Towards three-dimensional, multi-functional graphene-based nanocomposite aerogels by hydrophobicity-driven absorption†

Shibing Ye and Jiachun Feng*

By skillfully taking advantage of the high oil-absorption capacity of hydrophobic graphene aerogels (GAs), a novel, facile, scalable, and versatile approach is put forward for the preparation of three-dimensional, multi-functional graphene-based nanocomposite aerogels. Through the simple hydrophobicity-driven absorption of organic solutions containing functional modifiers, high-strength GA/polymer and magnetic GA/metal oxide aerogels were obtained.

Three-dimensional (3D) graphene aerogels (GAs), which generally exhibit continuously interconnected macroporous structures, extremely low densities, large internal surface areas, and high electrical conductivities, have marked a major step forward in the translation of the excellent properties of individual graphene layers into macroscopic structures.1–9 To date, GAs have proven to be a very promising material and have attracted much attention from both the scientific community and industry, since a number of emerging applications such as energy storage, electronic devices, and environmental protection have been explored. With the rapid development of the above-mentioned technologies, ameliorated mechanical properties or enhanced functionalities are urgently required for GAs.10–12

Recently, much effort has been dedicated to develop graphene-based nanocomposite aerogels (GNAs) via an in situ synthesis from graphene oxide (GO) precursors and other functional modifiers. By integrating polymers or various metal oxides into GAs, GNAs such as graphene/polymer aerogels or graphene/metal oxide aerogels can be obtained, respectively, which effectively improve the mechanical properties of GAs or creatively endow GAs with novel functionalities.13–20 By freeze-drying the GO/water-soluble polymer hydrogels without a reduction process, high-strength GO/polymer aerogels were easily produced.21–23 Recent works also obtained the graphene/thermoset polymer aerogels by infiltrating the monomers and curing agents into GAs, followed with a polymerization process.11,24 Xiao et al. reported a kind of superoleophilic graphene/polymer aerogel made by solvothermal reduction of the mixed dispersions of GO and polyvinylidene fluoride.25 Yu et al. and Yan et al. independently incorporated Fe3O4 nanoparticles into GAs in situ by a hydrothermal method and prepared hybrid aerogels with strong magnetism.12,26 However, these methods are usually multistep, and it is difficult to control the dispersion and structure of graphene in the resulting GNA matrices, which would reduce the repeatability in manufacture. Moreover, the majority of polymers, in particular cost-effective commodity polymers that are not water-soluble, but are oil-soluble, are hard to assemble into GAs through an in situ process. Therefore, it is necessary to develop a new and feasible approach that can produce structure-controlled GNAs on a large scale.

Herein, we propose a new design strategy to prepare GNAs by skillfully taking advantage of the high oil-absorption capacity of GAs. In this strategy, the ready-made, hydrophobic GAs automatically absorb the organic solutions of modifiers in large amounts, and the 3D GAs, which offer a large number of accessible open pores and cell walls,27 serve as the host frameworks to immobilise and support the guest modifiers (e.g. polymers or nanoparticles). A number of cases of hydrophobic GAs used as efficient sorbents for oils and organic solvents have been recently reported, and the absorption capacity can even reach up to 900 times the GAs’ own weights.4,12,25 Thus, our hydrophobicity-driven absorption method is expected to be a versatile route to obtain various GNAs since most commodity polymers and metal oxide precursors are oil-soluble. Compared with the common methods such as vacuum-assisted suction or the dip coating method,25,26 the hydrophobicity-driven absorption method can work within a short duration and without using any external forces. These advantages, together with the large-scale manufacture of GAs from low-cost GO, make the hydrophobicity-driven absorption method a very simple and

† Electronic supplementary information (ESI) available: Experimental section, the absorption ability of GA, the schematic of the preparation of GNAs, digital images of GA/SEBS, TGA curve and TEM images of Fe3O4. See DOI: 10.1039/c4ta01392a
scalable method for the preparation of GNAs. Moreover, by using pre-synthesized GAs as the host frameworks, it preserves the original 3D, continuously interconnected graphene networks in the resulting GNAs, which achieves structure control and good repeatability.

