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Supplementary Information

3D hierarchical MnO_2 nanorods/welded Ag-nanowire-network composites for high-performance supercapacitor electrodes

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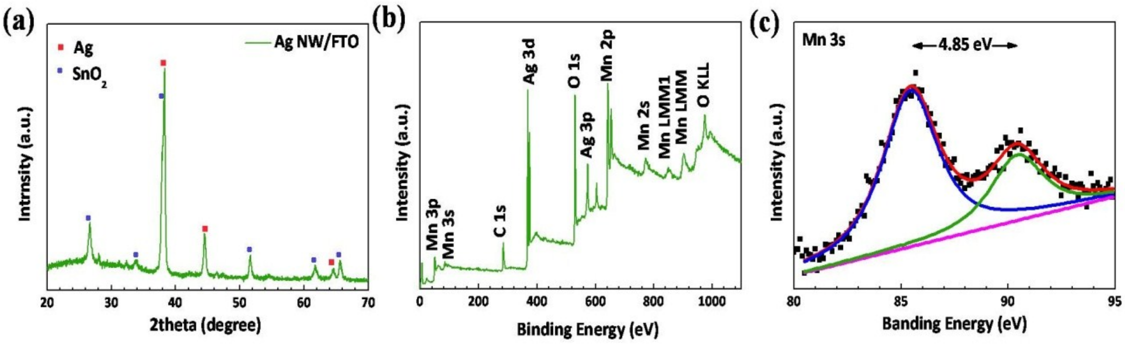

Fig. S1 (a) XRD patterns of the AgNW/FTO. (b) XPS full-survey-scan spectrum of the 3D MN/w-ANN composites, (c) XPS core-level spectra of Mn 3s.

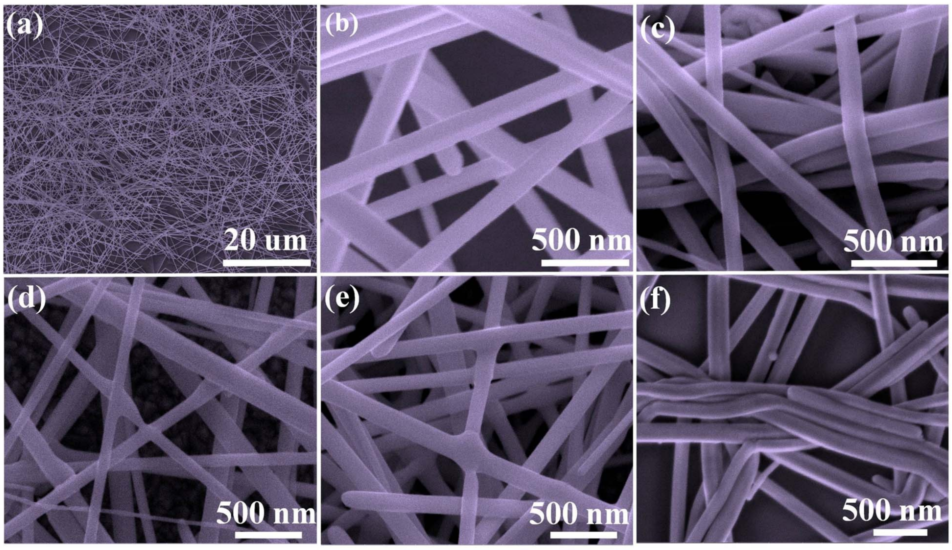

Fig. S2 SEM of AgNW network at different annealing temperature (a) and (b) room temperature; (c) 200 °C; (d) 250 °C ; (e) 300 °C; (f) 350 °C.

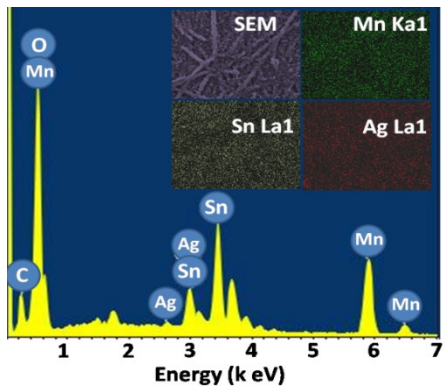

Fig. S3 EDX spectrum showing the elemental composition of the 3D MN/w-ANN composites, the insets show its SEM and elemental mapping of Mn, Sn and Ag.

