

Responsive aqueous foams stabilized by silica nanoparticles hydrophobised *in situ* with a conventional surfactant

Yue Zhu,^a Xiaomei Pei,^a Jiangzhong Jiang,^a Zhenggang Cui^{a*} and Bernard P. Binks^{b*}

^a*The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, 1800 Lihu Road, Wuxi, Jiangsu 214122, P.R. China*

^b*Department of Chemistry, University of Hull, Hull. HU6 7RX. UK*

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*Corresponding authors: cuizhenggang@hotmail.com; b.p.binks@hull.ac.uk

Abstract

In the recent past switchable surfactants and switchable/stimuli-responsive surface-active particles have been of great interest. Both can be transformed between surface-active and surface-inactive states *via* several triggers, making them recoverable and re-usable afterwards. However the synthesis of these materials is complicated. In this paper we report a facile protocol to obtain responsive surface-active nanoparticles and their use in preparing responsive particle-stabilized foams. Hydrophilic silica nanoparticles are initially hydrophobized *in situ* with a trace amount of a conventional cationic surfactant in water rendering them surface-active such that they stabilize aqueous foams. The latter can then be destabilized by adding equal moles of an anionic surfactant, and re-stabilized by adding another trace amount of the cationic surfactant followed by shaking. The stabilization-destabilization of the foams can be cycled many times at room temperature. The trigger is the stronger electrostatic interaction between the oppositely charged surfactants than that between the cationic surfactant and the negatively charged particles. The added anionic surfactant tends to form ion pairs with the cationic surfactant, leading to desorption of the latter from particle surfaces and de-hydrophobization of the particles. Upon addition of another trace amount of cationic surfactant, the particles are re-hydrophobized *in situ* and can then stabilize foams again. This principle makes it possible to obtain responsive surface-active particles using commercially available inorganic nanoparticles and conventional surfactants.

Keywords: Responsive surface-active particles; Responsive foams; Silica nanoparticles; ion pairs; electrostatic interaction

Introduction

There has been growing interest in switchable surfactants and switchable/responsive surface-active colloid particles [1-4] during the recent past. They can be transformed between surface-active and surface-inactive forms *via* certain triggers and can then be used to prepare switchable/responsive emulsions and foams. [3-6] These are important in practical processes such as fuel production, oil transport, emulsion polymerization, **foam flotation and foam flooding**, where the emulsions or foams need only to be temporarily stabilized and have to be destabilized ultimately. The switchable characteristics also make them re-usable and recoverable afterwards and they are thus among the “green” chemicals.

For switchable surfactants many triggers have been reported, [1] such as pH, **redox**, light, magnetic field, CO₂/N₂ and temperature.[7] **Among these**, the CO₂/N₂ trigger initially reported by Jessop and co-workers[8] is both low cost and environmentally benign and has been paid more attention recently. [9-13] Nonetheless, the switching on/off conditions are relatively rigorous (0-5 °C/50 °C), [4, 8] and moreover, high concentration (>>critical micelle concentration, cmc) is usually needed for preparing switchable emulsions and foams which are thermodynamically unstable.

In contrast, very stable emulsions and foams can be obtained using surface-active colloid particles, [14-16] due to the presence of a dense particle film at the oil-water or air-water interface which prevents droplets/bubbles from coalescence. However, these particular emulsions and foams can be difficult to destabilize. Switchable or responsive surface-active colloid particles are thus required for these systems where only temporary stability is needed. Indeed many attempts have been made to develop such particles and the triggers reported include pH, [17-23] temperature, [24-26] light, [27,28] magnetic field, [29-31] CO₂/N₂, [22,32-34] and pH-temperature, [36-40] light-temperature [41] and magnetic field intensity-temperature. [42,43] These switchable/responsive colloid particles are mostly functional polymer particles or organic/inorganic hybrids which are complicated to synthesize and are not easily supplied in large quantities.

In recent studies we have found that commercially available inorganic nanoparticles such as silica and calcium carbonate can be made surface-active by *in situ* hydrophobization.[44-47] Here the charged nanoparticles adsorb oppositely charged ionic surfactant *via* electrostatic

