# Supplementary Material:

# Pickering emulsions stabilized by carboxylated nanodiamonds over a broad pH range

Zhiwei Huang [a], Izabela Jurewicz [a], Edgar Muñoz [b], Rosa Garriga [c], Joseph L. Keddie [a, *]

[a] Department of Physics, Faculty of Engineering and Physical Sciences, University of Surrey, Guildford, GU2 7XH, UK
[b] Instituto de Carboquímica ICB-CSIC, Miguel Luesma Castán 4, 50018 Zaragoza, Spain
[c] Departamento de Química Física, Universidad de Zaragoza, 50009 Zaragoza, Spain

*E-mail: j.keddie@surrey.ac.uk

**Supplementary Material Index:**

**- Fig. S1**. A schematic diagram of the membrane emulsification system for oil-in-water emulsions.

**- Fig. S2**. The influence of injection rate during membrane emulsification on size distributions of emulsions stabilized by surfactant.

**- Fig. S3**. Schematic diagram of the method to measure the contact angle at the three-phase contact line of oil, ND coating, and water.

**- Fig. S4**. Schematic diagram to define the creaming index.

**- Fig. S5**. Schematic diagram of the method to measure the drying process of standard and β-carotene-containing ND Pickering emulsions.

**- Fig. S6**. AFM topographic image of the surface of an ND coating used to perform wettability studies by the three-phase contact angle method.

**- Fig. S7**. 'No surfactant' oil-in-water emulsions.

**- Fig. S8**. FTIR characterization of sunflower oil saponification.

**- Fig. S9**. Interfacial tensions of oil/water and oil/ND dispersion at pH 7.

**- Fig. S10**. Shaking stability of conventional emulsions and long-term stability of Pickering emulsions.

**- Fig. S11**. Optical microscope images of ND-stabilized emulsions after being stored for one year.

**- Fig. S12**. Optical microscope images of the Pickering emulsions prepared in 1 M NaCl and CaCl$_2$ solutions.

**- Calculation** of the number of ND in the shell of an oil droplet.

**- Video S1**. Shape changes and instability of a pH 10 NaOH aqueous drop (without ND) being immersed in sunflower oil for 15 min.

**- Video S2**. Effect of the addition of pH 12 buffer solution on the stability of ND Pickering emulsions.

**- Video S3**. The late stages of the drying of an ND Pickering oil-in-water emulsion with β-carotene as model active ingredient.
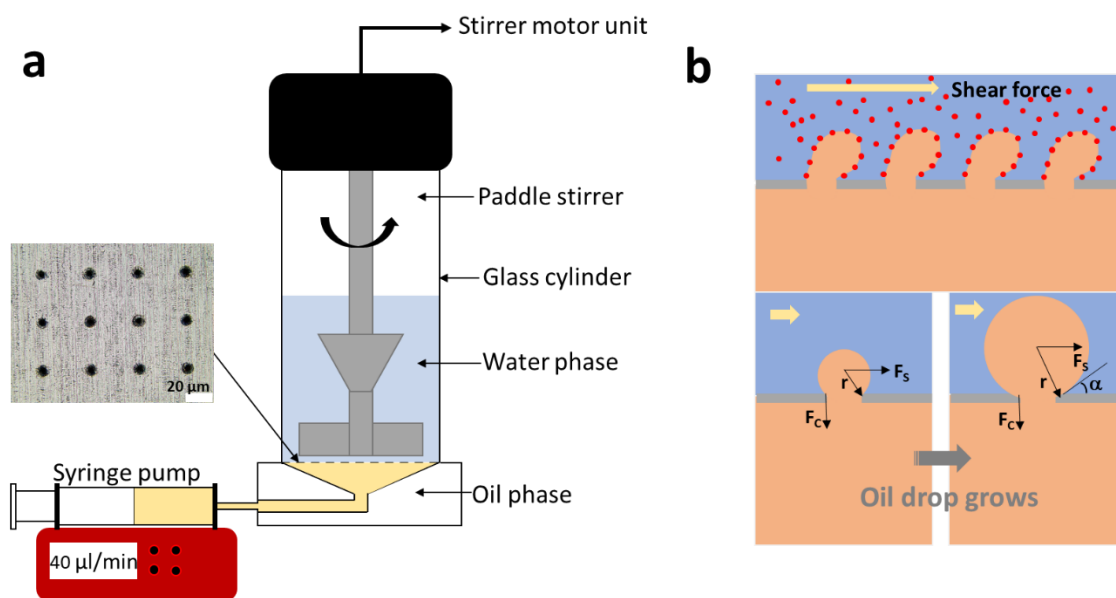
**Fig. S1**. (a) A schematic diagram of the membrane emulsification system for oil-in-water emulsions. The inset photograph shows a metal membrane where the pore diameter is 5 μm. (b) A schematic diagram showing how the emulsion droplets are formed, including a simplified force analysis of a single droplet on the surface of the membrane. At equilibrium, $M_{CZ} = F_S \times r \times cos\alpha$, where $F_S$ is the shear force, $r$ is the radius of the droplet, and α is the angle from the pore edge.

