Communications

Ultrastable Particle-Stabilized Foams**

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Aqueous foams are important in a variety of different applications, ranging from food and cosmetics to oil recovery, blast mitigation, and fire extinguishing.[1] Well-established and emerging applications that use foams as an intermediate structure to produce macroporous materials are also widely used in the field of engineering to fabricate thermal insulating materials and low-weight structures, as well as in medicine to produce artificial implants and scaffolds for drug delivery and tissue engineering.[2–4] The thermodynamically unstable nature of liquid foams is a critical issue in all these applications. Foam instability arises from the high energy associated with the gas–liquid interface, and constitutes a driving force for decreasing the total interfacial area of the foam through coalescence and disproportionation (Ostwald ripening) of the bubbles. Such processes can be partially hindered by using long-chain surfactants or biomolecules such as lipids and proteins to adsorb at the air–bubble surface and reduce the gas–liquid interfacial energy.[1] In addition to surfactants and biomolecules, colloidal particles have long been exploited to stabilize oil droplets in Pickering emulsions.[5–7] However, it was only recently recognized that partially hydrophobic particles can also attach to gas–liquid interfaces and stabilize air bubbles in surfactant-free diluted suspensions.[7–10] The attachment of particles at the gas–liquid interface requires an optimum balance between the solid–liquid, solid–gas, and liquid–gas interfacial tensions and is therefore dependent on the wetting behavior at the particle surface (Figure 1 a,b).[7]

A number of approaches have been described to change the lyophobicity and wetting properties of solid particles so as to favor their attachment at gas–liquid interfaces. In the flotation industry, for example, wetting is usually controlled through the adsorption of long-chain surfactants (typically > 10 carbon atoms) on the particle surface.[11–15] Hydrophobic silane species have also been deliberately grafted on to the surface of silica nanoparticles to enable model investigations in the absence of surfactants to be performed.[7–10, 16–20] However, in all the particle-stabilized foams reported so far, the concentration of modified particles in the liquid medium is not sufficiently high to stabilize a large gas–liquid interfacial area. Therefore, the initially aerated suspension undergoes extensive drainage and creaming before a stable floating foam is achieved on top of the liquid phase.[7–10, 16, 20] The stabilization of a high concentration of sub-millimeter-sized air bubbles that do not undergo drainage or creaming would, however, be highly advantageous in many foam applications.

We report here a simple and versatile approach to prepare ultrastable particle-stabilized foams that percolate throughout the entire liquid phase and exhibit no drainage or creaming effects. The novelty of our method is the fact that it enables the surface modification of a high concentration of colloidal particles in the liquid phase, thus allowing the stabilization of a large gas–liquid interfacial area against disproportionation, coalescence, drainage, and creaming. Herein we describe and discuss: 1) our approach to surface-modify a large number of particles in the liquid phase, 2) the resulting attachment of lyophobized particles at a gas–liquid interface, 3) the foaming behavior after surface modification, and finally 4) the foam stability achieved. The examples described herein illustrate the universal nature of the method, which in principle can be extended to any type of oxide or non-oxide particles regardless of their initial wetting behavior.

Colloidal particles of various chemical compositions (Figure 1 c) were surface-lyophobized through the adsorption of short-chain amphiphilic molecules on to the particle surface. A key feature of our approach is the use of short amphiphiles (typically < 8 carbon atoms) which exhibit high solubility and high critical micelle concentrations in the aqueous phase. This is a primary requisite to enable the

