Supporting Information

Role of Graphene Oxide Liquid Crystals in Hydrothermal Reduction and Supercapacitor Performance

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XPS analysis for contents of elements and groups

Table S1 shows the surface group distribution of dried GO, blade-rGO and spray-rGO films. Though hydrothermally reduced at identical conditions, the blade-rGO contains less oxygenated groups than the spray-rGO, owing to the trapped water in the original blade-GO film which exhibits LC feature.

Table S1. Surface group distribution (%) and atomic composition from by XPS analysis.

Name	C-C sp^2 (284.4 eV)	C-C sp^3 (285.2 eV)	C-O (286.2 eV)	C=O (287.7 eV)	COOH (288.7 eV)	C (at%)	O (at%)	C/O ratio
GO	42	4	38	12	4	73	27	2.7
Blade-rGO	62	10	18	6	4	86	14	6.2
Spray-rGO	55	9	24	7	5	77	23	3.4

Blade coating of LC GO films

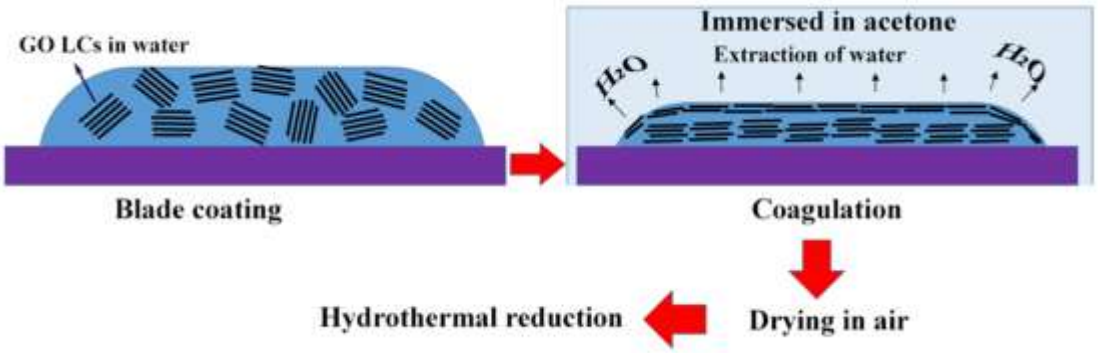

Figure S1. Illustration for the preparation process of graphene electrodes, including the blade coating of LC GO solution, coagulation in acetone, drying, and hydrothermal reduction.

The effect of reduction temperature on the capacitance

Blade-coated GO films were hydrothermally reduced at different temperatures, with the identical duration of 3 h. We fabricated symmetric supercapacitors using these

rGO films as electrodes and 1 M H_2SO_4 aqueous solution as electrolyte. Though high temperature favors the reduction of GO sheets, the shrinkage of rGO film has to be taken into account in device fabrication. As shown in Figure S2a, the rGO film lost almost half of its original area after 180 ^oC hydrothermal reduction. This film with rough surface detached off the substrate, not suitable for making solid-state supercapacitors with gelled electrolyte. The relationship of specific capacitance with reduction temperature is shown in Figure S2b. The rGO mass loading is around 0.8 mg/cm^2 for all samples, and the capacitance is deduced from galvanostatic CD curves at 1 A/g. When the reduction temperature is in the range of 140 ^oC to 160 ^oC, the capacitance is quite close. However, in the range of 160-180 ^oC the film suffers from severe shrinkage, and the rapid increase of specific capacitance can be attributed to the structural change of the film, as it reduces in area and increases in thickness, resulting in sponge-like 3D structure of the film. Wang *et al* studied the effect of hydrothermal reaction temperature on the capacitance of 3D graphene hydrogel.[1] In their work the 1 mg/ml GO aqueous dispersion was sealed in an autoclave and hydrothermally reduced to form graphene hydrogel. Samples that were reduced at 160 ^oC and 180 ^oC are quite close in specific capacitance, indicating that reaction in the range of 160-180 ^oC led to nearly stable reduction degree of rGO. Shi *et al* prepared 3D graphene hydrogel using 150 ^oC hydrothermal reduction, and the capacitance was measured to be 185 F/g at 2 A/g,[2] close to that of our 180 ^oC-reduced sample. We conclude that hydrothermal reduction of our LC GO films at high temperatures (160-200 ^oC) will lead to the formation of hydrogel.

