Supporting Information

Three dimensional cellular architecture of sulfur doped graphene: Selfstanding electrode for flexible supercapacitor, lithium ion and sodium ion

battery

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Experimental

Preparation of PEDOT:PSS functionalized GO in aqueous medium

As-prepared graphene oxide (GO) in the liquid crystal (LC) state (50 mg at 2 mg mL⁻¹) was mixed with 50 mg of PEDOT:PSS pellets (Orgacon DRY, Agfa) by continuous stirring for 12 h to obtain a homogeneous aqueous dispersion. The dispersion was then incubated at 40 °C for 24 h to develop π - π interactions of PEDOT:PSS on the GO surface. During low temperature ageing the sulfur groups of the PEDOT chains take part in a non-covalent interaction with the polar functional groups on the GO surface (Figure 1a) and create a soft polymer layer without having any negative effect on the liquid crystal property of the GO content. The incubated dispersion was then centrifuged to decant excess PEDOT:PSS from the solution and obtain liquid crystals of PEDOT:PSS functionalized graphene oxide (GO-PP) in water medium (Figure 1a).

Results and discussion

Table S-1. EDS quantitative analysis of the PEDOT:PSS and rGPPF composite carried out inFE-SEM.

	Carbon (C)	Oxygen (O)	Sulfur (S)	Content of PEDOT:PSS
Material	atom %	atom %	atom %	(%)
PEDOT:PSS	70.1	21.6	8.3	100
rGPPF	78.53	19.27	2.2	26.5

Thermogravimetric analysis



Figure S-1. Thermogravimetric analysis of the rGPPF in argon.

The thermogram of the rGPPF composite in Figure S-1 gives a clear view of the chemical alteration during the pyrolysis process in an inert atmosphere. As shown in Figure S-1, there was a small weight loss (~5 %) of the composite observed before 250 °C, which may have arisen from the surface adsorbed moisture and partial degradation of the residual oxygenated groups on the rGO surface.¹ The first major weight loss observed after 250 °C can be attributed to the rupture of the sulfone functional groups of the PSS chain.² The major weight loss that appears around 300 °C has certainly resulted from the destruction of the PEDOT:PSS polymer chains interacting with the graphene surface as they start producing sulfur-containing species for further atomic doping on the hexagonal carbon lattice of the graphene at higher temperature, such as after 500 °C. No substantial weight loss was observed at temperatures higher than 750 °C, suggesting that the decomposition of PEDOT:PSS and generation of doping species followed by S-doping had already been completed. With regard to this, the pyrolysis temperature was selected to be 800 °C for the preparation of the sulfur-doped network of graphene sheets in a self-standing 3D architecture.



Figure S-2. (a) Low and (b) high magnification FE-SEM images of rGO foam; (c) low and (d) high resolution FE-SEM images of GF.

Table S-2. Sp	pecific surface	area analysis	by the BET	method.
1		5	2	

Materials	Specific surface area (m ² g ⁻¹)
SGF	537
rGPPF	187
GF	108



Figure S-3. (a) XPS survey spectrum of rGPPF, (b) high resolution C 1s spectrum of GF, (c) high resolution C 1s spectrum of rGPPF, and (d) high resolution S 2p spectrum of rGPPF.

Table S-3. High resolution carbon region core level XPS analysis of SGF, rGPPF, and GF.

Samples	Carbon (C 1s) atom%				
	C–C/C=C	C-O/C=O/O-C=O	C–S–C		
SGF	85.89	8.94	5.17		
rGPPF	78.37	19.31	2.32		
GF	89.15	10.85			

Table	S-4	Hioh	resolution	sulfur	region	core	level	XPS	analysis	of SGE
1 ant	Б-- .	Ingn	resolution	Sullui	region	COLC	10,001	\mathbf{M}	anarysis	01 501.

