**Synthesis and Properties Single-crystal MnO2 nanorods**

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**Abstract** Single-crystal MnO2 nanorods were prepared by hydrothermal reaction of
single KMnO4 under acidic conditions. The nanorods have a diameter of
30–70 nm and a length up to 2 μm. The formation mechanism for the
MnO2 nanorods was investigated. Electrochemical properties of the MnO2
nanomaterials prepared for different hydrothermal times were characterized
by galvanostatic charge/discharge tests and cyclic voltammetry (CV) studies.
The results indicate that the MnO2 nanorods prepared for 5 and 8 h show fine
capacitive behaviour with high specific capacitances of 71.1 and 70.9 F g-1,

# Introduction

 one-dimensional (1D) nanostructures, including nanowires, nanorods and nanotubes, have attracted increas- ing attention due to their superior optical, electrical, catalytic and magnetic properties, which can be extensively explored as fundamental building blocks for nanoscale science and tech- nology. Therefore, much effort has been devoted to the fabrication of various 1D nanomaterials with alterable morphology, phase and distinctive performances.

MnO2 has many kinds of polymorphs, such as *α*, *β*,*γ* and *δ*-type according to different linkage ways of its basic MnO6 octahedral units. MnO2 has wide applications such as redox catalysts, molecular/ion sieves and electrode materials in batteries or capacitors. Recently, increasing interest has been focused on the fabrication of 1D MnO2 nanostructures. Various 1D MnO2 nanomaterials, such as *α*-MnO2 nanorods/nanowires, *β*-MnO2 nanorods/nanotubes, *γ* -MnO2 nanowires/nanotubes and *δ*-MnO2 nanofibres have been successfully prepared by oxidation of Mn2+ or reduction of KMnO4. In addition, single-crystal MnO2 nanowires of *α*, *β* and *γ* -type have also been conveniently prepared by simple hydrothermal treatment of commercial *γ* -MnO2 particles in water or ammonia solution. Further, it is found that these 1D MnO2 nanomaterials show finer electrochemical properties than their bulk counterparts, which can be adopted as promising electrode materials in Zn–MnO2 batteries, Li– MnO2 cells and electrochemical capacitors, etc

In this paper, we report the preparation of single-crystal *α*-MnO2 nanorods by direct hydrothermal decomposition of single KMnO4 under acidic conditions involving no templates or surfactants. The formation mechanism of such nanorods was studied by tracing their growth process at different reaction stages. Electrochemical properties of the as-prepared nanorods as electrode materials in electrochemical capacitors were also investigated with galvanostatic charge/discharge tests and cyclic voltammetry (CV) studies. The results show that these MnO2 nanorods display ideal capacitive behaviour, in which the MnO2 nanomaterials prepared for 5 and 8 h have high specific capacitances of 71.1 and 70.9 F g−1, respectively.

# Experimental methods

All the chemical reagents were analytical grade and used without further purification. All the hydrothermal reactions were performed in a 36 ml Teflon-lined stainless steel autoclave under autogenous pressure. In a typical synthesis, 2 mmol KMnO4 and 1 ml concentrated H2SO4 were added to 23 ml distilled water under stirring to form a solution, which was then loaded into the autoclave, sealed and heated in an oven at 150 ◦C for 12 h. After the reaction was complete, the autoclave was taken out and naturally cooled to room temperature. The resulting brown-black precipitates were filtered off, washed with distilled water several times to remove excess ions, and finally dried at 120 ◦C in air overnight.

X-ray powder diffraction (XRD) was taken on a Rigaku- D-Max rA 12 kW Diffractometer with Cu K*α* radiation (*λ* 0*.*154 06 nm) at an operation voltage and current of 40 kV and 300 mA, respectively. The Fourier transform infrared (FT-IR) spectrum was recorded on a US Nicolet-5DX Fourier-IR spectrometer with KBr pellets. Transmission electron micrographs (TEM), selected area electron diffraction (SAED) and high-resolution transmission electron micrographs (HRTEM) were obtained from a Hitachi H-800 transmission electron microscope and a JEOL-3010 high-resolution transmission electron microscope, respectively. Chemical composition of the as-obtained materials was analysed by an inductively coupled plasma emission spectrograph (ICP-ES). Average oxidation state of Mn in the final products was determined by chemical titration with sodium thiosulfate as described elsewhere