# The Influence of Injection Rate during Membrane Emulsification on Size Distributions of Emulsions Stabilized by Surfactant

## Experimental Method

Sunflower oil was injected into the water phase containing 20 mg/mL Tween 20 surfactant through 5 µm pore stainless steel membrane. The injection rate was increased from 40 µL/min to 400 µL/min in separate experiments. Microscope images of the resulting emulsions (Fig. S2 a – e) were obtained. Fig. S2f shows that only small difference in the average oil droplet size appeared. However, the coefficient of variation (CV) continuously increased from 8.6% (when the injection rate was 40 µL/min) to 32.16% (when the injection rate was 400 µL/min).
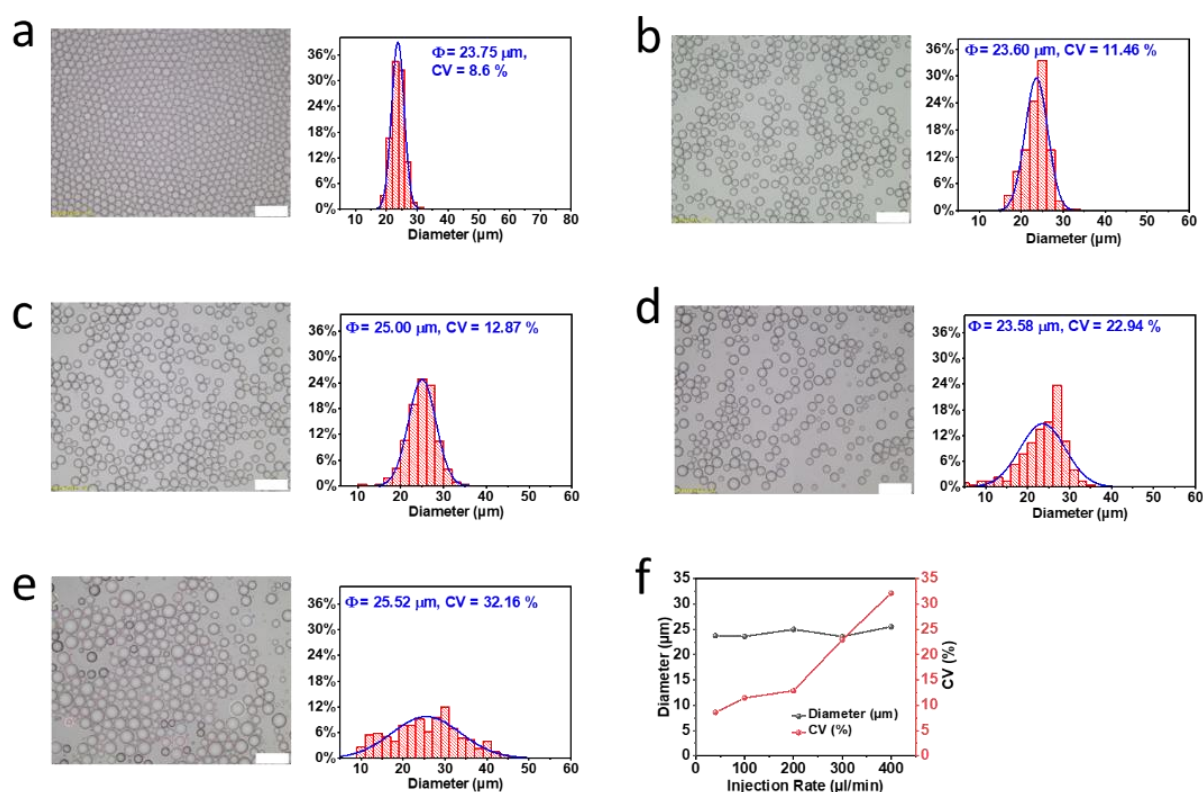


