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## Facile synthesis and characterization of ultrathin $\delta$ - $\text{MnO}_2$ nanoflakes

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Ultrathin  $\text{MnO}_2$  with a 2D structure is extremely attractive, especially in the field of energy storage, as its high surface area enables faradaic charge storage and provides short transport paths for electrons and ions. In this paper, we report a facile synthesis of ultrathin  $\delta$ - $\text{MnO}_2$  nanoflakes with wrinkled morphology via the reduction of potassium permanganate by ethanol in an aqueous solution. The obtained  $\delta$ - $\text{MnO}_2$  nanoflakes were potassium manganese oxide hydrate (K-birnessite) with the chemical formula  $\text{K}_{0.25}\text{MnO}_{2.06}\cdot0.51\text{H}_2\text{O}$  and had a lamellar structure with monoclinic symmetry. The lateral dimensions of the nanoflakes were in the range of 150–200 nm, as determined by transmission electron microscopy (TEM). A further high-resolution-TEM analysis indicated that these nanoflakes were composed of nanograins with a thickness of 4–5 nm. It is speculated that the nanoflakes assembled from crystal nuclei 4–5 nm in size, corresponding to ~7 lamellar layers, along the layer directions. As a result, the assembled nanoflakes inherited the ultrathin nature of these crystal nuclei. Cyclic voltammetry measurements demonstrated the excellent electrochemical properties of the nanoflakes, which can potentially serve as supercapacitor electrode materials.

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## Introduction

Two-dimensional (2D) materials have become one of the most exciting research fields in materials science over the years<sup>1</sup> because they present novel properties different from their bulk counterparts when reduced to their physical limits.<sup>2</sup> These materials have high surface areas and flexibility,<sup>3</sup> and some of them exhibit high mechanical strength, high electrical and thermal conductivities, and high dielectric constants.<sup>4,5</sup>

With its unique 2D nanostructure, layered  $\text{MnO}_2$  has been extensively investigated and widely used in the areas of ion-exchangers,<sup>6</sup> adsorbents,<sup>7</sup> catalysis,<sup>8</sup> and energy storage.<sup>9</sup> Layered  $\text{MnO}_2$  is typically a ternary phase with the general formula  $\text{R}_x\text{MnO}_2\cdot y\text{H}_2\text{O}$ , where water molecules and cationic species are located between the layers composed of  $\text{MnO}_6$  octahedral units<sup>10</sup> so as to balance the charges. The interlayer spacing between the octahedral layers is around 7 Å,<sup>11</sup> which is suitable for cation migration and thus leads to excellent ion-exchange properties and electrochemical performance.<sup>12</sup> In energy storage applications,  $\text{MnO}_2$  uses only a nanometer-thick portion of its surface to store charge; therefore, a high-surface area  $\text{MnO}_2$  nanoflake with nanometer thickness could be ideal for enhanced charge storage. Besides, the ultrathin  $\text{MnO}_2$  nanoflakes could tolerate volume alteration during the charge-

discharge cycles due to their flexibility, leading to improved stability.

Layered  $\text{MnO}_2$  can be synthesized through the reduction/decomposition of a Mn(vii) compound or the oxidization of a Mn(ii) compound. After years of effort, several synthetic routes such as co-precipitation,<sup>13</sup> hydrothermal,<sup>14</sup> sol-gel,<sup>15</sup> decomposition,<sup>16</sup> and microwave-assisted methods<sup>17,18</sup> have been developed. The morphology of layered  $\text{MnO}_2$  is affected by several synthetic parameters such as the type, concentration, and ratio of reactants, and the temperature and pH of the reaction. Liu *et al.*<sup>19</sup> reported a simple synthesis of acid K-birnessite nanoparticles by adding  $\text{NH}_2\text{OH}\cdot\text{HCl}$  to  $\text{KMnO}_4$  solution under ambient condition. The particle size could be decreased by adding an excess of the  $\text{NH}_2\text{OH}\cdot\text{HCl}$  reductant. Wang *et al.*<sup>20</sup> synthesized K-birnessite nanoparticles by a redox reaction between  $\text{KMnO}_4$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  at 90 °C. The morphology of the obtained nanoparticles was dominated by the reactant ratio of  $\text{KMnO}_4$  to  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ . The particles exhibited flower-like morphology when the reactant ratio was 0.5. When the ratio increased to 2.25, the surface of the nanoparticles became denser and the flower-like structure disappeared. Although much effort has been devoted to improving the fabrication methods to control the morphology of layered  $\text{MnO}_2$ , the obtained products are most often granular or have flower-like shapes. Extra exfoliation is usually required to achieve a flaky morphology. For instance, Beatriz *et al.*<sup>21</sup> reported a two-step exfoliation route to achieving flaky  $\text{MnO}_2$ . Firstly, he fabricated flower-shaped  $\text{MnO}_2$  nanostructures with a typical co-

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precipitation method, and then exfoliated them into nanoflakes with isopropanol. The obtained flakes possessed lateral dimensions of 20–40 nm and thickness of 3.2 nm. Omomo *et al.*<sup>22</sup> synthesized unilamellar two-dimensional crystallites of  $\text{MnO}_2$  with a thickness of ~0.8 nm by intercalating layered protonic  $\text{MnO}_2$  ( $\text{H}_{0.13}\text{MnO}_2 \cdot 0.7\text{H}_2\text{O}$ ) with tetrabutylammonium ions during an ion-exchange treatment. Besides, 2D  $\text{MnO}_2$  nanoflakes were also reported, synthesized with the aid of surfactants and templates. For example, Kang's group<sup>23,24</sup> synthesized amorphous  $\text{MnO}_2$  nanosheets *via* the reduction of  $\text{KMnO}_4$  aqueous solution dispersed in isoctane with sodium bis(2-ethylhexyl) sulfosuccinate. Zhao *et al.*<sup>25</sup> reported an *in situ* synthesis of  $\text{MnO}_2$  nanosheets from graphene oxide templates.