Sulfur (S 2p) atom%					
S 2p _{3/2}	S 2p _{1/2}	-SO _n -			
56.39	31.74	11.87			



Figure S-4. (a) Schematic illustration of the as-prepared symmetric supercapacitor assembled with SGF electrodes, Whatman filter paper used as separator, and 6 M KOH as electrolyte;

and (b) photograph of the supercapacitor device.



Figure S-5. (a) CV study of the GF symmetric supercapacitor at different scan rates, (b) CV study of the rGPPF symmetric supercapacitor at different scan rates, (c) Nyquist plot of SGF reveals the resistance of the assembled device, (d) CD study of the GF symmetric supercapacitor at different current densities, (e) CD study of the rGPPF symmetric supercapacitor at different current densities, and (f) CD profile of three SGF supercapacitor devices in series compared with a single device at 1 A g⁻¹ current density.



Figure S-6. (a) Low and (b) high magnification FE-SEM images of SGF after 30000 cycles continuous charge-discharge study in a symmetric supercapacitor reveals the stability of the sulfur doped cellular architecture after long electrochemical application. The sample was pill

out from the nickel foam, washed with water several times prior to run the microscopy.

Table S-5. Comparison of heteroatom-doped graphene materials used for supercapacitor

 electrode preparation in two electrode configurations.

Doped-	Type/	BET	Electrolyte/	Specific	
Graphene	Method	surface	Potential window	capacitance	Ref.
materials		area (m²/g)	(V)	(F/g)	
	Self-standing		6M KOH/	363 @ 100 mV/s	Present
SGF	foam/thermal	537	0 - 1	367 @ 1 A/g	work
	Self-standing				-
GF	foam/thermal	108	6M KOH/	121 @ 100 mV/s	Present
	process		0 - 1		work
3D N-	Foam/thermal		6M KOH/	180 @ 0.5 Δ/σ	3
graphene-CNT	process		-1.0 - 0	180 @ 0.5 A/g	
3D BN-	Foam/hydroth		PVA/H ₂ SO ₄ gel/		
Graphene	ermal process	249	0 - 0.8	132 @ 100 mV/s	4
N/S- flexible	Film/thermal	20.5	6M KOH		-
graphene	process	385	0 - 0.8	305 (<i>a</i>) 100 mV/s	5
paper	Powder/				
N-Graphene	plasma CVD		6M KOH/	282 @ 1 A/g	6
1	process		0 - 0.8		
N. Cranhana	Powder/hydrot		5M KOH/	170 @ 0.5 A/a	7
N-Graphene	hermal process		0 - 0.8	170 @ 0.3 A/g	,
Crumpled N-	Powder/therm		$1M[D_{11}]N]DE/$	248 @ 5 mV/c	
Graphene	al process	465	$\frac{11}{15} \frac{15}{15}$	240 @ 5 111 V/S	8
nanosheets			-1.5 - 1.5		
N Granhana	Powder/therm		0.5 M H ₂ SO ₄ /0 –	210 @ 1 A/g	9
N-Oraphene	al process		0.7	210 @ 1 A/g	-
B-graphene	Powder/therm	166	6M KOH/	160 @ 1 Δ/σ	10
nanoplatelets	al process	400	-1.0 - 0	100 @ 1 A/g	
porous	Powder/therm				
carbon/N-	al process	2927	$1 \text{M} \text{Na}_2 \text{SO}_4$	57 @ 200 mV/s	11
graphene			0-1.8		
Sandwich	Powder/therm		1M Et ₄ N BF ₄ -		
NG-sheets	al process	630	propylene	138 @ 1 A/g	12
			carbonate/ $0-4$		

Table S-6. Performance of the cellular SGF as anode material for lithium ion and sodium ion battery application compared with the previously reported heteroatom-doped graphene-based anode materials for similar application.

