

Electronic Supplementary Information

Janus amphiphilic nanoplatelets as smart colloid surfactants with
complementary face-to-face interactions

Jin Yong Lee^a, Kyu Hwan Choi^b, Jaemin Hwang^c, Minchul Sung^c, Ji Eun Kim^b, Bum Jun Park^{b*}, Jin
Woong Kim^{c*}

^aDepartment of Bionano Technology, Hanyang University, Ansan, 15588, Republic of Korea;

^bDepartment of Chemical Engineering, Kyung Hee University, Yongin, 17104, Republic of Korea;

^cSchool of Chemical Engineering, Sungkyunkwan University, Suwon, 16419, Republic of Korea.

Experimental section

Materials: Zirconyl chloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 98%), 3-aminopropyltriethoxysilane (APTES, 99%), anhydrous toluene (99.8%), triethylamine (TEA, 99.5%), anhydrous dichloromethane (MC, 99.8%), poly(ethylene glycol) methacrylate (PEGMA, $M_n \sim 360$), ethyl α -bromoisobutyrate (EBiB, 98%), α -bromoisobutyric acid (BiBA, 98%), copper(II) bromide (CuBr_2 , 99%), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDTA, 99%), tin(II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$, 92.5~100%), L-ascorbic acid (AscA, 98%), anhydrous anisole (99.7%), N,N-dimethylformamide (DMF, 99%), and sodium hydroxide (NaOH, 98%) were purchased from Sigma-Aldrich (USA). Phosphoric acid (H_3PO_4 , 85%) and hydrogen peroxide (H_2O_2 , 30%) were purchased from Junsei Chemical Co. (Japan). Tris(2-pyridylmethyl)amine (TPMA, 98%), hexyltrimethoxysilane (HTMS, 98%), and α -bromoisobutyryl bromide (Bibb, 98%) were supplied by Tokyo Chemical (Japan). n-Butyl methacrylate (BMA, 99%, Alfa Aesar, USA), 2-aminoethylmethacrylate hydrochloride (AMA, 90%, Morris Plains, USA), n-decane (99%, Daejung Chemical, Korea), and 2N-hydrochloric acid solution (HCl, Daejung Chemical, Korea) used in this study were reagent grade and were used without further purification. For all experiments, deionized double distilled water was used. A silicon wafer (polished, p++ type, boron doped, 1-30 Ω cm, 100mm diameter) was purchased from Silicon Technology (Japan).

Synthesis and surface modification of ZrHP NPLs: We synthesized the zirconium hydrogen phosphate (ZrHP) nanoplatelets (NPLs) by using the refluxing method¹. Firstly, 3.22g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was dissolved in 200 mL distilled water in a three-neck round bottom flask. After refluxing at 100 °C for 48 h, 6.0 M H_3PO_4 (200 mL) was added dropwise. Then, the reaction product was washed with distilled water and collected in the form of a white paste. The paste obtained was dried at 65 °C for 24 h. Secondly, the hydroxyl groups on the surface of ZrHP NPLs were modified with (3-aminopropyl)triethoxysilane

(APTES) and hexyltrimethoxysilane (HTMS). For this, 1 wt% of dried ZrHP NPLs was dispersed in 100 mL toluene at 110 °C after refluxing and then, 2.5 wt% of APTES and 2.5 wt% of HTMS were incorporated into the dispersion. The reaction was conducted for 24 h with slow stirring. Then, primary amine functionalized ZrHP-NH₂ NPLs were obtained by repeated centrifugation and redispersion in toluene, followed by drying under vacuum at 60 °C. For incorporation of ATRP-initiation sites, 1 wt% of ZrHP-NH₂ NPLs were dispersed in 100 mL of MC and 2 wt % of TEA was added after Ar purging at 0 °C. Then, 1 wt% of 2-bromoisobutryl bromide was dripped slowly into the dispersion. The reaction carried out for 24 h at room temperature. Finally, bromide functionalized ZrHP-Br NPLs were produced by centrifugation and redispersion in the mixture of MC and ethanol (5/5, v/v), followed by drying under vacuum at 60 °C.

