

Supporting Information for

**Mechanically Strong and Highly Conductive Graphene Aerogels and Its Use as
Electrodes for Electrochemical Power Sources**

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Experimental

Materials: All chemicals including graphite powder (200-325 mesh) and L-ascorbic acid were purchased from Beijing Chemical Reagents Company with their purity being of analytical grade. All chemicals were used without further purification. Graphene oxide used in this work was synthesized according to the procedure reported elsewhere (V. C. Tung, M. J. Allen, Y. Yang, R. B. Kaner, *Nat. Nanotechnol.*, 2009, 4, 25) and described in brief as follows: The concentrated 25 mL H₂SO₄ in a 100 mL beaker was heated up to 90 °C. K₂S₂O₈ (5 g) and P₂O₅ (5 g) were added in sequence with continuous stirring until the reactants were completely dissolved. The mixture was then cooled down to 80 °C. Graphite powder (6 g) was then added to above mixture. The resulting mixture was kept at 80 °C for 4.5 hours, after which the mixture was diluted with 1 L of DI water and left overnight. The mixture was then filtered and washed to remove all soluble substances, and the corresponding pretreated graphite was transferred to a drying dish and left overnight under ambient conditions. Another 230 mL H₂SO₄ was put into a 1 L Erlenmeyer flask and then cooled in an ice bath. The pretreated graphite and 30 g KMnO₄ were added slowly in sequence and allowed to dissolve completely. The mixture was then allowed to react at 35 °C for 2 hours, after that, 460 mL distilled water was slowly added. When the temperature of the mixture remained constant,

another 1.4 L of DI water was added to the mixture. The mixture was stirred for another 2 hours, thereafter 25 mL of 30% H₂O₂ was added to the mixture. The mixture was allowed to stand for at least 12 hours then the clear supernatant was decanted. The remaining mixture was washed with a great number of 5% HCl solution followed by DI water to remove the inorganic acid. The final solution was concentrated to 10 mg/mL.

Synthetic Method: In a typical procedure, 0.72 g L-ascorbic acid was added into a 200 mL beaker containing 60 mL 4.0 mg•mL⁻¹ graphene oxide aqueous solution with vigorous magnetic stirring until completely dissolving. The mixture was heated up to 40 °C and then left to stand for at least 16 hours to form graphene hydrogel. The obtained hydrogel was first purified in a large amount of distilled water for at least 1 week in order to wash out low molecular weight components of the system including excessive L-ascorbic acid and its oxidized product dehydroascorbic acid, and then freeze-dried to obtain the graphene aerogel. Or the purified hydrogel was further turned into the alcogel by using alcohol to replace the water within the network of the hydrogel, and then dried with supercritical CO₂ to obtain graphene aerogel. [The bulk densities of the resulting aerogels have been calculated by the mass of the graphene aerogel divided by its volume.](#)

Instrumentation: [The compression tests were carried out by a single-column system \(CMT6104\) with loading capacity from 10 to 104 N at a constant loading speed of 2 mm/min.](#)

SEM was conducted at a Hitachi S-4800 field-emission-gun scanning electron microscope at 5-10 kV and samples for SEM were prepared by incising very thin pieces of the resulting aerogels and then attaching them onto the silicon wafer via carbon adhesive tape. TEM was conducted at a FEI Tecnai 20 transmission electron microscopy. The imaging was performed