For the spray-coated GO film, the contraction after 180 ^{o}C hydrothermal reduction is not evident, due to absence of trapped water in the film. After 150 ^{o}C hydrothermal reduction, the specific capacitance measured using 1 M H_2SO_4 solution as electrolyte was 125 F/g (corresponding to 1 A/g). However, after 180 ^{o}C hydrothermal reduction, the capacitance measured with identical conditions was decreased to be 102 F/g, attributed to the restacking of rGO sheets.

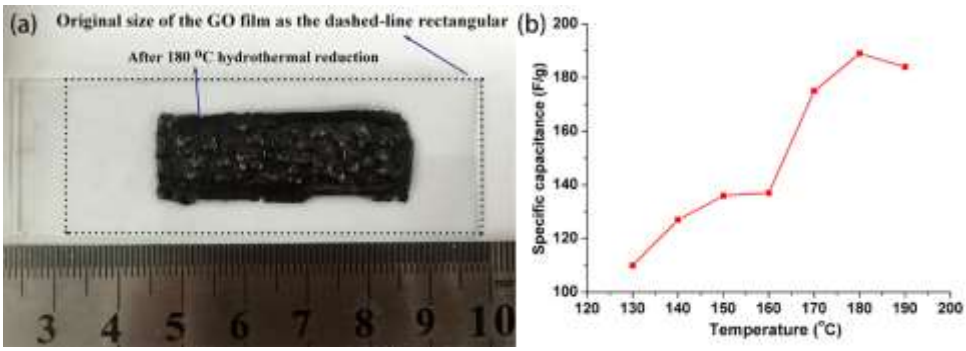

Figure S2. A photograph shows the severe shrinkage of rGO film after 180 ^{o}C hydrothermal reduction. (b) The relationship of specific capacitance with the reduction temperature.

SEM observation

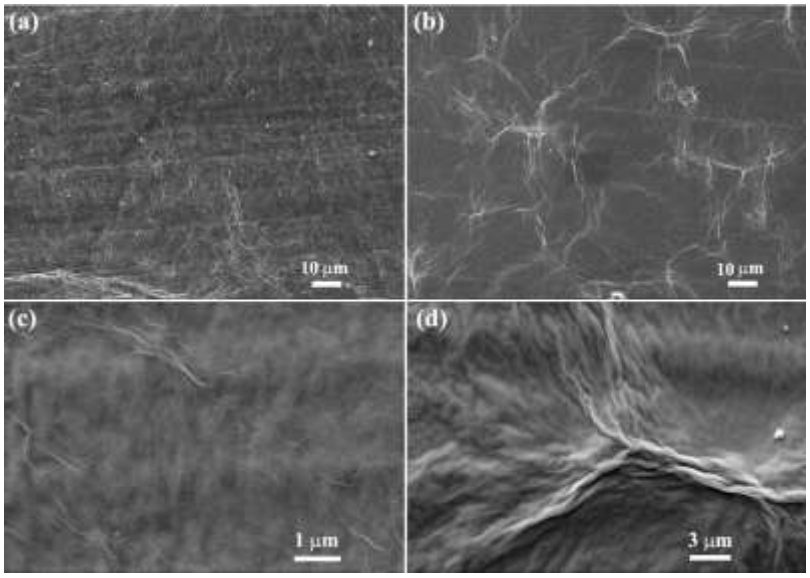

Figure S3. Top view FE-SEM images of air-dried (a, c) blade-rGO and (b, d) spray-rGO films. (a) and (b), taken in InLens mode; (c) and (d), taken in SE2 mode.