Synthesis of ANPLs via SI-ARGET ATRP: Two species of amphiphilic nanoplatelets (ANPLs) were synthesized by the surface-initiated activators regenerated by electron transfer ATRP method (SI-ARGET ATRP). The polymerization was done simultaneously in an oil-in-water emulsion state. First, 400 µL of 0.1M CuBr₂ as a catalyst, 400 µL of 1M TPMA as a ligand, and 40 µL of EBiB dissolved in DMF solutions as sacrificial initiator, 1g of ZrHP-Br as macro-initiator, and 0.5 g of (BMA as a hydrophobic monomer dispersed in 20 mL anisole were mixed in a three-neck round bottom flask at 80 °C, with vigorously stirring and continuous purging with Ar. Then, 400 µL of 1M Sn(Oct)₂ dissolved in DMF solution as a reducing agent was rapidly added into the solution. After a while, the water phase solution was dripped into the oil solution, which consists of 0.5 g of water-soluble monomers, PEGMA or PEGMA/AMA (8/2, w/w), 400 µL of 0.1M CuBr₂, 400 µL of 1M PMDTA, and 40 µL of 0.1M BiBA dissolved in DMF solution. Lastly, 400 µL of 1M AscA dissolved in DMF solution was quickly added. After 24 h polymerization, the ANPLs were purified by centrifugation and washed in different solvents (DMF, MC, ethanol).

Surface modification and polymer grafting of silicon wafers: Silicon wafers (SW) were cut into squares (1-2 cm²) and immersed in acetone while applying ultrasonication for 30 min to completely remove any contaminants on the surface. After rinsing with deionized water, the SW were dried in vacuum. Firstly, to prepare silanol terminated-silicon wafers (SW-OH), the SW were placed in a piranha solution (H₂SO₄/H₂O₂ = 2.5:1, v/v) for 30 min at room temperature. Subsequently, the SW were washed again with deionized water and dried in vacuum. Secondly, the SW-OH were modified with 2.5 wt% APTES and 2.5 wt% hexyltrimethoxysilane in anhydrous toluene for 24 h at room temperature, which leads to amino group modified-silicon wafers (SW-NH₂). After rinsing with anhydrous toluene to remove any excess reagent, the SW-NH₂ were dried under vacuum. Thirdly, the SW-NH₂ were placed in 20 mL of dichloromethane and then 2 wt % TEA was added under argon purging at 0 °C. After dripping slowly 1 wt% of 2-bromoisobutryl bromide into the solution, the reaction was conducted for 24 h at room temperature, which allowed us to produce the bromide modified-silicon wafers (SW-Br).

Using the SW-Br, the polymer-grafted SW were synthesized via SI-ARGET ATRP. The polymerization was done simultaneously in homogeneous solution. Firstly, to produce hydrophobic polymer grafted-SW (SW-pBMA), 1 mL of 0.1M CuBr₂ as a catalyst, 1 mL of 1M TPMA as a ligand, and 100 µL of EBiB

dissolved in DMF solutions as sacrificial initiator, the SW-Br and 5 g of BMA as a hydrophobic monomer dispersed in 20 mL anisole were vigorously stirred in a three-neck round bottom flask at 80 °C while Ar purging. Then, 1 mL of 1M Sn(Oct)₂ dissolved in DMF solution as a reducing agent was rapidly added into the reaction solution. After 24 h of polymerization, the polymer-grafted SW were washed with DMF, ethanol, and MC in that order. Secondly, to produce the hydrophilic polymer-grafted SW (SW-pPEGMA or SW-p(PEGMA-co-AMA)), 1 mL of 0.1M CuBr₂ as a catalyst, 1 mL of 1M PMDTA as a ligand, and 100 μL of BiBA dissolved in DMF solutions as sacrificial initiator, the SW-Br wafers and 5 g of hydrophilic monomer (PEGMA or PEGMA/AMA= 8/2, w/w) dispersed in 20 mL D.I water were mixed in a three-neck round bottom flask. Then, 1 mL of 1M AscA dissolved in DMF solution was quickly added while vigorously stirring the reaction mixture. After polymerization for 24 h, the SW-pPEGMA or SW-p(PEGMA-co-AMA) were rinsed by different solvents in the following order: DMF, MC, ethanol, D.I. water.

