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Preparation and electrochemical capacitance of MnO_2 thin films doped by $CuBi_2O_4$

A.A. Aref, A.A. Muneerah, D.M. Sun, H. Wang, C. Qing, Y.W. Tang *

Institute of Nanoscience and Nanotechnology, Central China Normal University, Wuhan 430079, PR China

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ABSTRACT

Manganese dioxide (MnO_2) and $CuBi_2O_4$-doped MnO_2 thin films with different nanostructures were deposited on indium tin oxide (ITO) glass and Ti foil substrates by using a chemical bath deposition (CBD) technique. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron microscopy (XPS). The effects of doping and substrates on electrochemical properties of MnO_2 and $CuBi_2O_4$-doped MnO_2 thin films on ITO glass and Ti foil were investigated. Capacitive properties of MnO_2 and $CuBi_2O_4$-doped MnO_2 thin films electrodes were studied using cyclic voltammetry and electrochemical impedance spectroscopy in a three-electrode experimental setup using 0.1 M Na_2SO_4 aqueous solution as electrolyte. Specific capacitance, obtained from electrochemical measurement for the $CuBi_2O_4$-doped MnO_2, exhibited a higher value of 338 F g^{-1} compared to the MnO_2 exhibiting value of 135 F g^{-1}. In addition, $CuBi_2O_4$-doped MnO_2 thin films on an ITO electrode had a better and satisfactory specific capacitance value, and exhibited more excellent electrochemical stability and reversibility than Ti foil substrates.

1. Introduction

Growing demands for systems and devices that require high performance power sources have stimulated researchers to focus on energy storage. Moreover, the growing environmental and economic impact of the production and use of fossil fuels have evoked the search for alternative energy sources, such as electrochemical energy batteries, and fuel cells. More recently, electrochemical capacitors have been studied extensively [1].

The electrochemical capacitors are classified into two types according to their charge storage principle [2]. The first is an electrical double-layer capacitor (EDLC) using activated carbon (AC) with high surface area and the other is a pseudocapacitor using metal oxides and conducting polymers [3]. Transition metal oxides, such as porous NiO_x [4], RuO_2 [5], CoO_x [6], Fe_2O_3 [7], SnO_2 [8] and MnO_2 [9–11], are promising candidates applicable as supercapacitors. Accordingly, cheaper candidates with good capacitive characteristics such as oxides of Mn, Mo, V, Ni, Co, etc. have attracted considerable attention. These oxides show specific capacitance varying between 100 F/g and 200 F/g. Among these candidates, MnO_2 has been considered to be the most suitable alternative because it is cheaper, more abundant, and more environment friendly than noble metal oxides and other transition metal oxides [12]. However, the resistivity and the equivalent series resistance (ESR) of MnO_2 electrode are very large. Therefore, its capacity is limited. In order to overcome this disadvantage, the composite electrode materials of the manganese oxide were prepared using conducting additives with carbon material (such as graphite, carbon nanotube, porous carbon, activated carbon, carbon aerogel, etc.) [13–15], conducting polymers [16,17], metal oxides

* Corresponding author. Tel.: +86 27 67867947; fax: +86 27 67861185.
E-mail address: ywtang@phy.ccnu.edu.cn (Y.W. Tang).

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[18–20], etc. Usage of the novel compound can be useful, and open a new way for preparing nanomaterials to control nanocrystal size, shape and distribution size [21].

Doping has been created as a powerful technique to improve the features of metal oxides [22]. The choice of metal precursor is a key step in the preparation of nanometal oxides [23]. Lee et al. [24] prepared Fe-doped manganese oxide thin films by anodic deposition and reported the specific capacitance of 212 F/g, which was 21% higher than that for plain manganese oxide. Wu et al. showed that addition of 1–8 wt% Ag to lithium manganese dioxide electrode could significantly improve battery performance due to the increase in conductivity [25]. Ding and Chin reported that the metal ion-doped MnO_2 exhibited a higher value of 36 mF/cm^2 compared to the non-doped MnO_2 value of 30 mF/cm^2. They observed that the doped metal ion influenced the morphology of MnO_2, and improved capacitance behavior of metal ion-doped MnO_2 was exhibited [22]. Several methods, such as a template method [26], sol–gel synthesis [27], electrodeposition technique [28,29], anodic deposition [30], and layer-by-layer assembly [31,32], have been developed for the synthesis of MnO_2 nanostructures on ITO glass. The CBD process has been reported for the deposition of MnO_2 thin film onto ITO glass substrates [33,34]. Yet, the effect of structure and morphology on the electrochemical capacitive performance of the thin film has not been explored in detail. So, the presence of $CuBi_2O_4$ may have tuned the morphology of MnO_2 thin film. Although there have been a lot of reports about MnO_2 thin film deposition as shown above, the preparation of MnO_2 nanoflower arrays on substrates is few. The effect of $CuBi_2O_4$ on MnO_2 1-D nanorod and 3D nanoflower thin film deposition has not yet been reported. In addition, an appropriate $CuBi_2O_4$ volume is critical for the construction of a nanoflower structure and the presence of $CuBi_2O_4$ can shorten the formation time of nanorods.

