Electronic Supplementary Material (ESI) for Nanoscale.

Three-dimensional nanotube electrode arrays for hierarchical tubular structured high-performance pseudocapacitors

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Supplementary Information

Optical images of electrode fabrication process

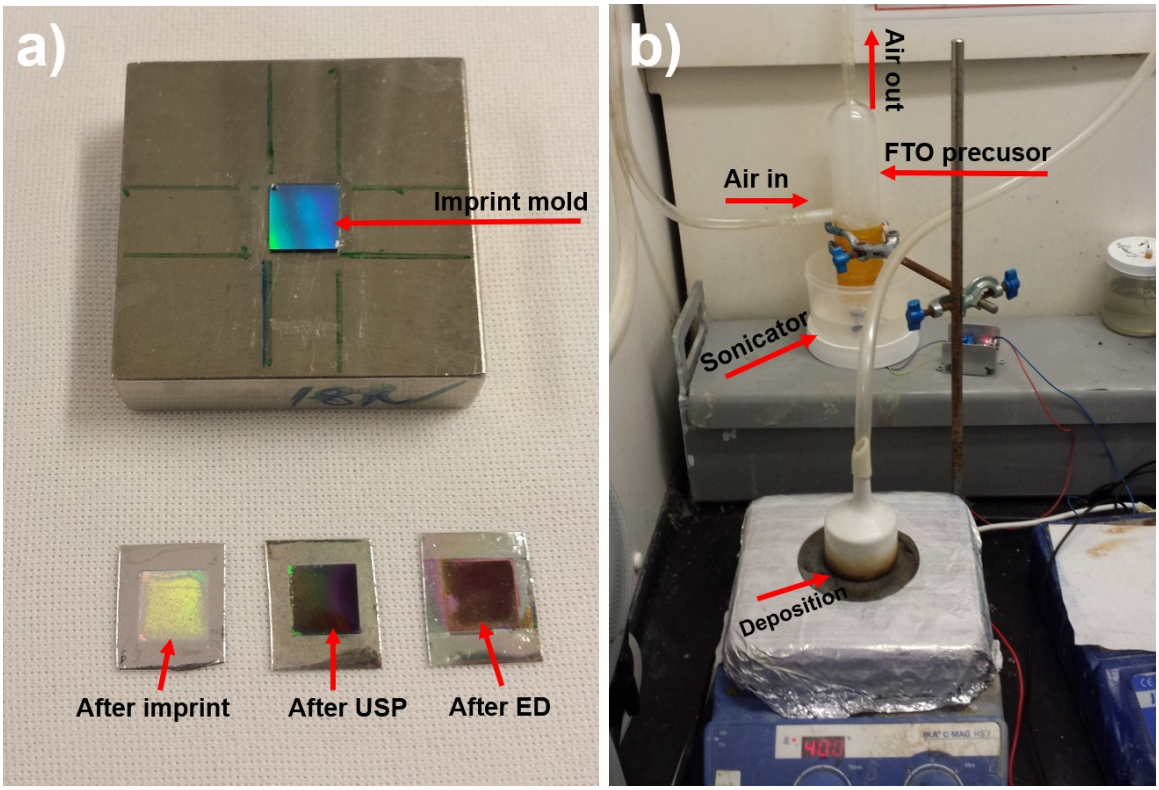
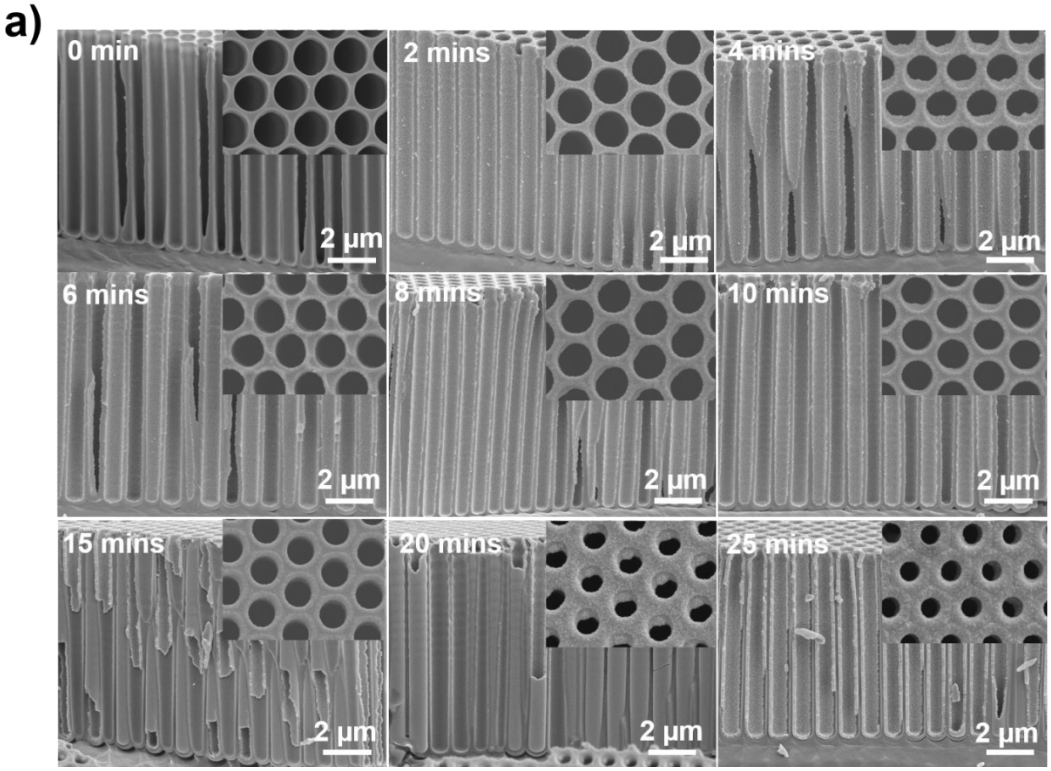
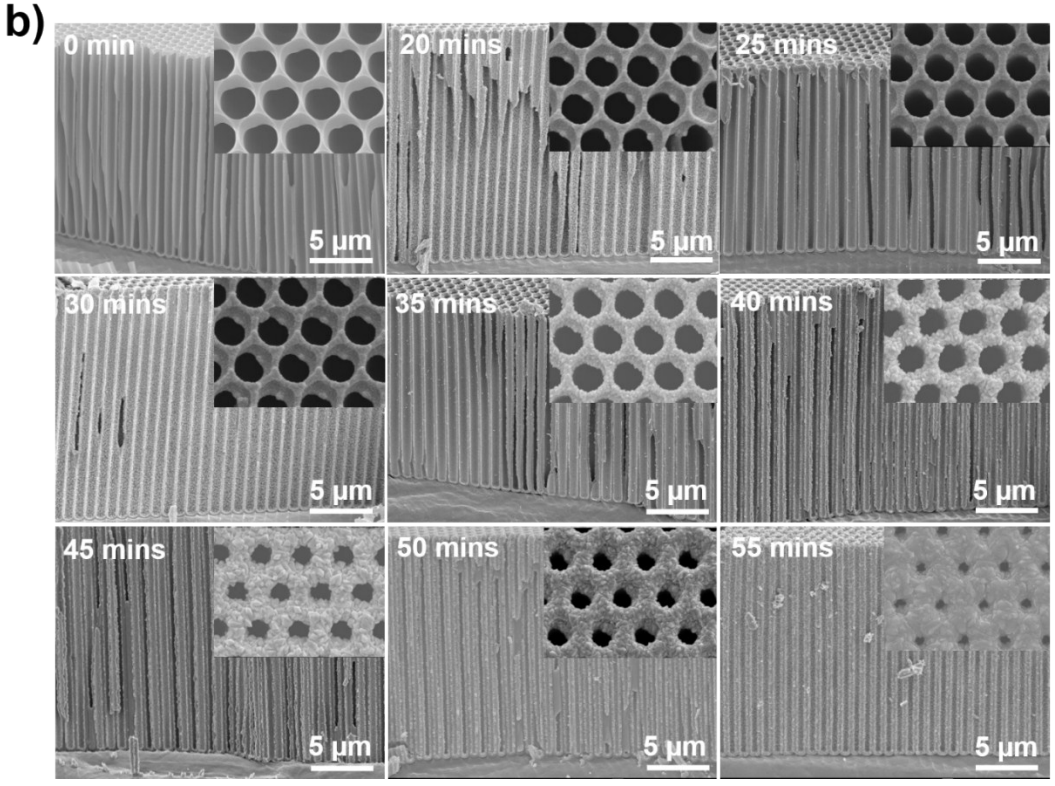


