Short Communication

Electrochemical Properties of Single-crystalline Mn$_3$O$_4$ Nanostructures and their Capacitive Performance in Basic Electrolyte

Hidayat Ullah Shah$^1$, Fengping Wang$^{1,*}$, Arbab Mohammad Toufiq$^{1,2,3}$, Abdul Muqsit Khattak$^4$, Azhar Iqbal$^4$, Zahid Ali Ghazi$^4$, Shujaat Ali$^1$, Xingyang Li$^1$, Ziya Wang$^1$

$^1$ Department of Physics, School of Mathematics and Physics, University of Science and Technology Beijing, Beijing 100083, P. R. China,
$^2$ Department of Physics, Hazara University Mansehra, Khyber Pakhtunkhwa, Mansehra, Pakistan
$^3$ UNAM-National Nanotechnology Research Center, Institute of Materials Science and Nanotechnology, Bilkent University, Ankara 06800, Turkey
$^4$ Laboratory for Nanomaterials, National Center for Nanoscience and Technology No. 11, Beiyitiao, Zhongguancun. Beijing 100190, PR China.
$^*$E-mail: fpwang@ustb.edu.cn

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Single-crystalline Mn$_3$O$_4$ square-shaped nanostructures have been successfully synthesized by hydrothermal method without using any surfactant. The as-prepared products were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), Transmission electron microscopy (TEM) and High Resolution transmission electron microscopy (HRTEM). To assess the potential properties of nanostructures, galvanostatic charging–discharging and cyclic voltammetry measurements were performed for their use in supercapacitors. The Mn$_3$O$_4$ nanoarchitectures used as supercapacitor electrode in 1mol L$^{-1}$ KOH electrolyte have a specific capacitance value of 355.5 F g$^{-1}$ at a low current density of 0.35 A g$^{-1}$. The device still retain 85.08% of its initial capacitance afterwards 2000 cycles at a current density of 5 A g$^{-1}$. The as-synthesized Mn$_3$O$_4$ nanostructures exhibited a good rate capability and stability for electrochemical properties. These results indicate their potential application as electrode material for high performance supercapacitor in basic medium.

**Keywords**: Hydrothermal Method; Optical Properties; Transition metal oxides; Supercapacitance; Electrochemical properties;

1. INTRODUCTION

In recent few years, the esteemed demand of energy increased the importance of renewable energy resources and energy storage devices. Cost effective, high power performance, fast charge and
discharge rates, long cycle life and low maintenance catalyst has been a demanding challenge to solve the current energy crisis [1-2]. Researchers in both academic world and industry have deliberately increased efforts over the past decades to fabricate such an advanced materials with magnitudes ranging from a few to several hundred nanometers. The reason is that when particles are synthesis within a limit of around 1–100 nanometers, the materials’ chemical and physical properties change considerably from those at bulk level. Nano-size materials are becoming increasingly significant for electrochemical energy storage [3].

Electrochemical capacitors (ECs), mostly referred by manufacturers in literature as “ultracapacitors,” or “supercapacitors” store energy using either fast surface redox reactions or ion adsorption. It can completely or less replace batteries in electrical energy storage appliances, where a high-power transfer is required. The ion desolvation approach in pores less than the solvated ions leads to higher capacitance for electrochemical double layer capacitors by means of carbon electrodes with nanometer pores, introduced new ways to construct high energy devices with different electrolytes. The discovery of carbon nanotubes brings revolution in electrochemical capacitors, permitting adaptable and innovative devices to be made [4-5].

Recently, different kinds of materials have been studied as possible supercapacitors electrodes, like, conducting polymers, carbonaceous materials, and transition metal oxides. Transition-metal oxides such as NiO [6], RuO$_2$ [7], Co$_3$O$_4$ [8] and MnO$_2$ [9] are mostly used electrode materials due to their large surface area, relatively better electrical conductivity and high capacitance. Among them, RuO$_2$ and MnO$_2$ are an ideal material for supercapacitors because of their variable oxidation states, good electrochemical and chemical stability, easy fabrication and high theoretical specific capacitance. However, toxic nature, high cost and low porosity of RuO$_2$ restricts its commercialization in supercapacitors. Currently, MnO$_2$ is considered as one of the most promising candidate for supercapacitor application because of its abundant natural resources, non-toxicity, high capacitance and environmental friendliness. Manganese oxides have various forms such as MnO$_2$, MnO, Mn$_2$O$_3$ and Mn$_3$O$_4$, due to its different oxidation states. Among these manganese oxides, Mn$_3$O$_4$ is one of the established mixed oxides state (Mn$^{2+}$ (Mn$^{3+}$)$_2$O$_4$) with spinel structure. Mn$_3$O$_4$ has been broadly used in different fields such as electrode material for supercapacitor and lithium batteries [10-13], an effective catalyst for the decay of waste gaseous products and an appropriate material to control the air pollution [12].

