

Supporting information

Ultra-light, Compressible and Fire-Resistant Graphene Aerogel as the Highly Efficient and Recyclable Absorbent for Organic Liquids

**Jihao Li,^{a,b} Jingye Li,^{*a} Hu Meng,^{a,b} Siyuan Xie,^{a,b} Bowu Zhang,^a Linfan Li,^a
Hongjuan Ma,^a Jianyong Zhang,^a and Ming Yu^a**

^a *TMSR Research Center and CAS Key Lab of Nuclear Radiation and Nuclear Energy
Technology, Shanghai Institute of Applied Physics, Chinese Academy of Sciences,
Shanghai, 201800, P. R. China. Fax & Tel: +86 21 3919 4505; E-mail:
jingyeli@sinap.ac.cn*

^b *University of Chinese Academy of Sciences, Beijing, 100049, P. R. China*

Materials:

Graphite flake (~500 μm) was obtained from Sigma-Aldrich, ethylenediamine (EDA), Concentrated H_2SO_4 (98 %), KMnO_4 , P_2O_5 , H_2O_2 (30 %) solution, $\text{K}_2\text{S}_2\text{O}_8$ were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received. Milli-Q water is used for all experiments unless otherwise stated.

Preparation of graphene aerogels:

GO was prepared from graphite powder through a modified Hummer's method as reported[1-3] (Figure S6). In a typical experiment for synthesis of a graphene aerogel of $4.4 \text{ mg}\cdot\text{cm}^{-3}$, 1g of ethylenediamine (EDA) was added into 50 ml ultrapure water, and then the mixture is slowly added with 50 mL $4 \text{ mg}\cdot\text{mL}^{-1}$ aqueous suspension of GO under magnetic stirring. Then 10ml of the mixture was sealed in a glass vial and heated at 80 $^\circ\text{C}$ for 24h without stirring. The extra EDA or ions were removed by dialysis with ultrapure water more than ten times. After freeze-drying, the as-prepared graphene aerogel was finally produced.

Characterization:

Compressive tests were performed by using INSTRON 5966 equipped with two flat-surface compression stages and 500 N load cells. The strain ramp rate was controlled to be $6 \text{ mm}\cdot\text{min}^{-1}$ for the tests. The cylindrical graphene aerogels (with size of 1.5~2 cm) were used. For the compression of graphene aerogel in butanol as an organogel, a glass dish filled with butanol was fixed on the bottom stage, and a graphene aerogel was placed in the center of dish. The graphene aerogel was completely immersed in the butanol during the compression cycles, and the aerogel can only expand its volume from the compressed state by absorbing surrounding liquid during unloading. To minimize the influence of incompressible liquid on the mechanical tests, the top compression stage was modified to the same cross-sectional

size to the aerogel sample to avoid direct compression on liquid surface.

Contact angle analysis was performed on a KSV INSTITUTION (Attention Company) instrument and the volume of the water drop is 5 μ L. Each sample was measured for three times on different positions and the average value was obtained.

XPS spectra were recorded on a SHIMADZU Kratos AXIS Ultra DLD XPS instrument equipped with a monochromated Al K α X-ray source. High resolution scans were acquired with 40 eV pass energy, wide-scan survey spectra were acquired with 160 eV pass energy.

XRD patterns were recorded on a RIGAKU D/Max 2200 X-Ray diffractometer with Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$) at a generator voltage of 40 kV and a generator current of 50 mA. All experiments were carried out in the reflection mode at ambient temperature with 2θ in the range of 3 $^\circ$ to 50 $^\circ$. The scanning speed was 8 $^\circ$ min $^{-1}$.

The morphologies of the aerogels were characterized on a field-emission scanning electron microscope (FESEM, JEOL, JSM6700F).

FT-IR spectra were collected by using KBr pellets on the transmission module of Thermo Nicolet Avatar 370 FT-IR spectrometer at 4 cm $^{-1}$ resolution and 32 scans.

TGA curves were obtained from a NETZSCH TG 209 F3 Tarsus - Thermo-Microbalance. The samples were heated at 10 $^\circ$ C min $^{-1}$ under 50 mL min $^{-1}$ of nitrogen purging in the temperature range from 20 $^\circ$ C to 600 $^\circ$ C. In order to eliminate the influence of absorbed water, all tests were set 10 min thermostating at 100 $^\circ$ C in the heating program.

The observation of the GO surface features was carried out on a Digital Nanoscope IIIa Multimode SPM Atomic Force Microscope (AFM).

