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Supporting Information

Electrolyte-assisted hydrothermal synthesis of holey graphene films for all-solid-state supercapacitors

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Experimental Methods

1. Preparation of graphite oxide (GO)

Graphite oxide was prepared from natural graphite (Jinglong Co., Beijing, China) according to a modified Hummers method: 120 mL 98 wt% H_2SO_4 was poured into a beaker containing a mixture of 5 g natural graphite and 2.5 g $NaNO_3$, and then the mixture was stirred in an ice bath for 30 min. 15 g $KMnO_4$ was added slowly into the mixture, which was allowed to react for 2 h at a temperature no more than 20°C. Then, the temperature was risen to 35°C, and the reaction was performed for another 2 h. After that, the reactant mixture was poured slowly into 360 mL distilled water under violent stirring condition so as to control the temperature no more than 90°C, followed by further reaction at 75°C for 1 h. After the mixture was diluted to 1.5 L, 50 mL 30 wt% H_2O_2 was added to consume the remaining $KMnO_4$ and the produced MnO_2. The as-obtained mixture was a bright yellow suspension. After filtered and washed with 5 wt% HCl and distilled water, the filter cake was freeze-dried for 24 h to obtain the graphite oxide.

2. Preparation of holey graphene oxide (HGO)

Holey Graphite oxide was prepared according to a defect-etching reaction as reported previously[1]: 10 mL 30 wt% H_2O_2 aqueous solution was added to 100 mL 2 mg mL^{-1} GO aqueous dispersion and then heated at 80 °C for 6 h under stirring. After filtered and washed with 5 wt% HCl and distilled water to remove the residual H_2O_2, the filter cake was freeze-dried for 24 h to obtain the HGO. The as-prepared HGO was re-dispersed in water by ultrasonication for 1 h to produce a homogeneous HGO aqueous dispersion with a concentration of 2mg mL^{-1}.

3. Electrochemical characterization and analysis.

The calculating of the electrochemical measurement results was described as what we reported previously.[2] From CV curves of a three-electrode system, the gravimetric capacitances were calculated according to the following equation: $C_{\mathrm{g}} = \frac{1}{2m \cdot \Delta E \cdot v}\left(\int i_{\mathrm{a}} dE + \int i_{\mathrm{c}} dE\right)$, where C_{g} represents the gravimetric capacitance of a single electrode, m is the mass of the active material in the working electrode, E is the working electrode potential, ΔE is the potential window of the scan, v is the scan rate, i_{a} is the anodic current during the anodic scan, and i_{c} is the cathodic current during the cathodic scan. From CV curves of a two-electrode system, the gravimetric capacitances were calculated according to the following equation: $C_{\mathrm{g}} = \frac{1}{m \cdot \Delta V \cdot v}\left(\int i_{\mathrm{charge}} dV + \int i_{\mathrm{discharge}} dV\right)$, where C_{g} represents the gravimetric capacitance of a single electrode, m is the average mass of the active materials in the two electrodes, V is the voltage of the supercapacitor, ΔV is the voltage window of the scan, v is the scan rate, i_{charge} is the charging current during the charge scan, and $i_{\mathrm{discharge}}$ is the discharging current during the discharge scan.

From galvanostatic charge/discharge measurements of a three-electrode system, the gravimetric capacitances were obtained from the acquired data using the following equation: $C_{\mathrm{g}} = \frac{i_{\mathrm{discharge}} \cdot \Delta t}{m \cdot \Delta E}$,where C_{g} represents the gravimetric capacitance of a single electrode, $i_{\mathrm{discharge}}$ is the constant discharging current during the discharge process, Δt is the discharge time, m is the mass of the active material in the working electrode, and ΔE is the discharge potential range. From galvanostatic charge/discharge measurements of a two-electrode system, the gravimetric capacitances were obtained from the acquired data using the following equation: $C_{\mathrm{g}} = \frac{2 i_{\mathrm{discharge}} \cdot \Delta t}{m \cdot \Delta V}$, where C_{g} represents the gravimetric capacitance of a single electrode, $i_{\mathrm{discharge}}$ is the constant discharging current during the discharge process, Δt is the discharge time, m is the average mass of the active materials in the two electrodes, and ΔV is the discharge voltage range.

