

Supporting information

Thinking outside the Box: Placing Hydrophilic Particles in Oil Phase for Formation and stabilization of Pickering Emulsions

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Synthesis of 200 nm silica nanoparticles

Spherical SiO₂ particles were prepared by hydrolyzing tetraethoxysilane in a water–ethanol mixture containing ammonia. The detailed recipe for SiO₂ particle is depicted in table 1.

Table S1: Experimental details for the synthesis of 200 nm silica nanoparticles based on the Stöber method

	ml	PM (g/mol)	ρ(g/ml)	g	Moles	Molar
Ammonia 30%	3.38	17.03	0.880	2.97	0.052	0.5
H ₂ O	5.91	18		5.91	0.33+1.12	4.5
TEOS	3.91	208.33	0.933	3.65	0.017	0.17
EtOH	86.80	46.07	0.789	68.49	1.49	
Total mL/g	100			81.02		
SiO ₂		60.09	2.0	1.02	0.017	

Characterization

Calculation of number of particles, example for SiO₂ particles with 200

Without losing precursor material and resulting in SiO₂ particles with 200 nm in diameter. The number of particle can be calculated as follows:

The volume per sphere is,

$$V_{1NP} = \frac{4}{3}\pi r^3 \sim 4.19 \times 10^6 \text{ nm}^3$$

The mass per SiO₂ sphere,

$$m_{1NP} = \rho_{SiO_2} V_{1NP} \times 1 \times 10^{-21} \sim 8.38 \times 10^{-15} \text{ g}$$

Thus, the total number of particles dispersed in 100 ml is:

$$\frac{\text{total mass of nanoparticles}}{m_{1NP}} = \frac{1.02 \text{ g}}{8.38 \times 10^{-15} \text{ g}} = 1.22 \times 10^{14}$$

Emulsification

Table S2: Detailed experimental composition of each of the emulsion systems tested for long-term stability and emulsion type.

	From aqueous dispersion			From HD dispersion		
	Aqueous phase		Oil phase	Aqueous phase	Oil phase	
NPs %	NPs dispersion	MQ water		MQ water	NPs dispersion	HD
0	0 μL	2000 μL	2000 μL	2000 μL	0 μL	2000 μL
0.05	85 μL	1915 μL	2000 μL	2000 μL	71 μL	1929 μL
0.1	171 μL	1829 μL	2000 μL	2000 μL	142 μL	1858 μL
0.25	427 μL	1573 μL	2000 μL	2000 μL	355 μL	1645 μL
0.5	855 μL	1145 μL	2000 μL	2000 μL	709 μL	1291 μL

Titration

For SiO₂ particles produced by the Stöber sol-gel method, the magnitude of the silanol group, that is, the number of OH groups per unit surface area is known as the Kiselev–Zhuravlev constant value. Hence, assuming that the SiO₂ surface is fully hydroxylated, that means it is not functionalized or there are no molecules adsorbed, it has a numerical value of 4.6 OH/nm² (least-squares method) (silanol number per unit surface).¹ To evaluate if the produced SiO₂ particles were hydroxylated to the maximum degree, we performed a potentiometric titration following a procedure reported by Fouilloux with slight modifications.² Accordingly, 9.52 ml of the SiO₂ particles dispersion (2.1 % wt., 5.4x10¹⁵ NPs/mL) were mixed with 6.48 mL of sodium chloride solution (49.38 g L⁻¹) giving a final volume of 16 mL. The estimated total surface area is 3.63x10¹⁹ nm². The titration was performed against 0.1 M HCl acid. After the addition of small volumes of HCl acid, the sample was allowed to equilibrate for at least 2 minutes.³ The results of potentiometric titration showed a decrease of surface charge with decreasing pH, as expected. The volume of HCl required to lower the pH from 6.5 to 2.5 was recorded as 3.08 mL. In addition a blank titration with 16 mL of a sodium chloride solution without SiO₂ NPs was performed and the volume of 0.61 mL of HCl was subtracted from the previous one. It is calculated that the silanol density is 4.1 OH/nm², which is close to the theoretical maximum value of 4.6 OH/nm² (note the adsorbed water on the surface of the SiO₂ particles may affect the results¹). Therefore, it is unequivocal that the silanol groups from the SiO₂ particle surface are exposed and the SiO₂ particles are hydrophilic.

