Supplementary Information for

Click chemistry as a route for the immobilization of well-defined polystyrene onto graphene sheets

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1. Experimental Section

1.1. Materials. Expandable graphite powders were kindly provided by Yingtai Co. (China). Without otherwise stated, all other reagents and solvents were purchased from commercial suppliers (Aldrich, TCI, Sinopharm etc.) and were used as received.

1.2. Instruments. Atomic force microscopic (AFM) images were obtained using a Multimode Nano 4 in the tapping mode. For AFM observations, the samples were dispersed in appropriate solvents (0.2 mg/mL) with the aid of sonication and then spin-coated onto freshly cleaved mica surfaces. X-ray diffraction (XRD) patterns were acquired by a PANalytical X'pert diffractometer with Cu Kα radiation. Raman spectra were collected on a Renishaw inVia Reflex micro-Raman spectrometer with 633 nm laser excitation. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Nexus 470 spectrometer. All FTIR samples were prepared as pellets using spectroscopic grade KBr. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere with a Perkin Elmer Thermal Analyzer at a heating rate of 20 ^{o}C/min. Molecular weight and polydispersity index (PDI) of PS were estimated by gel permeation chromatography (GPC) equipped with an Agilent 1100 with a G1310A pump, a G1362A refractive-index detector, and a G1314A variable-wavelength detector with THF as eluent phase and monodispersed polystyrene as standard. ^{1}HNMR was carried out on a Mercury Plus 400 Hz spectrometer with $CDCl_3$ as solvent.

1.3. Synthesis Procedure

1.3.1 Preparation of graphite oxide (GO) sheets. The GO sheets were synthesized from expandable graphite powders by a modified Hummers method.[1] 5 g expandable graphite powders and 115 mL concentrated H_2SO_4 were mixed and agitated in an ice bath. Then, 15 g potassium permanganate was added to the suspension slowly to prevent a rapid rise in temperature (less than 20 ºC). After keeping in the ice bath for 2 h, the reaction mixture was heated to 35 ºC and stirred continuously for 0.5 h. 115 mL distilled water was slowly added to the reaction vessel. The diluted suspension was stirred for another 15 min and further diluted with 700 mL warm distilled water (40 ºC) before adding 50 mL 30% H_2O_2. The resulting suspension was filtered, washed with 5% HCl and dialyzed for 7 days in the dark. Subsequently, the wet form of graphite oxide was freeze-dried, pulverized and finally vacuum dried at 60 ºC for 24 h.

1.3.2. Preparation of terminal alkyne modified graphene sheets. The terminal alkyne modified graphene sheets were synthesized according to a similar procedure to prepare terminal alkyne modified multi-wall carbon nanotubes.[2] The as-purified GO sheets (100 mg) were refluxed in 20 mL $SOCl_2$ at 70 ºC for 24 h. After removing excess $SOCl_2$ by rotary evaporation, the products were vacuum dried overnight. A mixture of propargyl alcohol (2 mL), distilled $CHCl_3$ (2 mL) and anhydrous TEA (1 mL) was added dropwise in an ice-water bath under vigorous stirring. The mixture was stirred at 0 ºC for another 1 h and then at room temperature for 24 h. The powders were obtained by filtering the mixture through a 220 nm PTFE membrane. The collected powders were redispersed in ethanol (200 mL) and separated by filtration for four times. Then, the collected powders was redispersed in distilled water (200 mL) and separated by filtration for another two times. After purification, the resulting powders were vacuum dried overnight at 35 ºC, and terminal alkyne modified graphene sheets were obtained.

