Electronic Supplementary Information for

Manganese Oxides Transformed from Orthorhombic Phase to Birnessite with Enhanced Electrochemical Performance as Supercapacitor Electrodes

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Experimental

Chemicals: Ammonium persulfate ($(NH_4)_2S_2O_8$), Manganese sulfate monohydrate ($Mn_2SO_4 \cdot H_2O$), Formaldehyde solution (37 wt %), Tetrathyl orthosilicate and Pluronic F-127 were purchased from SIGMA-ALDRICH. Phenol (AR grade) was supplied by MERCK Pty. All these chemicals were used as received without further purification.

Sample preparation

Orthorhombic γ-MnO_2. The urchin-like orthorhombic γ-MnO_2 were synthesized by a hydrothermal method according to a previous literature with a little modification.[1] Typically, 1.3522 g manganese sulfate monohydrate and 1.8256 g ammonium persulfate were dissolved in 100 mL deionized water under magnetic stirring at room temperature for 20 minutes to form a homogeneous solution. Then this solution was transferred into a 100 mL Teflon-lined stainless steel autoclave, which was sealed and placed into an oven, maintaining at 100 °C for 10 h, followed by natural cooling to room temperature. The obtained brown-black precipitates were rinsed with deionized water and ethyl alcohol several times and then dried in a vacuum oven at 60 °C for 12 h.

Phenolic resin. The phenolic resin was prepared following a literature method with some modification.[2] In a typical procedure, 10.0 g phenol was melted at 40 °C in a flask and mixed with 2.13 g NaOH aqueous solution (5 mol L^{-1}) under magnetic stirring for 20 min. Then 16.30 mL formaldehyde solution (37 wt %) was added dropwise at 45 °C, followed by increasing the temperature to 75 °C and keeping for 1 h. The mixture was cooled down to room temperature with the PH value adjusted to about 7.0 by HCl solution (1 mol L^{-1}). The final product was obtained by removing water via vacuum evaporation at 45 °C. 10.0 g of the as-prepared phenolic resin was dissolved in 40.0 g ethanol to make a 20 wt % phenolic resin / ethanol solution.

Mesoporous carbon. The ordered mesoporous carbon was also prepared according to a previous report.[2] Typically, 0.8 g triblock copolymer F127 was mixed with 0.5 g HCl solution (0.2 mol L^{-1}) in 8.0 g ethanol under magnetic stirring at 40 °C for 1h to form a clear solution. Then, 1.04 g Tetrathyl orthosilicate and 2.5 g 20 wt % phenolic resin / ethanol prepared above were added in sequence. After stirring for 2 h, the mixture was transferred into a dish, which was placed in a fume hood for 6 h at room temperature to evaporate ethanol, followed by thermopolymerization at 100°C in an oven for 24 h. The as-made product was taken off and transferred into a tubular furnace, where calcination was carried out at 350 °C for 3 h and then at 900 °C for 2 h under Ar flow to get mesoporous carbon-silica nanocomposites. The heating rate was 2 °C min^{-1} below 600 °C and 5 °C min^{-1} above 600 °C. The ordered mesoporous carbon was obtained by removing the silicon dioxides in a NaOH aqueous solution (2 mol L^{-1}) and rinsing with copious deionized water and ethanol, followed by drying at 60 °C in a vacuum oven for 12 h.

Comparison experiments. To investigate the influence of the mass ratio of orthorhombic γ-MnO_2 on the morphology and electrochemical performance of the composite, comparisons were made by decreasing the mass of orthorhombic γ-MnO_2 to 0.2 g and 0.1 g without changing other parameters. Also, to understand the phase transformation mechanism from birnessite to orthorhombic, comparative experiments have been conducted: (1) Orthorhombic MnO_2 was treated in 2 M NaOH aqueous solution at room temperature for 12 h; (2) Orthorhombic MnO_2 was calcined at 900 °C under Ar flow for 2 h and then treated in 2 M NaOH aqueous solution at room temperature for 12 h; (3) Manganese oxides/carbon composite were prepared through the same procedure as that of birnessite manganese oxide/carbon composites with 0.2 g orthorhombic MnO_2 but without the addition of TEOS; (4) Manganese oxides were prepared through the same procedure as that of birnessite manganese oxide/carbon composites with 0.2 g urchin-like MnO_2 but without the addition of phenolic resin. All the resulting samples were rinsed with deionized water and ethyl alcohol several times and then dried at 60 °C in a vacuum oven for 12 h.

