Capillary Foams: Stabilization and Functionalization of Porous Liquids and Solids

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S *Supporting Information*

ABSTRACT: Liquid foams are two-phase systems in which a large volume of gas is dispersed as bubbles in a continuous liquid phase. These foams are ubiquitous in nature. In addition, they are found in industrial applications, such as pharmaceutical formulation, food processing, wastewater treatment, construction, and cosmetics. Recently, we reported a new type of foam material, capillary foam, which is stabilized by the synergistic action of particles and a small amount of an immiscible secondary liquid. In this study, we explore in more detail the foam preparation routes. To illustrate some of the potential applications, we create vividly colored wet and dried foams, which are difficult to prepare using traditional methods, and load-bearing porous solids. The combined action of particles and immiscible secondary fluid confers exceptional stability to capillary foams and many options for functionalization, suggesting a wide range of possible applications.
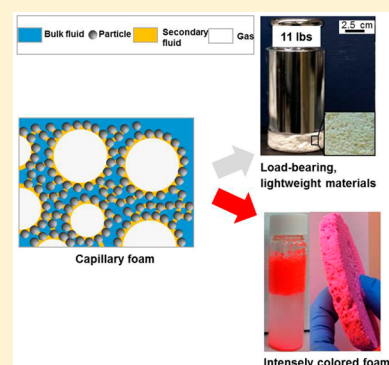
INTRODUCTION

Liquid suspensions of solid colloidal particles (Figure 1a) are ubiquitous in nature and are widely used in industry, including pharmaceutical formulations, foods, coatings, adhesives, and cosmetics.[1−3] Colloidal particles can adsorb strongly to liquid−gas or liquid−liquid interfaces of foams and emulsions and form a protective particle layer around gas bubbles or liquid droplets.[4−8] The adsorption of particles with appropriate wettability tends to lower interfacial energy so significantly that the particle attachment is practically irreversible.[4−10] Consequently, any coalescence of particle-covered bubbles or emulsion droplets results in an increase in interfacial particle concentration. Once a sufficiently high interfacial coverage is reached, further coalescence is effectively inhibited and the covered emulsion droplets or foam bubbles become highly stable.[10,11] Particle-stabilized emulsions or foams, often called "Pickering emulsions" or "Pickering foams", have been prepared by agitating particle suspensions with an added immiscible liquid or a gas. Depending on the wetting properties of particles, either oil-in-water or water-in-oil emulsions can be stabilized, if the added fluid is a liquid (Figure 1b),[12] and either particle-decorated ("armored") foam bubbles in liquid suspension or liquid drops ("liquid marbles") in a continuous gas phase can be stabilized, if the added fluid is a gas (Figure 1d,e).[12,13] Even more complex multiphase colloidal systems, such as combined dispersions of particles, oil, and air in an aqueous medium, have received less attention in the scientific literature, but they are nonetheless relevant industrially, e.g., for oil recovery, food products like ice cream, cosmetics, or pharmaceuticals.[14−16]

