Electronic Supplementary Information (ESI)

Ultrathin amorphous manganese dioxide nanosheets synthesized with controllable width

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Materials and Methods

1. Synthesis of two-dimensional MnO$_2$ nanosheets

The synthesis process of ultrathin MnO$_2$ nanosheet colloid is very simple and facile. KMnO$_4$ aqueous solution was firstly dispersed in isooctane and subsequently reduced by sodium bis(2-ethylhexyl) sulfosuccinate (Na(AOT)). Colloidal MnO$_2$ nanosheets were obtained by adding 0.1 mol L$^{-1}$ (M) KMnO$_4$ aqueous solution in a 0.1 M Na(AOT)/isooctane, which was subjected to ultrasound for 30 minutes to yield a brown colloidal solution as shown in Figure S1a.

![Diagram](image)

**Fig S1** (a) Schematic of a traditional route to synthesize ultrathin MnO$_2$ nanosheets. These nanosheets are generally peeled off from a layered bulk material by a mechanical or chemical method without a size-tunable process. (b) Schematic of a size-tunable rout and photo images of emulsion and MnO$_2$ nanosheet colloidal. Right shows the Tyndall effect of the colloidal. This is one step process from emulsion to colloidal. (c) Fourier transformation infrared spectra (FTIR) of Na(AOT) and MnO$_2$ nanosheet

We controlled the water-surfactant molar ratio ($W_0 = [\text{H}_2\text{O}]/[\text{AOT}]$) values to synthesize various MnO$_2$ nanosheets. The $W_0$ values are ranging from 15, 22, 30, to 45, which are denoted as sample A, B, C, and D, respectively. The product was separated, washed copiously several times with distilled water and ethanol, and dried at 80 °C in vacuum for 12 h. FTIR spectra of Na(AOT) and MnO$_2$ nanosheet (sample C) are showed in Fig S1c. In the curve of MnO$_2$, the band at frequency 3370 cm$^{-1}$ is representative of the O–H stretching vibration presented in the constitutional water. The bands observed in the low-frequency region ranging from 1000 cm$^{-1}$ to 400 cm$^{-1}$ reveal information about MnO$_6$ octahedral structure. The bands ranging from 1800 cm$^{-1}$ to 1000 cm$^{-1}$ in the curve of MnO$_2$
mainly represent the vibration due to interaction of Mn with surrounding species such as OH, O, and H. No characteristic peak of Na(AOT) are found in the curves of MnO₂, which indicates that the Na(AOT) are completely removed after washing process.

2. **Synthesis of zero-dimentional MnO₂ nanosphere**

100 mL 0.1 mol L⁻¹ KMnO₄ and 0.15 mol L⁻¹ Mn(CH₃COO)₂ aqueous solutions were prepared individually. 10 mL polyethylene glycol (PEG-400) was added in 100 mL Mn(CH₃COO)₂ solution, which has been stirred for 1 h. Then 100 mL 0.1 mol L⁻¹ KMnO₄ aqueous solution was added quickly and stirred for 4 h at room temperature. The product was separated, washed copiously several times with distilled water and ethanol, and dried at 80 °C in vacuum for 12 h.

3. **Synthesis of one-dimentional MnO₂ nanorod**

Chemical co-precipitation technique was also used to be reference. 100 mL 0.1 mol L⁻¹ KMnO₄ and 0.15 mol L⁻¹ Mn(CH₃COO)₂ was quickly mixed and stirred for 4 h at room temperature. A dark brown precipitate was immediately obtained according to equation (1)

\[
2\text{Mn(Ⅶ)} + 3\text{Mn(Ⅱ)} \rightarrow 5\text{Mn(Ⅳ)}
\]  

(1)

The product was separated, washed copiously several times with distilled water, and dried at 80 °C in vacuum for 12 h.

