Supporting Information

Pickering Emulsions of Alumina Nanoparticles and Bola-type Selenium Surfactant yield a fully Recyclable Aqueous Phase

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No. Pages: 18

No. Schemes: 1

No. Figures: 23

No. Tables: 5

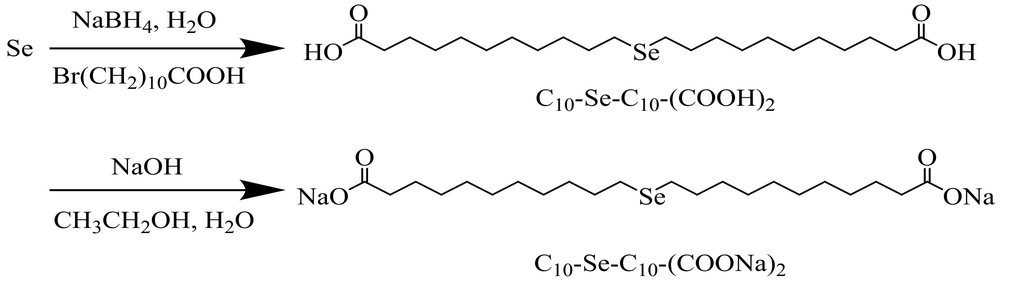
No. Equations: 3

1. Materials

Hydrophilic alumina (Al_2O_3) nanoparticles with a purity > 99.8% were purchased from Sigma, with a primary diameter of 13 nm and a Brunauer-Emmett-Teller (BET) surface area of 85-115 m^2/g according to the supplier. SEM and TEM images of the particles are shown in Figure S1. Sodium hydroxide, hydrochloric acid, hydrogen peroxide (30%), anhydrous sodium sulphite, selenium, 11-bromoundecanoic acid and sodium borodeuteride were analytical grade from Sinopharm Chemical Reagent Co., Ltd. Pure water (18.2 MΩ cm, pH = 6.1 (25 °C)) was purified using a Millipore pure water system (Merck Millipore, Shanghai). Dihendecylcarboxylic acid sodium selenide, C_{10}-Se-$C_{10}\cdot(COONa)_2$, was synthesized in our lab. (Scheme S1).

2. Synthesis of C_{10}-Se-$C_{10}\cdot(COONa)_2$ surfactant

The C_{10}-Se-$C_{10}\cdot(COONa)_2$ surfactant was synthesized as described in the literature.[1]



Scheme S1. Synthetic route for C_{10}-Se-$C_{10}\cdot(COONa)_2$ surfactant.

3. Preparation and characterization of emulsions

Alumina nanoparticles (0.1 wt.%) were dispersed in 7 cm^3 aliquots of surfactant solution or pure water (pH = 10) using an ultrasonic probe and then equal volumes of octane were added to prepare emulsions followed by homogenization using an ultraturrax homogenizer (8000 rpm, 2 min). The type of emulsion was determined by the drop test and by staining. Nile red was used to color the oil. Optical micrographs of the emulsion were recorded by a VHX-1000 microscope system (Keyence Co.). Redox reaction of the Pickering emulsion was performed by adding H_2O_2 or Na_2SO_3. For example, demulsification can be observed within a few seconds after a trace amount (20 μL) of H_2O_2 (20%) was added to the Pickering emulsion and a stable emulsion forms again with re-homogenization (Figure S20). The emulsification of the oxidized system containing particles and oxidized surfactant can be achieved by addition of 20 μL of aqueous Na_2SO_3 (6.53 M) with stirring for 2 h followed by homogenization (8000 rpm, 2 min).

4. Adsorption of C_{10}-Se-C_{10}·$(COONa)_2$ at alumina-water interface

The adsorption isotherm of C_{10}-Se-C_{10}·$(COONa)_2$ at the alumina particle-water interface was measured by the depletion method. Alumina nanoparticles (0.1 wt.%) were dispersed in aqueous C_{10}-Se-C_{10}·$(COONa)_2$ solutions of different concentration for 24 h at 25 °C to reach equilibrium. The surface tension of the dispersion was then measured by the du Noüy ring method. The equilibrium concentration of surfactant was calculated from the surface tension of the C_{10}-Se-C_{10}·$(COONa)_2$ solution without alumina particles as calibration.

5. Zeta potential

A series of C_{10}-Se-C_{10}·$(COONa)_2$ solutions of different concentration containing alumina nanoparticles (0.1 wt.%) were prepared using an ultrasonic probe and equilibrated in an incubator at 25 °C for 24 h. The zeta potentials were measured using a Brookhaven Zeta PLAS instrument. The average error is ± 0.5 mV.

6. ICP-MS

ICP-MS was carried out using a Thermo Fisher Scientific iCAP TQ instrument. The sample was digested with 5 vol.% nitric acid solution, and a series of concentrations of selenium solution were then prepared. The blank nitric acid solution and the sample solution were injected into the instrument and the concentration of Se element in the digestion solution was obtained according to the signal response values of the element to be tested and the internal standard element. The operating conditions of the ICP-MS are listed in Table S4. The calibration curve was drawn using ^{89}Y as the internal standard element to obtain $y = 21.444x-9.276$ ($R^2 = 0.998$) (Figure S14). The content of Se element in the sample was calculated according to equation S3. The limits of detection (LOD) and limits of quantitation (LOQ) were 0.0007 ppb and 0.002 ppb, respectively, which were determined as suggested by the International Union of Pure and Applied Chemistry (IUPAC). [2,3]

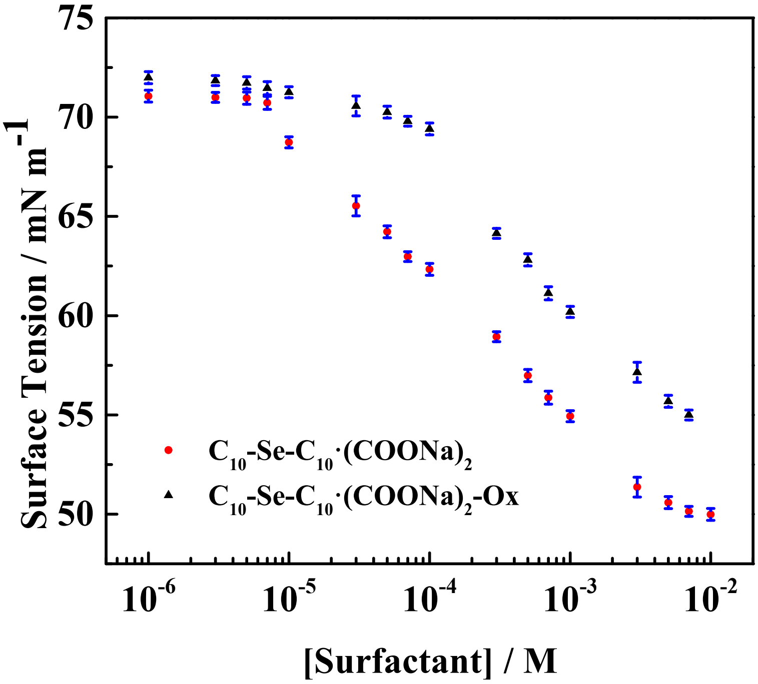


Figure S1. Surface tension of C_{10}-Se-$C_{10}\cdot(COONa)_2$ and C_{10}-Se-$C_{10}\cdot(COONa)_2$-Ox as a function of concentration at 25 °C.

