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Free-Standing Janus Graphene Oxide with Anisotropic Properties for 2D Materials as Surfactant

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Supporting Information

ABSTRACT: We present a simple and facile approach to creating asymmetrically modified graphene oxide sheets by grafting polymers with different polarities. Single-layered Janus graphene derivatives were prepared by grafting polymers with different polarities at the liquid-gas interface through one step functionalization. This approach allows obtaining free-standing monolayers of Janus graphene oxide sheets for large area, and also controlling the morphology (i.e., wrinkled Janus graphene oxide sheets) by a compression monolayer. A neutron reflectivity technique is used to check the functionalization on each side of the monolayer, and the results are compared with contact angles to determine its



amphiphilic nature. The free-standing Janus monolayers become robust after UV-irradiation, and are able to withstand various solvents. Because these robust Janus graphene films can maintain their anisotropic functionalities over time, this technique provides a new strategy for fabricating functional materials that require amphiphilic properties (i.e., oil-water separation membranes and chemical compatibilizers functioning as a 2D surfactant) and different electrical functionalities (i.e., flexible lightweight p-n junction semiconductors and stimuli-driven actuators).

KEYWORDS: Janus graphene oxide, Langmuir-Schaefer technique, free-standing structure, grafting polymers, amphiphilic properties, wrinkled structure, neutron reflectivity

INTRODUCTION

The fabrication of a single layer of graphene or a graphene derivative on a large scale represents a major technological challenge. For further development, it is necessary to use the graphene layer as a building block to obtain more tunable structures with the desired electronic and mechanical properties.^{1–11} Of particular interest is the creation of an anisotropic amphiphilic graphene single layer. This represents a new class of 2D amphiphiles with advanced functionalities.¹²⁻¹⁷ Based on previous studies on the fabrication methods of 2D Janus films and their applications,^{18,19} there is a growing interest in making graphene or graphene oxide with Janus structure.²⁰⁻²⁵ Through this process, graphene derivatives can provide completely different amphiphilicity along the thickness direction. Thus, "Janus graphene derivatives", is combined with the intrinsic advantages of graphene or graphene derivatives and amphiphilic functionality of coated layers. These consist of sheets in which the two sides have different properties in terms of chemistry or polarity, with potential for a broader range of application compared with their pristine counterparts.

Our 2D Janus graphene materials can be precisely controlled in thickness at the nanoscale level, as well as in terms of their morphology and free-standing surface properties. They have potential application in a variety of research fields, including as flexible lightweight semiconducting materials for electronics,²⁶⁻³² graphene-based separators for Li-S batteries,^{33,34} and stimuli-driven actuators.^{35,36} In recent theoretical studies of asymmetrically engineered graphene, extensive computational calculations were used to predict the widening of the bandgap in graphene through hydrogenation or halogenation. $^{37-42}$ Based of this theoretical work, experimental synthesis of Janus graphenes has also been reported.²⁶⁻³² Electrical properties were controlled by treating both sides with an n-type/p-type dopant on a chemical vapor deposition (CVD) single-layer graphene to enable electronic structure control. However, conventional synthesis approaches based on epitaxial growth or CVD processes have some limitations. For

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Figure 1. Schematic presentation of Janus GO film preparation using the LS technique. The $PS-NH_2$ dissolved in toluene is spread on GO suspension in deionized water. Due to the electrostatic interaction between amine groups of $PS-NH_2$ and oxidized groups of the GO, the exfoliated GO sheets are floated to the liquid–gas interface. The PAH aqueous solution is then injected to the subphase. The PAH is also attached to the GO sheet through electrostatic interaction. The UV was then irradiated to the Langmuir Janus GO monolayer. Whereby the amide bonds are formed between the attached polymers and the GO. By LS deposition, the free-standing Janus GO films are obtained on the perforated Cu foils.