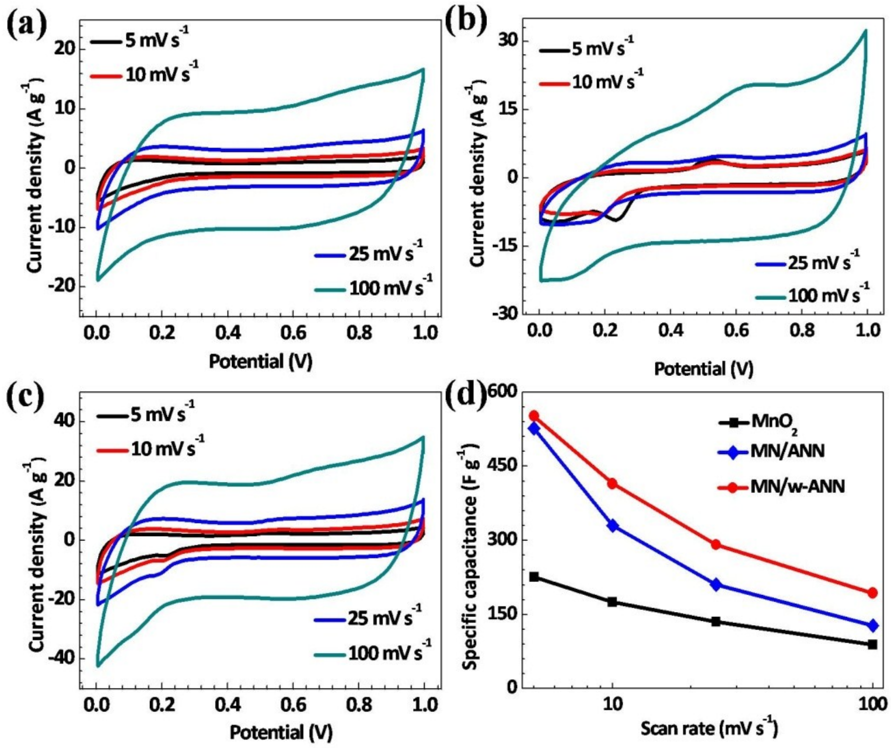

Fig. S4 CV curves for (a) the bare MnO_2, (b) the MN/ANN electrode and (c) the 3D MN/w-ANN composite electrode at different scan rates in 0.5 M Na_2SO_4 aqueous electrolyte; (d) Specific capacitances of the bare MnO_2, the MN/ ANN and the 3D MN/w-ANN composite electrode.

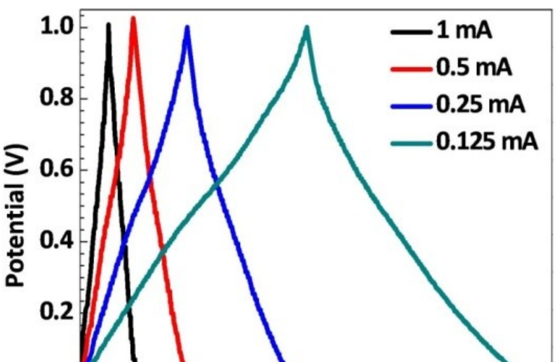

Fig. S5 GCD curves of the 3D MN/w-ANN composite electrode at different current.

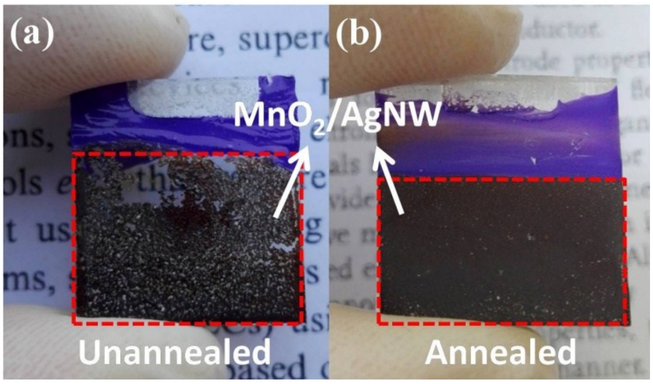

Fig. S6 Photo images of electrodes after GCD testing (a) the MN/ ANN electrode; (b) the 3D MN/w-ANN composite electrode.

Table S1. The mass ratio between MnO_2 and AgNW network in the 3D MN/w-ANN composite electrode s and the corresponding specific capacitance.

AgNWs spin-coated number	0	5	10	20	40	60	80	100
Mass ratio (MnO_2 :AgNW)	1 : 0	1:0.05	1:0.10	1:0.19	1:0.28	1:0.30	1:0.40	1:0.45
Specific capacitance (F g^{-1})	135.1	191.7	218.5	274.3	314.8	354.1	378.3	365.4

Table S2. Comparison of specific capacitance, cycle number and capacitance retention of the reported MnO_2 electrodes and the present work.

