

## Supporting Information

# The Directional Structure Transition of MnO<sub>2</sub> during Drying Process

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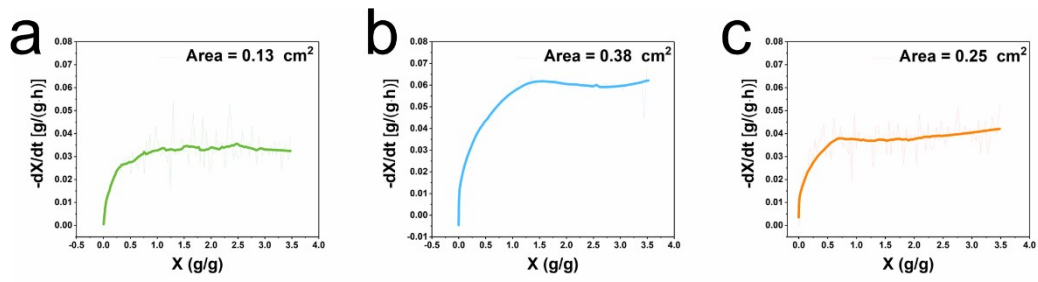
Number of Pages: 18 (S1 to S18)

Number of Figures: 11 (S1 to S14)    Number of Tables: 1 (S1)

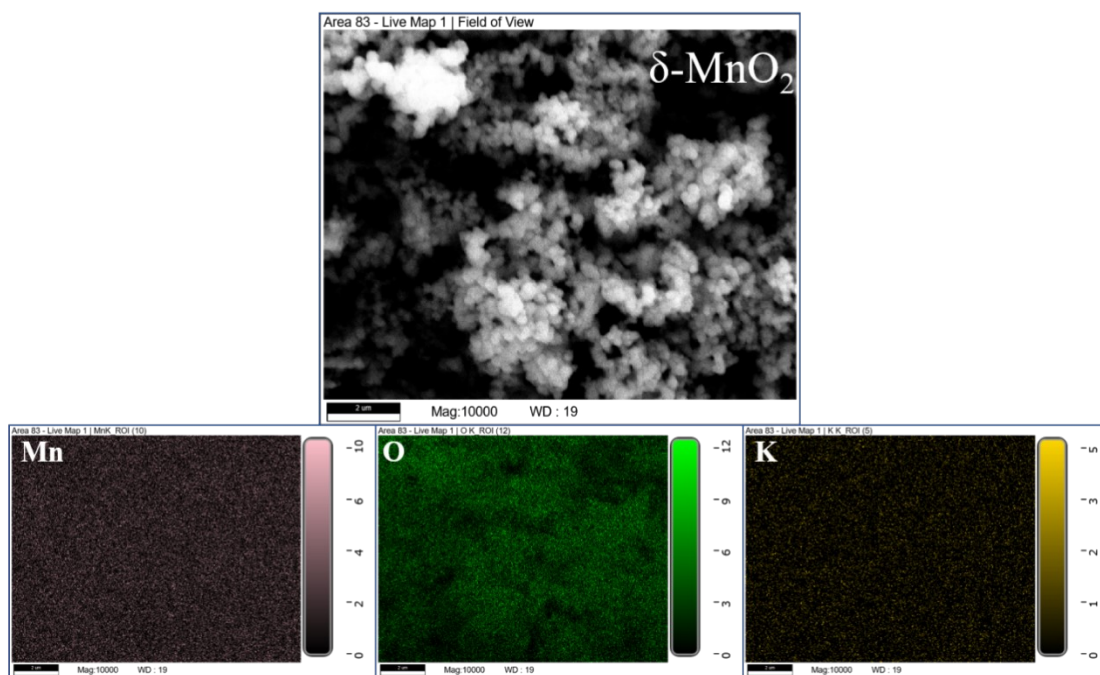
### **Preparation of Na<sup>+</sup>/δ-MnO<sub>2</sub>**

0.043 mol MnSO<sub>4</sub> was mixed in 100 mL of DI water via sonication for 15 min, after that, 100 mL of 0.05 mol NaMnO<sub>4</sub> was slowly added to the above solution within 5 min under vigorous magnetic stirring, followed by stirring at 80 °C for 100 minutes. After cooling down to room temperature, the precipitates were collected by centrifugation and washed several times with DI water.