The EIS tests were performed at open circuit conditions using sinusoidal signals with a frequency range of 105~0.01Hz and an amplitude of 10 mV. From an EIS plot of a two-electrode system, the gravimetric capacitances at different frequencies were calculated according to the following equation: $C_{\mathrm{g}} = -\frac{1}{\pi f \cdot m \cdot Z''}$,where C_{g} represents the gravimetric capacitance of a single electrode, f is the frequency of the sinusoidal signal, m is the average mass of the active materials in the two electrodes, and Z'' is the imaginary component of the complex impedance.

The volumetric capacitances were calculated using the following equation: $C_{\mathrm{v}} = \rho \cdot C_{\mathrm{g}}$, where C_{v} represents the volumetric capacitance of a single electrode, and C_{g} is the gravimetric capacitance of a single electrode, ρ is the density of the active materials, which was measured according to the following formula: $\rho = \frac{m}{S \cdot d}$,Where m (g) is the mass of the single dried electrode, S (cm^2) and d (cm) are the area and thickness of the film electrode, respectively. The gravimetric and volumetric energy densities were calculated using the gravimetric capacitances obtained from the galvanostatic charge/discharge tests according to the following equation: $E_{\mathrm{g}} = \frac{1}{8 \times 3.6} C_{\mathrm{g}} \cdot \Delta V^2$, $E_{\mathrm{v}} = \rho \cdot E_{\mathrm{g}}$, where E_{g} represents the gravimetric energy density against the mass of the active materials in the two electrodes, and E_{v} is the volumetric energy density against the volume of the active materials in the two electrodes.

The gravimetric and volumetric power densities were calculated according to the following equation: $P_{\mathrm{g}} = \frac{E_{\mathrm{g}}}{\Delta t}$, $P_{\mathrm{v}} = \rho \cdot P_{\mathrm{g}}$, where P_{g} represents the gravimetric power density against the mass of the active materials in the two electrodes, Δt is the discharge time, and P_{v} is the volumetric power density against the volume of the active materials in the two electrodes.

4. Measurement of the specific surface area of graphene films.

The specific surface area of rHGF was calculated using the methylene blue adsorption method. Methylene blue is a common dye probe used to determine the surface area of graphitic materials, with each molecule of adsorbed methylene blue representing 1.35 nm^2 of surface area.[3, 4] The surface area was calculated by adding a known mass of rHGF into a standard concentration of methylene blue in DI water. The rHGF was stirred in the methylene blue solution continuously at a rate of 300 rpm for a total of 48 h to reach maximum adsorption. The mixture was then allowed to settle and further centrifuged to remove any suspended material. The methylene blue concentration was determined by analyzing the supernatant through UV-vis spectroscopy at a wavelength of 665 nm and compared to the initial standard concentration of methylene blue prior to interacting with rHGF.

