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Short communication

Microwave–hydrothermal synthesis of birnessite-type MnO_2 nanospheres as supercapacitor electrode materials

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ABSTRACT

Birnessite-type MnO_2 (Bir-MnO_2) nanospheres have been successfully synthesized by the microwave–hydrothermal (M–H) method at 75 °C for 30 min under low pressure. The properties and electrochemical performance of the as-prepared MnO_2 are analyzed and evaluated by the field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) measurements and electrochemical tests. The Bir-MnO_2 appears mesoporous nanosphere structure with 70–90 nm in diameter, and it exhibits a large specific surface (SS) of 213.6 $m^2\,g^{-1}$ by the results of FE-SEM, XRD and BET. The electrochemical test results show that the specific capacitance (SC) is 210 $F\,g^{-1}$ at 200 $mA\,g^{-1}$ in 1.0 M Na_2SO_4 electrolyte, and the SC retention and coulombic efficiency are over 96% and 98% respectively after 300 cycles at 1.6 $A\,g^{-1}$. Compared with the conventional syntheses of MnO_2, the performance of the Bir-MnO_2 nanospheres synthesized by M–H method is significantly improved.

1. Introduction

As an energy storage device, an electrochemical capacitor (EC) or supercapacitor has caught much attention in recent years due to its high charge–discharge efficiency, high power density and long cycle life, its application has great potential in those fields ranging from aerospace field to consumer electronic devices [1–3]. However, in some new application fields, such as electric and hybrid vehicles, supercapacitor with higher capacitance and longer cycle life is necessary.

Manganese oxide (MnO_2), one of the potential alternatives with promising pseudo-capacitor performance in neutral electrolytes, has been taken into intensive investigations because of its superior electrochemical performance, low cost, abundance and environmental-friendliness [4–8]. The electrochemical performance of MnO_2 depends on various factors, such as particle size, structure, surface morphology, bulk density and homogeneity, which can influence the kinetics of H^+ or alkali metal cations (C^+) diffusing process, the adsorbability and utilization ratio of MnO_2 [9]. Different syntheses of MnO_2 make crystal growth environments vary, and thus leading to different physical and chemical properties, such as crystallinity, morphology, SS area and cycling stability [4,8,10]. A literature survey show that many routes or techniques for preparation of MnO_2 have been developed, such as sonochemical synthesis [10], solution-combustion [11], thermal decomposition [12], hydrothermal synthesis [2,13–15], microwave-assisted synthesis [1,4,16,17] electro-deposition [18] and sol–gel progress [6]. However, most of the methods require extensive mechanical mixing, long duration, high temperature, energy-wasting, etc. For example, microwave-assisted method is facile but it is easy to go to thermal runway [9], and the hydrothermal synthesis is beneficial to making smaller particles but it requires quite long time to complete a reaction [13]. M–H synthesis has inherent advantages, including rapid volumetric heating, good homogeneity, high yield, morphology controllability and the ability to produce narrow size distribution particles with high purity [19–22]. Incorporating rapid microwave heating into hydrothermal processing possesses a good potential for synthesizing inorganic materials, the M–H process is rapid and it enhances the crystallization kinetics of synthesis process and thus M–H process is energy-efficient and economical [14]. The process combines the advantages of hydrothermal and microwave-assisted synthesis, it not only needs short duration and low temperature and pressure but also overcomes aggregating of the synthesized materials.

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A literature survey reveals that few reports about M–H synthesis of MnO_2 as electrode materials can be found.

Here our group exploit M–H synthesis of Bir-MnO_2 nanospheres as supercapacitor electrode materials. This method is quite fast, facile, secure, controllable and energy-saving. In this work, the Bir-MnO_2 nanospheres synthesized by M–H method at 75 °C for 30 min under very low pressure show excellent electrochemical properties, high rate capacitance and good cycling stability for supercapacitor applications.

