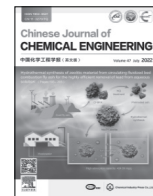




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## Full Length Article

## Fabrication of super-elastic graphene aerogels by ambient pressure drying and application to adsorption of oils

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## ABSTRACT

Three-dimensional graphene-based aerogels have promising applications in oil adsorption and environmental restoration. However, current research of graphene-based aerogels is often hindered by high preparation cost, poor mechanical properties and low recycling efficiency. Here, super-elastic graphene aerogel (SGA) was prepared through one-step freezing and twice hydrothermal reduction followed by drying under ambient pressure. The simple atmospheric drying provides a possibility for large-scale preparation of high performance graphene-based aerogels. The prepared SGA not only has the ability of highly repeatable compression rebound, but also exhibits excellent oil adsorption performance. And the overall performance of SGA is better than most of graphene-based aerogels prepared by freeze drying. After the SGA was cyclically compressed with 70% strain for 300 times, it can return to the original shape and height substantially. SGA retained about 90% of the initial adsorption capacity after 50 cycles of adsorption and compression regeneration for cyclohexane.

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## 1. Introduction

Oceanic petroleum and its derivatives spill can bring various pollution problem and threaten the survival of marine creature. In order to treat the water pollution caused by the leakage of petroleum and its derivatives, diverse countermeasures have been developed, such as physisorption, *in-situ* combustion and bioremediation [1–5]. Among these treatment methods, physical adsorption has attracted much attention of researchers for its simple, fast and efficient features.

Graphene aerogel is a new three-dimensional porous carbon material constructed by two-dimensional graphene sheets as skeleton material. Due to its high porosity [6], high specific surface area [7], ultra-low density [8] and other advantages, it shows great advantages in oil adsorption and environmental restoration [9–14]. However, the application of graphene aerogels in oil adsorption has many problems, such as high preparation cost, poor mechanical properties and low recycling efficiency. In order to prepare high-

performance graphene aerogels, many synthetic techniques have been reported, such as *in situ* self-assembly [15,16], chemical cross-linking [17], chemical vapor deposition (CVD) [18], electrochemical synthesis [19], and template-mediated assembly [20]. Except the CVD method, most of these approaches require specific drying techniques, such as supercritical drying [21–24] or freeze drying [25–27] to remove the solvent in the hydrogels, so as to obtain graphene aerogels without structure collapse and volume shrinkage. The supercritical drying needs to be carried out under high temperature or pressure, so it is difficult to attain commercial production due to its high cost and energy consumption. Vacuum freeze-drying needs long preparation cycle and high energy consumption, which is not conducive to mass production and has strict requirement on equipment. These specific drying methods have become one of the key factors limiting the commercial application of graphene aerogels.

The atmospheric pressure drying technique is performed under ambient pressure conditions. Compared with supercritical drying and freeze-drying, it has the advantages of low energy consumption, simple operation and short production cycle. It is more conducive to the manufacture of graphene aerogel. Nevertheless, there are very few reports on the preparation of graphene aerogel

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by atmospheric drying (especially as adsorbent for repeated oil adsorption). This is mainly because the frameworks of the graphene aerogel are normally not robust enough to resist the capillary pressure generated by solvent evaporation under ambient temperature and pressure conditions [28,29], which always causes severe volume shrinkage and structure collapse of the graphene aerogel. Therefore, how to realize the atmospheric drying of high-performance graphene aerogel materials is of great significance for industrial preparation of high-performance graphene aerogel and its commercial application.

In this work, ultralight, highly compressible super-elastic graphene aerogel (SGA) was prepared by one-step freezing and twice hydrothermal reduction methods under ambient pressure. The effects of reducing agent dosage, pre-reduction time and pH value on aerogel formation were discussed in detail. The prepared SGA has the ability of resisting solvent evaporation and has no obvious volume shrinkage during drying under ambient pressure. It not only has super light properties, but also shows the ability of highly repeatable compression rebound. The observation of morphology and surface properties of the prepared SGA were carried out, and adsorption properties of SGA on organic compounds and oily products were analyzed.

## 2. Experimental

### 2.1. Preparation of graphene aerogel

Schematic diagram of the preparation process of graphene aerogel (GA) is shown in Fig. 1. Graphite oxide (GO) powder was prepared using the modified Hummers' method [30,31]. GO was added into deionized water, through ultrasonic treatment, to prepare GO dispersion ( $5 \text{ mg}\cdot\text{mL}^{-1}$ ). Then, L-ascorbic acid was used as reducing agent and added based on the amount of GO (such as the mass ratio between GO/L-ascorbic acid was 1:1, 1:2, 1:3 and 1:4). The above mixture was charged into a hydrothermal reactor, a hydrothermal reduction (pre-reduction) was controlled at  $90^\circ\text{C}$  for a certain period of time (such as 20, 25, 30, 35 and 40 min). In the process of pre-reduction, the graphene hydrogel was formed by self-assembly and reduction of graphene oxide. The prepared hydrogel was then frozen under  $-30^\circ\text{C}$  for 1 h, thawed, it was hydrothermal again at  $90^\circ\text{C}$  for another 200 min. The graphene hydrogel was washed with ethanol until the ethanol has no yellow color, after that, the washed graphene hydrogel was dried in intelligent electro-thermostatic blast drier under  $50^\circ\text{C}$  or natural drying at room temperature to obtain graphene aerogel. In the freezing process, the formation of 3D porous structure of aerogel is facilitated by the formation of ice crystals, and the growth of ice crystals increases the folding of the pore wall, which is beneficial to improve the mechanical properties of aerogel [32,33], so freezing can also enhance the skeletal strength of the aerogel to resist the capillary pressure in the course of drying.

