Supporting information

Stabilization of high internal phase Pickering emulsions with millimeter-scale droplets using silica particles

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Synthesis of silica particles with varying a concentration of CTAB

The synthesis of anisotropic silica particle aggregates was conducted via a micelle-template method.[1] Specifically, 0.79 mol of ethanol, 1.66 mol of water, and 0.0002, 0.0004, 0.0006, and 0.0008 mol of CTAB were added to an Erlenmeyer flask, stirred at 300 rpm for 5 minutes, and then 10 ml of 1.25 wt% ammonia solution was added. The solution was stirred at 300 rpm for 5 minutes, and then 0.07v/v% of TEOS was added lastly. The reaction was carried out at room temperature for 3 hours. The synthesized particles were washed 4 to 5 times with water and ethanol, and then dried in the oven at 70°C for 24 hours.

When the amount of CTAB added during particle synthesis increases, the degree of particle aggregation, which is closely related to the stability of Pickering HIPEs, also increases, as shown in Fig. S1. Here, particle images were taken using SEM (JSM-7500F) operating at 10.0 kV accelerating voltage. In particular, the particle aggregations appear as branched structures and tend to elongate predominantly in one direction, resulting in more pronounced anisotropic shape as the aggregation becomes larger.
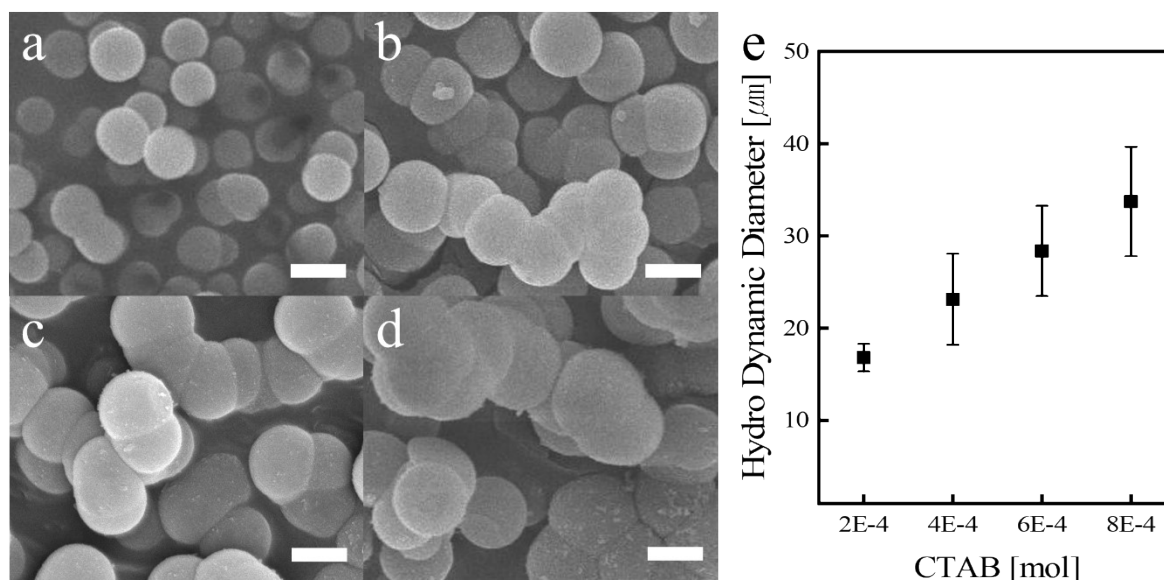

Fig. S1 SEM images showing silica particles prepared with varying amounts of CTAB in the particle synthesis process. (a) SEM image of silica particles prepared with 0.0002 mol of CTAB. The volume-averaged hydrodynamic diameter is 16.8±1.5 μm. (b) SEM image of silica particles prepared with 0.0004 mol of CTAB. The volume-averaged hydrodynamic diameter is 23.1±4.9 μm. (c) SEM image of silica particles prepared with 0.0006 mol of CTAB. The volume-averaged hydrodynamic diameter is 29.4±4.9 μm. (d) SEM image of silica particles prepared with 0.0008 mol of CTAB. The volume-averaged hydrodynamic diameter is 33.7±5.9 μm. (e) The graph of the volume-averaged hydrodynamic

diameter, measured by DLS versus the amount of CTAB. Scale bar: 1 μm.