The electrical conductivity of graphene aerogels and was measured by a two-probe method using a digital multimeter (VC 890D, Shenzhen Victor Hi-tech Co. Ltd.)

References:

- [1] H. Sun, Z. Xu, C. Gao, *Adv. Mater.*, 2013, **25**, 2554-2560.

[2] B.W. Zhang, Y.J. Zhang, C. Peng, M. Yu, L.F. Li, B. Deng, P.F. Hu, C.H. Fan,

J.Y. Li, Q. Huang, *Nanoscale*, 2012, **4**, 1742–1748.

[3] B.W. Zhang, L.F. Li, Z.Q. Wang, S.Y. Xie, Y.J. Zhang, Y. Shen, M. Yu, B. Deng,

Q. Huang, C.H. Fan, J.Y. Li, *J. Mater. Chem.*, 2012, **22**, 7775–7781.

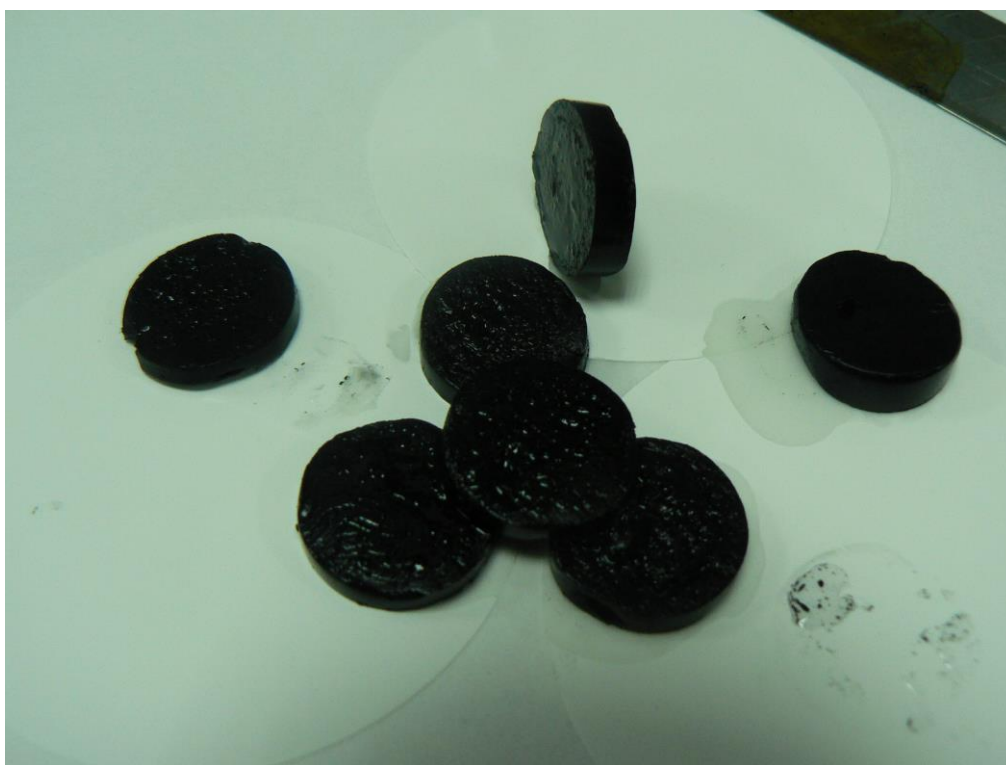


Figure S1. The hydrogel is good in mechanical property which can be cut into pieces by knife.

Table S2 Concentrations of various elements of GO and graphene aerogels.

Samples	C (Atomic Conc. %)	O (Atomic Conc. %)	C/O atomic ratio	N (Atomic Conc. %)	C/N atomic ratio
GO	69.49	29.59	2.35	< 1	>68.29
Graphene aerogel	81.74	9.40	8.69	7.22	11.32

The C/O atomic ratios were calculated according to the peak areas of C, O and N elements from XPS wide scans.