interaction in water, and the formation of a monolayer of surfactant enhances the hydrophobicity of the particle surfaces and thus renders particles surface-active. Interestingly, when a switchable surfactant with CO₂/N₂ trigger was employed, the hydrophilic silica nanoparticles which are negatively charged in water can be transformed to switchable surface-active nanoparticles with the same triggers, [4] where the switchable surfactant adsorbs/desorbs from particles surfaces in accord with switched on (as a cationic surfactant) and switched off (as an uncharged surfactant compound with limited solubility). Both switchable Pickering emulsions and switchable particle-stabilized foams have been obtained using the particle/switchable surfactant combination. [4,5] Compared with using switchable surfactant alone, this protocol needs only a trace amount of switchable surfactant (1/10 cmc) to obtain ultra-stable emulsions and foams. [4,5] However, the switching on/off condition is rigorous and difficult to realize at room temperature. In this paper, we report a more general and simple protocol to obtain switchable/responsive surface-active nanoparticles by using inorganic nanoparticles such as silica and conventional ionic surfactants which are all commercially available. The negatively charged particles are initially hydrophobized *in situ* by adsorbing a cationic surfactant, and then de-hydrophobized by adding equal moles of an anionic surfactant. The anionic surfactant prefers to form ion pairs with the cationic surfactant, leading to desorption of the cationic surfactant from particle surfaces. Once another trace amount of cationic surfactant is added, the *in situ* hydrophobization re-occurs and the particles become surface-active again. This hydrophobization-dehydrophobization can be cycled for many times until the total concentration of the individual surfactants is beyond the cmc. Using this protocol, responsive Pickering emulsions have been obtained [6] and here we focus on the formation of responsive particle-stabilized foams.

Experimental

Materials

Hydrophilic silica nanoparticles, HL-200, with a purity > 99.8 % were provided by Wuxi Jinding Longhua Chemical Co., China, and have a primary particle diameter of *ca.* 20 nm and a BET surface area of 200 ± 20 m²/g. Electron microscopy images of the particles are shown in Figure S1. The zeta potentials of the particles dispersed in water as function of pH at 25 °C

are shown in Figure S2. Cetyltrimethylammonium bromide (CTAB, 99 %) was purchased from Sinopharm Chemical Reagent Co. Dodecyltrimethylammonium bromide (DTAB, 98 %) and sodium dodecyl sulphate (SDS, 99 %) were purchased from Sigma. All other chemicals were analytically pure and purchased from Sinopharm Chemical Reagent Co. Ultrapure 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).

Methods

(a) Dispersion of silica nanoparticles in aqueous media

Powdered silica nanoparticles were weighed into a glass bottle (6.5 cm (h) \times 2.5 cm (d), 25 cm³), followed by adding either pure water or aqueous surfactant solution. The particles were then dispersed using an ultrasound probe (JYD-650, Shanghai) of tip diameter 0.6 cm operating at an output of 50 W for 1 min.

(b) Preparation and characterization of aqueous foams

A certain amount of silica nanoparticles was initially dispersed in pure water or surfactant solution *via* sonication. 10 cm³ of the dispersion was transferred to a 50 cm³ cylindrical graduated flask which was well stoppered and shaken up and down vigorously for 20 times by hand. After that the flasks were left at room temperature (20-25 °C) and photographed at different time intervals. In order to evaluate the stability of the foams, the decay of the foam volume with time was determined. For visualizing the microstructure of the foams, 10 cm³ of solution/dispersion was transferred to a bottle of 6.5 cm (h) \times 2.5 cm (d) (25 cm³) and shaken by hand for 20 times. A sample of the foam was immediately placed on a microscope slide using a pipette and micrographs were taken using a VHX-1000 microscope system (Keyence Co.).

(c) Switching of aqueous foams

Foams stabilized by 0.5 wt.% silica nanoparticles in combination with 0.3 mM CTAB were cycled between unstable, by adding 0.1 cm³ of 30 mM aqueous SDS followed by hand

shaking, and stable by adding 0.1 cm³ of 30 mM aqueous CTAB followed by hand shaking for 20 times.

(d) Zeta potential of silica nanoparticles in aqueous dispersion

The zeta potentials of 0.1 wt.% silica nanoparticles dispersed in pure water of different pH (adjusted by adding HCl and NaOH), and that of 0.5 wt.% silica nanoparticles dispersed in aqueous surfactant solutions of different concentration at 25 °C were measured using a ZetaPLAS instrument (Brookhaven) 24 hr after dispersion.

(e) Contact angles of surfactant solutions on glass slides in air

Microscope glass slides were immersed in 30 % aqueous NaOH solution for 24 hr, followed by rinsing with pure water and drying. A pre-treated slide was placed on the measuring table of a contact angle analyzer (Dropmeter A-100, Ningbo, China), and a drop of aqueous surfactant solution (1 μL) was released from a needle to form a sessile drop on the slide in air. The image was recorded at different times and the contact angle which no longer changed with time was determined using software.

(f) Adsorption of surfactant on particles in water

The adsorption isotherm of CTAB at the silica-water interface for equilibrium concentrations < cmc at 25 °C was measured by a depletion method after equilibrating 0.5 wt.% of silica particles with aqueous surfactant. The dispersions were stored for 24 hr in a plastic box whose temperature was controlled at 25 °C using an Air-Therm Heater (World Precision Instrument). The equilibrium concentration of CTAB after equilibration was determined by surface tension measurement without separating the particles (home-made du Nouüy ring method), where the surface tension of pure CTAB solutions was used as calibration.

All experiments were carried out at room temperature (20-25 °C) unless specified otherwise.

