Supporting Information

Structured Droplets Dominated by Interfacial Self-Assembly of Topology-Tunable Janus Particles towards Macroscopic Materials

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Experimental Section

Materials: Poly(vinyl alcohol) (PVA) was purchased from Acros Or-ganics. Decane (98%) was purchased from Shanghai Macklin Biochemical Co., Ltd. Gellan Gum was purchased from Sigma-Aldrich. PDMS Sylgard 184 was purchased from Dow Corning. All other reagents were purchased from J&K Scientific Ltd. Deionized water was used.

Fabrication of topology-tunable Janus particles: Bread-shaped, hemisphere-shaped and crescent-shaped Janus particles were precisely synthesized by emulsion interfacial polymerization.[1,2] Generally, 0.2 g polystyrene seeds (~ 1.2 μm) was dispersed in 20 mL aqueous sodium dodecyl sulfate solution (SDS, 0.25% w/v) under ultrasound. Then, a certain volume of 1-chlorodecane (CD) was add to 10 mL aqueous SDS solution, and they were emulsified to form CD-in-water emulsion. The CD-in-water emulsion was mixed with polystyrene seed solution at 40 °C for 20 h under stirring. Subsequently, the monomers (1.5 mL styrene, 1.0 mL divinyl benzene, 0.5 mL acrylic acid) and 40 mg 2,2′-azoisobutyronitrile were dispersed in 10 mL aqueous SDS solution, and they were emulsified to form monomer emulsion. The monomer emulsion was added to the seed solution and their mixture was stirred at 40 °C for 6 h. At last, 5 mL aqueous PVA solution (1% w/v) was added to the afore-mentioned mixture. After de-oxygenation, the polymerization was finished for 14 h at 70 °C. Noteworthily, bread-shaped, hemisphere-shaped and crescent-shaped Janus particles were prepared by using 5 μL, 20 μL, 100 μL CD agent, respectively. These Janus particles were repeatedly centrifuged and dispersed in ethanol or water more than four times for further use.

Interfacial self-assembly of Janus particles: Janus particle topology-manipulated interfacial self-assembly was observed by DataPhysics OCA20 (DataPhysics Company, Germany)

based on interfacial dilatational rheological measurement. 10 mg Janus particles were first uniformly dispersed in 2 mL deionized water under ultrasound. Then, a water-oil interface was created by injecting a pendent drop (8 μL) of Janus particle solution into decane phase at 30 °C. Volume and surface area of the pendent drop were monitored over time by a charge-coupled device (CCD) camera, which were programed into a sinusoidal variation at a chosen amplitude (5%) and frequency (0.01 Hz) by using a computer-controlled dosing system. Interfacial tension and dilatational modulus during self-assembly of Janus particles were analyzed by software employing the Laplace equation.

Interfacial adsorption behaviors of Janus particles: Interfacial adsorption behaviors of Janus particles at the oil-water interface were performed by a reported gel trapping technique.[2] In brief, a certain amount of decane was layered on the top of aqueous gellan solution (20 mg/mL) at 50 °C. A mixture of 250 μL Janus particle solution (1 mg/mL) and 250 μL 2-propanol was injected close to decane-water interface and kept for 6 h at 50 °C. Then, they were cooled to allow gellan gel to solidify at room temperature. Finally, Janus particles at the oil-water interface were transferred into solidified PDMS gel and washed in hot water.

Fabrication of macroscopic materials: In a typical synthesis, 1.5 mL St containing 40 mg 2,2′-azoisobutyronitrile was added into 40 mL aqueous solution of Janus particles (5 mg/mL) at 1000 rpm for 30 min to allow the fabrication of Janus particles-dominated structural droplets. After which, the droplets were polymerized at 70 °C for 4 h to fabricate macroscopic particles. After polymerization, these Janus particles could be recycled by treating the macroscopic particle solutions with ultrasound. In addition, magnetic macroscopic particles or fluorescent macroscopic

particles were controllably fabricated by only introducing the magnetic Fe_3O_4 nanoparticles or quantum dots in styrene monomer solutions.

Characterizations: The topologies of Janus particles and their adsorption behaviors at the oil-water interface were observed by a scanning electron microscopy (SEM, SU8010, Japan). The morphologies of pendent drops were acquired by a Dataphysics OCA20 with a CCD camera. Collision process between two droplets was recorded by a high-speed camera (i-SPEED 3, Olympus). Digital camera images were acquired by a digital camera (Canon EDS-60D, Japan). Microscope images were acquired by an optical microscope (Nikon Ti-E, Japan). Zeta potential was analyzed by a Zetasizer Nano ZS (Zen3600, UK).

