#### **Electronic Supporting Information**

# Ultrahigh-rate electrochemical capacitor based on solution-processed highly conductive PEDOT:PSS films for AC line-filtering

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#### 1. Experimental section

#### **1.1 Preparation of Electrodes**

**AT-PEDOT:PSS electrodes**. PEDOT:PSS solution (Clevios PH1000, Heraeus) was directly used after stirring for 2 h at room temperature. A cellulose paper was adhered onto the surface of a graphite foil (conductivity~16,000 S cm<sup>-1</sup>, thickness = 16  $\mu$ m, Emitac New Material Technology Co. Ltd, Suzhou, China) with the assistance of water wetting. Typically, PEDOT:PSS solution was slowly dropped on the semi-dried cellulose paper and spin-coated at 2,000 rpm for 30 s. The thickness of electrodes can be modulated by changing the concentration of PEDOT:PSS or by repeated spin-coating. Successively, the resulting films were immersed into concentrated H<sub>2</sub>SO<sub>4</sub> (98 wt.%) overnight at room temperature followed by washing in deionized water. Finally, the AT-PEDOT:PSS electrodes were dried under ambient condition.

**HNO<sub>3</sub>-treated PEDOT:PSS electrodes.** The control HNO<sub>3</sub> treated PEDOT-PSS electrodes were prepared through the same procedures described above except the time of acid treatment was reduced to as short as 15 min. The conductivity of HNO<sub>3</sub>-treated PEDOT:PSS is comparable to that of AT-PEDOT:PSS<sup>S1</sup> and the amount of residual polymer after HNO<sub>3</sub>-treating of PEDOT:PSS coated on graphite foil (2000 rpm min<sup>-1</sup>) is almost identical to that of 300 nm-AT-PEDOT:PSS. In this case, the cellulose skeleton was still remained; thus, this HNO<sub>3</sub> treated PEDOT:PSS electrode

is much thicker than that of the AT-PEDOT:PSS electrode with the same mass loading.

#### **1.2 Material characterizations**

Scanning electron micrographs were taken out on a Sirion 200 field-emission scanning electron microscope (FEI, USA). Raman spectra were recorded on a LabRAM HR Evolution (HORIBA Jobin Yvon, France) with a 514-nm laser, and X-ray photoelectron spectra (XPS) were conducted using an Escalab 250 photoelectron spectrometer (ThermoFisher Scientific, USA). Electrical conductivity measurements were carried out using a four-point probe test instrument (KDY-1) at room temperature. Mechanical testing were performed on an Instron 3342 universal testing machine (Instron, USA) with a loading rate of 0.5 mm min<sup>-1</sup> with a gauge length of 15 mm.

#### **1.3 Fabrication of ECs and electrochemical measurements**

All electrochemical measurements were carried out using a symmetrical twoelectrode cell configuration by stacking two identical electrodes ( $5 \times 5 \text{ mm}^2$ ) in a face to face manner with a porous separator of cellulose paper. 1.0 M aqueous solution of H<sub>2</sub>SO<sub>4</sub> was used as aqueous electrolyte and a H<sub>2</sub>SO<sub>4</sub>/PVA polymer gel <sup>S2</sup> was used as the solid electrolyte. The All-solid-state EC was constructed by sandwiching a H<sub>2</sub>SO<sub>4</sub>/PVA membrane between two identical AT-PEDOT:PSS/graphite foil electrodes and the thickness of electrode material was 300 nm. This device was dried at room temperature to evaporate excess water. Cyclic voltammograms, galvanostatic charge-discharge curves, and electrochemical impedance spectra (EIS) in the frequency range of 1-100 kHz with a 5 mV ac amplitude were carried out using a CHI 660D electrochemical workstation (CHI Instruments Inc., Austin, TX). For selfdischarge tests, the devices were first charged to 0.8 V at 0.02 mA and kept at 0.8 V for 10 min, and then the open potential of the device was measured as a function of time. It should be noted here that the electrode material is too light to be weighted accurately. Thus, the special capacitances of the ECs were evaluated in area ( $\mu$ F cm<sup>-2</sup>) and volume (F cm<sup>-3</sup>) units. The specific areal capacitance of EC devices,  $C_A$  ( $\mu$ F cm<sup>-2</sup>), was calculated from EIS spectra by equation S1:

$$C_{\rm A} = -1/s(2\pi f Z^{"})$$

eq S1

where f is frequency (Hz), Z" is the imaginary resistance ( $\Omega$ ) and s is the area of the electrode (cm<sup>2</sup>).

