

## Supporting Information for

# Constructing Hierarchically Structured Interphase for Strong and Tough Epoxy Nanocomposites by Amine-Rich Graphene Surfaces

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## 1. Raman results.

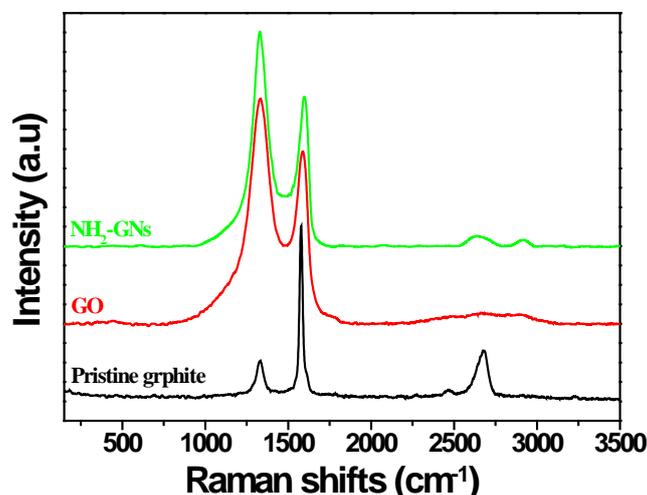


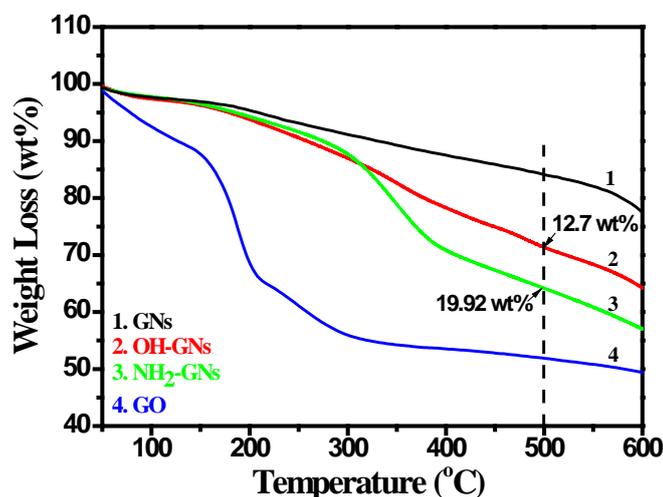
Figure S1 Raman spectra of pristine graphite, GO sheets and NH<sub>2</sub>-GNs.

The Raman spectra offer further support for covalent bonding between GNs and organic molecules. The structural changes occurred during treating pristine graphite to GO or to NH<sub>2</sub>-GNs, are reflected in several characteristic bands. In our measurements, powder samples were first deposited on the wafer and an identical excitation wavelength (631 nm) was used in all samples. The pristine graphite displays a prominent G band at 1580 cm<sup>-1</sup> corresponding to the first-order scattering of the E<sub>2g</sub> mode. The G band was broadened in GO and meanwhile, the D band at 1340 cm<sup>-1</sup>, activated in the first order scattering process of sp<sup>3</sup> carbons, becomes more prominent. In a recent study, Cancado et al.<sup>1</sup> have suggested that the intensity ratio of D and G bands can be used to characterize the crystallite size ( $L_a$ ) in graphene sheets, that is,

$$L_a(\text{nm}) = (2.4 \times 10^{-10}) \times \lambda_{\text{laser}}^4 (I_D / I_G)^{-1}$$

where  $\lambda_{\text{laser}}$  is the laser excitation wavelength, and ID and IG are the peak intensities of D and G bands. This offers a convenient approach to evaluate the covalent bonding between GNs and organic molecules or polymer. For the pristine graphite, its  $L_a$  equals 186.5 nm, which is much higher than that of GO (28.4 nm), implying a remarkable increase in disorder extent in GO, that is, more organic groups such as hydroxyl, carbonyl and carboxyl groups are introduced to GO surface. For the  $\text{NH}_2$ -GNs,  $L_a$  is 26.7 nm. Although it is slightly lower than that of GO, the value reflects prominent covalent bonding in view of amine functionalization of GNs was conducted after hydrazine reduction of GO; the latter means the restoration of order extent in graphene sheets. As a result, the Raman results provides a direct evidence for the covalent bonding between GNs and organic molecules.