at 200 kV. Raman spectra were recorded on a Renishaw system 1000 with a 50 mW He-Ne laser operating at 632.8 nm with a CCD detector. Atomic force microscope (AFM, Veeco NanoScope III, Veeco Co., USA, operated in tapping mode) was used to characterize the surface topography of the samples. X-Ray photoelectron spectroscopy (XPS) was performed using an AXIS Ultra spectrometer with a high-performance Al monochromatic source operated at 15 kV. The XPS spectra were taken after all binding energies were referenced to the C 1s neutral carbon peak at 284.8 eV, and the elemental compositions were determined from peak area ratios after correction for the sensitivity factor for each element. Nitrogen sorption measurements were performed with ASAP 2010 (Micromeritics, USA) to obtain pore properties such as the BET-specific surface area, pore size distribution, and total pore volume. Before measurement, the sample was outgassed under vacuum at 250 °C for ca. 10 h until the pressure less than 0.665 Pa. A Keithley 4200 Semiconductor Characterization System was used to measure the current-voltage curves (two-probe method) and electrical conductivities (four-probe method) of the samples. TGA was carried out using a PerkinElmer TGA7 thermogravimetric analyzer from room temperature to 900 °C at 10 °C/min heating rates with N₂ protection. The weight of samples is 6-10 mg in all cases. X-ray powder diffraction data were collected with an X'Pert Pro MPD (PANalytical, The Netherlands) diffractometer using monochromatic Cu K α 1 radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 40 mA. The diffraction patterns were optimized with a step length of 0.01°(2 θ) over an angular range 5-70° (2 θ) with a scanning speed of 0.01°/s. The electrochemical performances of the samples were measured in a two-electrode cell. The electrodes were prepared by pressing a mixture of 87 wt% of sample, 10 wt% of acetylene black and 3 wt% of PTFE binder into pellets (11 mm in diameter)

and then drying at 120 °C for 12 h. The capacitor was assembled into two-electrode system, among which two electrodes were separated by polypropylene membrane using 6 mol.L⁻¹ KOH aqueous solutions as electrolyte. The cyclic voltammetry (CV) and ac impedance spectroscopy were recorded by Solartron 1280B electrochemical workstation. The galvanostatic charge/discharge test was carried out on an Arbin cell tester (CT2001A) between 0 and 1 V. The specific capacitance (C) of a single electrode was determined with the formula $C = 2It / \Delta Vm$, where I is the discharge current (A), t is the discharge time (s), ΔV is the potential change in discharge (V) and m is the mass of the active material in a single electrode (g).

Tables

Table SII: Mechanical properties of the graphene aerogels dried by supercritical CO₂

Sample ID	A	B	C
Bulk density (mg/cm ³)	30.9	47.6	96.1
Young's modulus in the elastic region (MPa)	1.2	2.8	6.2
Yield strength (MPa)	0.04	0.15	0.66
Young's modulus in the yield region (MPa)	0.3	1.1	2.2