Fig. S1. a) Optical images of as-fabricated pseudocapacitor electrode and Si imprint mold. b) Optical image of USP setup.

SEM images after USP process





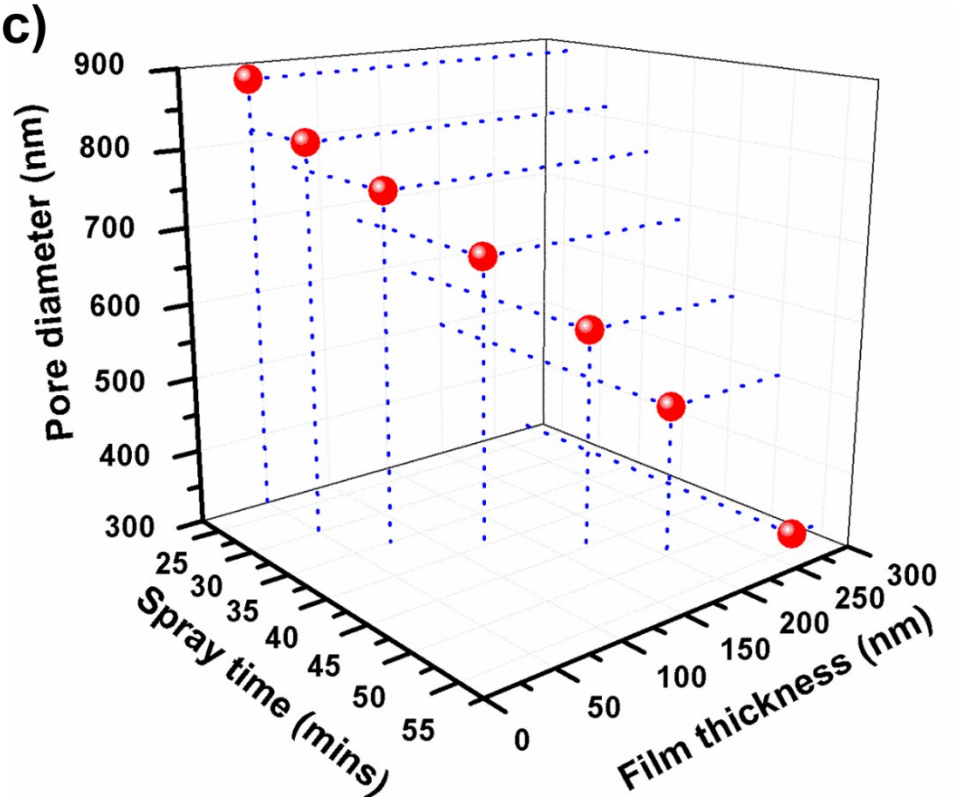


Fig. S2. a) SEM images of FTO tubular shells with the length of 10 μm at different spray time. b) SEM images of FTO tubular shells with the length of 20 μm at different spray time. c) The relationship among pore diameter, FTO film thickness and spray time of 20 μm FTO tubular shells.

Schematic diagram of surface area calculation

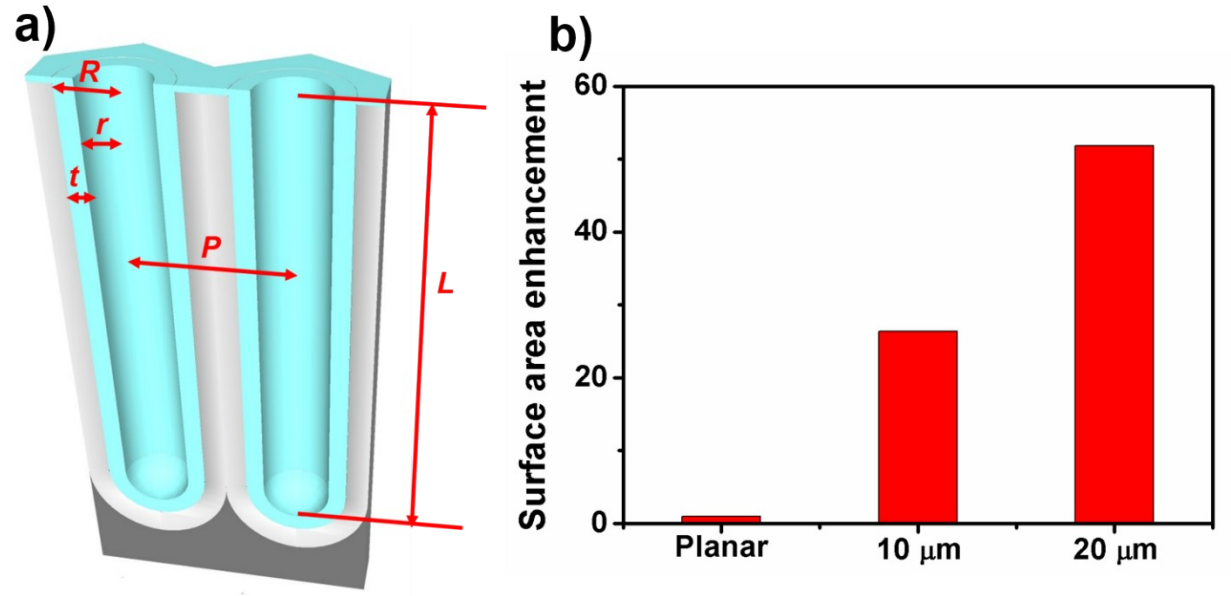


Fig. S3. a) Structural schematic for surface area calculation. b) Surface area enhancement of FTO tubular shells with the length of 10 μm and 20 μm as compared with planar structure.