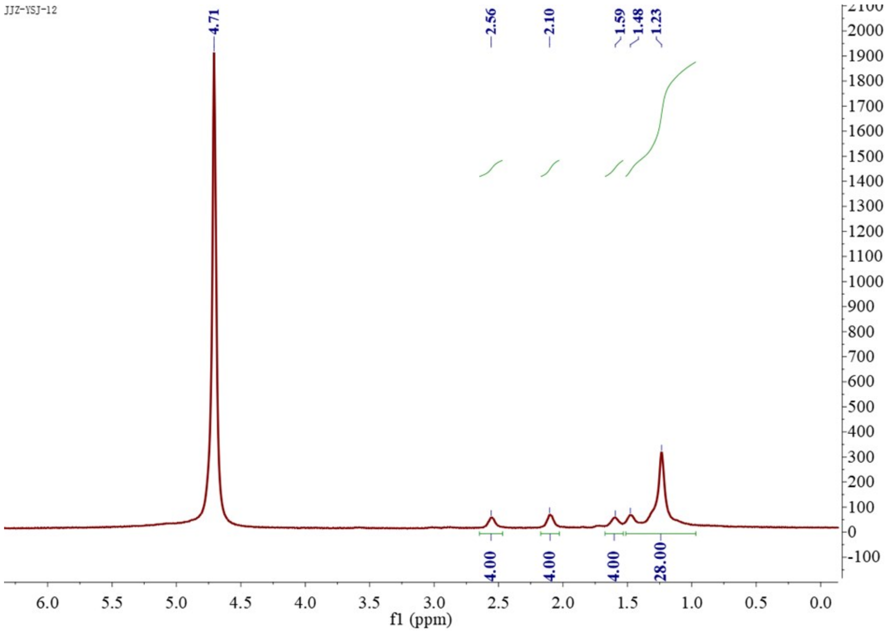


Figure S2. ^{1}H NMR spectrum of C_{10}-Se-$C_{10}\cdot(COONa)_2$.

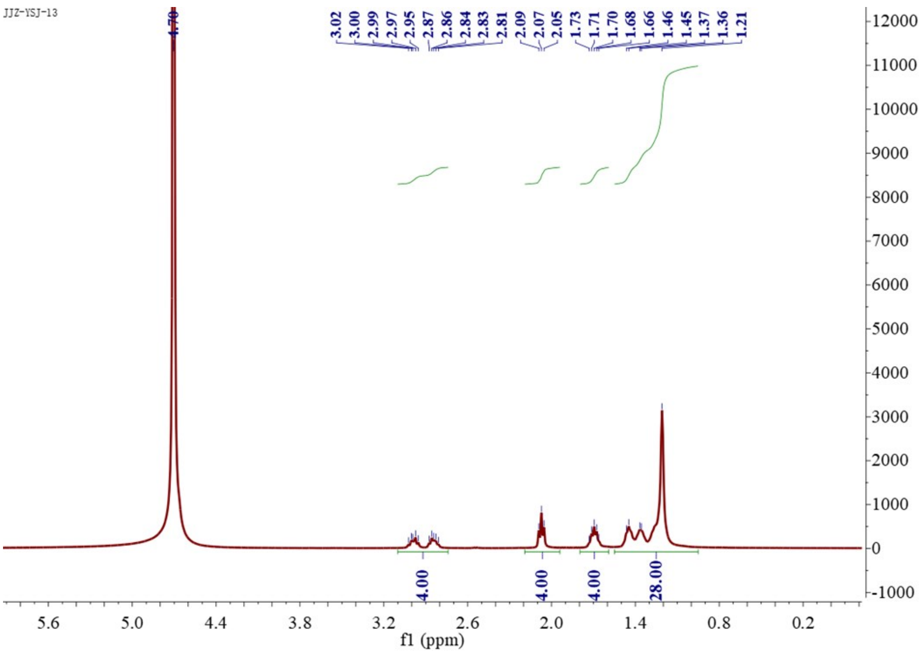


Figure S3. ^{1}H NMR spectrum of C_{10}-Se-$C_{10}\cdot(COONa)_2$-Ox.

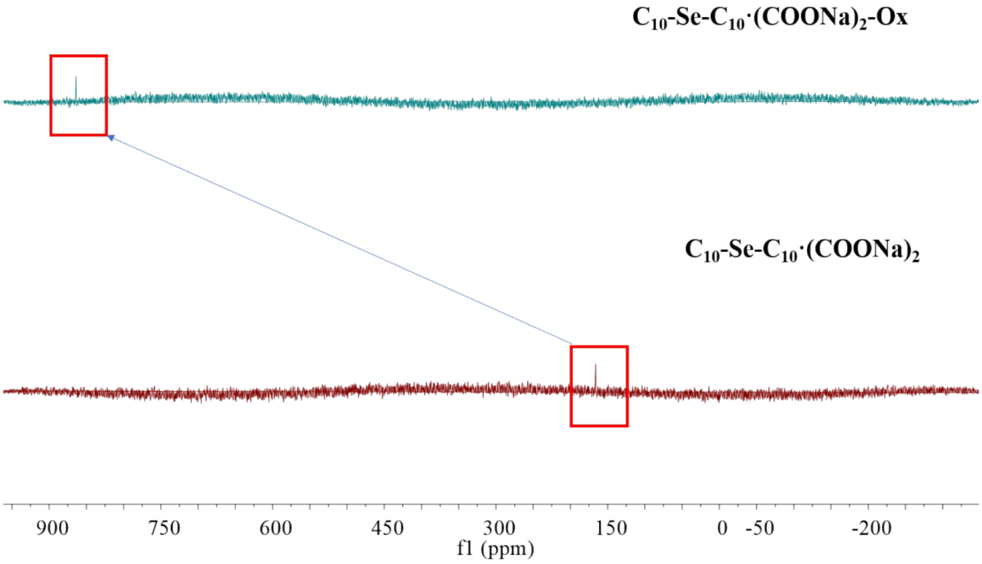


Figure S4. ^{77}Se NMR spectrum of C_{10}-Se-$C_{10}\cdot(COONa)_2$.

