Supporting information

Straightforward Synthesis of Conductive Graphene/Polymer Nanocomposites from Graphite Oxide

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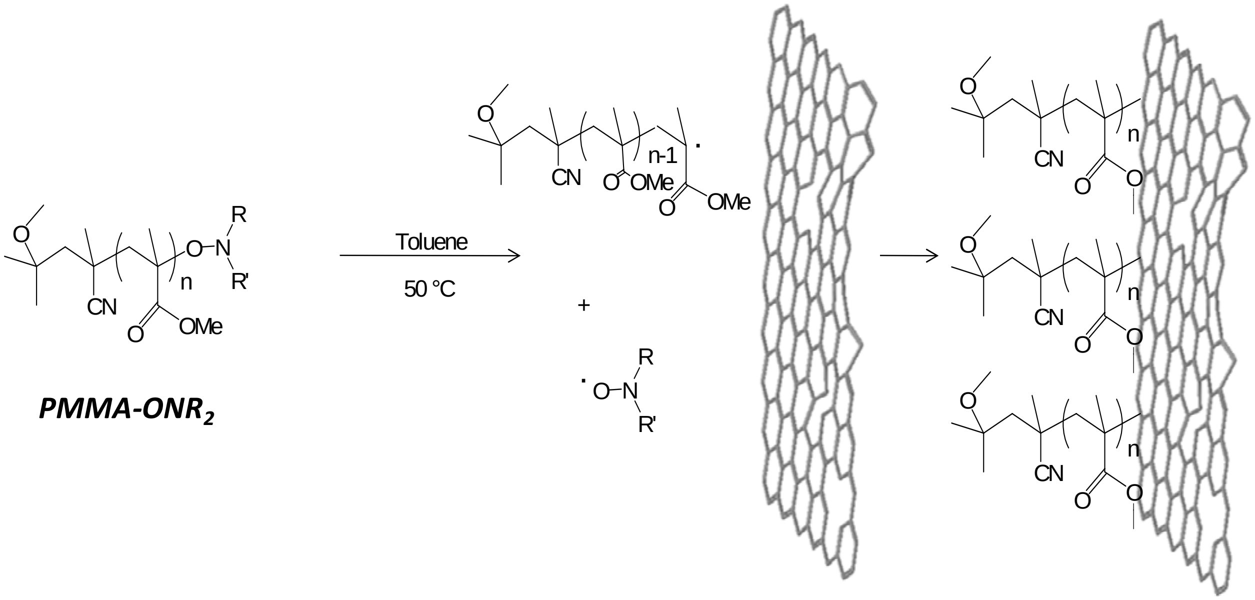

Scheme S1. Radical grafting of poly(methyl methacrylate) end-capped by an alkoxyamine (PMMA-ONR$_2$) onto graphene.

Materials

Methyl methacrylate (>99%, Aldrich), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) (Wako), $NaNO_3$ (Merck), $NaBH_4$ (>98%, Aldrich), $KMnO_4$(>99%, Aldrich), H_2SO_4 (95-97%, Merck), H_2O_2 (30%, Aldrich), $NaNO_2$ (Baker), 5μ graphite nanoplatelets (GP) (XGScience), poly(methyl methacrylate) (Diakon; Mn = 51600 g/mol, Mw/Mn = 1.70) are used as received. Methyl 2-methyl-3-nitro-2-nitrosopropionate (NMMA) is prepared starting from MMA, H_2SO_4 and $NaNO_2$ by a method described elsewhere.[1]

Characterizations

Size exclusion chromatography (SEC) is carried out in tetrahydrofuran (THF) (flow rate: 1mL min^{-1}) at 40°C with a Waters 600 liquid chromatograph equipped with a 410 refractive index detector and styragel HR columns (four columns HP PL gel 5μm 10^5Å, 10^4Å, 10^3Å, 10^2Å). Poly(methyl methacrylate) standards are used for calibration.

TGA analyses are carried out with a Hi-Res TGA Q500 from TA Instruments at a heating rate of 40°C/min under nitrogen.

