Supporting Information

CO$_2$-Switchable Emulsions with Controllable Size and Viscosity

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No. of scheme: 2

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Experimental Section

1. Materials

Hydrophilic silica nanoparticles with a purity > 99.8% were purchased from Sigma, with a primary diameter of 12-18 nm and a Brunauer-Emmett-Teller (BET) surface area of 168-188 m²/g, according to the supplier. 11-Bromohendecanoic acid, dimethylamine, and *n*-octane were purchased from Adamas. Ultrapure water (18.2 MΩ cm, pH = 6.5 at 25 °C) used in all experiments was produced from a Simplicity Pure Water System (Merck Millipore, Shanghai).

2. Methods

2.1 Preparation of oil-in-dispersion emulsions

The corresponding content of silica nanoparticles was dispersed in water or surfactant solutions in sample bottles using an ultrasonic processor. The emulsions were prepared by the mixture of oil phase (*n*-octane) and the aqueous phase by homogenization with an Ultra-turrax homogenizer (11000 rpm, 2 min). The particle concentration was calculated as a weight percent (wt.%) to the aqueous phase. The prepared emulsion was stored in a 25°C incubator. The macroscopic pictures and optical micrographs of the emulsion were taken by a digital camera and a VHX-1000 microscope system (Keyence Co.), respectively.

2.2 Determination of surface tension

The surface tension of the surfactant solutions with or without silica particles was measured by Du Noüy ring method at 25 °C.

2.3 CO_2/N_2 response performance of NCOONa measured by pH

The pH of NCOONa solution (0.3 mmol/L) was measured with a pH meter.

2.4 Effect of $NCOONa/N^+COONa$ on zeta potential of silica particles nanoparticles

Silica nanoparticles were dispersed in NCOONa or N^+COONa solution with an ultrasonic processor. After 12 hours of equilibrium in a 25 °C incubator, the zeta potential of silica particles was measured by Brookhaven Zeta PLAS instrument.

2.5 Optical contact Angle measurement

The negative charged silica particles were simulated with glass plate. The glass plate (1cm×2cm) is ultrasonically treated with an ethanol-water solution to remove dirt from the surface. Soak them in the solution for at least 12 hours to allow the surfactants to interact fully with the silica surface. Pour the surfactant solution for soaking glass plate into the clean quartz tank, then put two plastic supports into the tank to support the plate, build the device shown in Figure S17, and measure the contact angle

with a video contact angle measuring instrument (Figure S18).

3. Synthesis of NCOONa

The target product was synthesized according to the protocol in the literature (Scheme 1) [1]. 11-bromundecanoic acid and excess dimethylamine were reacted in an aqueous solution at room temperature for 12 h. After the reaction was completed, rotary evaporation was performed to obtain a yellow oil. The crude product was obtained after the yellow oil was dissolved in NaOH solutions. NCOONa ($(CH_3)_2N\text{-}C_{10}H_{20}\text{-}COONa$) with purity over 99% (Scheme 2) was received after recrystallization in ethanol-acetonitrile solution.
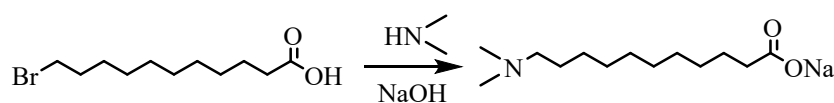
Scheme S1. Synthetic route of NCOONa
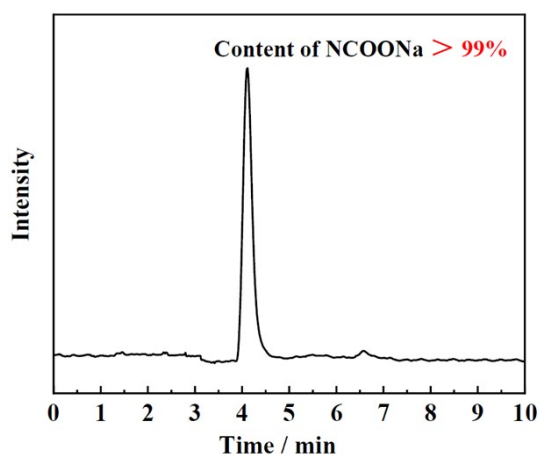
Scheme S2. HPLC of NCOONa. C_{18} Superb chromatographic column (5 um, 4.6 × 250 mm), flow rate: 1 mL/min, mobile phase: methanol/ultrapure water (3/7), UV detector (detection wavelength is 230 nm)。

4. Molecular cross-sectional area determination of NCOONa/N⁺COONa molecules at the air/water interface

According to the measured surface tension values of different concentrations of aqueous surfactant solutions, the γ_s-lgC$_s$ curve and $\dfrac{\partial \gamma_s}{\partial lgc_s}$ can be obtained. The interface excess concentration (

Γ_s) of the surfactant can be calculated with the formula as follow:

$$\Gamma_s = -\frac{1}{2.303RT}\left(\frac{\partial \gamma_s}{\partial lgc_s}\right)_T \qquad \text{equ. s1}$$

Among them, "T" is the experimental temperature (K), "R" is the ideal gas constant (8.314×10^7 erg/mol/K), and "C_s" is the surfactant concentration in the aqueous solution (mol/L).

Γ_s is brought into the following formula to obtain the molecular cross-sectional area of the surfactant at the interface (A):

$$A = \frac{10^{14}}{N \times \Gamma_s} \qquad \text{equ. s2}$$

5. Determination of adsorption amount and molecular cross-sectional area of N^+COONa on silica nanoparticle/water interface

The curve of $\gamma_{s,p}\text{-}lgC_{s,p}(i)$ and $\gamma_s\text{-}lgC_s$ were plotted. The concentration difference (ΔC) and the adsorption capacity of the active agent at the particle/water interface ($\Gamma_s(p/w)$) can be obtained by the formula as follow:

$$\Gamma_s(p/w) = \frac{V\Delta C}{x} = \frac{V[C_{s,p}(i) - C_{s,p}(e)]}{x} \qquad \text{equ. s3}$$

Among them, "$C_{s,p}(i)$" is the initial concentration of surfactant in the dispersion (mol/L), "$C_{s,p}(e)$" is the equilibrium concentration (mol/L), "V" is the volume of dispersion liquid (ml), "x" is the mass of particles contained in the dispersion (g).

Then, by plotting $\Gamma_s(p/w)$ against $C_{s,p}(e)$, the adsorption isotherm of the surfactant at the particle/water interface can be obtained. After the amount of surfactant adsorbed at the particle/water interface was calculated, the cross-sectional area of surfactant molecules at the solid particle/water interface ($a_s(p/w)$) can be obtained by the following formula:

$$a_s(p/w) = \frac{10^{21}S_P}{N\Gamma_s(p/w)} \qquad \text{equ. s4}$$

Among them, "S_P" is the specific surface area of the particle (m²/g).

6. Fluorescently labeled silica nanoparticles

1.759 g citric acid was placed in a single-mouth flask and heated to 200 °C for 20 minutes. The citric acid solid was gradually transformed into a brown liquid. The above liquid was dissolved in a small amount of ethanol and added to the ultra-pure aqueous dispersion containing 2 g silica particles

and 20 mL [3-(diethylamino) propyl] trimethoxysilane (KH792). After stirring for two minutes, the mixed solution was transferred to the hydrothermal reactor and heated at 100 °C for 3 h. After cooling, the water was removed to obtain a dry solid, which was washed twice with ethanol-water to obtain the final product.