Figures

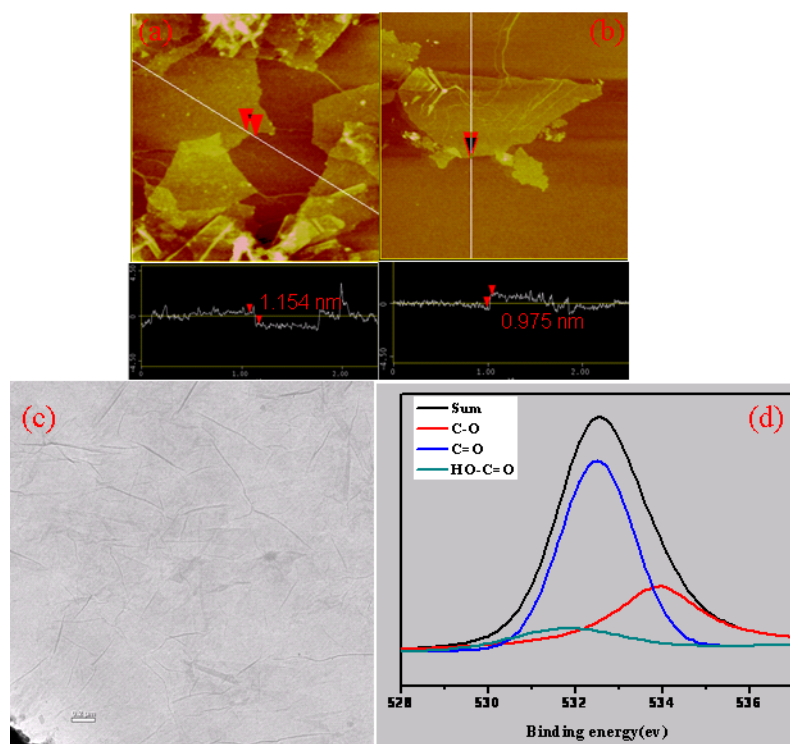


Fig.S11 AFM images of graphene oxide (a) and graphene (b), TEM image of graphene oxide (c), and O 1s XPS spectra of graphene (d)

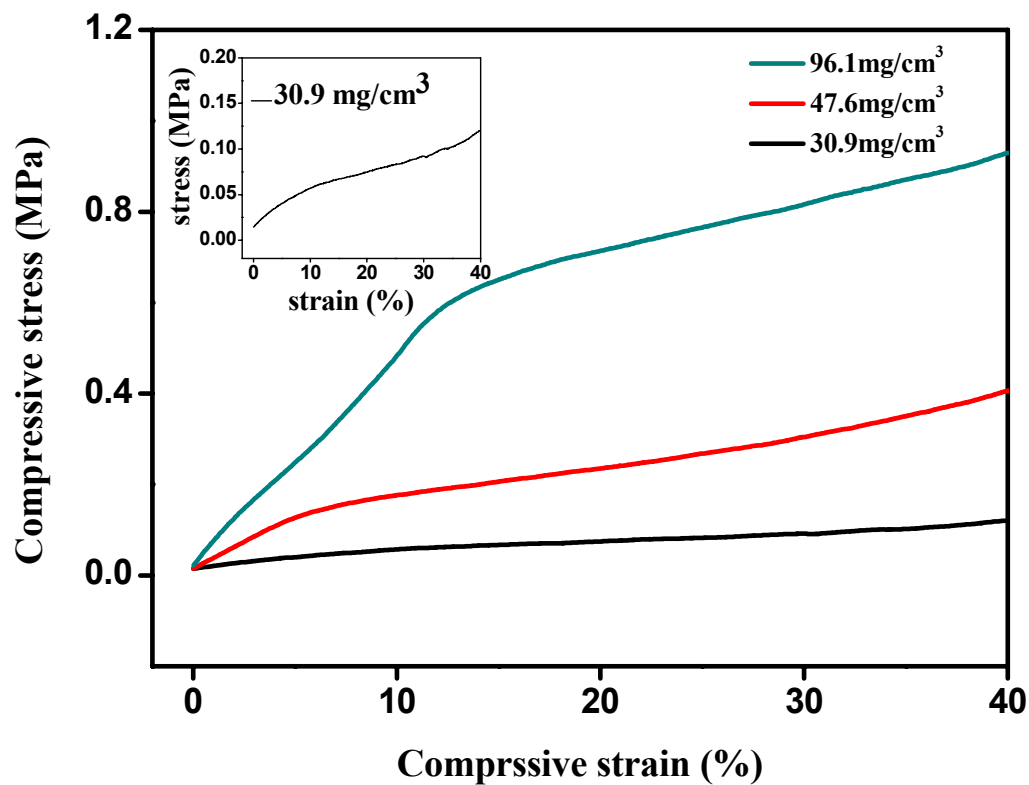


Fig.SI2 Compressive stress-strain curves of the graphene aerogel with supercritical CO₂ drying (Inset: enlarging stress-strain curve of the graphene aerogels with the density of 30.9 mg/cm³ for clearer observation of two strain regions.)