In 2011, it was reported that the addition of a small amount (0.05−10 wt %) of an immiscible secondary liquid to a particle suspension can transform the suspension from a viscous fluid into an elastic gel ("capillary suspension"), in which particles at a relatively low volume fraction form a system-spanning network (Figure 1c) held together by the capillary forces associated with small liquid bridges between the particles.[17−19] Recently, we have shown that a new type of foam material ("capillary foams") can be formed from a particle dispersion by introducing both gas bubbles and a small amount of an immiscible secondary liquid (Figure 1f).[20] In these foams particles again are connected via bridges of the minority liquid, and the resulting network partly serves to entrap and immobilize gas bubbles. More importantly, the particles and the secondary liquid can jointly adsorb at bubble surfaces and stabilize the foam bubbles in a synergistic manner: While particles alone are known to stabilize foams if their wetting properties are appropriate, the addition of a secondary liquid can lead to stable foams even when the particles do not have the required wetting behavior to stabilize foam bubbles. In the case of aqueous foams with an oil as the secondary liquid, for instance, particles may readily adsorb at the air−oil or oil−water interface (but not at the air−water interface) and thereby
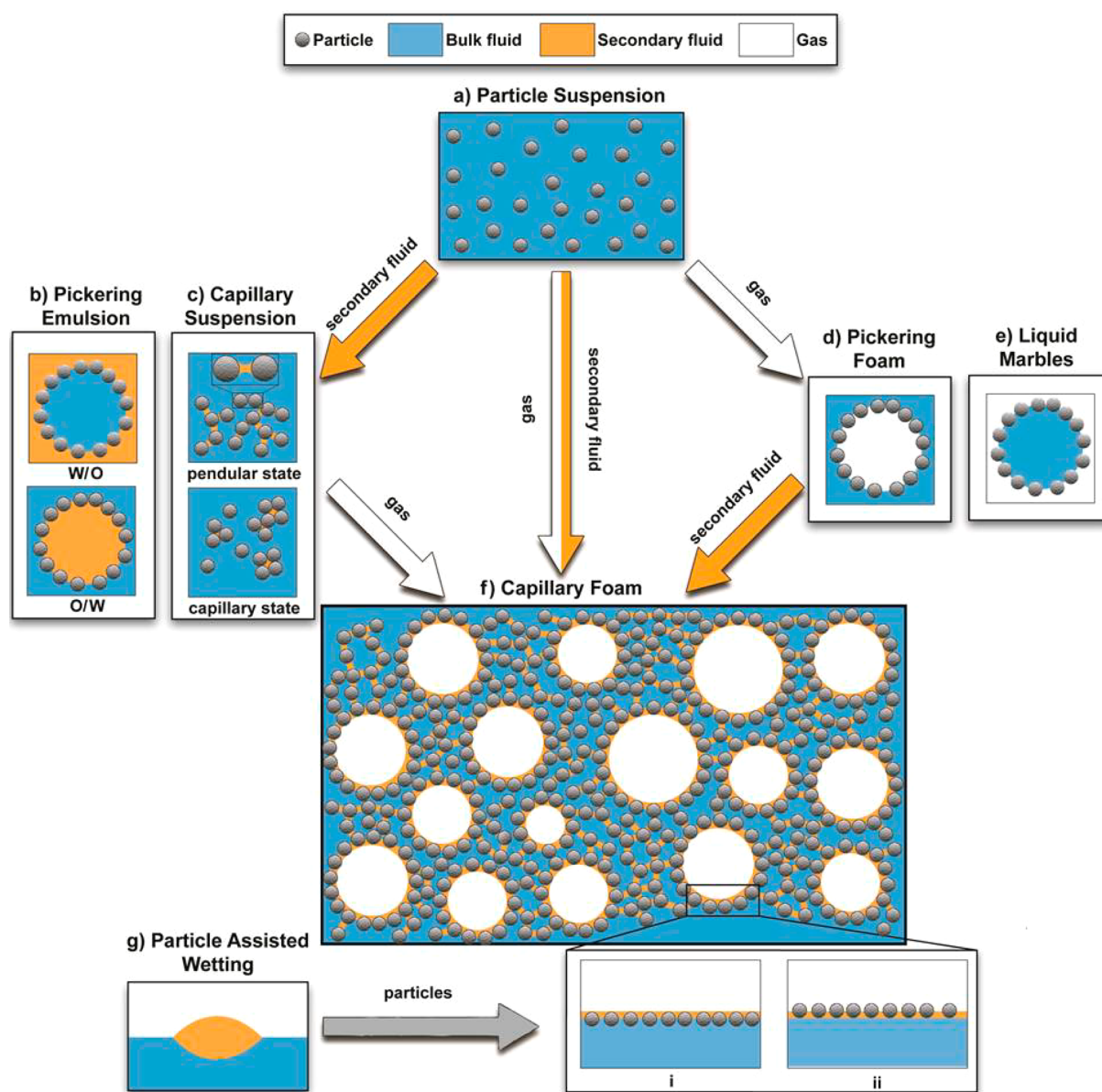
Figure 1. Multiphase colloidal systems prepared from particle dispersions. (a) Particle suspensions are the starting point. (b) Suspension mixing with a large amount of secondary liquid can result in "Pickering emulsion" drops of oil-in-water or water-in-oil stabilized with hydrophilic or hydrophobic particles, respectively. (c) Mixing with a small amount of secondary liquid can result in the formation of a capillary suspension, in which particles are connected by bridges of secondary liquid (forming either "pendular" menisci between particle pairs or the center of "capillary" agglomerates, depending on which liquid wets the particles preferentially). (d, e) Suspension mixing with a gas phase can lead to "armored bubbles" (particle-stabilized bubbles that connect, at high concentration, forming a "Pickering foam") or to "liquid marbles" (particle stabilized droplets in air), depending on the particle wettability. (f) In capillary foams, suspension particles and the secondary liquid jointly adsorb at the interface of the gas bubbles with the primary liquid. The decorated bubbles are further entrapped in a network of excess particles in the primary liquid bridged by a secondary liquid. (g) Particles adsorbing preferentially at the interface of the secondary liquid can mediate the spread of the secondary liquid film around the gas bubbles, which is directly analogous to the "particle-assisted wetting" of a macroscopic air−water interface by a drop of oil. Depending on their wetting properties, the particles can adsorb at the oil−water interface (i) or the oil−air interface (ii).

promote spreading of the oil around the gas bubbles,[20] in close analogy to the "particle-assisted wetting" of a planar water surface by an oil drop (Figure 1g).[21,22] In order to get stable capillary foams, the oil should successfully spread around the gas bubbles. In addition, the particle should have a strong affinity to adsorb at the oil−water interface (the outer interface of capillary foams).[20] In this paper, we show that capillary foams can be prepared alternatively either by introducing air and oil simultaneously to a particle suspension, by frothing a capillary suspension, or by mixing oil into a Pickering foam. To

illustrate some of the application potential, we demonstrate the preparation of intensely colored foams, which are notoriously difficult to achieve with traditional methods, and the preparation of load-bearing porous solids.