7. Debye length

The Debye length can be calculated from the equation as following:[2]

$$\kappa^{-1} = \left(\frac{RT\varepsilon_0\varepsilon}{1000N_A^2e^2\sum_i z_i^2 c_i} \right)^{1/2} = \left(\frac{RT\varepsilon_0\varepsilon}{2000N_A^2e^2 I} \right)^{1/2} \text{(m)} \qquad \text{equ. s5}$$

where ε_0 and ε are permittivity of the free space and water, respectively, R is the gas constant, T is the absolute temperature, N_A is the Avogadro constant, e is the charge of an electron, z_i is the valence of ith ion, c_i is the concentration of ith ion, and I is the ion strength in the solution.

For NCOONa, which has one negative charge, it is obtained:

$k^{-1}=0.304/\sqrt{C(NCOONa)} = 17.6$ (nm) ($C_{(NCOONa)}$=3 ×10^{-4} mol/L)
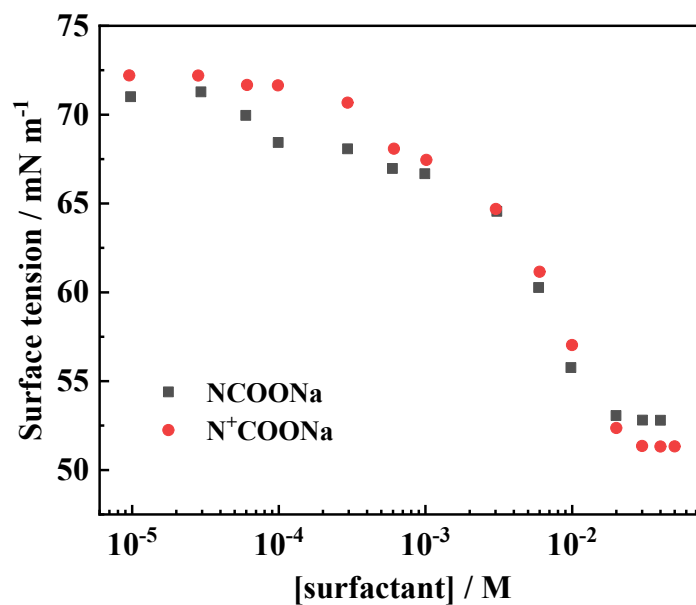
Figure S1. Variation curve of surface tension of NCOONa (pH=8.35±0.01) / N⁺COONa (pH=4.54±0.01) aqueous solution as a function of surfactant concentration.

Table S1. Surface activity parameters of NCOONa and N⁺COONa.[*]

Surfactant	cmc(mmol/L)	γ_{cmc}(mN/m)	Γ^{∞}(10^{-10}mol/cm^2)	A(nm^2/molec.)
NCOONa	16.47	52.76	3.08	0.54
N⁺COONa	21.78	51.33	1.83	0.91