Effect of pH on stability and droplet size of pickering HIPE

We emulsified the HIPE system while varying the pH of the continuous phase from 3.3 to 11.3 at a fixed particle concentration of 4 wt% and a fixed oil volume fraction of 0.85. In the manuscript, the particles were dispersed in deionized water, and the pH was measured to be 7.2. We adjusted the pH of the emulsion system to 3.3 and 5.2 by mixing 2ml of acetic acid with 10 mL of deionized water and by mixing 2 mL of acetic acid with 1 L of deionized water, respectively. In addition, we set pH to 9.3 and 11.3 using sodium hydroxide. Here, the aqueous sodium hydroxide solution was first prepared by adding 0.4 g of sodium hydroxide to 100 mL of deionized water. At pH-9.3, the continuous phase is given by mixing 0.02 mL of aqueous sodium hydroxide solution with 1 L of deionized water. At pH-11.3, the continuous phase was given by an aqueous solution of 0.2 mL of aqueous sodium hydroxide solution with 10 mL of deionized water.

As shown in Fig. S2a, the stable HIPE could be achieved when the emulsification was conducted at pH 3.3, but the size of the droplets was much smaller than that of the original case at pH 7.2. At this low pH, deprotonation of the silanol groups present on the particle surface is difficult, making the particles less hydrophilic. Less hydrophilic particles are easily adsorbed at the interface, resulting in smaller droplets primarily. In contrast, at a high pH value of 11.3, HIPE was not stabilized at all. This possibly occurs due to the high surface charge on the particle surface, which makes it difficult for the particles to adsorb to the interface, leading to HIPE destabilization. When emulsions were emulsified with a particle dispersion of pH 5.2 and pH 9.3, Fig. S2b and d, the droplets seemed to be almost identical in size compared to the emulsion stabilized with a particle dispersion of pH 7.2.
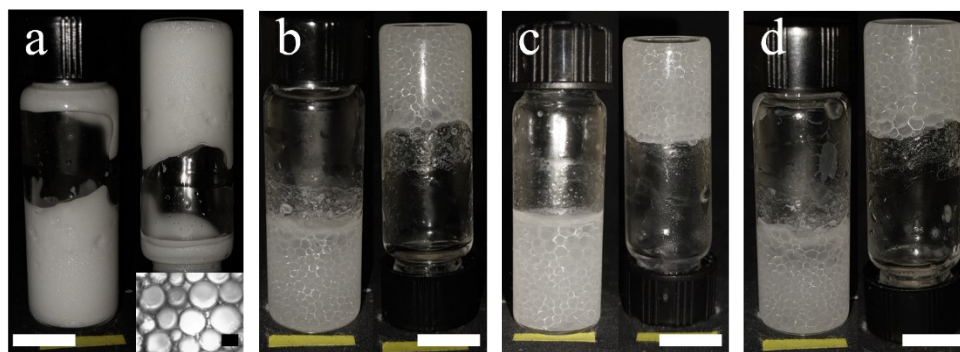

Fig. S2 Macroscopic Images of emulsions prepared at various pHs. All HIPEs were stabilized with 85 vol% of oil and 4wt% of particle concentration. (a) Macroscopic image of the emulsion stabilized at pH 3.3. An average diameter of droplets is reported to be 11.3±2.0 μm. Inset: Optical microscopic image of the HIPE with a scale bar of 10 μm. (b-d) Macroscopic images of the emulsions stabilized at pH 5.2 (b), pH 7.2 (c) and pH 9.3 (d), respectively. The average diameters of the droplets are reported as 1332.1±145.4 μm (b), 1331.6±193.7 μm (c), and 1363.2±179.4 μm (d). Scale bar: 1 cm.