 $C_{\rm V} = -1/\mathcal{V}(2\pi f Z^{\prime\prime}) \qquad \text{eq S2}$ 

where v is the volume of the two electrodes;  $v = 2d \times s$  and d is the thickness of a single electrode.

The  $C_A$  (µF cm<sup>-2</sup>) of EC devices measured by galvanostatic charge-discharge test was calculated by equation S3:

$$C_A = I\Delta t / s\Delta V \qquad eq S3$$

 $C_V$  (F cm<sup>-3</sup>) measured by galvanostatic charge-discharge test was calculated by equation S4:

$$C_V = I\Delta t / v \Delta V$$
 eq S4

The specific volumetric energy  $(E_V)$  and volumetric power density  $(P_V)$  derived from charging-discharging curves were calculated by using equations:

$$Ev=1/2C_VU^2$$
 eq S5

$$P_V = E_V / \Delta t$$
 eq S6

where *I* is the constant discharge current ( $\mu$ A cm<sup>-2</sup>),  $\Delta t$  is the discharge time (s),  $\Delta V$  is the discharge potential drop (V) (excluding IR drop), *s* is the area of the electrode, and U is the operating potential window.

# 2. Supplementary figures



Fig. S1 (a,b) Top view SEM images of a graphite foil before (a) and after (b) concentrated  $H_2SO_4$  treatment; (c) cross-section SEM images of a graphite foil; (d) Typical tensile stress-strain curve of a graphite foil before and after concentrated  $H_2SO_4$  treatment.



**Fig. S2** (a, b) S 2p XPS spectra (a) and Raman spectra (b) of pristine PEDOT:PSS and AT-PEDOT:PSS.

S 2p XPS spectra were taken out to analyze the composition difference between pristine PEDOT:PSS and AT-PEDOT:PSS. In Fig. S2a, the 164.4 eV band is related to the S atoms of PEDOT and the 168.6 eV band is assigned to the S atoms of PSS.<sup>S3</sup> The intensity of 168.6 eV band in the spectrum of AT-PEDOT:PSS is much weaker than that in the spectrum of pristine AT-PEDOT:PSS, implying the insulating PSS in PEDOT:PSS was partially removed by H<sub>2</sub>SO<sub>4</sub> treatment. Raman technique was applied to study the conformational changes of a PEDOT:PSS film upon H<sub>2</sub>SO<sub>4</sub> treatment. As shown in Fig S2b, the Raman bands in the spectrum of AT-PEDOT:PSS film are stronger and sharper than those in the spectrum of pristine PEDOT:PSS. The 1510 cm<sup>-1</sup> (A) and 1435 cm<sup>-1</sup> (B) bands are attributed to the antisymmetric and symmetric stretching vibrations of  $C_{\alpha}$ - $C_{\beta}$  bonds of neighboring thiophene rings.<sup>S1</sup> The intensity ratio of I<sub>A</sub>/I<sub>B</sub> for AT-PEDOT:PSS is much higher than that for pristine PEDOT:PSS, reflecting the former has longer conjugation lengths of PEDOT chains. These results indicate that the great increase in the conductivity of PEDOT:PSS upon H<sub>2</sub>SO<sub>4</sub> treatment is mainly caused by partially removing its insulating PSS and increasing the conjugation lengths of PEDOT chains.



**Fig. S3** Photographs of a cellulose paper, a graphite foil, and a PEDOT:PSS coated cellulose paper/graphite foil.



**Fig. S4** (a-d) The photographs of AT-PEDOT:PSS film before (a,b), under (c) and after violent stirring (300 rpm). The AT-PEDOT:PSS film strongly adhered to the surface of graphite foil and kept intact even after violent stirring.



**Fig. S5** (a) Comparison of the phase angles of EC-n at different frequencies; (b) Nyquist plots of EC-300 and AEC.



**Fig. S6** (a) The CV curves of EC-300 and EC-0 at a scan rate of 10 V s<sup>-1</sup>; (b) Plots of  $C_A$  versus frequency for EC-300 and EC-0.



Fig. S7 (a) The CV curves of EC-300 and  $H_2SO_4$ -treated graphite foil based EC (EC-A0) at a scan rate of 10 V s<sup>-1</sup>; (b) Plots of  $C_A$  versus frequency for EC-300 and EC-A0; (c) CV curves of EC-A0 at various scan rates; (d) Plot of discharge current density versus scan rates for EC-A0.



**Fig. S8** (a,b) Plot of  $C_A$  and  $C_V$  versus discharge current density for EC-300; (c) Ragone plot of energy densities versus power densities of EC-300; (d) Self-discharge curves of EC-300 and AEC after charging to 0.8 V and stabilizing at this voltage for 10 min;



**Fig. S9** (a-d) The comparison of various EIS parameters versus frequency for EC-300 before and after charging-discharging for 12,000 cycles at 2 mA cm<sup>-2</sup>; (a) phase angle, (b) impedance, (c)  $C_A$ , (d) C' or C".