However, the synthesis of perfect 2D  $\text{MnO}_2$  nanoflakes especially with an ultrathin feature is still challenging; the current synthesis procedures are generally multi-step, time-consuming, or high-cost, invariably involve toxic or expensive chemicals, and are not suitable for scale production. Therefore, it is necessary to spend some effort on developing a simple synthesis method for ultrathin 2D  $\text{MnO}_2$  nanoflakes. Moreover, their characterization and growth mechanism are also worth the attention. Herein, we report the preparation of 2D  $\delta\text{-MnO}_2$  nanoflakes by a simple chemical co-precipitation method. The chemical formula and structure of  $\delta\text{-MnO}_2$  were determined, and its growth mechanism was proposed based on TEM observation and structural analysis. Finally, we investigated the supercapacitive performance of the as-prepared  $\delta\text{-MnO}_2$  nanoflakes.

## Experimental

### Synthesis procedure

$\delta\text{-MnO}_2$  nanoflakes were prepared through a redox reaction between  $\text{KMnO}_4$  and  $\text{C}_2\text{H}_6\text{O}$ . The reagents with 99.5% purity were supplied by Sinopharm Chemical Reagent. In brief, 1 g of  $\text{KMnO}_4$  was dissolved in 500 ml of distilled water and excess of  $\text{C}_2\text{H}_6\text{O}$  was added dropwise under vigorous stirring. The reaction was carried out at ambient temperature for 2 h until the purple solution turned brown. The obtained precipitate was filtered under pressure, and washed with distilled water and then ethanol. Finally, the purified precipitate was desiccated at 80 °C for 12 h in an electric thermostatic drying oven, and a brown powder was obtained.

### Characterization

Chemical analysis was carried out using an inductively coupled plasma-atomic emission spectrometer (PerkinElmer Optima 7300 ICP-AES). The thermal decomposition was studied with a differential scanning calorimeter (DSC-214, NETZSCH) in an argon flow using an aluminum crucible. The valence state was determined by X-ray photoelectron spectroscopy (XPS) under ultra-high-vacuum condition using monochromatic  $\text{Al K}_\alpha$  X-rays (1486.6 eV). Powder X-ray diffraction (XRD) patterns were obtained using a diffractometer (Bruker D8 advance) with  $\text{Cu K}_\alpha$  radiation (30 kV, 30 mA,  $\lambda = 1.5406 \text{ \AA}$ ). TEM and selected area electron diffraction (SAED) were performed utilizing

a transmission electron microscope (FEI Tecnai G2 F30) at an accelerating voltage of 100 kV, equipped with a high-resolution accessory. A Fourier transform infrared spectroscope (FTIR Spectrum 400) was used to determine the crystal structure of the as-prepared  $\text{MnO}_2$ . Raman scattering spectra were recorded with a Raman spectrometer (HORIBA LabRAM HR800, Japan) at room temperature.

### Electrochemical measurements

To prepare the working electrode, 70 wt% of as-prepared  $\text{MnO}_2$ , 20 wt% acetylene black, and 10 wt% polytetrafluoroethylene (PTFE) were uniformly mixed using an agate mortar and pestle for 30 min. The mixture was dispersed in ethanol in an ultrasonic bath (37 kHz, 200 W) for 20 min. The dispersion was then dropped on a well-polished glassy carbon electrode and desiccated under infrared light. The electrochemical properties of the electrode were examined *via* cyclic voltammetry in a three-electrode electrochemical cell, which consisted of a  $\text{Ag}/\text{AgCl}$  reference electrode and a platinum-wire counter-electrode with 0.5 M  $\text{K}_2\text{SO}_4$  electrolyte (the pH was adjusted to 10 with a dilute buffer solution).

## Results and discussion

### Chemical composition and crystal structure

Prepared in a K-rich aqueous solution, the obtained powder is anticipated to contain K and crystal water. Thus, chemical analysis (by ICP-AES) and synchronous thermal analysis (by DSC) were carried out in sequence. The K and Mn content were determined as 8.72 wt% and 48.44 wt%, respectively. The DSC analysis detected two endothermic peaks in the temperature range from room temperature to 200 °C. A similar phenomenon was reported by Bach *et al.* In their DSC study of Na-birnessite, two departures of water were observed at 85 and 150 °C.<sup>26</sup> As shown in Fig. 1a, the peaks at 109.7 °C and 148.2 °C are believed to have originated from the evaporation of adsorbed water and interlayer water, respectively. The integration of both the peaks yields a vaporization heat of 163 J g<sup>-1</sup>, which, when compared to the standard vaporization heat of water (2.257 kJ g<sup>-1</sup>), gives an estimated water content of 7.22 wt%. In addition, the water content was determined by weighing the mass loss after the DSC test, which yielded a value of 8.62 wt%. The reported values of the water content of potassium manganese oxide hydrate range from 4.3 to 14.1 wt%.<sup>27–29</sup> This discrepancy is probably due to the presence of adsorbed water, which can vary with environmental humidity and preheating conditions. The valence state of Mn was determined by XPS (Fig. 1b). The  $\text{Mn}^{2p^{3/2}}$  peak was fitted with five multiplet components in conformity with the parameters established by Biesinger *et al.*<sup>30</sup> The atomic ratio of  $\text{Mn}^{3+} : \text{Mn}^{4+}$  was evaluated by their relative peak areas, and the average oxidation state of Mn was found to be 3.87. Finally, the chemical formula of the  $\text{MnO}_2$ -based powder was determined as  $\text{K}_{0.25}\text{MnO}_{2.06} \cdot 0.51\text{H}_2\text{O}$ . The co-precipitation reaction between  $\text{KMnO}_4$  and  $\text{C}_2\text{H}_6\text{O}$  can be described by the following equation:



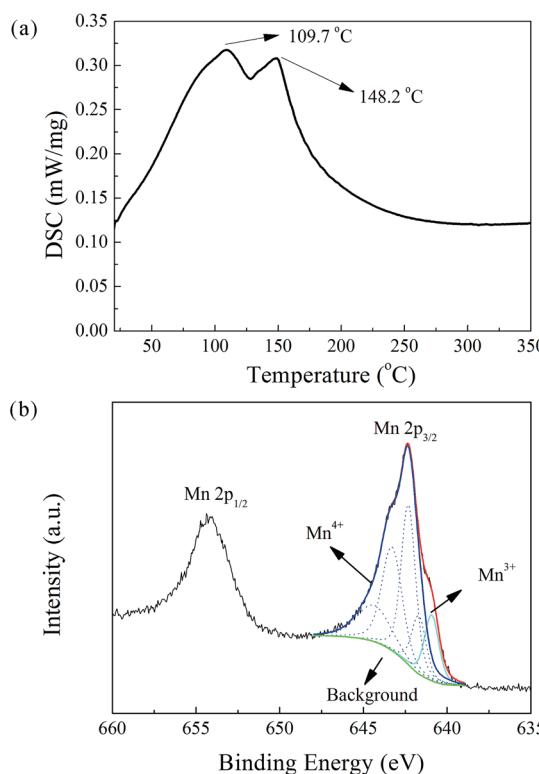
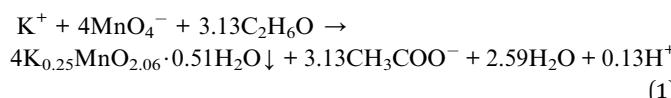


Fig. 1 Thermal decomposition and compositional analysis of the as-prepared powder. (a) DSC curve. (b) XPS spectra.



Phase determination of the as-prepared powder was carried out by XRD, and the result is presented in Fig. 2a. The pattern coincides well with the reference JCPDS00-042-1317 (potassium manganese oxide hydrate,  $\text{K}_{0.25}\text{MnO}_2 \cdot 0.75\text{H}_2\text{O}$ , star quality). The main peaks appear at  $12.48^\circ$ ,  $25.21^\circ$ ,  $36.74^\circ$ , and  $65.77^\circ$  corresponding to the (001), (002), (110), and (020) planes with interplanar spacing of  $7.09$ ,  $3.53$ ,  $2.45$ , and  $1.42$  Å, respectively. The reference phase ( $a = 5.150$  Å,  $b = 2.844$  Å,  $c = 7.159$  Å,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 100.64^\circ$ ) belongs to the face-centered (C) monoclinic crystal system. Its [010] axis has a two-fold rotational symmetry, and the vertical plane perpendicular to the [010] axis is a mirror symmetry plane. The XRD analysis hence confirmed the layered structure of the as-prepared powder, which can be denoted as K-birnessite or  $\delta$ - $\text{MnO}_2$ . The layered  $\delta$ - $\text{MnO}_2$  is commonly generated from the redox reaction between  $\text{KMnO}_4$  and  $\text{C}_2\text{H}_6\text{O}$ , and the presence of  $\text{K}^+$  is believed to stabilize its 2D layered structure.

In addition, the XRD peaks were significantly broad compared to the standard patterns. This phenomenon is attributed to the small crystalline grain size, as estimated by the Debye–Scherrer equation,  $D_{hkl} = f\lambda/\beta \cos \vartheta$ , where  $D_{hkl}$  is the mean size of the crystalline domains (or grain size),  $f$  is a dimensionless shape factor with a value close to unity

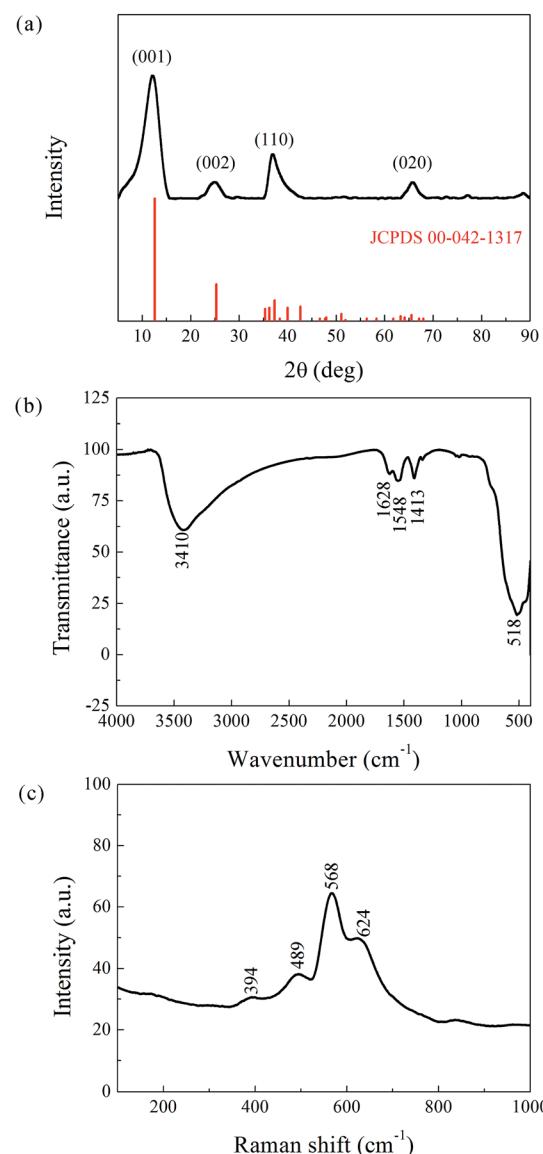


Fig. 2 Structural characterization of the as-prepared powder. (a) XRD pattern. (b) FTIR Spectra. (c) Raman scattering.

(typically 0.9),  $\lambda$  is the X-ray wavelength,  $\beta$  is the full width at half maximum (FWHM, expressed in radians), and  $\vartheta$  is the Bragg angle (in degrees). The corresponding results, listed in Table 1, indicate an ultrafine grain structure for the  $\delta$ - $\text{MnO}_2$  material.

