Supporting Information

Conversion of bile salts from inferior emulsifier to efficient smart emulsifier assisted by negatively charged nanoparticles at low concentrations

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EXPERIMENTAL

Materials

Silica nanoparticles HL-200 (99.8%) were purchased from Wuxi Jinding Longhua Chemical Co. Ltd., China. *n*-octane (purity > 99.8%), cyclohexene, sodium taurocholate, sodium glycodeoxycholate, sodium dehydrocholate, sodium ursodeoxycholate, sodium deoxycholate, sodium chenodeoxycholate, sodium cholate, sodium dodecyl sulfate, alumina nanoparticles, and Nile Red were purchased from Sigma (Shanghai). Ferric chloride, sodium hydroxide, olive oil, soybean oil, diesel oil, kerosene, toluene, liquid paraffin, and dimethicone were purchased from Sinopharm Chemical Reagent Co. Ltd., China.

Determination of surface and interfacial tension

The surface tension of NaDC solutions with or without silica nanoparticles was measured at 25 °C using the du Noüy ring method. A cover was used to minimize water evaporation. To obtain the equilibrium surface tension, measurements were made every 3 min until the change was below 0.03 mN m^{-1}. The surface tension of triple-distilled water was first measured at 25 ± 0.1 °C to calibrate the tensiometer. The p*c*20 value is defined as the negative logarithm of the surfactant concentration at which the surface tension of pure water is reduced by 20 mN m^{-1}:

$$pc20 = - \log c20 \quad (1)$$

The oil-water interfacial tension between an aqueous solution and oil was determined at 25 °C by the pendant drop method on an OCA15EC optical contact angle measuring instrument (Dataphysics, Germany).

Determination of zeta potential and particle diameter

The zeta potential/mean diameter of silica nanoparticles or montmorillonite particles at 0.1 wt.% dispersed in deionized water were measured using a Brookhaven Zeta PLAS instrument after incubation at 25 °C for 24 h.

Preparation of emulsions

Aqueous NaDC solutions were prepared by dissolving NaDC in pure water. Silica nanoparticles were then dispersed in 5 mL of the surfactant solution or pure water using an ultrasonic probe followed by adding 5 mL of *n*-octane, and then the mixture was homogenized using an UltraTurrax homogenizer (11,000 rpm for 2 min) to form emulsions. The nanoparticle concentration (wt.%) is relative to the aqueous phase. The emulsions were placed in a thermostat at 25 °C and were monitored by taking photos and using optical microscopy. The volume ratio of oil to water was 1:1.

Characterization of emulsions

The drop test method and fluorescence staining method were used to identify the type of emulsion. A few drops of emulsion were added into pure water which was observed to be dispersed well. Nile Red in ethanol (10 μL, 1mg/mL) was added to the oil phase, and emulsion droplets were observed to be red using fluorescence microscopy (Carl Zeiss Axio Imager Z2, Germany). Both suggest that the emulsion formed is oil-in-water.

Microstructure of emulsions

A small volume of emulsion was placed on a clean polished monocrystalline silicon wafer at 25 ° C to allow water and oil to evaporate completely. Then SEM images were recorded using a scanning electron microscope (Hitachi Corporation, S-4800).

Determination of turbidity and pH of NaDC solutions

The turbidity of 0.05 mM NaDC aqueous solution was measured by a WGZ-2B turbidity meter (Shanghai Xinrui Instrument Co., Ltd). The pH was measured by a FE20 pH meter (Mettler Toledo).

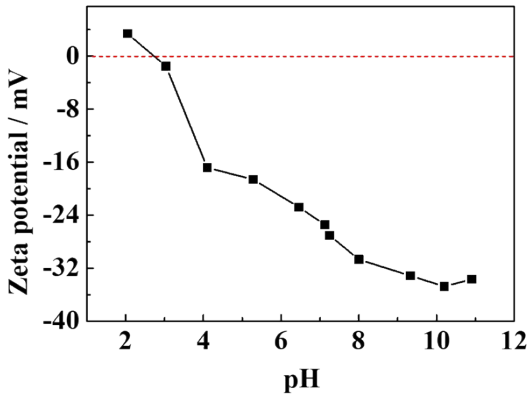

Figure S1. Zeta potential of 0.1 wt.% silica nanoparticles dispersed in water of different pH at 25 °C.