Figure 2. Characterization of surface amphiphilicity of Janus GO monolayers. Surface structure of Janus GO monolayers. AFM topography images of (a) GO/PS-NH₂/Si monolayers and (b) PAH/GO/PS-NH₂/Si monolayers (inset: schematic illustrations of the prepared monolayers). In both cases, the monolayers are deposited through LS deposition at the surface pressure of 20 mN/m. The corresponding cross-section profiles of the monolayer are obtained to measure the thickness of the each layer of Janus GO films. (c) Neutron reflectivity profile of *d*PS/Janus GO/*d*PS film on Si substrate. Janus GO layer consists of PAH/GO/(20 wt % *d*PS-NH₂ + 80 wt % PS-NH₂) and deposited by LS technique at the surface pressure of 30 mN/m. In order to enhance the contrast between the Janus GO monolayer and the Si substrate on the bottom side or air on the top side, the Janus GO monolayer was sandwiched between around 200 Å-thick *d*PS layers. The solid line is the best fit to the measured reflectivity data. (d) Corresponding scattering length density (SLD) profile derived for *d*PS/Janus GO/*d*PS film. Water contact angles of two Janus GO monolayers, namely, (e) PAH/GO/PS-NH₂/Si and (f) PS-NH₂/GO/PAH/Si which are prepared by LS and mLB techniques, respectively. The PAH/GO/PS-NH₂/Si monolayer has a hydrophilic PAH side exposed (the contact angle: $36 \pm 0.3^{\circ}$), whereas the PS-NH₂/GO/PAH/Si monolayer has a hydrophilic PAH side exposed (the contact angle: $30 \pm 0.4^{\circ}$).

instance, a polymer protection layer is necessary to transport the Janus graphene layer.^{17,43} This causes a major difficulty regarding the quality of the final product, owing to contamination with unremoved polymeric materials. Additionally, the previous methods require discontinuous multisteps of individual transfer process for each surface modification. These problems can be also found in a previous study for the GO where Janus GO sheets are decorated with other nanoparticles on both sides.⁴⁴ This method has the similar limitation that the GO may be desorbed from the substrate surface during the transfer process, and the process becomes complicated as well. In this work, we describe a simple approach for fabricating free-standing Janus graphene derivatives via grafting polymers with different polarities at the liquid–gas interface through one step functionalization. This approach was inspired by our previous work, in which we provided a convenient method to manipulate the coverage of graphene derivatives and morphologies of sheets.⁴⁵ Graphene oxide (GO) sheets in



Figure 3. UV-induced chemical bonding between GO and coated polymers. XPS C 1s and N 1s spectra of Janus GO films transferred on silicon substrates: (a), (b) pristine sample and (c), (d) UV irradiated sample. SEM images of Janus GO films on perforated Cu film with hole size = 300 μ m after UV irradiation (~350 nm). (e) PAH/GO/PS-NH₂ (PAH-side up) and (f) PS-NH₂/GO/PAH (PS-NH₂-side up). EDS results of copper (Cu) on (g) PAH/GO/PS-NH₂ (PAH-side up) and (h) PS-NH₂/GO/PAH (PS-NH₂-side up) after dyeing with Cu(ll) sulfate solution.

the aqueous subphase formed a densely packed Langmuir Janus monolayer with an amine-terminated polystyrene (PS- NH_2) monolayer spread at the liquid-gas interface and a poly(allylamine hydrochloride) (PAH) adsorbed from the subphase. Anisotropic polymer grafting on the GO surface is facilitated by the strong affinity of the electrostatic interaction between the negatively charged oxide groups on GO and positively charged amine groups on PS-NH₂ and PAH. The Janus sheets consist of a single layer of GO in large scale, with chemical asymmetry on their surfaces. Such sheets can be either deposited onto solid substrates or in the form of freestanding films; it is also possible to tune the coverage of polymers on graphene derivatives and control the morphology of sheets (i.e., wrinkling or flat structures). Due to importance of morphologies of graphene films for the high performance graphene-based materials, the technique employed in this study can provide a route for applications requiring wrinkled graphenes with amphiphilic properties, including water desalination membranes, and 2D sensors, and actuators.

