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Microwave-assisted Reflux Synthesis of Flower-like MnO_2 Nanostructure for Super capacitor Application

D. MuthuGnana Theresa Nathan[1], P. Shobha[1], R. Mahesh[1], P. Sagayaraj[1*]
[1]*Department of Physics, Loyola College (Autonomous), Chennai-600034, India*
**Corresponding Author's Email: psagayaraj@hotmail.com*

Abstract: In this work, flower-like MnO_2 nanostructure was successfully synthesized by reducing potassium permanganate in acidic condition employing microwave-assisted reflux method. The as-prepared samplewas characterized using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive X-ray analysis (EDX) and high resolution transmission electron microscopy (HRTEM). Electrochemical measurements were carried out with three electrode configuration by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS). The electrochemical results indicate that the prepared material can be used as electrode material for energy storage applications.

Keywords: Manganese dioxide, Microwave-assisted reflux, Nanostructure, Supercapacitors

Introduction

Manganese dioxides (MnO_2) with layered and tunnel structures have received greatattention because of their distinctive physicochemical properties, and their wide applications in catalysts, lithium ion batteries and supercapacitors [1-3]. MnO_2 exists in several crystallographic forms, such as α, β, γ, δ, λ and ε-type, when the basic MnO_6 octahedron unit links in different ways [4].Many methods have been developed for the preparation of nanostructures MnO_2, including hydrothermal [5], thermal decomposition [6] and electrodeposition [7] techniques. However, these synthesis methods mostly require prolonged reaction times. In recent years, microwave-assisted method has been increasingly employed to replace conventional heating methods in material synthesis as it provides fastand homogenous heat that significantly reduces processing time and cost [8, 9].Zhang et al. synthesized different MnO_2 nanostructures within minutes by microwave-assisted hydrothermal method [10].It has been recognized that the crystallographic structure, morphology and architecture of the MnO_2 materials can impose significant influences on theirproperties [11].

In this work, microwave-assisted reflux method was employed to synthesize flower-like MnO_2 nanostructure. The structure, morphology and elemental composition of the as-prepared sample was characterized by XRD, FESEM, HRTEM and EDX. The electrochemical performances were also investigated.

Experimental

In a typical procedure, 0.45 g of $KMnO_4$ and 1ml of HCl (37%) were added to 40 ml of distilled water under magnetic stirring. The mixture was transferred into a 250 ml round bottom flask and placed in a domestic microwave oven (2.45 GHz, 800 W) fitted with a reflux condenser. The reaction temperature was set to 140 °C and maintained for 15 min. The obtained black powder was washed with distilled water and ethanol several times, and dried at 80 °C overnight.

Characterization

The structure, phase and crystallinity of the as-prepared samplewere investigated by a X-ray diffraction system (XRD 3003 TT) using monochromatic nickel filtered CuK_α (λ = 1.5406 Å) radiation. Field emission scanning electron microscope (FESEM) was employed for morphological study using a CARL ZEISS SUPRA 55. It is attached with an energy dispersive X-ray analyzer (EDAX) for elemental analysis. The morphology and structure of the sample was further investigated by high resolution transmission electron microscopic (HRTEM) using a JOEL JEM 2100 advanced HRTEM.

Electrochemical measurement

The electrochemical performance was investigated using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) on a electrochemical workstation (VSP, Biologic) equipped with a standard three electrode cell configuration. The working electrode was made of active material (80 wt%), activated carbon (10 wt%) and polyvinylidene fluoride (10 wt%) slurry coated on a nickel foil current collector. All the measurements were performed using aqueous 1 M Na_2SO_4 electrolyte at ambient conditions.

Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) pattern of MnO_2. All the diffraction peaks can be conveniently indexed to the tetragonal phase of α-MnO_2 (JCPDS No. 44-0141). The sharp and intense diffraction peaks indicatethe good crystallinity of α-MnO_2.No other peaks corresponding to the impurities are observed, which suggests the high purity of the sample.

