Electronic Supplementary Material (ESI) for ChemComm.

Supporting information for:

Janus Nanosheets of Graphene Oxide

Brendan T. McGrail,[a] Joey Mangadlao,[b] Bradley J. Rodier,[a] Jordan Swisher,[a] Rigoberto Advincula,[b] and Emily Pentzer[a,*]

[a]Case Western Reserve University, Department of Chemistry

[b]Case Western Reserve University, Department of Macromolecular Science and Engineering

General Considerations. All reagents were purchased from commercial suppliers and used without purification. Unless otherwise noted, all operations were conducted under ambient conditions. All ^{1}H NMR shifts are reported relative to residual solvent peak, as noted. Photochemical reactions were performed in a cylindrical Rayonet photo-reactor, RPR-100, equipped with 10 x 4000 Å bulbs, λ=365 nm. FTIR spectra were acquired using an Aglient Cary 630 FT-IR in ATR mode. For analysis of samples by Raman spectroscopy, a sample in THF-DMF mixture (1 mg/mL) was dropcast onto a previously cleaned glass slide and allowed to dry at room temperature for 24 hours. Raman spectra were collected using BWTek I-Raman Plus equipped with a video microscope Raman sampling system. The laser (532 nm) was focused using a 20X objective onto areas with dense GO sheets and spectra were collected using 10% laser power and 30-second integration time; the area or the height of the D and G peak was used to ascertain the degree of functionalization.

Atomic force micrographs (AFMs) were acquired using a Digital Instruments Dimension 3100 AFM with a Nanoscope IIIa controller and Quadrex extension module in Tapping Mode using silicon probes (resonant frequency ~320 kHz). X-ray photoelectron spectra were acquired using a PHI Versaprobe 5000 X-ray photoelectron spectrometer with Al-K⍰ radiation and referenced to internal SiO_2. The surface behavior of Langmuir Blodgett films was investigated using a KSV-2000 system (KSV Instruments).

Pendant drop tensiometry and static contact angle measurements were performed using a CAM 200 optical contact angle meter (KSV Instruments) with CAM 200 software. For pendant drop tensiometry measurements, a sample in 1:1 Water:DMF (0.5 mg/mL) was used and an interface made by injecting a pendant drop of the sample solution into a dodecane bath. Five to ten pendant drops were measured and were averaged, with 1:1 Water:DMF mixture was used as a control. To perform pendant drop measurements at different pH, the sample was acidified by adding 10 μL portions of HCl (0.1 M) until pH =2 or by adding 10 μL portions of NaOH (0.1 M) to increase the pH to 13. Contact angle measurements were carried out by slowly moving upward the sample stage with the sample on top to come into contact with the liquid droplet (~1 μL) that was suspended at the tip of a 200 μL micro syringe. Contact angle values were determined by software-assisted drop profile fits and are reported as the average ± one standard deviation for four drops on each film. To prepare substrates for deposition, a silicon wafer (1 cm x 1 cm) was placed in a buffered oxide etchant (BOE) solution for 15 minutes to etch SiO_2; the BOE solution was prepared by dissolving of Ammonium Fluoride (NH_4F, 80 g) in DI water (120 mL) then adding 20 mL of 49% HF. The contact angle of the wafer before and after etching is 48° and 77°, respectively.

LB Assembly and Isotherm Collection. Prior to spreading the GO on the water subphase, the LB trough (width 150 mm, area 78 000 mm^2) and the Teflon-coated barriers were cleaned thoroughly with ethanol. The trough was then filled with Millipore water (resistivity >18 MΩ·cm, 20 °C) and 250, 500, and 1000 μL of 1 mg/mL dispersions of acrylate-GO-acrylate, acrylate–GO-PS_{40}, or PS_{40}-GO-PS_{40} in DMF/THF 60:40 (vol:vol) was slowly spread onto the air-water interface using a 50 μL glass syringe (9 experiments in total). The material was allowed to equilibrate for 20 minutes and was then compressed at 5 mm/min barrier speed. Langmuir-Blodgett transfer of platelets-on-water films to mica substrates was accomplished by driving to a trough area of 100 cm^2, equilibrating for 20 minutes, and inserting (downstroke) or withdrawing (upstoke) the mica substrate at 3 mm/min.