Results and discussion

(a) *Particle-stabilized foams of silica nanoparticles hydrophobized in situ with CTAB*

The strongly hydrophilic bare silica nanoparticles (primary diameter = 20 nm, Figure S1) as indicated by a zeta potential of -25.2 ± 0.4 mV at pH = 6.1 shown in Figure S2 can be well dispersed in pure water without sedimentation for a long time. As previously reported [5] they are not surface-active and cannot stabilize aqueous foams alone. The foamability and foam stability of the aqueous solutions of CTAB are low at concentrations \leq cmc (0.9 mM) as seen in Figure 1, and all foams disappeared 24 hr after shaking. However, dispersions of 0.5 wt.% silica nanoparticles in dilute (\leq cmc) aqueous CTAB solutions show increased foamability and foam stability, as shown by Figures 1 and 2. Some micrographs of the foams produced by shaking the dispersions in bottles are displayed in Figure 3, which shows that the average bubble size tends to decrease with increasing surfactant concentration but less obvious as observed for emulsion droplets stabilised by the same stabilizers [6]. Both the good foamability and high foam stability indicate that the foams of the dispersions are mainly stabilized by particles rather than surfactant [5], although the latter may also adsorb at the air-water interface.

The origin of the enhancement in the surface activity of the silica particles by *in situ* hydrophobization in the foaming systems is similar to that in emulsion systems and has been described earlier. [6] Briefly, in aqueous solution the cationic CTAB molecules adsorb on negatively charged silica particle surfaces *via* electrostatic interaction and form a monolayer at the particle-water interface with surfactant head groups towards the particle surface and hydrocarbon tails towards water. The neutralization of the charges on particle surfaces together with the head-on monolayer renders particle surfaces more hydrophobic than that of the bare particles. [6, 45] The zeta potential of the silica nanoparticles increases from negative values to positive values upon increasing the concentration of CTAB (Figure S3) as a result. The adsorption isotherm of CTAB at the silica particle-water interface [6, 45] given in Figure S4 supports this mechanism, where the adsorbed amount of 0.44 mmol/g at 8.3×10^{-4} M (close to the cmc) gives a molecular area of 0.75 nm²/molecule similar to that at the air-water interface [48] suggesting monolayer adsorption.

(b) *Cycling between foaming and defoaming by addition of SDS*

For a foaming system comprising 10 cm³ of 0.5 wt.% silica nanoparticles and 0.3 mM CTAB, defoaming occurs after adding 0.1 cm³ of a 30 mM SDS solution (cmc = 8 mM) followed by hand shaking (Figure 4). The number of moles of SDS added is equal to that of CTAB in the sample and the change in volume of the aqueous phase is negligible. However, once 0.1 cm³ of 30 mM aqueous CTAB solution was subsequently added, a stable foam was formed again after hand shaking. This foaming-defoaming behavior has been cycled for three times as shown in Figure 4, where the total concentration of CTAB reaches its cmc (0.9 mM). Beyond that, foaming is still good following the addition of 0.3 mM CTAB, but defoaming becomes less efficient with the accumulation of both surfactants in the system. For example, there were 4 cm³ and 6 cm³ of foam (initially 30 cm³) remaining in the fourth and fifth cycle after adding an equal number of moles of SDS. We have found that if a surfactant with low surface activity or high cmc was used, such as DTAB (cmc = 15 mM), this foaming-defoaming conversion starting at 1 mM can be cycled for 6 times with almost complete defoaming although the foam volume is lower (20 cm³) as shown in Figure 5. Similarly the efficiency of defoaming decreases with the accumulation of both surfactants in subsequent cycles.

(c) Mechanism for foaming/defoaming cycling

As previously reported [4-6,45], silica nanoparticles are negatively charged in aqueous solution and can be hydrophobized *in situ* with a cationic surfactant such as CTAB due to electrostatic interactions and thus adsorb to the air-water interface to stabilize foams. However, upon the addition of an anionic surfactant like SDS, the stronger electrostatic interaction between CTAB and SDS than that between CTAB and particle surfaces leads to formation of ion pairs between the surfactants. This results in desorption of CTAB molecules from particle surfaces, rendering particles hydrophilic again and surface-inactive. [5] Here we provide more evidence to support this mechanism.