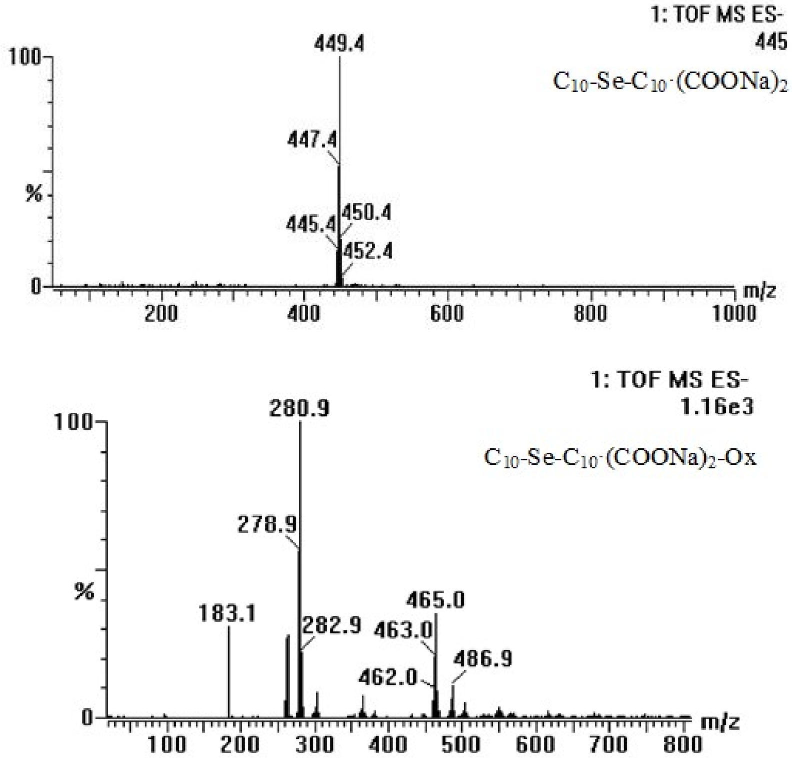


Figure S5. Mass spectrometry of C_{10}-Se-$C_{10}\cdot(COONa)_2$ and C_{10}-Se-$C_{10}\cdot(COONa)_2$-Ox.

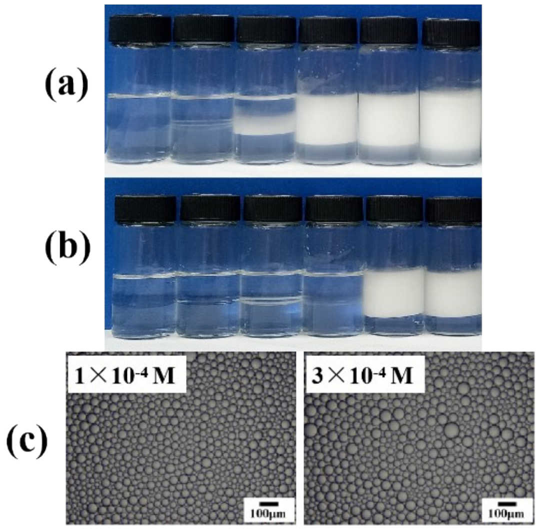


Figure S6. Digital photos (a and b) and selected micrograph (c) of octane-in-pure water emulsions stabilized by C_{10}-Se-$C_{10}\cdot(COONa)_2$ surfactant alone taken (a) immediately and (b, c) 24 h after preparation. Surfactant concentration in aqueous phase (for a and b) from left to right: 0, 1×10^{-5}, 3×10^{-5}, 6×10^{-5}, 1×10^{-4}, 3×10^{-4} M and as shown for (c).

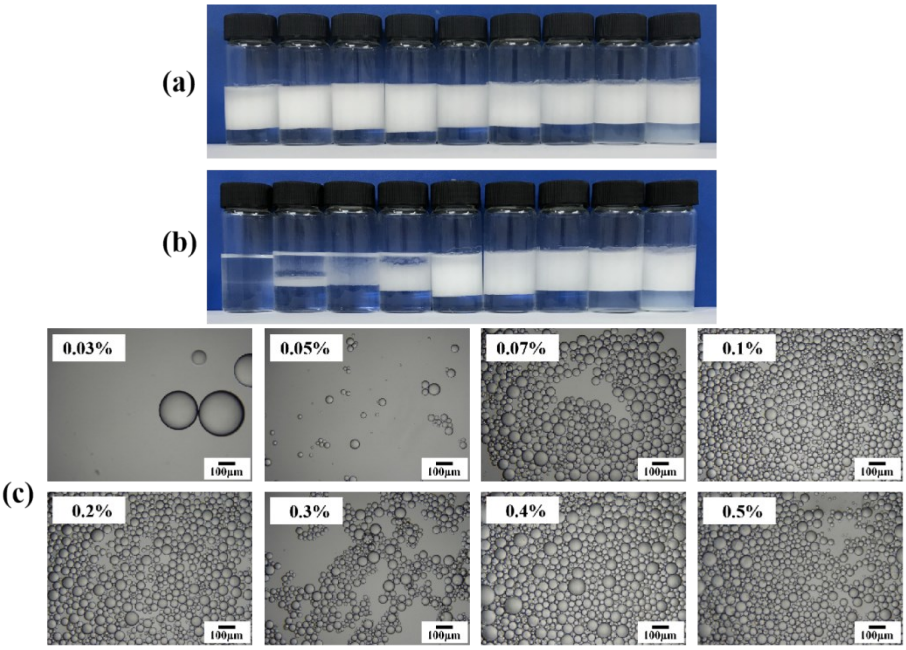


Figure S7. Digital photos of emulsions stabilized by 3×10^{-5} M C_{10}-Se-$C_{10}\cdot(COONa)_2$ surfactant in combination with alumina nanoparticles at pH = 10 taken: (a) 0 h and (b) 24 h after preparation. Alumina nanoparticle concentration in water from left to right: 0.01, 0.03, 0.05, 0.07, 0.1, 0.2, 0.3, 0.4, 0.5 wt.%. (c) Selected micrographs of emulsions corresponding to (b).