Determination of grafting density of polymer brushes on ANPLs: The molecular weight of bulk polymers (M_n and M_w) obtained after precipitation has been evaluated using GPC (Agilent 1100S, Agilent Technologies Inc., USA). Nitrogen adsorption-desorption isotherms were recorded at -196 °C on an adsorption volumetric analyzer BEL MINI. (Japan)². All the samples were degassed at 200 °C for 12 h under static vacuum prior to adsorption measurements. The specific surface area was determined from the N₂ adsorption isotherms in the relative pressure range 0.05–0.20 by using the Brunauer-Emmet-Teller (BET) method. The molecular weight of the polymer in solution obtained by GPC was $M_n = 9,600$; $M_w = 76,000$ g mol⁻¹. The amount of the grafted polymer determined by TGA was 20 wt. %. The grafting density (Equation 1) was determined by considering the surface area of the kaolinite particles, which was evaluated by BET measurements: $S_{BET} = 25.5$ m² g⁻¹ (N_A is the Avogadro's number; f_{pol} is the polymer mass fraction according to TGA analysis). The estimated value of the grafting density was ca. 0.54 chains/nm², which is comparable to the previously reported value of the grafting density, obtained using ARGET-ATRP on a SiO₂ substrate.

$$\Gamma \left(\frac{\text{chains}}{\text{nm}^2} \right) = \frac{f_{pol} N_A}{1 - f_{pol} M_n S_{BET}}$$

Production of ANPL-armored Pickering emulsions: To produce ANPL-armored Pickering emulsions, the ANPLs were finely dispersed in MC at 40 °C with vigorous stirring. Then, a given volume fraction of n-decane was added to the solution. To ensure fine dispersion of ANPLs, probe-type sonication was applied at 100% amplitude for 2 min. Then, MC was completely removed from the ANPL dispersion by using an evaporator at 40 °C for 15 min. We used a rapid vortex method to produce the Pickering emulsions. Upon adding the ANPL-suspended n-decane into water, rapid vortexing was conducted for 1 min. In the cases of adjusting pH and controlling salinity, we used aqueous solutions with different pH with or without 5 M NaCl. The pH values were tuned by using 0.1 M HCl solution and 0.1 M NaOH solution. The phase of Pickering emulsions was identified through conductivity measurements.

Rheological analysis: Rheological properties of Pickering emulsions were characterized using a DHR-1 rheometer (TA Instruments) in the oscillation frequency-control mode with a parallel plate geometry, the diameter of which is 40 mm and the gap is set to 500 μm . The concentration of ANPLs in Pickering emulsions was tuned from 0.1 wt % to 4 wt % and the oil volume fraction of *n*-decane oil was varied from 0.1 to 0.9. Before operation of the rheometer, equilibration was performed for all rheological measurements for 30 sec. Then, the sample was loaded onto the rheometer plate and surrounded by a solvent trap to prevent any evaporation of water. The range of the oscillation frequency was 400–0.1 rad s^{-1} . The strain amplitude was kept to 1.0 %. All measurements were conducted at 25 $^{\circ}\text{C}$.

Characterizations: The morphological characteristics of ANPLs were observed using a Scanning electron microscopy (SEM, MIRA3, Tescan, Czech Republic) and Energy-filtering transmission electron microscope (EF-TEM, LIBRA 120, Carl Zeiss, Germany). Cryo-Scanning electron microscopy (Cryo-SEM) was performed with a focused ion beam microscope (Quanta 3D FIB, FEI, USA) and cryo system (ALTO 2500, Gatan, Germany). The Dextran rhodamine-B labeled Pickering emulsions were then visualized using a fluorescence microscope (AX10 with Axiocam 503 mono, Carl Zeiss, Germany). Thermogravimetric analysis (TGA) results were obtained using an SDT Q600 device (TA Instruments Inc.) at a scan rate of 10 $^{\circ}\text{C min}^{-1}$. The zeta potential of the ANPLs were measured by dynamic light scattering (ELS-Z2, Otsuka electronics Japan) using a He-Ne laser with a wavelength of 632.8 nm. To confirm the Janus phase, one side was tagged with fluorescein sodium salt, then analyzed by using confocal laser scanning microscopy (CLSM, LSM710, Carl Zeiss, Germany). The contact angle measurement was used by Velcam digital color CCD camera (CVC5220, Koera).