Observation of multi-layered structures of silica particles

To observe the multi-layered structure formed during the compression process of silica particles, we first transfer the structure from the air-water interface to a silicon wafer which are immersed in water prior to the compression by gently sucking water to lower the water level. All processes were conducted at room temperature (~22°C). The particle structures reside on the silicon wafer was then imaged using SEM (JSM-7500F) operating at 10.0 kV accelerating voltage. As shown in Fig. S3, the multilayered structures of the silica particles are clearly observed. Specifically, Fig. S3a and b indicate that dark lines in the optical microscope images (Fig. 2b) actually correspond to multiple layers of overlapping particles. In addition, multilayer structures can be easily identified by the difference in height between the top of the particle layers and the empty bottom, as indicated in Fig S3c and d.
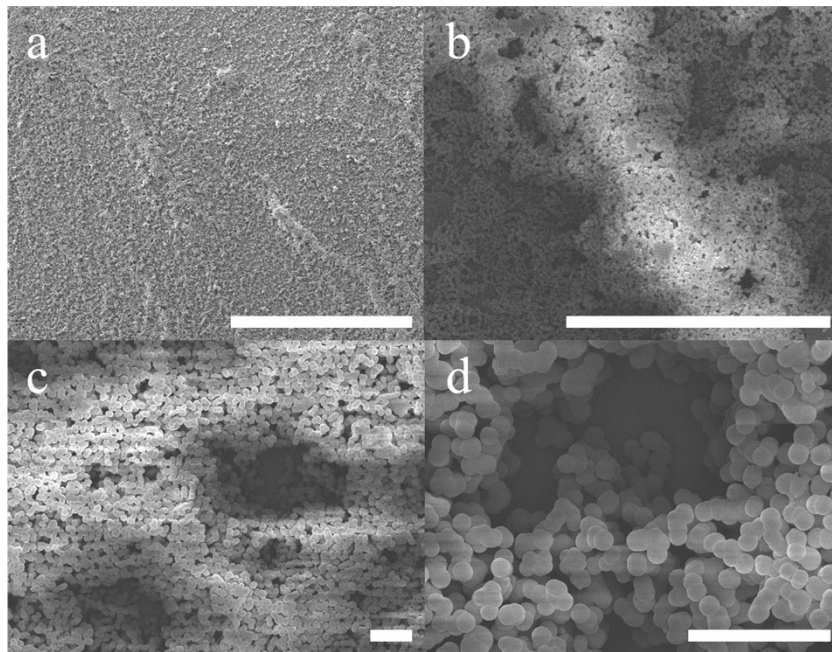

Fig. S3 SEM Images of the layered structure of particles that is transferred from the air-water interface to the silicon wafer with 4 different magnifications (a) Scale bar: 1 mm. (b) Scale bar: 1 mm. (c) Scale bar: 10 μm. (d) Scale bar: 10 μm.

Behavior of common silica particles at the air-water interface

We conducted the experiment for obtaining the isotherm of 621 nm-silica particles to which CTAB was not added during particle synthesis. Experimental details are as follows. First, spherical silica particle dispersion in ethanol with 10 wt% was spread with a micro-syringe onto the air-water interface, with a volume of 50 μl. After waiting for 30 minutes to achieve complete solvent evaporation, the compression process with a barrier speed of approximately 30 cm^2 was initiated. During image capture, we stopped compression for 10 seconds and then resumed it. All measurements were conducted at room temperature (~22°C).

As a result, unlike the isotherm result from the shape anisotropic silica particle aggregates, the compression only resulted in a surface pressure value of 0 mN/m due to the hydrophilic nature of pure silica particles, as indicated in Fig. S4.
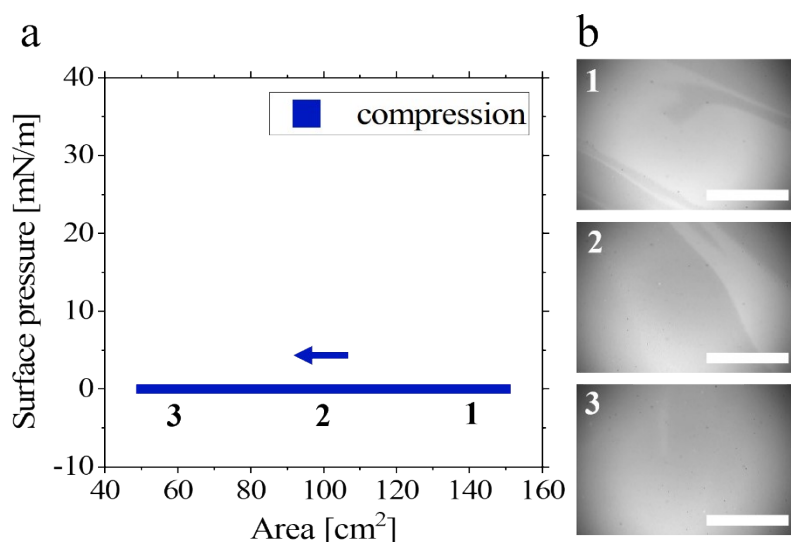

Fig. S4 (a) The area-surface pressure isotherm of pure silica particles during the compression (blue symbols). When the compression is performed, the surface pressure value is measured as a fixed value of 0 mN/m. (b) Microscopic image of the interfacial structure of particles during the compression. No closely packed particle structures are observed even at the lower interfacial area. Scale bar: 100 μm.

