Electronic Supplementary Information (ESI) for:

Capacitance enhancement of polyaniline coated curved-graphene supercapacitors in a redox-active electrolyte

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Experimental Section

1. Materials preparation

1.1 Materials

All chemicals used in this study were purchased from Sigma Aldrich and used as received.

1.2. Preparation of graphene oxide

Graphene oxide was prepared by a modified Hummers' method.[1,2] Typically, 75 ml of concentrated sulfuric acid (98%) was added to 1.5 g of graphite powder and 1.5 g of $NaNO_3$ in a beaker. The mixture was stirred for 15 min at room temperature and then placed in an ice bath. Subsequently, 9 g of $KMnO_4$ was added slowly into the mixture and kept in the ice bath for 30 min. The mixture was continued to be stirred for 48 h at room temperature. The formed brownish slurry was then added slowly into 138 ml of cold DI water under stirring for 10 min. Afterwards,

420 ml of warm water (~45 °C) was added followed by a slow addition of 30 ml of H_2O_2 to get a yellow suspension. The suspension was centrifuged and washed repeatedly by a mixed aqueous solution of 6 wt% H_2SO_4 and 1 wt% H_2O_2, and then by DI water until the PH of the suspension closes to 7.

1.3. Preparation of hydrothermally reduced graphene oxide (rGO)

The graphene oxide suspension was applied to probe ultrasonication (160 W) for 1 h followed by centrifugation at 5000 rpm for 10 min. The supernatant was collected for the preparation of rGO. Typically, 37 ml of ~2 mg/ml GO suspension was transferred to and sealed in a 45 ml Teflon-lined stainless steel autoclave and maintained at 180 °C for 6 h. It was then cooled to room temperature naturally. The resultant black product was filtered, washed by DI water and dried at 100°C under vacuum for 12 hours.

1.4. Preparation of reduced graphene oxide-polyaniline (rGO-PAni)

The rGO-PAni was prepared by in-situ chemical polymerization of aniline in the presence of rGO. Briefly, 100 mg of rGO was dispersed into 50 ml of HCl (1M) by bath sonication for 30 min. Then 0.1 g of K_2CrO_7 and 0.2 ml of aniline was added into the solution under stirring. The solution was continued to stir for 6 hours at room temperature. Finally, the product was filtered and washed by DI water and ethanol for several times before drying at 60 °C under vacuum for 10 hours. The polyaniline nanofibers were prepared in the same process without adding rGO.[3]

2. Materials characterization

The electrode materials were conducted by a detailed characterization, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD),

Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and nitrogen adsorption and desorption technique. The microstructure and morphology were characterized by SEM (Nova Nano 630, FEI), and TEM (Titan 80-300 kV (ST), FEI). The crystallographic structure of the samples was identified by XRD (D8 Advance bulk power XRD, Bruker). The vibrational characteristics were carried out by Raman (LabRAM ARAMIS, laser: 633 nm). The XPS analysis was taken on a Kratos AXIS Ultra DLD spectrometer. The BET surface area and pore size distribution were determined by nitrogen adsorption and desorption at a bath temperature of -195.85 °C (ASAP 2420, surface area and pore size analyzer, Micromeritics).

3. Electrochemical measurements

All electrochemical measurements were conducted at room temperature in a classical two-electrode configuration. For the preparation of supercapacitor electrodes, the rGO-PAni, acetylene black and polytetrafluoroethylene (PTFE) binder with a ratio of 85:10:5 were dispersed in 10 mL ethanol and stirred for an overnight to form electrode slurry. The slurry was pasted onto the graphitized carbon paper and vacuum dried at 60 °C for 12 hours. The mass of the electrode materials were determined by a microbalance (Mettler Toledo XP26, resolution of 1 μg) using the mass difference before and after materials loading. The mass loading of the electrode materials ranged from 8 mg to 10 mg (4-5 mg/cm^2), which is a relatively high mass loading for supercapacitor study. Two electrodes were isolated by a separator (Celgard 3501) with electrolytes in between for the assembly of the symmetrical button-like supercapacitors (MTI). The electrolytes used in this study are 1 M H_2SO_4 and 1 M H_2SO_4 with 0.4 M hydroquinone. The concentration of HQ was chosen according to the reported study.[4] The electrochemical performance was investigated by electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and galvonostatic charge-discharge (CD) measurements in a

VMP3 multi-channel electrochemical workstation (Biologic). The EIS was measured with frequency range between 100 kHz and 10 mHz. The CV was tested from 5 mV/s to 100 mV/s in a voltage range from 0 to 0.7 V for both H_2SO_4 and H_2SO_4+HQ electrolyte. The CD was recorded from 1 A/g to 30 A/g with the same voltage profile as the CV measurements.