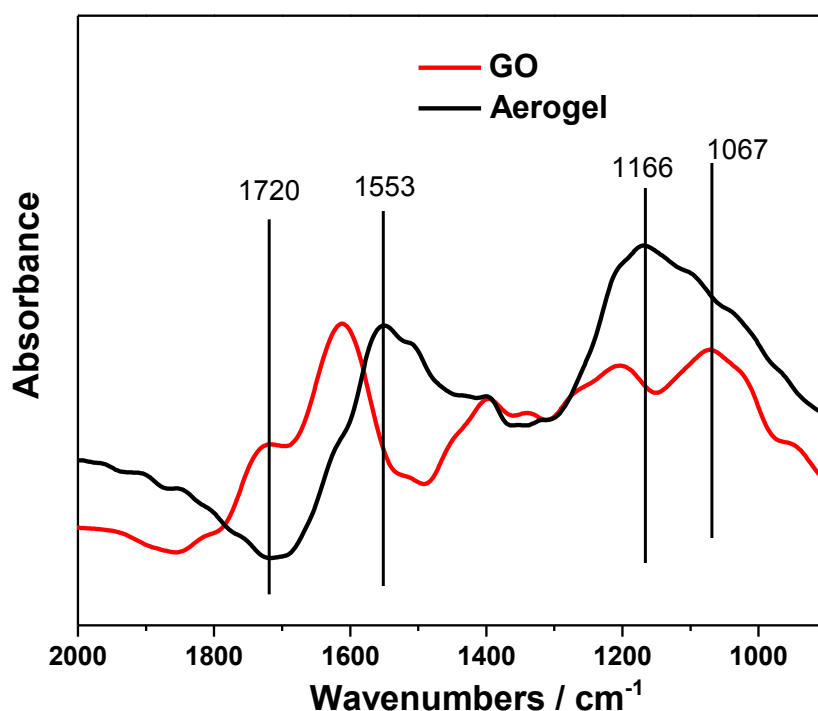


Figure S3. The FT-IR spectra of GO and the graphene aerogel ($\rho=4.4 \text{ mg cm}^{-3}$). Before the reaction with EDA, the stretching vibration band of C=O at 1720 cm^{-1} , and the stretching vibration bands C-O of epoxy and alkoxy at 1200 and 1067 cm^{-1} respectively demonstrate that the GO has abundant oxygen containing groups. After reaction with EDA, the intensities of the all FT-IR bands correlated to the oxygen containing groups decreased dramatically. Furthermore, there are two new broad bands: 1553 cm^{-1} which is associated with the vibration of N-H groups and 1167 cm^{-1} which is associated with the vibration of C-N bond. The results are consistent with the XPS analysis in Figure 1c, demonstrating the successful chemical reduction and also surface modification of GO with EDA.

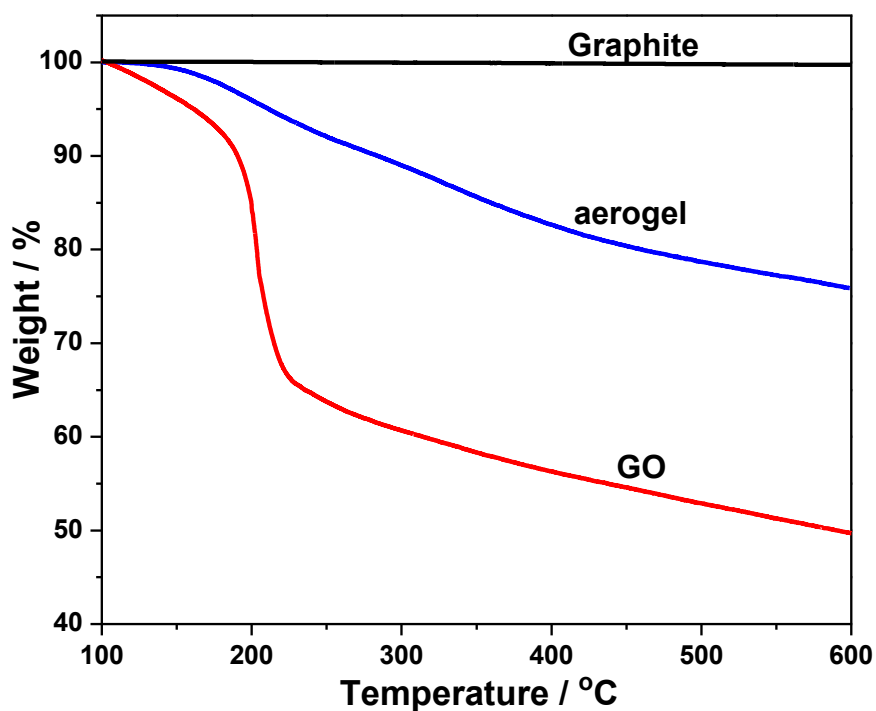


Figure S4. The TGA curves of graphite, GO and the graphene aerogel ($\rho=4.4$ mg cm^{-3}).

