1. Introduction

Aerogels, an extremely important aggregation state of various self-assembled nanoscale building blocks, have great potential in fields ranging from energy storage to thermal insulation. However, the porosity of aerogels makes them mechanically weak in most cases, and the chemical activity of the resulting aerogel needs consideration. Herein, chemically crosslinked graphene oxide (GO) 3D aerogels with large specific surface areas (up to 850 m² g⁻¹), outstanding mechanical performance (up to 20 MPa Young’s modulus, 1 MPa yield strength and 45 J g⁻¹ specific energy adsorption), and superhigh chemical activity (toward some reducing gases such as H₂S, HI, and SO₂), are fabricated by assembling 2D GO sheets edge-to-edge into uniform, 3D hydrogel networks with subsequent supercritical fluid drying. These aerogels are superior to other 3D frameworks (e.g. graphene aerogels) assembled via partial overlapping of the basal planes of the 2D building blocks.

Edge-to-Edge Assembled Graphene Oxide Aerogels with Outstanding Mechanical Performance and Superhigh Chemical Activity

Huan Huang, Pengwan Chen, Xuetong Zhang,* Yun Lu, and Wanchu Zhan

Aerogels, an extremely important aggregation state of various self-assembled nanoscale building blocks, are generally prepared from molecular precursors by sol-gel processing and subsequent supercritical fluid drying or freeze drying to replace the solvents in wet gels with air. Charming characteristics such as quite low density, large open pores, high specific surface area, etc., give aerogels great potential in fields ranging from energy storage to thermal insulation. However, the porosity of aerogels makes them mechanically weak in most cases, and the chemical activity of the resulting aerogel needs consideration. Herein, chemically crosslinked graphene oxide (GO) 3D aerogels with large specific surface areas (up to 850 m² g⁻¹), outstanding mechanical performance (up to 20 MPa Young’s modulus, 1 MPa yield strength and 45 J g⁻¹ specific energy adsorption), and superhigh chemical activity (toward some reducing gases such as H₂S, HI, and SO₂), are fabricated by assembling 2D GO sheets edge-to-edge into uniform, 3D hydrogel networks with subsequent supercritical fluid drying. These aerogels are superior to other 3D frameworks (e.g. graphene aerogels) assembled via partial overlapping of the basal planes of the 2D building blocks.

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thesized from the reduction of GO with L-ascorbic acid in the absence and presence of carbon nanotubes. Very recently, nitrogen and boron co-doped graphene aerogels have been fabricated by using GO and ammonia boron trifluoride as precursors via hydrothermal reaction and freeze-drying processes in sequence. However, all these reported graphene aerogel monoliths have been assembled based on partial overlapping of the graphene basal planes, and so our question is: is it possible to fabricate 3D aerogel frameworks based on 2D building blocks via edge-to-edge assembly?

Herein, we present a general but creative route to make GO aerogels by assembling 2D GO sheets edge-to-edge into uniform, 3D hydrogel networks with subsequent supercritical fluid drying. GO is an intermediate product to achieve mass production of graphene by solution chemistry, and holds carboxylic acid groups at the edges and hydroxyl as well as epoxide groups at the basal planes, which makes it an excellent 2D nanomaterial with promising applications in many fields including catalysis, sensors, drug delivery, and others. Although a few authors have mentioned the term ‘GO aerogel’ elsewhere, the method used is to directly freeze dry the GO suspension without using a sol-gel process, and thus the resulting products incur the problems of quite low surface area (much less than 100 $m^2/g$) and a great loss of active sites on both sides of the GO sheets due to serious overlapping of the basal planes during assembly, thereby seriously limiting their further application. However, the GO aerogels presented in this manuscript show large specific surface area (855 $m^2/g$), abundant pore volume ($\sim 3 \text{ cm}^3/g$), and high chemical activity toward some reducing gases (such as $H_2S$, $SO_2$) at room temperature and ambient pressure as the edge-to-edge assembled GO 3D framework can provide less overlapping of the GO basal planes. Furthermore, it has been demonstrated theoretically and experimentally that the oxidation process significantly decreases the in-plane Young’s modulus and fracture strength of GO sheets in comparison with those of graphene. However, the GO aerogels assembled edge-to-edge here exhibit a high Young’s modulus (10–20 MPa), yield strength (ca. 1.0 MPa), and energy adsorption capacity (approaching to 45 J g$^{-1}$), even higher than those of their graphene counterparts assembled via partial overlapping of the basal planes reported in our previous study.

