Electronic Supporting Information

Charge storage performances and mechanisms of MnO_2 nanospheres, nanorods, nanotubes and nanosheets

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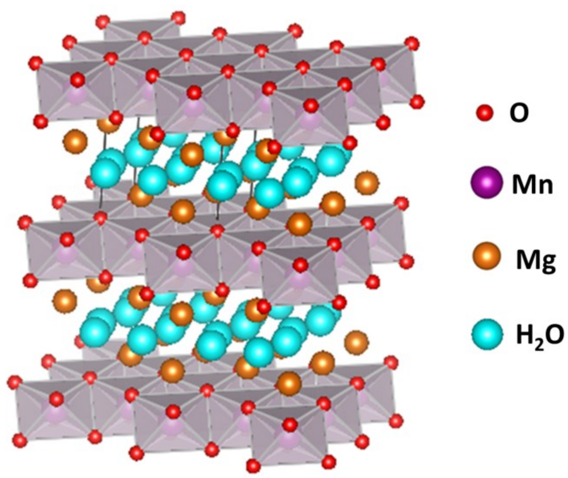

Fig. S1 2D layered structure of birnessite-type MnO_2 nanosheets intercalated with metal ions (K^+ or Mg^{2+}) and water molecules.

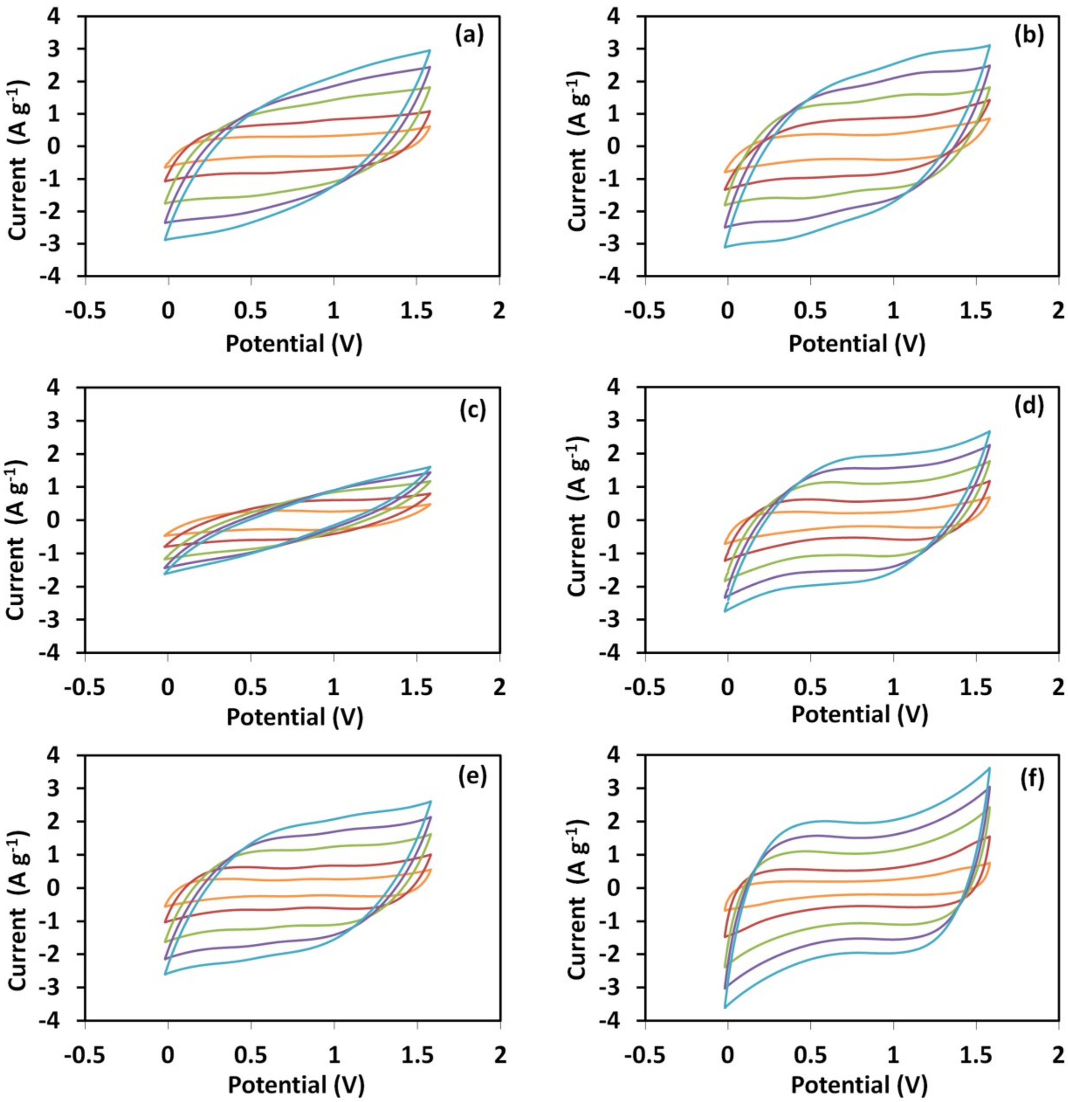

Fig. S2 CV curves of the as-assembled MnO_2 supercapacitors at different scan rates: (a) α-MnO_2 