Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information

Importance of polypyrrole in constructing 3D hierarchical carbon nanotube@MnO_2 perfect core-shell nanostructures for high-performance flexible supercapacitors

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1) The optimizing method to balance the charges on positive and negative electrodes in the asymmetric supercapacitor

The charges stored by each electrode depend on the specific capacitance (C_s), the potential window for the charge/discharge process (ΔU) and the mass of the active materials in electrodes (m) following the Equation (1):

$$Q = Cs \times \Delta U \times m \, , \quad (1)$$

So, the balance between the charges on positive and negative electrodes can be represented by

$$Cs^{+} \times \Delta U^{+} \times m^{+} = Cs^{-} \times \Delta U^{-} \times m^{-} \, , \quad (2)$$

That is

$$\frac{m^{-}}{m^{+}} = \frac{Cs^{+} \times \Delta U^{+}}{Cs^{-} \times \Delta U^{-}} \, , \quad (3)$$

In our study, the C_s were obtained from the CVs (shown in Figure S4) of single electrode at 10 mV s^{-1}, and they are 239.3 F g^{-1} and 217.6 F g^{-1} for the positive and negative electrodes, respectively. The potential ranges of positive and negative electrodes were from 0 to 1 V and from -1 to 0 V, respectively, so the ΔU is 2 V. Finally, 1.75 mg AC was matched in SSM/AC, according to the Equation (3) with the known mass of MnO_2 and PPy (0.7 mg) in positive electrode.

2) Supplementary figures

PPy treatments

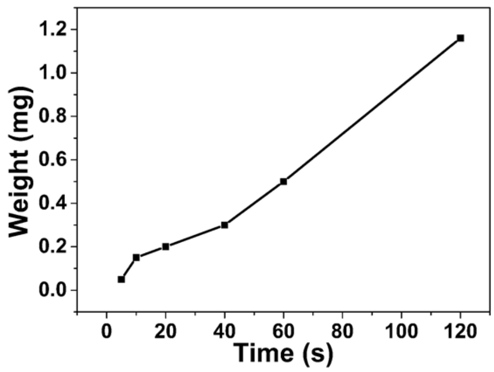

Fig. S1 time-dependent MnO_2 deposition mass.

After 5-s PPy treatment, the CNTs are unevenly coated with large numbers of PPy nanoparticles. When increasing the treatment time to 10s, the CNTs are uniformly coated with a shell of PPy. Thus, 10-s treatment is enough for our work. Further increasing the treatment time to 20s, there will form many PPy nanoclusters within the CNTs samples. Once, increasing the treatment time to 120s, the outer diameter of the CNT@PPy reaches about 500 nm, implying the formation of an over 200-nm PPy shell on CNTs.

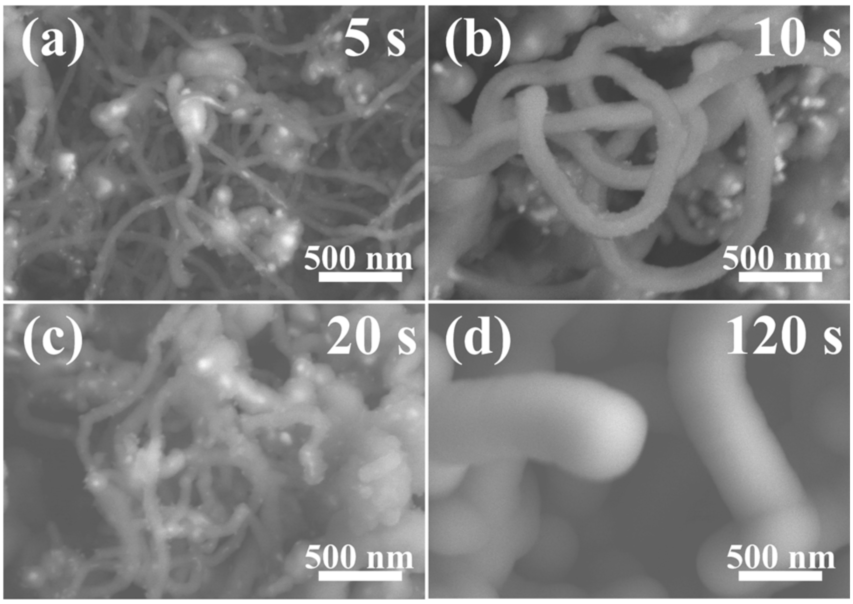

Fig. S2 SEM images of the PPy-treated samples with different time.