**Fig. S2**. Optical microscope images and histograms of oil-in-water emulsions stabilized by Tween 20 when the injection rate is (a) 40 µL/min, (b) 100 µL/min, (c) 200 µL/min, (d) 300 µL/min, (e) 400 µL/min. (f) Line chart shows the changes of size and CV of emulsion drops with increasing injection rates. The scale bars are 200 µm in all images.
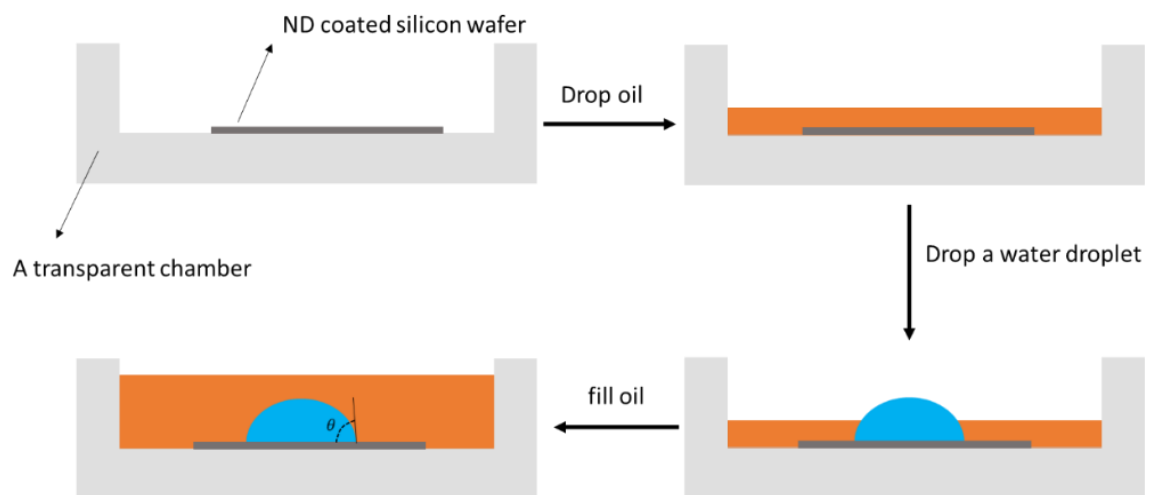
**Fig. S3**. Schematic diagram of the method to measure the contact angle at the three-phase contact line of oil, ND coating, and water.
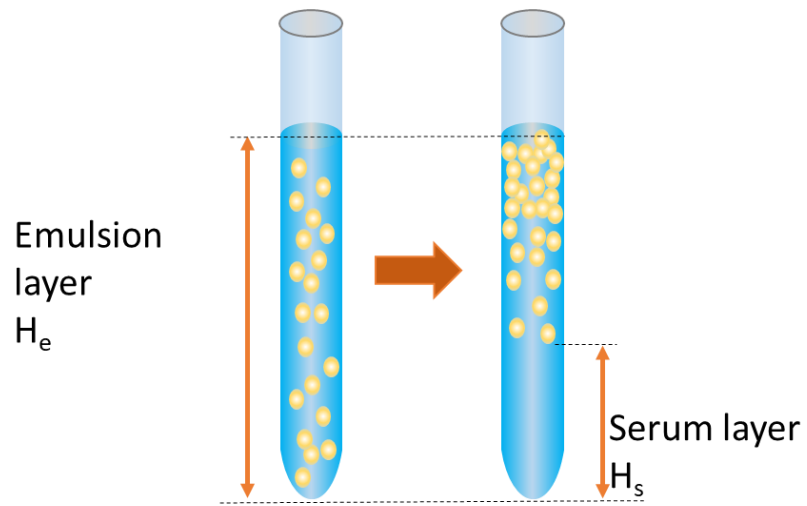
**Fig. S4**. Schematic diagram to define the creaming index as the thickness of the serum layer ($H_s$) divided by the thickness of the entire emulsion layer ($H_e$).
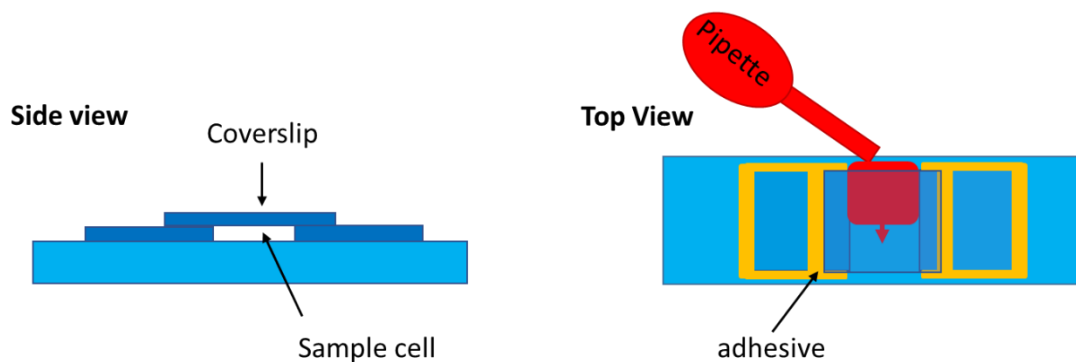
**Fig. S5**. Schematic diagram of the method to measure the drying process of standard and *β*-carotene- containing ND Pickering emulsions. The sample cell was constructed by stacking three coverslips on a glass microscope slide and sealing with an epoxy adhesive. Because of the capillary force, the sample cell was filled by the emulsion when it was dropped at the edge of the sample cell.
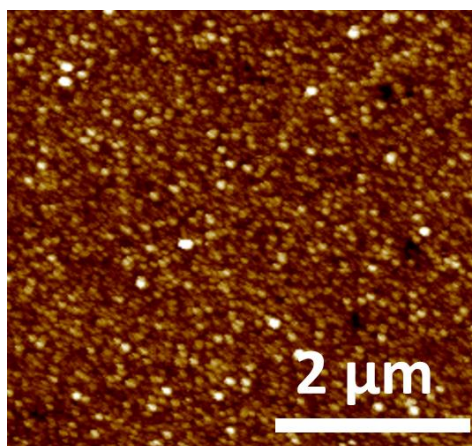


