/CNTs composite

Metrological amount of $FeCl_3$ was dissolved in methyl orange (MO) solution and then ultrasonically stirred in order to form a homogeneous solution. A flocculent precipitate appeared immediately after the stirring. Metrological amount of MnO_2/CNTs composite was added to the mixture. After using ultrasonic agitation for better dispersion, pyrrole monomers were slowly injected into the above mixture. Subsequently, the reaction was performed under static condition for 24 h at the temperature of −5 to 0 °C. After washing several times with distilled water and ethanol, the composite was dried under vacuum at 50 °C. The theoretical mass percentage of MnO_2, PPy and CNTs in the final composite is about 57.0%, 41.2% and 1.8%, respectively.

The PPy was synthesized following the similar procedures but adding the MnO_2/CNTs and performing corresponding ultrasonically stirred step was skipped.

2.3. Instrument and characterization

The powdered sample was dispersed in absolute ethanol by ultrasonication for 1 h in a KQ5200B ultrasonic bath. The crystalline structure in the samples was characterized by an X-ray diffraction (XRD, Japan Rigaku D/Max 2400) using Cu Kα radiation (λ = 1.5405 A) in the 2θ range of 10–60°). Fourier transform infrared (FT-IR) spectra were also taken on a BRUKER-EQUINOX-55 IR spectrophotometer. The morphologies of the products were firstly recorded by transmission electron microscopy (TEM, Model Hitachi H-600, 200 KV). The morphologies were also examined by scanning electron microscopy (SEM, Germany, Leo 1430 VP). High-resolution transmission electron microscopic (HRTEM) image was obtained by a JEOL-2010 High-resolution transmission electron microscope.

Electrodes for supercapacitors were prepared by mixing active materials (1 mg) with 15% acetylene black and 5 wt% polytetrafluorethylene (PTFE) to make more homogeneous slurry. The slurry was pressed on graphite current collector. Electrochemical studies were carried out in a three-electrode system, the freshly prepared PPy/MnO_2/CNTs composite on graphite, a platinum electrode, and a saturated calomel electrode were used as working electrode, counter electrode and reference electrode, respectively. The electrolyte was 1 mol/L Na_2SO_4 solution. Cyclic voltammograms and galvanostatic charge–discharge experiments were performed by using CHI660A electrochemical working station system at the room temperature.

3. Results and discussion

Fig. 1 showed the XRD patterns of pure PPy (a), MnO_2/CNTs (b) and PPy/MnO_2/CNTs composite (c). In XRD patterns of Fig. 1a, a broad peak which located in the range of 15–30° was the characteristic peak of amorphous PPy. There was a small change in intensity and position compared to the XRD pattern in the literature [22]. The highest diffraction peak at a 2θ value of 26.1° was ascribed to the typical reflection of CNTs in Fig. 1b. Moreover, the four major diffraction peaks of MnO_2 nanoparticles at 2θ = 34.8°, 41.1°, 54.1° and 58.5° (marked by asterisk), were assigned as the crystal planes of (3 0 1), (2 1 1), (4 0 2) and (3 1 2), respectively. These results coincided to the XRD signals of MnO_2 very well according to standard JCPDS date (42-1316). While the characteristic peaks of PPy/MnO_2/CNTs composite combined the characteristic peaks of MnO_2, PPy and CNTs as displayed in Fig. 1c. However, it is worthy to note that the PPy characteristic peaks of the PPy/MnO_2/CNTs composite exhibits a shift in positions as compared to pristine PPy. Thus, a structural order was presumed to be induced by PPy chains in this composite [23]. Compared Fig. 1c to Fig. 1b, the diffraction peaks of MnO_2 were weakened significantly. That could be a part of distortion in crystal structure of MnO_2 and also may because of the transformation from crystal structure into amorphous phase during the oxidation polymerization reaction of pyrrole monomer.

The molecular structure of pure PPy and PPy/MnO_2/CNTs nanocomposite were characterized by FT-IR, as shown in Fig. 2. The frequencies at 1541 and 1448 cm^{-1} are attributed to the antisymmetric and symmetric pyrrole ring vibration. The band at 1301 cm^{-1} is corresponded to in-plane vibration of C–H band. Transmittances peaks at 1151 and 1031 cm^{-1} are assigned to the C–N stretching vibrations and N–H in-plane deformation vibration, respectively, which implied the doping state of PPy [24]. The

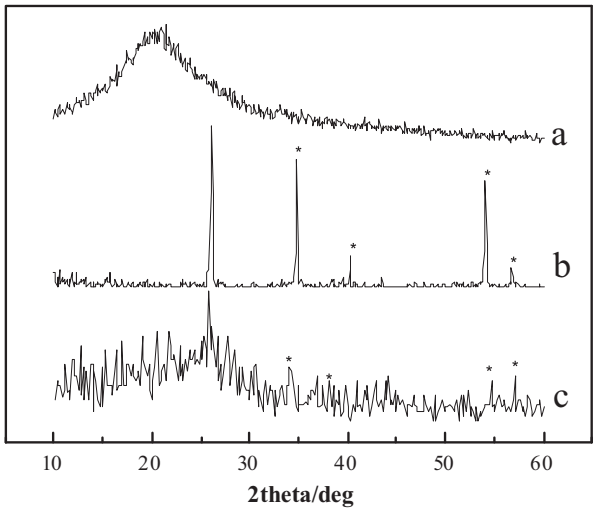

Fig. 1. X-ray diffraction patterns of the PPy (a), MnO_2/CNTs (b) and PPy/MnO_2/CNTs (c) nanocomposites.