Supporting information

Hierarchical porous C/MnO_2 composite hollow microspheres with enhanced supercapacitor performance

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Calculation Equations

For the three-electrode system, the specific capacitance (C_s, F g^{-1}) of the working electrode can be obtained from the GCD curves and the CV curves based on the following equations:

$$C_{s-CD} = \frac{I \times \Delta t}{m \times \Delta V} \quad \text{(S1)}$$

$$C_{s-CV} = \frac{\int IdV}{2 \times m \times s \times \Delta V} \quad \text{(S2)}$$

where I is the charge-discharge current (A), ΔV is the width of potential window (V), Δt is the time of discharge (s), m is the loading mass of active material (g), and s is the potential scan rate (V s^{-1}).

For ASCs, charge balance is required to optimize the capacitive performance. Generally, the charge balance (q^{+}=q^{-}) is decided based on the capacitive performance of each electrode. The charge balance is valuated from Equation S4 according to the specific capacitance (C_s) and potential range (ΔV).

$$q = m \times C_s \times \Delta V \quad \text{(S3)}$$

$$\frac{m_+}{m_-} = \frac{C_{s-} \times \Delta V_-}{C_{s+} \times \Delta V_+} \quad \text{(S4)}$$

where m_+ and m_- are the masses of anode and cathode active-materials.

The total specific capacitance (C, F g^{-1}), energy density (E, Wh kg^{-1}), and power density (P, W kg^{-1}), of ASCs are determined by the following equations:[33]

$$C = \frac{I \times \Delta t}{M \times V} \quad \text{(S5)}$$

$$E = \frac{1}{2} \times \frac{1}{3.6} \times C \times V^2 \quad \text{(S6)}$$

$$P = 3600 \times \frac{E}{\Delta t} \tag{S7}$$

where V is the width of the voltage window (V), Δt is the time of discharge (s), and M is the total mass of these two electrodes (g).

Table S1. BET specific surface areas (S_{BET}), pore volume (V_{total}) and average pore size (d_{pore}) of the samples.

Sample	S_{BET} ($m^2\ g^{-1}$)	V_{total} ($cm^3\ g^{-1}$)	d_{pore} (nm)
NHCS	1272	1.64	5.2
MnO_2-NHCS	158	0.30	7.5
MnO_2 HS	119	0.30	10.2