**Fig. S6.** An AFM topographic image of the surface of an ND coating deposited by spin-coating (at 3000 rpm) from a 5 mg/mL ND dispersion onto a Si substrate and used to perform wettability studies by the three-phase contact angle method.

**'No Surfactant' Oil-in-Water Emulsions**

Stable emulsions can be made by simply mixing pH 12 aqueous solutions with sunflower oil when no surfactants or ND particles are present. Oil was mixed with HCl solution (pH 2) and NaOH solution (pH 12) separately in vials. After shaking them for several seconds, an emulsion layer appeared in the NaOH solution, but only an oil layer was observed in the HCl solution. Subsequently, after keeping the vials static for 12 hours, the emulsion layer formed at pH 12 retained the same height in the NaOH solution, indicating a stable emulsion was prepared. The size of the oil droplets can be as large as the millimetre scale. This result can be explained by the saponification reaction at the interface of oil and aqueous alkaline solution. As a result of the saponification, anionic surfactants ($RCOO^-$) will be produced, where the hydrophilic heads $COO^-$ will be exposed to the surrounding aqueous media and the hydrophobic tails R will be in contact with oil. Thus, the oil drop is stabilized in aqueous media.
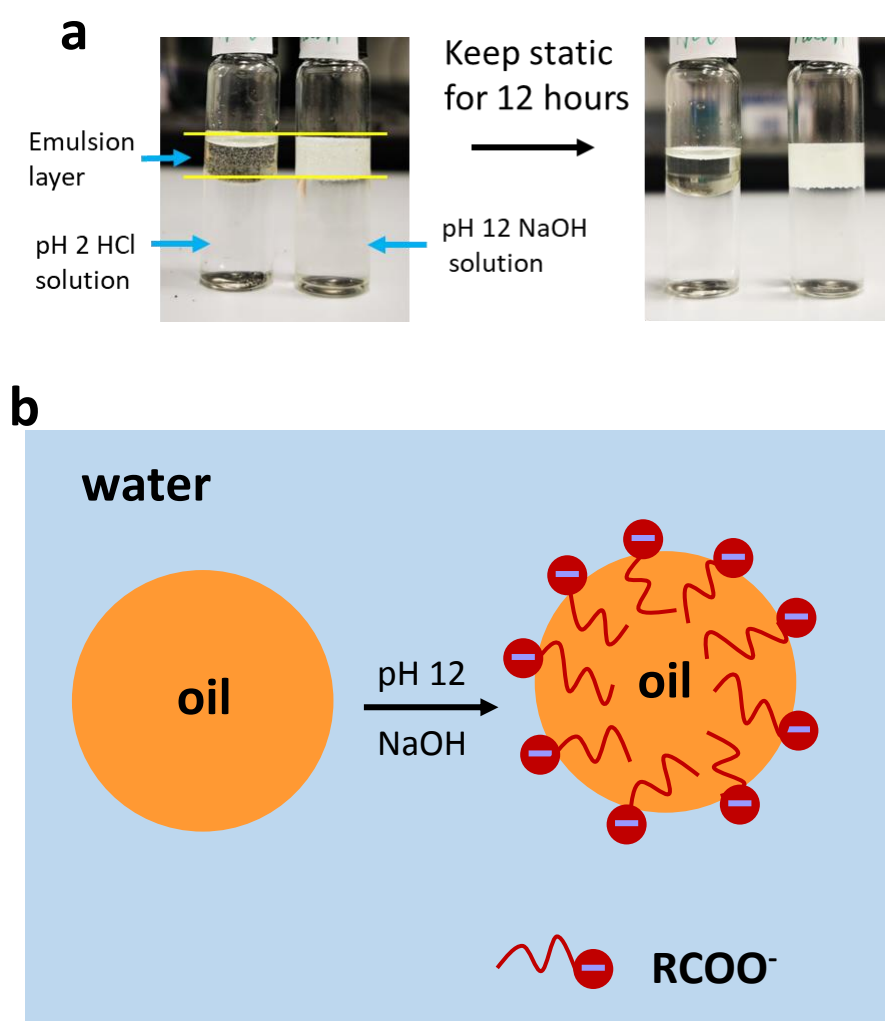


**Fig. S7**. (a) 'No Surfactant' Oil-in-Water Emulsions. Photographs showing oil mixed with pH 2 HCl solution and pH 12 NaOH solution by hand shaking, before (left) and after 12 hours of static ageing (right). (b) A schematic shows the saponification process.

