New strategy for integrating superior mechanical performance and high volumetric energy density into Janus graphene film for wearable solid-state supercapacitor

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1. Preparation of graphene oxides (GOs)

GOs were prepared through the modified Hummers' method. Briefly, expanded graphite (3.0 g, 50 meshes) was slowly added to concentrated sulfuric acid (200 mL) under constant stirring (200 rpm) at room temperature for 4 h. Potassium permanganate (9 g) was slowly added under an ice-bath and the mixture was stirred at 5 °C for 12 h. Then, 400 mL water was slowly added and the solution was stirred for another 4 h. Additionally cooled water (300 mL) was added to terminate the reaction, and then H_2O_2 (33%, 12 mL) was added dropwise until the color of the mixture turned to dark yellow. The GOs were obtained by repeatedly centrifugation and washed with HCL solution (10 wt %) at 8000 rpm for 2 times. Then the GOs suspension was centrifuged at 3000 rpm to remove non-exfoliated aggregates, followed by dialysis purification process to remove excess metal ions and HCl. The suspension was then concentrated by centrifugation at 10000 rpm for 30 min and the GOs suspension with high concentration was obtained.

2. Calculations

The electrochemical performances of the five JGFs with different thickness were studied in a three-electrode cell in $1 \text{ M H}_2\text{SO}_4$ electrolyte with Ag/AgCl and carbon rod as the reference electrode and counter electrode, respectively. The Nyquist plots of JGF and HIGF were obtained in a frequency range of 10 mHz to 100 kHz at an open circuit potential of 10 mV.

For three-electrode system, the specific areal capacitance (C_A) and volumetric capacitance (C_V) were calculated according to the following calculations:

$$C_A = \frac{Q}{A \times \Delta U}$$
$$C_V = \frac{Q}{V \times \Delta U}$$

where Q (C) is the average charge during the discharging process, U (V) is the potential window, A (cm⁻²) and V (cm⁻³) are the area and volume of the JGF, respectively.

For GSC device, the areal capacitance $(C_{Adevice})$ and volumetric capacitance $(C_{Vdevice})$ were calculated from the charge and discharge curves according to the following equations:

$$C_{Adevice} = \frac{i \times t}{A \times \Delta U}$$
$$C_{Vdevice} = \frac{i \times t}{V \times \Delta U}$$

where i is the discharge current, t is the discharge time, A (cm⁻²) is the area of the JGF and V (cm⁻³) is the total volume of the GSC device including the JGFs and solid state electrolyte, ΔU is the potential window.

Volumetric energy density (E, Wcm⁻³) and power density (P, W cm⁻³) of the GSC device are obtained from the following equations:

$$E = \frac{1}{2 \times 3600} C_{Vdevice} \Delta U^2$$
$$P = \frac{E}{t}$$

where t is discharge time calculated from the discharge curve.

For MSC device, the areal capacitance ($C_{Adevice}$) is calculated from the CV curves according to the following equations:

$$C_{Adevice} = \frac{1}{v(V_f - V_i)} \int_{V_i}^{V_f} I(V) dV$$

where v is the scan rate, V_f and V_i are the integration potential limits of the voltammetric

curves and I(V) is the voltammetric discharge current.

The areal energy density (E_A) and power density (P_A) are obtained by

$$E_A = \frac{C_{Adevice} \Delta U^2}{2 \times 3600}$$
$$P_A = \frac{3600 \times E_A}{t}$$

where t is the discharging time derived from charge-discharge curves.



Figure S1. (a) AFM image of GO sheet. (b) Height profile of GO sheet on mica. (c)

	SEM	image	of	GO	sheets	on	а	silicon	substrate
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Figure S2. SEM cross sectional morphology of (a) JGF0.3 and (b) JGF2.0. (c) SEM images of JGFs with different thickness (scale bar: 5 μ m). (d) The variation of the thickness of the JGFs with the colloid height.



Figure S3. The average pore diameter of our graphene film and other reported works^[1-6]



Figure S4. (a) Stress-strain curves of JGFs with different thickness. (b) The reinforcing mechanism of SFGFs.