EDX before and after MnO_2 electrodeposition

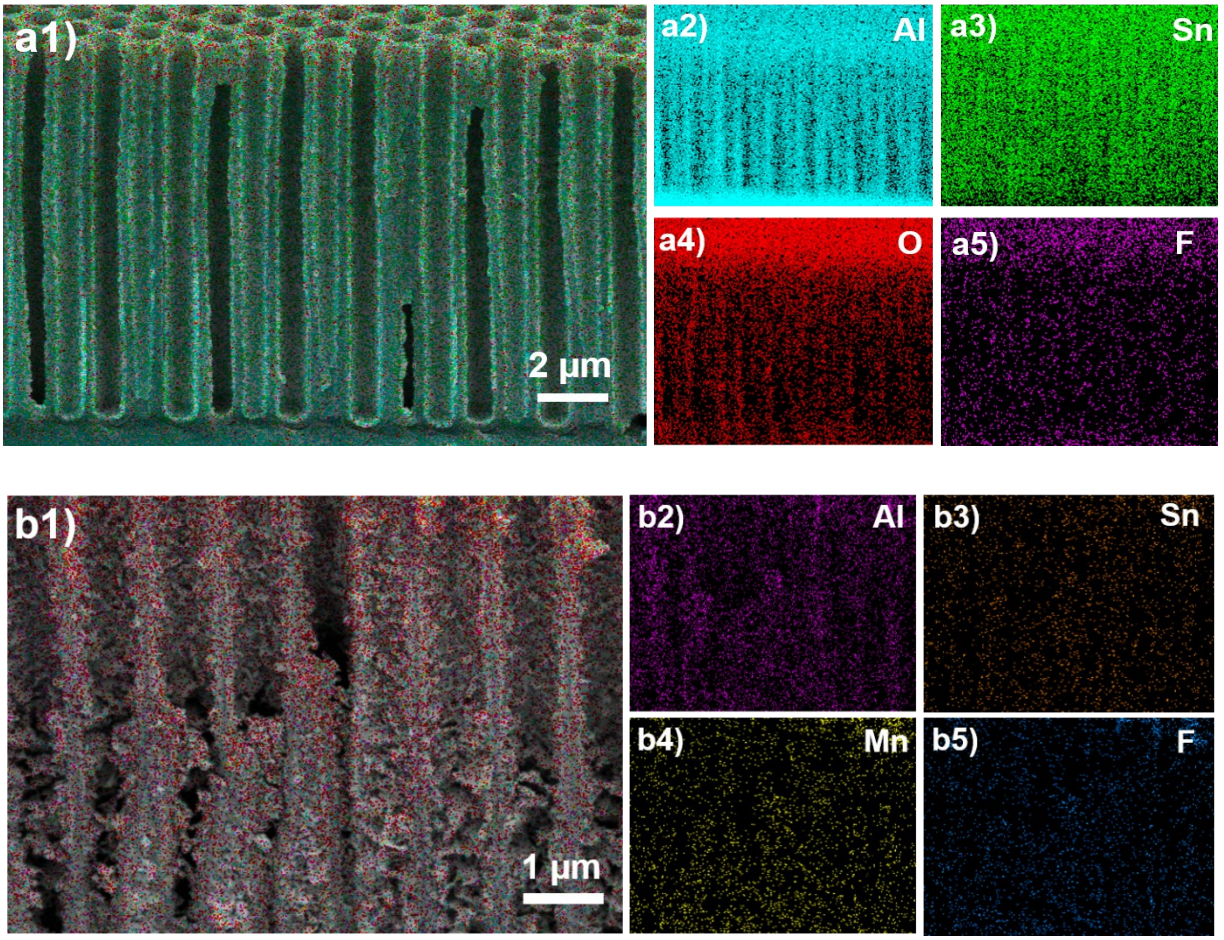


Fig. S4. a) EDX of FTO tubular shells before electrodeposition. b) EDX of FTO tubular shells after MnO_2 electrodeposition.

Capacitance calculation based on total electrode weight and volume

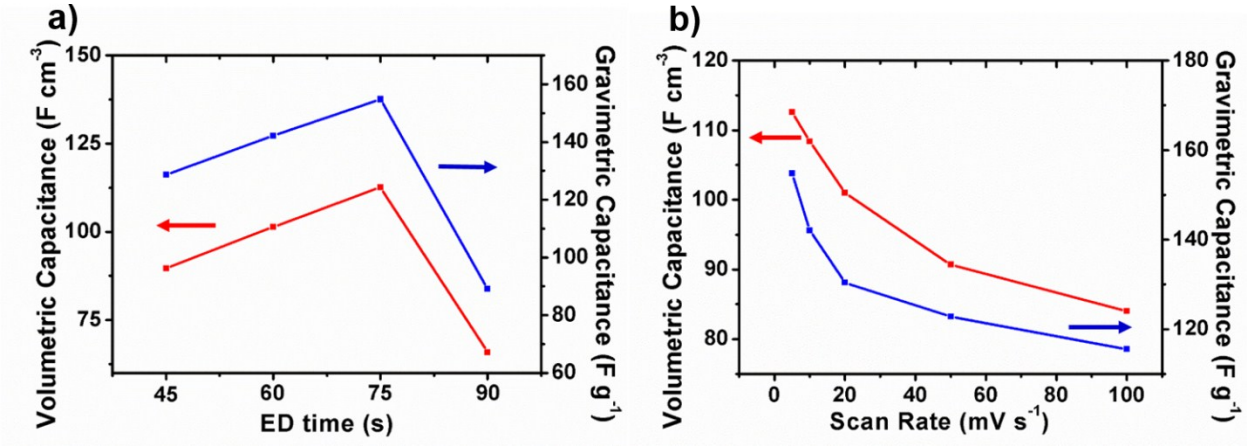


Fig. S5. a) Volumetric and Gravimetric capacitance calculated based on total electrode volume/ weight with different electrodeposition time. b) Volumetric and Gravimetric capacitance calculated based on total electrode volume/ weight with different scan rate after 75 s electrodeposition.

