Electronic Supplementary Material (ESI) for RSC Advances
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Supporting Information (SI)

One-pot preparation of unsaturated polyester nanocomposites containing functionalized graphene sheets *via* a novel solvent-exchange method

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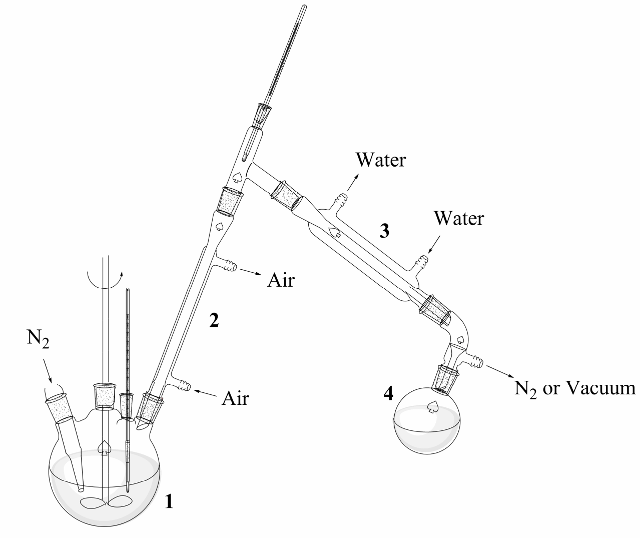
SI.1 Experimental apparatus for the one pot preparation of composites

Figure S1 shows the fractional distillation device that can be used for the preparation of unsaturated polyester resin (UPR), GO/EG dispersions, and FGS/UPR composites.



1-Reactor; 2-Fractionating Tube; 3-Condensation Tube; 4-Receiving Flask

Fig. S1 Fractional distillation device for the preparation of UPR, GO/EG dispersions, and FGS/UPR composites.

SI.2 Origin AFM image of GO in EG solvent

Figure S2 shows the AFM image of GO on a mica substrate from EG dispersions after the solvent-exchange process. The sample was prepared by spin-coating the sonicated solution onto a freshly-exfoliated mica substrate.

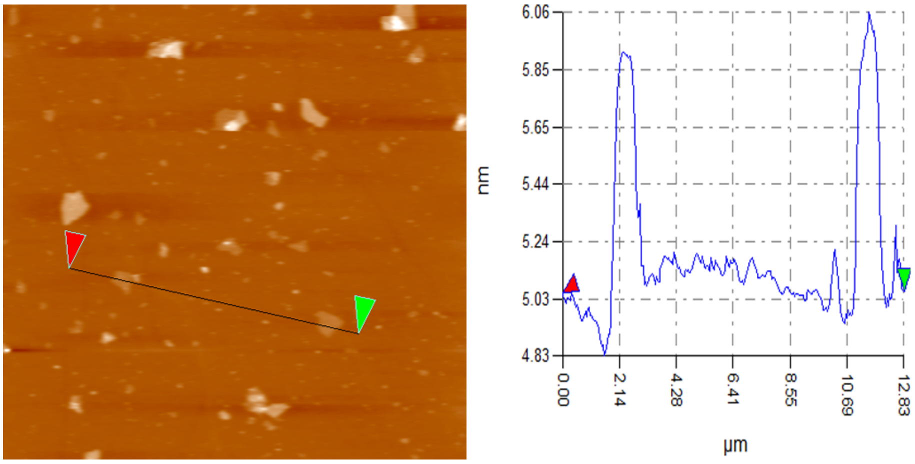


Fig. S2 AFM image and line profile of the GO samples exfoliated in EG solvent.

SI.3 Analysis of functionalized graphene sheets (FGS) in UPR nanocomposites

In order to determine whether the chemical state of GO sheets changed during the high temperature polycondensation process, the GO sheets (in EG solvent without and with addition of hydroquinone) were experienced the same thermal treatment as the polycondensation process. Typically, the dispersions of GO sheets in EG solvent were heated to about 200 ºC (EG's boiling point) for 4 h, in the absence of all the other chemicals (MA, PA, etc.). Then the EG solvent in the dispersions were mostly removed by rotary evaporation and the residues were dried by a vacuum bake oven at 80 °C for 48 h. The two obtained products (heat treated in EG solvent without and with addition of hydroquinone) were labeled as Sample-1 and Sample-2, respectively. On the other hand, some dried GO sheets were prepared by drying GO/H_2O dispersions in an ordinary bake oven at 50 °C for 24 h and then in a vacuum bake oven at 50 °C for 48 h. The mild experimental conditions were employed here to avoid the reduction of GO sheets. All the obtained samples were analyzed by FT-IR, XRD, and TGA.