## 2. Thermogravimetric Analysis (TGA) results.

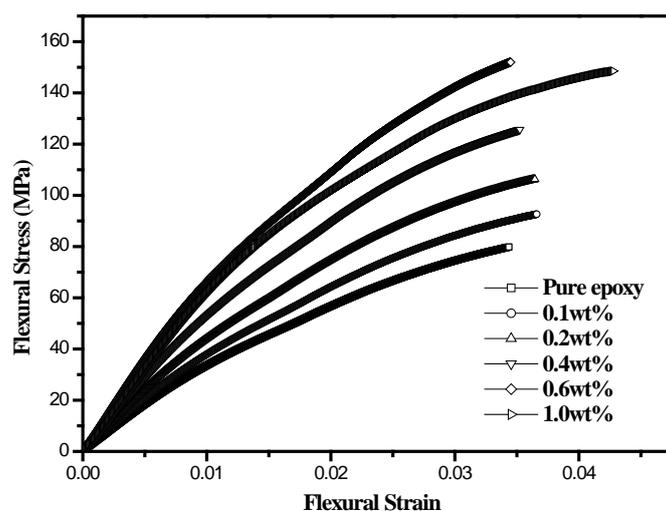


**Figure S2** TGA curves of graphene (GNs), graphene oxide (GO), hydroxyl- and amine-functionalized graphene (HO-GNs and  $\text{NH}_2$ -GNs).

TGA was used to estimate the grafting density of  $\text{NH}_2$  groups on graphene nanosheets (GNs). All measurements were conducted under the same condition: heating exhaustively dried samples from room temperature to 600 °C at 20 °C/min in nitrogen. Unlike thermally reduced GNs, a small amount of residual groups there still exist so that about 20 wt% mass loss at 600 °C, including loss of part of carbon atoms due to the breaking of carbon-carbon bonds. By comparison, graphene oxide (GO) is very unstable and significant mass loss occurs around 150 °C, which is one of important causes for us to choose GNs rather than GO to

improve epoxy resin. Grafting organic molecules, in particular aromatic compounds such as MDA and MDI, usually enhance to some extent the thermal stability of GNs due to their weak thermal conductivity and relatively high thermal stability (higher residual char contents than aliphatic compounds). As a consequence, it is reasonable the mass loss of phenyl ethanol is used to estimate the grafting density, provided that we assume an exhaustive capture of MDI to hydroxyl groups on GNs. In other words, it is more accurate to calculate the grafting density of  $\text{NH}_2$  groups with 12.7 wt% of HO-GNs than with 19.9 wt% of  $\text{NH}_2$ -GNs, because the mass of the residual char from the decomposition of MDI and MDA is hard to be deducted. In light of the mass loss of HO-GNs, we obtain a grafting density of one  $\text{NH}_2$  group/69 carbon atoms for  $\text{NH}_2$ -GNs.

### 3. Representative results of flexural measurements.



**Figure S3** Representative stress-strain curves for the pristine epoxy and composites, obtained by flexural measurements at room temperature

All measurements were conducted at room temperature with a crosshead rate of 1 mm/min, following ASTM D790 standard. The flexural properties of each material were tested repeatedly at least five times. Remarkable enhancements in stress at break and Young's modulus are always observed, along with a slight increase in elongation at break. Flexural strength was defined as the value of stress at break while the Young's modulus was obtained

