

Fiber-reinforced Three-dimensional Graphene Aerogels for Electrically Conductive Epoxy Composites with Enhanced Mechanical Properties^{*}

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Abstract To enhance the mechanical properties of three-dimensional graphene aerogels with aramid fibers, graphene/organic fiber aerogels are prepared by chemical reduction of graphene oxide in the presence of organic fibers of poly(*p*-phenylene terephthalamide) (PPTA) and followed by freeze-drying. Thermal annealing of the composite aerogels at 1300 °C is adopted not only to restore the conductivity of the reduced graphene oxide component but also to convert the insulating PPTA organic fibers to conductive carbon fibers by the carbonization. The resultant graphene/carbon fiber aerogels (GCFAs) exhibit high electrical conductivities and enhanced compressive properties, which are highly efficient in improving both mechanical and electrical performances of epoxy composites. Compared to those of neat epoxy, the compressive modulus, compressive strength and energy absorption of the electrically conductive GCFA/epoxy composite are significantly increased by 60%, 59% and 131%, respectively.

Keywords Electrical conductivity; Mechanical properties; Graphene aerogels; Epoxy composites; Thermal annealing

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INTRODUCTION

As a promising two-dimensional carbon nanomaterial with outstanding electrical and thermal conductivities, graphene sheets are widely used to improve the mechanical, thermal and electrical properties of various polymers^[1–4], including epoxy-based polymers^[3–5], polypropylene^[6–8], polylactic acid^[9] and polystyrene^[10]. However, to efficiently construct an interconnected conductive network within a polymer matrix by improving the dispersion of graphene sheets is a common but challenging issue because of the strong van der Waals forces between graphene sheets and the intrinsic incompatibility with most polymers^[11, 12]. Different from *in situ* formation of a three-dimensional (3D) conducting network of graphene sheets during melt compounding or solution mixing, the 3D conductive network could also be constructed before compounding or mixing with polymers by assembling graphene sheets into 3D aerogels^[13–15], foams^[16–19] and porous films^[20–22]. Many methods have been developed to fabricate the 3D porous graphene architectures, including *in situ* reduction^[23–25], template-assisted approach^[26–28] and crosslinking methods^[27–29]. The assembly of graphene sheets into 3D

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porous architectures can effectively avoid the aggregation of graphene sheets and provide a preformed conductive network for electrically conductive polymer nanocomposites.

Polymer nanocomposites fabricated by infiltration of monomers or polymers into porous architectures are expected to remarkably improve their mechanical and electrical properties, but such an expectation is often frustrated by the poor mechanical strength of 3D porous networks due to their inherent brittleness and low density^[30]. So far, there are mainly two typical approaches to reinforce graphene aerogels and foams. One is to enhance the skeletons of aerogels by using a polymer to bridge graphene sheets of aerogels^[31, 32]. The other is to develop hybrid or composite aerogels. For example, Zhang *et al.*^[33] filled silica aerogel with aramid fibers, and the resulting composite aerogel showed improved mechanical performances. However, the drawback of using polymeric fibers as mechanical enhancers is the decrease of the electrical conductivity of the composites due to their intrinsic electrical insulation. To improve the electrical conductivity of hybrid aerogels, organic fibers were annealed at high temperature for converting them to carbon fibers with higher mechanical strength^[34] and electrical conductivity^[35].

The purpose of present work is to reinforce the graphene aerogels with organic aramid fibers, by which the mechanical properties of their conductive epoxy composites can be enhanced. Herein, we report the fabrication of graphene-based composite hydrogels *via* chemical reduction of graphene oxide (GO) in its aqueous suspension with organic fibers of poly(*p*-phenylene terephthalamide) (PPTA) using hydroiodic acid (HI) as the reducing agent. It is found that the 3D composite aerogels with chemically reduced GO sheets (RGO) and PPTA aramid fibers are formed by freeze-drying of the hydrogels. Furthermore, to enhance the electrical conductivity of the composite aerogels, thermal annealing at 1300 °C is adopted not only for restoring the conductivity of the RGO component but also for converting the insulating PPTA organic fibers to conductive carbon fibers by carbonization. The resulting graphene/carbon fiber aerogels (GCFAs) exhibit excellent electrical conductivities ($> 10^2$ S/m), 4 orders of magnitude higher than those of reported graphene aerogels formed by chemical reduction^[36]. The carbon fibers increase the mechanical properties of aerogel with a high density of ~ 70 mg/cm³. Thanks to the reinforced porous architecture of GCFA, the compressive strength and energy absorption of its epoxy composite are enhanced by 59% and 131%, as compared with those of neat epoxy, respectively. To the best of our knowledge, this is the first example to reinforce graphene aerogels with organic fibers, by which the mechanical and electrical properties of epoxy composites are highly improved.