The PPy-treated or untreated samples were sent to a Teflon-lined stainless steel autoclave containg 0.03 M $KMnO_4$ solution. And then, the MnO_2 depositions were conducted 60 °C for 0.5, 1, 3, 5, and 7 h. After deposition, the resulting samples were rinsed with DI water for several minutes and naturally dried at room temperature. Via this series of optimization experiments, it is found that the optimized time is 3 h for our case.

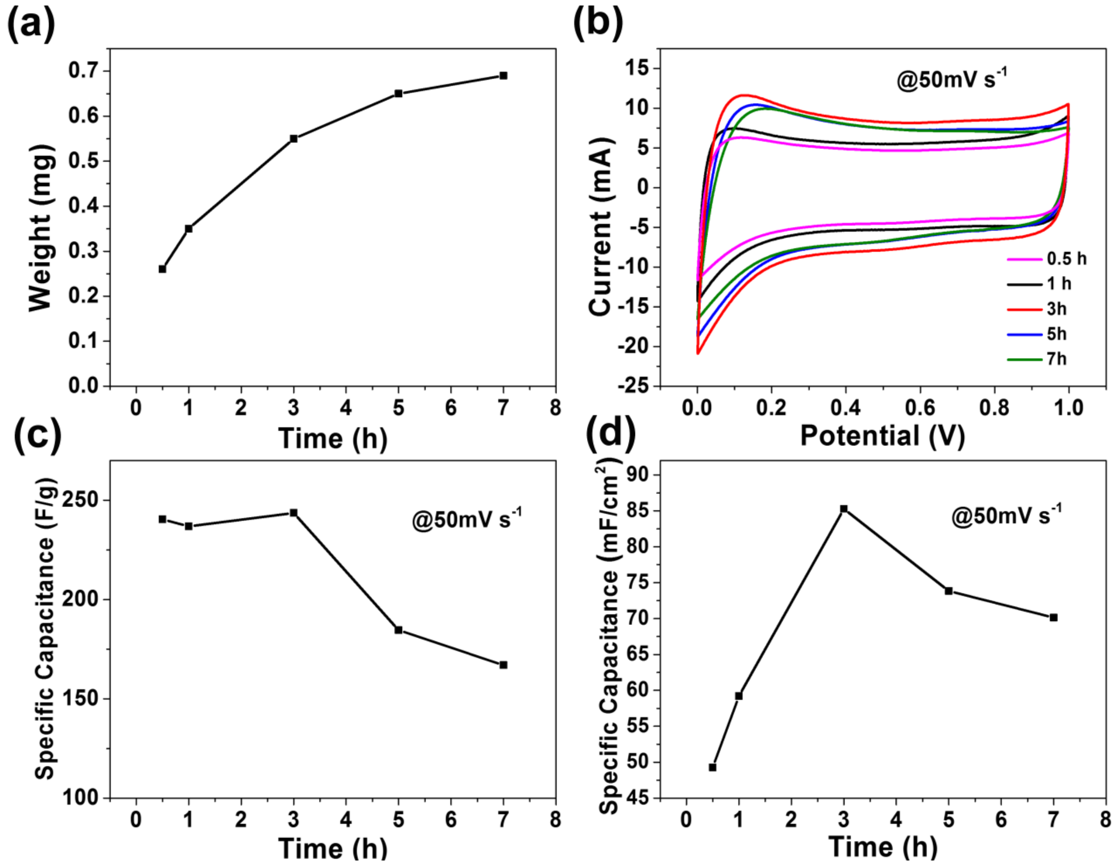

Figure S3 (a) time-dependent MnO_2 deposition mass, (b) CV curves of the electrodes with different MnO_2 deposition time, (c) specific capacitance and (d) capacitance per unit area as a function of MnO_2 deposition time.