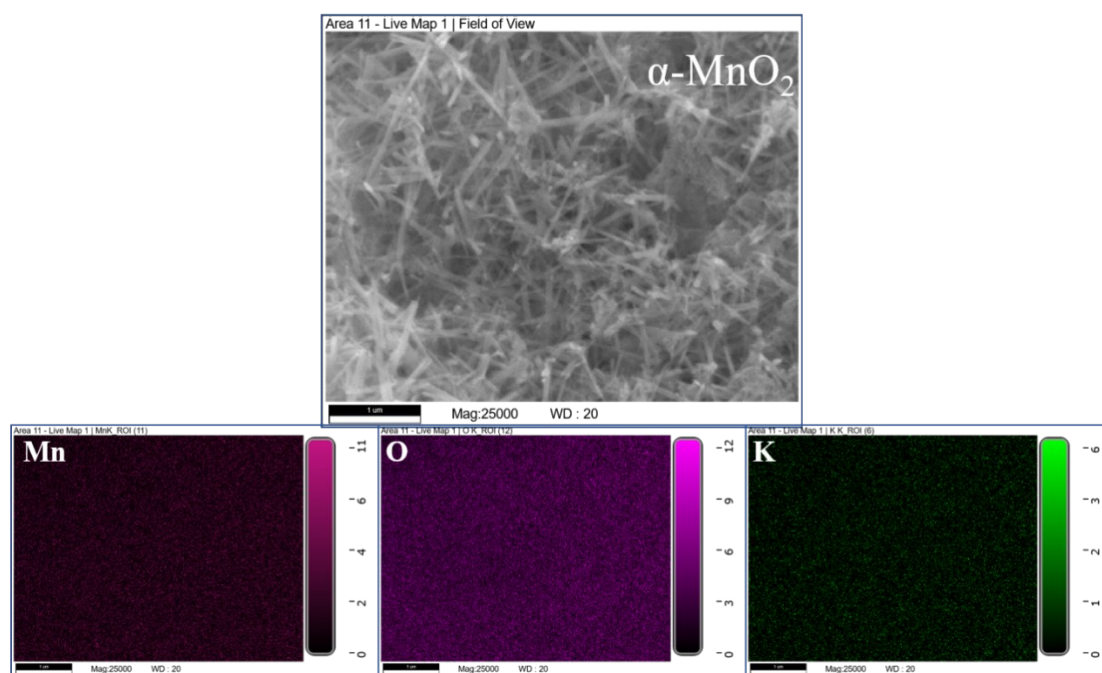
After washing, equal amount of wet materials were put into three identical containers, each container was sealed with a cap with a small hole, and the drying rate of the materials in the container was adjusted by changing the size of the hole.



