Supplementary Information

Three-dimensional “Skin-Framework” Hybrid Network as Electroactive Material Platform for High-Performance Solid-state Asymmetric Supercapacitor

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S1. Calculations

1. 1. Calculation of the areal specific capacitance of the single electrode

(1) The areal specific capacitance of the electrodes was calculated from the CV curves using Equation (1):

\[ C_a = \frac{Q}{\Delta U \times S} \]  \hspace{1cm} (1)

where \( C_a \) (mF/cm²) is the areal specific capacitance, \( Q \) is the average charge during electrode charging and discharging, \( \Delta U \) (V) is the working voltage window of the electrode, and \( S \) (cm²) is the test area of the electrodes.

(2) \( C_a \) was calculated by galvanostatic charging-discharging using Equation (2):

\[ C_a = \frac{I \times \Delta t}{\Delta U \times S} \]  \hspace{1cm} (2)

where \( I \) is the current during electrode discharging (A), and \( \Delta t \) (s) is the DC discharge time of the electrode.

(3) The mass specific capacitance with respect to the three-electrode configuration was derived from galvanostatic charging-discharging based on Equations (3) and (4):

\[ C_i = \frac{Q(MnO_2+MWCNT) - Q(MWCNT)}{\Delta U_1 \times m_1} \]  \hspace{1cm} (3)

\[ C_i = \frac{Q(AC+MWCNT) - Q(MWCNT)}{\Delta U_2 \times m_2} \]  \hspace{1cm} (4)

where \( C_i \) is the mass specific capacitance, \( Q \) is the charge obtained from the galvanostatic charging-discharging based on the MnO₂-MCN, AC-MCN and MCN electrodes, \( \Delta U_1 (=0.8 \text{ V}) \) and \( \Delta U_2 (=1.0 \text{ V}) \) constitute the voltage range, \( m_i \) is the mass of MnO₂ loaded on the MnO₂-
MCN electrode, and \( m_2 \) is the mass of AC loading on the AC-MCN electrode.

1. 2. Calculation of volume specific capacitance, power density, and energy density of the \( \text{MnO}_2\text{-MCN} /\text{AC-MCN} \) solid-state ASC device

(1) The volume specific capacitance of the electrodes was calculated from the CV curves and from Equations (5) and (6):

\[
C_{\text{cell}} = \frac{Q}{\Delta U} \quad (5)
\]

\[
C_V = \frac{C_{\text{cell}}}{V} = \frac{Q}{V \times \Delta U} \quad (6)
\]

where \( C_{\text{cell}} \) is the capacitance and \( C_V \) is the volume specific capacitance of the device, \( Q \) is the average charge during electrode charging and discharging, \( \Delta U \) (V) is the working voltage window of the device. \( V \) (cm\(^3\)) is the volume of the device, including the volumes of the positive and negative electrode pieces, gel electrolyte, and diaphragm. The area, thickness, and volume of the \( \text{MnO}_2\text{-MCN} /\text{AC-MCN} \) solid-state ASC device were 1.0 cm\(^2\), 521 μm (see Fig. S9), and 0.521 cm\(^3\), respectively.

(2) The specific capacitance of the device was calculated from the discharging curve using Equations (7) and (8):

\[
C_{\text{cell}} = \frac{I \times \Delta t}{\Delta U} \quad (7)
\]

\[
C_s = \frac{C_{\text{cell}}}{m} = \frac{I \times \Delta t - C_{\text{MWCNT}} m_{\text{MWCNT}}}{m \times \Delta U} \quad (8)
\]

where \( C_{\text{cell}} \) is the capacitance and \( C_s \) is the mass specific capacitance of the device; \( I \) is the
current during the device discharging (A), and \( \Delta t \) (s) is the DC discharge time of the device; \( \Delta U \) (V) is the working voltage window of the device; \( m \) (g) is the mass of the active material, where \( m \) includes the MnO\(_2\) and AC.

(3) Equations (9)–(11) were used to calculate the energy density \( (E, \text{ mWh/cm}^3) \), equivalent series resistance \( \text{(ESR, i.e., the internal resistance of the capacitor, } \Omega) \), and power density \( (P, \text{ mW/cm}^3) \) of the device, respectively:

\[
E = \frac{1}{2 \times 3600} C_v \Delta U^2 \quad (9)
\]

\[
ESR = \frac{iR_{\text{drop}}}{2 \times I} \quad (10)
\]

\[
P = \frac{\Delta U^2}{4 \times ESR \times V} \quad (11)
\]

where \( C_v \) is the volume specific capacitance of the device, \( \Delta U \) (V) is the working voltage window, and \( iR_{\text{drop}} \) is the voltage drop.

