

## **A three-dimensional graphene aerogel containing solvent-free polyaniline fluid for high performance supercapacitors**

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### **1. Experimental Section**

#### **1.1 Materials**

Aniline and ammonium peroxydisulfate (APS) were purchased from Gelest, Inc. (USA). Nonylphenol polyoxyethylene ether sulphate (NPES,  $\text{CH}_3(\text{CH}_2)_8\text{-C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_{10}\text{OCH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$ ) was bought from Sigma-Aldrich Corporation (Saint Louis, USA). Graphite powder was provided by XFNANO Materials Tech Co., Ltd. (325 mesh, purity is more than 99.8 wt%, imported high purity, Nanjing, China).

#### **1.2 Synthesis of GO and self-suspended PANI**

GO was prepared by natural graphite powder with a modified Hummers method.<sup>1</sup> S-PANI was obtained according to our previous method.<sup>2</sup> Specifically, 1.86 g aniline and 4.56 g

APS were dissolved in 50 mL acetone containing 7.62 g NPES, respectively. After freezing to 0 °C, the two solutions were mixed rapidly and transferred into a three-necked flask for polymerization under moderate stirring. The temperature of the reaction medium was kept below 5°C using an ice/water mixture around the flask. After 8 h polymerization, the polymer solution was dialyzed to remove the low molecular weight compounds using a cellulose dialysis membrane/bag (8200 molecular weight cut off) by circulating deionized water around the dialysis bag for 72 h. Finally, the PANI doped with long-chain NPES was dried in a vacuum at 150 °C for 8 h.

### **1.3 Fabrication of RGO/S-PANI Aerogel**

Typically, 60 mg GO was dispersed in 15 ml distilled water by sonication for 2 h to obtain a 4 mg/ml GO suspension. Meanwhile, 15 ml S-PANI aqueous solution (4 mg/ml) was prepared by the same way. Then the above GO and S-PANI aqueous solutions were mixed and sonicated for 30 min. The mixture was transferred into a 50 ml Teflon-lined stainless-steel autoclave, and treated hydrothermally at 180 °C for 20 h. After naturally cooled to room temperature, the RGO/S-PANI hydrogel was obtained. The as prepared hydrogel was washed several times with distilled water to remove the residues. Subsequently, the washed hydrogel was frozen drying for 48 h to completely remove water. Pure reduced RGO aerogel was prepared with the same procedure for comparison.

### **1.4 General Characterization**

Fourier transform infrared FTIR spectra analysis of the composites was carried out by employing a Nexus IR measurement system (Thermo Nicolet Nexus, USA) using KBr

pellets. X-ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCALAB 250Xi Photoelectron spectrometer (Thermo Fisher, USA). HRSEM images were obtained with an S-4800 scanning electron microscope (HITACHI, Japan) at 5 kV. Scanning electron microscopy (SEM) images were obtained by JSM-5610LU SEM (Hitachi, Japan). Nitrogen adsorption and desorption were determined by nitrogen physisorption at 77 K on a Micromeritics ASAP 2020M analyzer.

### **1.5 Electrochemical measurement**

All electrochemical measurements were conducted using CHI660E electrochemical workstation (Shanghai Chenhua Co. Ltd., China). The working electrode was prepared by casting a nafion-impregnated sample onto a glassy carbon electrode with a diameter of 3 mm. Typically, 3 mg of the composite was dispersed in 1 ml dimethyl formamide (DMF) solution containing 5  $\mu$ l of nafion solution (5 wt% in water) by sonication for 30 min. Then 3  $\mu$ l of the suspension was dropped onto the glassy carbon electrode and dried in an oven before the electrochemical test. Electrochemical performances were carried out in a conventional three-electrode cell in 1 M H<sub>2</sub>SO<sub>4</sub> electrolytes at a constant temperature of 20 °C. Platinum foil and saturated calomel electrode were used as the counter and reference electrodes, respectively. The specific capacitance is calculated based on the equation:

$$C = I\Delta t/m\Delta V \quad (1)$$

where  $I$ ,  $\Delta t$ ,  $m$  and  $\Delta V$  are the current density, discharge time, mass of the active material and the voltage change excluding the IR drop during the discharge process, respectively.