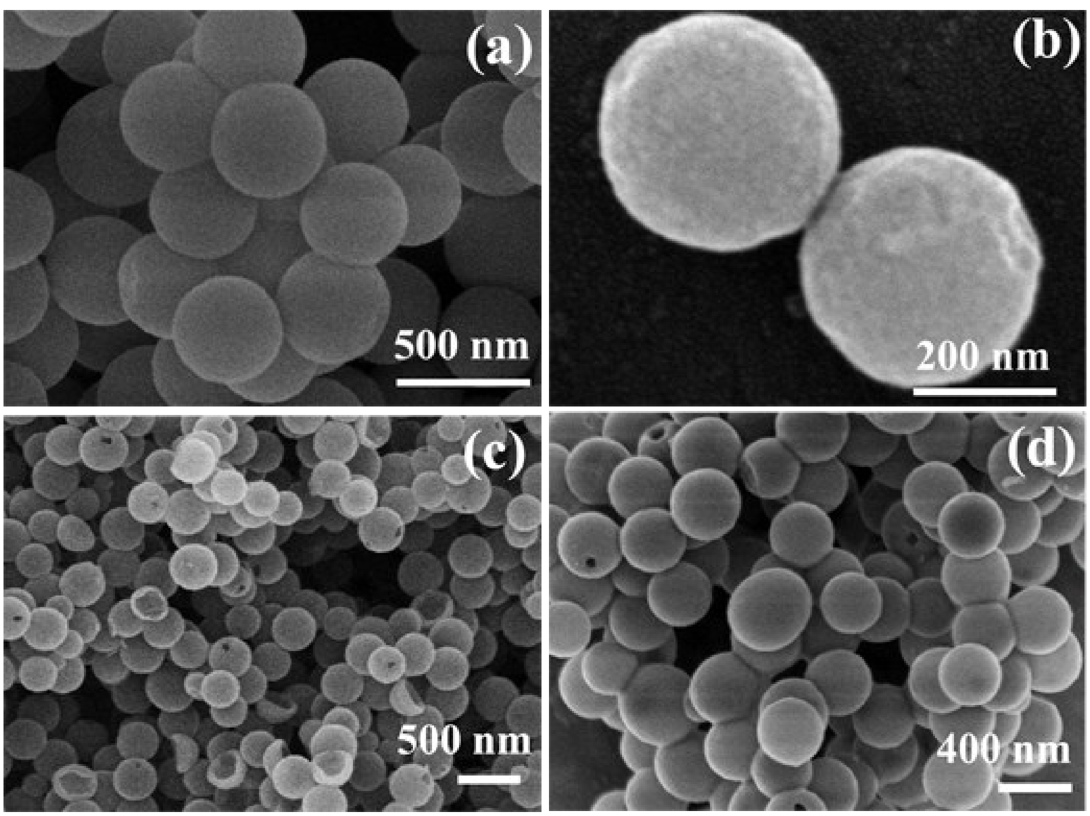

Figure S1. FESEM images of (a, b) SiO_2@PDA spheres and (c, d) NHCS.

