

Pickering emulsions responsive to CO₂/N₂ and light dual stimuli at ambient temperature

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ABSTRACT

A dual stimulus-responsive *n*-octane-in-water Pickering emulsion with CO₂/N₂ and light triggers is prepared using negatively charged silica nanoparticles in combination with a trace amount of dual switchable surfactant, 4-butyl-4-(4-N,N-dimethylbutoxyamine) azobenzene bicarbonate (AZO-B4) as stabilizers. On one hand, the emulsion can be transformed between stable and unstable at ambient temperature rapidly *via* the N₂/CO₂ trigger, and on the other hand a change in droplet size of the emulsion can occur upon light irradiation/re-homogenization cycles without changing the particle/surfactant concentration. The dual responsiveness thus allows for a precise control of emulsion properties. Compared with emulsions stabilised by specially synthesized stimuli-responsive particles or by stimuli-responsive surfactants, the method reported here is much easier and requires relatively low concentration of surfactant ($\approx 1/10$ cmc), which is important for potential applications.

INTRODUCTION

Pickering emulsions, which are stabilised solely by colloidal particles, have been known for more than a century.¹⁻⁸ Such emulsions can be super-stable against coalescence due to the adsorption of colloid particles at the interface of two immiscible liquids such as oil and water, which renders emulsions very stable compared with those stabilised by surfactants.⁵ Studies on Pickering emulsions are therefore important in both understanding the fundamentals and developing potential applications.⁶

In some practical applications, such as fossil fuel production, oil transport and emulsion polymerization, emulsions need to be temporarily stabilised and subsequently demulsified. The

super stability of Pickering emulsions is thus desired initially but unwanted later due to difficulties in demulsification. In this case, switchable or stimuli-responsive Pickering emulsions, which have a controllable stability on demand, are therefore desirable and have received considerable attention in recent years.^{7,8} For this purpose the colloid particles used as stabilizers at a range of fluid interfaces should be convertible between surface-active and surface-inactive in response to environmental triggers. Various triggers such as pH,⁹⁻¹⁴ temperature,¹⁵⁻¹⁸ magnetic field,¹⁹⁻²¹ CO₂,²²⁻²⁴ specific ion concentration^{25, 26} and light irradiation have been reported.²⁷⁻³⁰ Among these triggers CO₂ is low cost, environmentally benign, easily removed and thus makes systems free of contamination.³¹⁻³³ However, the destabilisation of CO₂-responsive systems has usually to be carried out at high temperature (65°C).²² Light irradiation is another superior trigger without the need to add chemicals, and the wavelength, polarization direction and intensity of the light can be easily controlled. With this trigger, spiropyran-conjugated particles have been synthesized and used to prepare responsive Pickering emulsions.²⁷ However, the multi-step synthesis of the particles is complicated.

Recently, many attempts have also been reported on multi-responsive Pickering emulsions, where the combination of multiple stimuli widens the controllable range or improves the degree of precision for a given system. Pickering emulsions or particle-stabilised foams responding to dual triggers such as pH-temperature,³⁴⁻³⁷ magnetic field-temperature,³⁸⁻⁴⁰ pH-magnetic field⁴¹ and temperature–ionic strength⁴² have been investigated. In addition, Lee and Klajn⁴³ have recently reported on aqueous dispersions of metallic nanoparticles co-functionalised with UV and CO₂-sensitive ligands. However, the reversible conversion of the particles relies on simultaneous stimuli of UV irradiation and CO₂ addition, and no responsive phenomenon was observed when either stimulus was applied alone.

Herein we report a novel dual stimulus-responsive Pickering emulsion stabilised by silica nanoparticles in combination with a trace amount of a dual switchable surfactant, 4-butyl-4-(4-N,N-dimethylbutoxyamine) azobenzene bicarbonate, abbreviated as AZO-B4 (Scheme 1), where the dual triggers of CO₂/N₂ and light employed by the switchable surfactant can be transferred to silica nanoparticles through *in situ* hydrophobization in water.

The molecule of AZO-B4 contains both a charged amine group and an azobenzene group, which are CO₂/N₂-sensitive and photo-active, respectively. Bubbling an aqueous solution with N₂ or air converts the amphiphilic ammonium bicarbonate (surface-active form) to an uncharged tertiary amine (surface-inactive form), whereas bubbling the latter solution with CO₂ enables protonation back to its surface-active form. The interconversion can be monitored by measuring the conductivity of the aqueous solution (Figure S1). On the other hand, the azobenzene group can be easily photo-isomerized between *cis* (more polar) and *trans* (less polar) states upon UV or blue light irradiation, respectively,⁴⁴⁻⁴⁹ which has been introduced into surfactant molecules, *e.g.* AzoTAB,^{47,48} for stabilising photo-controlled aqueous foams. The photo-conversion can be observed by measuring the UV–Vis spectra (Figure S2), and both the critical micelle concentration, cmc (1.0×10^{-3} M) and the surface tension at the cmc, γ_{cmc} (29.1 mN m⁻¹) of *trans*-AZO-B4 are lower than those of *cis*-AZO-B4 (2.0×10^{-3} M and 34.7 mN m⁻¹ respectively, Figure S3).

