

Journal of Materials Chemistry A

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

ARTICLE

A Facile Method to Prepare Highly Compressible Three-Dimensional Graphene-only Sponge

Jinhui Li^{a,b}, Songfang Zhao^{a,b}, Guoping Zhang^{a,*}, Yongju Gao^{a,c}, Libo Deng^a, Rong Sun^{a,*}, Ching-Ping Wong^{d,e}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x
www.rsc.org/

Abstract Endowing compressibility and conductivity into graphene sponge offers the possibility to regenerate piezoresistivity and is therefore of great interest in the field of sensor. In this work, the highly compressible three-dimensional graphene-only sponge (CGS) was prepared through a facile method by using ammonium sulfide and ammonia solutions under mild condition. The morphologies and microstructures of the as-prepared CGSs can be controlled by adjusting the mass ratio of graphene oxide (GO) to ammonium sulfide which changed from metallic sheen bulk with leaf-shaped structure to a black sponge with cellular structure. Besides, by simply change the concentrations of GO, CGSs with different porosity, conductivity as well as mechanical strength were obtained. Moreover, the resultant CGSs show ultralow density (as low as 4.9 mg cm⁻³), high porosity (as much as 99.8%), great compressibility (as much as the strain of 80%), excellent stability (100 cycles) during the compression. Furthermore, the sensitive variation of electrical resistances and cycle stability were validated under the compressive strain of 50% which make them great candidates for pressure-responsive sensors, elastic conductors and other applications.

Introduction

The carbon nano-materials represented by carbon nanotube (CNT) and graphene have been desired to form a connected, three-dimensional structure so as to exploit their numerous possibilities for many fields such as electrochemical energy materials¹⁻³, catalyst⁴, absorbents^{5, 6} and chemical sensors⁷ because of their superior physical and chemical properties⁸⁻¹⁰. Among these materials, three-dimensional compressible carbon sponge or foam has attracted much attention¹¹⁻¹⁴. Thereinto, compressible graphene sponge (CGS)^{6, 15, 16}, combining the thinnest, strongest and stiffest properties as well as excellent conductivity of graphene sheets and the special three-dimensional structure possesses great compressibility, ultralow density as well as excellent electrical property. Meanwhile, a great deal of attention has been paid on the application of CGS such as piezoresistive sensors¹⁷, elastic conductors¹⁸, electronic skin¹⁹ and recyclable absorbent for organic liquids²⁰. Therefore, developing facile and accessible methods to prepare CGS is highly desirable. As well as known, chemical vapor deposition (CVD) method has been adopted to prepare the three-

dimensional elastic macroscopic graphene network while this method needs high temperature, special gases and the assistance of porous substrates¹³. Another general method, organic compounds or polymer binders including ethylenediamine^{20, 21}, paraphenylene diamine²², poly(vinyl alcohol)²³, poly(acrylic acid)²⁴, polyurethane^{17, 18} and poly(dimethylsiloxane)²⁵, had been reported to prepare CGS by crosslinking graphene oxide (GO) nanosheets and further reduction. In fact, introducing organic components into the three-dimensional graphene sponge improved the compressibility but disserved the conductivity^{18, 26}. Besides the two methods mentioned above, hydrothermal process was also employed to prepare CGS^{16, 27}, however high temperature, high pressure and special devices were necessary in the process.

Even though much progresses, it is still a challenge to prepare graphene-only bulk with super elasticity and conductivity under mild conditions¹⁵. Special reducing agents such as hydrazine hydrate, HI, NaHSO₃, Na₂S and ascorbic acid (vitamin C) had been reported to prepare graphene sponge (GS)²⁸⁻³². However, none of them have referred to CGS. One possible reason may be that the reduction can't form tight connection with high strength between GO sheets during the process of reduction and self-assembly²¹. Here we tried to prepare the compressible three-dimensional graphene-only sponge by ammonium sulfide and ammonia solutions under mild conditions.

Ammonium sulfide, a cheap, safe and high-efficient reduction agent were used in this study for reduction of GO. The low valence states of sulfur (S²⁻) provide the high reducibility and the reduction and self-assembly process can be completed at 90 °C during 3 h or 8 days at room temperature. To the best of our knowledge, this is the first report about the formation of graphene hydrogel (GH) at room temperature. After the treatment by ammonium solution at 90 °C for 1 h, the ultra-light and compressible graphene-only sponge was obtained after freeze-drying. The microstructure, porosity,

^a Shenzhen Institutes of Advanced Technology, University of Chinese Academy of Sciences, Shenzhen 518055, China. E-mail: gp.zhang@siat.ac.cn or rong.sun@siat.ac.cn; Fax: +86-755-86392104; Tel: +86-755-86392104.

^b Shenzhen College of Advanced Technology, University of Chinese Academy of Sciences, Shenzhen 518055, China.

^c Nano Science and Technology Institute, University of Science and Technology of China (USTC), Suzhou 215123, China.