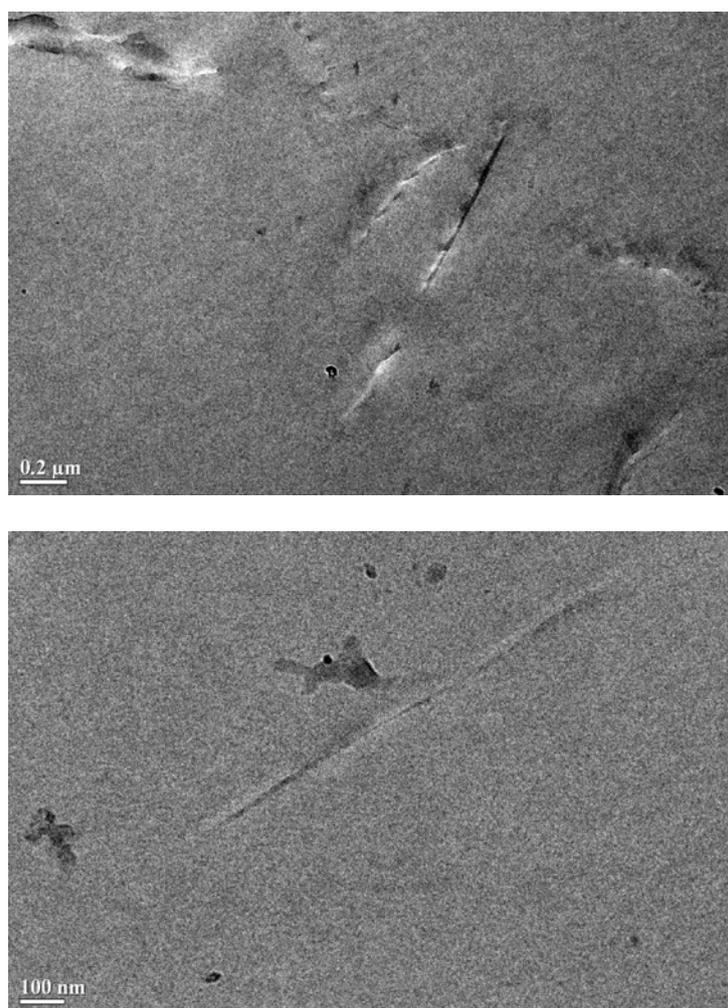
from the slope of linear region of stress-strain curves. Fracture toughness was acquired by integrating these stress-strain curves. The results presented in Table 1 are the average values over several measurements and meanwhile, the corresponding errors are also included.

**Table 1.** Thermal and mechanical properties of the pristine epoxy and nanocomposites

<sup>a</sup> GN Content, wt %	<sup>b</sup> Modulus, GPa	<sup>c</sup> Strength, MPa	<sup>d</sup> Fracture Toughness, MPa.m <sup>1/2</sup>	<sup>e</sup> T <sub>g</sub> , °C	<sup>f</sup> CRR Length, nm
0	2.77±0.18	78.7±2.81	1.63±0.004	165.0	2.65±0.11
0.1	3.25±0.11	90.64±3.35	2.05±0.007	161.9	2.26±0.09
0.2	3.58±0.23	103.95±4.64	2.24±0.183	160.7	2.06±0.08
0.4	4.43±0.47	121.31±6.48	2.82±0.201	157.4	1.99±0.08
0.6	5.42±0.35	151.33±6.03	3.16±0.344	-	-
1.0	5.06±0.58	148.44±7.35	4.10±0.042	-	-

<sup>a</sup>The weight percentage of GNs without organic layers; <sup>b</sup>obtained from the slopes of linear areas in stress-strain curves; <sup>c</sup>defined as the stress at the fracture point; <sup>d</sup>calculated by integrating stress-strain curves; <sup>e</sup>from the peak temperature of tan δ curves in dynamic mechanical analysis; <sup>f</sup>calculated in terms of the method described in ref. [2,3].

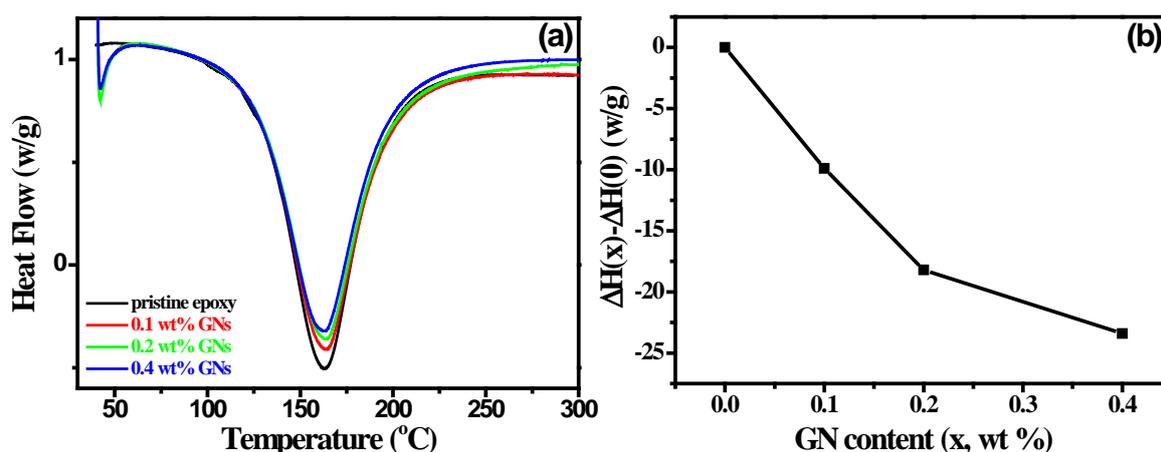
#### 4. TEM observation



**Figure S4** TEM image of nanocomposites with 1.0wt% GNs.

TEM observation is used to confirm the uniform dispersion of GNs in epoxy composites. In our observation, no aggregates are found and also no debonding occurs, which reflects the effectiveness of amine functionalization of GNs for improving dispersion and interface adhesion.