EXPERIMENTAL

Materials

Fumed silica nanoparticles (HL-200, purity > 99.8%, primary particle diameter \approx 20 nm, Brunauer-Emmett-Teller (BET) surface area = 200 ± 20 m²/g) were provided by Wuxi Jinding Longhua Chemical Co., China. Octane (purity > 98%) was purchased from Sinopharm Chemical Reagent Co., China. High purity N₂ and CO₂ were provided by Wuxi Xinnan Chemical Gas Co. Ltd. The dual switchable surfactant AZO-B4 was synthesized in-house using the procedure described in the Supporting Information. Pure water with a resistance of 18.2 M Ω cm and a pH of 6.1 at 25 °C was produced from a simplicity pure water system (Merck Millipore, Shanghai).

Preparation and characterization of dispersions and emulsions

Silica nanoparticles were dispersed in pure water or surfactant solution using an ultrasonic probe (JYD-650, Shanghai) of tip diameter 0.6 cm operating at an output of 50 W for 1 min. For preparing emulsions, equal volumes (7 cm³) of aqueous phase with either surfactant or silica nanoparticles or both and oil were put in a glass vessel of volume 25 cm³ (7.5 cm (h) \times 2.5 cm (d)) followed by homogenization at 7,000 rpm for 2 min using an Ultraturrax homogenizer (IKA T18 basic, S18N-10G head). The particle and surfactant concentrations are expressed as weight percent (wt.%) and moles per litre (M) relative to the water phase, respectively. The emulsion type was determined using the drop test,⁵⁰ and micrographs of the emulsion droplets were recorded using a VHX-1000 microscope system (Keyence Co.).

Light irradiation

On a macroscopic scale, an emulsion (2 mL) was placed in a quartz tube and then irradiated by UV or visible light in a dark room at 20 °C (Figure S4(a)). The UV light was from a UV-100D point light (9 W) which has a diameter of 10 mm and a wavelength of 365 ± 5 nm. The blue light was from a LED light (9 W) with a wavelength of 436 nm. On a microscopic scale,

several droplets of emulsion were placed on a glass slide and subsequently irradiated with UV light (wavelength = 365 ± 5 nm) from 1 cm above as illustrated in Figure S4(b).

Surface tension

The air-water surface tension of the surfactant solution with and without particles was measured using the du Noüy ring method at 25 °C using a tensiometer as described elsewhere.⁵⁰

Zeta potential

The zeta potentials of 0.1 wt.% silica nanoparticles ultrasonically dispersed in surfactant solutions were measured at 25 °C using a Brookhaven Zeta PLAS instrument 24 h after dispersion.

Adsorption of AZO-B4 at the particle-water interface

The adsorption isotherm of AZO-B4 at the silica particle-water interface at equilibrium concentrations $<$ cmc at 25 °C was measured by the depletion method. The equilibrium concentration of the surfactant in a series of 0.1 wt.% silica dispersions after adsorption for 24 h was calculated based on the surface tension of the dispersions using the surface tension of AZO-B4 solution without silica particles as calibration.

Rheology

The static rheological properties of emulsions with and without UV irradiation were measured by means of a HAAKE rotational rheometer using a cone and plate geometry (gap 1000 μ m) at a shear rate ranging from 0 to 50 s^{-1} . All measurements were carried out at room temperature (25 ± 0.5 °C).

Contact angles at oil-water-solid interface

A glass slide was cut into strips 1.5 cm wide and soaked in 30% aqueous sodium hydroxide for 24 h. They were then washed with deionized water and dried. Then a clean glass strip was placed inside a glass cuvette of 35 mm (L) × 25 mm (D) × 20 mm (H), with its two ends being supported by standing legs. The cuvette was then filled with surfactant solution until the glass strip was immersed, as shown in Figure S5. After 2h (for adsorption), an octane droplet (0.5 μ L) was released from a U-shaped needle in solution below the glass strip, which was then captured to form an inverted sessile droplet. The contact angle through the oil droplet was measured using a Dropmeter A-100 contact angle instrument and converted to the contact angle through the aqueous phase. The temperature was kept at 25 °C using an air bath during measurement.