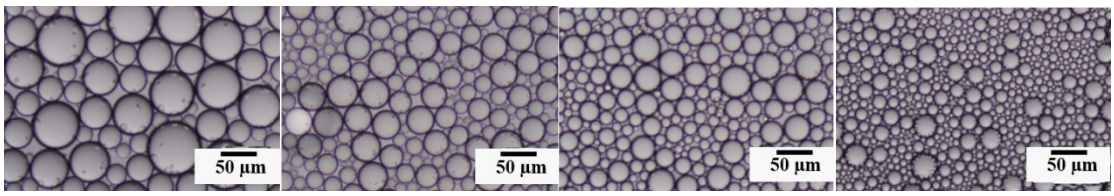

Figure S2. Optical micrographs of emulsions stabilized by 0.1 wt.% silica nanoparticles in combination with NaDC of different concentration taken 24 h after preparation. [NaDC]/mM from left to right: 0.01, 0.06, 0.1, 0.2.

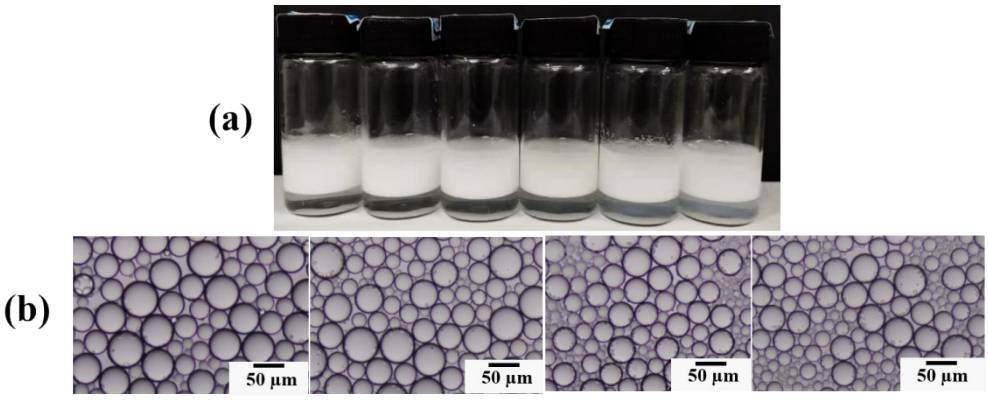

Figure S3. (a) Digital photos of emulsions stabilized by 0.05 mM NaDC in combination with silica particles of different concentration taken 12 h after preparation. [particle]/wt.% from left to right: 0.01, 0.03, 0.05, 0.1, 0.3, 0.5. (b) Optical micrographs of above emulsions with [particle]/wt.% from left to right: 0.01, 0.03, 0.05, 0.5.