CV and GCD comparison between bare FTO and pseudocapacitor electrode

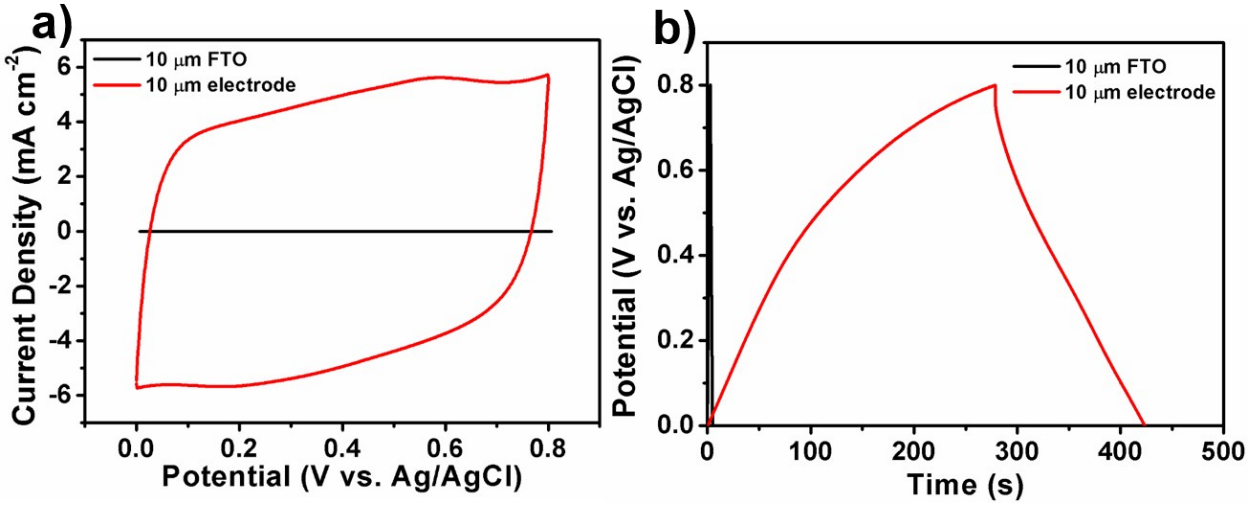


Fig. S6. a) CV of bare FTO and electrode at the scan rate of 50 mV s^{-1}. b) GCD of bare FTO and electrode at the discharge current density of 0.6 mA cm^{-2} (normalized to the projected area of electrode).

CV curves and capacitance calculation of electrode with 10 µm thickness

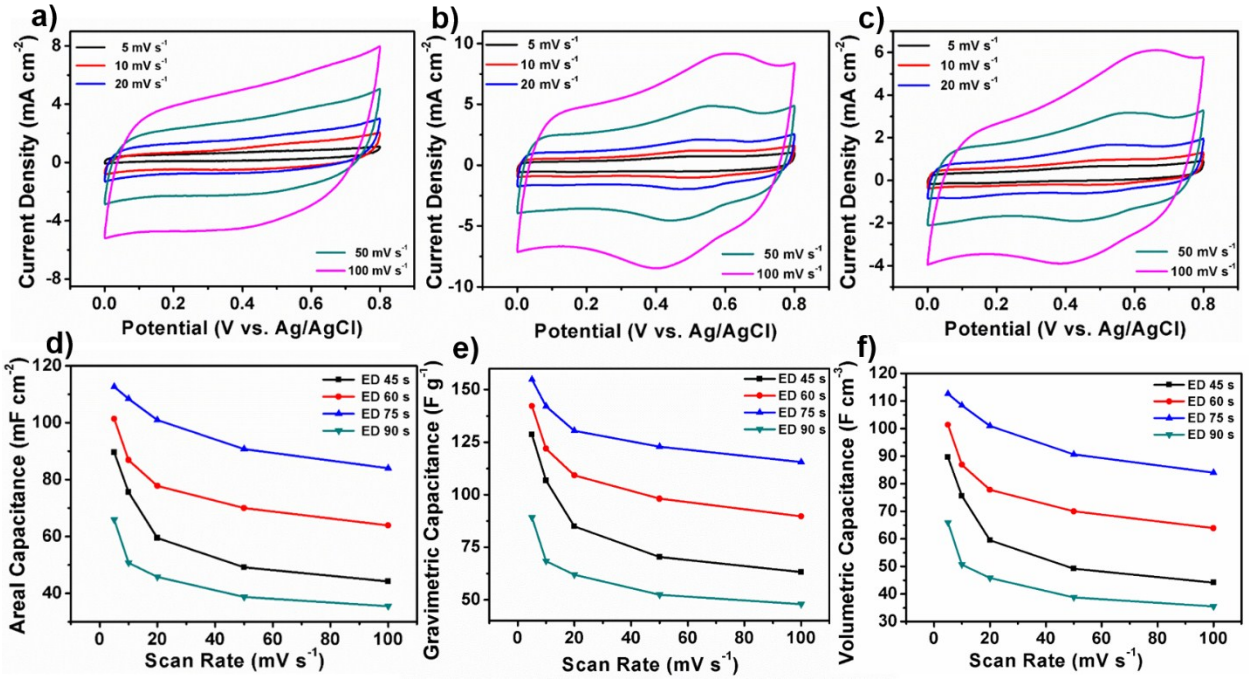


Fig. S7. a) CV of 45 s electrodeposition at different scan rates. b) CV of 60 s electrodeposition at different scan rates. c) CV of 90 s electrodeposition at different scan rates. d) Areal capacitance after different deposition time as the function of scan rates. e) Gravimetric capacitance after different deposition time as the function of scan rates. f) Volumetric capacitance after different deposition time as the function of scan rates.