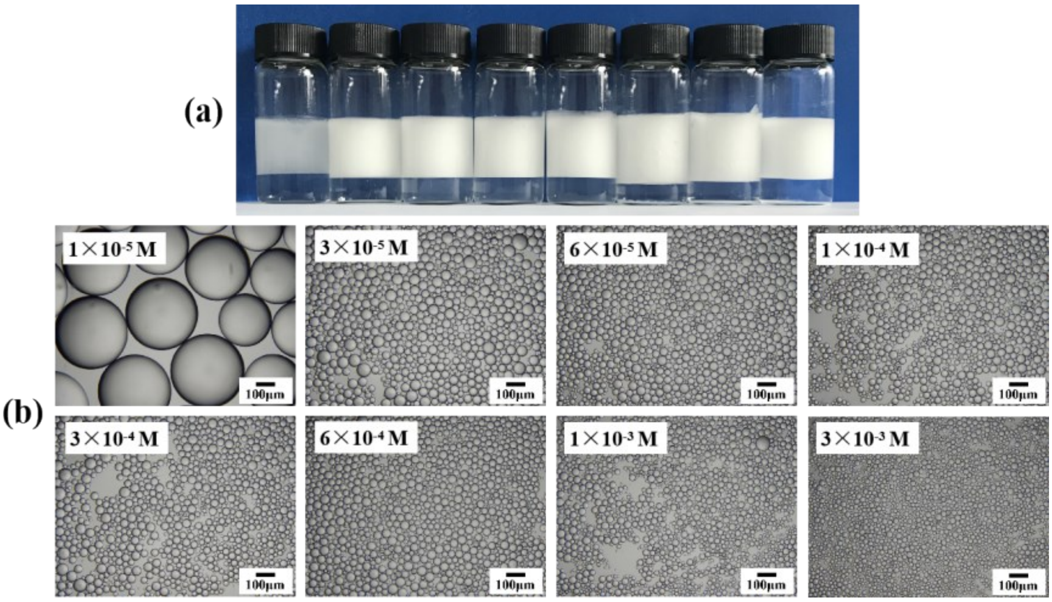


Figure S8. Digital photos of Pickering emulsions stabilized by 0.1 wt.% alumina nanoparticles and C_{10}-Se-$C_{10}\cdot(COONa)_2$: (a) 1 month after preparation. [surfactant] in aqueous phase from left to right: 1×10^{-5}, 3×10^{-5}, 6×10^{-5}, 1×10^{-4}, 3×10^{-4}, 6×10^{-4}, 1×10^{-3}, 3×10^{-3} M. (b) Corresponding optical micrographs.

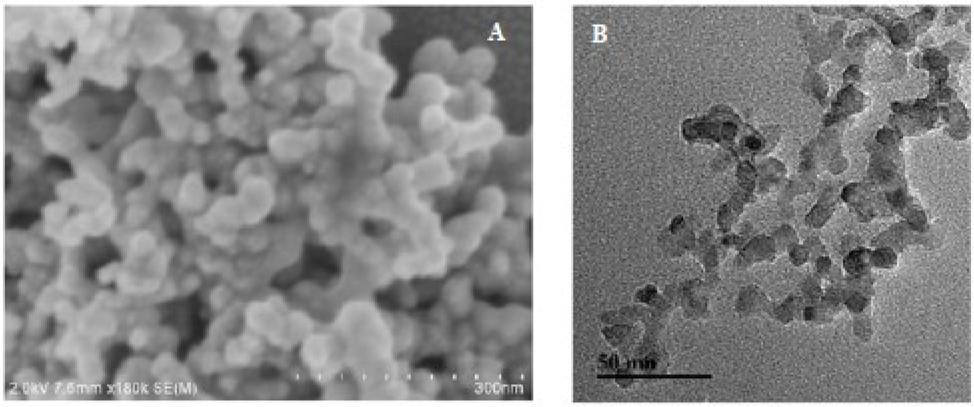


Figure S9. (A) SEM image of alumina nanoparticles forming aggregates of average diameter (d_{av}) 192 nm, (B) TEM image of alumina nanoparticles of primary diameter 13 nm.

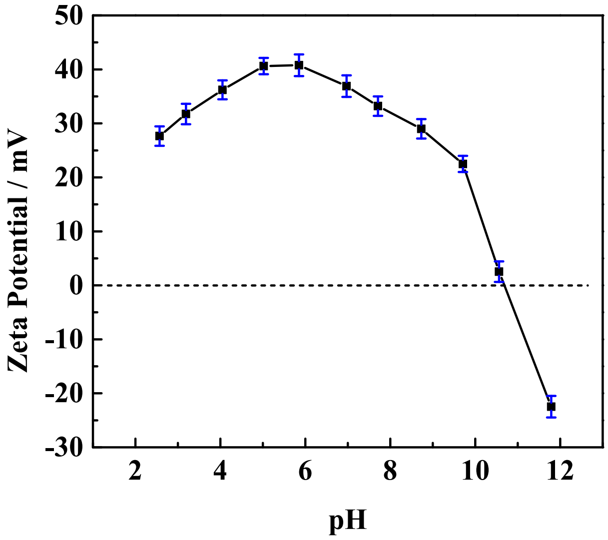


Figure S10. Zeta potential of alumina nanoparticles (0.1 wt.%) dispersed in water of different pH at 25 °C.

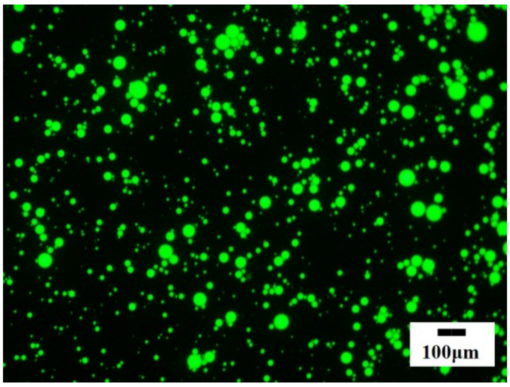


Figure S11. Fluorescence microscopy image of octane-in-water Pickering emulsion stabilized by 1×10^{-3} M C_{10}-Se-C_{10}·$(COONa)_2$ in combination with 0.1 wt.% alumina nanoparticles with the oil phase stained with Nile red.