CLSM images of the particles at the interface

To investigate the particle structures at the interface in detail, a confocal laser scanning microscope (CLSM, LSM 800 BIO, Carl Zeiss) was used with a 561nm-Laser (10mW). Here, Sudan Red dye whose emission wave length is 615 nm when excited at 560 nm, was utilized, and the dye was dissolved in the oil phase at a concentration of 0.026 wt%. Interestingly, the dye molecules appeared to adhere well to the particle surface, making it easy to observe the adsorbed particles on the droplets using CLSM. The Pickering HIPE with an oil fraction of 75 vol%, was stabilized with a particle concentration of 4 wt%.

When observing cross-sections of the droplets, a red-colored thin layer was apparently observed at the interface (Fig. S5a), strongly indicating that the silica particle aggregates are closely packed at the interface. This is further supported by the CLSM images of the particles at the droplet surface, as shown in Fig. S5c. Furthermore, in the more magnified CLSM image (Fig. S5b), it was also observed that relatively thick particle domains are occasionally present, which agrees well with the observations in the optical microscopic images shown in the manuscript.
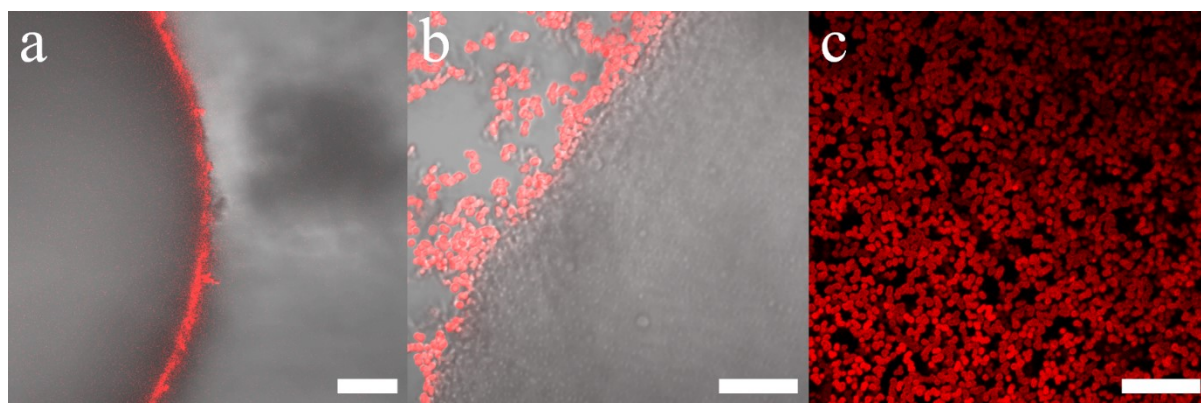

Fig. S5 Microscopic images of emulsion droplets, taken by CLSM. (a) A cross-sectional image shows the presence of particles at the oil-water interface, taken using a 10x lens. The scale bar is 50 μm. (b) A cross-sectional image taken using a 63x lens shows the presence of particles at the interface. The scale bar is 20 μm. (c) A CLSM image taken using a 63x lens shows the closely packed particle layer at the particle surface. The scale bar is 20 μm.

Emulsion stabilized with the dispersed phase with low volume fractions

We conducted an emulsification experiment under the condition that the volume fraction of oil was less than 75%. First, at a fixed particle concentration of 4 wt%, we formed emulsions with oil fractions of 30 vol% and 60 vol%. As a result, quite small droplets were mainly observed, with average sizes of 130.9 μm and 402.1 μm at 30 vol% and 60 vol%, respectively, as shown in Fig. S6a and b. This may have occurred due to the low volume fractions of the dispersed phase, compared to that of the HIPE. It appears that decreasing the volume fraction of oil can reduce coalescence occurrence in the droplets formed at the beginning of emulsification, and accordingly, the size of droplets of 60 vol% is significantly smaller than that of the HIPE, and the size in 30 vol% is even smaller than that of 60 vol%.

Furthermore, we also reduced the particle concentration proportionally to the dispersed phase fraction, setting it to 1.4 wt% and 2.8 wt% for 30 vol% and 60 vol%, respectively. These low particle concentrations can cause more coalescence between the droplets formed at the beginning of emulsification, resulting in larger droplets compared to those at 4 wt%, as shown in Fig. S6c and d.
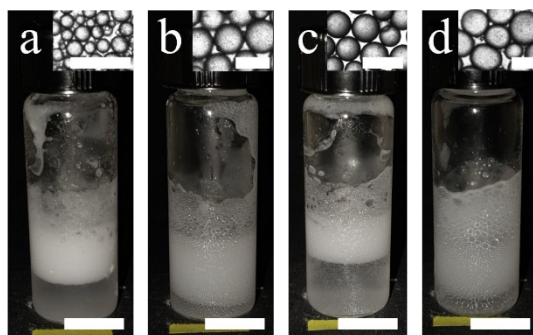