Firstly, the zeta potentials of 0.5 wt.% silica nanoparticles during foaming/defoaming cycling shown in Figure 4 was monitored, as shown in Figure 6. It was found that the zeta potential increases from -25.2 mV in pure water (no foaming) to +7.4 mV in 0.3 mM CTAB solution (Figure 4-A and Figure 6-A, foaming). It decreases to -25.0 mV (Figure 4-B and

Figure 6-B, defoaming) and increases to +7.1 mV (Figure 4-C and Figure 6-C, foaming) following the addition of SDS and then CTAB **respectively** in the first cycle. The corresponding data are -24.6 mV and +8.1 mV for the second cycle (Figure 4-D and Figure 6-D, defoaming and Figure 4-E and Figure 6-E, foaming), and -24.6 mV and +7.5 mV for the third cycle (Figure 4-F and Figure 6-F, defoaming and Figure 4-G and Figure 6-G, foaming). It is thus suggested that in the absence of SDS, CTAB molecules adsorb at the particle-water surface to neutralize the negative charges on particle surfaces and render particles partially hydrophobic and hence surface-active. Coated particles can then adsorb at the air-water interface to stabilize foams and none remain in water, as indicated by a clear aqueous phase in Figure 4-A. In the presence of SDS however, CTAB molecules desorb from particle surfaces probably forming ion pairs with SDS in water, rendering particles hydrophilic again and thus surface-inactive. The particles thus return to the aqueous phase, as indicated by the increase in turbidity seen in Figure 4-B, D and F, and bubbles are destroyed.

Secondly, foaming does not occur for dispersions of 0.5 wt.% silica particles in equimolar mixtures of CTAB and SDS solutions up to an individual concentration of 1 mM (Figure S5). Consistent with this, the zeta potential of the particles in these dispersions remains more or less constant at -24.7 ± 0.2 mV, similar to that in pure water, as shown in Figure 6 by the filled squares. Moreover, in the absence of silica nanoparticles, aqueous solutions of equimolar mixtures of CTAB and SDS up to an individual concentration of 3 mM do not foam either, as shown in Figure S6. It is believed that monomer molecules of both surfactants are used in the formation of ion pairs and are thus not available for adsorption at the air-water surface to stabilize air bubbles. The neutral ion pairs exhibit low hydrophilicity and may precipitate at high enough concentration. This is evidenced by the reduction of the transmittance of solutions with increasing concentration as shown in Figure S7, from which a solubility as low as 8.5×10^{-5} M is estimated for the equimolar mixture, which is much lower than the respective cmc's. The monomer concentrations (equal to the mixed cmc) in the equimolar mixture can be predicted from non-ideal micellization theory [48]. The cmc in this mixture is $< 2 \times 10^{-6}$ M based on an interaction parameter $\beta^M = -25.5$ for DTAB+SDS [48], which is much smaller than the solubility of the mixture. Here, equimolar mixtures of both CTAB and SDS and DTAB and SDS behave as defoaming agents at individual concentrations

lower than their cmc. Although good foaming properties have been reported in the literature for some other cationic+anionic surfactant mixtures, [49, 50] these systems all have one surfactant in excess and at high concentration.

Finally, the contact angles of aqueous CTAB solutions on hydrophilic glass slides in air were measured and their change upon addition of SDS was examined, as shown in Figure 7. It was found that the contact angle increases with increasing CTAB concentration, from less than 10° at low concentration to a maximum approaching 50° at 0.3 mM, and then decreases dramatically to less than 20° . The initial increase corresponds to the formation of a monolayer and the subsequent decrease corresponds to the formation of a bilayer or hemi-micelle formation. At 0.3 mM corresponding to maximum contact angle, **by adding a drop of SDS solution (0.5 μ L) of the same concentration into a drop of CTAB solution (0.5 μ L) already on a slide**, the contact angle was lowered significantly to 16° (Figure 7, unfilled circle), implying a hydrophilic surface. This means that upon addition of SDS, changes occur at both the air-water and the solid-water interfaces, with CTAB most likely being desorbed from the latter. Moreover, aqueous solutions of equimolar mixtures of CTAB and SDS up to an individual concentration of 1 mM exhibit low contact angles of between 5° and 14° , also suggesting a hydrophilic surface. In other words, the equimolar mixture does not result in hydrophobisation of the charged surface.

The decrease in defoaming efficiency occurring at high equimolar mixture concentrations (beyond the cmc) seems to be caused by the accumulation of ion pairs in the aqueous phase. It was observed that in the absence of particles the aqueous phase appears turbid and the ion pairs do not sediment completely after 24 hr (Figure S6 (B)). The dispersed ion pairs probably in the form of small crystals are thus beneficial to the stabilization of the residual foams. In the presence of particles, partial flocculation and sedimentation of the particles/ion pairs occurs (Figure S5 B), but many of them are present in the continuous phase which results in an enhancement in stability of the residual foams. The micrographs in Figure S8 indicate that the continuous phase surrounding bubbles is not clear but contains ion pairs/particles, which are difficult to distinguish from the optical image unfortunately. Nevertheless the cycling between foaming and defoaming of the systems at low surfactant concentration is successful, and a full understanding of the concentrated systems is worthy of future study.

