Electronic Supplementary Material (ESI) for Nanoscale

Supplementary Information for

Hierarchical Nanostructures of Polypyrrole @ MnO_2 Composite Anodes for High Performance Solid-State Asymmetric Supercapacitors

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1. The areal capacitance with respect to three-electrode configuration is calculated by the following equation:

$$C_s = \frac{Q_e - Q_s}{\Delta U \cdot S} \quad (1)$$

where C_s is the areal capacitance of the electrode, Q_e is the charge obtained from the discharge curve of the PPy-MnO_2-CC electrode, and Q_s is from the substrate of CC, ΔU is the voltage range during the discharge process, S is the area of the electrode. The volumetric specific capacitance is derived from the same formula in which S is replaced by the volume of the electrode.

2. The areal capacitance with respect to two-electrode full cell is calculated by the following equation:

$$C_s = 2 \times \frac{Q_e - Q_s}{\Delta U \cdot S} \quad (2)$$

where C_s is the areal capacitance, Q_e is the charge obtained from the discharge curve of the PPy-MnO_2-CC//AC-CC full cell device, and Q_s is from the substrate of CC, ΔU is the voltage range during the discharge process, S is the area of per electrode. The volumetric specific capacitance is derived from the same formula in which S is replaced by the total volume of the device.

The specific capacitance with respect to two-electrode full cell is calculated by the following equation:

$$C_{sp} = \frac{C_s}{M} \quad (3)$$

where C_{sp} is the specific capacitance , C_s is the areal capacitance, M is the total mass of active materials per 1 cm^2 in the anode and cathode.

3. The energy density and average power density derived from the discharge process of the device can be calculated from the following equations:

$$D_E = 0.5 C_s (\Delta U)^2 \quad (4)$$

$$D_P = 3600\, D_E / \Delta t \quad (5)$$

where D_E is the energy density, C_s is the areal capacitance which can be obtained through Eq. 2, ΔU is the voltage range during the discharge process, D_P is the average power density and Δt is the discharge time.

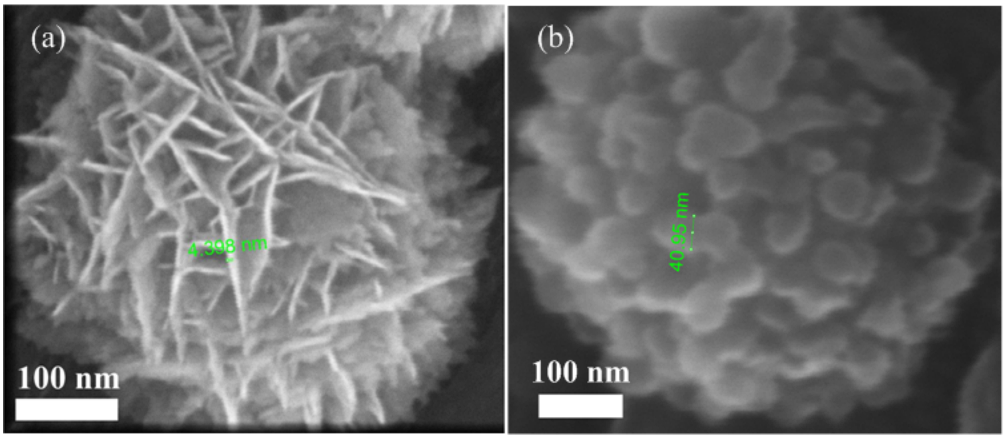

Figure S1. (a) a high resolution SEM image shows that the thickness of the nanowall in a MnO_2 nanoflower is about 4.4 nm. (b) a SEM image shows that the PPy film wrapped on MnO_2 nanowalls is about 18.3 nm.

