Electronic Supplementary Information for

Versatile Pickering Emulsion Gel Lubricants Stabilized by Cooperative Interfacial Graphene Oxide-Polymer Assemblies

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S1: Experimental Section

Materials

Single-layer graphene oxide (GO) nanosheets were purchased from XFNANO Co. Ltd., China. Diaminopropyl-terminated polydimethylsiloxane (NH_2-PDMS-NH_2) with a molecular weight of ~27000 g mol^{-1} was obtained from Macklin Inc., China. Dimethyl silicone oil (DSO, H201-100), hydrochloric acid (HCl, 36-38%), and sodium hydroxide (NaOH) were received from Sinopharm Chemical Reagent Co. Ltd, China. All the chemicals have a purity of no less than 98% and were used as received. Ultrapure water (ρ = 18.25 mΩ·cm) was used to prepare all the sample solutions and gels.

Preparation of the Pickering Emulsion Gels

The attractive water-in-oil Pickering emulsion gels were prepared by directly mixing aqueous dispersions of GO nanosheets and oil solutions of NH_2-PDMS-NH_2 at desired concentrations and pH values under vortexing for about 10 min. Stable Pickering emulsion gels could then be obtained after standing at room temperature within 5 h. Aqueous NaOH and HCl solutions (1 mol L^{-1}) were used to regulate the pH values of GO dispersions. All the gel samples were stored in glass serum bottles sealed with tightly covered parafilms to avoid water evaporation. Their water contents before and after stored for 30 days were 51.0 ± 0.5 wt% and 50.3 ± 0.6 wt%, respectively, demonstrative of no significant water loss.

Characterization

Transmission electron microscopy (TEM, JEM-1011, JEOL, Japan) was used to determine the morphology of GO nanosheets at an acceleration voltage of 100 kV. Optical microscopy (OM, Axioskop, Zeiss, Germany) was used to determine the internal microstructures of a Pickering emulsion gel. Fluorescence microscopy (FM, Axio Scope A1, Zeiss, Germany) was utilized to measure the type of the Pickering emulsion gels. A hydrophilic dye sodium fluorescein (Aladdin Biochemical Technology Co. Ltd., China) was used to stain the dispersed aqueous phase for FM imaging. All the optical and fluorescent micrographs were taken from the same batch of samples after desired days of storage. Field-emission scanning electron microscopy (FE-SEM, JSM-760F, Zeiss, Germany) was employed to characterize the surface topography of a steel substrate after lubricated with different materials or submerged in water for different periods with or without surface coating of the Pickering emulsion gels. All the metal surfaces were directly visualized without deposition of additional conductive materials in advance due to their inherent high conductivity. A zeta potential analyser (ZetaNano ZS90, Malvern, UK) was used to measure the zeta potential values of a GO dispersion at different studied pH values. A thermal conductivity analyser (TPS 2500S, Hot Disk, Sweden) was utilized to measure the thermal conductivity of water, DSO and Pickering emulsion gels with different water volume fractions. The viscoelasticity and thixotropy of the Pickering emulsion gels were measured using a rheometer (MCR-302, Anton Paar, Austria) in 25-mm (in diameter) parallel-plate geometry. No slippage was discovered during the whole measuring process. The testing stress was set to be between 0.1 and 30 Pa, the studying frequency range was from 0.01 to 100 Hz, and the testing strain was between 0.01% and 100%. Freshly prepared gel samples were used in each test. The measuring temperature was set to be 25 ± 1 ºC. The volume of the grease-like gels was controlled by setting the sample gap at constant at 1.0 mm, and the excess gels were trimmed after the final gap height was reached. No solvent trap for the emulsion gels was used in this study.

Interfacial Property Analysis

The interfacial tension of the water/DSO interface after adsorbed with the GO nanosheets, the NH_2-PDMS-NH_2 polymers, and the GO/NH_2-PDMS-NH_2 cooperative assemblies was measured using constrained drop surfacetometry. Constrained drop surfactometry is a new-generation droplet-based tesiometry technique developed by Zuo et al..[1-3] It employs a 3-mm (in diameter) sessile water droplet to accommodate adsorbed polymer and/or nanoparticle films. The droplet is “constrained” on a carefully machined hydrophilic pedestal using its knife-sharp edge to prevent film leakage at low interfacial tensions and is enclosed in a quartz cuvette filled with pure DSO or the oil solutions of NH_2-PDMS-NH_2 to generate a water/oil interface. The interfacial film can be compressed and expanded either quasi-statically or dynamically by precisely controlling liquid flow out of and into the droplet with a motorized syringe. The interfacial tension was determined according to the shape of the aqueous droplet in real-time using closed-loop axisymmetric drop shape analysis (CL-ADSA).[3, 4] Specifically, the shape of sessile droplets is controlled by the mechanical balance between the interfacial tension and local gravity. And the interfacial tension can be determined from the shape of the droplet once gravity is known according to the Laplace equation of capillary $\Delta P = \gamma\left(\frac{1}{R_1}+\frac{1}{R_2}\right) = \frac{2\gamma}{R_0} + \Delta\rho g z$, where ΔP refers to the Laplace pressure, γ is the oil/water interfacial tension, R_1 and R_2 are the two principal curvature radii at the studied point of the interface, R_0 refers to the curvature radius at the apex of the sessile droplet, $\Delta\rho$ is the density difference across the interface, g refers to the local acceleration of gravity, and z is the vertical distance between the apex and the studied point.

The interfacial jamming of the GO/NH_2-PDMS-NH_2 nanoparticle surfactant was studied both using the constrained drop surfactometry and an optical contact angle meter (Attension® Theta Flex, Biolin Scientific, Finland) in pendent drop configurations. The GO-covered solid substrate for contact angle measurements was prepared by depositing high-concentration aqueous GO dispersions onto a glass substrate and then drying at ambient temperature. Such process was repeated for several times until the whole glass surface turned completely black. A commercial multi-functional tensiometer (K100, Krüss, Germany) was employed to study the squeezing and detaching behaviour between aqueous GO droplets in the continuous oil phase. Specifically, two freshly prepared GO droplets (~ 5 μL) were placed at the bottom and suspended on the top of the container, respectively. The bottom droplet then slowly approached and squeezed the top droplet at a rate of 0.01 mm s^{-1}. It started to detach from the top droplet when the repulsive force reached ~-14.7 μN and the weight-displacement curves can be recorded during the process.

Tribological Measurements

A commercial UMT friction and wear tester (UMT-TRIBOLAB, Bruker, Germany) with a reciprocating ball-on-disc configuration using a Si_3N_4 ball (d = 10 mm) and steel substrate (d = 24 mm) or a Si_3N_4 ball (d = 10 mm) and silicone wafer (d = 10 mm) as counterparts was used to determine the tribological performance of the water-in-oil Pickering emulsion gels. Both the ball and substrate were cleaned ultrasonically in petroleum ether and methanol before each measurement. The under-water friction and wear tests were conducted by submerging the measuring ball and substrate in a steel tank filled with water and the substrate was fixed onto the bottom of the tank to avoid any possible slips or movements of the substrate during the measurements. The testing temperature was set to be 25 °C, the applied normal loads were 10-200 N for the Si_3N_4/steel tribopair and 5-80 N for the Si_3N_4/silicone tribopair, respectively, and the sliding velocities were 20-160 mm s^{-1} for both the tribopairs. A 3D surface profilometer (MicroXAM-800, KLA-Tencor, USA) was utilized to measure the resultant wear volume and abrasive scar of a steel substrate after lubricated with different materials. All the tribological measurements were repeated for at least three times to ensure good reproducibility.

Anti-Corrosion Tests

Polished steel blocks with or without coating of a small amount of Pickering emulsion gels were immersed in deionized water at 50 °C for 10 and 72 h, respectively. The testing media were encapsulated in centrifugal tubes sealed with tightly covered parafilms to minimize volatilization. And the centrifugal tubes were placed in a water bath for an accurate temperature control.