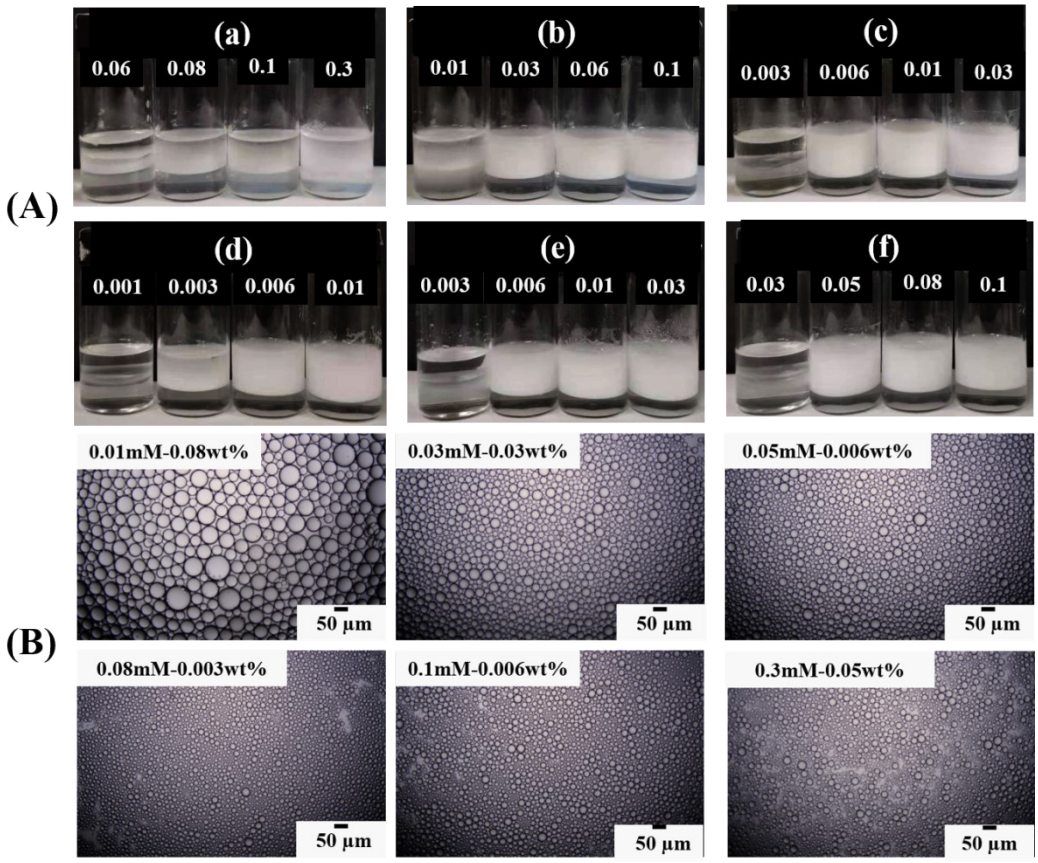

Figure S4. (A) Digital photos of emulsions stabilized by NaDC in combination with silica particles of different concentration (wt.%) as shown on vessels taken 12 h after preparation. [NaDC]/mM from (a) to (f): 0.01, 0.03, 0.05, 0.08, 0.1 and 0.3. (B) Optical micrographs of emulsions stabilized by the minimum silica particle concentration in combination with NaDC of different concentration taken 24 h after preparation. The concentrations of surfactant and particles are shown on the images.

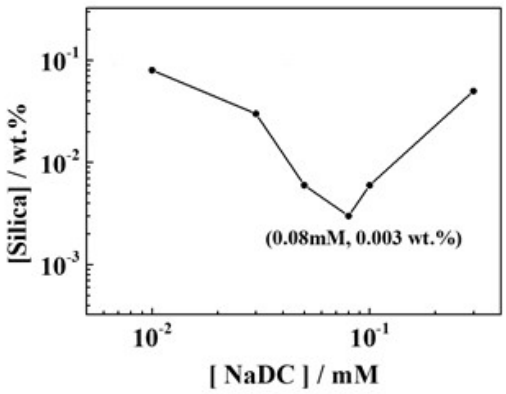

Figure S5. Variation of the minimum concentrations of silica nanoparticles and NaDC required for stabilization of *n*-octane-in-water emulsions.

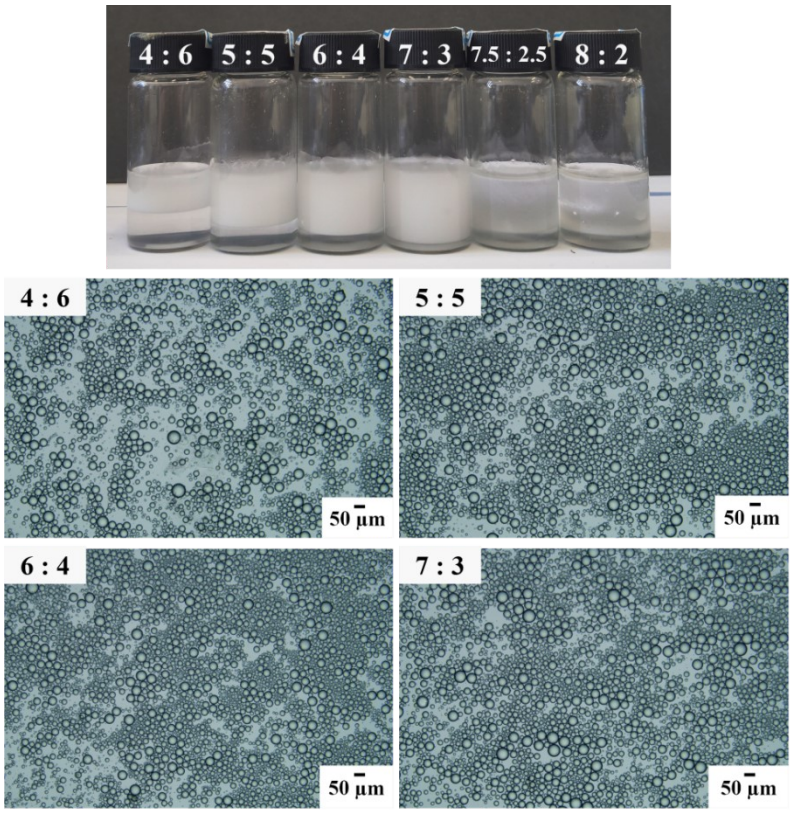

Figure S6. Digital photos and optical micrographs of *n*-octane-in-water emulsions stabilized by 0.05 mM NaDC in combination with 0.1 wt.% silica nanoparticles at different oil:water volume ratios as shown taken 2 weeks after preparation. They are unstable to coalescence at 75 and 80% oil.