2. Experimental

2.1. Preparation of MnO_2

MnO_2 is synthesized by the M–H technique under mild conditions. In a typical experiment procedure, $KMnO_4$ (Analytically Pure (AP), Beijing Chemical Factory) and $MnSO_4{\cdot}H_2O$ (AP, Sinopharm chemical Reagent Co., Ltd., China) (molar ratio is 2:3) are dissolved in 140.0 mL doubly deionized water and stirred strongly to form a homogeneous solution, and then the mixture solution is transferred into a Teflon (PTFE)-lined autoclave assembled in the matched experiment microwave oven (NJL07-3, Nanjing Jiequan Microwave Development Co., Ltd., China). The autoclave is sealed and maintained at 75 °C for 30 min by microwave under certain frequency and power. Then the autoclave is cooled down to room temperature and the as-prepared black precipitate is filtered and washed copiously with doubly deionized water and absolute ethyl alcohol respectively, finally dried at 75 °C under vacuum.

2.2. Characterization of structure and morphology

The crystallographic structure of the materials is determined by a Marcogroup diffractometer (MXP21 VAHF) with a Cu-Kα radiation source (λ = 1.54056 Å). The morphology of the samples is investigated by FE-SEM (Zeiss SuprATM 55 microscope, German). And the surface area of the materials is studied using Brunauer–Emmett–Teller measurements (BET, Quantachrome, QUADRASORB SI-MP).

2.3. Electrochemical characterization

The electrochemical properties of the materials are studied by cyclic voltammetry (CV), galvanostatic charge–discharge (GC) technologies in a VMP2 electrochemical workstation (Princeton Applied Research, USA). And the electrochemical tests are taken in 1.0 M Na_2SO_4 electrolyte using a three electrode cell comprising a saturated calomel electrode (SCE) as reference, Pt as counter and MnO_2-based electrode (MnO_2:acetylene black:PVDF = 70 wt%:20 wt%:10 wt%) as the working electrode.

3. Results and discussion

The FE-SEM images of the MnO_2 synthesized by M–H method are given in Fig. 1, which show homogeneous nanosphere structure, 70–90 nm in diameter. During the reacting process, the microwave irradiation makes the vibrations of the MnO_2 lattice increase, and the mutual repulsion of MnO_2 increases correspondingly, which prevents MnO_2 nanospheres from growing up and agglomerating together. The MnO_2 nanospheres tend to grow homogeneously in a short period of time because the MnO^{4-} and Mn^{2+} are selectively heated by microwave irradiation due to their large dipole moments [23]. This MnO_2 nanosphere electrode has a high electrode interfacial reaction area between electrode and electrolytic solution, which is important to the improvement of these electrochemical properties.