XRD analysis

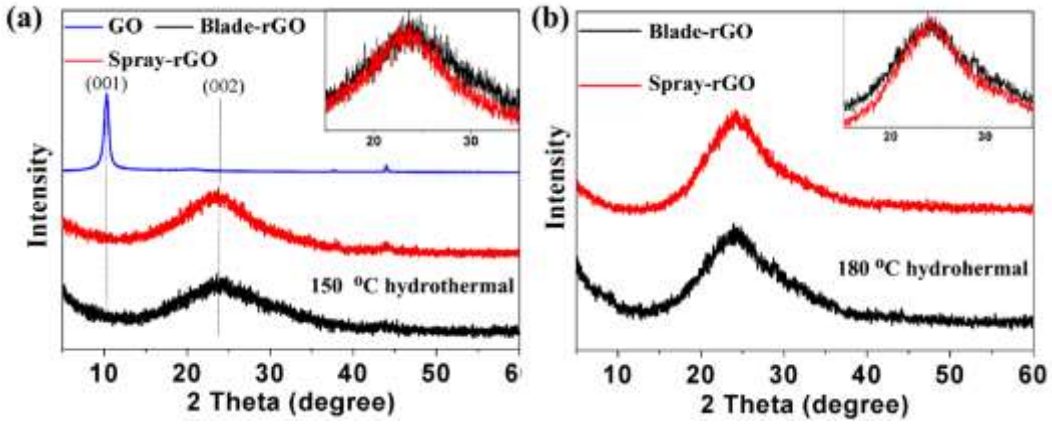

Figure S4. (a) XRD patterns of the GO, spray-rGO, and blade-rGO films for reduction

at 150 °C. Inset is high-magnification image of peaks for better comparison of the full width at half maximum. (b) XRD patterns of the spray-rGO, and blade-rGO films for reduction at 150 °C. Inset is high-magnification image of peaks for better comparison of the full width at half maximum.

XPS analysis for O 1s region

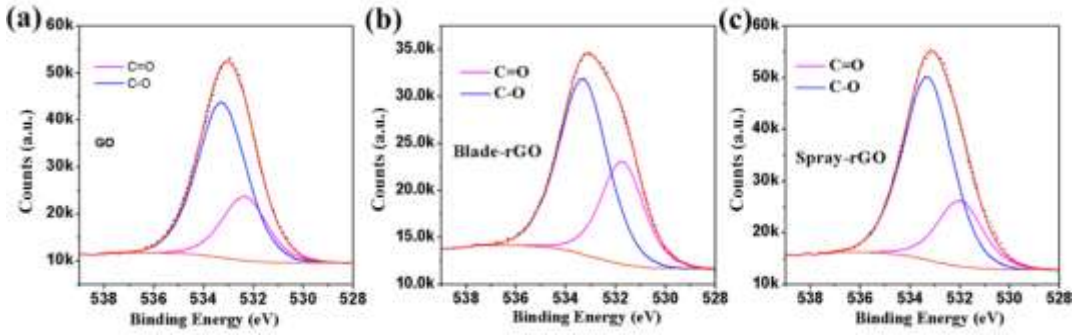

Figure S5. Deconvolved XPS spectra of the O1s regions of (a) GO, (b) blade-rGO, and (c) spray-rGO samples.

TGA of dried GO

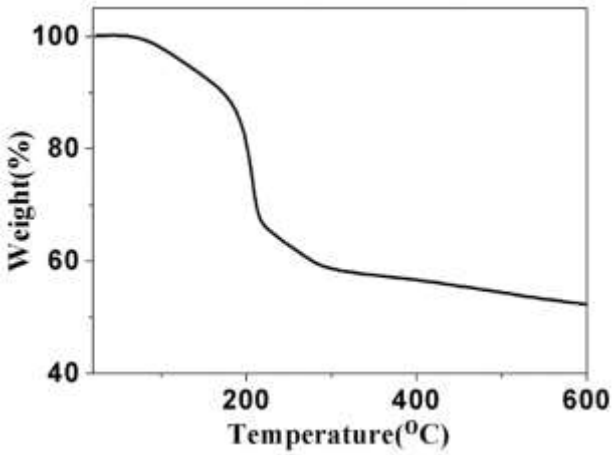

Figure S6. TGA of freeze-dried GO, heated in Ar at 5 °C/min.

XPS analysis

XPS analysis of two different blade-coated rGO films, derived from freshly-prepared and well-dried films, respectively. This comparison is to reveal the effect of trapped water in GO film on the reduction degree.