We thus suggest that in the particle-stabilized foams stabilized by silica nanoparticles hydrophobized *in situ* by a conventional cationic surfactant, once a conventional anionic surfactant is added the electrostatic interaction between the oppositely charged surfactants is much stronger than that between cationic surfactant and particle surfaces, which leads to de-hydrophobisation of particles. Once a trace amount of cationic surfactant is added however, *in situ* hydrophobisation is re-established. The differential electrostatic interaction is therefore the trigger. This protocol of using silica nanoparticles in combination with conventional ionic surfactants to construct responsive surface-active nanoparticles and thereby responsive particle-stabilized foams may be suitable for other inorganic nanoparticles which are either positively or negatively charged in aqueous media, avoiding complicated synthesis of functional particles and rigorous switching conditions.

Conclusions

We have demonstrated that particle-stabilized foams can be prepared using negatively charged silica nanoparticles hydrophobized *in situ* with a trace amount of a conventional cationic surfactant. Such foams can be made unstable by adding equal moles of a conventional anionic surfactant. The foaming-defoaming behavior can be cycled many times until the concentration of the individual surfactants is not far beyond their cmc's. The trigger is the differential electrostatic interaction between the oppositely charged ionic surfactants and between the cationic surfactant and particle surfaces. The added anionic surfactant tends to form ion pairs with the cationic surfactant, which desorbs from particle surfaces. This access to responsive particle-stabilized foams is quite facile compared with that employing switchable surfactants, switchable polymers, switchable surface-active particles or particles hydrophobised *in situ* with switchable surfactants, as it avoids both the complicated synthesis and the rigorous switching conditions. The particles and ionic surfactants are all commercially available, and the ionic surfactants used are in trace amount (\ll cmc) if only one or a few responsive cycles are needed. We anticipate that this principle will also apply to positively charged particles. Although the accumulation of surfactants in the system is a problem, the surfactant added is in trace amount and is therefore negligible compared with the systems

stabilized solely by surfactants.

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Captions

Figure 1. Foam volume as a function of surfactant concentration for both aqueous CTAB solutions and dispersions of 0.5 wt.% silica nanoparticles in aqueous CTAB solutions, measured immediately (V_0), 30 min ($V_{0.5}$) and 24 hr (V_{24}) after shaking 10 cm^3 of solution/dispersion.

Figure 2. Photographs of vessels containing aqueous foams stabilized by 0.5 wt.% silica nanoparticles in combination with CTAB at different concentrations, taken immediately (A) and 30 min (B) after shaking 10 cm^3 of solution/dispersion. [CTAB]/mM from left to right are: 0.01, 0.03, 0.06, 0.10, 0.20, 0.30 and 0.60.

Figure 3. Micrographs of the bubbles in foams produced by shaking 10 cm^3 of a dispersion of 0.5 wt.% silica particles in CTAB solution at different concentration taken immediately after shaking. [CTAB]/mM from A to F: 0.01, 0.03, 0.06, 0.10, 0.20 and 0.30.

Figure 4. Photographs showing the cycling between foaming and defoaming of a dispersion (10 cm^3) of 0.5 wt.% silica nanoparticles in 0.3 mM aqueous CTAB (foaming) by adding equal moles of SDS (0.1 cm^3 solution in 30 mM, defoaming) and another amount of free CTAB (0.1 cm^3 solution in 30 mM, foaming again) alternately. The photographs were taken 10 min after shaking **and the total CTAB/SDS concentration in mM is shown above the vessels.**

Figure 5. Photographs showing cycling between foaming and defoaming of a 10 cm^3 dispersion of 0.5 wt.% silica nanoparticles in aqueous DTAB solution (initially 1 mM and foaming, then defoaming by adding equal moles of SDS, then foaming by adding 1 mM DTAB *etc.*). The photos were taken 10 min after shaking.

Figure 6. **Zeta potentials of 0.5 wt.% silica nanoparticles dispersed in water containing an equimolar mixture of CTAB and SDS (squares) and in water accompanying cycling between**

foaming and defoaming by addition of CTAB (0.3 mM) then SDS (0.3 mM) alternately (points A-G) as a function of total CTAB concentration.

Figure 7. Contact angle of aqueous surfactant solutions on hydrophilic glass slides in air at 25°C as a function of CTAB concentration. The unfilled circle was measured by adding a drop of SDS solution into a drop of CTAB solution already on a slide both at a concentration of 0.3 mM.