Materials Preparation

Preparation of graphene oxide (GO):[1–3] A typical preparation of graphene oxide by a modified Hummers' method proceeded as follows: In a 50 mL round-bottom flask equipped with a magnetic stir bar, flake graphite (2.0 g) was slowly added to a solution of phosphorous pentoxide (1.00 g, 3.5 mmol) and potassium persulfate (1.01 g, 3.7 mmol) in 98% H_2SO_4 (3mL) that had been previously heated to 80 °C over a steam bath to produce a thick blue-black suspension. Additional H_2SO_4 (0.5 mL) was added to reduce the viscosity of the suspension and the flask was removed from heat and allowed to stir while cooling to room temperature over the course of 2 hours. The mixture was diluted with deionized water (30 mL), which caused the solution to heat up, and was then allowed to cool to room temperature with stirring. This "pre-oxidized" graphite was collected by suction filtration and washed with H_2O (about 3.5 L) until the pH of the eluent from washing was 5.5-6 (determined by pH paper) and was then immediately transferred to a 500 mL beaker cooled on a salt-ice bath to -5°C. The pre-oxidized graphite was suspended in concentrated H_2SO_4 (46 mL) and stirred with a magnetic stir bar until homogenized, then potassium permanganate (3 g, 19 mmol) was added slowly while monitoring the temperature to ensure that the solution remained below 20 °C. After the complete addition, the suspension was warmed to 35 °C, and within 5 minutes thin films of the suspension on a glass rod showed a dark emerald green color while the bulk suspension remained black. After 35 minutes, deionized water (96 mL) was added and the temperature rapidly rose to ~70 °C. The mixture was allowed to cool to room temperature over approximately two hours and was then treated with deionized water (46 mL) and 30% hydrogen peroxide (0.5 mL). The black solid was collected by filtration and washed with H_2O (~5 L), giving a filtrate pH of 5.5-6. Collection and purification of the GO by centrifugation (50mL fractions, 10 min, 5000 rpm) was also effective for removal of residual ions (wet yield: 7.6 g, dry yield: 2.3 g after 14 days drying over P_2O_5).

Preparation of Acr-GO-Acr via the Pinner reaction: GO (50 mg) was suspended in a water (100 mL) in an Erlynmeyer flask equipped with magnetic stir bar, and the suspension was sonicated for 30 seconds to ensure platelet dispersion. Acrylonitrile (5 mL) was then added neat to the suspension of GO. The reaction mixture was stirred vigorously at room temperature, open to air for 30 minutes, and the resulting functionalized platelets (acrylate-GO-acrylate) were isolated by centrifugation, and washed with deionized water and THF to remove residual acid and any unreacted acrylonitrile. The functionalized platelets were characterized by FTIR (carbonyl stretch of ester at 1725 cm^{-1} and C=C acrylate stretch at 1426 cm^{-1}).

Preparation of PS_{40}-SH. Thiol-termianted polystyrene (PS_{40}-SH) was prepared using RAFT polymerization of styrene and removal of the chain-transfer agent, as previously reported.[4,5] Briefly, styrene (100 mL, 0.8698 mol) was passed through a plug of alumina to remove any inhibitor and collected into a 500 mL Schlenk flask. Cyanomethyldodecyl trithiocarbonate (0.259 g, 0.894 mmol) and toluene (100 mL) were added, and the mixture was degassed by three consecutive freeze-pump-thaw cycles. The reaction mixture was placed under nitrogen and stirred at 110 °C for 22 hours; the polymerization was terminated by cooling to room temperature and then further cooling in an acetone-dry ice bath and exposing to air. The product was precipitated by dropwise addition of the reaction mixture into stirred methanl (200 mL), and then collected by centrifugation. Once collected, the precipitated polymer was dissolved in THF/H_2O (10/1 v/v, 200 mL) and $NaBH_4$ (169.1 mg, 4.47 mmol, 5 eq. to the chain-transfer agent) was added; the solution was stirred at room temperature for 24 hours. The thiol-terminated polymer (PS_{40}-SH) was precipitated into methanol to afford an off-white solid which was isolated by centrifugation and dried under vacuum. Deprotection of the thiol was confirmed by absence of the trithiocarbonate group in FTIR spectrum (C=S band ~ 1065 cm^{-1}) and ^1H NMR. Mn = 39,000; Đ = 1.13.

Preparation of PAA_5-SH. Acrylic acid (10 mL, 0.146 mol) was passed through a plug of alumina to remove any inhibitor and collected into a 100 mL round bottom flask charged with a stir bar and 40 mL an ethanol:water mixture (2:1 vol:vol). Dibenzyl trithiocarbonate (0.58 g, 0.002 mol) was added and the mixture was sparged with nitrogen to degas. The reaction mixture was stirred at reflux under a nitrogen environment for 6 hours and the polymerization was terminated by cooling to room temperature and exposing the mixture to air. Without isolation, the polymer was dissolved in ethanolic sodium hydroxide solution (20 mL, 2:1 EtOH:H_2O, ~0.1 M NaOH, pH 8-9) and treated with five equivalents of sodium borohydride, then stirred overnight under dinitrogen to give PAA_5-SH. The product was isolated by cooling the mixture in an ice water bath and precipitating into two volumes (40 mL) of ethyl acetate, then collecting by centrifugation.

Preparation of PS_4-GO-PS_{40}. In a 100 mL round bottom flask equipped with a stir bar, acrylate-GO-acrylate (30 mg) was dispersed in DMF/THF (60/40 vol/vol, 50 mL total) and a solution PS_{40}-SH (200 mg) in THF (30 mL) was added. The resulting suspension was placed under nitrogen and sonicated to ensure dispersion and then irradiated at 365 nm for 3-4 h. The resulting PS_{40}-GO-PS_{40} was isolated by addition of saturated NaCl in water (0.5 mL) followed by letting the reaction sit 10 minutes, resulting in the separation of the aqueous and organic phases. The organic phase was collected and centrifuged; the supernatant was decanted and discarded. PS_{40}-GO-PS_{40} is recovered as a black brown solid and washed (suspension, centrifugation, supernatant discarded) with chloroform (3x 25 mL) to remove unreacted PS_{40}-SH and with acetone (2x 10 mL), then dried under vacuum. The symmetrically functionalized PS-GO-PS resuspended in THF after bath sonication.