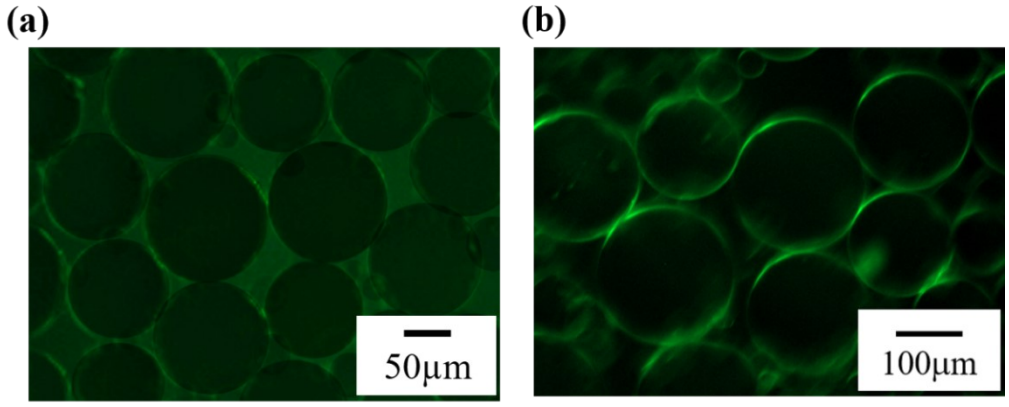

Figure S7. (a) Fluorescence microscopy image of the oil-in-dispersion emulsion of 0.05 mM NaDC and 0.1 wt% silica particles using labeled silica. (b) Fluorescence microscopy image of the Pickering emulsion stabilized by 0.05 mM CTAB and 0.1 wt.% silica particles using labeled silica. The labelled silica particles at the interface emit green light.[1]

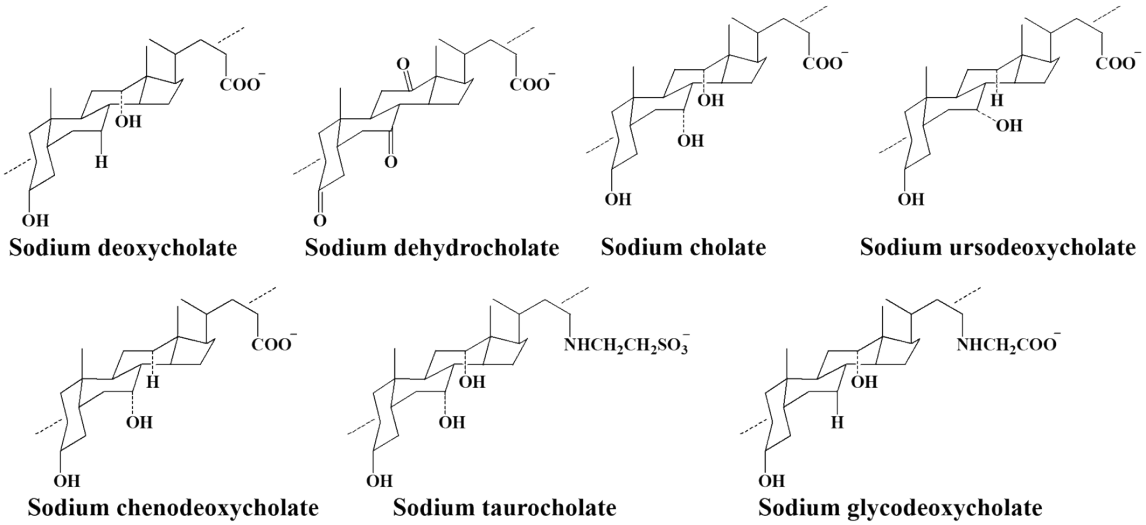

Figure S8. Name and structural formula of different bile salts.

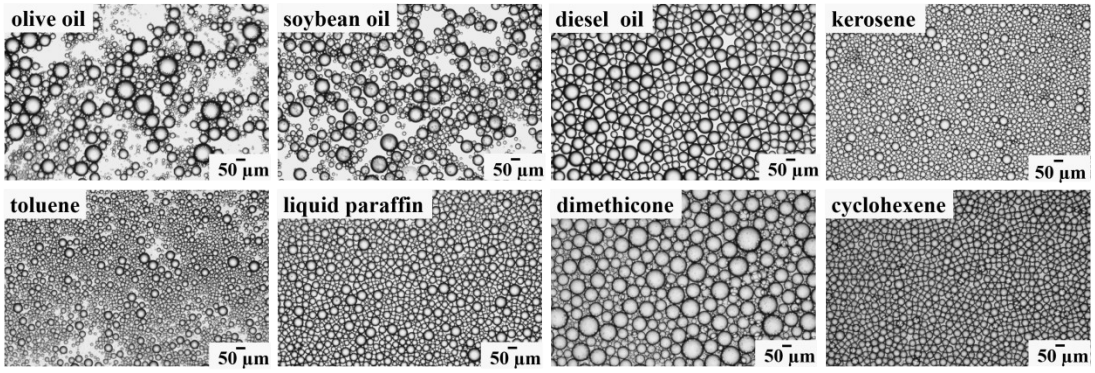

Figure S9. Optical micrographs of oil-in-water emulsions stabilized by 0.05 mM NaDC in combination with 0.1 wt.% silica particles using different oils as shown taken 2 weeks after preparation.