RESULTS AND DISCUSSION

Emulsions containing either surfactant or particles or their mixture

In an initial experiment, the ability of *trans*-AZO-B4 alone to stabilise an *n*-octane-in-water (1:1) emulsion was investigated. As shown in Figure S6, no stable emulsion can be formed at concentrations lower than the cmc, and the emulsions formed at higher concentration (1-3 mM) destabilised completely after one week, indicating that *trans*-AZO-B4 cannot stabilise an emulsion at concentrations \leq 3 mM.

The bare silica nanoparticles (primary diameter = 20 nm) are highly negatively charged at neutral pH, as indicated by a zeta potential, $\zeta = -28.8 \pm 0.2$ mV for 0.1 wt.% particles dispersed in pure water (pH = 6.1) at 25 °C. The zeta potential of bare silica nanoparticles in pure water as a function of pH is shown in Figure S7. They are thus too hydrophilic to stabilise an *n*-octane-in-

water emulsion alone^{52,53} (Figure S6). However, the particles can be hydrophobized *in situ* by addition of cationic surfactants enabling them to stabilise oil-in-water Pickering emulsions.^{3,4} When the silica nanoparticles (0.5 wt.%) were dispersed into aqueous solutions of *trans*-AZO-B4, *n*-octane-in-water emulsions (1:1) were formed, which were stable to coalescence for over a week at surfactant concentrations between 0.01 and 3.0 mM (Figure 1a and b). Moreover, the stability to creaming of the emulsions increases upon increasing the surfactant concentration, due mainly to a reduction of the average droplet size (Figure 1c).

Influence of N₂/CO₂ bubbling

In our previous studies, the switching on/off of the Pickering emulsions or foams containing the same silica nanoparticles in combination with a CO₂/N₂ switchable surfactant (N'-dodecyl-N,N-dimethyl-acetamidinium) had to be carried out at low (0–5 °C) and high (65 °C) temperature, respectively and usually took a long time (80 min) which is practically inconvenient.²² Here however, we observed that rapid conversion between emulsification/demulsification can be achieved at ambient temperature using the CO₂/N₂ trigger (Figure 2). For an emulsion stabilized by silica nanoparticles (0.5 wt.%) together with *trans*-AZO-B4 (0.06 mM), when N₂ was bubbled through the emulsion at a steady rate of 0.1 L minute⁻¹ at 35°C (Figure 2a), the emulsion partially coalesced releasing oil within 20 min (Figure 2b) and demulsified almost completely in 40 min (Figure 2c). In addition, a stable emulsion was re-formed by bubbling CO₂ through the oil-water mixture (Figure 2c) at 20 °C for 30 min followed by re-homogenization for 2 min (Figure 2d), with droplet diameters (50-150 µm) similar to that in the initial emulsion. According to conductivity measurement (Figure S1), upon bubbling N₂ or air through the aqueous solution, the bicarbonate surfactant was deprotonated to the neutral state and desorbed from particle surfaces, rendering silica nanoparticles hydrophilic again thus

returning them to the aqueous phase resulting in demulsification. The desorption of the surfactant from particle surfaces is evidenced by the different Fourier Transform Infra Red (FT-IR) spectra of the particles separated from aqueous dispersion with and without bubbling N₂, as shown in Figure S8. Compared with the FT-IR spectra of bare silica (Figure S8(a)), the FT-IR spectra of silica with adsorbed surfactant (Figure S8(b)) shows several peaks at about 2900 cm⁻¹ and 1467 cm⁻¹ indicative of the stretching vibration band of -CH₃, -CH₂ and -N=N- respectively, whereas these peaks disappear or appreciably weaken in the FT-IR spectra of silica separated from the dispersion after bubbling N₂ (Figure S8(c)). Whilst bubbling CO₂ through the broken emulsion, the neutral tertiary amine was protonated to be surface-active again enabling adsorption onto silica nanoparticles allowing stable emulsions to be re-formed. The conversion between stable (after homogenization) and unstable Pickering emulsions can be cycled several times by bubbling CO₂ and N₂ alternately. This rapid conversion under ambient conditions using the CO₂/N₂ trigger may result from the appropriate basicity of *trans*-AZO-B4, which strongly influences the switching rates of the switchable surfactants.³¹⁻³³ The *trans*-AZO-B4 (pK_a = 10.2) is less basic than alkylacetamidine (pK_a ≈ 12.2) and is thus easily switched on/off by bubbling with CO₂/ N₂.

