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Three dimensional graphene aerogels and their electrically conductive composites

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Abstract

A three dimensional (3D) graphene aerogel was prepared by in situ reduction-assembly method. *p*-phenylene diamine (PPD) was used as the reducing and functionalizing agent of graphene oxide (GO) in an aqueous medium with ammonia. The prepared 3D graphene-PPD aerogel has highly porous structure, low density, high electrical conductivity and good mechanical properties. Further, this aerogel based epoxy composites were also prepared by vacuum-assisted impregnation process. These materials also exhibited good electrical conductivity and compressive properties. For e.g., only 0.21 vol% of graphene, electrical conductivity was 4×10^{-2} S/m; and with 0.95 vol% of graphene, compressive strength of the composite increased by ~178% as compared to neat epoxy.

1. Introduction

Graphene has received immense attention recently because of its excellent thermal, electrical and mechanical properties [1], which can be imparted, though partly, to polymers [2-11]. The relatively modest improvement in properties of these composites was attributed to poor dispersion of graphene in polymers. The strong π - π interactions between graphene sheets was believed to be an important reason for this behavior. Even with the solvent casting approach, graphene sheets aggregate during the volatilization process of the solvent, yielding inferior nano-architecture [12,13]. This destroys the large accessible surface area of graphene, and thus resulting in inferior properties of the composite.

To overcome the above-mentioned problem, efforts were put forward to assemble individual graphene sheets into 3D graphene macroscopic materials resulting in hydrogels, aerogels, and macroporous films [14-21]. Subsequently, macromolecules are infiltrated through the graphene template. These graphene based composites exhibited significantly improved electrical conductivities compared to the composites prepared by conventional dispersion of graphene sheets [10,22,23]. For example, Chen et al. infiltrated 3D graphene prepared by chemical vapor deposition with polydimethylsiloxane [24]. The polydimethylsiloxane composite showed an electrical conductivity of about 1000 S/m at a low loading of ~0.5 wt%. Zhang et al. also manufactured a sensing device for differentiating organic solvents with different polarity by backfilling polydimethylsiloxane into a 3D

conducting network with a graphene loading of 0.35 vol% [25]. In another study, graphene/carbon nanotube (CNT) aerogel was infiltrated with polydimethylsioxane to fabricate highly conductive and stretchable composites [12]. The electrical conductivity of the composite reached ~280 S/m with 0.57 vol% of graphene/CNT aerogel. Despite these high conductivity values, the structural integrity of the aerogels during compounding process is still a challenge.

Current methods to prepare 3D graphene macrostructures involve template-directing method, cross-linking method, directed chemical vapor deposition, and in situ reduction-assembly method [26]. In general, GO is quite suitable to be used as a precursor for fabricating 3D graphene assemblies considering its rich functional groups and good dispersability in aqueous medium. It was shown that under hydrothermal treatment or in the presence of reducing agents, GO could be reduced to graphene and in situ self-assemble into a 3D architecture with pore sizes from sub-micrometer to several micrometers [19]. Driving forces for this self-assembly were believed to be hydrophobic interactions and π - π stacking between the reduced sheets. However, as mentioned before, most of the obtained aerogels are brittle. But in one of studies, Li et al have prepared a graphene aerogel with high elasticity because of the biomimetic cork-like structure [27]. It was also shown that the addition of pyrrole or ethylenediamine during the reducing-assembly process could result in tough aerogels [28,29]. But these aerogels have not been used to prepare polymer composites.

In our previous study, we have shown that PPD can simultaneously reduce and functionalize GO in the presence of ammonia solution under mechanical stirring [30]. Based on this work, here, we developed an effective method to prepare tough 3D graphene architectures from GO suspensions with concentrations as low as 1 mg ml⁻¹. The as-prepared 3D graphene-PPD aerogel (GPA) was infiltrated with epoxy monomer to fabricate electrically conductive composites.

2. Experimental

2.1. Materials

Natural graphite flakes with an average diameter of 48 μm were supplied by Huadong Graphite Factory (Pingdu, China). Potassium chlorate (98%), fuming nitric acid (65-68%), concentrated sulphuric acid (95%-98%), hydrochloric acid (36-38%) and dichloromethane (99.5%) were obtained from Beijing Chemical Factory (China) and used as received. PPD was bought from Tianjin Guangfu Chemical Research Institute (China). Epoxy resin, diglycidyl ether of bisphenol A, with the trade name of Epon-828 was purchased from Shell Co. (Britain). Curing agent, polyetheramine, with the trade name of JEFFAMINE[®] D2000 (D2000) was purchased from Huntsman (USA).

2.2. Preparation of GPA

GO was synthesized from natural graphite using modified Staudenmaier method [31]. The resultant solution with a pH $\sim$ 7 was ultrasonicated for 2 h in ice-water bath to obtain GO

suspension. The concentration of GO in the suspension was determined by drying some suspension in a vacuum oven at 80 °C for 24 h and then weighing the dried GO. Various suspensions with different concentrations of GO were produced by controlling the time of centrifugation.

In situ reduction-assembly using PPD as the reducing and functionalizing agent in the presence of ammonia solution was carried out to prepare GPA. In a typical procedure, PPD (112 mg) and ammonia solution (135 μ L) were added to GO suspension (5 ml) with a concentration of 4.5 mg ml⁻¹. Subsequently, the mixture was magnetically stirred for 10 min and then placed in an oil bath at 90 °C for 6 h without stirring. The resulting cylindrical structure of graphene hydrogel was dipped in water for 48 h to remove residual impurities and then the wet hydrogel was lyophilized to obtain GPA. A schematic of this process is shown in Fig. S1. To investigate the effect of ammonia on the reduction, GO was reduced by PPD alone without ammonia under the same conditions and the resultant graphene was designated as GO-PPD.

2.3. Preparation of epoxy/graphene composites

The epoxy/graphene composites were fabricated by two methods: vacuum-assisted suction and conventional solution mixing. In the suction method, the epoxy monomer and curing agent (D2000) in a 10:26.3 weight ratio was infiltrated into the previously prepared GPA. The obtained complex was degassed in a vacuum oven, pre-cured in an oven at 90 °C for 2 h and

then post-cured at 120 °C for 6 h. In the solution mixing process, grounded GPA was dispersed and exfoliated in dichloromethane using the ultrasonicator for 1 h. The resulting suspension was then mixed with epoxy monomer and curing agent, D2000. After homogenizing for 2 h using an IKA T18 homogenizer (Germany) at ambient temperature, the mixture was heated for 6 h at 60 °C in the vacuum oven to thoroughly remove the residual solvent. Afterwards, the mixture was poured into stainless steel moulds, pre-cured at 90 °C for 2 h followed by post-curing at 120 °C for 6 h.

2.4. Characterization

The morphology of the prepared GPA was observed with a JEOL FE-JSM-6701F field-emission scanning electron microscope (SEM) at an accelerating voltage of 5 kV. X-ray diffraction (XRD) spectra were recorded using a Bruker AXS D8 Advance diffractometer with CuK α radiation ($\lambda = 1.54 \text{ \AA}$) at a generator voltage of 40 kV and a generator current of 40 mA with a scanning speed of 10°/min from 3 to 40°. The surface composition of GO and GPA were characterized by a ThermoVG RSCAKAB 250X high-resolution X-ray photoelectron spectroscope (XPS). Fourier-transform infrared spectroscopy (FTIR) was measured with a Nicolet Nexus 670 spectrometer. Raman spectra were recorded with a Renishaw inVia Raman microscope (Britain) using an excitation wavelength of 514.5 nm. Thermogravimetric analysis (TGA) was carried out on a TA Q50 thermal analyzer under a nitrogen atmosphere at a heating speed of 10 °C/min. The PPD content in GPA was measured

with an Elementar Analysensysteme GmbH Vario EL cube elemental analyzer. The volume conductivities of GPA and the epoxy composites were measured with a 4-Probes-Tech RTS-8 four-probe resistivity meter (China) when the conductivity is higher than 1×10^{-4} S/m, whereas a Keithley Instruments 6517B resistivity meter (USA) was used when the conductivity was lower than 1×10^{-4} S/m. Compression properties of GPA and its epoxy composites were measured using an Instron 1185 testing machine (UK) at a constant strain rate 1 mm/min. A Hot Disk Techmax TPS1500 thermal meter (Sweden) was used to characterize the thermal conductivities of GPA.

3. Results and discussion

3.1. Synthesis and morphology of GPA

In a typical synthesis procedure of GPA, a dark brown colored solution of GO (4.5 mg ml^{-1}), PPD and ammonia is transformed to a black ‘free-standing’ hydrogel, which is subsequently converted to GPA after freeze-drying (Fig. 1a). It is interesting to note that the volume shrinkage is negligible using this methodology. This is quite different from graphene hydrogels prepared by other methods where drastic reduction in volume was observed [19,28]. In the current work, it is presumed that PPD with its conjugated structure and $-\text{NH}_2$ groups plays an important role as it easily attaches to surfaces and galleries of GO sheets through π - π interactions or H-bonding. In addition, PPD could be grafted onto the sheets through the nucleophilic substitution reaction between the epoxide groups of GO and the

amine groups of PPD during the reduction process. PPD grafted or adsorbed on the sheets would prevent the self-stacking of GO during the reduction, and in turn preventing the volume shrinkage. A similar result was reported by Qu et al. with pyrrole [29]. The content of PPD in GPA is ~39 wt% according to elemental analysis.

Fig. 1. (a) Pictorial representation of the fabrication of GPA; (b) and (c) SEM images of GPA at different magnifications; (d) GPA in diverse shapes (and volumes); and (e) a digital image showing that GPA can support a 500 g weight, which is 6000 times its own weight.

This property of negligible volume shrinkage is extremely important to retain deserved shapes, and therefore, the current reduction-assembly methodology provides an opportunity to exploit these graphene aerogels in different applications. As shown in Fig. 1b and c, GPA exhibits a highly porous structure. Despite this, GPA shows good structural integrity as it

does not collapse or crumble even when loaded with a weight of more than 6000 times its own weight (Fig. 1e).

3.2. Efficiency of the reduction process

To have a thorough understanding of the reduction process of GO with PPD and ammonia solution, different techniques like FTIR, XPS, XRD, Raman spectroscopy and TGA were used. This section highlights the results based on these various techniques from different viewpoints. Fig. 2 compares the FTIR spectra of GO, GO-PPD and GPA. The spectrum of GO, as expected, exhibits the presence of strong peaks corresponding to oxygen-containing groups, such as 1704 cm^{-1} (C=O stretching vibration from carbonyl and carboxylic groups), 1620 cm^{-1} (C=C in aromatic ring), 1390 cm^{-1} (C-OH deformation vibration), 1056 cm^{-1} (C-O-C in epoxide). Besides these sharp features, the broader peak around 3405 cm^{-1} is assigned to hydroxyl groups. However, in the spectrum of GPA, the intensities of these peaks corresponding to oxygen-containing groups are reduced significantly suggesting the reduction of GO with PPD in the presence of ammonia. Furthermore, a new peak at 1570 cm^{-1} corresponding to the N-H bending vibration appeared, implying the formation of -C-NH-C- bonds resulting from the nucleophilic substitution reaction between the epoxide group and the amine group.

Fig. 2. FT-IR spectra of PPD, GO and GPA.

Similar conclusions were also derived from XPS measurements (Fig. 3). In Fig. 3a, the three different peaks at 286, 400 and 533 eV are related to C, N and O, respectively. The atomic ratio of carbon and oxygen (C/O ratio) increased from 2.8 for GO to 6.1 for GO-PPD. This ratio further increased to 8 with ammonia solution. This implies that most of the oxygen-containing groups have been removed. This is evident even when comparing the intensities of the peaks related to oxygen-containing groups in GO, GO-PPD and GPA in their C1s XPS spectra (Fig. 3c and d). Besides, the appearance of the new characteristic peak corresponding to C–N bond (286.8 eV) indicates the successful covalent bonding between GO and PPD.

Fig. 3. XPS spectra of (a) general spectra, (b) GO, (c) GO-PPD and (d) GPA.

In Fig. 4 XRD patterns of GO, GO-PPD and GPA are shown, which reveal information on their structural evolution. GO exhibits an interlayer distance of 0.69 nm corresponding to 2θ of $\sim 12.8^\circ$ pointing to an ordered structure. For GO-PPD, the interlayer spacing increased to 1.1 nm (8.2°) owing to the chemical grafting of PPD onto GO by nucleophilic substitution reaction. The appearance of a broad peak at 25.9° is an indication of the restacking of exfoliated graphene sheets. By adding ammonia solution, a broad peak appears at 7.5° (1.2 nm) suggesting a poor ordering of graphene sheets due to higher extent of intercalation than that of GO-PPD. This result shows that GPA is composed of few-layer stacked graphene

sheets [19,25].

Fig. 4. XRD patterns of GO, GO-PPD, and GPA.

To further elaborate on the order/disorder in the sp^2 network, Fig. 5 shows the Raman spectra of graphite, GO, GO-PPD and GPA. Two main characteristic peaks are well known for graphene materials, the G mode due to first order scattering of the E_{2g} photon of sp^2 C atoms ($\sim 1575\text{ cm}^{-1}$) and the D mode resulting from a breathing mode of κ -point photons of A_{1g} symmetry ($\sim 1350\text{ cm}^{-1}$). As expected, the G band of natural graphite is located at 1581 cm^{-1} and no obvious D band is observed owing to its structural perfection. However, GO, GO-PPD and GPA exhibit a D peak centered at $\sim 1345\text{ cm}^{-1}$ as a result of the oxidation-induced defects. Also, GPA and GO-PPD show higher intensity ratios of D-band to G-band as

~1.23 and 1.18, respectively, compared to that of GO (~0.93). The higher ratio quantifying the density of defects in sp^2 carbon atoms suggests an increase in the number of smaller graphene domains [32,33].

Fig. 5. Raman spectra of graphite, GO, GO-PPD and GPA.

Generally, it is believed that the thermal stability of GO would be improved due to the removal of its oxygen functionalities. GPA shows an improved thermal stability in comparison with GO-PPD and GO (Fig. 6). GO exhibits a major mass loss of 27.4 wt% around 250 °C, which is ascribed to the removal of labile oxygen-containing functional groups, yielding CO_2 , CO and steam. The mass loss of GO is 34.6 wt% at 400 °C due to the removal of more stable oxygen functionalities. Whereas, the mass losses at 400 °C for GO-

PPD and GPA are 25.0% and 18.3%, respectively, indicating the extent of reduction consistent with XRD and Raman results.

Fig. 6. TGA curves of (1) PPD, (2) GO, (3) GO-PPD and (4) GPA.

3.3. Compressive properties

Previous studies have demonstrated compressive recovery for foam-like CNT and graphene materials [17,28], which is also observed in the case of GPA. The stress-strain curve in Fig. 7a exhibits a linear regime at below 50% strain and a non-linear regime between 50% and 60% strain values. The deformation during the whole loading process is still recoverable as shown in Fig. 8. This could be explained by elastic bending and elastic buckling of cell walls [17,34]. Furthermore, it is seen that the stress-strain behavior changes with a clear yield point for GPA with higher starting GO concentration of 20 mg ml⁻¹ (Fig. 7b). It is evident that the

behavior of low density GPA fits the first regime, a linear-elastic region where cell walls only bend and buckle. For GPA with high density, the compressive curve includes the whole three regions, linear elastic region, collapse region and densification region, indicating an irreversible process of collapse of cell walls. This is evident from the crumbled aerogel with starting GO concentration of 20 mg ml^{-1} (inset of Fig. 7b). But the specimen with a low starting GO concentration of 4.5 mg ml^{-1} recovers its original macroscopic shape.

Fig. 7. Compressive stress-strain curves of GPA with various starting GO concentrations of (a) 4.5 mg ml^{-1} and (b) 20 mg ml^{-1} .

Fig. 8. Digital images showing recovery of GPA (starting concentration of GO is 4.5 mg mL^{-1}).

Nevertheless, both compressive strength and modulus increase with GO concentration as shown in Fig. 9. When the starting GO concentration increase from 1 to 10 mg mL^{-1} , the compressive strength of GPA increased by nearly 18 times from 7.7 to 146 kPa, and similarly, the compressive modulus of GPA is improved from 20.4 to 856 kPa. A typical compressive stress-strain behavior of foams is shown in Fig. S2 [35].

Fig. 9. Mechanical properties of GPA with different starting GO concentrations.

3.4. Electrical and thermal conductivities

Thermal and electrical conductivities of GPA with different starting concentrations of GO are listed in Table 1. Although electrical conductivity values are as expected, due to the porous

3D structure, the in-plane thermal conductivity of GPA could reach only $0.04 \text{ W m}^{-1} \text{ K}^{-1}$ and is close to widely used heat insulating materials such as polyurethane foam [36]. But the thermal conductivity of (non-porous) graphene is as high as $3000 \text{ W m}^{-1} \text{ K}^{-1}$ [1].

Table 1. Thermal and electrical conductivities of GPA with different starting GO concentrations.

GO concentration (mg/ml)	Sample ID	Thermal conductivity (W/mK)	Electrical conductivity (S/m)
1.0	GPA-1	0.040	1.5×10^{-2}
4.5	GPA-4.5	0.041	4.3×10^{-1}
10.0	GPA-10	0.044	5.7×10^{-1}
20.0	GPA-20	0.053	1.0

Besides the aerogel, electrical conductivities of the epoxy/graphene composites prepared by the two different methods (solution mixing and vacuum-assisted impregnation) based on GPA were also studied. From Fig. 10, it is evident that the ultrasonication-assisted dispersion of GPA is nominal in improving the electrical conductivity of epoxy composite compared to vacuum-assisted impregnation process. A percolation threshold of 0.91 vol% is observed with the former process, which is similar to that obtained with fully reduced (at 250°C) epoxy/graphene composites [10]. With $\sim 1.5 \text{ vol\%}$ graphene, the solution-casted epoxy composite yielded a value of $\sim 2 \times 10^{-11} \text{ S/m}$. But with the vacuum-assisted impregnation, the electrical conductivity value reaches $4 \times 10^{-2} \text{ S/m}$ with only $\sim 0.21 \text{ vol\%}$ graphene. This is almost 13 orders of magnitude higher than that of neat epoxy. In fact this value of electrical conductivity of the GPA/epoxy composite is nearly 2 orders of magnitude higher than the

best value reported for the composites filled with 2D graphene nanosheets at the similar loading [1]. This excellent electrical conductivity results from the conductive graphene network and its good wetting with the epoxy matrix [12,37], which keeps the matrix and the conductive component from segregation or agglomeration (Fig. 11).

Fig. 10. Electrical conductivities of epoxy/graphene composites prepared by (a) solution mixing and (b) vacuum-assisted impregnation.

Fig. 11. SEM images of the epoxy/graphene composite with 0.47 vol% of graphene prepared by the vacuum-assisted impregnation at different magnifications.

Furthermore, the compressive strength of these composites prepared by vacuum-assisted

impregnation is impressive. The compressive strength at the strain of 10% for the composite with 0.47 vol% graphene is increased by 92.6% to 0.53 MPa relative to the basic resin. As shown in Fig. 12, further improvement to compressive strength is realized (0.75 MPa) on increasing graphene loading to 0.95 vol%.

Fig. 12. Compressive strength at 10% strain of epoxy/graphene composites prepared through vacuum-assisted impregnation.

4. Conclusions

We developed a simple method to prepare graphene aerogel with highly porous structure, low density, robust mechanical properties and improved electrical conductivity. The in situ reduction-assembly method was used in combination with PPD and NH_3 solution. Especially, through the vacuum-assisted impregnation, as-prepared aerogel can be used to manufacture

electrically conductive epoxy/graphene composites with improved mechanical properties. We believe that the strategy developed here can be applied for a variety of applications due to its simplicity, scalability and functionality.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version.

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Research highlights

- Graphene aerogel was prepared from graphene oxide by an in situ reduction-assembly
- The aerogel exhibits high electrical conductivity and good mechanical property
- The epoxy composite exhibits an high electrical conductivity
- The compressive strength of epoxy is increased by ~178% with 0.95 vol% of graphene