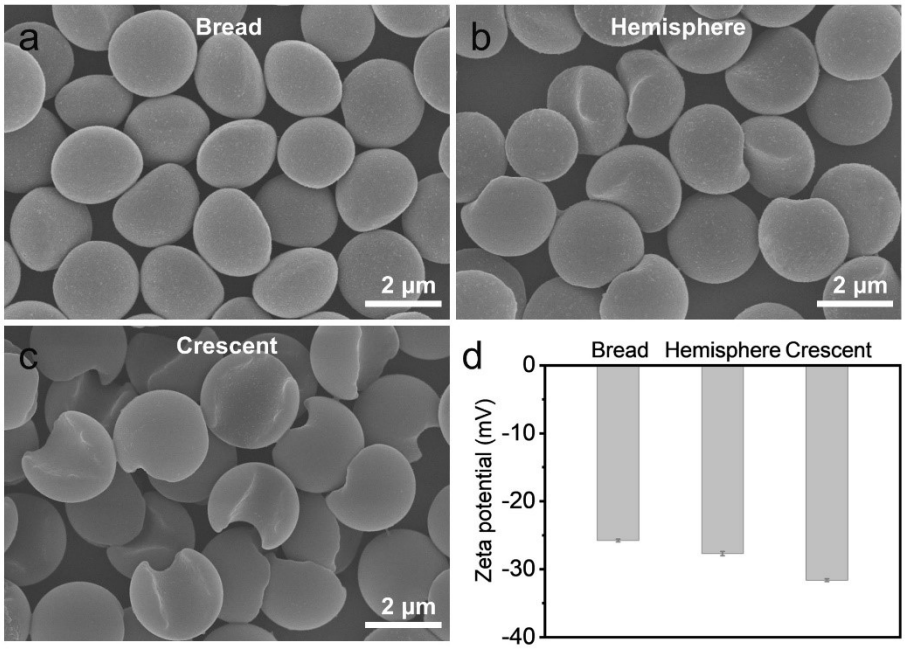

Fig. S1 The characterizations of Janus particles. (a-c) SEM images of Janus particles. (d) Zeta potential of Janus particles (1 mg/mL) dispersed in deionized water.

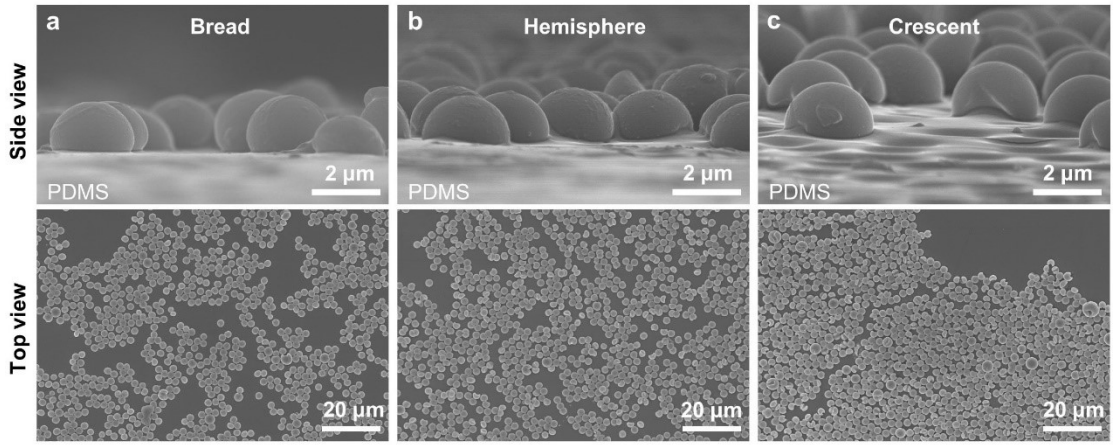

Fig. S2 Janus particle topology-manipulated interfacial adsorption behaviors. SEM images of (a) bread-shaped Janus particles, (b) hemispherical-shaped Janus particles and (c) crescent-shaped Janus particles at the decane-water interfaces.