■ MATERIALS AND METHODS

Materials. Polyvinyl chloride particles (Vinnolit SA1062/7, average particle size 14.8 μm, particle density 1.41 g/cm^3) were obtained from Vinnolit, Germany. The polyethylene (PE) particles were purchased from Polysciences, Inc. The morphologies and size distributions of particles used in this study are shown in Figure S1 of the Supporting

Information. Trimethylolpropane trimethacrylate (TMPTMA) and sodium dodecyl sulfate (SDS) were purchased from Sigma-Aldrich, and benzoin isobutyl ether was purchased from TCI America. Nile Red, Allura Red, Oil Blue N, and FD&C Blue No. 1 dye were purchased from Sigma-Aldrich. Ultrapure water with a resistivity of 18.2 MΩ·cm (Barnstead) was used as the bulk phases of the foams in this study.

Preparation and Characterization of Load-Bearing, Lightweight, Porous Materials. The main processing steps can be summarized as the dispersion of particles, the introduction of secondary fluid and gas bubbles, and the solidification and drying of foams (as shown in Figure 2): (1) A suspension of particles in water as
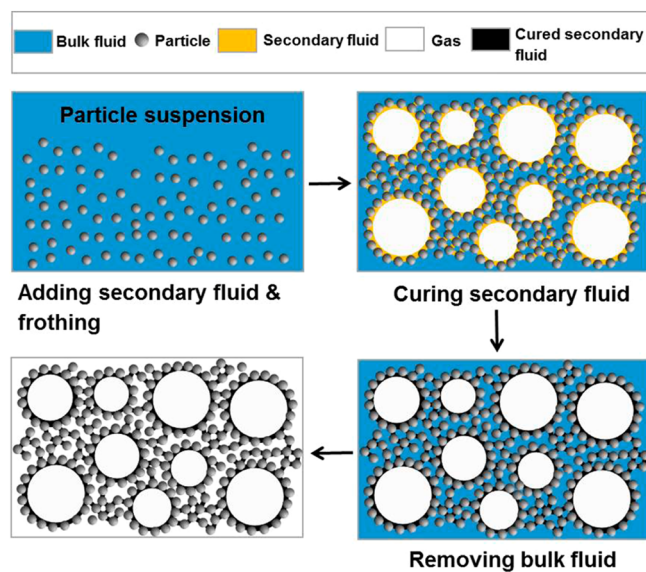

Figure 2. Processing steps for the preparation of load-bearing, lightweight, porous solids.

the primary liquid was obtained by dispersing the initially dried particles with the help of sonication. (2) A small amount (0.14−6%) of immiscible secondary fluid (the mass percentage of secondary fluid is with respect to water bulk in this study, unless otherwise noted) was added to the resulting particle suspension and frothed using a rotor–stator homogenizer (IKA UltraTurrax T10, stator diameter of 8 mm and rotor diameter of 6.1 mm) at 30 000 rpm or a hand mixer (Rival 5-Speed Hand Mixer) at the maximum speed. The TMPTMA was treated with Al$_2$O$_3$ to remove inhibitor and enriched with 6 wt % of the photoinitiator benzoin isobutyl ether. (3) The wet foam containing TMPTMA was cured by exposure to UV light (SpectroLine Longlife Filter, wavelength 365 nm) and then dried in an atmospheric oven (Fisher Scientific Co.) at 70 °C.

The porosity (ε) of dried foam was calculated by using $\varepsilon = 1 - (\rho_b/\rho_p)$, where ρ_b is the bulk density of the foams and ρ_p is the particle density. The ρ_b of foam was calculated by measuring sample mass and volume.

Preparation and Characterization of Colored Foams. Colored foams stabilized by SDS surfactant were formed by hand-shaking the water dispersion of surfactant and dye 20 times. Colored particle-stabilized foams (Pickering foam) were prepared by frothing a suspension of particles and dissolved dye using a rotor–stator homogenizer (IKA UltraTurrax T10, stator diameter of 8 mm and rotor diameter of 6.1 mm, 30 000 rpm). For the preparation of colored capillary foams, a suspension of particles in water was obtained by dispersing the particles via sonication, and then the dye solution, consisting of dye dissolved in the oil phase, was added. The resulting suspension was frothed using a rotor–stator homogenizer (IKA UltraTurrax T10, with a stator diameter of 8 mm, and a rotor diameter of 6.1 mm) at 30 000 rpm. The wet foam was characterized using a

Zeiss LSM 510 VIS confocal microscope (excitation at 543 nm and emission above 560 nm).

Spectral Acquisition of Foam Area Using Hyperspectral Technology. The foams were collected from each sample using a small, clean metal spatula and placed on a microscope slide, covering about a 0.5 × 0.5 mm^2 area (with no coverslip). Using a PARISS hyperspectral imaging system (LightForm, Inc., Asheville, NC), the color (in specular reflectance mode) of each foam was acquired under a Nikon 80i microscope outfitted with a monochrome Retiga 2000DC CCD camera (QImaging). Wavelength calibration was performed with a MIDL Hg$^+$/Ar$^+$ emission lamp (LightForm, Inc.), and accuracy was recorded and verified to be better than 2 nm using a 50 μm slit. To avoid heterogeneity of data due to complex surface geometry, a lack of plane focus, and sometimes movement of the foam, only one snapshot of spectral acquisition was done (taking less than 30 ms), covering a 5 × 0.005 mm^2 line across the foam surface, with a 10× objective. All spectra (ranging from 400 to 900 nm) from one individual sample (line) showing >99% closeness of fit were identified by one or two single representative spectra. Percent reflectance was calculated by dividing the sample spectra by that of a silver mirror reference standard with optimal reflectance in the range of visible wavelengths (Thorlabs, Newton, NJ).