### 2.2. Characterization

The functional group structures of GO and SGA were analyzed by a Fourier transform infrared spectroscopy (FTIR, Thermo Scientific IS10 type). The crystal structures of GO and SGA were analyzed using an X-ray diffractometer (XRD, Dutch X'pert DXR Microscope type). The microstructures of SGA were observed using a scanning electron microscope (SEM, Hitachi S-4800 type). The stress-strain curve of the SGA was tested by a WDW100d type microcomputer controlled electronic universal testing machine equipped with 0.3N pressure sensor.

### 2.3. Performance of saturated adsorption capacity for SGA on pure organics

To determine the saturated adsorption capacity for aerogels on pure organics, a block of SGA weighing  $m_1$  (g) was putted into a syringe, with the syringe nipple being sealed. Then the total mass  $m_2$  (g) of the SGA and syringe was weighed. Plenty of organic matter was added into the syringe, standing for a period of time, and the SGA reached adsorption saturation. Then, the bottom end of the syringe was opened to release the excess organic compound, and the total mass  $m_3$  (g) of syringe and SGA after the adsorption process was weighed. The saturated adsorption capacity ( $q$ ,  $\text{g}\cdot\text{g}^{-1}$ ) of SGA was calculated by Eq. (1).

$$q = \frac{m_3 - m_2}{m_1} \quad (1)$$

## 3. Results and Discussion

### 3.1. The influence of different factors on aerogel molding

#### 3.1.1. Effect of reducing agent dosage

In order to investigate the influence of reducing agent dosage on aerogel molding effect, the mass ratio between GO/L-ascorbic acid was controlled at 1:1, 1:2, 1:3 and 1:4, respectively (Fig. S1, in Supplementary Material). It can be seen that with the increase of reducing agent (L-ascorbic acid), the contraction degree of aerogels being more and more significant. The reason is that with the increase of the amount of reducing agent, the degree of deoxidation increased, the  $\pi$ - $\pi$  interaction force between the graphene sheets increased, and thus the volume of the formed three-dimensional graphene aerogel decreased.

#### 3.1.2. Effect of pre-reduction time

The pre-reduction time was adjusted to 20, 25, 30, 35 and 40 min respectively to explore the effect of pre-reduction time (Fig. S2). The results show that the pre-reduction time can directly affect the volume of the GA. When the pre-reduction time was 20 min, the GA was brittle and the aerogel molding was imperfect. Perfect three-dimensional graphene aerogel was gradually formed with the increase of the pre-reduction time. However, when it increased to 40 min, the formed three-dimensional graphene aerogel shrank significantly. This is because when the pre-reduction time is short, the reduction amount of GO is low, and there are a large number of oxygen-containing functional groups on the graphene sheets. And the  $\pi$ - $\pi$  force between the sheets is weak, which is insufficient to form a complete three-dimensional skeleton structure. With the prolongation of pre-reduction time, the degree of deoxidation gradually increased, the  $\pi$ - $\pi$  force between the graphene sheets gradually increases to form a structurally complete three-dimensional aerogel. When the pre-reduction time exceeds a certain range, the  $\pi$ - $\pi$  force is so large, that it results in severe stacking between the graphene sheets, and thus the aerogel volume shrinks seriously. As shown in Fig. 2(a)–(c), when the pre-reduction time is short (30 min), the aerogel can rebounded to its original shape after being compressed under pressure of more than 1300 times its own mass (compressed to about 50% of its height), which indicated that the aerogel prepared under a shorter pre-reduction time shows good compression and resilience property.

As shown in Fig. 2(d)–(f), when the pre-reduction time is long enough (40 min), the aerogel can retain its original shape under pressure of more than 1300 times its own mass, indicating that the aerogel prepared is rigid. This shows that the pre-reduction time has a critical value between 30 and 40 min, which makes the GA change from elastic to rigid. The study of García-bordejé *et al.* [34] also showed that the aerogels were compressible and

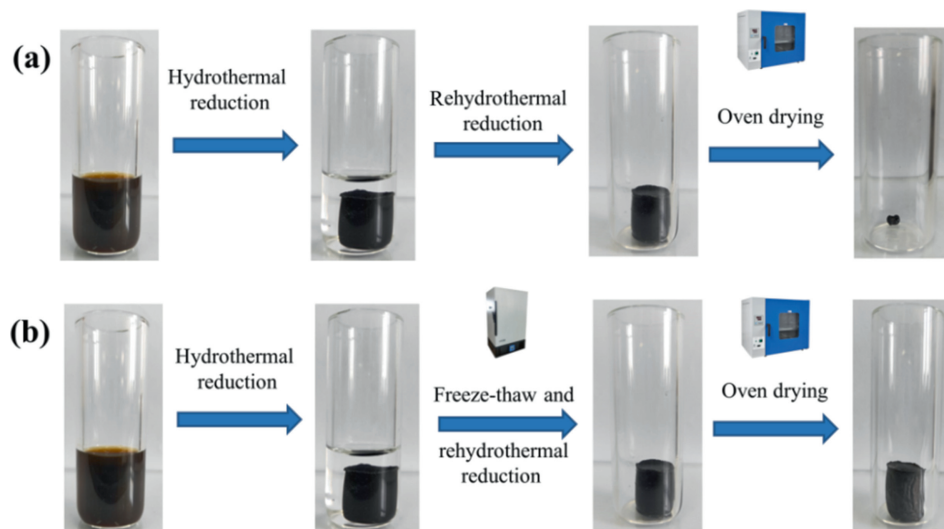


Fig. 1. Preparation process of GA: (a) without freeze-thaw treatment and (b) with freeze-thaw treatment.

elastic when the reduction time was relatively short, that is, the aerogel was deformed under pressure, and the initial shape was restored after releasing the pressure, whereas aerogels became rigid for longer reduction time. The reason is that the graphene sheets are stacked to a greater extent when the pre-reduction time is longer. The arrangement of graphene sheet layers is relatively dense. The aerogel has a lower porosity and loses its elasticity. Therefore, by controlling the time of pre-reduction, graphene aerogels with excellent elasticity or mechanical strength can be obtained.