RESULTS AND DISCUSSION

Fabrication of Janus GO Monolayers. In order to achieve the formation of Janus GO monolayers, first, the PS-NH₂ ($M_w = 10$ kDa) solution in toluene was spread on the GO-suspended subphase; this induces the surface anchoring of the GO at the liquid–gas interface (Figure 1). Then we obtained the amphiphilic Janus GO monolayers by adsorption of the PAH ($M_w = 16$ kDa) to another side of the GO monolayer at the interface after injecting the PAH into the subphase as illustrated in Figure 1. In this manner, we prepared a large-area Janus GO monolayer with the PS-NH₂ on one side and PAH on another side at the air–water interface, which could then be deposited on solid substrates using Langmuir–Schaefer (LS) techniques, namely parallel deposition by simply juxtaposing the substrate surface with the liquid–gas interface.

Characterization of Surface Amphiphilicity of Janus GO Monolayers. AFM technique was employed to measure the surface structure of the Janus GO monolayer after deposition on silicon substrates. Figure 2a and b show AFM images of the GO monolayers with the PS-NH₂ monolayer before and after adding the PAH into the subphase. The cross-section profiles clearly show a difference in the thickness of the platelet monolayer before (2.9 nm) and after PAH adsorption (4.4 nm). The thickness of the adsorbed PAH layer (1.5 nm) corresponded to ~0.12 radius of gyration (R_g). This layer was strongly adsorbed onto the GO surface; thus, it was not detached or delaminated after thorough rinsing with water.

To verify the Janus functionalization, the NR technique was applied. By using this technique, we obtained values of material composition, interface structure, and thickness along the depth of Janus GO thin films. Particularly, for polymers on the GO, the difference between hydrogenated polymers and deuterated polymers is distinguished from neutron scattering by substituting deuterium with high scattering length dense (SLD) for neutron. Therefore, we used deuterated PS-NH₂ (denoted dPS-NH₂). We prepared a mixed solution (denoted mPS-NH₂) with 20 wt % deuterated PS-NH₂ (denoted dPS-NH₂) and 80 wt % PS-NH₂. The scattering length density (SLD) values of the mPS-NH₂ and PAH were obtained to be 2.5×10^{-6} and 0.5×10^{-6} Å⁻², respectively, which is sufficient to distinguish each polymer layer on the GO surfaces. We measured normalized reflectivity profiles as a function of the momentum transfer normal to the surface, $q_z = 4\pi \sin \theta / \lambda$, where θ is the grazing angle of incidence and λ is the neutron wavelength (Figure 2c). After removing the background of the neutron reflectance measurement and correcting the foot print, analyze the data by fitting the data using Parratt formalism based on the proposed SLD profile. The structure along the depth of Janus GO films grafted with mPS-NH₂, and PAH on each side was measured using the NR technique.

Adding the *d*PS layers to the top and bottom of the Janus film provides an enhanced sensitivity and better spatial resolution of SLD profiles derived from NR data of Janus GO monolayers due to interferometic enhancement.⁴⁶ Using the NR technique, monolayers in a large area $(50 \times 75 \text{ mm})$ was measured. The structural information obtained from the NR results was an average over the entire length of the sample, in contrast to the limited local structure that was obtained from



Figure 4. Effect of UV irradiation on the resistance of free-standing Janus GO film against the toluene. SEM images of free-standing Janus GO films transferred on Cu grids at the surface pressure of 30 mN/m by LS technique: (a)-(d) The pristine samples and (e)-(h) UV-irradiated samples before and after rinsing with toluene. The magnified SEM images (b, d, f, and h) were measured with tilting 55° to show more clear surface on Janus GO.

the AFM or SEM measurements. For this reason, NR was considered an appropriate method to investigate the large-area Janus GO structure. Figure 2c shows the NR profiles of the Janus GO monolayer with mPS-NH₂ and PAH sandwiched between two dPS thin films as a function of q_z . The SLD profile clearly shows that the GO monolayer was asymmetrically functionalized with mPS-NH₂ and PAH, with the mPS- NH_2 on the bottom and PAH on the top (Figure 2d). The thicknesses of the mPS-NH₂ and PAH layers were 1.7 and 2.0 nm, respectively, which is in good agreement with the AFM results. To the best of our knowledge, there is no previous report to characterize the structure and composition of each layer in the 2D Janus sheets on the nanoscale. This is the first time it was verified that the asymmetric functionalization of the Janus GO monolayer consisted of different polymers by using neutron reflectivity.