Physical characterization

The crystallographic structures of the synthesized materials were determined by a powder X-ray diffraction system (XRD, Rigaku D/MAX 2550V) equipped with Cu Kα radiation (λ=0.15406 nm). The morphologies of the materials were characterized by field-emission scanning electron microscopy (FESEM, HITACHI S4800) and high-resolution transmission electron microscopy (HRTEM, JZM-2100). Raman spectra were measured on an Iuvia Refl Raman spectrometer using a 531.4 nm laser as the excitation source. Nitrogen adsorption / desorption isotherms were measured on a Micromeritics ASAP-2010 surface area analyzer. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas with the adsorption data, and the pore volumes and pore size distributions were obtained using the Barrett-Joyner-Halenda (BJH) model. The MnO_2 content in the nanocomposites was determined by thermogravimetric analysis (TGA, NETZSCH STA 449F3) from room temperature to 800 °C in air at a heating rate of 40/10.0 (K/min).

Electrochemical measurement

The specific capacitance (C, F g^{-1}) of the electrode materials can be calculated from the galvanostaic discharge according to the following equation:

$$C = (I\,\Delta t) / (m\,\Delta V) \qquad \text{(S1)}$$

Where I is the discharge current (A), Δt is the discharge time (s), m is the mass of the electroactive materials in the working electrodes (g) and ΔV is the potential range in the discharge process (V).

The specific capacitance (C, F g^{-1}) of the electrode materials can also be calculated based on the CV curves according to the following equation:

$$C = (\int I\,dV) / (\upsilon\, m\, V) \qquad \text{(S2)}$$

Where I is the response current density (A g^{-1}), V is the potential (V), υ is the potential scan rate (mV s^{-1}), and m is the mass of the electroactive materials in the working electrodes (g).

The electrochemical performance of solid-state asymmetric supercapacitors (ASC) was evaluated by a two-electrode testing system using manganese oxides as positive electrode, mesoporous carbon as negative electrode, and Na_2SO_4/PVA as electrolyte, respectively. To achieve the maximum performance of the assembled ASC, we balanced the capacity (Q) of the positive and negative electrode based on Equation S3, which is associated with capacitance (C), potential window (ΔV) and mass of active materials (Equation S4).

$$Q_- = Q_+ \qquad \text{(S3)}$$

$$Q = C \times \Delta V \times m \qquad \text{(S4)}$$

Combining Equation S3 and S4, the mass ratio of manganese oxides to mesoporous carbon on positive and negative electrodes respectively should satisfy the Equation S5.

$$m_+/m_- = (C_- \times \Delta V_-) / (C_+ \times \Delta V_+) \qquad \text{(S5)}$$

Energy density (E, Wh kg^{-1}) and power density (P, W kg^{-1}) are two important parameters for evaluating the electrochemical performance of supercapacitors, terms which can be calculated using Equation (S6) and Equation (S7) below:

$$E = CV^2 / 2 \qquad \text{(S6)}$$

$$P = E / t \qquad \text{(S7)}$$

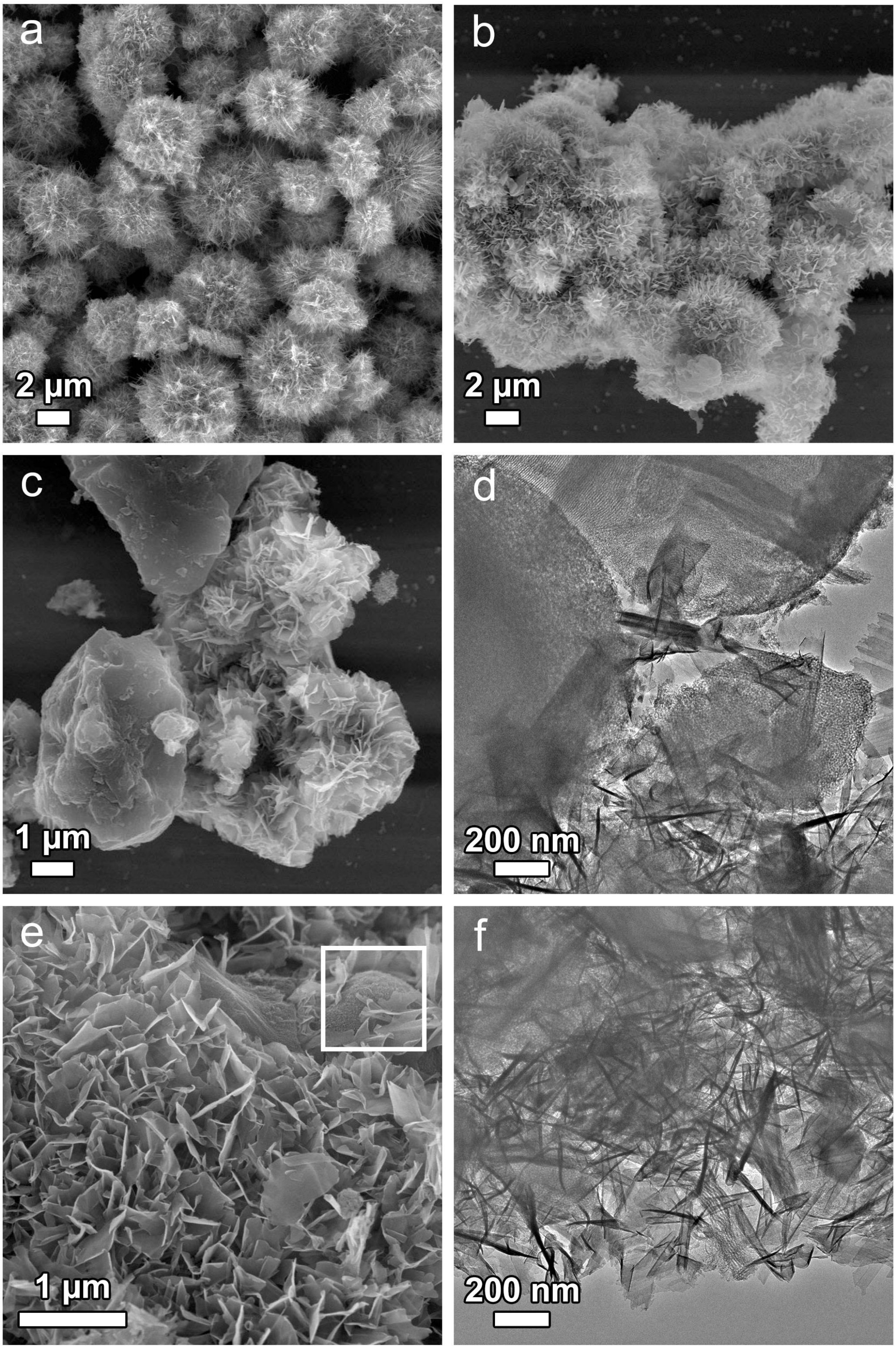

Fig. S1 (a) Low-magnification SEM image of pristane orthorhombic γ-MnO_2. (b) Low-magnification SEM image of the transformed birnessite δ-MnO_2/carbon (Mn/C63). SEM and TEM images of Mn/C18 (c, d) and Mn/C30 (e, f).