**Characterization**

Powder X-ray diffraction (XRD) patterns of MnO₂ powders were obtained by using TW3040/60 diffractometer (Tanlytical Company, Holland) in which Cu-Kα was used as the source. Fourier transformation infrared spectra (FTIR) of the samples were measured from KBr sample pellets on a VERTEX 70 spectrometer. Morphology of MnO₂ was examined using transition electron microscope (Jeol JEM2100F), electron microscope (SEM, Hitachi, S-5200). The surface topography of the sample was visualized using atomic force microscopy (AFM, Shimadzu, SPM9600) instrument in tapping mode. X-ray photoelectron spectroscopy (XPS) studies were conducted with a VG Escalab 220i-XL instrument using X-rays magnesium anode (monochromatic Kα X-rays at 1253.6 eV) as a source. XPS spectra were analyzed and fitting using XPSPEAK software (version 4.1). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) for both samples were recorded in the temperature
range from ambient to 600 °C in nitrogen atmosphere at a heating rate of 10 °C per min using Sta449C (Netzsch) tester. The Raman spectroscopy measurements have performed by Renishaw RM-1000 tester.

Electrochemical tests were performed with an Im6e (Zahner) electrochemical station. MnO$_2$ power was well-dispersed and drop coated on titanium substrate, which was further dried in vacuum at room temperature for 8 h. All electrodes with a loading mass of 0.25 ± 0.01 mg cm$^{-2}$ were coated as the working electrode. The typical three-electrode assembly, in which a piece of platinum gauze and saturated calomel electrode were assembled as the counter and reference electrode, was employed.

All samples were subjected to cyclic voltammetric tests in 1 mol L$^{-1}$ Na$_2$SO$_4$ solution. The potential range is from 0.0 to 0.8 V versus saturated calomel electrode (SCE) with sweep rates ranging from 2 to 100 mV s$^{-1}$. The specific capacitance ($C$) of electroactive material can be estimated using half the integrated area of the CV curve to obtain the charge ($Q$), and subsequently being divided the charge by the mass of the active material ($m$) and the width of the potential window ($\Delta V$):

$$C = \frac{Q}{\Delta V m}$$

(2)

1. MnO$_2$ nanosheets

SEM images of MnO$_2$ nanosheets

![Fig. S2 SEM image of sample C](image.png)

TEM images and AFM images of MnO$_2$ nanosheets

As is showed in Fig S3, both AFM and TEM images present sample C and sample D is ultrathin, with the average thickness of ca. 2 nm. Fig S3c’ and Fig 3d’ clearly indicate that the average widths of sample C and D are ca. 15 and 20 nm, respectively.
**Fig. S3** AFM images of sample C (a) and sample D (b). Some cross-sectional analysis are also listed, which is indicated by inserted lines (line AB and line CD). TEM images of sample C (c and c’) and sample D (d and d’). Scale bar are (c) 20nm, (c’) 5nm, (d) 20nm, and (d’) 5nm.

**XRD patterns of MnO₂ nanosheets**

XRD patterns of sample A, B, C, and D are exhibited in Figure S4. It shows that all samples possess similar XRD profiles. All profiles are emerged with a few of broad peaks, which indicate that all samples present in an amorphous state.

![XRD patterns](image)

**Fig. S4** XRD patterns of sample A, B, C and D

**Raman spectra analysis of MnO₂ nanosheets**

The Raman spectra of sample A, B, and D are shown in Figure S5. The spectrum of sample C is shown in Figure S7. It can be seen that all samples present in an amorphous state.
XPS spectra analysis of MnO$_2$ nanosheets

The manganese average state for MnO$_2$ can be calculated from the signal of the Mn-O-Mn and Mn-OH components according to following equation:

\[
\text{Average state} = \left( \frac{4^* (S_{\text{Mn-O-Mn}} - S_{\text{Mn-OH}}) + 3^* S_{\text{Mn-OH}})}{S_{\text{Mn-O-Mn}}/3} \right)
\]  