[*] Γ^{∞} and A are the saturated surface concentration and area per surfactant molecule, respectively.
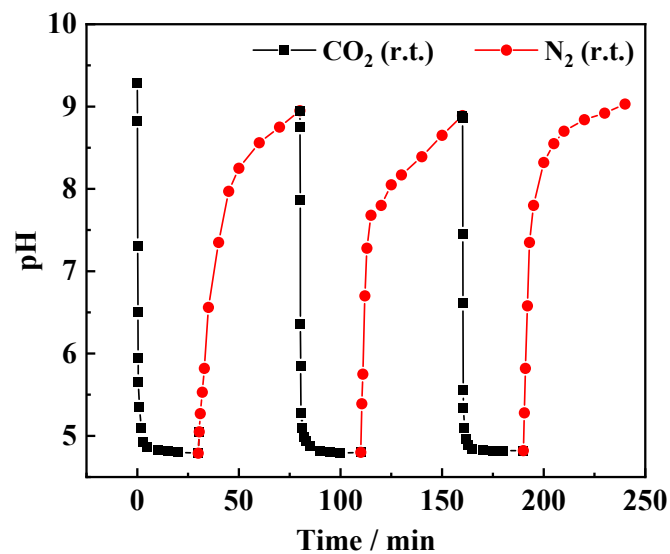
Figure S2. The pH value of 0.3 mM NCOONa solution after bubbling CO_2 or N_2 (V_{CO_2}=25 mL/min, V_{N_2}=50 mL/min, 25°C)
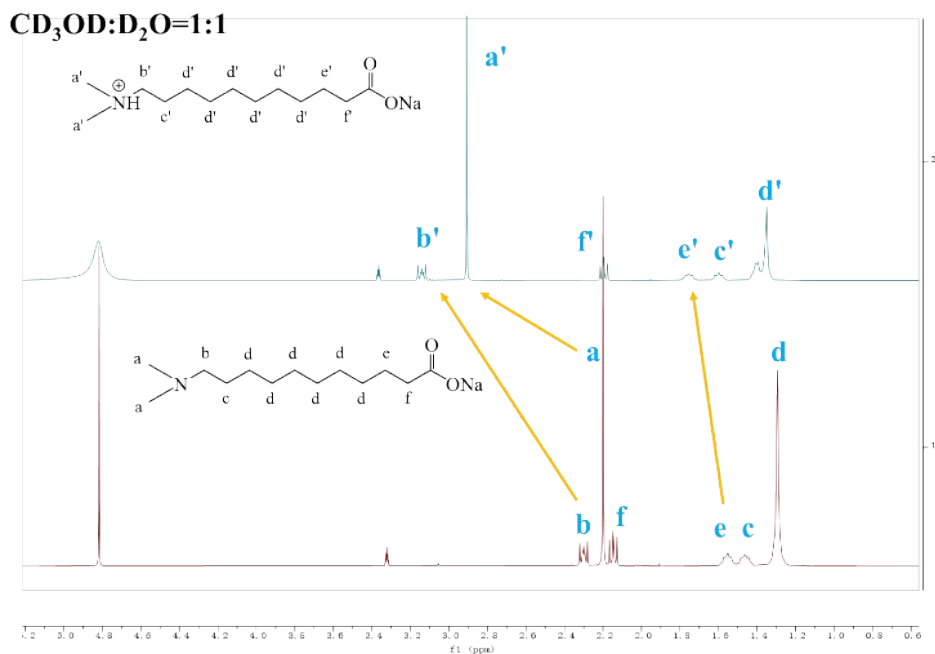
Figure S3. The change of ^{1}H-NMR spectrum before (pH=8.35) and after CO_2 (pH=4.54) is introduced into the solution (CD$_3$OD/D$_2$O).
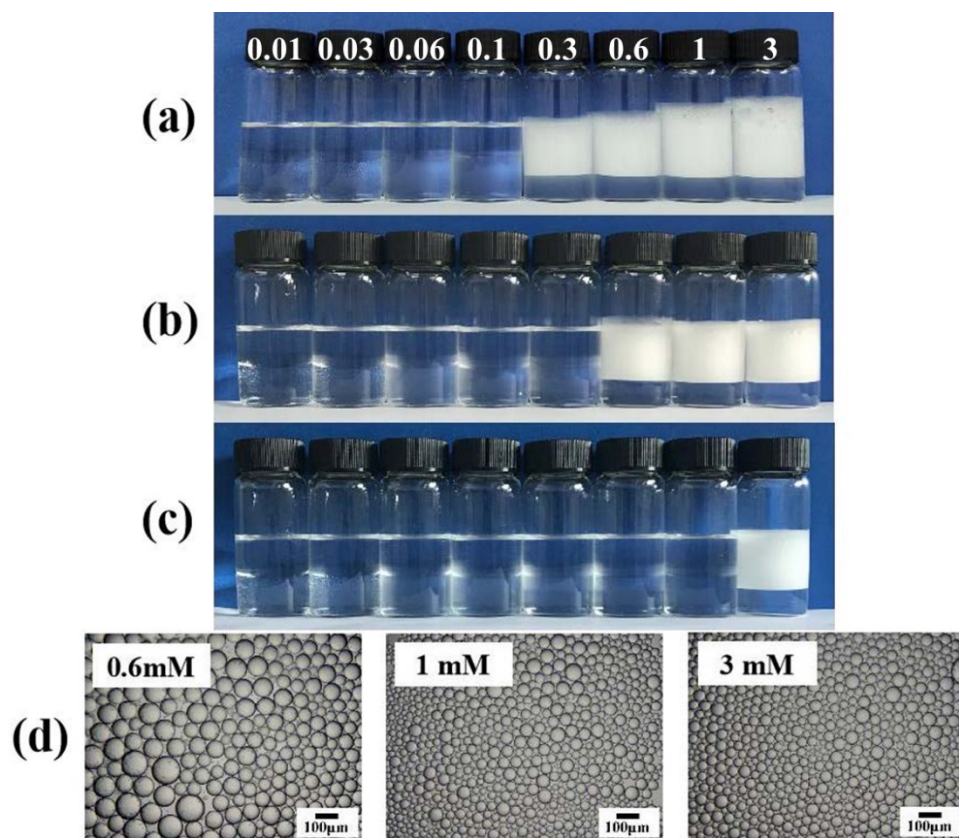
Figure S4. Digital photos of the emulsions stabilized by NCOONa alone (pH=8.35) at different concentrations (shown in mM). (a) taken immediately after preparation, (b and d) 24 h after preparation, (c) 48 h after preparation.
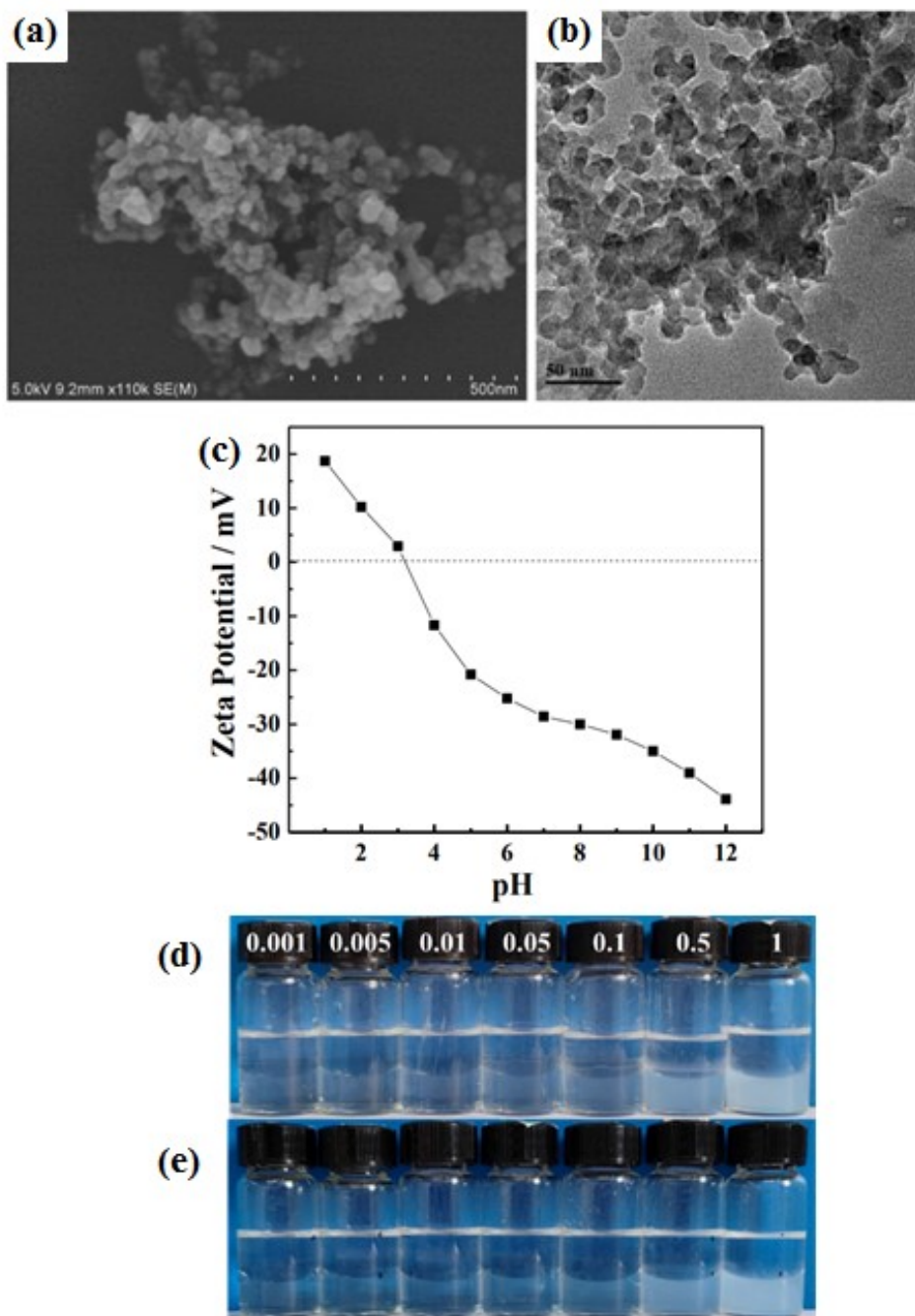
