Electronic Supplementary Information (ESI)

Electrostatic-Attraction-Induced High Internal Phase Emulsion for Large-Scale Synthesis of Amphiphilic Janus Nanosheets

Dan Luo,[*a] Fanghao Zhang,[a,b] Haotian Zheng,[c] Zhensong Ren,[a] Lili Jiang,[a] Zhifeng Ren*[*a]*

[a]Department of Physics and TcSUH, University of Houston, Houston, Texas 77204, United States.

[b]Department of Chemistry, University of Houston, Houston, Texas 77204, United States

[c]Department of Electrical & Computer Engineering and Materials Science and Engineering Program, University of Houston, Houston, Texas 77204, USA

Corresponding Authors:

*zren@uh.edu

*danluo1101@gmail.com

Materials and Methods

Synthesis of Amphiphilic Janus Nanosheets

Graphene oxide (GO) was first synthesized by the previously reported method.[1] 200 mg GO was then dispersed in deionized (DI) water to obtain 1 mg/mL concentration via sonication. 500 mg octadecylamine (ODA) purchased from Sigma-Aldrich was completely dissolved in 50 mL kerosene (Sunnyside Corporation), and the solution was added drop-by-drop into the as-prepared GO dispersion with the assistance of a certain amount of NaCl. The mixture was subjected to stirring at a speed of 900 rpm for 18 hours at room temperature. After washing sequentially by ethanol and DI water using a centrifuge at a low speed, amphiphilic Janus nanosheets were obtained.

Characterization

The Fourier transform infrared spectroscopy (FTIR) spectrum was detected using a Nicolet iS50 FTIR Spectrometer equipped with an attenuated total reflectance (ATR) accessory. Zeta potentials were measured using a Malvern Zetasizer Nano ZS by generating kerosene droplets in DI water (pH=4). The chemical information of the GO and amphiphilic Janus nanosheets were also characterized by X-ray photoelectron spectroscopy (XPS) (Physical Electronics Model 5700). UV-Vis spectra were further recorded via a Cary 5000 UV-Vis-NIR spectrophotometer. The morphology of the amphiphilic Janus nanosheets was examined by using a JEOL 2010F transmission electron microscope (TEM). The distribution of particle sizes was determined by a Malvern NanoSight NS300 using a diluted dispersion.

DLVO Modeling

We calculated the interactions for both the GO-kerosene/water interface and GO particles themselves using classical DLVO theory by considering the balance of van der Waals and electrostatic interactions.

For van der Waals (Φ_{vdw}), we assumed both GO and the interface as infinite plates. The equations are given as,[2]

$$\Phi_{vdw} = -\left(\frac{H}{12\pi}\right)\left(\frac{1}{d^2} + \frac{1}{(d+t_1+t_2)^2} - \frac{1}{(d+t_1)^2} - \frac{1}{(d+t_2)^2}\right)$$

$$H \approx \frac{3hv_e}{8\sqrt{2}\,(n_1{}^2 + n_3{}^2)^{1/2}(n_2{}^2 + n_3{}^2)^{1/2}\left\{(n_1{}^2 + n_3{}^2)^{1/2} + (n_2{}^2 + n_3{}^2)^{1/2}\right\}} \frac{(n_1{}^2 - n_3{}^2)(n_2{}^2 - n_3{}^2)}{}, \quad n_1 = n_2.$$

In these equations, H is the hamaker constant, d is the distance between the two plates, t is the thickness of the plates, h is the the Planck constant, v_e is the primary electronic absorption frequency in the UV region, and n is the the refractive index in the visible regime. v_e is approximated as: $v_e = v_1\sqrt{3/(n_i{}^2 + 2)}$, where v_1 is the absorption frequency of a Bohr atom (3.3×10^{15} s^{-1}) and n_i is the refractive index.

For the electrostatic interaction,[2]

$$\Phi_{ele} = \frac{2\sigma_1\sigma_2}{\varepsilon_0\varepsilon_m\kappa} exp(-\kappa d)$$

$$\sigma = \frac{2\varepsilon_0\varepsilon_m\kappa kT}{e} sinh\left(\frac{e\psi}{kT}\right)$$

$$\kappa = \left[2e^2 N_A I/(\varepsilon_0\varepsilon_m kT)\right]^{1/2}$$

$$\varepsilon_m = 87.73 \times 10^{-0.002(T - 273.15)}$$

In these equations, ε_0 is the vacuum permittivity; ε_m is the solvent permittivity; σ is the surface charge density; ψ is the surface potential, which is approximated using the zeta potential ξ; κ is the inverse Debye length; e is the elementary charge; N_A is the Avogadro constant; I is the ionic strength; k is the Boltzmann constant; and T is the absolute temperature. We assumed that the temperature was at 298.15 K and calculated the temperature-dependent dielectric constant of water by $\varepsilon_m = 87.73 \times 10^{-0.002(T - 273.15)}$.[3]

Finally, the total interactions were calculated as,

$$\Phi_{DLVO} = \Phi_{vdw} + \Phi_{ele}$$

The thicknesses of GO and the kerosene-water interface in the calculations were chosen as 1 nm and 0.3 nm, respectively. The refractive indices for GO and DI water were determined as 1.58 and 1.33, respectively. The zeta potential for the kerosene-water interface was measured as -62.0 $\pm$ $7.2mV$ while -38.0 mV for GO at pH=4. After adding ODA at 10 mg/mL, the zeta potential for the interface was changed to + 68.0 $\pm$ $4.9mV$. The ionic strength was calculated as 0.17 M for 1 wt% NaCl while 10^{-6} M for the DI water due to the dissolution of CO_2 in the atmosphere.