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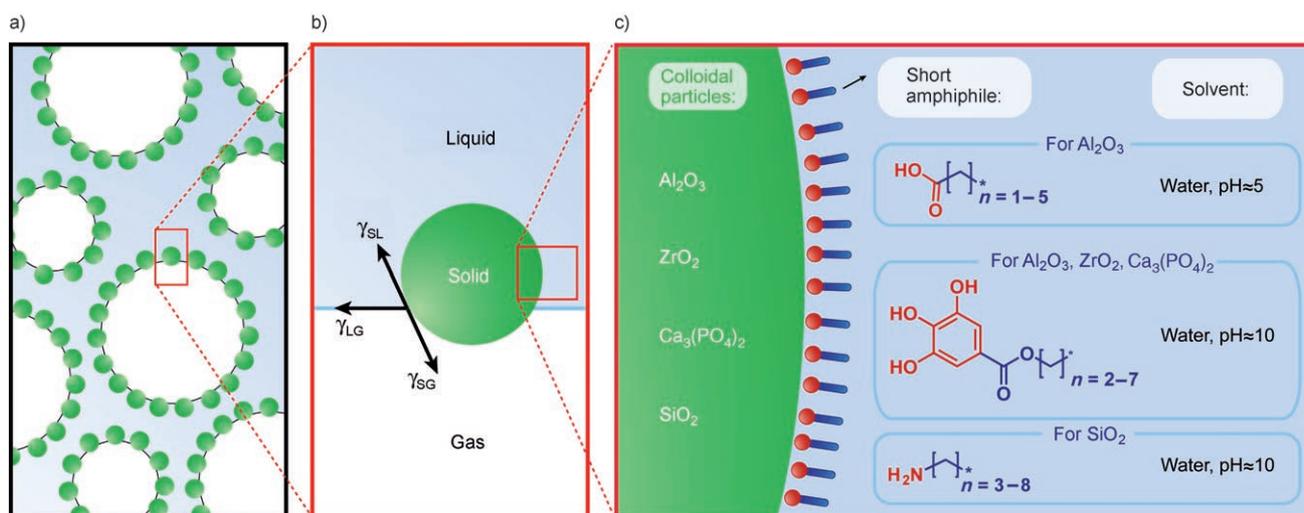*Angew. Chem. Int. Ed.* **2006**, *45*, 3526–3530

Figure 1. Possible approaches to attach colloidal particles at gas–liquid interfaces by tuning their surface-wetting properties. a) Schematic illustration of the stabilization of gas bubbles with colloidal particles (the particle size is exaggerated for clarity). b) The adsorption of partially lyophobic particles at the gas–liquid interface, illustrating the balance in tension (γ) responsible for the attachment of particles. c) The approaches used to tune the wetting properties of originally hydrophilic particles to illustrate the universality of the foaming method developed. The same principles can be easily extended to other types of particles, by using different surface modifiers as well as liquid and gaseous phases.

surface modification of a high concentration of colloidal particles in the liquid phase. By choosing appropriate anchoring groups and pH conditions (Figure 1c), particles were surface-lyophobized through the adsorption of short amphiphiles through electrostatic interactions (carboxylates and amines) and ligand-exchange reactions (gallates).[21] Figure 2a shows an example of the electrostatic-driven adsorption of anionic carboxylate amphiphiles onto positively charged alumina particles in a suspension under acidic conditions (Figure 1c). The lyophobization achieved by adsorption of the amphiphile was confirmed by contact-angle measurements of aqueous solutions of valeric acid ($0.05\ mol\,L^{-1}$; pH 4.75) deposited on polycrystalline alumina substrates: angles of approximately 60° were measured through the aqueous phase. Lyophobization occurs as a result of the relatively strong interaction between the anchoring group and the particle surface, thus leaving the amphiphile's hydrophobic tail in contact with the aqueous solution. In the case of the example shown in Figure 2a, the adsorption of negatively charged carboxylate ions on to the alumina surface screened the surface positive charge at acidic pH values, thereby reducing the zeta potential of the particle in water. Therefore, addition of carboxylate amphiphiles beyond the concentrations depicted in Figure 2a led to strong coagulation of the particles as a result of van der Waals and hydrophobic attractive forces.[22–25]