^d School of Materials Science and Engineering, Georgia Institute of Technology, 771 Ferst Drive, Atlanta, GA 30332, USA

^e Department of Electronic Engineering, Faculty of Engineering, The Chinese University of Hong Kong, Hong Kong, China

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

conductivity, mechanical strength and piezoresistivity of the as-prepared CGSs were comprehensively investigated in the following work.

Experimental

Materials

Graphite powder (CP) and ammonium sulfide solution (20% w/w aq.) were supplied by Aladdin (Shanghai, China) and used as received. The chemicals included potassium permanganate (KMnO_4), sodium nitrate (NaNO_3), concentrated sulfuric acid (98%), hydrochloric acid and ammonia solution were all reagent grade purchased from Sinopharm Chemical Reagent Beijing Co., Ltd.

Preparation of CGSs

GO was prepared from natural graphite powders by a modified Hummers method²⁷. GH was prepared by reduction and self-assembly of GO with ammonium sulfide solution. In a typical process, 10 mL of GO solution (2 mg mL^{-1}) was sealed in a 20-mL glass bottle with the addition of 1 mL ammonium sulfide solution (the mass ratio of GO and to ammonium sulfide was 1:10). After standing at 90°C for 3 h, the bottle was cooled freely and GH was obtained. The GH was washed by deionized water for several times and then treated in ammonia solution (14 v/v%) at 90°C for 1 h in a sealed vessel and CGS was obtained after freeze-drying. Other samples were prepared by 1 mg mL^{-1} , 3 mg mL^{-1} and 5 mg mL^{-1} GO solutions according to the above mentioned way. The resultant sponges were referred as CGS-1, CGS-2, CGS-3 and CGS-5, respectively. In contrast, graphene sponge without the treatment of ammonia solution was named as GS.

Measurements

Fourier transform infrared (FTIR) spectra were recorded with Bruker Vertex 70 spectrometer (Bruker Optik GmbH, Ettlingen, Germany) in the range of $4000\text{--}400 \text{ cm}^{-1}$. Thermal gravity analysis (TGA) was made on a TA SDTQ600 thermo-gravimetric analyzer; the microbalance has a precision of $\pm 0.1 \mu\text{g}$. Samples of about 10 mg were placed into $70 \mu\text{L}$ alumina pans. The samples were heated from 30°C to 800°C under a nitrogen flow of 100 mL min^{-1} . Scanning electronic micrographs (SEM) were recorded with a Nova NanoSEM 450. The Raman spectra were measured by LabRAM HR Raman Spectrometer (HORIBA Jobin-Yvon, France) with a laser at the excitation wavelength of 632.8 nm and 15.7 mW power irradiation. The collection time for each spectrum was 60 s. The scattered light was detected with a thermoelectric cooled (-70°C) charge coupled device detector (CCD). All the measurements were carried out directly over the sample. Powder X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (RiGSKU D/Max 2500) with monochromated $\text{Cu K}\alpha$ radiation ($\lambda=1.54 \text{ \AA}$) at a scanning rate of 2° min^{-1} . Atomic Force Microscopes (AFM) were recorded with MFP-3DTM (Asylum Research, USA) and operated in air in AC mode. The compressive tests were performed in a Dynamic mechanical analysis (DMA, TA Instruments DMA 2980) in controlled strain mode with a strain rate of 50% per minute at room temperature. X-ray photoelectron spectroscopy (XPS) analyses were conducted with a XSAM800 system, where $\text{Al K}\alpha$ excitation source was used. The electrical resistance variation is measured by a two-probe method under mechanical deformation. During the measurement, two copper sheets sever as electrodes to connect to sponges and a Keithly 2410 Source Meter instrument (Keithly Inc. USA).

Results and discussion

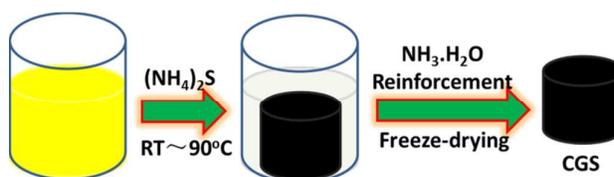


Figure 1. Schematic illustration for the preparation of CGS.

The typical fabrication process of CGS is illustrated in Figure 1. First, GO colloidal solution was reduced and assembled to graphene hydrogel by ammonium sulfide at mild reaction condition. Second, the resultant hydrogel was reinforced by ammonia solution and freeze-dried to prepare the desired CGS. The as-prepared GO in the aqueous dispersion is of a single layer with the width about several micrometers as shown in Figure S1, demonstrating the successful preparation of GO nanosheets. During the reduction process, GO solution turned black at room temperature very quickly which indicated the excellent reducibility of ammonium sulfide solution (Figure S2). Furthermore, the hydrogel could be formed obviously in 10 minutes at 90°C or 2 days at room temperature which indicated the quickly self-assembly process as shown in Figure 2a and Figure S3. After 3 h at 90°C or 8 days at room temperature the volume of hydrogel didn't change any more and the self-assembly process was finished completely. During the process of reduction and self-assembly, the hydrophobicity and the π - π conjugated structures of the reduced GO sheets were increased gradually and the rod-shaped hydrogel was formed at the end. In order to remove the residuary ammonium sulfide the hydrogel was immersed in de-ionized water and washed for several times. After treated by ammonium solution at 90°C for 1 h and freeze-drying the ultra-light CGS was obtained. Compared with CGS, GS without the reinforcement of ammonium solution can't be compressible as shown in Figure S4. The possible reason can be ascribed that the low freezing point of ammonia reduced the expansion of ice during freeze drying as the expansion ratio was about 1.1 when water became ice and retarded the freezing of the hydrogel which kept the porous structure undestroyed³³.

