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Gas Bubbles

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Generation of Superstable, Monodisperse Microbubbles Using a pH-Driven Assembly of Surface-Active Particles

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Bubbles are everyday objects and easy to make? Not so, when one is trying to generate and maintain tiny bubbles with accurately defined volumes in the nanoliter range or even smaller. This follows from the fact that the gas/liquid interface (the bubble boundary) is energetically expensive. As a consequence, this interface has a tension γ and the bubble has a spherical shape (with radius R), which minimizes the surface area for a given volume. To maintain the curvature of the bubble in equilibrium, a pressure drop ΔP across the interface is required, which can be described according to the Young–Laplace law [Eq. (1)].

$$\Delta P = \frac{2\gamma}{R} \quad (1)$$

From this relationship it is clear that as bubbles get smaller, their internal pressure increases to infinity. As a consequence, very small bubbles are not only difficult to make, but are even more difficult to maintain because the contained gas, which is generally soluble in the surrounding liquid, goes into the solution, leaving behind an even smaller bubble at an even higher pressure, which dissolves even more rapidly etc. This leads to a vicious circle that ultimately results in the disappearance of the bubble.

The interest in generating and stabilizing tiny bubbles at accurately controlled volumes is manifold from a fundamental and applied perspective. For example, introducing a small amount of tiny bubbles into a liquid dramatically changes its compressibility, whilst its density remains virtually unchanged. Such modifications have a dramatic effect on the acoustic properties of the liquid,[1] which is why they are employed as contrast agents for ultrasound examinations.

The aggregation of a large number of bubbles leads to the construction of foams, which, if all the bubbles have the same volume, self-organize under the force of gravity or compaction into highly crystalline structures.[2–4] These may be polymerized in situ[5,6] to obtain microporous, multiscale materials with large surface-to-volume and rigidity-to-weight ratios,[7] or to form materials for other purposes.[8]

Producing stable bubbles for such purposes requires that the coalescence of neighboring bubbles is avoided. In recent years it has become possible, in the case of bubbles in aqueous solutions, to avoid both—bubble dissolution and coalescence—by transferring the concept of “Pickering emulsions” (liquid/liquid dispersions)[9] to foams (air/liquid dispersions): bubbles are stabilized solely by solid particles of nano- or micrometric dimensions, whose surfaces are chemically modified to be partially hydrophobic.[*][9–15] Similar to soap molecules, these particles prefer, on energetic grounds, to be at the gas/liquid interface, to which they are irreversibly adsorbed since the size of the particles makes the desorption energies orders of magnitude higher than those provided by thermal fluctuations.[16,17] If the density of the particles at the interface is sufficiently high, they form a rigid “armor”,[10,18–21] which not only inhibits dissolution of the gas, but also prevents neighboring bubbles from coalescing. Individual bubbles and liquid foams made in such a way can be stable for up to several months.[10–12,15,22] Contrary to intuition and to the Young–Laplace law stated above, such particle armors can maintain nonisotropic surface stress and therefore do not need to be spherical at equilibrium.[19]

A major challenge lies, however, in creating such bubbles or foams reproducibly with sufficient control over the volume, and at reasonable production rates. The decoration of the interfaces with a large number of particles requires that the particle surfaces are sufficiently hydrophobic. This requirement means, unfortunately, that one can only dissolve small amounts of the particles in the liquid used to generate the bubble. Furthermore, the generally charged particles experience energy barriers that hindere their adsorption at the interface.[14,18,21,23] These barriers can be overcome by using the inertial energy input of turbulent bubbling methods[12,22] or shear flow underneath the interface.[18] These methods suffer, however, from lack of control over the bubble size or low production rates, respectively.

Park et al.[24] recently proposed a technique which offers an elegant solution to all these challenges simultaneously by turning one of the key problems into a very useful tool: CO_2-filled bubbles dissolve in an aqueous dispersion of particles

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[*] These particles are not to be confused with “Janus particles”, which—like soap molecules—are truly amphiphilic, that is, they have one hydrophobic and one hydrophilic half. These also make very stable bubbles and droplets, but are much more difficult to produce.

whose hydrophobicity increases significantly with decreasing pH values (Figure 1). The dissolution of the CO_2 decreases the pH value in the vicinity of the bubble ($CO_2 + OH^- \leftrightarrow HCO_3^-$), which increases substantially the hydrophobicity of the particles in this region, thus forcing them out of solution to the gas/liquid interface. As the bubble continues to shrink, more and more particles arrive at the interface, where they are simultaneously compacted because of the shrinkage of the bubble surface. The dissolution of the bubble stops when the particles are densely packed—in the case of monodisperse particles (with low charge), this is when the particles are in a close-packed arragement (Figure 2).[18] Similar experiments, but on complex foam structures and with an externally controlled pH value, have been presented recently by Binks et al.[25]

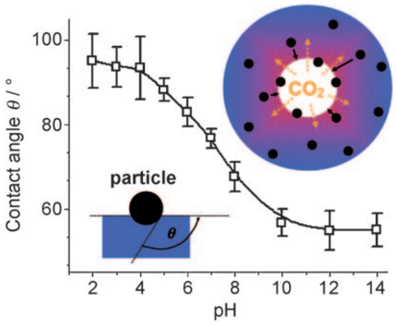

Figure 1. Dependence of the hydrophobicity (measured by the contact angle θ) of a PS-*co*-PAA surface on the pH value of an aqueous NaOH solution (obtained from contact angle measurements of an aqueous drop in air on a PS-*co*-PAA film). The bottom inset shows how the position of a particle at a gas/liquid interface is determined by the wetting angle of the liquid on the particle surface. The top inset shows how the pH-sensitive particles in a dispersion are driven to the surface of a CO_2 bubble, which is dissolving and hence renders the surrounding dispersion increasingly acidic.

