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Electronic Supplementary Information

Introduction of Benzoxazine onto the Graphene Oxide Surface by Click Chemistry and the Properties of Graphene Oxide Reinforced Polybenzoxazine Nanohybrids

Fanbin Meng[a] Hatso Ishida[b] and Xiaobo Liu*[a]

a Research Branch of Functional Materials, Institute of Microelectronic & Solid State Electronic, High−Temperature Resistant Polymers and Composites Key Laboratory of Sichuan Province, University of Electronic Science and Technology of China, Chengdu, People’s Republic of China

b Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106

1 Experimental Section

1.1 Materials

GO was synthesized using a modified Hummers method from natural graphite powder.[1] propargyl benzoxazine was prepared according to the previously reported.[2] Sodium azide and copper iodide were used as–received from Acros Organics. Pentaerythritol tribromide was obtained from TCI America. Other reagents, such as toluene diisocyanate (TDI) (98%), chloroform ($CHCl_3$) (99.9%), dimethyl sulfoxide (DMSO) (99.5%), anhydrous N,N–dimethylformamide (DMF) and N,N,N',N',N''–pentamethyldiethylenetriamine (PMDETA, 99%), were obtained from Sigma–Aldrich and used without further purification.

1.2 Synthesis of 2,2,2–tris(azidomethyl)ethanol

A solution of pentaerythritol tribromide (10.0 g) and Sodium azide (NaN_3) (6 g) in DMSO (50 mL) was stirred and heated at 80 °C for 48 h to give a finally pale yellow solution. This was diluted with water (250 mL) and extracted with $CHCl_3$ (3 × 50 mL). The combined extracts were washed with water (3 × 50 mL) and dried over sodiumsulfate anhydrous. After filtration, the $CHCl_3$ was removed from the solution (the temperature should be sufficient to achieve only this) by evaporation under reduced pressure, leaving a pale yellow oil. Yield, 5.2 g. IR spectra (KBr, cm^{-1}): 2105, 3248. ^{1}H–NMR (300 MHz, $CDCl_3$) 3.58 (s ,2H, CH_2OH), 3.37 (s, 6H, CH_2N_3).

1.3 Preparation of triazido functionalized graphene oxide (GO–N_3)

Tris(azidomethyl) ethanol modified graphene oxide sheets were synthesized by TDI as the bridging unit. In a typical procedure, TDI (0.343 mL, 2.4 mmol) and tris(azidomethyl) ethanol (0.504g, 2.4 mmol) were dissolved in anhydrous DMF (2 mL). The solution was stirred at room temperature for 24 h under nitrogen atmosphere. Then the as–reparied GO solution dispersed in anhydrous DMF (33 mL, 1.2 mg/mL) was added, and the mixture was stirred under nitrogen for 10 h at 80 ^oC. After the reaction, the suspension was diluted with 20 mL of DMF and filtered over a 0.2 μm PTFE microporous membrane. The obtained triazido GO was washed thoroughly using DMF with the assistance of sonication and then dried under vacuum overnight.

1.4 Synthesis of benzoxazine functionalized graphene oxide via Click Chemistry (GO–BZ)

To a 50 mL Schlenk flask, GO–N_3 (30 g) and propargyl benzoxazine (80 mg, 4.62 mmol) was dissolved in 30 mL DMF and degassed. Under an nitrogen atmosphere, CuI (0.571 g, 3 mmol) and N,N,N’,N”,N” –pentamethyldiethylenetriamine (PMDETA) (0.626 mL, 3 mmol) were successively added. This mixture was stirred for 24 h at room temperature. The obtained product was by filtration through a 0.2 μm polytetrafluoroethylene (PTFE) membrane membrane for several times. The precipitate was washed with $CHCl_3$ five times and the excess propargyl benzoxazine and other impurities can be removed, which included sonication, filtration (discarding the filtrate). The final products were dried at 40 ^{o}C under vacuum overnight to yield benzoxazine functionalized graphene oxide.

1.5 Characterization

Fourier transform infrared (FITR) spectra were recorded on a PerkinElmer spectrum GX FTIR system with attenuated total reflectance (ATR) accessory. The 1H NMR spectra were recorded using a Varian Oxford AS300 spectrometer at a proton frequency of 300 MHz. a proton frequency of 300 MHz with $CDCl_3$ as the solvent. The Raman spectra were collected using a Raman spectrometer (Renishaw) with a 514 nm laser. Scanning electron microscopic (SEM) images were taken on JSM, 6490LV, transmission electron microscopy (TEM) was measured on the Hitach H-600. X–ray diffraction (XRD) was measured on the Rigaku RINT2400 with Cu kα radiation. X-ray photoelectron spectroscopic (XPS) measurements were carried out on a VG Microtech ESCA 2000 using a monochromic Al X-ray source (97.9 W, 93.9 eV). Atomic force microscopy (AFM) was performed on an Agilent 5500 atomic force microscope. The sample was prepared by spincoating from the corresponding solution on Si substrates. Differential scanning calorimetry (DSC) measurements were conducted with a TA Instruments DSC Q–100 at a heating rate of 10 °C/min under a N_2 atmosphere. Thermogravimetry analysis (TGA) was conducted using a TA Instruments TGA Q–50 at a heating rate of 20 °C/min from room temperature to 800 °C under a N_2 atmosphere.