SEM images after MnO_2 electrodeposition

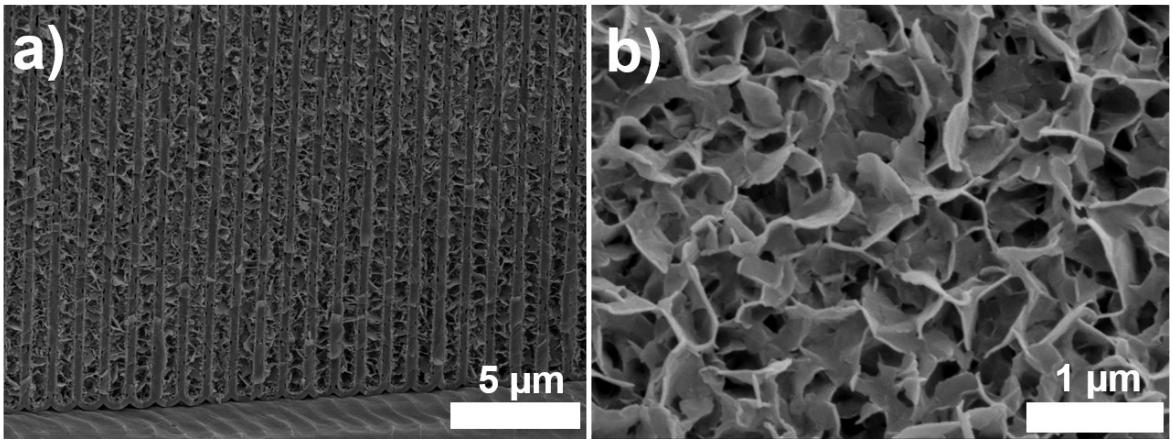


Fig. S8. SEM images of 20 µm hierarchical tubular electrode. a) side view, b) top view.

Materials characterization of pseudocapacitor electrode

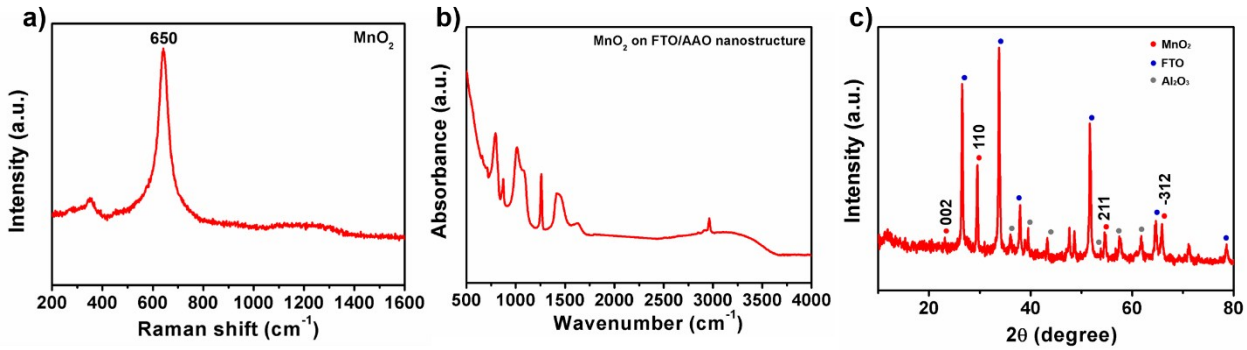


Fig. S9. a) Raman spectrum for MnO_2. b) FTIR of materials components for pseudocapacitor electrode. c) XRD characterization of pseudocapacitor electrode.