It should be noted that the capacitance of the capacitor depends mostly on the capacity of electrode material expressed in farad/gram (F.g$^{-1}$), while the voltage and the resistance of such device depends mainly on the electrolyte. Lota et al. tried to find the inert electrolyte, such as Na$_2$SO$_4$, Na$_2$SO$_3$, K$_2$SO$_4$, Li$_2$SO$_4$, (as well as for comparison 1 M H$_2$SO$_4$ and 6 M KOH) and evaluate their effect on the capacitance of electrode materials (two activated carbons and carbon nanotubes) to the electrochemical capacitor. The highest values of conductivity were obtained for 1 M H$_2$ SO$_4$ and 6 M KOH, while MgSO$_4$ has the lowest conductivity from electrolytes which were selected. [13].

In our previous work, we have reported 3D nanostructures, self-assembled with single-crystalline Mn$_3$O$_4$ nanoparticles and their multiple PL emissions in visible region without any surface modification [14]. Wu et al. have studied the electrochemical performances of porous calcium carbide-derived carbon (CCDC) material for supercapacitors in different aqueous electrolytes such as KOH,
K₂SO₄, KCl and KNO₃. Among all the tested electrolytes, KOH solution has shown the highest specific capacitance that is endorsed to the fast mobility of OH⁻ ions [15]. To the best of our knowledge, very less literature is available about Mn₃O₄ material been checked in basic medium. In this study, we synthesis pure Mn₃O₄ nanostructure by hydrothermal method and estimated the electrochemical performances in 1 M KOH solution. The supercapacitor exhibited excellent cycling performance as the device retain 85.08% of its initial capacitance after 2000 cycles at a current density of 5 A.g⁻¹.

2. EXPERIMENTAL DETAILS

2.1. Sample preparation

The chemical reagents used in this research work were of analytical grade and used without any additional refinement. In a typical reaction, 1.5g of manganese Chloride Tetrahydrate (MnCl₂.4H₂O) was dissolved in 40ml deionized water through magnetic stirring for 20 minutes at room temperature. After that, 1.6 g of NaOH was mixed to the solution and stirred further for 20 minutes. Finally, the homogeneous solution was transferred into a 40 mL Teflon-lined stainless steel autoclave and hydrothermally reacted at 180°C for 18 h in an oven. The reaction suspension was centrifuged, filtered and washed several times with H₂O and ethanol to remove the residual traces. The brown precipitate were dried at 90°C for 6 h.

2.2. Sample Characterizations

The crystallographic and phase study of the as-prepared product were investigated by X-ray diffractometer (X’Pert MPD-XRD) having Cu Kα radiation (λ= 0.154nm, 40 KV, 40mA), field emission scanning electron microscopy (FESEM, ZEISS SUPPER™ 55) and high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED JEM 2010). The electrochemical properties were measured with 1M KOH as the electrolyte in a three-electrode configuration. The electrode (working) was prepared by mixing 70 wt.% Mn₃O₄ powder as an active materials, 25 wt.% acetylene black, as the conductive filler and 5 wt.% polyvinylidene fluoride (PVDF), as the binder. Proper quantity of water was added to this mixture to make homogenous slurry, further pasted on Ni-foam which acts as working electrode and as current collector. The cyclic voltammetry (CV) and galvanostatic charge–discharge tests were conducted with CHI 660C electrochemical workstation.

3. RESULTS AND DISCUSSION

3.1. XRD analysis

The XRD pattern of Mn₃O₄ is depicted in fig. 1. All the diffraction peaks are well indexed to the Hausmannite (Mn₃O₄) tetragonal crystal structure (JCPDS file No. 80-0382) [16-17]. No other characteristic peaks from impurities are found, demonstrating the high purity of the as-prepared product. The sharp diffraction peaks of the XRD patterns specify that the as-prepared products are well
crystallized. The EDX analysis illustrated in the upper inset of Fig. 1, shows that the final brown precipitate comprises only Mn and O which shows that the as-synthesized products are made of pure Mn$_3$O$_4$.

