Supporting information for

Flexible supercapacitors based on carbon nanotube/MnO_2 nanotube hybrid porous films for wearable electronic devices

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Capacitance compared with previous reports:

Single electrode

In the conventional way, the areal capacitance (C_a) of the electrode can be calculated by the following equations according to the discharge curves:

$$C_a = \frac{I\Delta t}{A\Delta U}$$

where I is the discharge current, Δt is the discharge time, A is the effective area of the working electrode and ΔU is the potential window. Therefore, in this work, the areal capacitance of the freestanding CNT/MnO_2 NT hybrid electrode calculated by the above conventional method is 295.3 mF cm^{-2} at a current density of 0.5 mA cm^{-2} and 229.5 mF cm^{-2} at a current density of 1 mA cm^{-2}. These values are better than that reported in previous, as shown in Table S1.

Table S1 Comparison of the areal capacitance of the freestanding CNT/MnO_2 NT hybrid electrode with that in previous reports.

Electrode materials	**Areal capacitance (mF cm^{-2})**	**Reference**
Freestanding CNT/MnO_2 NT hybrid	295.3 (0.5 mA cm^{-2}) 229.5 (1 mA cm^{-2})	This work
Freestanding VN/CNT hybrid	178 (1.1 mA cm^{-2})	1
Hydrogenated MnO_2 nanorods	220 (0.75 mA cm^{-2})	2
Functionalized carbon nanotube	150 (1 mA cm^{-2})	3
Hydrogenated ZnO@ZnO-doped MnO_2 nanocables	138.7 (1 mA cm^{-2})	4
MnO_2 nanowires & Fe_2O_3 nanotubes	150.0 (1 mA cm^{-2}) 180.4 (1 mA cm^{-2})	5
Hydrogenated TiO_2@MnO_2 nanowires	70 (2 mA cm^{-2})	6

SC device

Similarly, the volumetric capacitance (C_v) of the whole device can be calculated by the following equations according to the discharge curves:

$$C_v = \frac{I\Delta t}{V\Delta U}$$

where *I* is the discharge current, *Δt* is the discharge time, *V* is the volume of the whole SC device and *ΔU* is the voltage. Hence, using the above conventional method, the value of this work is 7.7 F cm^{-3} at 16 mA cm^{-3}, which is much higher than that of other solid-state SC devices reported in previous papers, as listed in Table S2.

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Table S2 Comparison of the volumetric capacitance of the SC device with that in previous reports.

Supercapacitor Devices	**Volumetric capacitance (F cm^{-3})**	**Reference**
Freestanding CNT/MnO_2 NT hybrid based SC	7.7	This work
VN/CNT hybrid based SC	7.9	1
H- MnO_2 & RGO based asymmetric SC	0.72	2
Functionalized carbon nanotube based SC	3.0	3
MnO_2 nanowires & Fe_2O_3 nanotubes based asymmetric SC	1.5	5
H-TiO_2@MnO_2 & H-TiO_2@C based asymmetric SC	0.71	6
Worm-like MnO_2 nanowries based SC	0.44	7
NiF_2 based SC	3.2	8
MnO_2 nanotubes based SC	4.4	9
MnO_2 & Fe_2O_3 based asymmetric SC	1.2	10

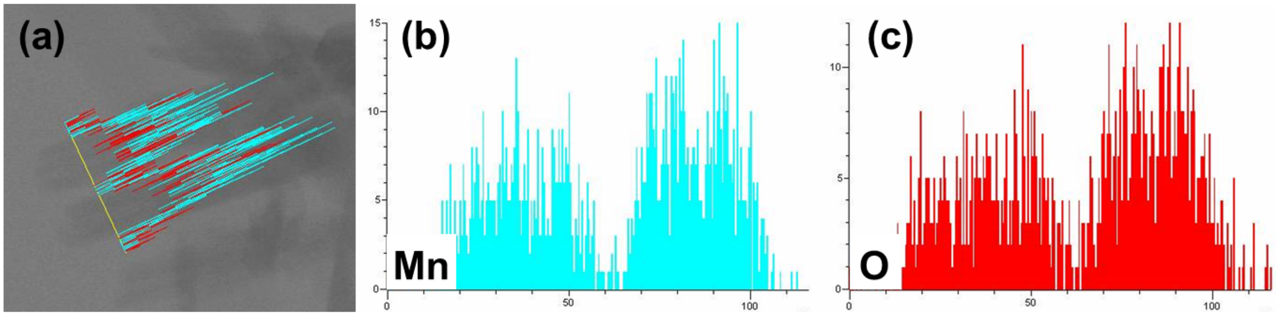

Fig. S1 (a) STEM image of a MnO_2 nanotube and EDS line scan curves of elements (b) Mn and (c) O along the line shown in the leftmost panel.