1.3.3. Preparation of 3-azidoethyl 2-bromoisobutyrate (AEBiB). The azido terminated ATRP initiator AEBiB was prepared by the esterification reaction of 3-azido-1-ethanol with 2-bromoisobutyrate bromide in the presence of TEA according to previous report[3]. A 250 mL round bottom flask was charged with 3-azido-1-ethanol (8.7 g, 0.10 mol), TEA (11.11 g, 0.11 mol) and 120 mL CH_2Cl_2. The reaction mixture was cooled by an ice-water bath, while 2-bromoisobutyrate bromide (25.3 g, 0.11 mol) in 30 mL CH_2Cl_2 was added dropwise under vigorous stirring. After the addition was completed, the reaction mixture was stirred overnight at room temperature. After filtration and removing all solvents, the residues was further purified by a silica gel column chromatograph using CH_2Cl_2 as eluent, affording AEBiB a colorless liquid (9.63

g, 69.2%). ^{1}HNMR ($CDCl_3$): δ 4.34 (t, 2H, CH_2 close to azido), δ 3.52 (t, 2H, CH_2 close to C=O), δ 1.96 (s, 6H, CH_3).

1.3.4. Preparation of azido-functionalized polystyrene (PS) via atom transfer radical polymerization (ATRP). AEBiB (45.4 mg, 0.19 mmol), CuBr (27.6 mg, 0.19 mmol), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, 80 µL. 0.41 mmol), styrene (distilled, 2 g, 20 mmol) and chlorobenzene (distilled, 2 g) were mixed in a dry schlenk flask. After three freeze-pump-thaw cycles, the flask was sealed and the reaction proceeded at 90 ºC for 8 h. The polymerization was quenched by liquid nitrogen. After adding a spot of THF, the polymer solution passed though a short alumina column to remove the catalyst, and then precipitated in methanol. The collected solid was vacuum dried to yield azido-functionalized PS. ^{1}H NMR: δ 0.87-1.04 (br), δ 1.16-2.10 (br), δ 6.31-7.22 (br). GPC: $M_n = 4600$ g/mol, $M_w/M_n = 1.04$.

1.3.5. Click reaction of azido-functionalized PS with terminal alkyne modified graphene sheets via Cu(I)-catalyzed 1,3-dipolar cycloaddition reaction. A 50 mL flask was charged with terminal alkyne modified graphene sheets (20 mg), azido-functionalized PS (4600, 200 mg, 0.043 mmol), CuBr (6.2 mg, 0.043 mmol), PMDETA (10µL, 0.051 mmol) and DMF (distilled, 15 mL). After three freeze-pump-thaw cycles, the reaction mixture was stirred under nitrogen at room temperature for 48 h. As the cycloaddition reaction finished, the mixture was dissolved in 100 mL THF and filtered through a 220 nm PTFE membrane for five times. The collected powders was vacuum drying to afford the PS-grafted graphene sheets.

2. TGA and DTG curves of GO and azido-PS

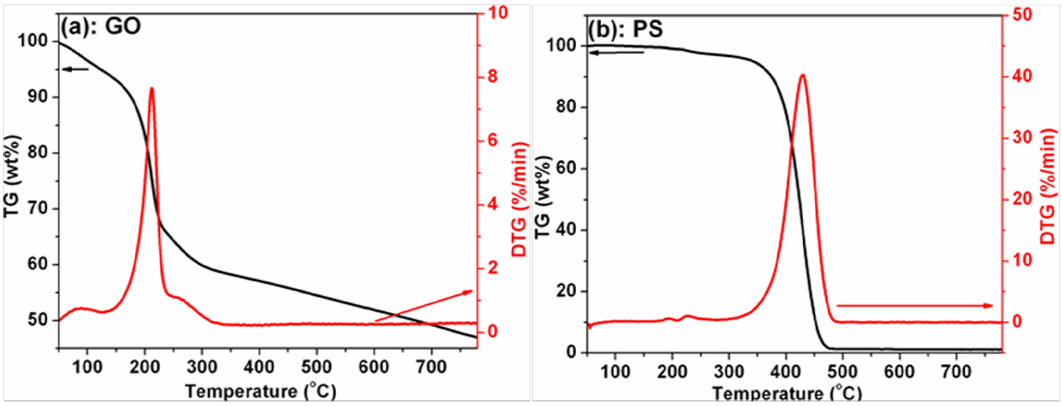

Fig. S1. TGA and DTG traces of (a) GO and (b) azido-PS.

References

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