Supporting Information

Mordant Inspired Wet-spinning of Graphene Fibers for High Performance Flexible Supercapacitors

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MATERIALS & METHODS

Materials. Natural graphite flakes (300 μ m) were obtained from Asbury Graphite Mills USA. KMnO₄, HI acid (55%), CaCl₂, AlCl₃, and FeCl₃ were purchased from Sigma-Aldrish and used as received. Concentrated H₂SO₄ (98%), HNO₃, HCl (36.5%), glacier acetic acid, ethanol and H₂O₂ (30%) were purchased from Fisher Chemical.

Synthesis of GO. GOs were prepared from graphite powders following a modified Hummers' method.¹⁻² Graphite powder (2 g) was added to a H_2SO_4 (98%, 100 mL) and HNO_3 (33 mL) mixture, stirring for 24 hours at room temperature. Then, the mixture was poured slowly into 1 L de-ionized (DI) water, followed by filtration to collect the solid. The solid was washed using DI water to neutralize pH and dried at room temperature to obtain the intercalated graphite compounds.

The intercalated graphite compounds were thermally expanded using a microwave (750 W) for 5 seconds to obtain worm-like expanded graphite (EG). EG was added to a 500 mL flask containing H_2SO_4 (98%, 267 mL) in an ice bath (0°C). KMnO₄ (10 g) was then added slowly to the mixture under continuous stirring. After the introduction of KMnO₄, the mixture was kept at room temperature and stirred for 12 hours. 1.5 L water was then added slowly to an ice bath (0°C). Shortly after the dilution with DI water, 30 mL $H_2O_2(30\%)$ was added to the mixture, resulting in a bright yellow, bubbling solution.

We left the mixture to settle for 2 days after we decanted the clear supernatant. The remaining mixture was washed with HCl solution (10 %) and DI water successively until neutral, followed by dialysis for 2 weeks.

Fabrication of rGO fibers. With a lab-scale, home-built wet-spinning apparatus depicted in

Fig. 1, a GO spinning dope (15 mg mL⁻¹) was extruded through a spinneret (24 gauge) into the rotating coagulation bath, yielding a draw ratio of 1.3. The coagulation baths tested include 0.5 M AlCl₃, 0.5 M FeCl₃, 0.5 M CaCl₂ in H₂O/ethanol (3/1 v/v), and glacier acetic acid, respectively.

Subsequently, as-spun wet-state GO fibers from AlCl₃, CaCl₂, and FeCl₃ coagulation baths were washed with DI water. The reduced GO (rGO) fibers were prepared with hydroiodic acid (HI) reduction at 80°C for 12 hours, followed by cleansing with water and ethanol, and drying at 60 °C in vacuum for 8 hours.

Structure Characterizations. The morphology of rGO fibers were characterized using a scanning electron microscope (SEM). Electrical conductivity of rGO fibers were measured by standard four-probe method. Mechanical properties were measured using a Q-test system with 1 mm/min extension rate and 1 cm gauge distance. All the electrical conductivity and mechanical properties were the average results of at least 5 samples. The orientation degree of rGO sheets was evaluated by polarized Raman spectroscope (BaySpec Nomadic Raman Spectrometer) with 785 nm laser excitation. The intensity ratios of $I \parallel / I \perp$ were calculated by averaging five positions along fiber axis.

The SSA of rGO fibers were measured by methylene blue adsorption method.³⁻⁴ Generally, around 10 mg of rGO fibers were put into a flask and 100 µL of 1 mg/mL of MB solution were added at regular time. Then the remnant concentration of MB was measured by UV-Vis spectrophotometer at 664 The SSA calculated the equation: nm. was by $SSA = (m_{MB}/M_{MB})A_VA_{MB}(1/m_{fiber})$, where m_{MB} is the mass of the adsorbed MB, M_{MB} is the molar molecular weight (319.87 g mol⁻¹) of MB, A_V is Avogadro's number (6.02 ×

10²³/mol), A_{MB} is the area covered by one MB molecule (assumed to be 1.35 nm²) and m_{fiber} is the mass of rGO fibers.

Electrochemical Performance Characterizations. Electrochemical measurements, including the CV, GCD, and EIS were conducted in the solid state using electrochemical workstation (Autolab, Metrohm, USA). Two rGO fibers were aligned in parallel, soaked with gel electrolyte of H_2SO_4 /polyvinyl alcohol (PVA)/ H_2O (1/1/10 in weight), and dried at room temperature.