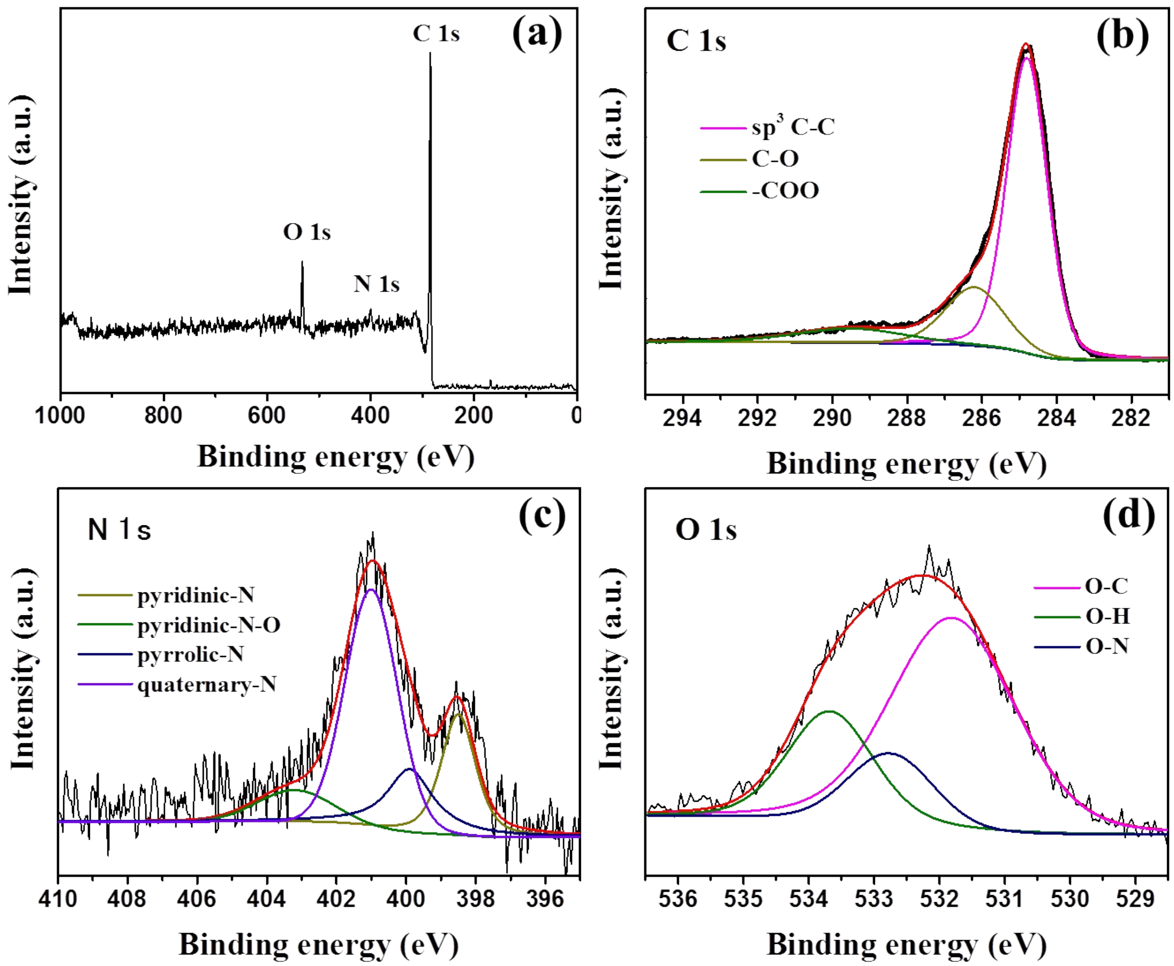

Figure S2. XPS spectra of the NHCS sample: (a) survey spectrum; (b) C 1s spectrum; (c) N 1s spectrum; (d) O 1s spectrum.

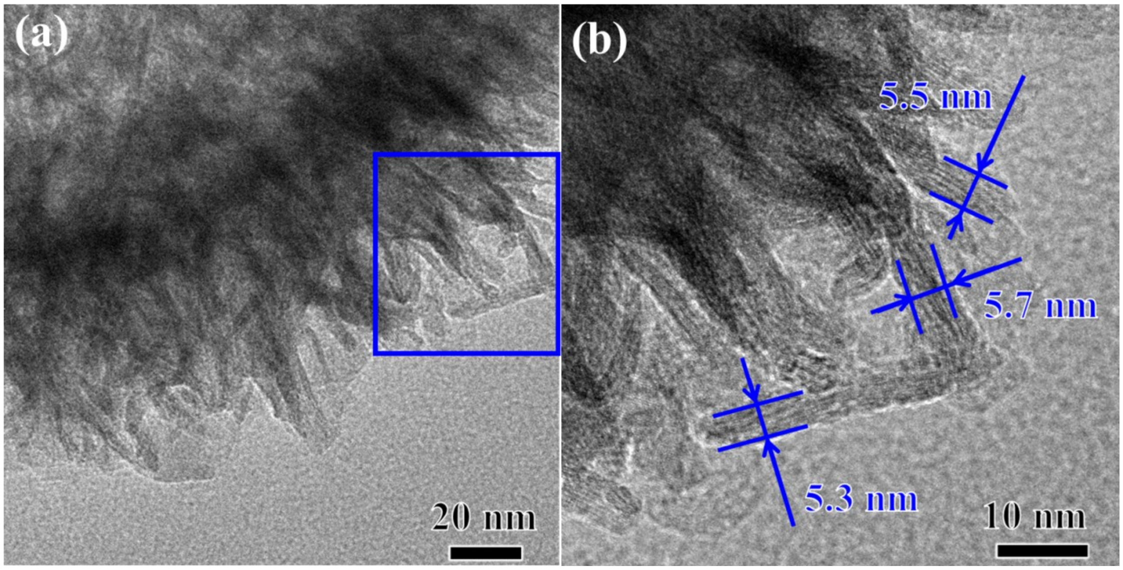

Figure S3. TEM images of NHCS@MnO2 at high magnification.