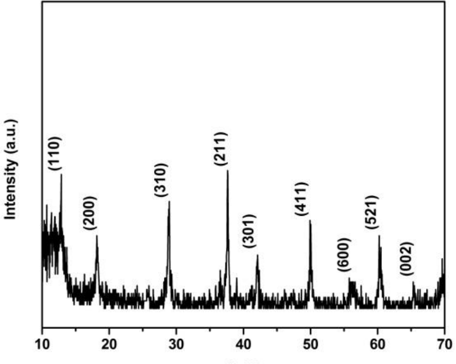

Fig.1 XRD pattern of MnO_2

The structure and morphology of MnO_2 sample were investigated by FESEM and HRTEM. The FESEM image (Fig. 2a) depicts flower-like sphere structure with diameter about 1-1.2 μm. It is observed that the sphere structure consists of crumpled nanosheetsabout 10 nm in thickness. The EDX spectrum (Fig. 2b) confirms the presence of Mn and O elements only and thus underlining the purity of sample. The observed result is consistent with the XRD data. The HRTEM image (Fig. 3a) reveals the core-corona architecture of the microsphere. It is observed that the nanosheets in the corona are grown perpendicular to the core [12]. Fig. 3b clearly exhibits the lattice fringes, which indicates that the prepared MnO_2 microspheres are well crystallized. The selected area X-ray diffraction (SAED) pattern (inset image) illustrates a polycrystalline nature of the flower-like MnO_2nanostructure.

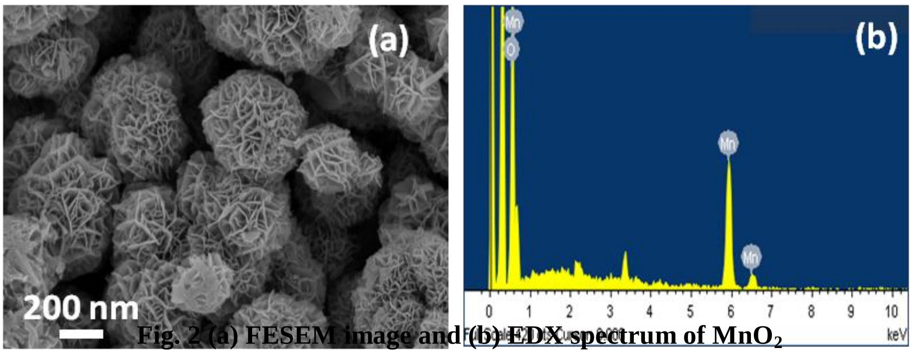

Fig. 2 (a) FESEM image and (b) EDX spectrum of MnO_2

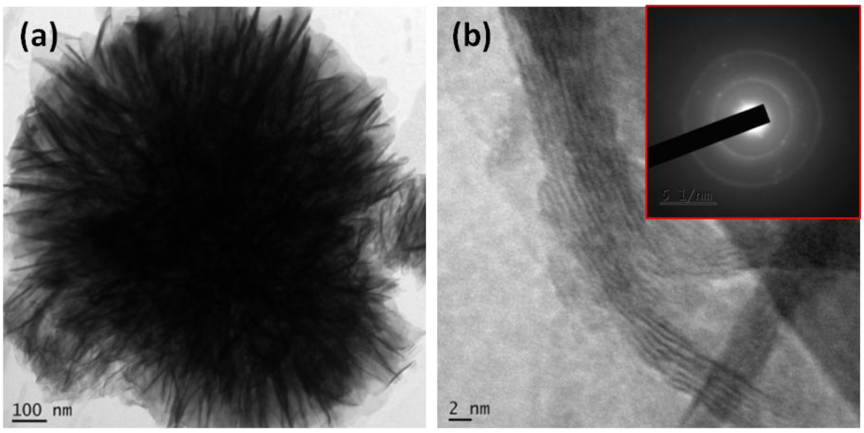

Fig. 3 HRTEM images of MnO_2 (Inset: SAED pattern)

Figure 4 shows the cyclic voltammetry (CV) curves of MnO_2 at different scan rates in the potential window between 0 and 0.8 V. The CV curves exhibit nearly symmetric rectangular shape, which indicates ideal capacitive behavior of MnO_2 [13].The area of the CV curves is found to increase with the of scan rate, suggesting the excellent capacitive nature and fast diffusion of electrolyte ions into electrode surface. Galvanostatic charge-discharge cycles of MnO_2 at different current densities are depicted in Fig. 5. Specific capacitance can be calculated from galvanostatic charge-discharge curves using the following equation:

$$C_s = \frac{I\Delta t}{m\Delta V} \qquad (1)$$

Where, C_s is specific capacitance (F g^{-1}), I is the applied constant current (A), Δt is discharge time (s), ΔV is discharge potential (V) and m is mass of the active material (g). According to equation (1), a maximum specific capacitance of 347 F g^{-1} was calculated at current density of 1 A g^{-1}. The enhanced capacitance may be attributed to unique morphology which provides pathway for rapid diffusion of electrolyte.