Preparation of PS_{40}-GO-Acr by photochemical method: In a 250 mL, single neck round bottom flask, acrylate-GO-acrylate (0.025 g) was dispersed in water (50 mL) by sonication to give a black suspension. PS_{40}-SH (0.2g, 1.81 x10^{-3} mmol) was dissolved in toluene (25 mL) with vigorous stirring and then added to the acrylate-GO-acrylate dispersion, forming a two-phase system. The flask was purged with nitrogen and capped. Emulsification of this biphasic system was achieved by vigorous shaking (by hand) with intermittent sonication (~5 min). The emulsion was irradiated at 365 nm for 3 h without stirring to initiate the photocemical thiol-ene click reaction and prepare acrylate-GO-PS$_{40}$. After reaction, a solution of saturated NaCl in water (1 mL) was added and the reaction allowed to stand for 10 minutes. After centrifugation, the supernatant was decanted and discarded. Acrylate-GO-PS$_{40}$ was then recovered as a black brown solid and washed with chloroform (3x 25 mL) to remove unreacted PS$_{40}$-SH and with acetone (2x 10 mL), then dried under vacuum.

Redispersal of the Janus platelets proved difficult. Solvents tried include EtOH, MeOH, IPA, DMSO, DMSO/CHCl$_3$, 0.5 M NEt$_3$ in DMSO, DMF, THF, 0.1 M NaOH in THF, ^{t}BuOH in 9:1 acetone:MeOH, and 0.1 M NH$_4$OH in 9:1 Acetone/MeOH, as well as various ratios of THF/DMF mixtures. Successful redispersal of the Janus PS-GO-Acr platelets was ultimately realized in DMF/THF mixtures, with 40-70% DMF and bath sonication for at least one hour.

Preparation of PS$_{40}$-GO-Acr by thiol-Michael addition: To an identical suspension of acrylate-GO-acrylate (0.025 g) in water (50mL), a solution of PS40-SH (0.2 g) and diisopropylethylamine (0.027g, 0.208 mmol) dissolved in toluene (25 mL) was added. The mixture was emulsified by sonication and shaking, then kept at room temperature for 18 h. The monofacially functionalized platelets (acrylate-GO-PS40) were isolated as outlined above for the photochemical reaction.

Preparation of PS$_{40}$-GO-PAA$_5$. To perform the double thiol-ene click reaction on acrylate-GO-acrylate, a toluene-in-water emulsion stabilized by the platelets was prepared as before (see above, prep of acrylate-GO-PS$_{40}$), with the aqueous phase containing PAA$_5$-SH (0.129 g, 0.026 mmol) and the toluene phase containing PS$_{40}$-SH (0.2 g). The flask was purged with nitrogen and capped then shaken vigorously shaking (by hand) with intermittent sonication. The emulsion was irradiated at 365 nm for 3 h without stirring to initiate the photochemical thiol-ene click reaction and prepare PS$_{40}$-GO-PAA$_5$.

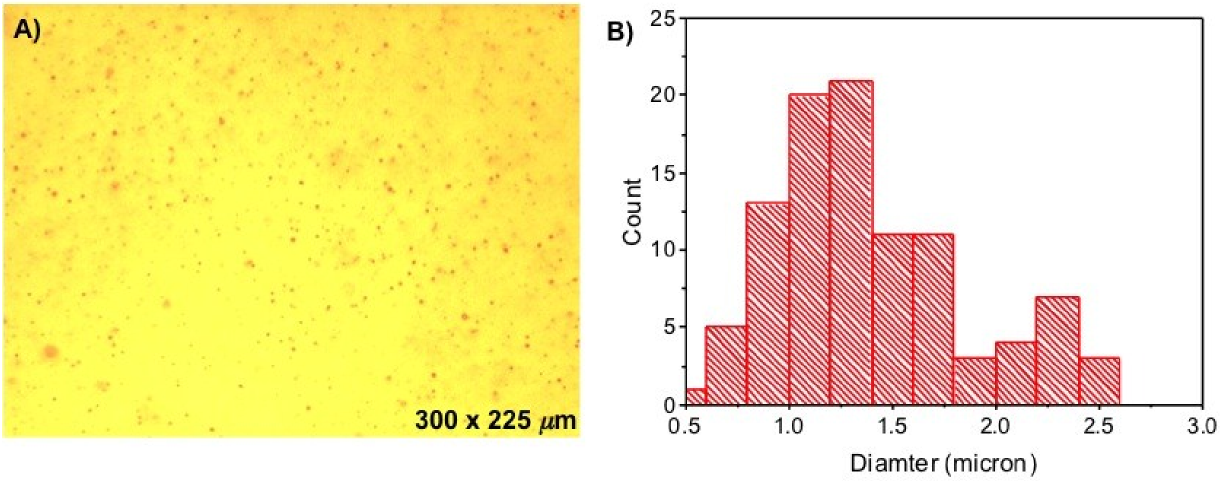

Figure S1. A) Optical image of the Pickering-type emulsions prepare using GO as a surfactant; B) Size distribution of emulsion droplets.