Molecular Dynamics (MD) Simulations

A monolayer of graphene with dimensions of 24.9 Å× 25.9 Å was constructed as a substrate containing 238 carbon atoms. 4 carboxyl groups were attached to the edges of the graphene, along with 24 epoxy groups and 28 hydroxyl groups built on the bottom, top, and edges. To construct the amphiphilic Janus nanosheet, 5 octadecylamine molecules were further connected to one side of the previously established graphene through ring-opening of epoxy groups. All of the construction works were performed on PyMOL.[4] The topology files were produced by TPPmktop.[5] GROMACS 5.1.4. was employed for MD simulation with the use of the OPLS-AA force field.[6] The time step was set to 2 fs. After an energy minimization, the simulation further underwent a 5 ns NVT ensemble equilibration at 300 K and also a 5 ns NPT ensemble equilibration at 1 bar, followed by a production run (100 ns). The LINCS algorithm was used for the bond length constraint. A cutoff of 1.2 nm was set for Lennard-Jones (LJ) interactions and the real part of the long-range electrostatic interactions, which were calculated via the particle-mesh Ewald (PME) method. 0.16 nm grid spacing was used for PME. The system information was recorded every 100 ps. The periodic box size was 60 Å × 60 Å × 90 Å (length × wide × height). 444 Heptane molecules were distributed on the top part of the box (60 Å × 60 Å × 30 Å). 7587 water molecules were

randomly distributed throughout the entire box. An amphiphilic Janus nanosheet was initially put in the center of the box.

Figures

Figure S1. Emulsions generated using 5 mL kerosene and different concentrations of graphene oxide (GO) at fixed 10 mg/mL octadecylamine (ODA), except for the leftmost bottle containing only GO and kerosene (no emulsion was generated).

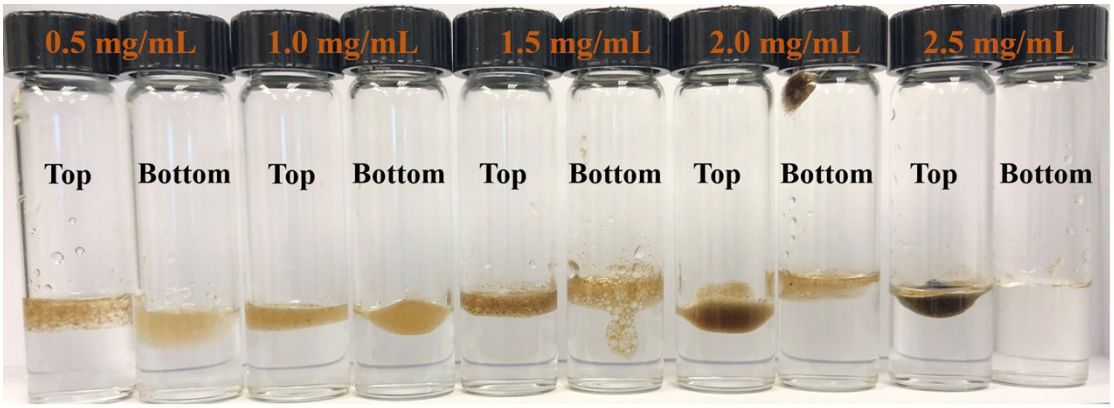


Figure S2. Dilution tests for emulsions generated in Fig. S1 at the top and bottom parts.