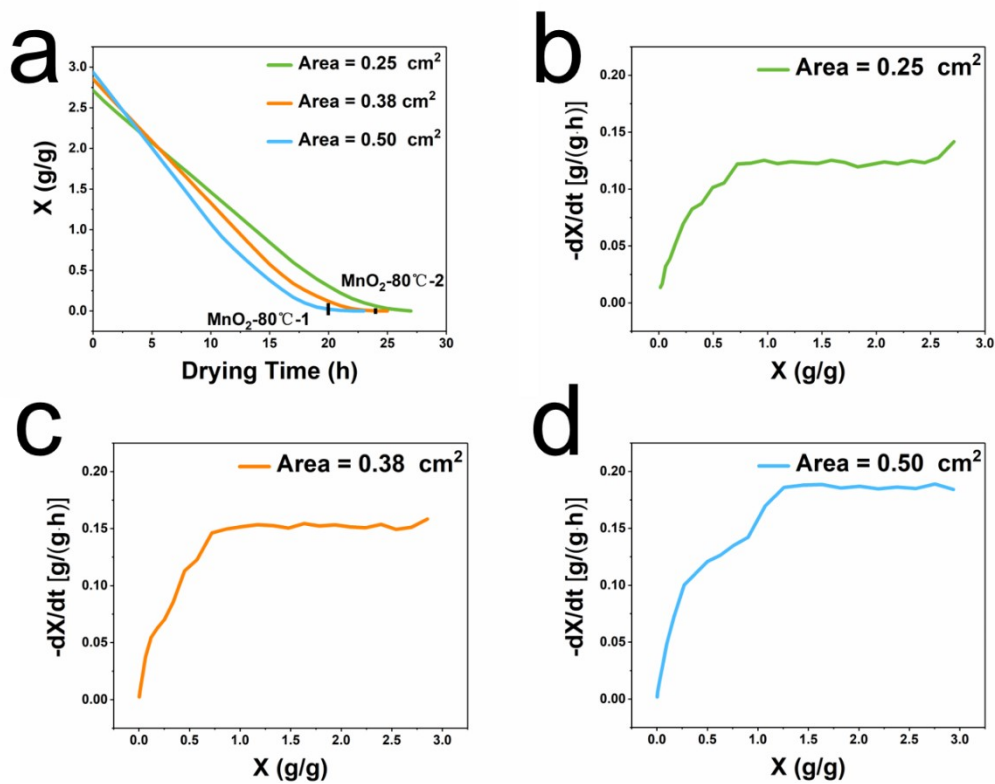
**Fig. S1** The drying rate curves (a) in the case of Area = 0.13 cm<sup>2</sup>, (b) in the case of Area = 0.38 cm<sup>2</sup>, (c) in the case of Area = 0.25 cm<sup>2</sup>.



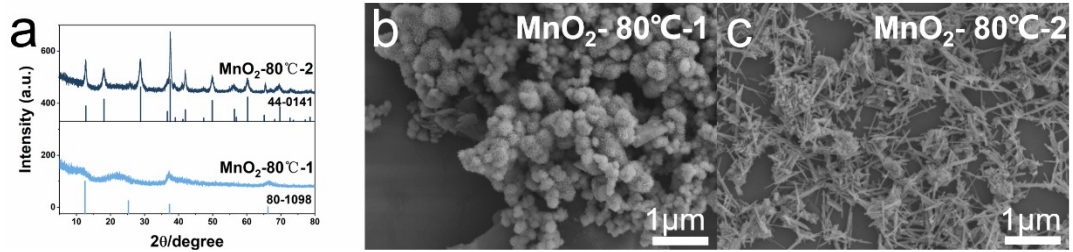
**Fig. S2** EDS mapping of  $\delta\text{-MnO}_2$ .



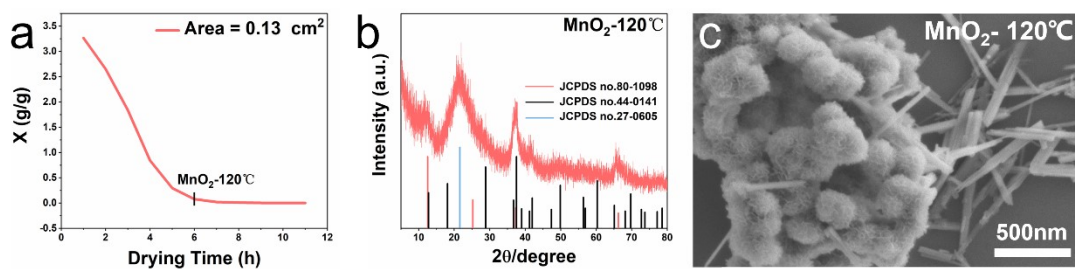
**Fig. S3** EDS mapping of  $\alpha\text{-MnO}_2$ .



**Fig. S4** The drying curves (a) in the case of Area = 0.25 cm<sup>2</sup>, Area = 0.38 cm<sup>2</sup> and Area = 0.50 cm<sup>2</sup>. The drying rate curves (b) in the case of Area = 0.25 cm<sup>2</sup>, (c) in the case of Area = 0.38 cm<sup>2</sup>, (d) in the case of Area = 0.50 cm<sup>2</sup>.