An electrochemical workstation (CHI660E, Shanghai Chenhua, China) with a three-electrode configuration was employed to analyse the anti-corrosion performance and mechanism of the Pickering emulsion gels. A steel electrode covered with a small amount of the Pickering emulsion gels with an exposed area of 0.07 cm^2 was used as the working electrode in the electrochemical measurements. A platinum electrode and a saturated calomel electrode were selected as the counter electrode and the reference electrode, respectively. A 3.5 wt% aqueous NaCl solution was used as the testing media. The measuring potential range was set to be between -1.0 and 1.0 V, and the scanning rate was set to be 5 mV s^{-1}. All the working steel electrodes were placed in the testing media for about 1 h to stabilized the open-circuit potential (OCP) before each measurement. The electrochemical impedance spectroscopy (EIS) was obtained in a range between 0.01 and 100 kHz with a potential amplitude of 10 mV at the OCP. Control experiments were performed with bared steel electrodes immersed in the saline and pure DSO, respectively. Each measurement was repeated for at least three times to ensure good reproducibility.

Under-Water Printing of the Pickering Emulsion Gels

Aqueous GO dispersions stained with different dyes were used to prepare colourful Pickering emulsion gel inks for 3D printing. The spiral and snake-shaped patterns were created using a commercially available pressure-driven 3D printer (Bio-Architect® SR, REGENOVO, China) that uses G-code commands to control the trajectories of the print head. The other 2D geometries and 3D structures were obtained by direct extrusion printing of the Pickering emulsion gel inks into water with a syringe.

S2: Supplementary Figures

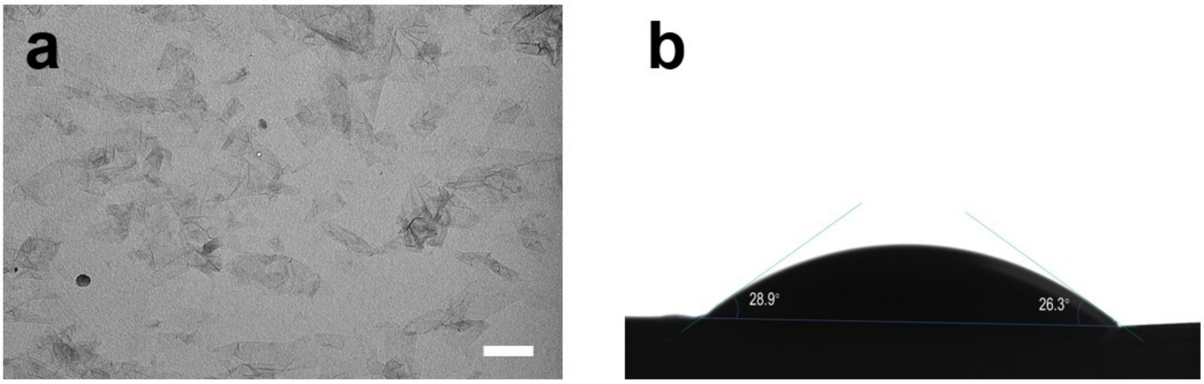

Fig. S1 (a) TEM observation of the GO nanosheets used for assembling Pickering emulsion gels. Scale bar = 1 μm. (b) Contact angle of a pure water droplet deposited onto a GO-covered glass substrate. T = 25 °C.

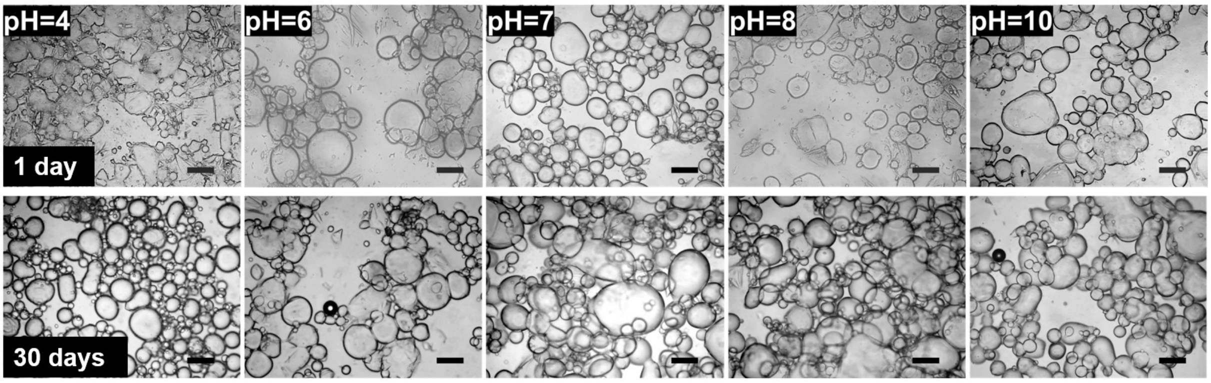

Fig. S2 Optical micrographs of the internal microstructure of the Pickering emulsion gels at different studied pH values. Scale bar = 100 μm. c_{GO} = 0.3 mg mL^{-1}. $c_{NH2\text{-}PDMS\text{-}NH2}$ = 10 mg mL^{-1}. V_W% = 50%. T = 25 °C.

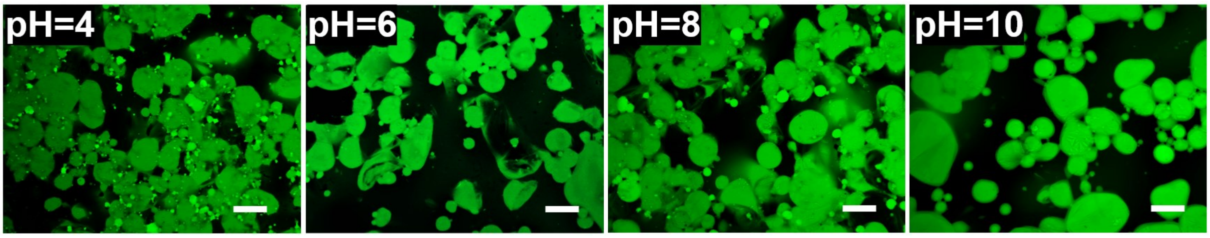

Fig. S3 Fluorescent micrographs of the Pickering emulsion gels stained with a fluorescent dye sodium fluorescein at different pH values. Scale bar = 100 μm. c_{GO} = 0.3 mg mL^{-1}. $c_{NH2\text{-}PDMS\text{-}NH2}$ = 10 mg mL^{-1}. V_W% = 50%. T = 25 °C.

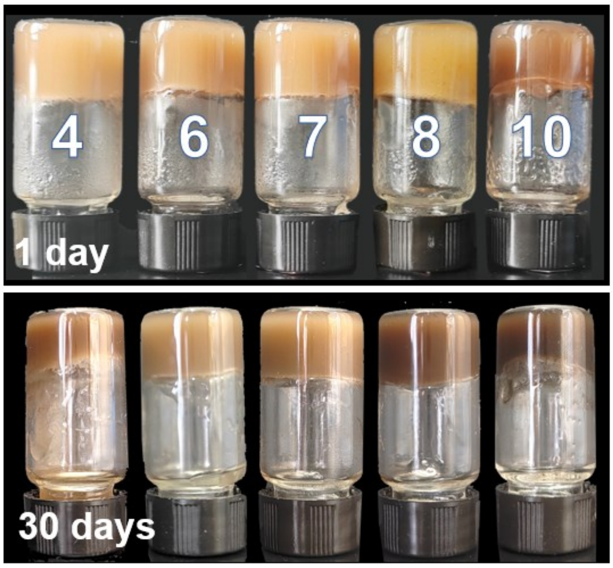

Fig. S4 Photographs of the Pickering emulsion gels at different studied pH values after stored at room temperature for 1 and 30 days. Scale bar = 100 µm. c_{GO} = 0.3 mg mL^{-1}. $c_{NH2\text{-}PDMS\text{-}NH2}$ = 10 mg mL^{-1}. V_W% = 50%.