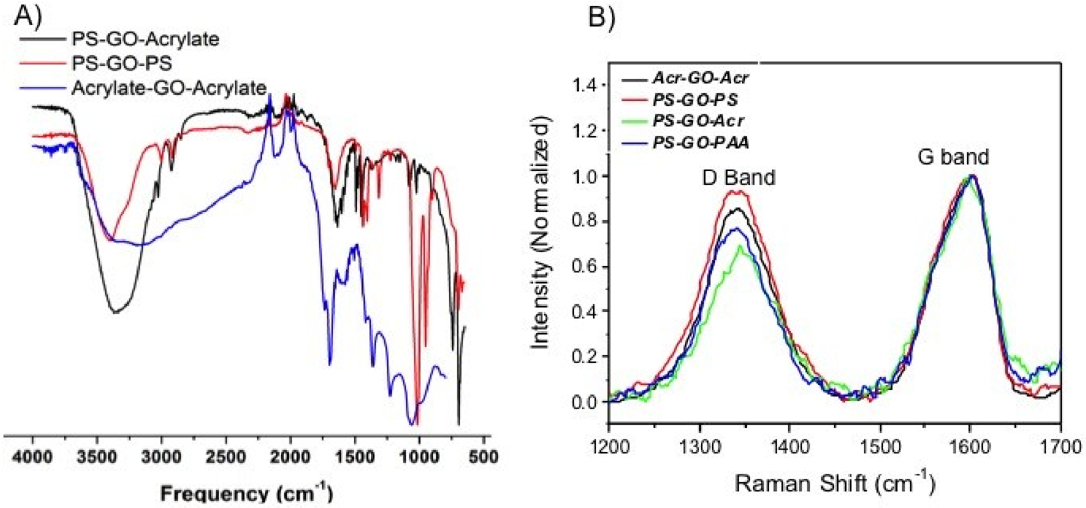

Figure S2. A) FTIR spectra and B) Raman spectra of Acr-GO-Acr, Acr-GO-PS$_{40}$, and PS$_{40}$-GO-PS$_{40}$. I_D:I_G ratios are 0.86 (Acr-GO-Acr), 0.93 (PS$_{40}$-GO-PS$_{40}$), and 0.69 (PS$_{40}$-GO-Acr).

Characterization of platelets by FTIR and Raman spectroscopy.

The FTIR spectrum of GO Acr-GO-Acr (Figure S2A, blue trace) displays a sharp peak at ~1725 cm^{-1} due to the ester functionality of the acrylate group, as well as a broad stretching frequency at 2500-3500 cm$_{-1}$ due to unreacted hydroxyl groups and carboxylic acid groups of GO as well as residual water (GO is difficult to dry without heating, which causes reduction). After functionalization with PS, both the hydroxyl and ester peak are attenuated and peaks corresponding to aliphatic C-H stretches (~2900 cm^{-1}) are apparent, attributed to the PS backbone and olefinic C-H stretch from styrene.

Raman spectroscopy is a powerful tool to study graphene-based materials' electronic and structural properties. It is particularly useful in determining the degree of functionalization (oxidation) of GO, and can also be affected by the local environment (i.e., the presence of polymers). Typically, the Raman spectrum of GO is characterized by a G band (graphitic band, ~1580 cm^{-1}) and a D band (disorder band, ~1350 cm^{-1}) and the ratio of the intensity of D and G bands is related to the extent of "disorder" or functionalization of the basal plane of GO. The I_D/I_G ratio for the GO used is 0.62 (Table S1), and this increases for all functionalized GO platelets (0.69-0.93).[6,7] The I_D/I_G ratio of Acr-GO-Acr is 0.86, while that of PS-GO-PS further increases to 0.93. While the I_D/I_G ratio of PS$_{40}$-GO-Acr (0.69) and PS$_{40}$-GO-PAA$_5$ (0.77) are lower than that of Acr-GO-Acr, this can be attributed to slight reduction of the basal plane during functionalization. However, the effects of functionalization of the platelets with polymer cannot be distinguished or separated from reduction in the basic conditions used.

Table S1. I_D/I_G ratios for GO and its functionalized derivatives, as calculated from Raman spectra of Figure S1B.

Sample	$\mathbf{I_D/I_G}$
GO	0.62
Acr-GO-Acr	0.86
PS_{40}-GO-PS_{40}	0.93
PS_{40}-GO-Acr	0.69
PS_{40}-GO-PAA_5	0.77