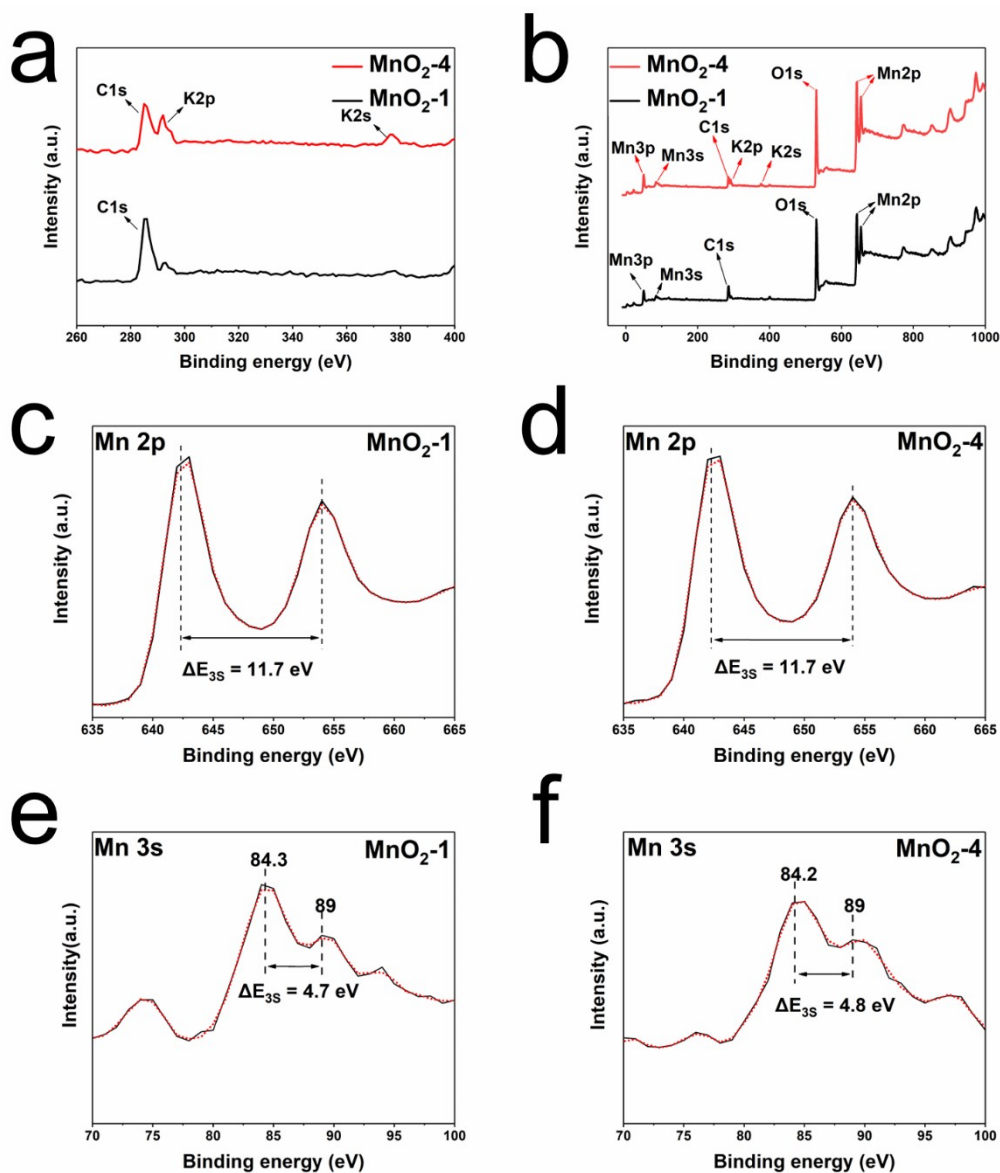


**Fig. S5** XRD patterns (a) and SEM images (b and c) of MnO<sub>2</sub>-80°C-1, MnO<sub>2</sub>-80°C-2.



**Fig. S6** The drying rate curves (a) in the case of Area = 0.13 cm<sup>2</sup>, XRD patterns (b) and SEM images (c) of MnO<sub>2</sub>-120°C.





