

# Supporting Information

## Materials and Methods

### Fabrication of CNT-sponge and MnO<sub>2</sub>-CNT-sponge electrodes

To prepare CNT ink, single walled carbon nanotubes (SWNTs, Carbon Solution Inc.) and sodium dodecylbenzenesulfonate (SDBS) (Sigma Aldrich) were dispersed in DI water (Milli Q, 18.2 MΩ) at concentration of 0.8 mg/mL and 10 mg/mL, respectively. The solution was ultrasonicated (Brason 3510) at room temperature for 8 hours before using. A macroporous commercially available sponge was cleaned by water and acetone for several times, followed by completely drying and cutting into small pieces with thickness of ~ 1 mm and width by length of 1×2 cm<sup>2</sup>. All sponge pieces were dipped into CNT ink by a simple “dipping and drying” method. Upon drying at 120°C in oven for 1 hour, the sponges were washed with abundant amount of water to remove the surfactant. After that, the sponges were put in a vacuum oven at 120°C for three hours to remove water completely. The sheet resistance of the conductive CNT-sponge was measured by a four-point sheet resistance meter (EDTM). The galvanostatic electrochemical deposition of MnO<sub>2</sub> was performed using a solution of 20 mM Mn(NO<sub>3</sub>)<sub>2</sub> and 100 mM NaNO<sub>3</sub> (Sigma Aldrich). The three electrode configuration was used for the electrodeposition (CH Instruments, electrochemical workstation, Model 660D), with Ag/AgCl as reference electrode (Bio-logic), Pt wire as counter electrode (Bio-logic), and conductive CNT-sponge or platinum foil (0.25 mm thick, 25mm×25mm, Sigma Aldrich) as working electrode. A very small current density of 500 μA/cm<sup>2</sup> was used for the electrodeposition. The deposited mass of MnO<sub>2</sub> can be controlled by deposition time and the deposition area is 1×1 cm<sup>2</sup>. The mass differences were measured by microbalance (Mettler Toledo XP26, resolution of 1 μg) before and after CNT loading and MnO<sub>2</sub> deposition.

### Microscopic characterization

Supercapacitor electrodes based on MnO<sub>2</sub>-CNT-sponge and CNT-sponge have been characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) surface area measurements. The microstructure of the samples was characterized by SEM (Quanta 600 FEG, FEI) and TEM (Titan 80-300 kV (ST) TEM, FEI) equipped with X-ray energy dispersive spectroscopy (EDS). The crystal structure of MnO<sub>2</sub> was identified by XRD (D8 Advance bulk power XRD, Bruker). BET surface area measurement (ASAP 2420, surface area and pore size analyzer, Micromeritics) was conducted by Argon adsorption and desorption at bath temperature of -185.86 °C. In order to get enough powder for XRD and BET analyses, MnO<sub>2</sub> was deposited on platinum foil for extended times (multiple 10-hour runs).

### Cell assembly of supercapacitor devices

Two identical pieces of MnO<sub>2</sub>-CNT-sponge (each with area of 1×1 cm<sup>2</sup>) were sandwiched by a monolayer polypropylene separator (25μm thick, Celgard 3501), and placed in a coin cell (CR2032, MTI),

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with 1 M Na<sub>2</sub>SO<sub>4</sub> (Sigma Aldrich) in DI water as electrolyte. The MnO<sub>2</sub>-CNT-sponge works as both electrodes and current collectors. The same process was done for CNT-sponge devices.

## Electrochemical characterization

All electrochemical measurements were carried out by both two- and three-electrode configurations using Model 660D electrochemical workstation (CH Instruments). For the three-electrode configuration, the MnO<sub>2</sub>-CNT-sponge or CNT-sponge acts as working electrode, Ag/AgCl as reference electrode, and Pt wire as counter electrode. For the two-electrode configuration, an assembled coin cell was used for the measurements. Cyclic voltammogram (CV), galvanostatic charge-discharge (CD) and electrochemical impedance spectroscopy (EIS) were performed to evaluate the electrochemical performance of sponge supercapacitors. The CVs were tested in a voltage window between 0 and 1 V at a wide range of scan rates, ranging from 1 mV/s to 200 V/s. The CDs were measured in the same voltage window under a wide range of current densities, from 1 A/g to 100 A/g. The EIS was performed in the frequency range from 100 kHz to 10 mHz at open circuit voltage by applying a 5 mV signal. All measurements were taken using 1 M Na<sub>2</sub>SO<sub>4</sub> at room temperature.