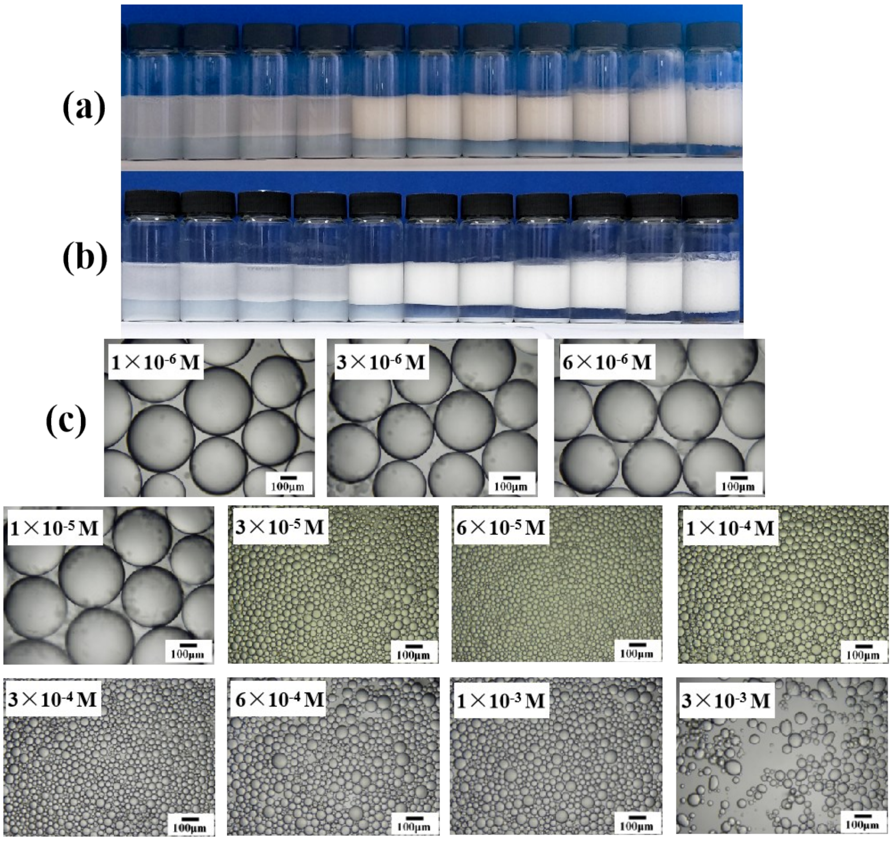


Figure S12. Digital photos (a and b) and micrographs (c) of Pickering emulsions stabilized by 0.5 wt.% alumina nanoparticles in combination with C_{10}-Se-C_{10}·$(COONa)_2$ at different concentrations (from left to right for a and b): 1×10^{-6}, 3×10^{-6}, 6×10^{-6}, 1×10^{-5}, 3×10^{-5}, 6×10^{-5}, 1×10^{-4}, 3×10^{-4}, 6×10^{-4}, 1×10^{-3}, 3×10^{-3} M and as shown for (c), taken (a) immediately and (b and c) 24 h after preparation.

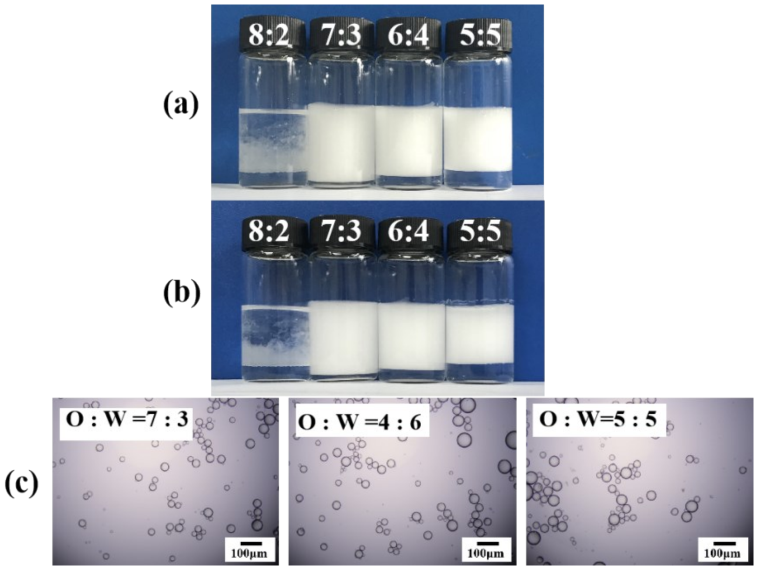


Figure S13. Digital photos (a and b) and corresponding micrographs (c) of Pickering emulsions stabilized by 0.1 wt.% alumina nanoparticles in combination with 3×10^{-5} M C_{10}-Se-C_{10}·$(COONa)_2$ at different oil:water ratios as shown, taken (a) immediately and (b and c) 24 h after preparation.

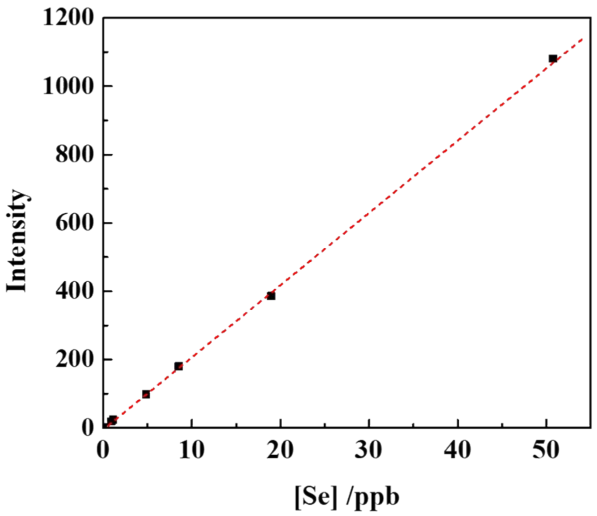


Figure S14. Calibration curve for the determination of Se using ICP-MS.

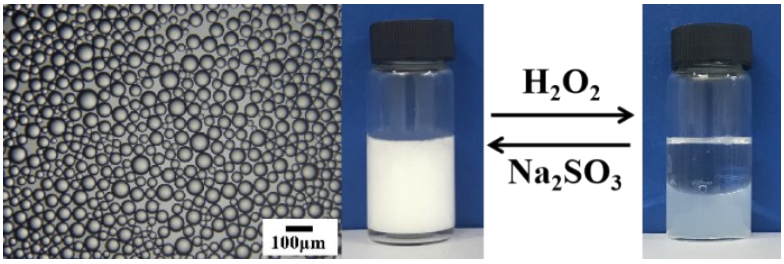


Figure S15. Digital photos and micrograph of toluene-in-water (7 mL/7 mL) Pickering emulsion stabilized by 0.1 wt.% alumina nanoparticles in combination with 3×10^{-4} M C_{10}-Se-C_{10}·$(COONa)_2$ undergoing switching on/off cycles induced by addition of H_2O_2/Na_2SO_3.

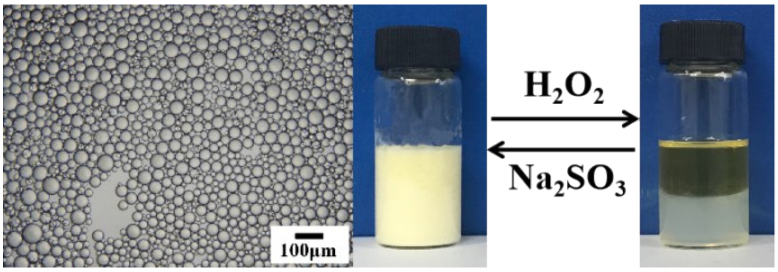


Figure S16. Digital photos and micrograph of olive oil-in-water (7 mL/7 mL) Pickering emulsion stabilized by 0.1 wt.% alumina nanoparticles in combination with 3×10^{-4} M C_{10}-Se-C_{10}·$(COONa)_2$ undergoing switching on/off cycles induced by addition of H_2O_2/Na_2SO_3.