Optical Density Acquisition of Bulk Liquid of Foam. Bulk liquid aliquots (200 μL) from each sample were placed in wells of a UV transparent 96-well plate (Corning Costar). Each well was scanned for optical density (percent transmittance) using a Spectramax I3 (Molecular Devices, Sunnyvale, CA), with a 1 nm incremental step from 230 to 930 nm.

RESULTS AND DISCUSSION

Water-Based Capillary Foams Can Be Prepared by Introducing Air and Oil Simultaneously or by either Frothing a Capillary Suspension or Mixing Oil into a Pickering Foam. Starting with 10 wt % PE particle suspension (Figure 3a), mechanical frothing produced PE particle-stabilized foam (Figure 3b). Figure 3c shows an image of a particle suspension prepared with 2 wt % TMPTMA, followed by stirring (60 rpm, 30 min). Figure 3g is a SEM image of the corresponding dried suspension from Figure 3c. Figure 3g shows that particles are connected by bridges of TMTPMA, confirming that capillary suspensions are formed in the bulk liquid of the suspension in Figure 3c. To study the possible routes of preparing capillary foams, we prepared foams by (1) introducing air bubbles and TMPTMA simultaneously into the PE particle suspension in which 2 wt % TMPTMA was initially added to the container of the suspension and then introduced to the whole suspension simultaneously with air bubbles by mechanical frothing (Figure 3e), (2) mechanically frothing a capillary suspension (Figure 3f), and (3) introducing TMPTMA to a PE particle-stabilized foam in which 2 wt % TMPTMA was added and the mixture was frothed again (Figure 3d). Parts h, i, j of Figure 3 show SEM images of the stabilized bubble of the corresponding dried foams in parts d, e, f, respectively. For the dried capillary suspension and foams, the secondary fluid was first solidified by photopolymerization, and then the water was removed by drying. It is known that photopolymerization of TMPTMA films already yields a solidlike gel at a conversion degree of only 3−4%.[23] As a conversion of only a few percent does not substantially change the polarity of the organic liquid, it is assumed that its contact angles and three-dimensional structure are retained at this point and remain unchanged as conversion proceeds further in the now solidified oil. The images in Figure 3h−j indicate that solidified TMPTMA spreads around gas bubbles and connects the particles in the bulk water phase and are taken to reflect the structure in the liquid state prior to TMPTMA polymerization.
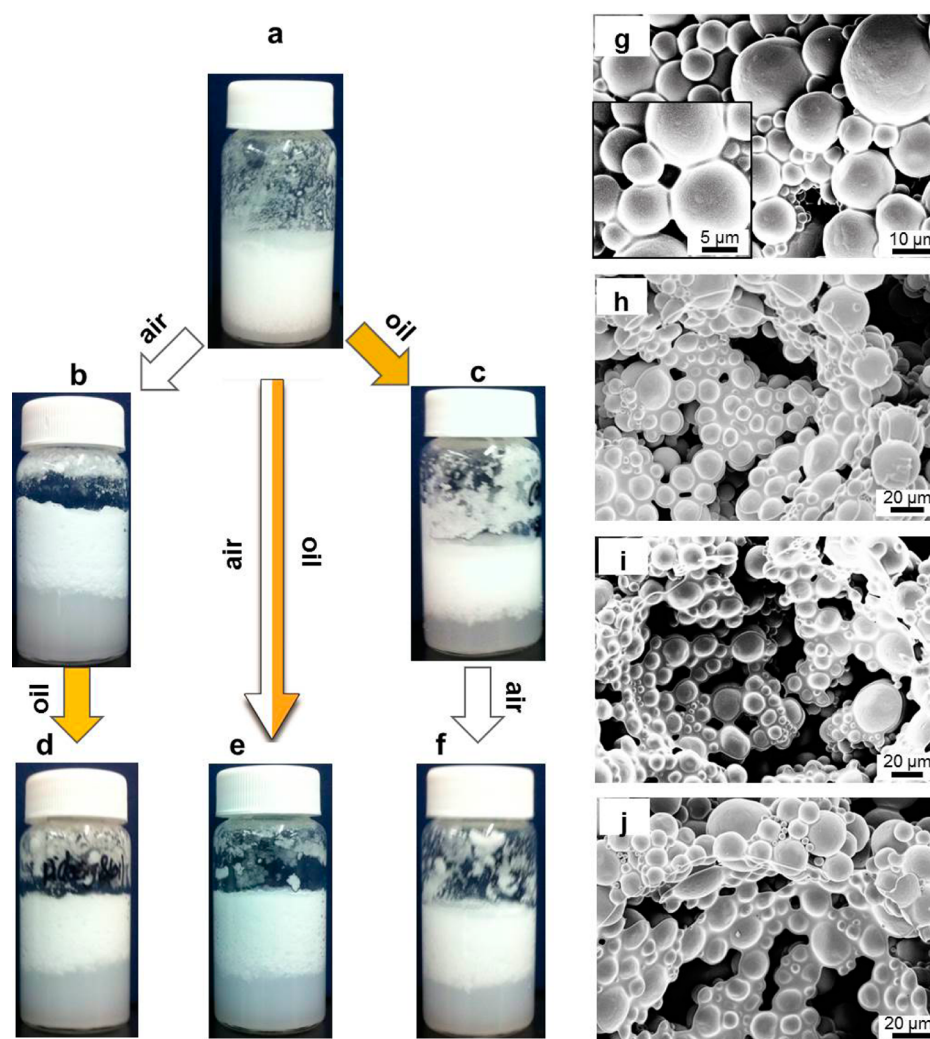
Figure 3. Capillary foams were prepared through multiple routes. (a) 10 wt % PE particle suspensions. (b) Mechanical frothing of the suspension produced a Pickering foam. (c) Suspension mixing with 2 wt % oil (TMPTMA) resulted in the formation of a capillary suspension. Capillary foams were prepared by (d) mixing 2 wt % oil (TMPTMA) with a Pickering foam, (e) introducing 2 wt % oil (TMPTMA) and air bubbles simultaneously to a particle suspension, and (f) introducing air bubbles to a capillary suspension. TMPTMA was treated with Al_2O_3 to remove inhibitor and enriched with 5 wt % of the photoinitiator benzoin isobutyl ether. (g) SEM image of dried capillary suspension in part c. The particles were bridged by the minority oil phase. (h, i, j) SEM images of corresponding dried foam in parts d, e, and f, respectively. Both particles and a thin oil film adsorbed on the bubble surface. For a dried capillary suspension and foam, the secondary liquid was first solidified by photopolymerization, and then the water was removed by drying.