Figure 1. Schematic synthesis of both La$^{3+}$ and polyethylenimine (PEI)-crosslinked GO aerogels (GDL in the figure stands for gluconolactone).

2. Results and Discussion

The procedure for fabricating GO aerogels, as shown in Figure 1, contains two important steps, namely, the synthesis of GO hydrogels, and subsequent supercritical fluid drying. As discussed in our previous work, GO hydrogels can be easily obtained by using metal ions or polyamines to crosslink the GO sheets in the presence of gluconolactone (GDL) as the gel promoter. The pH value of the GO solution was initially adjusted to ca. 8.0, then either La(OH)$_3$ or polyethylenimine (PEI) was added to the GO solution to form the stable mixtures, and finally GDL was added to the mixtures with sonication for 30 s to initiate gelation. In these systems, GDL can slowly hydrolyze in aqueous solution and thus decrease the pH value of the mixtures, which can subsequently control the release of La$^{3+}$ from La(OH)$_3$ or protonate the amino groups attached to PEI to crosslink the GO sheets, to form uniform hydrogel networks. Both La$^{3+}$ and protonated amino groups have a strong electrostatic interaction with carboxyl groups at the edge of GO sheets, which guarantees the connection of the edges of one GO sheet to another. This way to form GO 3D assemblies was demonstrated to be efficient to get uniform hydrogels, which is crucial to further obtain GO aerogels. In addition, we have observed that re-dispersed GO hydrogels are easily flocculated from the dispersion, indicating that small GO sheets have been assembled into large ones after such fabrication. After the formation of the GO hydrogels, they were washed with plenty of water to get rid of unhydrolyzed GDL, hydrolyzed product of the GDL, and superfluous crosslinkers (either protonated PEI or La$^{3+}$ ions), and then the solution was solvent-exchanged with acetone several times. Supercritical CO$_2$ drying of these hydrogel precursors was the final step to obtain the corresponding GO aerogels.