The specific volumetric capacitance (C_v), and area capacitance (C_A) of the electrode in a two-electrode cell was calculated according to $C_V = 2C/V_{fiber}$, and $C_A = 2C/S_{fiber}$, respectively, where C is the measured two-electrode configuration FSC capacitance, V_{fiber} and S_{fiber} are the volume, mass and surface area of the single fiber respectively. C could be obtained from CV test: $C = (1/2v) \times \oint I dU/\Delta U$, where v is the scan rate, I is the instantaneous current, ΔU is the voltage range. C could also be from GCD test: $C = t \times I/(\Delta U - U_{drop})$, where t is the discharge time, I is the discharge current, ΔU is the potential window, U_{drop} is the voltage drop in the discharge curve.

For the solid-state FSC, the volumetric capacitance ($C_{V-device}$) of the device was derived from the equation: $C_{V-device} = C/V_{device}$, where V_{device} is the volume of two fiber electrodes. The volumetric energy density (E_V) and power density (P_V) of the FSC can be obtained from $E_V = C_{v-device} \times U^2/7200$, $P_V = E_v \times 3600/t$.



Figure S1. Size distribution of Graphene Oxide (GO) sheets. (a) an SEM image of GO sheets drop-casted onto a silica wafer; (b) the corresponding size distribution of the GO sheets. The average size of GO sheets is calculated to be $ca.16 \mu m$.



Figure S2. SEM images with high magnification of rGO fibers. (a) acetic acid coagulated rGO fiber; (b) Ca²⁺ coagulated rGO fiber; (c) Fe³⁺ coagulated rGO fiber; (d) Al³⁺ coagulated rGO fiber.

Density functional theory calculations. The revised Perdew-Burke-Ernzerhof (RPBE)⁵ generalized gradient approximation (GGA)⁶ functionals in conjunction with the projector augmented wave (PAW)⁷ pseudopotentials were employed in our density functional theory (DFT)⁸⁻¹¹ calculations using the Vienna Ab Initio Simulation package (VASP)¹²⁻¹⁵. The plane-wave cutoff energy was set as 500 eV. The atomistic structures in our calculations were allowed to relax to the tolerance of atomic force at 0.01 eV/Å. Our graphene-oxide (GO) model was constructed from a perfect graphene structure (Fig. S3). A GO layer was placed in a simulation cell with a size of 12.82 Å × 12.34 Å in the basal plane and with at least 13 Å vacuum in the normal direction. A 3×3×1 Monkhorst-Pack grid¹⁶ was used to sample the Brillouin zone in our calculations.

The binding energy of hydrated cation on GO surface ${\binom{E_b}{b}}$ was calculated as:

$$E_b = E_{tot} - E_{M - OH}$$

where, E_{tot} is the DFT calculated energy of the optimized structure with metal hydrated cation adsorbed on GO and $E_M - OH$ is the DFT calculated energy of an isolated hydrated cation (*i.e.*, ion chelated by two OH groups).

To evaluate the strength of the cross-link formed by Al, Fe, and Ca between two GO layers, we calculated the energies of breaking the crosslink through removal of the bonds linked to either the upper or the lower GO layer. Namely, we performed the following two calculations for each crosslink.

$$E_{BD-up} = E_{M-GO-down} + E_{GO-up} - E_{tot}$$

$$E_{BD-down} = E_{M-GO-up} + E_{GO-down} - E_{tot}$$
where, E_{BD-up} and $E_{BD-down}$ denote the energies for breaking the bonds with the upper and

lower GO layer, $E_{M-GO-down}$ and $E_{M-GO-up}$ are the DFT calculated energies of the relaxed lower and upper GO layer with metal atom adsorbed on, and E_{GO-up} and $E_{GO-down}$ are the DFT calculated energy of the relaxed upper and lower GO layer, respectively. Thus, the activation energy to break the crosslink is defined as the lower value of E_{BD-up} and $E_{BD-down}$.



Figure S3. Atomistic structure of (a) single-layer graphene and (b) optimized structure of single layer graphene oxide (GO). In the figure, carbon, oxygen and hydrogen atoms are plotted as the black, red and white balls, respectively.



Figure S4. Top view (top) and lateral view (bottom) of metal cations adsorption configuration on a graphene layer through cation- π interaction and optimized by DFT method.