GCD and CV together with capacitance calculation of 20 µm electrode

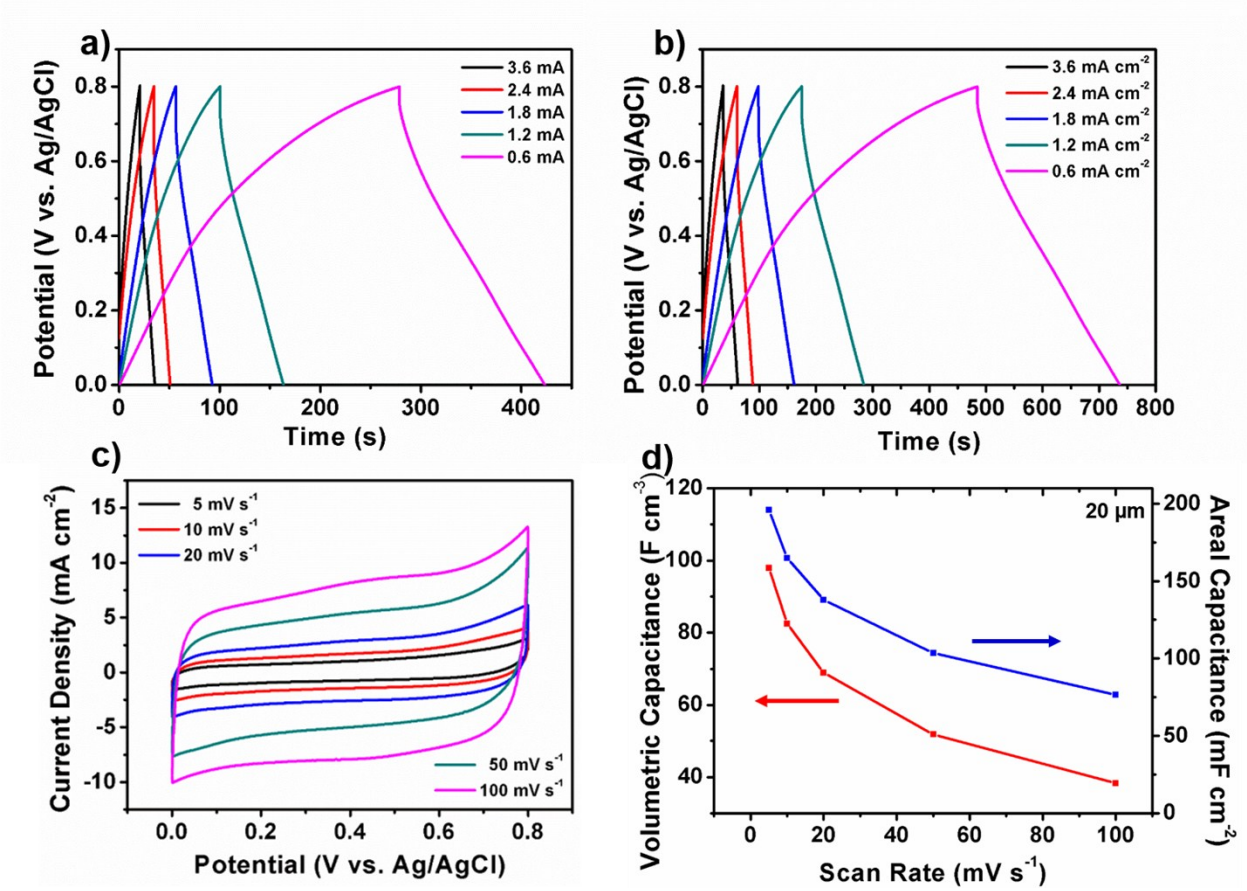


Fig. S10. a) GCD of 10 µm hierarchical tubular electrode at different current densities. b) GCD of 20 µm hierarchical tubular electrode at different current densities. c) CV curve of 20 µm hierarchical tubular electrode at different scan rates. d) Volumetric capacitance and areal capacitance of 20 µm hierarchical tubular electrode as the functions of scan rates.

Optical images of electrode after cycling test

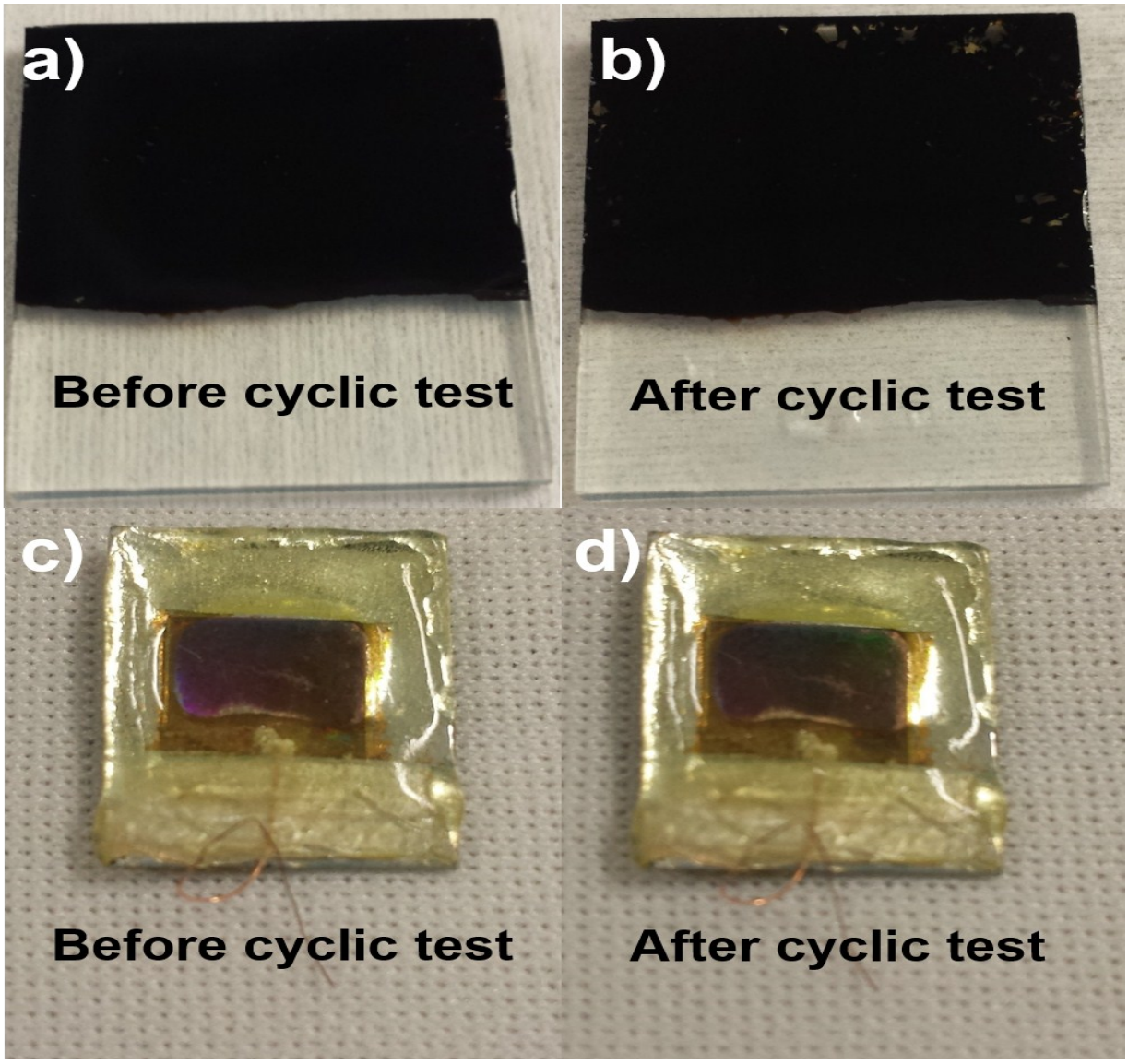


Fig. S11. a-b) Optical images of planar electrode after cyclic test. c-d) Optical images of hierarchical tubular electrode after cyclic test.