As depicted in Figure S3b, the dense shell inherited from the alignment of nematic phase GO sheets along the substrate enhances the mechanical strength via the compact stacking structures and strong π - π stacking interactions. In addition, the well-aligned pore structures derived from the microgel stacking, forming physical self-crosslinking sites to reduce the tendency towards displacement and deformations between the graphene sheets for the enhanced mechanical strength.



Figure S5. Cross sectional SEM images of HIGF.



Figure S6. The i-t curves of JGF bended with different angles (I and II are the photographs of JGF bended at 0° and 180°, respectively).



Figure S7. Raman spectra of the GOF and JGF.

For the sake of keeping certain processability of GO and maintaining as much as conjugated domains, the graphene oxide with relative low oxidation degree is chose for the film preparation. The structure and composition of the low oxidized graphene oxides are characterized by XRD and Raman spectroscopy. As shown in Fig. 1d (red line), the XRD pattern of graphene oxide film exhibits an diffraction peak at 10.9° corresponing to an interlayer spacing about 0.811 nm, which is narrower than reported values, confirming the relative low oxidation degree of graphene oxides.^[7] In addition, Figure S4 shows that the graphene oxides exhibit a low I_D/I_G ratio due to its low oxidation levels. The average crystallite size of the sp² domains (L_a) are caculated to be 20.51 nm according to the following equation:^[7]

$$L_a(nm) = \frac{(2.4 \times 10^{-10})(\lambda)^4}{I_D / I_G}$$

where λ is the input laser energy, I_D and I_G are the intensity of the D band and G band, respectively. The large average crystallite size of the sp² domains confirm the low oxidation degree of the graphene oxides.^[8] The increase in the 2D band is due to the restoration the stacking order due to the reduction of the GO.



Figure S8. (a) The POM photo of GO solution after AA was added for 150 min, where the microgel was formed completely. (b) Variation of UV-vis absorption spectra for

GO	during	the	reduction	process
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 Figure S9. (a-c) SEM images of the graphene microgels formed during the fabrication

 process. (d) Schematic illustrations of Janus graphene film formation processes via the

 RES
 method.



Figure S10. Performance of the JGF0.3 electrode: (a) CV curves at different scan ratesin 1 M H_2SO_4 . (b) Charge-discharge curves and (c) areal specific capacitance atdifferentcurrentdensities.



Figure S11. Performance of the JGF0.5 electrode: (a) CV curves at different scan ratesin 1 M H_2SO_4 . (b) Charge-discharge curves and (c) areal specific capacitance atdifferentcurrentdensities.



Figure S12. Performance of the JGF1.0 electrode: (a) CV curves at different scan ratesin 1 M H_2SO_4 . (b) Charge-discharge curves and (c) areal specific capacitance atdifferentcurrentdensities.



Figure S13. Performance of the JGF1.5 electrode: (a) CV curves at different scan ratesin 1 M H_2SO_4 . (b) Charge-discharge curves and (c) areal specific capacitance atdifferentcurrentdensities.



Figure S14. Performance of the HIGF electrode: (a) CV curves at different scan ratesin 1 M H_2SO_4 . (b) Charge-discharge curves and (c) areal specific capacitance atdifferentcurrentdensities.



Figure S15. (a) CV curves of GSC device in different potential windows at 50 mV s⁻¹.

(b) CV curves cycled for 1th and 10000th at 50 mV s⁻¹.



Figure S16. Photographs of JGF2.0 soaking in 1 M H₂SO₄ solution for different time.



Figure S17. a) CV curves of GSC device at different bending angle. b) CV curves of GSC device bended for 1 and 1000th. c) CV curves of GSC device folded for 1, 30 and 100th. Scan rate is 100 mV s⁻¹.



Figure S18. Optical images of a LED powered by three GSC devices (charged to 2.7

V), which can be illuminated for more 2 min.



Figure S19. Optical images of an electronic watch powered by three GSC devices (charged to 2.7 V), which can support power to the electronic watch at least 2 h.



