Supporting Information

Ultrathin Manganese Dioxide Nanosheets Grown on Mesoporous Carbon Hollow Spheres for High Performance Asymmetrical Supercapacitors

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Materials. Absolute ethanol, $NH_3 \cdot H_2O$ (25 wt%), formaldehyde (37 wt%), $KMnO_4$ and Na_2SO_4 were purchased from Sinopharm Chemical Reagent Co., Ltd. Tetrapropyl orthosilicate (TPOS), tetraethyl orthosilicate (TEOS), resorcinol, hydrofluoric acid (HF, 40 wt%) and 1-methyl-2-pyrrolidinone (NMP) were obtained from Aladdin Industrial Co., Ltd. The obtained HF solution was diluted to 5 wt% for next use. Other chemicals were of analytical grade and directly used in experiment.

Calculation of loading rate of MnO_2 in MCHS/MnO_2 hybrid materials. The mass loading of MnO_2 in MCHS/MnO_2 is calculated by the difference between MCHS/MnO_2 and residual MCHS obtained by MCHS/MnO_2 reacting with the excess dilute hydrochloric acid. Therefore, the loading rate of MnO_2 in MCHS/MnO_2 is calculated to be ~94.4% according to above mentioned difference.

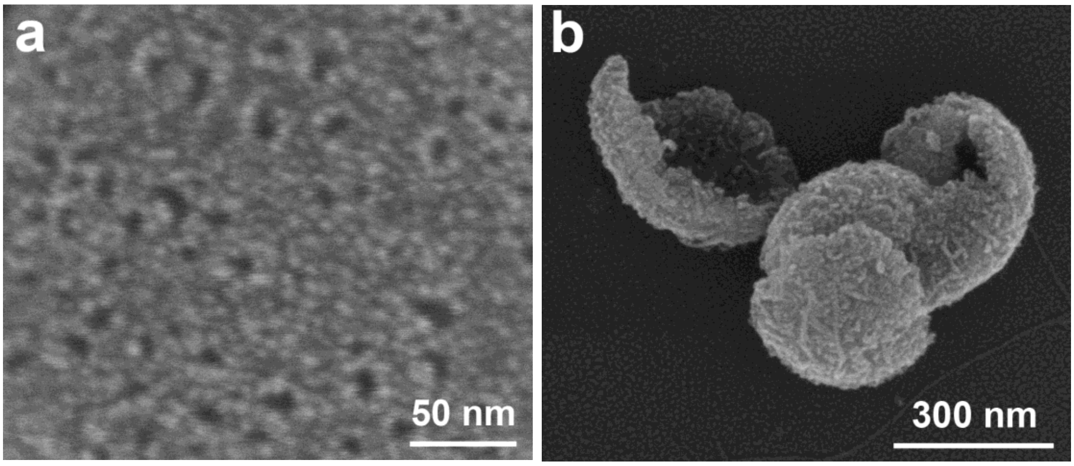

Figure S1. (a) High magnification SEM image of the surface of MCHS; (b) SEM image of broken MCHS/MnO_2 treated by ultrasound.