In this work, chemical bath deposition (CBD) was applied to deposit MnO_2 thin film onto ITO glass and Ti foil to compare the effect of substrate. In the chemical bath deposition method, the oxidation could take place on some metallic substrate, so the substrate material was carefully selected to avoid the substrate dissolution into the chemical reaction [35,36]. The obtained nanostructured manganese dioxide was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The electrochemical feature of MnO_2 was extensively investigated by cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) methods. To date, MnO_2 nanoflower thin films grown onto ITO glass and Ti foil in the presence of $CuBi_2O_4$ by using CBD has not yet been reported.

2. Experimental

2.1. Preparation of MnO_2 and $CuBi_2O_4$ doped-MnO_2 films

In this work, manganese dioxide (MnO_2) and $CuBi_2O_4$-doped MnO_2 thin films were deposited onto the substrates ITO glass and Ti foil using the CBD technique. The substrates of ITO glass and Ti foil were ultrasonically cleaned in distilled water, acetone and absolute ethanol for 10 min in each solvent and then dried at room temperature. MnO_2 thin film was prepared by first mixing 30 mL of 1 M manganese sulfate ($MnSO_4.H_2O$) and 30 mL of 1 M potassium persulfate ($K_2S_2O_8$) to the beaker in the following sequence: first $K_2S_2O_8$ and then followed by $MnSO_4 \cdot H_2O$. The mixture was poured into a beaker and immersed into the heated water bath. The solution was stirred to ensure homogeneous dissolution for 5 min. Thereafter, 30 mL of 0.05 M copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) was added into the solution in the beaker under stirring condition. Subsequently, the pre-clean substrates were submerged into the solution with the top of the beaker covered with a Parafilm. The solution was magnetically stirred in the beaker at 80 °C for 8 h. Dark brown precipitates were immediately obtained based on the following formula:

$$\mathbf{5MnSO_4} + 5\mathbf{K_2S_2O_8} + 10\mathbf{H_2}O \rightarrow 5\mathrm{Mn}\mathbf{O_2}\downarrow + \mathbf{K_2SO_4} + 4\mathbf{H_2SO_4} + 10\mathrm{KHS}\mathbf{O_4}$$

After completing the film deposition, the samples were removed from the beaker and immediately rinsed with deionized water to remove soluble impurities and then dried in the vacuum at 60 °C overnight. For the deposition of $CuBi_2O_4$-doped MnO_2 thin films onto ITO glass and Ti foil, the above steps were repeated in the presence of $CuBi_2O_4$ with different concentrations at 0.01, 0.03 and 0.05 g for ITO glass, and Ti foil under stirring condition. It was to ensure the complete dissolution of $CuBi_2O_4$. $CuBi_2O_4$ was synthesized by the group as previously reported [37].

2.2. Characterization

The purification phase of the samples was characterized by X-ray powder diffraction (XRD) using an X-ray diffractometer (Y-2000) with Cu Kα radiation ($\lambda = 1.5418$ Å). Scanning electron microscopy (SEM) images were obtained by a JEOL JSM-6700F microscope operated at 5 kV. A Large Area X-ray Photoelectron Spectroscopy (LAXPS) equipped with an Al Kα 300 W X-ray radiation ($h\nu = 1486.6$ eV) source for the excitation and energy dispersive spectra obtained it using X-ray dispersive spectrum spectroscopy (SUTW-SAPPHIRE) with 20.0 kV accelerating voltage. All of the spectra were calibrated to C 1s peak at 284.6 eV. The electrochemical behavior of MnO_2 and $CuBi_2O_4$-doped MnO_2 was characterized by cyclic voltammetry and charge–discharge tests. Cyclic voltammetry (CV), charge–discharge testing, and electrochemical impedance spectroscopy were performed using a computer controlled electrochemical system (CHI440A Instruments, Chenhua Co., Shanghai). Measurements were performed in a three-electrode cell. As a counter-electrode and reference electrode, a Pt plate and a saturated calomel electrode were used. The MnO_2 and $CuBi_2O_4$-doped MnO_2 on ITO glass and Ti foil electrodes were used as working electrodes. The measurements were performed at room temperature in 0.1 M Na_2SO_4 electrolyte.

3. Results and discussion

3.1. Structure and morphology characterization

3.1.1. XRD

Fig. 1 shows XRD patterns of MnO_2 and $CuBi_2O_4$-doped MnO_2 thin films prepared by CBD on ITO glass and Ti foil.