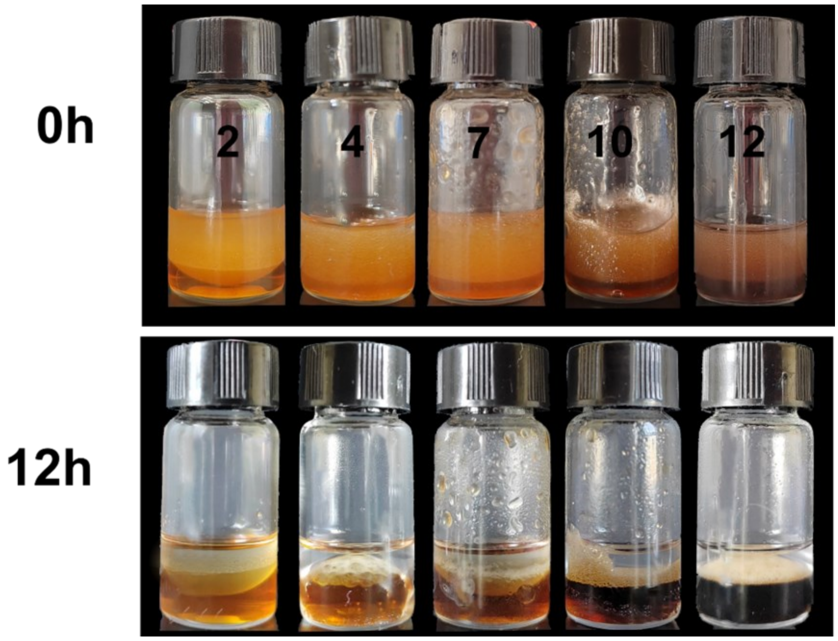

Fig. S5 Photographs of DSO/water mixtures stabilized by GO independently at different pH values at 25 °C. c_{GO} = 0.5 mg mL^{-1}. V_W% = 50%.

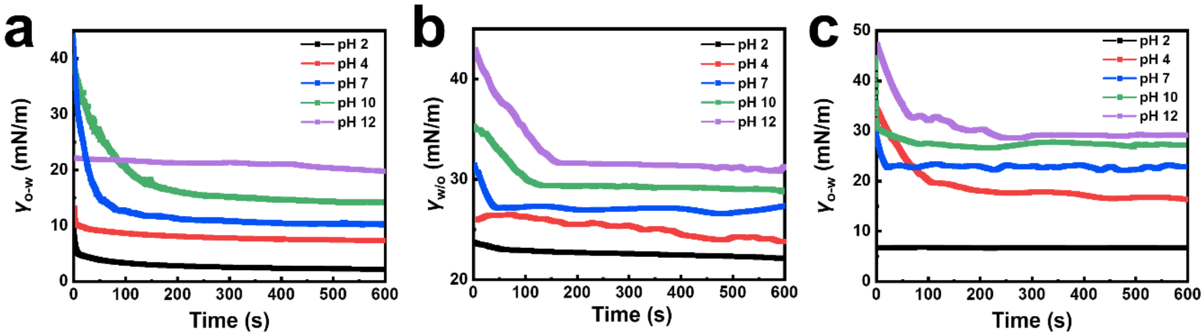

Fig. S6 Equilibrium water/oil interfacial tension of the (a) GO/NH_2-PDMS-NH_2 nanoparticle surfactant, (b) pure GO nanosheets, and (c) pure NH_2-PDMS-NH_2 ligands at different pH values. c_{GO} = 0.3 mg mL^{-1}. $c_{NH2\text{-}PDMS\text{-}NH2}$ = 10 mg mL^{-1}. T = 25 °C.

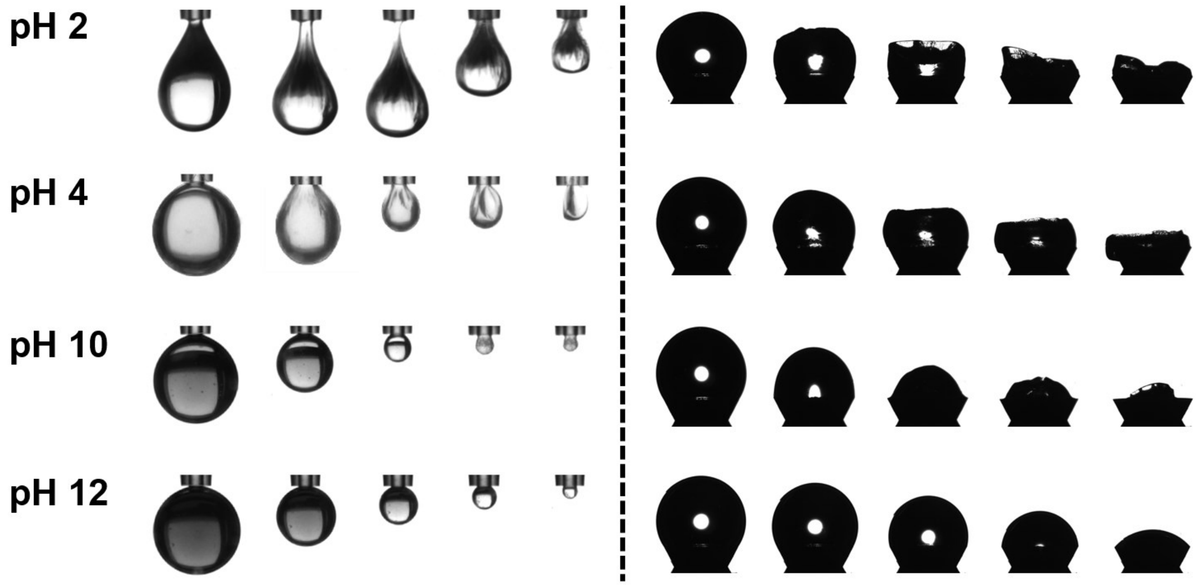

Fig. S7 Snapshots of the aqueous GO droplets immersed in the NH_2-PDMS-NH_2 oil solutions with different pH values upon slowly withdrawing the internal dispersed phase under both pendant drop (left) and constrained sessile drop (right) configurations. c_{GO} = 0.3 mg mL^{-1}. $c_{NH2-PDMS-NH2}$ = 10 mg mL^{-1}. T = 25 °C.

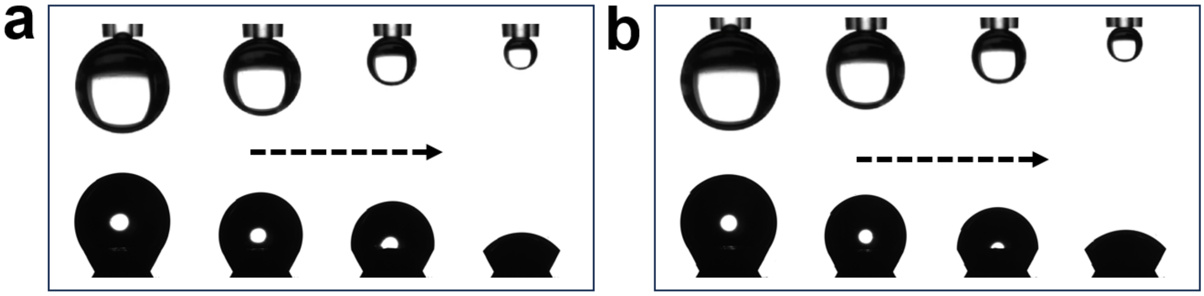

Fig. S8 Snapshots of (a) pure water droplets immersed in the NH_2-PDMS-NH_2 oil solutions and (b) the aqueous GO droplets immersed in pure oil upon slowly withdrawing the internal dispersed phase under both pendant drop (top) and constrained sessile drop (bottom) configurations. c_{GO} = 0.3 mg mL^{-1}. $c_{NH2\text{-}PDMS\text{-}NH2}$ = 10 mg mL^{-1}. pH = 7. T = 25 °C.