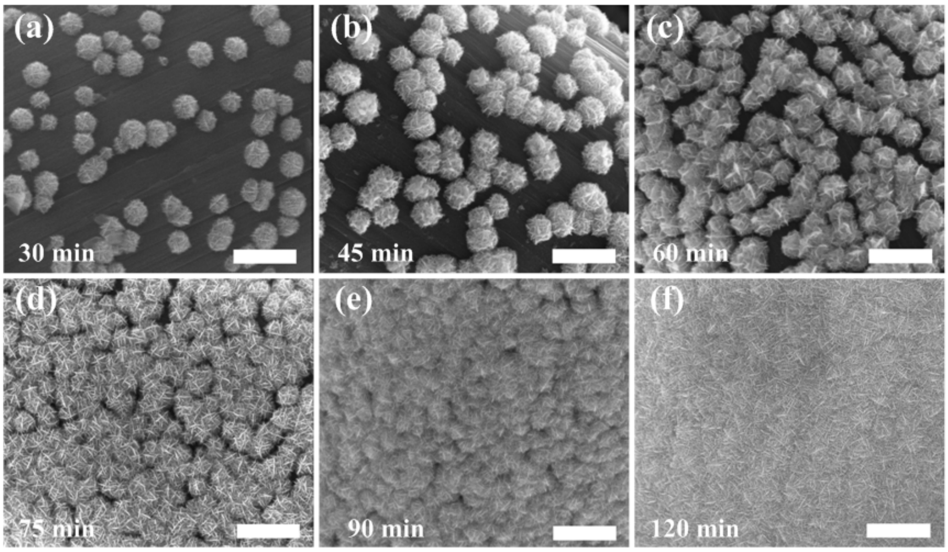

Figure S2. (a-g) SEM images of MnO_2 nanoflowers of different deposition time: 30, 45, 60, 75, 90, 120 min, respectively. All the scale bars: 1 μm. This figure clearly revealed the growth process of MnO_2 nanoflowers.

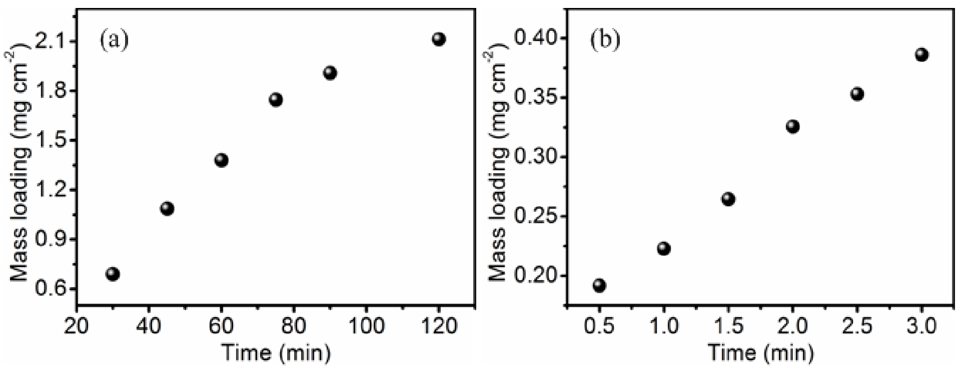

Figure S3. (a) The mass loading of MnO_2 as a function of depositing time. The areal density is ~1.75 mg cm^{-2} at the time of 75 min. (b) The mass loading of PPy as a function of depositing time. The areal density is ~0.35 mg cm^{-2} at the time of 2.5 min.