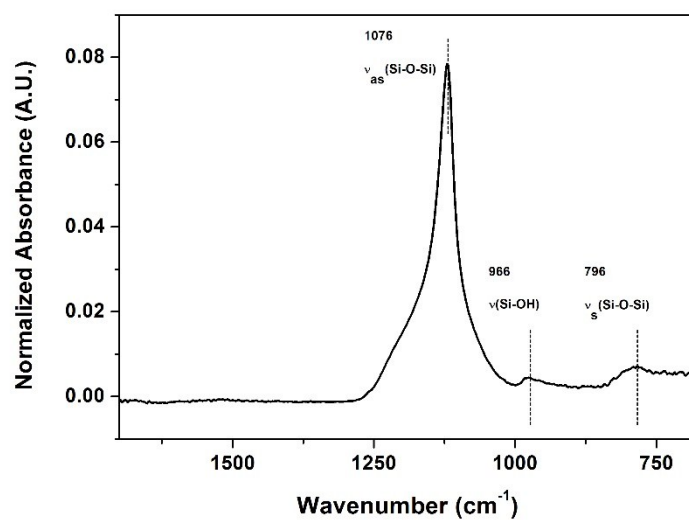


Figure S1. FTIR spectra of the SiO₂ particles prepared by Stöber sol-gel method. The spectrum shows the absorption bands arising from asymmetric vibration of Si–O (1076 cm⁻¹), asymmetric vibration of Si–OH (966 cm⁻¹), and symmetric vibration of Si–O (796 cm⁻¹).⁴

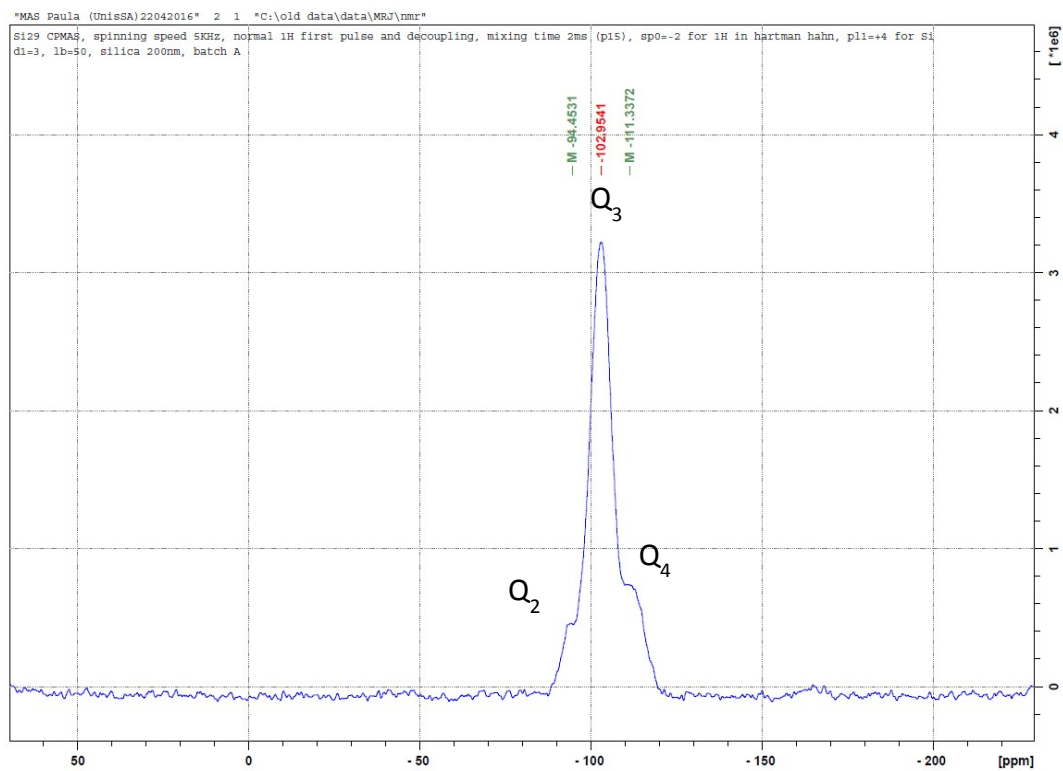


Figure S2. ^{29}Si NMR spectrum of the SiO_2 particles prepared by Stober sol-gel method. Q_2 (≈ -92 ppm) represents germinal Si-OH, Q_3 (≈ -102 ppm) isolated Si-OH and Q_4 (109 ppm) the surficial silanol bridge.

