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Microwave-assisted synthesis of Zn–WO_3 and $ZnWO_4$ for pseudocapacitor applications

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ABSTRACT

Nanosized Zn–WO_3 and $ZnWO_4$ materials have been prepared by microwave irradiation method. The physico-chemical characterization of the prepared nanomaterials was carried out by X-ray diffraction (XRD) and high resolution-scanning electron microscopy (HR-SEM) techniques. The size and shape of the $ZnWO_4$ material can be controlled by changing the temperature. The XRD analysis revealed the formation of monoclinic phase of the calcined nanopowder. The HR-SEM images showed the sphere and plate shape particles. The electrochemical behavior of the $ZnWO_4$ modified electrodes was investigated using electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) techniques. The synthesized material shows the pseudocapacitance. The specific capacitance of 35.70 F/g was achieved for the Zn–WO_3 nanopowder.

1. Introduction

Advanced nanostructured materials are mainly used in energy conversion and storage devices and they are getting notable attention especially for supercapacitors. Supercapacitors are gaining great technical and industrial attention due to their promising applications in hybrid-electric vehicles, pacemakers and memory devices [1–3]. In recent years, researchers are trying to develop efficient energy storage devices for example battery and supercapacitors; however, the high power energy density storage is not yet achieved. The development of alternate energy storage devices in combination with the existing battery and supercapacitor will probably fulfill the efficient solutions for energy storage. Supercapacitors can be classified into two groups such as (i) Electrical double layer capacitor (EDLC) where the capacitance ascribed by the accretion of charges at the electrode/electrolyte interface and (ii) Redox capacitors, where a real battery-type redox reaction occur leading to the pseudocapacitance. Carbon based material with high surface area especially activated carbon and carbon fiber are used in EDLC [4–6]. (iii) Metal oxides and conducting polymers are used as electroactive-materials in pseudocapacitors [7–10]. The carbon is predicted as promising electrode materials for EDLC due to its life cycle and specific capacitance (C_{sp}). However, the carbon based materials suffer from poor energy density and limited cell voltage due to the minimum C_{sp} [11,12]. Recently, most of the research work has been devoted on the pseudocapacitor because of their high C_{sp} and energy density. So far several metal oxides, such as RuO_2 and V_2O_5 [13–14] have been studied in order to use them as electrode materials in pseudocapacitor. These materials are very expensive and hence these materials may not be suitable for commercial device applications. Therefore, searching for a low cost pseudocapacitive material has been the prime focus in electrochemical capacitor research. Recent literature clearly indicates that the transition metal oxides are having good conductivity behavior, so that it could be used in several device applications including supercapacitors [15–35]. Metal doped WO_3 nanoparticles and metal tungstate shows excellent capacitance performance which is suitable for electrochemical capacitors [36–38]. Recently, X. F. Cheng et al. reported that nanomaterials of Zn–WO_3 have higher catalytic performance compare to WO_3 because the doping of zinc into the tungsten oxide lattices permits more absorption capability of visible light and thus more reactivity [39]. Similarly, we assumed that Zn–WO_3 nanomaterials could be a possible and suitable material to achieve high specific capacitance. It has been reported that the enhanced performance of $ZnWO_4$ nanomaterials was observed when it was used in the batteries due to electrochemical activity of both Zn and W metals [38]. The above observation stimulated us that these materials could produce high specific capacitance when applied in supercapacitors. Hence, we synthesized the both Zn–WO_3 and $ZnWO_4$ nanomaterials for pseudocapacitor applications. Zinc tungstates have been prepared by various methods and reported in literatures [40–44]. It should be indicated that the reported methods necessarily need high

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power and time to prepare tungstate based materials ($ZnWO_4$). So, alternate methods are desirable for materials preparation. Microwave irradiation method is a right choice for nanomaterial synthesis including $ZnWO_4$ nanopowder. Microwave heating is a superior technology whose applications have been rapidly growing due to its special effects such as rapid volumetric heating, shortened reaction time and energy saving. Moreover, the technique is effortless, cost effective and very less time consuming compared with other existing technologies. In the present work, we synthesized Zn–WO_3 and $ZnWO_4$ nanopowders by microwave irradiation method and subsequently physical and chemical characterization was also carried out. This approach unbolts up an original pathway to synthesize many different inorganic materials on a large scale for commercial applications. The present study clearly indicates that the synthesized Zn–WO_3 and $ZnWO_4$ nanopowders are promising candidate for pseudocapacitor applications.

2. Experimental

2.1. Materials preparation

The Zn–WO_3 and $ZnWO_4$ were prepared by microwave irradiation method. In a typical experimental procedure, first, 0.1 M of zinc acetate tetrahydrate ($C_4H_6O_4Zn \cdot 2H_2O$) was dissolved in polyethylene glycol solution under the invariable pH at 4.5–5.5. Then, 1 ml of equimolar solution of sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$) was added into the reaction mixture with strong stirring and subsequently a precipitate was obtained. The resultant precipitate was washed with deionized water for a number of times to remove the impurities from the precipitate. The final active precipitate was exposed to microwave radiation of 160 W for 10 min. The microwave irradiated powder emerged in light greenish yellow color powder, which was then heat treated at 400 °C and 500 °C in a muffle furnace for 2 h to obtain crystalline $ZnWO_4$ nanopowder. Fig. 1 clearly shows the schematic representation of synthetic method.

