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Templating Interfacial Nanoparticle Assemblies via in Situ Techniques

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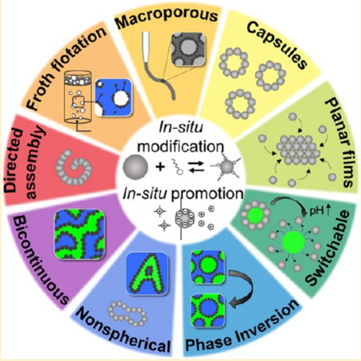
ABSTRACT: In situ surface modification of nanoparticles has a rich industrial history, but in recent years, it has also received increased attention in the field of directed self-assembly. In situ techniques rely on components within a Pickering emulsion system, such as amphiphiles that act as hydrophobizers or ionic species that screen charges, to drive the interfacial assembly of particles. Instead of stepwise procedures to chemically tune the particle wettability, in situ methods use elements already present within the system to alter the nanoparticle interfacial behavior, often depending on Coulombic interactions to simplify operations. The surface modifications are not contingent on specific chemical reactions, which further enables a multitude of possible nanoparticles to be used within a given system. In recent studies, in situ methods have been combined with external means of shaping the interface to produce materials with high interfacial areas and complex geometries. These systems have facilely tunable properties, enabling their use in an extensive array of applications. In this feature article, in honor of the late Prof. Helmuth Möhwald, we review how in situ techniques have influenced the development of soft, advanced materials, covering the fundamental interfacial phenomena with an outlook on materials science.



INTRODUCTION

In situ surface modification of particles has a century-old tradition in the mining industry.[1] However, in the last decade, this simple approach of controlling the wettability of solid particulates has regained attention in the field of interfacial nanoparticle self-assembly, where structures are created from the system finding a local energy minimum. In nanoparticle self-assembly, tuning the properties of a single particle can result in complex, collective structures. The ability to control the interfacial attachment of a nanoparticle by simply adsorbing organic molecules has innovated the fabrication of materials via self-assembly. Currently, the application potentials of technologies derived from in situ modifications are being developed to advance separation membranes,[2] lightweight materials,[3] microencapsulation,[4] optical materials,[5] biomedical engineering,[6] and catalysis.[7]

This feature article, in honor of the late Prof. Helmuth Möhwald, aims to provide the reader with a historical perspective on the development of in situ techniques for interfacial particle attachment and highlights current developments and emerging directions in this field.

As director of the Max Planck Institute of Colloids and Interfaces, Helmuth Möhwald endeavored to translate fundamental laboratory discoveries toward applications. Most well known for his pioneering work of introducing polyelectrolyte layer-by-layer assembly for encapsulation applications,[8] Möhwald has also contributed significantly to the understanding of nanoparticle self-assembly at interfaces. His research group was the first to show that nanoparticles with dimensions below 10 nm require contact angles close to 90° and low charge densities to strongly attach to interfaces.[9−11] Research in Möhwald's department also revealed interfacial behavior of colloidal particles by means of the Langmuir trough, allowing for measurement of the nanoparticle contact angle or the interfacial characterization of thermoresponsive particles.[12−15] In his department, novel encapsulation strategies were devised based on interfacial particle assemblies, resulting in various colloidosomes[16,17] that can be useful for applications, as evidenced by his work on nanocontainer-doped, self-repairing coatings.[4,18] Here, in situ nanoparticle functionalization rendered commercially available nanoparticles partially hydrophobic to mediate their interfacial attachment, facilitating the preparation of high-end encapsulation systems via a cost-efficient, industrially viable approach.[18] To date, various encapsulation methods have been established based on analogous in situ techniques.[19−23] Interestingly, Möhwald's team also investigated the opposite approach, of rendering strongly hydrophobic nanoparticles partially hydrophilic via in situ modification, resulting in interfacial mono- and multilayers with potential applications in magnetic information storage and processing.[24]

During this time, in situ surface functionalizations were already recognized as a critical step in processing macroporous ceramics and polymers, templated from particle-stabilized, high-internal-phase emulsions.[25] In situ particle modification

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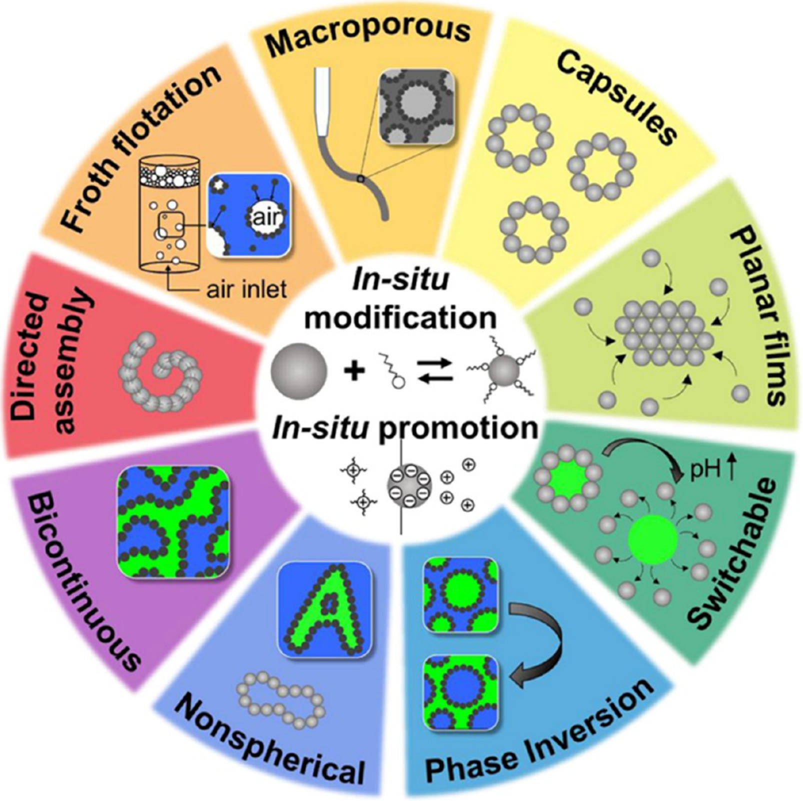

Figure 1. Graphical table of contents.

methods allow for generating materials using large particle quantities from a broad selection of inorganic and organic nanoparticles. Most recently, macroporous materials fabricated with in situ techniques have been three-dimensional (3D)-printed, forming scaffolds with hierarchical pore sizes.[3,26] With these feature sizes and the wide range of possible particle compositions, these materials have potentials in biomedical, energy, and catalytic applications.

Besides bulk materials, in situ techniques have also advanced planar nanoparticle assemblies for the formation of films. The planar interface enabled the development of another method for interfacial nanoparticle attachment, termed in situ promotion.[27,28] Both in situ surface modifications and in situ promotion play an important role in the particle assembly process. The findings of these studies are especially relevant for reflective surfaces and inkjet printing.

Another useful aspect of in situ techniques is the possibility to attach/detach nanoparticles from interfaces on demand. This feature has recently been developed to design smart windows,[5] photoresponsive films,[29] and separation technologies.[30]

Beyond the flexibility of particles that can be used, in situ modifications also allow for manipulation of the interface shape. Systems with intricate interfacial geometries are industrially desirable for their designability and high interfacial surface areas. With in situ, surface-modified nanoparticles, fluid−fluid interfaces of any curvature can be rigidified, facilitating the formation of emulsions into nonequilibrium shapes, including bicontinuous structures. These systems can be facilely produced with in situ hydrophobizations, with tunable feature sizes, ranging from millimeters to submicron.[31−33]

In situ modifications are a particularly valuable tool for the directed self-assembly of nanoparticles into complex structures. Recent research has shown that nanoparticles can be ordered into elaborate arrangements from the influence of an underlying liquid crystalline, elastic field.[23] This material can have periodic, heterogeneous chemical patches, relevant for optical and energy applications.

The first part of this review provides an overview of in situ techniques used to obtain the interfacial attachment of particles. The second part of this review details how these in situ techniques can be coupled with external methods of shaping the interface. In honor of Prof. Möhwald, this review covers these advances in interfacial phenomena from the lens of materials development (Figure 1). We highlight the relevance of these techniques in applications and end by discussing future directions.

■ IN SITU TECHNIQUES FOR INTERFACIAL PARTICLE ASSEMBLY—A MATERIALS PERSPECTIVE

An air bubble passing through a suspension can collect solid particles on its surface and retain those while ascending. Numerous particle-coated bubbles together create a stable foam without additional stabilizers. Emulsion droplets can be protected against coalescence virtually indefinitely by the deposition of solid particles on the liquid−liquid interface. The particles can be very persistent in resisting removal to the bulk phases and can be irreversibly attached to the interface. Sometimes, the droplets can be dramatically deformed while remaining metastable, apparently violating the surface area minimization normally required by surface tension. In such cases, a dense particle crust on the interface is formed and

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interfacial jamming of the particles leads to mechanical rigidity. Such observations were published first by Ramsden in 1903[34] and Pickering in 1907,[35] but the driving force for particle attachment was not understood at this time.