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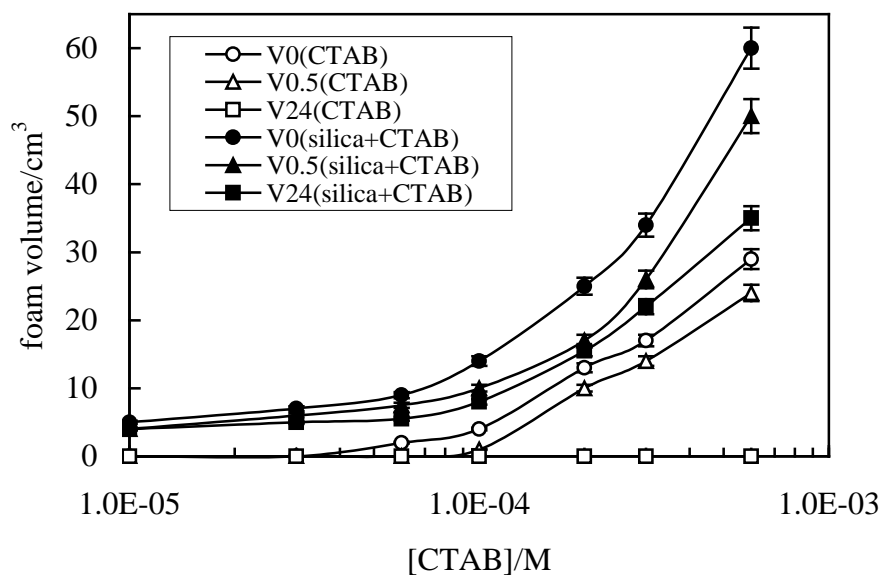


Figure 2. Photographs of vessels containing aqueous foams stabilized by 0.5 wt.% silica nanoparticles in combination with CTAB at different concentrations, taken immediately (A) and 30 min (B) after shaking 10 cm³ of solution/dispersion. [CTAB]/mM from left to right are: 0.01, 0.03, 0.06, 0.10, 0.20, 0.30 and 0.60.

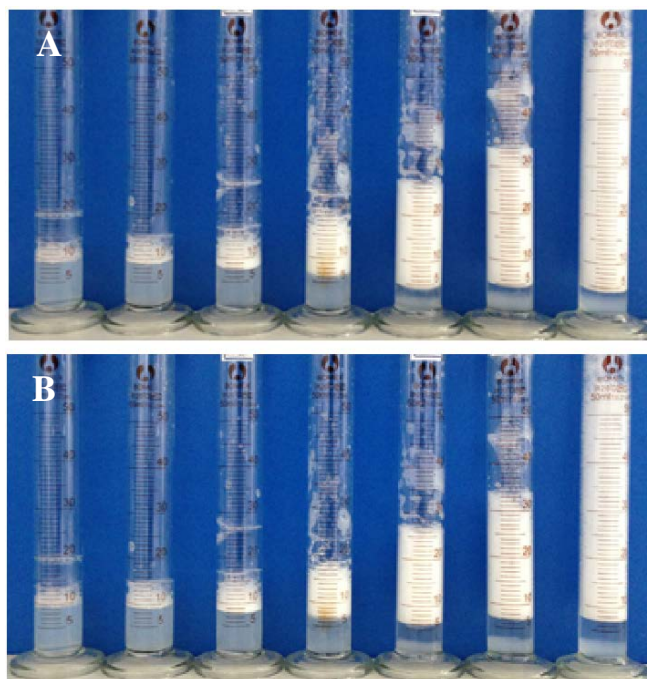


Figure 3. Micrographs of the bubbles in foams produced by shaking 10 cm³ of a dispersion of 0.5 wt.% silica particles in CTAB solution at different concentration taken immediately after shaking. [CTAB]/mM from A to F: 0.01, 0.03, 0.06, 0.10, 0.20 and 0.30.