In order to investigate the effect of pre-reduction time on the hydrophobicity of aerogels, the contact angles of water drops on the aerogels with different pre-reduction time were tested. As shown in Fig. 3(a) and (b), the hydrophobic angle is about  $96.0^\circ$  for the aerogel prepared under pre-reduction time of 25 min, and that is about  $36.1^\circ$  when the pre-reduction time was prolonged to 35 min. The aerogel prepared under a pre-reduction time of 25 min has a rough surface, while the aerogel prepared under a pre-reduction time of 35 min has a smooth surface. Theoretically, the longer the reduction time, the greater the degree of deoxidation of the aerogel, the larger the hydrophobic angle of the mate-

rial, but the experimental results are just the opposite. This indicates that the hydrophobicity of the material is not only related to the deoxidation degree, but also to the surface roughness of the material, and the latter shows greater impact in this work. It is expected that materials with different hydrophobicity can be obtained by controlling the pre-reduction time.

### 3.1.3. Effect of pH value

Graphene aerogels prepared from GO dispersions with different pH values showed significant differences both in macroscopic (apparent density and total pore volume) and microscopic scale (surface chemistry and GA nanosheets morphology) [28]. Fig. S3(a) and (b) shows graphene oxide dispersions and graphene aerogels states under different pH values (pH values being controlled at 3, 7 and 10 from left to right, respectively). pH values were adjusted by NaOH addition. It is found that the color of graphene oxide dispersion gradually deepened with the increase of pH value. As shown in Table 1, the volume and porosity of the graphene aerogel prepared under acidic condition (GA-3) are significantly larger than under alkaline condition (GA-10), and the apparent density is significantly lower. The porosity calculation of graphene aerogels is

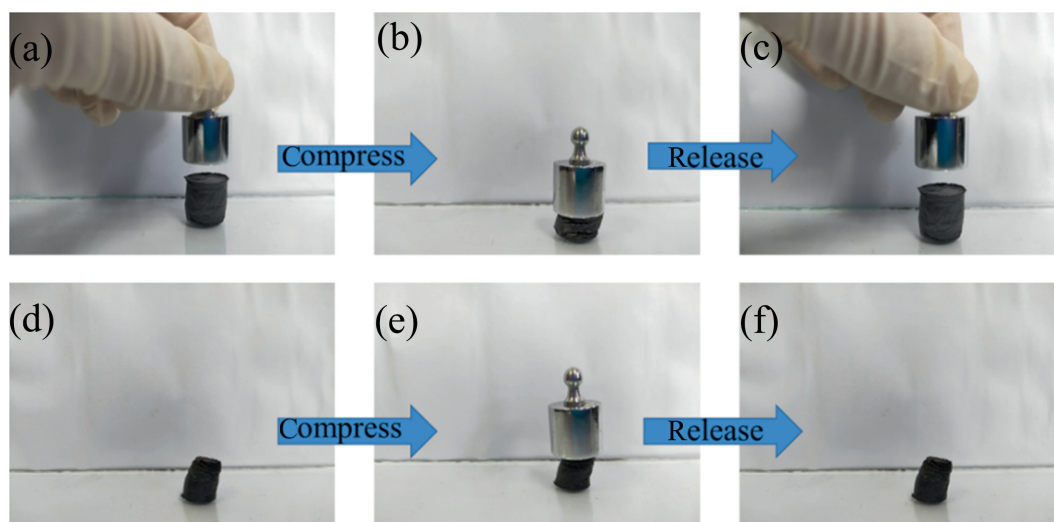


Fig. 2. (a)–(c) and (d)–(f) are compression test pictures of aerogel with pre-reduction time of 30 min and 40 min, respectively.

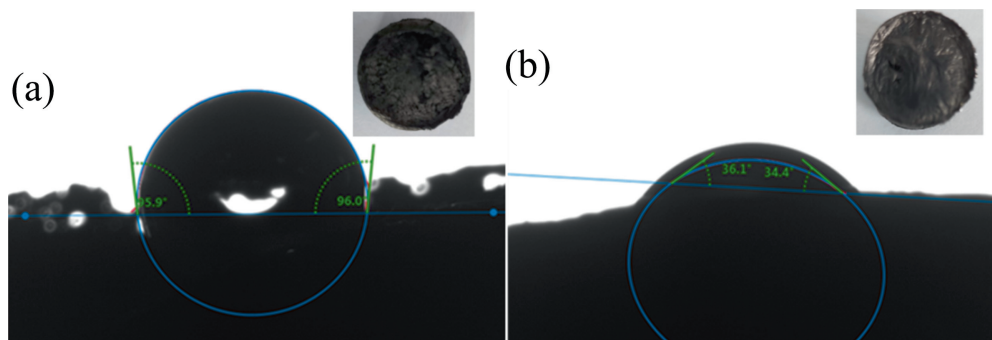


Fig. 3. (a) and (b) are the contact angle pictures of the aerogel pre-reduction time of 25 min and 35 min, respectively.