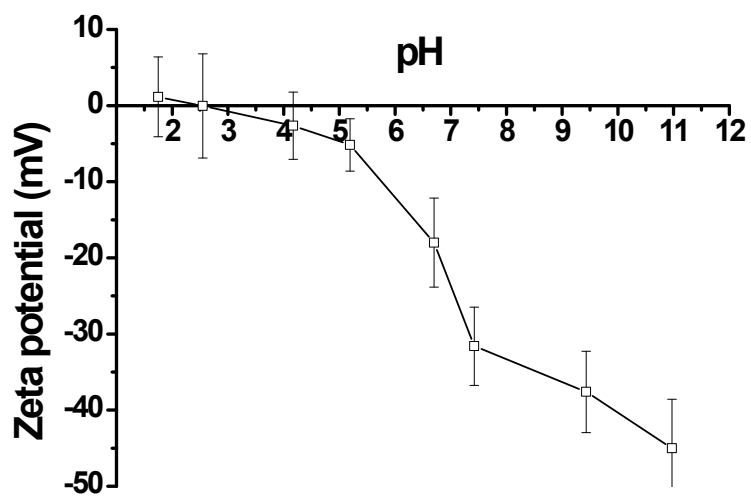


Figure S3. Zeta potential of 200 nm SiO₂ particles in function of pH

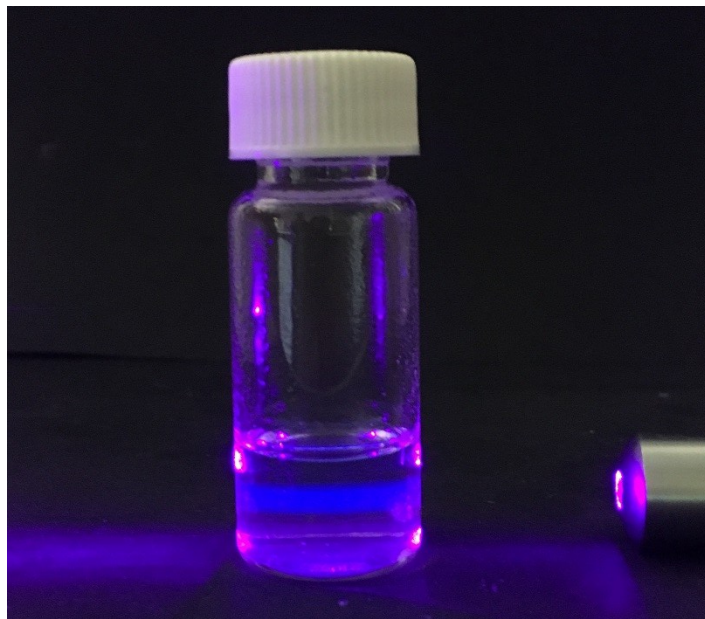


Figure S4. Digital photograph of the Tyndall effect of SiO_2 particle (200 nm) dispersion in HD.