A particle located between two immiscible fluids (e.g., oil (o) and water (w)) reduces their interfacial contact area by occupying space on the interface. Spontaneous particle attachment takes place when the associated oil (o)/water (w) interfacial energy reduction (ΔG_{ow}) is larger than the interfacial energy gain between the particle (p) and the immiscible fluids ($\Delta G_{\mathrm{po}} + \Delta G_{\mathrm{pw}}$). Neglecting gravity, the total energy reduction upon attachment of a single spherical particle can be expressed by summing all interfacial energy changes, as was done by Koretsky and Kruglyakov[36,37]

$$\Delta G_{\mathrm{attach}} = \Delta G_{\mathrm{po}} + \Delta G_{\mathrm{pw}} + \Delta G_{\mathrm{ow}}$$
$$= -\pi \cdot r^2 \cdot \gamma_{\mathrm{ow}} \cdot (1 - \cos\theta)^2$$

with r being the particle radius, γ_{ow} being the water/oil interfacial tension, and θ being the contact angle measured through the aqueous phase. In Figure 2a, the individual contributions to the attachment energy are plotted for a particle with 40 nm radius against the contact angle.

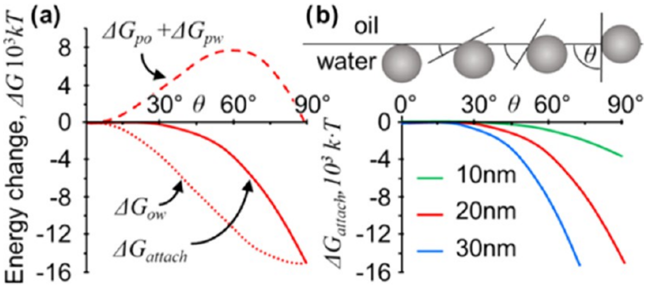

Figure 2. Interfacial attachment energy. (a) Individual contributions to attachment energy in dependence of particle contact angle, θ: sum of particle/oil and particle/water surface energy change ($\Delta G_{\mathrm{po}} + \Delta G_{\mathrm{pw}}$), oil/water interfacial energy change ΔG_{ow}, and attachment energy $\Delta G_{\mathrm{attach}}$. (b) Depiction of the contact angle θ (top) and attachment energy for particles with different radii (bottom).

For θ larger than 30°, the reduction of ΔG_{ow} exceeds $\Delta G_{\mathrm{po}} + \Delta G_{\mathrm{pw}}$ and interfacial attachment is strongly favored. Note that above 40°, the attachment energy corresponds to more than 1000 times the thermal energy of the particle in kT. These high attachment energies result in irreversible particle attachment, in stark contrast to attachment of surfactant molecules of only a few kT. Moreover, the particle attachment energy increases further when the particle size is increased, as can be seen in Figure 2b.

We have seen that the control parameter governing particle attachment is the contact angle θ. For a given oil/water interface, θ is a function of the particle surface chemistry. Hydrophilic particles often have contact angles too low to enable strong interfacial attachment. The contact angle of such particles can be altered by covalently binding hydrophobic groups to the particle surface. However, practically, this often requires tedious reaction and purification steps. A more simple and versatile approach is the in situ hydrophobization or promotion of particle attachment. In fact, in situ techniques have a long history and are currently applied for many material fabrication methods, as we shall see in the following.

Froth Flotation—A Historical Application. Rayleigh famously concluded in 1899 that oleic acid forms a molecular monolayer when spread on the surface of water.[38] Inspired by this, Langmuir proposed in 1917 that molecular monolayers can also be formed on solid surfaces.[39] He showed that the deposition of a monolayer of oleic acid considerably increases the contact angle of a water droplet on the sulfide mineral galena.[40] On the other hand, no changes in contact angle were observed for the same treatment on a glass surface. Oleic acid adsorbed on galena, rendering it partially hydrophobic, but it did not adsorb on glass.

This selective hydrophobization explains why fine particles of galena attach to air bubbles in the presence of small amounts of oleic acid, while quartz particles do not. Even today, this principle is of great importance in the mining industry, where mineral separation is accomplished by froth flotation, a process in which air is bubbled through a slurry of fine mineral particles.[1] For a mix of galena and quartz particles, only hydrophobized galena particles attach to ascending air bubbles, allowing them to be selectively harvested from the froth on top.

Collectors are surface active organic reagents that impart hydrophobicity to minerals when they adsorb on mineral surfaces. In the 1920s, highly effective collectors for sulfide minerals were discovered, including thiocarbanilide,[41] xanthanes,[42] and dithiophosphates. These sulfur-containing collectors adsorb specifically on sulfite minerals by chemical bonding, allowing highly selective separations of sulfide minerals via froth flotation.[43]

Besides sulfide minerals, oxides and silicates can also be hydrophobized via the in situ adsorption of organic molecules.[44] The molecular structure of an in situ surface modifier is composed of a polar head group and an apolar moiety. The polar head group binds to the mineral surface by either chemisorption or physisorption. In this section, we focus on the electrostatically driven physisorption of in situ modifiers with charged polar head groups on oppositely charged mineral surfaces.

Fuerstenau first proposed that the adsorption of ionic surfactants on mineral surfaces is accompanied by the formation of surfactant aggregates.[45] Figure 3a-i shows that the adsorbed amount of dodecylammonium acetate (DAA) on quartz increases gradually when increasing the solution concentration from 10^{-5} to 10^{-4} mol/t of the mineral (t).[46] In this region, adsorption is primarily driven by electrostatic attraction between the positively charged head group and the negative surface charges. However, above 10^{-4} mol/t, the adsorbed amount of DAA increases steeply with increasing concentration. This indicates that lateral, hydrophobic interactions between the surfactant tails enhance the adsorption process, acting in tandem with electrostatic attraction to form a surfactant monolayer on the particle surface, as depicted in Figure 3a-ii. In close analogy to surfactant aggregates in solution, the resulting two-dimensional surfactant aggregates are termed hemimicelles.[46] The contact angle, illustrated in the bottom of Figure 3a-ii, and the flotation recovery both increase with analogous trends. The correlation between surfactant adsorption, contact angle, and flotation recovery demonstrates how these three phenomena are connected by the effect of in situ hydrophobization on interfacial phenomena. The surfactant concentration then serves as a control parameter for in situ surface modification.

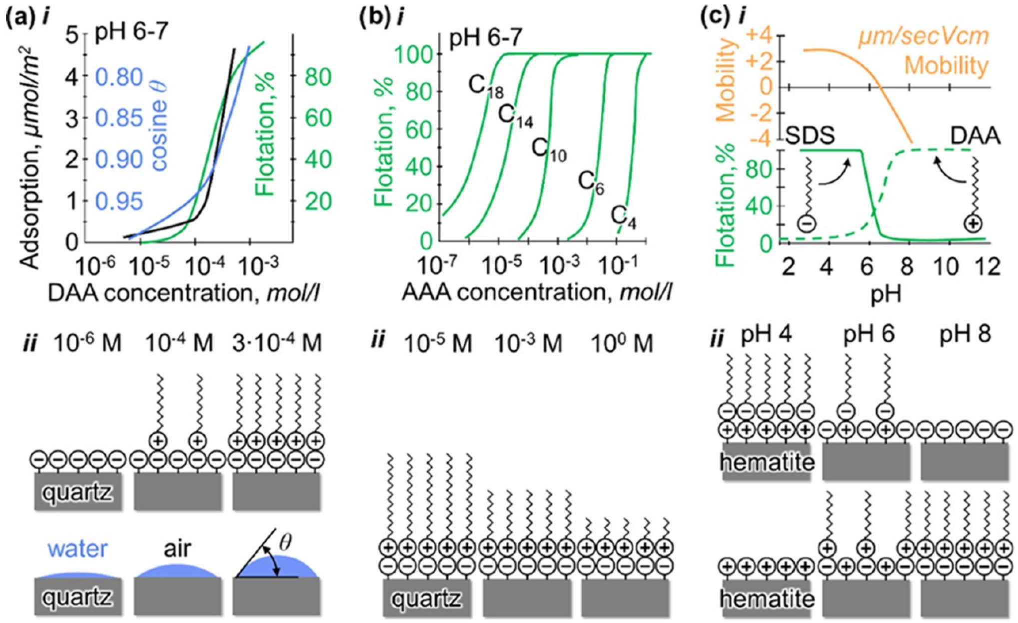

Figure 3. Physisorption of ionic surfactants on oppositely charged mineral surfaces. (a) (i) Adsorption isotherm, contact angle, and flotation recovery for dodecylammonium acetate (DAA) adsorption on quartz. Adapted with permission from ref 46. Copyright 1964 AIME's Member Society, SME. (ii) Illustration of surfactant adsorption and contact angle increase upon adsorption. (b) (i) Effect of hydrocarbon chain length of alkylammonium acetates (AAA) on flotation recovery of quartz. Adapted with permission from ref 46. Copyright 1964 AIME's Member Society, SME. (ii) Illustration of adsorption of surfactants with different chain lengths. (c) (i) Electrophoretic mobility of unmodified hematite and flotation recovery of hematite in-situ modified with DAA (cationic) or sodium dodecyl sulfate (anionic, SDS) in dependence of pH value. Adapted with permission from ref 48. Copyright 1960 AIME's Member Society, SME. (ii) Schematics of DAA and SDS adsorption on hematite in dependence of pH value.

Hemimicelle formation depends strongly on the alkyl chain length, another control parameter. Figure 3b-i shows that with increasing chain length, the flotation recovery reaches its maximum at lower surfactant concentrations.[46] These trends reveal how surfactants with longer alkyl chains have lower critical hemimicelle concentrations, as illustrated in Figure 3b-ii.