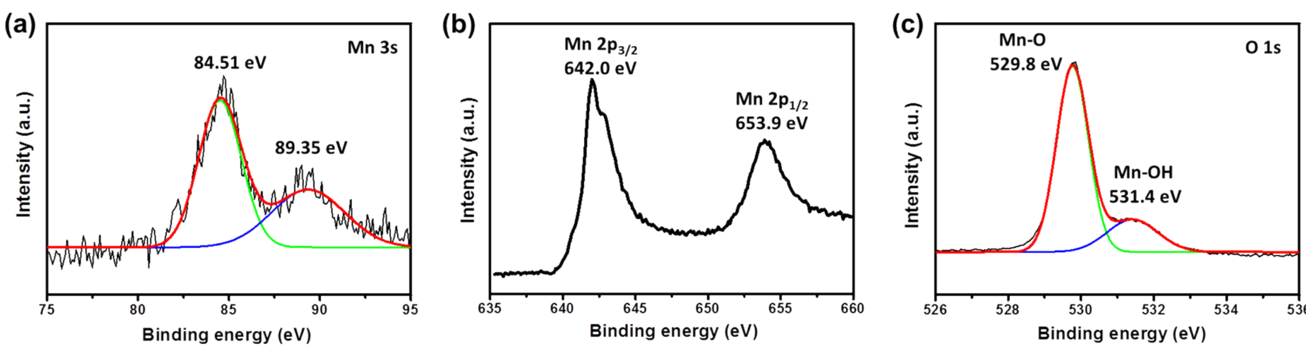

Fig. S2 XPS spectra of (a) Mn 3s, (b) Mn 2p and (c) O 1s collected from the MnO_2 NTs. As report in previous,[11, 12] the oxidation state of element Mn can be determined from the binding energy width (ΔE) between the separated Mn 3s peaks caused by multiple splitting. By reference to the ΔE data of 4.78, 5.41, 5.50 and 5.79 eV acquired from genuine samples of MnO_2, Mn_2O_3, Mn_3O_4 and MnO, respectively, the possible valence of Mn in this samply (ΔE=4.84 eV) is +3.95. Mn 2p3/2 and Mn 2p1/2 peaks were located at 642.0 and 653.9 eV, which are consistent with the previous reported values for MnO_2. The peaks at 529.8 and 531.4 eV can be indexed to the oxygen bond of Mn-O and Mn-OH, respectively.[5]

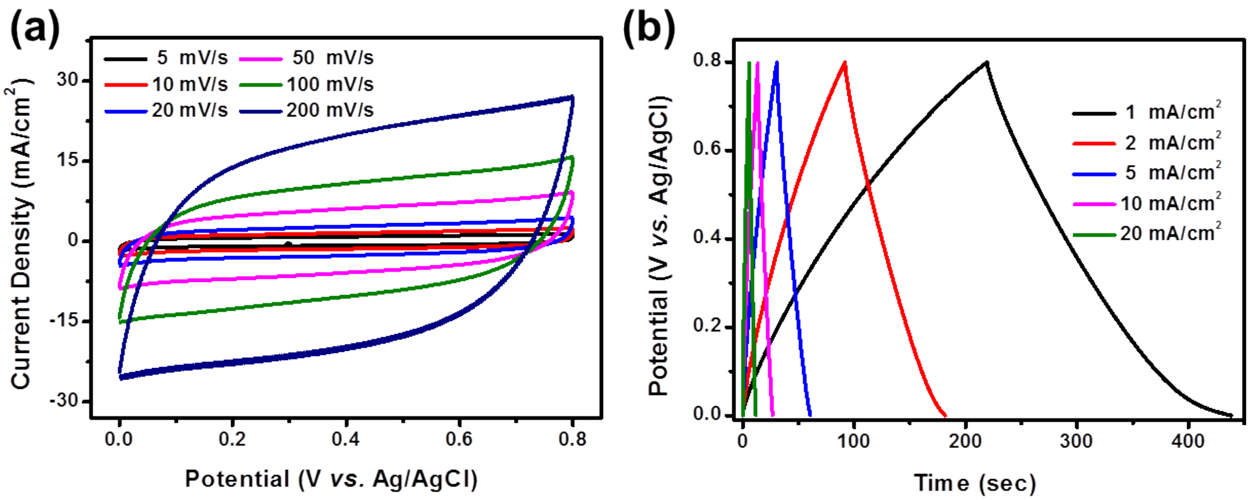

Fig. S3 (a) CV curves collected at different scan rates and (b) Galvanostatic charge-discharge curves at various current densities for hard MnO_2 NTs electrodes.