Upon monolayer compression, the GO platelets became closely packed. This minimized the gap between the sheets at a surface pressure (π) of 30 mN/m (Supporting Information (SI) Figure S1). Two interfacial configurations (PAH/GO/PS-NH₂/Si and PS-NH₂/GO/PAH/Si) were obtained by the LS and a modified Langmuir-Blodgett (mLB) methods, respectively, as shown in insets of Figure 2e and f. In order to check the amphiphilic natures of the Janus GO, we measured the water contact angles of the monolayers deposited onto the Si substrates. The contact angles were obtained to be $80 \pm 0.4^{\circ}$ and 36 \pm 0.3°, when the hydrophobic PS side (i.e., PS-NH₂/ GO/PAH/Si) and the hydrophilic PAH side (i.e., PAH/GO/ PS-NH₂/Si) were exposed, respectively. This indicates the formation of amphiphilic Janus GO with distinctly different surface hydrophobicity. In addition, Raman spectra exhibited typical peaks of GO sheets, such as G, D, G + D, and 2D bands (SI Figure S2), indicating that Janus GO forms a stable hybrid monolayer by grafting of the polymer at the air-water interface, and their structures are maintained during the LS deposition process.

Formation of Robust Free-Standing Janus Films by UV Irradiation. We also used UV irradiation technology to improve the mechanical properties of the Janus thin films through covalent bonding between the GO and the polymers. This is important for practical applications requiring free-

standing forms, such as advanced gas separation and desalination membranes. We conducted XPS measurements to check the chemical bonding between GO and coated polymers (i.e., PS-NH₂ and PAH) after UV irradiation. Figure 3 shows the XPS spectra of Janus GO films before and after UV irradiation (~350 nm) for 1 h. Prior to UV irradiation, the C1 XPS spectrum of the Janus GO film exhibited several major peaks (Figure 3a). The peak at 285.7 eV corresponds to C-N in the amino group of PS-NH2 and PAH, while the peaks at 284.7, 284.1, and 287.5 eV correspond to typical characteristic of GO sheets. The small peak at 291.1 eV is assigned to $\pi - \pi$ bonding between aromatic rings in PS and GO.47,48 In addition, N1 XPS spectrum was obtained before UV irradiation to verify the amino groups of PS-NH₂ and PAH (Figure 3b), showing two major peaks at 399.9 and 402.2 eV, corresponding to NH₂ and NH₃⁺, respectively. However, after UV irradiation, the C1 XPS spectrum exhibited two additional peaks at 286.8 and 288 eV, corresponding to C-O-C and O=C-N (amide), respectively (Figure 3c). Note that the peak at 287.5 eV corresponding to C-O dramatically decreased from 26.0% to 2.18% after UV irradiation. Although the peak intensity at 288 eV is not significant, this is probably due to the fact that covalently bonded amide groups were formed between carboxylic acid groups on GO and amine groups on the PAH and PS-NS₂. The N1 XPS spectrum also shows the additional peak at 401.5 eV corresponding to amide bond. Note that XPS results of the pristine GO shows that the GO sheets were not affected by the UV irradiation (SI Figure S3). We also analyzed the O 1s region before and after UV (SI Figure S4). However, the spectrum shows a single peak without any shoulder. It is therefore difficult to accurately interpret each O-bond individually.