Metal cations	Ionic radius (Å)	Hydration shell thickness (Å)	electronegativit y	Charge density (C mm ⁻³)
Ca ²⁺	1.00	1.71	1.01	52
Fe ³⁺	0.65	2.88	1.83	349
Al^{3+}	0.50	3.24	1.61	770

Table S1.	Physicoche	mical Propert	ties of the	Cations ¹⁷⁻¹⁸



Figure S5. TOF SIMS secondary ion images of (a) Ca²⁺, (b) Al³⁺ and (c) Fe³⁺ acquired from corresponding rGO fibers along fiber axis direction, confirming the existing of cations in rGO fibers. TOF-SIMS measurements were conducted with an ION-TOF TOF-SIMS V instrument with bismuth beam for analysis and cesium beam for sputtering.



Figure S6. (a) Schematic illustration of the wrinkling direction of rGO sheets in each rGO fibers. (b) Cross-sectional SEM images of rGO fibers. rGOF-Al³⁺ has the most wrinkled structure through fiber cross-section (perpendicular to fiber axis), but still maintain good alignment along fiber axis.



Figure S7. Typical polarized Raman spectroscopy of rGOF-Al³⁺ fiber with the incident laser beam parallel and perpendicular to the fiber axis, respectively. The Raman ratio, which is determined from the ratio between the G peak intensities of the two spectra (parallel $^{I} \parallel vs$. perpendicular $^{I} \perp$), provides a useful probe for the relative degree of alignment.

Table S2. G peak intensities ratios (parallel $I \parallel vs$. perpendicular $I \perp$) of rGO fibers. The ratio is the average of five measurements made over different positions of each fiber.

Sample	rGO-Al ³⁺	rGO-Fe ³⁺	rGO-Ca ²⁺	rGO-Acetic acid	
I_{\parallel}/I_{\perp} ratio	2.36±1.03	1.80±0.97	1.67±0.37	1.92±0.45	



Figure S8. XRD patterns of rGO fibers. Fixed Time mode, step size 0.05 degree, dwell time 4 second. Wavelength to compute d-spacing 1.54059 Å, Cu/K-alpha 1.



Figure S9. Equivalent circuit for fitting Nyquist plots in the high frequency region by Z-view.

Fitting	R _s /	Wo			CPE _{dl}	
Parameters	Ω	$R_W\!/\Omega$	T_W / s	α	Y_0/F	α
rGOF-Al ³⁺	227	889	20.13	0.53	0.51	0.92
rGOF-Fe ³⁺	349	1046	50.18	0.47	0.49	0.89
rGOF-Ca ²⁺	285	3379	299	0.99	0.14	0.65
rGOF-acetic acid	424	3890	357	0.99	0.08	0.59

Table S3. Z-view fitting results for Nyquist plots in Figure 3d with the equivalent circuit shown

in Figure S6.



Figure S10. The calculated specific capacitance of rGOF-Al³⁺ FSC at different current density.

Fiber electrode	CA	Cv	См	CL	EA	Ev
	(mF cm ⁻²)	(F cm ⁻³)	(F g ⁻¹)	(mF cm ⁻¹)	(μWh cm ⁻²)	(mWh cm ⁻³)
GO@H ₂ O, AlCl ₃ bath, HI	286.59 @0.53	382.12		2.7		13.26
reduced (this work)	$mA cm^{-2}$	100.4	(0.5	1.4	5.10	()
GO@NMP, ethyl acetate bath,	149.5	199.4	69.5	1.4	5.12	6.8
HI reduced ¹	$(a)0.15A g^{-1},$					
NI COQUO apotio apid	0.55 IIIA CIII -	226	111 V S ·	/	/	7 26
NL $OO(a)H_2O$, accur actu	(0.2 A and and	220		/	/	7.20
Datil, HI Teduced	(0.02 A g^2)	@0.2 A	@0.2 A			
	0.005 IIIA CIII	g , 0.085 mA cm ⁻²	g,			
GO&CNT@H2O. CaCl2 bath.	177	158	/		/	3.5
HI reduced ²⁰	$@0.1 \text{ mA cm}^{-2}$	@0.1 mA				
	U	cm ⁻²				
CNT coated carbon fiber by	86.8	14.1	11.1	/	/	0.14
spray coating ²¹	@0.38 mA cm ⁻	@5 mV	@5 mV			
	2	s ⁻¹	s ⁻¹			
GO@H ₂ O, CaCl ₂ bath, 800°C	391.2 @0.1				8.7	
annealed followed by dip	mA cm ⁻²					
coating & carbonization ²²						
GO&CNC@H ₂ O, AA bath, HI		155.8	123.3			5.1
reduced ²³		@0.126	@ 0.1			
		A cm ⁻³	A g ⁻¹			
$GO@H_2O$, $CaCl_2$ bath, $800^{\circ}C$	36.25 @0.1				0.8	
annealed, $plasma^{24}$	mA cm ⁻²	16			4.55	1.0
GO&PEDOT:PSS, VC	115 @0.1 mA	46			4.55	1.8
reduced ²³	cm-2				a 0.02	
GO&CNT_chitosan/AA_bath		38.8 @		0.35	IIIA CIII-2	1
HI reduced ^{26}		mA cm-3		0.55		1
GO&PPy&CNF, FeCl ₃ &HCl	218 @0.1 mA	334		4.2	7.4	7.4
bath, HI reduced ²⁷	cm ⁻²					
GO&Mn ₃ O ₄ @DMF, ethyl						
acetate bath ²⁸						
GO@H ₂ O, NaOH/methanol	16.7 @ 1 A g ⁻¹		245			
bath, 650°C reduced, coating						
MnO_2^{29}						
GO&MnO ₂ @H ₂ O, acetic acid	82.6 @60 mA	66.1				5.8
bath, hydrazine reduction ³⁰	cm ⁻³					