Park et al.[24] have made use of a microfluidic technique to obtain spherical bubbles with very low polydispersity (less than 5%) at high rates (up to several hundred bubbles per second; Figure 2). In this approach, bubbles are generated by simultaneously injecting CO_2 at constant pressure and an extremely basic ($pH \approx 14$) particle dispersion at a constant flow rate Q_L into a microfluidic T-junction device.[26] The initial size of the bubbles can be controlled by adjusting the gas pressure, the flow rate Q_L of the dispersion, and the dimensions of the T junctions.[27]

The standard dispersion used by Park et al. is an aqueous NaOH solution containing monodisperse, micrometer-sized poly(styrene-*co*-acrylic acid) (PS-*co*-PAA) particles. Protonation of the carboxylic groups on the particle surface results in the hydrophobicity of these particles increasing significantly as the pH value of the surrounding solution decreases. Figure 1 shows this effect for the example of an extended PS-*co*-PAA film, where the hydrophobicity of the surface was characterized by the contact angle with the aqueous solution.

After their generation, the bubbles travel along the microchannel, where the CO_2 rapidly goes into solution (order of seconds), which decreases the pH of the dispersion and forces the particles to the interface. The dissolution of the bubble comes to a halt when the particles are closely packed on the surface, as shown in Figure 2, bottom left. Such an interplay of processes means that one can accurately control the final size of the particle-stabilized bubbles by carefully tuning the initial bubble volume V_o, the flow rate Q_L, the particle concentration C_P and the pH value of the particle dispersion. Figure 3 shows a typical example of how the final bubble diameter $D_f = 2R$ and the relative change of the bubble volume $\Delta V/V_o$ depend on the flow rate Q_L of the dispersion in the microfluidic device.

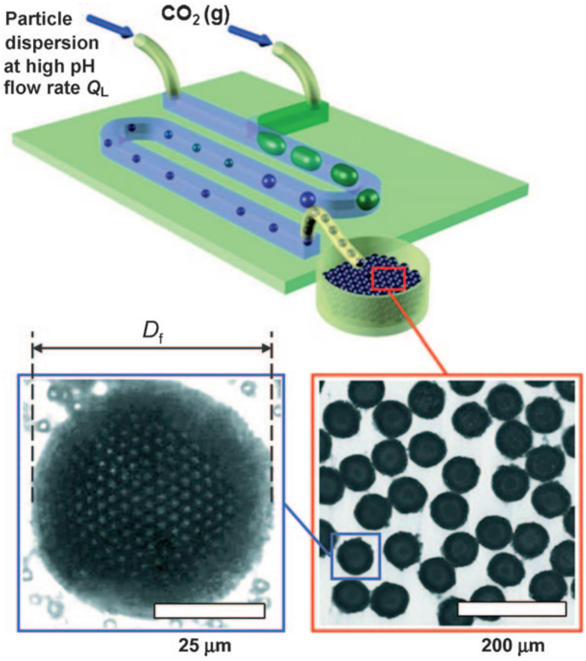

Figure 2. Highly monodisperse bubbles are generated by injecting CO_2 and a dispersion of micrometer-sized particles at high pH value simultaneously in a microfluidic device. As the bubbles travel along the channel, the CO_2 dissolves rapidly, thus rendering the dispersion increasingly acidic. This drives the pH-sensitive particles to the bubble surface where they form a close-packed rigid armor which makes the bubbles extraordinarily stable against further dissolution and coalescence.

Park et al.[24] have illustrated the general applicability of their approach by successfully decorating bubbles with other

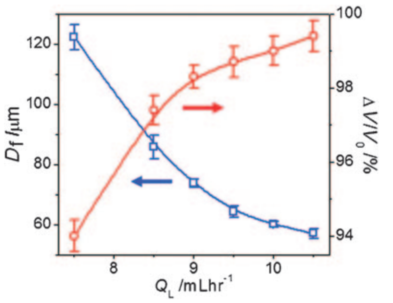

Figure 3. Dependance of final bubble diamter D_f and the relative change of volume $\Delta V/V_o$ on the flow rate Q_L of the dispersion in the microfluidic device.

anionic particle species such as carboxylated silica particles (20 nm diameter) with and without CdSe/ZnS core-shell quantum dots (QDs), and even with the protein bovine serum albumin labeled with fluorescein isothiocyanate (FITC-BSA at pH 7).

A disadvantage of this method is that the various controlling parameters are coupled in intricate ways. Changing, for example, the flow rate Q_L of the dispersion simultaneously influences the initial bubble volume,[28] the rate of dissolution of the CO_2, and the number of particles transported into the vicinity of the bubble. Hence, even if initial attempts at modeling this process were made by Park et al.,[24] a proper quantitative description will require significantly more complex modeling studies. In the meantime, however, thorough calibration of experiments should provide satisfactory control over the final size of the bubbles and thus provide a route to the development of a range of interesting materials. This will certainly include the application of this method to the generation of particle-stabilized droplets. An interesting extension to this method would be the controlled destruction of stabilized bubbles or droplets for drug-delivery purposes, for example.

Park et al.[24] generated bubble sizes of the order of 50 micrometers, but there is no apparent reason why this technique could not be used to produce significantly smaller final bubbles (by using appropriately sized particles) and therefore generate micro- or even nanoporous materials with very unusual light- or heat-transport properties.[29] For this purpose, a significant up-scaling of bubble production needs to be envisaged, for example, by parallelization of this technique.[30,31]

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