nanospheres, (b) δ-MnO_2 nanosheets, (c) as-calcined nanosheets, (d) α-MnO_2 nanorods, (e) as-calcined nanorods, and (f) α-MnO_2 nanotubes. Note, 10 mV s^{-1} (orange), 25 mV s^{-1} (brown), 50 mV s^{-1} (green), 75 mV s^{-1} (purple), and 100 mV s^{-1} (blue).

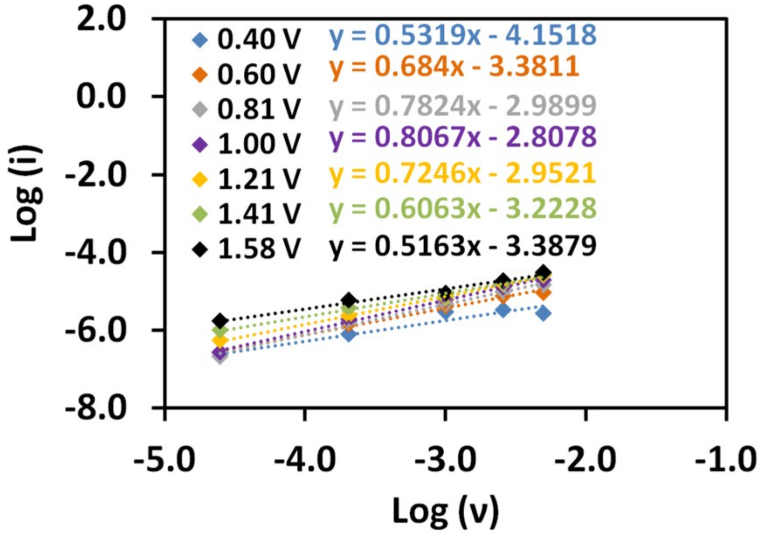

Fig. S3 Power's law dependence of log(i) vs. log(v) of δ-MnO_2 nanosheet supercapacitor.

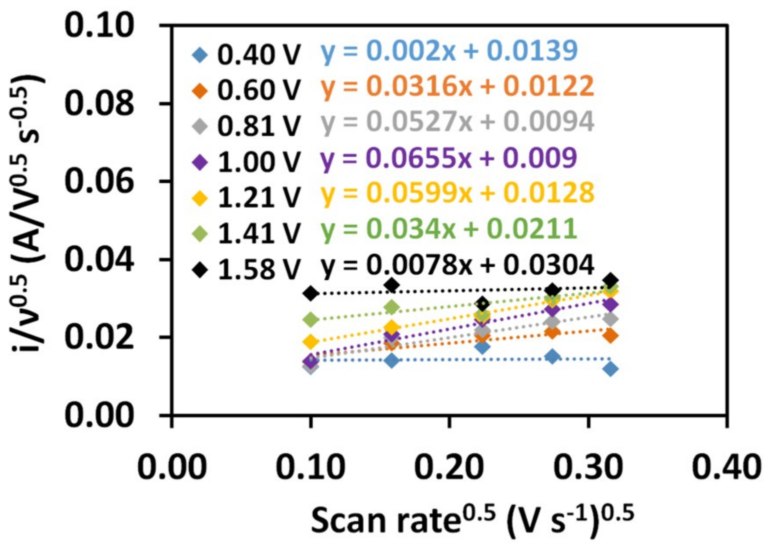

Fig. S4 The plots of $v^{1/2}$ vs. $i(V)/v^{1/2}$ of δ-MnO_2 nanosheet supercapacitor.