Figure 3h–j suggest that both particles and a thin oil film adsorb on the bubble surface, and therefore, capillary foams were formed in Figure 3d–f. We can conclude that capillary foams can be prepared through multiple routes.

Figure 1 illustrates the connection between capillary foams and other colloidal multiphase systems, such as capillary suspensions or Pickering foams, and that the latter can be intermediates in the preparation of capillary foams. It would nonetheless be wrong to think of capillary foams simply as a Pickering foam with some added oil or as a capillary dispersion with some added gas bubbles: some particles suitable for capillary foams simply do stabilize an intermediate Pickering foam, and the ones that do require a major rearrangement, as oil adsorbs at the previously particle stabilized air–water interface. Similarly, the bubbles added to a capillary dispersion do not simply become entrapped in the existing particle network but also get "coated" via joint adsorption of oil and

particles, and as shown previously, the formation of a capillary network is not sufficient to stabilize capillary foams.[20]

Load-Bearing, Lightweight, Moldable, Porous, Solid Foams. Mold-casting, which is widely used in fabrication processes, is inexpensive and easy to control. To show that capillary foams are in principle amenable to this technique, we prepared wet capillary foams as described before and transferred them into different simple molds by hand, cured them under UV light, and then dried them in an oven at 70 °C overnight (Figure 4a,b). Figure 4 demonstrates that capillary foams can be molded into various shapes, and the moldability supports the application of these foams as materials for various applications.

In capillary foams, particles and an oil film jointly adsorb on the bubble surface, and the resulting mixed particle/oil coated bubbles are entrapped in a network of excess particles connected by bridges of oil.[20] Dried capillary foam consists of pores originating from the original gas bubbles and the
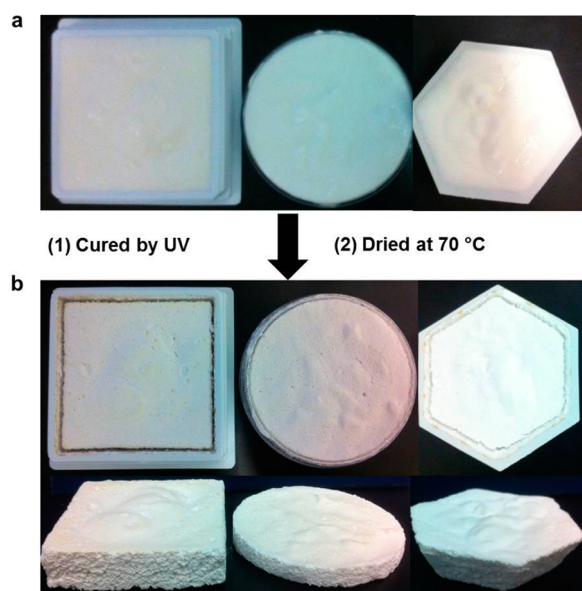
Figure 4. Mold-casting of capillary foams. (a) The prepared capillary foams with 25.2 vol % PVC 1062/7 particle concentration and 2.92 wt % TMPTMA were molded into containers of various shapes by hand. (b) Capillary foams were cured under UV light and then dried in an oven.