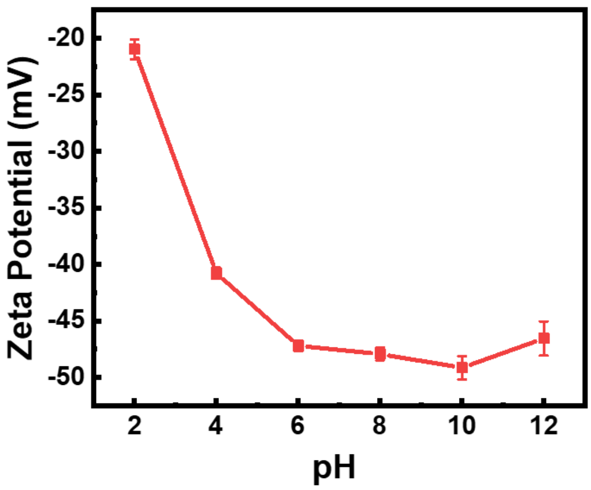

Fig. S9 Variations in the zeta potential values of aqueous GO dispersions as a function of the pH value. c_{GO} = 0.3 mg mL^{-1}. T = 25 °C.

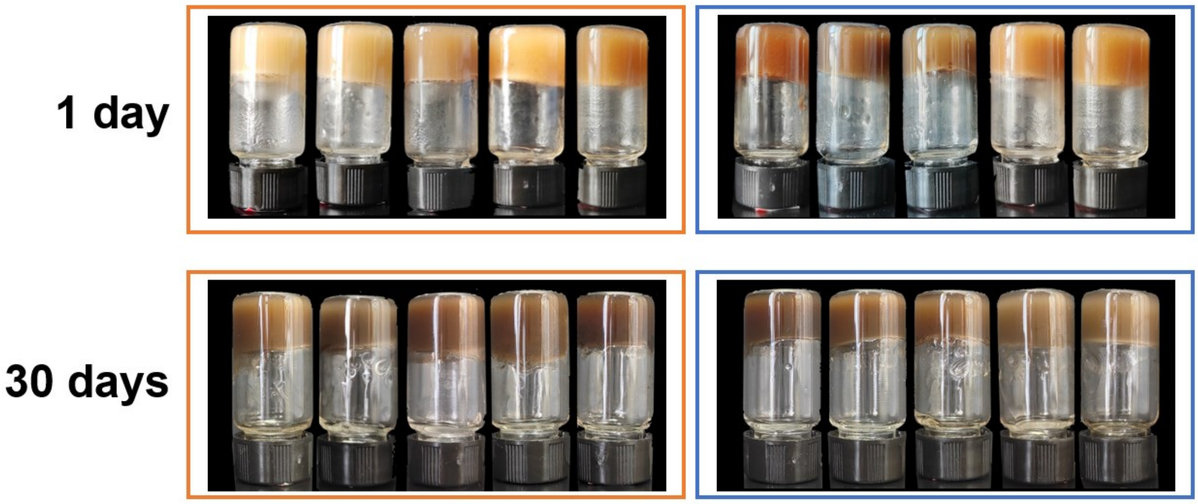

Fig. S10 Photographs of the Pickering emulsion gels shown in Figure 2a after stored at ambient temperature for 1 and 30 days.

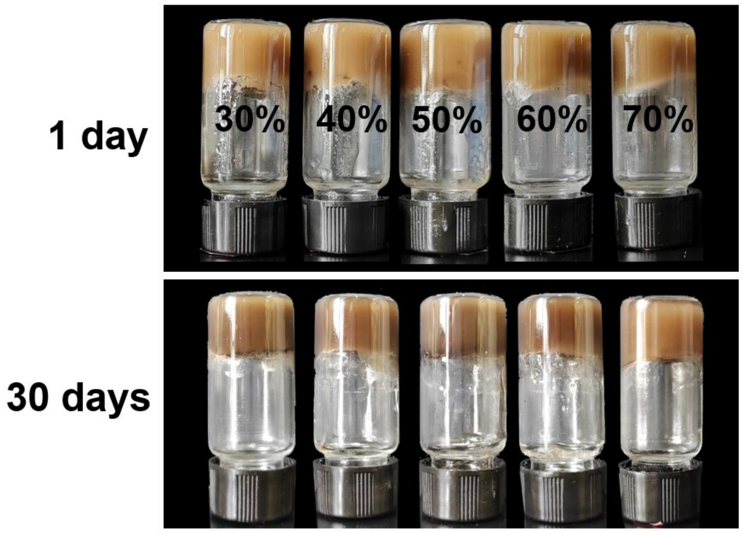

Fig. S11 Photographs of the Pickering emulsion gels prepared with different water volume fractions after stored at room temperature for 1 and 30 days. c_{GO} = 0.3 mg mL^{-1}. $c_{NH2\text{-}PDMS\text{-}NH2}$ = 10 mg mL^{-1}. pH = 7.

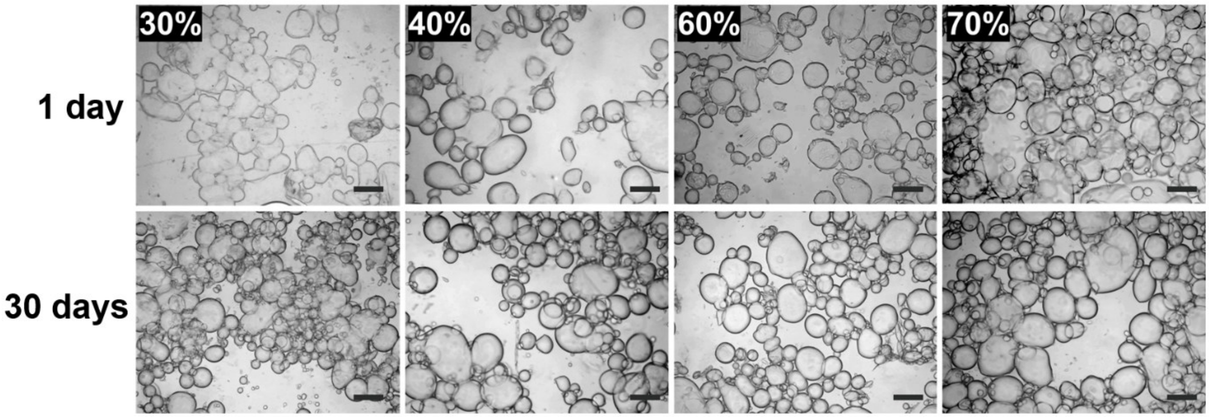

Fig. S12 Optical micrographs of the Pickering emulsion gels prepared with different water volume fractions after stored at ambient temperature for 1 and 30 days. c_{GO} = 0.3 mg mL^{-1}. $c_{NH2\text{-}PDMS\text{-}NH2}$ = 10 mg mL^{-1}. pH = 7.