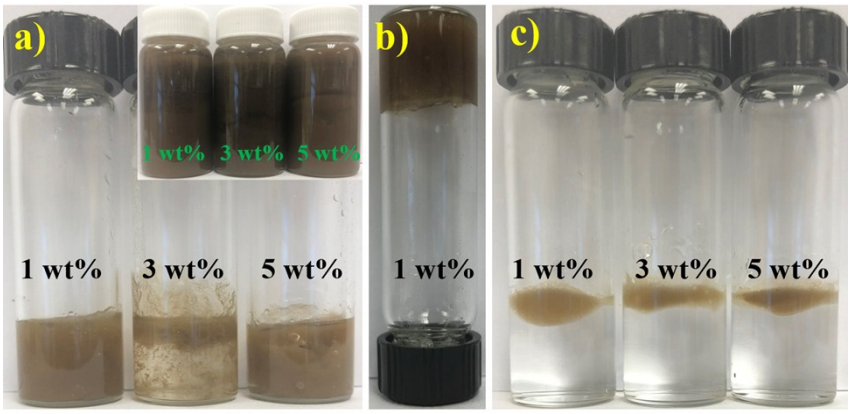
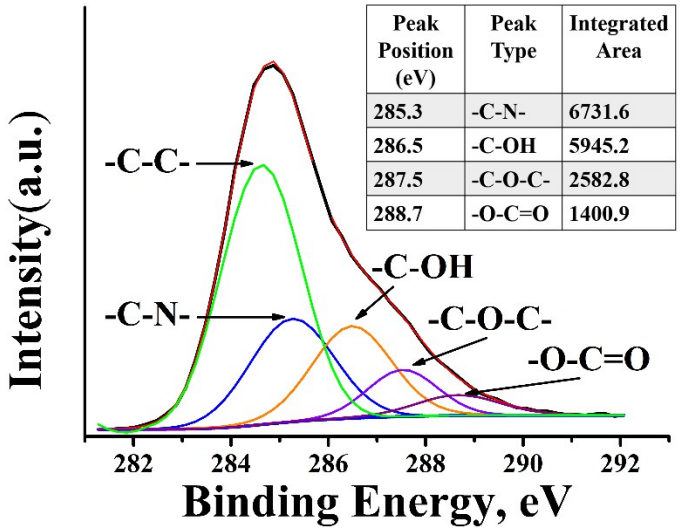


Figure S3. (a) Emulsions generated using 1 mg/mL GO and 10 mg/mL ODA at different NaCl concentrations. **(b)** Demonstration of the high viscosity of the emulsion formed using 1 wt% NaCl. **(c)** Dilution tests at different NaCl concentrations.



Peak Position (eV)	Peak Type	Integrated Area
285.3	-C-N-	6731.6
286.5	-C-OH	5945.2
287.5	-C-O-C-	2582.8
288.7	-O-C=O	1400.9

Figure S4. Convolution of C1s spectrum of amphiphilic Janus nanosheets.

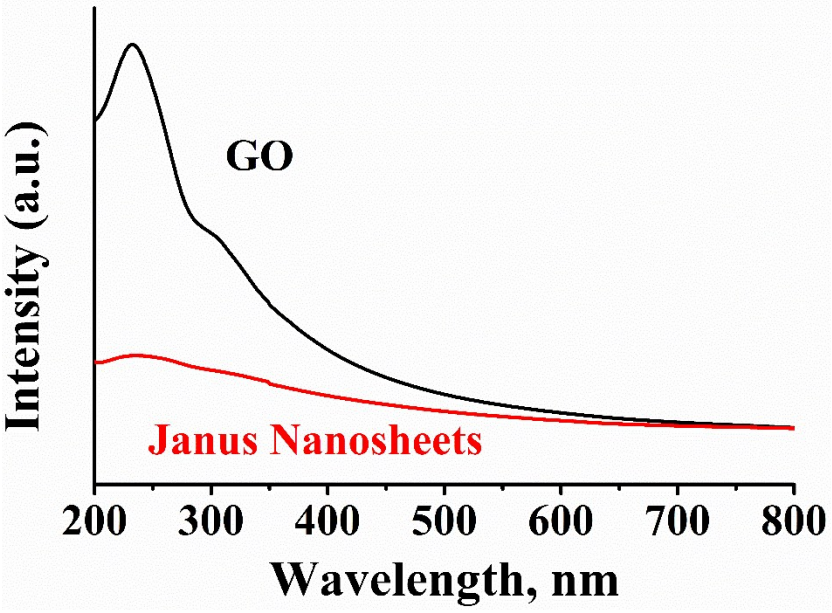


Figure S5. UV-Vis spectrum of GO and amphiphilic Janus nanosheets.

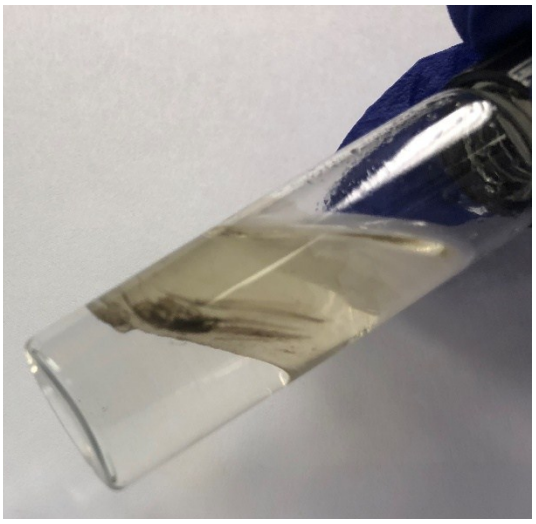


Figure S6. Wrinkles showing on the interfacial film formed by amphiphilic Janus nanosheets when tilting the vial.

Figure S7. Emulsion generation using 0.02 wt% amphiphilic Janus nanosheets at the 8:1 ratio of water volume to oil volume.

References

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