As examples, poly(styrene-\(\beta\)-(ethylene-co-butylene)-\(\beta\)-styrene) (SEBS) and Fe\(_2\)O\(_3\) were selected as the functional modifiers, and GA/SEBS and GA/Fe\(_2\)O\(_3\) aerogels were fabricated to demonstrate the hydrophobicity-driven absorption method. As expected, the obtained GA/SEBS aerogels not only have excellent mechanical properties but also maintain fine electrical conductivity even with a high SEBS loading amount. The as-prepared GA/Fe\(_2\)O\(_3\) aerogels exhibit strong magnetism, having potential in serving as recyclable oil sorbents. From the viewpoint of material fabrication, we believe that the hydrophobicity-driven absorption method can achieve the mass production of GNAs with low costs and simple steps.

The host GAs from the GO precursor were synthesized through a freeze-casting process and a subsequent thermal treatment.\(^2\) By this cost-effective method, a set of GAs with desired shapes, a low density (0.028 g cm\(^{-3}\)), and a high specific surface area of 270 m\(^2\) g\(^{-1}\) were readily obtained in large quantities. The scanning electron microscopy (SEM) image shown in Fig. 1a demonstrates that the resultant GAs exhibit a cellular and hierarchical structure, which possesses an interconnected porous network with most of its pores having a size of several micrometers. The detailed observation in Fig. 1b reveals a curved and crumpled morphology of the graphene cell walls, which can prevent neighboring graphene sheets from restacking with one another. Similar to the GAs prepared by other methods,\(^4\) the hydrophobic GAs in this work have an excellent oil-absorption capacity for various organic liquids including common organic solvents, that is, 50–130 times their own weights (Fig. S1†). These results demonstrate the great promise of GAs as host frameworks for loading guest polymers or nanoparticles in large amounts.

SEBS, an oil-soluble commodity polymer, was selected as the guest polymer to demonstrate the hydrophobicity-driven absorption method. In a typical preparation (Fig. S2†), a weighted, cylindrical GA was immersed into cyclohexane solutions containing 1, 2, 5, and 10 wt% SEBS for 30 min, followed by the removal of solvents in a mild drying process. The final nanocomposite aerogels were denoted as GA/S1, GA/S2, GA/S5, and GA/S10, respectively. Due to the intrinsic hydrophobicity of GAs, the cyclohexane solutions of SEBS could easily infiltrate into the pores of the GAs under a hydrophobicity-driven ‘force’. The backfilled GA/SEBS aerogels have similar dimensions and sizes as those of the bare GAs, but the bulk densities of the GA/SEBS aerogels are 0.04, 0.08, 0.14, and 0.23 g cm\(^{-3}\), respectively, greater than that of the GAs and strongly dependent on the concentration of the SEBS solutions. Similarly, the SEBS content in the GA/SEBS aerogels, accurately estimated from the thermal gravimetric analysis (TGA) curves (Fig. 2a), are 32, 65, 78, and 87 wt\%, respectively, gradually increasing with the increasing concentration of the SEBS solutions. Different morphologies compared to the GA are observed in the cross-sections of the GA/SEBS aerogels. For GA/S2, the SEBS partially but homogeneously fills the aerogel, and no evidence is seen of interfacial separation or cracking in the foam structure (Fig. 1c). Zooming in on the graphene walls reveals relatively thick and dark blocks (Fig. 1d), indicating that the SEBS fills the crumples of graphene and coats the surfaces of graphene walls. The \(\pi-\pi\) interactions between the graphene sheets and the styrene segments of SEBS may lead to the strong absorption of the SEBS into the GAs.\(^{27,28}\) Increasing the SEBS concentration to 10 wt\% results in a more dense infiltration of SEBS, where only a few voids can be detected (Fig. 1e). The crumles and ravines are almost completely filled and covered by the SEBS, resulting in a flat and smooth surface (Fig. 1f).

The incorporation of SEBS is expected to improve the mechanical properties of GAs. As shown in Fig. S3†, the as-prepared GAs are fragile, just strong enough to permit careful handling, while the reinforced aerogels show robust mechanical properties. All of the compressive stress–strain curves of the GA/SEBS aerogels (Fig. 2b) exhibit three regimes of deformation (a nearly linear elastic regime, a relatively flat stress plateau, and an abrupt stress increasing regime), similar to cork and other elastomeric foams.\(^3\) Increasing the SEBS loading has a significant effect on the mechanical properties of the GA/SEBS aerogels. The compressive stress of GA/S1 is \(-0.27\) MPa at 80\% strain, which is one order of magnitude higher than the

![Fig. 1](image_url) SEM images of the microstructures of GAs (a and b), GA/S2 (c and d), and GA/S10 (e and f).

