# Graphene Size-dependent Modulation of Graphene Framework Contributing to Superior Thermal Conductivity of Epoxy Composite

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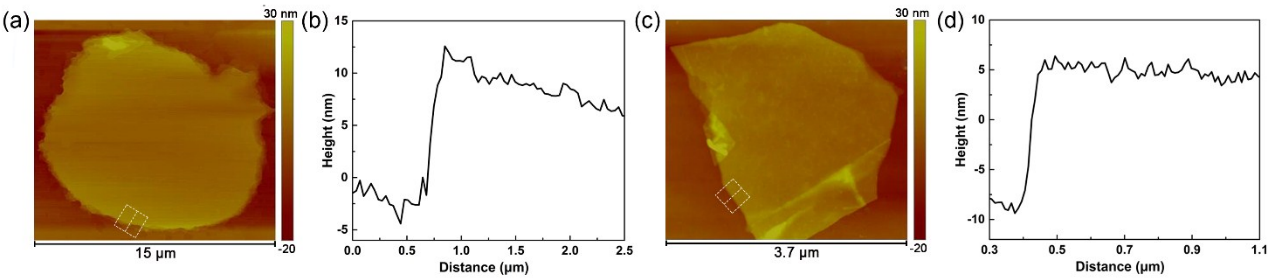


Figure S1 AFM images and thickness of (a-b) large and (c-d) small graphene sheets, respectively.

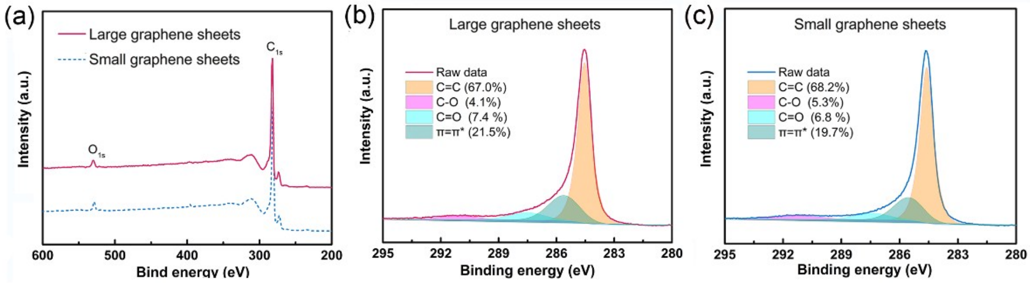


Figure S2 (a) XPS survey spectra of large and small graphene sheets. XPS-C1s spectrum of (b) large and (c) small graphene sheets.

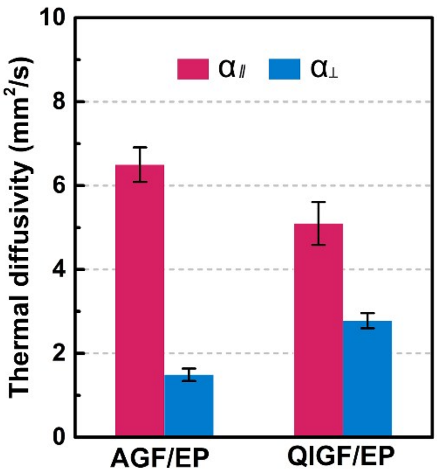


Figure S3 In- and through-plane thermal diffusivities of AGF/EP and QIGF/EP.