EXPERIMENTAL

Materials

Potassium permanganate (KMnO₄), concentrated sulfuric acid (H₂SO₄, 98%), hydrochloric acid (HCl, 36%), hydrogen peroxide (H₂O₂, 38%), HI and ascorbic acid were supplied by Beijing Chemical Factory (China). Graphite flakes (48 μm) were purchased from Huadong Graphite Factory (China). Short PPTA aramid fiber pulps (Nomex) were supplied by DuPont Co. with an average length of 2 mm and average diameter of 0.5–2 μm. Epoxy resin (JY-257) with an epoxy value of 0.53–0.55 mol/100g was provided by Changzhou Jiafa Chemical Co. (China). Methyl hexahydrophthalic anhydride as the curing agent and tris-(dimethyl aminomethyl) phenol as the curing accelerator were bought from Alfa Aesar (China).

Preparation of Graphene/Organic Fiber Aerogels and Graphene/Carbon Fiber Aerogels

Graphite oxide was synthesized by oxidation of graphite flakes with a modified Hummers' method^[37, 38]. A homogeneous and yellow-brown suspension of GO was firstly prepared by ultrasonication of graphite oxide using a bath sonicator for 30 min, and PPTA fibers were then incorporated on the basis of GO/PPTA mass ratios of 1/1, 1/4, 1/10 and 1/20. After the resulting mixture was stirred vigorously for 5 min and HI was added to chemically reduce GO to RGO based on a HI/GO mass ratio of 3/1, it was sealed in a glass beaker at 90 °C for 12 h to produce graphene/PPTA fiber hydrogels. The obtained hydrogels were washed with deionized water for 24 h to remove the residual impurities and then freeze-dried at –50 °C using a FD-1C-50 freeze drier (China) for 48 h to obtain graphene/organic fiber aerogels (GOFAs). Furthermore, GOFAs were thermally annealed at

1300 °C in an argon atmosphere for 2 h in order to improve their conductivities by removing more residual oxygen-containing groups and carbonize the organic PPTA to be carbon fibers. The resulting composite aerogels were designated as GCFA x - y , where x was the initial GO concentration and y was the initial mass ratio of PPTA fiber to GO. For comparison, neat graphene hydrogel and aerogel (GA) were also prepared using the similar methodology. However, to prevent the dramatic shrinkage of neat graphene hydrogel during the reduction of its GO component, ascorbic acid was used as a mild reducing agent rather than the strong reducing agent of HI.

Fabrication of Electrically Conducting Epoxy Composites

GCFA/epoxy composites were fabricated using a vacuum-assisted impregnation method. Typically, the epoxy monomer, the curing agent, and the curing accelerant were mixed in a planetary centrifugal vacuum mixer, and then GCFA was immersed and backfilled by the mixture in a vacuum oven for 3 h, and cured at 80 °C for 2 h, 120 °C for 2 h and 160 °C for 2 h. The fabricated epoxy composites were used for morphological observation, and electrical and mechanical properties characterizations.

Characterizations

The morphology and microstructure of aerogels and their epoxy composites were observed with a Hitachi S4700 field-emission scanning electron microscope (SEM). X-ray diffraction (XRD) measurements were carried out by using a Rigaku D/Max 2500 diffractometer with Cu K α radiation ($\lambda = 0.154$ nm) at a generator voltage of 40 kV. GO and its aerogels were scanned with a Thermo VG RSCAKAB 250X X-ray photoelectron spectroscope (XPS), and a Renishaw in Via Raman microscope (Britain) at an excitation wavelength of 514.5 nm. Compression measurements were performed on an Instron 5567 testing machine at a constant crosshead speed of 5 mm/min. The volume conductivities of aerogels and their epoxy composites were measured with a RTS-8 four-probe resistivity meter (China) when the conductivity was higher than 1×10^{-4} S/m, whereas a Keithley 6517B resistivity meter (USA) was used when the electrical conductivity was smaller than 1×10^{-4} S/m. Silver paste was used to minimize the contact resistance between the probes and the samples.