![Fig. 2](image_url) (a) TGA curves of the SEBS and GA/SEBS aerogels under a N\(_2\) atmosphere. (b) Compressive stress–strain curves of the GA/SEBS aerogels; inset are the compressive stress–strain curves of the GA/S10 up to the maximum strain of 50\% for 50 cycles. (c–f) Photographs of the GA/S10 under a compressing and releasing cycle.
reported value of bare GAs,\(^3\) and this value increases to \(~0.63\) MPa for GA/S10. Additionally, an approximately reversible structural recovery could be observed for the SEBS-reinforced GAs. As a representative sample, a piece of the GA/S10 underwent 50 successive compression cycles up to 50% strain without recovery time. Except for the first compression cycle, the subsequent ones nearly retrace each other (inset of Fig. 2b), indicating that the structure and height of GA/S10 changed very little. Actually, along the in-plane direction, the GA/SEBS aerogels can be squeezed into a pellet under pressure but recover most of their material volume elastically without any cracks once the external pressure is removed, with the exception of GA/S1 (Fig. 2c–f and S4†). Compared with the compressible GAs from other assembly approaches,\(^4\) the SEBS-reinforced aerogels fabricated by the hydrophobicity-driven absorption method exhibit larger compressibility and a more rapidly reversible compression–recovery process, which should be attributable to the incorporation of the SEBS elastomer. Interestingly, the combination of GA and SEBS significantly improves the thermal stability of the SEBS, that is, the temperature for the thermal degradation of the GA/SEBS aerogels is approximately 100 °C higher than that of pure SEBS (Fig. 2a).

Due to the preformed consecutive graphene networks, the GA itself shows high electrical conductivity (\(~120\) Ω) before incorporation of SEBS. To illustrate the influence of a backfilling polymer on the bulk electrical resistance of the GAs, the electrical resistance ratios (\(R_E/R_G\), where \(R_G\) and \(R_E\) represent the resistance of the GAs before and after backfilling with SEBS, respectively) were calculated and plotted against the SEBS content, as shown in Fig. 3a. With regard to GA/S1, the values of \(R_E/R_G\) along the in-plane and out-of-plane directions are \(~1.5\) and \(~1.7\), respectively, meaning that the electrical conductivity of the reinforced GAs is slightly decreased, but have an appreciable retention. More interestingly, \(R_E/R_G\) is almost constant as the SEBS content increases from 32 wt% to 87 wt% in the GAs, which indicates that the 3D, interconnected, conducting graphene networks could effectively retain their original structure after absorbing the polymer and, just like wires, are covered with a layer of insulation. We also investigated the resistance variation ratios of the GA/SEBS aerogels during the compression process, \(R_E/R_G\), where \(R_G\) is the initial resistance of the GA/SEBS aerogels and \(R_E\) is the resistance of the GA/SEBS aerogels under pressure. As shown in Fig. 3b, for all of the four samples, \(R_E/R_G\) decreases as the compression strain is increased from 0 to 80%.

We suspect that there are plentiful micro-defects in the preformed graphene network, which are also observed in the SEM image (Fig. 1a). When the pressure was imposed on the GA/SEBS aerogels, these broken joints come into contact with each other, inducing substantial contact in the network and reducing the conductive pathway disruption to a great extent. The resistance variation of the GA/SEBS aerogels can be directly revealed by the reading change of a multimeter or the brightness change of a light-emitting diode (LED) light integrated into the circuit of the GA/SEBS aerogels. The reading of the multimeter gradually decreases as the pressure is imposed, until a minimum is reached (Fig. 3c–e). Similarly, the LED light becomes bright upon compressing and becomes dark when the pressure is released (Fig. 3f–i). These results reveal that the GA/SEBS aerogels have both electrical conductivity and elastic properties, which are needed for the fabrication of flexible displays, stretchable electronic implants, electrically actuated elastomers, etc.\(^4,11,29–31\) Based on the above unique properties, a GA/SEBS aerogel is able to work as a pressure-sensitive material.

