Electronic Supporting Information

Robust graphene composite films for multifunctional electrochemical capacitors with an ultrawide range of areal mass loading toward high-rate frequency response and ultrahigh specific capacitance

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1. Experimental section

1.1 Preparation of GO sheets and rGO powder

GO sheets were prepared by the harsh oxidation of 12,000 mesh nature graphite powder (purchased from Qingdao Huatai Lubricant Sealing S&T Co. Ltd.) according to modified Hummers method. Typically, sodium nitrate (NaNO₃, 4.5 g) and graphite powder (9 g) were carefully added into concentrated sulfuric acid (H₂SO₄, 210 mL) under mild stirring in an ice bath, followed by the addition of potassium permanganate (KMnO₄, 27 g) slowly in small portions to control the temperature of the suspension lower than 10 °C. Successively, the reaction system was transferred to a 35°C oil bath for 30 min. Then 500 mL water was added dropwise by a peristaltic pump, after that the system was stirred at 95 °C for another 15 min. Additional 1500 mL water was added, followed by the addition of 20 mL H_2O_2 (30% aqueous solution) to eliminate the unreacted KMnO₄ and terminate the reaction. The mixture was filtered and washed with 1000 mL diluted hydrochloric acid aqueous solution (1:10 by volume) to remove metal ions, followed by washing with ultrapure water. The resulting mud-like solid was dispersed in water, and then the dispersion was purified by dialysis with a dialysis membrane (8,000–14,000 g mol⁻¹) for 2 weeks to remove the remaining acid. GO sheets were directly used after ultrasonic treating the aqueous dispersion of GO sheets.

Reduced graphene oxide (rGO) hydrogel were prepared via hydrothermal treatment of GO aqueous dispersion at 180 °C for 12 h. The resultant hydrogel was washed and dried at room temperature to produce rigid rod-like rGO monolith. rGO powder were obtained by ball-milling the rGO monolith for 12 h, and the as-prepared rGO powder was collected after sieving with a 200 mesh filter.

1.2 Material characterizations

Scanning electron micrographs (SEM) and Energy-dispersive spectroscopy (EDS) were taken out on a Sirion 200 field-emission scanning electron microscope (FEI, USA). Raman spectra were conducted using a LabRAM HR Evolution (HORIBA Jobin Yvon, France) with a 532-nm laser, and Electrical conductivity measurements were carried out via a four-point probe test instrument (KDY-1) at room temperature. Mechanical testing were performed on Instron 3342 universal testing machine (Instron, USA) with a loading rate of 0.5 mm min⁻¹ with a gauge length of 8 mm. The

specific surface area (SSA) of the rGO powder was measured by methyl blue (MB) adsorption (a standard method for evaluating the SSAs of graphite materials). X-ray photoelectron spectra (XPS) were recorded on an Escalab 250 photoelectron spectrometer (ThermoFisher Scientific, USA). Mechanical compression was performed on an Infrared Tablet Press (FW-5A, BoTianShengDa Co. Ltd., Tianjin, China) under a pressure of 5 MPa for 1 min.

1.3 ECs fabrication and electrochemical measurements

First, PEDOT:PSS aqueous solutions (Clevios PH1000, Heraeus) were filtered through a 0.45 µm syringe filter. Successively, rGO powder was added to the PEDOT:PSS aqueous solution with a mass ratio of 4:1, and then this system was vigorous stirring and keeping for 12 h to obtain a homogeneous suspension. For the electrodes with areal mass loading less than 0.6 mg cm⁻², the mixture was directly coating on the surface of a UV-ozone treated graphite foil (conductivity~16,000 S cm^{-1} , thickness = 16 µm, Emitac New Material Technology Co. Ltd, Suzhou, China) via blade coating method. The mass loading of electrodes can be precisely modulated by changing the coating thickness. Then, the electrodes were drying under ambient condition, followed by post-treatment with 1 M H₂SO₄ at 90 °C for 12 h to remove insulating PSS. Finally, the as-fabricated electrodes were washed by1 M H₂SO₄, and then directly used to construct symmetrical ECs. For the electrodes with areal mass loading higher than 0.6 mg cm⁻², additional Methyl-2-pyrrolidionne (NMP) was dropped into the PEDOT:PSS/rGO mixture with a volume fraction of 20%. The NMP in the mixture is critical to keep the film gel-like state and make the filtration process more controllable, because the critical point for aqueous system is difficult to capture. After stirring for another 20 min, a certain amount of the new mixture was filtered through hydrophobic PTFE filter membrane (0.45 µm pore size) by vacuum suction. The filtration was terminated once the gel-like film forming without flowing mixture upon it. The as-prepared gel-like film was immediately transferred to a beaker and immersed in 1.0 M H₂SO₄ aqueous solution to undergo post-treatment at 90 °C for 12 h. The resultant film were washed by 1 M H₂SO₄, and then mechanical compressed before using as electrodes.