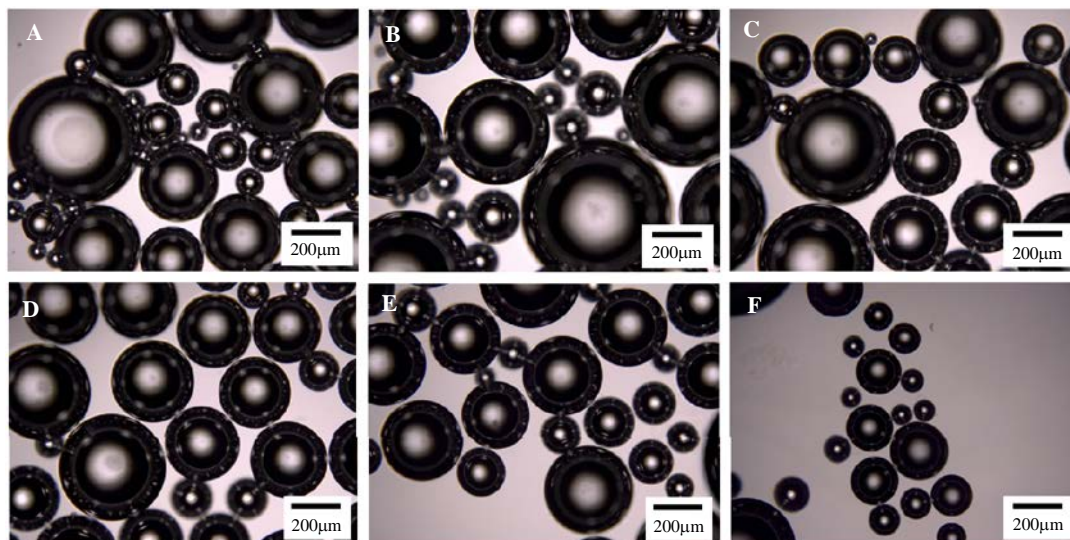


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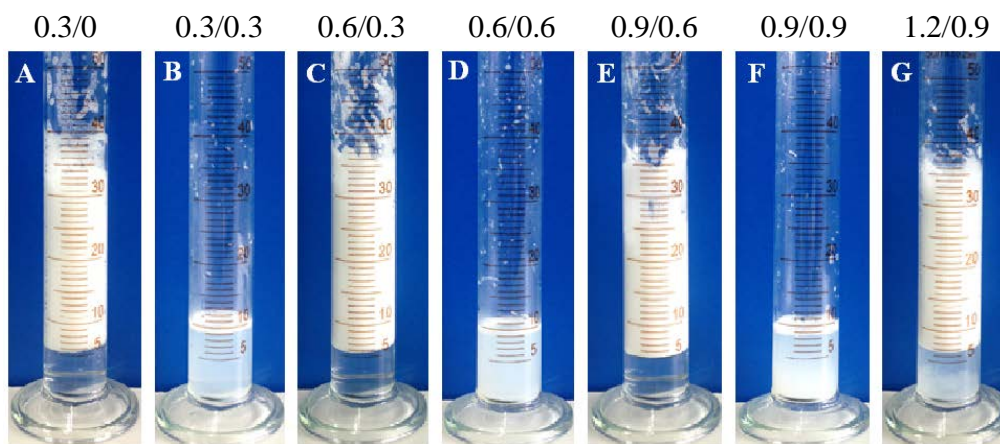


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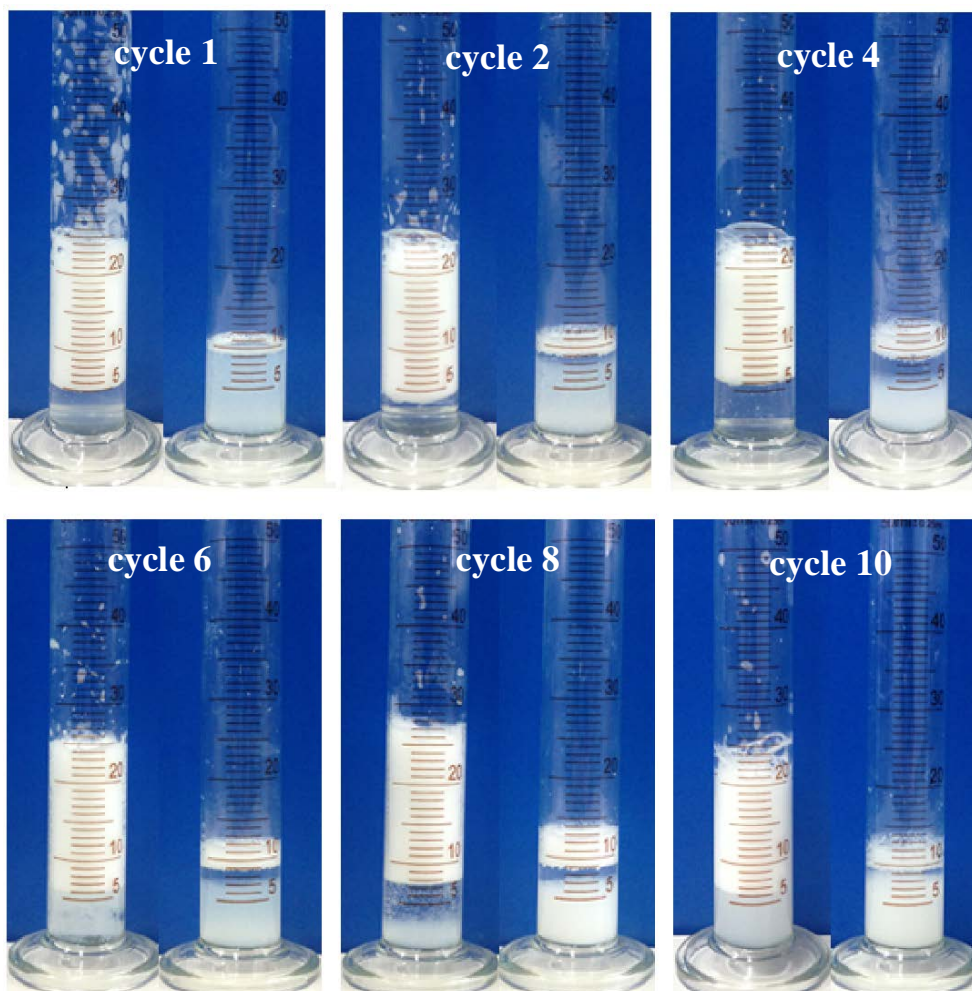