The charge balance in the asymmetric supercapacitor was ensured by matching the mass of MnO_2 and PPy in positive (CNTs@PPy@MnO_2) and AC in negative (SSM/AC) electrodes. The CV of CNTs@PPy@MnO_2 was measured within a potential range from 0 to 1 V, while that of SSM/AC was measured within a potential range from -1 to 0 V at the same scan rate of 20 mV/s, as shown in Figure 5 (d). Both CVs are relatively rectangular in shape and exhibit near mirror-image current response on voltage reversal, indicating an ideal capacitive behavior and approximately equal charge for both electrodes.[1] The specific capacitances calculated from the CVs are 347.5 F/g for CNTs@PPy@MnO_2 electrode, and 139 F g^{-1} for SSM/AC electrode. So, SSM/AC with 1.75 mg AC have been matched according to the constant mass of PPy (0.15 mg) and MnO_2 (0.55 mg) in CNTs@PPy@MnO_2.

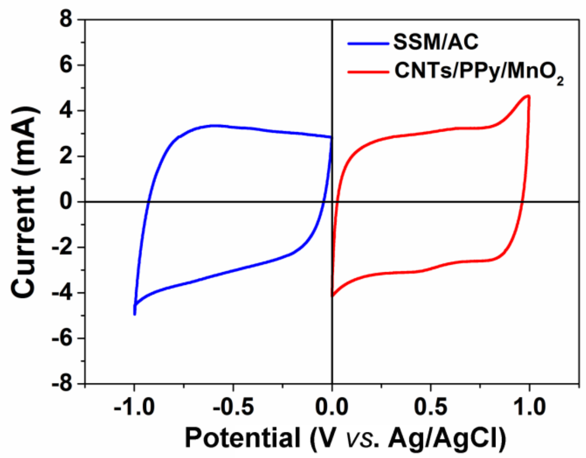

Figure. S4. Comparative CVs of CNT@PPy@MnO_2 and SSM/AC electrodes at a scan rate of 20 mV s^{-1}.

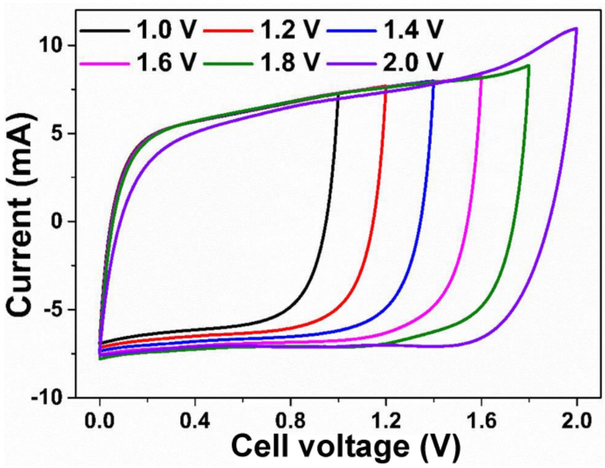

Fig. S5 CV curves of the optimized asymmetric supercapacitor measured at different potential windows in 1 M Na_2SO_4 aqueous solution at a scan rate of 50 mV s^{-1}.

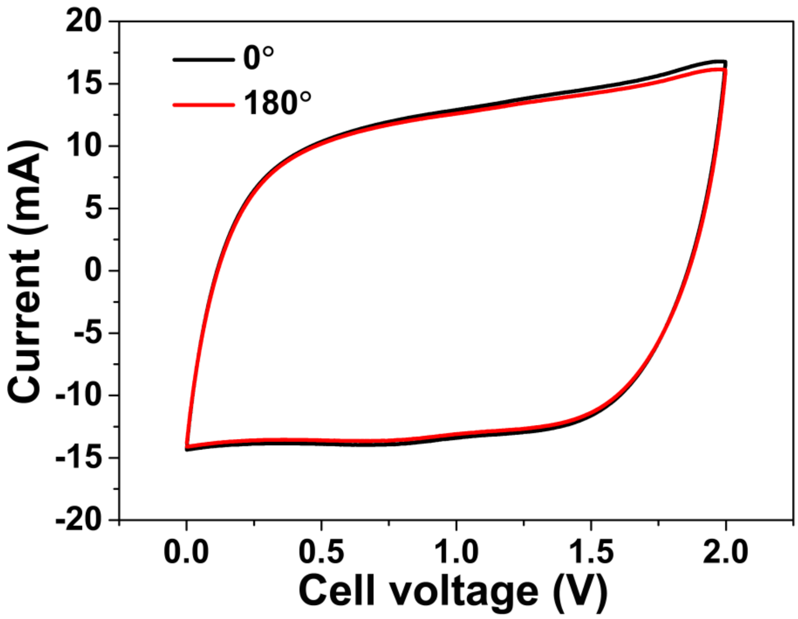

Fig. S6 CVs of the assembled asymmetric supercapacitor under flat and bending conditions (scan rate: 100 mV s^{-1}).