## Calculation of specific capacitance, areal capacitance and specific energy and power

1. The specific capacitance with respect to three-electrode configuration is derived from cyclic voltammogram based on equation 1:

$$C_s = \frac{Q_{(CNT + MnO_2)} - Q_{(CNT)}}{\Delta V \cdot m} \quad (1)$$

where  $C_s$  is the specific capacitance,  $Q$  is the charge obtained from the discharge scan of the CV curves based on MnO<sub>2</sub>-CNT-sponge and CNT-sponge electrodes,  $\Delta V$  is the voltage range (1V), and  $m$  is the mass of MnO<sub>2</sub> on MnO<sub>2</sub>-CNT-sponge electrode. Here, the mass loading of CNTs on MnO<sub>2</sub>-CNT-sponge electrode and CNT-sponge electrode are the same.

2. The specific capacitance with respect to two-electrode full cell is derived from cyclic voltammogram based on equation 2:

$$C_s = 2 \times \frac{Q_{(CNT + MnO_2)} - Q_{(CNT)}}{\Delta V \cdot m} \quad (2)$$

where  $C_s$  is the specific capacitance,  $Q$  is the charge got from the discharge scan of the CV curve based on MnO<sub>2</sub>-CNT-sponge and CNT-sponge full cell device,  $\Delta V$  is the voltage range, and  $m$  is the mass of MnO<sub>2</sub> per MnO<sub>2</sub>-CNT-sponge electrode. Here, the mass loadings of CNTs on both MnO<sub>2</sub>-CNT-sponge device and CNT-sponge device are kept the same.

3. Specific energy and specific power derived from galvanostatic charge-discharge of two-electrode full cell are calculated from the following equations:

$$E = \frac{1}{2} C \cdot (\Delta V)^2 / M \quad (3)$$

where  $E$  is the specific energy,  $C$  is the measured capacitance,  $\Delta V$  is the voltage range and  $M$  is the mass of active material on MnO<sub>2</sub>-CNT-sponge electrodes.

$$P = \frac{(\Delta V)^2}{4RM} \quad (4)$$

where  $P$  is the specific power,  $\Delta V$  is the voltage range,  $R$  is the internal resistance obtained from voltage drop at the beginning of discharge (equation 5), and  $M$  is the mass of active material on MnO<sub>2</sub>-CNT-sponge electrodes.

$$R = \frac{V_{IR}}{2I} \quad (5)$$

4. The average discharge current is calculated based on the following equation (equation 6):

$$I_d = \frac{A}{2\Delta V} = \frac{\int_0^1 I dV}{2 \Delta V} \quad (6)$$

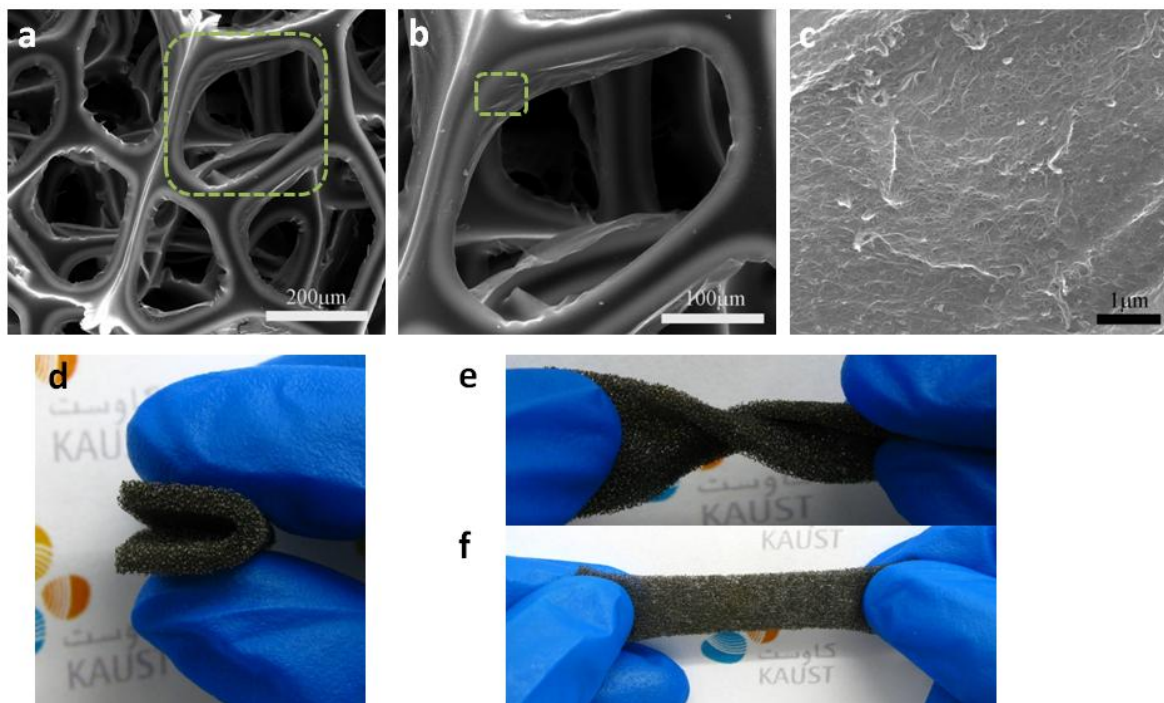
where  $A$  is the area of the CV curve integrated from 0 to 1 V, and  $\Delta V$  is the voltage range (1 V).