![Figure 1. XRD pattern of as-prepared Mn$_3$O$_4$ nanostructures](image)

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![Figure 2. (a) FESEM (b) TEM and HRTEM images of as-prepared Mn$_3$O$_4$ nanostructure](image)

Figure 2. (a) FESEM (b) TEM and HRTEM images of as-prepared Mn$_3$O$_4$ nanostructure

The morphology of the Mn$_3$O$_4$ nanostructures was primarily imaged by FESEM as shown in Fig 2 (a). The FESEM image shown in Fig. 2a demonstrates that as-prepared Mn$_3$O$_4$ consists of squared-shape, identical, and uniform nanoparticles with diameter of about 70nm. More detailed information regarding the structural aspects of the Mn$_3$O$_4$ nano-structures has been investigated by TEM and HRTEM. Fig. 2b illustrates the TEM image of Mn$_3$O$_4$ nanostructures, which is in agreement with FESEM observations. The HRTEM image taken from a randomly distributed nanoparticle given in lower inset of fig.2 (b) demonstrated the singlet set of parallel planes with inter-planer ($d$) spacing of 0.24nm, which correspond to the $d$ spacing of [211] plane of Mn$_3$O$_4$ in the XRD spectrum. The single
crystalline structure of as-prepared Mn₃O₄ nanostructures is also verified by the SAED pattern presented in the upper inset of fig.2 (b).

3.2. Electrochemical Characterization

Electrochemical properties of Mn₃O₄ electrode were examined by cyclic voltammetry (CV) and galvanostatic charge–discharge tests in 1 M aqueous KOH electrolyte. The specific capacitance can be determined by integrating the area under the curve (CV) to obtain the charge (Q) and then dividing by the mass of the electro active material (m), the scan rate (v), and the potential window (ΔV = Va− Vc) according to the equation 1.

\[ C = \frac{Q}{\Delta V} = \frac{1}{mv(\Delta V)} \int_{V_a}^{V_c} I(V) \, dV \]

Furthermore, the specific capacitance was computed from the galvanostatic charging–discharging curves using equation 2.

\[ C = \frac{I \Delta t}{m \Delta V} \]

Where C stands for specific capacitance, I is the current density, Δt for discharge time, ΔV is the potential window and m is the active mass of material [18].

Fig. 3(a,b) shows the Cyclic voltammetric (CV) analysis carried out in the voltage range of -0.25 to 0.45 V vs. Ag/AgCl in 1 M KOH solution. Fig. 3(a) shows the CV curves of Mn₃O₄ electrode at different scan rates of 10, 20, 50, 80,100 and 200 mV s⁻¹, respectively. The cathodic and anodic peaks observed in the cyclic voltammograms point towards the reversible oxidation and reduction reaction. More specifically, a pair of redox reaction peaks in the CV curves of the synthesized Mn₃O₄ nanoparticles clearly suggesting the pseudo-capacitance behavior that can be attributed to the redox transitions of interfacial oxidation species at various Mn oxidation states (i.e., Mn²⁺ and Mn³⁺). The pseudo-capacitance mechanism of Mn₃O₄ electrode can be explained using following relations [19];

\[
\begin{align*}
3\text{Mn (OH)}_2 + 2\text{OH}^- & \leftrightarrow \text{Mn}_3\text{O}_4.2\text{H}_2\text{O} + 2\text{e}^- + 2\text{H}_2\text{O} \quad (1) \\
\text{Mn}_3\text{O}_4.2\text{H}_2\text{O} + \text{OH}^- & \leftrightarrow 2\text{MnOOH} + \text{Mn (OH)}_3 + \text{e}^- \quad (2)
\end{align*}
\]

In Fig.3a, it can be seen that even at high sweep rate of 200 mV s⁻¹, the CV curve of Mn₃O₄ electrode retains its shape which reveals the enhanced electrochemical reversibility of the faradic redox reaction of Mn₃O₄ electrode. Furthermore, an ideal capacitive behavior is evident by the increase in redox current with respect to the scan rate which also verify the good rate capability of our synthesized material [20]. It can be observed that the redox peaks undergoes negative and positive shifts by increasing the scan rate, which can be attributed to the resistance of the electrode [18]. The electrochemical stability of the as-synthesized Mn₃O₄ electrode material was investigated by repeating the CV test measured at a scan rate of 80 mVs⁻¹ for 500 cycles shown in Fig 3b. The CV curves shows no significant variation after 500 cycles which indicates the excellent cycling stability of the Mn₃O₄ electrode. The CV investigations reveal stable electrochemical performance and suggests that as-prepared Mn₃O₄ electrode has potential application due to the enhanced capacitive behavior.