Measurements of the three-phase contact angle: The three-phase contact angle θ was measured by using a tensiometer. Each of the polymer-grafted substrates (SW-Br, SW-pBMA, SW-pPEGMA, and SW-p(PEGMA-co-AMA)) was placed on a glass container filled with *n*-decane. A sessile drop was formed on the substrate surface by gently placing 5 μL of water (resistivity = 18.2 $\text{M}\Omega\cdot\text{cm}$). The contact angle between the sessile drop and the substrate was determined by analyzing the optical image.

Calculations of interface attachment energy: The Hit-and-Miss Monte Carlo method was used to numerically calculate the attachment energy of an ANPL to an oil-water interface.³ When the ANPL dispersed in water is adsorbed to the interface, the attachment energy is given by $\Delta E_{Iw} = E_{Int} - E_w$, where E_{Int} is the surface free energy when the ANPL is trapped at the interface and E_w is the energy when the particle is completely submerged in water. Each free energy is expressed as $E_{Int} = \gamma_{ow}(S_{Int}^{tot} - S_{Int}) + \gamma_{Pw}S_{Pw} + \gamma_{Po}S_{Po} + \gamma_{Aw}S_{Aw} + \gamma_{Ao}S_{Ao} + \gamma_{Sw}S_{Sw} + \gamma_{So}S_{So}$ and $E_w = \gamma_{ow}S_{Int}^{tot} + \gamma_{Pw}S_{Pw} + \gamma_{Aw}S_{Aw} + \gamma_{Sw}S_{Sw}$, where S_{ij} and γ_{ij} are the surface area and surface tension between i and j , respectively, S_{Int}^{tot} is the total area of the oil-water interface, and S_{Int} is the interface area displaced by the particle. The subscripts A , P , S , w , and o indicate apolar, polar, side, water, and oil, respectively, and Int is the interface. By combining the Young's equation, the attachment energy can be expressed as $\Delta E_{Iw} = \gamma_{ow}(S_{So}\cos\theta_S + S_{Ao}\cos\theta_A + S_{Po}\cos\theta_P - S_{Int})$. Similarly, the interface attachment energy from the oil

phase is expressed as $\Delta E_{Io} = -\gamma_{ow}(S_{Sw}\cos\theta_s + S_{Aw}\cos\theta_A + S_{Pw}\cos\theta_P + S_{Int})$. The equilibrium configuration of the ANPLs is determined by minimizing ΔE_{Iw} , which is calculated as functions of the orientation angle φ and of the vertical displacement d_I against the interface. The equation of ΔE_{Io} results in the same equilibrium configuration, and therefore, ΔE_{Iw} is evaluated unless otherwise noted. The ANPL has a polygonal geometry with a thickness of ~ 40 nm and a diameter of ~ 300 nm. For simplification, we assumed that the ANPL adopts a circular disk shape with 40 nm in thickness and 300 nm in diameter. The contact angles of 117.6° for the SW-pBMA surface and 59.4° for the SW-p(PEGMA-co-AMA) surface (Figure S5) are used as θ_A and θ_P , respectively. Because it is unlikely that the side region of the ANPL is coated exclusively with either PBMA or p(PEGMA-co-AMA), the θ_s value was assumed to be neutral wetting with 93.5° , which corresponds to the contact angle of the SW-Br surface. To determine the equilibrium configuration, $\Delta E_{Iw}(d_I, \varphi) = \Delta E$ is calculated with varying the d_I values at a constant $\varphi = \Theta$, and the minimum attachment energy $\Delta E_{min}(\varphi = \Theta)$ is found. The same procedure is repeated for different values of φ from 0° to 180° . Finally, the global energy minimum ($\min(\Delta E_{min})$) is evaluated from the values of ΔE_{min} .