Fig. S6 Macroscopic images of emulsions with low volume fractions of oil, 30 vol% and 60 vol%. (a) Macroscopic image of the emulsion with 30 vol%-oil at a particle concentration of 4 wt%. The average diameter of droplets was 130.9±21.5 μm. (b) Macroscopic image of the emulsion with 60 vol%-oil at a particle concentration of 4 wt%. The average diameter of droplets was 402.1±56.2 μm. (c) Macroscopic image of the emulsion with 30 vol%-oil at a particle concentration of 1.4 wt%. The average diameter of droplets was 308.6±39.1 μm. (d) Macroscopic image of the emulsion made with 60 vol%-oil at a particle concentration of 2.8 wt%. The average diameter of droplets was 527.9±59.9 μm. Scale bar: 1 cm. Inset: optical microscopic images of emulsions. Scale bar: 500 μm.

SEM images of PolyHIPEs with varying the particle concentration

Based on the previous study on the photo-polymerization of Pickering HIPEs,[2] we synthesized PolyHIPEs with large droplets. In order to observe the internal structures of a PolyHIPE monolith in detail, the middle part of the sample was cut into thin slices, and SEM images were then taken using SEM (JSM-7500F) operating at 10.0 kV accelerating voltage. Here, we also took SEM images of PolyHIPEs with particle concentrations of 4 wt% and 16 wt%. As shown in Fig. S7, the PolyHIPE with 4 wt% has an open-cell structure where large pores (~1.6 mm) with pore-throats were mainly observed, while the PolyHIPE with 16 wt% appears to have a completely closed-cell structure with a pore size of ~0.5 mm. Accordingly, these results are consistent with the findings from the optical microscopic images in the manuscript
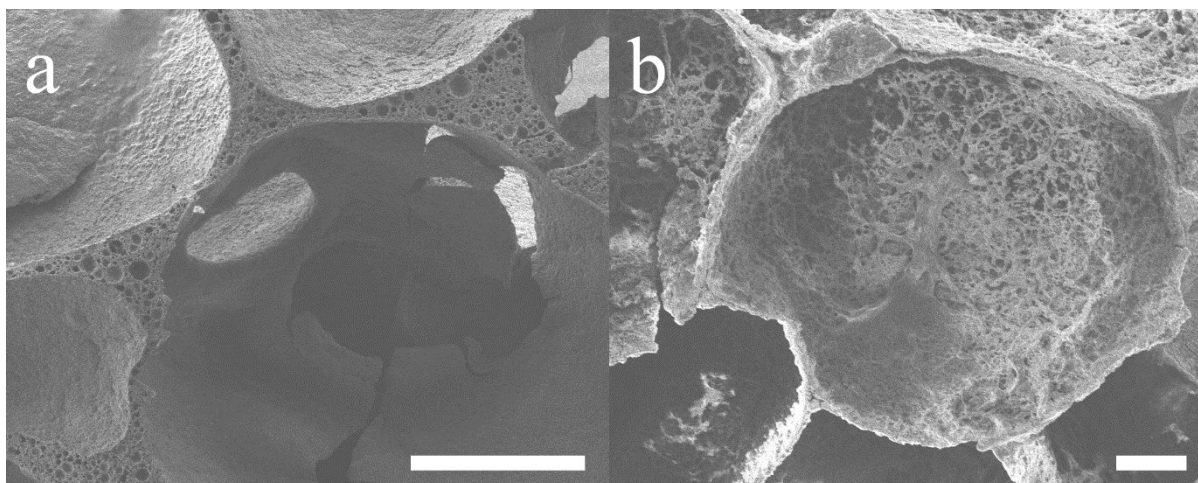

Fig. S7 SEM images of the PolyHIPEs prepared from HIPEs with an oil fraction of 85vol% and at particle concentrations of 4 wt% and 16 wt%. (a) The PolyHIPE prepared from a HIPE with a particle concentration of 4 wt% clearly show pore throats. Scale bar: 1 mm. (b) The PolyHIPE prepared from a HIPE with a particle concentration of 16 wt% provides a completely closed pore. Scale bar: 100 μm.

References

1   Y. Bao, T. Wang, Q. Kang, C. Shi and J. Ma, *Scientific Reports 2017 7:1*, 2017, **7**, 1–14.

2   S. Kim, J. Q. Kim, S. Q. Choi and K. Kim, *Polym Chem*, 2022, **13**, 492–500.