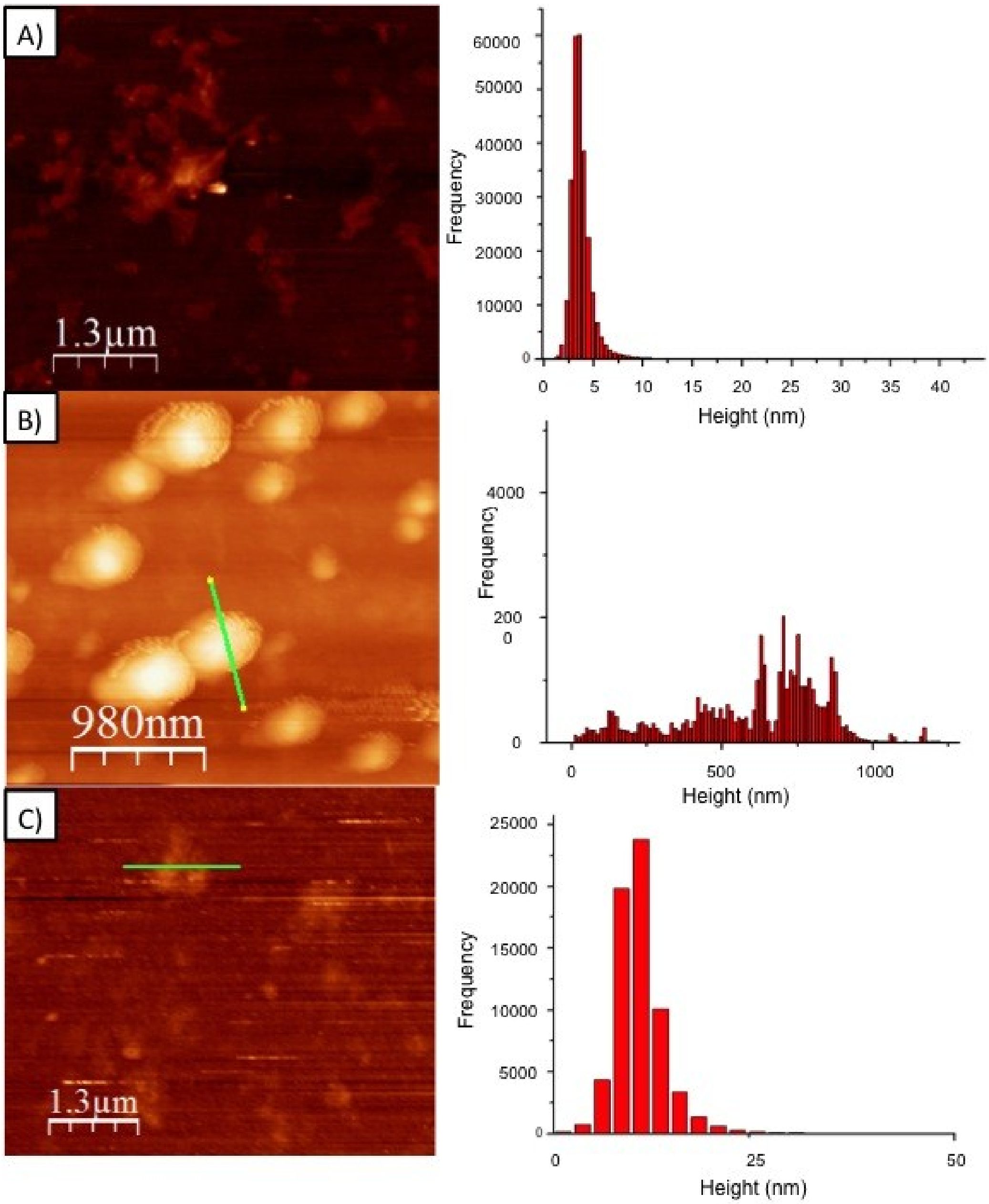

Figure S3. Representative atomic force micrographs and histograms of platelet heights of A) Acr-GO-Acr (4.0 ± 1.4 nm); B) PS_{40}-GO-PS_{40} (361.8 ± 49.3 nm); and C) PS_{40}-GO-Acr (18.2 ± 4.1 nm).

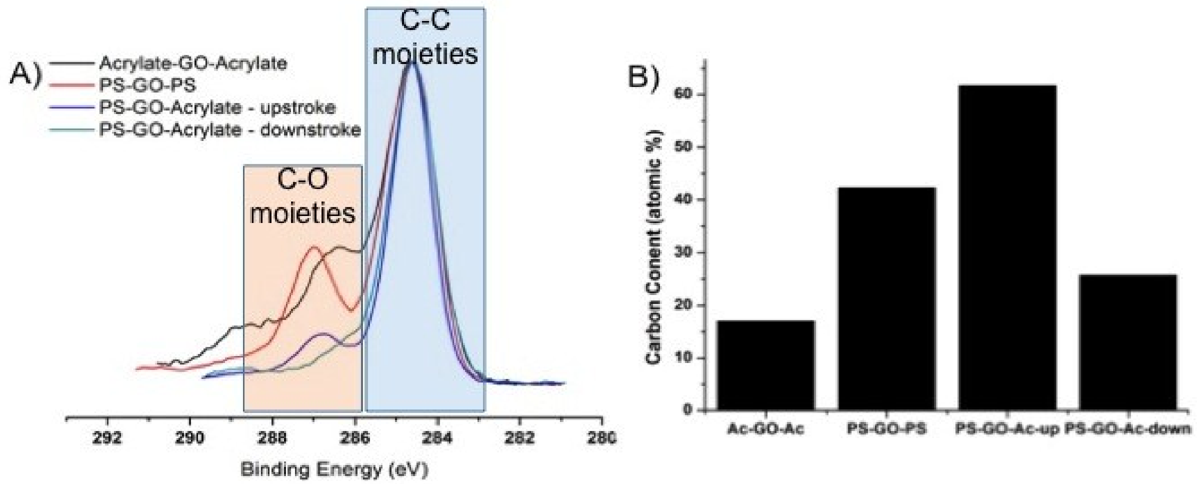

Figure S4. High resolution C(1s) X-Ray photoelectron spectra of Acr-GO-Acr (black), PS_{40}-GO-PS_{40} (red), and PS_{40}-GO-Acr deposited by upstroke (blue) and downstroke methods (green).