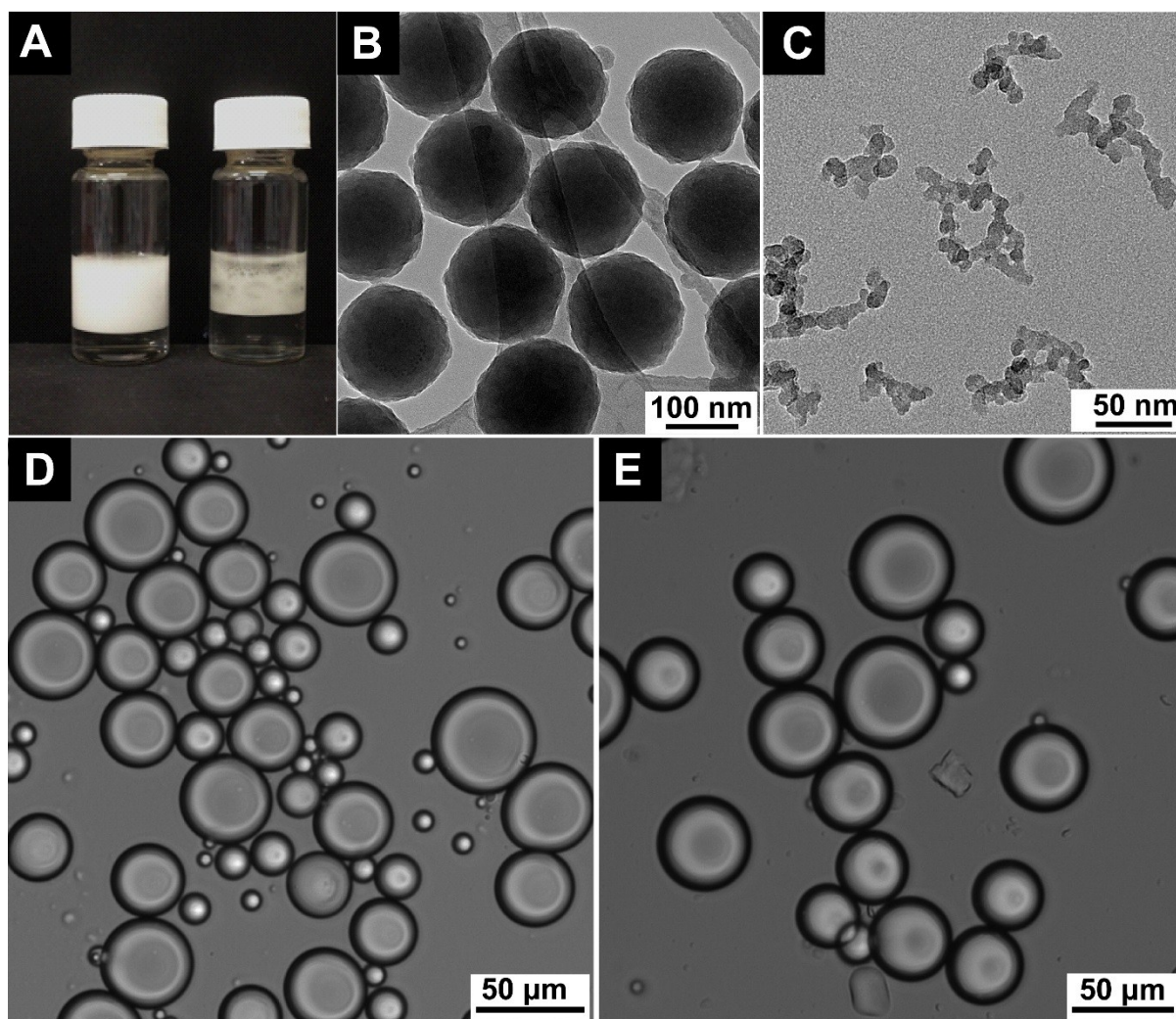


Figure S5. (A) Digital photograph illustrating oil-in-water Pickering emulsions obtained using 50% Milli-Q water and 50% HD containing commercial hydrophilic SiO₂ particles (left 160 nm and right 50-86 nm) as emulsifiers. TEM images of the commercial (B) SiO₂ particles with size of 160 nm (microParticles GmbH) and (C) Aerosil® SiO₂ aggregates (50-86 nm) composed of small 11 nm SiO₂ NPs. The corresponding optical microscopy images of the Pickering emulsions stabilized by (D) 160 nm SiO₂ particles and (E) 50-86 nm SiO₂ aggregates.