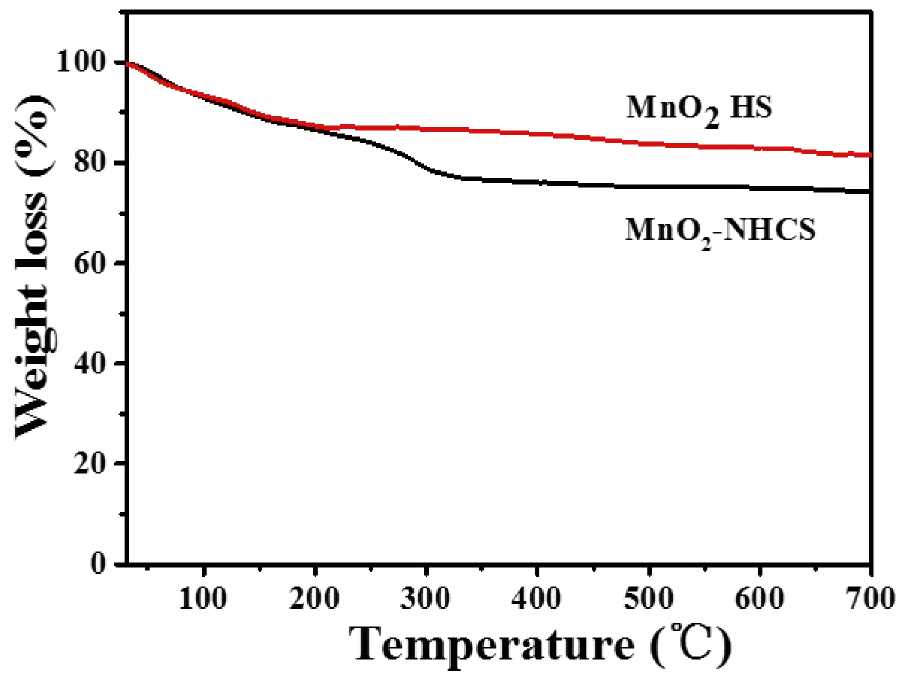

Figure S4. TGA curves of MnO_2-NHCS and MnO_2 HS. This pyrolysis process was carried out in air at a heating rate of 10 °C min^{-1}.

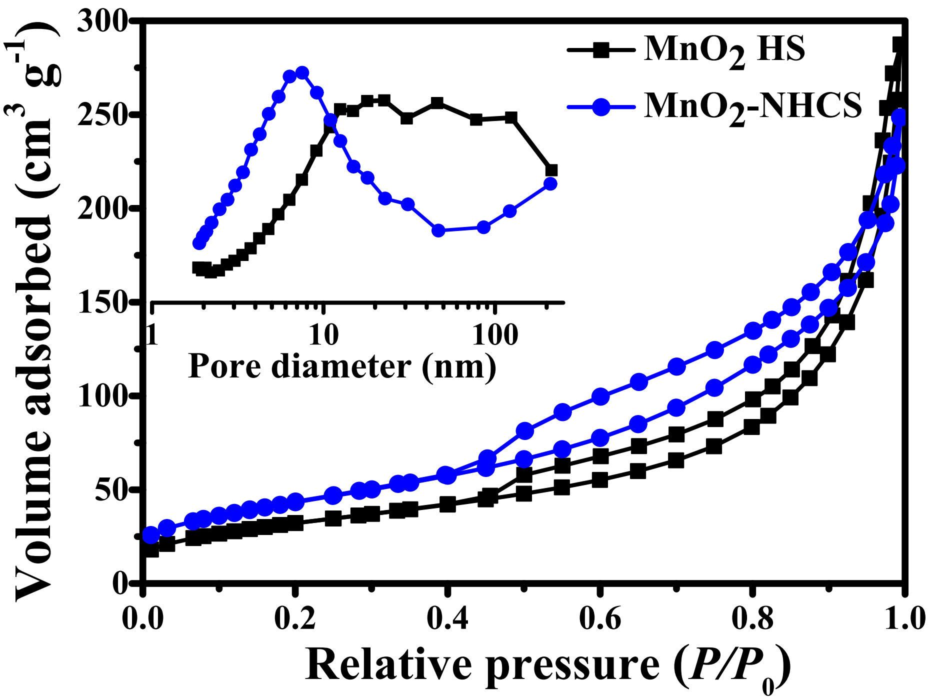

Figure S5. N_2 adsorption/desorption isotherms of MnO_2-NHCS and MnO_2 HS, with the inset exhibiting the pore size distributions.

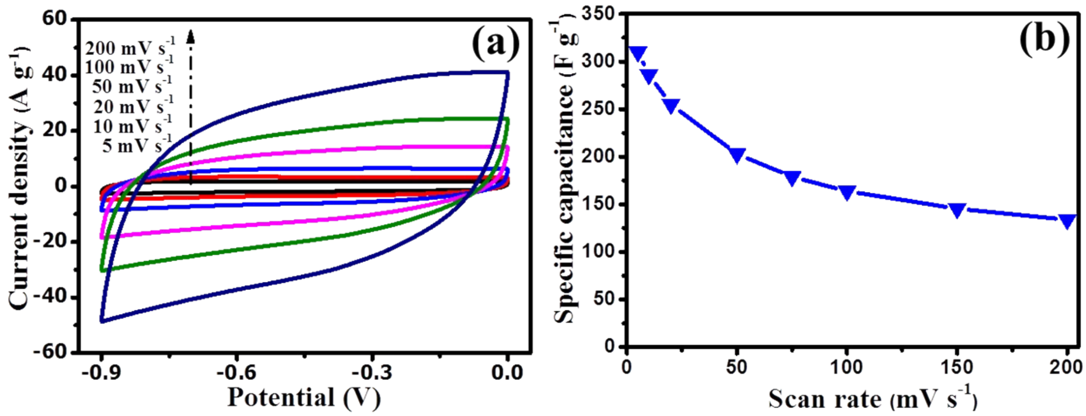

Figure S6. CV curves (a) and specific capacitances at different scan rates (b) of NHCS.