4. Calculation of specific capacitance

The cell capacitance was calculated from galvanostatic charge-discharge curves based on the following equation[5]:

$$C = \frac{I}{dV/dt} \qquad (1)$$

where C is the cell capacitance, I is the applied current, and dV/dt is the slope of the discharge curve after voltage drop.

$$C_s = \frac{4C}{M} \qquad (2)$$

where Cs is the specific capacitance, M is the total mass of active materials on the two electrodes.

Supporting Figures

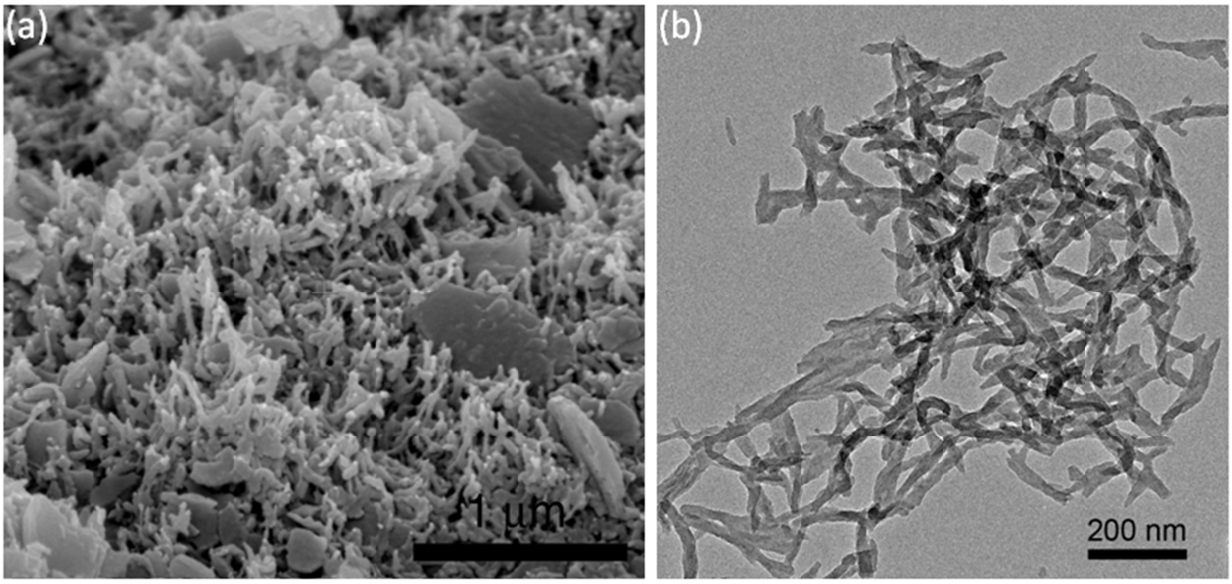

Fig. S1 (a) SEM and (b) TEM of polyaniline nanofibers.