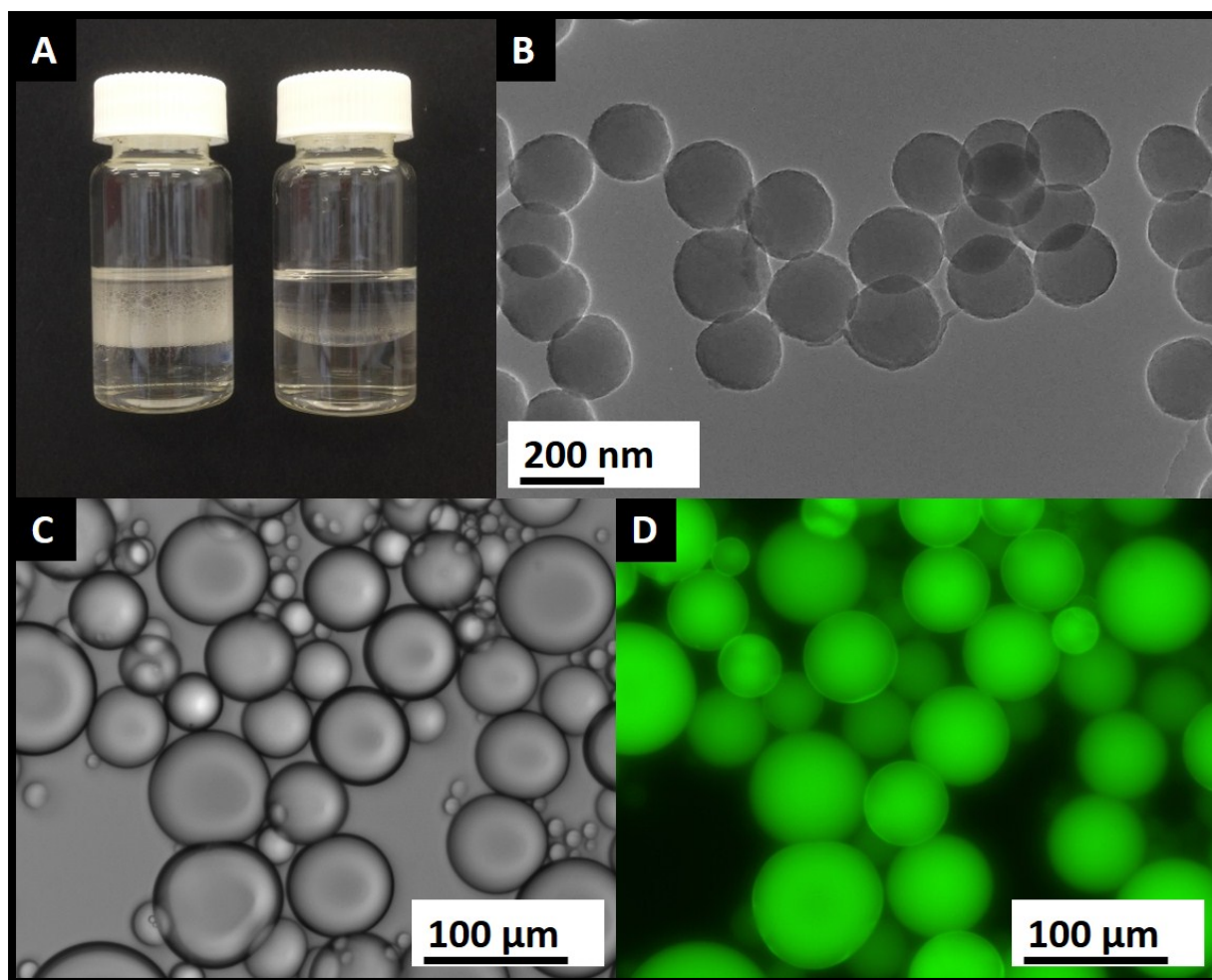


Figure S6. (A) Digital photograph illustrating (left) stable Pickering emulsions obtained when the hydrophilic PDA particles were initially dispersed in HD phase, (right) no Pickering emulsion was observed when the PDA particles were initially dispersed in the aqueous phase. (B) TEM image of the PDA particles. (C) Optical microscope image and (D) fluorescence microscope image of Pickering emulsion prepared when the PDA particles were initially dispersed in HD.