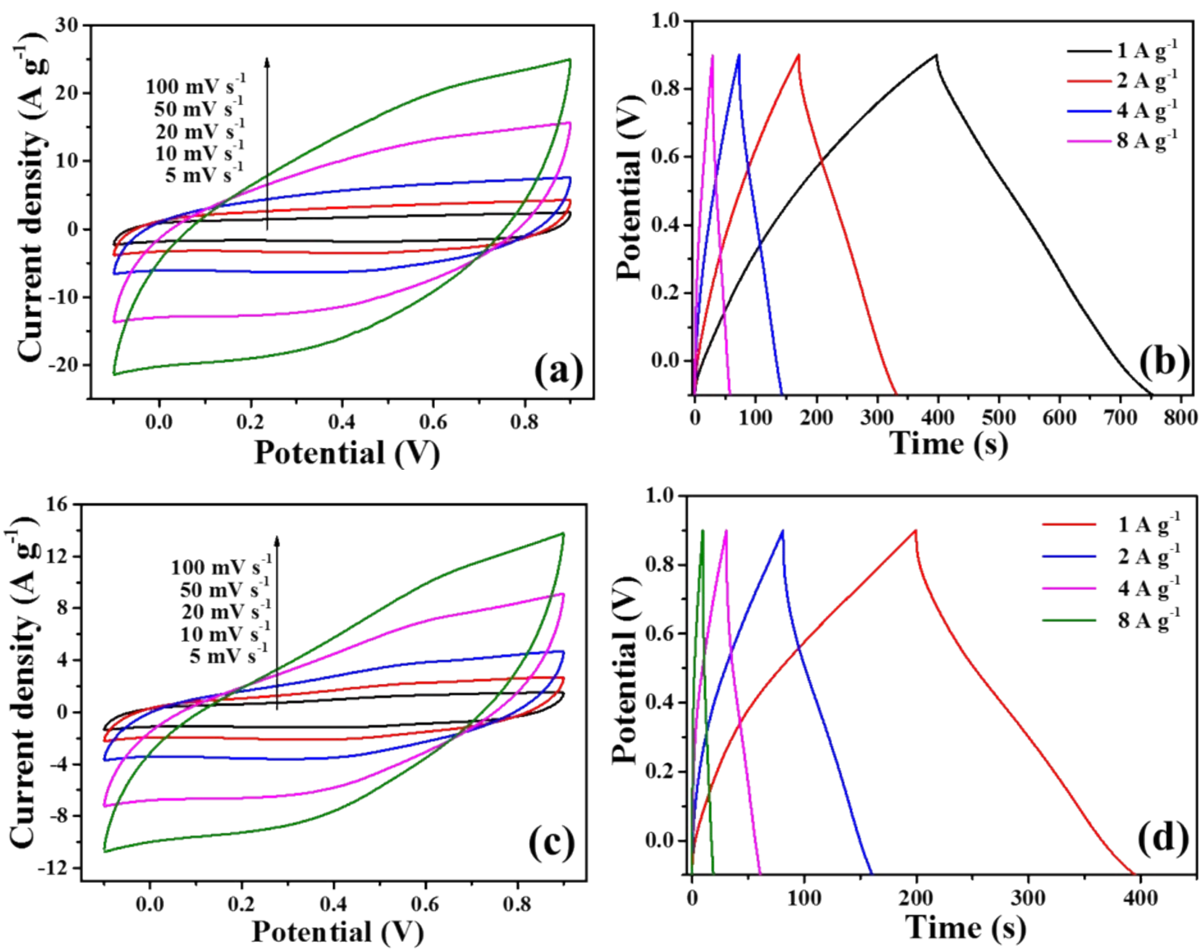

Figure S7. (a) CV curves at different scan rates and (b) GCD curves at various current densities of MnO_2-NHCS composite. (c) CV curves at different scan rates and (d) GCD curves at various current densities of MnO_2 HS. These curves were measured in a three-electrode system in 1 M Na_2SO_4 aqueous solution.