5. The mean areal cell capacitance ( $C_m$ ) is obtained from the slope of the straight line (red line) in Figure 3c, which can be calculated from the following equation (equation 7):

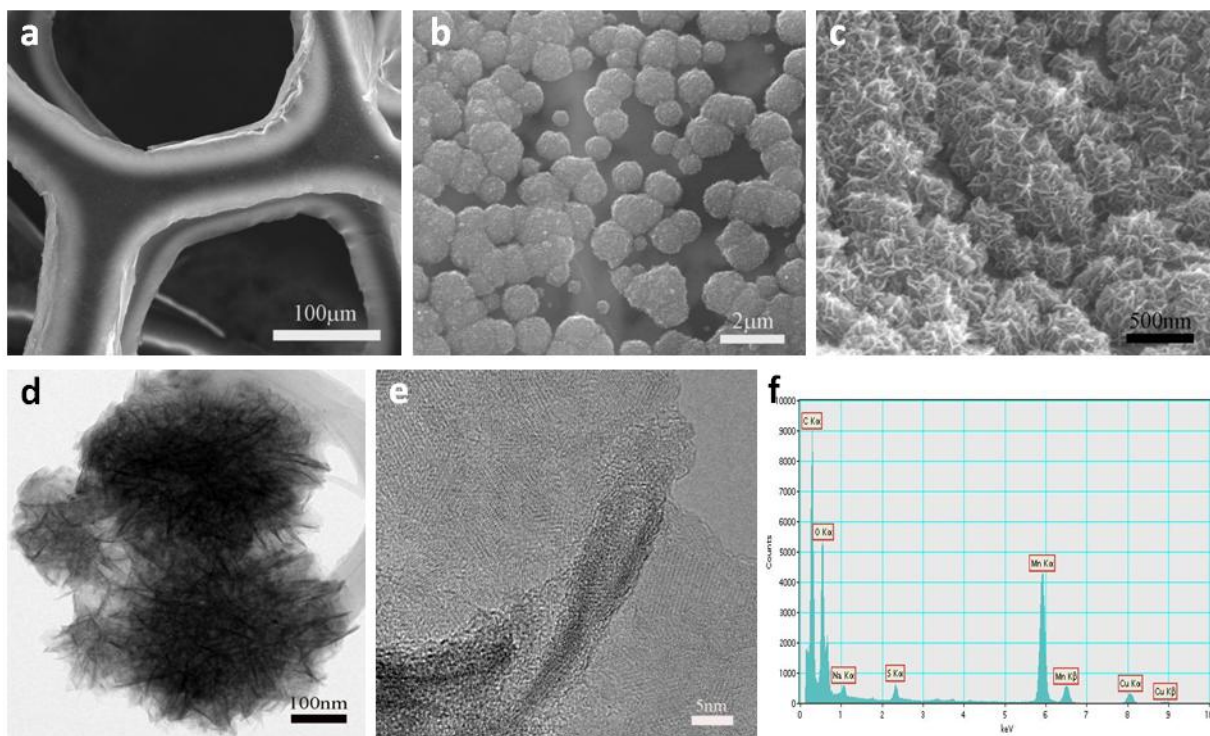
$$C_m = slope = \frac{\Delta I}{2\Delta s} \quad (7)$$

where  $\Delta I$  and  $\Delta s$  are the difference of discharge currents and scan rates of two points picked on the straight line (red line), and the factor 2 refers to the total area of the positive and negative electrodes, which is 2 cm<sup>2</sup> in all full cell devices.