Influence of UV/visible irradiation

An emulsion stabilised by *trans*-AZO-B4 alone at 0.6 mM was observed for demulsification with and without UV irradiation in a quartz tube, as shown in Figure S9. The emulsion with UV irradiation demulsified more extensively than that without UV irradiation. The Pickering emulsion stabilised by 0.5 wt.% silica nanoparticles in combination with 0.06 mM *trans*-AZO-B4 was similarly observed for its response to both UV and visible light irradiation. The original emulsion is of average droplet diameter ~ 50 μm (Figure 3(a)), which increases to

more than 90 μm after 1.5 hr of UV light irradiation (Figure 3(b)). The original droplet size can be recovered when the emulsion was exposed to blue light for 5 hr with stirring in the presence of CO_2 followed by homogenization for 2 min (Figure 3(c)). During this process the appearance of the emulsion shows no significant change except a little more aqueous phase was separated. In particular, no coalesced oil phase was observed. The presence of the second photo-trigger, therefore, makes it possible to manipulate the droplet size of the emulsion by controllable light irradiation without changing the emulsifier concentration.

In order to investigate other influences of UV illumination on the emulsions, their rheological properties with and without UV light illumination were measured, since these can be related to the macroscopic stability of an emulsion.^{3,4} The steady state shear rate dependence of the shear stress of the emulsion stabilised by 0.5 wt.% silica nanoparticles plus 0.06 mM *trans*-AZO-B4 is given in Figure 3(d). It shows that the application of shear causes deformation of the emulsion, resulting in a yield stress (at the maximum). Once the applied shear rate exceeds the yield stress, the emulsion behaves as a non-Newtonian fluid.⁵⁴⁻⁵⁷ It is clear that the yield stress is significantly affected by UV irradiation as it changes from 30.1 Pa to 14.3 Pa following UV irradiation. In addition, the apparent viscosity of the emulsion decreases with increasing shear rate, typical of shear-thinning flow behavior, Figure 3(e). The viscosity of the emulsion after UV irradiation is lower than that of the original one. These rheological changes together with those of the droplet size indicate that the emulsion stabilised by silica nanoparticles plus a trace amount of AZO-B4 is responsive to light illumination.

In another test, some droplets of the Pickering emulsion stabilized by 0.5 wt.% silica nanoparticles in combination with 0.06 mM *trans*-AZO-B4 were spread on a glass slide and subsequently irradiated with UV point light from 1 cm above (Figure S4(b)). No coalescence of

oil droplets occurred without UV irradiation (Figure 4(a) and (b)) but coalescence was observed to start after 2 min UV irradiation and was almost complete within 5 min, as shown in Figure 4(c) and (d). The increase in emulsion droplet size following UV irradiation shown in Figure 3 may thus be caused by coalescence.

In order to reveal the interactions between the dual switchable surfactant (AZO-B4) and silica nanoparticles, the zeta potentials (ζ) of the particles dispersed in aqueous solutions of AZO-B4 (in surface-active form) with and without UV irradiation and in the neutral state (inactive form) were measured (Figure 5(a)). For surfactant-free dispersions ($[AZO-B4] = 0$ mM), a value of -28.8 mV was measured regardless of the illumination conditions indicating a high density of negative charges on silica particle surfaces. In the absence of UV irradiation, the zeta potential of the particles increases upon increasing the concentration of *trans*-AZO-B4, and changes sign indicating adsorption of the surfactant at the particle-water interface. The change in sign of the zeta potential at a concentration close to the *cmc* suggests bilayer or hemi-micelle adsorption,²² which can be quantitatively analysed by measuring the adsorption isotherm. Figure 5(b) shows that the adsorbed amount of *trans*-AZO-B4 at the particle-water interface increases with increasing surfactant concentration between 0.01 and 1 mM, in parallel with the change of the zeta potential. The adsorbed amount of 0.03 mmol/g at 0.06 mM corresponds to a molecular area of 11.2 nm²/molec, which is much larger than that (0.70 nm²/molec) at the air-water interface at saturated adsorption ($\Gamma_{\infty} = 2.38 \times 10^{-10}$ mol/cm²), suggesting monolayer adsorption. At 0.56 mM (~ 0.5 cmc), the adsorption increases to 1.42 mmol/g, giving a molecular area of 0.23 nm²/molec, smaller than that at the air-water interface at saturated adsorption, suggesting double layer or hemi-micelle adsorption, which coincides with the concentration at which the zeta potential changes from negative to positive (Figure 5(a)). Based on the above results, we can

conclude that the cationic surfactant AZO-B4 molecules adsorb onto particle surfaces from aqueous solution *via* electrostatic attraction with their hydrophobic tails exposed towards water, which leads to *in situ* hydrophobization of the particles.^{53, 58} The particles thus become surface-active and can stabilise *n*-octane-in-water Pickering emulsions (Figure 1(a)).