FTIR and Raman characterizations further elucidated the crystal structure of the nanoflake grains. Fig. 2b shows the IR spectra of  $\delta$ - $\text{MnO}_2$ . The bands at  $3410$  cm $^{-1}$  and  $1400$ –

Table 1 XRD data for the Debye–Scherrer equation

No.	$2\vartheta$ (°)	$d$ (Å)	$\beta$ (rad)	$(hkl)$	$D_{hkl}$ (Å)
1	12.48	7.09	0.038	(001)	40.34
2	25.21	3.53	0.043	(002)	36.96
3	36.74	2.45	0.021	(110)	76.18
4	65.77	1.42	0.034	(020)	53.62

1650 cm<sup>-1</sup> correspond to the stretching<sup>31</sup> and bending<sup>32</sup> vibrations of H<sub>2</sub>O, respectively, and the presence of several O-H bending vibration modes in the 1400–1650 cm<sup>-1</sup> range indicates the co-existence of adsorbed and crystal water.<sup>33</sup> Another important observation is the band at 518 cm<sup>-1</sup>, which represents the Mn-O bond vibration.<sup>34</sup> Fig. 2c shows the Raman spectra of  $\delta$ -MnO<sub>2</sub>, where an intense band at 568 cm<sup>-1</sup> and three weak bands at 394, 489, and 624 cm<sup>-1</sup> are observed. The Raman band located at 624 cm<sup>-1</sup> can be attributed to the symmetric stretching vibration  $\nu_2$ (Mn-O) of MnO<sub>6</sub>. The band at 568 cm<sup>-1</sup> is generally attributed to the  $\nu_3$ (Mn-O) stretching vibration in the MnO<sub>6</sub> layer, and its strong intensity is believed to be related to the high content of quadrivalent Mn atoms in the birnessite structure. The bands at 489 and 394 cm<sup>-1</sup> are assigned to the  $\nu_5$ (Mn-O) and  $\nu_7$ (Mn-O) stretching vibrations of MnO<sub>6</sub>, respectively. These features correspond to a layered birnessite MnO<sub>2</sub> material consisting of layers composed of MnO<sub>6</sub> units,<sup>35</sup> in which six oxygen atoms surround a central manganese atom in an approximate octahedral coordination, and crystal water between the layers, as shown in Fig. 3a. Based on the above characterization, crystal parameters, and data from Table 1, we determined the structure of a typical  $\delta$ -MnO<sub>2</sub>

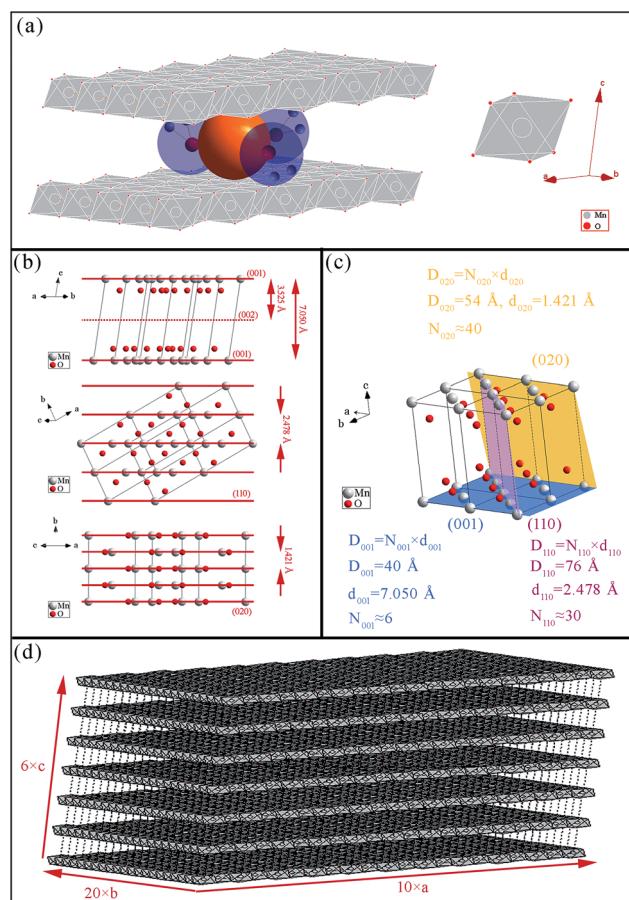


Fig. 3 Schematic of  $\delta$ -MnO<sub>2</sub> structure. (a) MnO<sub>6</sub> octahedral units, water, and K<sup>+</sup>. (b) View of the crystal cell along a direction parallel to the (001), (110), and (020) planes; (c) (001), (010), and (110) planes in the 3D crystal cell. (d) Typical  $\delta$ -MnO<sub>2</sub> grain with lamellar structure.

grain (Fig. 3d). Three independent lattice planes—(001), (110), and (020)—were chosen to estimate the dimensions of a typical grain (Fig. 3b).  $N_{hkl}$  is the number of atomic layers in a grain in its  $[hkl]$  direction, and is calculated as  $D_{hkl}/d_{hkl}$  (Fig. 3c).  $N_{100}$ ,  $N_{010}$ , and  $N_{001}$  were calculated as 10, 20, and 6, and a 7-layer 3D grain was accordingly drawn in Fig. 3d.

### Morphology observation and analysis

A TEM image of the as-prepared  $\delta$ -MnO<sub>2</sub> is displayed in Fig. 4a, which shows a typical layered flake-shape morphology. The wrinkling, along with the highly transparent flake border, points to ultrathin nanoflakes. In the figure, one can distinguish wrinkled flakes with a lateral size of 150–200 nm. Despite their nanoscale dimensions, these individual nanoflakes are not monocrystals (Fig. 4d), but, on the contrary, exhibit dozens of crystalline grains within an HR-TEM-analyzed region, with a lateral size of about 5 nm. Lamellar stripes are observed along the border or the wrinkled region of these nanoflakes. As shown in Fig. 4b, two obvious distinctions can be made between these stripes and the ordinary crystal lattice stripes. First, the stripe spacing is much wider for the lamellar structures, *i.e.*, 6–7 Å measured here, as opposed to the ordinary crystal lattice stripe