Table S4. Comparison of specific capacitance (based on a single electrode) and energy density (based on device) of solid-state FSC.

Note: in wet spinning method, unless other mentioned, the spinning dopes are aqueous pure GO dispersion.

References

1. Gilje, S.; Han, S.; Wang, M.; Wang, K. L.; Kaner, R. B., A chemical route to graphene for device applications. *Nano Lett.* **2007**, *7*, 3394-3398.

2. Xu, Z.; Peng, L.; Liu, Y. J.; Liu, Z.; Sun, H. Y.; Gao, W. W.; Gao, C., Experimental Guidance to Graphene Macroscopic Wet-Spun Fibers, Continuous Papers, and Ultralightweight Aerogels. *Chem. Mater.* **2017**, *29*, 319-330.

3. Chen, S.; Ma, W.; Cheng, Y.; Weng, Z.; Sun, B.; Wang, L.; Chen, W.; Li, F.; Zhu, M.; Cheng, H.-M., Scalable non-liquid-crystal spinning of locally aligned graphene fibers for high-performance wearable supercapacitors. *Nano Energy* **2015**, *15*, 642-653.

 Aboutalebi, S. H.; Jalili, R.; Esrafilzadeh, D.; Salari, M.; Gholamvand, Z.; Yamini, S. A.; Konstantinov, K.; Shepherd, R. L.; Chen, J.; Moulton, S. E.; Innis, P. C.; Minett, A. I.; Razal, J. M.; Wallace, G. G., High-Performance Multifunctional Graphene Yarns: Toward Wearable All-Carbon Energy Storage Textiles. *ACS Nano* 2014, *8* (3), 2456-2466.

Zhang, Y.; Yang, W., Comment on ``Generalized Gradient Approximation Made Simple".
 Phys. Rev. Lett. 1998, *80*, 890-890.

6. Perdew, J. P.; Chevary, J.; Vosko, S.; Jackson, K. A.; Pederson, M. R.; Singh, D.; Fiolhais,

C., Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Phys. Rev. B* **1992**, *46* (11), 6671.

7. Blöchl, P. E., Projector augmented-wave method. *Physical Review B* 1994, 50, 17953.

8. Hohenberg, P.; Kohn, W., Inhomogeneous electron gas. *Phys. Rev.* 1964, 136, B864-B871.

9. Kohn, W.; Sham, L. J., Self-consistent equations including exchange and correlation

effects. Phys. Rev. 1965, 140, A1133-A1138.

10. Parr, R. G.; Yang, W., *Density-functional theory of atoms and molecules*. Oxford university press: 1989; Vol. 16.

11. Martin, R. M., *Electronic structure: basic theory and practical methods*. Cambridge university press: 2004.

12. Kresse, G.; Hafner, J., Ab initio molecular-dynamics simulation of the liquid-metalamorphous-semiconductor transition in germanium. *Phys. Rev. B* **1994**, *49*, 14251.

13. Kresse, G.; Furthmüller, J., Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54*, 11169.

14. Kresse, G.; Furthmüller, J., Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computat. Mater. Sci.* **1996**, *6*, 15-50.

15. Kresse, G.; Joubert, D., From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, *59*, 1758.

 Monkhorst, H. J.; Pack, J. D., Special points for Brillouin-zone integrations. *Phys. Rev. B* 1976, 13, 5188.