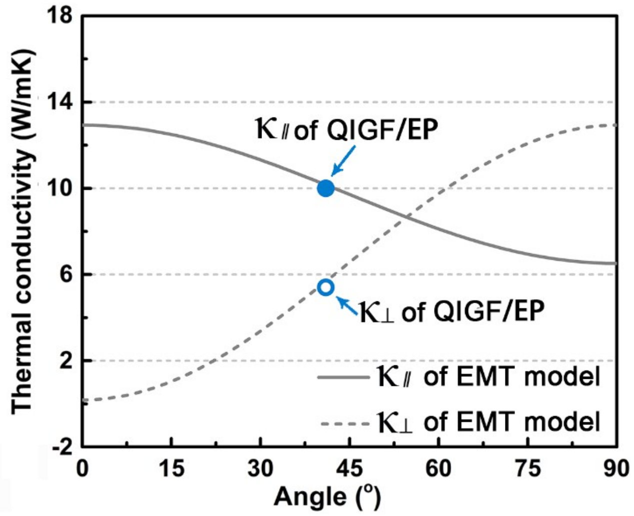


Figure S4 Deflection angle-dependent thermal conductivities of QIGF/EP composites calculated based on EMT model.

In order to explain the anisotropic ratio of QIGF/EP in theory, the thermal conductivity along in- and through-plane direction can be calculated by the effective medium theory (EMT) model, which is usually used to predict the thermal conductivity of laminate fillers/polymer system.[1] As the model describes, $\kappa_{//}$ and $\kappa_{\perp}$ as the function of deflection angles of laminate fillers can be estimated based on the equation (1) and (2), respectively:

$$\kappa_{\parallel} = \kappa_m \left\{ \frac{2+V_f\left[\frac{\kappa_p}{\kappa_m}\left(1+\langle\cos^2\theta\rangle\right)\right]}{2-V_f\left[\frac{\kappa_p h-\kappa_m h-R_{bd}\kappa_p\kappa_m}{\kappa_p h}\left(1-\langle\cos^2\theta\rangle\right)\right]} \right\} \quad (1)$$

$$\kappa_{\perp} = \kappa_m \left\{ \frac{1+V_f\left[\frac{\kappa_p}{\kappa_m}\left(1-\langle\cos^2\theta\rangle\right)\right]}{1-V_f\left[\frac{\kappa_p h}{h+R_{bd}\kappa_p}\langle\cos^2\theta\rangle\right]} \right\} \quad (2)$$

where $\kappa_m$ is the thermal conductivity of the matrix material; $\boldsymbol{\kappa_p}$ is the thermal conductivity of laminate fillers in parallel direction; $R_{bd}$ is the thermal boundary resistance between fillers and matrix; $\theta$ is the deflection angles of laminate fillers; $V_f$ is the volume fraction of fillers; $h$ is the average thickness of laminate fillers. According to the previous reports,[2, 3] the thermal conductivity of exfoliated graphene is ranged from 250 to 600 W/mK, and an average value (425 W/mK) was employed for this calculation. $R_{bd}$ was taken to be $7.7 \times 10^{-8}$ Km$^2$/W, which were derived from literature.[4] $\kappa_m$ for the epoxy matrix (0.18 W/mK) was obtained by direct measurement of an epoxy. $V_f$ was 3.1 vol% by conversion from the mass fraction of 5.5 wt%. $h$ was around 15 nm by a statistical analysis of graphene sheets using AFM.

As a result, the evolution of theoretical thermal conductivity as a function of deflection angles of graphene sheets along in- and through-plane directions is presented in Figure S4, which is predicted from EMT model. In our work, the average angle of graphene sheets in QIGF/EP was ≈ 41°. Based on this, Figure S4 indicates a good agreement between theoretical and measured thermal conductivities (both of $\kappa_{//}$ and $\kappa_{\perp}$) of QIGF/EP. Moreover, the anisotropic ratio of theoretical value (1.88) is also close to the measured one.

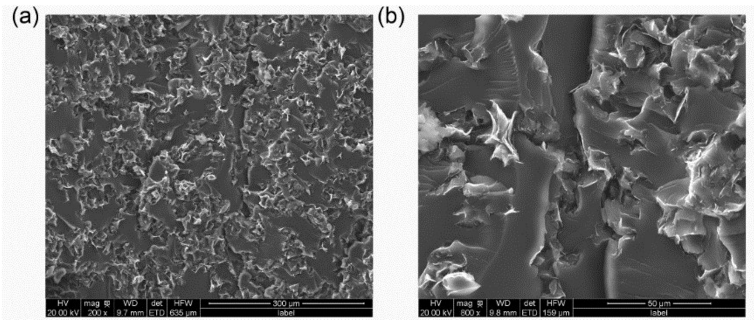


Figure S5 (a-b) SEM images of DG/EP.