Doned granhane materials	Li-ion performance	Na-ion performance	Rof	
Dopeu graphene materiais	(mAh/g) on 2 nd cycle	(mAh/g) on 2 nd cycle	NCI ,	
SGE	1697 @ 100 mA/σ	$472 \oslash 50 \text{ mA/g}$	Present	
501	1097 @ 100 IIIA/g	472 @ 50 mA/g	work	
rGPPF	982 @ 100 mA/g	263 @ 50 mA/g	Present	
	,		work	
GF	317 @ 100 mA/g	58 @ 50 mA/g	Present	
			work	
Composite of S-	1670 @ 100 mA/g		13	
graphene/MoS ₂				
N/S-co-doped graphene	896 @ 200 mA/g		14	
N-doped carbon sheets	845 @ 100 mA/g		15	
S/N-graphene aerogel	880 @ 100 mA/g		16	
N,S-co-doped porous	957 @ 100 m A/g		17	
graphene	937 @ 100 III Vg			
N-doped graphene/graphite	775 @ 37 mA/g		18	
N-graphene	872 @ 50 mA/g		19	
N/S-graphene quantum dots	254.2 @ 37 mA/g		20	
N-graphene/graphite foam	642 @ 100 mA/g		21	
S-doped GNS	830 @ 372 mA/g		22	
N-carbon sandwich		$208 \odot 50 \text{ m} \text{ /}a$	23	
nanosheets		598 @ 50 mA/g		
S covalently bonded graphene		385 @ 50 mA/g	24	
S-mesoporous carbon sheets	1300 @ 100 mA/g	395 @ 20 mA/g	25	
3D N-graphene foam		1057 @ 100 mA	26	
Amorphous				
Phosphorus/Nitrogen-doped		1500 @ 200 mA/g	27	
graphene				
Self-standing S-graphene		377 @ 100 mA/g	28	
N-graphene nanosheets		260 @ 50 mA/g	29	

The following equations from reports in the previous literature have been used to analyze the electrochemical performance of the as-prepared symmetric supercapacitors.^{1, 6, 8, 10, 30}

Gravimetric capacitance (C_s) for a single electrode of the symmetric supercapacitor device was calculated from the CV curves by using the following equation:

$$C_{s} = \frac{2}{mv(V_{a} - V_{c})} \int_{0}^{1} I(V) dV$$
(S1)

Where *I* is the current (A), *V* is the voltage, *v* is the scan rate (V s⁻¹), and *m* is the mass (g) of both electrodes in the device.

The gravimetric capacitance (C_s) for a single electrode of the symmetric supercapacitor device was calculated from the charge-discharge curve by using the following equations:

$$C_T = \frac{I \times \Delta t}{\Delta V \times m} \tag{S2}$$

$$C_s = 4 \times C_T \tag{S3}$$

Where *I* is the discharge current in Amperes, Δt , the discharge time in seconds, ΔV , the voltage change in the discharge process excluding the *IR* drop, *m*, the total mass of both electrodes in grams, $C_{\rm T}$ is the total capacitance of the assembled device, and $C_{\rm s}$ is the specific capacitance of a single electrode in the device. The multiplier of 4 adjusts the capacitance of the cell to the mass of a single electrode.

The energy density (E) and power density (P) of the assembled symmetric supercapacitor device were calculated from the following equations:

$$E = \frac{1}{2}C_s(\Delta V)^2 / 3.6$$
(S4)

1

$$P = \frac{E \times 3600}{t}$$

Where C_s , ΔV , and *t* are the specific capacitance of the device, the potential window (*V*) of the supercapacitor, and the discharge time (s), respectively.

The volumetric capacitance (C_{vs} , F cm⁻³) of the self-standing SGF electrode was calculated based on the volume v (cm³) of the electrode according to the following equation:

$$C_{vs} = \frac{C_s \times m}{v} \tag{S6}$$

Where C_s is the specific capacitance, *m* is the mass of the electrode, and *v* is the volume of

the material after it is pressed on the Ni foam current collector electrode.

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