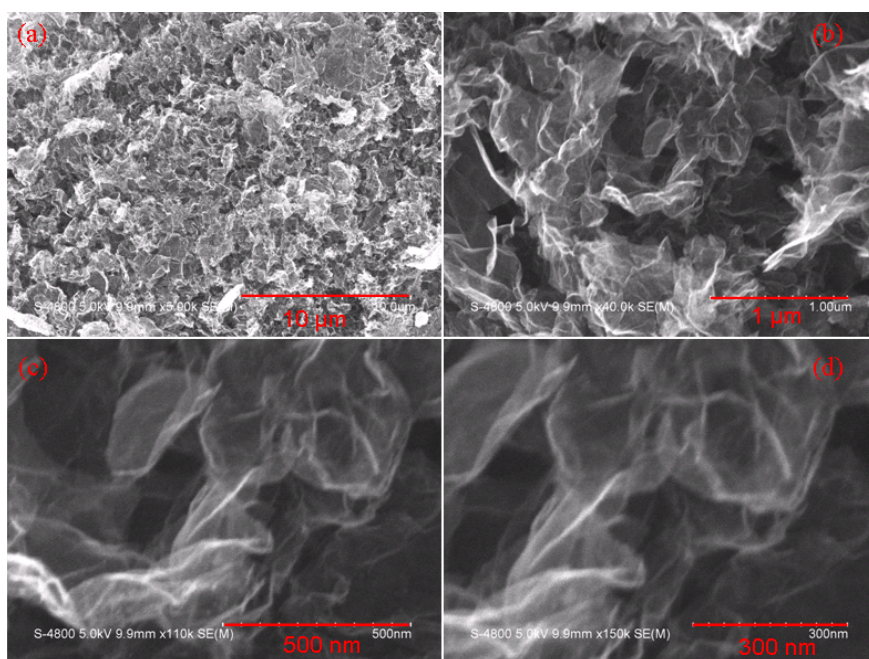


Fig.S13 SEM images of graphene aerogel with supercritical CO₂ drying

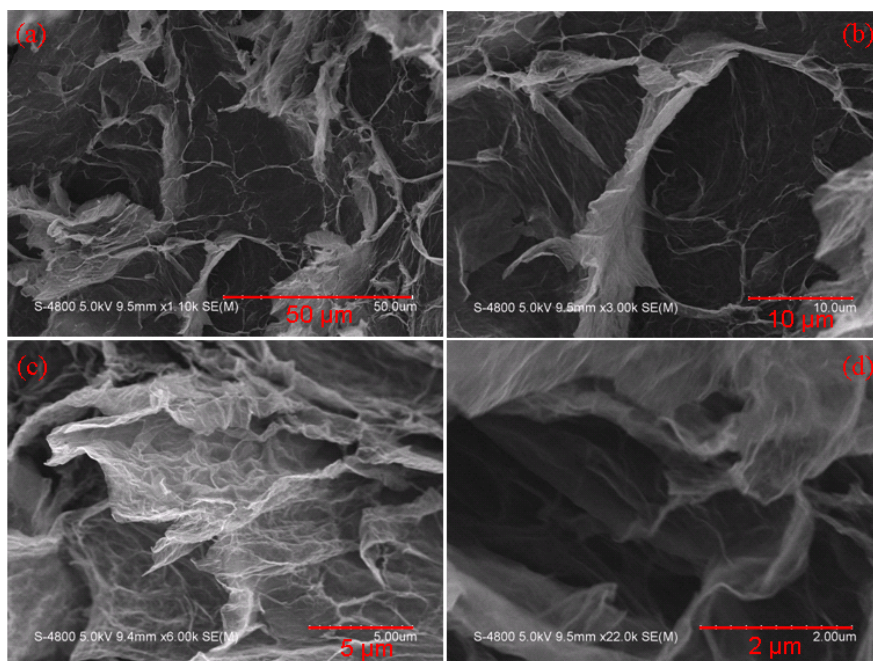


Fig.SI4 SEM images of graphene aerogel with freeze drying

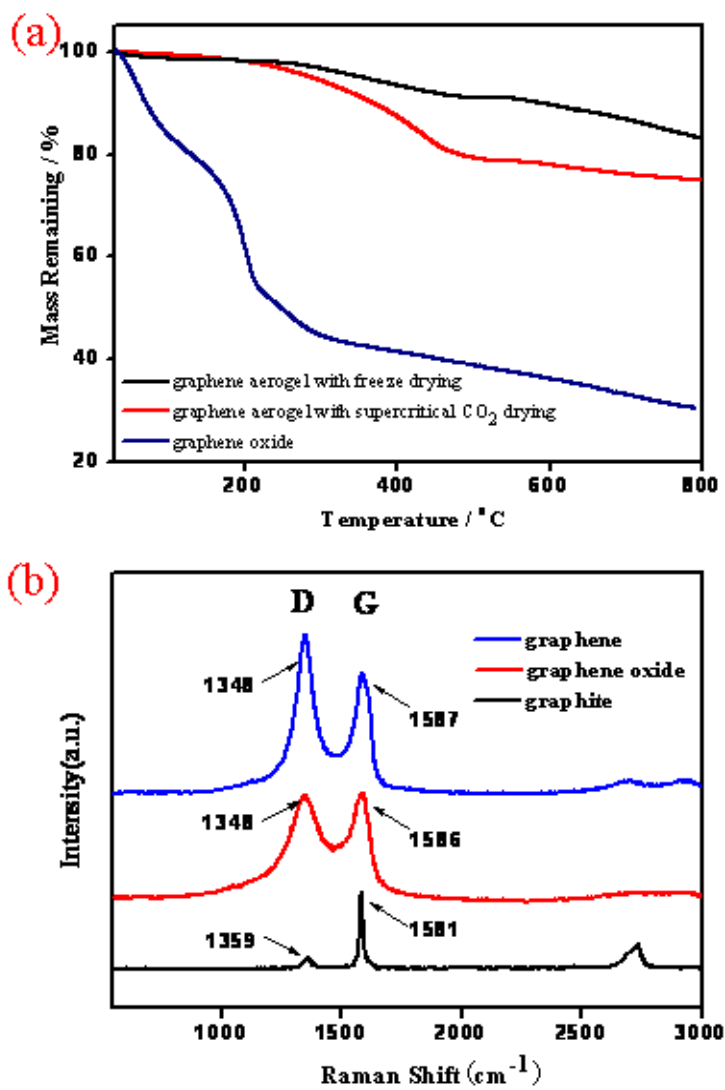
