Supplementary Information

Ultrahigh Stability in High-Power Nanofibrillar PEDOT Supercapacitors

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Calculations:

The specific capacitance C_{cell} (F/g) of a symmetric supercapacitor was calculated from GCD curves using equation 1.

$$C = It/mV$$
(1)

Where I (mA) is the discharge current, t (s) is the discharge time, V (V) is the potential change (1 V and 1.2 V) during discharge, and m (mg) is the total mass of the active material in both electrodes.

The energy density E (Wh/kg) of a symmetric supercapacitor was calculated from GCD curves using equation 2.

 $E = C_{cell} V^2 / (2 \times 3.6) \tag{2}$

Where Ccell (F/g) is the specific capacitance of a symmetric supercapacitor, V (V) is the potential change during the discharge.

The power density P(W/kg) of a symmetric supercapacitor was calculated from GCD curves using equation 3.

$$P=3600 \times E/t$$
 (3)

where E (Wh/kg) is the energy density, t (s) is the discharge time.

It is important to note that the specific capacitance for electrode materials usually derived from three-electrode measurements involving the reference and counter electrodes is much higher than the actual cell capacitance from a two-electrode measurement. In our system, the absolute specific capacitance ($C_{electrode}$ in F/g) was obtained from equation 4.

$$C_{\text{electrode}} = 4C_{\text{cell}}^{1,2} \tag{4}$$

Where Ccell is the specific cell capacitance for a two-electrode supercapacitor derived from GCD curves.

Coulumbic efficiencies (CE) are calculated using equation 5. $CE = (Q_{out}/Q_{in}) \times 100$ (%) (5)

Where Q_{out} is the amount of charge that exits the battery during the discharge cycle in mA.h Q_{in} is the amount of charge that enters the battery during the charging cycle in mA.h.

The Coulumbic efficiencies can never be 100% because of losses in charge, largely because of secondary reactions, such as the electrolysis of water or other redox reactions in the cell and can quantitatively be determined from Galvanostatic charge discharge (GCD).

For pseudocapacitor with a non-linear discharge profile, the equation (2) overestimates the energy density, hence integration of discharge profile is done as below. The GCD plot below is for a device of total mass 1 mg, cycle at 1 V, at a current density of 0.2 Ag^{.1}. The area under the shaded region is considered for calclating the reported energy densities at different current densities.



Figures:



Fig. S1. a) Sequence of images of an aqueous FeCl₃ micro-droplet inside a CVD chamber during evaporative vapor phase polymerization of PEDOT on hard carbon paper after reactor reaches 130 °C. b) Optical micrograph of the back of this EVPP-PEDOT-coated hard carbon paper shows the deposition of insulating white colored ferrous chloride crystals.



Fig. S2. C-1s core-level spectra of (a) hard carbon paper washed with methanol and (b) washed with methanol and then treated with a FeCl₃ nitromethane solution. O-1s core-level spectra of (c) hard carbon paper washed with methanol only and (d) washed with methanol and then treated with a FeCl₃ nitromethane solution. The enhanced peak intensity for oxidized carbon (C=O, C-O, O-C=O) in (b) and (d) increases after treatment with a FeCl₃ nitromethane solution.



Fig. S3. a) C-1s core-level spectra of pristine hard carbon paper (black curve), and washed with methanol, treated with a FeCl₃ nitromethane solution, and dried in oven at 100 °C (red curve). b) O-1s core-level spectra of pristine hard carbon paper (black curve), and washed with methanol, treated with a FeCl₃ nitromethane solution, and dried in oven at 100 °C (red curve). The enhanced peak intensity for oxidized carbon (C=O, C/O, O-C=O) post a FeCl₃ nitromethane iron treatment stays consistent.



Fig. S4 a) Digital image of tape test on grafted PEDOT showing minimum delamination on the tape. Corresponding optical microscopic and SEM image showing higher adhesion of PEDOT nanofibers to the carbon fibers. b) Similar sequence of images for non grafted PEDOT on carbon paper showing significant peeling off the PEDOT film.



Fig. S5. Elemental composition and morphology of uncycled EVPP-PEDOT-coated hard carbon paper washed in 6 M HCl. a) XPS show the removal of any presence of iron. b) SEM shows nanofibrillar morphology.



Fig. S6 a) Three-electrode GCD profiles and b) two-electrode GCD profiles recorded at different current densities magnified at higher current densities for clarity.



Fig. S7. a) Coulombic efficiencies of PEDOT nanofiber electrode and a device vs the current density. b) Cycling stability as a function of Coulombic efficiency during cycling for a device with mass loading of 7 mg/cm^2 , cycled at 1 V at a current density of 10 A/g.



Fig. S8. CV of hard carbon paper cycled in 1 M H_2SO_4 illustrates its negligible contribution to total capacitance.



Fig. S9. A rendered image of a two electrode device encased in epoxy for long term stability tests.



Fig. S10. a) ESR Plot of three devices after 50,000 cycles. b) ESR profile of a one week old uncycled device shows that upon testing, its ESR continues to increase with cycle number. Note that the ESR is an order of magnitude higher than a device initially cycled after fabrication.



Fig. S11. Cycling stability of device at current densities of 10 A/g and 5 A/g cycled at 1 V. The device is initially cycled at 10 A/g followed by 5 A/g and still retains 90 % of its capacitance for 150,000 cycles.



Fig. S12. a) Comparison of cycling stability of our device where nanofibrillar PEDOT (1 mg/cm²) is grafted onto the current collector with a control device where EVPP PEDOT is deposited in absence of nitromethane. b) Comparison of the cycling stabilities of two devices with two mass loadings, indicating that mass loading do not affect capacitance retention.

Supporting multimedia information:

Movie S1: An aquoues $FeCl_3$ droplet evaporating on a flat glass substrate while temperature ramps from 30 °C to 130 °C (a) on a concave slide (b). The video for droplet evaporation on a concave substrate is accelerated by a factor of 3 in order to match that of a droplet on a flat substrate.

Movie S2: Comaparison of evaporation of an aquoues $FeCl_3$ droplet evaporating on flat glass slide (a) and on hard carbon paper (b). The video of droplet evaporation on hard carbon paper substrate is made 3.5 times faster to match the time on flat substrate.

Movie S3: Additional filter processed video of an aquoues FeCl₃ droplet evaporating on hard carbon paper to enhance the visual effect of polymer skin formation.

Movie S4. Comparison of a standard tape test performed using scotch tape (3M), on grafted EVPP-PEDOT on carbon paper (left panel) and non-grafted EVPP PEDOT on carbon paper (right panel), showing that non-grafted PEDOT peels off easily, and a probable chemical bond between the grafted PEDOT and the underlying carbon paper.

References:

- 1 T. Chen, L. Dai, J. Mater. Chem. A 2014, 2, 10756.
- 2 M. D. Stoller, R. S. Ruoff, Energy Environ. Sci. 2010, 3, 1294.