X-ray diffraction analysis (XRD) is carried out with a powder diffractometer Siemens D5000 (Cu Kα radiation with λ=0.15406 nm, 50 kV, 40 mA, Ni filter, $\theta/2\ \theta$ geometry) at room temperature for 2θ varying from 1.65° to 50° by 0.04° steps.

Dynamic rheological measurements are carried out with an ARES G2 rheometer from TA instrument. Compression-molded samples at 180°C for 1min with diameter 25 mm, thickness 2 mm, are run at 180 °C with a strain of 1%.

TEM analysis is realized on a TEM, Philips CM100. Ultrathin sections (50–80 nm) are prepared with an Ultramicrotome Ultracut FC4e, Reichert-Jung of compression-molded samples at 180°C for 1min. No staining is used since the graphene sheets are contrasting enough in the polymer matrix.

Electrical measurements are performed with a Vector Network Analyser Model Wiltron 360B operating over the frequency range 40MHz-40GHz. Each nanocomposite sample to be characterized consists of a compression-molded, at 180°C for 1min, thin plate of

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[1] Detrembleur, C.; Claes, M.; Jérôme, R. *ACS Symposium Series, American Chemical Society (ACS)* **2003**, *854*, 496.

same thickness (1 mm) and surface (4x4 mm^2) and is used as a microwave substrate on which a ground plane and a microstrip line are deposited.

Raman scattering spectroscopy is performed on powder samples with a LabRam Spectrometer (Jobin-Yvon) equipped with a confocal microscope and an Andor BR-DD CCD detector. The excitation is at 647.1 nm from a Spectra Physics krypton laser.

Synthesis of PMMA-ONR$_2$. The synthesis of PMMA-ONR$_2$ is carried out by optimizing the procedure reported elsewhere.[1] 0.075 g of methyl 2-methyl-3-nitro-2-nitrosopropionate (NMMA) (0.426 mmol) and 0.13 g of 2,2'-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) (0.421 mmol) are added in a 500 ml round bottomed flask and degassed by several vacuum-nitrogen cycles. Degassed MMA (200 mL, 1.88 mol) is then added and the mixture is heated at 50°C for 3h. A sample is picked out for the monomer conversion (26 %). THF (200 mL) is added and the polymer was precipitated in MeOH (4L). After filtration and drying the polymer under vacuum, the polymer is dissolved in THF and analyzed by SEC using a PMMA calibration. Mn = 60000 g/mol, Mw/Mn = 1.3.

Synthesis of GO. GO is prepared by oxidation of graphite following the method developed by Hummer et al.[2] H_2SO_4 (12 mL) are placed in a 250 mL erlenmeyer at 0 °C and then charged with 250 mg GP, 250 mg $NaNO_3$ and 1.8 g $KMnO_4$. The green mixture is placed under stirring at room temperature for 18h. H_2O (20 mL) is then added dropwise to the brown reaction mixture. After 0.5h, when the mixture warms at 90°C, another 50 mL of water is added and then 1.5 mL of 30% aq. H_2O_2. The yellow mixture obtained is centrifuged 15 min at 10000 round/min. The obtained solid is dried and analyzed by Raman spectroscopy (**Figure 2d**).

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[2] W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.

Synthesis of RGO grafted with PMMA. 100 mg GO are placed in H_2O (100 mL) under stirring for 1 h. Then, a solution of PMMA-ONR_2 (1 g) in toluene (100 mL) is added. The solution is yellow in the water phase and colorless in toluene phase. The mixture is placed 10 min under sonication, degassed and then placed at 50°C under stirring (1000 rpm) and inert atmosphere (argon). Then, $NaBH_4$ (380 mg) is added. The reaction mixture turns black in the toluene phase after 5h. The organic phase is then poured into MeOH (5L) for precipitating the nanocomposite that is filtered and dried under vacuum. The nanocomposite is then analyzed by transmission electron microscopy (TEM) (**Figures 2a** and **b**, and **Figure S3**). In order to determine the amount of polymer grafted to RGO, the product is re-dispersed in toluene (50 ml) and filtered on a 0.2 μm filter. This step is repeated twice to remove excess of ungrafted PMMA. RGO grafted by PMMA is finally dried under vacuum and analyzed by TGA (20% PMMA-ONR_2 grafted on the RGO; **Figure S2**) and Raman spectroscopy **(Figure 2d)**. The elemental analysis of RGO: C 86.08; H 1.49; O 12.43. This RGO is stable for the TGA conditions **(Figure S2)**.