Supplementary Figures and Tables

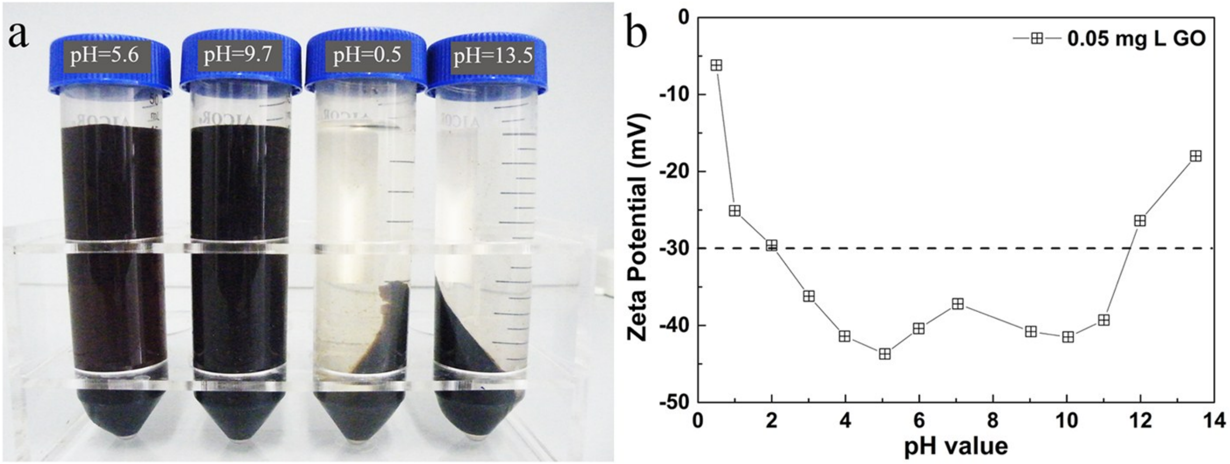

Figure S1. Surface properties of GO. (a) Dispersion state of 2 mg mL^{-1} GO at different pH after centrifuged at 10000 r min^{-1} for 10min. (b) Zeta potentials of GO as a function of pH, in aqueous dispersions at a concentration of ~0.05 mg ml^{-1}.

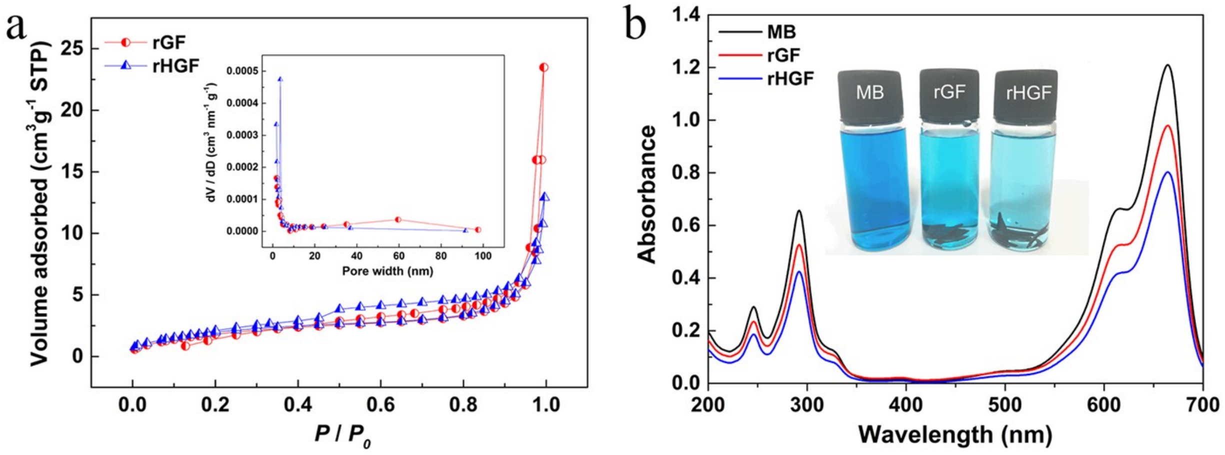

Figure S2. (a) N_2 adsorption-desorption isotherms and pore size distribution curves of rGF and rHGF. (b) UV-vis absorption spectra and photos of MB solution after 48 h absorption by rGF and rHGF.

Table S1. The surface area of the rGF and rHGF measured by the N_2 adsorption-desorption and methylene blue adsorption method

Sample	S_{N2} [a] [m^2 g^{-1}]	Adsorption [b] [mg ads./mg]	S [b] [m^2 g^{-1}]
rGF	7.28	0.1052	257.8
rHGF	7.82	0.1945	473.2

[a] SSA calculated with BET method from the N_2 adsorption isotherm. [b] Adsorption capacity and corresponding SSA calculated with methylene blue adsorption method.