**Fig. S7** (a) XPS spectra of C 1s, K 2p and K 2s for MnO<sub>2</sub>-1 (δ-MnO<sub>2</sub>) and MnO<sub>2</sub>-4 (α-MnO<sub>2</sub>). XPS survey spectra of MnO<sub>2</sub>-1 (δ-MnO<sub>2</sub>) and MnO<sub>2</sub>-4 (α-MnO<sub>2</sub>) (b). Mn 2p XPS spectra of the MnO<sub>2</sub>-1 (c) and MnO<sub>2</sub>-4 (d). Mn 3s XPS spectra of the MnO<sub>2</sub>-1 (e) and MnO<sub>2</sub>-4 (f).

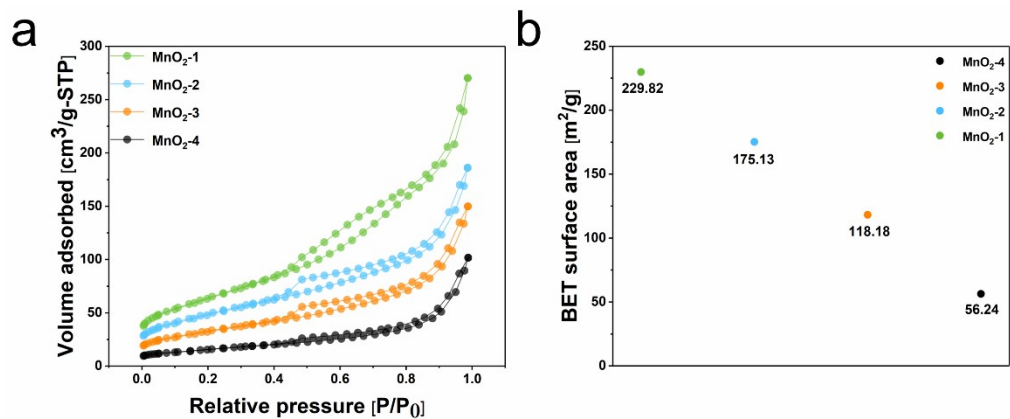


$\delta\text{-MnO}_2$

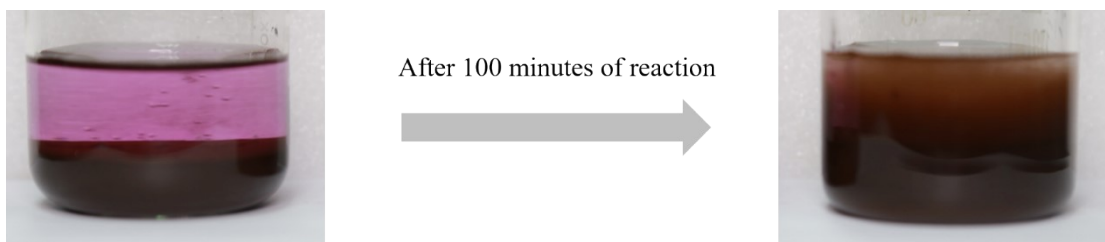


$\alpha\text{-MnO}_2$

**Fig. S8** Picture of synthesized  $\text{MnO}_2\text{-1}$  ( $\delta\text{-MnO}_2$ ) (left) and  $\text{MnO}_2\text{-4}$  ( $\alpha\text{-MnO}_2$ ) (right).



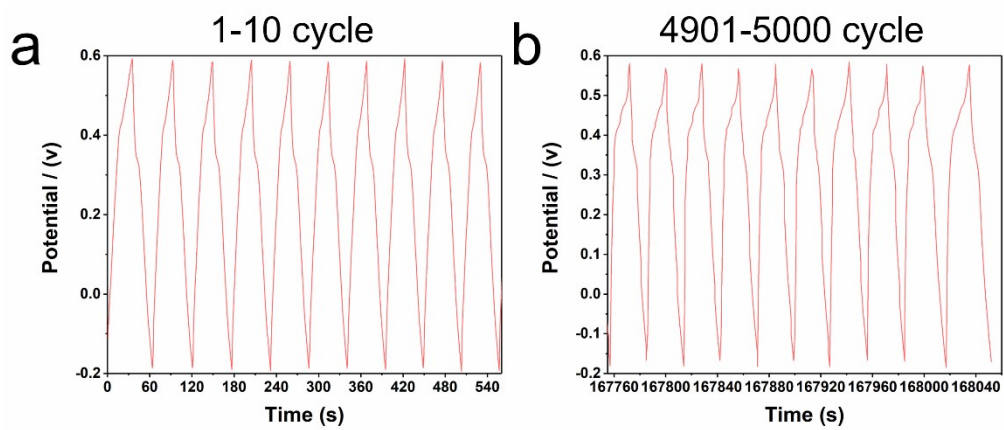
**Fig. S9** Brunauer-Emmett-Teller (BET) analysis of MnO<sub>2</sub>-1, MnO<sub>2</sub>-2, MnO<sub>2</sub>-3, and MnO<sub>2</sub>-4.