RESULTS AND DISCUSSION

Reduction Efficiency of GO and Structural Evolution of the Composite Aerogels during the Chemical Reduction Process and Subsequent Thermal Annealing

Figure 1 illustrates the process for fabricating GCFA composite aerogel and its epoxy composite. PPTA organic fibers as the mechanical enhancer are mixed into the yellow-brown aqueous suspension of GO, and the mixture is then subjected to chemical reduction with HI as the chemical reducing agent of GO component at 90 °C for 12 h to obtain a black graphene/organic fiber hydrogel. It is noted that, in the absence of PPTA fibers, the neat GO suspension requires a longer time for gelation under the same conditions, indicating that the amine groups of PPTA fibers have electrostatic interactions with the carboxyl groups of GO. It can link the GO sheets together and promote the gelation process^[39]. It is interesting that the incorporation of sufficient organic fibers alleviates the volume-shrinkage of 3D hydrogel during the chemical reduction process. For instance, at the GO/PPTA mass ratio of 1/1, the volume of composite hydrogel is about half of initial volume of the mixture with the GO concentration of 8 mg/cm³. Interestingly, when the mass ratio is 1/20, the hydrogel has almost no volume-shrinkage. Apparently, PPTA fibers benefit the preparation of a robust graphene hydrogel with negligible shrinkage. The GOFA aerogel prepared by freeze-drying of its hydrogel counterpart is thermally annealed at 1300 °C for 2 h, by which the PPTA component is carbonized to carbon fibers and the residual oxygen-containing groups are removed from the RGO component. An electrically conductive GCFA aerogel is formed with an excellent porous network for accommodating epoxy resin using a vacuum-assisted impregnation process.

Figure 2 shows the SEM micrographs of freeze-fractured surfaces of GOFAs and GCFAs with different GO/PPTA mass ratios. Both GOFAs and GCFAs exhibit interconnected porous structures. The diameters of carbon fibers in GCFAs become much smaller than those of the organic fibers in GOFAs due to the carbonization of PPTA fibers. During the thermal annealing at 1300 °C, the non-carbon elements of PPTA fibers are eliminated by volatilizing H₂O, CO₂, HCN, benzene, toluene and benzonitrile^[40, 41]. The PPTA organic fibers

are carbonized to be carbon fibers with a mass loss of nearly 68 wt%^[42]. It is also seen that the graphene sheets provide beddings where fibers attach on or insert in the aerogel matrix. Such porous architectures are obviously observed in GCFA, where graphene sheets and carbon fibers are combined tightly. With the increase of PPTA content, the porous walls of aerogel matrix tend to be overlapped with each other.

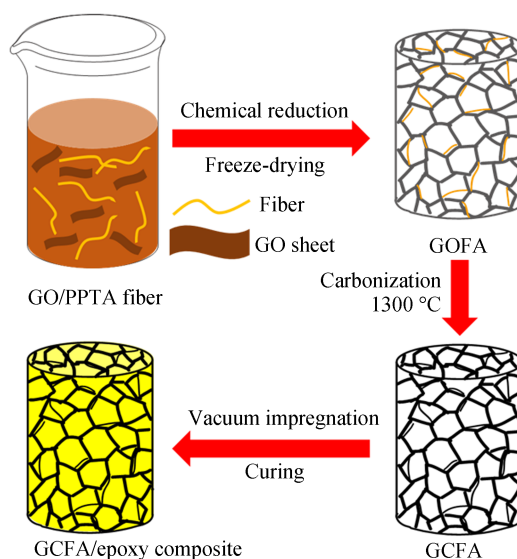


Fig. 1 Schematic diagram of the fabrication process of GCFA architecture and the conductive epoxy composite