Raman spectroscopy and X-ray powder diffraction (XRD) were used to confirm the formation of GO aerogels and explore their particular characteristics as shown in Figure 2a,b. For GO powder, two apparent peaks located at 1348 $cm^{-1}$ and 1594 $cm^{-1}$ correspond to well-documented G and D bands, respectively. After sol-gel and supercritical drying processes, G and D bands can still be observed from both La$^{3+}$ and PEI-crosslinked GO aerogels with no or little changes in both their position and intensity ratios, as shown in Figure 2a. Although a slight increase in $I_D/I_G$ and a little blueshift of the G band occurred for the PEI-crosslinked GO aerogel due to the slight reducibility of PEI, the existence of GO in both aerogels can be sufficiently evidenced. In
addition, the X-ray photoelectron spectroscopy (XPS) investigation in our previous work strongly confirmed that the existence of N or La elements in the resulting GO aerogel precursors and the driving force for precursor assemblies is the coordination interaction between carboxyl groups attached to the GO sheets, and metal ions released from their colloidal precursors by GDL or between carboxyl groups attached to the GO sheets, and ammonium ions attached to the PEI macromolecules.\(^{[28]}\) The bands at 1728 cm\(^{-1}\) (C=O stretching vibrations from carbonyl and carboxylic groups) in GO’s FTIR spectrum (see Supporting Information Figure SI1) shifts to a lower position at 1710 cm\(^{-1}\) after the formation of the aerogels. This suggests that both La\(^{3+}\) and PEI interact with carbonyl or carboxylic groups attached to the GO sheets.\(^{[18]}\) It can be seen from Figure 2b that GO powder shows a sharp peak at around 2\(\theta = 10.7^\circ\), corresponding to the (001) reflection, indicating that the interlayer space (0.82 nm) is much larger than that of pristine graphite (0.34 nm) due to the introduction of oxygen-containing functional groups on the graphite sheets. But why can we not observe the XRD peaks of GO sheets in these aerogels, as shown in Figure 2b? This phenomenon could be explained by the good distribution and no overlapping of the GO sheets in the supercritical fluid-dried aerogels. In contrast, GO sheets in freeze-dried hydrogels were impelled to overlap one another by the gradual growth of ice crystals during freezing, which has resulted in the obvious peaks in their XRD patterns.\(^{[28]}\) Furthermore, if we do a comparison between the XRD patterns of graphene aerogel\(^{[12]}\) and its GO counterpart, two different assembly mechanisms can be revealed. In the graphene aerogel, a \(\pi-\pi\) interaction dominates the assembly and causes overlapping of the graphene sheets, which was strongly confirmed by its XRD patterns. However, as discussed above, GO sheets dispersed well in the GO aerogels and no significant overlapping happened, as the crosslinkers (La\(^{3+}\) or PEI) have grasped carboxyl groups at the edges of different GO sheets by strong electrostatic forces, which has resulted in junctions of these 2D GO sheets. The formation of junctions between crosslinkers and carboxyl groups (only appearing at the edges of the GO sheets) indicates that a novel assembly mode, namely edge-to-edge, has worked well in our case.

To further confirm the edge-to-edge assembly mode in our crosslinked GO aerogels, high-resolution transmission electron microscopy (TEM) images have been recorded, as shown in Figure 2c–f. By taking advantage of the contrast difference, we can easily recognize the edges (indicated by arrows ‘B’ or the red circles) of the GO sheets from wrinkles (indicated by arrows ‘A’) of the GO sheets in these TEM images. For PEI-crosslinked GO aerogels, some edges of the GO sheets are very smooth, and no protrusive nanostructures are observed. For La\(^{3+}\)-crosslinked GO aerogels, all edges of the GO sheets are smooth, and no protrusive nanostructures are observed.

![Figure 2](image-url). Raman spectra (a) and XRD patterns (b) of the resulting GO aerogels, and high-resolution TEM images of both PEI- (c,d) and La\(^{3+}\) (e,f) crosslinked GO aerogels, from which edge-to-edge assembled GO sheets can be easily recognized and labeled by the red circles. In addition, arrows ‘A’ highlight the wrinkle in the same GO sheet, while arrows ‘B’ indicate the edge of one GO sheet standing on the another GO sheet.
This is because the La$^{3+}$ ion adsorbed to the edges of the GO sheets are too small to be observed from TEM imaging. However, we still can observe that two ends of the different GO sheets have been connected, as shown in Figure 2f, which is attributed to the crosslinking effect of the metal ions via electrostatic interactions. This again confirms the edge-to-edge assembly mode in our crosslinked GO aerogels.