The third important control parameter determining in situ surface modification is the surface charge of the mineral. For oxide and silicate minerals, amphoteric, surface hydroxyl groups are generally assumed to control this charge. Depending on the mineral type, an equilibrium between protonated $-OH^+$, neutral $-OH$, and deprotonated $-O^-$ exists at any given pH value.[47] Figure 3c-i (top) shows the electrophoretic mobility measurement of hematite, a quantity that represents the isoelectric point and the overall sign of the surface charge.[48] The corresponding flotation recovery of hematite in the presence of the surfactants sodium dodecyl sulfate (SDS) or DAA is also shown in Figure 3c-i (bottom).

Hematite can be recovered via froth flotation by in situ hydrophobization with negatively charged SDS below pH 6 and with positively charged DAA above pH 6. Figure 3c-ii illustrates the corresponding pH-dependent adsorption for the two different surfactants. Below pH 6, positively charged hydroxyls allow SDS to adsorb, but above pH 6, negatively charged hydroxyls inhibit SDS adsorption. The opposite is the case for DAA, which adsorbs only above pH 6.

In industrial froth flotation, the electrostatically driven physisorption of surfactants plays a minor role for the separation of minerals. This is due to the nonspecificity of physisorption. Charged surfactants readily adsorb on any oppositely charged surface, irrespective of the material type, making them ineffective for mineral separations. Sulfur-containing collectors are predominant in froth flotation due to their highly specific adsorption characteristics.

However, for the innovation of soft materials, physisorption is advantageous. In situ modification by ionic surfactants has been widely applied in the production of soft materials with designable features, as research in the last decade has shown. In the following, we review the fabrication of a broad array of new materials that exploit in situ surface modification to coordinate the interfacial assembly of dispersed, hydrophilic particles.

Macroporous Materials. Foams are used beyond froth flotation, as seen in everyday cosmetics and cleaners, as well as in modern, macroporous materials. These advanced materials can have selective characteristics that enable their applications as chemical sensors, filtration membranes, electrodes for batteries and solid oxide fuel cells, insulators, as well as scaffolds for bone replacement and tissue engineering.[49] Researchers have employed multiple, low-cost, in situ surface hydrophobizations to generate particle-stabilized, high-internal phase emulsions and foams for templating macroporous materials. The methods used can be divided into two main techniques: by producing (1) oil-in-water (o/w) emulsions or (2) water-in-oil (w/o) emulsions.

Macroporous Materials from o/w Emulsions. The first approach to creating macroporous materials involves the slight hydrophobizations of particles via physisorption. Gonzenbach et al. investigated foams stabilized with in situ, hydrophobized colloidal particles of aluminum oxide, zirconium oxide, calcium phosphate, and silica.[50] The particle surface modification was realized with short amphiphiles (e.g., propionic acid or butyl gallate) adsorbing either electrostatically or via ligand-exchange reactions on particle surfaces.[51] The use of short-chain amphiphiles (number of carbons in chain <8) allowed for the hydrophobization of large quantities of colloidal particles

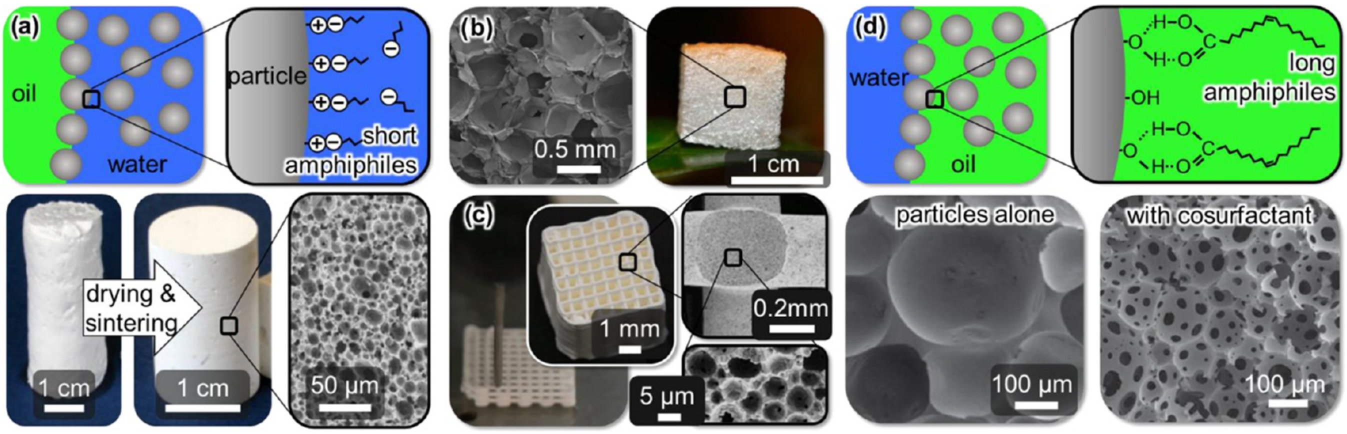

Figure 4. Fabricating macroporous materials with in-situ hydrophobized particles. (a) Illustration of nanoparticle-stabilized, o/w emulsion via particle hydrophobization with short amphiphiles. Below: emulsion-templated macroporous ceramics. Adapted with permission from ref 25. Copyright 2008 John Wiley and Sons. (b) In-situ hydrophobized, nanofibrillated, cellulose fiber stabilized o/w emulsion made with a soft, foam scaffold. Adapted with permission from ref 52. Copyright 2016 American Chemical Society. (c) 3D-printing of concentrated, nanoparticle-stabilized emulsions for creating hierarchically porous materials. Adapted with permission from ref 3. Copyright 2016 John Wiley and Sons. (d) Illustration of nanoparticle-stabilized w/o emulsion via particle hydrophobization with long amphiphiles. Below: particle-stabilized, high-internal w/o emulsion for templating macroporous polymer scaffolds with open pore structures. Adapted with permission from ref 53. Copyright 2010 John Wiley and Sons.

(15 vol % of 200 nm particles), resulting in foams with high yield strengths. Akartuna et al. later used this approach to stabilize high internal phase emulsions with up to 35 vol % of silica, alumina, and iron oxide particles.[25] Drying and sintering of these emulsions resulted in macroporous ceramics with compressive strengths as high as 13 MPa (Figure 4a).

Using similar in situ surface functionalizations with short amphiphiles, highly absorbent soft foams were fabricated in the group of Wågberg (Figure 4b). Surface-modified, nanofibrillated cellulose fibers were in situ hydrophobized with octylamine. Gentle drying of the foam in air resulted in a macroporous cellulose material with 98% porosity and a density of 30 mg/cm^3.[54] The homogeneity of the pore structure of the dry foam was also improved in a later study.[52]

Current research thrusts for macroporous materials involve the development of hierarchically organized scaffolds with pore features on both millimeter and micron scales. Studart's group demonstrated the fabrication of complex geometries by the 3D printing of in situ hydrophobized, particle-stabilized emulsions and foams with fine-tuned rheological properties (Figure 4c).[3] This approach allows for the formation of both closed and open pore structures via the addition of the polymeric co-stabilizer, poly(vinyl alcohol). Compressive strengths of up to 16 MPa for samples with 88% porosity were obtained. The same technique has been recently used by the Lewis group to make honeycomb lattice structures for 3D-printed foams.[26] Also noteworthy is the wet spinning of high-internal-phase emulsions, stabilized with in situ hydrophobized, laponite clay disks, resulting in macroporous fibers for controlled release applications.[55]

Macroporous Materials Templated from w/o Emulsions. The second approach to generating macroporous materials is to substantially hydrophobize particles for the stabilization of w/o emulsions (Figure 4d, top). In the group of Bismarck, adsorption of oleic acid via hydrogen bonding[56] was employed to hydrophobize titania and silica particles for the stabilization of high-internal-phase w/o emulsions.[57,58] Here, the adsorption step was carried out separately in an organic phase. The polymerization of the oil phase resulted in macroporous polymers (Figure 4d, bottom left). Upon introducing the polymeric surfactant Hypermer 2296, polymer scaffolds with open pore structures and high permeabilities were obtained (Figure 4d, bottom right).[53]

Most recently, Bian et al. have used the physisorption of cetyltrimethylammonium bromide (CTAB) to colloidal particles composed of MXenes to manufacture macroporous materials. The resultant materials have the potential to be implemented as rechargeable batteries, supercapacitors, fuel cells, and sensors.[59]

In summary, in situ hydrophobizations of various particles have enabled the fabrication of macroporous materials. Approaches to tailor the pore interconnectivity and mechanical strength have been developed. Three-dimensional printing of these materials now facilitates the design of advanced materials with prospective applications as filters, electrodes, insulators, and tissue engineering scaffolds.[49]

Droplets, Capsules, and Particles. Particle-stabilized emulsions are used to engineer not only macromaterials, but also materials down to the micron and submicron scales, such as colloidosomes, miniemulsions, and composite polymer particles. These objects are relevant for drug delivery, anticorrosive coatings,[60] foods,[61] and oil recovery,[62] so developing methods for the facile production of these materials is industrially significant. The technique of in situ particle hydrophobization facilitates the straightforward fabrication of a wide array of hydrophilic building blocks, such as inorganic nanoparticles, cellulose nanocrystals, or metal-organic frameworks. In this section, we review the two main approaches for controlling the interaction between in situ modifiers and nanoparticles in making droplets, capsules, and particles: (1) the modifier and the particle can interact within the aqueous phase or (2) they are dispersed in opposite, immiscible phases and interact only at the interface.