The attachment of the resulting partially lyophobic particles at the air–water interface was indirectly evidenced by surface-tension measurements on a droplet of the suspension at various concentrations of added amphiphilic molecules (Figure 2b). A relatively abrupt decrease in surface tension was observed for amphiphile additions above a certain critical concentration. Since a fraction of the added amphiphiles does not adsorb at the particle surface (Figure 2a), part of the observed reduction in the surface tension

was caused by the adsorption of free amphiphilic molecules at the air–water interface. To investigate this issue, the individual contributions of the free amphiphiles and of the partially lyophobic particles to the reduction in the overall surface tension was measured. Figure 3 shows as an example the case of suspensions with butyric acid. The contribution of the amphiphile alone was evaluated by measuring the surface tension of aqueous solutions containing amphiphile concentrations corresponding to the fraction of non-adsorbed molecules given in Figure 2a. The results shown in Figure 3 indicate that the contribution of amphiphiles ($\Delta\gamma_{amph}$) to the overall surface tension increases steadily below the critical amphiphile concentration, whereas the contribution of modified particles ($\Delta\gamma_{part}$) remains constant. However, a drastic increase in the contribution of modified particles to the overall surface tension is observed for amphiphile concentrations above the critical point. This finding indicates that a significant fraction of modified particles attach at the air–water interface at amphiphile concentrations beyond the critical condition. This result was also evidenced by the formation of a thin stiff skin on the surface of suspensions prepared with amphiphiles above this critical concentration.

The presence of partially lyophobized particles in the suspension enabled the preparation of foams simply by incorporating air bubbles through mechanical frothing. Foams prepared by vigorous mechanical shearing of concentrated alumina suspensions (35 vol% solids) showed a five- to sixfold increase in volume at optimum concentrations of carboxylic acid (Figure 2c). This volume increase corresponds to an amount of incorporated air of approximately 85% air with respect to the total volume of the foam. A bubble-size distribution ranging typically from 10 to 100 μm is formed through this foaming process under conditions that produce the maximum amount of foam. Narrower bubble-size distributions are achieved by increasing the particle lyophobicity.
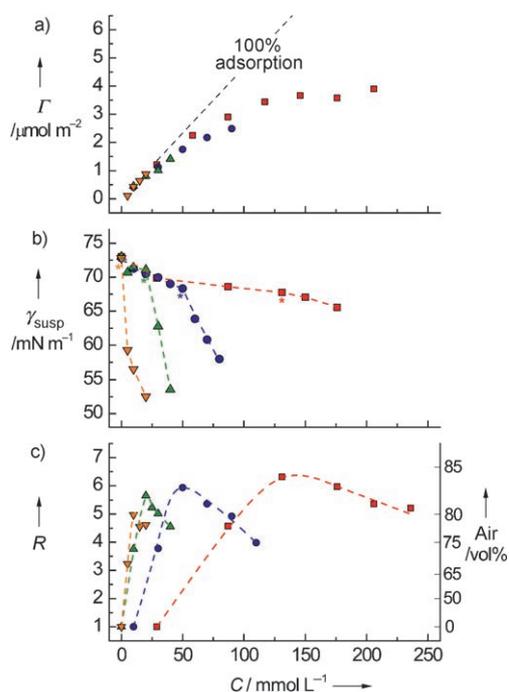
Figure 2. Example of surface lyophobization and foaming behavior using alumina particles and short fatty acids as amphiphiles (■: propionic acid (C₃), ●: butyric acid (C₄); ▲: valeric acid (C₅), ▼: enanthic acid (C₇)). a) Surface lyophobization of colloidal particles accomplished through the electrostatic-driven adsorption of negatively charged carboxylic acids on to positively charged alumina particles. The symbols Γ and C denote the amount of amphiphile adsorbed per unit surface area of alumina and the initial concentration of the amphiphile added to the suspension, respectively. b) The ability of lyophobized particles to attach at air–water interfaces results in a significant decrease in the surface tension of colloidal suspensions (γ_{susp}). The asterisks (*) indicate the critical concentration at which the particles are supposed to attach at the gas–liquid interface. c) The decrease in surface tension resulted in remarkably high foamability upon high mechanical shearing. R is the foam expansion ratio given by the volume of foam divided by the volume of the initial suspension. The volume percentage of air incorporated in the foams is also indicated on the right *y*-axis in (c). All data were obtained from 35 vol% alumina suspensions at pH 4.75.