interparticle spaces in the initially liquid part of the foam. Because the walls of such dry foams consist of a porous (particle) network, these foams can achieve high overall porosity and low mass density. Moreover, the secondary liquid originally connecting the particles reinforces the particle network, enhancing its mechanical strength. For example, it is possible to solidify the secondary liquid prior to the removal of the primary liquid, thereby avoiding the need to apply high-temperature thermal sintering that is often used to enhance the mechanical properties of porous solids prepared from particles.[24,25] Dried capillary foams, such as those shown in Figure 5a, show promise as lightweight, load-bearing, functional materials. In this case, the secondary liquid TMPTMA was solidified by UV-initiated polymerization prior to removal of the bulk water.[21,22] We expect that the optimization of foam mechanical properties can be attained through the adjustment
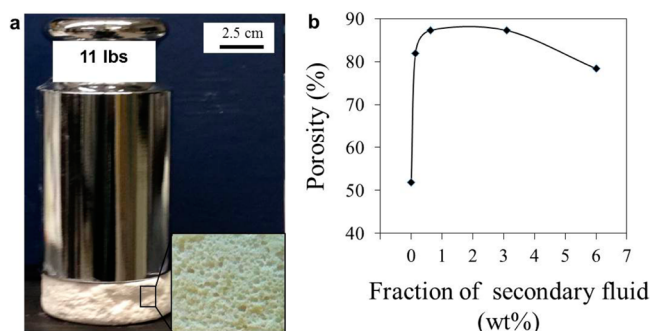

Figure 5. Functional load-bearing, lightweight, porous materials from capillary foams. (a) Photograph of an 11 lbs weight on a cured and dried foam with a density of 0.24 g/cm^3 and porosity of 82.97%. The foams were prepared from PVC (Vinnolit SA 1062/7) particles with a solid content of 21 vol % and 1.5 wt % TMPTMA by a hand mixer (Rival 5-Speed Hand Mixer) running at the maximum speed. (b) Variation in porosity with the amount of secondary fluid phase for prepared porous solids from capillary foam.

of preparation and drying conditions, as well as through alternative methods of solidifying the secondary fluid. Similarly, it is conceivable that properties can be tuned for use in thermal and acoustic insulation, packaging, transportation, shock absorption, and tissue scaffolding. Although the adaptation of capillary foams for a particular use is beyond the scope of this study, we anticipate that this new type of foam material will be a robust subject for future application-oriented research.

We investigated the effect of the amount of secondary fluid on the porosity of dried capillary foams and found a dramatic dependence of porosity on the concentration of added secondary liquid. Figure 5b shows the porosity of materials with an initial PVC 1062/7 particle loading of 10 vol % and various amounts of TMPTMA. As the fraction of secondary fluid increased, porosity first increased rapidly and then reached a plateau of 87.3%. (The corresponding mass density of foams initially decreased from 0.68 g/cm^3 and then reached a plateau of 0.18 g/cm^3.) However, porosity began to decrease to 78.37% (mass density 0.30 g/cm^3) at 3.09 wt % oil concentration. The increase of porosity at low oil concentration is caused by the incorporation of (oil- and particle-coated) gas bubbles into a tenuous network of particles stabilized by oil bridges. The decrease of porosity at high oil concentration may be attributed to the reduction of the volume of particle networks caused by the formation of larger number of attractive capillary bridges, resulting in a denser particle network in the suspension. In all cases, the porosity is higher than both that of the corresponding Pickering foam without secondary fluid and that of capillary suspensions without introduction of gas bubbles.[26,27]

Intensely Colored Capillary Foam. Aqueous foams are inherently unstable. Their instability arises from the large gas–water interfacial energy, which the foam systems tend to reduce by decreasing the total interfacial area via bubble coalescence and Ostwald ripening. Surfactant, such as SDS, is typically added to reduce interfacial energy by its adsorption at the air–water interface. Figure 6a shows the results of foaming a colored aqueous liquid with 0.050 wt % SDS, indicating an intense color in the bottom solution but weak coloration of the foam phase. The color intensity of the bulk liquid phase was determined by transmitted light spectrometry. Measuring the color intensity of the foam phase by using transmitted light spectrometry is difficult due to the diffusion and scattering of incident light in foams.[28] The color intensities of foams were measured by using hyperspectral imaging in reflectance mode. Quantitative analysis of the color intensity of dyes in the bulk liquid and foam phase is shown in Figure 6b,c, which demonstrates the strong absorbance in bulk liquid and weak reflectance for the foams at wavelengths of 500 and 630 nm. It appears that the majority of dye is concentrated in the bulk solution rather than in the thin films between the bubbles, as is observed qualitatively in the images. This appearance is typical of surfactant-stabilized foams made from colored liquids.[28]