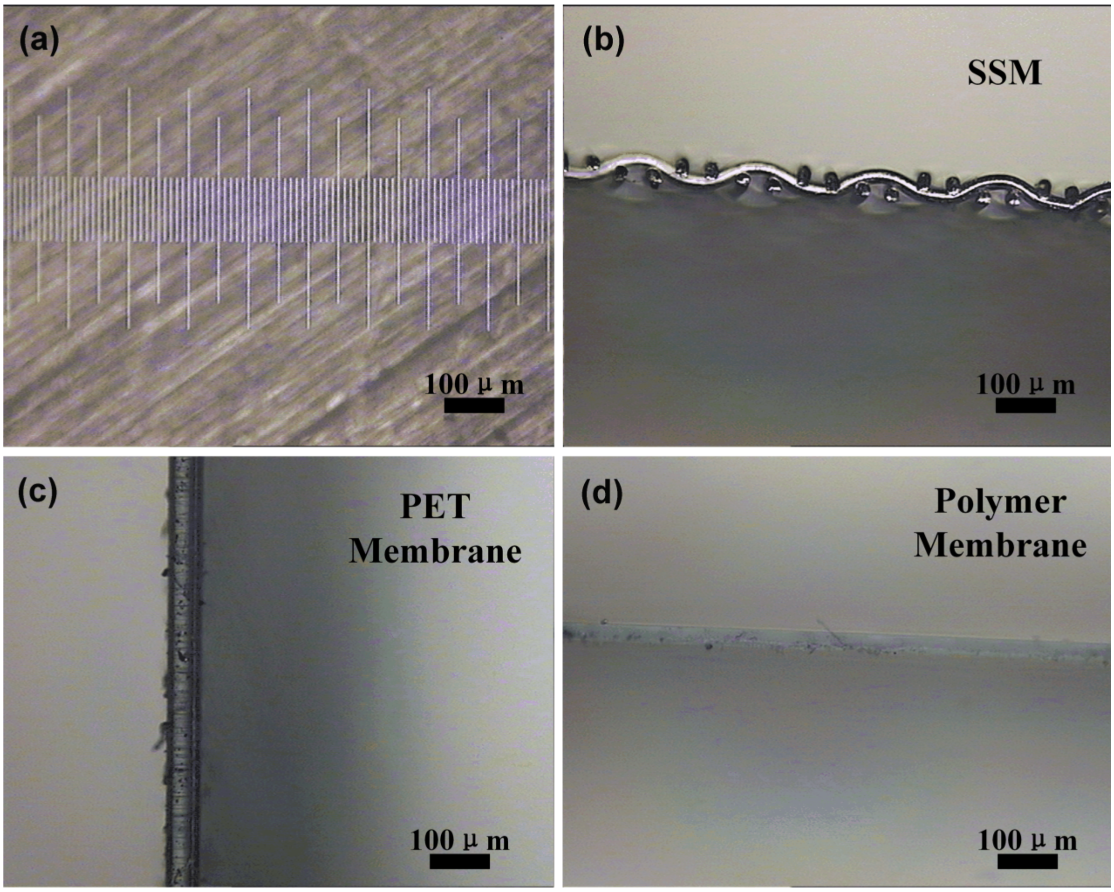

Fig. S7 Optical images of (a) micro ruler, (b) SSM, (c) PET membrane, and (d) polymer membrane.

Their thicknesses are evaluated to be ~50, 40, and 30 μm, respectively. Thus, the total thickness of the device can be roughly estimated to be (50×2+40×2+30) = 210 μm.

1. Z. Fan, J. Yan, T. Wei, L. Zhi, G. Ning, T. Li, F. Wei, *Adv. Funct. Mater.* **2011,** 21 (12), 2366-2375.