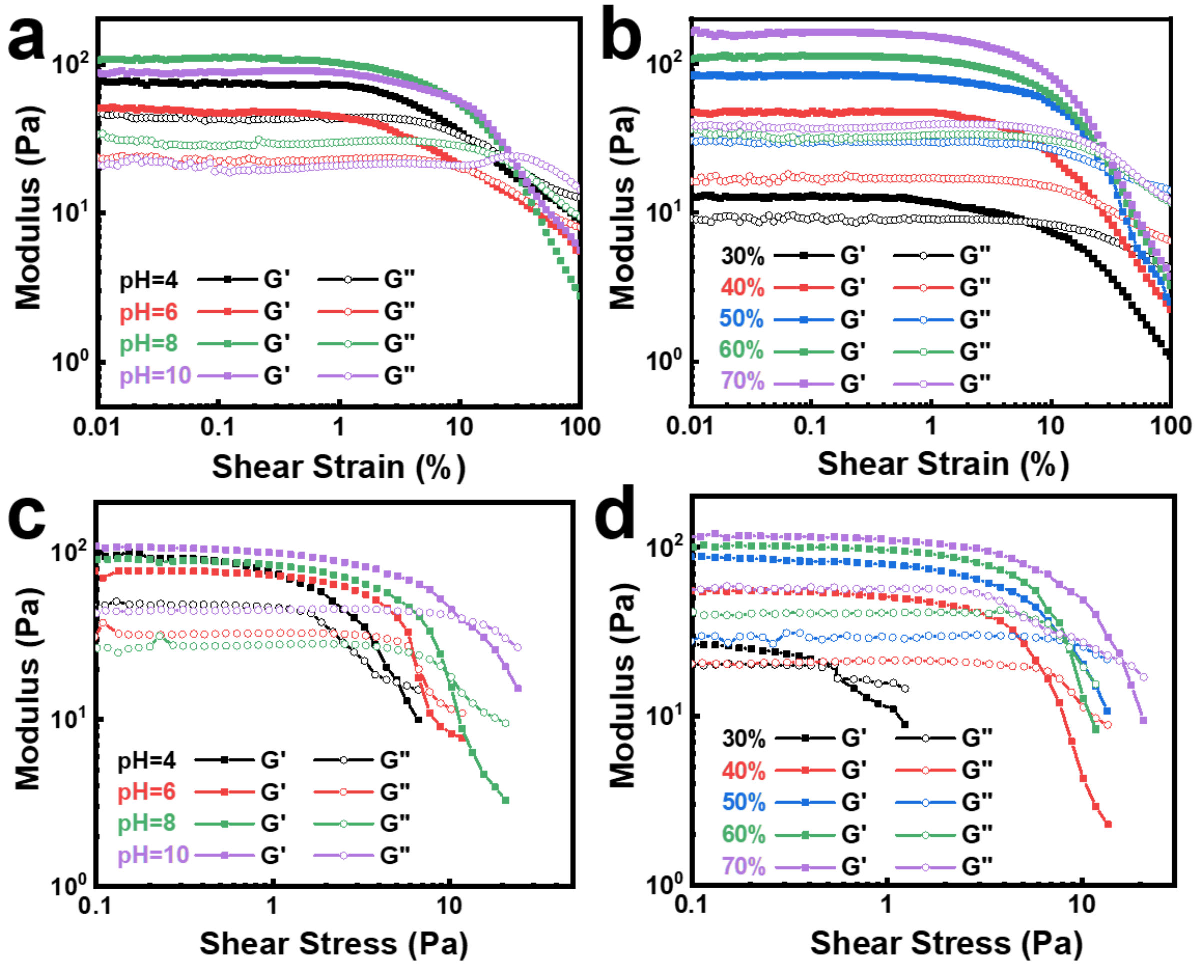

Fig. S13 Strain and stress sweeps of the Pickering emulsion gels at (a, c) different studied pH values and a constant water volume fraction of 50% and (b, d) different water volume fractions and a constant pH value of 7 at 25 ºC. The measuring shear frequency was 1 Hz. c_{GO} = 0.3 mg mL^{-1}. $c_{NH2\text{-}PDMS\text{-}NH2}$ = 10 mg mL^{-1}.

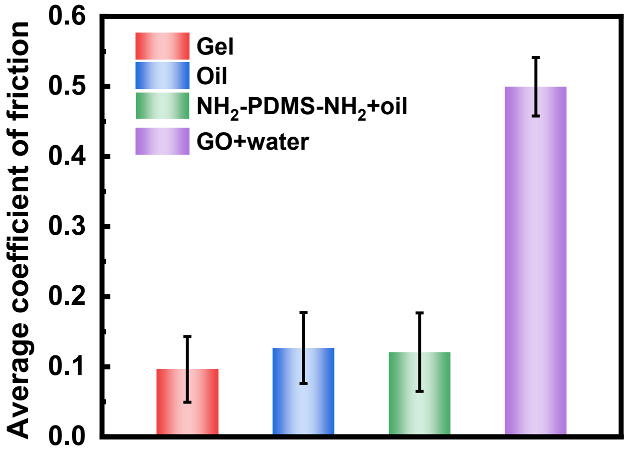

Fig. S14 Average CoF of the Pickering emulsion gel and its different compositions calculated from multiple (n ≥3) reproducible measurements at 30 N and 80 mm s^{-1}. T = 25 °C.

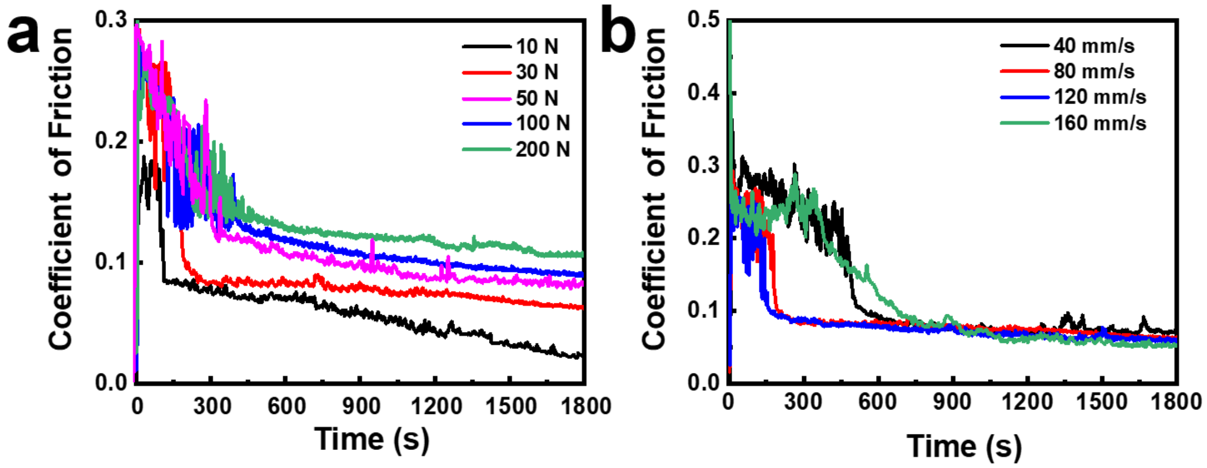

Fig. S15 CoF of the Pickering emulsion gel lubricant at (a) a constant sliding velocity of 80 mm s^{-1} and different applied normal loads and (b) a fixed normal load of 30 N and different sliding velocities at room temperature. c_{GO} = 0.3 mg mL^{-1}. $c_{NH2\text{-}PDMS\text{-}NH2}$ = 10 mg mL^{-1}. V_W% = 50%. pH = 7.