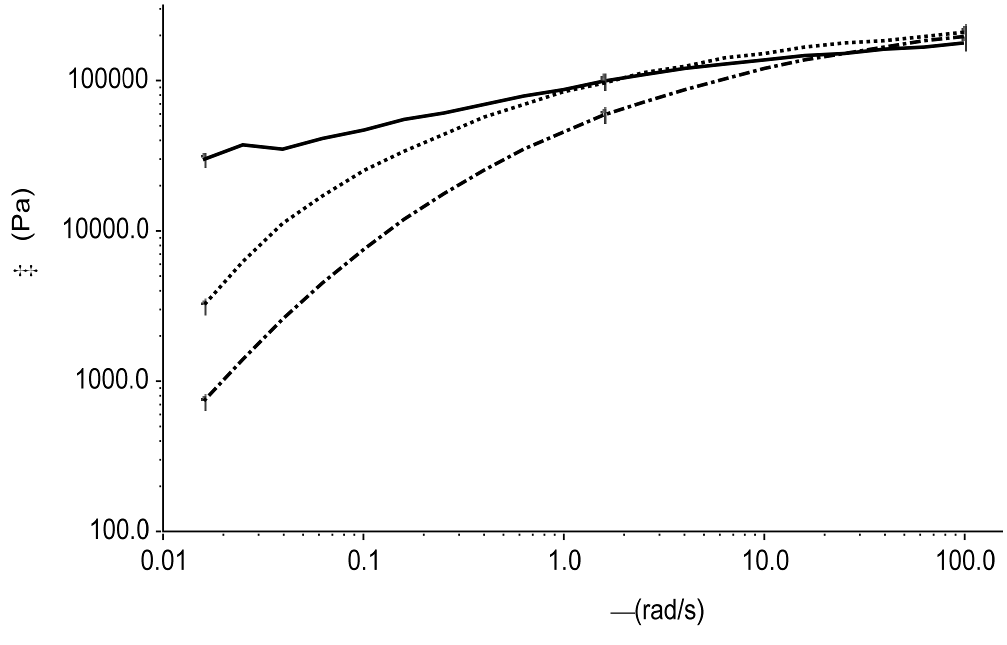

Figure S1. Storage modulus as a function of frequency for : PMMA (dashed-dot line), PMMA/graphene (5wt%RGO-g-PMMA) prepared using the reactive biphasic procedure (solid line), PMMA nanocomposite (5wt% GP-g-PMMA) prepared by grafting PMMA-ONR_2 on pristine graphite (dot line).

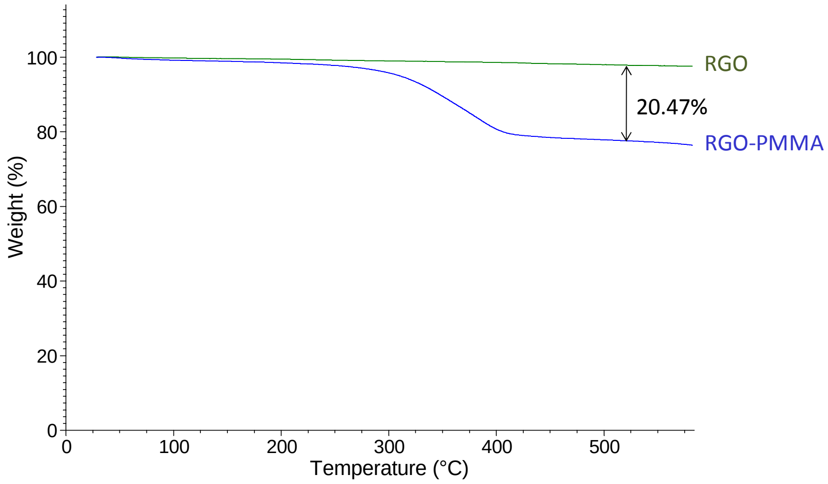

Figure S2. Thermogravimetric analysis (TGA) of RGO (in green) and RGO grafted by PMMA (in blue) under nitrogen (RGO-g-PMMA).