The electrodes used for the electrochemical measurements were prepared by mixing the as-prepared MnO2 samples, acetylene black and PTFE latex with a mass ratio of 80:10:10 to form a slurry. The slurry was dried at 120 ◦C, and then filled into a Ni mesh, which was then roll pressed and dried again. The capacitor was assembled with the MnO2 positive electrode and MnO2 negative electrode, separated by a polypropylene separator. The masses of the positive-electrode and the negative-electrode active materials are kept the sameGalvanostatic charge/discharge tests of the MnO2 capac- itors were performed using a Land battery test system in a two-electrode system, in which MnO2 electrodes were used as the positive electrode and the negative electrode. All the tests were performed between 0 and 1.0 V at a specific current of 300 mA g−1 in a 0.5 M Na2SO4 electrolyte at room temper- ature. Discharge specific capacitances of the capacitors were calculated according to the formula *C It/m∆V* (where *I* is the discharge current, *t* is the discharge time, *∆V* is the differ- ence in discharge voltage and *m* is the total mass of active ma- terials of the two electrodes). Cyclic voltammetry (CV) stud- ies were carried out on a CHI-660 electrochemical workstation with a three-electrode configuration, in which a MnO2 elec- trode was used as the working electrode, Pt wire as the counter and a saturated calomel electrode (SCE) as the reference. CV tests were done between 0*.*2 and 1.0 V in a 0.5 M Na2SO4 electrolyte at different scan rates of 5, 10 and 20 mV s−1, re- spectively.

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# Results and discussion

Figure [1](#_bookmark0) shows the XRD pattern of the resultant MnO2 product. All the peaks can be indexed to the pure tetragonal phase of *α*-MnO2 (JCPDS No. 44-0141) with lattice constants of *a* 0*.*982 nm and *c* 0*.*286 nm. No peaks for other types of manganese oxides are observed, indicating that the as-prepared products are phase-pure *α*-MnO2 nanorods. The sharp diffraction peaks reveal that the products are well crystalline. In addition, it is worth noting that the relative intensity of the (110) peak (51.0%) is much stronger than that of the standard JCPDS card (37.0%). Likewise, the relative intensity of the (220) peak (7.5%) is 1.5 times of the value from the standard JCPDS card. However, the relative intensities of other diffraction peaks are basically comparable to those of the standard JCPDS card. Thus, these MnO2 nanorods might have a preferential growth along the [001] direction

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**Figure 1.** Typical XRD pattern of the as-prepared MnO2 products.

Figure [2](#_bookmark1)(a) gives a panoramic TEM image of the as- obtained *α*-MnO2 samples. It is found that all the MnO2 samples are composed of nanorods with diameters 30–70 nm and lengths up to 2 *μ*m. Figure [2](#_bookmark1)(b) shows a representative TEM micrograph of a single nanorod with uniform diameter. As indexed in the SAED pattern taken from this rod (inset image of figure [2](#_bookmark1)(b)), a series of dots arrayed in a single line and perpendicular to the rod can be seen clearly, implying that it is a single-crystal rod. The HRTEM image of part of an individual rod demonstrates that the nanorod has uniform lattice fringes as shown in figure [2](#_bookmark1)(c). The lattice spacing is calculated to be 0.69 nm (figure [2](#_bookmark1)(d)), which corresponds to the (110) plane of *α*-MnO2.



**Figure 2.** ((a), (b)) TEM images of the as-prepared *α*-MnO2 nanorods; the inset shows the corresponding SAED pattern. ((c), (d)) HRTEM images of the *α*-MnO2 nanorods.

Figure [3](#_bookmark2) shows the FT-IR spectrum of the resulting nanorods. The bands at around 3416.6 and 1642.3 cm−1 correspond to the O–H vibrating mode of traces of absorbed water. The bands at about 709.9, 528.6 and 470.3 cm−1 that are below 750 cm−1 can be attributed to the Mn–O vibrations of MnO6 octahedra in *α*-MnO2 nanorods. The relatively simple FT-IR pattern is ascribed to the highly structural symmetry of *α*-MnO2 nanorods. The IR analysis here is consistent with the results reported in the literature.