The hydrophobicity-driven absorption method was also successfully applied to prepare graphene/metal oxide aerogels, which follows the previous search for carbon/metal oxide aerogels.\(^4,12\) Typically, the GAs were impregnated in an ethanol solution of ferric nitrate (0.05 M) for a few minutes, followed by thermal treatment at 400 °C for 3 h under Ar to obtain the GA/Fe\(_2\)O\(_3\) (Fig. S2†). The GA can absorb amounts of the ethanol solution up to 75 times its own weight. From the TGA curves (Fig. S5†), the content of Fe\(_2\)O\(_3\) in the GA/Fe\(_2\)O\(_3\) was calculated to be \(~27\) wt%. The content of metal oxide in the GAs can be easily adjusted by controlling the concentration of the organic solutions. The SEM image (Fig. 4a) reveals that the GA/Fe\(_2\)O\(_3\) also possesses a 3D morphology featured with randomly macroporous frameworks. The high-magnification SEM image (Fig. 4b) and the transmission electron microscopy (TEM, Fig. S6†) images clearly show that the Fe\(_2\)O\(_3\) nanoparticles with a size of 50–200 nm are uniformly anchored on the surfaces of the graphene sheets. X-ray powder diffraction (XRD) was used to identify the crystal structure of the resulting GA/Fe\(_2\)O\(_3\) (Fig. 4c). The five peaks at 30.2, 35.5, 43.1, 57.0, and 62.7° can be assigned to \(\gamma\)-Fe\(_2\)O\(_3\) (JCPDS no. 33-0664), which is the cubic spinel crystal of the bulk maghemite.\(^19,20\) Notably, the introduction of the magnetic \(\gamma\)-Fe\(_2\)O\(_3\) makes the GA/Fe\(_2\)O\(_3\) capable of being manipulated by a bar magnet (Fig. 4d). Moreover, even under...
the resultant GA/Fe$_2$O$_3$ aerogel has enormous potential in the applications of magnetic oil-sorbents. Taken together, our results confirm that the hydrophobicity-driven absorption method is feasible and efficient in preparing graphene/polymer aerogels and graphene/metal oxide aerogels, and is of great interest in the industrial field.

**Conclusions**

In summary, we have developed a novel, facile, scalable, and versatile method to fabricate graphene-based nanocomposite aerogels. Different from previous works, our hydrophobicity-driven absorption method takes full advantage of the intrinsic hydrophobicity of graphene aerogels, which overcomes the problem that it is difficult to incorporate commodity polymers into GAs, and makes it possible to prepare graphene/metal oxide aerogels on a large scale and through simple steps. By such means, the GA/SEBS and GA/Fe$_2$O$_3$ aerogels were successfully obtained. The former materials not only have improved mechanical properties and thermal stability, but also demonstrate an interesting elastic response in the electrical conductivity. Combined with the unique properties of Fe$_2$O$_3$, strong ultrasonic treatment, the final GA/Fe$_2$O$_3$ powder in solution can be readily collected by a magnetic bar (Fig. 4e), which suggests that the Fe$_2$O$_3$ nanoparticles are firmly attached onto the graphene sheets. Considering the high oil-absorption capacity of GAs, our GA/Fe$_2$O$_3$ has potential application as an ultralight magnetic sorbent with high selectivity and sorption capacity, easy collection and recyclability. As shown in Fig. 4f, the collection of the GA/Fe$_2$O$_3$ from the organic solvent can be readily accomplished with a bar magnet, while the recycling and reuse of such a sorbent could be achieved by releasing the organic chemicals through evaporation or burning.

**Acknowledgements**

This work was financially supported by the Natural Science Foundation of China (51373042 and 21174032) and National Basic Research Program of China (2011CB605704).

**Notes and references**


---

**Fig. 4** (a and b) SEM images of the microstructures of GA/Fe$_2$O$_3$. (c) XRD patterns of the GA and GA/Fe$_2$O$_3$. (d) A piece of the GA/Fe$_2$O$_3$ could be manipulated by a magnetic bar. (e) The GA/Fe$_2$O$_3$ powder could also be collected by a bar magnet. (f) Pictures of the recycling of the GA/Fe$_2$O$_3$ after absorbing cyclohexane dyed with Sudan I.