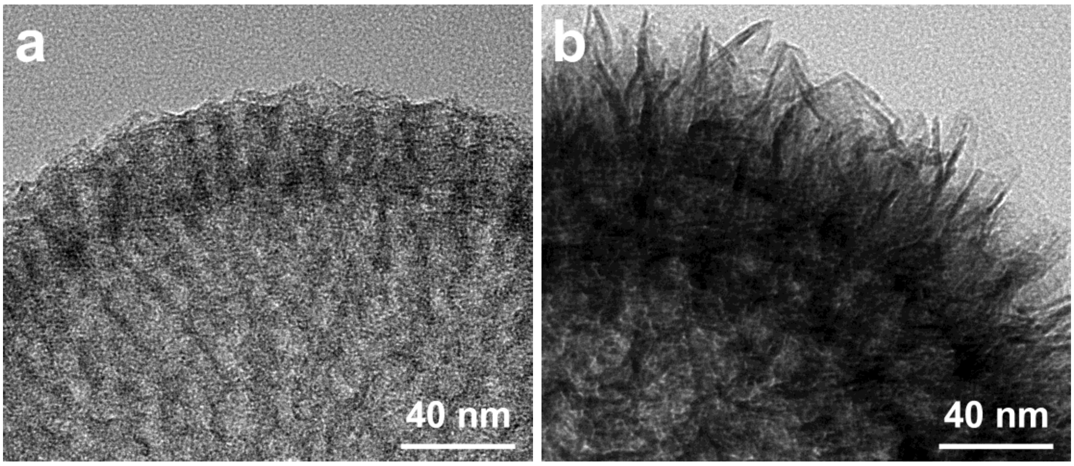

Figure S2. TEM images of (a) MCHS and (b) MCHS/MnO_2.

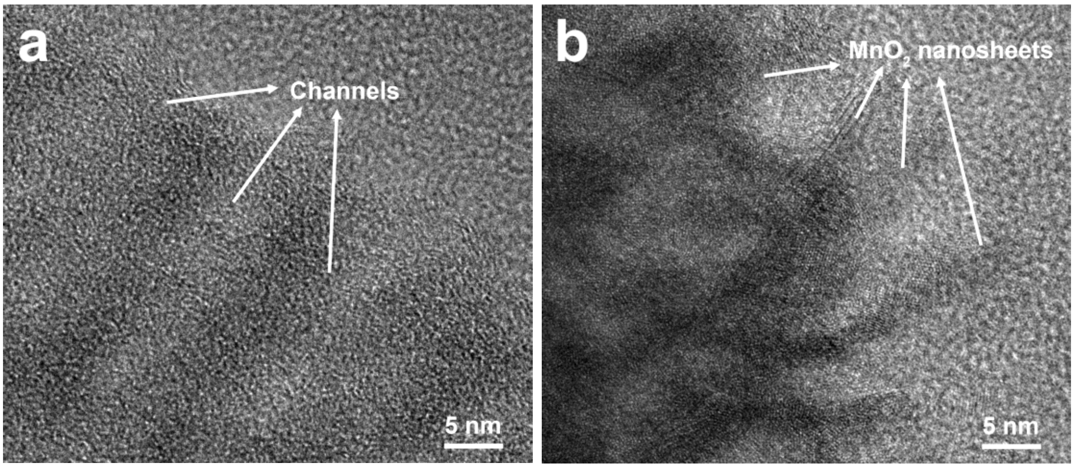

Figure S3. HRTEM images of (a) MCHS and (b) MCHS/MnO_2.