The change of the zeta potential is also evidence of desorption of the surfactant following bubbling with N₂. When dispersed in an aqueous solution of 0.06 mM surfactant (pH = 5.1), the zeta potential increases from -28.8 mV (in pure water, pH = 6.1) to -2.17 mV due to neutralization of the negative charges by adsorbed surfactant. However the zeta potential decreases to -21.74 mV following bubbling with N₂ (pH = 6.0). As a reference, the zeta potential of silica in pure water decreased from -18.82 mV to -28.8 mV only as pH increased from 5.1 to 6.0 (Figure S7). The significant decrease of the zeta potential in surfactant solutions following bubbling with N₂ is thus mainly due to desorption of the surfactant molecules, which are deprotonated to the neutral, surface-inactive form upon bubbling N₂ or air through emulsions or dispersions. The desorption of the surfactant from particle surfaces renders particles hydrophilic again, which detach from the oil-water interface resulting in demulsification (Figure 2(c)). However, the deprotonation is usually incomplete²² and the adsorption of the residual AZO-B4 at particle surfaces leads to a zeta potential of the particles slightly higher than that of bare silica (Figure 5(a)). On the other hand by bubbling CO₂ through the oil-water mixture after demulsification, the AZO-B4 molecules are re-protonated and can adsorb on particle surfaces again enabling emulsification.

The effect of surfactant concentration on demulsification of silica + surfactant stabilized emulsions was examined. As shown in Table 1, demulsification of the emulsion can be easily triggered by bubbling N₂ at 35 °C for surfactant concentrations between 0.01 mM and 0.2 mM,

but becomes difficult at concentrations above 0.3 mM. However, this difficulty can be overcome by increasing the temperature, since the bicarbonate salt can be easily decomposed at high temperature.³¹

Furthermore, the zeta potential of the particles and the adsorbed amount of surfactant can be reduced by UV illumination as well (Figure 5). The *cis*-AZO-B4 induced by UV irradiation has a higher polarity and a large steric hindrance compared with *trans*-AZO-B4 and thus adsorbs less on particle surfaces.⁵⁹ Accordingly, particles are less hydrophobic and less surface-active (Figure S3). However, the decrease in adsorption at particle surfaces after UV irradiation is limited. For example, at 0.06 mM, the adsorbed amount of the surfactant decreases from 0.03 mmol/g before UV irradiation to 0.01 mmol/g after UV irradiation. This reduction is much less than that induced by bubbling N₂ or air. As a result, complete demulsification does not occur but a noticeable droplet size increase occurs due to coalescence (Figure 4) following UV irradiation.

The effect of light illumination can be further probed by evaluating the change in wettability of a negatively charged glass slide (mimic of bare silica particle surface) immersed in the surfactant solution. For this, the contact angle of a captured *n*-octane drop in water was measured, as shown in Figure 6. The contact angle measured through the aqueous phase before UV irradiation increases gradually with increasing surfactant concentration between 0.003 mM and 0.3 mM, reaching as high as 130° (Figure 6(d), Table S1). Interestingly, a similar contact angle increase was observed after UV irradiation or when the surfactant is in the neutral amine state (surface-inactive form), but the angles are all lower than above. Similar to what occurs on silica nanoparticle surfaces, the cationic surfactant *trans*-AZO-B4 molecules adsorb at both the oil-water interface and at the negatively charged glass slide surface *via* electrostatic interactions and form a hydrophobic monolayer at low concentration (0.001 - 0.1 mM). After bubbling N₂,

desorption of the surfactant from the glass slide occurred as evidenced by the contact angle decrease shown in Figure 6, from 128° to 87° at a surfactant concentration of 3×10^{-4} mol/L.

However, since the active *trans*-AZO-B4 cannot be deprotonated completely by bubbling N₂ or air through the solution, a moderate increase of the contact angle with increasing surfactant concentration in the neutral state can still be observed, consistent with the zeta potential measurements (Figure 5(a)). It is observed that the contact angle is also reduced by UV irradiation (yielding *cis* isomer), which is consistent with the decrease in both the zeta potential of particles and the adsorbed amount of surfactant (Figure 5). This is shown by the inverted photographs of *n*-octane drops immersed in an aqueous solution of 0.3 mM *trans*-AZO-B4 before and after UV irradiation (Figure 6(a)-(c)). In the absence of UV, the contact angle was 128° which declines to 106° or 80° following UV irradiation (1 h) or in solution where the surfactant is in the neutral state, respectively.

Finally, the effect of combining both light and N₂ stimuli on demulsification of a particle+surfactant-stabilised emulsion was examined (Figure S10). It was found that the destabilization of the emulsion can be achieved within 30 min, which is faster than that obtained by applying the N₂ stimulus alone (40 min). The deprotonation of the surfactant in combination with its photo-isomerization thus accelerates the desorption of surfactant from particle surfaces with subsequent easier demulsification.