The calculation details of relaxation time constant (τ_0)

The relaxation time constant can be calculated by the following eq. (S1):

$$\tau_0 = 1/2\pi f_0 \quad \text{(S1)}$$

where f_0 is the resonance frequency determined from the intersection of $|P|/|S|$ and $|Q|/|S|$ plot, $|S|$ is the complex power obtained from active power or real part ($|P|$) and reactive power or imaginary part ($|Q|$) as shown in eq. (S2).

$$S(\omega) = P(\omega) + jQ(\omega) \quad (S2)$$

The $P(\omega)$ and $Q(\omega)$ can be calculated from eq. (S3) and (S4), respectively

$$P(\omega) = \omega C''(\omega)|\Delta V_{rms}|^2 \quad (S3)$$

$$Q(\omega) = -\omega C'(\omega)|\Delta V_{rms}|^2 \quad (S4)$$

where $|\Delta V_{rms}|^2 = \Delta V_{max}/\sqrt{2}$ with V_{max} being the maximum amplitude of the ac signal, $C'(\omega)$ is the real part of the complex capacitance, and $C''(\omega)$ is the imaginary part of the complex capacitance. The $C'(\omega)$ and $C''(\omega)$ are given by following equation:

$$C'(\omega) = -Z''(\omega)/\omega\ |Z(\omega)|^2 \quad (S5)$$

$$C''(\omega) = Z'(\omega)/\omega\ |Z(\omega)|^2 \quad (S6)$$

where $Z'(\omega)$ and $Z''(\omega)$ are the real and imaginary parts of the complex impedance ($Z(\omega)$), respectively and $\omega = 2\pi f$.

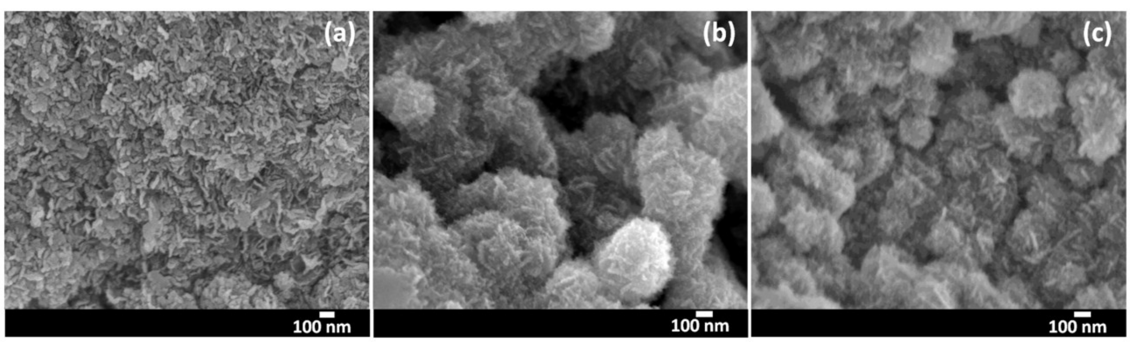

Fig. S5 FE-SEM images of (a) MnO_2 nanosheet powder, (b) MnO_2 nanosheets on positive electrode after cycling stability, and (c) MnO_2 nanosheets on negative electrode after cycling stability.

Table S1 Elemental composition in Mg-birnessite that coated on CFP materials measured by X-ray fluorescence spectroscopy.

Elements	Concentration
Mn	14.9%
K	2.18%
Mg	1.26%
Si	695 ppm
F	464 ppm
S	312 ppm
Ca	40.3 ppm