Table 1

Basic performance parameters of aerogels prepared at different pH values

| Aerogel | pH | $V_c/\text{cm}^3\cdot\text{g}^{-1}$ | Density/ $\text{mg}\cdot\text{cm}^{-3}$ | $V_p/\text{cm}^3\cdot\text{g}^{-1}$ | $\eta/\%(\text{vol})$ |
|---------|----|-------------------------------------|-----------------------------------------|-------------------------------------|-----------------------|
| GA-3    | 3  | 103.68                              | 9.65                                    | 102.74                              | 99.09                 |
| GA-7    | 7  | 89.93                               | 11.12                                   | 88.94                               | 98.90                 |
| GA-10   | 10 | 69.09                               | 14.48                                   | 68.12                               | 98.60                 |

Note:  $V_c$  is the apparent volume per unit mass of GA,  $\text{cm}^3\cdot\text{g}^{-1}$ ;  $V_p$  is the pore volume per unit mass of GA,  $\text{cm}^3\cdot\text{g}^{-1}$ ;  $\eta$  is the porosity of GA,  $\eta = V_p/V_c$ , (v)%. The  $V_c$  and  $V_p$  are calculated through Eqs. (S1) and (S2), respectively.

based on the method in our previous reports [10]. This indicates that the pH value affects the microstructure of graphene nanosheets. The graphene nanosheets undergo strong deoxidation under alkaline conditions, and the stacking between the layers is more severe than under acidic condition. Under acidic condition,

the graphene nanosheets with abundant oxygen-containing groups are accumulated by hydrogen bonds, and finally form aerogels with lower density and higher porosity than under alkaline condition. It is expected that with the addition of NaOH, some negative oxygen-containing groups on GO surface will be removed, causing

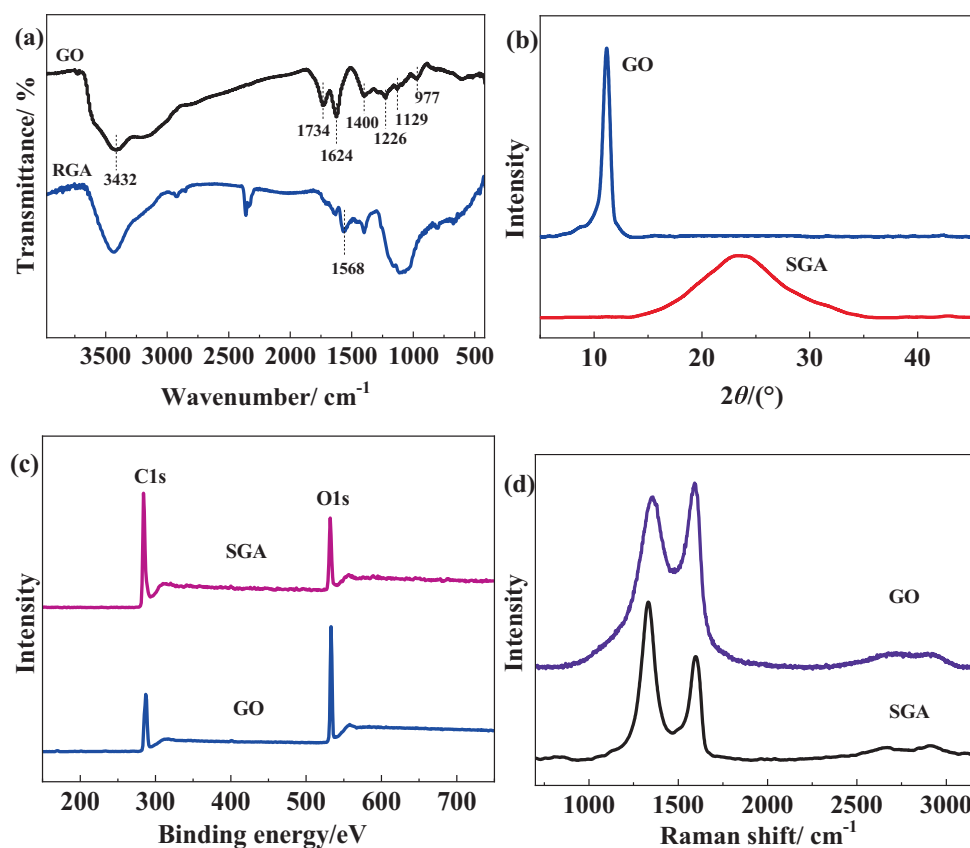


Fig. 4. The FTIR (a), XRD (b), XPS (c) and Raman (d) spectra of GO and SGA.

alkali deoxygenation reduction [35]. Therefore, the degree of lamellar stacking in aerogel can be controlled by controlling the pH.

Through the investigation on the amount of reducing agent, pre-reduction time and pH value, the optimal experimental conditions were determined as follows, *i.e.*: the mass ratio of GO/L-ascorbic acid (reducing agent) being 1:3, pre-reduction time being 30 min, and pH value being 3. The aerogel fabricated under the best experimental conditions was called as SGA. And the related performance of SGA was evaluated in the following sections.