Interaction within the Aqueous Phase. Long-chain ionic surfactants allow for the efficient hydrophobization of nanoparticles at low concentrations of the in situ modifier (Figure 3b). Negatively charged nanoparticles are most frequently hydrophobized with quaternary alkylammonium

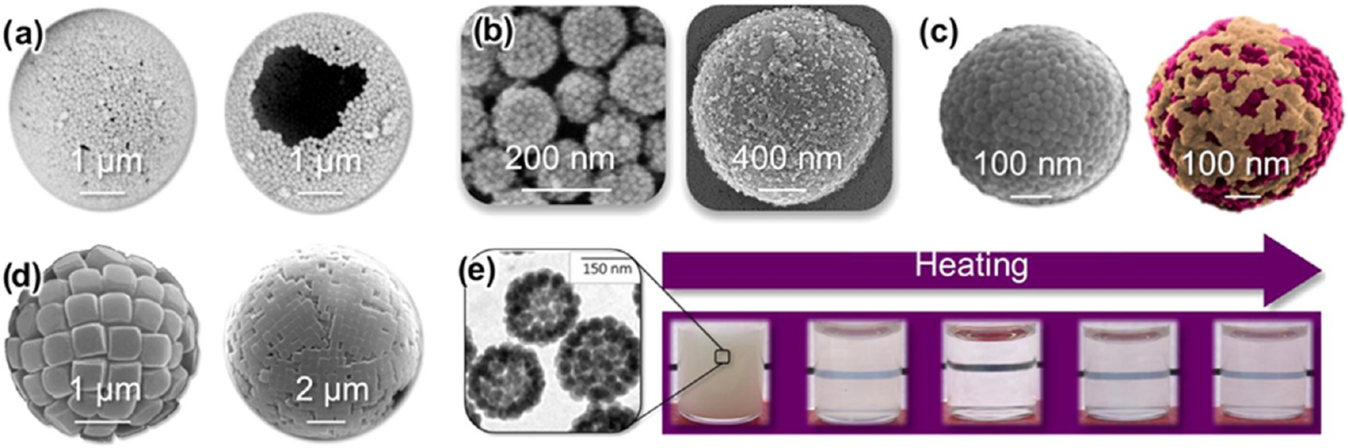

Figure 5. Electron micrographs of colloidosomes and particles. (a) Polyelectrolyte reinforced colloidosomes. Adapted with permission from ref 19. Copyright 2009 American Chemical Society. (b) Corrosion-inhibitor-doped silica/polymer composite particles. Adapted from refs 4 and 18 with the permissions of John Wiley and Sons, and American Chemical Society. (c) Mono- and bi-functional (false colored) colloidosomes from inverse miniemulsions. Adapted with permission from ref 6 Copyright 2013 American Chemical Society, Adapted with permission from ref 20. Copyright 2014 John Wiley and Sons. (d) Colloidosomes with metal organic framework wall. Adapted with permission from ref 84. Copyright 2013 American Chemical Society. e) Transparent inverse miniemulsions obtained by partial water evaporation from droplets. Adapted with permission from ref 86. Copyright 2017 American Chemical Society.

salts. Silica nanoparticle- or cellulose nanocrystal-stabilized emulsions have been achieved with CTAB at concentrations as low as 0.01 mM.[22,63] On the other hand, positively charged particles are frequently hydrophobized with alkyl sulfates. For instance, alumina, calcium carbonate, and layered double hydroxide particles can be hydrophobized with SDS to obtain both o/w and w/o emulsions.[63−65] However, a disadvantage of in situ surface functionalization with long-chain surfactants is that the resulting emulsions are often flocculated since the adsorbed alkyl chains reduce the particle charge and interact with the alkyl chains on particles of adjacent droplets.

Small organic molecules with charged groups significantly reduce the flocculation problem when used as in situ hydrophobizers of particles with an opposite surface charge. However, depending on the size of the organic moiety, higher concentrations of these in situ hydrophobizers are needed. Based on this, Akartuna et al. introduced a general route for colloidosome fabrication.[19] Short amphiphile-hydrophobized colloidal particles of alumina, silica, and iron oxide were employed to stabilize o/w emulsions. After reinforcing the particle-stabilized droplets with polyelectrolytes, drying and electron microscopy observation of the colloidosomes were possible (Figure 5a). Using similar charged short amphiphiles, various particle-stabilized, o/w emulsions have been obtained.[66,67] Notably, weak interactions between zwitterionic or nonionic small organic molecules and hydrophilic particles also facilitated synergistic emulsion stabilization.[68,69]

An intriguing concept is the multifunctionality of in situ surface hydrophobizers. In the department of Möhwald, this idea was realized with 8-hydroxyquinoline (8-HQ) acting simultaneously as the in situ hydrophobizer and as the encapsulated agent. The organic corrosion inhibitor 8-HQ was dissolved at high concentrations (40 wt %) in styrene and emulsified with silica particles in water. Upon pH value reduction, small amounts of protonated 8-HQ electrostatically hydrophobized the silica particles and stable miniemulsion droplets were obtained. Polymerization of the 8-HQ-filled droplets resulted in colloidal containers with applications in self-repairing, anticorrosive coatings (Figure 5b).[4,18] Similar concepts of multifunctionality have previously been employed in miniemulsions, where 4-vinylpyridine acts simultaneously as a comonomer and in situ hydrophobizer of silica.[70,71] Moreover, for emulsion polymerization, 2,2-azobis-(isobutyramidine)dihydrochloride has been employed simultaneously as a radical initiator and in situ hydrophobizer.[72] Another, more recent example involves the in situ modifier altering the anchoring of liquid crystal molecules, and thereby changing the particle assembly behavior. This is discussed in greater detail in the last section of this review.[23]

Interaction at the Interface between Immiscible Fluids. Aggregation of nanoparticles and flocculation of emulsion droplets can be further avoided when the in situ modifier is water-insoluble. In such systems, the hydrophilic nanoparticles are dispersed in water, and the surfactant is dissolved in oil.[73]

Electrostatic interactions can still drive the adsorption process when nanoparticles and surfactants meet at the oil/water interface. Classical studies describe the synergistic emulsion stabilization of barium sulfate particles with oleic acid and calcium carbonate particles with stearic acid.[74,75] More recently, Whitby et al. have demonstrated synergistic stabilization of o/w emulsion with well-dispersed, negatively charged, laponite clay particles in water and octadecylamine dissolved in dodecane.[76] Whitby showed that the interactions between fatty amines and silica nanoparticles result in the formation of viscoelastic films on the oil−water interface.[77] This principle has been extensively employed by the Russell group for the controlled formation of emulsions with nonspherical shapes and complex curvatures, considered later in this review.[78]

Interestingly, emulsion droplets with submicron dimensions stabilized synergistically by surfactants and nanoparticles of the same charge have recently been described. The group of Glatter showed that adsorption of negatively charged and water-soluble oleic acid on silica particles dispersed in water allows for the formation of particle-stabilized, octadecene droplets with sizes between 100 and 200 nm.[79,80] The adsorption increases both the charge of the particles and the hydrophobicity. Although ζ-potential and X-ray measurements

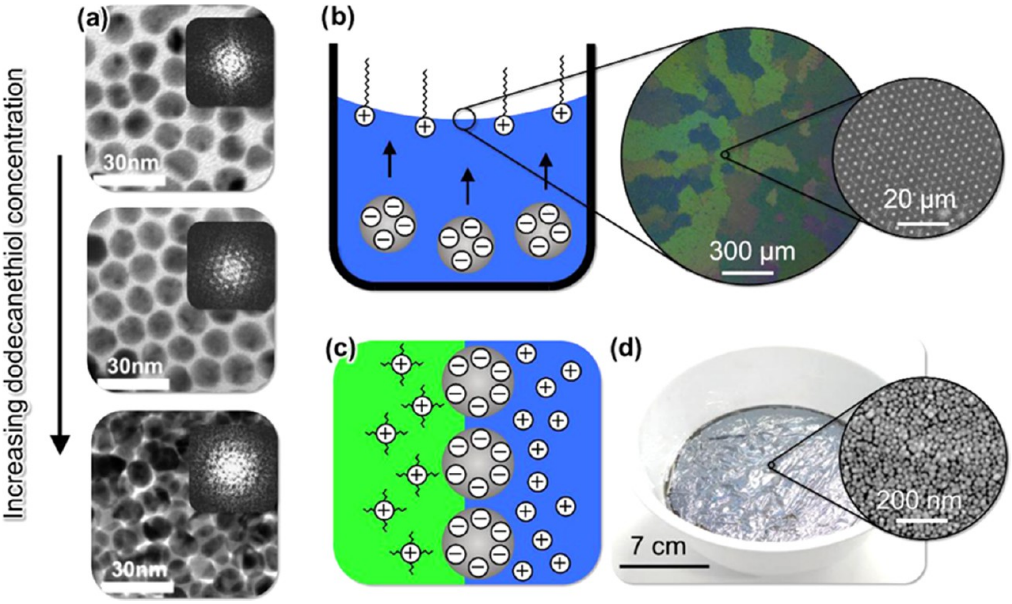

Figure 6. Planar film formation with nanoparticle interfacial attachment via in-situ promotion. (a) Transmission electron micrographs and diffraction patterns (insets) of interfacially-assembled gold nanoparticles. Adapted with permission from ref 91. Copyright 2007 American Chemical Society. (b) Polycrystalline, interfacial nanoparticle layer formation with ultralow concentrations of oppositely charged surfactants (~CMC/1000). Adapted with permission from ref 28. Copyright 2018 American Chemical Society. (c) Attachment of nanoparticles at the interface of two immiscible electrolytes (ITIES). (d) Silver nanoparticle film assembled at the interface of two immiscible electrolyte solutions, converted into free standing film via polymer precipitation. Adapted with permission from ref 94. Copyright 2017 John Wiley and Sons.