## FTIR Characterization of Sunflower Oil Saponification

An effect related to saponification, called 'salting out', occurs when the fatty acid forms an insoluble (or poorly soluble) salt in the presence of cations at high concentration. Salting out is a very useful way to separate fatty acid salts (anionic surfactants) from mixtures of basic solutions and vegetable oil. Specifically, when adding some salt, such as NaCl, into an alkaline aqueous phase, a fatty acid salt will form and separate out from the oil interface into the water. It will finally phase separate from the aqueous phase as a result of the surfactant's reduced water solubility.[1]

An experiment was performed in which oil was mixed and sonicated with pH 12 buffer solution. The aqueous phase was collected and dried on a glass slide. A layer of white powder (*i.e.* the "carboxylate salt" or surfactant-like substance) was scraped off and was used for a transmission IR measurement.

IR Spectra in the wavenumber range of 4000-400 cm$^{-1}$ were recorded on an Agilent Technologies Cary 600 Series FT-IR spectrometer using Agilent Resolutions Pro software. Samples were analysed by attenuated total reflection (ATR). A blank measurement was subtracted for each sample measurement.

Spectra were normalized with respect to the intensity of the absorbance band at 1744 cm$^{-1}$ for stretching C=O (ester). The absorbance peak that appears at 1562 cm$^{-1}$ is specific to the COO$^{-}$ asymmetric stretching, and that of 868 cm$^{-1}$ can be assigned to glycerin,[2,3] which confirms the formation of saponified oil (anionic surfactant) and its removal to the aqueous phase.
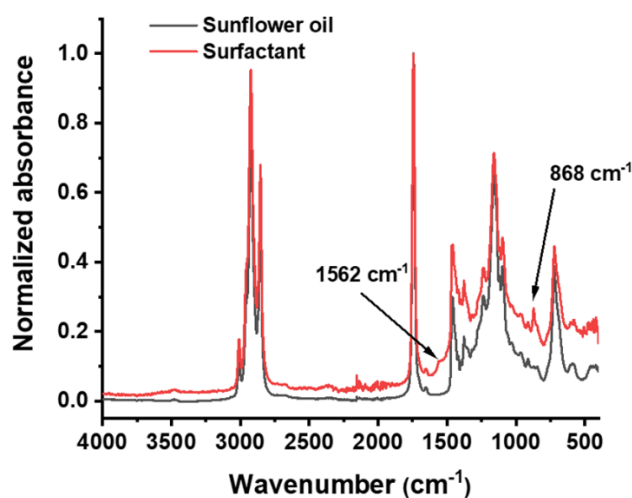


**Fig. S8**. FTIR spectra of oil and anionic surfactants produced by mixing pH 12 buffer with sunflower oil.

### References

[1] H. Schott and A. E. Royce, *J. Pharm. Sci.*, 1984, 73, 793–799.

[2] G. Poulenat, S. Sentenac, and Z. Mouloungui, Fourier-Transform Infrared Spectra of Fatty Acid Salts - Kinetics of High-Oleic Sunflower Oil Saponification. *Journal of Surfactants and Detergents*, 6(4), October 2003, 305.

[3] M.E.S. Mirghani, Y.B. Che Man, S. Jinap, B.S. Baharin, and J. Bakar. FTIR Spectroscopic Determination of Soap in Refined Vegetable Oils. *JAOCS*, 79(2), 2002, 111-116.

**Interfacial Tensions of Oil/Water and Oil/ND Dispersion**
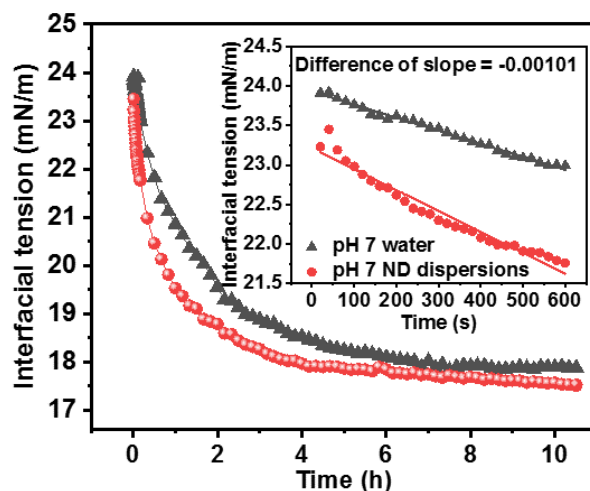


**Fig. S9.** The interfacial tension of water and oil (gray triangles) compared to that of an ND dispersion in DI water (0.5 mg/mL) and oil (red circles) The inset figure shows the differences of the slopes of the dynamic interfacial tension during the initial 600 s.