A further increase in the surface lyophobicity leads, however, to strong coagulation between particles in the liquid media, thus hindering the attachment of particles at the gas–liquid interface and thus hindering the foaming process.

In general, foam formation was favored by increasing the particle concentration or decreasing the particle size in the initial suspension. Such trends are explained by the fact that an increase in particle concentration and a decrease in particle size reduce the time required for the modified particles to diffuse and adsorb on to the surface of the air bubble.[26–28] For the particle size used in the example reported in Figure 2 (diameter: ca. 200 nm), a minimum colloid concentration of 15 vol% was necessary to obtain relatively stable, high-volume foams. However, this lower concentration limit could be reduced to approximately 5 vol% by using highly mobile partially lyophobized nanoparticles (diameter: ca. 70 nm) as foam stabilizers (see the Supporting Information). The production of fresh bubbles at very high rates
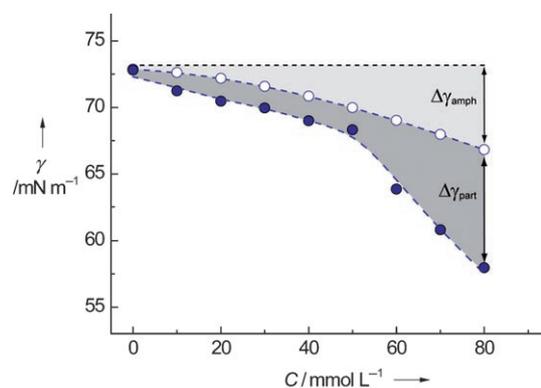

Figure 3. Reduction in surface tension resulting from free amphiphiles (open symbols) and by the combined effect of surface-modified particles and free amphiphiles (filled symbols). Butyric acid is the amphiphile used in this example. The graph illustrates the individual contribution of the free non-adsorbed amphiphiles ($\Delta\gamma_{amph}$) and that of the modified particles ($\Delta\gamma_{part}$) to the overall decrease in the surface tension of the suspension. All data were obtained at pH 4.75, either from 35 vol% alumina suspensions (filled symbols) or aqueous solutions of butyric acid containing the concentration of non-adsorbed amphiphiles depicted in Figure 2a (open symbols).

during air incorporation was also observed to be crucial for the preparation of foams that can percolate throughout the entire volume of the initial suspension. The aforementioned general foaming behavior was observed for all the examples outlined in Figure 1c (see the Supporting Information).

The adsorption of lyophobic particles at the air–water interface of our foams was also confirmed by confocal microscopy images of air bubbles obtained from the dilution of concentrated fluorescent silica foams. A large number of extremely stable air bubbles or hollow colloidosomes[29] were produced upon dilution of the foam (Figure 4). Small clusters of particles were adsorbed at the air–water interface, thus suggesting the existence of an attractive colloidal network around the air bubbles.