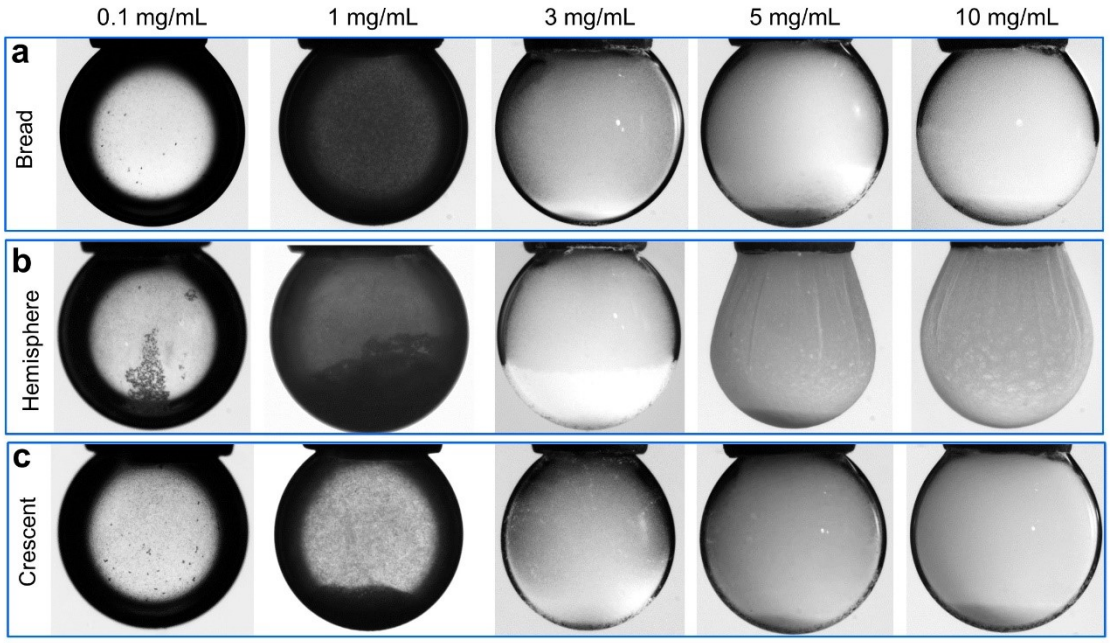

Fig. S3 Concentration-dependent interfacial self-assembly of Janus particles.

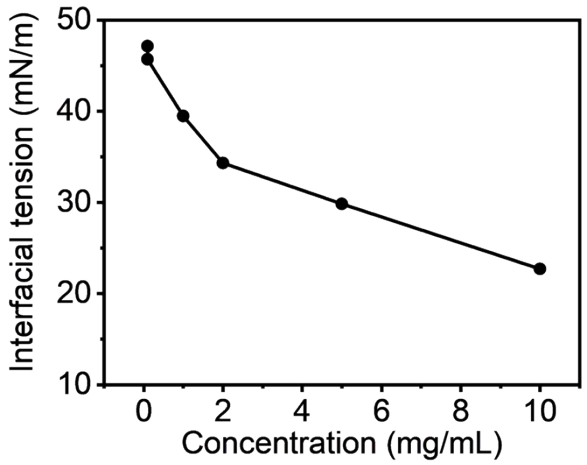

Fig. S4 The interfacial tension was gradually reduced with the increase of concentrations of Janus particles.

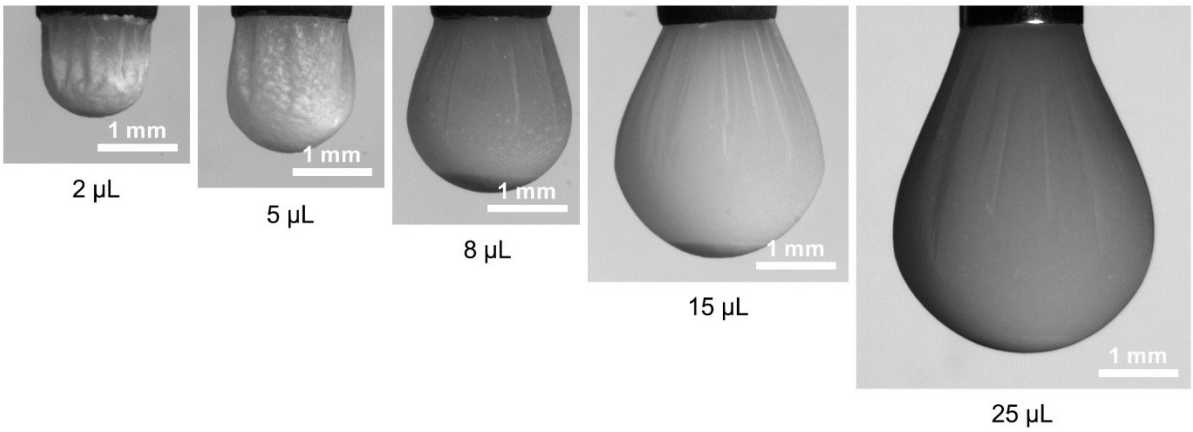

Fig. S5 Tunability of solid-like membranes. The solid-like membranes could also be successfully fabricated when the volumes of water droplets were increased from 2 μL to 25 μL.