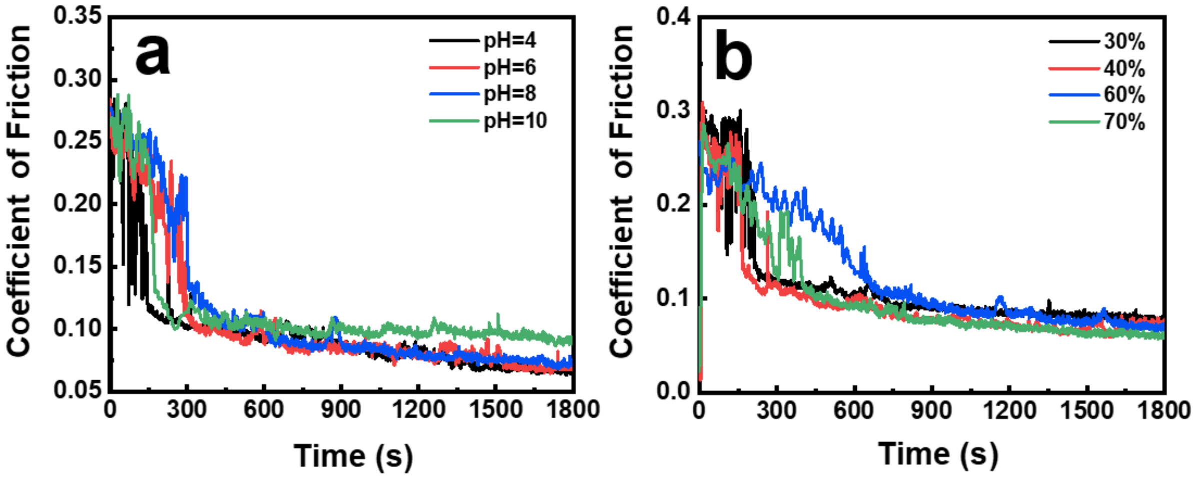

Fig. S16 Effect of the (a) pH value and (b) water volume fraction on the CoF of a Pickering emulsion gel. c_{GO} = 0.3 mg mL^{-1}. $c_{NH2\text{-}PDMS\text{-}NH2}$ = 10 mg mL^{-1}. T = 25 °C.

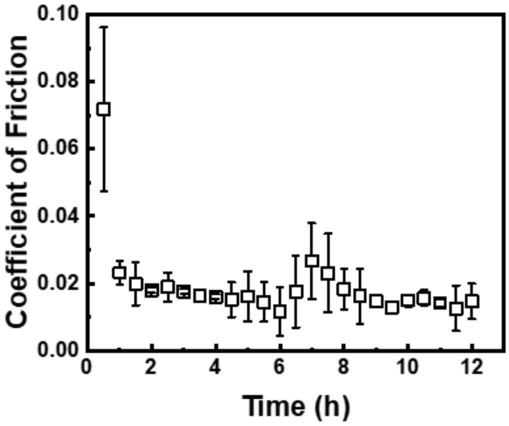

Fig. S17 Variations in the CoF of the Pickering emulsion gel lubricant over time at ambient temperature. c_{GO} = 0.3 mg mL^{-1}. $c_{NH2\text{-}PDMS\text{-}NH2}$ = 10 mg mL^{-1}. V_W% = 50%. pH = 7.

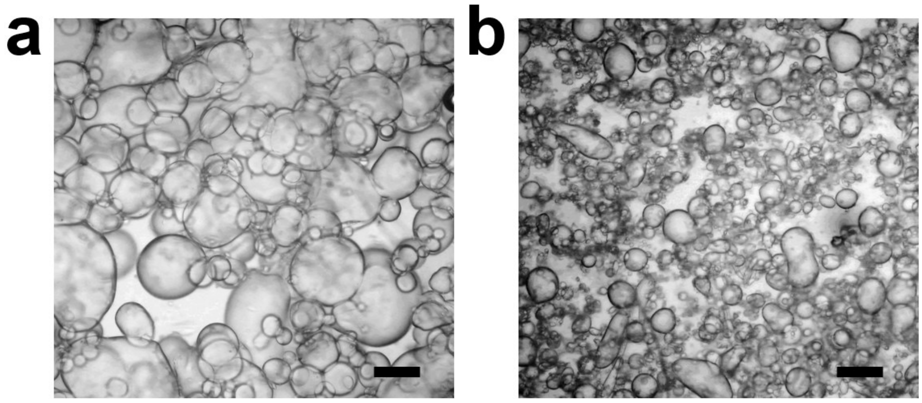

Fig. S18 OM observations on the Pickering emulsion gels (a) before and (b) after the friction tests. Scale bar = 100 μm. T = 25 °C.

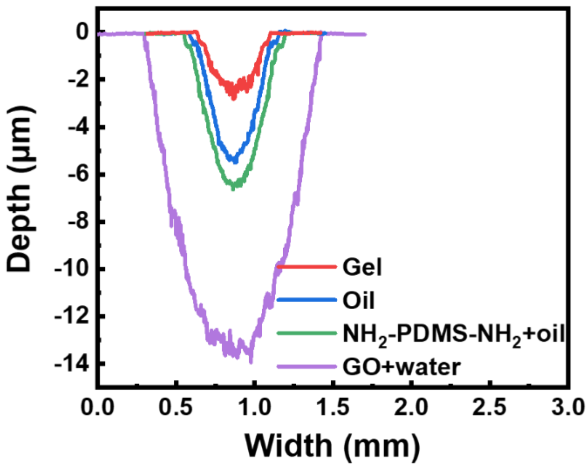

Fig. S19 Width and depth of the wear scar on a steel substrate lubricated with the Pickering emulsion gel and its different compositions. T = 25 °C.

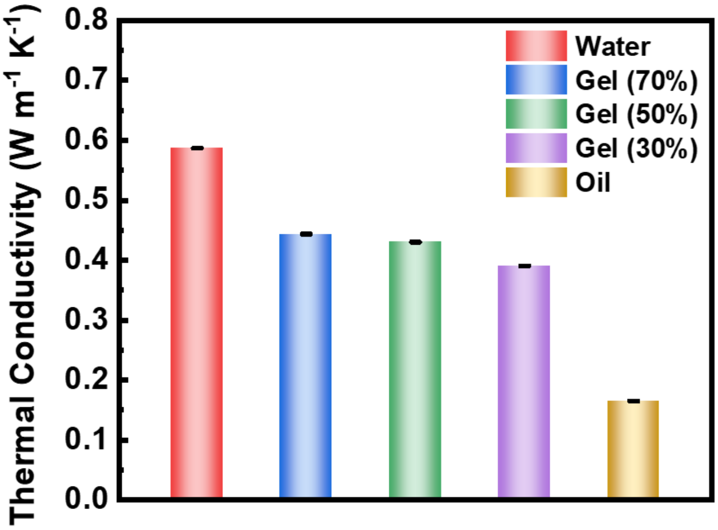

Fig. S20 Thermal conductivity of the deionized water, DSO and Pickering emulsion gels with different water volume fractions at 25 °C. c_{GO} = 0.3 mg mL^{-1}. $c_{NH2\text{-}PDMS\text{-}NH2}$ = 10 mg mL^{-1}. pH = 7.

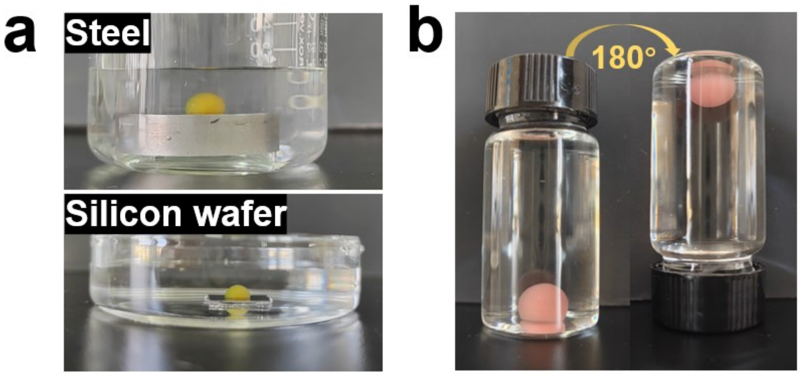

Fig. S21 Photographs of the Pickering emulsion gel lubricants adhering on different substrates. Dyes including sodium fluorescein and methyl red were used to stain the gels for better visualization. c_{GO} = 0.3 mg mL^{-1}. $c_{NH2\text{-}PDMS\text{-}NH2}$ = 10 mg mL^{-1}. V_W% = 50%. pH = 7. T = 25 °C.