Experimental Data

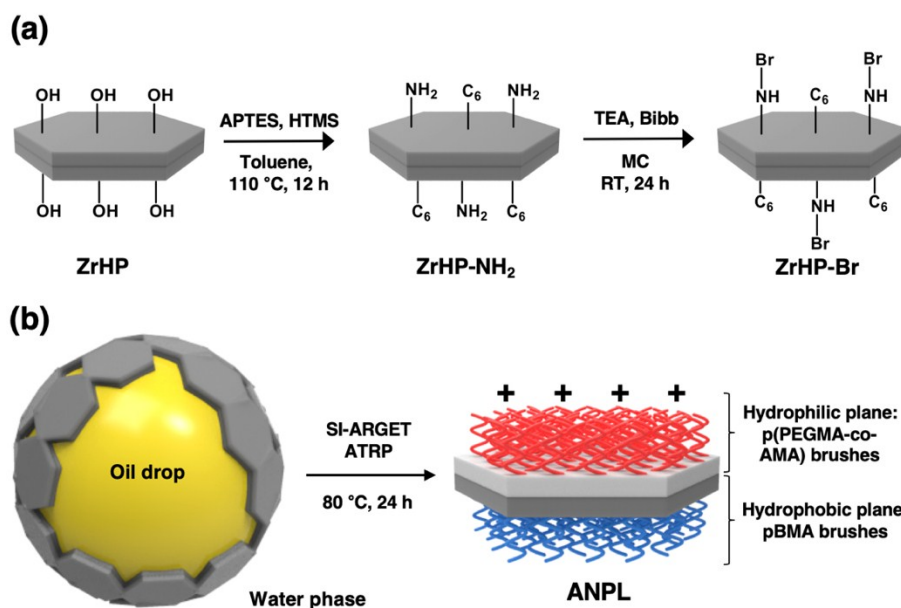


Figure S1. Schematic illustration for synthesis of ANPLs. (a) Incorporation of initiation sites on a bare ZrHP NPL. (b) SI-ARGET ATRP at the interface. Hydrophilic monomer, BibA, PMDTA, CuBr₂, and AsCA were located in the water phase. Hydrophobic monomer, Ebib, TPMA, CuBr₂, and Sn(Oct)₂ were in the anisole phase.

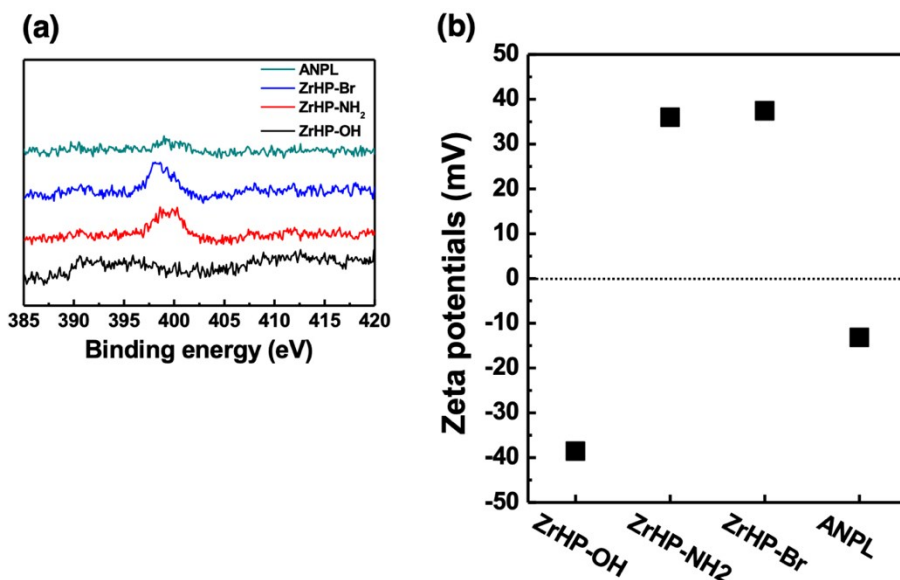


Figure S2. XPS patterns of ZrHP NPLs and ANPLs: (a) high resolution spectra of N 1s. (b) Zeta potentials of NPLs in each step of surface modification and ANPLs after SI-ARGET ATRP. In this study, ANPLs with p(PEGMA-co-AMA) and pBMA brushes were used.