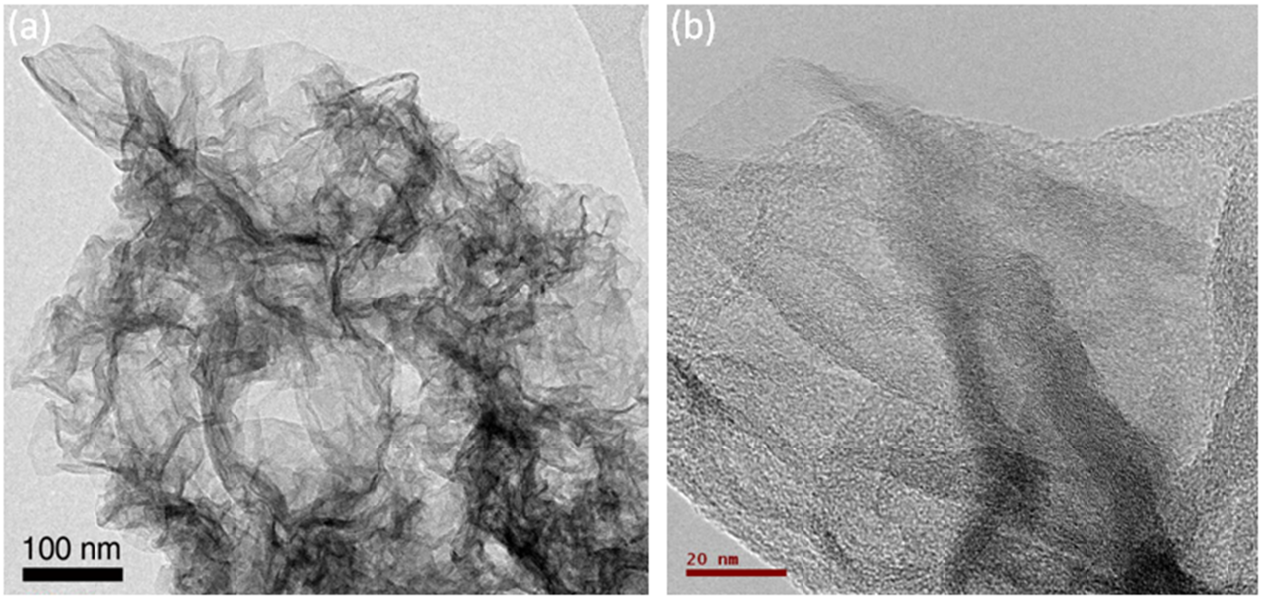

Fig. S2 (a) TEM and (b) HRTEM of rGO-PAni.

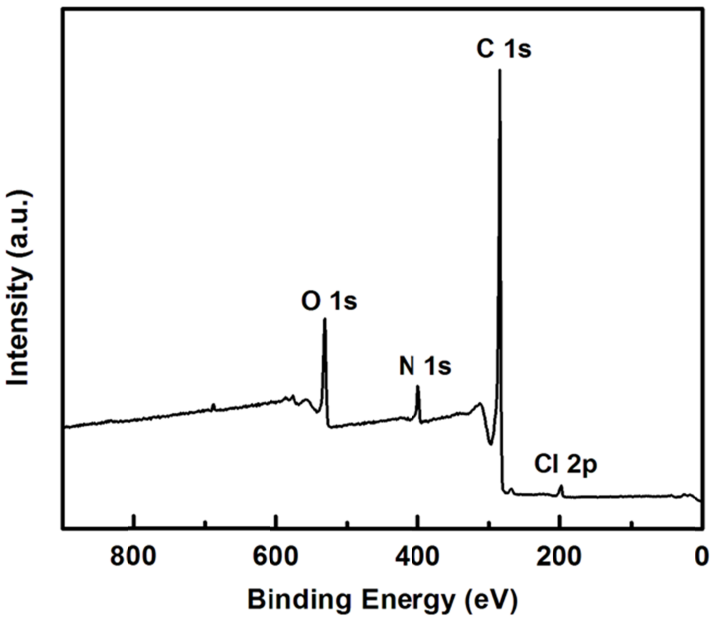

Fig. S3 XPS survey scan of rGO-PAni.

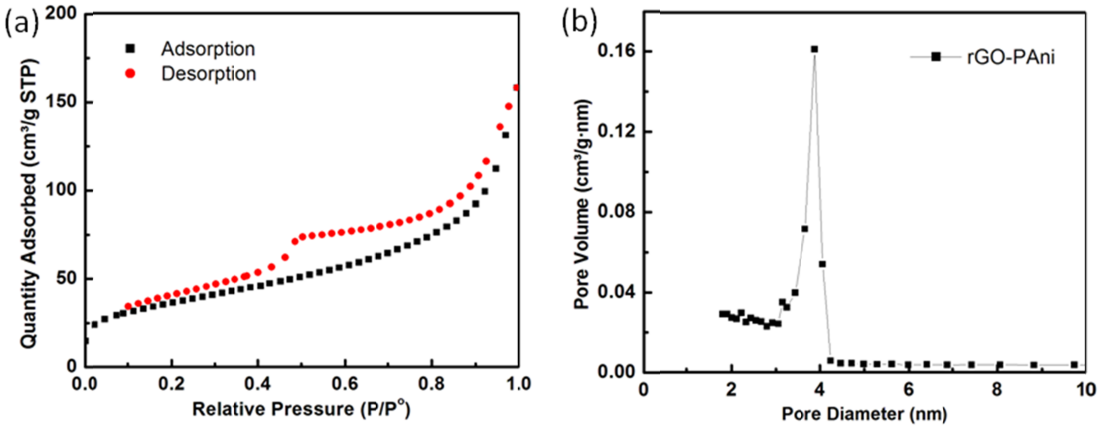

Fig. S4 (a) Nitrogen adsorption and desorption isotherm and, (b) pore size distribution of rGO-PAni.