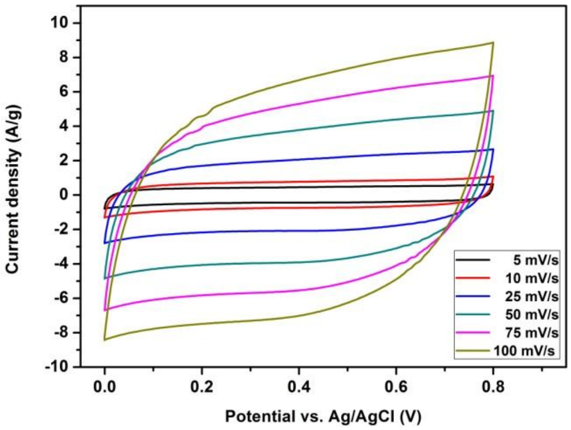

Fig. 4 Cyclic voltammograms of MnO_2 at different scan rates

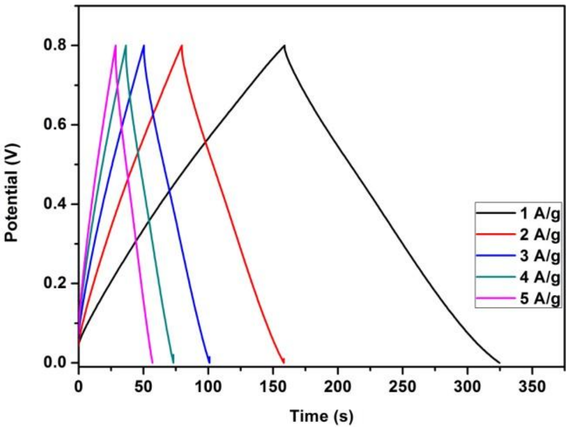

Fig. 5Galvanostatic charge-discharge curves of MnO_2 at different current densities

Electrochemical impedance spectroscopy (EIS) is a powerful tool to assess the frequency behavior and equivalent series resistance (ESR) of a supercapacitor. The EIS measurement was performed at open circuit potential in the frequency range from 0.1 Hz to 100 kHz. As shown in Fig. 6, the Nyquist plot of MnO_2 consists of high frequency semicircle and low frequency vertical line. The semicircle of the high frequency reflects the charge transfer process at the interface between active component and electrolyte.The high frequency intercept at Z′ axis correspondsto ESR, which consists ofelectrolyte resistance, intrinsic resistance of active material and electrical contact resistance [14]. The low frequency slopping line is called Warburg resistance, which is related to the electrolyte ion diffusion.

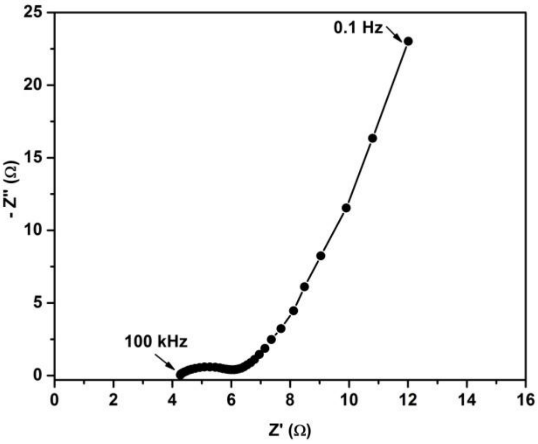

Fig. 6 Nyquist plot of MnO_2

Conclusion

We have successfully synthesized flower-like MnO_2 microspheres employing microwave-assisted reflux method. The formation of flower-like nanostructure was authenticated by FESEM and HRTEM analyses. As electrode material for supercapacitors, MnO_2 microspheres exhibited a high specific capacitance of 347 F g^{-1} at 1 A g^{-1}. The improved electrochemical performance of MnO_2 microspheres may be attributed to their unique morphology. These results manifest that the prepared material is a potential candidate for fabricating energy storage devices.

Acknowledgements

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