Supplementary Information for

A new insight into the in situ thermal reduction of graphene oxide dispersed in polymer matrix

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1. Experimental Section

Materials: Natural graphite in the production of graphene oxide (GO) was supplied by Qingdao BCSMA Co. Ltd. (Qingdao, China). Poly(octene-ethylene) (POE), ethylene-vinyl acetate copolymer (EVA), polymethyl methacrylate (PMMA), poly (styrene-b-(ethylene-co-butylene)-b-styrene) (SEBS), and polystyrene (PS) were provided by China PetroChemical Corporation. The chemical structural formulas of these polymers is shown in **Fig S1**. Other reagents were purchased from commercial suppliers (Aldrich and Sinopharm) and used without further purification.

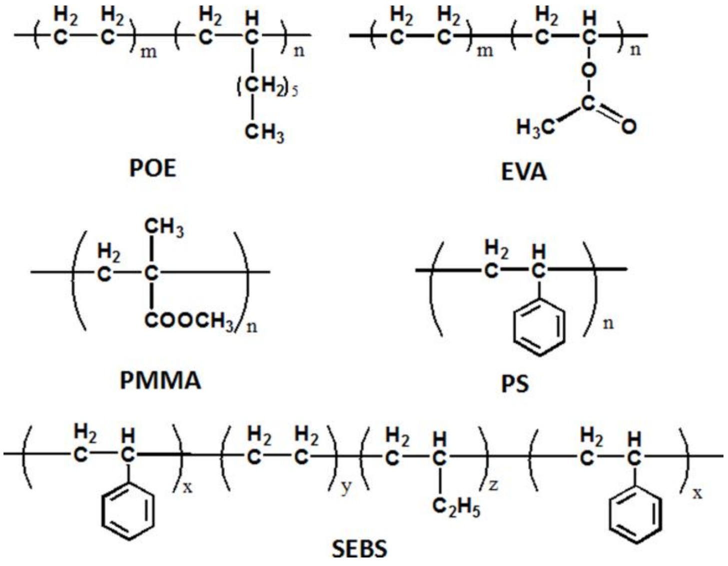

Fig. S1 The chemical structural formulas of POE, EVA, PMMA, PS and SEBS.

Preparation of graphite oxide: Graphite oxide was synthesized from natural graphite by following modified Hummers method. In the typical procedure, 5 g of graphite, 5 g of $NaNO_3$ and 115 mL of H_2SO_4 (98%) were stirred together in an ice bath. Next, 15 g of KMnO4 was slowly added in 30 min and the mixture was stirred for about 0.5 h. Then the ice bath was removed, 230 mL of deionized (DI) water was added and the solution was stirred for 30 min at 35 ^oC while the color of the solution changed from black to yellowish brown. In the next step, 50 mL of H_2O_2 (30%) was added and immediately the color turned to golden yellow, followed by slow addition of 700 mL of DI water. The warm solution was then centrifuged for several times until the PH was ~7. The resulting concentrated GO solution was suddenly frozen in liquid nitrogen and then the ice cube was freezes dried using a FD-1A-50 lyophilizer (Boyikang Co. Ltd., China) at -50 ^oC and less than 20 Pa. After 5-day lyophilization process, low-density, loosely packed graphite oxide powders were finally obtained.

Preparation of polymer/GO nanocomposites: Polymer/GOS nanocomposites with an accurate GO loading of 10 wt% were fabricated in a preparation as follows: solid polymers were dissolved in solvent under violent stirring, while GO dispersions were obtained by dispersing graphite oxide in corresponding solvents with the aid of ultrasonication. The mixtures of polymer solutions and GO dispersions were stirred for 2h and then casted in film form on glass dishes. After that, the solvents were subsequently evaporated by drying at room temperature in air for 2 weeks, and the polymer/GO samples were further dried under vacuum at 50 ^oC for 2 days to remove the residual solvents. For PMMA, PS, and SEBS, tetrahydrofuran as the good solvent was used; For POE and EVA, they could only be dissolved in toluene at 60 ^oC.

