Supplementary Material (ESI) for Nanoscale

Supporting Information

Preparation and Characterization of Polypropylene-graft-Thermally Reduced Graphite Oxide with an Improved Compatibility with Polypropylene-based Nanocomposite

EXPERIMENTAL SECTION

Materials

Natural graphite powder (Alfa Aesar) was used as the starting material for the preparation of graphite oxide (GO). The graphite had a particle size of ~70 μm with a purity of 99.9995% and a density of 2.25 g/cm3. 1,6-diaminohexane (Alfa Aesar, purity > 98 %) was used without further purification. Polypropylene-graft-maleic anhydride (PP-g-MA, 8-10 wt% MA) with an average Mw of ~9,100 was obtained from Sigma-Aldrich Co Ltd. Polypropylene (average Mw ~190,000, melt index= 35 g/10 min) was purchased from Sigma-Aldrich Co Ltd. and used as the matrix. Anhydrous stabilized tetrahydrofuran (THF) was supplied by Lancaster Co., Eastgate, White Lund, Morecambe, England.

Preparation of GO and thermally reduced graphite oxide (TRGO)

Natural graphite powder was oxidized using the Staudenmaier method.[1] In this method, graphite (5 g) was first mixed with sulfuric (87.5 mL) and nitric (45 mL) acid, and then stirred. Once the graphite had become uniformly dispersed, potassium chlorate (55 g) was slowly added, and stirring was continued for at least 96 hours. After the completion of the oxidation reaction, the mixture was poured into deionized water and then filtered. The GO was rinsed repeatedly and redispersed in a 5% aqueous solution of HCl three times. It was then washed repeatedly with deionized water until the pH of the filtrate was neutral. The GO slurry was then dried and pulverized twice. Finally, the GO was heated to 1050 °C in an inert gas atmosphere and held in a furnace for 30 s to form TRGO.

Functionalization of TRGO directly with 1, 6-diaminohexane

TRGO prepared as described above (500 mg) was suspended in THF (200 mL) and sonicated for 30 min in an ultrasonic bath. The suspension was then transferred into a three-neck flask and pre-purged with N_2. A THF solution (50 mL) containing 1, 6-diaminohexane (DAH) (1.45 g) was added with stirring. The mixture was heated to 80 °C and refluxed for 24 h under N_2.

The mixture was then cooled, and separated by filtration through a 0.2 μm polytetrafluoroethylene (PTFE) membrane, thoroughly washed with anhydrous THF and acetone to remove the residual 1,6-diaminohexane, and then dried in a vacuum oven at 80 °C overnight to remove the solvent.

Grafting of polypropylene on TRGO and preparation of PP/PP-g-TRGO nanocomposites

PP-g-MA was grafted on to TRGO-DAH using a solution process. Toluene was first heated to 120 °C under N_2 and PP-g-MA was added and stirred until its complete dissolution to form a homogeneous light-yellow solution. TRGO-DAH was then added into the resulting homogeneous solution (the weight ratio of PP-g-MA: TRGO-DAH was 2:1) and refluxing at 120 °C was continued for a further 24 h under N_2.

The mixture was next cooled to room temperature and the modified TRGO was then isolated by filtration through a 0.2 μm polytetrafluoroethylene (PTFE) membrane, and thoroughly washed with methanol several times to remove any impurities, and then dried in a vacuum oven at 80 °C overnight to remove the solvent. This yielded the polypropylene-grafted-thermally reduced graphite oxide (PP-g-TRGO).

The PP-g-TRGO was homogenized and blended with a iPP matrix using a Brabender, and the molten compounds were formed. Mixing parameters of 180 °C and 10 min were used, with a rotational speed of 50 rpm. For comparison, nanocomposites of iPP/TRGO with various TRGO contents (0.1, 0.25, and 0.5 wt% based on the neat TRGO contents determined by TGA) were also prepared under the same processing conditions.

Characterization and Instruments

X-ray photoelectron spectra (XPS) measurements were performed using a PHI Quantera SXM/AES 650 Auger Electron Spectrometer (ULVAC-PHI INC., Japan) equipped with a hemispherical electron analyzer and a scanning monochromatic Al Kα (hυ=1486.6 eV) X-ray source. A small spot lens system allowed the analysis of samples that had an area of less than 1 mm^2. X-ray diffraction (XRD) was carried out at room temperature at a scan rate of 2° min^{-1} using a Shimadzu XD-5 X-ray diffractometer (40 kV, 30 mA, $\lambda = 0.1542$ nm) with a copper target and a Ni filter. The Raman spectroscopy was carried out on a Stellar-PRO confocal Raman microscopy system (MODU-LASER, LLC), with a laser wavelength of 488 nm. Transmission electron microscopy

(TEM) analyses were conducted using a JEM-2100 electron microscope at 200 kV, and the TRGO-DAH and PP-g-TRGO for the TEM measurements were prepared using one drop casting on a lacey copper grid followed by evaporation of the solvent in air at room temperature. Ultrathin sections of iPP/TRGO and iPP/PP-g-TRGO nanocomposites with a thickness of less than 100 nm were prepared by cutting with a diamond knife using a microtome technique, and collected on 300-mesh copper grids. The fractured surfaces of iPP/TRGO and iPP/PP-g-TRGO nanocomposites were investigated using a field emission-scanning electron microscope (FE-SEM, JEOL JSM-6330, Japan) with an accelerating potential of 15.0 kV. DSC measurements were conducting using a differential scanning calorimeter (Perkin-Elmer, diamondDSC, USA) in a nitrogen atmosphere. The samples were first heated from 25 ^{o}C to 190 ^{o}C (10 ^{o}C min^{-1}) and held at that temperature for 5 min in order to remove the thermal history. Afterwards, the samples were cooled back to 25 ^{o}C with a rate of 10 ^{o}C min^{-1}. Thermogravimetric analysis (TGA) was carried out using a DuPont-TGA951 at a heating rate of 10 °C min^{-1} in an N_2 atmosphere.