The continuous three-dimensional network indicates the strong interconnection between building blocks. CGS exhibits a cellular structure inside with interconnected pores ranging from tens to hundreds of micrometers by microscopic observation (Figures 2b and c). The pore walls are made up of assembled graphene sheets during the reduction and self-assembly process. In addition, wrinkles and twists can be observed in the edge of graphene sheets (Figure 2d) which could dedicate to the excellent mechanical strength and especially compressibility. However, it should be noticed that the morphologies, gloss and internal structures of these graphene sponges were influenced greatly by the mass ratio of GO to ammonium sulfide (Figure 3). It can be seen that the internal structure changed from leaf-shaped structure to the continuous porous structure with the increasing of the proportion of ammonium sulfide solution which is similar with the rGO sponge prepared by mercaptoacetic acid³⁴. Meanwhile, the volume of hydrogels get bigger and the mechanical strength become weaker. The GH even couldn't hold its shape during the washing process

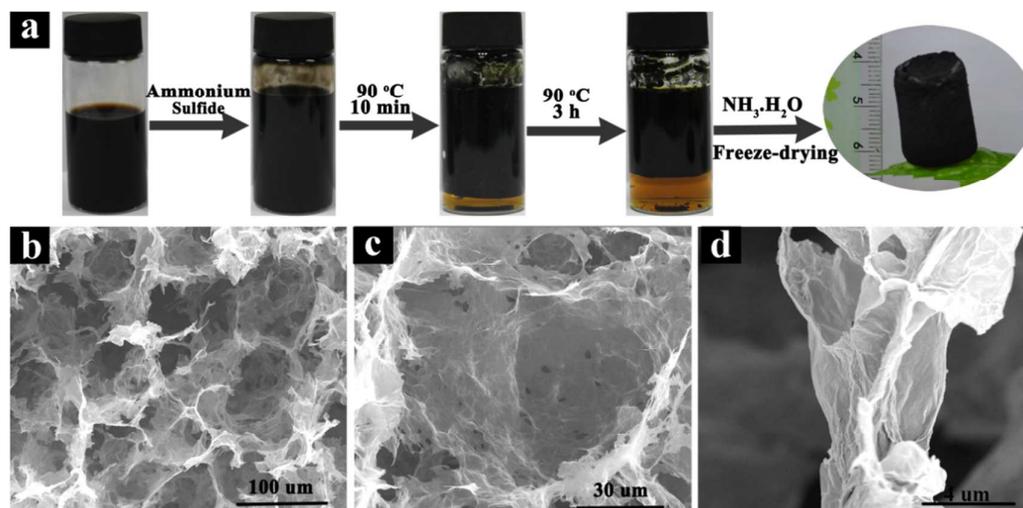


Figure 2. (a) Illustration of the reduction and self-assembly process of the graphene hydrogel and the digital image of CGS obtained from 5 mg mL^{-1} GO solution. (b-d) SEM images of cellular structure of CGS at different magnification.

