# **Excellent Rate Capability Supercapacitor Based on Free-standing**

# **PEDOT:PSS Film Enabled by Hydrothermal Method**

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## S1. Experimental

### Materials

Aqueous PEDOT:PSS (Clevios PH1000) was purchased from Xi'an Polymer Light Technology Corporation. Sulfuric acid ( $H_2SO_4$ ) (98.3 wt%) were purchased from Shanghai Laboratorial Equipment Co. Ltd. The nano-porous polypropylene membranes (Celgard 3501) with a pore size of 0.064 µm was purchased from Celgard LLC.

## **Preparation of free-standing PEDOT:PSS films**

First, 1 mL PH1000 solution was vacuum-filtered onto the nano-porous polypropylene membrane in air for 1 h to form PEDOT:PSS film. The films were dried at 50 °C for 2 h in drying oven and then peeled it from the polypropylene membrane to obtain free-standing PEDOT:PSS films. The free-standing films were hydrothermal treated with  $H_2SO_4$  solvent (98.3 wt%) for 10 h in the closed container. The films were rinsed with deionized water for five times to remove the excess of  $H_2SO_4$  and naturally dried to obtain the resultant free-standing PEDOT:PSS film.

### **Preparation of PEDOT:PSS-based SC**

PVA powder (2.0 g),  $H_2SO_4$  (2.0 g) and deionized water (20.0 mL) were mixed together at 45 °C for 0.5 h. The mixture was heated at 75 °C with stirring for 3 h to obtain gel electrolyte. The obtained gel electrolyte was then coated on the free-standing PEDOT:PSS films followed by drying in air at room temperature. Finally, PEDOT:PSS films coated by electrolyte were assembled to be SCs.

### **Characteristics**

The morphology and thickness of free-standing PEDOT:PSS film was characterized through scanning electron microscopy (SEM, Apreo S HiVac, Thermo Scientific, USA) at 5 kV. The structure was analyzed by X-ray diffractometer (XRD, Rigaku Ultima IV, Japan) using a Cu K $\alpha$  source operated at 40 kV with a scan rare of 0.3°/min and X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Scientific, USA) using Al K $\alpha$  rays at 12 kV. Atomic force microscope (AFM, Dimension ICON, Bruker, USA) was employed to explore the topography and phase images with a tapping mode. Thermogravimetric analysis was carried out to analysis the weight loss from room temperature to 800 °C at a speed of 10 °C/min. Sheet resistance was measured by using the four-probe technique (RS-4, Probes Tech, China). Electrochemical performance, including cyclic voltammetry (CV) and galvanostatic charge-discharge measurements (GCD), were measured by an electrochemical workstation (CHI660E, CH Instruments, Shanghai, China). The cycle life was determined by a battery test system (MTI). The specific capacitance is calculated according to the following equations:

$$C = I\Delta t / \Delta E \tag{1}$$

$$C_{v1} = I\Delta t / V\Delta E \tag{2}$$

where C is the total capacitance,  $C_{v1}$  is the specific capacitance, I is the discharge current,  $\Delta t$  is the discharge time,  $\Delta E$  is the potential window during the discharging process after the IR drop, and  $V_I$  is the volume of PEDOT:PSS films. The volumetric energy density (E) and power density (P) was calculated as follows:

$$C_{v2} = I\Delta t / V\Delta E \tag{3}$$

$$E = C_{v2} \Delta E^2 / 2 \tag{4}$$

$$P = E/\Delta t \tag{5}$$

where  $C_{v^2}$  is the volumetric capacitance of the flexible device, *I* is the discharge

current,  $\Delta t$  is the discharge time,  $\Delta E$  is the potential window during the discharging process.  $V_2$  is the device volume including the two electrodes.

### S2. The changes during hydrothermal process

When PEDOT:PSS films are soaked into  $H_2SO_4$  solutions.  $H_2SO_4$  dissociates into  $H^+$  and  $HSO_4^-$  in water (Formula 1-1). As the temperature gradually increases,  $H^+$  associates with PSS<sup>-</sup> to form PSSH (Formula 1-2). The total reaction could be written as formula (1-3). This reaction leads to the replacement of some PSS<sup>-</sup> with  $HSO_4^-$  as the counter anions of PEDOT (Fig.S1a and b) [1,2]. Noticeably, PSSH chains are neutral and do not have Coulombic interaction with PEDOT. Hence, insulating PSSH is effectively removed. As temperature and pressure continue rising, the structure is degraded.

$$H_2SO_4 \rightarrow H^+ + HSO_4^-$$
(1-1)

$$H^{+} + PSS^{-} \rightarrow PSSH$$
 (1-2)

$$H_2SO_4 + PSS^- \rightarrow HSO_4^- + PSSH$$
 (1-3)



Fig.S1 Molecular structures of PEDOT:PSS before and after H<sub>2</sub>SO<sub>4</sub> treatment

### S3. The detailed discissions about XPS

As shown in Fig.2b, the intensity of PSS is HT-RT>HT-100>HT-120>HT-80

under the same intensity of PEDOT peaks. Namely, HT-80 exhibits the lowest intensity, indicating the insulating PSS of HT-80 is effectively detached. The phenomenon is associated with dielectric constant of H<sub>2</sub>SO<sub>4</sub> solutions under different temperatures, which affects the removal of PSS [3]. High dielectric constant of solution is beneficial for the removal of PSS. As the temperature rising, the dielectric constant of solution increases first and then declines due to the polarizations increasing and then decreasing. Hence, the content of PSS decreases first and then increases. Namely, HT-80 shows the lowest content of PSS. Yet, the PSS content of HT-120 is lower than HT-100. This is mainly because the structure is destroyed at 120 °C, which leads to PSS washing away. Moreover, we also find that binding energies of samples, treated by temperature, shifts to a lower position. This is due to the protonation of the PSS-SO<sub>3</sub>-[3]. For the PEDOT, the binding energy of HT-80 is lower than HT-RT by ~0.5 eV, which can be ascribed to a reduction of the insulating PSS component and a possible ion-exchange by acid treatment [3,4].





S5. The SEM images of (a) HT-RT, (b) HT-80, (c) HT-100, and (d) HT-120 (the scale bar is 500 nm)



S6. The CV profiles of (a) HT-RT, (b) HT-80, (c) HT-100, and (d) HT-120 from 200 to 1300 mV s<sup>-1</sup>



## References

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