Table S1. Analysis of the deconvoluted (a) C1s peaks and (b) N1s peaks obtained from XPS and their relative atomic percentages for TRGO, TRGO-DAH, and PP-g-TRGO; (c) ATR-FTIR assignments for TRGO-DAH, PP-g-TRGO, and PP-g-MA.

(a)

Sample Name	C1s fitting Binding energy (eV) (Relative atomic percentage %)									
	C=C[2] (sp^2)	C-C[2] (sp^3)	$C-NH_2$[3]	C-OH[4-5]	C-N-C[7]	C-O-C[4-5]	N-C=O[6]	C=O[4-5]	O-C=O[4-5]	π-π*
TRGO	284.2	285.1	-	285.8	-	286.5	-	288.2	289.4	291
	(71.1)	(10.6)		(4.74)		(5.09)		(3.03)	(2.78)	(2.57)
TRGO-DAH	284.0	284.8	285.4	285.8	286.1	286.5	-	288.2	289.2	291
	(60.9)	(17.3)	(3.93)	(4.51)	(3.93)	(1.51)		(2.43)	(2.81)	(2.61)
PP-g-TRGO	284.2	284.8	-	385.5	286.1	286.5	287.9	288.2	289.2	291
	(51.2)	(38.5)		(1.77)	(2.19)	(1.19)	(2.32)	(0.70)	(1.53)	(0.58)

(b)

Sample Name	N1s fitting Binding energy (eV) (Relative atomic percentage %)					
	NH_2-C (primary amine)[7-9]	C-NH-C (secondary amine)[10]	C-N(C)-C (tertiary amine)[7, 11-12]	N-C=O (amide)[9,11]	- $NH^{\delta+}$ - (hydrogen bonding of secondary amine)[10]	$-NH_3^+$ (Protonated amine)[9,13]
TRGO	-	-	-	-	-	-
TRGO-DAH	398.5	399.3	400.3	-	401.1	401.6
	(39.0)	(23.2)	(13.0)		(13.8)	(11.0)
PP-g-TRGO	-	399.2	-	400.5	-	-
		(45.8)		(54.2)		

(c)

Sample Name	**Wavenumber (cm^{-1})**	**Assignment**	**Bond**
TRGO-DAH	1731	C=O stretching	-COOH
PP-g-TRGO	1772	Anhydride C=O stretching	-C(O)O
	1708	C=O stretching	-COOH
	1650	Secondary amide C=O stretching	-CO-NH-
PP-g-MA	1776	Anhydride C=O stretching	-C(O)O
	1711	C=O stretching	-COOH

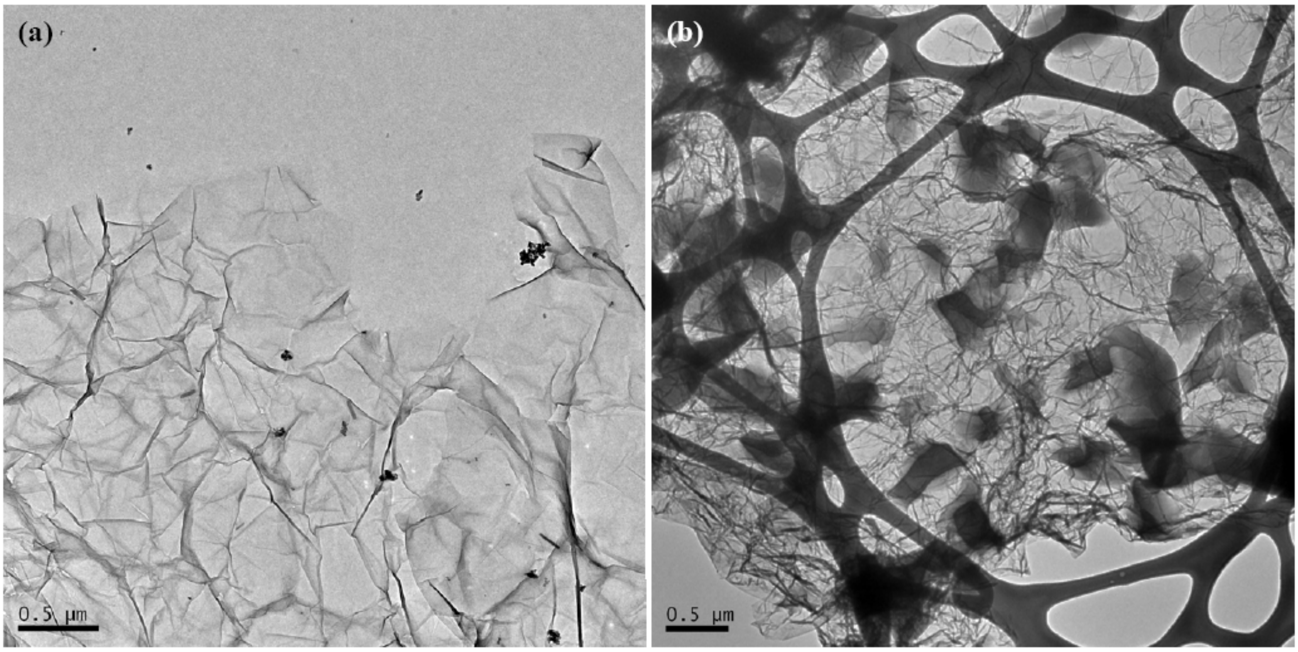

Figure S1. TEM images of (a) TRGO and (b) PP-g-TRGO.

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