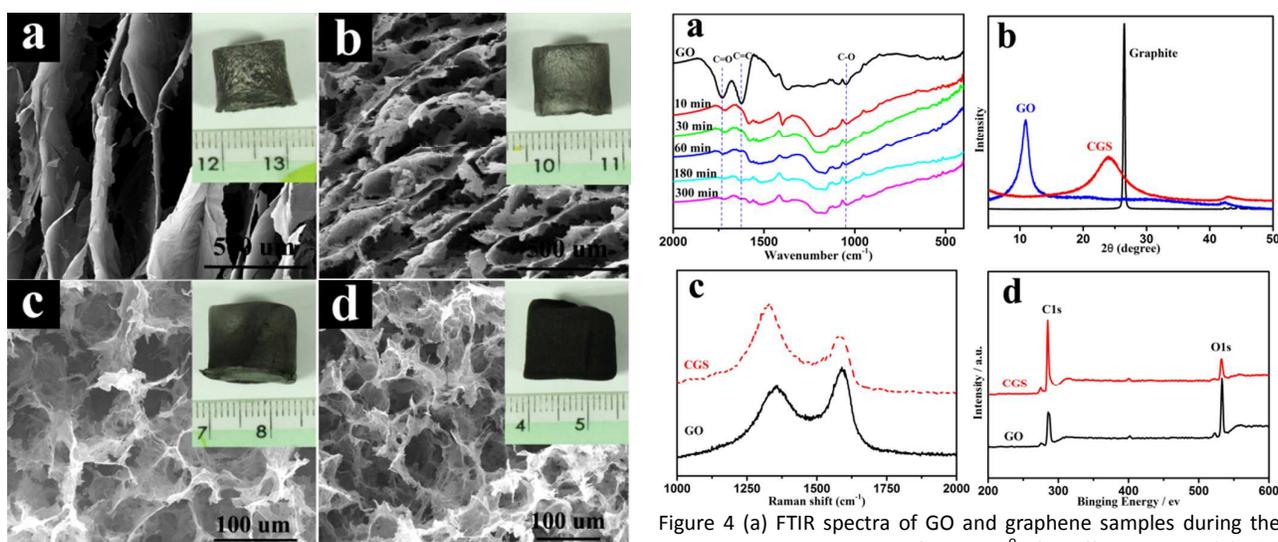


Figure 3 The internal microstructure of as-prepared graphene-only sponge at different mass ratio of GO to ammonium sulfide from (a) 2:5, (b) 1:5, (c) 1:10 to (d) 1:20.

when the mass ratio of GO to ammonium sulfide reached to 1:20. The as-prepared graphene sponge also lost the metallic sheen gradually as shown in the insets of Figure 3. Therefore, the mass ratio of GO to ammonium sulfide has significant effect on mechanical strength as well as morphology of the graphene hydrogel and sponge (Figure S5). All the phenomena can be ascribed that when the reducing agent was excess, the GO sheets were reduced quickly into graphene sheet and the assembly happened at the same time and during the progress all the sheets hardly moved and the porous structures formed immediately. Otherwise, the reduction of GO sheets happened slowly and the sheets have enough time to move together and compactly layer structure was obtained at last. In order to prepare graphene sponge with 3D cellular structure, lower density and stronger mechanical strength, the mass ratio of 1:10 of GO to ammonium sulfide was employed in this work.

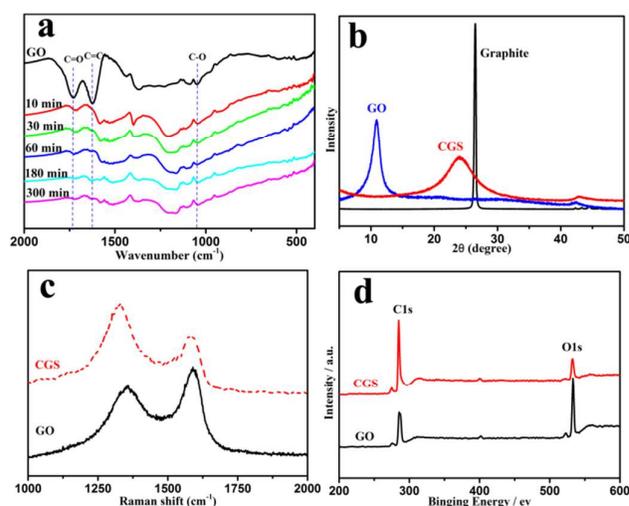


Figure 4 (a) FTIR spectra of GO and graphene samples during the reduction by ammonium sulfide at 90°C for different times. (b) XRD patterns of graphite, GO and CGS. (c) Raman spectra of GO and CGS. (d) XPS spectra of GO and CGS.

FTIR spectra of the intermediates and products during the reduction-assembly process were shown in Figure 4a. Before reduction, the typical stretching vibration band of C=O and C-O at 1730 cm^{-1} and 1047 cm^{-1} respectively demonstrates that the GO has abundant oxygen containing groups. After the reduction by ammonium sulfide, the intensities of all FTIR bands correlated to the oxygen containing groups decreased dramatically^{35, 36}. The reduction of GO to the final sponge was also examined by XRD, Raman spectroscopy and XPS (Figures 4b, c and d). In the XRD patterns, the peak of graphite is at $2\theta = 26.46^\circ$ (d-spacing 3.36 \AA) while the diffraction peak for GO appears is around $2\theta = 11^\circ$ (d-spacing 8.10 \AA). After the reduction and freeze-drying, a new broadened diffraction peak at $2\theta = 24.06^\circ$ (d-spacing 3.69 \AA) appeared in the sponge, which is close to the d-spacing 3.36 \AA of the graphite. All these results suggest the chemical reduction happened successfully during the process³⁷. The Raman spectra of GO and CGS have two remarkable bands at around 1326 and 1585 cm^{-1} and they are assigned to the D- and G-bands of carbon. GO

shows an I_D/I_G ratio of 0.78 while the corresponding value of CGS was increased up to 1.48. These results indicate that the GO sheets were reduced to rGO and their conjugated structures were partly restored during the reduction process by ammonium sulfide^{30,38-40}. The C/O mole ratio increased from 1.6 up to 4.9 as shown in the XPS spectra (Figure 4d). It also demonstrated that large numbers of oxygen containing groups were reduced successfully by ammonium sulfid at comparatively mild condition⁴¹. Besides all the analysis above, the TGA curve of CGS displayed a slowly downward sloping line compared with that of GO, which means its enhanced thermal stability due to the removal of oxygen-containing groups³⁴ (Figure S6).

Table 1 Properties of different CGSs.