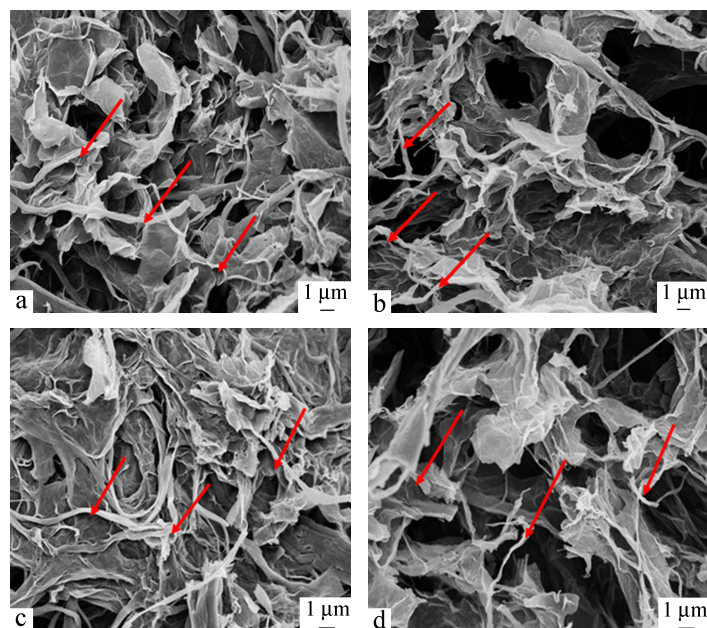


Fig. 2 SEM images of (a) GOFA and (b) GCFA with the GO/PTTA mass ratio of 1/4, and (c) GOFA and (d) GCFA with the GO/PTTA mass ratio of 1/10 (The red arrows point to the fibers.)

Figures 3(a)–3(d) show the XPS spectra of GO, GOFA and GCFA. It is seen that the C/O ratio increases from 2.2 for GO to 4.6 for GOFA due to the chemical reduction of GO with HI and the introduction of PPTA fibers (Fig. 3a). A much higher C/O ratio of 47 is present for GCFA because of the highly efficient thermal reduction at 1300 °C, and the carbonization of PPTA fibers. The evolutions of functional groups of GO, GOFA

and GCFA are well reflected in their C1s spectra. The C1s peaks of GO at 284.8, 286.5, 287.4 and 288.7 eV (Fig. 3b) are assigned to C—C/C=C in aromatic rings, hydroxyl (C—OH), epoxide (C—O—C) and carboxyl (C=O) groups, respectively^[36, 43]. These peaks for the oxygen-containing groups of GO are apparently weakened in the C1s spectrum of GOFA, indicating the partial removal of these groups (Fig. 3c). Compared to the chemical reduction with HI, the thermal annealing at 1300 °C is more efficient in removing the oxygen-containing groups, including the removal of residual oxygen-containing groups of GO and the carbonization of PPTA fibers, evidenced by the greatly weakened peaks in the C1s spectrum of GCFA (Fig. 3d). The structural