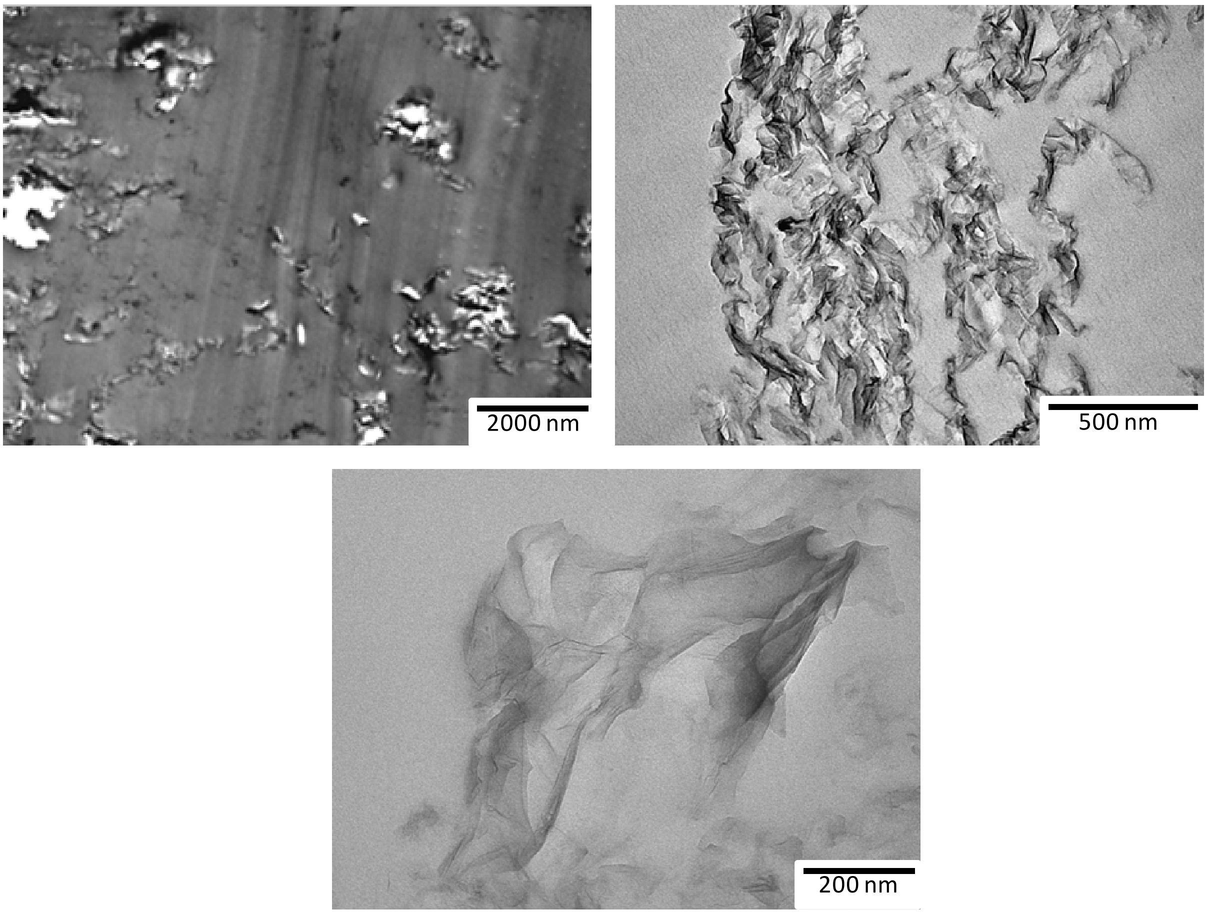

Figure S3. TEM micrograph of RGO dispersed in PMMA using the reactive biphasic procedure (RGO-g-PMMA/PMMA).