Figure S5. (a) SEM and (b) TEM images of silica nanoparticles. (c) the zeta potential of 0.1 wt% silica particles in aqueous solutions at different pH values. (d) Digital photos of *n*-octane/water emulsions stabilized by silica particles alone at different particle concentrations (wt.%), taken immediately after preparation. (e) Digital photos of the emulsions in (d), taken 24 h after preparation.
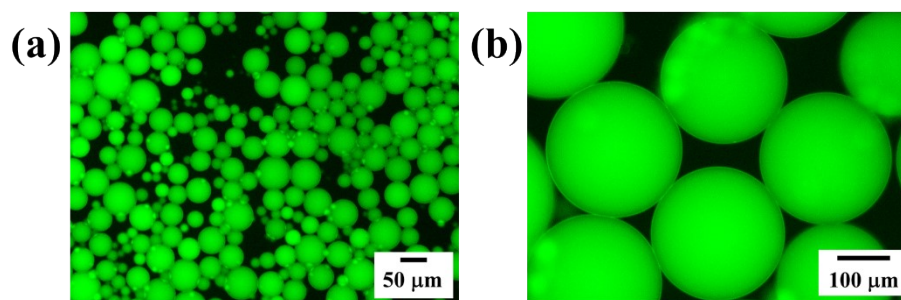
Figure S6. Fluorescence photographs of emulsion droplets stabilized with 0.3 mM surfactant and 0.1 wt.% silica particles. (a) NCOONa (pH=8.35), (b) N$^+$COONa (pH=4.54).
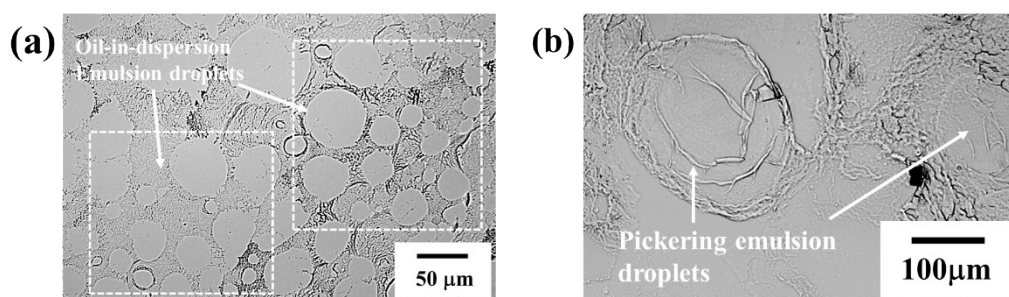
Figure S7. Optical photos of drying morphology of emulsion droplets stabilized with 0.3 mM surfactant and 0.1 wt.% silica particles. (a) NCOONa (pH=8.35), (b) N$^+$COONa (pH=4.54).
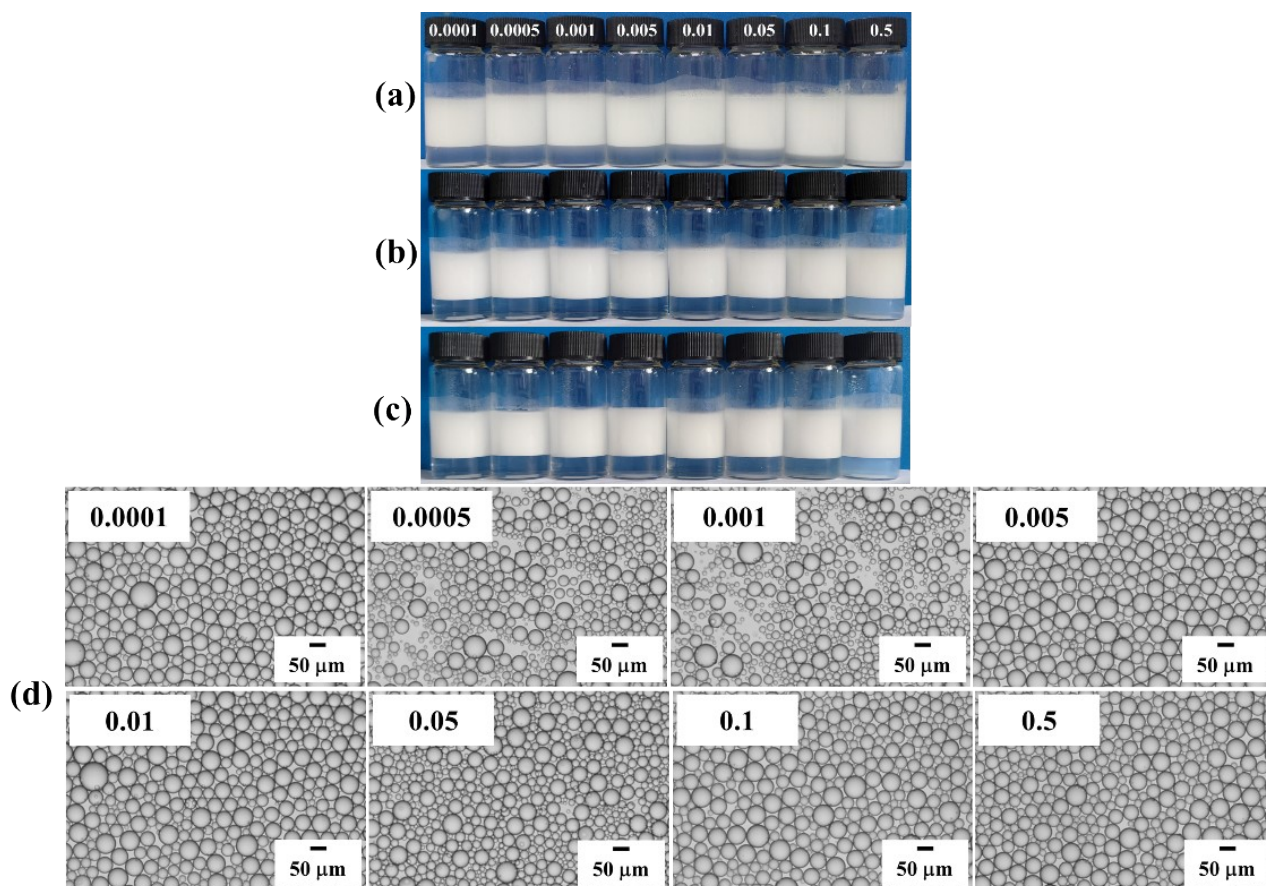