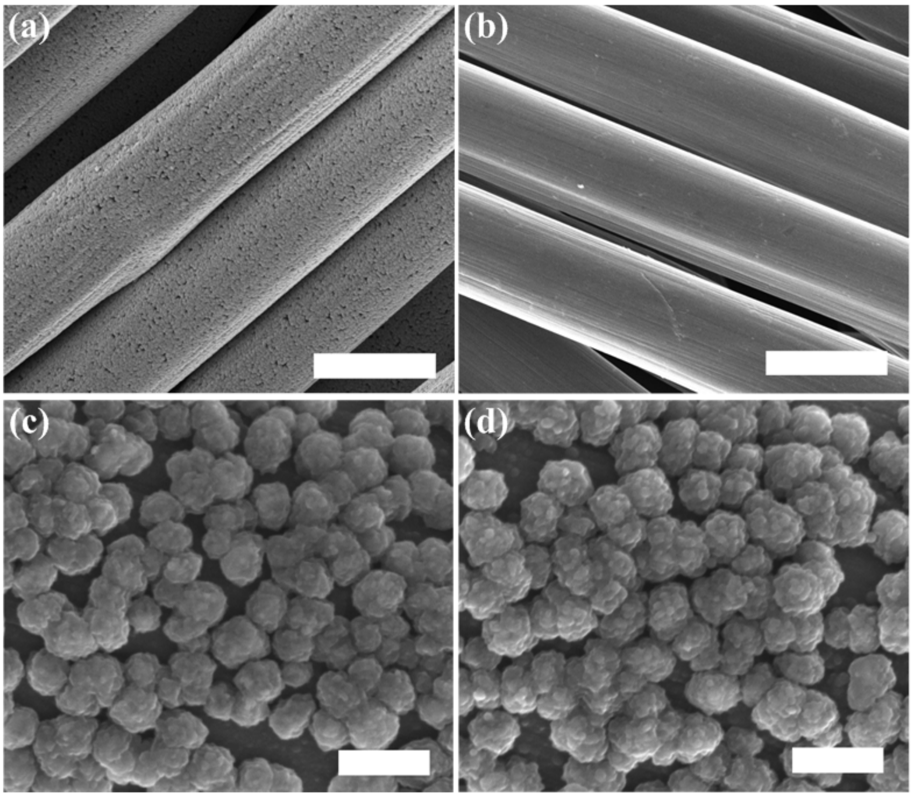

Figure S4. (a, b) SEM images of MnO_2-CC electrodes before and after being immersed into acid solution: (a) before; (b) after being immersed into H_3PO_4 solution of 16.7 wt. % for 12 h. Scale bars: 10 μm; (c, d) SEM images of PPy-MnO_2-CC electrodes before and after being immersed into acid solution: (c) before; (d) after being immersed into H_3PO_4 solution of 16.7 wt. % for 12 h. Scale bars: 1 μm . It was clear to see that PPy could prevent MnO_2 nanoflowers from corrosion by acid electrolyte.

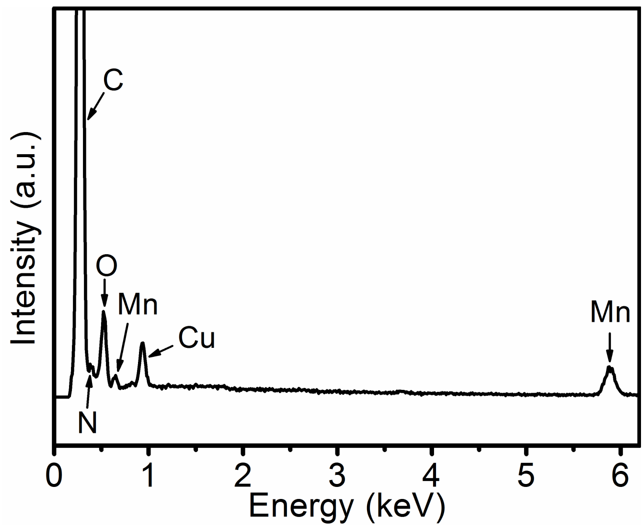

Figure S5. A typical EDS plot of the PPy-MnO_2-CC hybrid structure, in which Cu signal came from the sample stage and N signal came from PPy.

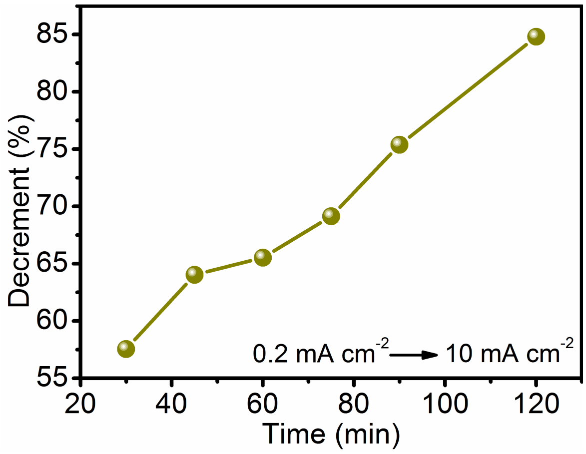

Figure S6. The areal capacitance decrement of MnO_2-CC electrode at different MnO_2 depositing time when the discharge current density enlarged 50 times (from 0.2 mA cm^{-2} to 10 mA cm^{-2}).

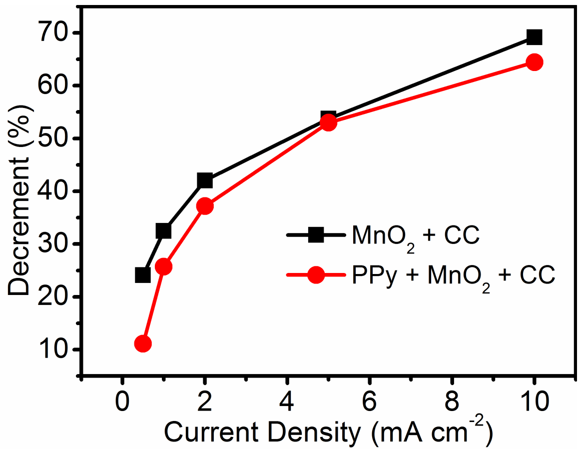

Figure S7. A plot of the areal capacitance decrement of PPy-MnO_2-CC electrode and MnO_2-CC electrode, showing that there is slight improvement of the decrement when discharge current density increased after PPy integration.