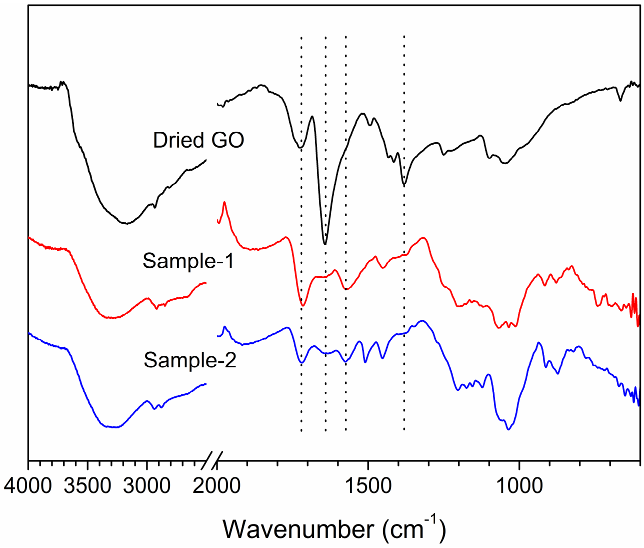


Fig. S3. FT-IR spectra of GO and the samples obtained by heat treatment of GO dispersions.

Figure S3 shows FT-IR spectra of GO and the two treated GO samples. Several characteristic peaks were observed in the spectrum of GO sheets: hydroxyls (3600 cm^{-1} to 2500 cm^{-1} with a maximum at 3182 cm^{-1}, strong and broad), C=O on carbonyl groups (1723 cm^{-1}, moderate), C=O on carboxyl groups or intercalated water (1641 cm^{-1}, strong), C-OH (1384 cm^{-1}, moderate), and C-O (1000-1300 cm^{-1}, moderate).[1-8] However, after the thermal treatment, the bands at 1641 cm^{-1} and 1384 cm^{-1} in the treated samples almost disappeared, indicating the reduction of carboxyl groups. Meanwhile, a new peak at around 1571 cm^{-1} representing C=C skeletal vibrations of unoxidized graphitic domains appeared, which means the structures of treated GO samples are more close to the graphene domain.[1-8] All of these results suggest that the GO sheets were reduced to FGS during the *in situ* melt polycondensation process.

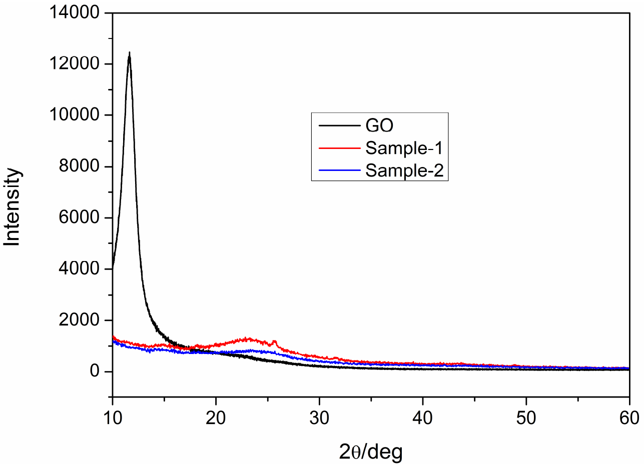


Fig. S4. XRD patterns of GO sheets and the samples obtained by heat treatment of GO dispersions.

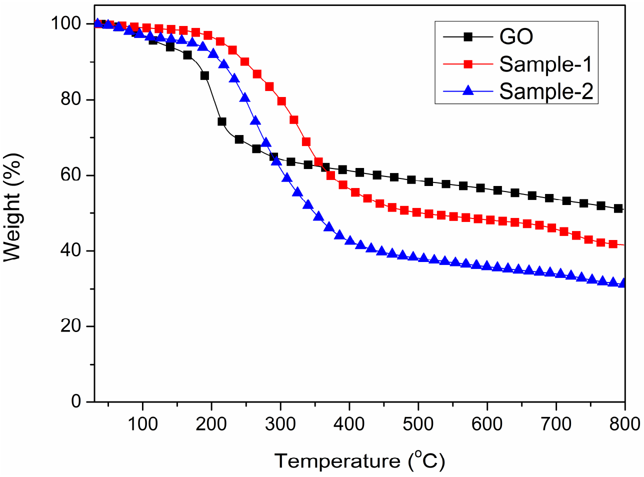


Fig. S5. TGA thermograms of GO sheets and the samples obtained by heat treatment of GO dispersions.