### 3.2. Characterization analysis

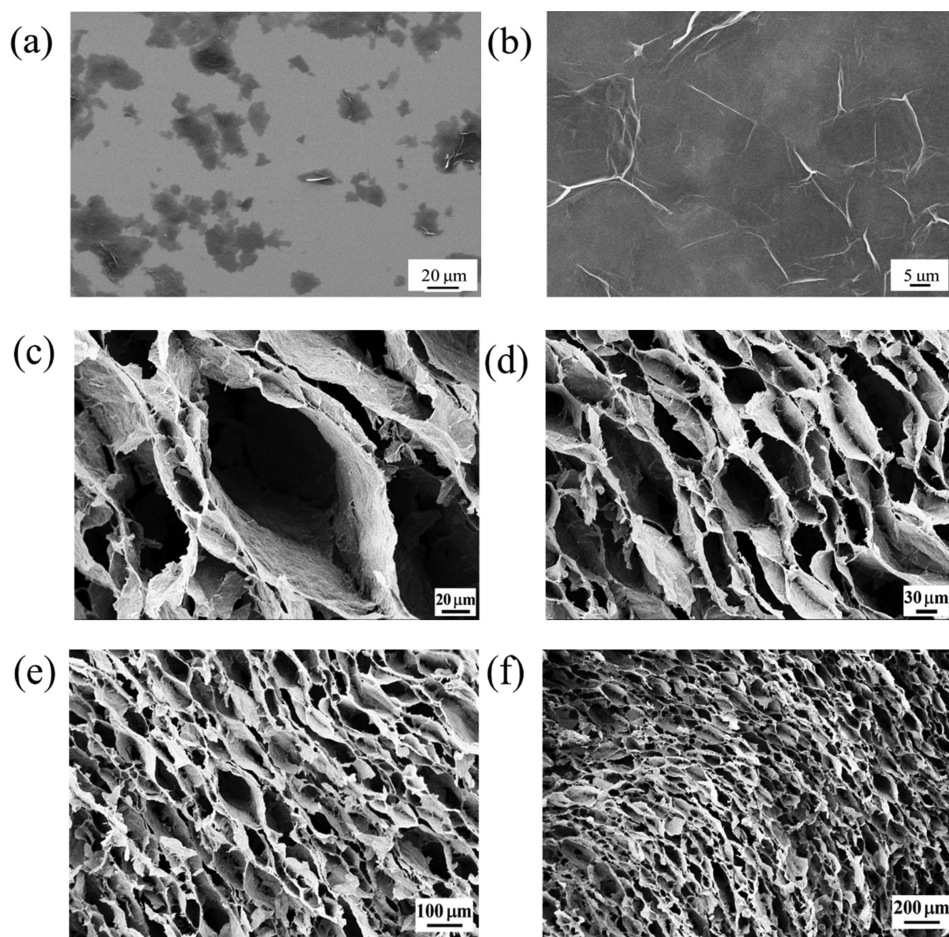
The FTIR spectrum of Fig. 4(a) shows that the oxygen-containing functional groups in SGA are significantly weakened or even disappeared after twice hydrothermal reduction. As represented in the XRD spectrum of Fig. 4(b), the GO characteristic peak at  $2\theta = 11.17^\circ$  disappears in the spectrum, while a broad diffraction peak appears at  $2\theta = 24.26^\circ$ , and the interlayer spacing is reduced from the original 0.791 nm to 0.367 nm. Furthermore, the XPS spectrum of Fig. 4(c) shows that the atomic ratio of C/O changes from 1.87 of GO to 5.23 of SGA. This further proves that GO is effectively reduced. Fig. 4(d) shows the Raman spectrum of GO and SGA. The D peak at about  $1350\text{ cm}^{-1}$  is used to analyze the structural disorder or defect degree of carbon materials. The G peak of about  $1590\text{ cm}^{-1}$  is used to analyze the integrity of  $\text{sp}^2$  hybrid bond

structure in carbon materials.  $I_D/I_G$  of GO and SGA is 0.86 and 1.51, respectively, indicating that more defects are generated in SGA sheets after hydrothermal reduction. The increase of defect sites can improve the adsorption performance of SGA [31].

Fig. 5(a) and (b) shows that the GO prepared in this work is a multi-layer disordered lamellar structure with wrinkles on the lamellar surface. The sizes of the lamellar are in several microns to tens of microns. After hydrothermal reduction and ice crystal induction, GO flakes were self-assembled into SGA. Fig. 5 indicates that the SGA has a three-dimensional network structure, and the graphene sheets is interconnected, rich in pore structures, with the pore size ranges from a few microns to a few hundred microns. In addition, the SEM images of SGA demonstrates that the reduced graphene sheets have many small protrusions, folds, and micron-sized porous structures, which contribute to the formation of ultra-light properties of the aerogel.

### 3.3. Resilience property test

As shown in Fig. 6(a), the SGA can easily stand on green bristle-grass without deformation of it, indicating that the SGA has ultra-light properties. Fig. 6(b)–(d) shows a simple resilience property test for the SGA (video 1). It can be seen that SGA has good resilience property. For the  $\sim 93\%$  compression ( $\varepsilon = 93\%$ ), SGA recovers to its original height and no surface damage was observed after the force was removed.



**Fig. 5.** Scanning electron microscopy (SEM) photographs: (a) GO, 20  $\mu\text{m}$  (Mag = 500 $\times$ ); (b) GO, 5  $\mu\text{m}$  (Mag = 1500 $\times$ ); (c) SGA, 20  $\mu\text{m}$  (Mag = 400 $\times$ ); (d) SGA, 30  $\mu\text{m}$  (Mag = 200 $\times$ ); (e) SGA, 100  $\mu\text{m}$  (Mag = 100 $\times$ ); (f) SGA, 200  $\mu\text{m}$  (Mag = 50 $\times$ ).

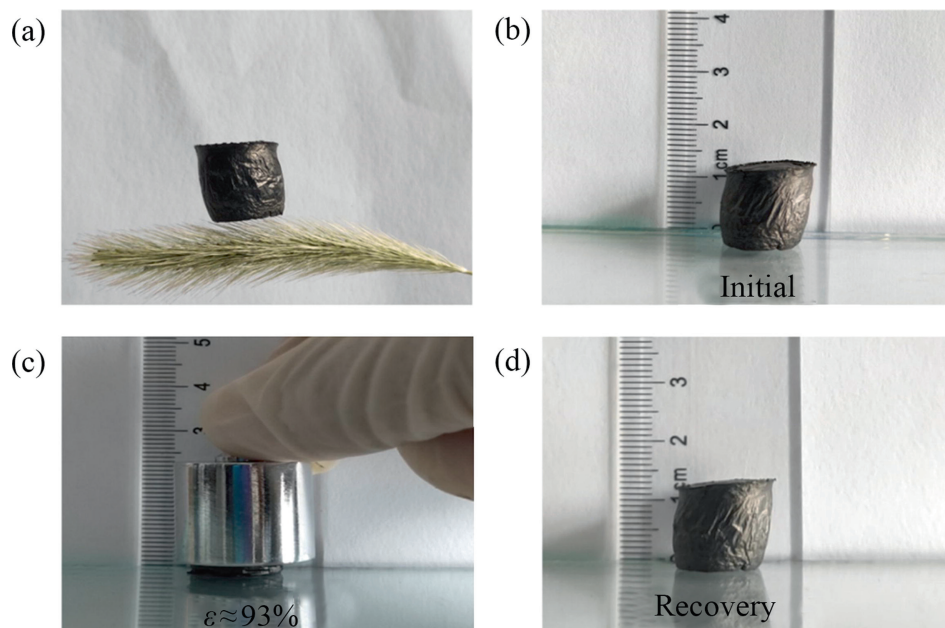


Fig. 6. (a) Picture of SGA standing on green bristlegrass; (b)–(d) SGA simple compression rebound test.