CONCLUSIONS

We have demonstrated that a dual stimulus-responsive Pickering oil-in-water emulsion with CO₂/N₂ and light triggers can be prepared using negatively charged silica nanoparticles in combination with a trace amount of dual switchable surfactant AZO-B4. On one hand, the

emulsion can be transformed between stable and unstable at ambient temperature rapidly *via* the N₂/CO₂ trigger, and on the other hand a **recoverable** change in droplet size and rheological properties of the emulsion can occur upon light irradiation/re-homogenization cycles without changing the particle/surfactant concentration. Compared with emulsions stabilised by specially synthesized stimuli-responsive particles or by stimuli-responsive surfactants, the method reported here is much easier and requires relatively low concentration of surfactant ($\approx 1/10$ cmc), which is important for potential applications.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website. Experimental details for the synthesis and characterization of the surfactant and emulsions.

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Notes

The authors declare no competing financial interest.

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Table 1. Time required for complete demulsification of o/w emulsions stabilised by 0.5 wt.% silica nanoparticles plus the switchable surfactant at different concentrations by bubbling with N₂.

[<i>trans</i> -AZO-B4]/mM	Time/min
0.01	10 ^a
0.06	40 ^a
0.10	60 ^a
0.15	85 ^a
0.20	130 ^a
0.30	10 ^b
3.00	60 ^c

^a 35 °C; ^b 50 °C; ^c 65 °C

Scheme 1. Chemical structure of 4-butyl-4-(4-N,N-dimethylbutoxyamine) azobenzene bicarbonate (AZO-B4, middle) and its CO₂/N₂ and light dual stimuli responses.

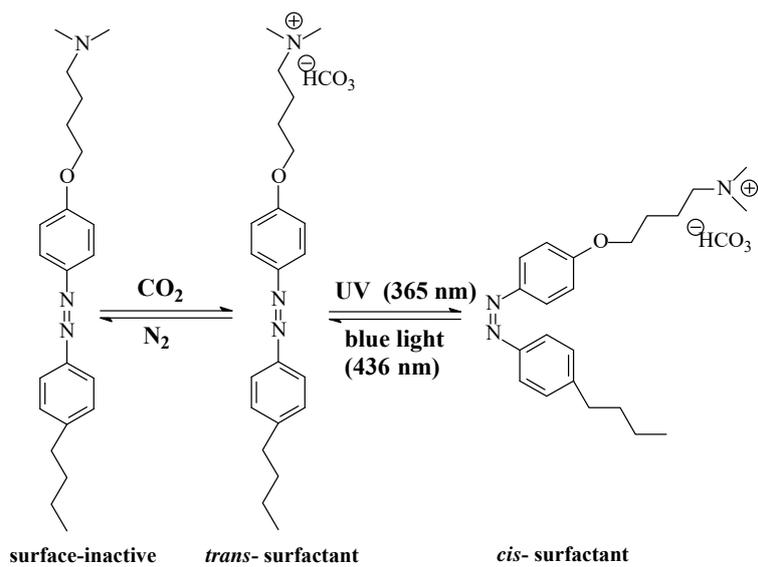


Figure 1. Photographs and selected optical micrographs of *n*-octane-in-water emulsions ($7 \text{ cm}^3/7 \text{ cm}^3$) stabilized by silica nanoparticles (0.5 wt.%) in combination with *trans*-AZO-B4, taken 24 h ((a) and (c)) and 1 week (b) after preparation. Concentration of *trans*-AZO-B4 in the aqueous phase from (1) to (6) is 0.01, 0.03, 0.1, 0.3, 1.0 and 3.0 mM, respectively.