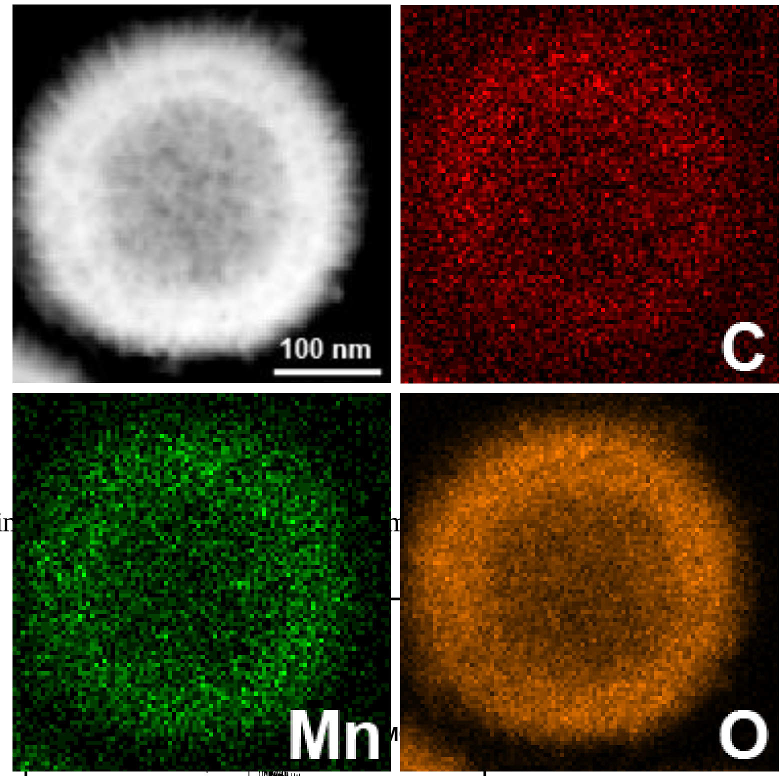

Figure S4. HAADF-STEM in

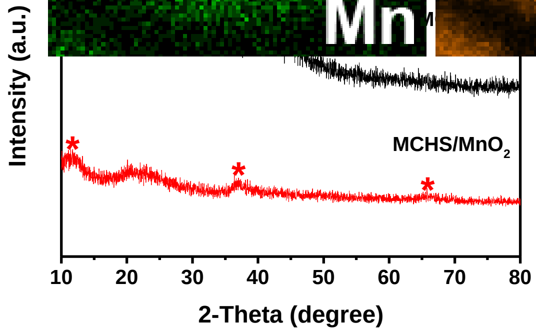

Figure S5. XRD patterns of MCHS and MCHS/MnO_2.

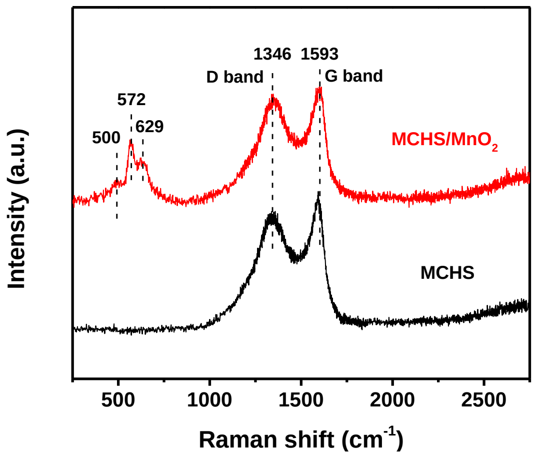

Figure S6. Raman spectra of MCHS and $MCHS/MnO_2$.

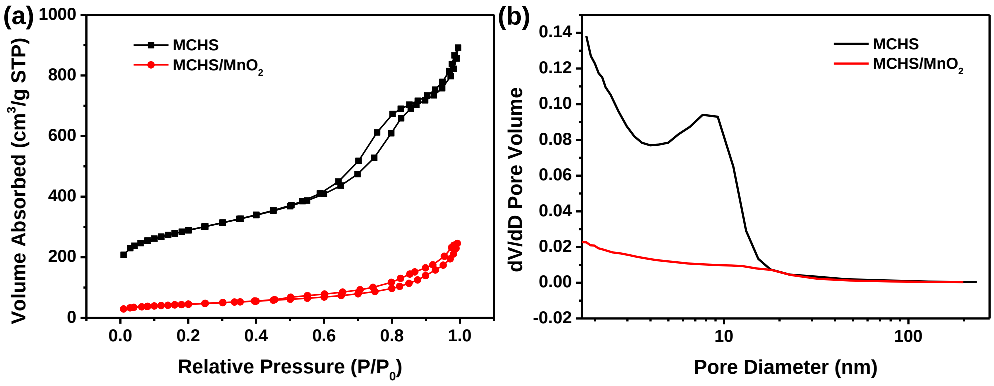

Figure S7. (a) N_2 adsorption/desorption isotherms of MCHS and $MCHS/MnO_2$ with specific surface areas of 956.7 and 154 m^2/g respectively calculated by BET; (b) Pore size distribution of MCHS and $MCHS/MnO_2$.