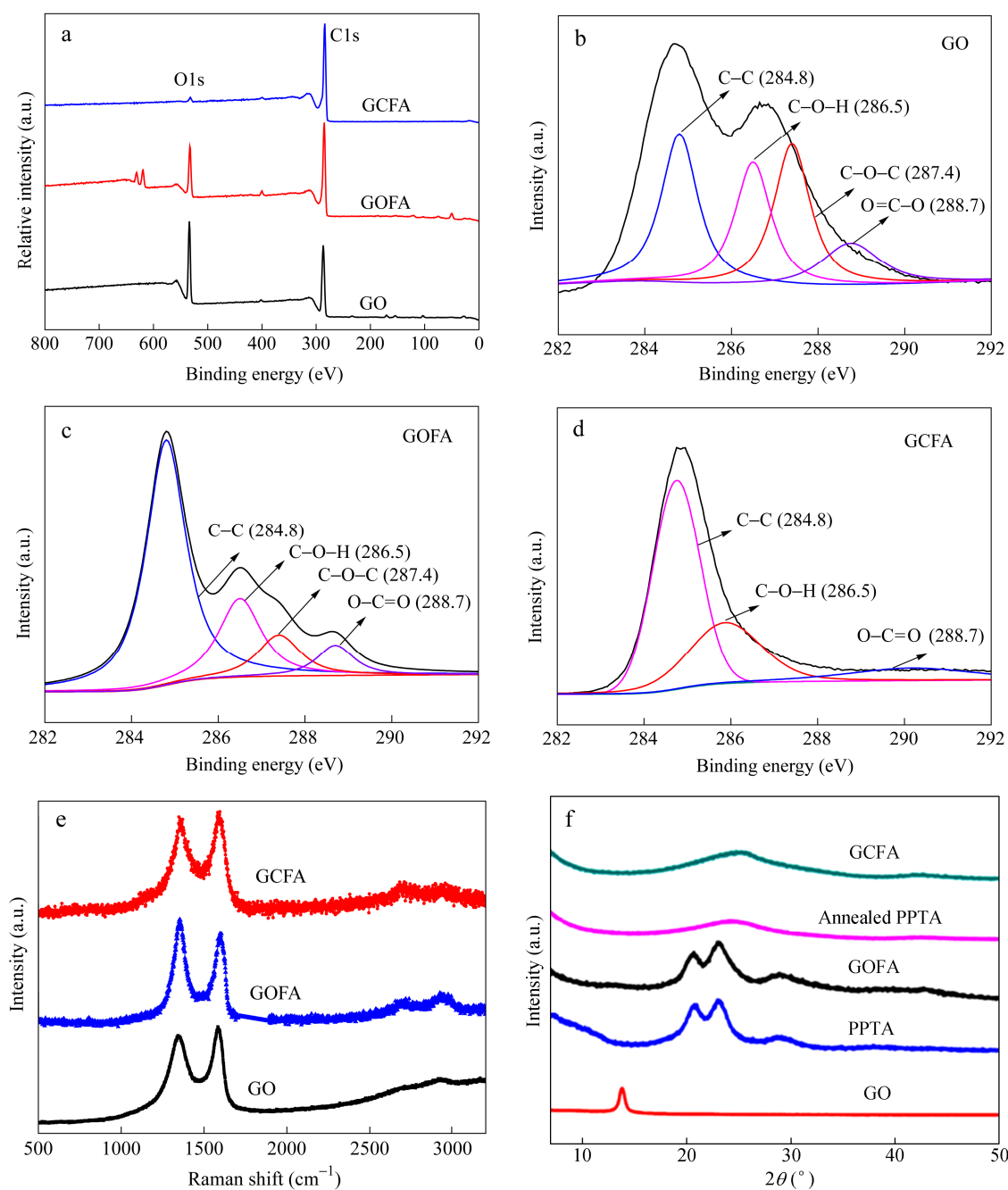


Fig. 3 (a–d) XPS spectra, (e) Raman spectra and (f) XRD patterns of GO, GOFA, GCFA, and pristine and annealed PPTAs

evolution of GO during the chemical reduction and subsequent thermal annealing is evaluated with Raman spectra (Fig. 3e). Typically, the Raman spectrum of GO exhibits two peaks: D band (1352 cm^{-1}) and G band (1592 cm^{-1}), corresponding to the sp^3 carbon atoms of the defect structure and the sp^2 -hybridized carbon atoms from the aromatic structure, respectively. The intensity ratio of D- to G-band peaks (I_D/I_G) is used to assess the density of defects in sp^2 carbon. The I_D/I_G ratio increases from 0.91 for GO to 1.05 for GOFA, implying an increase of structural defects in GOFA after the partial removal of oxygen-containing groups by HI. The average size of sp^2 domains decreases upon the reduction of GO due to the defects caused by the release of oxygen-containing groups^[44]. Interestingly, the I_D/I_G ratio is decreased from 0.91 of GO to 0.72 for GCFA, which is attributed not only to the further removal of the oxygenated groups from the chemically reduced GO component, but also to the recovery of the sp^2 conjugated carbon structure during the thermal annealing at $1300\text{ }^\circ\text{C}$ ^[44].

XRD analysis (Fig. 3f) is used to demonstrate the interlayer spacing evolution. The XRD trace of pristine PPTA fibers is characterized with two crystalline peaks at 19° and 22° indexed as 110 and 200 reflections, corresponding to a monoclinic (pseudo-orthorhombic) unit cell^[45]. In the XRD pattern of GOFA, the typical peaks of PPTA show no obvious change and the characteristic peak of GO at 11.8° disappears, suggesting a good stability of PPTA during the reduction process of GO and the disordered distribution of RGO sheets in the resulting GOFA. After thermal annealing at $1300\text{ }^\circ\text{C}$, both peaks of PPTA and RGO components disappear in the XRD pattern of GCFA because of the thermal pyrolysis of PPTA and the disorderly distributed graphene sheets^[46]. Instead, a new broad peak at 25° appears, corresponding to the graphitic profile (002) with an interlayer spacing of 0.35 nm . The appearance of this peak can be attributed to the turbostratic structure of carbon converted from the highly organized aromatic rings of PPTA during the thermal annealing^[47], and to the further elimination of functional groups of RGO, thus leading to the decrease in interlayer spacing.

Compressive and Electrical Properties of the Composite Aerogels

Figure 4 shows the compressive properties of GCFA. When the initial concentration of GO is 5 mg/mL and the initial GO/PPTA mass ratios for GOFAs are 1/1, 1/10 and 1/20, the graphene/carbon fiber mass ratios in GCFA are changed to be 1.3/1, 1/7.6 and 1/15, respectively. The thermally annealed neat graphene aerogel has a density of 6 mg/cm^3 , and its modulus is about 1.9 kPa . The presence of more carbon fibers leads to a denser architecture and a further increase in the modulus of GCFA. Compared to the neat graphene aerogel with a compressive modulus of $\sim 31.9\text{ kPa}$ and a compressive strength of $\sim 9.5\text{ kPa}$ at 30% strain, the GCFA5-20 composite aerogel exhibits a modulus of $\sim 174\text{ kPa}$ and a compressive strength of $\sim 55.7\text{ kPa}$ at 30% strain, with significant improvements of 445% and 486%, respectively. The GCFA are even stronger than many graphene aerogels reported in the literature because the carbon fibers generated by the *in situ* carbonization of PPTA structurally reinforce the porous architecture and provide further interconnections between individual graphene sheets^[48, 49].

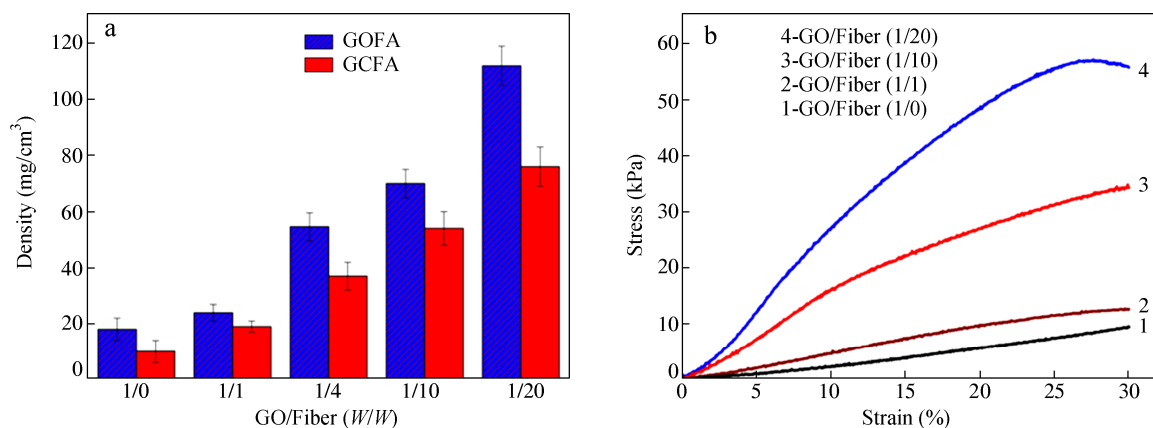


Fig. 4 (a) Densities of GOFAs and GCFA and (b) compressive stress-strain curves of GCFA prepared from the 5.0 mg/mL GO dispersions with various GO/fiber ratios

The electrical conductivity of GOFA has not been improved because the PPTA organic fibers are electrically insulating. For example, GOFA has an electrical conductivity of 27 S/m, similar to those of the most reported physically cross-linked graphene aerogels and foams (0.1–10 S/m)^[48, 50]. Interestingly, the thermal annealing at 1300 °C greatly enhances the electrical conductivity of the composite aerogels (Fig. 5). The electrical conductivity of GCFA is determined to be 1.48×10^3 S/m, ~ 3 orders of magnitude greater than those reported for 3D graphene aerogels^[36, 48]. This value is even close to the conductivity reported for graphene sheets ($\sim 8 \times 10^3$ S/m) produced by thermal reduction of GO at 700 °C under hydrogen atmosphere^[51, 52]. At a fixed initial GO concentration of 8 mg/mL, the electrical conductivities of GOFAs show a slightly decrease at high content of fibers, resulting from the insulating PPTA fibers and the loose network of graphene sheets. On the contrary, the electrical conductivities of GCFAs exhibit an increasing trend at high fiber content, because numerous conducting carbon fibers are formed *in situ* during the annealing at 1300 °C^[42]. In addition, at a given PPTA content of 80%, the electrical conductivity of GCFAs increases with the initial GO concentration due to the denser conducting networks constructed by more graphene sheets (Fig. 5b).