Characterization and measurements: Atomic force microscopic (AFM) image was acquired using a Multimode Nano 4 in the tapping mode. Scanning electron microscopy (SEM, TESCAN 5136MM) was applied to observe their surface morphologies at an operating voltage of 20 kV. Raman spectra were collected on a Renishaw inVia Reflex micro-Raman spectrometer with 633 nm laser excitation. XRD patterns were collected using a PANalytical X’pert diffractometer with Cu Kα radiation at an accelerating voltage of 40 kV and a current of 25 mA. In order to determine the reduction temperature of GO in the matrices, DSC and TGA measurement were conducted for polymer/GO nanocomposites and pure GO from 100 to 250 ^{o}C at a heating rate of 5 ^{o}C/min under nitrogen atmosphere. To conform the reduction temperature, PMMA/GOS and SEBS/GOS nanocomposites were selected to be thermally annealed at 150 and 195 ^{o}C for 4h in nitrogen, respectively, and the electrical conductivity of all the thermally treated samples were measured by a four-probe method at room temperature.

2. TGA curves of various polymer/GO nanocomposites

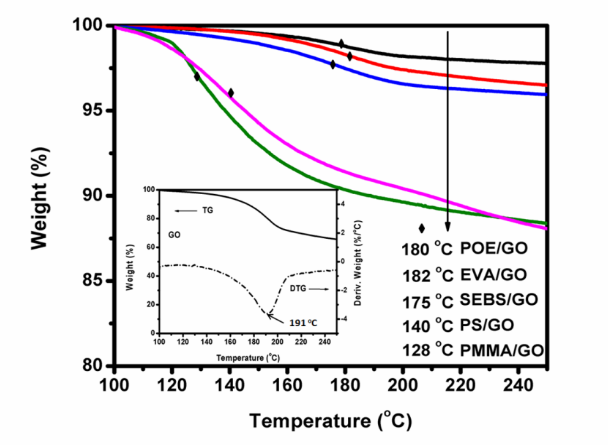

Fig. S2 TGA curves of the polymer/GO nanocomposites.

3. XRD and DSC results for PMMA/GO nanocomposites with different GO concentrations

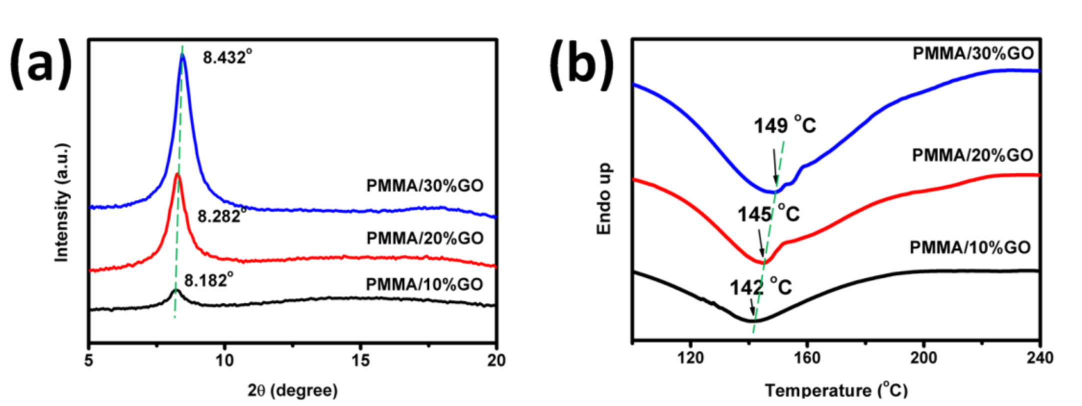

Fig. S3 XRD patterns (a) and DSC curves (b) of PMMA/GO nanocomposites with different GO concentrations.