Synthesis of RGO dispersed in PMMA without grafting

10 mg GO are placed in H_2O (10 mL) under stirring for 1 h, then a solution of PMMA (Mn = 51600 g/mol, Mw/Mn = 1.70; 100 mg) in toluene (10 mL) is added. The solution is yellow in the water phase and colorless in the toluene phase. The mixture is placed 10 min under sonication and then $NaBH_4$ (40 mg) is added to the solution under stirring (1000 rpm). The reaction mixture (both water and toluene phases) turns into black after 5h. The organic phase is then poured into MeOH (200 mL) for precipitating the nanocomposite that is filtered and dried under vacuum. TEM analysis of the composite evidences the poor RGO dispersion with the presence of large RGO aggregates **(Figure S4)**. The product is then re-dispersed in toluene and filtered on a 0.2 μm filter. This step is repeated twice. The final product is finally dried under vacuum and analyzed by TGA until 600°C **(Figure S5)**. Less than 2wt% PMMA is adsorbed on RGO.

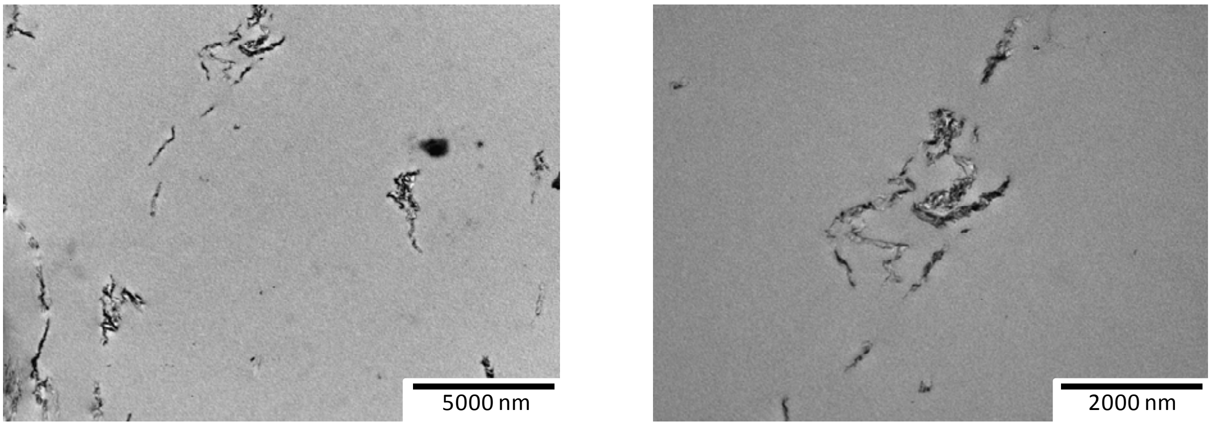

Figure S4. TEM micrograph of RGO dispersed in PMMA without polymer grafting using the biphasic procedure.