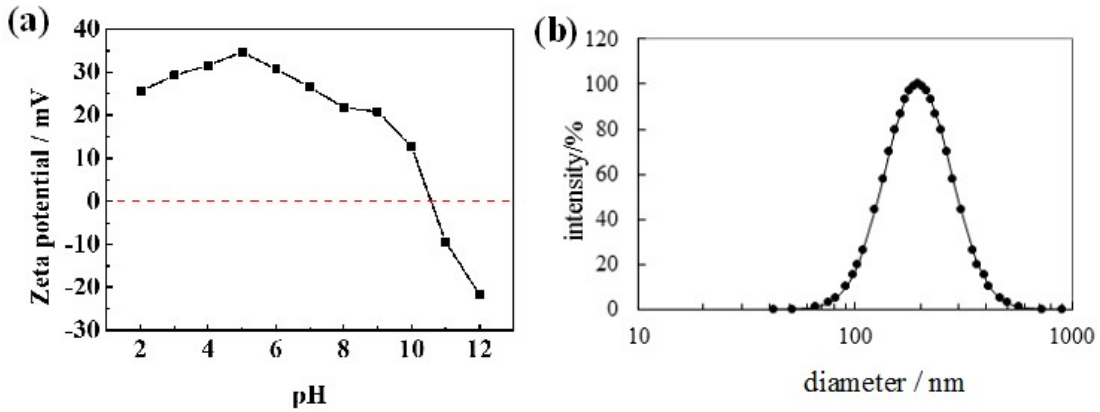

Figure S10. (a) Zeta potential *versus* pH and (b) size distribution of 0.1 wt.% alumina nanoparticles dispersed in water at pH 7.

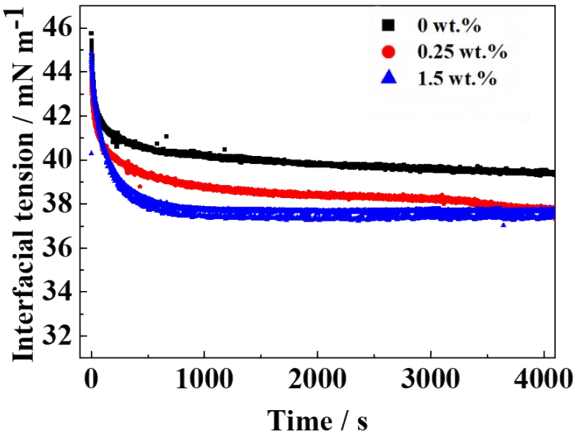

Figure S11. Interfacial tension between aqueous SDS (0.1 mM) without and with silica nanoparticles (0.25 wt%, 1.5 wt%) and *n*-octane measured by the pendant drop method at 25 °C.

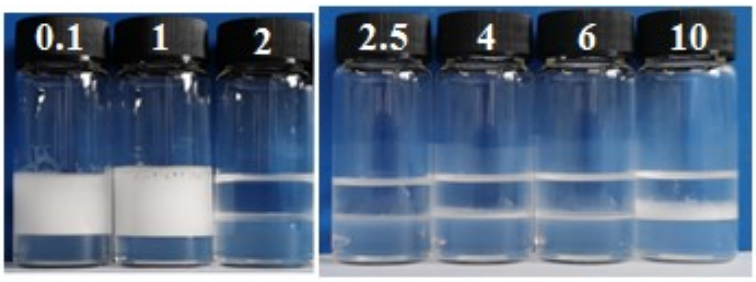

Figure S12. Digital photos of *n*-octane-in-water emulsions stabilized by 0.1 wt.% silica particles in combination with different concentrations of NaDC (mM) taken 3 days after preparation.