corroborate the adsorption of negative amphiphiles to particles of the same charge, the exact mechanism was not discussed.[80] Possibly related to this is the study by Durán-Álvarez.[81] Through streaming potential measurements and molecular dynamics simulations, they found that the adsorption of positively charged dodecyltrimethylammonium bromide (DOTAB) on positively charged calcite depends upon electrostatic screening by counterions and water molecules. Furthermore, Bollhorst et al. described the formation of submicrometer-sized colloidosomes based on oil-soluble surfactants of the same charge (positive or negative) as the water-dispersed nanoparticles.[20] In situ modification of alumina particles with stearyl amine and silica particles with stearic acid enabled the formation of submicron w/o emulsions. Bollhorst et al. suggested that the oil-soluble surfactants induce agglomeration of particles as they act as local electrolytes at the interface. Centrifugation of the water droplets from the oil phase into the water phase resulted in stable colloidosomes (Figure 5c). Later, they further refined their approach and developed diamondosomes as well as bifunctional colloidosomes stabilized by silica and iron oxide for potential biomedical applications.[6,82]

Additionally, nonionic surfactants dissolved in oil have been used to hydrophobize water-dispersed, colloidal particles. Wang et al. found that the nonionic surfactant Span-80 hydrophobizes layered double hydroxides more strongly than laponite clay particles.[83] The group of Eddaoudi generated astounding colloidosomes via the modification of metal-organic framework cubes with Span-80 for applications in catalysis (Figure 5d).[84,85] Sihler et al. investigated the stabilization of inverse miniemulsions (submicron w/o droplets) with silica particles in situ hydrophobized by a variety of surfactants, including block copolymers and lecithin.[21] Based on their technique, they later developed highly transparent emulsions via refractive index matching for applications in confocal microscopy, light-induced reactions, and spectroscopic studies (Figure 5e).[86]

Summarizing this section, in situ hydrophobizations have helped to advance the fabrication of functional droplets, capsules,[19] and particles.[70] They made possible the direct combination of a broad selection of hydrophilic nanomaterials, such as ceramics, cellulose, and metal-organic frameworks, with hydrophobic oils—without need for additional surface treatment steps. Furthermore, attractive interactions between oppositely charged as well as like-charged particle/surfactants pairs have given rise to the fabrication of submicron colloidosomes, relevant for biomedical applications,[20] corrosion protection,[4] and catalysis.[85]

Planar Nanoparticle Films. In situ hydrophobized particles can assemble not only on droplets but also into sheets at planar liquid interfaces. These assemblies are relevant for the development of antireflective coatings, sensors, and inkjet printing. The planar nanoparticle films are directly usable on the fluid–fluid interface (for instance, as liquid mirrors), or they can be harvested from the interface to be integrated into devices. The planar, liquid interface can also template patterns after evaporation of the liquid, as is the case for inkjet printing. In these applications, the particle wettability can be controlled by in situ methods. However, besides particle in situ hydrophobization, there exist other in situ techniques that do not rely on the surface modification of particles. Consequently, this section is divided in two parts: planar nanoparticles films formed by (i) in situ modification and (ii) in situ promotion.

Planar Film Formation via in Situ Modification. A drying sessile droplet of a colloidal suspension typically leaves behind a ring-shaped deposit due to evaporation-driven capillary flow.[87,88] Inhibiting this effect is crucial during inkjet printing, as it affects the uniformity of the printout. Anyfantakis et al. found that the coffee ring effect can be suppressed for drying

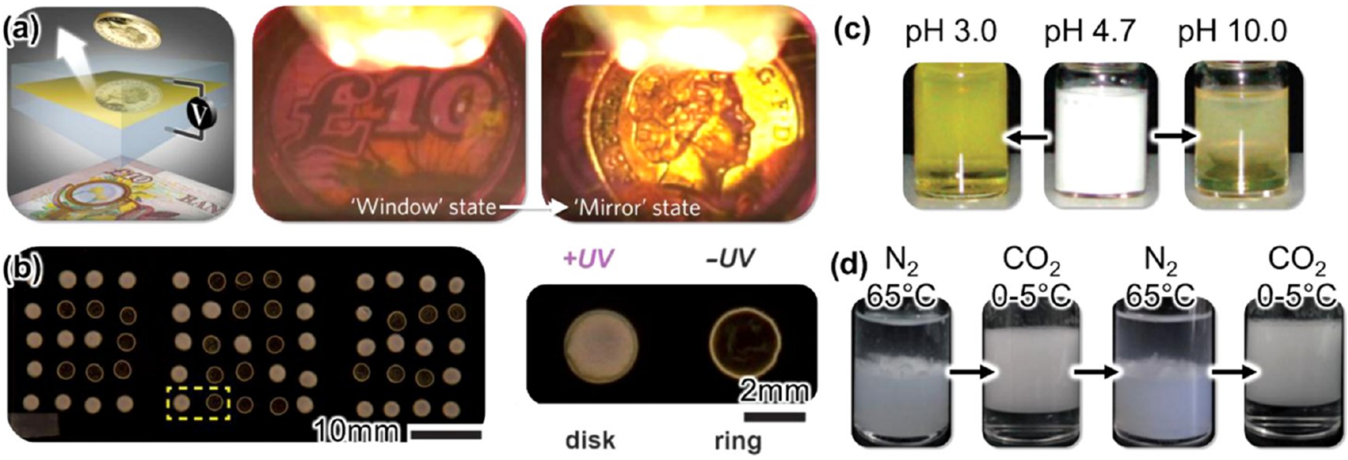

Figure 7. Switchability of interfacial assemblies. (a) Schematic and photographs of voltage triggered transition from transparent to reflecting interfacial gold nanoparticle film. Adapted with permission from ref 5. Copyright 2017 Springer Nature. (b) Photograph of light-triggered drying pattern based on controlling stickiness of in-situ modified nanoparticles. Adapted with permission from ref 29. Copyright 2014 John Wiley and Sons. (c) Pickering emulsion destabilization by pH induced charging of an amphoteric in-situ modifier. Adapted from ref 18 with the permissions of American Chemical Society. (d) Pickering emulsion destabilization by CO2 and temperature-induced charging of in-situ hydrophobizer. Adapted from ref 97 with permission of the Royal Society of Chemistry.

droplets with in situ hydrophobized colloidal particles.[89,90] The hydrophobized particles generated a skin on the liquid/gas interface resulting in a homogeneous disk of particles on the substrate after drying. This technique was further applied for light-switchable particle deposition, as discussed in the following section.

Interfacial assemblies of metallic nanoparticles are important for materials with designed optical, magnetic, and electronic properties. Nanoparticles made of gold and silver are of interest in optical and sensing applications due to the collective, oscillatory behavior of their conducting band electrons, a phenomenon known as surface plasmon resonance. Park et al. showed that in situ hydrophobization of gold particles with 1-dodecanethiol results in their interfacial assembly.[91] It was further found that intermediate dodecanethiol concentrations facilitated ordered and void-free monolayers of gold nanoparticles (Figure 6a). Similar assemblies of gold nanoparticles in situ modified by octadecylamine or dodecyltrimethylammonium can be obtained via the Langmuir−Blodgett method.[92,93] Based on surface plasmon resonance, these films can be used for understanding the adsorption of molecules in small quantities via surface-enhanced Raman scattering (SERS). Indeed, this technique was exploited to confirm that certain molecules did not adsorb to the nanoparticles, while still helping to promote nanoparticle interfacial attachment. These in situ promoters are described in the following section.

Planar Film Formation via in Situ Promotion. Most recently, a new principle of assembling ordered interfacial films of colloidal particles was discovered. Anyfantakis et al. created a planar film of negatively charged polystyrene particles.[28] The polystyrene particles did not attach to interfaces on their own. However, with the addition of dodecyltrimethylammonium bromide (DOTAB) concentrations roughly 1000 times below the critical micelle concentration (CMC), interfacial particle attachment occurred with polycrystalline ordering (Figure 6b). ζ potential measurements showed that the particle charge was not reduced at these low DOTAB concentrations, nor was the particle contact angle of 30° increased. Instead, Anyfantakis et al. concluded that the adsorption of the cationic surfactant at the air/water interface reduced the electrostatic barrier between the interface and the particles for the particles to adsorb.

In situ promotion of interfacial particle attachment without surface modification is also possible at the interface of two immiscible electrolyte solutions (ITIESs) (Figure 6c). An organic electrolyte, such as the cations of tetraalkylammonium and the anions of tetraphenylborate, can be dissolved in the oil phase, while an inorganic electrolyte, such as sodium chloride, is additionally dissolved in water (Figure 6c). Su et al. demonstrated that negatively charged gold nanoparticles can be reversibly attached at the ITIES.[27] Xu et al. showed that this concept can be extended to titania and silica nanoparticles. Through SERS while using gold nanoparticles, it was shown that the organic ions did not adsorb on the particles.[95] Instead, organic ions screened the Coulombic repulsion between negatively charged particles through the oil, allowing interfacial particle attachment driven by interfacial energy reduction. The interparticle spacing was determined by the balance of the attractive van der Waals force and the electrostatic repulsion and was controllable through the organic ion concentration.[96] Xu et al. showed in a separate work that the particle film can be harvested from the interface after precipitating a polymer film on the particles in the oil phase (Figure 6d).[94]

Research on planar interfaces has employed both in situ modification and in situ promotion for interfacial particle assembly. More control over the ordering of particles on the interface was realized based on balancing attractive and repulsive particle interactions. Furthermore, in situ promotion can facilitate reversible particle adsorption, since the particle aggregation is subdued. This stands in contrast to in situ surface modifications employed in Macroporous Materials section for particle-stabilized emulsions and foams, which often result in particle aggregation at the interface and in the bulk. Planar interfaces do not have the requirement of particle jamming for the interface to be stabilized. This allows for the study of in situ techniques that greatly moderate particle aggregation, enabling well-ordered particle assemblies and reversible interfacial adsorption. The next section describes how this feature of reversibility can be exploited for technological applications.