Characterization of platelets by XPS.

The XPS spectra of the functionalized GO platelets are shown in Figure S4A, while Figure S4B shows the atomic percentage of carbon atoms. As expected, Acr-GO-Acr (black trace) exhibits comparable amounts of C-O and C-C moieties. Surprisingly, PS-GO-PS shows more C-O bonds than PS-GO-Acr. The Janus structure collected from LB films by the upstroke method are expected to expose GO for characterization, while PS will be exposed for characterization for platelets collected by downstroke method. Comparison of these two samples shows that the GO-exposed face of the Janus structures has a higher population of -C-O-C-, -C-OH,-C=O and HO-C=O groups compared to the PS-face of the platelets. Taken together, these spectroscopic results further solidifies the preparation of Janus GO platelets.

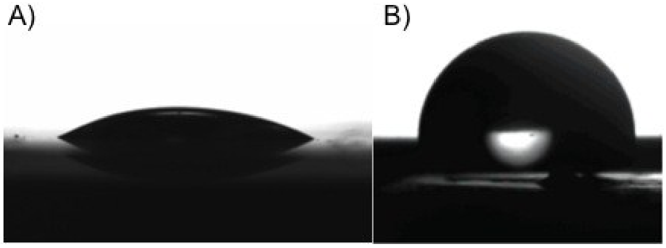

Figure S5. Water contact angles of A) Acr-GO-Acr; and B) PS thin film.[8]

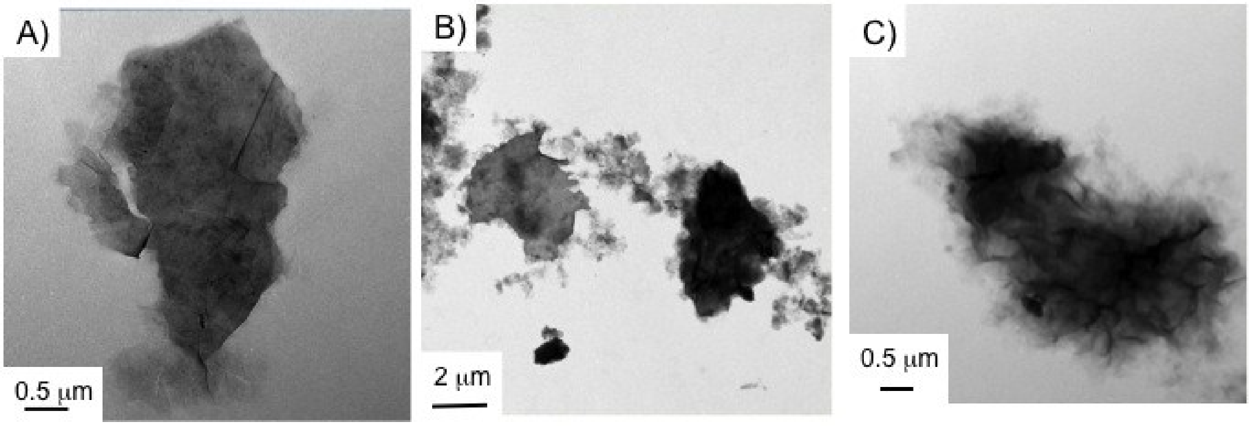

Figure S6. TEM images of A) Acr-GO-Acr, B) PS_{40}-GO-Acr, and C) PS_{40}-GO-PS_{40}.