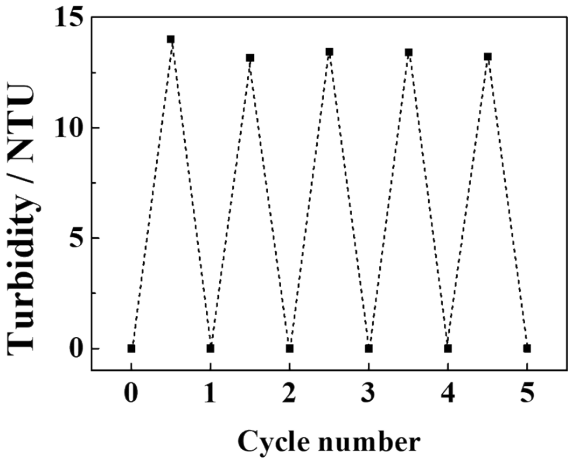

Figure S13. Turbidity of 20 mL of 0.05 mM NaDC aqueous solutions after bubbling first CO_2 (10 min, 25 mL/min) and then N_2 (10 min, 25 mL/min) alternately at 25 °C.

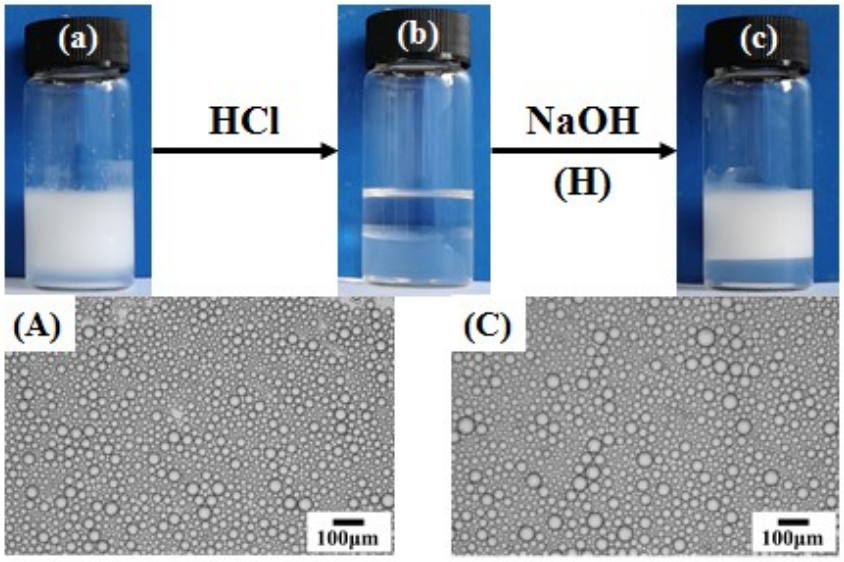

Figure S14. Digital photos and optical micrographs of oil-in-water emulsions stabilized by 0.05 mM NaDC in combination with 0.1 wt.% silica after adding HCl (pH = 4) and NaOH (pH = 10).

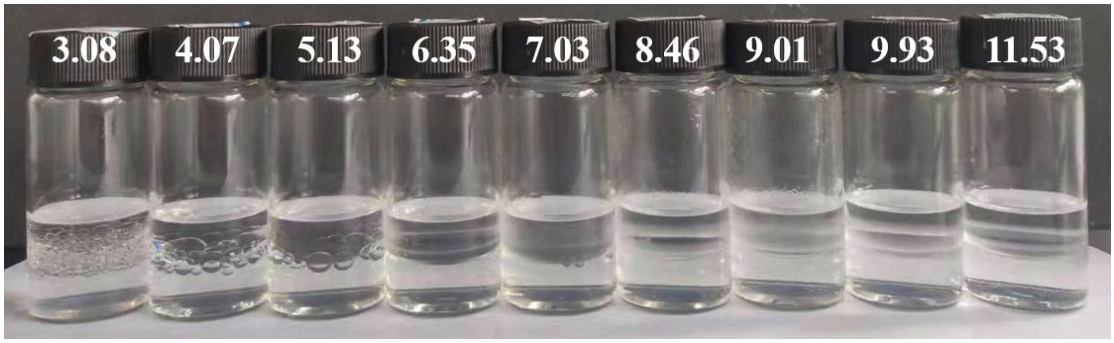

Figure S15. Digital photos of emulsions stabilized by 0.1 wt.% silica nanoparticles alone at different pH (given) immediately after preparation.