Switchable Interfacial Particle Attachment. Reversibly attaching/detaching colloidal particles from interfaces has multiple purposes: For planar assemblies of plasmonic nanoparticles, reversibility enables switchable mirrors with potential uses as smart windows. In biphasic catalysis, where droplets are stabilized by catalyst particles, reversibility expedites the separation of reactants, products, and catalysts.[30] By controlling concentration, charge, or molecular conformation of in situ modifiers and promoters, interfacial particle attachment/detachment can be triggered. In the following, we review different stimuli that trigger the activity of in situ modifiers and promoters.

An electrotunable, nanoplasmonic liquid mirror has been recently introduced by Montelongo et al.[5] Negatively charged, 16 nm gold particles were assembled at the ITIES (Figure 6c). The particles attached and packed tightly upon concentrating organic cations near the interface by applying a voltage of −200 mV. At this state, the interface reflected 22% of the incoming light at 620 nm. Transparency of the interface was induced by inverting the polarization of the electrode. At +200 mV, the particles detached since the organic cations near the interface were removed. The process was fully reversible because aggregation of particles on the interface was inhibited by precise control of the interparticle repulsion. Particle attachment/detachment takes several hours due to the slow diffusion kinetics of the nanoparticles, but miniaturization of the system allows for more rapid responses (Figure 7a).

Patterning nanoparticle films with light illustrates another original application of switchable, in situ modifiers. Anyfantakis et al. discovered that the drying pattern of droplets, discussed in the previous section, can be controlled by light irradiation.[29] The photosensitive cationic surfactant azobenzene trimethylammonium bromide (AzoTAB) is adsorbed on negatively charged polystyrene particles in a drying sessile droplet. At a given AzoTAB concentration, sessile droplet irradiation with blue or UV light controls whether the drying of the droplet deposits a ring or a homogeneous disk on the substrate. The light irradiation tunes the stickiness of the in situ hydrophobized nanoparticles and thereby their interfacial assembly, due to the trans−cis conformation change of AzoTAB. This technique was applied to create patterns composed of multiple dried droplets with a photomask (Figure 7b).

The destabilization of Pickering emulsions can also be switched with potential applications in biphasic catalysis[98] and oil recovery.[62] The switch from metastable to unstable emulsions is typically achieved by desorbing the in situ modifier from the particle surface. To this end, electrostatic interactions between the particle and the in situ modifier are inhibited. This is possible by adjusting the pH value to neutralize or invert charges of weak acid or base groups, either on the particle surface or on the in situ modifier (Figure 7c).[18,99] Alternatively, redox reactions can also be employed to tune charges in the system.[100,101] As a consequence, particles return to their hydrophilic state and detach from the liquid−liquid interface, resulting in the coalescence of droplets.

However, after particle detachment to the water phase, nanoparticles are often aggregated, and the system does not return completely to its initial state. Furthermore, if emulsion stabilization/destabilization is repeated multiple times by subsequent additions of acid or base, ions accumulate in the system, leading to further particle aggregation over time. This drawback can be avoided when gas-responsive in situ modifiers are employed. This concept was introduced by Jiang et al., where the surfactant *N*′-dodecyl-*N*,*N*-dimethylacetamidine is switched from neutral to cationic upon carbon dioxide exposure, a transition that is reversible by removal of carbon dioxide with nitrogen.[102] Stable emulsions are obtained when silica nanoparticles are in situ hydrophobized by the cationic form of the surfactant, while destabilization occurs with the neutral form of the surfactant (Figure 7d).[97,103]

Controlling interfacial particle attachment via stimuli-responsive, in situ modifiers and promoters has allowed for applications ranging from switchable mirrors and light-patterned particle assemblies, to controllable emulsion destabilization. While these approaches have introduced means to interrupt the interaction between nanoparticles and the interface, other in situ modifications can be employed to shape nanoparticle-decorated interfaces and are reviewed in the next section.

■ FORMING INTERFACES FOR MATERIALS WITH COMPLEX CURVATURES

Altering the particle interfacial behavior is essential for arresting droplets into the desired metastable state. From adjusting the particle characteristics, the type of emulsion can be determined, as seen with systems in prior sections. However, depending on the particle properties alone limits the system geometries and interfacial shapes. The ability to not only accommodate but also manipulate interfaces with complex curvatures is essential for the development of materials with high surface areas and intricate shapes, properties that can be vital for materials to function within the desired application. As previously discussed, particles can kinetically arrest a system away from equilibrium, stabilizing Pickering emulsions. However, these emulsions can be pushed even further from equilibrium by having particles freeze the oil−water interface into shapes beyond the surface-tension-minimizing sphere by: first, fine control of the three-phase contact angle and second, external means of manipulating the interface. The former is achievable through the distinctive ways in which in situ surface modification can tune the particle surface chemistry, as covered in the last sections.

The effect of the contact angle in selecting interfacial shape boils down to a geometric argument. The greater the contact angle (θ) of a particle is, the more it prefers to wet the oil phase (Figure 8). For both $\theta < 90°$ and $\theta > 90°$, particles pack at the interface to geometrically prefer a surface with positive Gaussian curvature, with particles having $\theta < 90°$ curving to form o/w emulsions and particles having $\theta > 90°$ curving to form w/o emulsions (Figure 8, bottom, left, and middle). Particles can curve toward either phase equally with θ close to 90°, where both the water and the oil phases are equally wetted by the particles, allowing for negative Gaussian curvature of the interface to be accommodated (Figure 8, bottom right).

As mentioned in Section 1, the three-phase contact angle determines the magnitude of the particle attachment energy, with a maximum at $\theta = 90°$. For nanoparticles ranging from a few nanometers to microns, the attachment energy can be several to hundreds of thousands times greater than kT. This strong attachment typically results in arrest of the interface shape, with solidlike nanoparticle assemblies potentially competing against surface-area-minimizing, interfacial tension. This solidlike characteristic of nanoparticle assemblies at the interface has already been noted in the first study of particle-

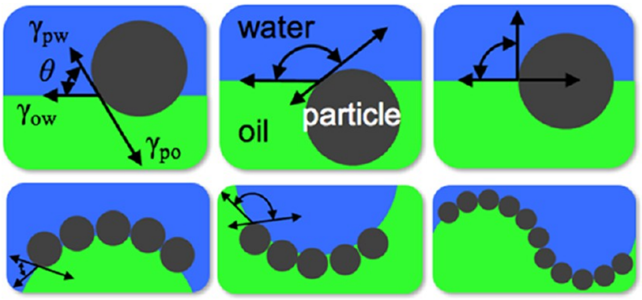

Figure 8. Role of contact angle in stabilizing and shaping emulsions. As the contact angle (θ) of a particle increases, the particle immerses itself more into the oil phase (top row). With $\theta < 90°$, o/w emulsions are preferred due to the favorable geometrical packing of particles at the interface (bottom row, left, and middle). With $\theta > 90°$, w/o emulsions are preferred for the same reason. Particles with $\theta < 90°$ can accommodate interfaces with negative Gaussian curvature from the equal preference for either oil or water (bottom right).

stabilized emulsions by Ramsden and Gotch in 1903, in which they observed "solid or viscous-like coatings" at the free surface of their emulsions.[34] The shear moduli of particle-laden interfaces have been studied and measured[104] using compression and dilation within Langmuir troughs,[105−107] oscillatory shear rheometers,[108] magnetic needle rheology,[109] optical tweezers,[110] single particle tracking,[111] simulations and X-ray scattering,[14] as well as pendant and sessile drop elastometry.[112]

More than half a century after Ramsden and Gotch's work, in 1957, the exact role of the three-phase contact angle in Pickering emulsion behavior was first investigated by Schulman and Leja, when they executed emulsion phase inversion with changes in the contact angle.[74] The fundamental principles behind this work and that of Ramsden and Gotch are now used to fabricate capsules and particles with nontrivial geometries, as well as the latest manifestation of Pickering emulsions called bicontinuous interfacially jammed emulsion gels—bijels, a material with potential for broad applications. In this section, we review studies of the phase inversion of Pickering emulsions, highlighting how these studies laid the groundwork for the development of new materials with complex curvatures. We also bring out the potential of these materials and the advantages of their shapes both for fundamental investigations in physics and chemistry and for industrial applications.

Phase Inversion. An interesting aspect of the method of in situ surface modification of nanoparticles for Pickering emulsions is the phenomenon of emulsion phase inversion. A w/o emulsion can become an o/w emulsion by tuning system parameters, with the essential parameter being the particle wettability, defined by the three-phase contact angle—versatilely tunable within a given system by in situ surface modification.