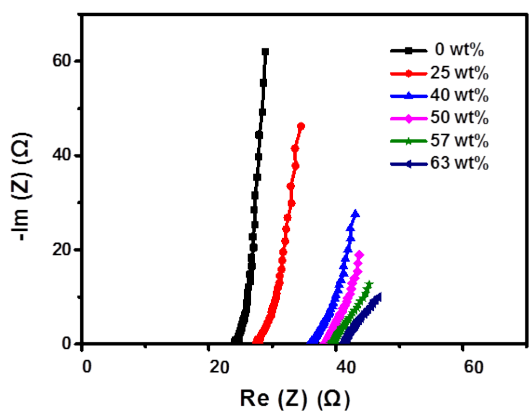

Fig. S4 Nyquist plots of the CNT/MnO_2 NT hybrid films with different weight percentages of MnO_2 NTs.

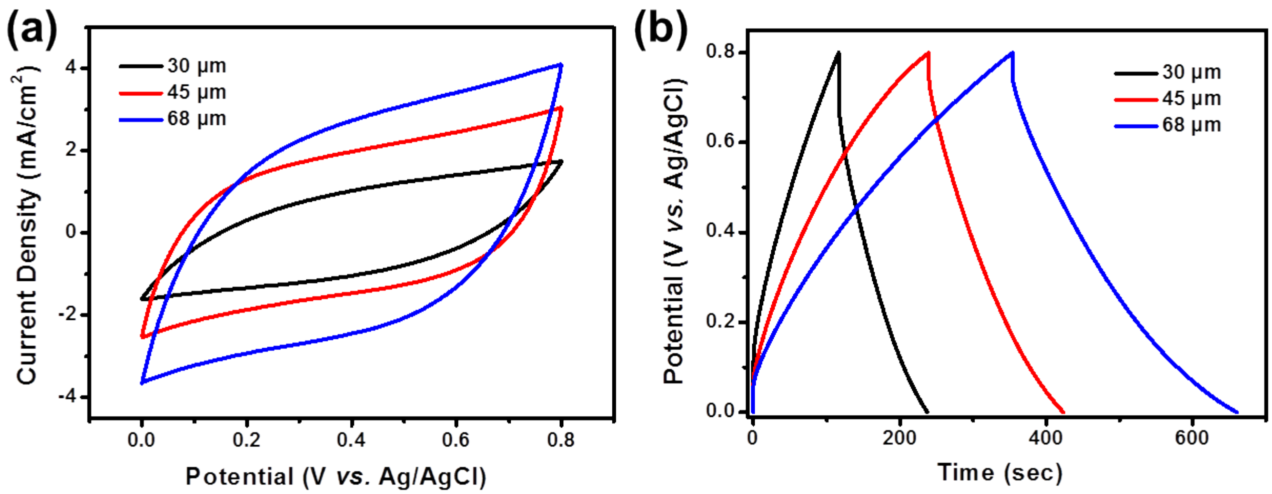

Fig. S5 Comparison study among the flexible CNT/MnO_2 NT hybrid electrodes with different thickness: (a) CV curves measured at 10 mV s^{-1} and (b) Galvanostatic charge-discharge curves at 1 mA cm^{-2}. These films have the same weight percentage of MnO_2 (57 wt%).

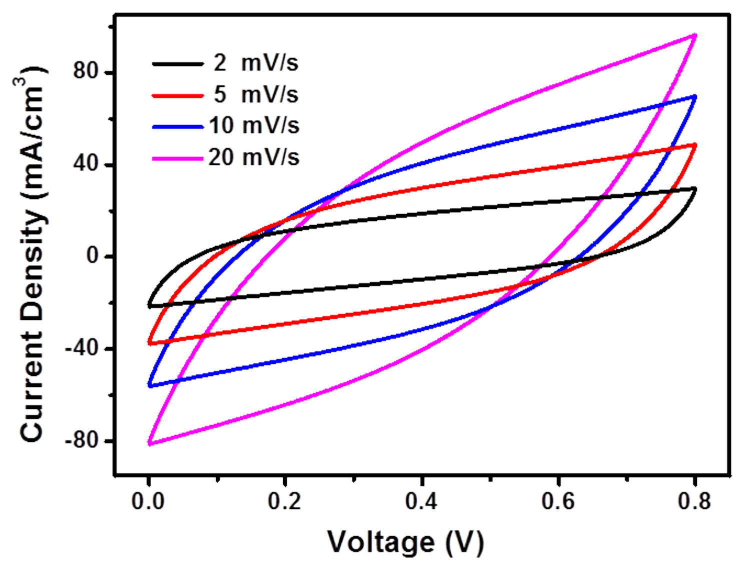

Fig. S6 Electrochemical performance of the flexible solid-state SCs based on freestanding CNT/MnO_2 NT hybrid electrodes, CV curves collected at various scan rates.

Notes and references

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