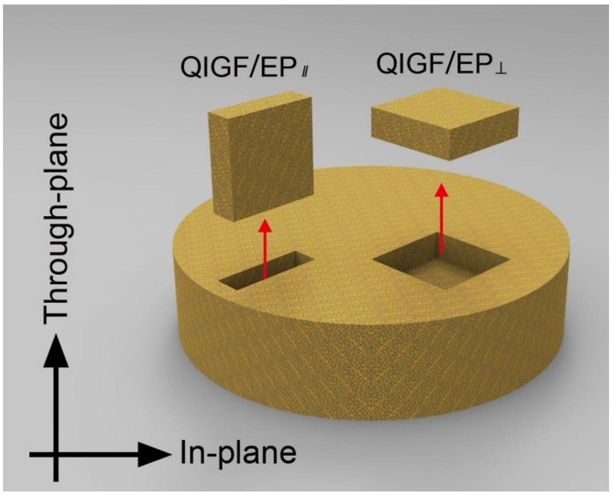


Figure S6 Schematic of the preparation of QIGF/EP$_{\perp}$ and QIGF/EP$_{//}$.

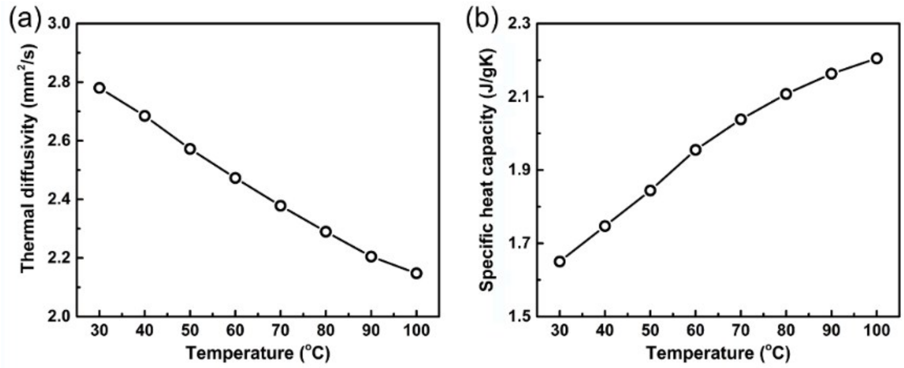


Figure S7 The variation of (a) $\alpha_{\perp}$ and (b) $C_p$ of QIGF/EP as a function of environmental temperature.

Table S1 Comparison of thermal conductivity of our QIGF/EP composite with reported graphene/epoxy composites.

| Filler | Tc (W/mK) | Fraction (wt%) | Direction | Reference |
|---|---|---|---|---|
| Graphene oxide sheets | 0.85 | 5 | Isotropic | 5 |
| Multilayer Graphene | 1.5 | 5.7 | Isotropic | 6 |
| Functionalize graphene nanosheets | 1.91 | 4 | Isotropic | 7 |
| Functionalized Graphene Flakes | 1.53 | 10 | Isotropic | 8 |
| Graphene-CNT | 0.321 | 1 | Isotropic | 9 |
| Graphene-Silica | 0.29 | 1.5 | Isotropic | 10 |
| Graphene coated PMMA balls | 1.41 | 1 | Isotropic | 11 |
| Pu foam templated graphene framework | 1.51 | 5 | Isotropic | 12 |
| Ni templated 3D graphene framework | 2<br>8.8 | 8.3 | Through-plane<br>In-plane | 13 |
| Hydrothermal graphene framework | 2.13<br>0.63 | 1.9 | Through-plane<br>In-plane | 14 |
| QIGF | 5.4<br>10 | 5.5 | Through-plane<br>In-plane | This work |

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