The stability of our high-volume particle-stabilized foams was compared to that of foams known to be very stable in cosmetic and food applications. No liquid drainage, creaming, or bubble disproportionation was observed in the particle-stabilized foams four days after their preparation (see the Supporting Information). Highly stable foams were actually only produced with amphiphile additions higher than the critical concentrations depicted in Figures 2b and 3, thus indicating that the stable foams prepared in this work are indeed stabilized by partially lyophobized colloidal particles. The outstanding stability of the particle-stabilized foams contrasts to the markedly higher drainage and disproportionation rates of food and cosmetic wet foams. Liquid foams containing conventional long-chain surfactants adsorbed at the air–water interface collapse much faster—typically within a couple of minutes—than the foams investigated here.[10] The remarkable resistance of our particle-stabilized foams to coalescence and disproportionation is most likely imparted by the strong attachment of particles at the air–water interface (Figure 4) and by the formation of an attractive particle network at the interface and throughout the foam lamella.[8, 9]
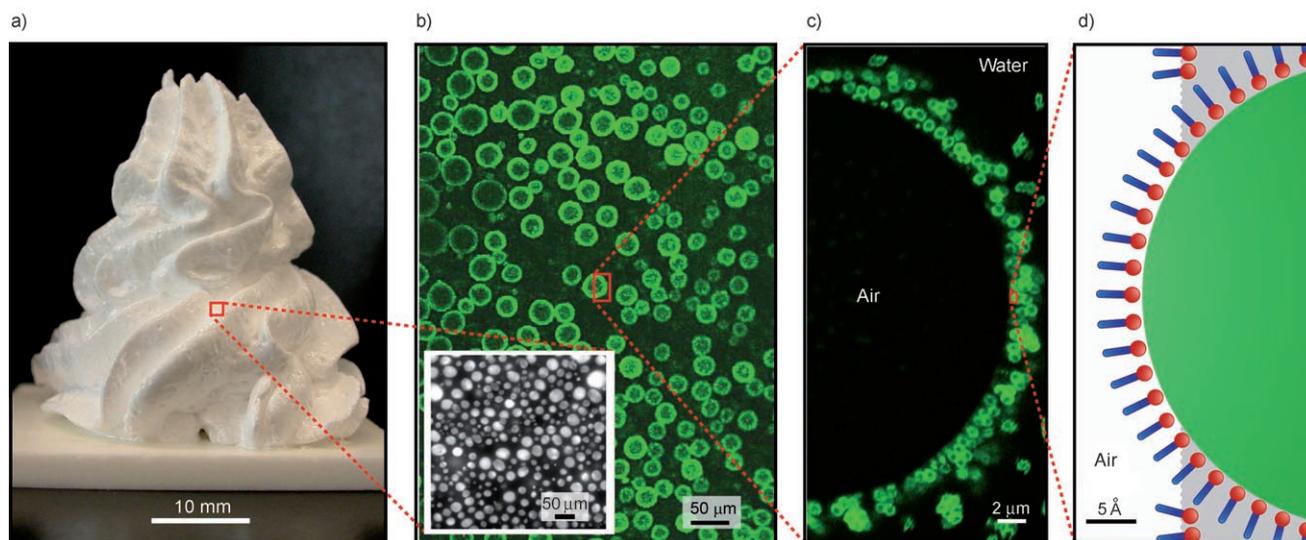
Figure 4. Hierarchical features of the particle-stabilized foams containing short amphiphilic molecules. High-volume macroscopic foams (a) with bubble sizes within the range 10–50 μm (b) are formed through the adsorption of submicrometer-sized colloidal particles at the air–liquid interface (c). Particles attach at the air–water interface as a result of the surface hydrophobicity imparted by the adsorbed amphiphilic molecules, as indicated schematically in (d). The confocal images shown in (b) and (c) were obtained after dilution of concentrated foams (inset in b) containing fluorescently labeled silica particles and hexylamine as amphiphile.

The unique colloidal architecture responsible for the long-term stability of the foam depicted in Figure 4 is based on the sequential assembly of amphiphiles on the surface of the particles and of particles on the surface of air bubbles, which leads to a hierarchical structure spanning over more than five orders of magnitude in length scale. Foam assembly involves a high degree of synergism between the individual components of different length scales, which lead ultimately to the intricate hierarchical structure depicted in Figure 4.

High-volume wet foams with remarkable long-term stability and bubble size as small as 10–100 μm can be prepared for cosmetic and food applications by using the described method. The strong attachment of particles at the air–water interface also enables the fabrication of an enormous number of hollow colloidosomes (Figure 4b) for a variety of emerging applications.[29] Additionally, the outstanding stability of the foam has allowed us to fabricate bulk macroporous structures with a variety of different ceramic, polymeric, and metallic materials by drying and heat treating the wet foams (see the Supporting Information). Macroporous materials prepared by this simple and straightforward method can be used as low-weight structural components, porous media for chemical and biological separation, thermal and electrical insulating materials, catalyst supports, refractory filters for molten metals, and scaffolds for tissue engineering and medical implants.[2–4] Therefore, we expect this novel technique to open up new opportunities in a wide number of areas, including food, cosmetics, engineering, biology, and medicine.

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