## 2. Figures and Tables

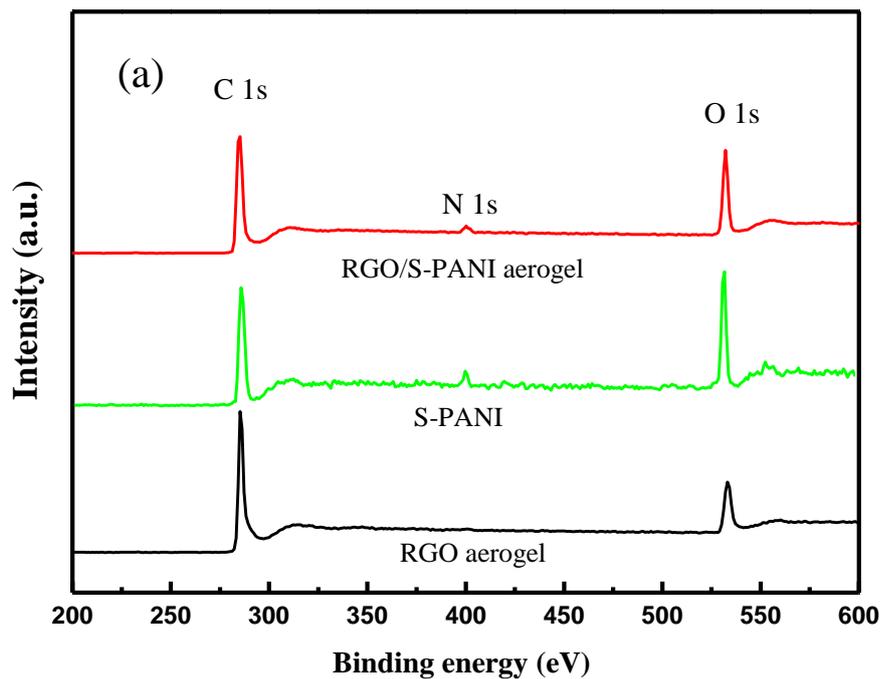


Figure S1 Wide scan survey spectrum of RGO and RGO/S-PANI aerogel

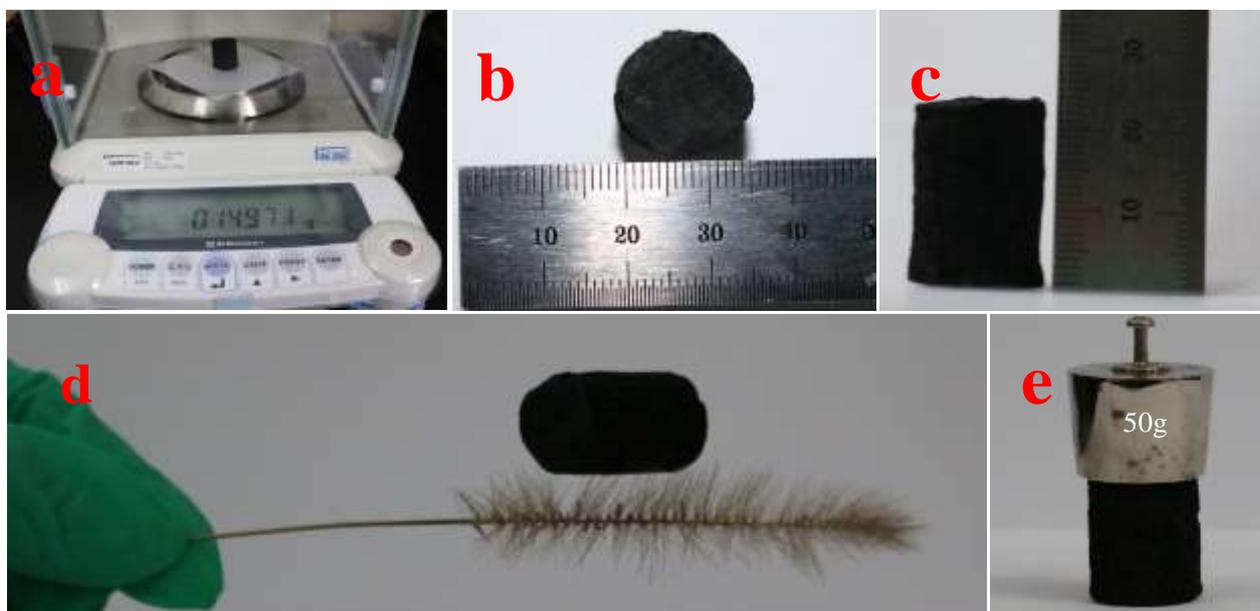


Figure S2 Digital images of RGO/S-PANI aerogel. (a-c) Mass and Size of RGO/S-PANI aerogel. (d) A RGO/S-PANI aerogel standing on a bristle grass. (e) A 4 cm<sup>3</sup> RGO/S-PANI aerogel supporting a weight of 50 g.

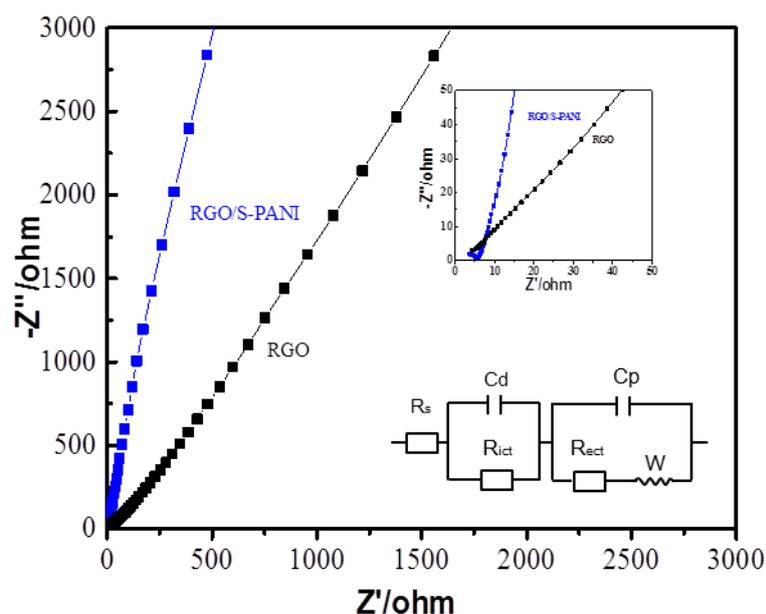


Figure S3 Nyquist plots for RGO and RGO/S-PANI electrodes using a sinusoidal signal of 2.5 mV over the frequency range from 0.01 Hz to 100000 Hz.  $Z'$  and  $Z''$  are referred to the real and imaginary impedances, respectively.

Table S1 The performance of graphene and PANI composites for supercapacitors

Materials on 3D graphene	Synthesis methods	Specific capacitance ( $F g^{-1}$ )	Stability	Ref.
PANI nanowires	In-suit polymerization	385 at $0.5 A g^{-1}$	88% (5000 cycles at $5 A g^{-1}$ )	3
RGO-PANI hollow sphere	Layer-by-layer assembly	380 at $0.5 A g^{-1}$	83% (1000 cycles at $0.5 A g^{-1}$ )	4
PANI-PAMPA	In-suit reduce of graphene oxide	223.82 at $0.4 A g^{-1}$	87% (5000 cycles at $10 A g^{-1}$ )	5
PANI nanoparticles	In-suit polymerization	438.8 at $0.5 A g^{-1}$	76.5% (2000 cycles at $2 A g^{-1}$ )	6
PANI nanowires		520.3 at $0.25 A g^{-1}$ 330.0 at $2 A g^{-1}$	500 cycles	7
Solvent-free PANI fluid	Directly self-assembly	480 at $1 A g^{-1}$ 344 at $40 A g^{-1}$	96.1% (10000 cycles at $10 A g^{-1}$ )	This work

### 3. References

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