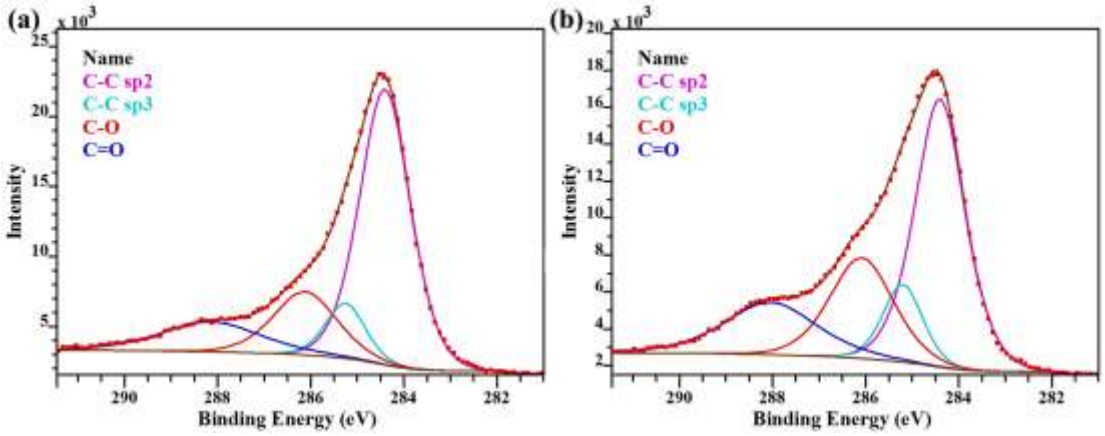

Figure S7. Deconvolved XPS spectra of the C1s regions of two rGO films obtained by

hydrothermally reducing blade-coated LC GO films at identical conditions. Before reduction, the GO films were: (a) naturally dried and have water trapped between sheets; (b) well-dried and lost the LC feature.

Impedance measurement

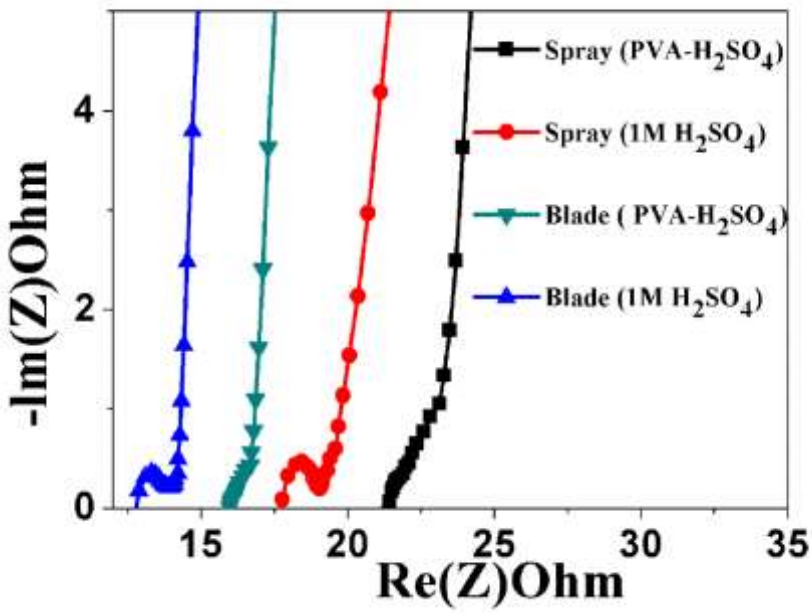

Figure S8. Nyquist plots of the blade-rGO and spray-rGO films in 1M H_2SO_4 aqueous electrolyte and PVA-H_2SO_4 gelled electrolyte.