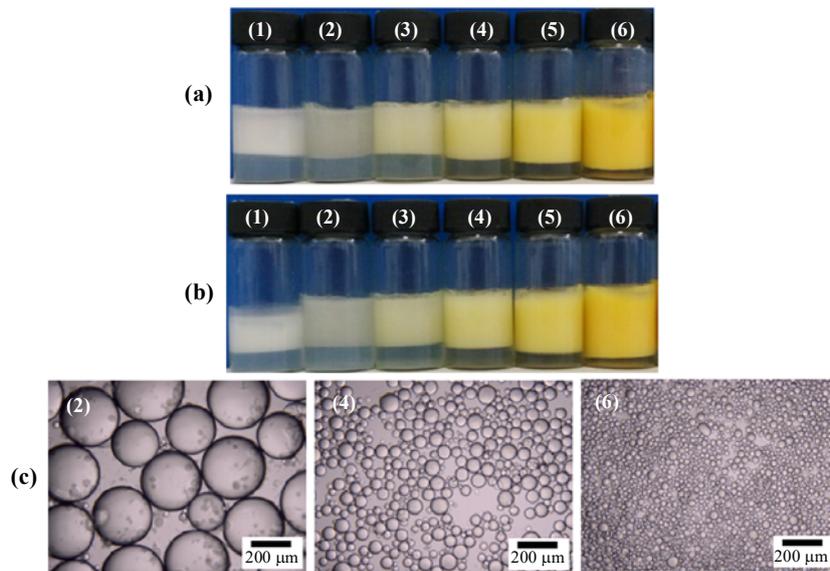


Figure 2. Photographs and corresponding optical micrographs of *n*-octane-in-water Pickering emulsions stabilised by silica nanoparticles (0.5 wt.%) in combination with *trans*-AZO-B4 (0.06 mM) undergoing switching off/on cycle. (a) Stable Pickering emulsion, (b) after bubbling N₂ through the emulsion at 35 °C for 20 min, (c) after bubbling N₂ at 35 °C for another 20 min, (d) after bubbling CO₂ through the oil-water mixture at 20 °C for 30 min followed by homogenization for 2 min, taken 24 h (b and c) and 1 week (a and d) after operation.

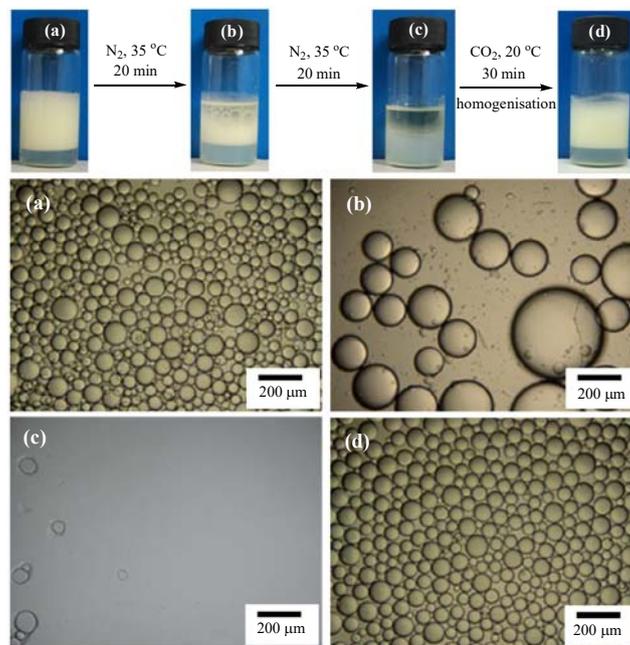


Figure 3. Optical micrographs of *n*-octane-in-water Pickering emulsions stabilised by 0.5 wt.% silica nanoparticles plus 0.06 mM AZO-B4 (a) before UV irradiation taken 24 h after preparation, (b) after UV irradiation at 20 °C for 1.5 h and (c) then irradiated by blue light for 5 h followed by homogenization. (d) Shear stress *versus* shear rate and (e) apparent viscosity *versus* shear rate of the emulsions (1) before and (2) after UV irradiation.

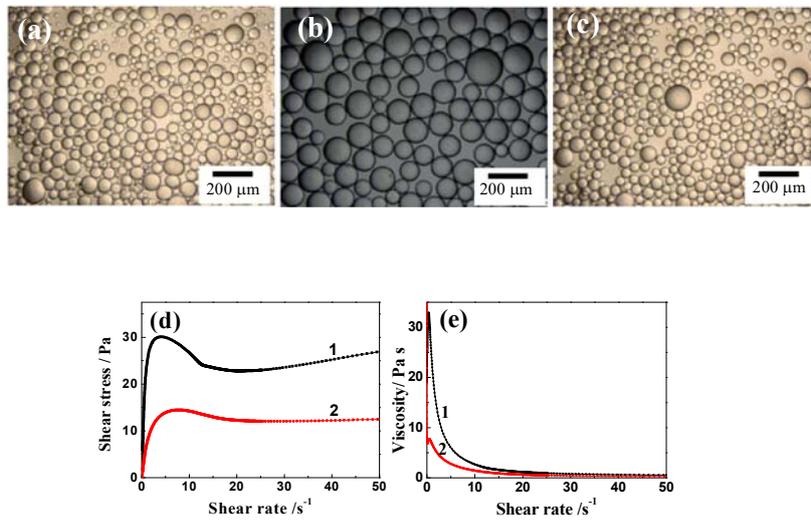


Figure 4. Optical micrographs of *n*-octane-in-water Pickering emulsions stabilised by 0.5 wt.% silica nanoparticles plus 0.06 mM *trans*-AZO-B4 on a glass slide following light irradiation. (a) Original emulsion, (b) 5 min later without UV irradiation, (c) 2 min after UV irradiation, (d) 3 min after UV irradiation.