In order to confirm the amide bond between the GO and polymers, we also conducted the FT-IR spectroscopy measurement (SI Figure S5). The FT–IR spectra of Janus GO show a peak at 1626 cm⁻¹ that is assigned to the carbonyl stretching of carboxylic group present in the GO. However, after UV irradiation, the appearance of characteristic peaks of carbonyl stretching of amide at 1605 cm⁻¹ and NH bending of amide at 1184 and 1495 cm⁻¹ indicate successful covalent bond in Janus graphene.

SEM images of the UV-irradiated Janus GO films were measured after transferring onto perforated copper (Cu) plates by the LS technique. Figures 3e and f are the SEM images of the Janus GO films with the PAH and PS-NH₂ facing up, by turning the sample upside down, respectively. In both cases, due to UV-induced enhancement of mechanical property, the free-standing structure was maintained over the large area of 300 μ m-diameter hole during the drying process. In addition, we investigated the UV effect on chemical stability of freestanding Janus GO monolayers. The Janus films were deposited on TEM copper grids, which were followed by UV irradiation ($\lambda = \sim 350$ nm for 1 h of exposure). This freestanding structure formed on TEM grids was maintained even after thorough rinsing with toluene (Figure 4g and h), whereas the Janus GO films without UV treatment were easily ruptured by toluene (Figure 4c and d). The improvement in the mechanical property and chemical stability of these Janus films can be also achieved when UV irradiation is applied directly to the Janus GO Langmuir monolayer at the liquid-gas interface (SI Figure S6). The structure of these both Janus GO films deposited both on largely perforated substrates and on the Si substrate was retained after rinsing with toluene as shown in SI Figures S6 and 7, respectively. As a result, UV irradiation can strengthen the Janus thin films and stabilize them against solvent by bonding between coated polymers and covalent bonds between GO-polymers, but this UV effect can not be expected when applied to the monolayer only consisted of the GO.

In order to distinguish the PAH side from the PS-NH₂ side in the films, both PAH/GO/PS-NH₂ and PS-NH₂/GO/PAH were stained with Cu(ll) sulfate solution and analyzed by a SEM-EDS. Figure 3g and h show their EDS chemical mapping results for Cu. The free-standing Janus film with the PAH facing up (i.e., PAH/GO/PS-NH₂) interacts with more Cu sulfate than that with the PS-NH₂ facing up (i.e., PS-NH₂/ GO/PAH). This result is not surprising since Cu sulfate selectively adsorbs to the amine groups contained in the PAH much more than PS-NH₂. This finding provides additional evidence for anisotropic functionality of the free-standing Janus GO film in large areas.

Wrinkled Structure of Janus GO Monolayers. In addition, the morphology of Janus films, (i.e., flat or wrinkled structure), was also tunable by monolayer compression at the liquid-gas interface. Figures 5a and b show AFM images of Janus films on silicon substrates transferred by LS techniques at surface pressures of 20 and 38 mN/m, respectively. Although there were some small gaps between the sheets, the flat Janus GO film covered up to 90.5% of the substrate at 20 mN/m. The flat morphology and small nanopore structure of the free-standing Janus GO films were also determined by SEM measurements. The diameters of the nanopores in the flat Janus GO monolayer ranged from 74 to 240 nm. Upon further compression of the Janus GO monolayer ($\pi = 38 \text{ mN/m}$), extensive wrinkles appeared on the surface (Figure 5b). The root-mean-square of the roughness of the wrinkled structure was determined to be 9.1 nm, while the roughness of the Janus GO film at the surface pressure of 20 mN/m was 0.2 nm based on the AFM results. The cross-section profiles of Figure 5c and d clearly show the difference in the roughness between flat and wrinkle Janus GO monolayers. To improve the strength of the membrane, the wrinkled Janus GO monolayers were UVirradiated at the liquid-gas interface prior to deposition. The SEM results showed that a free-standing wrinkled film was also



Figure 5. Nanowrinkled Janus GO formation. AFM topography images and cross-section profiles of Janus GO film transferred on silicon substrates by LS technique at the surface pressure of (a, c) 20 and (b, d) 38 mN/m. Corresponding SEM images of free-standing Janus GO films deposited at (e) 20 and (f) 38 mN/m.

obtained after deposition on the bare TEM copper grids (Figure 5f). This wrinkled morphology might be useful for applications requiring greater specific surface areas, for example, gas and metal ion adsorption. The anisotropic functionality of Janus films may improve selectivity for various materials with different hydrophilicity or ionic charges.