2.2. Materials characterization

The XRD patterns of prepared samples were measured on a (XPERT-PRO) diffractometer with monochromatic CuKα – radiation ($\lambda = 1.5406$ Å). The HR-SEM images were recorded on a Quanta FEG using an accelerating voltage of 20.00 kV. Electrochemical test was done using a three-electrode cell equipped with an Hg/HgO as reference electrode, platinum foil as counter electrode and nickel mesh as working electrode. The electrochemical properties of Zn–WO_3 and $ZnWO_4$ modified electrodes, including EIS, CV, GCD were examined using an electrochemical work station (biologic –SP 300) at room temperature.

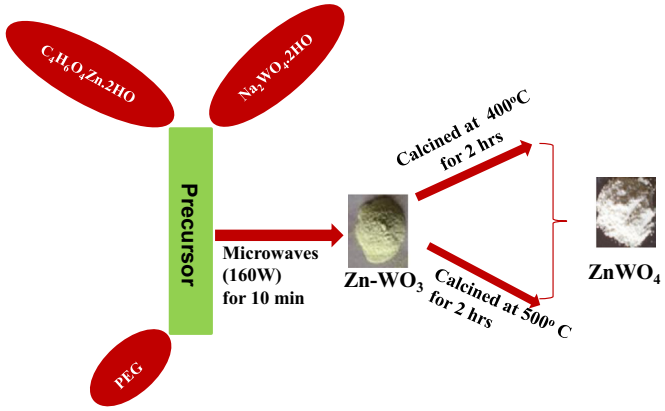

Fig. 1. Schematic representation of synthetic method.

2.3. Preparation of electrodes

The electrode preparation is very important in electrochemical investigations. The working electrodes were prepared by mixing an electro-active material, acetylene black and polytetrafluoroethylene (PTFE), with a ratio of 75:15:10. This mixture was continuously grinded for 10 min in a mortar and then the desired film was coated. The film was pressed on Ni mesh to use as a current collector.

3. Results and discussion

3.1. XRD analysis

XRD pattern (Fig. 2(a)) of the as-prepared powder shows the peaks at 24.2° and 22.9° and those assigned peaks may be due to (200) and (002) crystalline planes of orthorhombic phase (β-WO_3). The observation well matches with the JCPDS card no: 89-4480. The as-synthesized (Zn–WO_3) sample shows the corresponding peaks of WO_3 only and no peak was observed for Zn. However, the author already described in previous work about the presence of Zn in as-prepared sample [45]. The samples calcined at 400 °C and 500 °C show (Fig. 2(b) and (c)) the XRD peaks at 30.5° and 36.3° and those peaks could be assigned to (111) and (021) crystalline planes of monoclinic phase $ZnWO_4$ which is in accordance with the JCPDS card no: 89-7624. The crystallite size of as-prepared, 400 °C and 500 °C calcined samples were calculated using Scherer's equation. The average crystallite sizes of about 44, 17 and 52 nm were achieved for as-prepared, 400 °C and 500 °C calcined samples, respectively.

3.2. HR-SEM

Fig. 3 shows HR-SEM micrographs of the synthesized powder. Fig. 3(a) shows the HR-SEM image of as-prepared sample and it clearly reveals the spherical shape nanoparticles. The surface morphology of calcined samples show different morphologies

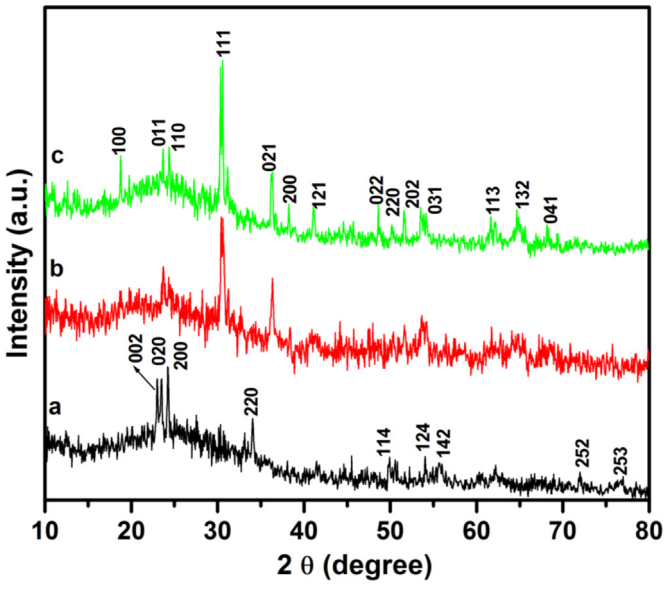

Fig. 2. XRD patterns of (a) as-prepared sample (Zn–WO_3), (b) sample heat treated at 400 °C for 2 h and (c) sample heat treated at 500 °C for 2 h.