All electrochemical measurements were carried out using a symmetrical twoelectrode cell configuration with a porous separator of cellulose paper. 1.0 M H_2SO_4 aqueous solution was used as aqueous electrolyte and a H_2SO_4 /PVA polymer gel was used as the solid electrolyte. Cyclic voltammograms (CV), galvanostatic chargedischarge (GCD) tests , and electrochemical impedance spectroscopy (EIS) were carried out using a CHI 660D electrochemical workstation (CHI Instruments Inc., Austin, TX). For self-discharge tests, the devices were first charged to 1 V at 0.5 mA and kept at 1 V for 30 min, and then the open potential of the device was measured as a function of time. The leakage current was recorded by charging the device to 1.0 V at 3 mA and then keeping the potential at 1.0 V for 2h. It should be noted here that the electrode material with ultra-low mass loading for AC line-filter application is evaluated in area (μ F cm⁻²) units. The areal specific capacitance (C_A) of the EC was calculated from EIS spectra by equation S1and S2:

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

where f is frequency (Hz), Z" is the imaginary resistance (Ω); s is the area of the electrode (cm²).

eq S1

For the electrodes with high mass loading, the capacitive performance is evaluated by gravimetric specific capacitances (C_g), areal specific capacitance (C_A) and volumetric specific capacitances (C_v) of single electrode, which is measured by GCD test.

 $C_{\rm g}$ was calculated by equation S2:

area of the electrode.

$C_{\rm g} = 2I\Delta t/m\Delta V$	eq S2
$C_{\rm A}$ was calculated by equation S3:	
$C_{\rm A} = 2I\Delta t/s\Delta V$	eq S3
$C_{\rm v}$ was calculated by equation S4:	
$C_v = 2I\Delta t / v\Delta V$	eq S4

where *I* is the constant discharge current, Δt is the discharge time, ΔV is the discharge potential drop (V) (excluding IR drop), *m* is the mass of single electrode, and *s* is the

2. Supplementary figures and table



Fig. S1 (a) SEM image of GO sheets (inset: the corresponding histograms of size distributions of GO sheets).



Fig. S2 C1s XPS spectra of (a) GO and (b) rGO.



Fig. S3 Cross-sectional SEM image of uncompressed graphene/PEDOT:PSS film



Fig. S4 Plots of the real or imaginary part of areal specific capacitance (C' or C") of GO_{0.012}-based EC versus frequency.



Fig. S5 The electrochemical performance of $GP_{0.037}$ -based EC. (a) Cyclic voltammogram (CV) curves at different scan rates (V s⁻¹). (b) Nyquist plot (c) Plot of phase angle versus frequency. (d) Areal specific capacitance as a function of frequency.



Fig. S6 (a) Self-charge curve of the GP_{12} -based EC after charging at 1 V for 30 min; (b) Leakage current curve of the GP_{12} -based EC in aqueous electrolyte.



Fig. S7 Electrochemical characterization of the GP_{33} -based EC. (a) CV curves at different scan rates; (b) GCD curves at different current densities (A g^{-1}); (c) C_g as a function of discharge current density; (d) Cross-sectional SEM image of GP_{33} electrode.



Fig. S8 TGA curves of (a) H_2SO_4 -treated PEDOT:PSS; (b) rGO and rGO/PEDOT:PSS composite film.



Fig. S9 Electrochemical characterization of pure PEDOT:PSS film. (a) CV curves of PEDOT:PSS_{0.24} (0.24 represents the mass loading in milligram per square centimetre) at different scan rates; (b) CV curves of PEDOT:PSS₅ at different scan rates; (c) Nyquist plots of two kinds of PEDOT:PSS-based ECs; (d) C_g versus different current densities for two kinds of ECs.



Fig. S10 Electrochemical performance comparison between the EC prepared by PEDOT:PSS as binder and EC prepared by PTFE as binder. (a) C_g versus different current densities for two kinds of ECs; (b) Nyquist plots of two kinds of ECs.



Fig. S11 Variations in relative resistance of flexible electrode versus bending angle.



Fig. S12 S 2p XPS spectra of pristine PEDOT:PSS and graphene/PEDOT:PSS film treated by $1 \text{ M H}_2\text{SO}_4$.

S 2p XPS spectra were taken out to analyze the composition difference between pristine PEDOT:PSS and 1 M H_2SO_4 treated graphene/PEDOT:PSS composite film. The 164.4 eV band is related to the S atoms of PEDOT and the intensity of 168.6 eV band is assigned to the S atoms of PSS. The spectra were normalized by the intensity of 164.4 eV band. The intensity at 168.6 eV in the spectrum of graphene/PEDOT:PSS composite film is much weaker than that in the spectrum of pristine PEDOT:PSS, implying that the insulating PSS in graphene/PEDOT:PSS was partially removed after 1 M H_2SO_4 treatment.

Electrode	$C_v (F cm^{-3})$	C _A (mF	$C_{f}(F^{2} cm^{-5})$	Areal mass	Current	Reference
		$cm^{-2})$	$\times 10^3$	loading	density	
				$(mg \ cm^{-2})$	$(mA cm^{-2})$	
PG _n	235	2270	574	12	12	
	223	2508	577	14	14	
	221	2940	650	17	17	This work
	220	3660	805	21	21	
	203	5365	1089	33	33	
Holey graphene	18.4	860	15.8	30	30	S1
Crumpled graphene	75	3000	225	20	2	S2
Graphene fabric	44.7	4470	199.8	30	20	S3
Activated wood	48	3600	173	30	1	S4
Graphene film	172	1293	222	10	10	S5
Graphene/PPD	711	390	277	0.85	0.425	S6

Table S1 Comparison of the capacitive performance (C_A , C_V and C_f) of various ECs with high C_A and/or C_v .

3. Supplementary references

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