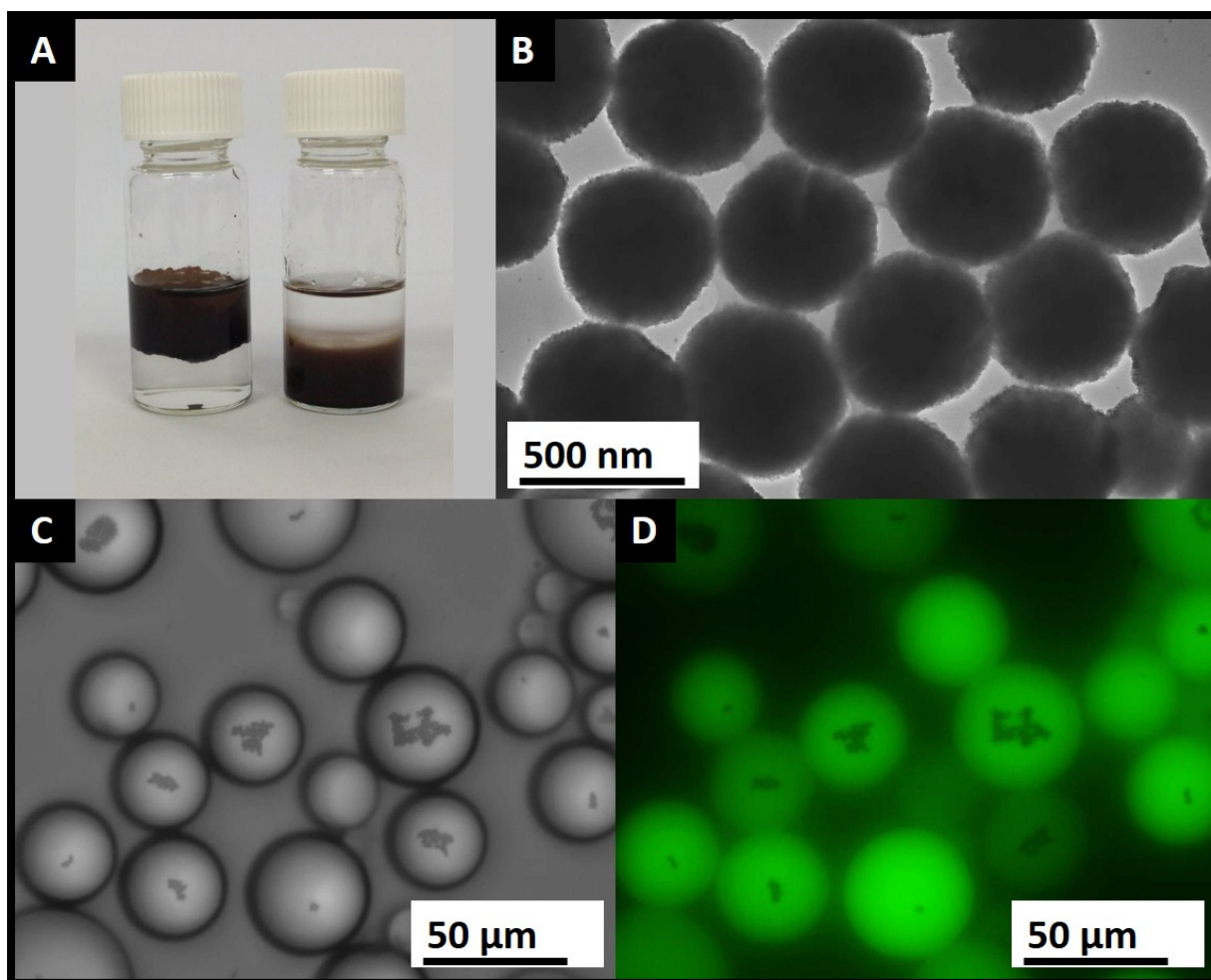


Figure S7. (A) Digital photograph illustrating (left) stable Pickering emulsions were obtained when the hydrophilic $\text{Fe}_3\text{O}_4@\text{PAA}$ particles were originally dispersed in HD, (right) no Pickering emulsion was obtained when the $\text{Fe}_3\text{O}_4@\text{PAA}$ particles were originally dispersed in the aqueous phase. (B) TEM image of the $\text{Fe}_3\text{O}_4@\text{PAA}$ particles. (C) Optical microscope image and (D) fluorescence microscope image of Pickering emulsions.

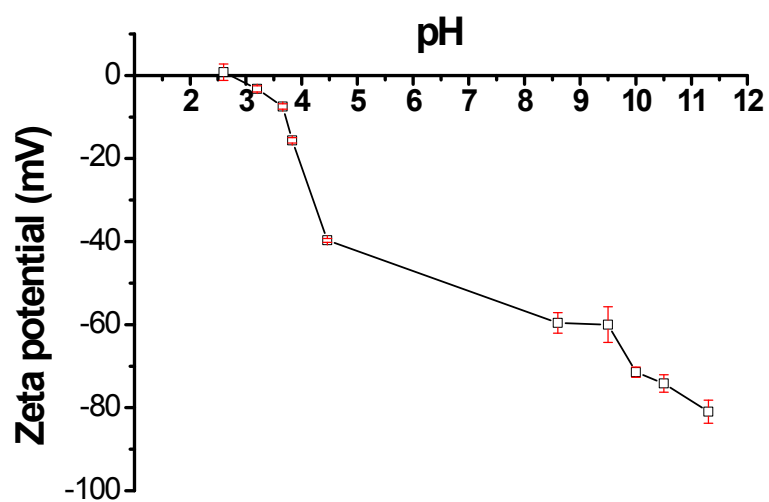


Figure S8. Zeta potential measurements of pristine HD droplets dispersed in degassed MQ water adjusted at different pH.

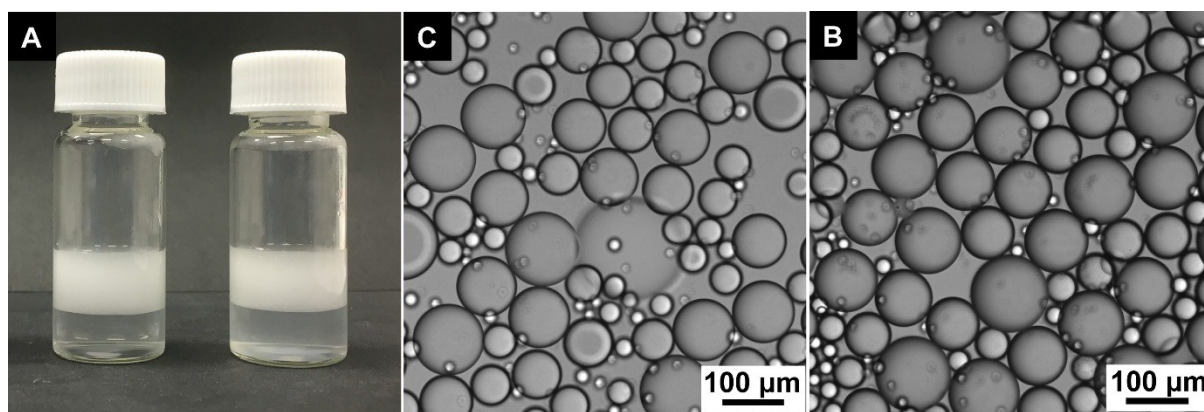


Figure S9. (A) Digital photograph of Pickering emulsions prepared using 50% Milli-Q water and 50% oil containing 200 nm SiO₂ particles, the oil phase is octane (left) and dodecane (right). Optical microscopy images of the Pickering emulsions prepared with (B) octane and (C) dodecane as oil phase.

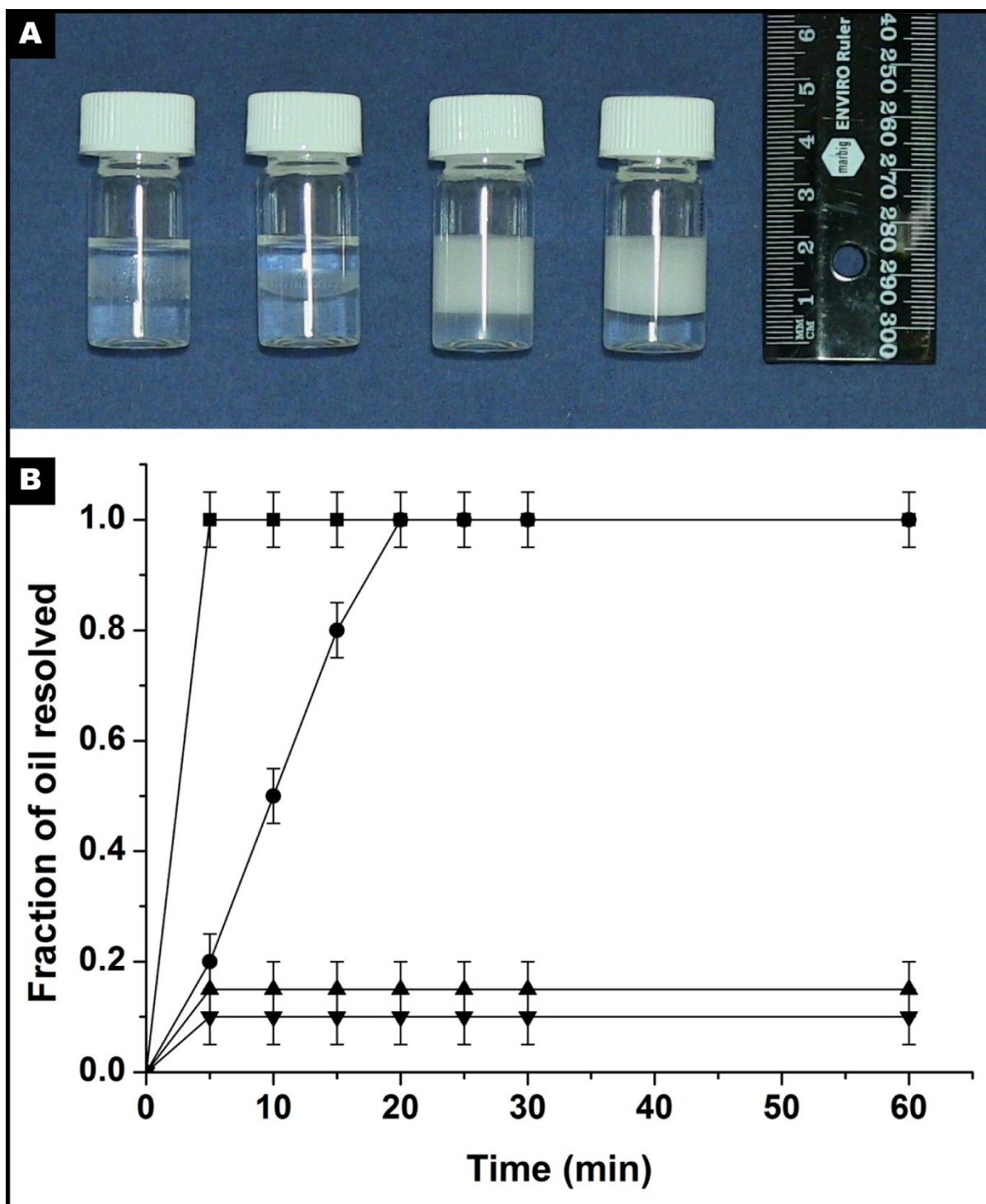


Figure S10. Stability of Pickering emulsions stabilized by hydrophilic SiO₂ particles (initially dispersed in water) at pH around the isoelectric point (pH = 2.5). (A) Concentration in percentage weight of SiO₂ particles from left to right 5.6, 11.2, 16.8, and 22.4 %. (B) Graphic displaying the fraction of oil resolved in function of time for each of the emulsion systems. ■ 5.6 wt%, ● 11.2 wt%, ▲ 16.2 wt%, ▼ 22.4 wt%.

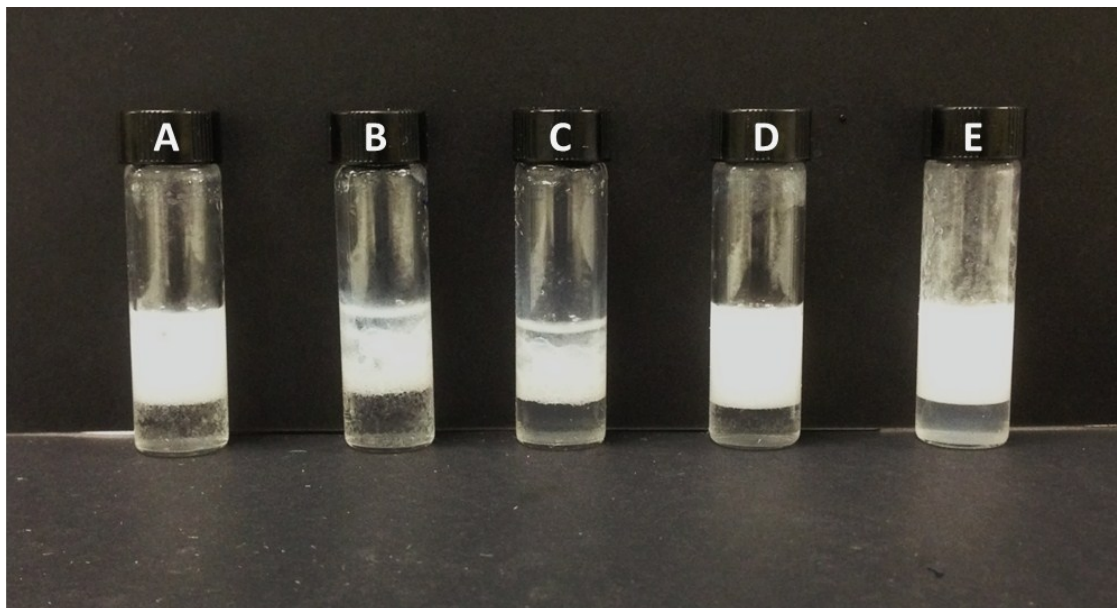


Figure S11. Photograph of the Pickering emulsions prepared when hydrophilic SiO₂ particles were originally dispersed in HD, the pH of water phase is (A) 2.86, (B) 3.83, (C) 6.10, (D) 8.40, (E) 10.45.

References

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2. S. Fouilloux, F. Malloggi, J. Daillant and A. Thill, *Soft Matter*, 2016, **12**, 900-904.
3. J. Lützenkirchen, T. Preočanin, D. Kovačević, V. Tomišić, L. Lövgren and N. Kallay, *Croat. Chem. Acta*, 2012, **85**, 26.
4. S. L. Warring, D. A. Beattie and A. J. McQuillan, *Langmuir*, 2016, **32**, 1568-1576.