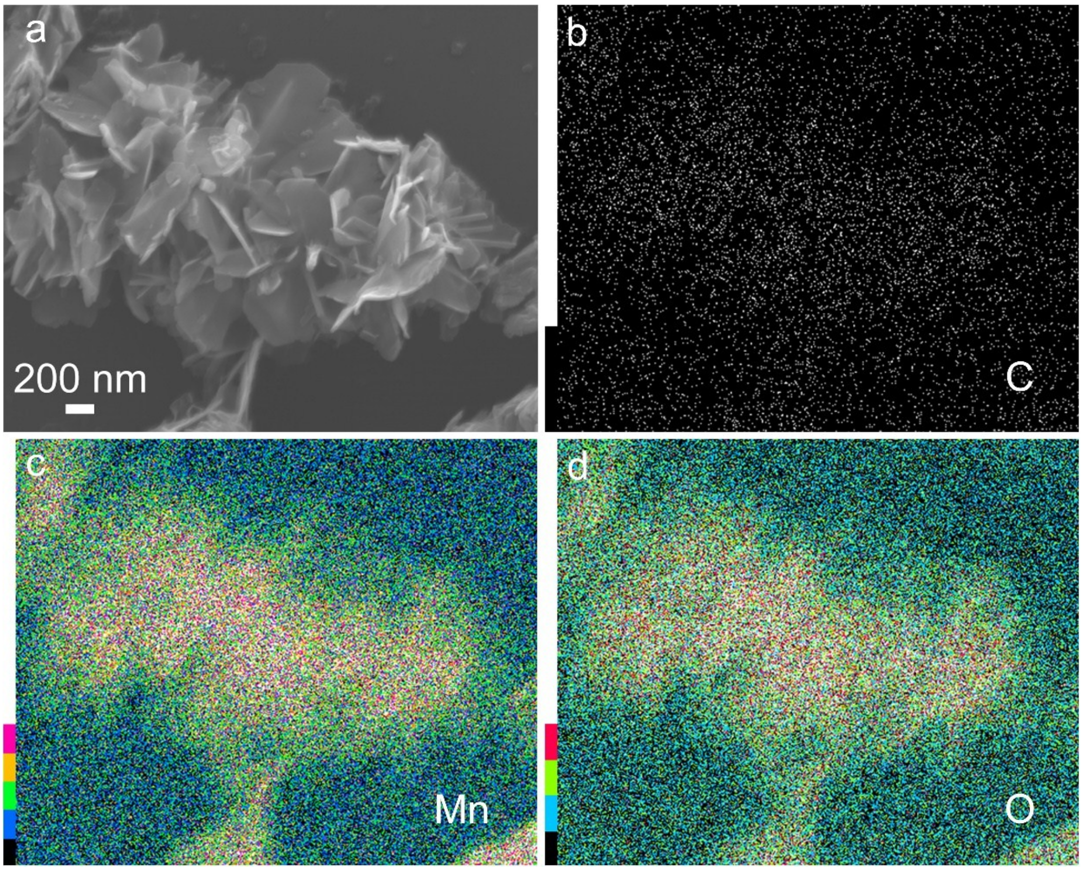

Fig. S2 (a) SEM image of Mn/C63 on Si substrate. (b, c, d) EDS mapping of C, Mn and O elements.

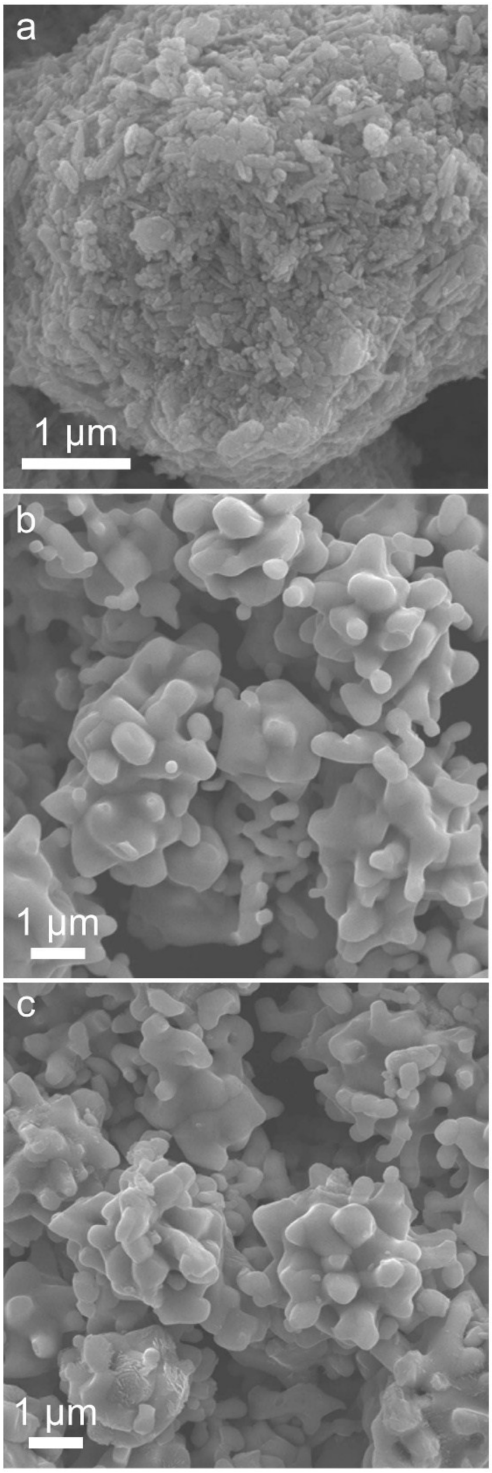

Fig. S3 SEM images of pristine MnO_2 after (a) soaking in 2 M NaOH solution for 12 h, (b) calcination at 900 °C under Ar flow for 2 h, and (c) calcination at 900 °C under Ar flow for 2 h followed by soaking in 2 M NaOH solution for 12 h.