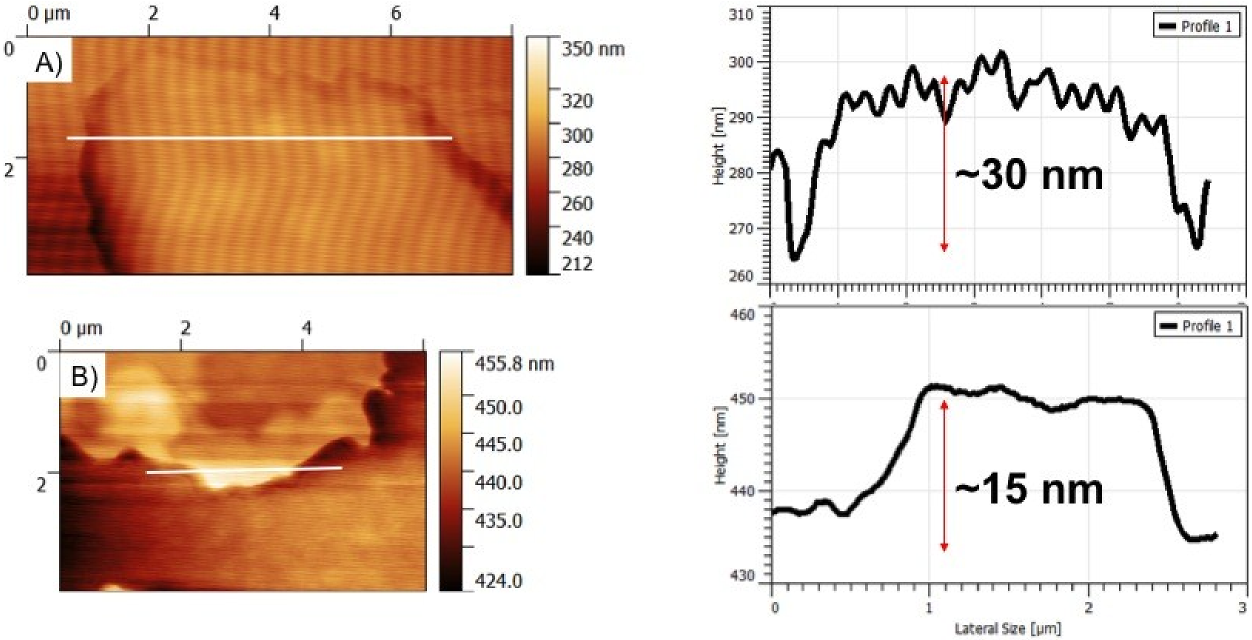

Figure S7. AFM topography image and line profile of PS40-GO-Acr collected by A) upstroke and B) downstroke deposition

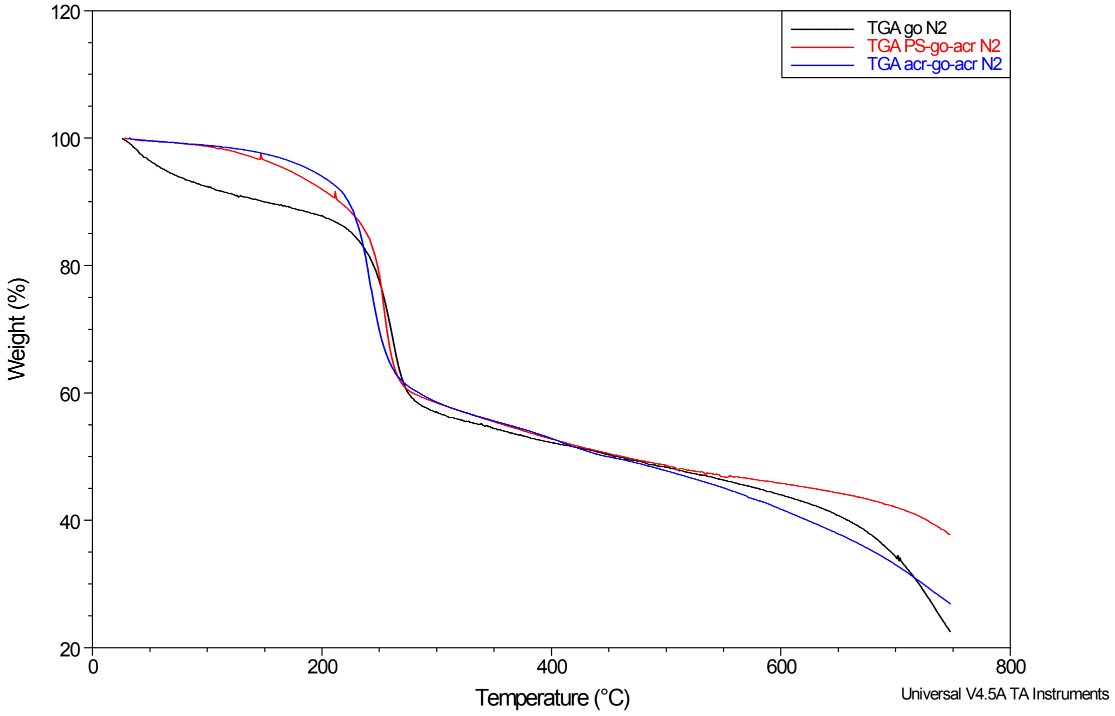

Figure S8. TGA weight loss profiles of GO (black trace) Acr-GO-Acr (blue trace), PS$_{40}$-GO-Acr (red trace).

Table S2. Summary of the properties of symmetrically and asymmetrically functionalized GO.

	Acr-GO-Acr	PS$_{40}$-GO-Acr	PS$_{40}$-GO-PS$_{40}$
Interfacial tension (mN/m)	N.D.	14.79 ± 0.3	16.5 ± 0.4
Contact angle	17.9 ± 2.3	Upstroke: 60.0 ± 4.3 Downstroke: 27.5 ± 5.7	29.5 (PS thin film ~86)[8]
AFM height average	4. 0 ± 1.4	18.2 + 4.1	362 ± 49
I$_D$/I$_G$	0.860	0.69	0.93
Carbon % (from XPS)	N.D.	Upstroke: 62 Downstroke: 26	N.D.