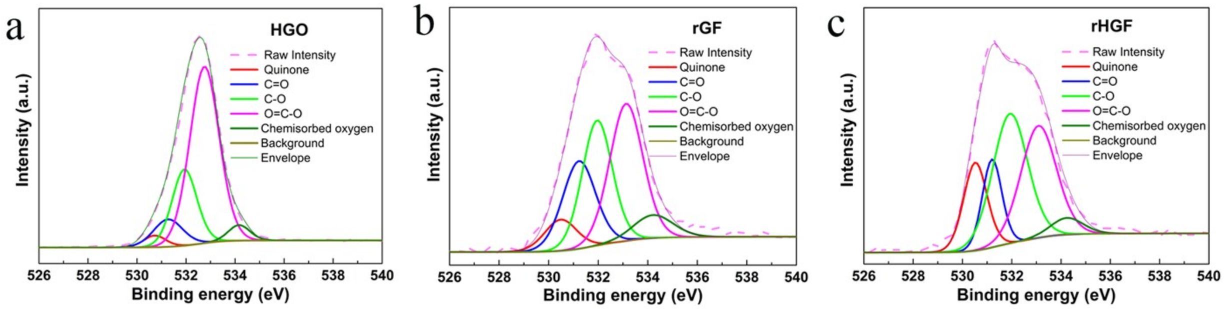

Figure S3. O1s XPS spectra of (a) HGF, (b) rGF and (c) rHGF.

Table S2. Surface elemental concentrations and relative contents of functional groups derived from C1s XPS spectra of HGO, rGF and HrGF

Samples	Carbon (at.%)	Oxygen (at.%)	C1s fitting binding energy (eV; relative percentage,%)				
			C=C(sp^2)	C-C(sp^3)	C-O	C=O	O-C=O
HGO	68.7	31.3	284.8 (45.91)	285.29 (8.88)	286.91 (34.08)	287.54 (6.27)	288.70 (4.91)
rGF	85.88	14.12	284.8 (63.81)	285.41 (12.29)	286.21 (10.61)	287.22 (5.6)	288.76 (7.69)
rHGF	82.31	17.69	284.8 (55.78)	285.81 (15.94)	286.7 (14.78)	288.14 (7.09)	288.70 (6.41)

Table S3. Relative contents of functional groups derived from O1s XPS spectra of HGO, rGF and HrGF

Samples	O1s fitting binding energy (eV; relative percentage, %)				
	Quinone	C=O	C-O	O=C-O	Chemisorbed oxygen
HGO	530.72 (3.06)	531.27 (9.52)	531.93 (22.41)	532.75 (61.06)	534.16(3.95)
rGF	530.49 (7.67)	531.23(22.09)	531.96(28.63)	533.13 (34.67)	534.22(6.94)
rHGF	530.52 (16.07)	531.2(13.39)	531.93(35.30)	533.2 (31.06)	534.24(4.19)

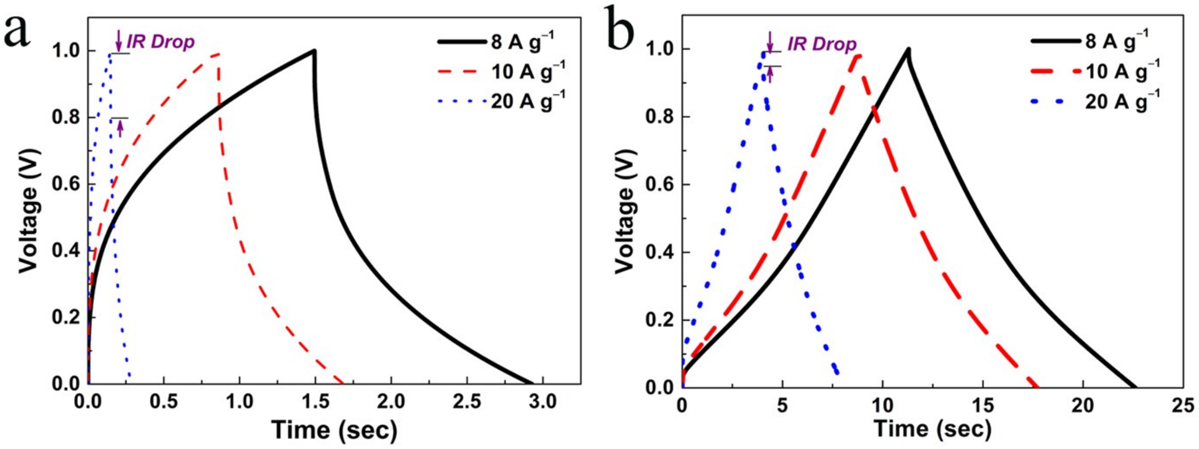

Figure S4. Electrochemical characterization of as-prepared electrodes in a two-electrode system. (a,b) Charge/discharge curves obtained at different current densities of rGF and rHGF.