Figure S4 shows the XRD patterns of GO sheets and the samples obtained by the heat treatment of GO dispersions. GO had a typical diffraction peak at 11.6°, which indicates typical hydrated graphite oxide feature.[9] However, after the thermal treatment, this peak disappeared and new weaker bands appeared at 20 to 30°. These results also indicate that the GO has been reduced to FGS.[5, 6, 10]

Figure S5 shows TGA curves of dried GO sheets and the samples obtained by heat treatment of GO dispersions. The GO sheets showed a significant weight loss at around 200 ºC due to the pyrolysis of carboxyl and hydroxyl groups, while Sample-1 and Sample-2 showed significant weight losses at around 335 ºC and 262 ºC, respectively. Besides, the weight losses below 150 ºC for Sample-1 and Sample-2 are lower than that for GO. This means the obtained FGS contain lower content of intercalated water than GO due to the hydrophobic character of FGS.[5] Hence, it is concluded that the obtained FGS showed considerable improved thermal stability because of the reduced functional groups. At last, it was observed that the FGS samples demonstrated larger weight losses than GO over 400 ºC, which may result from the loss of EG molecules linked to GO. During the high-temperature thermal treatment, the EG can possibly react with functional groups on GO to form covalent bonds through esterification, ring-opening reaction, etc. Thus it can be expected that GO has linked to polyesters during the *in situ* melt polycondensation process.

In summary, it can be expected that GO sheets have been reduced into FGS during the *in situ* polycondensation process. And with/without addition of hydroquinone has no obvious difference on the structures of the obtained FGS, but will slightly affected the reduction extent of them.

SI.4 Raman spectra of dried GO sheets from an aqueous solution

Figure S6 shows Raman spectra of the dried GO sheets recorded by (a) a MultiRAM Stand Alone FT-Raman spectrometer (BRUKER Corporation) with λ_{ex} = 1064 nm (b) a LabRAM Aramis Raman spectrometer (HORIBA Corporation) with λ_{ex} = 632.8 nm. It is observed that the Raman spectroscopy (λ_{ex} = 1064 nm) used in this work is not sensitive to the GO sheets, while the other Raman spectroscopy (λ_{ex} = 632.8 nm) can clearly demonstrate the characteristic peaks of D band (1341 cm^{-1}) and G band (1596 cm^{-1}) in GO sheets. The *I*(D/G) value is about 1.60.

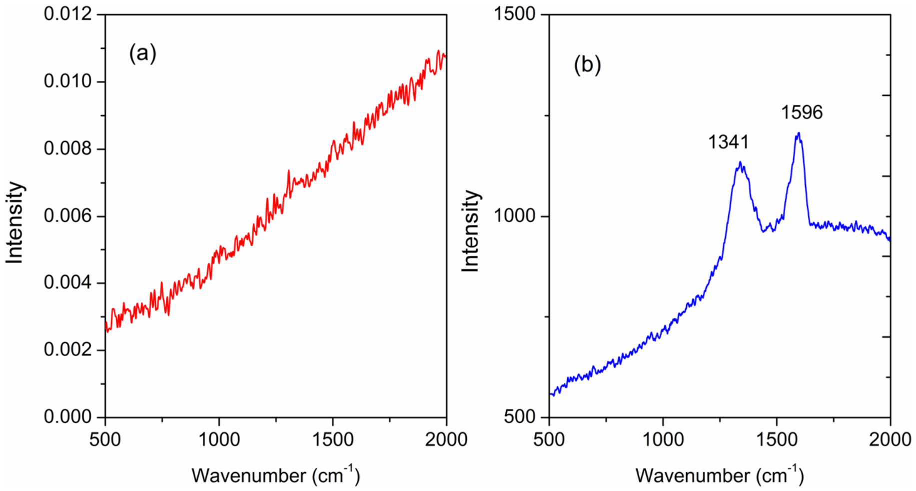


Fig. S6 Raman spectra of GO nanosheets recorded by (a) a MultiRAM Stand Alone FT-Raman Spectrometer with λ_{ex} = 1064 nm (b) a LabRAM Aramis Raman Spectrometer with λ_{ex} = 632.8 nm.

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