The interfacial tension (IFT) of the sunflower oil and DI water, shown in Fig. 9, decreases strongly during the first several hours of the measurement before starting to stabilise. We attribute this downward trend to the presence of trace impurities in the oil or possibly to chemical changes in the oil. Although the value for the IFT of oil with the ND dispersion in water is slightly lower in Figure S9, the difference is comparable to the uncertainty of the measurement, on the order of 1 mN/m. There is a small difference in the slopes of IFT *versus* time during the first initial 600 s (presented in the inset) for the two systems, but the differences are within the resolution of the measurement.

We attempted measurements of the interfacial tension of the oil and ND dispersions at lower pH values of 2 and 4. However, at the lower pH, the size of the ND clusters is larger and the zeta potentials are lower (see Fig. 2), so that the NDs are subject to sedimentation during the measurement, leading to unreliable measurements.

**Shaking Stability of Conventional Emulsions and Long-Term Stability of Pickering Emulsions**
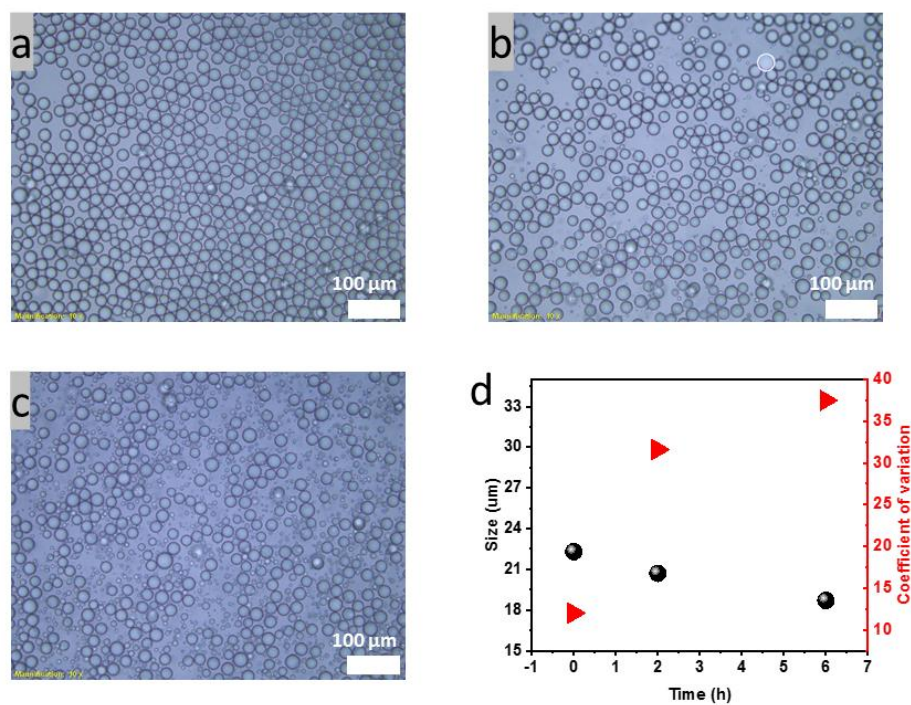