CONCLUSIONS

In summary, we prepared free-standing Janus GO films by grafting polymers using the LS technique. Hydrophobic PS-NH₂ and hydrophilic PAH were used for asymmetric modification on the surface of GO monolayers. The amine groups on PS-NH₂ and PAH interacted with oxide groups on the GO via electrostatic interaction at the liquid-gas interface. The Janus GO films consisted of hydrophobic PS and hydrophilic PAH on each side of the GO monolayer; these two sides exhibited different water contact angles, $80 \pm 0.4^{\circ}$ and $36 \pm 0.3^{\circ}$, respectively. The different functionalization on each side of the GO were also confirmed by EDS analysis and NR measurement. UV irradiation was used to improve mechanical property and chemical stability of free-standing Janus GO films. The XPS results confirm UV-induced covalent bonding between the oxide groups on the GO and amine groups on PS-NH₂ or PAH. This new approach for Janus GO sheets facilitates large area deposition of the robust freestanding single layer with different chemical functionality on each side of the GO and the formation nanowrinkle structure of Janus-type two-dimensional sheet by monolayer compression. Since morphologies and anisotropic functionality of graphene films are closely correlated to the performance improvement of graphene-based materials, the technique employed in this study can provide a route for applications requiring more specific surface area and selective adsorption,

such as membrane materials for desalination and electrode materials for Li-ion batteries and supercapacitors.

EXPERIMENTAL SECTION

Preparation of Janus Graphene Oxide. GO was obtained by a modified version of Hummers and Offeman's method from graphite flakes (Sigma-Aldrich, St. Louis, MO, USA), as previously described in detail.49 ⁻⁵¹ GO was dispersed in the deionized (DI) water (pH 7.4) at the concentration of 100 ppm, and the LS technique was used to fabricate the Janus GO monolayer at the liquid-gas interface. PS-NH₂ (10 kDa, M_w/M_n = 1.10, purchased from Polymer Source Inc. (Dorcal, Quebec, Canada)) dissolved in toluene (1 mg/mL) was gently spread on the surface of the prepared GO suspension (total area $(A) = 367 \text{ cm}^2$ in a Langmuir trough (KSV 2000, KSV NIMA, Espoo, Finland) at room temperature (the spread volume of the PS- NH_2 solution, $v = 25 \ \mu L$). Owing to Coulomb interactions between the oxidized function groups on the GO and the amine groups on the PS-NH₂, the GO sheets suspended in the DI water floated to the interface. After 15 min, the GO/PS-NH₂ hybrid film was compressed by motorized barriers at a speed of 5 cm^2/min , with monitoring of the surface pressure-area $(\pi - \hat{A})$ isotherm using a 25 mm wide platinum Wilhelmy plate suspended from a microbalance. After the desired surface pressure was achieved, the GO suspension was carefully replaced with DI water in the trough. Outside of the compressed barriers, water was supplied at one end and the GO suspension was aspirated at the other end. Thereafter, PAH (16 kDa, $M_w/M_p = 1.6$, purchased from Polymer Source Inc. (Dorcal, Quebec, Canada)) solution in DI water was injected into the subphase until the final PAH concentration reached 0.05 mg/mL. The subphase was exposed to UV (~350 nm) for 15 min sequentially, to enhance the covalent bonds between the GO and polymers. Then, either the hydrofluoric acid etched silicon substrates or transmission electron microscopy (TEM) grids (Ted Pella, Redding, CA) were juxtaposed and touched to the Langmuir film at the air-suspension interface. The substrates were horizontally lifted. The substrates with attached Janus GO sheets were gently washed several times with DI water and annealed under vacuum at 80 °C for 2 h.