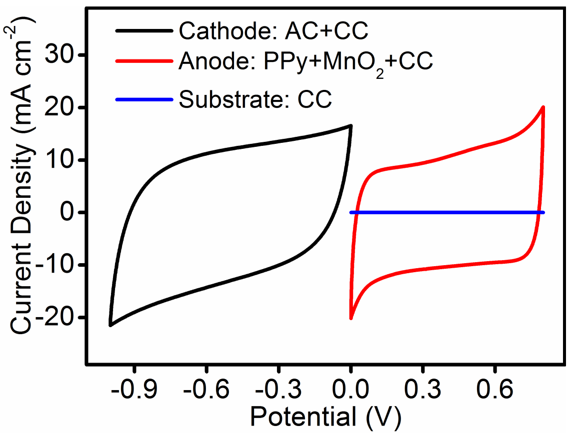

Figure S8. CV curves of the anode, the cathode and the substrate at the same scan rate of 10 mV s^{-1}. The two electrodes are matched well when the mass loading of AC on the cathode is ~ 3.3 mg cm^{-2}, and the capacitance of the substrate is much smaller than that of the electrodes, which can be negligible.

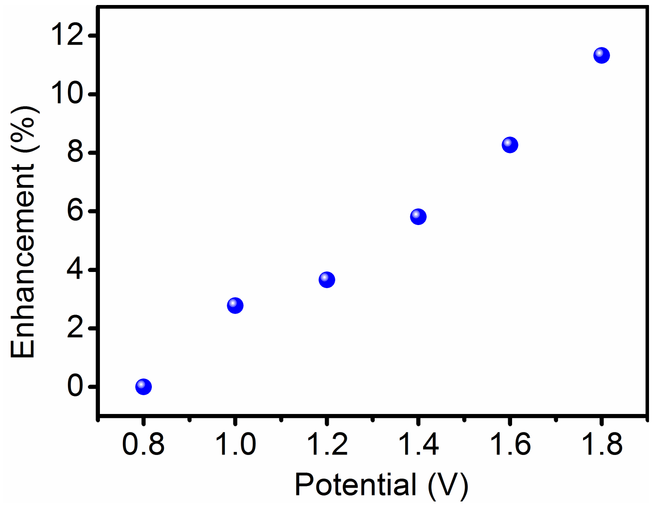

Figure S9. The enhancement of areal capacitance at different potential windows. When the potential window is 1.8 V, the areal capacitance of the device increases of 11.3 % (compared with the potential window of 0.8 V).

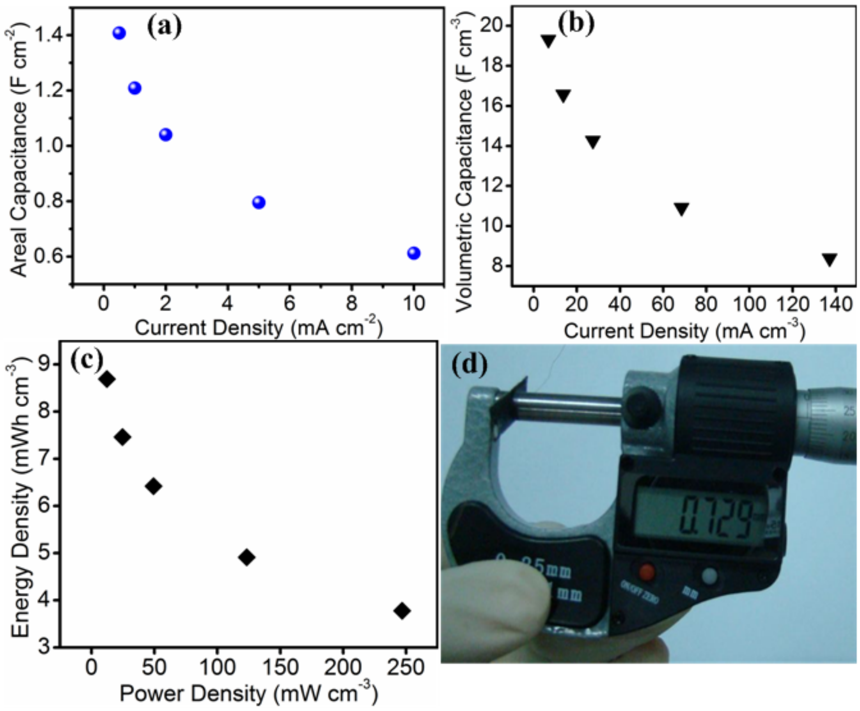

Figure S10. (a, b) The capacitances of the as-fabricated solid-state asymmetric SC calculated from discharge current density curves. (c) Volumetric energy and power density plot. (d) A photograph showing the thickness of the whole device.