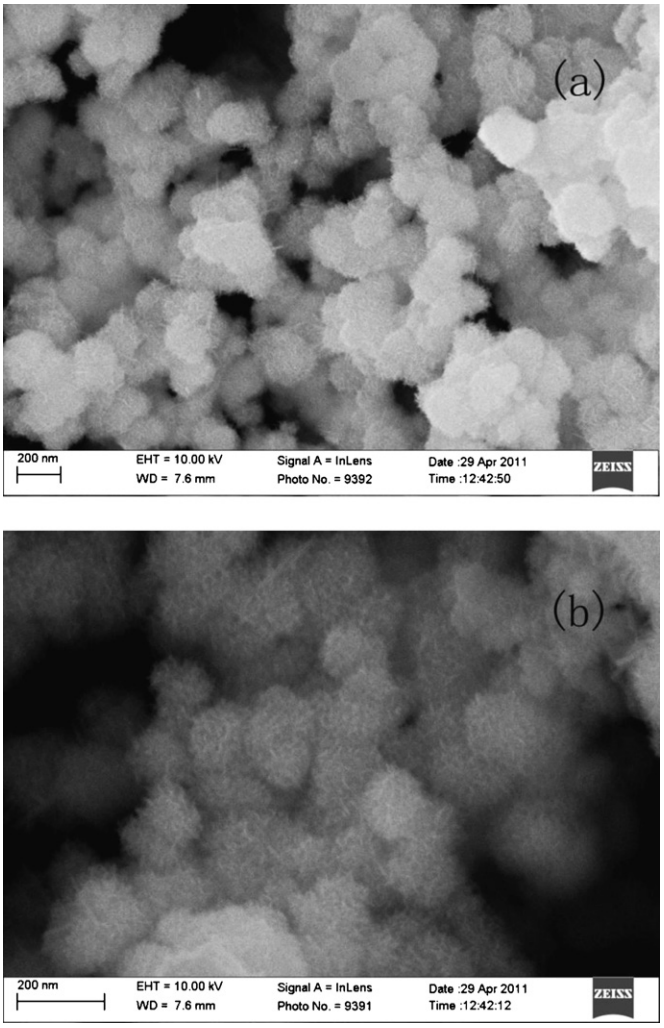

Fig. 1. FE-SEM images of MnO_2 synthesized at 75 °C for 30 min by M–H method: (a) 100k× and (b) 200k×.

XRD measurement is used to identify the crystalline phase of MnO_2 nanospheres and the result is presented in Fig. 2. Significant XRD peaks at $2\theta = 12.36°$, 37.10° and 65.70° can be well assigned to the (0 0 2), (0 0 6) and (1 1 9) planes of MnO_2 with a birnessite

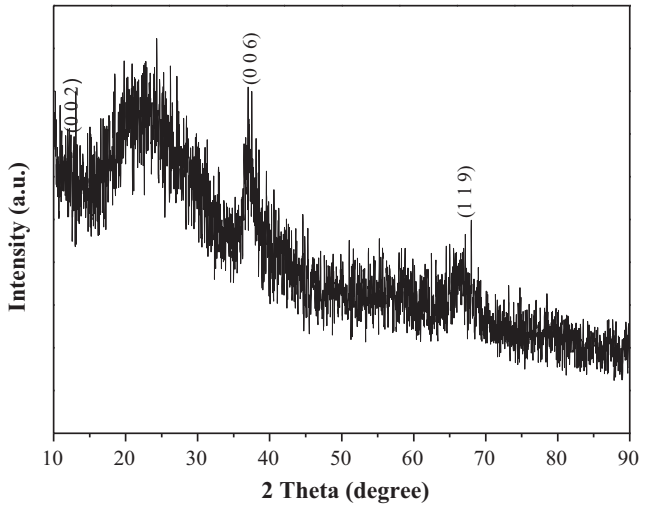

Fig. 2. XRD pattern of MnO_2 synthesized at 75 °C for 30 min by M–H method.

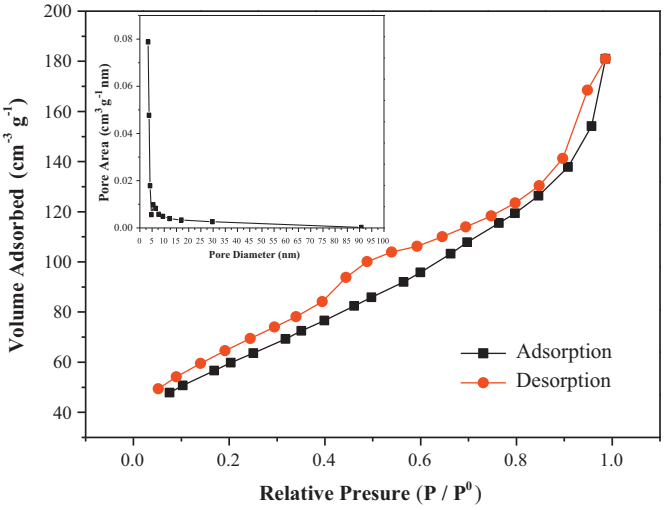

Fig. 3. N_2 adsorption–desorption isotherms for MnO_2 synthesized at 75 °C for 30 min by M–H method.