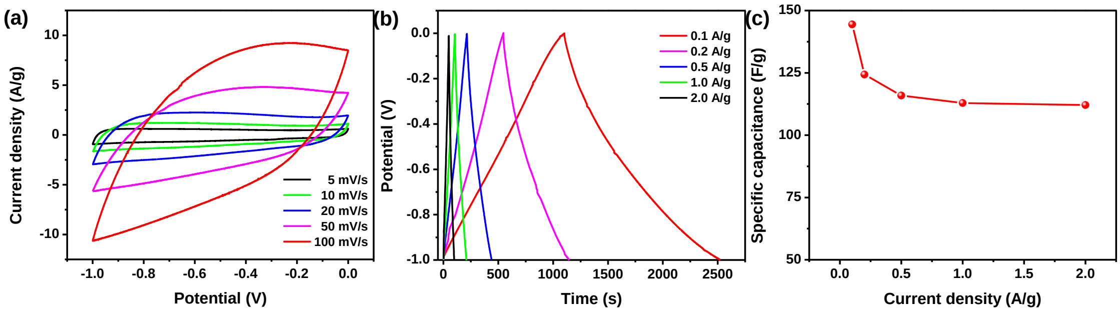

Figure S8. (a) CV curves of MCHS at various scan rates of 5−100 mV/s; (b) GCD curves of MCHS at various current densities of 0.1−2.0 A/g; (c) Calculated specific capacitance of MCHS from GCD curves as a function of current density.

The electrochemical performance of prepared MCHS was characterized by electrochemical station with three-electrode system in 1 M KOH aqueous electrolyte solution. The Ni foam coated by prepared MCHS slurry, Pt plate and saturated calomel electrode were respectively served as working, counter and reference electrodes. The applied potential windows in CV and GCD tests are -1−0 V. Benefited from the hollow and mesoporous structure, MCHS exhibits the excellent electrochemical performance. The rectangle-like shape of all CV curves in Figure S8a shows the typical characteristic of electric double layer capacitance (EDLC), and the integral area increases with the scan rate and there are no distorted curves appear even at larger scan rates, indicating the well capacitance behavior of MCHS. GCD curves plotted in Figure S8b present the GCD process of MCHS at different current densities from 0.1 to 2.0 A/g, they all exhibit the approximately symmetrical triangle shape which is the typical feature of EDLC, indicating the fast electron transfer rate and ion diffusion rate of MCHS. As shown in Figure S8c, specific capacitance of MCHS calculated from GCD curve as a function of current density is plotted. Apparently, MCHS shows excellent specific capacitance of 144.4, 124.3, 115.9, 112.9 and 112.1 F/g at current density of 0.1, 0.2, 0.5, 1.0 and 2.0 A/g, respectively, and about 77.6% retention of capacitance is still achieved when current density increases from 0.1 to 2.0 A/g, indicating the well rate capability of MCHS.

Table S1. Comparison of electrochemical properties of supercapacitor devices.

Electrode		Electrochemical performance (device)		Reference
Positive	Negative	Operating voltage /V	Maximum energy density/Wh·kg^{-1}	
MCHS/MnO_2	MCHS	2	64.6	Our work
$MnCo_2O_4$@$Ni(OH)_2$	AC	1.6	48	15
$NiCo_2O_4$@ppy	AC	1.6	58.8	17
Ni@rGO-Co_3S_4	Ni@rGO-Ni_3S_4	1.3	55.16	18
CBC-N2@LDH-0.4	CBC-N2	1.6	36.3	19
NiS/NHCS	AC	1.5	38.3	23
PMNC	AC	1.4	41	24
CC/SnO_2/MnO_2	Ni foam/NiO	1.5	64.4	29
MnO_2	MEGO	1.6	25.8	30
MnO_2-NHCS	NHCS	1.8	26.8	40

The listed references are numbered in Table according to main text.