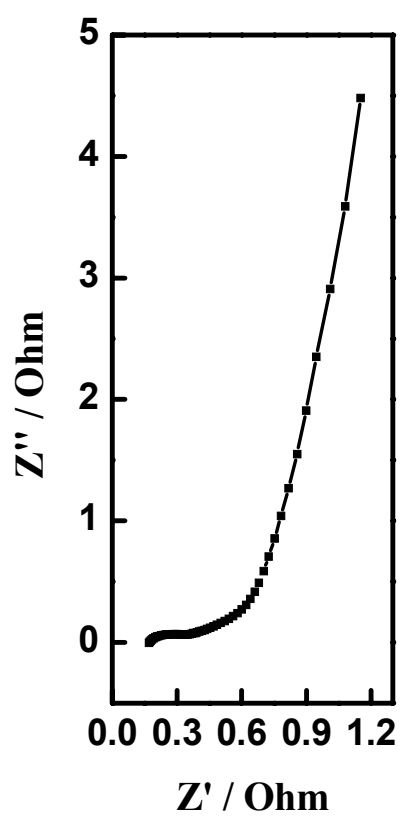


Fig.S15 TG curves of graphene aerogel (a),
and Raman spectra of graphene aerogel precursor (b)



[Fig.SI6](#) Nyquist plots for EDLCs based on graphene aerogel dried by supercritical CO_2