The repeated compression and resilience of graphene aerogel is an important basis for evaluating its mechanical properties. Fig. 7 shows the stress–strain curve of the SGA, where the universal testing machine was loaded at  $300 \text{ mm} \cdot \text{min}^{-1}$  and unloaded at  $55 \text{ mm} \cdot \text{min}^{-1}$ . As shown in Fig. 7, for a 70% strain, there are hysteresis loops in the stress–strain curves, which indicates that the mechanical response of the SGA during compression is a typical viscoelastic behavior. This behavior is associated with stress relax-

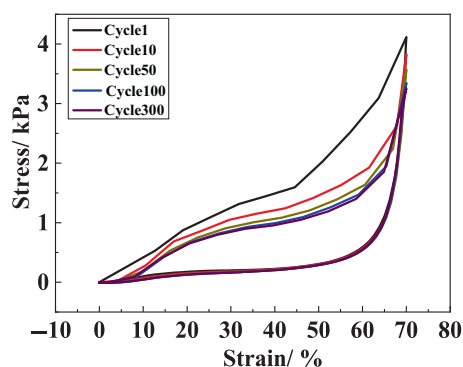


Fig. 7. Stress–strain curve with 70% SGA strain.

Table 2

The comparison of compression times of different graphene-based aerogels prepared by freeze-drying without obvious damage

| Materials                                               | Strain/% | Compression times | Ref.      |
|---------------------------------------------------------|----------|-------------------|-----------|
| Cellulose/graphene aerogel                              | 50       | 100               | [9]       |
| Magnetic carbon nanospheres/graphene composite aerogels | 50       | 10                | [12]      |
| Graphene sponge                                         | 25       | 8                 | [38]      |
| Graphene aerogels                                       | 50       | 10                | [39]      |
| Anisotropic graphene aerogels                           | 50       | 10                | [40]      |
| Graphene/nanofiber aerogels                             | 50       | 500               | [41]      |
| SGA                                                     | 70       | 300               | This work |

ation, which occurs in almost all compressible carbon materials [36,37]. After the SGA was cyclically compressed at 70% strain for 300 times, the structure did not undergo collapse (Fig. S4), which is better than most graphene-based aerogels reported [9,12,38–41] (The comparison of maximum compression times of different graphene-based aerogels prepared by freeze-drying without obvious damage were shown in Table 2). When the external force is removed, the three-dimensional network structure can rebound

Table 3

Adsorption data of SGA on organics with different densities

| Organic species      | Density/ $\text{g} \cdot \text{cm}^{-3}$ | Adsorption capacity/ $\text{g} \cdot \text{g}^{-1}$ |
|----------------------|------------------------------------------|-----------------------------------------------------|
| <i>n</i> -Hexane     | 0.658                                    | 62.54                                               |
| <i>n</i> -Octane     | 0.702                                    | 71.60                                               |
| Cyclohexane          | 0.778                                    | 76.01                                               |
| Toluene              | 0.865                                    | 82.78                                               |
| Dimethyl sulfoxide   | 1.100                                    | 100.32                                              |
| Carbon tetrachloride | 1.592                                    | 142.32                                              |

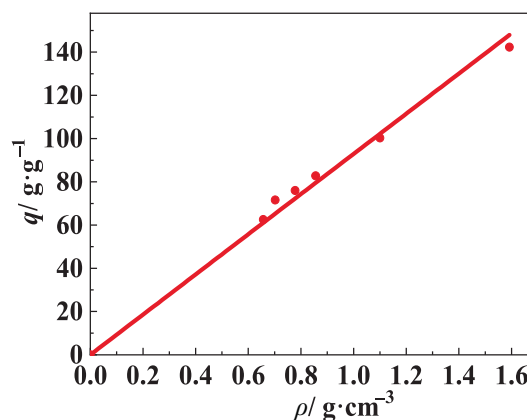


Fig. 8. Relationship between the saturated adsorption capacity of SGA for organic compounds and the density of organic compounds.

quickly, returning to the original shape and height substantially, with no significant damage exist on the surface and in the structure, indicating that the SGA has excellent resilience performance. It is expected that this performance can be used in the efficient recovery of the adsorbed organic compounds and repeated use of the SGA can be realized.

### 3.4. Saturated adsorption capacity of SGA on pure organic compounds

Graphene aerogels not only retain the structural advantages of most carbon nanomaterials, but also have porosities higher than 99%, and their rich porous network structures make them exhibit excellent adsorption properties for organic compounds and oils [40–42].

The apparent density of SGA prepared in this work is  $9.65 \text{ mg}\cdot\text{cm}^{-3}$ , the pore volume is  $102.74 \text{ cm}^3\cdot\text{g}^{-1}$ , and the porosity is 99.09%. The aerogel was used to adsorb pure organic compounds having different densities, such as *n*-hexane, cyclohexane, *n*-octane, toluene, dimethyl sulfoxide and carbon tetrachloride. As can be seen from Table 3, the adsorption capacity of SGA for the above compounds is in the range of  $62.54\text{--}142.32 \text{ g}\cdot\text{g}^{-1}$ . The relationship between the saturated adsorption capacities and densities of organic compounds is shown in Fig. 8. As you can see that the adsorption capacity and organic compounds density shows a linear relationship as Eq. (2).