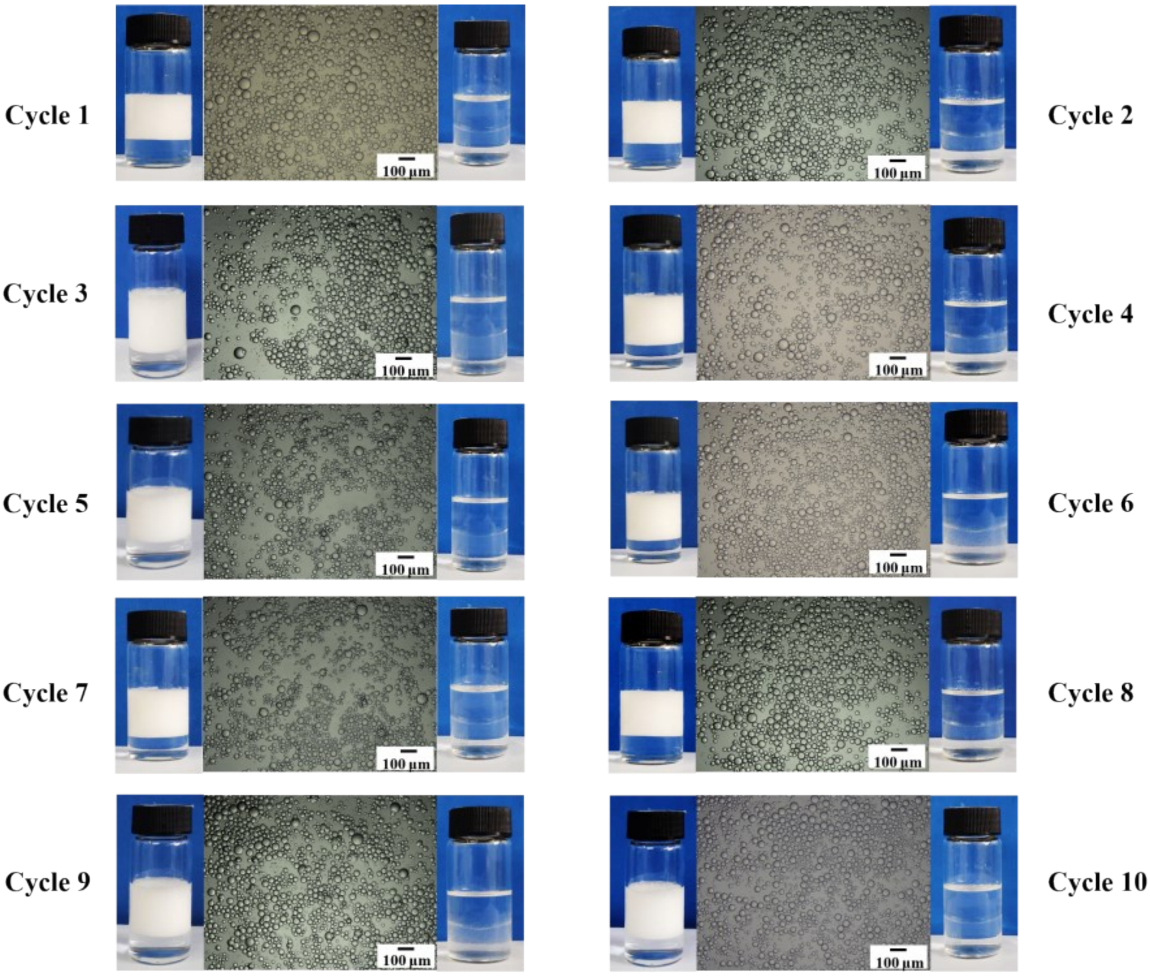


Figure S17. Digital photos and micrographs of Pickering emulsions stabilized by 0.1 wt.% alumina nanoparticles in combination with 3×10^{-5} M C_{10}-Se-C_{10}·$(COONa)_2$

undergoing ten switching on/off cycles induced by addition of H_2O_2/Na_2SO_3. The ICP-MS of Se element in oil phase after ten cycles is 0.0035 ppb.

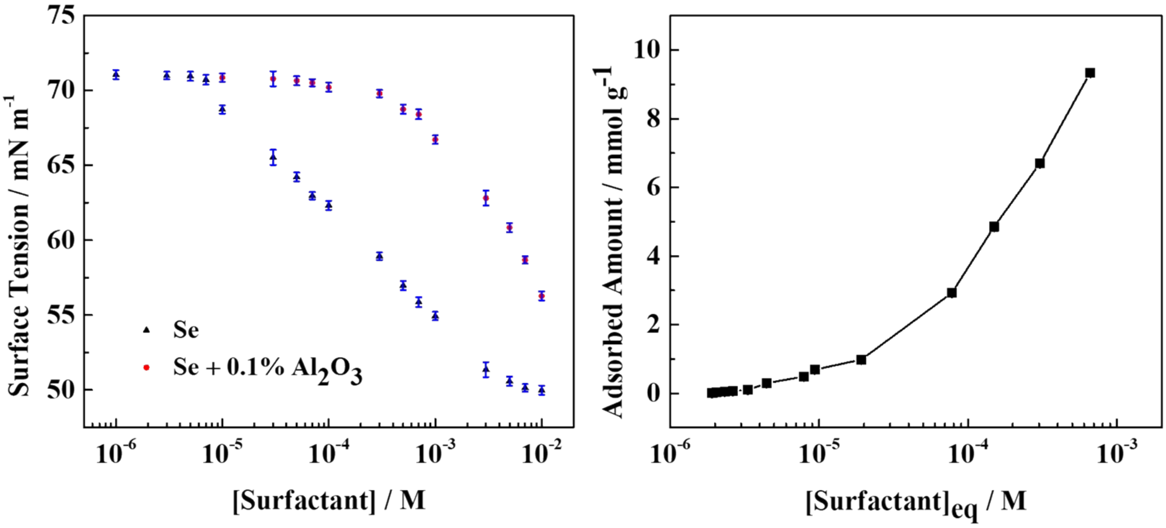


Figure S18. (a) Surface tension of aqueous solutions of C_{10}-Se-C_{10}·$(COONa)_2$ without and with 0.1 wt.% alumina nanoparticles as a function of initial surfactant concentration at 25 °C. (b) Adsorbed amount of C_{10}-Se-C_{10}·$(COONa)_2$ at the alumina-water interface as a function of equilibrium surfactant concentration at 25 °C (average error ± 0.001 mmol g^{-1}).