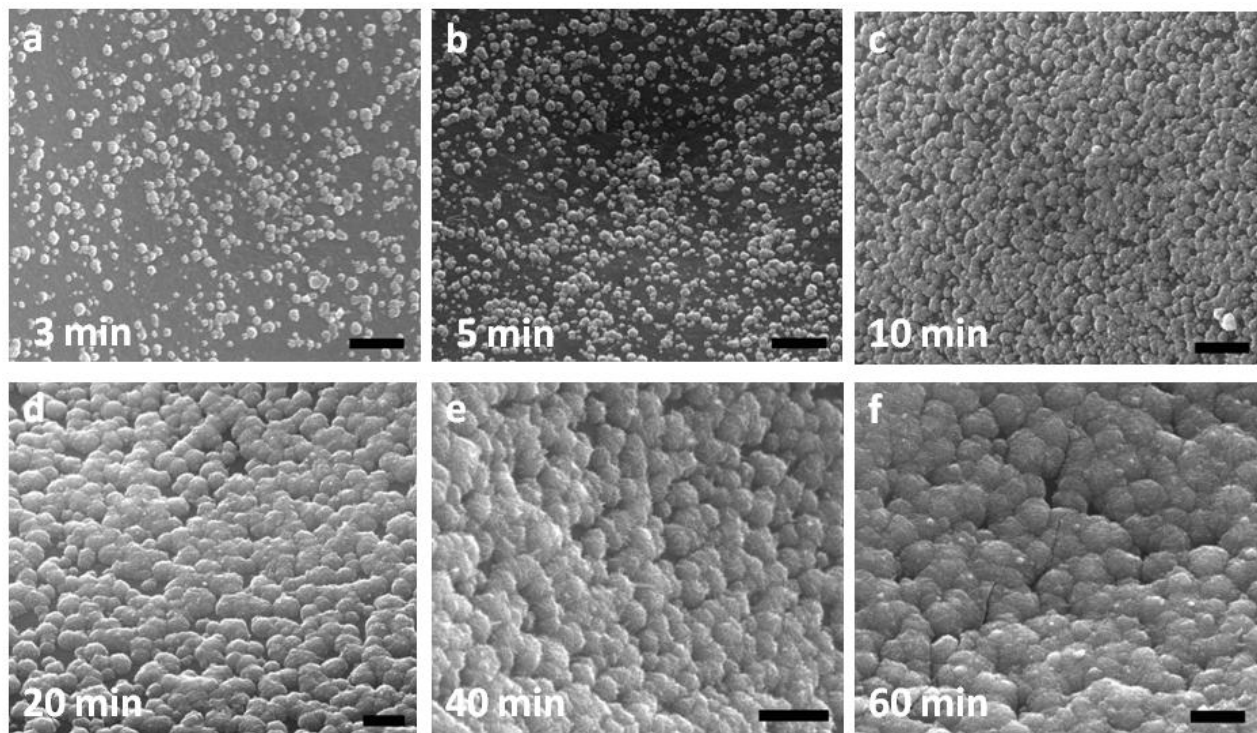
## Supporting Figures



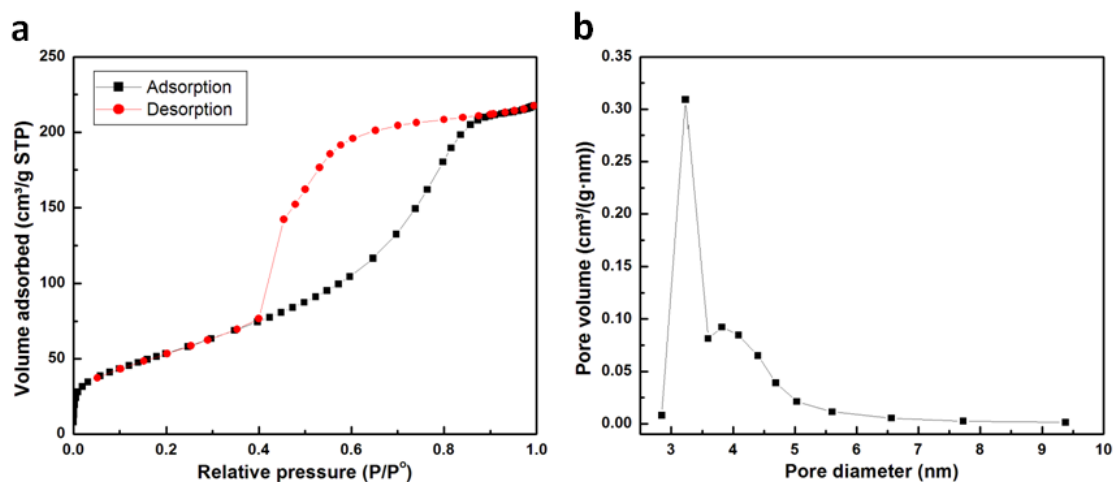
**Figure 1S.** (a, b, and c) Macroporous CNT-sponge in low, medial and high magnification, respectively; The CNT-sponge can be folded (d), twisted (e), and stretched (f) without any deformation.