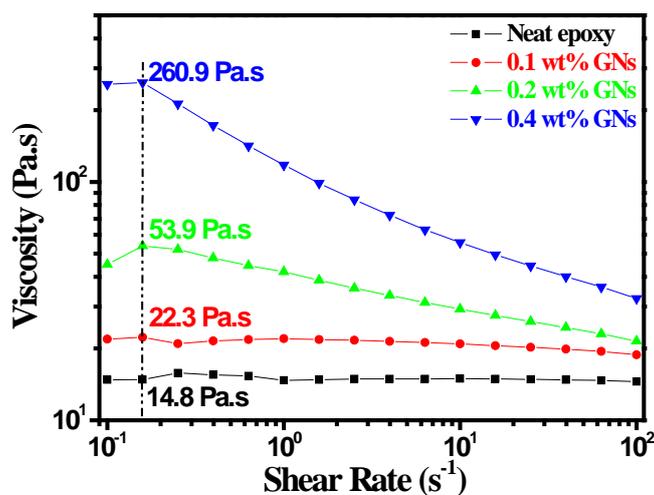
### 5. Calorimetric characterization of cure kinetics.



**Figure S5** Differential Scanning Calorimetry (DSC) monitoring of cure behaviors of the pristine epoxy and mixtures with different GN contents under the same condition: 10 °C/min heating rate in nitrogen atmosphere. (a) original DSC curves and (b) reactive enthalpy differences of all samples relative to the pristine epoxy.

Differential scanning calorimetry (DSC) was used to monitor the cure kinetics of epoxy and composites, with a heating rate of 10 °C/min in nitrogen. No significant difference in the cure kinetics was probed when GNs were added, except small decreases in reaction enthalpy, for example, ~23 J/g for the 0.4 wt% sample. This implies that the addition of extremely low loadings of GNs (0.1 to 0.4 wt%) did not substantially change the kinetic behavior, which should be beneficial to those existing processing procedures of epoxy composites. That is, there is no need to adjust process parameters for the formation of composite containing GNs. Nevertheless, the change in the network structure can be prominent because of the presence of amine-rich surface and the increase of viscosity of reactive systems, see below.

## 6. Steady-state shear viscosities of epoxy and GN mixtures without the curing agent.



**Figure S6** Steady-state shear viscosities versus shear rates of the epoxy resin and mixtures with different GN contents (no curing agents were added for all samples).

Rheological characterization of the graphene-epoxy suspensions was carried out on a Thermal Analysis ARES rheometer with cone-plate geometry (diameter 60 mm and gap 0.108 mm). A 30-min rest time was applied to the samples after setting them between cone and plate so that the suspensions relax and are in the same reference state before loading. All measurements were performed using steady shear testing at room temperature and the shear rate is in the range of 0.1-100 s<sup>-1</sup>

The steady-state shear viscosities ( $\eta_0$ ) of epoxy suspensions with different NH<sub>2</sub>-GN contents can be approximately estimated using the viscosity values ( $\eta$ ) at 0.16 s<sup>-1</sup>. Drastically increased  $\eta_0$  relative to the pristine resin can be observed, from 14.8 to 260.9 Pa.s, an increase of 17 times. We believe such a disparity in the rheological behaviors would affect the formation of epoxy networks, for example, by suppressing the diffusion rate of reactive groups.

## Reference

- 1 Cancado, L.; Takai, K.; Enoki, T.; Endo, M.; Kim, Y. A.; Mizusaki, H.; Jorio, A.; Coelho, L. N.; Magalhaes-Paniago, R.; Pimenta, M. A. *Appl. Phys. Lett.* **2006**, *88*, 163106.
- 2 Donth, E. *J. Non-Crystal. Solids*, **1982**, *53*, 325.
- 3 Yamamuro, I. Tsukushi, A. Lindqvist, S. Takahara, M. Ishikawa, T. Matsuo, *J. Phys. Chem. B*, **1998**, *102*, 1605.