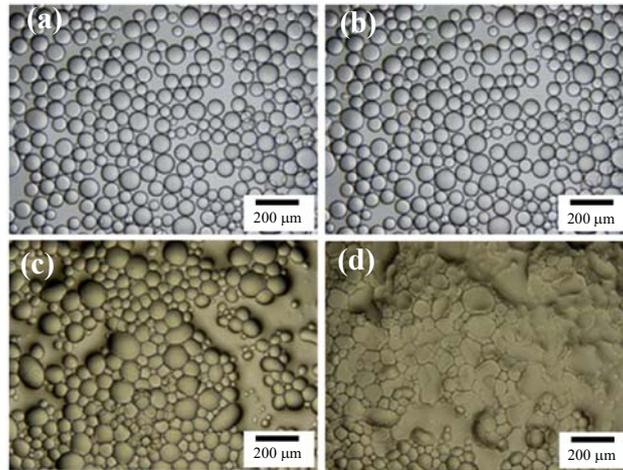


Figure 5. (a) Zeta potentials of 0.1 wt.% silica nanoparticles dispersed in aqueous solutions of AZO-B4 before UV irradiation (active, ■), after UV irradiation (active, ●) and in the neutral state (inactive, ▲) as a function of initial surfactant concentration. (b) Adsorption isotherm of AZO-B4 at the silica-water interface as a function of equilibrium surfactant concentration before UV irradiation (*trans*-AZO-B4, ■) and after UV irradiation (*cis*-AZO-B4, ●).

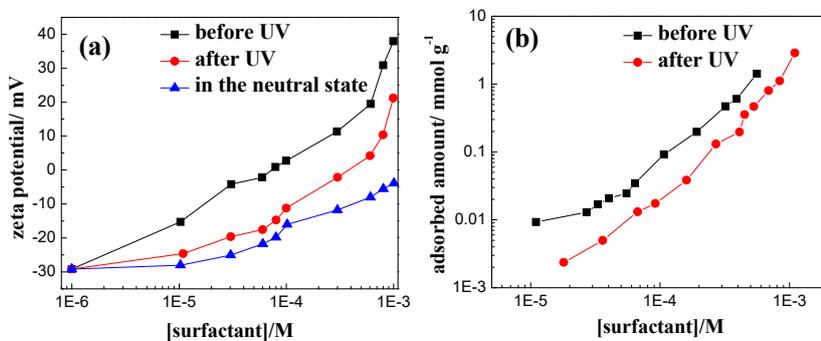
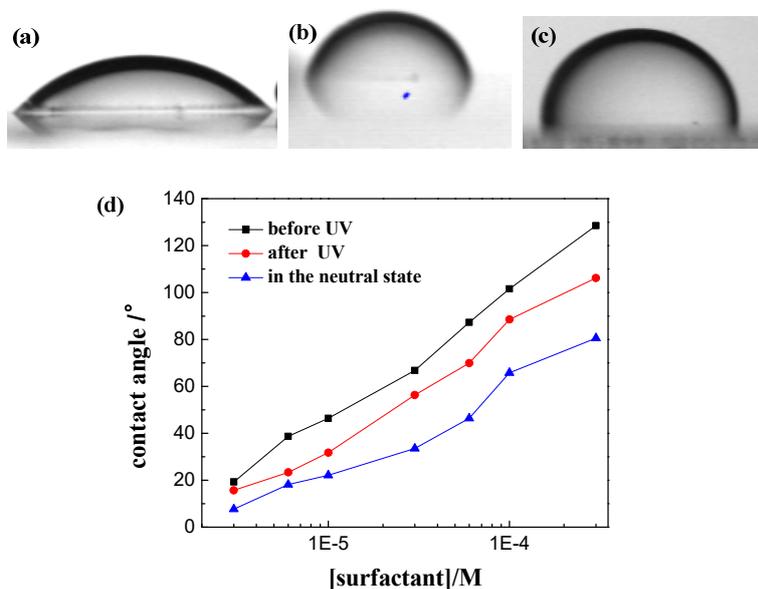


Figure 6. Inverted photographs of *n*-octane drops immersed in aqueous solutions of 0.3 mM AZO-B4 on glass slides at 25 °C; (a) before UV irradiation (active form), (b) after UV irradiation (active form), (c) surfactant in neutral state (inactive form). (d) Contact angle at the oil-water-glass interface measured through the aqueous phase as a function of surfactant concentration.



Graphical Abstract