**Figure 2S.** (a) SEM image of the skeleton of MnO<sub>2</sub>-CNT-sponge; (b and c) low and high magnification SEM images of MnO<sub>2</sub> nanoparticles deposited on CNT-sponge, respectively; (d and e) low and high resolution TEM of MnO<sub>2</sub> flower-like nanoparticles, respectively; (f) EDS of MnO<sub>2</sub> obtained from TEM.

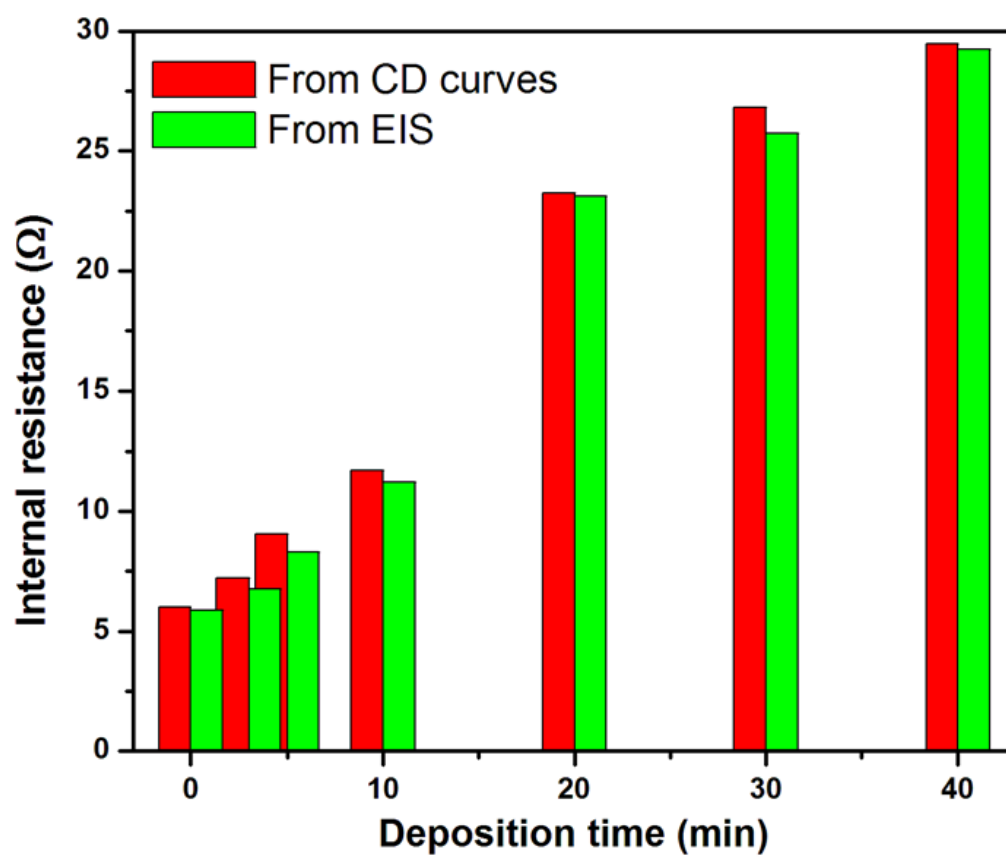


**Figure 3S.** SEM images of the morphology evolution of  $\text{MnO}_2$  on  $\text{MnO}_2\text{-CNT-sponge}$  at different deposition time, from 3 to 60 min. All scale bars are 2  $\mu\text{m}$ .



**Figure 4S.** (a) Argon adsorption and desorption isotherm of  $\text{MnO}_2$ ; (b) pore size distribution of  $\text{MnO}_2$ .





**Figure 5S.** Internal resistances obtained from galvanostatic charge-discharge (CD) curves and electrochemical impedance spectroscopy (EIS).