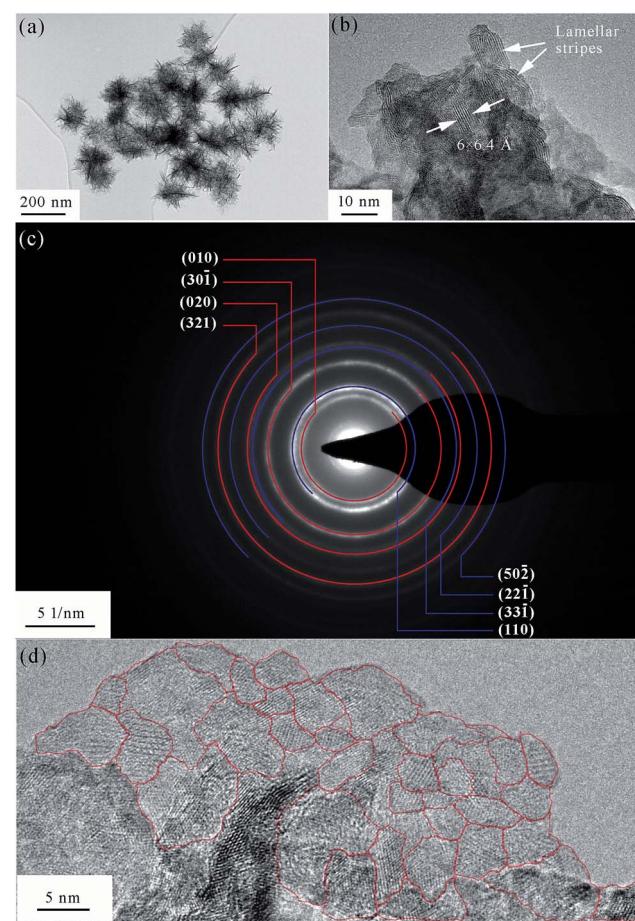


Fig. 4 TEM analysis of the as-prepared  $\delta$ -MnO<sub>2</sub>. (a) TEM and (b) HR-TEM image of lamellar stripes within the nanoflakes. (c) SAED pattern and (d) HR-TEM image of polycrystalline grains.



spacing of 1–3 Å. Second, while the ordinary crystal lattice stripes are equidistantly aligned, the lamellar stripes can be flexuous in shape. From the measurements of these lamellar stripes, the average thickness of the nanoflakes was determined to be 4 nm, similar to the lateral crystalline grain size. It is noteworthy that the observation of the lamellar structure is the most direct visual identification of the product as a layered birnessite.

As expected, the SAED pattern (Fig. 4c) consisted of polycrystalline rings. Since the incident electron beam was vertical to the  $\delta$ -MnO<sub>2</sub> nanoflake plane (*i.e.*, along its [001] normal direction), only the planes vertical to the (001) plane would generate rings in the SAED image. Table 2 lists the planes that are approximately vertical to the (001) plane, their corresponding *d*-spacing values, and the angles they form with the (001) plane. The *d*-spacing values obtained from the SAED polycrystalline rings are also given in Table 2, as well as the theoretical value of the (001) plane spacing and the measured value obtained from the HR-TEM images. The theoretical *d*-spacing values are about 1.1 times larger than the measured ones. The narrowing of the  $\delta$ -MnO<sub>2</sub> interlayer spacing (*d*<sub>001</sub>) has already been reported,<sup>33</sup> and is believed to be induced by dehydration caused by exposure to an electron beam in vacuum. In this paper, we found that not only *d*<sub>001</sub>, but also *d*<sub>010</sub> and *d*<sub>110</sub> reduced at the same rate after the dehydration of  $\delta$ -MnO<sub>2</sub>. In other words, hydration expands the  $\delta$ -MnO<sub>2</sub> unit cell at the same rate in all directions.

### Growth mechanism

Considering that the  $\delta$ -MnO<sub>2</sub> nanoflakes assembled from layered nano-grains, as illustrated in Fig. 3d, we propose a possible growth mechanism of these flakes. In the first stage,  $\delta$ -MnO<sub>2</sub> crystal nuclei with a lamellar structure consisting of MnO<sub>6</sub> octahedron layers, cations, and water were generated. These negatively charged crystal nuclei repulsed each other while attracting K<sup>+</sup>. The crystal nuclei therefore tended to

Table 2 Theoretical and experimental values of the interplanar spacing<sup>a</sup>

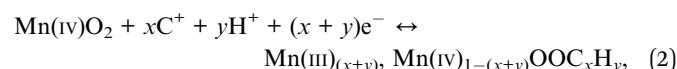
Plane ( <i>hkl</i> )	Theoretical angle with (001) plane <sup>#</sup>	<i>d</i> (Å)		
		Theoretical <sup>#</sup>	Measured	<i>R</i> <sup>+</sup>
(010)	90°	2.843	2.61 <sup>^</sup>	1.09
(110)	85°	2.478	2.24 <sup>^</sup>	1.11
(301)	87°	1.714	1.59 <sup>^</sup>	1.08
(311)	87°	1.468	1.37 <sup>^</sup>	1.07
(020)	90°	1.421	1.30 <sup>^</sup>	1.09
(221)	85°	1.240	1.13 <sup>^</sup>	1.10
(321)	88°	1.094	1.01 <sup>^</sup>	1.08
(502)	84°	1.024	0.92 <sup>^</sup>	1.14
(001)	0°	7.050	6.40*	1.10

<sup>a</sup> 1. Data marked with <sup>#</sup> are calculated from the monoclinic crystal parameters (*a* = 5.150 Å, *b* = 2.844 Å, *c* = 7.159 Å,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 100.64^\circ$ ). 2. Data marked with <sup>^</sup> are derived from the electron diffraction rings. 3. Data marked with \* were obtained from the direct measurement of the lamellar spacing. 4. *R*<sup>+</sup> = *d*<sub>Theoretical</sub> : *d*<sub>Measured</sub>.

assemble along the lamellar directions, yielding the nano-grains observed by HR-TEM in Fig. 4d, and shown by the parallel lines in Fig. 5. This self-assembly is believed to be controlled by coulombic interactions<sup>36</sup> and driven by surface energy reduction. However, defects inevitably formed during the self-assembly and finally led to an imperfect wrinkled nanoflake morphology. It is worth mentioning that  $\delta$ -MnO<sub>2</sub> nanoflakes were assembled along the lamellar directions, and hence, their thicknesses were determined by the thicknesses of their component crystal nuclei. A sufficient condition to achieve ultrathin  $\delta$ -MnO<sub>2</sub> nanoflakes is to control the thicknesses of their original crystal nuclei.