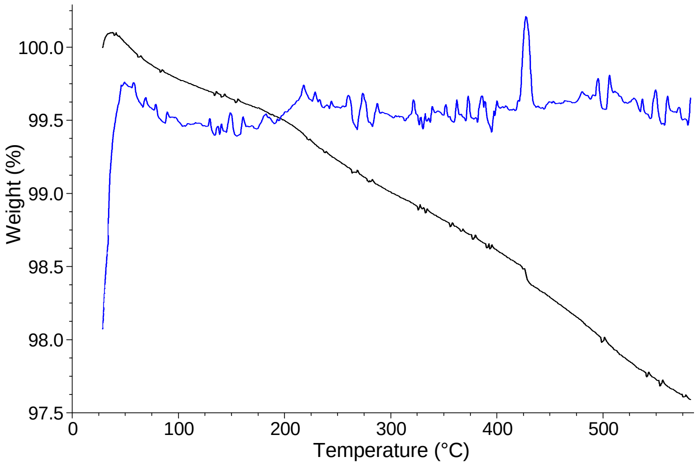

Figure S5. Thermogravimetric analysis (TGA) of RGO after PMMA washing

Synthesis of pristine graphite (GP) grafted with PMMA

100 mg GP and 2 g of PMMA-ONR_2 are added in a 250 mL round bottomed flask and degassed by several vacuum-nitrogen cycles. Degassed toluene (200 mL) is then added and the mixture is placed under sonication for 5 min and then heated under vigorous stirring (1000 rpm) at 50 °C for 5 h. The composite is precipitated in MeOH (2 L) and dried under vacuum and the dispersion of GP in the PMMA is analyzed by TEM **(Figure S7)** and DRX (**Figure 2c** in main text). Only aggregates are evidenced by these techniques. After removal of the non-grafted polymer by washing with toluene (3×50 mL), the residue is dried under vacuum and analyzed by TGA (20wt% grafted PMMA on GP; **Figure S6**).

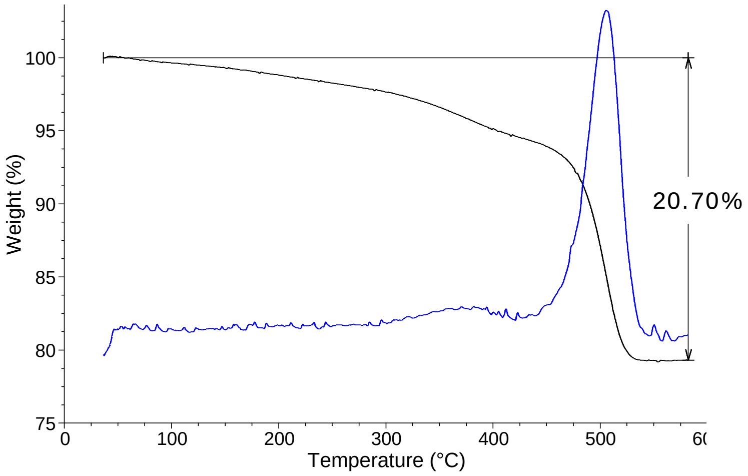

Figure S6. Thermogravimetric analysis (TGA) of pristine graphite grafted by PMMA, under nitrogen.

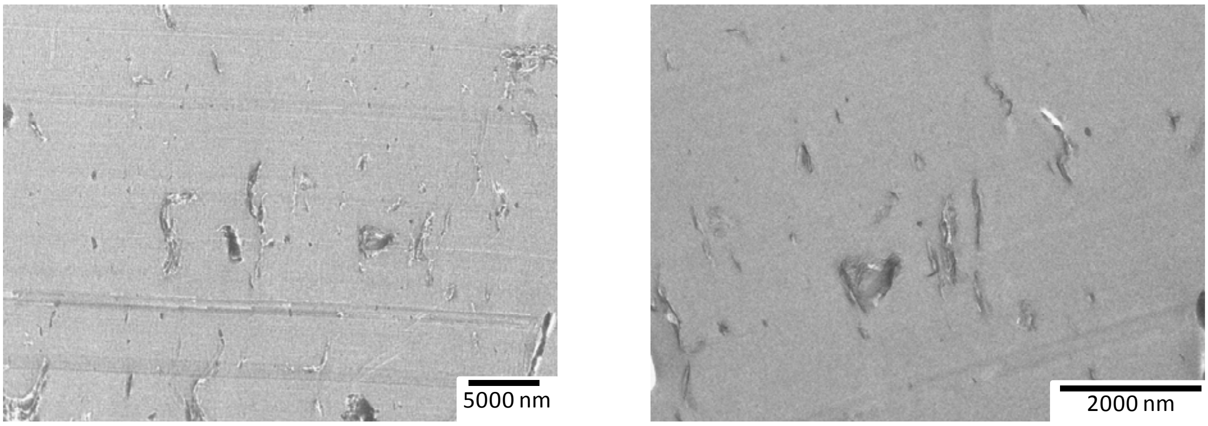

Figure S7. TEM micrograph of the pristine graphite (GP)/PMMA nanocomposite prepared by reaction of PMMA-ONR_2 in solution with pristine graphite.