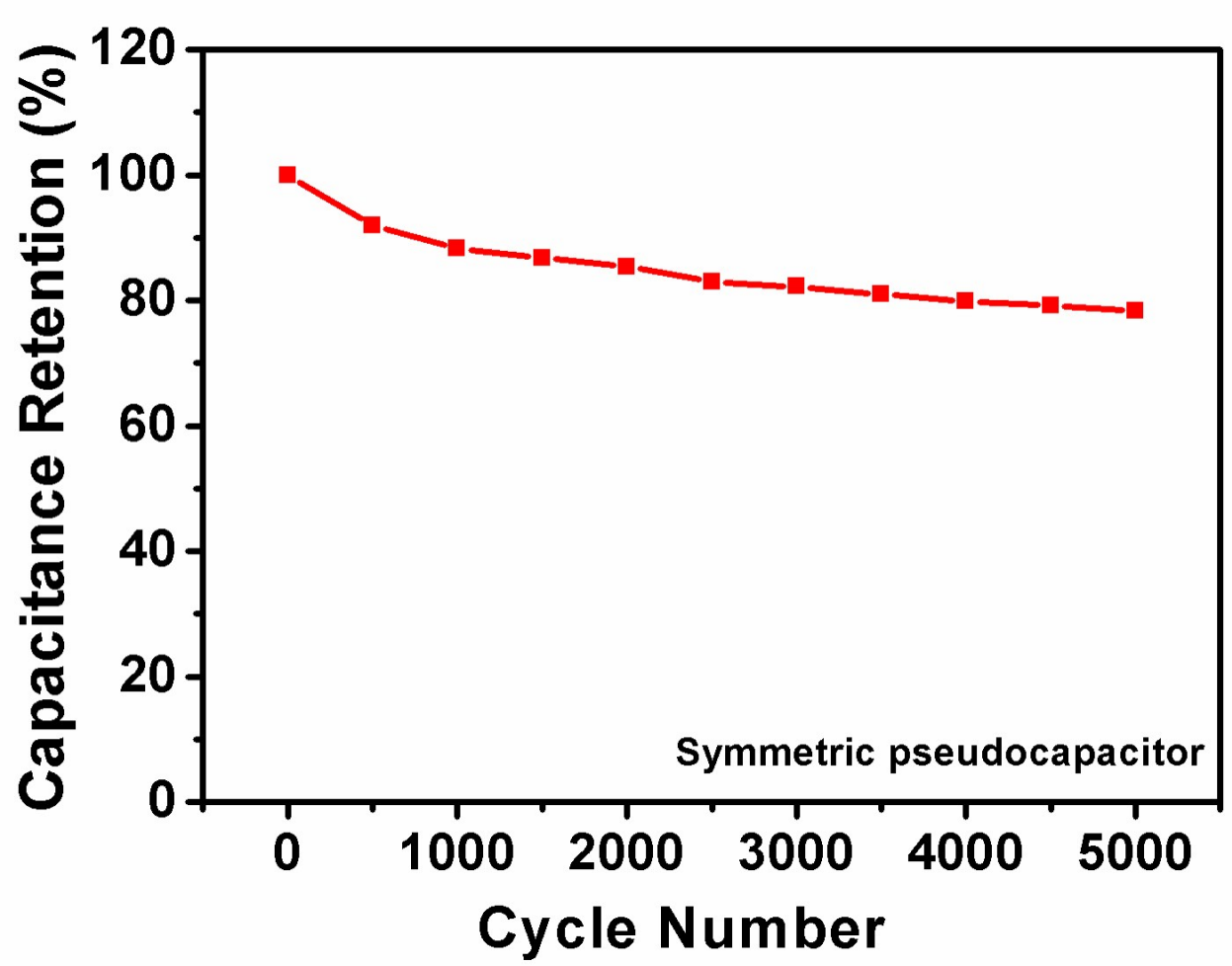


Fig. S12. Cyclic stability test for the symmetric pseudocapacitor device at the scan rate of 100 mV s^{-1}.

Surface Area Calculation equations

As shown in Fig. S3a, surface area (S cm^{-2}) of FTO tubular arrays in an 1 cm^{-2} projected area can be calculated using the following equation:

$$S = \frac{4\sqrt{3}}{3P^2}\pi r L * 10^8 + 1 \quad (1)$$

$$r = R - d \quad (2)$$

Where L is the length of FTO tubular arrays, P is the theoretical value of the pitch, which represents the center-center distance between two neighbouring tubes, r is the radius after FTO deposition, R is the radius after pore size enlargement, and d is the thickness of FTO film. The value of r, R, and d are measured by SEM.

As shown in Fig. S3b, surface area enhancemnet is defined as total surface area divided by projected area.

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