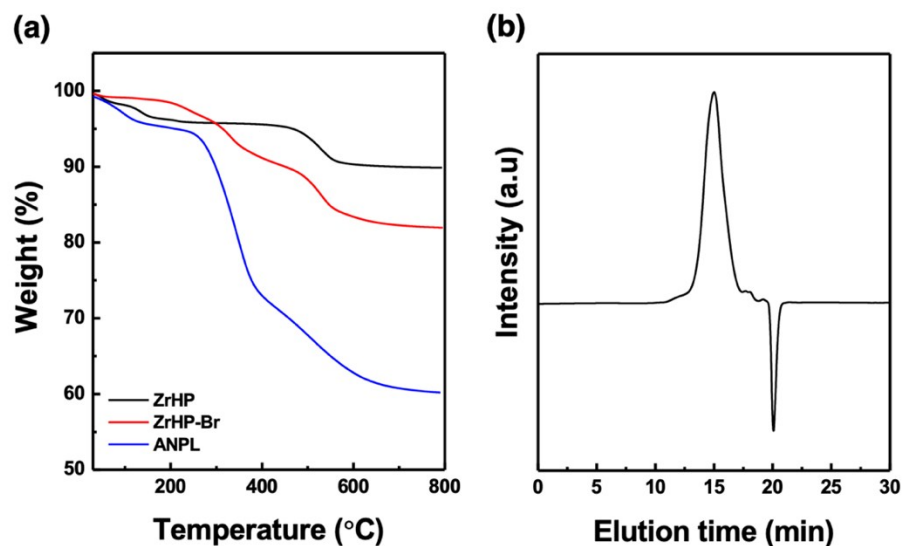


Figure S3. (a) TGA curves of bare NPLs and ANPLs. (b) GPC trace of grafted polymer on the surface of ANPLs. In this study, ANPLs with p(PEGMA-co-AMA) and pBMA brushes were used.

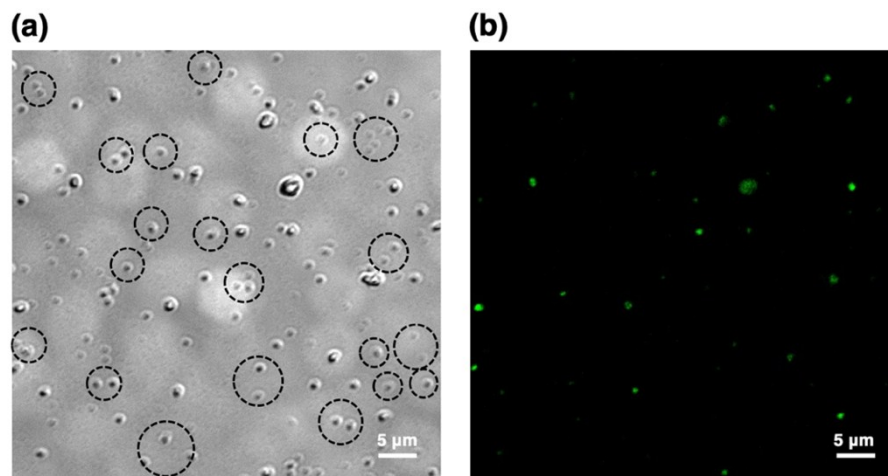


Figure S4. (a) Bright-field microscope image of ANPLs in the differential interference contrast (DIC) mode. (b) CLSM image of ANPLs of which hydrophilic plane was selectively labelled with fluorescein sodium salt. In this study, ANPLs with p(PEGMA-co-AMA) and pBMA brushes were used.