Where $S$ stands for signal of the different components of the O 1s spectra. Since all manganese atoms are bonded to an oxygen atom, the Mn-O-Mn signal should represent the contribution of two species: hydroxide MnOOH and oxide MnO$_2$. Hence, the XPS signal related to Mn(IV) species can be calculated by subtracting the contribution of hydroxyl group (MnOOH) from the Mn-O-Mn signal. Figure S4 shows the XPS spectra of Mn 2p and O 1s.
Table. S1 XPS peak analysis of MnO₂ samples. The deconvoluted data for the Mn 2p\textsubscript{3/2} and O 1s spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn 2p\textsubscript{3/2} BE (eV)\textsuperscript{a}</th>
<th>O 1s</th>
<th>Eb (eV)</th>
<th>Area %</th>
<th>(\Delta BE_{\text{Mn-O}})\textsuperscript{b} (eV)</th>
<th>Average state\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>642.11</td>
<td>Mn-O-Mn</td>
<td>529.47</td>
<td>69.56</td>
<td>112.64</td>
<td>3.72</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn-OH</td>
<td>531.04</td>
<td>19.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H-O-H</td>
<td>532.92</td>
<td>10.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn-O-Mn</td>
<td>529.46</td>
<td>68.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>642.04</td>
<td>Mn-OH</td>
<td>531.22</td>
<td>20.04</td>
<td>112.58</td>
<td>3.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H-O-H</td>
<td>533.01</td>
<td>11.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn-O-Mn</td>
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<td>70.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>642.21</td>
<td>Mn-OH</td>
<td>531.56</td>
<td>21.61</td>
<td>112.74</td>
<td>3.69</td>
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<td></td>
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<td>7.68</td>
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<tr>
<td></td>
<td></td>
<td>Mn-O-Mn</td>
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<td>63.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>641.79</td>
<td>Mn-OH</td>
<td>530.90</td>
<td>25.21</td>
<td>112.59</td>
<td>3.64</td>
</tr>
<tr>
<td></td>
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<td>H-O-H</td>
<td>532.87</td>
<td>11.30</td>
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</tr>
</tbody>
</table>

\textsuperscript{a} Binding energies of peak position.
\textsuperscript{b} The separation of peak position between Mn 2p\textsubscript{3/2} and O 1s at the lowest position.
\textsuperscript{c} The Mn mean state was obtained by the relative area calculation of the O 1s components.

CV plots of MnO₂ nanosheets

![CV plots of sample C at various sweep rates.](image)

Fig. S7 CV plots of sample C at various sweep rates.

Cycle performance of MnO₂ nanosheets
Fig. S8 Cycle performance of MnO₂ nanosheets

2. 0D sphere and 1D rod

XRD patterns of 0D sphere and 1D rod

XRD patterns of 0D MnO₂ sphere and 1D MnO₂ rod are exhibited in Figure S8. It shows that 0D sphere and 1D rod possess similar XRD profiles with 2D nanosheet. All profiles are emerged with a few of broad peaks, which indicate that all samples present in an amorphous state. 0D sphere and 1D rod MnO₂ samples possess similar crystalline structure with 0D sphere and 1D rod samples.

Fig. S9 XRD patterns of 0D sphere and 1D rod

SEM images of 0D MnO₂ sphere and 1D MnO₂ rod
The SEM images of 0D sphere are shown in Figure S10, which indicates that this MnO$_2$ sample exhibits a spherical shape with ~30 nm in diameter.

![Fig. S10 SEM images of 0D MnO$_2$ sphere at low (a) and high (b) resolutions](image)

The SEM images of 1D rod are shown in Figure S11, which indicates that this MnO$_2$ sample exhibits a rod shape with ~12 nm in diameter and ~100 nm in length.

![Fig. S11 SEM images of 1D MnO$_2$ rod at low (a) and high (b) resolutions](image)

3. **Samples of heat treated sample C**

To further investigate the properties of MnO$_2$ sheet, sample C was annealed at 200, 300, 450 and 600 °C in air condition for 10 h, which are denoted as C-200, C-300, C-450, and C-600, respectively.

**TEM images of sample C-300 (a1 and a2), C-450 (b1 and b2)**
**Fig. S12** TEM images of sample C-300 (a1 and a2), C-450 (b1 and b2).

**TG and DSC curves of sample C**

The thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) curves of sample C show ca. 20% weight loss and endotherm around 100 °C, which correspond to dehydration of the powders (Figure S13). Small weight loss and exotherm around 450 °C could attribute to the loss of oxygen from MnO$_2$ lattice resulting in phase transition from MnO$_2$ to Mn$_2$O$_3$. 

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Fig. S13 TG and DSC curves of sample C

Raman spectra of sample C, C-200, C-300, C-450 and C-600

Fig. S14 Raman spectra of C, C-200, C-300, C-450 and C-600

CV plots of sample C-200, C-300, C-450 and C-600
Fig. S15 CV plots of sample C-200, C-300, C-450 and C-600