Fig. S22 Photographs of a Pickering emulsion gel after adhering on a glass bottle bottom for 90 days. c_{GO} = 0.3 mg mL^{-1}. $c_{NH2\text{-}PDMS\text{-}NH2}$ = 10 mg mL^{-1}. $V_W\%$ = 50%. pH = 7. T = 25 °C.

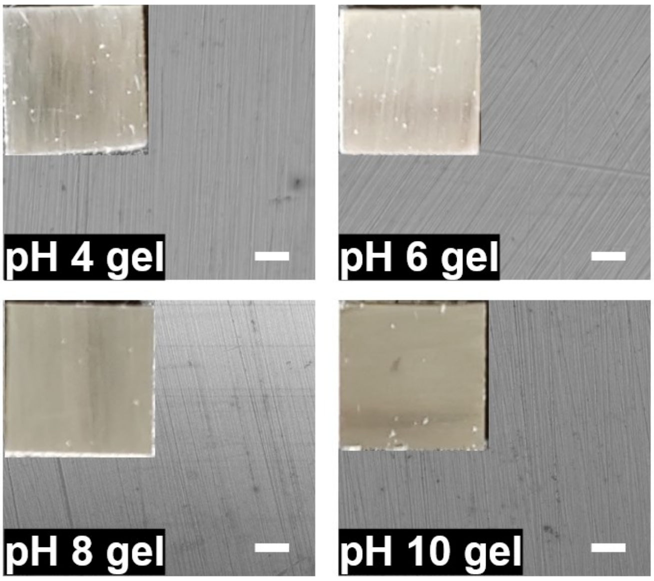

Fig. S23 Photographs and SEM images of the steel blocks pre-coated with a small amount of Pickering emulsion gels after placed in deionized water for 72 h at 50 ºC. Scale bars = 10 μm. c_{GO} = 0.3 mg mL^{-1}. $c_{NH2\text{-}PDMS\text{-}NH2}$ = 10 mg mL^{-1}. V_W% = 50%.

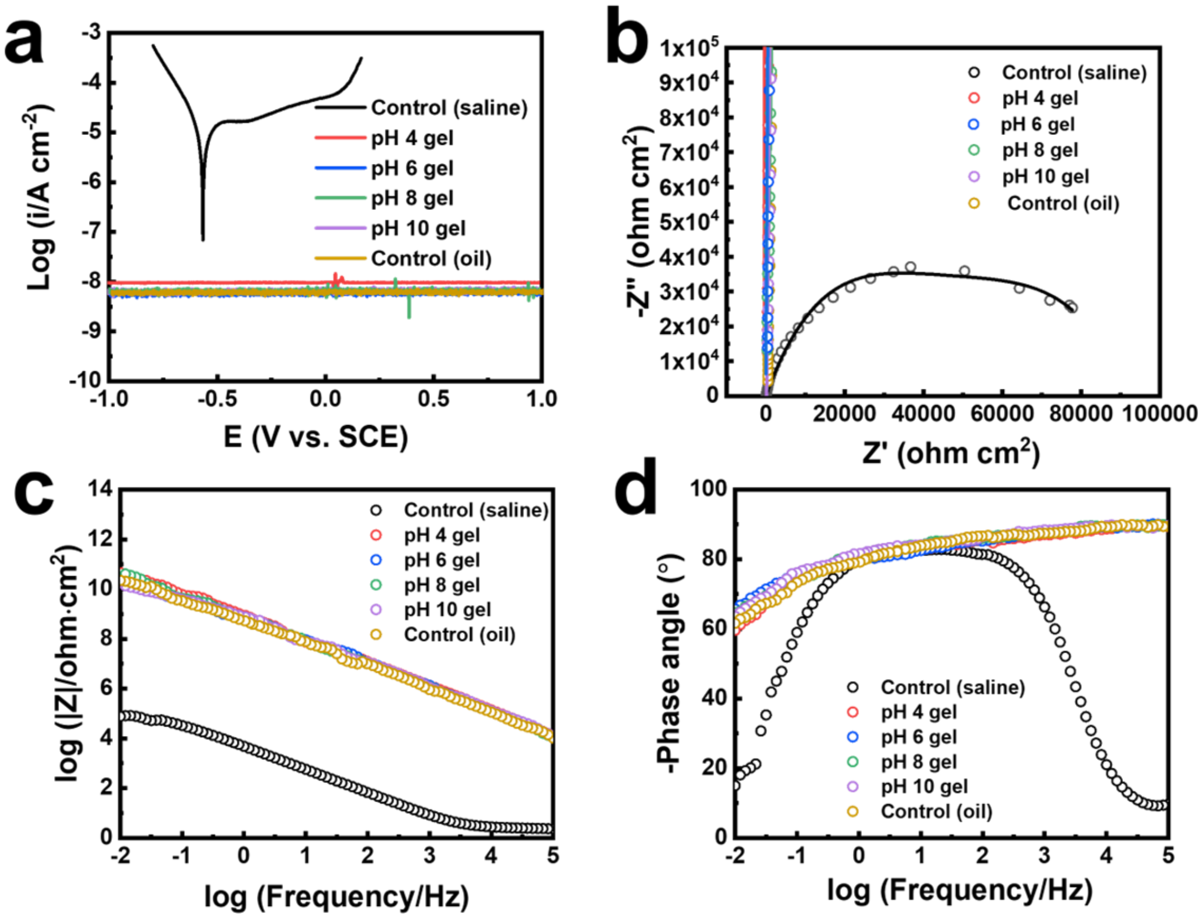

Fig. S24 (a) Polarization curves, (b) Nyquist plots, (c) impedance curves, and (d) the body phase angles of the steel working electrodes upon either directly submerged in 3.5 wt% NaCl solutions and oil or pre-covered with a small amount of the Pickering emulsion gels and then placed in the saline. c_{GO} = 0.3 mg mL^{-1}. $c_{NH2\text{-}PDMS\text{-}NH2}$ = 10 mg mL^{-1}. V_W% = 50%. T = 25 °C.

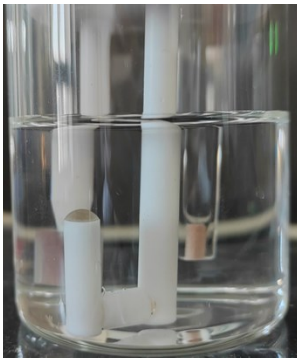

Fig. S25 Photograph of a gel-covered steel working electrode submerged in saline at 25 °C.

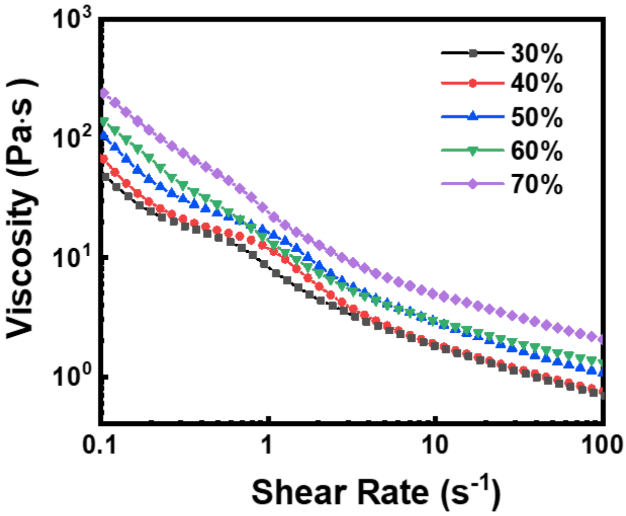

Fig. S26 Variations in the shear viscosity of the Pickering emulsion gels with different water volume fractions as a function of external shear rate. c_{GO} = 0.3 mg mL^{-1}. $c_{NH2\text{-}PDMS\text{-}NH2}$ = 10 mg mL^{-1}. pH = 7. T = 25 ºC.