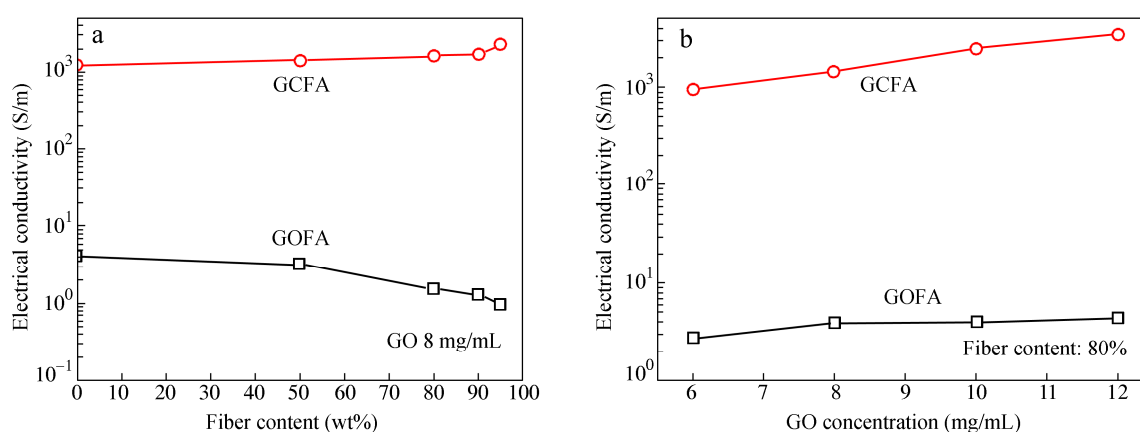


Fig. 5 Plots of electrical conductivity for GOFAs and GCFAs as function of (a) the initial fiber content and (b) the initial GO content

Enhanced Compressive and Electrical Properties of the Epoxy Composites

Since the filled individual graphene sheets often aggregate in their polymer matrices^[53], pre-construction of highly interconnected graphene networks before compounding or mixing with polymers is used to avoid aggregation of the graphene sheets to fully take their advantages^[54]. Figure 6 shows the plot of electrical conductivity of epoxy composites as a function of graphene content. A remarkable 14 orders of magnitude increase in electrical conductivity achieves for the epoxy composite in the presence of carbon fibers, when the graphene content is only 0.05 wt%, the initial GO concentration is 2 mg/mL and PPTA content is 20 times of GO. The 3D porous architecture, constructed with graphene sheets and carbon fibers, is an excellent electrically conducting network and renders epoxy with substantially improved electrical conductivity at such low graphene contents. The carbonized fibers structurally reinforce the porous architecture with sufficient mechanical stability during the vacuum-assisted impregnation of epoxy monomer, and enhance the interconnected graphene network for electrical conduction.

In addition to the improved electrical conductivity, the mechanical properties of epoxy are also enhanced by GCFAs. Figure S1 (in supporting information, SI) shows the compressive stress-strain curves of the epoxy composites with GCFAs, and the relevant results are listed in Table 1. With increasing the fiber content, both compressive modulus and strength of epoxy are apparently increased because of the reinforcement of fibers in the epoxy composites. It is also seen that the epoxy/GCFA8-20 composite can be compressed up to a strain of $\sim 13\%$ without any loss in stress, suggesting a good mechanical resistance supplied by the enhanced interconnecting network. The compressive stress-strain curves present a stress plateau region, indicating that

these composites can absorb compressive energy. The energy absorption during the compression is calculated by integrating the area under the stress-strain curve. The energy absorption of epoxy composite is higher than that of neat epoxy (Table 1). For example, the GCFA8-20 composite exhibits high energy absorption, which is ~160% higher than that of neat epoxy matrix. It indicates the effective enhancement of GCFA and their potential application for dissipating energy in a crash event.