Sample	Density (ρ) /mg cm ⁻³	Conductivity /S m ⁻¹	Porosity /%
CGS-1	4.9	0.18	99.8
CGS-2	7.5	0.20	99.7
CGS-3	7.7	0.28	99.7
CGS-5	8.1	0.40	99.6

The graphene sponges have an ultralow density (ρ) that ranges from 4.9 to 8.1 mg cm⁻³ controlled by variation of the GO concentration from 1 mg mL⁻¹ to 5 mg mL⁻¹ (Table 1 and Figure S7). The as-prepared graphene-only sponges can be considered as ultralight material because densities of all CGSs are in the range of below 10 mg cm⁻³ as reported⁶. Meanwhile, the conductivities of CGSs were improved with increasing the weight densities (Table 1). Typically, CGS-5 has a conductivity of about 0.40 S m⁻¹, and this value is comparable to that of graphene sponge prepared by severe hydrothermal reduction of GO. Furthermore, the porosity is calculated based on the followed equation²¹ which can be achieved as high as 99.6–99.8%. Therefore, the CGSs obtained here were of great electrical conductivity, ultralight as well as high porosity.

$$\varepsilon = 1 - \rho/\rho_0$$

where ε represent the porosity, ρ is the density of the as prepared graphene-only sponge while ρ_0 is the density of graphite which is assumed to be 2.2 g cm⁻³.

Taking advantage of the special architecture of as-prepared graphene-only sponge, the interlock and twist of graphene sheets composed of pore wall which improved the mechanical strength of graphene sponge and make the sponges compressible. A set of real-time images of a compressing sample and the following recovering process were shown in Figure 5a. It can be seen that CGS-2 can be pressed to a very small height under stress and once the external pressure is removed, the CGS-2 could recover to the original shape immediately. The compression stress (σ)-strain (ε) curves with the stress loaded along the honeycomb cell axis direction of CGS-1 to CGS-5 are shown in Figures 5b, c, d and e. The stress-strain curves with different strains were tested by DMA. It shows that about compressible structures, all the curves under compression contain three steps, which includes an initial linear region at $\varepsilon < 10\%$, a gradually increasing slope and finally a quick increase in the stress which is similar to other reports^{20,27}. Take CGS-2 for example, the loading process exhibits a linear-elastic region for $\varepsilon < 8\%$ with an elastic modulus of 2.25 KPa, a plateau region for $8 < \varepsilon < 65\%$, and a steep slope region for $\varepsilon > 65\%$ where stress rises steeply with compression, which is because the cell walls begin to impinge upon each other^{18,42}. The hysteresis loops formed by the loading and unloading represent a typical σ - ε curve for elastomeric open-cell foams^{43,44}. Additionally, the curves under release give a stress that

stays above zero until $\varepsilon=0\%$, suggesting the sponge can rapidly and completely recover to its original volume, which is consistent with the observation in Figure 5b to Figure 5e. Meanwhile, the stress of CGS-1 increased from 1.04, 3.5 to 15.71 KPa under the strain of 30%, 50% and 80% respectively. By simply increased the concentration of GO solution, the densities increased gradually as shown in Table 1 which resulted into the increase of the compression strength. For example, the stress at $\varepsilon=50\%$ increase from 3.5 to 10.6 kPa (Figure 6a and Figure S9) for CGSs with the increase of the density of the samples and the compression stress were much higher than the CNT sponge with the density of 17.9 mg mL⁻¹ at the same strain which indicated the strong mechanical strength by this method⁴⁴. Besides, all the CGSs show great retention of stress with the coefficient of more than 88.57% with the stain of 50% after 10 cycles (Figure 6b). It should be noticed that after 10 cycles of compress-release process the retention of stress increased from CGS-1 to CGS-3 and then decreased for CGS-5. The possible reason could be that there were too much graphene sheets in the cell wall of the sponge and which could be broken during the compression because of the severe crush (Figure S8).

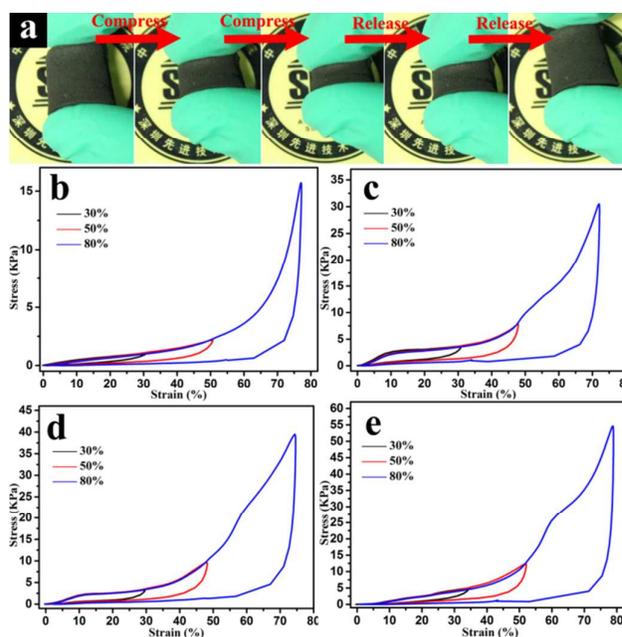


Figure 5. (a) A set of real-time images of CGS-2 showing the recovering process. The stress-strain curves with the strain of 30%, 50% and 80% of (b) CGS-1, (c) CGS-2, (d) CGS-3, (e) CGS-5.