### Supercapacitive performance

The CV measurements of the  $\delta$ -MnO<sub>2</sub> electrode were performed at a scanning rate in the range of 1–100 mV s<sup>-1</sup> (Fig. 6a). The nearly rectangular shapes of the CV curves indicate a nearly ideal supercapacitive behavior. The area under the CV curve increases with increasing scanning rate, while the curve retains its shape. According to Simon's mechanism,  $\delta$ -MnO<sub>2</sub> stores the charges mainly by pseudo-capacitive reactions occurring at the surface and bulk of the solid MnO<sub>2</sub> phase, as shown below:<sup>37</sup>



where C<sup>+</sup> = Li<sup>+</sup>, Na<sup>+</sup>, or K<sup>+</sup>. Since the oxidation state of Mn can be tailored reversibly and continuously during the pseudo-capacitive reactions of  $\delta$ -MnO<sub>2</sub>, we can hardly observe any typical pseudocapacitance peak in the CV curves. For the surface pseudo-capacitive reaction, cations can electrochemically adsorb onto the surface of  $\delta$ -MnO<sub>2</sub> through the charge-transfer process, which is kinetically more facile and is referred to as redox pseudocapacitance. For the bulk pseudo-capacitive reaction, charge storage is achieved by the intercalation/deintercalation of protons and cations into the interlayer gaps of layered  $\delta$ -MnO<sub>2</sub>. This process involves the long-range diffusion of ions through interlayer gaps, and hence, the intercalation/deintercalation is relatively slower and is known as intercalation pseudocapacitance. The

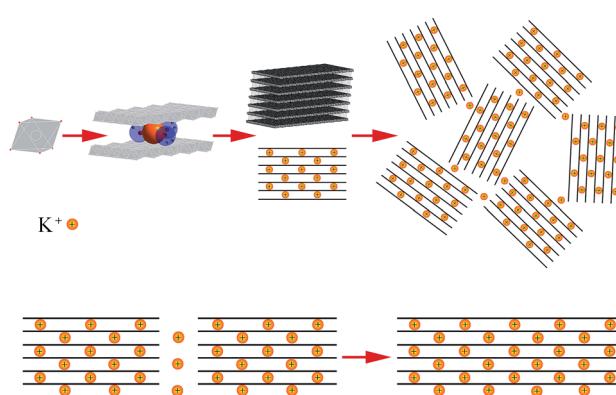


Fig. 5 Schematic of the growth mechanism of  $\delta$ -MnO<sub>2</sub> nanoflakes.

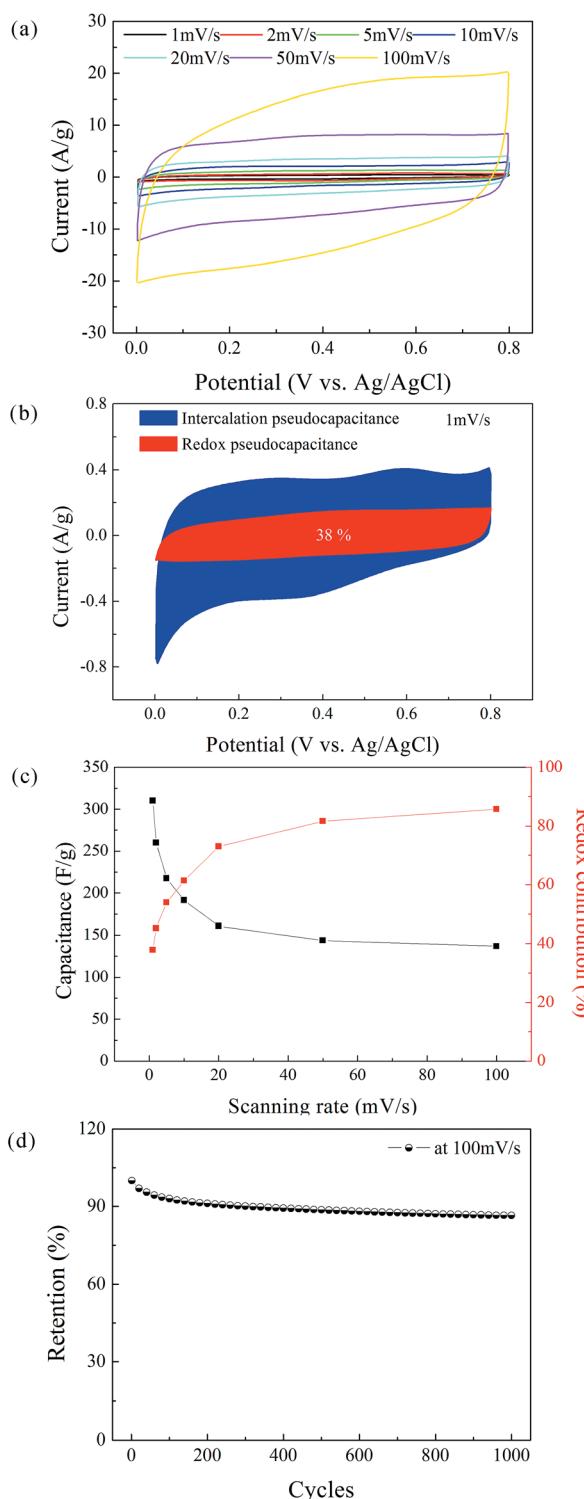


Fig. 6 (a) CV curves of the  $\delta$ -MnO<sub>2</sub> electrode at potential scanning rates of 1, 2, 5, 10, 20, 50, and 100 mV s<sup>-1</sup>. (b) Redox and intercalation contributions to charge storage of  $\delta$ -MnO<sub>2</sub> electrode at 1 mV s<sup>-1</sup>. (c) Specific capacitance of the  $\delta$ -MnO<sub>2</sub> electrode and its redox contribution as a function of the potential scanning rate. (d) Cycling performance of the  $\delta$ -MnO<sub>2</sub> electrode at a potential scanning rate of 100 mV s<sup>-1</sup>.

contribution of redox and intercalation pseudocapacitance can be divided according to Dunn's work,<sup>38-40</sup> as shown in Fig. 6b.