In their seminal work of 1957, Schulman and Leja switched an emulsion of benzene, oleic acid, and water, stabilized by barium sulfate particles, from o/w to w/o by adjusting the system pH, discovering that the pH altered the contact angle of barium sulfate with water and benzene.[74] At neutral pH, only one hydrocarbon chain of oleic acid attached to one barium atom, resulting in contact angles less than 90° and o/w emulsions. At higher pH, two hydrocarbon chains associated with one barium atom. The higher hydrocarbon density gave contact angles greater than 90°, resulting in a switch to w/o emulsions of the same system.

The importance of the contact angle continues to be explored another half century later in other Pickering emulsion systems. Notably, in 2000, Binks and Lumsdon coined catastrophic versus transitional phase inversion for whether phase inversion was obtained through changing the ratio of either water to oil[113] or of hydrophobic to hydrophilic particles within a system.[114] Both investigations demonstrated the crucial role of the contact angle in determining the emulsion type obtained. However, without the ability to subtly alter the particle wettability within these last two systems, the transition from one emulsion type to another occurred only once. Only with in situ surface modification is double phase inversion attainable, i.e., o/w to w/o back to o/w and vice versa.

The interaction between particle surfaces and a corresponding in situ modifier accommodates varied surfactant structures on the particle surface that alter particle wettability and are adjustable by the in situ modifier concentration. In 2009, Binks and Rodrigues succeeded in the double phase inversion of silica-stabilized Pickering emulsions with the use of didecyldimethylammonium bromide (di-DEDAB), a dichain, cationic surfactant, as the in situ surface modifier.[115] The double chain of the modifier was needed to obtain particles that were hydrophobic enough (with $\theta = 165°$)[115] to induce an inversion from o/w to w/o emulsions, upon increasing the di-DEDAB concentration. This transition did not occur with the single-chain surfactant CTAB because the particle was not rendered hydrophobic enough (maximum $\theta \sim 110°$) with this surfactant. By increasing the di-DEDAB concentration further, a second phase inversion, from w/o to o/w, took place. This second inversion is due to two factors.[115] First, bilayer formation of the dichain surfactant at the particle surface via hydrophobic interactions of the hydrocarbon chains leaves the particles partly charged and hydrophilic. With preferential wetting of the water phase, o/w emulsions become energetically favorable. Second, excess surfactant molecules also adsorb onto the free, droplet interface. The formation of an o/w emulsion is further favored, since the dichain surfactant by itself, without particles, creates o/w emulsions. The changes in θ from the adsorption and structuring of surfactant at the particle surface, vital for double phase inversion, have since been directly verified in experiments by freeze-fracture shadow-casting cryo-scanning electron microscopy.[116]

Double phase inversion has been discovered in other systems ranging from particles that are platelike and needlelike, to cellulose nanocrystals and clay, using various modifiers from anionic, cationic, and even nonionic surfactants.[22,64,65,117−119] For a Pickering emulsion system to phase invert, the shape and chemistry of the particles does not matter. For all cases, the essential system features are, first, the changing of the three-phase contact angle from surfactant structuring itself at the particle surface with varying concentration and, second, the competitive adsorption of particles and surfactants to the free oil−water interface. These two factors determine the favorable interfacial curvature of systems and can be harnessed to fabricate new materials.

Nonspherical Emulsions. For the previous phase-inverted systems, as the contact angle is adjusted in situ, the particle attachment energy subsequently changes as well. At certain in situ modifier concentrations, the prepared emulsions have nonspherical shapes as a result of the attachment energy increasing to the extent that particles can arrest and freeze the

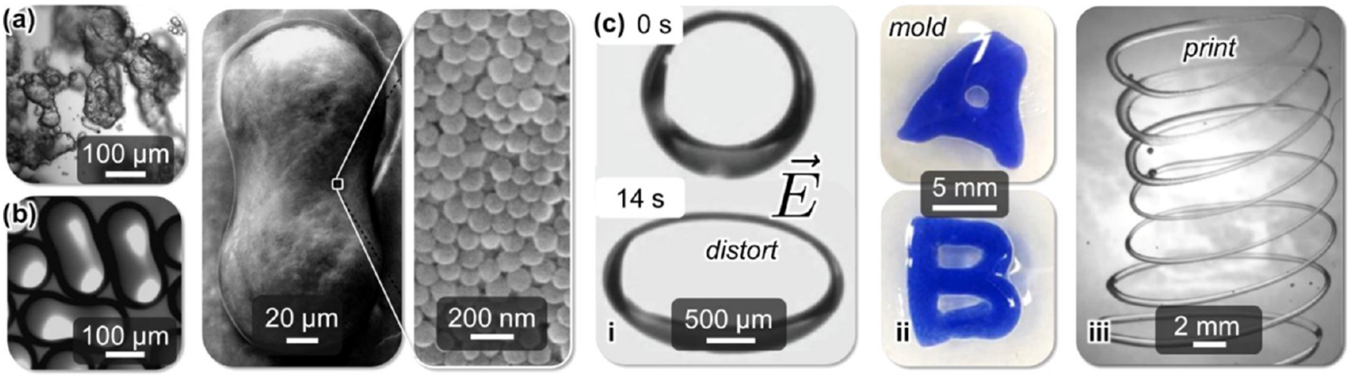

Figure 9. Nonspherical emulsion droplets. (a) n-dodecane droplets in an aqueous solution of 2 wt % Ludox CL and 1 mM SDS, formed by homogenization. Adapted with permission from ref 63. Copyright 2007 American Chemical Society. (b) The interfaces of neighboring droplets of oil in water (pH 8) are frozen in mid-coalescence by silica nanoparticles functionalized with 0.4 mM CTAB. Multilayers of silica particles are visualized in regions where two droplets merge with electron microscopy (right, inset). Adapted with permission from ref 120. Copyright 2009 American Chemical Society. (c) (i). Carboxylated polystyrene particles in the water phase are surface functionalized by amine-terminated polydimethylsiloxane (PDMS-NH2) from the oil phase, freezing in the structure of a water droplet that has been distorted by an electric field (4.6 kV cm-1) Adapted with permission from ref 78. Copyright 2013 The American Association for the Advancement of Science. (ii). Cellulose nanocrystals are functionalized by PDMS-NH2 to interfacially assemble at the interface of an aqueous droplet constructed within a mold, via a similar mechanism as ii Adapted with permission from ref 32. Copyright 2018 John Wiley and Sons. (iii). An aqueous solution of carboxylic-acid functionalized nanoparticles can be printed into a silicone oil solution containing PDMS-NH2 to fabricate nanoparticle stabilized, liquid fibers. Adapted with permission from ref 33. Copyright 2018 John Wiley and Sons.

interface into shapes distorted by the shearing required to create them (Figure 9a).[64,65,115,121] The nonspherical shape of the emulsions arises from the solidlike mechanics of the interfacial particle assemblies, as first noted by Ramsden and Gotch in 1903[34] and is often a signature of the emulsions being particle-stabilized.[63,65,119,121−123] The production of particles and colloidosomes with nonspherical shapes is of interest in the study of self-assembled structures[124,125] for the development of optical[126] and bioinspired materials[127] and capsules for use in drug delivery, foods, and fragrances.[128,129] However, the nonspherical emulsions produced by homogenization are often nonuniform and disordered. For Pickering emulsions to be useful in the fabrication of particles or capsules with nonspherical, but designable shapes, the mechanical control of liquid interfaces is necessary.

One common method of manipulating liquid−liquid interfaces is by tailoring flow fields with microfluidics to tune emulsion formation. Studart et al. used microfluidics to create monodisperse o/w Pickering emulsions stabilized by silica particles that have been modified by the adsorption of CTAB.[120] Monodisperse droplets collected from the microfluidic device were arranged into arrays, where neighboring droplets began to coalesce (Figure 9b, left). However, because of the high adsorption energy of nanoparticles to the interface, the coalescence process was kinetically arrested by the jamming of silica particles at the droplet surfaces, as shown in the electron micrographs of Figure 9b (right). The solidlike behavior of the interfacially adsorbed silica particles trapped the emulsions into shapes only seen in transient states, facilitating the creation of dumbbell-shaped particles after UV polymerization of the oil phase.

Droplets can be dynamically deformed away from the sphere, not only by arrested coalescence, but also by the application of an external field. Cui et al. exploited the typical dielectric difference between oil and water to deform water droplets by the application of an electric field.[78] With carboxylated polystyrene nanoparticles dispersed in the aqueous phase and the in situ modifier, amine-terminated poly(dimethylsiloxane) (PDMS-NH_2) mixed within the silicone oil, the particles in their investigation only become functionalized through interactions at the interface, as previously mentioned. Earlier studies of this technique detail how separating particles and the corresponding surfactant into opposite phases moderates particle aggregation while maintaining the synergistic effects of the particle and the surfactant in stabilizing emulsions.[76,83] As the electric field stretched the droplet, although the volume remained constant, the droplet surface area increased. More particles adsorbed onto the newly created interface to again arrest the droplet surface, but into an anisotropic shape that remained even with removal of the electric field (Figure 9c-i).

Electric and flow fields can easily deform a droplet, but to design these fields to yield droplets with arbitrary, anisotropic shapes is nontrivial. This degree of droplet shape design is possible with the use of molds. Shi et al. extended the last-discussed work by using molds and rodlike, cellulose nanocrystals as the nanoparticles. Cellulose nanocrystals can rapidly associate with the PDMS-NH_2 surface modifier and can strongly bind to the oil−water interface.[32] By placing the aqueous cellulose nanocrystal solution into a mold of a complex shape, such as the letter A or B, and then submerging this mold into a bath of carbon tetrachloride containing PDMS-NH_2, they fabricated droplets that retained the shape of the mold (Figure 9c-ii). As with the previous study, the wetting properties of the cellulose nanocrystals were modified through the interface by PDMS-NH_2, arresting the interfacial shape. Molds were created with the use of a 3D printer, accessing droplet shapes on the millimeter scale.

