Supporting Information

High-Performance Supercapacitors Based on MnO₂ Tube-in-Tube Arrays

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Material characterization

The morphology and microstructure of the fabricated materials are characterized by field-emission scanning electronmicroscopy (FE-SEM, JSM-6330F), X-raydiffractometry (XRD, D8ADVANCE), transmission electron microscopy (TEM, TecnaiTM G2 F30). The chemical composition of the samples was characterized by energy-dispersive X-ray spectroscopy (EDS, INCA 300) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250). All XPS spectra were corrected using the C 1s line at 284.6 eV. Inductively coupled plasmaatomic emission spectroscopy (ICP, SPECTRO) was used to analyze the loading of manganese dioxide. The mass loading of MnO₂ TTAs and STAs is 0.32 and 0.16 mg/cm², respectively.

Calculation methods of C_{sp} , power density and energy density

The specific capacitance (C_{sp}) determined from the cyclic voltammometric curves were calculated

according to Eqs. (1~2):

$$C_{\rm sp} = \frac{1}{A\Delta V} \int_{\rm y}^{\rm x} i dt \tag{1}$$

$$C_{\rm sp} = \frac{1}{w\Delta V} \int_{y}^{x} i dt \qquad (2)$$

Where *i*, ΔV , *A* and *w* were the current (mA), voltage range of one scanning segment (V), electrode area (cm²) and weight of the electrode material (mg), respectively.

The specific capacitance (Csp) determined from the chronopotentiometric curves were calculated according to Eqs. (3~4):

$$C_{\rm sp} = \frac{I\Delta t}{A\Delta V} \tag{3}$$

$$C_{\rm sp} = \frac{I\Delta t}{w\Delta V} \tag{4}$$

The energy density (*E*), and power density (*P*) were also calculated from the chronopotentiometric curves according to Eqs $(5\sim6)$:

$$E = \frac{1}{2} C_{sp} (\Delta V)^2$$
(5)
$$P = \frac{E}{\Delta t}$$
(6)

Where *I* is the charge/discharge current, Δt is the time for a full charge ordischarge, *w* is the mass of the active electrode material, and ΔV is the voltage change after a full charge/discharge.



Figure S1. (a-e) Optical images of carbon fiber cloth (CFC) at normal states and various bending states, indicating the excellent flexible ability of the CFC; (f) Typical SEM image of carbon fibers in the CFC.



Figure S2. SEM images of various precursors: (a) ZnO MRAs/CFC, (b) ZnO@MnO₂MRAs/CFC, (c)

 $ZnO@MnO_2@ZnOMRAs/CFC, \ and \ (d) \ ZnO@MnO_2@ZnO@MnO_2MRAs/CFC.$



Figure S3. SEM images of the MnO_2 tube-in-tube arrays (TTAs) with different magnifications on Ti substrate.



Figure S4. SEM image of MnO₂ STAs/CFC.



Figure S5. (a) TEM image, (b) HRTEM image and SAED (inset in (b)) of MnO₂ STAs.



Figure S6. The XPS full spectrum of MnO₂TTAs/CFC.



Figure S7. XPS spectrum of O_{1s} of the MnO₂ TTAs/CFC.



Figure S8. CVs of MnO₂ TTAs/CFC, MnO₂ STAs/CFC, and CFC at 100 mV/s.



Figure S9. (a) GCD curves of MnO₂ TTAs/CFC at different current densities among 6.25~37.5 A/g. (b) The dependence of C_{sp} on current densities for MnO₂ TTAs/CFC among 6.25~37.5 A/g.



Figure S10. (a) CVs of MnO_2 STAs/CFC at different scan rates, (b-c) GCD curves of MnO_2 STAs/CFC at different current densities.



Figure S11. SEM image of MnO_2 STAs/CFC after 2000 cycles.



Figure S12.SEM image of MnO₂ TTAs/CFC after 2000 cycles.



Figure S13. Nyquist plots of MnO₂ STAs/CFC before and after 2000 cycles.



Advantages of CFC



Figure S14. The fast ion and electron transmissions and high utilization rate in MnO_2 TTAs/CFC. (a) Schematic illustration for fast ion and electron transmissions in MnO_2 TTAs/CFC electrode; (b) TTAs architecture provides "highways" for ions and high utilization for MnO_2 TTAs/CFC electrode.



Figure S15. C_{sp} of MnO₂ TTAs/CFC-SSC and STAs/CFC-SSC as a function of scan rate.



Figure S16. C_{sp} retention of MnO₂ TTAs/CFC-SSC device measured at different bend angles. Insets are the pictures of the device under different bend conditions and the schematic illustration of bend angle.



Figure S17. (a) CVs of MnO_2 STAs/CFC-SSC at different scan rates and (b) GCD curves of MnO_2 STAs/CFC-SSC at different current densities.



Figure S18. Ragone plots of MnO₂ TTAs/CFC-SC and MnO₂ STAs/CFC-SSC.