The repeated compression rebound test of CGS-2 with the strain of 50% was shown in Figure 7a and the curves of the repeated 10 cycles show reproducible results with the maximum stress of 5.7 KPa. The retention of maximum stress and stress loss were also as shown in Figure 7b. It can be seen that the maximum stress decreased by only about 5% and tended to be stable in the first 10 cycles (Figure 7b). Besides, the stability of CGS during the compression was test by repeated compression rebound as much as 100 cycles and SEM as shown in Figure S10 and Figure S11. Figure S10 shows that there is hardly any loss for the maximum stress of the CGS-3. The retention of maximum stress was as much as 94.5% after 100 cycles which means that the mechanical property is quite stable during the compression rebound. The SEM pictures during the compression were also collected in Figure S11. It can be seen

that before compression CGS showed round shape cells of the sponge (Figure S11a) and during the compression the round cell of the original sponge had been pressed into narrow shape while the three-dimensional structure was still remained (Figure S11b). The cells were undamaged during the compression. And after the compression the round cell structure of CGS recovered (Figure S11c). Furthermore, Figure S11d showed the inner structure of CGS after 100 cycles and it can be seen that the continuous three-dimensional porous structure was still remained. This phenomenon provides that CGS possesses great stability during compression cycle. Therefore, the CGSs hold not only great elasticity but also wonderful stability and durability as a result of the special 3D structure as well as excellent mechanical strength.

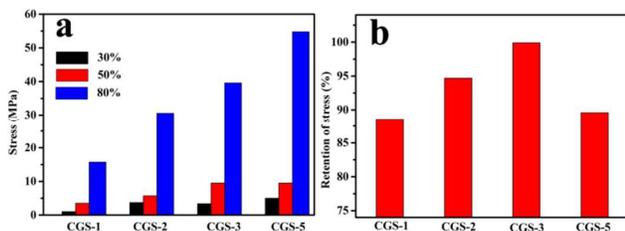


Figure 6 (a) The stress of CGSs with the strain of 30%, 50% and 80%, respectively. (b) The retention of maximum stress of CGSs with the strain of 50% after 10 cycles.

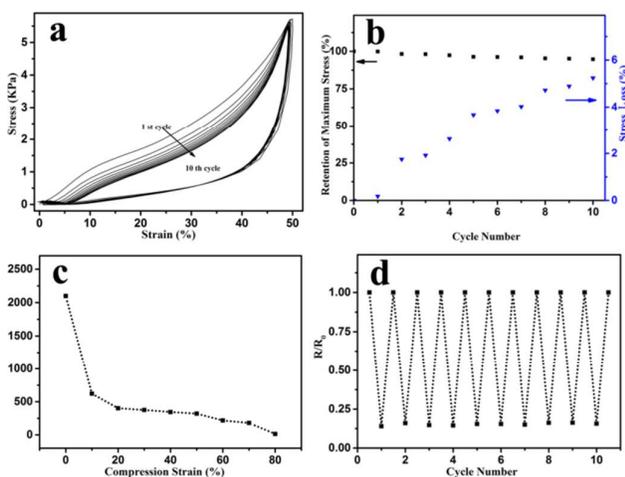


Figure 7 (a) Compressive stress-strain curves of the first 10 cycles of CGS-2 under the strain of 50%. (b) Retention of maximum stress at 50% strain and the stress loss of the maximum during the first 10 compression cycles (calculated from Figure 7a). (c) The electrical resistance of the CGS-2 as a function of strain. (d) Electrical resistance changes of CGS-2 recorded in the first 10 compression and release cycles with the strain of 50%.

We were excited by the excellent properties of the great elasticity and electrical conductivity and further investigate the relationship between elasticity and electrical conductivity for CGS. Then the curve of the electrical resistance (R) to the strain (ϵ) during the compression of CGS-2 was collected in Figure 7c. When the CGS was connected in a circuit ($\epsilon=0\%$), the electrical resistance (R_0) was 2.1 k Ω and when $\epsilon=10\%$ the electrical resistance decreased greatly and which was 623 Ω . With the increase of the compressive strain the electrical resistance decreased slowly and when $\epsilon=80\%$ the electrical resistance was about only 15 Ω . The density of contact spots between the graphene skeletons increases rapidly with the

process of compression, resulting into the decrease of electrical resistance. This phenomenon makes it possible to be used as pressure-responsive sensors⁴⁵⁻⁴⁷ and elastic conductors⁴⁸. The change in the electrical resistance is reproducible, which can be demonstrated by measuring the electrical resistance of the original sponge and the sponge was loaded to $\epsilon=50\%$ for 10 times (Figure. 7d) where the electrical resistance is only determined by the compressive strain. The constant relationship between compression strain and electrical resistance resulted from the high mechanical strength and stability of the structure. In other words, we can determine the repeated deformation of CGS and the sponge may be applied in pressure sensing graphene systems.