Porosity of the resulting GO aerogels is revealed by nitrogen sorption investigation and scanning electron microscopy (SEM). Figure 3a shows typical sorption and pore size distribution curves of both La$^{3+}$- and PEI-crosslinked GO aerogels. The typical Type IV isotherm characteristic with an adsorption hysteresis was observed from the sorption curves, suggesting that plenty of mesopores exist in these aerogels. The pore size distribution curves (inset in Figure 3a), determined by Barret-Joyner-Halenda method, show that pore diameter lies in the range 2–100 nm with high pore volumes (2.0 cm$^3$ g$^{-1}$ for La$^{3+}$-crosslinked aerogels and 2.9 cm$^3$ g$^{-1}$ for PEI-crosslinked aerogels). Details of the porosity of the resulting GO aerogels are shown in Table SI1. It is worth mentioning that the BET surface area was 854 m$^2$ g$^{-1}$ for La$^{3+}$-crosslinked GO aerogels and 674 m$^2$ g$^{-1}$ for PEI-crosslinked GO aerogels. As far as we know, these GO aerogels possess the highest surface area among the GO based bulk materials as shown in Figure 3b, e.g., 1.5 times higher than that of GO powder,[29] 1.4 times higher than that of GO frameworks, and 14 times higher than that of GO 3D porous assemblies.[31] among other examples.[29–37] What’s more, specific surface areas of the resulting GO aerogels are comparable with carbon/graphene composite aerogels[38] and even much higher than that of their graphene counterparts[32] and graphene/CNT composite aerogels.[13] We suppose that the great advantage in specific surface area lies in the microscopic edge-to-edge connection of GO sheets, which saves abundant surface area compared to those assembled by the partial overlapping of basal planes. Figure 3c and d show SEM images of La$^{3+}$- and PEI-crosslinked GO aerogels, respectively. All samples exhibit a well-defined and
interconnected 3D porous network. The macropores have diameters in the range of hundreds of nanometers (no less than 50 nm) and can be clearly recognized. Obviously these macropores cannot be detected by N\textsubscript{2} sorption investigations, due to instrumentation limitation. As no overlapping has occurred for these GO sheets, we can conclude that these macropore walls are composed of the well-dispersed GO sheets (almost the same as those in the GO aqueous dispersion) and these macropore walls are close to one another to form the mesopores observed by N\textsubscript{2} sorption investigation.

Quasi-static compression tests were conducted for as-prepared GO aerogels to analyze their mechanical properties. Under compression, both La\textsuperscript{3+}- and PEI-crosslinked GO aerogels experienced three stages of deformation as shown in Figure 4a,b, similar to aerogel materials reported elsewhere\cite{39} a linearly elastic region with small compressive strain (<4%) attributing to the elastic bending of GO sheets; a yield region with slight hardening up to 60% compressive strain attributing to buckling of the GO sheets as well as collapsing of the mes c. Figure 3) and macro pores of the aerogel, and a densification region with compressive strain attributing to bending and ultimate overlapping of the GO sheets. The background pictures in Figure 4a,b exhibit the appearance of aerogels before and after compression. With straight compression, the height of the aerogels reduced about 80%, but diameters were maintained and no cracks were observed in the compressed GO aerogels. In contrast, many other native or polymer-enhanced inorganic aerogels expand greatly and even crack after compression. The randomly distributed macropores in the original GO aerogels turned out to be smaller and denser, and some of the macropores seem to have disappeared after compression, as shown in Figure 3c,f. XRD patterns after compression (shown in Figure 2b) possess new prominent peaks at ca. 9° indicating that the randomly distributed GO sheets have stacked to some degree, and the larger the strain applied, the higher the degree of stacking observed (see Figure SI2). To further quantify the aerogels’ mechanical property, the Young’s modulus, yield strength, and energy adsorption are calculated from these stress–strain curves. The Young’s modulus is calculated from the initial linear region of the stress–strain curves, the value of yield strength is obtained from the end of the initial linear region, and the energy adsorption is defined as the area below the stress–strain curve from 0 to 80% strain. Young’s moduli of La\textsuperscript{3+}- and PEI-crosslinked aerogels are 10 MPa and 20 MPa, respectively, and the yield strengths are 0.9 MPa and 1.0 MPa, respectively. We noticed that PEI-crosslinked aerogels exhibit better performance than that of La\textsuperscript{3+}-crosslinked aerogels, possibly because the former is denser (60 mg mL\textsuperscript{−1}) than the latter (55 mg mL\textsuperscript{−1}), or because the introduction of polymer molecules—even just as the crosslinker—can enhance the mechanics of the GO aerogels to some extent.

