FREEZE-CAST GRAPHENE AEROGELS AND THEIR EPOXY COMPOSITES WITH ULTRALOW PERCOLATION THRESHOLD

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Abstract
A novel unidirectional freeze casting method is used to fabricate graphene aerogels (GAs) having a highly aligned porous structure. The high orientation of graphene sheets in the as-fabricated GAs results from the expulsion of graphene oxide (GO) sheets by rapidly advancing ice fronts, forcing them to gather between the aligned ice crystals. The resulting unidirectional GAs (UGAs) possess ultralow densities with high porosities, large surface areas and excellent electrical conductivities after reduction. Solid UGA/epoxy composites are fabricated by vacuum-assisted infiltration of liquid epoxy into the pores of UGA, followed by curing. The composites exhibit an extremely low percolation threshold of 0.007 vol% due to the 3D interconnected, aligned conductive networks of UGA. This value, to the authors' best knowledge, is among the lowest percolation thresholds for all graphene/polymer composites reported in the open literature. In addition, significant anisotropic electrical conductivities of the composites are observed, which is potentially useful for many niche applications. An improved analytical model is developed based on the interparticle distance concept to predict the percolation behavior of the current UGA/epoxy composites. Critical factors that control the percolation threshold of nanocomposites are identified, including the orientation states and the aspect ratio of fillers.

1. Introduction

Conductive polymer composites are of interest for a number of important applications, such as rechargeable batteries and electromagnetic interference (EMI) shielding devices [1, 2]. Generally, conductive polymer composites are fabricated by incorporating conducting fillers into the polymer matrixes. With gradually increasing the filler content, the composites will exhibit an insulator-to-conductor transition, known as the percolation phenomenon, and the percolation threshold can be determined by a sharp rise in conductivity curve [3]. Previous theoretical and experimental studies have shown that the percolation threshold depends mainly on the geometry, volume fraction and the aspect ratio of fillers in particular. Thanks to its ultrafast electron mobility and extremely high aspect ratio, graphene has been extensively studied to fabricate conductive polymer composites with high performance. However, the electrical properties obtained are still far from those anticipated from the inherent properties of graphene even though many strategies have been explored, including alignment of graphene sheets and self-assembly of graphene inside the polymer matrix [4, 5]. In light of this, a new approach has been taken to synthesize three-dimensional (3D) graphene with interconnected conductive networks.

Amongst several different types of 3D graphene materials, graphene aerogels (GAs) have attracted tremendous attention [6] because of their unique properties and potential applications. However, the gelation process of GO dispersion during the formation of hydrogels inevitably resulted in

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agglomeration of GO sheets, limiting their performance. More recently, a freeze casting method was employed to fabricate GAs, effectively eliminating the agglomeration issue to achieve ultralow densities [7]. As a wet shaping technique, the freeze casting method can be used to produce materials with complex shapes and desired morphologies if the freezing conditions are properly controlled [8]. This paper reports the fabrication of unidirectional GAs (UGAs) that possess unusual characteristics arising from the anisotropic porous structure, including ultralow densities, large surface areas and excellent electrical conductivities. The UGA/epoxy composite made therefrom presents unique anisotropic electrical conductivities along with one of the lowest percolation thresholds among all epoxy-based composites reported in the literature. A theoretical model is developed to explain the percolation behavior of the composites and the effect of filler orientation on percolation threshold of aligned composites.

2. Experimental

2.1. Fabrication of UGAs and UGA/epoxy composites

GO dispersion was prepared based on the modified Hummers method using natural graphite flakes (supplied by Asbury Graphite Mills) following our previous studies [9]. A unidirectional freeze casting method was employed to fabricate UGAs using an apparatus shown in Fig. 1a. Briefly, GO dispersions with concentrations ranging from 0.2 to 3.0 mg/ml were poured into a polypropylene (PP) container with aluminum bottom for effective thermal conduction between the inside GO dispersion and the underneath liquid nitrogen. The PP container was tightly wrapped with a thermal insulator Styrofoam and placed on the top surface of a metal scaffold, which in turn rested in a pool of liquid nitrogen with the identical depth as the metal scaffold. Therefore, a large temperature gradient was established between the bottom (–196 ℃) and the top (room temperature (RT)) of the GO dispersion, so that the ice crystals grew vertically. After freeze drying (SuperModulyo, Thermo Fisher) of the freeze-cast GO dispersion, a GO aerogel with an aligned porous structure was formed. The GO aerogel was subsequently reduced to UGA by stabilizing in air at 200 ℃ for 2 h and then thermally treating at 900 ℃ in a dry N_2 environment for 2 h at a constant heating rate of 5 ℃/min.

UGA/epoxy composites were fabricated using a vacuum infiltration method, as shown in Fig. 1b. Briefly, epoxy resin (LY1556), curing agent (triethylenetetramine), and acetone were mixed by vigorous stirring at an epoxy to curing agent to acetone weight ratio of 100:12:10. The diluted epoxy/curing agent mixture was placed in a vacuum oven to evaporate acetone for 2 h at RT, and then heated to 60 ℃ to lower the resin viscosity. The obtained mixture was poured into the UGA, followed by infiltration under vacuum at 60 ℃ for 1h. Finally, the resin-infiltrated UGA was cured at 80 ℃ for 30 min and post-cured at 110 ℃ for 2 h.

2.2. Characterization

The surface chemistry of UGAs was evaluated by X-ray photoelectron spectroscopy, and the degree of reduction of UGAs and the anisotropic graphene structure inside the composites were examined using Raman spectroscopy. The morphologies of UGAs were characterized on a scanning electron microscope (SEM) using secondary electron beams at an acceleration voltage of 20 kV. The surface areas of UGAs were measured based on the Brunauer-Emmett-Teller (BET) method, and the nitrogen adsorption/desorption isotherm curves were obtained at 77 K on an automated adsorption device. The electrical conductivities of UGAs and UGA/epoxy composites were measured using the four–point probe method. The contact points between the probes and the sample surface were coated with silver paste to reduce the contact resistance.

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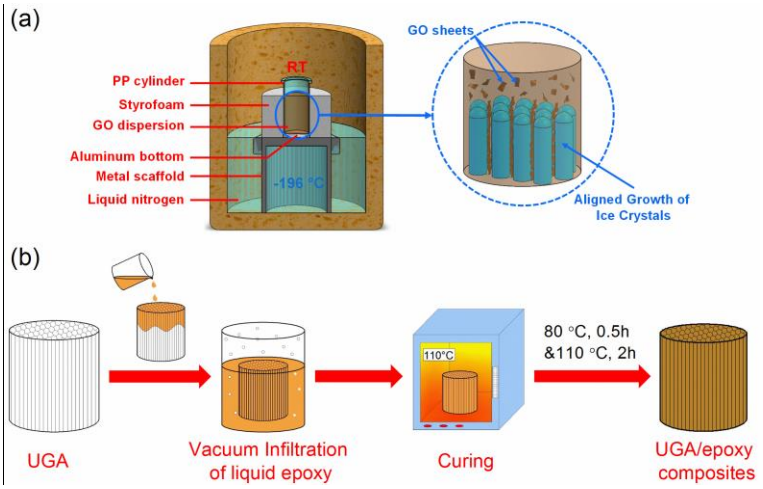

Figure 1. (a) The apparatus used for unidirectional freeze casting of GO dispersion and the mechanism of forming aligned graphene structure; and (b) the fabrication process of UGA/epoxy composites.

3. Results and discussion

3.1. Morphologies and properties of UGAs

Fig. 2 gives the typical morphologies of the UGAs produced using different GO concentrations. The UGAs made with GO concentrations of 1.0 and 2.0 mg/ml showed highly aligned porous structures resulting from the unidirectional freeze casting process, during which GO sheets were expelled by the rapidly advancing ice front and gathered between the aligned ice crystals [10]. As highlighted in Fig. 2b and 2c, the long and continuous graphene main skeleton was connected by ribbon-like short ligaments in the transverse direction to form a 3D interconnected structure. The UGAs made with GO at a low concentration of 0.5 mg/mL, however, did not show similar aligned and continuous graphene sheets, as shown in Fig. 2a. Instead, they exhibited loosely interconnected graphene sheets with little alignment. The GO sheets were too far from each other in the dispersion made with a low GO concentration, unable to form continuous and aligned graphene sheets.

The XPS and Raman spectra present the chemical compositions of GO and UGA, as shown in Fig. 3a and b. The XPS C 1s deconvoluted spectra (Fig. 3a) indicate that the oxygenated functional groups, including epoxy, carboxyl and carbonyl groups, were almost fully removed after the thermal reduction at 900 °C, leading to a dramatically increased C/O atomic ratio from 2.2 for GO to 37.5 for the UGA. The Raman results (Fig. 3b) further confirmed the reduction: the D- to G-band peak intensity ratio, I_D/I_G, decreased from 2.53 to 1.73 after reduction, as a consequence of the removal of oxygenated functional groups from the GO basal plane. The efficient reduction process used in this work gave the resulting UGAs excellent electrical conductivities as high as 0.17 S/cm and ultralow densities as low as 0.23 mg/cm^3, as shown in Fig. 3c. Both the density and electrical conductivity presented an increasing trend with increasing GO concentration, owing to the formation of increasingly denser conductive networks. Apart from the excellent electrical conductivities, a large BET surface area of 432 m^2/g was achieved for the UGAs fabricated using a GO concentration of 2.0 mg/ml. These excellent properties make the UGA an ideal filler for fabricating composites with outstanding functional capabilities at very low filler contents.

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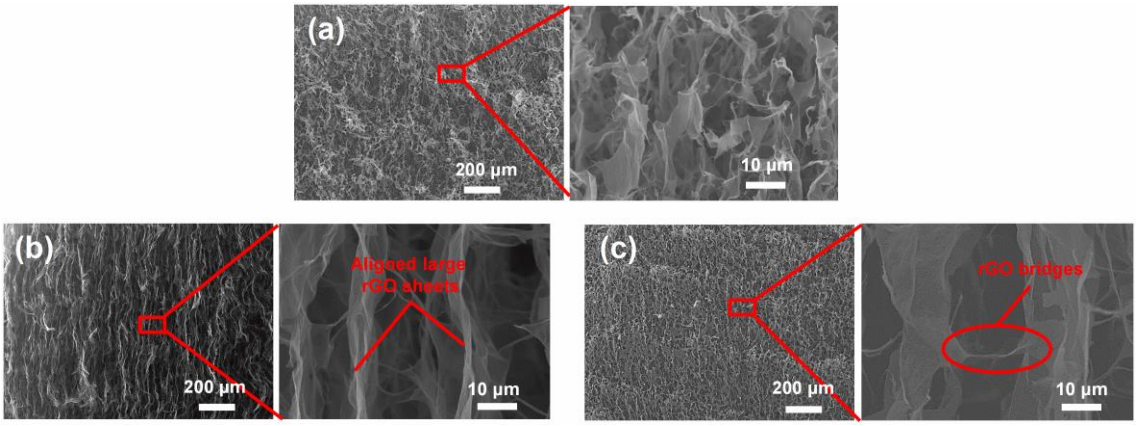

Figure 2. Morphologies of UGAs made with GO concentrations of (a) 0.5, (b) 1.0, and (c) 2.0 mg/ml.

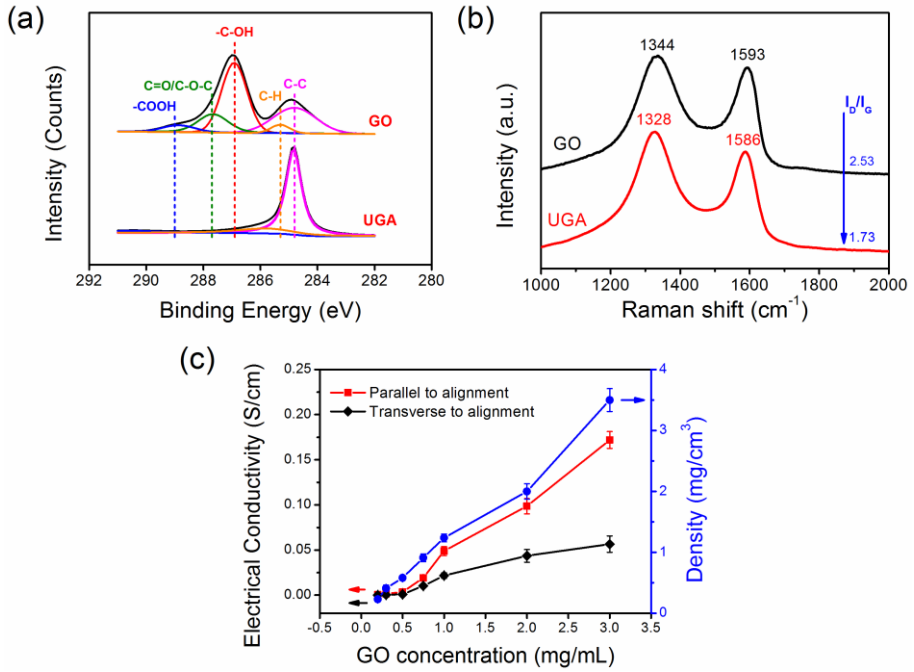

Figure 3. (a) XPS C 1s deconvoluted spectra; (b) Raman spectra of GO and UGA; and (c) densities and electrical conductivities measured in the orthogonal directions of UGAs plotted as a function of GO concentration.

3.2. Electrical properties of UGA/epoxy composites

Fig. 4a shows the electrical conductivities of the UGA/epoxy composites along the two orthogonal directions as a function of graphene content. With the addition of only 0.01 vol% graphene, the conductivity increased by almost eight orders of magnitude from 10^{-12} S/cm for the neat epoxy to 10^{-4} S/cm for the composites. It should be noted that 0.01 vol%, or an equivalent GO dispersion of 0.2 mg/mL, was the lowest graphene content that could form a GA, and further lowering the GO concentration was very difficult because the small amount of GO sheets could not be assembled into a stable 3D structure, giving rise to only very low conductivities of the composites made therefrom. The conductivity of the composites increased with graphene content and a further increase in graphene content beyond 0.08 vol% resulted in saturation with a high value of ~0.12 S/cm, which is considered

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to be sufficient for many practical applications. The percolation threshold of the composites, ρ_c, was measured using the power law equation [11]:

$$\phi_c = \phi_f(\rho - \rho_c)^n \quad (1)$$

where ϕ_c is the conductivity of the composite, ϕ_f is the conductivity of filler and ρ is the filler content. The inset of Fig. 4a shows a log–log plot of ϕ_c as a function of $(\rho-\rho_c)$, giving the percolation threshold of ρ_c = 0.007 vol%. To the best of our knowledge, this value is the lowest percolation threshold achieved for all graphene/polymer composites.

It is obvious from Fig. 4a that the conductivities were higher in the alignment direction than that perpendicular to it. The anisotropic electrical conductivities are the consequence of the anisotropic graphene structure within the composites, which was also proven by the polarized Raman spectra (Fig. 4b). There were significant differences in intensity of the Raman G- and D-bands obtained along the two orthogonal directions. The much higher intensity when measured in the alignment direction indicates a higher resonance, confirming significant alignment of graphene sheets in the composites [5].

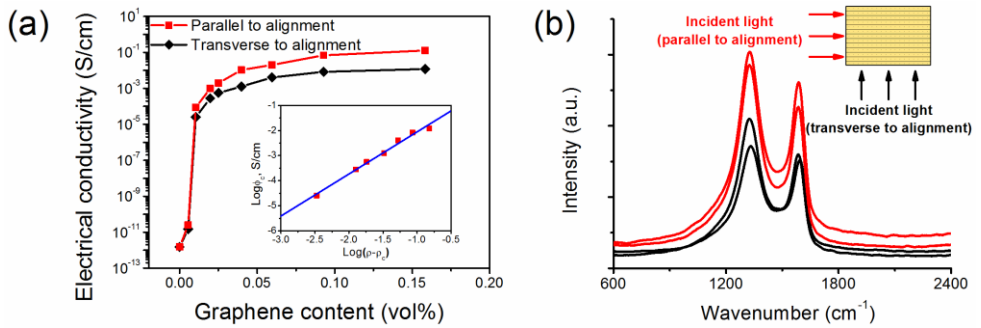

Figure 4. (a) Electrical conductivities of UGA/epoxy composites, ϕ_c, measured in the orthogonal directions, as a function of graphene content, ρ. Inset: log–log plot of the conductivity as a function of $(\rho-\rho_c)$; and (b) polarized Raman spectra for composites at a graphene content of 0.16 vol%.

3.3. Prediction of percolation threshold

An analytical model was developed to predict the percolation threshold of the current UGA/epoxy composites based on the average interparticle distance (IPD) theory [3]. According to the IPD model, the volume fraction, V_c, required for a single type of fillers with various shapes to form conductive networks is given by:

$$V_c = \frac{\pi}{4}\left(\frac{1}{R}\right) \quad (2)$$

where R is defined as the 'percolation factor' that depends on the size, shape and the orientation state of the fillers in the composites. For 2D disk-shaped fillers with large aspect ratios (D/t) such as graphene, the percolation factor, R_S, is defined as:

$$R_S \approx \left(\frac{D}{t}\right)\langle cos^2\,\theta\rangle^3 \quad (3)$$

where D and t are the diameter and thickness of graphene, respectively, and $\langle cos^2\theta \rangle$ is the average orientation angle between the fillers and the direction of preferred orientation. In the IPD model, it is assumed that the composite is divided into cubic elements, each containing one filler in the center, and the percolation occurs when the unit volume is filled with single type of cubic elements. Similarly, for composites containing two different groups of fillers, we may assume that the percolation occurs when

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the unit volume is filled with two groups of cubic cells, as shown in Fig. 5a. Therefore, the percolation factor for the current UGA/epoxy composites containing two groups of graphene, R_T, is obtained as:

$$R_T = \frac{\frac{V_1}{V_2}R_1 + R_2}{1+\frac{V_1}{V_2}} = \frac{D}{t}\left(\frac{\frac{V_1}{V_2}\langle\cos^2\theta_1\rangle^3 + \langle\cos^2\theta_2\rangle^3}{1+\frac{V_1}{V_2}}\right) \quad (4)$$

where R_1 and R_2 are the percolation factors of Group 1 and 2, and V_1 and V_2 are their volume fractions in the composite, respectively. Therefore, the corresponding percolation threshold, V_c, can be calculated by combining Eqs. (2) and (4):

$$V_c = \frac{\pi}{4\left(\frac{D}{t}\right)}\left[\frac{\left(1+\frac{V_1}{V_2}\right)}{\frac{V_1}{V_2}\langle\cos^2\theta_1\rangle^3 + \langle\cos^2\theta_2\rangle^3}\right] \quad (5)$$

According to Eq. (5), to predict the percolation threshold of UGA/epoxy composites, several critical factors, such as the aspect ratio, V_1/V_2, and mean orientation angles need to be determined. The aspect ratio of graphene sheets used here was ~16000, consistent with our previous study [9]. V_1/V_2 and the mean orientation angles were determined from the orientation distribution analysis of graphene sheets in the SEM images of UGAs using the Image Pro Plus software. Typically, at least 200 graphene sheets were randomly selected from the SEM images, then a reference line was drawn on each image and acute angles formed between the reference line and graphene sheets were recorded. The graphene sheet orientation histograms corresponding to the SEM images of UGA made using different GO concentrations, shown in Figs. 5b–d, were fitted using the GaussAmp peak function to obtain the orientation distribution function curve, $N(\theta)$:

$$N(\theta) = N_0 + Ae^{-\frac{(\theta-\theta_c)^2}{2w^2}} \quad (6)$$

where θ_c is the angle corresponding to the center of the peak, N_0 is the height of the baseline, A is the amplitude of the peak, and w depends on the full width at half maximum (FWHM), presenting the angle of deviation from the center of the peak, which follows the relation:

$$w = \frac{FWHM}{2\sqrt{ln4}} \quad (7)$$

It is seen from Figs. 5b–d that the three different UGAs showed similar orientation distributions containing two obvious peaks, namely a high peak centered at ~0° corresponding to the continuous and aligned graphene sheets (Group 1) and a low peak centered at ~±90° corresponding to the ligaments in the transverse direction (Group 2). In the current study, V_1/V_2 was determined from N_1/N_2, because Groups 1 and 2 contained the same kind of graphene sheets, thus their volume fractions are proportional to the number of fillers in the respective Groups. N_1 and N_2 were determined from the orientation histograms by calculating the total filler numbers in the range of angles corresponding to Group 1 and 2, respectively. $\langle\cos^2\theta_1\rangle$ and $\langle\cos^2\theta_2\rangle$ were calculated using Eqs. (8) and (9) [12]:

$$\langle\cos^2\theta\rangle = \int_0^{\pi/2} N(\theta)\cos^2\theta\sin\theta\, d\theta \quad (8)$$

$$\int_0^{\pi/2} N(\theta)\sin\theta\, d\theta = 1 \quad (9)$$

The percolation thresholds, V_c, were predicted using the filler parameters, $\langle\cos^2\theta_1\rangle$, $\langle\cos^2\theta_2\rangle$, and V_1/V_2, and the percolation factors, which are listed in Table 1. The prediction ranged from 0.0087 to 0.0135 vol%, which in general agreed well with the experimental result of 0.007 vol%.

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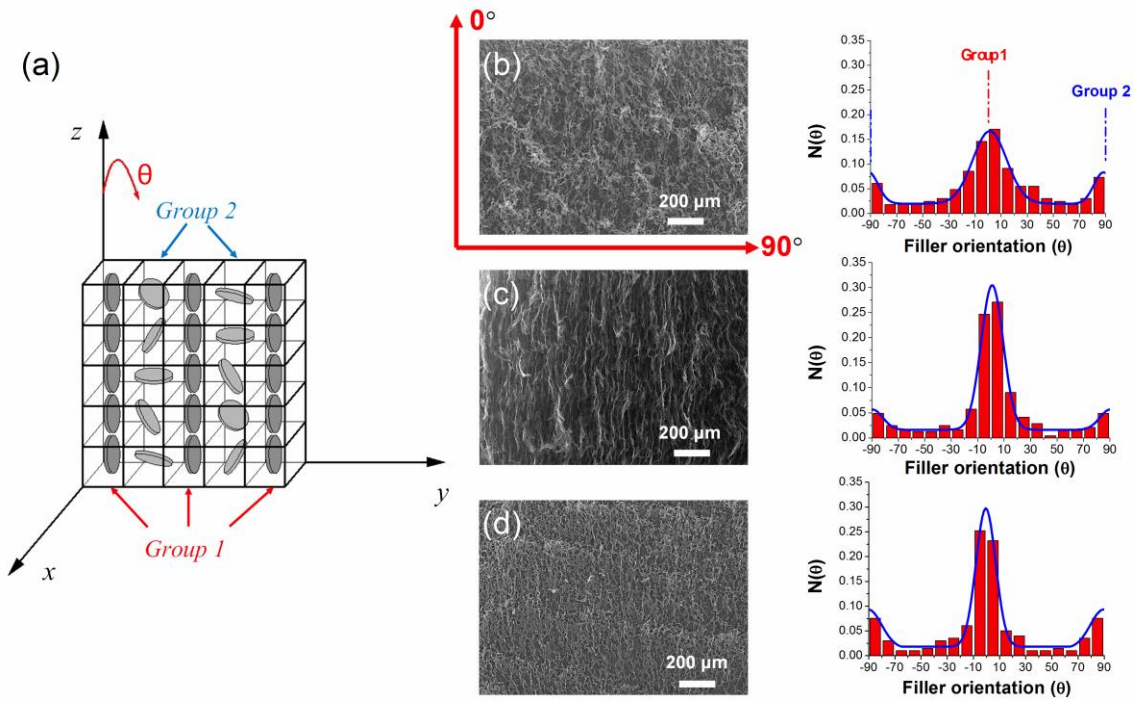

Figure 5. (a) Schematic of the IPD model for UGA/epoxy composites with two groups of graphene sheets; SEM images and the corresponding graphene orientation distributions of UGAs made with GO concentrations of (b) 0.5, (c) 1.0 and (d) 2.0 mg/mL, equivalent to graphene contents of 0.025, 0.06 and 0.09 vol%, respectively.

Table 1. The percolation thresholds, V_c, of the UGA/epoxy composites predicted using the filler parameters, $\langle\cos^2\theta_1\rangle$, $\langle\cos^2\theta_2\rangle$ and V_1/V_2 determined from the orientation distribution analysis of graphene sheets in Fig. 5, and the calculated R values for different GO concentrations.

Concentration of GO used to make UGA (mg/mL)	$\langle\cos^2\theta_1\rangle$	$\langle\cos^2\theta_2\rangle$	V_1/V_2	R	*Predicted* V_c (vol%)
0.5	0.78	0.08	3.05	5811	0.0135
1.0	0.87	0.04	4.30	8607	0.0090
2.0	0.91	0.06	3.00	9023	0.0087

4. Conclusions

A novel unidirectional freeze casting method was developed to fabricate UGAs with ultralow densities, high porosities and large surface areas. UGA/epoxy composites was fabricated by infiltrating liquid epoxy resin under vacuum, followed by curing of the liquid epoxy. The composites delivered an ultralow percolation threshold of 0.007 vol% with significant anisotropic electrical properties in two orthogonal directions. An interparticle distance model was developed to predict the percolation thresholds of UGA/epoxy composites. The percolation threshold of nanocomposties depended on several important factors, including the orientation state and the aspect ratio of fillers. The predicted percolation threshold agreed very well with the experimental results.

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