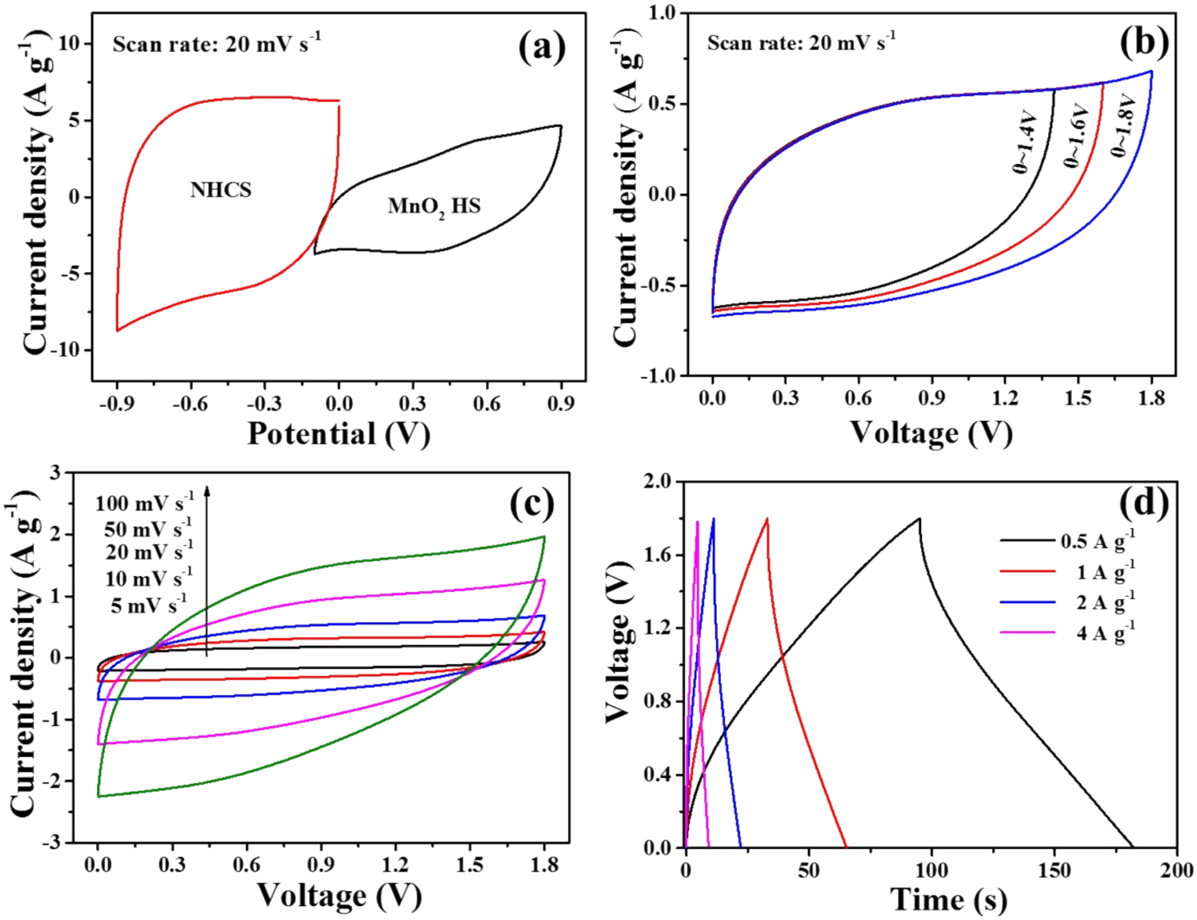

Figure S8. (a) CV curves of NHCS and MnO_2 HS measured in a three-electrode system at a scan rate of 20 mV s^{-1}. Electrochemical performance of an asymmetric supercapacitor with MnO_2 HS as positive electrode and NHCS as negative electrode: (b) CV curves at different cell voltage, (c) CV curves at different scan rates with a cell voltage of 1.8 V, (d) GCD curves at various current densities. The electrolyte was 1 M Na_2SO_4 aqueous solution.