As the porous solid is quite low in density, GO aerogels with mechanical properties like these are really strong. In order to demonstrate this, the data are divided by the aerogel’s density. In this way, we can see from Figure 4c that these as-prepared GO aerogels exhibit better performance than that of many native aerogel materials, including fiber-reinforced carbon...
They are even stronger than the graphene aerogel reported in our previous study[12] and the cellular graphene monolith reported very recently,[48] but weaker than thermally annealed graphene aerogels.[11] In addition, the specific energy adsorption is 42.0 J g$^{-1}$ for La$^{3+}$-crosslinked GO aerogels and 44.5 J g$^{-1}$ for PEI-crosslinked GO aerogels. These values are higher than those of many porous materials including SiC–N ceramics, Kevlar, steel, etc.[12,13,39,41,45,47,49] as shown in Figure 4d. High specific energy adsorption would provide our GO aerogels with great potential for various military and civil uses. It has been confirmed that the oxidation process can significantly decrease mechanical performance of the GO sheets in comparison to that of the graphene sheets. Why is GO aerogel still stronger than its graphene counterpart? It is well known that the elasticity of a substance results from the stretching (or compression/distortion) of the bonds formed among its atoms, and the Young’s modulus of the substance is the cumulative measurement of the moduli of these bonds.[50] The weakest connection in GO aerogels, lying in the electrostatic interaction (100–350 kJ mol$^{-1}$)-induced crosslinking at the edges of the 2D sheets, is still higher than the weakest connection in graphene aerogels, lying in the π–π interaction (0–50 kJ mol$^{-1}$)-induced partial overlapping of the basal planes. This is why GO aerogels have performed better in mechanics than their graphene counterparts observed herein.

Chemical activity of the resulting GO aerogels is demonstrated by their reaction with the reducing gas H$_2$S. A piece of GO aerogel was packed into the middle of one glass tube, then the in-situ formed H$_2$S was passed through the GO aerogel, as shown in Figure 5a. Reaction between GO and H$_2$S must occur due to the following observations: (1) a lot of water droplets, confirmed by infra-red spectroscopy (see Figure S13), appear on the wall of the glass tube close to the aerogel sample, and (2) the resistance of the aerogel sample has decreased sharply from $10^6$ Ω or higher (actually exceeding the upper limit of the meter) to $10^4$ Ω, indicating that GO was reduced to graphene during H$_2$S passage. The reaction between GO aerogels and in-situ formed H$_2$S is further validated by Raman spectroscopy (see Figure S14), XRD patterns (see Figure S15), and XPS analysis (see Figure S16). Figure 5c,d show SEM images of La$^{3+}$- and PEI-crosslinked GO aerogels exposed to H$_2$S for 28 h. Few sheet-like structures can be observed from the H$_2$S-treated aerogel samples in comparison with the native GO aerogels (Figure 3c,d). Instead, a large amount of columnar nanostructures have appeared, attributed to the S element oxidized from H$_2$S by GO. Many pores with diameters of hundreds of nanometers can be clearly distinguished in the SEM images. These observations indicate that GO aerogels reacting with H$_2$S gas provide a facile way to make graphene/S hybrids, which may have great potential in fields related to Li ion batteries. To further quantify the chemically adsorbed H$_2$S, curves of mass change for aerogel samples vs. exposure time (to H$_2$S) were recorded as shown in Figure 5b. It can be clearly seen that the mass of both La$^{3+}$- and PEI-crosslinked GO aerogels increased gradually until plateaus appeared after 28 h exposure time, suggesting that reaction equilibrium was achieved and thus adsorption capacities reached their maxima. From these curves, the H$_2$S adsorption capacities were calculated to be 63.5 mmol g$^{-1}$ for La$^{3+}$-crosslinked GO aerogel and 46.7 mmol g$^{-1}$ for PEI-crosslinked GO aerogel, which are much higher than those for activated carbon (all less than 20 mmol g$^{-1}$),[51] sewage sludge-derived fertilizer,[52] or metal-organic frameworks[53] as sorbents. The resulting GO aerogels were also applied to adsorb other reducing gases such as SO$_2$, HI, CO, and H$_2$, and the results show that similar chemical reactions took place between GO aerogels and SO$_2$ (oxidized to SO$_3$) or HI (oxidized into I$_2$). However no chemical reactions have been observed between GO aerogels and CO or H$_2$ due to their relatively low reducing capacity. All these gas adsorption investigations have been done at ambient atmosphere and room temperature, which provides a great advantage for the GO aerogels over some conventional sorbents such as activated carbon[51] as GO aerogels can remove high concentrations of poisonous gases such as SO$_2$, HI, and H$_2$S under normal conditions by turning them into non-volatile solids.