$$q = k\rho \quad (2)$$

where  $q$  is the saturated adsorption capacity of the aerogel,  $\text{g}\cdot\text{g}^{-1}$  and  $\rho$  is the density of the adsorbed organic compound,  $\text{g}\cdot\text{cm}^{-3}$ . According to the meaning of  $q$  and  $\rho$  in Eq. (2), it can be inferred that the linear slope  $k$  means the volume ( $\text{cm}^3\cdot\text{g}^{-1}$ ) of the organic compound adsorbed by the SGA per unit mass. The fitted slope,  $k$ , of the data in Fig. 8 is  $92.94 \text{ cm}^3\cdot\text{g}^{-1}$  with the determination coefficient  $R^2 = 0.9907$ . This indicates that the adsorption of the SGA to the organic compound should be a volume filling behavior, that is, the amount of liquid adsorbed by the unit mass SGA is constant, regardless of the type of organic compounds to be adsorbed [43]. As a result, the porosity of the aerogel has a great influence on its saturated adsorption capacity. Enlarging the volume of internal pores of the graphene-based aerogel will facilitate its adsorption of organic solvents and oils.

The volume filling degree of organic solvents in graphene aerogels pores should be an important indicator of their practical applications. Therefore, the occupancy rate of organic solvent in the pores of SGA is defined through Eq. (3).

$$\eta_0 = \frac{V_{\text{org}}}{V_p} \quad (3)$$

where  $\eta_0$  is the pore occupancy rate organic solvent in the pores of of SGA;  $V_{\text{org}}$  refers to the volume of adsorbed organic compounds per unit mass of SGA,  $\text{cm}^3\cdot\text{g}^{-1}$ ;  $V_p$  is the pore volume of unit mass of SGA,  $\text{cm}^3\cdot\text{g}^{-1}$ . It can be seen from Fig. 8, the pore occupancy of SGA is 90.46% when adsorbing pure organic compound, which is less than 100%, indicating that the pores of the SGA was not filled

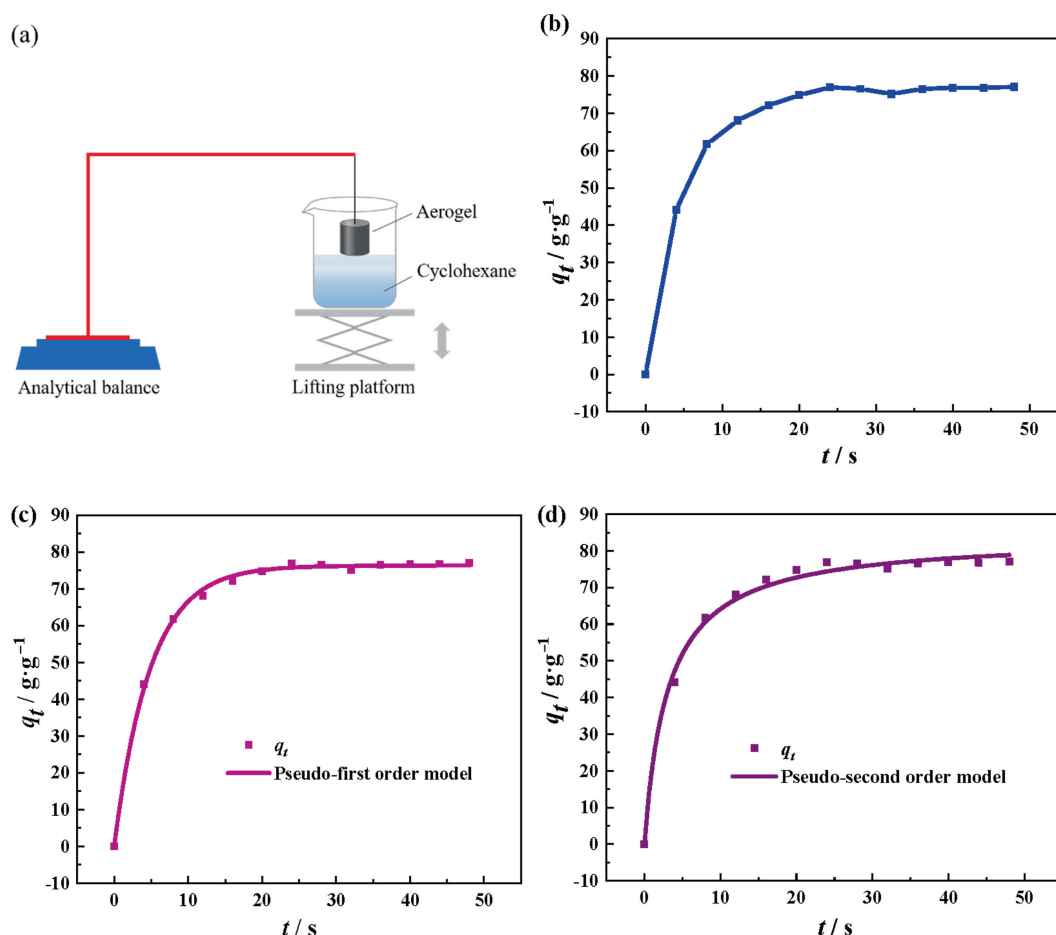
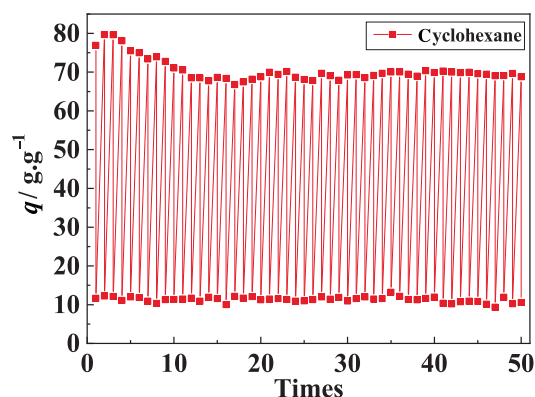


Fig. 9. (a) Schematic diagram of adsorption experimental device. (b) The amount of cyclohexane adsorbed by SGA varies with time. (c) PFO fitting diagram of cyclohexane adsorbed by SGA. (d) PSO fitting diagram of cyclohexane adsorbed by SGA.