Figure S8. The oil-in-dispersion emulsions stabilized by 0.3 mM NCOONa and different concentrations (wt.%) of silica particles (pH=8.35), taken immediately (a), 24 hours (b), and seven days (c,d) after preparation.
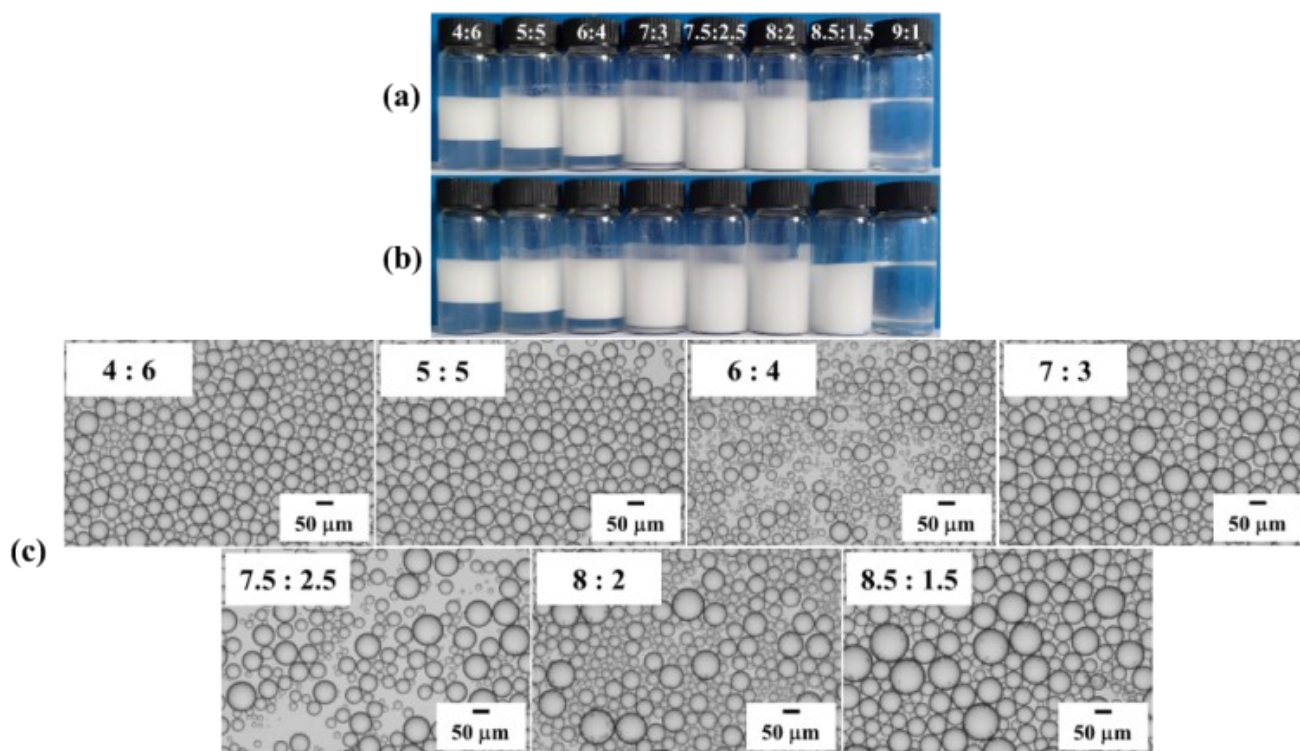
Figure S9. Photographs (a,b) and micrographs (c) of the emulsion stabilized by 0.3 mM NCOONa and 0.1 wt.% silica particles at different oil/water ratios (pH=8.35), taken 24 hours (a) and seven days (b,c) after preparation.
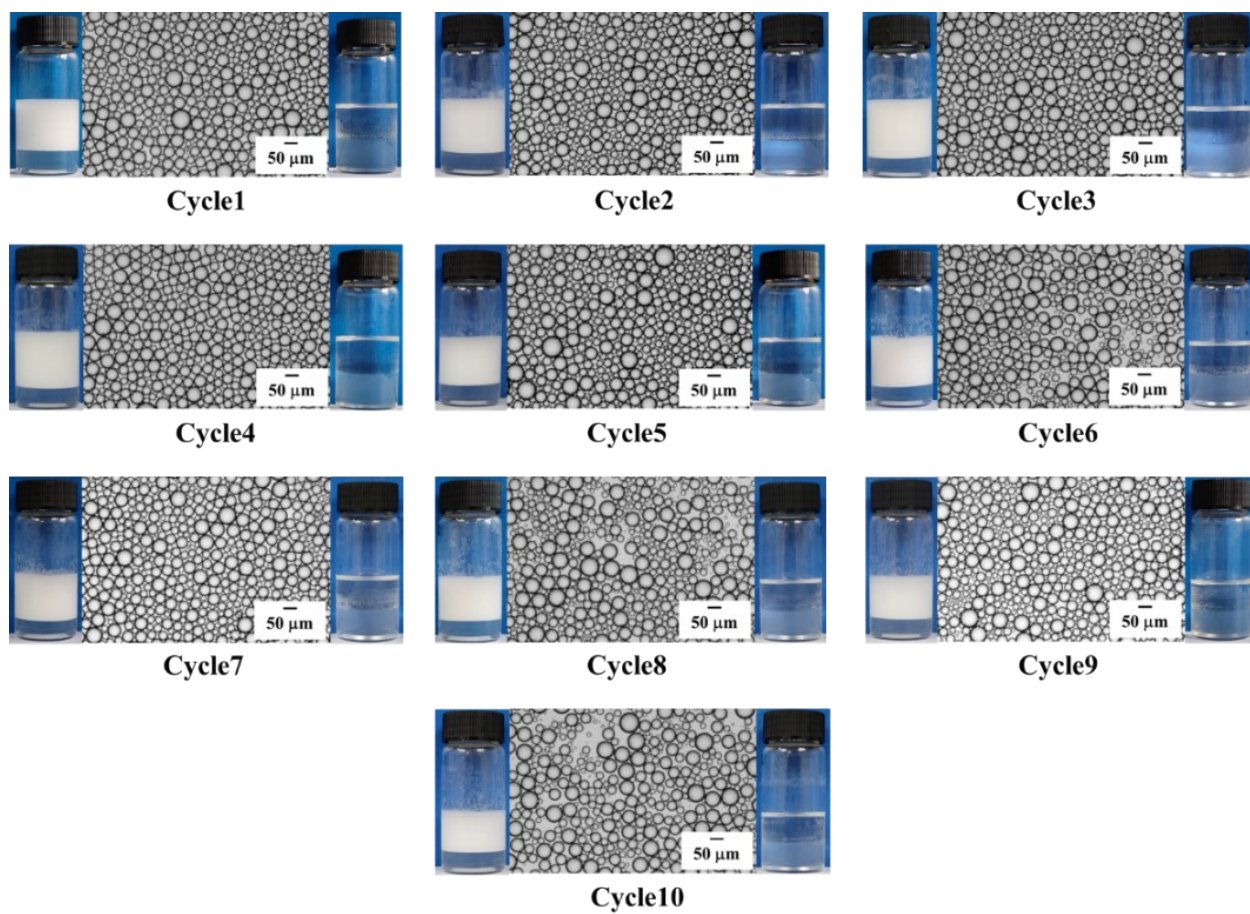
Figure S10. Digital photos and micro photos of the emulsion prepared by 0.3 mM NCOONa and 0.1 wt.% silica particles undergoing demulsification and re-homogenization with new oil phase for 10 times.
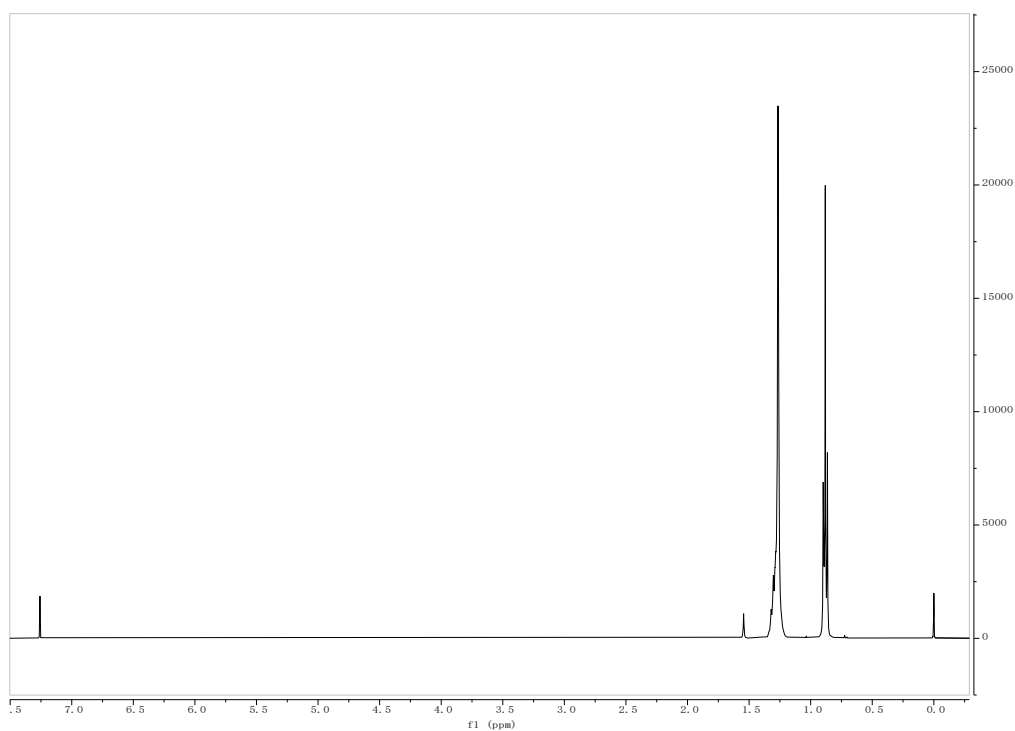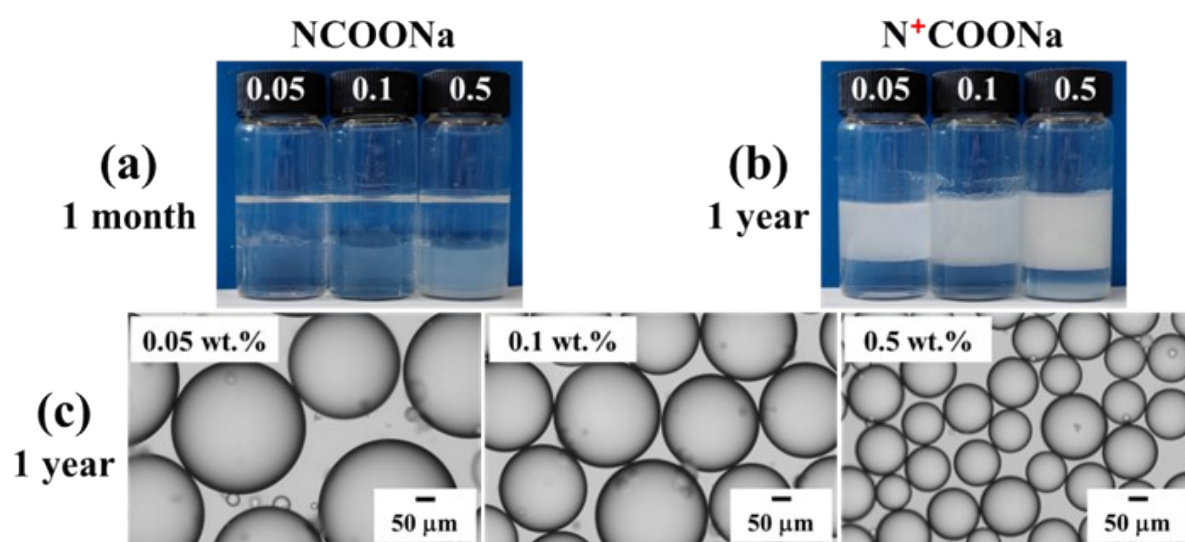
Figure S11. The ^{1}H-NMR spectrum of the separated *n*-octane