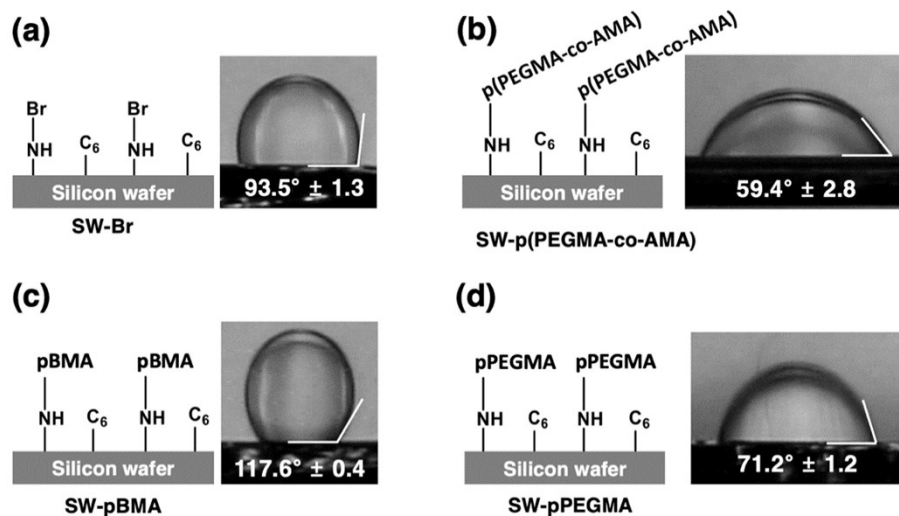


Figure S5. Contact angle measurements of water droplet in n-decane on surface treated silicon wafers: (a) SW-Br, (b) SW-p(PEGMA-co-AMA), (c) SW-pBMA, and (d) SW-pPEGMA.

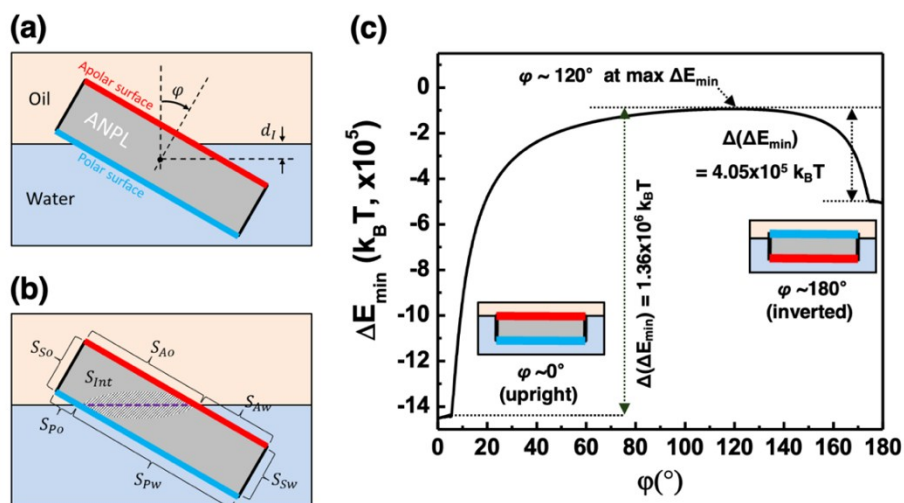


Figure S6. Schematic illustration of the geometry of ANPLs at the oil-water interface: (a) orientation angle φ and vertical displacement d_l of interface-trapped ANPLs and (b) surfaces of polar, apolar, and side regions exposed to each fluid phase. (c) Attachment energy profile of an ANPL with p(PEGMA-co-AMA) and pBMA brushes to the oil-water interface, assuming that $\theta_s = 86.5^\circ$.

[ANPL] (wt%)	Oil volume fraction (ϕ_{oil})					
	0.1	0.2	0.3	0.4	0.6	0.8
4						
3						
2						
1						
0.5						
0.1						

Figure S7. Actual appearance of Pickering emulsions armored with ANPLs with p(PEGMA-co-AMA) and pBMA brushes. All the photographs were taken after storage for 24 h at room temperature.

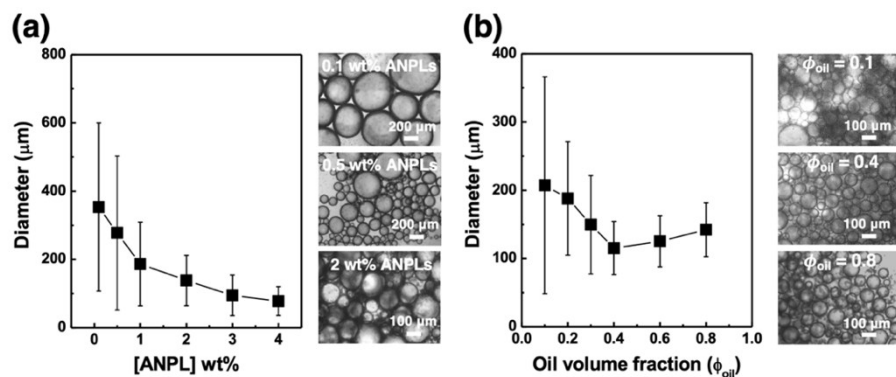


Figure S8. Size variation and optical images of Pickering emulsion droplets according to (a) [ANPL] (at fixed $\phi_{\text{oil}} = 0.2$) and (b) ϕ_{oil} (at fixed [ANPL] = 1 wt%). ANPLs with p(PEGMA-co-AMA) and pBMA brushes were used.