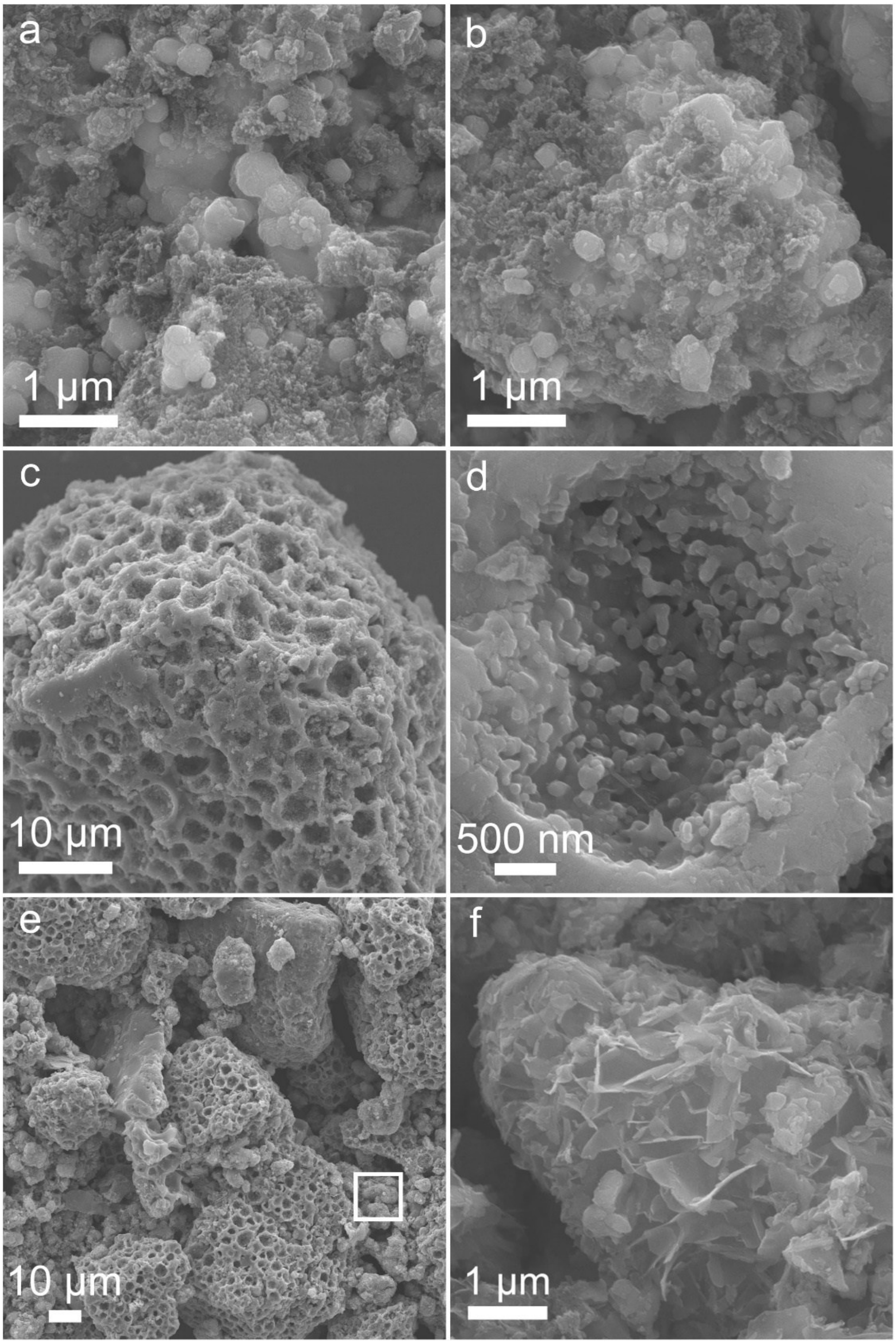

Fig. S4 SEM images of pristine MnO_2 after (a) calcination with only phenolic resin, (b) calcination with only phenolic resin followed by soaking in NaOH solution, (c) calcination with only SiO_2, and (e) calcination with only SiO_2 followed by soaking in NaOH solution. (d) and (f) are the amplified SEM images of (c) and (e), respectively.