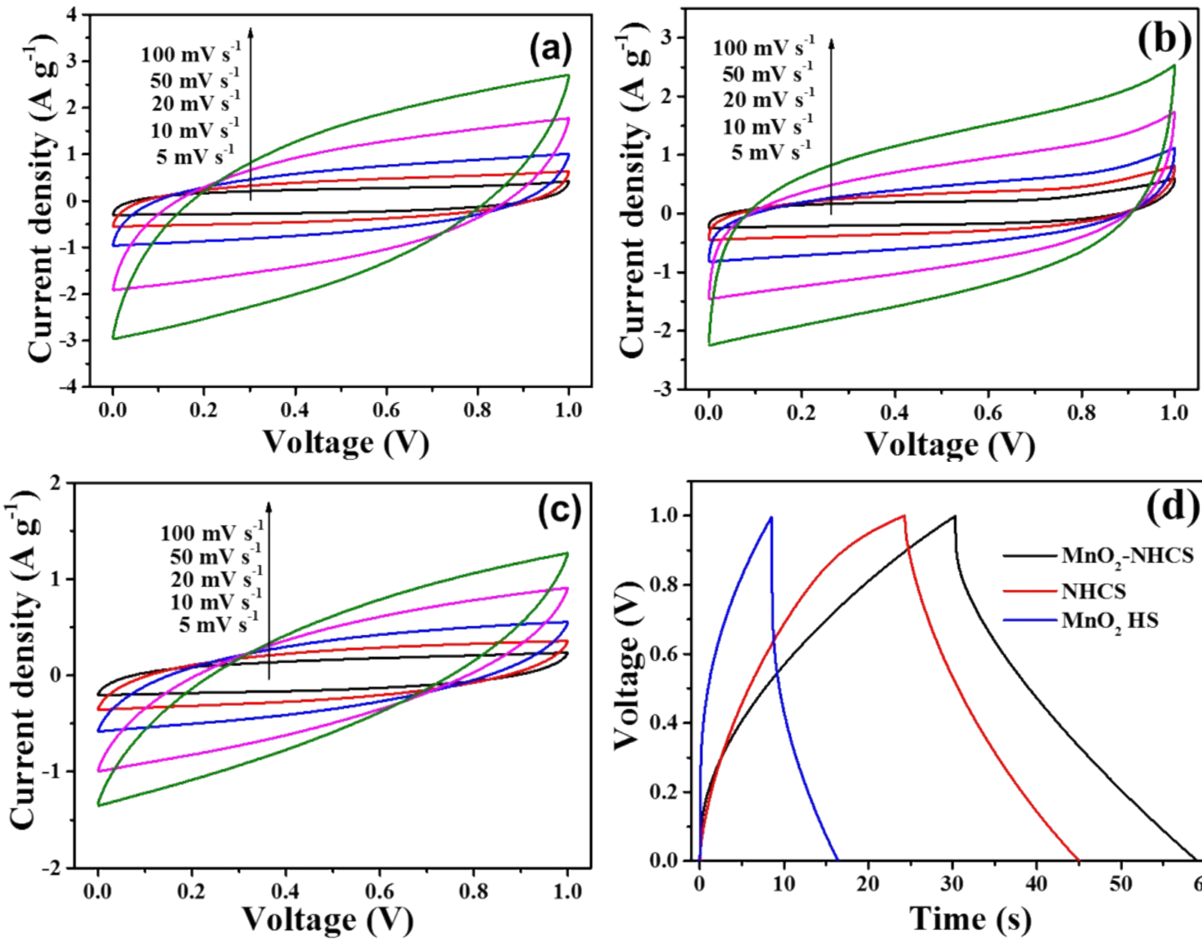

Figure S9. CV curves at different scan rates of the as-assembled symmetric supercapacitors (SC), (a) MnO_2-NHCS// MnO_2-NHCS, (b) NHCS//NHCS and (c) MnO_2 HS//MnO_2 HS. (d) GCD curves of MnO_2-NHCS// MnO_2-NHCS, NHCS//NHCS, and MnO_2 HS//MnO2 HS at the current density of 1 A g^{-1}.