17. Marcus, Y., Thermodynamics of solvation of ions. Part 5.-Gibbs free energy of hydration at 298.15 K. *Journal of the Chemical Society, Faraday Transactions* **1991**, *87*, 2995-2999.

18. Tansel, B.; Sager, J.; Rector, T.; Garland, J.; Strayer, R. F.; Levine, L.; Roberts, M.; Hummerick, M.; Bauer, J., Significance of hydrated radius and hydration shells on ionic permeability during nanofiltration in dead end and cross flow modes. *Sep. Purif. Technol.* **2006**, *51*, 40-47.

19. He, N.; Pan, Q.; Liu, Y.; Gao, W., Graphene-Fiber-Based Supercapacitors Favor N-

Methyl-2-pyrrolidone/Ethyl Acetate as the Spinning Solvent/Coagulant Combination. ACS Appl. Mater. Interfaces 2017, 9, 24568-24576.

20. Kou, L.; Huang, T.; Zheng, B.; Han, Y.; Zhao, X.; Gopalsamy, K.; Sun, H.; Gao, C., Coaxial wet-spun yarn supercapacitors for high-energy density and safe wearable electronics. *Nat. Commun.* **2014**, *5*, 3754.

21. Le, V. T.; Kim, H.; Ghosh, A.; Kim, J.; Chang, J.; Vu, Q. A.; Pham, D. T.; Lee, J.-H.; Kim, S.-W.; Lee, Y. H., Coaxial Fiber Supercapacitor Using All-Carbon Material Electrodes. *ACS Nano* **2013**, *7*, 5940-5947.

22. Zheng, X.; Zhang, K.; Yao, L.; Qiu, Y.; Wang, S., Hierarchically porous sheath-core graphene-based fiber-shaped supercapacitors with high energy density. *J. Mater. Chem. A* **2018**, *6*, 896-907.

23. Chen, G.; Chen, T.; Hou, K.; Ma, W.; Tebyetekerwa, M.; Cheng, Y.; Weng, W.; Zhu, M., Robust, hydrophilic graphene/cellulose nanocrystal fiber-based electrode with high capacitive performance and conductivity. *Carbon* **2018**, *127*, 218-227.

24. Meng, J.; Nie, W.; Zhang, K.; Xu, F.; Ding, X.; Wang, S.; Qiu, Y., Enhancing electrochemical performance of graphene fiber-based supercapacitors by plasma treatment. *ACS Appl. Mater. Interfaces* **2018**, *10*, 13652-13659.

25. Li, B.; Cheng, J.; Wang, Z.; Li, Y.; Ni, W.; Wang, B., Highly-wrinkled reduced graphene oxide-conductive polymer fibers for flexible fiber-shaped and interdigital-designed supercapacitors. *J. Power Sources* **2018**, *376*, 117-124.

26. Ma, Y.; Li, P.; Sedloff, J. W.; Zhang, X.; Zhang, H.; Liu, J., Conductive Graphene Fibers for Wire-Shaped Supercapacitors Strengthened by Unfunctionalized Few-Walled Carbon

Nanotubes. ACS Nano 2015, 9, 1352-1359.

27. Mo, M.; Chen, C.; Gao, H.; Chen, M.; Li, D., Wet-spinning assembly of cellulose nanofibers reinforced graphene/polypyrrole microfibers for high performance fiber-shaped supercapacitors. *Electrochim. Acta* **2018**, *269*, 11-20.

28. Chen, S.; Wang, L.; Huang, M.; Kang, L.; Lei, Z.; Xu, H.; Shi, F.; Liu, Z.-H., Reduced graphene oxide/Mn3O4 nanocrystals hybrid fiber for flexible all-solid-state supercapacitor with excellent volumetric energy density. *Electrochim. Acta* **2017**, *242*, 10-18.

Zhang, J.; Yang, X.; He, Y.; Bai, Y.; Kang, L.; Xu, H.; Shi, F.; Lei, Z.; Liu, Z.-H., δ-MnO
 2/holey graphene hybrid fiber for all-solid-state supercapacitor. *J. Mater. Chem. A* 2016, *4*, 9088-9096.

30. Ma, W.; Chen, S.; Yang, S.; Chen, W.; Cheng, Y.; Guo, Y.; Peng, S.; Ramakrishna, S.; Zhu, M., Hierarchical MnO2 nanowire/graphene hybrid fibers with excellent electrochemical performance for flexible solid-state supercapacitors. *J. Power Sources* **2016**, *306*, 481-488.