**Fig. S10** (a-c) CV curves at 10 V s<sup>-1</sup> (a), plots of phase angle versus frequency (b), plots of  $C_A$  versus frequency (c) for EC-300 and the EC with pristine PEDOT:PSS/cellulose paper/graphite foil electrodes (EC-P); the feeding mass loadings of PEDOT:PSS for both ECs are the same.



**Fig. S11** (a,b) CV curves at 10 V s<sup>-1</sup> (a), plots of  $C_A$  versus frequency (b) for EC-300 and the EC with pristine PEDOT:PSS/graphite foil electrodes (EC-DP) without using cellulose paper; the  $C_A$ s of both ECs were measured to be the same by charging-discharging tests.



**Fig. S12** The electrochemical performance of HNO<sub>3</sub>-treated PEDOT:PSS-based EC (the conductivity and the weight of the electrode material are nearly equal to those of 300 nm-thick AT-PEDOT:PSS); (a) CV curves at 10, 50, 100, 200, 500 V s<sup>-1</sup>, respectively; (b) Galvanostatic charge–discharge curves at various current densities in the range from 0.1 to 5 mA cm<sup>-2</sup>; (c) Nyquist plots (inset: an expanded view of high frequencies); (d) Plot of impedance phase angle versus frequency; (e) Plot of C<sub>A</sub> as a function of frequency; (f) Plots of the real or imaginary part (C' or C'') of specific capacitance versus frequency.



**Fig. S13** (a-d) CV curves of EC-90 (a), EC-240 (b), EC-390 (c), and EC-600 (d) at different scan rates (V  $s^{-1}$ ), respectively.



**Fig. S14** The electrochemical performance of all-solid-state AT-PEDOT:PSS-based EC-300. (a) CV curves at 10, 100, 500 and 800 V s<sup>-1</sup>, respectively; (b) Galvanostatic charge–discharge curves at various current densities in the range from 0.1 to 5 mA cm<sup>-2</sup>; (c) Plot of  $C_A$  as a function of the discharge current density; (d) Cycling stability and coulombic efficiency of this EC at a discharging current density of 2 mA cm<sup>-2</sup>; (e) Nyquist plots under flat and folded states; (e) Plots of C' or C'' versus frequency of the EC at its flat or folded state.

Electrode	$\tau_{RC}$ (µs)	$\tau_0 (ms)$	<i>f</i> <sub>-45</sub> °(Hz)	-Phase	C <sub>A</sub> (µF cm <sup>-</sup>	Thickness	C <sub>V</sub> (F cm <sup>-3</sup> )
				angle (°)	<sup>2</sup> )	(µm)	
AT-PEDOT:PSS <sup>a</sup>	99	0.152	6560	85.7	230	0.09	12.78
	101	0.347	2885	85.6	661	0.24	13.77
	146	0.585	170	83.6	994	0.30	16.57
	178	0.849	1178	82.2	1671	0.39	21.42
	255	1.497	668	78.9	2426	0.60	20.22
VOGN <sup>S4</sup>	200	0.067	15000	82.0	88	0.60	0.73
VOGN <sup>85</sup>	N/A	0.159	6300	85.0	265	2.00	0.66
ErGO <sup>S6</sup>	1350	0.238	4210	84.0	283	20.00	0.07
G/CNT <sup>S7</sup>	195	0.820	1343	81.5	230	10.00	0.23
CNT <sup>S8</sup>	199	0.702	1425	81.0	600	<1.60	
CNT <sup>S9</sup>	181	0.501	1995	82.2	282	0.30	4.74
CB <sup>S10</sup>	354	1.560	641	75.0	559	1.00	2.80
MC <sup>S11</sup>	319	0.371	4200	78.0	172		
PEDOT <sup>S12</sup>	800	3.3	400	65.0			
EG/PH1000 <sup>S13</sup>	597	1.5	708	75.0	28	0.08	1.83

**Table S1** Comparison of the performance parameters ( $\tau_{RC}$ , Phase angle,  $C_A$  and  $C_V$  at 120 Hz) of various ECs for AC line filtering.

a, this work; VOGN, vertically oriented graphene nanosheets; ErGO, electrochemically reduced graphene oxide; G/CNT, 3-dimensional (3D) graphene/carbon nanotube carpets; CB, carbon black; MC, camphor-derived meso/macroporous carbon; EG/PH1000, exfoliated graphene/PEDOT:PSS.

## **3.** Supplementary references

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