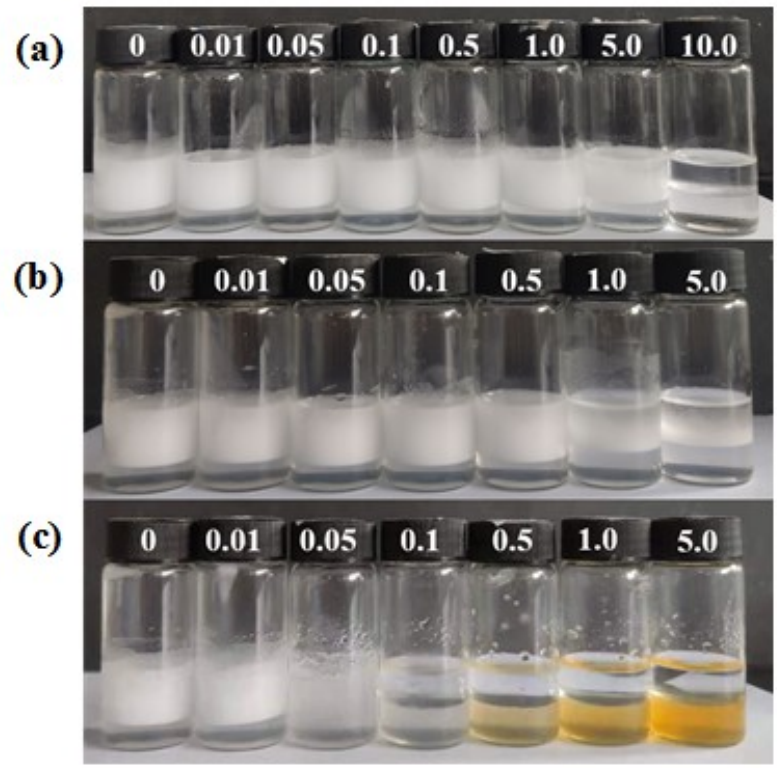

Figure S16. Digital photos of *n*-octane-in-water emulsions stabilized by 0.05 mM NaDC in combination with 0.1 wt.% silica particles at different concentrations of salt (mM given) for (a) NaCl, (b) $CaCl_2$, (c) $FeCl_3$.

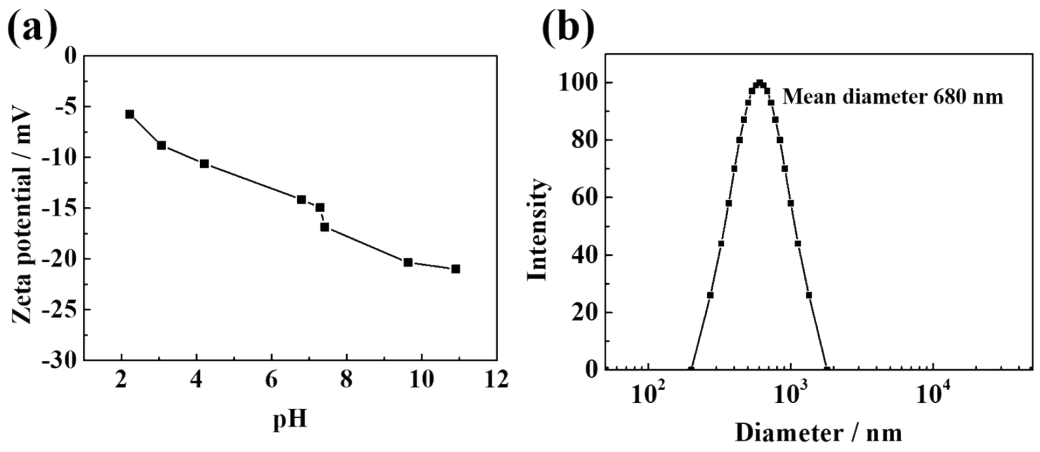

Figure S17. (a) Zeta potential *versus* pH and (b) particle size distribution of 0.1 wt.% montmorillonite particles dispersed in water at pH 7.

Figure S18. Digital photos of *n*-octane-in-water emulsions stabilized by montmorillonite particles alone immediately after preparation. [montmorillonite]/wt.% from left to right: 0.01, 0.05, 0.1, 0.5 and 1.0.

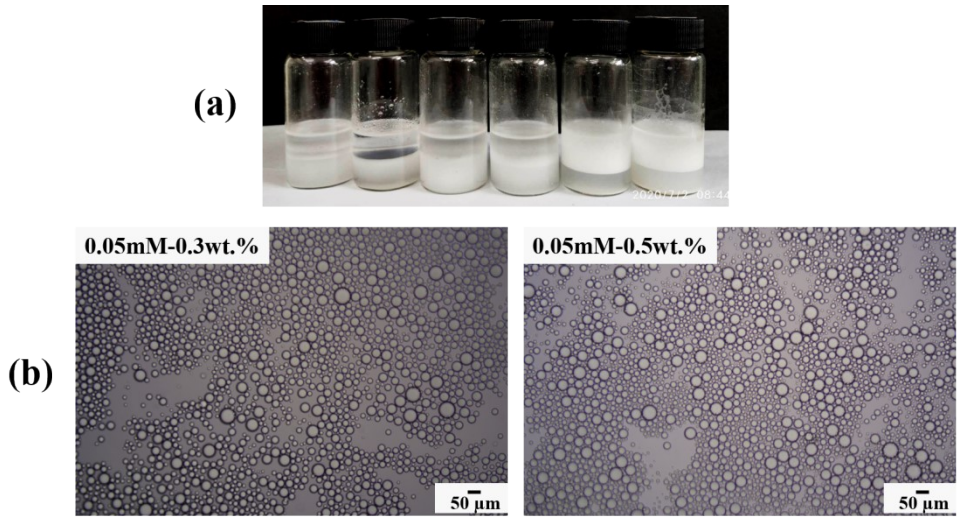

Figure S19. (a) Digital photos of *n*-octane-in-water emulsions stabilized by 0.05 mM NaDC in combination with different concentrations of montmorillonite. [montmorillonite]/wt.% from left to right: 0.005, 0.01, 0.05, 0.1, 0.3, 0.5. (b) Selected optical micrographs of the above emulsions with the concentration of NaDC and montmorillonite particles shown.

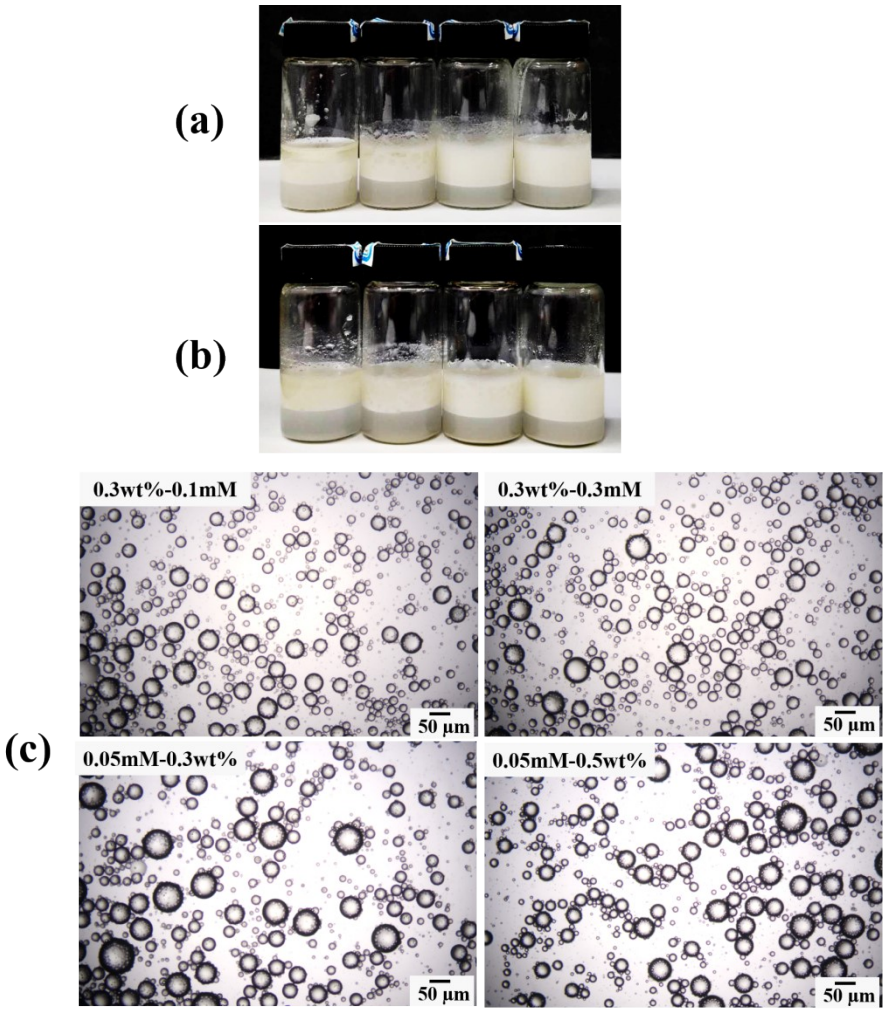

Figure S20. (a) Digital photos of soybean oil-in-water emulsions stabilized by 0.05 mM NaDC in combination with montmorillonite particles of different concentration. [montmorillonite]/wt.% from left to right: 0.05, 0.1, 0.3 and 0.5. (b) Digital photos of soybean oil-in-water emulsions stabilized by 0.3 wt.% montmorillonite particles in combination with NaDC of different concentration. [NaDC]/mM from left to right: 0.01, 0.05, 0.1 and 0.3. (c) Selected optical micrographs of emulsions with concentration of NaDC and montmorillonite particles shown.

Reference

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