Electrochemical measurement of supercapacitors with liquid H_2SO_4 electrolyte

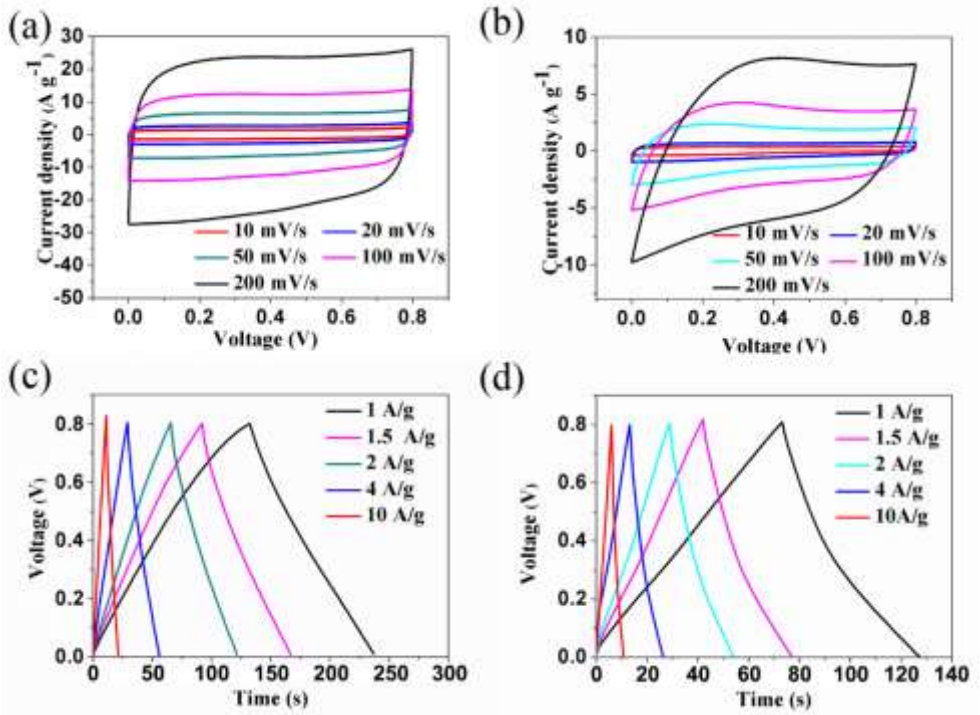

Figure S9. Electrochemical measurements of graphene supercapacitors using 1M H_2SO_4 aqueous electrolyte. (a) and (b) CV curves of the two devices based on spray-rGO and blade-rGO films, respectively. (c) and (d) Galvanostatic CD curves of the two devices based on spray-rGO and blade-rGO films, respectively.

Capacitance retention and cycle stability

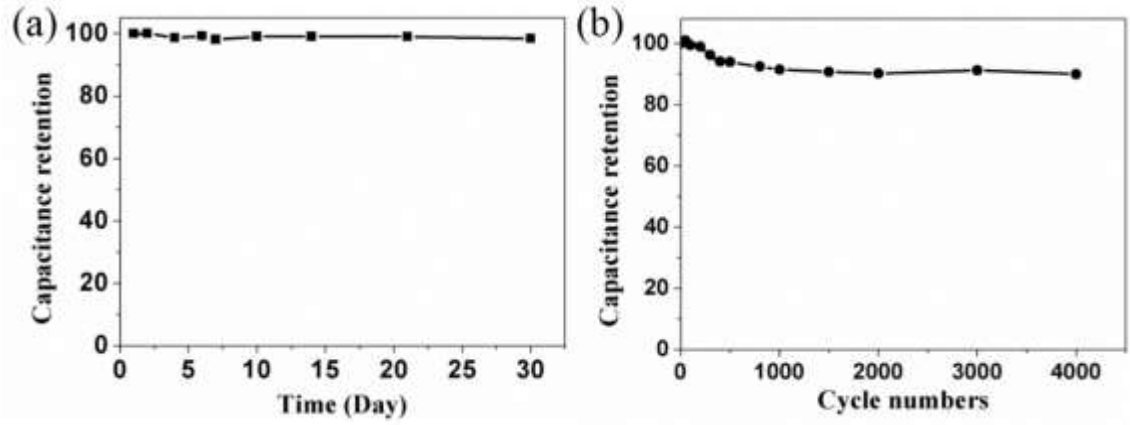

Figure S10. (a) The capacitance retention of the device measured after different days.

(b) Cycling stability of the device at a current density of 1 A/g.

References

1. Wang, J. D.; Peng, T. J.; Sun, H. J.; and Hou, Y. D. Effect of the Hydrothermal Reaction Temperature on Three-Dimensional Reduced Graphene Oxide's Appearance, Structure and Supercapacitor Performance. Acta. Phys. Chim. Sin. 2014, 30, 2077-2084.

2. Shi, J. L.; Du, W. C.; Yin, Y. X.; Guo, Y. G.; Wan, L. J. Hydrothermal Reduction of Three-Dimensional Graphene Oxide for Binder-Free Flexible Supercapacitors. J. Mater. Chem. A 2014, 2, 10830-10834.