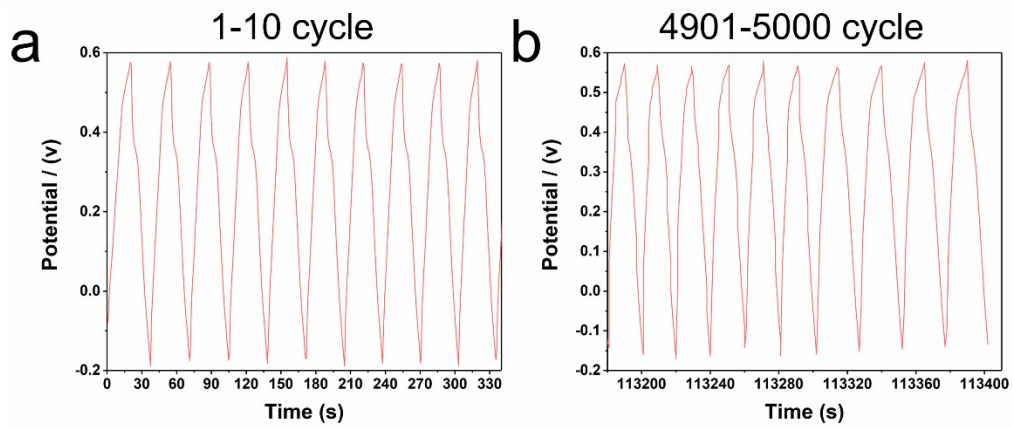
**Fig. S10** Photo of solution after 100 minutes of thermal reaction.