3. Conclusion

The novel edge-to-edge assembled GO aerogels with specific surface areas of up to 850 m$^2$ g$^{-1}$ were obtained for the first time by choosing high-quality GO hydrogels as precursors with supercritical CO$_2$ drying. The resulting GO aerogels show excellent mechanical properties (up to 20 MPa Young’s modulus and ca. 1 MPa yield strength) with superb adsorption capacity in mechanical energy (up to 45 J g$^{-1}$ specific...
energy adsorption). Moreover, these as-prepared GO aerogels possess unique chemical activities toward some reducing gases such as H\textsubscript{2}S, HI, and SO\textsubscript{2}. All of these characteristics can make the resulting GO aerogel a promising candidate in the field of environmental or mechanical engineering. The work presented here might also give inspiration to fabricate a series of graphene-based composite aerogels such as graphene/S hybrids.

4. Experimental Section

Materials: All chemicals including graphite powder, LaCl\textsubscript{3}·6H\textsubscript{2}O, glucose-δ-lactone (GDL), polyethylenimine (PEI), NaOH, acetone, and FeS were purchased from Beijing Chemical Reagents Company with analytical grade purity and were used without further purification. GO used in this paper was synthesized according to the procedure reported in our previous work.[28] After the formation of the hydrogels, these precursors were initially washed with a large amount of deionized water for about 1 week to remove the hydrolysis product of GDL, then washed with acetone to replace the water in the hydrogel network by the solvent-exchange process, finally supercritically dried with CO\textsubscript{2} (60 °C, 11 MPa) for 16 h.

Mechanical Property Tests: The quasi-static compression tests were conducted with the electronic universal testing machine (CMT4305). Aerogel samples used in the compression tests were chose to be about the same size with the shape of cylinder (ca. 1 cm in diameter, ca. 1 cm in height). During the compression, a force was put straightly onto the sample and moved from up to bottom with the strain rate of 0.005 s\textsuperscript{-1}. All the samples were compressed up to 80% strain to avoid the damage to the machine. (All the aerogels would not be broken down, even compress to the end).

Reaction with Reducing Gases: both La\textsuperscript{3+}- and PEI-crosslinked GO aerogels were first heated to 50 °C for 2 h under vacuum to remove moisture, and then packed into a glass tube as shown in Figure 5a. H\textsubscript{2}S was constantly released to pass through these aerogel samples deposited onto a glass slide and measured by irradiating with laser light at 632.8 nm in a Renishaw system 1000. The morphology of the crosslinked aerogels were observed with SEM (Hitachi S-4800). To clearly view the interior microstructures, the aerogel samples were cut into small pieces and then coated with gold by a sputter coater. TEM was performed at a FEI Tecnai 20 operating at 200 kV. The specific surface area, pore size distribution and pore volume were characterized with the ASAP 2010 (Micromeritics, USA) nitrogen sorption device. Before the measurement, samples were outgassed under vacuum at 120 °C for ca. 10 h until the pressure less than 0.665 Pa.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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