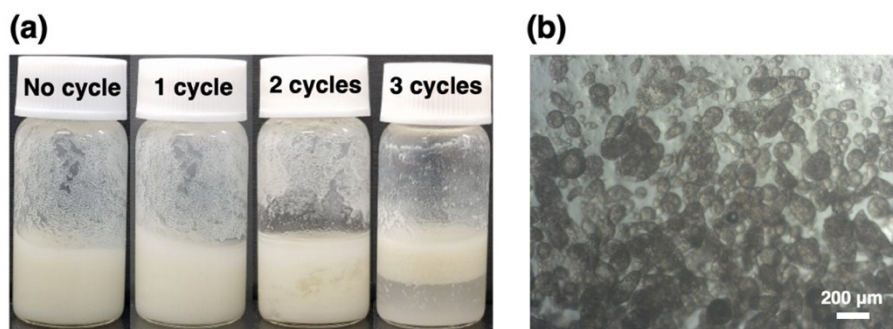


Figure S9. (a) Appearance of ANPL-armed Pickering emulsions after freeze-thawing test. (b) Optical microscope image of ANPL-armed Pickering emulsion drops after 3 cycles of freeze-thawing. ANPLs with p(PEGMA-co-AMA) and pBMA brushes were used. $\phi_{\text{oil}} = 0.2$. [ANPL] = 2 wt%.

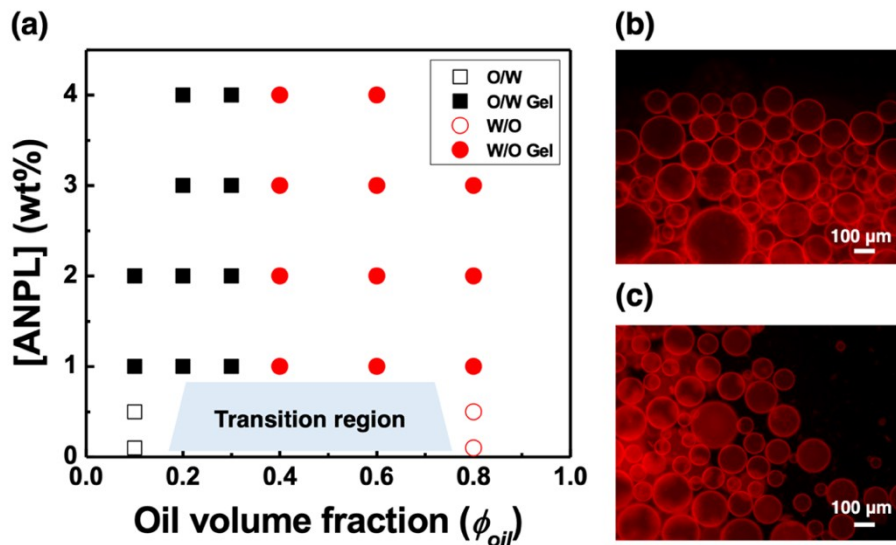


Figure S10. (a) Phase diagram of ANPL-armed Pickering emulsions. Fluorescence microscope images of ANPL-armed Pickering emulsions: (b) O/W emulsion drops with Nile red in n-decane dispersion phase and (c) W/O emulsion drops with Dextran tetramethylrhodamine in water dispersion phase. ANPLs with pPEGMA and pBMA brushes were used.

References

- 1 A. F. Mejia, A. Diaz, S. Pullela, Y.-W. Chang, M. Simonetty, C. Carpenter, J. D. Batteas, M. S. Mannan, A. Clearfield and Z. Cheng, *Soft Matter*, 2012, **8**, 10245-10253.
- 2 H. S. Kim, M. A. Abbas, M. S. Kang, H. Kyung, J. H. Bang and W. C. Yoo, *Electrochim. Acta*, 2019, **304**, 210-220.
- 3 B. J. Park and D. Lee, *ACS Nano*, 2012, **6**, 782-790.