Materials	**Electrolyte**	**Testing condition**	**Specific capacitance**	**Cycle number**	**Capacitance retention**	**Ref.**
Mesoporous MnO_2	1 M Na_2SO_4	**0.4 A g^{-1}**	229 F g^{-1}	2000	97.3%	1
MnO_2 nanowires	0.1 M Na_2SO_4	77 mA g^{-1}	167.5 F g^{-1}	3000	88%	2
MnO_2 nanorod arrays	0.5 M Na_2SO_4	**3 A g^{-1}**	485.2 F g^{-1}	1500	**123 %**	3
Free-standing MnO_2 nanorods	0.5 M Na_2SO_4	**3 A g^{-1}**	355.7 F g^{-1}	1500	**115%**	3
MnO_2/CNTs	1 M Na_2SO_4	**1 A g^{-1}**	201 F g^{-1}	10000	100%	4
MnO_2@polyaniline	1 M Na_2SO_4	**1 A g^{-1}**	437 F g^{-1}	3000	100%	5
ZnO@MnO_2 core-shell arrays	1 M Na_2SO_4	0.5 A g^{-1}	423.5 F g^{-1}	3000	92%	6
Ag NP/MnO_2	1 M Na_2SO_4	10 mV s^{-1}	272 F g^{-1}	—	—	7
Ag/MnO_2/RGO	3 M KOH	5 mV s^{-1}	126.2 F g^{-1}	1000	**134%**	8
Ag/PANI/MnO_2	1 M Na_2SO_4	**0.1 A g^{-1}**	518 F g^{-1}	1600	88.4%	9

Ag-doped MnO_2	0.5 M Na_2SO_4	2 mV s^{-1}	770 F g^{-1}	—	—	10
Hair-like Ag/MnO_x	1 M Na_2SO_4	**2 A g^{-1}**	237 F g^{-1}	800	78%	11
Ag/MnO_2 hybrid electrode	1 M Na_2SO_4	10 mV s^{-1}	293 F g^{-1}	5000	92.5%	12
MnO_2/a-AgNW	**0.5 M Na_2SO_4**	**6 A g^{-1}**	**663.4 F g^{-1}**	**7000**	**157%**	**The work**

Loading mass calculation of AgNW network and MnO_2

The AgNW/FTO substrates are obtained by spin-coating AgNW ink on FTO conducting glass. Firstly, we weight 20 pieces of cleaned FTO conducting glass with cut into 2*2 cm^2, and the mass is denoted as m_1. Then, AgNWs ink is spun on the surface of total FTO substrates at a 3000 rpm rotation speed for 5 times, respectively. Finally, the total AgNW/FTO substrates are weighted, and their loading mass is m_2. Thus, the mass m^* of each AgNW network layer on FTO can be calculated by equation (1):

$$m^* = \frac{m_2 - m_1}{20} \quad (1)$$

Loading mass of the other AgNW network layer by different spin-coating number can be obtained using the above method.

The electrochemical deposition process was carried out via the potentiostatic method under 1.0 V. And assuming 100% current effciency via the reaction, shown as follows:

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^- \quad (2)$$

Thus, the loading mass of electrodeposited MnO_2 is calculated using below equation:

$$m^* = \frac{(\int Idt)M}{2eN_A} \quad (3)$$

where I is the current, t is the electrochemical deposition time, m is the electrochemical deposition mass of MnO_2 on the AgNW/FTO substrate, e is the electron charge, N_A is the Avogadro's number, and M is molar mass of MnO_2 (86.9 g mol^{-1}).[12] Therefore, the loading mass of MnO_2 on the AgNW/FTO substrate is around 0.30 mg.

Specific capacitance calculation of MnO_2/a-AgNW electrode

Specific capacitance (C_{sp}) is the capacitance per unit mass for one electrode. In Cyclic voltammetry

(CV) measurements, the C_{sp} is calculated from:

$$C_{sp} = \frac{\int I\, dV}{2m\Delta V \nu_0} \quad (4)$$

where I is the current, V is the voltage, ΔV is the voltage window, ν_0 is the scan rate, and m is the loading mass of MnO_2.

In galvanostatic charge/discharge (GCD) measurements, the C_{sp} is calculated from:

$$C_{sp} = \frac{I\, \Delta t}{m\Delta V} \quad (5)$$

where I is the discharge current, Δt is the discharge time, the ΔV is the voltage difference of discharge, and m is the loading mass of MnO_2.[13]

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