Conclusions

In summary, we successfully prepared compressible graphene-only sponges via reduction and self-assembly of GO by ammonium sulfide at comparatively mild conditions. All results indicate that the GO was reduced by ammonium sulfide successfully and yielded the compressible graphene-only sponge by reinforcement of ammonia solution. It has also been demonstrated that the reduction and self-assembly of GO could be completed at room temperature. We found that with the changing of the mass ratio of GO to ammonium sulfide, not only the mechanical strength of the resultant GHs but also the appearance and the internal structure of CGSs changed greatly. Meanwhile, structure, porosity, conductivity as well as mechanical strength of CGSs can be regulated easily by changing the concentration of GO solution. All CGSs could be compressed as much as 80% of the strain and showed excellent durability. The conductivity can be as high as 0.40 S m⁻¹ and the electrical resistance of the sponge is variable under compression and is proportional to the strain, which make them candidates for potential applications in pressure sensing and elastic conductors. Besides, the piezoresistivity shows great stability in the cycles of compression rebound test. We believe that the strategy developed here can be applied for a variety of applications due to its simplicity, scalability and functionality.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (Grant No. 21201175), Guangdong and Shenzhen Innovative Research Team Program (No.2011D052, KYPT20121228160843692), and R&D Funds for basic Research Program of Shenzhen (Grant No. JCYJ20120615140007998).

Notes and references

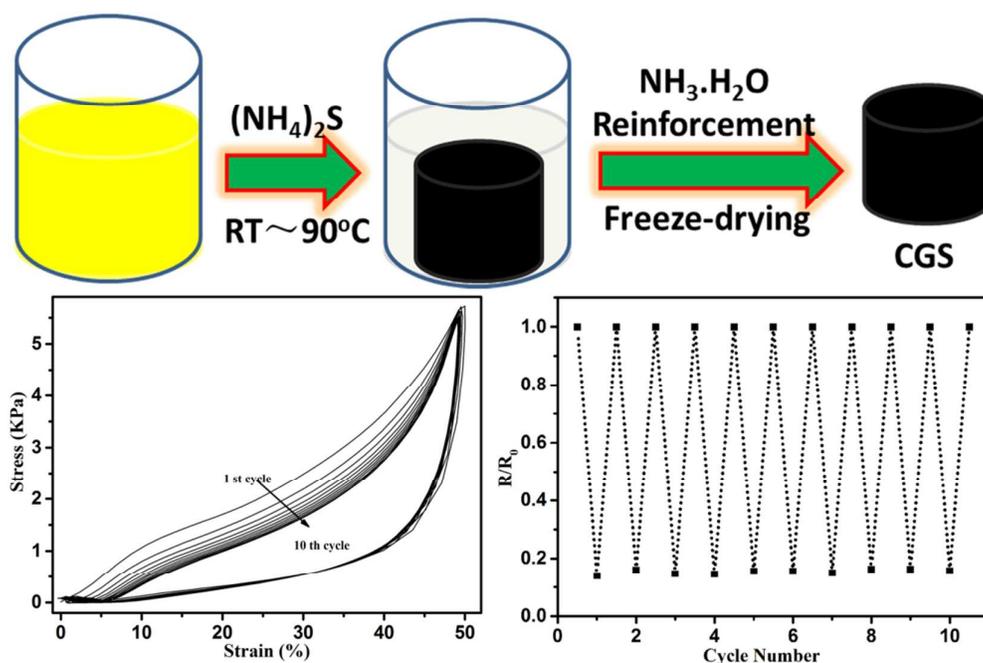
1. L. Kou, T. Huang, B. Zheng, *Nat. Commun.*, 2014, **5**, 3754.
2. K. Gopalsamy, Z. Xu, B. Zheng, *Nanoscale*, 2014, **6**, 8595.
3. L. Kou, Z. Liu, T. Huang, *Nanoscale*, 2015, **7**, 4080.
4. L. Peng, Y. Zheng, J. Li, *ACS Catal.*, 2015, **5**, 3387.
5. H. Bi, X. Xie, K. Yin, *Adv. Funct. Mater.*, 2012, **22**, 4421.
6. H. Sun, Z. Xu and C. Gao, *Adv. Mater.*, 2013, **25**, 2554.
7. M. W. Jung, S. Myung, W. Song, *ACS Appl. Mater. Interfaces*, 2014, **6**, 13319.
8. S. Nardecchia, D. Carriazo, M. L. Ferrer, *Chem. Soc. Rev.*, 2013, **42**, 794.
9. C. Li and G. Shi, *Nanoscale*, 2012, **4**, 5549.