The weight loss stage of starting GO starts from 150 °C to 230 °C. As an alternative, the TGA curve of graphene aerogel displays a slowly downward sloping line, which means its enhanced thermal stability due to the removal of oxygen-containing groups. Certainly, graphite was more stable than the graphene aerogel, suggesting the presence of fewer organic groups in it.

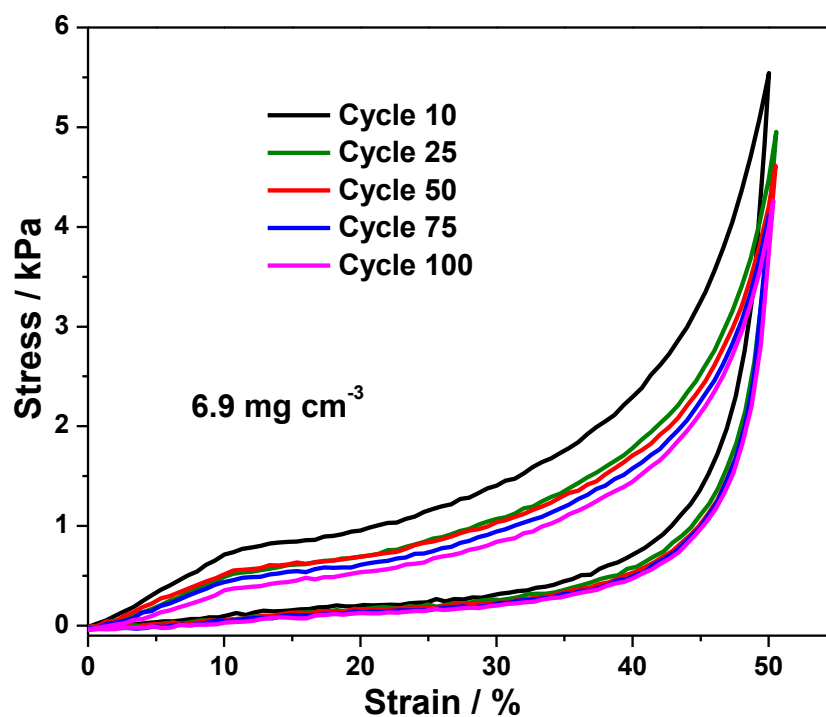


Figure S5. The Stress-Strain curves at different cycles for the graphene aerogel with ($\rho=6.9 \text{ mg cm}^{-3}$).

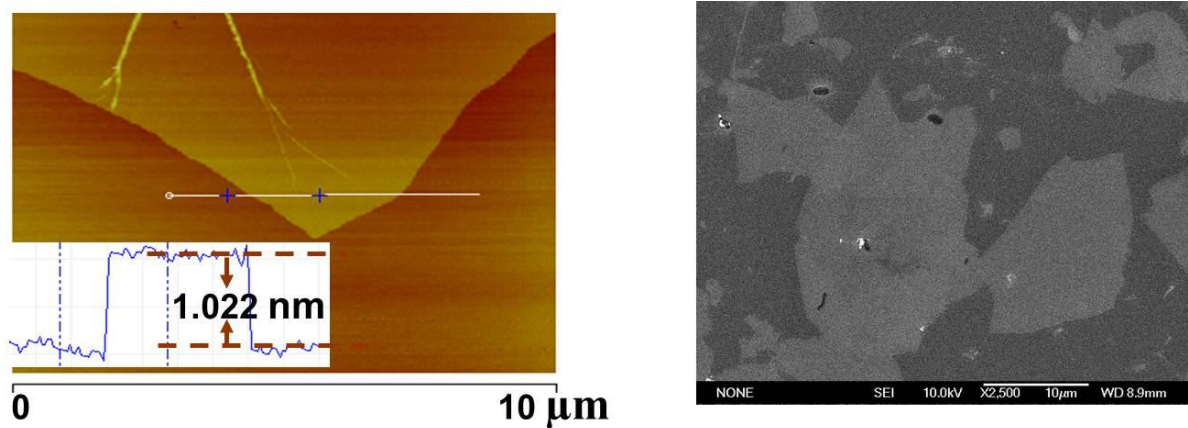


Figure S6. AFM (left) and SEM (right) images of the GO sheets obtained.

The as-prepared GO is of a single layer with a height of about 1 nm from the crossing section profile curve (Left) and an average lateral width of about 5-20 μm (Right), demonstrating the successful preparation of GO sheets.