**Fig. S10**. Influence of the time of mechanical shaking on the mean oil droplet size and CV of emulsions prepared by membrane emulsification using Tween 20 as the emulsifier. (a) Original emulsion. (b) After 2 h of shaking. (c) After 6 h of shaking. (d) The mean oil droplet size (black circles) and CV (red triangles) in the emulsions at the three shaking times.
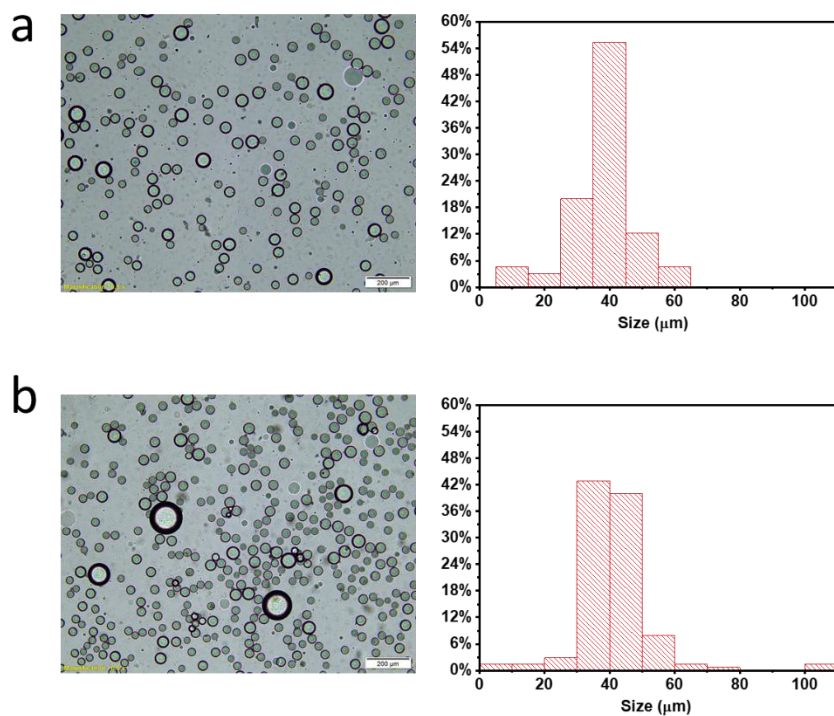
**Fig. S11**. Optical microscope images of ND-stabilized emulsions after being stored for one year. The emulsions were prepared by membrane emulsification (injection rate of 40 µl/min and membrane size of 5 µm) using buffered ND solutions with (a) pH 1.5 and (b) pH 4. The scale bars are 200 µm in each image. Histograms of the size distribution are shown in the panels on the right side. The emulsion in (a) has a mean size of 38 µm and CV of 26.6%; and (b) has a mean size of 41 µm and CV of 28.4%.
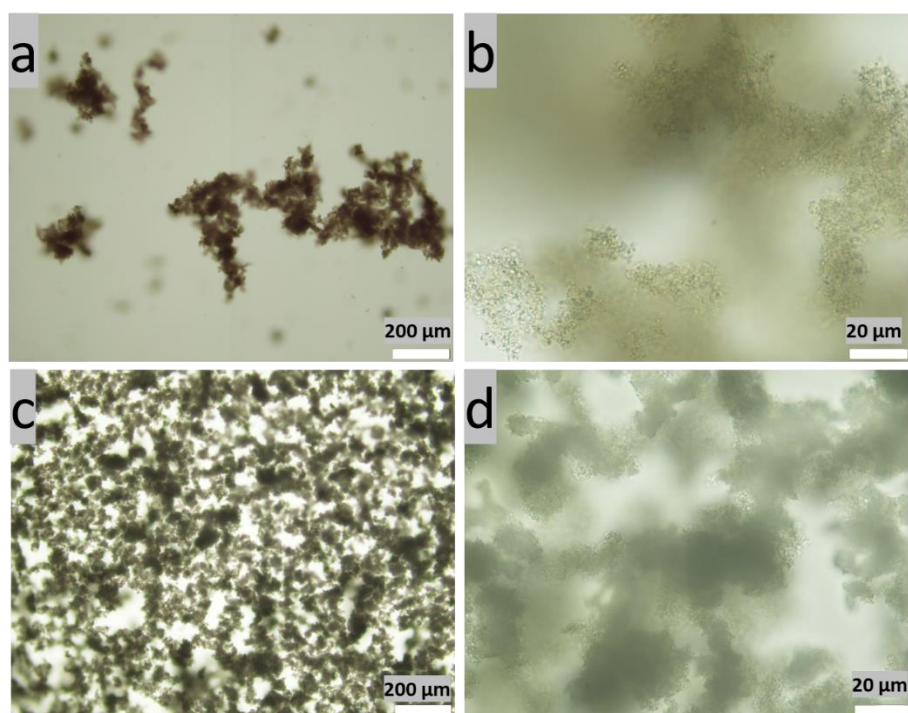
**Fig. S12**. Optical microscope images of the Pickering emulsions prepared in (a, b) 1 M NaCl solutions and (c, d) 1 M $CaCl_2$ solutions. The scale bars are shown in the lower right side of each image.

**Calculation of the Number of ND in the Shell of an Oil Droplet**

Based on the two assumptions below, a calculation of the number of ND needed to create an interfacial shell around oil drops is made. This number is compared to the number of ND in 0.1 mg/mL ND dispersions used in an emulsion.

**Assumptions**

1. Our DLS shows that the ND does not exist as primary particles in water at a pH of 4, where emulsions are made. Instead, it exists in aggregates of with a diameter, $D$, of 33 nm. We assume that these aggregates stabilize the emulsions. We estimate that the density of the ND aggregates is 70% of solid primary ND particles. The density of detonation ND particle is reported to be 1.6 g/cm³ [4]. Considering space-filling by hard spheres, the density of ND aggregates is then *estimated* to be

$\rho_{ND} = 1.6 \, \text{g}/cm^3 \times 70\% = 1.12 \text{g}/cm^3.$

2. The three-phase contact angle $\theta$ is equal to 90°, and hence the ND is assumed to be exactly half in the water and half in the oil. Then, a spherical emulsifier particle with diameter, $D$, will be modelled as a disc of diameter $D$ at the oil/water interface. (For an oil-in-water emulsion, $\theta$ is expected to be < 90°, but its value should be close to 90°, allowing this approximation.)