To obtain droplets of arbitrary shapes and curvatures across greater length scales, the droplets themselves must be printed. Building upon these last works, instead of distorting droplets with fields or confining them within a mold, Forth et al. directly printed an aqueous solution of nanoparticles into a viscous silicone oil solution containing PDMS-NH_2.[33] By this method, the Russell group formed long liquid fibers of arbitrary curvatures and lengths (Figure 9c-iii). Junctions

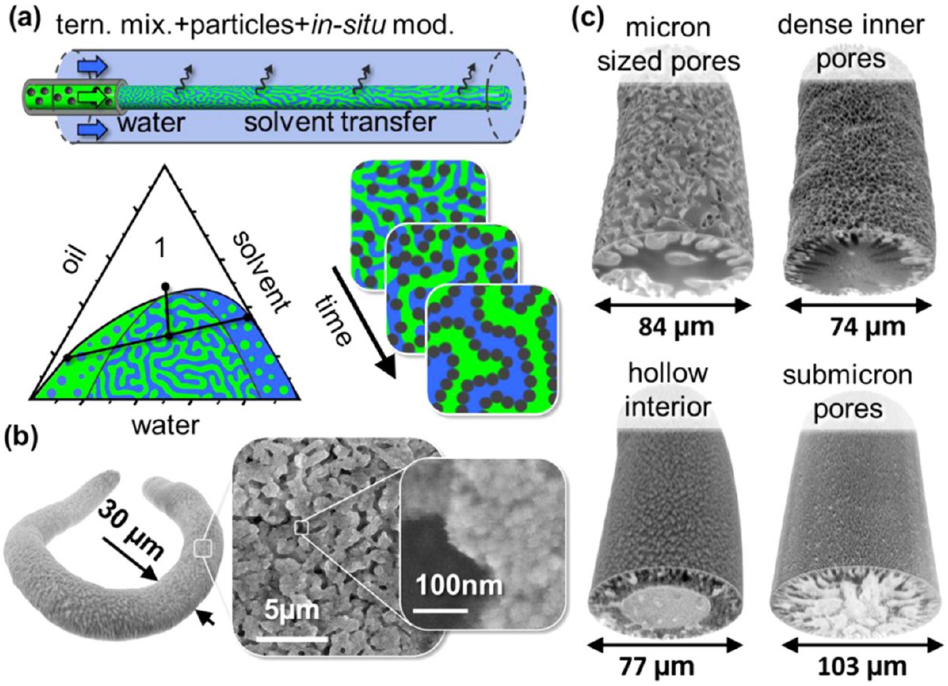

Figure 10. (a) Solvent Transfer Induced Phase Separation (STrIPS) requires the injection of a homogeneous mixture of three liquids into a continuous phase. One of the liquids is a solvent that allows homogeneous mixing of the other two liquids, (e.g. an oil and an aqueous phase), which are immiscible on their own. During the course of injection (top), this solvent is extracted into the continuous phase, leading to spinodal decomposition. The ternary phase diagram qualitatively depicts this process. During phase separation, surface active particles within the ternary mixture attach to the interface between the oil- and water-rich phases to arrest phase separation and stabilize the bicontinuous structure. (b) Electron microscopy magnification of the surface of a flexible fiber formed by STrIPS. The inset shows the interfacially jammed silica nanoparticles (20 nm) on the spinodal surface structures. (c) 3-dimensional confocal laser scanning micrographs of STriPS bijel fibers. Adapted from ref 31 with permission of John Wiley and Sons.

within the fibers were also printable, creating fiber networks with branches for transport within the still-liquid channels. Furthermore, they showed that the principle of particle functionalization is purely Coulombic by stabilizing liquid fibers with arbitrary particle compositions, from cellulose nanocrystals to even gold nanoparticles. With broad possibilities of material composition at the fiber interface, Forth et al. established the potential use of these fibers for diverse applications, such as for biphasic chemical synthesis.

Exploiting the mechanics of particle-stabilized interfaces, these investigations utilized flow fields, electric fields, confinement, and extrusion to shape interfaces into complex geometries that are subsequently arrested into configurations far from equilibrium. Ultimately, these systems are made metastable by the high attachment energy of surface-functionalized nanoparticles. The particles of Pickering emulsions jam at the interface, imparting onto it the solidlike characteristics that are vital for casting liquids into intricate architectures.

Bijels. Pickering emulsions are unique in being printable liquids, as Forth et al. have proven.[33] Their printability opens up the potential for these emulsions to be used as networks for biphasic reaction or mass transfer. The downside of direct printing of one phase into the other is the resolution and printing time. Maximizing the interfacial area of Pickering emulsions is advantageous for many industrially relevant processes, so submicron system features are desirable. Direct printing of network features is limited to the micron scale and, even if feasible, is time consuming. To maximize the system interfacial area, the Pickering emulsions must form these system features themselves via self-assembly, with system properties tuned to arrest them.

In 2005, Stratford et al. simulated a new material that they termed a bicontinuous interfacially jammed emulsion gel (bijel), where liquid networks are formed via spinodal decomposition, a type of liquid−liquid phase separation that generates interconnected channels of two immiscible fluids.[130] For these interconnected channels to be arrested in place by a solidlike particle film, the surface chemistry of the particles must be adjusted precisely to guarantee neutral wetting of both fluids ($\theta \approx 90°$), essential for accommodating the complex curvatures created by spinodal decomposition (Figure 8). In 2007, bijels were experimentally realized in the group of Clegg.[131] However, in this system, the particle wettability was difficult to control. In situ surface modification of the particle wettability enables the facile adjustment of the three-phase contact angle to kinetically arrest these structures.

Haase et al. initiated the use of in situ surface modification, in tandem with solvent transfer-induced phase separation (STrIPS), to fabricate bijels. STrIPS enables phase separation of two immiscible fluids (such as an oil and aqueous phase) by injection of a homogeneous mixture of these two fluids plus a third solvent into a continuous phase (Figure 10a, top).[31] The third solvent facilitates mixing of the two immiscible fluids, as depicted in the white region of the ternary phase diagram in Figure 10a (bottom left). While the ternary mixture is immersed within the continuous phase, this solvent is extracted into the continuous phase, leading to movement down the ternary phase diagram, past the binodal line where spinodal phase separation of the two immiscible fluids occurs. Incorporating nanoparticles and a corresponding in situ surface modifier into the initial ternary mixture enables the particles to be attached to the interface as the interface is being formed in

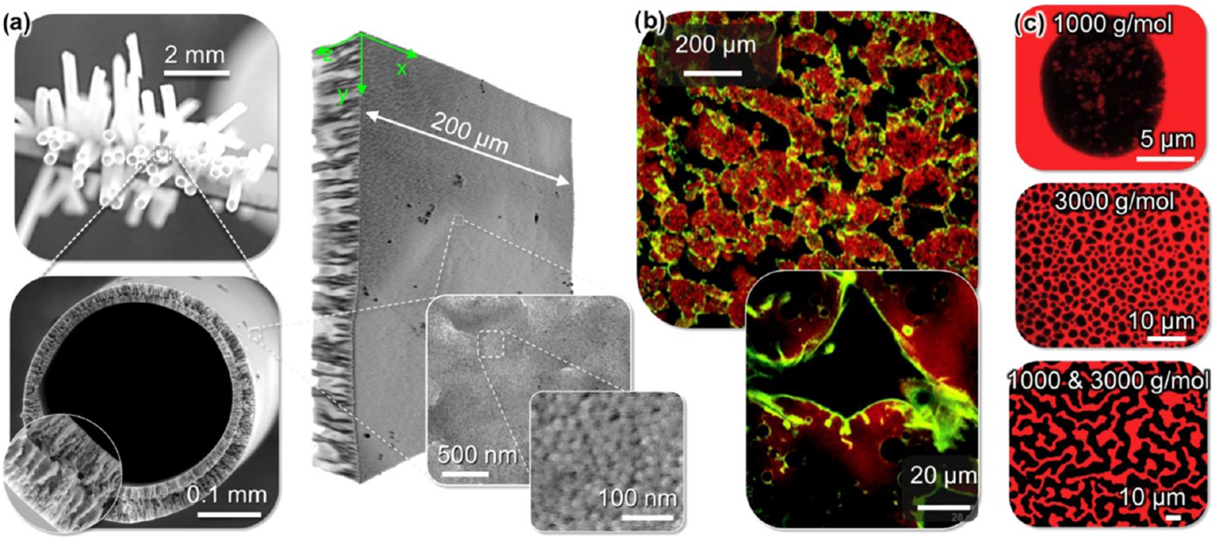

Figure 11. (a) Hollow fiber and planar membranes are fabricated from UV polymerization of bijels produced by STrIPS. Adapted from ref 2 with permission of Springer Nature. (b) Confocal micrographs of bijels at different magnifications, formed by direct mixing of silicone oil (red) in a glycerol phase, stabilized by 14 nm silica particles that are fluorescently labeled with fluorescein isothiocyanate (FITC). Adapted with permission from ref 132. Copyright 2017 Royal Society of Chemistry. (c) