



Decoration of defect-free graphene nanoplatelets with alumina for thermally conductive and electrically insulating epoxy composites

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ABSTRACT

Although graphene can significantly improve the thermal conductivity of polymers due to its high aspect ratio and excellent thermal conductance, it causes serious reduction in electrical insulation and thus limits the wide applications of its polymer composites in the thermal management of electronics and systems. To solve this problem, electrically insulating Al_2O_3 is used to decorate high quality (defect-free) graphene nanoplatelets (GNPs). Aided by supercritical carbon dioxide (scCO_2), numerous Al_2O_3 nanoparticles are formed on the inert GNP surfaces by fast nucleation and hydrolysis of $\text{Al}(\text{NO}_3)_3$ precursor followed by calcination at 600°C . Alternatively, by controlling nucleation and hydrolysis of $\text{Al}_2(\text{SO}_4)_3$ precursor with a buffer solution, $\text{Al}_2(\text{SO}_4)_3$ slowly nucleates and hydrolyzes on GNPs to form aluminum hydroxide, which is then converted to Al_2O_3 nanolayers without phase separation by calcination. Compared to the Al_2O_3 @GNP hybrid with the assistance of scCO_2 , the hybrid prepared with the help of a buffer solution is highly efficient in conferring epoxy with excellent thermal conductivity while retaining its electrical insulation. Epoxy composite with 12 wt% of Al_2O_3 @GNP hybrid exhibits a high thermal conductivity of $1.49\text{ W}/(\text{mK})$, which is 677% higher than that of neat epoxy, indicating its high potential as thermally conductive and electrically insulating fillers for polymer-based functional composites.

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1. Introduction

With high integration and miniaturization of electronic devices, the rapid and efficient dissipation of accumulated heat has become more and more crucial for the normal function of various high-performance devices [1–7]. Thermally conductive polymer composites are one class of important thermal management materials for heat transport and dissipation, which are widely applied in applications including light-emitting diode (LED) and electronic packaging due to their lightweight and ease of processing [1–11].

Owing to the low thermal conductivity of most polymers ($\sim 0.2\text{ W}/(\text{mK})$) [10,11], various thermally conductive fillers are used to enhance their thermal conductivities. Among these fillers, electrically insulating ceramic fillers, such as Al_2O_3 [12], BN [13] and AlN [14], can confer upon polymers high thermal conductivity while the filled composites maintain electrically insulating. Usually high loading ($>50\text{ wt}\%$) is required to obtain polymer composites with satisfactory thermal conductivities, which seriously damages the mechanical properties of polymers and causes processing difficulties of the composites [5,7,11].

Compared to ceramic fillers, two-dimensional graphene has a higher thermal conductivity ($\sim 5300\text{ W}/(\text{mK})$) and is thus more efficient in improving the thermal conductivity of polymers [11,15]. However, its high electrical conductivity makes it impossible to prepare thermally conductive but electrically insulating polymer/graphene composites because electrical conductivity is more sensitive to the content of graphene than thermal conductivity, and high electrical conductivity can be readily achieved at low loadings

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of fillers [16,17] before obvious increases in thermal conductivity of polymer composites are found. If thermally and electrically conductive polymer composites are used for electronic devices, special structural design of electronic components has to be made to avoid electric short circuit occurring inside the devices [3].

To fully utilize the excellent thermal conductivity of graphene for electrically insulating polymer composites, various techniques have been developed to suppress its high electrical conductivity by constructing insulating nanoparticles or nanolayers on graphene surfaces [3,4,11]. Hsiao et al. [1] coated thermally reduced graphene oxide (TGO) with silica by a sol-gel method. With 1 wt% of the TGO-silica hybrid, its epoxy composite exhibited a thermal conductivity of 0.32 W/(mK) and an electrical insulating property ($2.96 \times 10^9 \Omega \text{ m}$). However, the poor intrinsic thermal conductivity of silica coating and the low loading of the hybrid were responsible for the limited increase in thermal conductivity. Compared to TGO, which is usually thermally reduced at a moderate temperature of 1050 °C and still bears oxygen-containing groups and defects and thus has a moderate thermal conductivity, high quality (defect-free) graphene nanoplatelets (GNPs), which are prepared by thermal annealing of TGO sheets at 2200 °C, are more thermally conductive [18–20]. For instance, a high thermal conductivity of 1.35 W/(mK) was obtained for polyethylene glycol composite with only 5.3 wt% of defect-free GNPs [18].

Although defect-free GNPs are highly thermally conductive, their inert surface makes it difficult to be coated or decorated by electrically insulating nanomaterials. Fortunately, eco-friendly supercritical carbon dioxide (scCO₂) fluid has been confirmed to be effective in wetting the inert surfaces owing to its zero surface tension and high diffusivity, precursors of inorganic nanoparticles can be adsorbed onto the surfaces of GNPs and are subsequently converted to nanoparticles and nanosheets by calcination. With the help of scCO₂, AlOOH [21] and MnO₂ [22] were well decorated onto the inert surfaces of graphene [21–24]. However, the separated nanoparticles generally lead to loose and porous structures which will decrease the thermal conductivity of the hybrids. Recently, Zhang et al. [25] encapsulated carbon nanotubes (CNTs) with integrated Al₂O₃ layers by using a buffer solution. The same surface feature of graphene as CNTs should make it possible to construct compact and solid Al₂O₃ layers on GNPs. Nevertheless, to our best knowledge, few literature reported on the synthesis of thermally conductive but electrically insulating hybrids by coating electrically insulating layers onto the defect-free GNPs in the presence of scCO₂ fluid or buffer solutions.