3. All ND at the interface are hexagonally packed in a monolayer and no ND remains in the water phase. The packing fraction $f$ of the interfacial area is set to be $0.91 (f = \frac{\pi}{2\sqrt{3}} \approx 0.91)$ which applies to the hexagonal close packing of discs.

A drawing of the model of a stabilised oil drop is shown here. The ND aggregates are assumed to be packed into a dense shell around the oil drop.

The volume of one oil drop: $V = \frac{4}{3}\pi R^3$, where $R = 18$ µm for emulsions obtained by the membrane emulsification method, measured by optical microscopy.



An oil drop of radius, $R$, that is fully covered with close-packed spherical ND aggregates of diameter, $D$.

The total volume of oil drops is

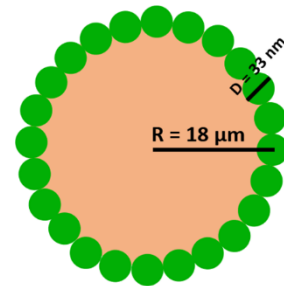$$V_{oil} = 3 \, mL = 3 \, cm^3 = 3 \times 10^{12} \, µm^3$$

The number of oil drops in this volume is $N = \frac{V_{oil}}{\frac{4}{3}\pi R^3}$

The surface area of an individual oil drop is $S_{oil} = 4\pi R^2$

The total area of all oil drops will be $A_{TOT} = N \times S_{oil}$

The diameter of a ND aggregate (drawn as the green particles) is $D = 33$ nm according to DLS.

The cross-sectional area of an ND aggregate (a disc at the hemisphere) is $A_{ND} = \pi(\frac{D}{2})^2$

**The total number of ND aggregates** needed for a densely-packed shell layer around all oil droplets is

$$N_{TOT} = \frac{f \times A_{TOT}}{A_{ND}} = \frac{f \times \frac{V_{oil}}{\frac{4}{3}\pi R^3} \times 4\pi R^2}{\pi(\frac{D}{2})^2} = \frac{12 f V_{oil}}{\pi R D^2} = 4.7 \times 10^{14}$$

In total, an emulsion, there is a mass of $m = 3$ mg of ND in a 30 mL dispersion in water (for a ND concentration of 0.1 mg/mL).

The total volume of ND is $V_{TOT} = \frac{m}{\rho} = 1.3 \times 10^{-3} \; cm^3 = 1.3 \times 10^{18} \; nm^3$

The occupied volume of a single ND aggregate is $V_{ND} = \frac{4}{3}\pi(\frac{D}{2})^3 = \frac{\pi D^3}{6}$.

**The number of ND aggregates** in a 30 mL dispersion is

$$N_{ND} = \frac{V_{TOT}}{V_{ND}} = \frac{6m}{\pi\rho D^3} = 1.9 \times 10^{14}$$

We find that $N_{ND}$ is approximately within a factor of two of $N_{TOT}$. The estimates suggest that a ND dispersion with a concentration of 0.1 mg/mL contains approximately 40% of the number of ND aggregates required to make a densely packed shell around the oil droplets - provided that all of the ND aggregates adsorb at the oil/water interface. However, we note that we have made numerous assumptions.

A ND concentration greater than 0.3 mg/mL should ensure that there is a sufficient number of ND aggregates to make a densely-packed layer of NDs around every oil drop of the size observed.


**Particle coverage of the oil drops formed by ultrasound compared to membrane emulsification**

Take the emulsion prepared in pH 2 by sonication as an example.

The oil drop diameter from sonication is $D_S = 3$ µm.

The oil drop diameter from membrane emulsification is $D_m = 36$ µm.

One large oil drop can be divided into $N = \frac{\frac{4}{3}\pi(\frac{D_m}{2})^3}{\frac{4}{3}\pi(\frac{D_S}{2})^3} = (\frac{D_m}{D_S})^3$ small oil drops.

Compared to the large oil drop, the total surface area is increased by a factor $\frac{N \times 4\pi(\frac{D_S}{2})^2}{4\pi(\frac{D_m}{2})^2} = \frac{D_m}{D_S} = 12$ times.

The surface coverage on the smaller, sonicated oil drops is $\frac{1}{12}$ of the surface coverage of the large oil drops from membrane emulsification.

As is calculated above, 0.1mg/mL ND can cover 40% of the oil droplets from membrane emulsification.

So we estimate that the coverage of the sonicated drops at the same ND concentration is $40.4\% \times \frac{0.5}{0.1} \times \frac{1}{12} = 3.4\%$

When ND concentration is increased to 0.5 mg/mL, which is used in our work, the surface coverage is thus $3.4\% \times 5 = 17\%$. In consideration of the numerous approximations, we will express this value as 20%.