**Figure 3.** FT-IR spectrum of the as-synthesized *α*-MnO2 nanorods.

The production yield of MnO2 is repeatedly above 95% based on Mn in our experiments. The molar ratio of K*/*Mn in the MnO2 products is about 0.15 determined by ICP-ES analysis. The average oxidation state of Mn in the products is 3.84 according to the chemical titration analysis.

In our synthesis of MnO2 nanorods, the source materials were merely KMnO4; no templates or surfactants were used. To investigate the formation process of *α*-MnO2 nanorods, a series of samples were prepared by hydrothermal reaction for different times. Figure [4](#_bookmark3) shows the XRD patterns of the samples hydrothermally prepared for 1.5, 5, 8 and 12 h, respectively. Clearly, the main reflection peaks of the products prepared for 1.5 h can be indexable to the *α*-MnO2 phase. In addition, a small amount of Mn7O13 5H2O (JCPDS No. 23- 1239) can also be observed. When the hydrothermal time is increased to 5 h, the products are composed of single- phase *α*-MnO2, and no peaks for other manganese oxides are detected any more. Meanwhile, the diffraction peaks become narrower and sharper along with the prolongation of hydrothermal time, indicating the crystallinity of the products enhances with increased reaction time. TEM micrographs of the products hydrothermally synthesized at different times are shown in figure [5](#_bookmark4). Figures [5](#_bookmark4)(a)–(c) show the TEM images of the samples hydrothermally prepared for 1.5 h. We can see that the products are composed of flower-like nanoarchitectures and some aggregates of nanorods. In addition, few individual nanorods are also detected. The SAED pattern taken from an individual nanorod (inset image of figure [5](#_bookmark4)(c)) demonstrates that it is a single crystal, though it is not very uniform in diameter. When the hydrothermal reaction was prolonged to 5 h, the products are all composed of nanorods, and no flower-like aggregates are detected, as shown in figures [5](#_bookmark4)(d) and (e). Besides, some nanorods have congregated and stacked together. Figure [5](#_bookmark4)(f) shows the TEM image of the products obtained after hydrothermal reaction for 8 h. It is evident that the products exhibit fine rodlike morphology with the prolongation of the hydrothermal treatment

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 **Figure 4.** XRD patterns of the manganese oxides prepared at different hydrothermal times.



**Figure 5.** TEM images and SAED patterns of the resulting manganese oxides prepared at different hydrothermal times. ((a)–(c)) 1.5 h; ((d), (e)) 5 h; (f) 8 h.

Based on the above experimental results, the formation mechanism of these nanorods is deduced as follows. Firstly, KMnO4 is generally unstable in acidic conditions, which would decompose into MnO2 and O2. This decomposition reaction would be accelerated considerably under a sealed hydrothermal environment, resulting in a large quantity of MnO2 colloids. Next, the produced MnO2 colloids tended to form some larger agglomerates due to their relatively high concentration and surface energies. Meantime, minor colloids might grow into a few small nanorods because of their 1D growth habits under the specific experimental conditions. As the reaction proceeded, the reaction rate would be slowed down due to the decrease of the reactants. After the KMnO4 was consumed completely, the whole system would thus tend to be thermodynamically stable. Subsequently, a dissolution–recrystallization process should be involved. That is, the amorphous and poorly crystalline components in the agglomerates would dissolve again and grow into nanorods. This process obeyed the well-known ‘Ostwald ripening process’, in which the larger nanorods grew at the cost of the small ones because of their energy differences. The growth process of the *α*-MnO2 nanorods presented here is somewhat different from those reported in the literature

# Conclusion

In conclusion, single-crystal *α*-MnO2 nanorods were prepared via a facile hydrothermal approach involving no templates and surfactants. Based on our experimental results, a dissolution–recrystallization followed by an ‘Ostwald ripening process’ should be responsible for the formation of nanorods. Electrochemical studies indicate that the MnO2 materials show ideal capacitive behaviour, in which the MnO2 samples prepared after 5 and 8 h have high specific capacitances of 71.1 and 70.9 F g−1, respectively. This simple synthetic approach may provide a convenient route for the fabrication of *α*-MnO2 nanorods with alterable particle size and other cation-doped MnO2 1D nanomaterials on a large scale. Further, these MnO2 nanorods may find potential applications in catalysis and electrochemical power sources.

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