Foam bubbles can alternatively be stabilized by colloidal particles, and the resulting foams are often called "Pickering foams". Colored Pickering foams stabilized by PE particles are shown in Figure 6d. Like the colored foams stabilized by surfactant, Figure 6d shows intense coloration in the bulk liquid phase and weak coloration of the foam areas. Figure 6e,f quantifies this with strong absorbance for the bulk liquid phase but weak reflectance for foams at wavelengths of 500 and 630 nm. The majority of colorants are concentrated in the bulk solution. The color intensity of the very thin films between the bubbles is insufficient to impart intense color to the foam. Kim
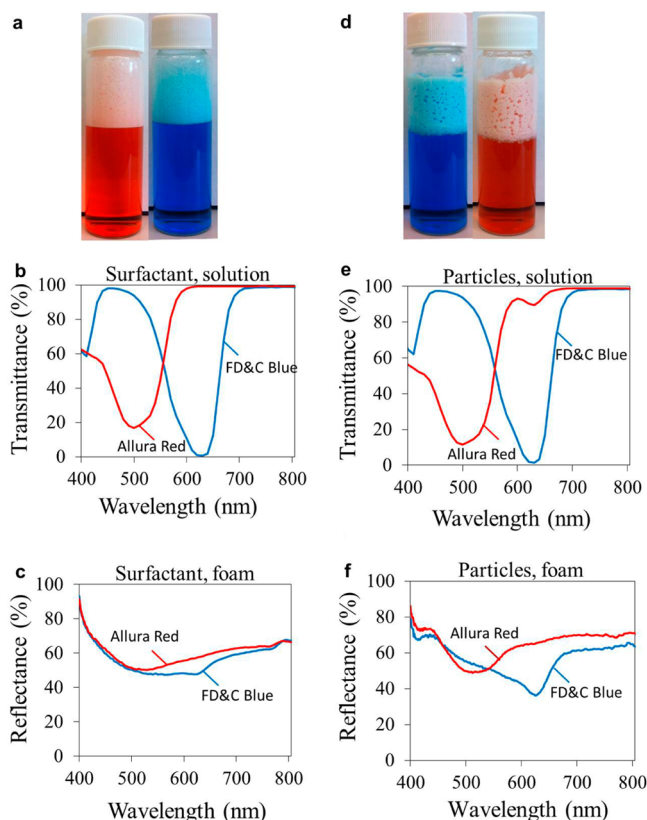
Figure 6. Photographs and spectra of colored foams formed by traditional foaming methods. (a) Photographs of foams stabilized by 0.05 wt % SDS surfactant and colored by 0.003 wt % Allura Red (left) or FD&C Blue No. 1 (right) dyes. (b) Transmittance spectra of the bulk liquid suspension of the foam in part a. (c) Reflectance spectra of the foam area of the foam in part a. (d) Photographs of foams stabilized by 7.41 wt % PE particles and colored by 0.0028 wt % Allura Red (right) or FD&C Blue No. 1 (left). (e) Transmittance spectra of the bulk suspension of the corresponding foams stabilized by PE particles in part d. (f) Reflectance spectra of the foam area of the corresponding foams stabilized by PE particles in part d.

and co-workers[28] reported a method of imparting intense color to foams stabilized with cellulose particles in which the dye was embedded in the particles during the synthesis process. However, it is not straightforward to dye many of the particles used to stabilize foams in industry, for example, silica and alumina particles.

The utilization of both particles and an oil phase in the capillary foams described above suggests an alternative method for incorporating a dye into the thin liquid films surrounding foam bubbles. To demonstrate this principle, described schematically in Figure 7, particles were dispersed in the water and the dye was dissolved in the oil phase, the oil-based dye solution was added to the aqueous dispersion and the mixture was frothed. On the basis of our previous study, we expect that the particles facilitate spreading of oil−dye solution around the air bubbles.[20] In the region between the gas bubbles, the particles are expected to be bridged by the dye solution. Figure 8a,c shows images of intensely colored capillary foams prepared in this manner, indicating weak coloration in the bulk phase but intense coloration of the foam area. Figure 8b,d quantitatively demonstrates the weak absorbance for the liquid phase and strong reflectance for the foam phase. Figure 8a,c shows confocal microscopy images of wet capillary foams
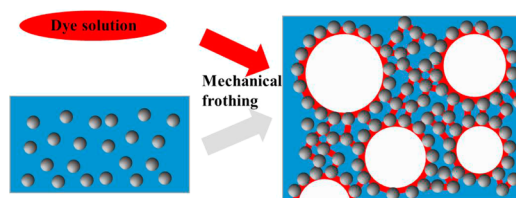

