Supporting Information

A supramolecular approach toward organo-dispersible graphene nanosheets and fabrication of polymer nanocomposites therefrom

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Experimental Procedures:

Preparation:

a) **Im-OH/TFSI/RGO:** Practically, reduced graphene sheets (RGO) were prepared by reducing exfoliated graphene oxide (GO) in the presence of functional imidazolium ionic liquid. Typically, GO was synthesized from natural graphite through a modified Hummers method [1], and Im-OH/TFSI was prepared by anion exchange between bromide and TFSI following a reported procedure.[2] To prepare RGO/Im-OH/TFSI, 20 mg Im-OH/TFSI was added into a 6 mL aqueous dispersion of graphite oxide (1 mg mL^{-1}). Successively, 10 mL hydrazine was injected into the solution and the reaction was carried out at 80 °C overnight. The resulting black precipitate was subsequently washed to remove excess hydrazine and Im-OH/TFSI before freeze-drying.

b) **Graphene/PCL nanocomposites**: For graphene/PCL nanocomposites, an appropriate amount of ImTFSI/RGO (depend on final Graphene loading requirements) were readily dispersed and exfoliated in ε-caprolactone monomer (5 mL) by sonication at room temperature. A stable homogeneous black dispersion was formed in contrast to RGO dispersion without any stabilizer. After adding tin (II) octate catalyst the mixture was deoxygenated by vacuum/dry nitrogen for several cycles. The flask, charged with the above reactants, was placed in a preheated oil bath at 70 °C to perform ring opening polymerization under a nitrogen atmosphere and constant stirring. After a 20 h period, the black hard solid, preferably the graphene/PCL nanocomposite was isolated by freeze rupturing the flask.

Characterization:

Transmission electron microscopic (TEM) measurements were carried out using Philips CM200 with a tungsten filament ken with CCD Gatan digital camera. X-ray diffraction (XRD) patterns were acquired on a Siemens D5000 x-ray diffractometer (Cu Kα). The Raman spectra were obtained by using a Renishaw Raman system Model 3000 spectrometer equipped with an integral microscope (Olympus BH2-UMA). Radiation from a He–Ne laser (633 nm) was used as the excitation source. The FTIR were recorded using a Bruker Infrared Spectrometer. Spectra were obtained using 32 scans and a 4 cm^{-1} resolution. The thermal behaviours of the MWCNTs were studied by using a TA instruments Q500 TGA at a heating rate of 10 $^{\circ}$C /min under inert atmosphere. X-ray photoelectron spectroscopy (XPS) was used to control the elemental composition of the samples. All reported spectra were recorded at a 90° take-off angle relative to the substrate with a VG ESCALAB 220iXL spectrometer using the monochromatised Al Kα radiation (1486.6 eV). A survey spectrum was first recorded with pass energy of 100 eV, the core level lines with pass energy of 31 eV. The core level lines analyzed (C1s, O1s, N1s, S2p, Na1s, F1s) were referenced with respect to the C 1s binding energy conventionally set here at 285.0 eV and characteristic of aliphatic moeities. XPS results were analyzed by curve-fitting of the C1s, O1s and N1s signals by using mixed Gaussian–Lorentzian curves after a linear background subtraction. The storage modulus of resulting graphene/PCL nanocomposites was measured using dynamic mechanical thermal analyses (DMTA). The measurements were performed under ambient atmosphere using a 2980 DMTA apparatus from TA Instruments in a dual cantilever. The measurements were carried out at a constant frequency of 1 Hz, a temperature range from -100 to 50 °C at a heating rate of 5 °C min^{-1}. Three samples were characterized for each composition.
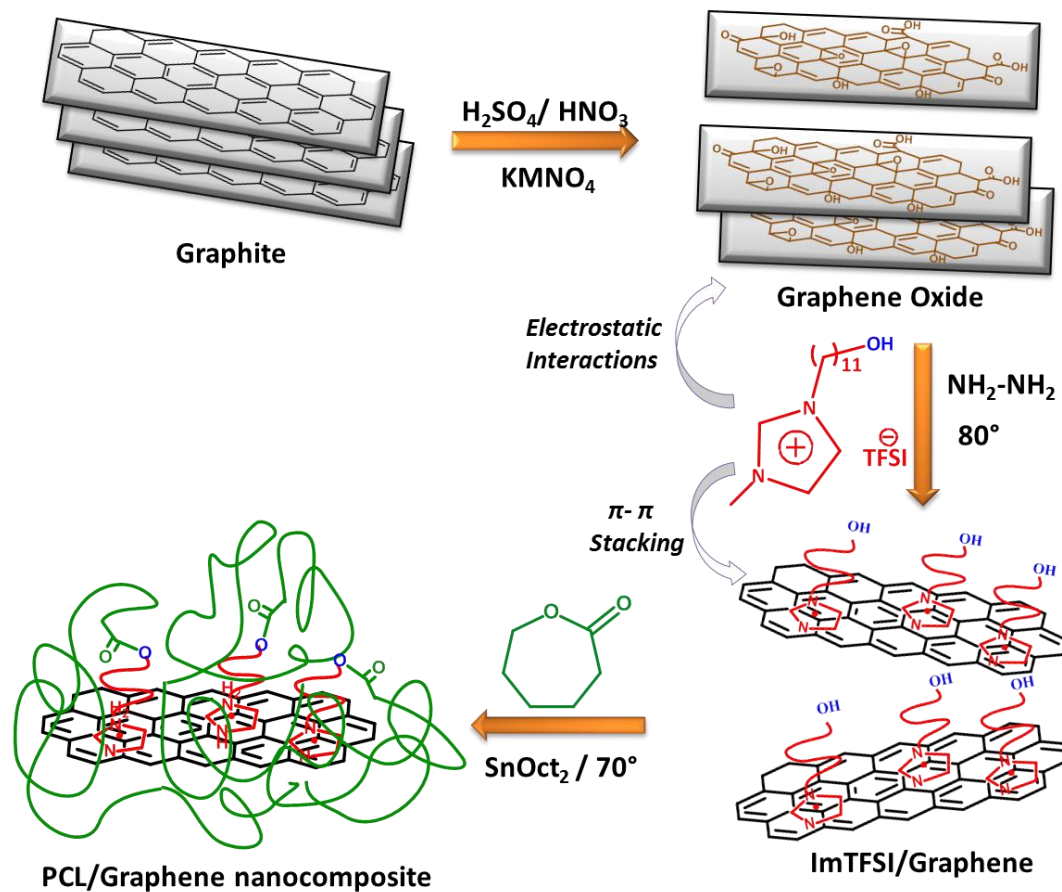
Scheme S1. Schematic illustration of the synthetic process of ImTFSI/Graphene and PCL nanocomposites preparation via ROP.
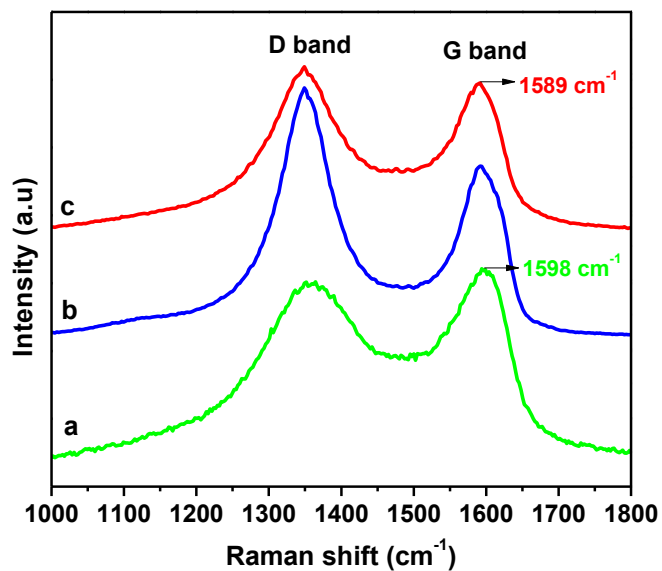
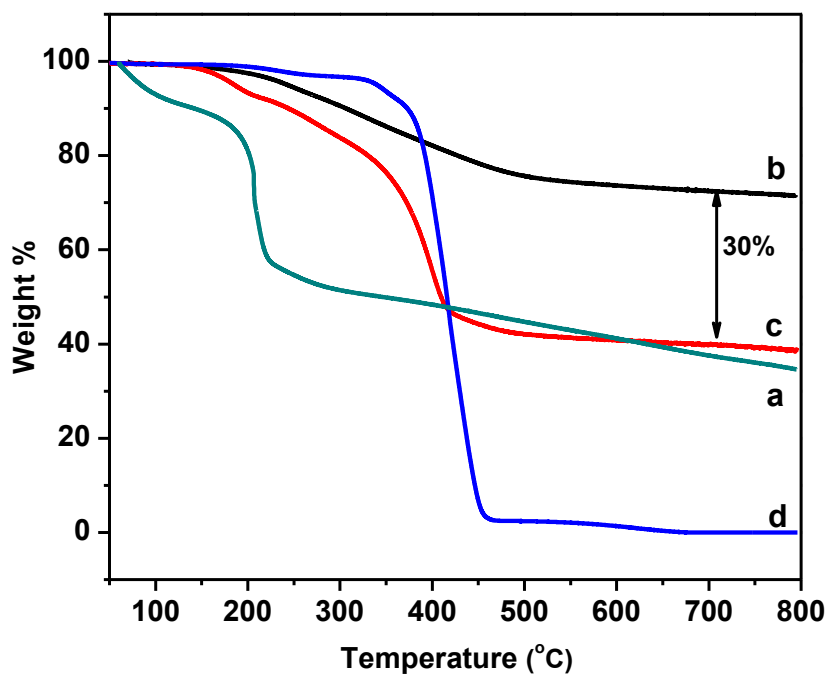**Figure S1**: Raman spectra of GO (a), RGO (b) and Im-OH/TFSI/RGO (c).

Figure S2: Thermogravimetric analysis of GO (a), RGO (b), Im-OH/TFSI/RGO (c) and imidazolium salt (d).
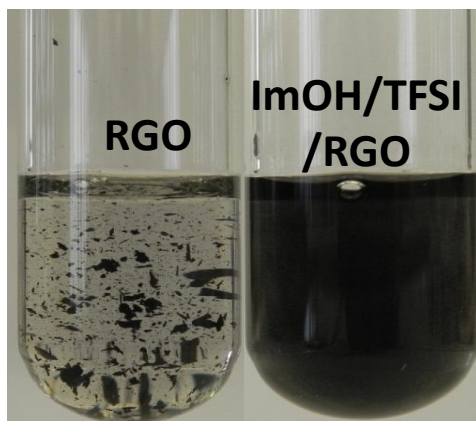
Figure S3: Dispersions of pristine graphene and imidazolium functionalized graphene in caprolactone (CL) monomer.

References:

1. a) Xu,Y.; Bai, H.; Lu, G.; Li, C., Shi, G. *J. Am. Chem. Soc.* **2008**, *130*, 5856. b) Hummers, W. S.; Offeman, R. E. *J. Am. Chem. Soc.,* **1958**, *80*, 1339.

2. Alcalde, E. ; Dinares, I.; Ibanez, A.; Mesquida, N. *Chem. Commun*, **2011**, *47*, 3266.