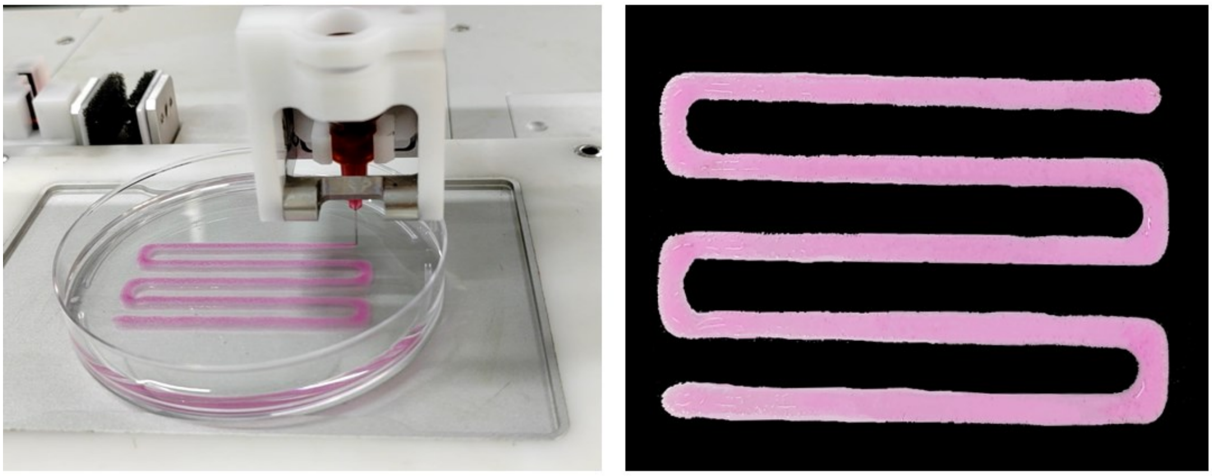

Fig. S27 Photographs of under-water 3D printing of the Pickering emulsion gels and the resultant snake-shaped pattern. c_{GO} = 0.3 mg mL^{-1}. $c_{NH2\text{-}PDMS\text{-}NH2}$ = 10 mg mL^{-1}. $V_W\%$ = 50%. pH = 7. T = 25 °C.

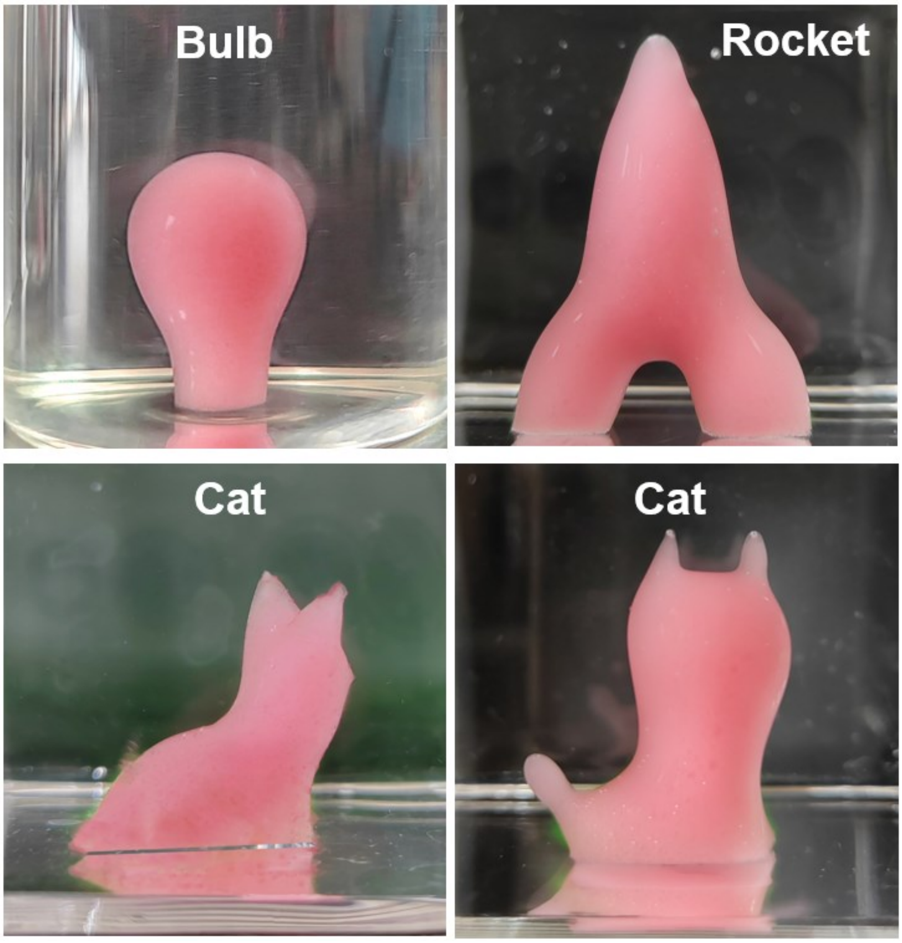

Fig. S28 Printed different 3D structures from direct extrusion of the Pickering emulsion gels into water. c_{GO} = 0.3 mg mL^{-1}. $c_{NH2\text{-}PDMS\text{-}NH2}$ = 10 mg mL^{-1}. V_W% = 50%. pH = 7. T = 25 °C.

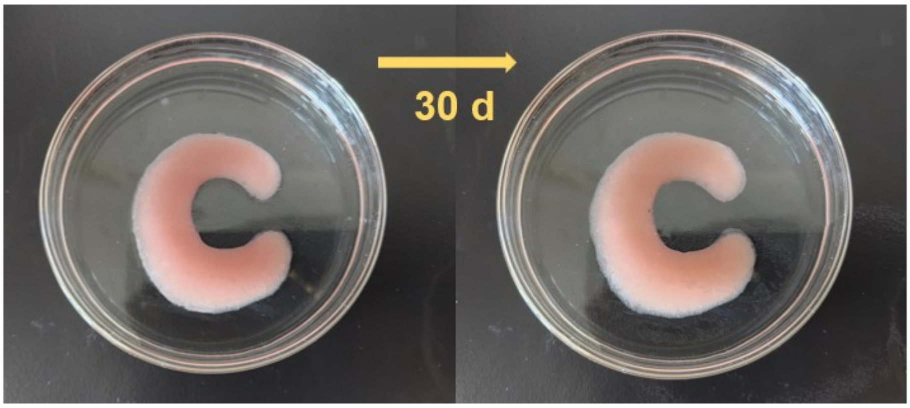

Fig. S29 Printed letter "C" after submerged in water for continuous 30 days at 25 °C.

Movie S1. Squeezing and detaching process of two aqueous GO droplets enclosed in an NH_2-PDMS-NH_2 oil solution.

Movie S2. Under-water printing of the Pickering emulsion gel inks into a 2D spiral pattern.

Movie S3. Under-water printing of the Pickering emulsion gels into a 3D configuration.

References

S1. R. P. Valle, T. Wu and Y. Y. Zuo, *ACS Nano*, 2015, **9**, 5413-5421.
S2. G. Li, X. Xu and Y. Y. Zuo, *J. Colloid Interface Sci.*, 2023, **630**, 21-27.
S3. J. Yang, K. Yu and Y. Y. Zuo, *Langmuir*, 2017, **33**, 8914-8923.
S4. K. Yu, J. Yang and Y. Y. Zuo, *Langmuir*, 2016, **32**, 4820-4826.