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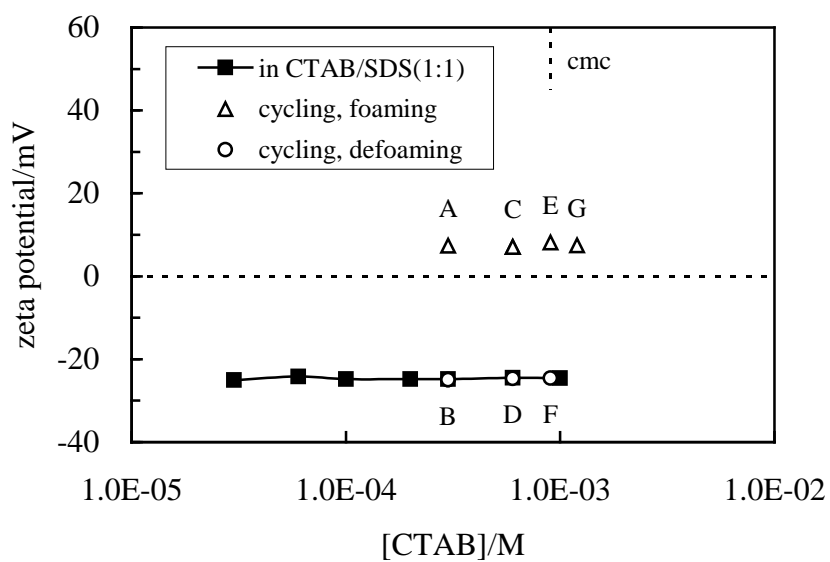
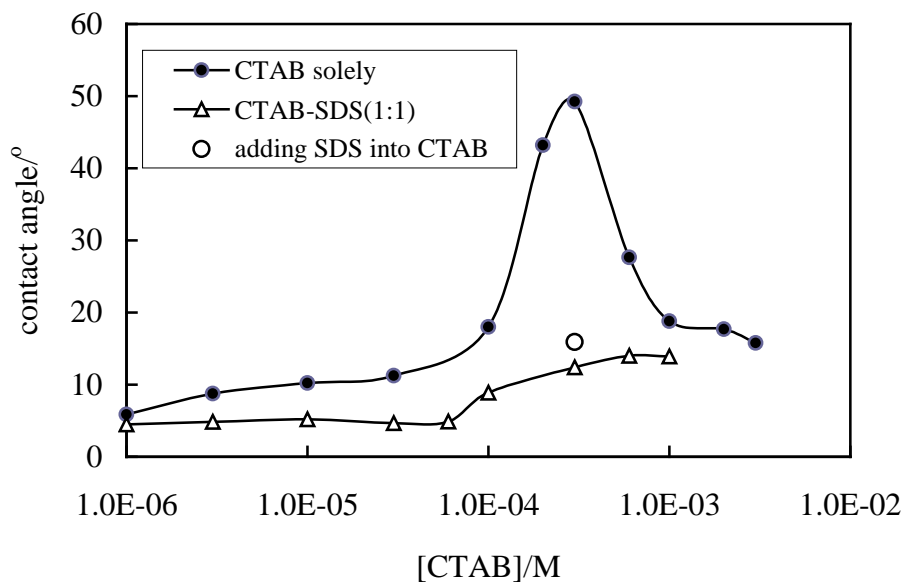
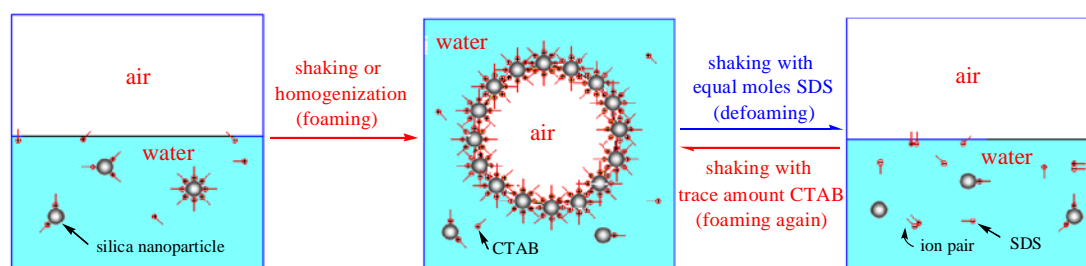


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TOC Graphic



Responsive particle-stabilized aqueous foams can be obtained by using commercially available silica nanoparticles and conventional ionic surfactants. The negatively charged silica nanoparticles are initially hydrophobized *in situ* with trace amount of a conventional cationic surfactant to become surface-active, and can then be de-hydrophobized *in situ* by adding an equal amount of anionic surfactant. The latter prefers to form ion pairs with the cationic surfactant, making it desorb from particle surfaces and thus rendering the particles surface-inactive. Once another trace amount of cationic surfactant is added, the particles are hydrophobized *in situ* again. The stronger electrostatic interaction between oppositely charged ionic surfactants than that between the cationic surfactant and particles is the trigger.