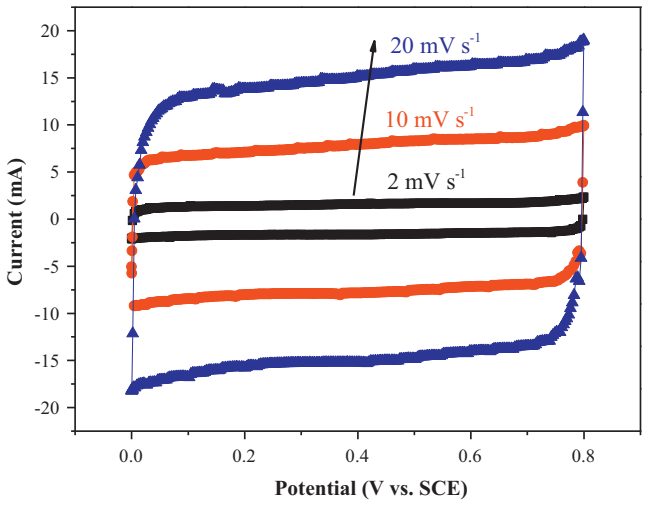

Fig. 4. CV of MnO_2 at scan rates of 2, 10, and 20 mV s^{-1}.

structure, respectively (JCPDS 18-802, $a = 5.82$ Å, $c = 14.62$ Å). The broadness of the peaks indicates that the crystallites of the synthesized material are of nanoscale character. The crystallite size is calculated using Scherrer's formula for various reflections (due to particle size <100 nm, data from FE-SEM) [24], and the crystallite size is about 6.22 nm, because the nanospheres are consisted of crystallites, which will be discussed in the following paragraph. The XRD pattern suggests that MnO_2 nanospheres can be easily prepared by this M–H method.

The N_2 adsorption–desorption isotherm and corresponding pore size distribution of the MnO_2 nanospheres are shown in Fig. 3. The BET surface area of the MnO_2 nanospheres is 213.6 m^2 g^{-1}, which is much larger than that of MnO_2 synthesized by some other methods [2,6,25]. And the porosity of the MnO_2 nanospheres is calculated by Barret–Joyner–Halenda (BJH) method, which reveals a narrow distribution of the mesopores with the average pore diameter of 5.24 nm (Fig. 3, inset), indicating the mesoporous nature of this nanospheres. The mesoporous structure is corresponding to the results of the XRD and FE-SEM. Fine tunings of pore structures can further improve the capacitance and cycling efficiency of the electrochemical system [2]. The porosity and the surface area of the Bir-MnO_2 nanospheres have always shown a corresponding impact on the electrochemical properties as discussed later.

Electrochemical properties of the products are studied by CV and GC technologies. The CV test result in 1.0 M Na_2SO_4 electrolyte is shown in Fig. 4. The CV test curves exhibit almost ideal rectangular shapes, implying a reversible capacitive behavior. Although the scan rate increased from 2 to 20 mV s^{-1}, the ideal rectangular shape still remains on the CV test interface, which implies that these Bir-MnO_2 nanospheres have good pseudo-capacitor properties. In addition, the nanospheres have also superior charge–discharge properties and cycle stability. It exhibits high SCs of 210, 200, 186 and 165 F g^{-1} at the current densities of 200, 400, 800 and 1600 mA g^{-1} respectively, as shown in Fig. 5(a). And the electrochemical stability test shows that the SC can still be stable and the coulombic efficiency is maintained over 97% after 300 charge–discharge cycles at current density of 1.6 A g^{-1}, as shown in Fig. 5(b), indicating the as-prepared MnO_2 nanospheres bear superior cycle stability and good electrochemical reversibility.