Galvanostatic charge/discharge curves of Mn₃O₄ electrode for the first 10 cycles at constant current density of 10 A.g⁻¹ are plotted in figure 3(d). The charge/discharge curves shows the pseudo-capacitance nature of the Mn₃O₄ electrode. Figure 6(c) shows the discharge curves of Mn₃O₄ electrode.
at different current densities (i.e., 0.35, 0.5, 0.8, 1, 2.5, 5 and 10 A.g\(^{-1}\)). These curves show that at higher current density the specific capacitance values decreases due to the intercalation of ions at the surface of the active materials in the electrode/electrolyte interface whereas at low current density the specific capacitance increases due to the intercalation/de-intercalation of ions at surface and inner matrix of the active materials.

Figure 3. CV and charging-discharging curves, corresponding specific capacitance, and capacitance retention of Mn3O4 electrode. (a) CV curves of Mn\(_3\)O\(_4\) electrode at different potential scan rates from 10 to 200 mV s\(^{-1}\); (b) Cycling stability of Mn\(_3\)O\(_4\) electrode at 80 mV/s; (c) charge-discharge curves of Mn\(_3\)O\(_4\) electrode at different current densities from 0.35 to 10 A.g\(^{-1}\); (d) First 10 Galvanostatic charge-discharge curves of Mn\(_3\)O\(_4\) electrode at the current density of 10 A.g\(^{-1}\); (e) the corresponding specific capacitance as a function of current density; (f) Capacitance retention of the Mn\(_3\)O\(_4\) electrode at 5 A.g\(^{-1}\) as a function of cycle number.
The specific capacitances of the synthesized Mn$_3$O$_4$ electrode material as a function of different current densities are shown in Fig. 3(e), which are in agreement to the results obtained from the discharge curves plotted in Fig. 3d.

The electrochemical stability is a key property of an electrode material for potential applications of supercapacitors at high current density. Therefore, the cyclic stability test has been accomplished at high current density of 5 A g$^{-1}$ in the potential range of -0.25 to 0.45 V vs. Ag/AgCl in 1 M KOH solution. The stability curve plotted in Fig. 3(f), evident that the as-prepared Mn$_3$O$_4$ electrode demonstrates excellent stability over 2000 cycles with negligible capacitance degradation. The value of capacitance measured at first cycle is calculated to be 258.57 F g$^{-1}$ which reduced to 220 F g$^{-1}$ after 2000 cycles that corresponds to a capacitance loss of 85.08%. These results indicate that the as-synthesized Mn$_3$O$_4$ nanostructure is highly stable in the long term repeated charge/dischage cycles as supercapacitors electrode material. We believe, that the enhanced stability at high current density values may be attributed to the uniform particle morphology which enables the electron transport from the electrode/electrolyte interface and low resistance of the electrode material. These structural and electrochemical results strongly suggests that the as-prepared Mn$_3$O$_4$ nanomaterial has potential applications to be used as supercapacitors.

The calculated capacitance value 355.5 F g$^{-1}$ is much higher than the reported values for Mn$_3$O$_4$. Yuqing Qiao et al. reported a specific capacitance of 286 F g$^{-1}$ (in 1 mol L$^{-1}$ Na$_2$SO$_4$ electrolyte at a low current density of 0.5 A g$^{-1}$) for micro/nano-structured Mn$_3$O$_4$ fabricated by a facile solvothermal approach [21]. A specific capacitance of 263 F g$^{-1}$ (in 4 M NaOH electrolyte at a current density of 1 A·g$^{-1}$) for Mn$_3$O$_4$ nanorods grown on Ni foam synthesized by hydrothermal method have also been reported [22], Guo-rong et al. reported a specific capacitance of 230 F g$^{-1}$ (in 0.5 mol L$^{-1}$ Na$_2$SO$_4$ electrolyte at a current rate of 0.25 A·g$^{-1}$) for Ni–Mn$_3$O$_4$ nanocomposite prepared by chemical method [23].

4. CONCLUSION

In summary, we reported the evolution of single crystalline square-shaped Mn$_3$O$_4$ nanostructures with uniform using hydrothermal-growth method. The as-prepared material can improve not only the initial discharge capacity, but also the cycling stability during subsequent cycles. Furthermore, this research effort can give rise to an enhanced performance in the case of graphene/Mn$_3$O$_4$ composite. A high specific capacitance of 355.5 F g$^{-1}$ at 0.35 A·g$^{-1}$ measured for the as-synthesized Mn$_3$O$_4$ nanostructures makes this material interesting for potential applications in supercapacitors electrode material and rechargeable lithium-ion batteries.

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