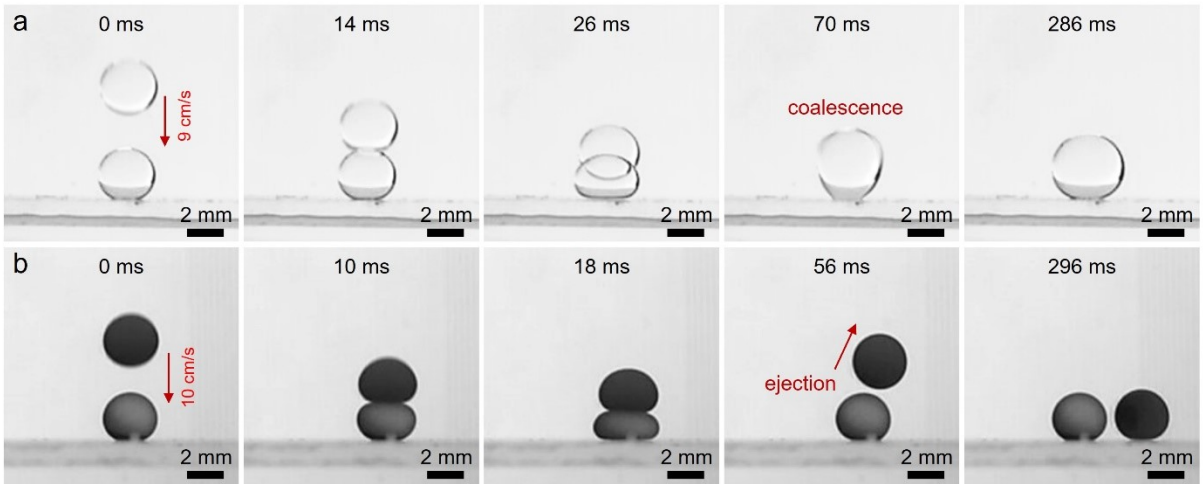

Fig. S6 Snapshots of collision process between two droplets under oil. (a) A pure water droplet collided a pure water droplet, and they were coalesced together. (b) One Janus particles-dominated structural droplet collided the other Janus particles-dominated structural droplet, and was ejected from the surface.

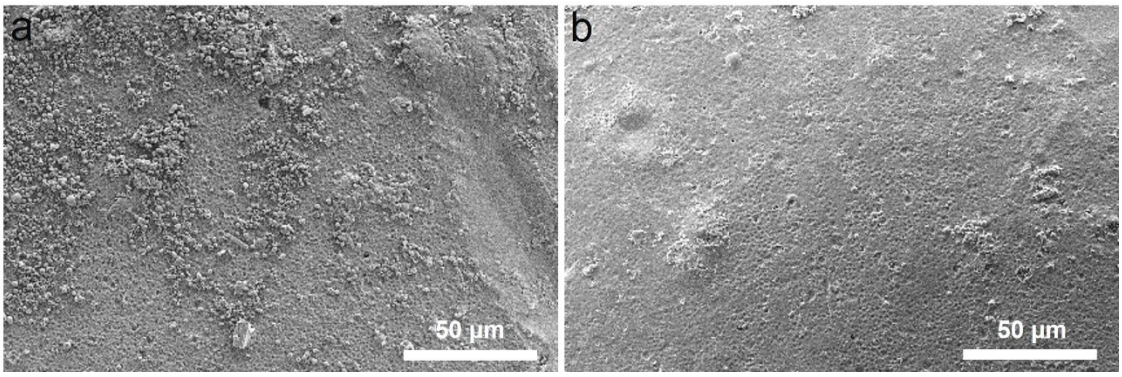

Fig. S7 SEM images of the surfaces of macroscopic particle materials. (a) The surface of macroscopic particle materials before removing Janus particles. (b) The surface of macroscopic particle materials after removing Janus particles.

Supporting Movies

Movie S1: A water droplet (8 μL) containing Janus particles (5 mg/mL) was immerged into decane, and then was periodically expanded and compressed under the frequency of 0.5 Hz to allow the self-assembly of Janus particles.

Movie S2: The structural droplet with solid-like membrane could largely bend or wrinkle when extracting the liquid, and it enabled to stretch back to the origin after reinjecting reversibly the liquid.

Reference

1 J. B. Fan, Y. Song, H. Liu, Z. Lu, F. Zhang, H. Liu, J. Meng, L. Gu, S. Wang and L. Jiang, *Sci. Adv.*, 2017, **3**, e1603203.

2 W. Zhai, Y. Song, Z. Gao, J. B. Fan and S. Wang, *Macromolecules*, 2019, **52**, 3237-3243.