There have been two mechanisms proposed for the charge storage in MnO_2-based electrodes [25], the mechanisms claim that large SS and suitable porosity are very important to MnO_2 as an electrode material. The homogeneous Bir-MnO_2 nanospheres with large SS and mesopore structure not only improve utilization ratio of MnO_2 but also accelerate diffusion process of H^+ or the alkali cation ion Na^+ in MnO_2 electrodes. The microwave irradiation enhances the reaction and prevents MnO_2 nanospheres from agglomerating [26]. Besides, the hydrothermal reaction creates a good homogeneous growth environment [27]. The homogeneous Bir-MnO_2 nanospheres can be fast synthesized controllably by M–H method at 75 °C for 30 min under low pressure in this study. And the properties of Bir-MnO_2 nanospheres are greatly improved with

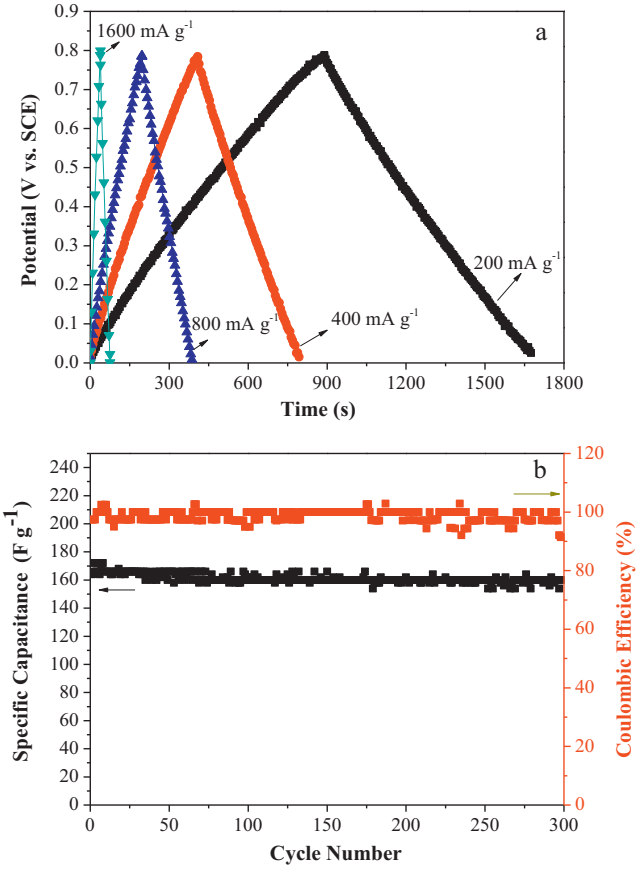

Fig. 5. (a) GC of MnO_2 at current densities of 200, 400, 800, and 1600 mA g^{-1}. (b) Cycle life of MnO_2 electrode in 1.0 M Na_2SO_4 at current density of 1.6 A g^{-1}.

large SS, high SC, high coulombic efficiency and good cycle stability [2,12,14,15,18,6,25].

4. Conclusions

Bir-MnO_2 nanospheres have been successfully synthesized by M–H method at 75 °C for 30 min under low pressure. According to the results of the FE-SEM, XRD, BET, CV and GC tests, as-prepared Bir-MnO_2 appears mesoporous nanosphere structure with 70–90 nm in diameter, the SS of the nanospheres is as large as 213.6 $m^2\,g^{-1}$ and the SC is as high as 210 $F\,g^{-1}$ at 200 $mA\,g^{-1}$ in 1.0 M Na_2SO_4 electrolyte. Cycle life test shows that the SC retention and coulombic efficiency are still over 96% and 98% respectively after 300 cycles at 1.6 $A\,g^{-1}$. The Bir-MnO_2 nanospheres show superior electrochemical performance and excellent cycling stability as supercapacitor electrode materials. Compared with the results of the literatures, the performance of the Bir-MnO_2 nanospheres synthesized by M–H method is significantly improved, and this M–H synthesis will be a very promising method to synthesize MnO_2 as a supercapacitor electrode material.

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