Figure 7. Schematic of the formation of a colored capillary foam. The dye is dissolved in the secondary fluid. During the foaming process, dyes adsorb onto the bubble surfaces, and they are bridged by particles in the region between bubbles.
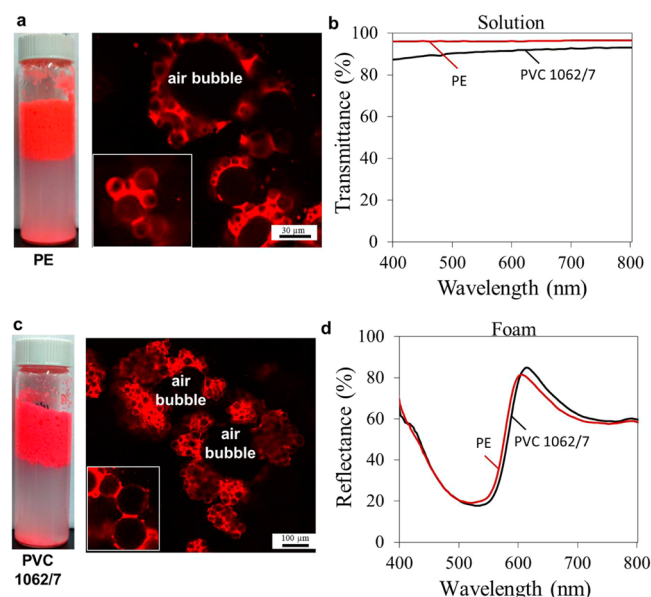

Figure 8. Intensely colored capillary foam. (a, c) Photographs and confocal microscope images of colored foams stabilized by 2 wt % dye solution (0.37 mg of Nile Red was dissolved in 0.5 g of TMPTMA) and 7.41 wt % PE or PVC 1062/7 particles. Insets in parts a and c are confocal microscopic images of the particle network among the bubbles. The additional zoom factors for the insets are 1.61 and 3.05, respectively. (b) Transmittance spectra of the bulk suspension of the corresponding capillary foam. (d) Reflectance spectra of the foam area of the corresponding capillary foams.

dyed with Nile Red, in which both the particles and the oil are adsorbed on the surfaces of the air bubbles. In addition, the particles between the bubbles are connected by oil bridges, as shown in the insets of Figure 8a,c. Therefore, the colorant is concentrated both on the bubble surfaces and in the liquid films between the bubbles.

Capillary foam retained its intense coloration even after drying, as shown in Figure 9a,b. Figure 9c shows that the dried color foam retained its strong reflectance. By contrast, the corresponding wet foams stabilized by surfactant or by particles did not yield intensely colored dried foams. The surfactant-stabilized colored foams coalesced and fully disintegrated during the drying process. For particle-stabilized colored foams, dyes concentrated on the external surfaces rather than within the interior of the dried foam, as shown in Figure 9d.

■ CONCLUSION

In this paper, we reported that capillary foams can be prepared either by introducing air and oil simultaneously to a particle suspension, by frothing a capillary suspension, or by mixing oil into a Pickering foam. In addition, capillary foams provide a
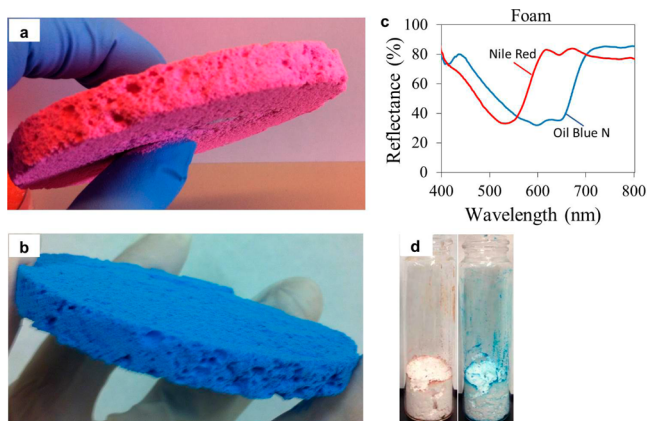
Figure 9. Images of dried color foams. (a) Dried capillary foams stabilized by the synergistic action of 18.5 vol % PVC 1062/7 particles and 4 wt % TMPTMA (1.5 mg of Nile Red was dissolved in 2 g of TMPTMA). (b) Dried capillary foams formed from the synergistic action of 10 vol % PVC 1062/7 particles and 5 wt % TMPTMA (10.2 mg of Oil Blue N was dissolved in 2 g of TMPTMA). (c) Reflectance spectra of the corresponding dried foams in parts a and b. (d) Dried Pickering foam stabilized by 7.41 wt % PE particles and colored by 0.003 wt % Allura Red (left) or FD&C Blue No. 1 (right).

general, novel processing route for preparing load-bearing porous solids and intensely colored liquid or solid dried foams. Porous solids formed from capillary foams have porosity on different length scales originating from the original gas bubbles and the particle network in the original liquid phase. Moreover, the secondary liquid originally connecting the particles in the wet foam could be polymerized to further reinforce the particle network before removal of the primary liquid. We also successfully prepared intensely colored liquid and dried foams by introducing an oil-based dye solution and gas bubbles to an aqueous particle suspension. Capillary foams retained their intense coloration even after drying, whereas foams stabilized by surfactant or particles did not allow for intense coloring in either the wet or dry state. Clearly, the presence of the minority liquid phase in capillary foams gives rise to many new opportunities for foam processing, further examples of which shall be explored in a forthcoming paper.

ASSOCIATED CONTENT

Ⓢ Supporting Information

SEM images and size distributions of particles used in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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