The specific capacitance of the electrode can be obtained from the area under the CV curve using the following equation:<sup>41-43</sup>

$$c = \int i \frac{dV}{2mV\Delta V} \quad (3)$$

where  $i$  is the current (A),  $V$  is the voltage (V),  $\int idV$  is the area under the CV curve,  $v$  is the scan rate (V s<sup>-1</sup>),  $m$  is the mass (g) of the electrode, and  $\Delta V$  is the potential window (V). The specific capacitance values of the MnO<sub>2</sub> electrode were found to be 310, 260, 218, 191, 161, 144, and 137 F g<sup>-1</sup> at scanning rates of 1, 2, 5, 10, 20, 50, and 100 mV s<sup>-1</sup> (Fig. 6c), respectively. In addition, the specific redox pseudocapacitance was quantified as 117 F g<sup>-1</sup>, which is independent of the scanning rate.

At a high scanning rate, cation diffusion through interlayer gaps is restricted; therefore, the redox pseudocapacitance at the surface of  $\delta$ -MnO<sub>2</sub> is the major contributor to the capacitance (86% at 100 mV s<sup>-1</sup>). By contrast, the capacitance mainly originates from the insertion and extraction of cations into and from the  $\delta$ -MnO<sub>2</sub> layers at a low scanning rate, and the redox pseudocapacitance contributes only 38% of total capacitance at 1 mV s<sup>-1</sup>. Note that the theoretical specific capacitance of  $\delta$ -MnO<sub>2</sub> (chemical formula:  $K_{0.25}MnO_{2.06} \cdot 0.51H_2O$ ) can be obtained according to Cao's method,<sup>44</sup> which was calculated as 862 F g<sup>-1</sup>. Considering the 7-layered lamellar structure of  $\delta$ -MnO<sub>2</sub>, the surface redox pseudocapacitance provides only one-seventh of the theoretical capacitance. The poor rate performances shown in Fig. 6c are mainly due to the structure of  $\delta$ -MnO<sub>2</sub>. On one hand, the large lateral dimensions of  $\delta$ -MnO<sub>2</sub> nanoflakes result in a long-range diffusion path for ions through the interlayer gaps, and the intercalation pseudocapacitance becomes dependent on the scan rate in the concerned range. On the other hand, the lamellar layer number of the  $\delta$ -MnO<sub>2</sub> nanoflakes is not small enough to provide a large redox pseudocapacitance. To further evaluate the stability of the  $\delta$ -MnO<sub>2</sub> electrode, long-term cycling was carried out at 100 mV s<sup>-1</sup>; the corresponding result is shown in Fig. 6d. The  $\delta$ -MnO<sub>2</sub> electrode exhibited about 86.5% of the initial specific capacitance after 1000 cycles. The good electrochemical stability indicates that a highly reversible redox reaction occurred at the surface and in the interlayer gaps of the  $\delta$ -MnO<sub>2</sub> electrode.

## Conclusions

In summary,  $\delta$ -MnO<sub>2</sub> nanoflakes were synthesized *via* the reduction of KMnO<sub>4</sub> by C<sub>2</sub>H<sub>6</sub>O in an aqueous solution. The so-obtained  $\delta$ -MnO<sub>2</sub> nanoflakes exhibited a lamellar structure and wrinkled morphology. In the first stage of nanoflake formation, nuclei with a size of  $\sim$ 4 nm, corresponding to  $\sim$ 7 lamellar layers, crystallized as  $K_{0.25}MnO_{2.06} \cdot 0.51H_2O$  in the face-centered (C) monoclinic crystal system. Then, the nuclei self-assembled into nanoflakes with a thickness of  $\sim$ 4 nm and lateral dimensions in the range of 150–200 nm. Defects formed during the self-assembly, which led to the observed wrinkled morphology. However, the obtained nanoflakes exhibited excellent electrochemical properties. In 0.5 M K<sub>2</sub>SO<sub>4</sub> aqueous solution, the specific capacitance of the  $\delta$ -MnO<sub>2</sub> electrode



reached  $310 \text{ F g}^{-1}$  at a scanning rate of  $1 \text{ mV s}^{-1}$ , and 86.5% of the initial specific capacitance remained after 1000 cycles at  $100 \text{ mV s}^{-1}$ .

## Conflicts of interest

There are no conflicts to declare.

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## Notes and references

- 1 T. M. Higgins, D. McAteer, J. C. Coelho, S. B. Mendoza, Z. Gholamvand, G. Moriarty, N. McEvoy, N. C. Berner, G. S. Duesberg and V. Nicolosi, *ACS Nano*, 2014, **8**, 9567–9579.
- 2 G. R. Bhimanapati, Z. Lin, V. Meunier, Y. Jung, J. J. Cha, S. Das, D. Xiao, Y. Son, M. S. Strano and V. R. Cooper, *ACS Nano*, 2015, **9**, 11509–11539.
- 3 F. Bonaccorso, L. Colombo, G. Yu, M. Stoller, V. Tozzini, A. C. Ferrari, R. S. Ruoff and V. Pellegrini, *Science*, 2015, **347**, 1246501.
- 4 C. Lee, X. Wei, J. W. Kysar and J. Hone, *Science*, 2008, **321**, 385–388.
- 5 A. K. Geim and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 183–191.
- 6 L. Chen, X. Xu, J. Song, X. Zhu and Z. Qi, *Sep. Sci. Technol.*, 2015, **51**, 1–9.
- 7 J. Zhao, J. Liu, N. Li, W. Wang, J. Nan, Z. Zhao and F. Cui, *Chem. Eng. J.*, 2016, **304**, 737–746.
- 8 G. Zhao, J. Li, X. Ren, J. Hu, W. Hu and X. Wang, *RSC Adv.*, 2013, **3**, 12909–12914.
- 9 X. Sun, H. Wang, Z. Lei, Z. Liu and L. Wei, *RSC Adv.*, 2014, **4**, 30233–30240.
- 10 X. Zhang, X. Sun, H. Zhang, C. Li and Y. Ma, *Electrochim. Acta*, 2014, **132**, 315–322.
- 11 K. S. Abou, M. Askar and R. Schöllhorn, *Solid State Ionics*, 2002, **150**, 116.
- 12 M. Toupin, T. Brousse and D. Bélanger, *Chem. Mater.*, 2004, **16**, 3184–3190.
- 13 Q. Feng, L. Liu and K. Yanagisawa, *J. Mater. Sci. Lett.*, 2000, **19**, 1567–1570.
- 14 L. Liu, Q. Feng, K. Yanagisawa and Y. Wang, *J. Mater. Sci. Lett.*, 2000, **19**, 2047–2050.
- 15 S. Ching, D. J. P. And, M. L. Jorgensen and S. L. Suib, *Inorg. Chem.*, 1997, **36**, 883–890.
- 16 X. Hu, L. Shi, D. Zhang, X. Zhao and L. Huang, *RSC Adv.*, 2016, **6**, 14192–14198.
- 17 X. Zhang, W. Miao, C. Li, X. Sun, K. Wang and Y. Ma, *Mater. Res. Bull.*, 2015, **71**, 111–115.
- 18 L. Wang, W. Ma, Y. Li and H. Cui, *J. Sol-Gel Sci. Technol.*, 2017, **82**, 85–91.
- 19 L. Liu, Y. Luo, W. Tan, Y. Zhang, F. Liu and G. Qiu, *J. Colloid Interface Sci.*, 2016, **482**, 183–192.
- 20 J. Wang, J. Li, C. Jiang, P. Zhou, P. Zhang and J. Yu, *Appl. Catal., B*, 2017, **204**, 147–155.
- 21 C. João, M.-S. Beatriz, P. Henrik, P. Anuj, K. M. Eva, L. Edmund, M. Lorcan, P. B. Alan and N. Valeria, *2D Mater.*, 2015, **2**, 025005.
- 22 Y. Omomo, T. Sasaki and M. Watanabe, *J. Am. Chem. Soc.*, 2003, **34**, 3568–3575.
- 23 C. Xu, S. Shi, Y. Sun, Y. Chen and F. Kang, *Chem. Commun.*, 2013, **49**, 7331–7333.
- 24 S. Shi, C. Xu, C. Yang, Y. Chen, J. Liu and F. Kang, *Sci. Rep.*, 2013, **3**, 2598.
- 25 G. Zhao, J. Li, L. Jiang, H. Dong, X. Wang and W. Hu, *Chem. Sci.*, 2012, **3**, 433–437.
- 26 P. L. Goff, N. Baffier, S. Bach, *et al.*, *Mater. Res. Bull.*, 1996, **31**, 63–75.
- 27 R. Chen, P. Zavalij and M. S. Whittingham, *Chem. Mater.*, 1996, **8**, 1275–1280.
- 28 K. L. Holland, *Clays Clay Miner.*, 1996, **44**, 744–748.
- 29 J. E. Posr, *Am. Mineral.*, 1990, **75**, 477–489.
- 30 M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson and R. S. C. Smart, *Appl. Surf. Sci.*, 2011, **257**, 2717–2730.
- 31 L. Kang, M. Zhang, Z.-H. Liu and K. Ooi, *Spectrochim. Acta, Part A*, 2007, **67**, 864–869.
- 32 F. Qi, *J. Mater. Sci. Lett.*, 2003, **22**, 999–1001.
- 33 K. S. Abou, *Solid State Ionics*, 2002, **150**, 407–415.
- 34 Q. Feng, K. Yanagisawa and N. Yamasaki, *J. Mater. Sci. Lett.*, 1997, **16**, 110–112.
- 35 C. Julien, M. Massot, R. Baddour-Hadjean, S. Franger, S. Bach and J. P. Pereira-Ramos, *Solid State Ionics*, 2003, **159**, 345–356.
- 36 D. Yan, P. X. Yan, G. H. Yue, J. Z. Liu, J. B. Chang, Q. Yang, D. M. Qu, Z. R. Geng, J. T. Chen, G. A. Zhang and R. F. Zhuo, *Chem. Phys. Lett.*, 2007, **440**, 134–138.
- 37 P. Simon and Y. Gogotsi, *Nat. Mater.*, 2008, **7**, 845–854.
- 38 X. Xiong, C. Yang, G. Wang, Y. Lin, X. Ou, J. Wang, B. Zhao, M. Liu, Z. Lin and K. Huang, *Energy Environ. Sci.*, 2017, **10**, 1757–1763.
- 39 V. Augustyn, P. Simon and B. Dunn, *Energy Environ. Sci.*, 2014, **7**, 1597–1614.
- 40 P. Simon, Y. Gogotsi and B. Dunn, *Science*, 2014, **343**, 1210–1211.
- 41 A. Bello, F. Barzegar, D. Momodu, J. Dangbegnon, F. Taghizadeh and N. Manyala, *Electrochim. Acta*, 2015, **151**, 386–392.
- 42 P. Yang and W. Mai, *Nano Energy*, 2014, **8**, 274–290.
- 43 X. Xiong, D. Ding, D. Chen, G. Waller, Y. Bu, Z. Wang and M. Liu, *Nano Energy*, 2015, **11**, 154–161.
- 44 J. Cao, X. Li, Y. Wang, F. Walsh, J. Ouyang, D. Jia and Y. Zhou, *J. Power Sources*, 2015, **293**, 657–674.