To get a better understanding of the reinforcement mechanism of epoxy composites, the SEM images of the fracture surfaces of compressive specimens are shown in Fig. 7. The brittle nature of epoxy matrix is observed in its smooth fracture surface with flow patterns in Figs. 7(a) and 7(b), whereas the fracture surface of epoxy/GCFA

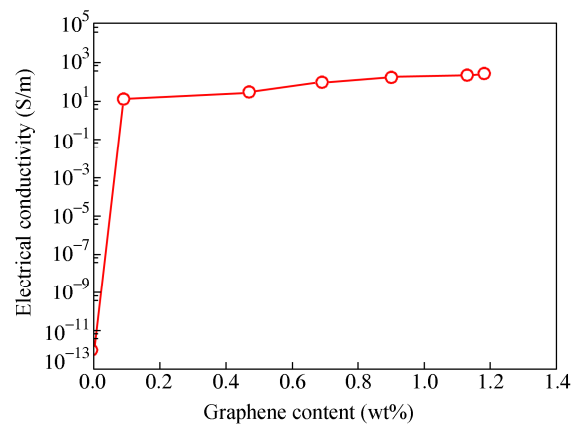


Fig. 6 Plot of electrical conductivity of GCFA/epoxy composites as a function of graphene content in the presence of the *in situ* formed carbon fibers

Table 1 Compressive properties of epoxy/GCFA composites

Sample	Fiber/graphene content (wt%)	Compressive modulus (GPa)	Compressive strength (MPa)	Energy absorption (MJ/m ³)
Epoxy	0/0	1.30	79.3	0.35
Epoxy/GA	0/1.30	1.48	99.0	0.59
Epoxy/GCFA8-4	2.25/0.75	1.94	124.0	0.69
Epoxy/GCFA8-10	3.98/0.52	2.09	126.5	0.81
Epoxy/GCFA8-20	5.86/0.39	1.85	106.4	0.91

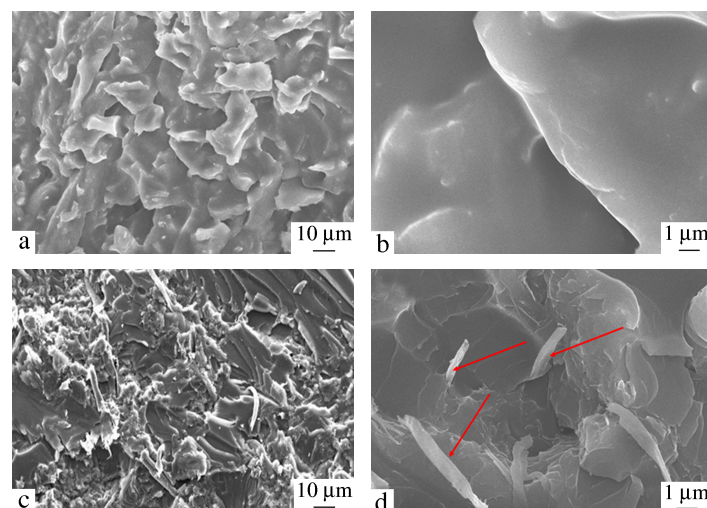


Fig. 7 SEM images of the compression-fracture surfaces of (a, b) epoxy/GA composite and (c, d) epoxy/GCFA8-10 composite (The red arrows point to the drawn carbon fibers.)

composite is rougher and has irregular cleavages with deeper valleys (Figs. 7c and 7d). The carbon fibers are embedded in the epoxy matrix and can reinforce the architecture and prevent the crack growth, evidenced by the drawing and pulling out of the carbon fibers from the epoxy matrix.

CONCLUSIONS

PPTA fiber-reinforced graphene aerogels are prepared by chemical reduction of GO in the presence of PPTA organic fibers followed by freeze-drying. To further enhance the electrical conductivity of the composite aerogels, thermal annealing at 1300 °C is adopted to restore the conductivity of RGO component and to convert the insulating PPTA fibers to conductive carbon fibers by the carbonization. Because the *in situ* formed carbon fibers reinforce the porous architecture and provide further interconnections between graphene sheets, the resulting GCFAAs exhibit both enhanced compressive properties and high electrical conductivities, which are highly efficient in improving the mechanical and electrical properties of epoxy matrix. In the presence of the carbon fibers, a remarkable 14 orders of magnitude increase in electrical conductivity is observed for the epoxy/GCFA composite with 0.05 wt% of graphene component. Compared to those of neat epoxy matrix, the compressive strength, compressive modulus and energy absorption of the epoxy/GCFA composite are significantly increased by 59%, 60% and 131%, respectively.

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