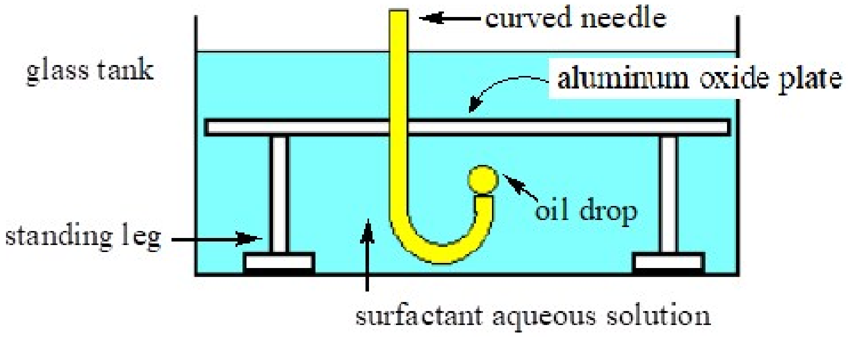


Figure S19. Schematic diagram of setup to measure the contact angle of an oil drop under an aqueous phase on an aluminium oxide plate.

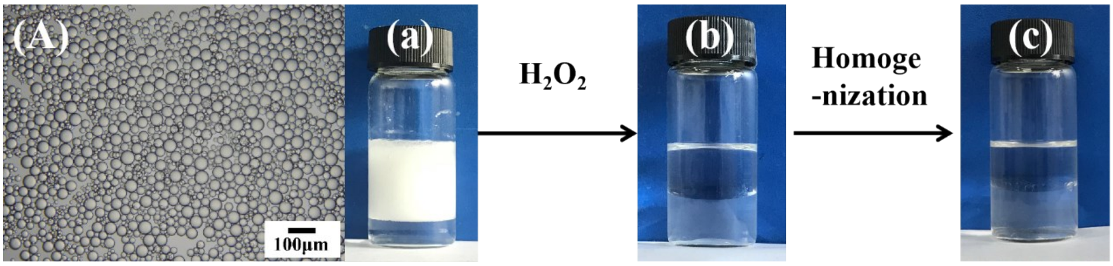


Figure S20. Digital photos and micrographs of Pickering emulsions stabilized by 3×10^{-5} M C_{10}-Se-C_{10}·$(COONa)_2$ surfactant and 0.1 wt.% alumina nanoparticles undergoing oxidation reaction: (a) initial emulsion, (b) after addition of H_2O_2, (c) oxidized system after re-homogenization.

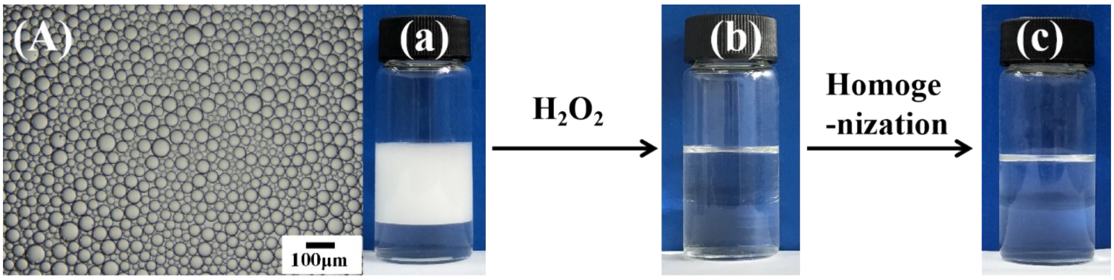


Figure S21. Digital photos and micrograph of emulsions stabilized by 1×10^{-4} M C_{10}-Se-C_{10}·$(COONa)_2$ surfactant alone undergoing oxidation reaction: (a) initial emulsion, (b) after addition of H_2O_2, (c) oxidized system after re-homogenization.

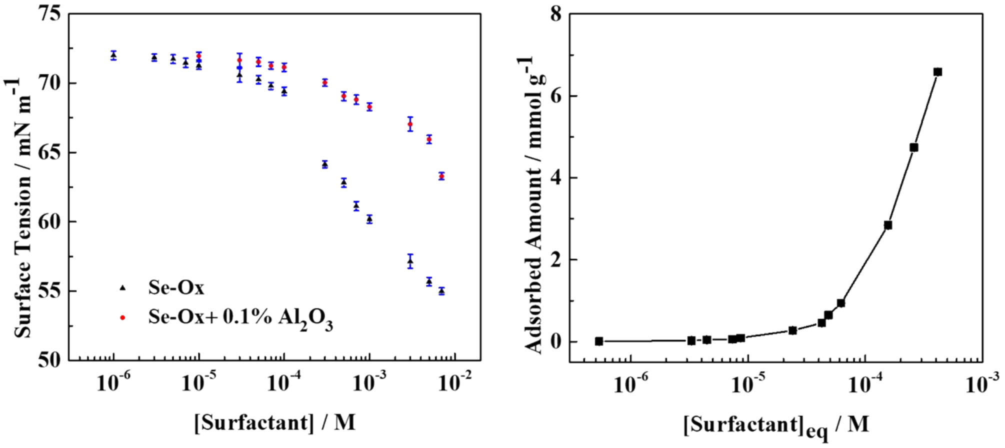


Figure S22. (a) Surface tension of aqueous solutions of C_{10}-Se-C_{10}·$(COONa)_2$-Ox without and with 0.1 wt.% alumina nanoparticles as a function of initial surfactant concentration at 25 °C. (b) Adsorbed amount of C_{10}-Se-C_{10}·$(COONa)_2$-Ox at the alumina-water interface as a function of equilibrium surfactant concentration at 25 °C (average error ± 0.001 mmol g^{-1}).