Figure S12. Digital photos of (a) OID emulsions (one month, pH=4.54) and (b) Pickering emulsions (one year, pH=8.35) stabilized by 0.3 mM NCOONa/N$^+$COONa and different concentrations of silica nanoparticles (wt.%). (c) micro photos of the Pickering emulsion in (b) taken one year after preparation.
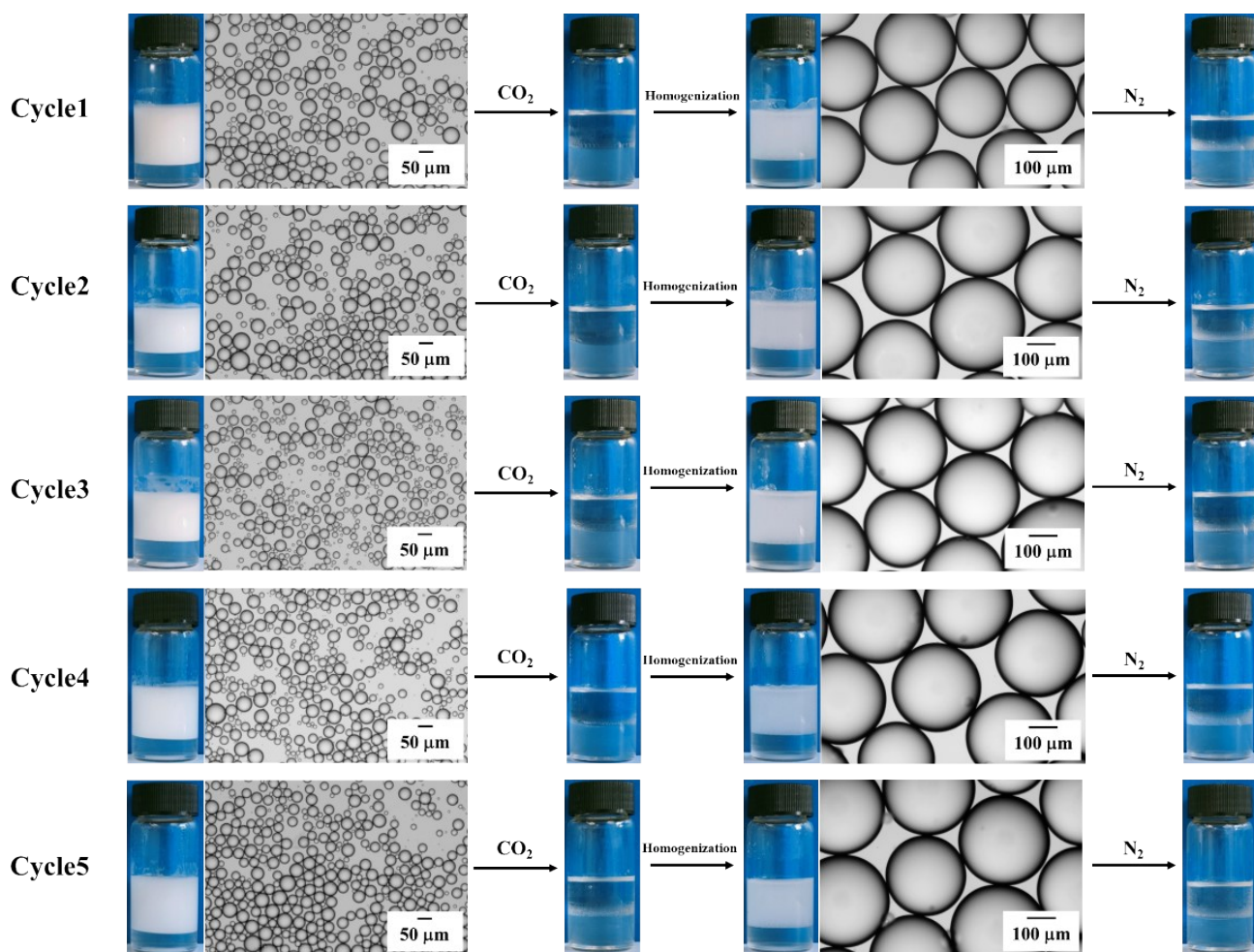
Figure S13. The transformation between the oil-in-dispersion and Pickering emulsions stabilized by 0.3 mM NCOONa and 0.1 wt.% silica particles by CO_2/N_2 trigger for five cycles.
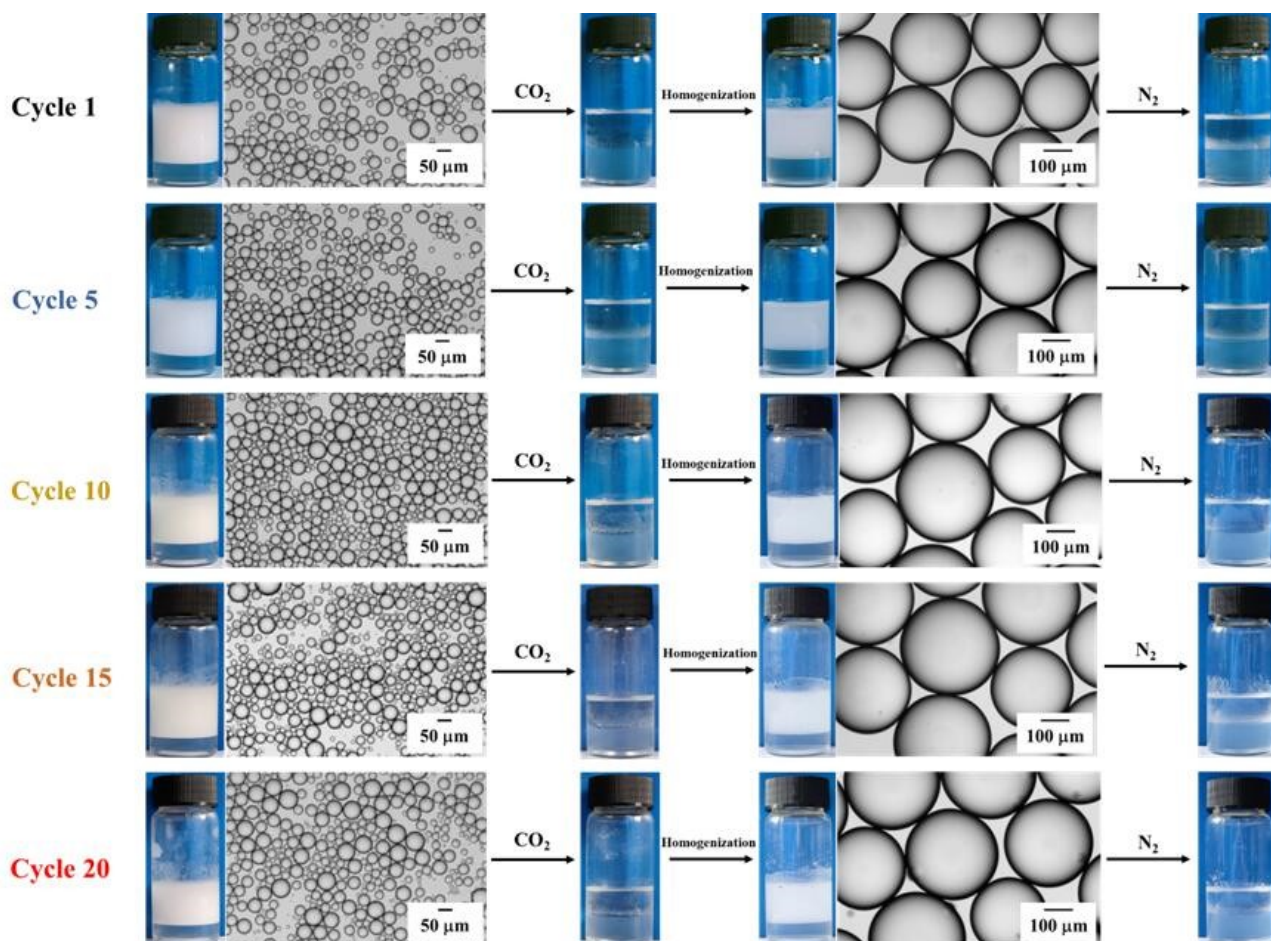
Figure S14. The CO_2-induced transformation between the oil-in-dispersion emulsions and Pickering emulsions of 0.3 mM NCOONa and 0.1 wt.% silica particles for 20 cycles.
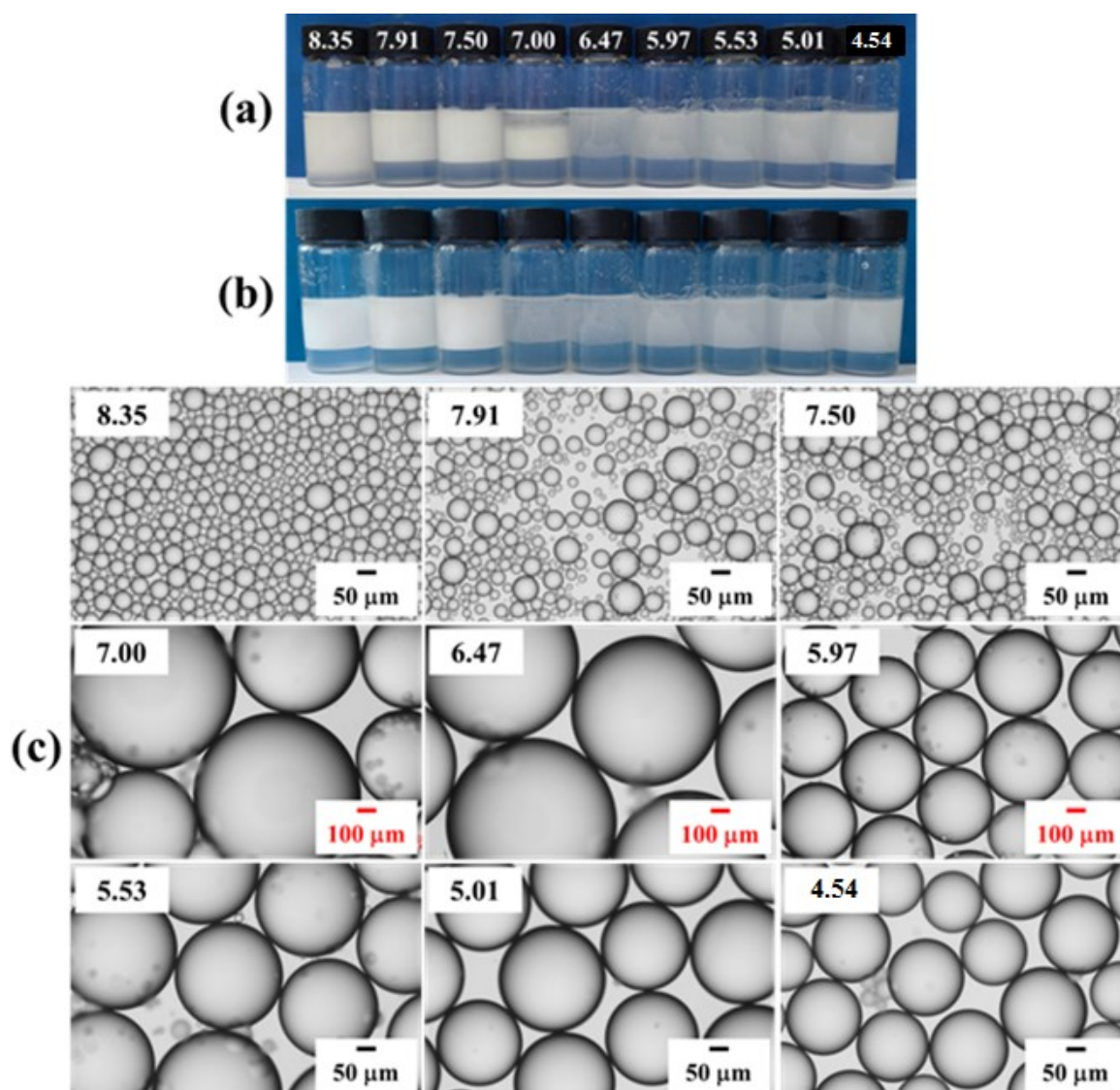
Figure S15. Digital photos (a,b) and micro photos (c) of the emulsions stabilized by 0.3 mM NCOONa and 0.1 wt.% silica particles at different pH, taken immediately (a) and 24 h (b, c) after preparation. The pH value was listed on vials and photos.
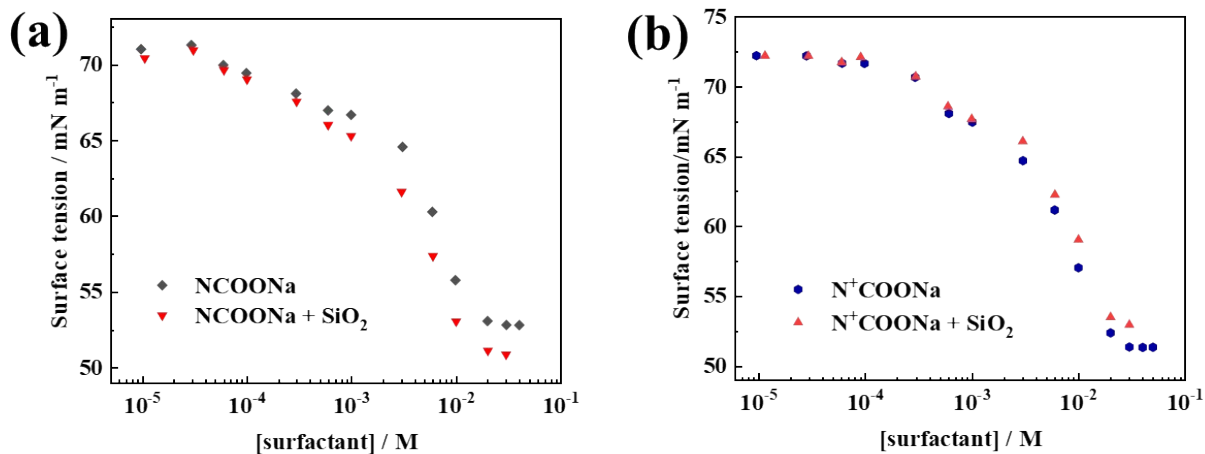
Figure S16. (a) The curve of surface tension of NCOONa aqueous solution as a function of NCOONa concentration before and after adding 0.1 wt.% silica particles (pH=8.35); (b) The curve of surface tension of N$^+$COONa aqueous solution as a function of N$^+$COONa concentration before and after adding 0.1 wt.% silica particles (pH=4.54).
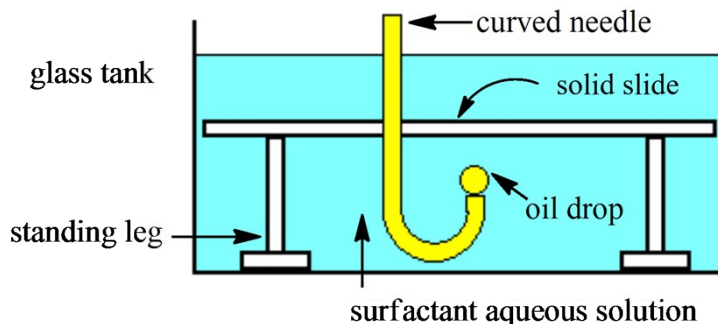

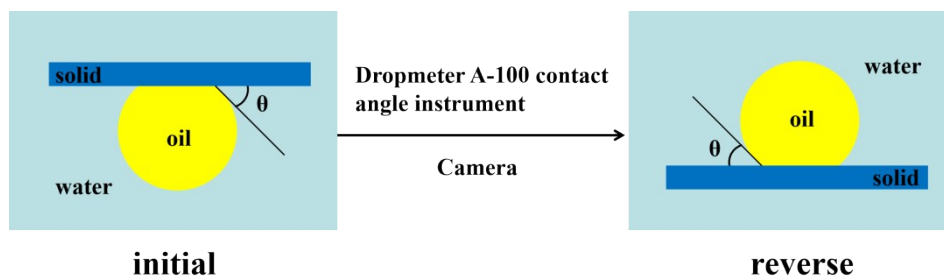**Figure S17**. Schematic diagram of instrument for measuring the contact angle.

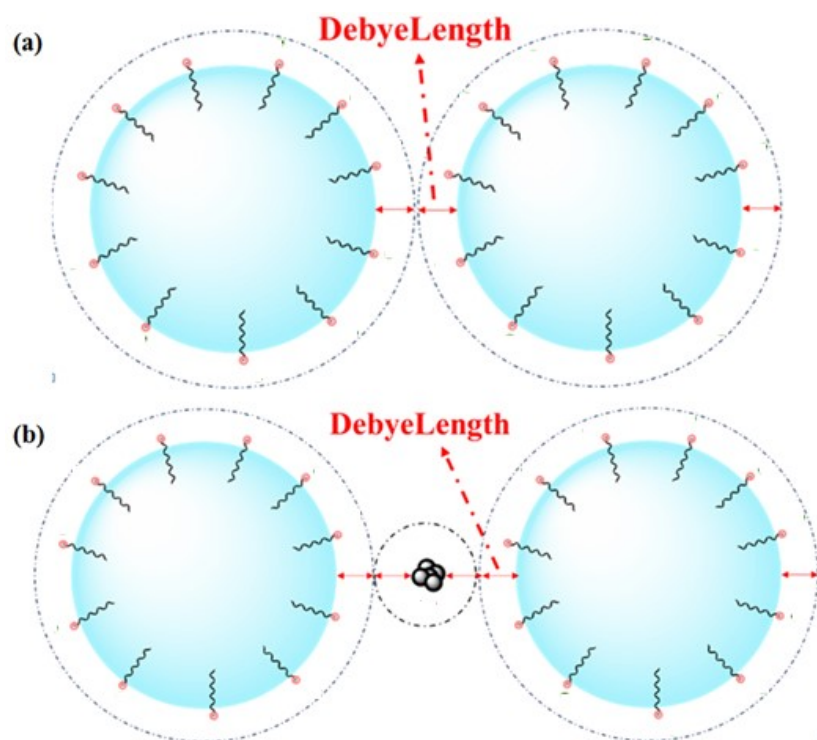**Figure S18**. Schematic diagram of the side view of the inverted sessile drops.

Figure S19. Illustration of the distance between two droplets before (a) and after (b) adding silica particles.[2]

Reference:

[1].J. Jiang, S. Yu, W. Zhang, H. Zhang, Z. Cui, W. Xia and B. P. Binks, *Angew. Chem. Int. Edit.*, 2021, **60**, 11793-11798.

[2].J.N. Israelachvili. Intermolecular and Surface Forces, London: Academic Press, 2011.