**Table 4**

The fitting results of kinetic for cyclohexane adsorbed by SGA

| T/K | Pseudo-first-order model         |                     |        | Pseudo-second-order model        |                                                    |        |
|-----|----------------------------------|---------------------|--------|----------------------------------|----------------------------------------------------|--------|
|     | $q_e/\text{g}\cdot\text{g}^{-1}$ | $k_1/\text{s}^{-1}$ | $R^2$  | $q_e/\text{g}\cdot\text{g}^{-1}$ | $k_2/\text{g}\cdot\text{g}^{-1}\cdot\text{s}^{-1}$ | $R^2$  |
| 303 | 76.3249                          | 0.2055              | 0.9981 | 83.9463                          | $3.86 \times 10^{-3}$                              | 0.9933 |

**Fig. 10.** SGA adsorption cyclohexane recycling.

completely by organic compounds. This means that there should exist “unreachable” part inside the SGA, *i.e.* some pores may be closed, leading to no organic compounds enter, or there may exist micropores with excessive diffusion resistance, which are difficult to be filled by organic compounds during the experiment.

### 3.5. Adsorption properties of cyclohexane by SGA

#### 3.5.1. The kinetic analysis of cyclohexane adsorbed by SGA

The cyclohexane adsorption experiment of SGA was carried out by self-made device, as shown in Fig. 9(a). The SGA was suspended on a bracket connected to an analytical balance, the lifting platform was adjusted so that the cyclohexane just touches the bottom of the SGA, and the mass changes of the system were recorded. The adsorption capacity of SGA is calculated by Eq. (S3). Fig. 9(b) shows that the cyclohexane can be rapidly adsorbed by SGA, and the adsorption equilibrium can be reached in about 20 s. Pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic equations (Eqs. (S4) and (S5)) were used to fit the adsorption process, the fitting results were shown in Table 4. Although the  $R^2$  fitted by pseudo-first-order kinetics model and pseudo-second-order kinetics model is greater than 99%, the equilibrium adsorption capacity fitted by pseudo-first-order kinetics model ( $76.3249 \text{ g}\cdot\text{g}^{-1}$ ) is closer to the saturated adsorption capacity measured in the experiment ( $76.01 \text{ g}\cdot\text{g}^{-1}$ ). As a result, the adsorption kinetics of cyclohexane by SGA is fitted with the pseudo-first-order kinetic model.

#### 3.5.2. Regeneration and re-adsorption of SGA

For a high performance adsorbent, it should not only have high adsorption capacity, but also have good reusability in practical applications. Up to now, the main regeneration means of graphene aerogel adsorbing oil and organic solvents include thermal evaporation method [3], solvent cleaning method [44], and direct combustion method [38]. Compared with the above methods, the mechanical extrusion method can not only recycle oil and organic solvents, but also with low external energy consumption. Considering that the SGA has remarkable elasticity performance, mechanical squeeze and re-adsorption was performed for the saturated aerogel. The material has stable adsorption capacities for cyclohex-

**Table 5**

The comparison of cycle adsorption times of different graphene-based aerogels prepared by freeze-drying on oil

| Materials                                              | Cycle times | Ref       |
|--------------------------------------------------------|-------------|-----------|
| Cellulose/graphene aerogels                            | 10          | [9]       |
| Magnetic carbon nanospheres/graphene composite aerogel | 10          | [12]      |
| Graphene aerogels                                      | 10          | [39]      |
| Graphene/nanofiber aerogels                            | 10          | [41]      |
| Polyimide/graphene aerogel                             | 10          | [45]      |
| SGA                                                    | 50          | This work |

ane during cyclic extrusion regeneration and re-adsorption. As shown in Fig. 10, after 50 cycles of compression and re-adsorption, the adsorption capacity of the SGA remain about 90% of the initial value, which is obviously better than the recently reported graphene-based aerogels [9,12,39,41,45] (The comparison of cycle adsorption times of different graphene-based prepared by freeze-drying on oil were shown in Table 5). These results showed that the SGA prepared had excellent recycling ability, and showed great application prospects in the adsorption and treatment of oil and organic compounds.

## 4. Conclusions

In summary, a highly compressible, super-elastic SGA was successfully prepared from GO and L-ascorbic acid by one-step freezing and two hydrothermal reduction steps under ambient pressure. The effects of reducing agent dosage, pre-reduction time and pH value on aerogel formation were discussed in detail. The simple atmospheric drying method can be manufactured graphene-based aerogels for commercial application.

Graphene aerogels have excellent compression resilience and fatigue strength. After 300 cycles of SGA compression to 70% of its own, the surface and the structure of SGA were not damaged, and can be restored to the original shape and height. The 1–300 times stress–strain curves of SGA all have hysteresis loops, which indicates that the mechanical response of SGA during compression is a typical viscoelastic behavior.

The adsorption of the SGA to the organic compounds is a volume filling behavior, and the porosity is the main factor affecting its saturated adsorption capacity. The adsorption capacity of unit mass SGA showed for organic compounds is  $92.94 \text{ cm}^3\cdot\text{g}^{-1}$ , and it has superior cyclic adsorption ability for organic compounds. Cyclic adsorption capacity of SGA for oil was tested with cyclohexane as the adsorbent. SGA of cyclohexane adsorbed by cyclohexane was recycled by mechanical extrusion. After 50 times cyclic adsorption, it was found that the adsorption capacity of cyclohexane by SGA could remain about 90% of the original value, which is much greater than recently reported graphene-based aerogels. Due to the good properties of SGA prepared by simple atmospheric drying process, it will have widespread applications prospect in oil adsorption.

## Data availability

Data will be made available on request.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2021.09.031>.

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