Characterization of Janus Graphene Oxide. For the PAH/ GO/PS-NH₂/Si, we transferred the monolayer by applying the LS technique (namely, downstroke deposition); therefore, the hydrophobic PS face was in direct contact with the substrate, whereas the hydrophilic PAH face was exposed. For the PS-NH₂/GO/PAH/Si, we employed an mLB technique (namely, upstroke deposition) to obtain the opposite configuration. The surface morphology of the Janus GO monolayer on a silicon substrate was characterized using atomic force microscope (AFM, Nanoscope IIIa; Veeco Instruments Inc., NY, USA), in the tapping mode with a silicon nitride tip (size = 5 nm). To compare the surface hydrophobicity of samples, water contact angles were measured with a contact angle meter (Phoenix 150, Surface Electro Optics, Korea). Unpolarized Raman spectra were recorded for the Janus GO monolayer. An InVia Raman microscope (Renishaw Ltd., Gloucestershire, UK) was used, with an excitation source (incident power of 2 mW) of the 633 nm line from a He-Ne laser. The elemental composition and functional groups of the Janus GO monolayer were characterized using X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo VG Scientific, USA). Scanning electron microscopy (SEM, Magellan 400, FEI, Hillsboro, OR, USA) was also used for measuring the surface morphology of the Janus GO monolayer, and Cu stained on the Janus GO film was analyzed by SEM-energy dispersive spectrometry (EDS). The accelerating voltage was 5 kV. The functional groups were investigated by Fourier-transform infrared spectroscopy (FT-IR, Nicolet iS50, Thermo Fisher Scientific Instrument, MA, USA) for the PAH, PS-NH₂, GO, and Janus GO.

A neutron reflectivity (NR) was used to investigate the large area of the Janus GO monolayer. We added 20 wt % of deuterated PS-NH₂ (dPS-NH₂) to 80 wt % of PS-NH₂ (mPS- NH₂) to obtain a distinct contrast from the PAH layer. The dPS-NH₂ (16 kDa, $M_w/M_n = 1.6$, was purchased from Polymer Source Inc. (Dorcal, Quebec, Canada). The Janus GO monolayer was sandwiched between two deuterated polystyrene (dPS) thin films to obtain a better scattering length density (SLD) profile. The SLD values were calculated to be 2.5 × 10⁻⁶ and 0.5 × 10⁻⁶ Å⁻² for mPS-NH₂ and PAH, respectively. The specular NR measurements were performed with an NG7 reflectometer beamline at the Cold Neutron Facility of the National Institute of Standards and Technology (Gaithersburg, MD, USA). The NR data were obtained as a function of the wave vector transfer, q_z (~4 π sin θ/λ), where θ is the grazing angle of the incidence neutron beam in the specular NR experiments. The obtained NR data were corrected for footprints and background, and analyzed using computational reflectivity profiles with a Parratt formalism.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsanm.9b00660.

Characterization (AFM and SEM) of Janus GO monolayers transferred on silicon substrates depending on the surface pressure; Raman spectra of PAH, PS-NH₂, GO, and Janus GO films; XPS spectra of GO, and XPS O 1s spectra of Janus GO films transferred on silicon substrates; FT-IR spectra of PAH, PS-NH2, GO, and Janus GO films; SEM and AFM images of UVirradiated Janus GO films after rinsing with toluene (PDF)

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Author Contributions

^{II}H.L. and K.-I.C. contributed equally to this work. J.K. conceived and designed the experiments. H.L., K.-I.C., and J.-H.C. performed Janus GO film fabrication and SEM/AFM measurements. J.Y. and Y.-S.S. performed Raman measurements and advised on data analysis. H.L., S.S., and J.K. conducted neutron reflectivity measurements and analyzed the data. H.L. performed XPS measurements. J.K. and H.L. wrote the paper. All authors discussed the results and commented on the manuscript.

Notes

The authors declare no competing financial interest.

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