Figure S20. Optical images of the microelectrode patterns. Scale bars, 100 μ m.



Figure S21. CV curves of the MSC device (a) on a centrifuge tube, (b) under bended

state and bended for 1000 cycles and (c) under folded state and folded for 1000 cycles.

Entry	Thickness (um)	o (O sa ⁻¹)	σ (S cm ⁻¹)	Tensile Strength	Elongation	
Entry	T mekness (µm)	p _s (22 sq)	0 (3 cm)	(MPa)	(%)	
JGF0.3	3.8	19.27	136.6	71.58	1.88	
JGF0.5	5.2	14.17	135.7	56.15	1.83	
JGF1.0	8.3	11.08	108.7	58.80	2.34	
JGF1.5	11.3	8.81	100.5	99.8	2.38	
JGF2.0	12.4	5.02	160.6	75.48	3.15	

 Table S1. Properties of the as-prepared JGFs.

Materials	Electrode Thickness (µm)	Configuration	Electrolyte	C _{area} (mF/cm²)	V _{vol} (F/cm ³)	E (mWh/ cm ³)	P (mW/cm ³)	References
Free-standing GO films	NA	Symmetric	EMIM BF4/MeCN	5.02 (25 mA cm ⁻³)	~0.6 (25 mA cm ⁻³)	1.36	800	[9]
rGO/niquel nanocone3D substrate	45	Symmetric	PVA/Na ₂ SO ₄	6.84 (0.01 mA cm ⁻²)	1.72 (0.05 mA cm ⁻²)	0.15	4	[10]
G/PAN/G film	≈15	Symmetric	PVA/H ₂ SO ₄	107 (2 mA cm ⁻²)	NA	5.3	70	[11]
MVNNs/CNT	48	Symmetric	PVA/H ₃ PO ₄	NA	7.9 (25 mA cm ⁻³)	0.54	400	[12]
TiN//Fe ₂ N	NA	Asymmetric	PVA/LiCl	NA	NA	0.55	200	[13]
PEDOT paper	NA	Asymmetric	PVA/LiCl	118 (0.4 mA cm ⁻²)	144 (0.5 A cm ⁻³)	1	52	[14]
(Ni,Co) _{0.85} Se//porous Graphene film	NA	Asymmetric	1.0 M KOH	529.3 (1 mA cm ⁻²)	6.33 (1 mA cm ⁻²)	2.85	10.76	[15]
Bamboo-like fiber	NA	Symmetric	PVA/H ₃ PO ₄	NA	2.1 (33 mA cm ⁻³)	0.24	6100	[16]

 Table S2. Comparisons of graphene-based solid state supercapacitors and other film supercapacitors.

α -Fe ₂ O ₃ /PPy on Carbon Cloth	NA	Asymmetric	PVA/LiCl	382.4 (0.5 mA cm ⁻²)	0.8355 (10 mV s ⁻¹)	0.22	153.6	[17]
MWCNT films	2.5	Symmetric	PVA/H ₃ PO ₄	3.8 (1A g ⁻¹)	NA	0.58	390	[18]
VO _x //VN	NA	Asymmetric	PVA/LiCl	NA	1.35 (0.5 mA cm ⁻²)	0.61	85	[19]
WO _{3-x} /MoO _{3-x} on fabrics	NA	Asymmetric	PVA/H ₃ PO ₄	216 (2 mA cm ⁻²)	NA	1.9	31.67	[20]
H-TiO 2 @MnO 2 //H-TiO 2 @C	NA	Asymmetric	PVA/LiCl	NA	0.7 (0.5 mA cm ⁻²)	0.3	230	[21]
CNT/PPy	50	Symmetric	PVA/H ₂ SO ₄	NA	4.9 (50 mA cm ⁻³)	0.26	150	[22]
				49.6 (0.2 mA cm ⁻²)	20 (80.6 mA cm ⁻³)	2.78	40.3	This work
GSC	12.4	Symmetric	PVA/H ₂ SO ₄	23.4 (5 mA cm ⁻²)	9.4 (2015 mA cm ⁻ ³)	0.62	2016.13	This work

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