N.D. = not determined

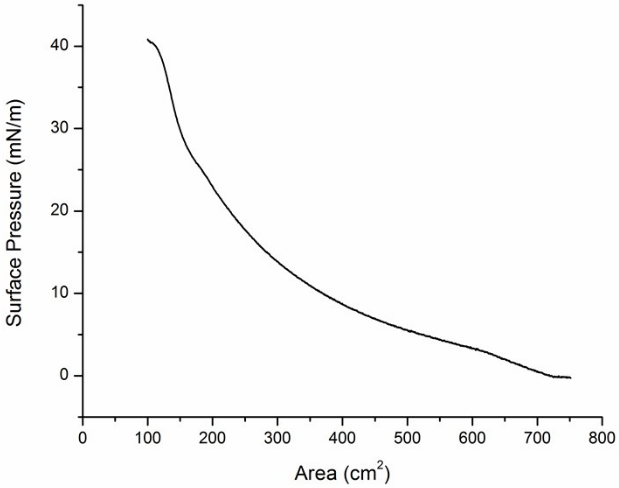

Figure S9. Surface-area isotherm of PS_{40}-GO-PAA_5.

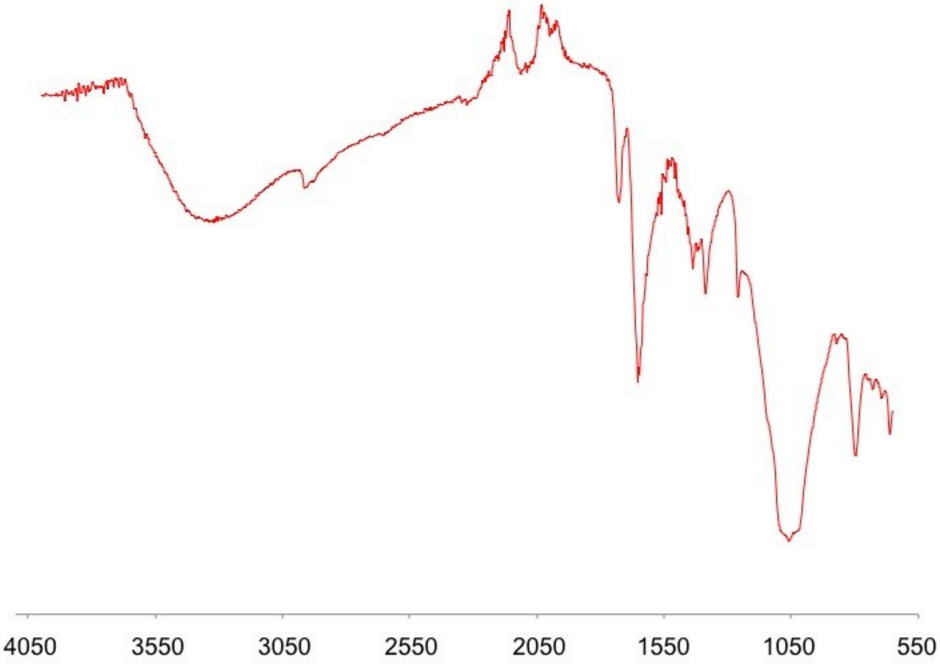

Figure S10. FTIR spectrum of PS_{40}-GO-PAA_5.

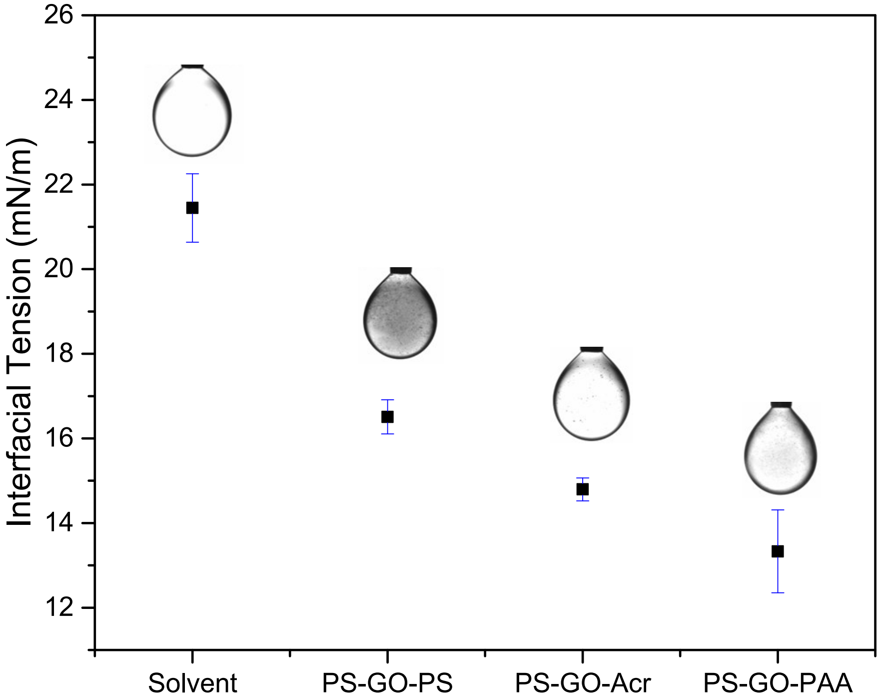

Figure S11. Shapes of pendant drop of solvent, PS_{40}-GO-PS_{40}, PS_{40}-GO-Acr, and PS_{40}-GO-PAA_5, (neturalized) obtained by suspending the platelets in 1:1 H_2O:DMF and injecting the sample into a dodecane bath.

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