1 W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339–1339.

2 Y. C. Wu and S. W. Kuo, *Polymer*, 2010, **51**, 3948–3955

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Table S1. Atomic Concentrations of GO, GO–N_3 and GO–BZ

Sample	C (wt%)	O (wt%)	N (wt%)	C/O ratio
GO	65.77	32.62	1.61	2.02
GO–N_3	67.71	25.38	6.91	2.67
GO–BZ	74.19	17.65	8.16	4.20

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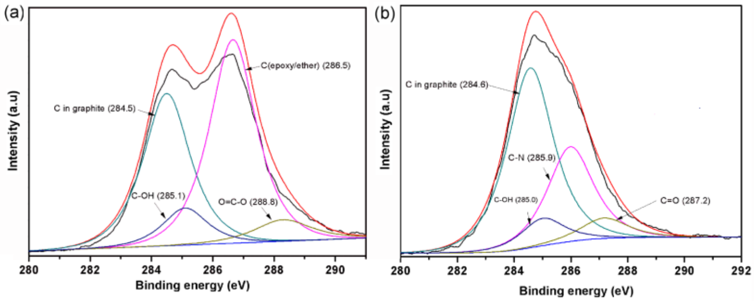

Fig. S1 the high-resolution C1s spectra for GO and GO−BZ, respectively.

From Fig. S1, it can be seen that the intensity of C-OH peak at 285.1 eV for GO significantly decreased, even the C=O-OH peak at 288.8 eV almost disappeared after the surface functionalization, indicating the hydroxyl group and carboxyl group on the surface of GO has been linked with an isocyanate group, which is consistent with the results of FTIR. Futhermore, the additional component at 285.9 eV in the GO-BZ C1s spectrum could be ascribed to the propargyl benzoxazine or TDI funtional triazide.

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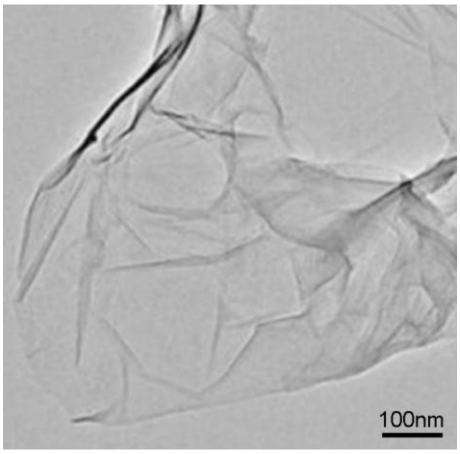

Fig. S2 HR-TEM images of GO.

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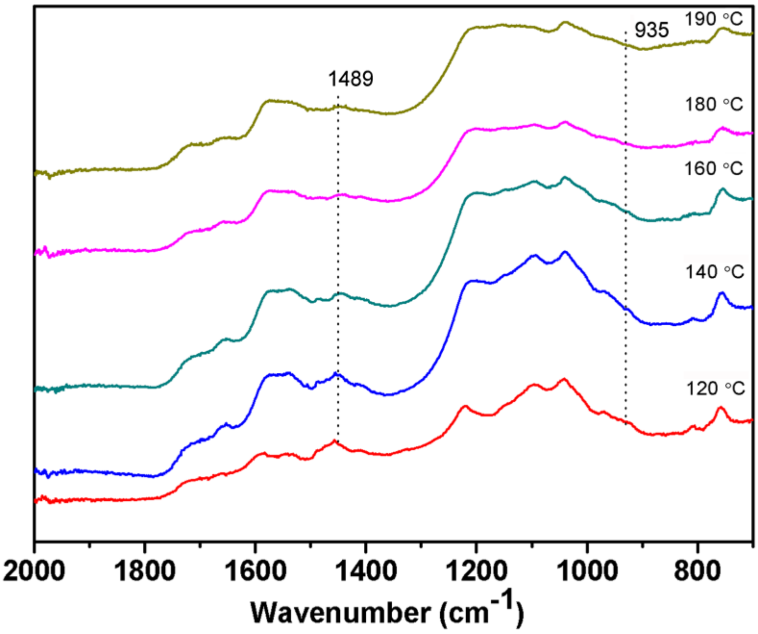

Fig. S3 FTIR spectra of GO–BZ after each cure stage.