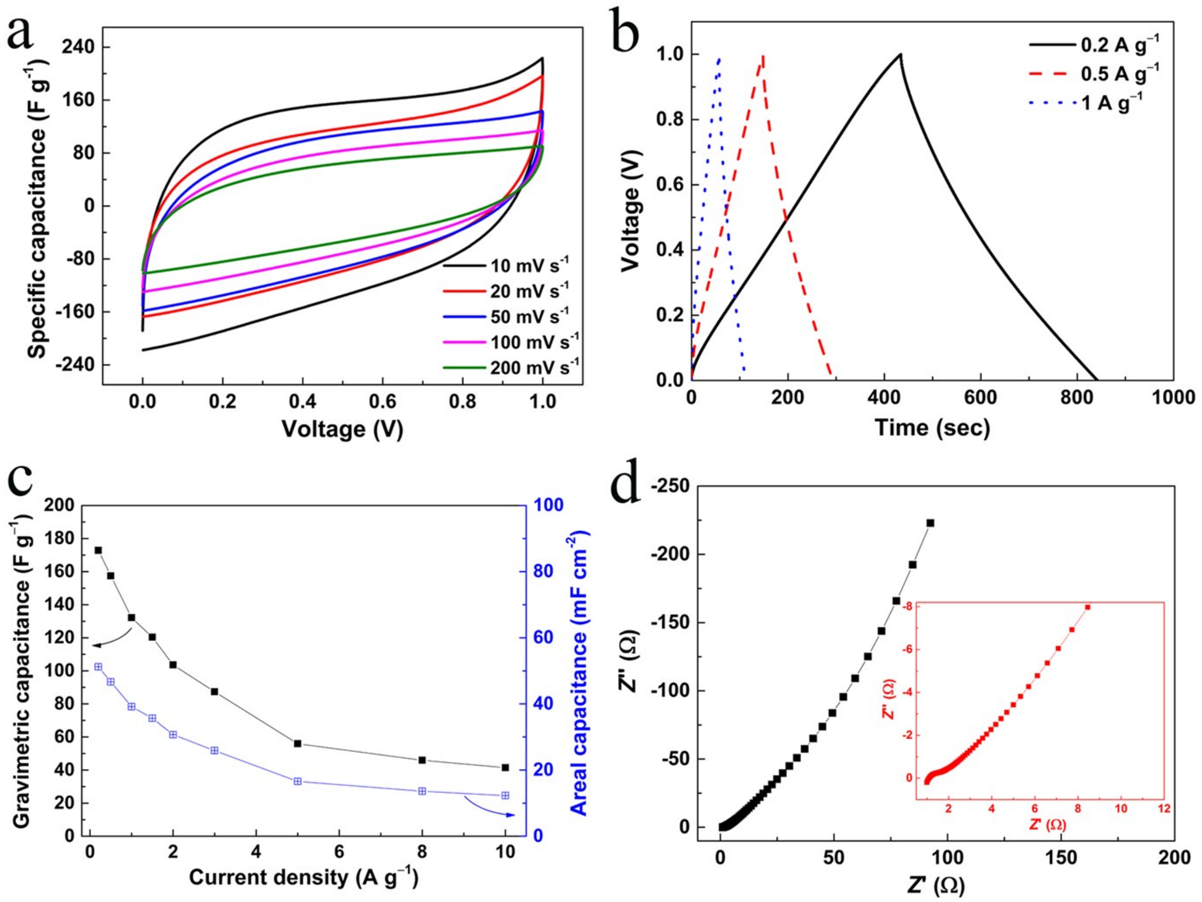

Figure S5. Electrochemical characterization of rHGF-based all-solid-state supercapacitor (based on electrode). (a) Relationship curves of the capacitance and potential at different scan rates. (b) Galvanostatic charge/discharge curves at different current densities. (c) Relationship plots between gravimetric capacitance values/areal capacitance and current densities. (d) Nyquist plots of the EIS for the all-solid-state supercapacitor.

Supplementary References

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