- 10.A. Cao, P. L. Dickrell, W. G. Sawyer, *Science*, 2005, **310**, 1307.
- 11.J. Suhr, P. Victor, L. Ci, *Nat. Nanotechnol.*, 2007, **2**, 417.
- 12.D. P. Hashim, N. T. Narayanan, J. M. Romo-Herrera, *Sci. Rep.*, 2012, **2**, 363.
- 13.H. Huang, H. Bi, M. Zhou, *J. Mater. Chem. A*, 2014, **2**, 18215.
- 14.K. H. Kim, Y. Oh and M. Islam, *Nat. Nanotechnol.*, 2012, **7**, 562.
- 15.L. Qiu, J. Z. Liu, S. L. Chang, *Nat. Commun.*, 2012, **3**, 1241.
- 16.Y. Wu, N. Yi, L. Huang, *Nat. Commun.*, 2015, **6**, 6141.
- 17.H. B. Yao, J. Ge, C. F. Wang, *Adv. Mater.*, 2013, **25**, 6692.
- 18.C. Wu, X. Huang, X. Wu, *Adv. Mater.*, 2013, **25**, 5658.
- 19.C. Hou, H. Wang, Q. Zhang, *Adv. Mater.*, 2014, **26**, 5018.
- 20.J. Li, J. Li, H. Meng, *J. Mater. Chem. A*, 2014, **2**, 2934.
- 21.H. Hu, Z. Zhao, W. Wan, *Adv. Mater.*, 2013, **25**, 2219.
- 22.G. Tang, Z.-G. Jiang, X. Li, *Carbon*, 2014, **77**, 592.
- 23.J. Y. Hong, B. M. Bak, J. J. Wie, *Adv. Funct. Mater.*, 2014, **25**, 1053.
- 24.H. Ha, K. Shanmuganathan and C. J. Ellison, *Acs Appl. Mater. Interfaces*, 2015, **7**, 6220.
- 25.M. Chen, L. Zhang, S. Duan, *Adv. Funct. Mater.*, 2014, **24**, 7548.
- 26.C. Wu, L. Fang, X. Huang, *Acs Appl. Mater. Interfaces*, 2014, **6**, 21026.
- 27.Y. Li, J. Chen, L. Huang, *Adv. Mater.*, 2014, **26**, 4789.
- 28.W. Lv, Y. Tao, W. Ni, *J. Mater. Chem.*, 2011, **21**, 12352.
- 29.Y. Liu, C.-L. Liang, R.-Y. Bao, *RSC Adv.*, 2015, **5**, 10.
- 30.Y. Liu, G.-Q. Qi, C.-L. Liang, *J. Mater. Chem. C*, 2014, **2**, 3846.
- 31.W. Chen and L. Yan, *Nanoscale*, 2011, **3**, 3132.
- 32.X. Zhang, Z. Sui, B. Xu, *J. Mater. Chem.*, 2011, **21**, 6494.
- 33.Z. Han, Z. Tang, P. Li, *Nanoscale*, 2013, **5**, 5462.
- 34.M. Chen, C. Zhang, X. Li, *J. Mater. Chem. A*, 2013, **1**, 2869.
- 35.H. Bi, K. Yin, X. Xie, *Adv. Mater.*, 2012, **24**, 5124.
- 36.G. Wang, B. Wang, J. Park, *Carbon*, 2009, **47**, 68.
- 37.R. Li, C. Chen, J. Li, *J. Mater. Chem. A*, 2014, **2**, 3057.
- 38.Q. Wu, Y. Xu, Z. Yao, *ACS nano*, 2010, **4**, 1963.
- 39.X. Wu, J. Zhou, W. Xing, *J. Mater. Chem.*, 2012, **22**, 23186.
- 40.S. Yang, L. Zhang, Q. Yang, *J. Mater. Chem. A*, 2015, **3**, 7950.
- 41.S. Pei, J. Zhao, J. Du, *Carbon*, 2010, **48**, 4466.
- 42.J. Zou, J. Liu, A. S. Karakoti, *Acs Nano*, 2010, **4**, 7293.
- 43.Y. Si, J. Yu, X. Tang, *Nat. Commun.*, 2014, **5**, 5802.
- 44.S. Zhao, Y. Gao, G. Zhang, *Carbon*, 2015, **86**, 225.
- 45.S. Zhao, G. Zhang, Y. Gao, *Acs Appl. Mater. Interfaces*, 2014, **6**, 22823.
- 46.S. Zhao, Y. Gao, J. Li, *Acs Appl. Mater. Interfaces*, 2015, **7**, 6716.
- 47.Y. A. Samad, Y. Li, A. Schiffer, *Small*, 2015, DOI: 10.1002/sml.201403532.
- 48.K. H. Kim, M. Vural and M. F. Islam, *Adv. Mater.*, 2011, **23**, 2865.

Graphical abstract

A Facile Method to Prepare Highly Compressible Three-Dimensional Graphene-only Sponge

Jinhui Li^{a,b}, Songfang Zhao^{a,b}, Guoping Zhang^{a,*}, Yongju Gao^{a,c}, Libo Deng^a, Rong Sun^{a,*}, Ching-Ping Wong^{d,e}



Highly compressible three-dimensional graphene-only sponge (CGS) was prepared through a facile method. CGAs show ultralow density, high porosity, great compressibility, excellent stability which make them great candidates for pressure-responsive sensors, elastic conductors and other applications.