4. FESEM images of the fracture surfaces of SEBS/GO and PMMA/GO treated at different temperature.

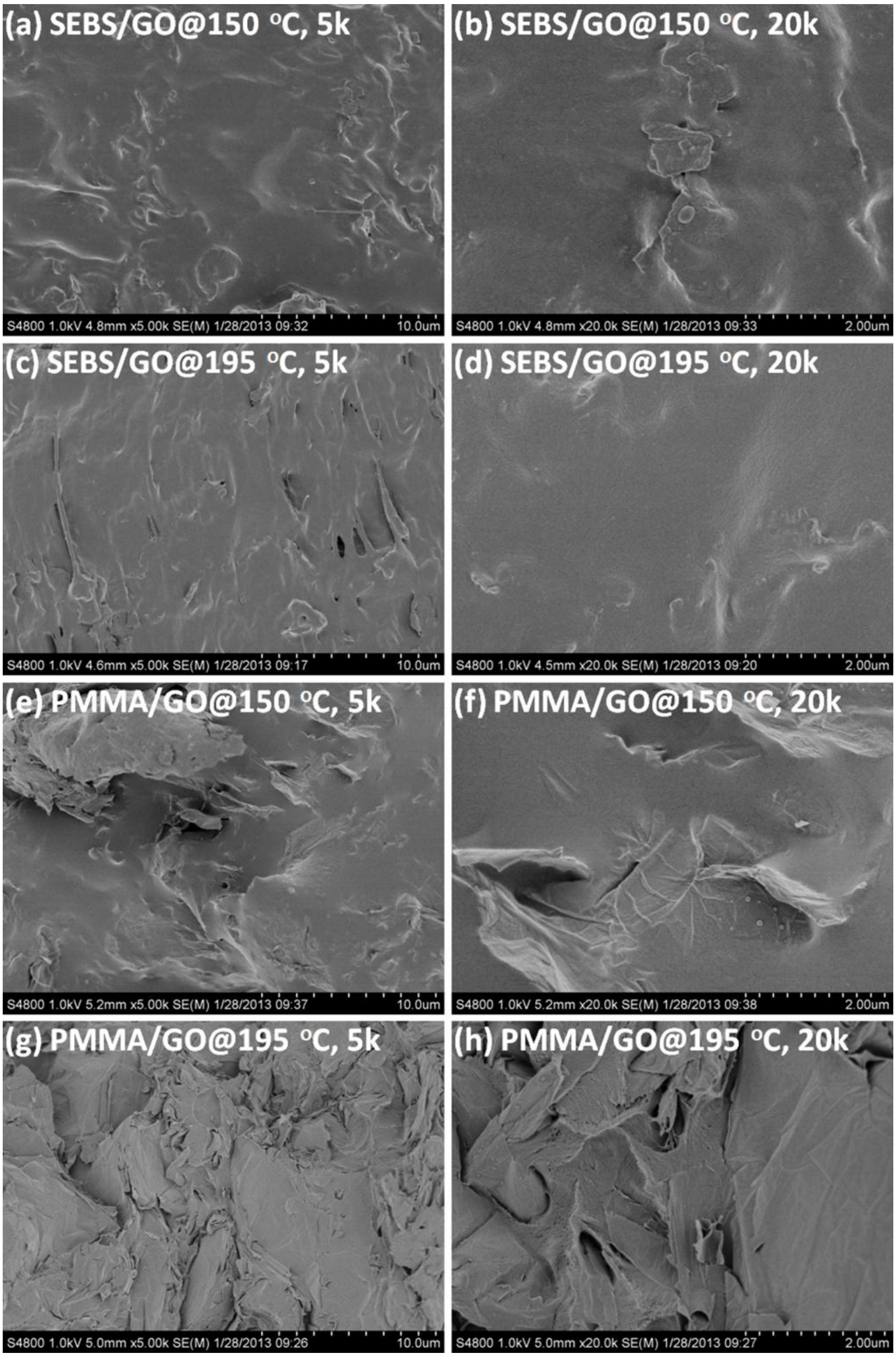

Fig. S4 FESEM images of the fracture surfaces of (a,b) SEBS/GO@150 ^{o}C, (c,d) SEBS/GO@195 ^{o}C, (e,f) PMMA/GO@150 ^{o}C, and (g,h) PMMA/GO@195 ^{o}C.

5. XRD patterns and Raman spectra of PMMA/GO and SEBS/GO treated at 150 and 195 °C, respectively

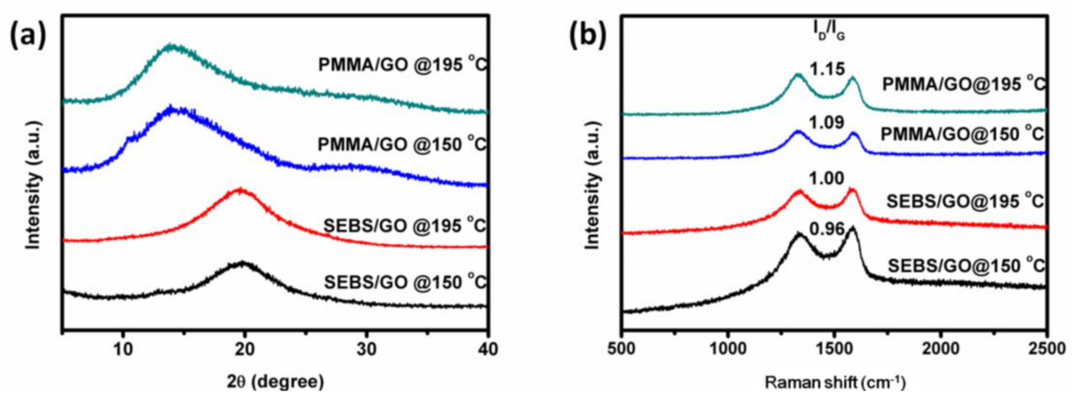

Figure S5 XRD patterns (a) and Raman spectra (b) of the PMMA/GO and SEBS/GO that treated at 150 and 195 °C, respectively.

6. TGA curves and Raman spectra of GO, X-RGO and O-RGO

To confirm the hypothesis that benzene rings, which can form π-π stacking with GO sheets, impact the RT of GO, a comparative experiment that GO is thermal treated at 100 °C for 1h in xylene and octane respectively has been conducted. The results of TGA and Raman of the resulting RGOs (called X-RGO and O-RGO) show that, despite the same temperature and time, X-RGO and O-RGO achieve different reduction degree when it is treated with xylene and octane (Fig.S6). This result agrees with the literatures as well as the similar effect observed in the polymers.

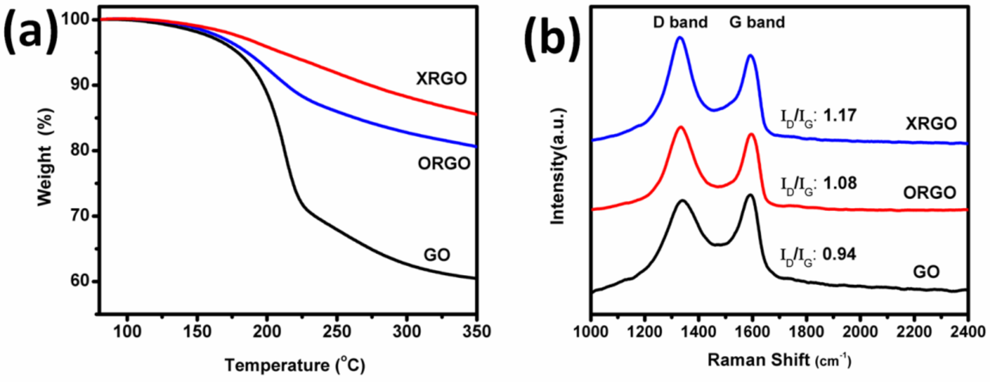

Fig. S6 (a) TGA curves and (b) Raman spectra of GO, X-RGO and O-RGO.

7. DSC curves for polyacrylamide (PAM)/GO nanocomposites

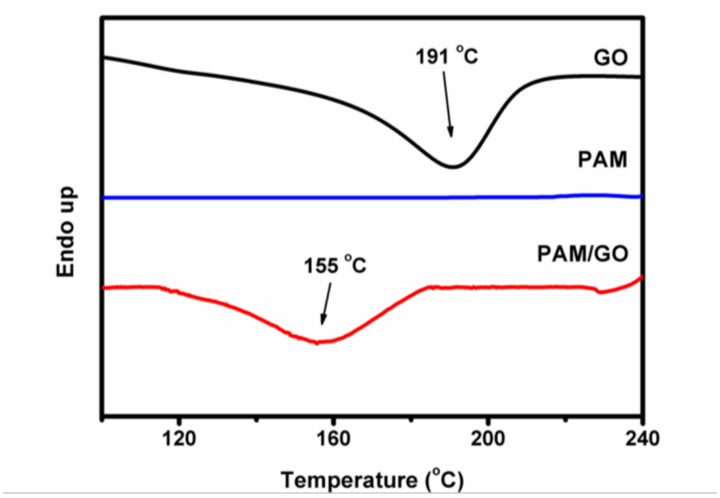

Fig. S7 DSC curves of PAM/GO nanocomposites and pure PAM.

8. DSC and TGA data for various nanocomposites

Table S1. DSC and TGA data for polymer/GO nanocomposites

Sample	RT from DSC (°C)	RT from TGA (°C)
GO	191	191
POE/GO	190	180
SEBS/GO	185	175
PS/GO	153	140
EVA/GO	186	182
PMMA/GO	142	128