Herein, by controlling the nucleation and hydrolysis process, Al₂O₃ nanoparticles and nanolayers are grown on GNPs with the assistance of scCO₂ fluid and in a buffer solution, respectively. The synthesized Al₂O₃@GNP hybrids are efficient in enhancing the thermal conductivity of epoxy resin and retaining the electrical insulation of epoxy. 1 wt% of GNPs are already sufficient to make epoxy electrically conductive. The maximum loadings for keeping an electrical insulation of the epoxy composites are increased to 10 wt% for the hybrid prepared with the assistance of scCO₂ (Al₂O₃@GNP-SC) with a thermal conductivity of 0.96 W/(mK) and 12 wt% for the hybrid prepared in a buffer solution (Al₂O₃@GNP-BS) with a thermal conductivity of 1.49 W/(mK). These thermal conductivities are much higher than those publicly reported for thermally conductive and electrically insulating composites with much higher filler loadings [26,27], indicating the promising potential as efficient thermally conductive fillers for polymer composites. In addition, the influence of microstructures of the anchored Al₂O₃ on the composite properties is also investigated.

2. Experimental

2.1. Materials

Defect-free GNPs, prepared by thermal exfoliation of graphite oxide at 1050 °C followed by annealing at 2200 °C in an argon atmosphere, were supplied by Shanghai Chaoqian New Materials Technology Co. Ltd. (China) [18]. Al(NO₃)₃·9H₂O, Al₂(SO₄)₃·18H₂O, formic acid, and ammonium formate were purchased from J&K Sci. Co. Ltd. (China). CO₂ gas (99.99%, Yanglike Gases), epoxy monomer (NPEL-128, Nanya Plastics), 4,4'-diamino-diphenylmethane (DDM, Aladdin-Reagent), commercial α -Al₂O₃ (Honghe Chemicals), BN (Dandong Rijin), multiwalled CNTs (TNGM2, Timesnano) and commercial GNPs (M15, XG Sciences) were used as-received without further purifications.

2.2. Preparation of Al₂O₃@GNP hybrids

Al₂O₃@GNP hybrids were prepared using two different approaches. For the scCO₂-assisted approach [21,28], 1.0 g GNPs and 6.0 g Al(NO₃)₃·9H₂O were dispersed in 100 ml ethanol by sonication and the resulting mixture was loaded into a high-pressure autoclave. The autoclave was then filled with CO₂ of 6 MPa and the supercritical state of CO₂ was achieved by increasing the temperature to 140 °C. After the reaction had lasted for 12 h under vigorous stirring, the autoclave was cooled down to room temperature and depressurized slowly. The resultant was centrifuged and washed repeatedly with ethanol, dried at 80 °C for 24 h, and finally calcined at 600 °C for 3 h in an inert atmosphere to remove the absorbed water and residual precursor. The obtained powder was designated as Al₂O₃@GNP-SC hybrid, in which uniformly dispersed Al₂O₃ nanoparticles were coated onto the GNPs. In the buffer solution-assisted approach [25], Al₂O₃@GNP hybrids were synthesized with a buffer solution (pH = 4.4) consisting of formic acid and ammonium formate aqueous solution (0.2 M). 0.2 g GNPs mildly treated with HNO₃ and 1.2 g Al₂(SO₄)₃·18H₂O were then dispersed in 500 mL formic acid/ammonium formate buffer solution. After the suspension reacted at 85 °C for 2 h, the resultant was washed, dried and calcined at 600 °C for 3 h, which were the same calcination conditions as that for the scCO₂-assisted approach. The product was labeled Al₂O₃@GNP-BS hybrid, in which uniform Al₂O₃ nanolayers without phase separation were coated on GNPs.

2.3. Preparation of epoxy/Al₂O₃@GNP composites

Thermally conductive epoxy/Al₂O₃@GNP composites were prepared by solution mixing. First, Al₂O₃@GNP/ethanol suspension was prepared by mild sonication, mixed with epoxy monomer at 75 °C for 1 h, and then the temperature was increased to eliminate air bubbles and evaporate the residual ethanol. After the curing agent of DDM (DDM/epoxy = 1/2.6, w/w) was added under continuous stirring followed by another bubble removal process, the mixture was poured into a polytetrafluoroethylene mold, cured at 80 °C for 2 h, and post-cured at 130 °C for 3 h. For comparison, epoxy-based composites filled with commercial fillers were also prepared using similar mixing and curing procedures.

2.4. Characterization

Microstructures of Al₂O₃@GNP hybrids and their epoxy composites were observed with a Hitachi S-4700 field emission scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDX) and a JEOL JEM-3010 high-resolution transmission electron microscope (TEM). The structural and chemical changes of GNPs and their hybrids were characterized

using a Bruker AXS D8 advance X-ray diffraction (XRD), a Thermo VG RSCAKAB 250× high-resolution X-ray photoelectron spectrometer (XPS), and a Renishaw inVia Raman microscope (UK). Al₂O₃ contents in the hybrids were determined with a TA Q50 thermogravimetric analyzer (TGA) under an air atmosphere from 30 to 1000 °C. The measurements of alternating current (AC) electrical conductivity were conducted on an Agilent 4294A precision impedance analyzer in the frequency range from 100 Hz to 100 MHz at room temperature. Direct current (DC) volume electrical conductivities of epoxy composites were measured with a Keithley Instruments 4200-SCS semiconductor characterization system ($>10^{-6}$ S/m) and a Keithley Instruments 6517B resistivity meter ($<10^{-6}$ S/m). Through-plane thermal conductivities (κ) of the epoxy composites were calculated according to Eq. (1):

$$\kappa = \alpha \times C_p \times \rho \quad (1)$$

where α is thermal diffusivity, C_p specific heat capacity and ρ density. Thermal diffusivities of epoxy composites with dimensions of $10 \times 10 \times 1.5$ mm³ were examined with a Netzsch LFA467 light flash apparatus at 25 °C. Specific heat capacities and densities (1.15 – 1.25 g/cm³) of the composites were measured with a Perkin-Elmer Pyris 1 differential scanning calorimeter (DSC), and a Mettler-Toledo balance equipped with a density measurement kit (Switzerland) in accordance with ASTM792-00, respectively.

3. Results and discussion

3.1. Synthesis of Al₂O₃@GNP hybrids assisted by scCO₂ fluid and in a buffer solution

It is confirmed that high temperature annealing of TGO can enhance its thermal and electrical conductivities by removing the defects and residual oxygen-containing groups of TGO [18–20,29] and the resultant defect-free GNPs exhibit a chemically inert surface, which makes the decoration or coating of GNPs difficult. Fig. 1a illustrates the decoration of GNPs with electrically insulating Al₂O₃ by a scCO₂ fluid anti-solvent approach [21] and a buffer solution assisted deposition approach [25]. In the scCO₂ fluid approach, the ethanol solution of Al(NO₃)₃ is swollen by scCO₂ and the solubility of Al(NO₃)₃ is thus greatly reduced, resulting in severe supersaturation and simultaneous nucleation of Al(NO₃)₃. GNPs are readily wetted by scCO₂ and provide abundant surfaces for nucleation of Al(NO₃)₃. Assisted by scCO₂, Al(NO₃)₃ is hydrolyzed at 140 °C forming aluminum hydroxide on GNPs [21,30], which is then converted to Al₂O₃ nanoparticles by calcinating at 600 °C. Alternatively, in a formic acid/ammonium formate buffer solution, the amount of ionized hydroxyl ions is moderate and stable, which makes Al₂(SO₄)₃ slowly nucleate and hydrolyze on GNP surfaces to form aluminum hydroxide nanolayers, which are then converted to Al₂O₃ nanolayers by calcination at 600 °C. Note that the nucleation and hydrolysis should be carefully balanced by adjusting the supply of hydroxyl ions by controlling the initial pH value of the solution to ensure the formation of uniform and thin aluminum hydroxide nanolayers rather than nanoparticles. The synthesized Al₂O₃@GNP hybrids are mixed with epoxy monomer to prepare thermally conductive but electrically insulating epoxy based composites. It is expected that the presence of the decorated Al₂O₃ can greatly suppress the electrical conductivity of the epoxy composites by preventing the direct contact of GNPs while both thermally conductive Al₂O₃ and GNPs components can afford the effective phonon transfer in the epoxy matrix.

Fig. 1b–d shows the morphologies of Al₂O₃@GNP hybrids synthesized through different approaches. In contrast to the smooth surfaces of GNPs (Fig. S1), Al₂O₃@GNP-SC hybrids exhibit

homogeneous Al₂O₃ particles on inert GNPs (Figs. 1b, S2–S4) with the assistance of scCO₂ fluid with high diffusivity and zero surface tension [24,30]. The thickness of Al₂O₃ particles observed from the cross-section SEM image is less than 50 nm (inset of Fig. S3a). It is seen that GNPs are well anchored by the electrically insulating Al₂O₃ nanoparticles despite the presence of porous space between them, which can interrupt possible direct connections of the electrically conductive graphene sheets and thus hinder charge transfers within the epoxy composites. However, it is interesting that Al₂O₃@GNP-BS hybrid shows an obviously distinct morphology. There is no granular particle but a thin layer of compact and flat Al₂O₃ is observed (Figs. 1c, S2, S3). The thickness of the Al₂O₃ layer is estimated to be ~36 nm from the cross-section image. By contrast, when Al₂(SO₄)₃ precursor is dissolved in water instead of the buffer solution, no precipitation could be formed on GNPs due to the low initial pH value of 3.7 (Fig. S5). Similarly, if the pH value of Al₂(SO₄)₃ aqueous solution is increased to 6.5, only large agglomerates are observed due to the fast hydrolysis and nucleation of Al³⁺ (Fig. S5). The formation of compact and solid Al₂O₃ layer is further verified by the TEM image. The substrate GNPs are completely covered by anchored Al₂O₃ (Fig. 1d). Moreover, the uniform distributions of C, O and Al elements also confirm the complete and compact coating of Al₂O₃ layers on GNPs (Fig. S6). The coating of Al₂O₃ nanolayers would favor the hybrids forming thermally conductive but electrically insulating network in the polymer matrix.

The Al₂O₃ coating greatly enhances the thermal stability of GNPs (Fig. 2). Under air atmosphere, GNPs are completely decomposed and burnt and no residue is left (Fig. 2a). However, both Al₂O₃@GNP hybrids exhibit significantly improved thermal stability because the thermally stable Al₂O₃ coating acts as insulator and mass transport protective barrier, thereby reducing the decomposition rate and delaying the escape of volatile products released as GNPs decompose [31]. As shown in Fig. 2b, the maximum decomposition temperatures (T_d) of Al₂O₃@GNP-SC and -BS hybrids are 102 and 112 °C higher than 698 °C of GNPs, respectively. This is attributed to the protective effect of the dense Al₂O₃ coating on the oxidative degradation of GNPs [1,4,5], which are more effective than those provided by MgO/graphene [8], TGO-silica [1], and alumina coated graphite sheets [5] whose maximum T_d are about 10, 50 and 70 °C higher than their carbon substrates, respectively. Since GNPs are completely decomposed, the residue should be the thermally stable Al₂O₃ component. Thus, the contents of Al₂O₃ are determined to be 36 wt% for Al₂O₃@GNP-BS hybrid and 38 wt% for Al₂O₃@GNP-SC hybrid. TGA curves of epoxy and its composites filled with Al₂O₃@GNP hybrid in air atmosphere are shown in Fig. S7. The results show that the thermal stability of epoxy composites is comparable to or even better than neat epoxy, which is very crucial for practical applications.

Fig. 2c shows the XRD patterns of GNPs and Al₂O₃@GNP hybrids. The diffraction peak at 26.4° appeared in all the samples corresponds to the highly graphitized GNPs [18]. There are no new characteristic peaks emerging for Al₂O₃@GNP-BS and Al₂O₃@GNP-SC hybrids, indicating the amorphous feature of the Al₂O₃ coated particles and layers. Note that the hydrophilic treatment of GNPs by HNO₃, made before the coating of Al₂O₃ layers by the buffer solution approach, does not damage their crystalline structure and cause structural defects (Fig. S8). GNPs and their hybrids are evaluated by Raman spectroscopy (Fig. 2d). The typical D (1348 cm⁻¹) and G (1580 cm⁻¹) bands usually correspond to the occurrence of defects and the in-plane stretching motion between pairs of sp² carbon, respectively [32]. The absence of D band for GNPs again confirms the high quality of GNPs after annealing at 2200 °C [18,20,29]. However, a weak D band peak is observed for Al₂O₃@GNP-SC and Al₂O₃@GNP-BS hybrids whose I_D/I_G intensity

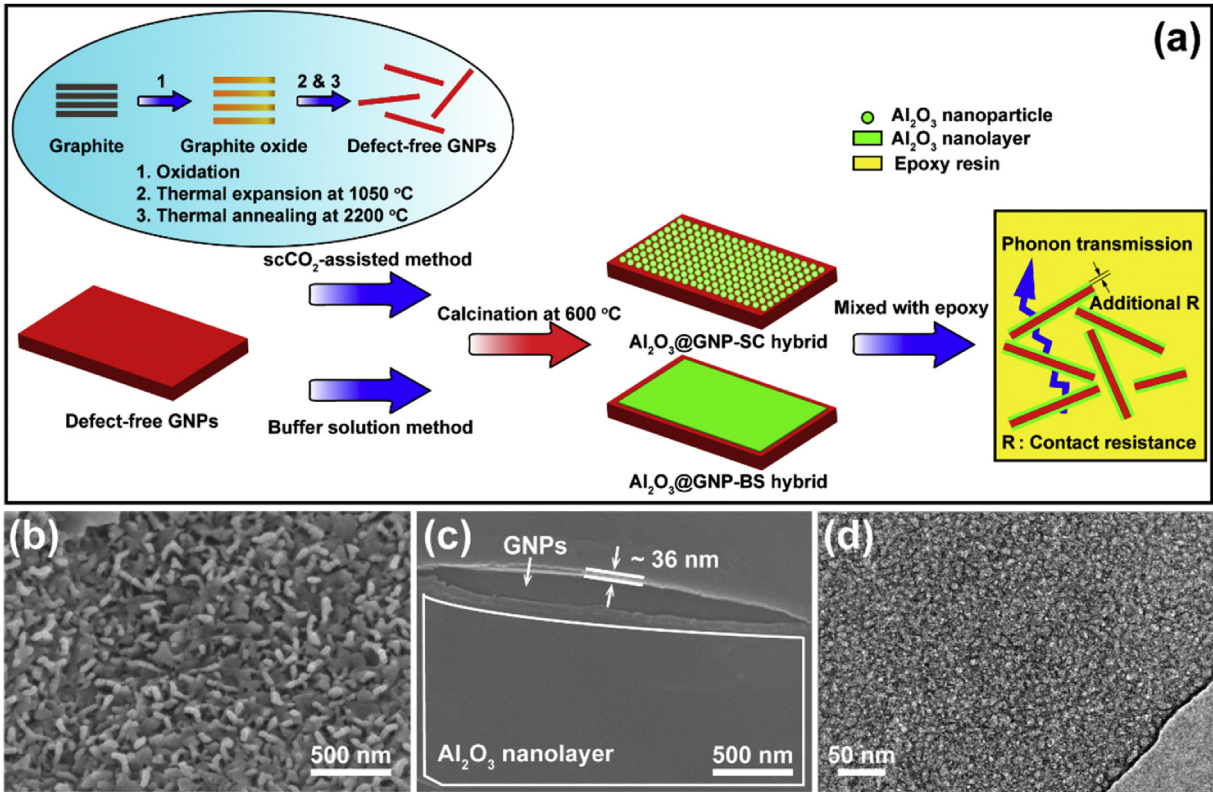


Fig. 1. (a) Schematic illustrating the synthesis routes of Al_2O_3 @GNP hybrids and their epoxy composites; SEM images of (b) Al_2O_3 @GNP-SC and (c) Al_2O_3 @GNP-BS hybrids; and (d) TEM image of Al_2O_3 @GNP-BS hybrid.

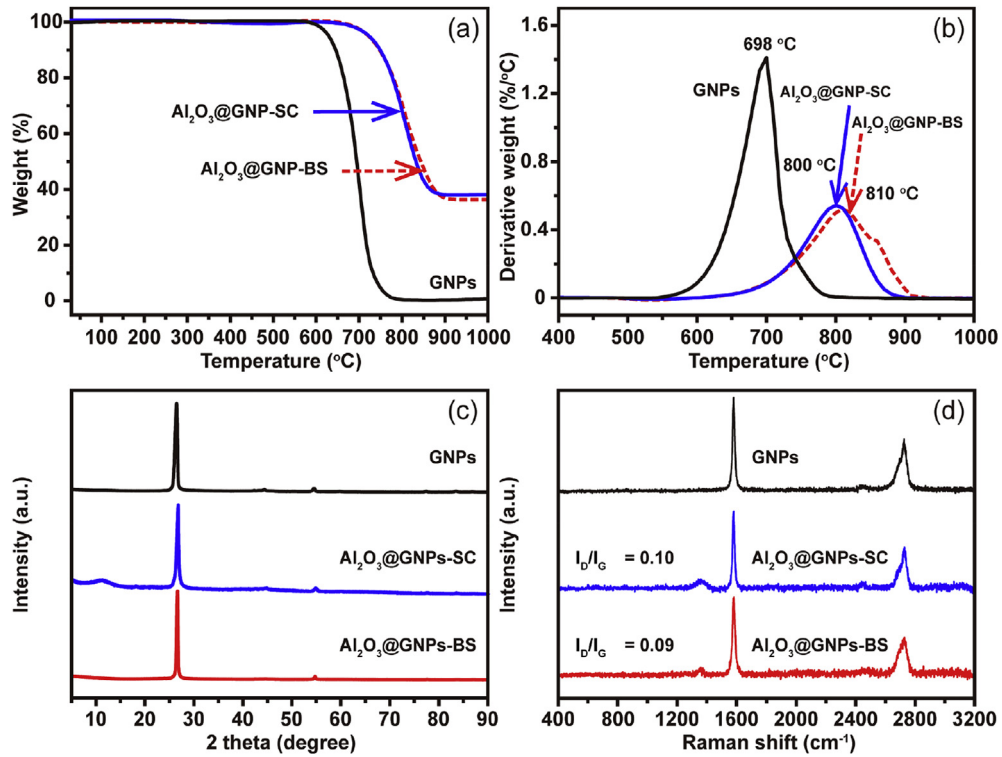


Fig. 2. (a) Mass loss and (b) derivative mass curves of GNPs and Al_2O_3 @GNP hybrids under air atmosphere; (c) XRD patterns and (d) Raman spectra of GNPs and Al_2O_3 @GNP hybrids.

ratios are 0.10 and 0.09, respectively, which may infer the formation of interactions between the GNP substrate and Al_2O_3 .

The chemical compositions of GNPs and Al_2O_3 @GNP hybrids are also evaluated with XPS spectra (Fig. 3). It is seen that GNPs have a quite low content of oxygen-containing groups as evidenced by its high C/O ratio (54.6) and the almost disappeared O 1s peak (Fig. 3a and Fig. S9). However, the C/O ratios of Al_2O_3 @GNP-BS and Al_2O_3 @GNP-SC hybrids are significantly decreased to 2.0 and 2.7, respectively, due to the presence of the Al_2O_3 coating (Fig. 3a and b). In addition, the formation of Al_2O_3 in the hybrids is also confirmed by the characteristic peaks of Al–O–Al and Al–OH bonds in the O 1s spectrum and the peak at 74.6 or 74.7 eV in the Al 2p spectrum (Fig. 3c and d) [21].

3.2. Electrically insulating performance of the epoxy composites

Al_2O_3 @GNP hybrids are used to prepare thermally conductive and electrically insulating epoxy composites. Fig. 4a shows the plots of AC conductivity as a function of frequency for the epoxy composites. As an insulator, neat epoxy has a typical frequency-dependent characteristic with a resistive behavior at low frequencies and a capacitive behavior at high frequencies [9,33]. However, the addition of only 1 wt% GNPs leads to an increase of 5–6 orders of magnitude in electrical conductivity with an almost frequency-independent conductivity behavior. A complete frequency-independent feature is observed for epoxy composite with 3 wt% GNPs, indicating this loading is already sufficient to form an electrically conducting network. The high intrinsic electrical conductivity and large aspect ratio of GNPs are responsible for the rapid transition from electrical insulating to conducting at low loadings [18,34,35], implying that it is not possible to prepare thermally conductive but electrical insulating epoxy composites by

using GNPs. Interestingly, the coating of Al_2O_3 effectively suppresses the electrically conducting feature of GNPs. The epoxy composites with Al_2O_3 @GNP hybrids exhibit typical frequency-dependent AC conductivity, and are still electric insulating at loadings less than 10 wt% for Al_2O_3 @GNP-SC hybrid and 12 wt% for Al_2O_3 @GNP-BS hybrid (Fig. 4b and c) [9,33].

To compare the electrical properties more exactly, Fig. 4d shows the AC conductivities at 100 Hz of different epoxy composites. Adding only 1 wt% of GNPs rapidly increases the electrical conductivity of epoxy to 1.2×10^{-5} S/m from 6.0×10^{-10} S/m, and the electrical conductivities of epoxy composites are more than 10^{-2} S/m at higher loadings. However, Al_2O_3 @GNP hybrids do not notably improve the electrical conductivity of epoxy, which is still smaller than 10^{-8} S/m even at much higher loadings, maintaining the electrically insulating feature. For example, electrical conductivities of the composites with 10 wt% Al_2O_3 @GNP-SC and 12 wt% Al_2O_3 @GNP-BS are as low as 3.6×10^{-9} and 6.7×10^{-9} S/m, respectively. In addition, the DC conductivities of different epoxy composites are compared in terms of weight contents of fillers and volume contents of GNPs (Fig. S10), which are in good agreement with the AC conductivity results.

Compared to epoxy/ Al_2O_3 @GNP-SC composites, Al_2O_3 @GNP-BS composites exhibit better electrically insulating performance (Fig. 4 and Fig. S10), which correlates well with the different morphologies of Al_2O_3 on GNP surfaces (Fig. 1). For the Al_2O_3 @GNP-SC, although the formed Al_2O_3 particles can cover most of the GNP surface, some pores and naked area on the edges of GNPs will facilitate electron transport and thus impair the insulating performance (Fig. S3). In the Al_2O_3 @GNP-BS hybrid, however, the compact and solid Al_2O_3 nanolayers encapsulate the GNPs well and thus effectively suppress the electron transport between the coated GNPs [1–7], retaining better electrical insulation.

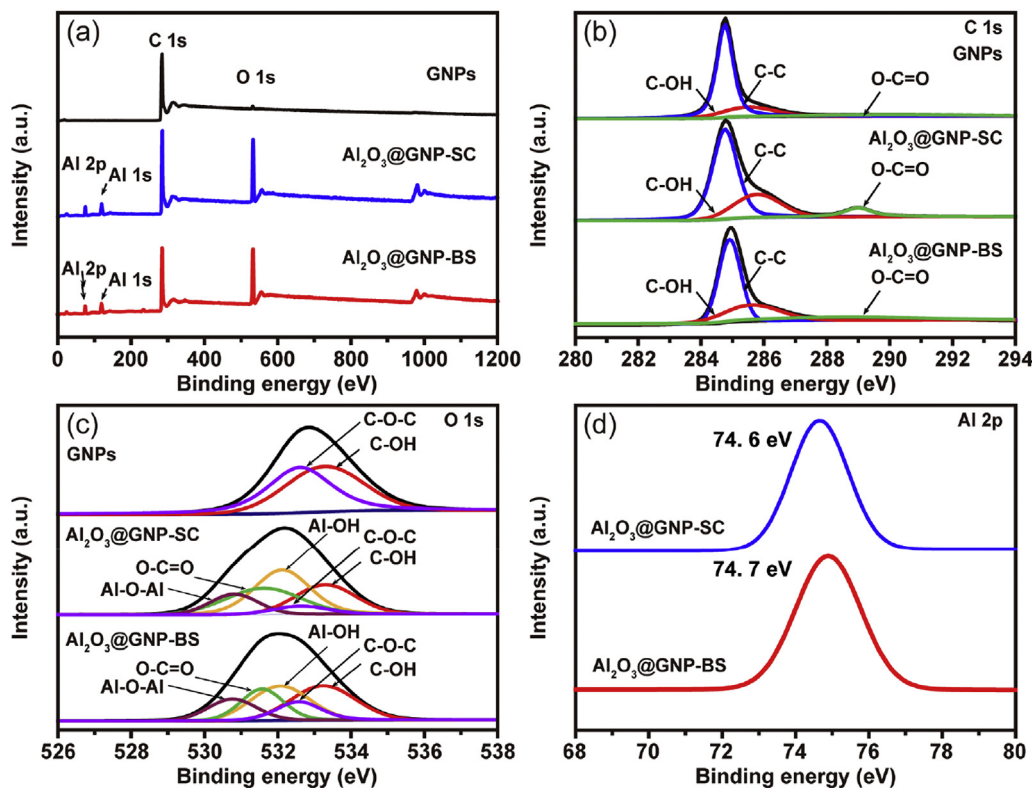


Fig. 3. XPS spectra of GNPs and Al_2O_3 @GNP hybrids: (a) survey scans, (b) C 1s, (c) O 1s, and (d) Al 2p.

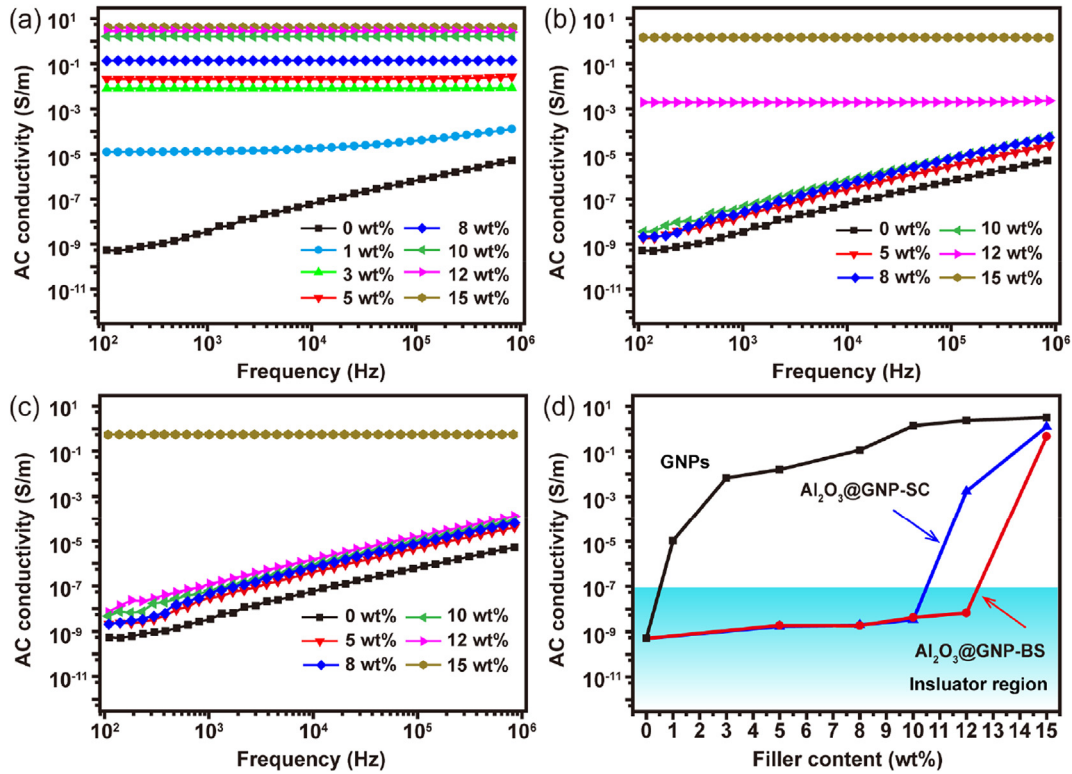


Fig. 4. Plots of AC conductivity versus frequency of epoxy composites containing: (a) GNPs; (b) Al₂O₃@GNP-SC; (c) Al₂O₃@GNP-BS hybrids; and (d) comparison of electrical conductivities of epoxy composites filled with GNPs and their hybrids at 100 Hz.

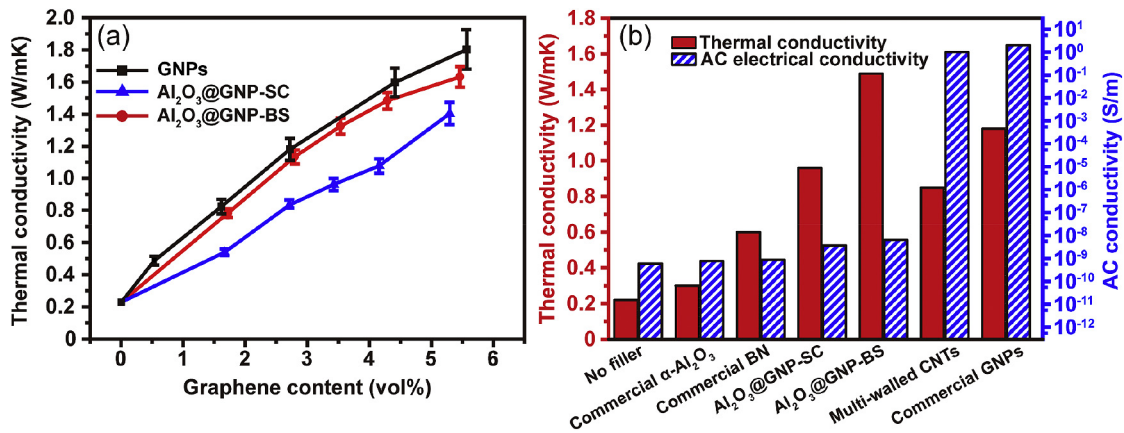


Fig. 5. (a) Plots of thermal conductivity versus GNP volume content of epoxy composites. Note that the GNP contents in the hybrids are determined based on their TGA results (Fig. 2a) and the densities of GNPs, Al₂O₃ and epoxy used are 2.26, 3.60 and 1.18 g/cm³, respectively. (b) Comparisons of thermal conductivity and AC electrical conductivity at 100 Hz for epoxy composites filled with various fillers. Note that the mass contents of commercial BN, Al₂O₃@GNP-SC and the other fillers are 15, 10 and 12 wt%, respectively.

3.3. Thermally conductive performance of the epoxy composites

Fig. 5a and Fig. S11 show the thermal conductivities of the epoxy composites filled with GNPs and Al₂O₃@GNP hybrids. Clearly, the thermal conductivity increases gradually with increasing GNP content for all three types of composites. Epoxy/GNP composites show a thermal conductivity of 1.80 W/(mK) with 5.6 vol% of GNPs, which is slightly higher than 1.40 W/(mK) for epoxy/Al₂O₃@GNP-SC composite and 1.62 W/(mK) for epoxy/Al₂O₃@GNP-BS composite at similar GNP loadings. This is because of the relatively lower thermal conductivity of the Al₂O₃ coating than that of the GNPs. Thus, thick Al₂O₃ nanolayer would reduce the thermal conductivity of

Al₂O₃@GNP hybrids and their epoxy composites. For example, the increase of Al₂O₃ content in Al₂O₃@GNP-SC hybrid from 38 to 55 wt% causes the reduction of thermal conductivity from 0.96 to 0.77 W/(mK) for epoxy composites. Compared to the Al₂O₃@GNP-SC hybrid consisting of large Al₂O₃ particles (Fig. 1b), the more compact and solid Al₂O₃@GNP-BS hybrid affords better thermal conductivities. As can be seen in Fig. 1a, Figs. S2 and S3, there are numerous pores among the spherical Al₂O₃ particles in Al₂O₃@GNP-SC hybrid, which can severely deteriorate heat conduction and cause lower thermal conductivity for epoxy/Al₂O₃@GNP-SC composites as compared to its counterpart. Although GNPs offer better thermal conductivities to epoxy than Al₂O₃@GNP hybrids at similar

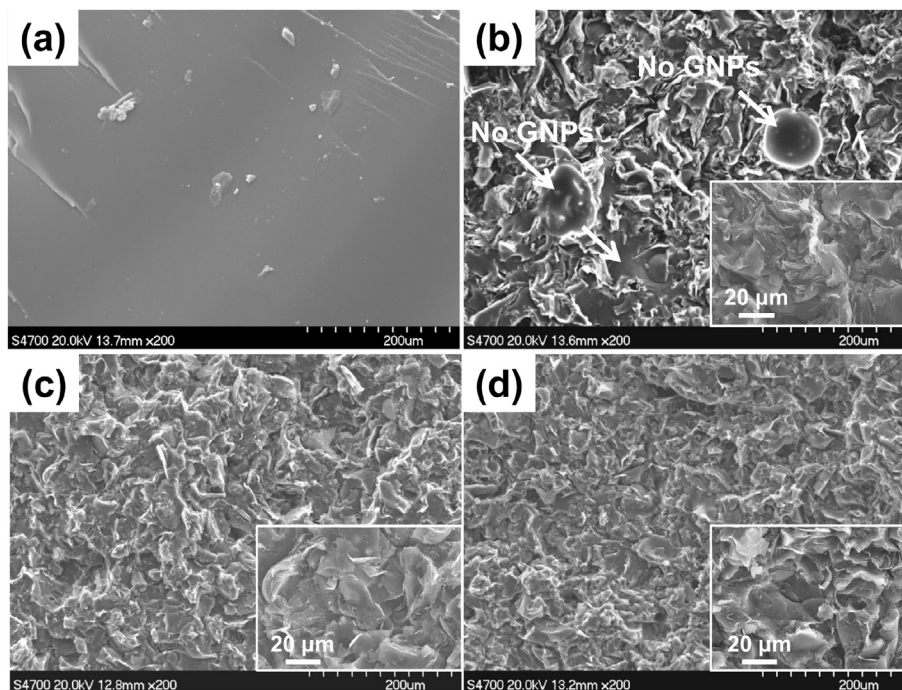


Fig. 6. SEM images of freeze-fractured surfaces of (a) neat epoxy, and epoxy composites with 12 wt% of (b) GNPs, (c) Al_2O_3 @GNP-SC, and (d) Al_2O_3 @GNP-BS hybrids.

loadings, their maximum loading to retain electric insulation of the epoxy composite is lower than 1.0 wt% (Fig. 4 and Fig. S10), at which the thermal conductivity is as low as 0.50 W/(mK) (Fig. 5 and Fig. S11). The advantages of the epoxy/ Al_2O_3 @GNP composites are obvious when both excellent thermal conductivity and electrical insulation behaviors are simultaneously required. The maximum filler contents for thermally conducting but electrically insulating epoxy composites are 10 wt% for Al_2O_3 @GNP-SC and 12 wt% for Al_2O_3 @GNP-BS, and their corresponding thermal conductivities are 0.96 and 1.49 W/(mK), which are much higher than those reported in the literature for thermally conductive but electrically insulating composites (Table S1) [36–39]. These results indicate the high potential of Al_2O_3 @GNP hybrids as thermally conductive and electrically insulating fillers for functional polymer nanocomposites.

To further illustrate the superiorities of the Al_2O_3 @GNP hybrids, epoxy composites filled with various fillers are compared in terms of thermal conductivity and electric insulation (Fig. 5b). Independent of the electrical insulating feature, the epoxy composites with commercial α - Al_2O_3 and BN show rather poor thermal conductivities of less than 0.60 W/(mK). Although epoxy composites with multi-walled CNTs and commercial GNPs show much better thermal conductivities, high AC conductivities of ~ 1.0 S/m are invariably obtained. Only the Al_2O_3 @GNP hybrids can well balance the excellent thermal conductivity and electrical insulation. Epoxy composites with Al_2O_3 @GNP-BS exhibit the highest thermal conductivity of 1.49 W/(mK) with a satisfactory electrical insulation of 6.7×10^{-9} S/m. Hence, it is possible to fully utilize the thermally conducting nature of defect-free GNPs and suppress their high electrical conductivity by an Al_2O_3 coating that is thermally conducting but electrically insulating.

The microstructures of the epoxy composites filled with different types of fillers are compared in Fig. 6. Compared to the rather smooth and brittle fracture surfaces of neat epoxy (Fig. 6a), the composites exhibit rougher surfaces due to the presence of the fillers. Some GNP aggregates also show clear interfaces in the

epoxy/GNP composites because of the incompatibility between the chemically inert GNPs and epoxy matrix (Fig. 6b). Interestingly, the interfacial interactions are improved by the coated Al_2O_3 nanolayer on the GNPs and better filler dispersion is thus achieved in the epoxy composites filled with both Al_2O_3 @GNP hybrids (Fig. 6c and d), which is a critical factor for forming a thermally conducting network within the epoxy composites.

4. Conclusion

We utilize a scCO_2 -assisted method to decorate the inert defect-free GNP surfaces with numerous Al_2O_3 nanoparticles by using fast nucleation and hydrolysis of $\text{Al}(\text{NO}_3)_3$ precursor followed by calcination at 600 °C. Besides, a buffer solution-assisted deposition approach is applied to deposit the $\text{Al}_2(\text{SO}_4)_3$ precursor, which is slowly nucleated and hydrolyzed on GNPs to form aluminum hydroxide; subsequently, this is converted to Al_2O_3 nanolayers without phase separation after a similar calcination process. The formation of Al_2O_3 nanoparticles or nanolayers significantly improves the thermal stability of GNPs by 102 and 112 °C for Al_2O_3 @GNP-SC and Al_2O_3 @GNP-BS hybrids, respectively. Most importantly, uniquely high thermal conductivity and good electrical insulation could be obtained in epoxy composites filled with these hybrids. Maximum filler loadings for electrical insulation are found to be 10 wt% for Al_2O_3 @GNP-SC and 12 wt% for Al_2O_3 @GNP-BS, leading to much higher thermal conductivities of 0.96 and 1.49 W/(mK), respectively. These excellent properties make them strong candidates for thermal management of electronic packaging and electronic devices.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.compscitech.2016.10.017>.

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