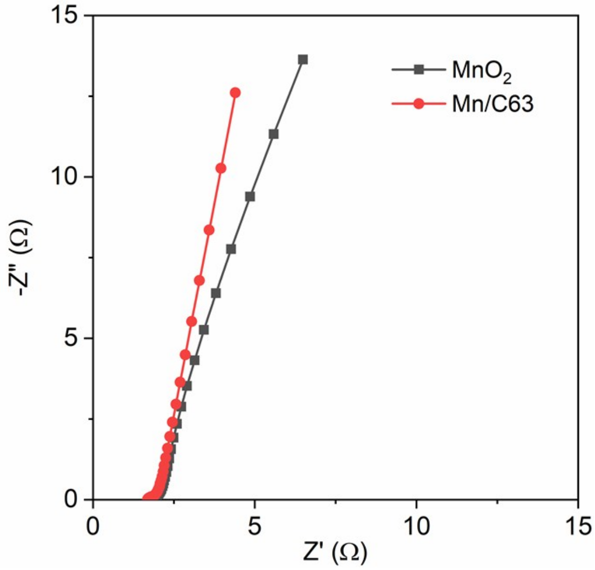

Fig. S5 EIS comparison of pristine MnO$_2$ and Mn/C63.

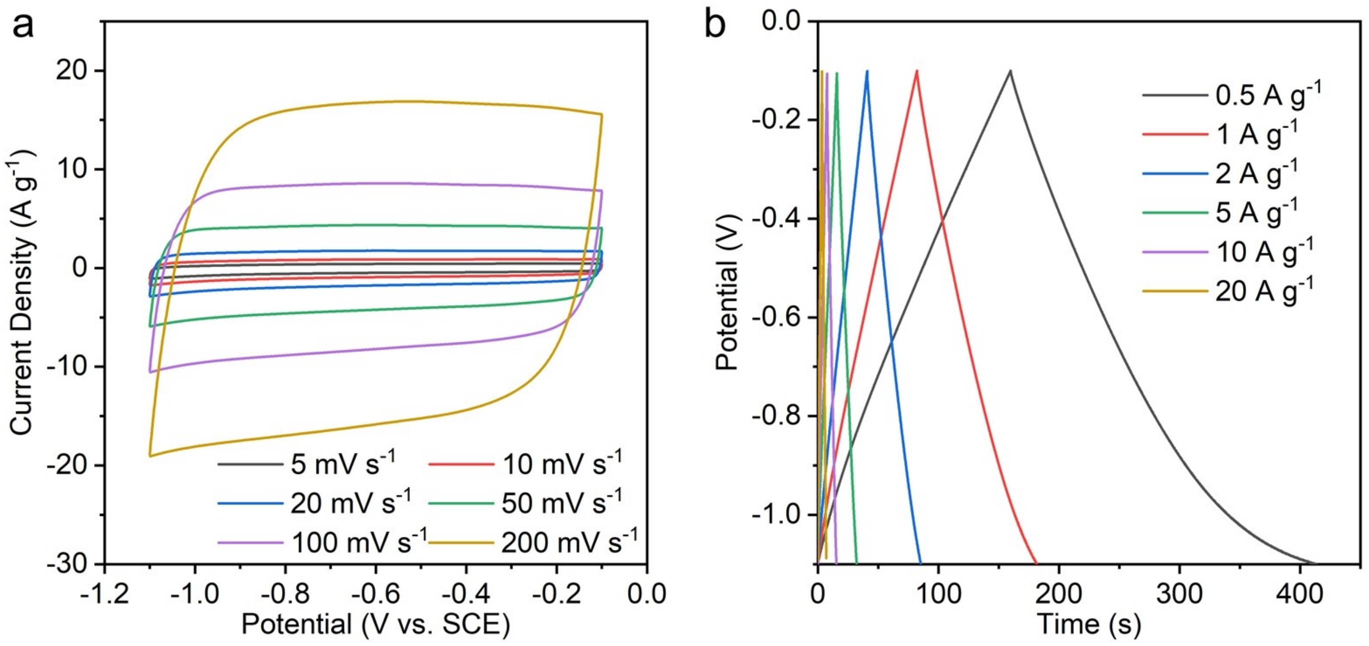

Fig. S6 (a) CV curves at different scan rates and (b) GCD curves at different current densities of mesoporous carbon in 1 M Na_2SO_4.