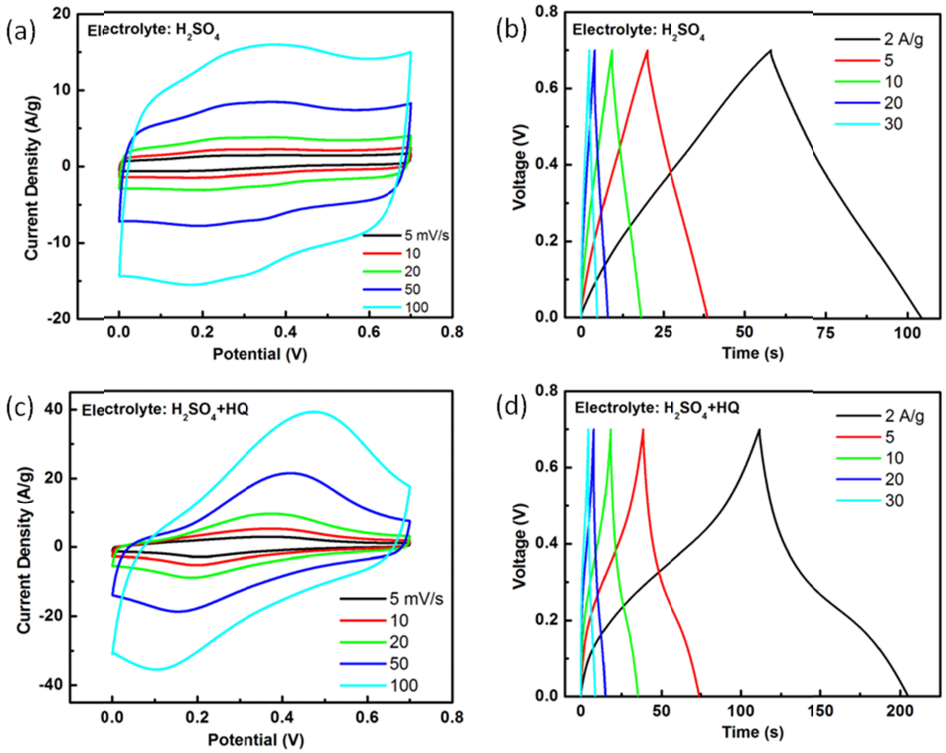

Fig. S5 (a) CV and (b) CD curves of the rGO-PAni supercapacitor in 1M H_2SO_4 electrolyte; (c) CV and (d) CD curves of the rGO-PAni supercapacitor in 1M H_2SO_4+0.4M HQ electrolyte.

Table 1. Summary of capacitances of graphene-polyaniline supercapacitors

Materials	Electrode configuration	Mass loading of materials	Electrolyte	Capacitance	Cycling	Ref.
PAni coated graphene	Two	8-10 mg (4-5 mg/cm^2)	1 M H_2SO_4	288 F/g @ 1 A/g, 243 F/g @ 30 A/g	240 F/g after 50000 cycles @ 10 A/g	This work
			1 M H_2SO_4 + 0.4 M HQ	553 F/g @ 1 A/g, 466 F/g @ 30 A/g	327 F/g after 50000 cycles @ 10 A/g	
Graphene-PAni nanofiber film	Two	---	1 M H_2SO_4	210 F/g @ 0.3 A/g	155 F/g after 800 cycles @ 3 A/g	6
Graphene-PAni nanofiber composites	Three	Very low (on glassy carbon electrode)	1 M H_2SO_4	480 F/g @ 0.1 A/g, 210 F/g @ 1 A/g	70% retention after 1000 cycles @ 1.5 A/g	7
PAni grafted graphene	Three	Very low (on glassy carbon electrode)	1 M H_2SO_4	250 F/g @ 100 mV/s	---	8
Functionalized graphene-PAni	Three	Very low (on glassy carbon electrode)	1 M H_2SO_4	420 F/g @ 2 mV/s, 388 F/g @ 1 A/g		9
	Two	2-3 mg		395 F/g @ 10 mV/s, 345 F/g @ 2 A/g	85% retention after 1000 cycles @ 2 A/g in two-electrode setup	
Graphene-PAni nanofiber hybrids	Three	Very low (on glassy carbon electrode)	2 M H_2SO_4	579.8 F/g @ 0.3 A/g, 361.9 F/g @ 1 A/g, 282 F/g @ 3 A/g	96% retention (270 F/g) after 200 cycles	10
Graphene oxide doped PAni	Three	2-14 mg	1 M H_2SO_4	531 F/g @ 0.2 A/g	---	11
PAni nanowire arrays on graphene	Two	---	1 M H_2SO_4	555 F/g @ 0.2 A/g, 227 F/g @ 2 A/g	92% retention after 2000 cycles	12
Graphene-PAni paper	Three	---	1 M H_2SO_4	233 F/g @ 2 mV/s	100% retention after 1500 cycles	13

Supporting references

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