**Table S1** Comparison of specific capacitance between MnO<sub>2</sub> based materials

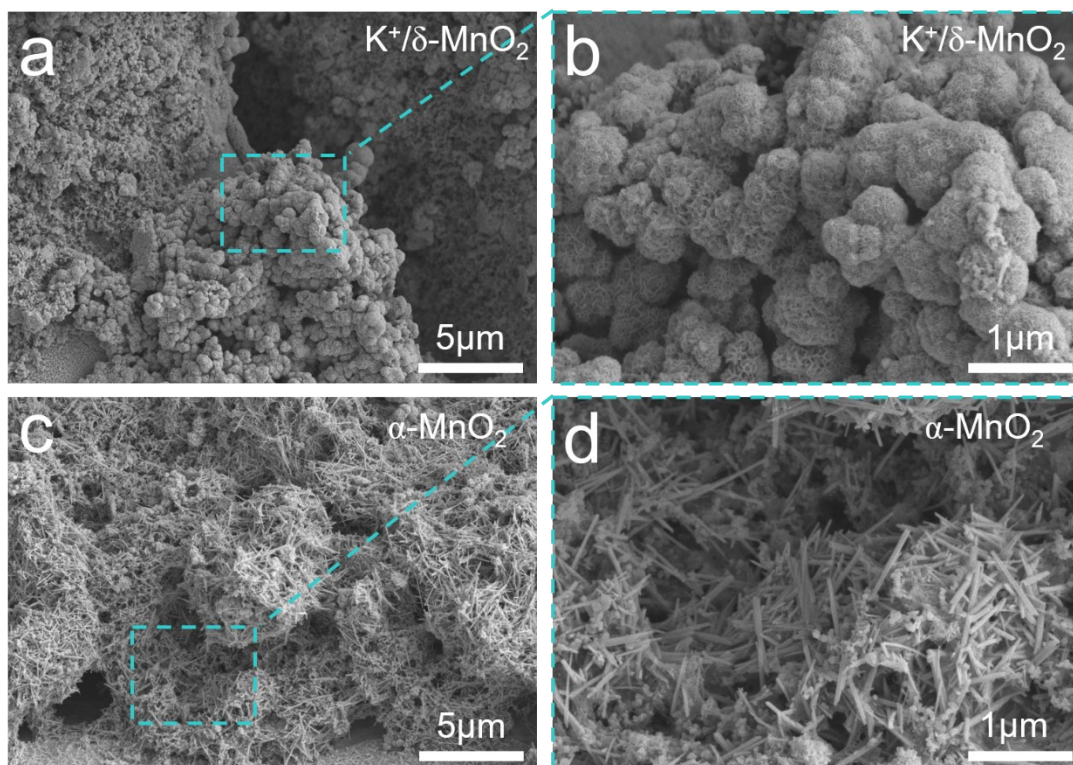
Electrode	Current density (A g <sup>-1</sup> )	Specific capacitance (F g <sup>-1</sup> )	Electrolyte	Ref.
$\delta$ -MnO <sub>2</sub> + $\alpha$ -MnO <sub>2</sub>	1.8	178	LiCl	1
Co <sub>9</sub> S <sub>8</sub> @ MnO <sub>2</sub>	1	711.5	NaSO <sub>4</sub>	2
$\delta$ -MnO <sub>2</sub> @ $\alpha$ -MnO <sub>2</sub>	0.25	206	Na <sub>2</sub> SO <sub>4</sub>	3
MnO <sub>x</sub> @rGO	1	405	KOH	4
Fe: MnO <sub>2</sub>	2	173	Na <sub>2</sub> SO <sub>4</sub>	5
K <sub>0.17</sub> MnO <sub>2</sub>	1	206	K <sub>2</sub> SO <sub>4</sub>	6
$\alpha$ -MnO <sub>2</sub>	0.5	535	KOH	7
MnO <sub>2</sub>	3	304	Na <sub>2</sub> SO <sub>4</sub>	8
MnO <sub>2</sub> -TEA	1	417.5	Na <sub>2</sub> SO <sub>4</sub>	9
$\delta$ -MnO <sub>2</sub>	1	565	KOH	This work



**Fig. S11** The cycling tests of  $K^+/\delta\text{-MnO}_2$  electrode at the  $10 \text{ A g}^{-1}$ .

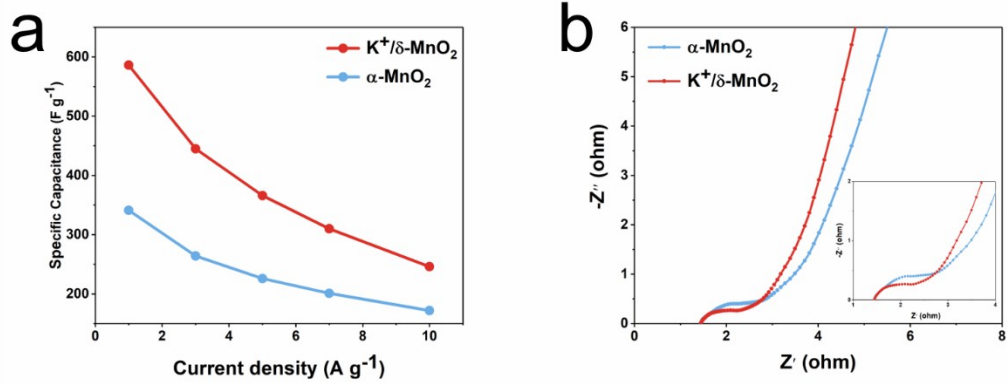


**Fig. S12** The cycling tests of  $\alpha$ - $\text{MnO}_2$  electrode at the  $10 \text{ A g}^{-1}$ .



**Fig. S13** SEM images of the (a, b)  $K^+/\delta\text{-MnO}_2$  electrode and (c, d)  $\alpha\text{-MnO}_2$  electrode after 5000 cycles at  $10 \text{ A g}^{-1}$ .





**Fig. S14** (a) specific capacitance of K<sup>+</sup>/δ-MnO<sub>2</sub> and α-MnO<sub>2</sub> at a series of current densities; (b) EIS curves of K<sup>+</sup>/δ-MnO<sub>2</sub> and α-MnO<sub>2</sub>.

## References

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