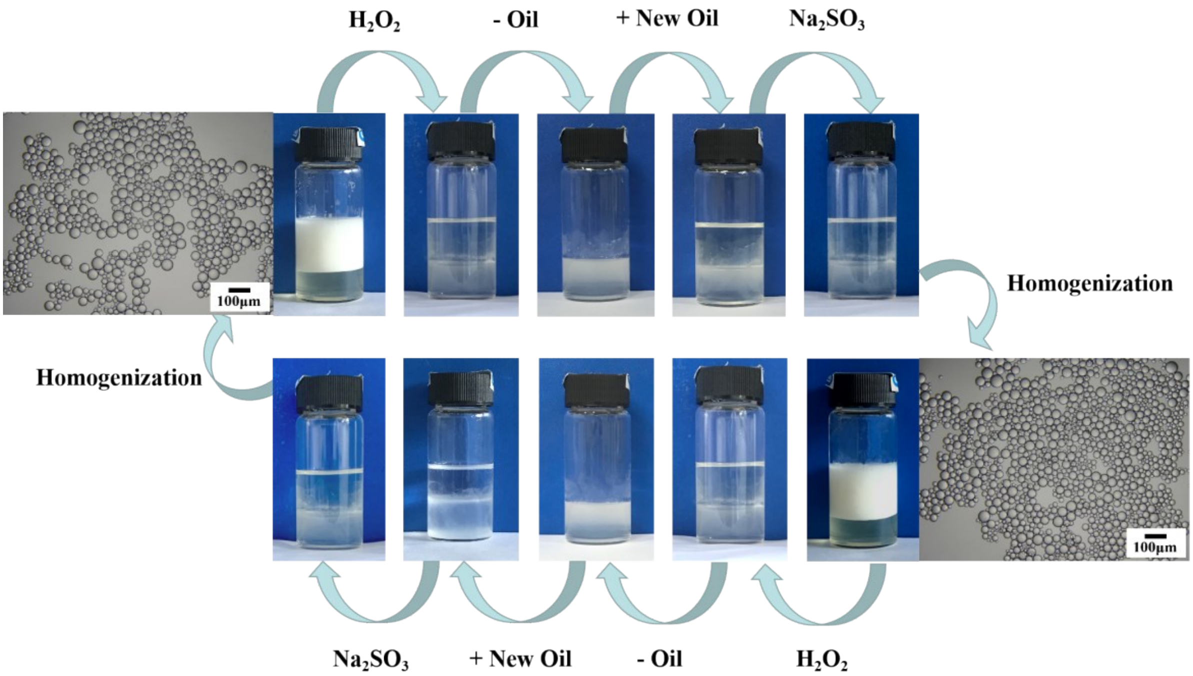


Figure S23. Digital photos and micrographs of gasoline-in-water (7 mL/7 mL) Pickering emulsion stabilized by 0.1 wt.% alumina nanoparticles in combination with $3\text{x}10^{-4}$ M C_{10}-Se-$C_{10}\cdot(COONa)_2$ undergoing switching on/off cycles induced by addition of H_2O_2/Na_2SO_3, in which the initial oil was removed and new oil was added. The residual amount of surfactant and aluminum in oil is 0.008 and 0.18 ppb, respectively.

Table S1. Advantages and disadvantages of demulsification methods.

Method	Advantage	Disadvantage
pH*	Fast separation	Chemical contamination of emulsion; hazardous to environment
Membrane*	Low chemical contamination of emulsion; high oil removal efficiency	Fouling; requires cleaning process; relatively low permeate flux
Electrical*	No chemical contamination of emulsion; environmental credibility;	Need high electric voltage; formation of secondary droplets in water-in-oil emulsions
Microwave irradiation*	Fast heating of emulsion; no chemical contamination of emulsion	Need additional chemical demulsifier to reach the desired separation efficiency
Biological *	Environmental compatibility and biodegradability	Might be sensitive/vulnerable to operational/treatment conditions
Current	Fast separation; recyclable	Al_2O_3 nanoparticles might be

method	emulsifier (surfactant and nanoparticles); low chemical contamination of emulsion; lower energy cost than conventional heating or centrifugation	hazardous to humans or environment

* Zolfaghari, R.; Fakhru'l-Razi, A.; Abdullah, L.C.; Elnashaie, S.S.E.H.; Pendashteh, A. *Sep. Purif. Technol.* 2016, **170**, 377-407

Table S2. Minimum concentration of surfactant to stabilize conventional emulsions to coalescence.

Surfactant	Concentration/M	Ref.
CTAB	$> 0.9 \times 10^{-3}$	Landfester, K.; Bechthold, N.; Tiarks, F.; Antonietti, M. *Macromolecules* 1999, **32**, 2679-2683
SDS	$> 1 \times 10^{-3}$	Rong, F.; Liu, D.; Hu, Z. *Pet. Sci. Technol.* 2018, **36**, 2157-2162
FTMA(ferrocenyl)	$>3 \times 10^{-3}$	Takahashi, Y.; Koizumi, N.; Kondo, Y. *Langmuir* 2016, **32**, 7556-7563

Table S3. Time for complete demulsification with different amounts of H_2O_2 at pH 10 (3×10^{-5} M C_{10}-Se-$C_{10}\cdot(COONa)_2$, 0.1 wt.% alumina nanoparticles).

Dose of H_2O_2	Time
10 μL (10 wt.%)	6 h
10 μL (20 wt.%)	60 min
15 μL (20 wt.%)	15 min
20 μL (20 wt.%)	50 s

Table S4. Interfacial tension between fresh octane or separated octane after demulsification and pure water.

Oil type	Oil-water interfacial tension (mN/m)
Fresh	50.3
First separated	50.3
Second separated	50.3
Third separated	50.3
Fourth separated	50.3

Fifth separated	50.3
Sixth separated	50.4
Seventh separated	50.3
Eighth separated	50.4
Ninth separated	50.3
Tenth separated	50.3

Table S5. Operating conditions for the determination of Se by ICP-MS.

Condition	Value
Power	1550 W
Sample uptake rate	0.65 mL min^{-1}
Plasma gas flow rate	15 L min^{-1}
Carrier gas flow rate	0.8 L min^{-1}
Sampling depth	8 mm
Nebulizer temp.	140 °C
Flow rate of added He	5 mL/min
Peltier-cooler multipass condenser temp.	2 °C
Determination points per peak	3
No. repeats	3
CeO^+/Ce^+	< 0.2%
Internal standard	^{89}Y
m/z	78

Calculating adsorption of surfactant at particle-water interface:

$$A = V (C_0 - C) / m \qquad \text{(eq. S1)}$$

where A is adsorbed amount of surfactant on particle surfaces, V is the volume of aqueous surfactant solution, C_0 is the concentration of surfactant before adsorption, C is the equilibrium concentration of surfactant after adsorption, m is the weight of alumina nanoparticles.

The surface coverage of droplets by particles (φ) can be estimated through:

$$\varphi = \frac{Mx \times s}{mS_t} \times 100\% \qquad \text{(eq. S2)}$$

where M is the total mass of silica nanoparticles in the emulsion, x is the mass fraction of silica adsorbed on the surface of oil droplets, s is largest area per bare silica particle on the surface of droplets, m is the mass per silica particle and S_t is the total interfacial area of oil droplets (assuming all of the droplets in the emulsion to be spherical and the radius is the median obtained from light scattering).

The content of Se element was calculated according to the following formula:

$$X = \frac{(\rho - \rho_0) \times V \times f}{m \times 1000} \qquad \text{(eq. S3)}$$

where X is the content in the sample in mg/kg or mg/L, ρ is the mass concentration (μg/L) of the tested element in the sample solution, ρ_0 is the mass concentration of the tested element in the sample blank solution (μg/L), V is the volume of the sample digestion fluid (mL), f is the dilution multiple, m is the weight or volume of the sample (g or mL).

References

1. Jiang, J.; Zhang, D.; Yin, J.; Cui, Z. Responsive, switchable wormlike micelles for CO_2/N_2 and redox dual stimuli based on selenium-containing surfactants. *Soft Matter* **2017**, *13*, 6458-6464.
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3. Kallam, S.R.; Srikanth, J.; Prakash, K.V. Development and Validation of an Inductively Coupled Plasma Mass Spectrometry (ICP-MS) Method for the Determination of 17 Trace Metals in Ingenol Mebutate (API), *IOSR J. Pharm. Biol. Sci.* **2016**, *11*, 6-11.