S2. Various graphs and curves

Fig. S1 (a) Mass loading and areal specific capacitance of the MnO\(_2\)-MCN electrode as a function of reaction times; (b) areal capacitance; and (c) capacitance retention rate of the MnO\(_2\)-MCN electrode as functions of the current density.
As expected, and as shown in Fig. S1a, when MCN is used as the active material platform, the mass loading of MnO\textsubscript{2} increases proportionally with the reaction time. However, the areal specific capacity of the MnO\textsubscript{2}-MCN electrode initially increases and then decreases with time. This is because MnO\textsubscript{2} nanoparticles substantially aggregates on the MWCNT surface with increasing the reaction time, with adverse effects on the electrochemical performance of the MnO\textsubscript{2}-MCN electrode. Fig. S1b and c show the electrodes area specific capacity and capacity retention as a function of current density at different times. Obviously, the MnO\textsubscript{2}-MCN electrode prepared with reaction time for 6h has a larger area specific capacity and a better capacity retention. The experimental results thus indicate an optimal reaction time of 6h, and this was adopted for further electrochemical investigation in this work.

Fig. S2 Display of large-scale preparation of the MCN hybrid materials.
**Fig. S3** Histogram of the specific surface area of the NF, MCN, and MnO$_2$-MCN electrode materials.

**Fig. S4** XPS full spectra of the MnO$_2$-MCN electrode.

**Fig. S5** (a) GCD curves of the MCN and MnO$_2$-MCN electrodes collected at a current density of 5 mA/cm$^2$; (b) Nyquist plots of the MCN and MnO$_2$-MCN electrodes with the equivalent circuit diagram used for fitting the EIS data (inset); (c) Nyquist plots of the
MCN and MnO$_2$-MCN electrodes with the corresponding high-frequency parts; and (d) cycle performance of the MnO$_2$-MCN electrode at current density of 10 mA/cm$^2$.

As shown in Fig. S5 (b), the equivalent circuit diagram used for the fitting of the EIS data includes the equivalent series resistance ($R_s$), the charge transfer resistance ($R_{ct}$), the diffusion impedance ($Z_w$), and the constant phase element (CPE) to account for the double layer capacitance. It is seen that the MCN electrode had smaller $R_s$ and $R_{ct}$ compared with the MnO$_2$-MCN electrode. This mainly attributed to the poor electronic conductivity of nano-MnO$_2$ (1×10$^{-5}$ to 1×10$^{-6}$ S/cm) loaded onto the MCN platform, resulting in a large $R_{ct}$ of the MnO$_2$-MCN electrode. Further, when the MnO$_2$ nanoparticles was loaded, the insufficiently developed porous structure of the MnO$_2$-MCN electrode combined with the poor liquid absorption ability led to the increase in the $Z_w$ of the MnO$_2$-MCN electrode to become large.

![Fig. S6](image_url)

**Fig. S6** (a) GCD curves of the MCN and AC-MCN electrodes collected at a current density of 5 mA/cm$^2$; (b) cycle performance of the AC-MCN electrode at a current density of 10 mA/cm$^2$; (c) Nyquist plots of the AC-MCN electrode with the equivalent circuit
diagram used for fitting the EIS data (inset); and (d) Nyquist plots of the AC-MCN electrode with the corresponding high-frequency part.

The equivalent circuit diagram used for the fitting of the EIS data is presented in inset of Fig. S6 (c), which includes the equivalent series resistance ($R_s$), the charge transfer resistance ($R_{ct}$), the diffusion impedance ($Z_w$), and the constant phase element (CPE) to account for the double layer capacitance. As shown in Fig. S6 (d), It can be seen that the AC-MCN electrode had a low $R_s$ (1.32 Ω) and $R_{ct}$ (0.49Ω). This mainly attributed to the good electronic conductivity of MCN electroactive platform.

**Fig. S7** (a) CV curves of the MnO$_2$-MCN//AC-MCN solid-state ASC device collected at scan rates of 5–100 mV/s; (b) GCD curves of the ASC device within various operation voltage windows at a current density of 10 mA/cm$^2$; and (c) cycle performance of the MnO$_2$-MCN//AC-MCN solid-state ASC device and (inset) photograph of an LED indicator (3 V) powered by two 1 cm $\times$ 1 cm units of the ASC device in series.
**Fig. S8** Cross-sectional SEM image of the AC-MCN electrode sheet.

**Fig. S9** Cross-sectional SEM image of the MnO$_2$-MCN//AC-MCN solid-state ASC device.

**S3. Video**

**Video S1** Demonstration of the structural stability of the MWCNT/CNF “skin” in the MCN platform by ultrasonic treatment.

**Video S2** Demonstration of the good wettability of the MCN, MnO$_2$-MCN and AC-MCN electrodes.