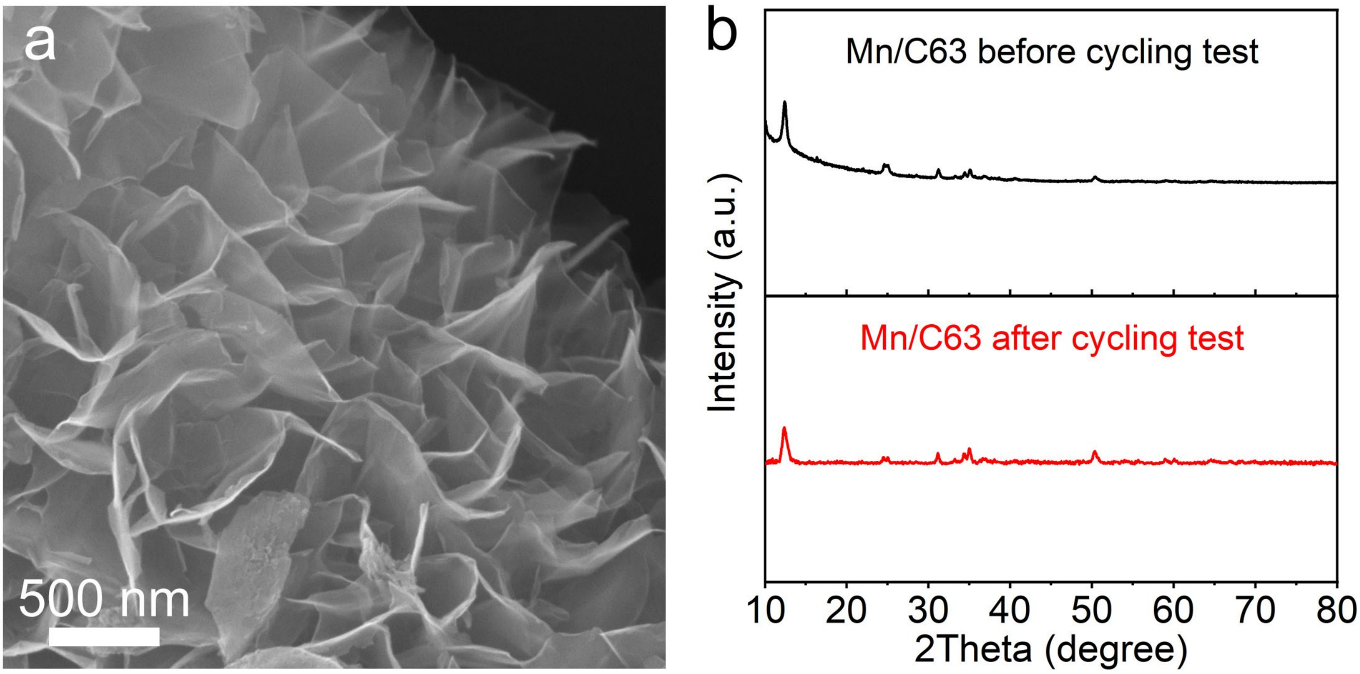

Fig. S7 SEM image (a) and XRD pattern (b) of birnessite δ-MnO_2/carbon composite after 2000 CV cycles at a scan rate of 100 mV s^{-1}.

Reference

1. M. Zhu, Y. Hu, Y. Li, H. Jin and Z. Zhu, *Phys. Status Solidi C*, 2012, **9**, 122-127.

2. R. Liu, Y. Shi, Y. Wan, Y. Meng, F. Zhang, D. Gu, Z. Chen, B. Tu and D. Zhao, *J. Am. Chem. Soc.*, 2006, **128**, 11652-11662.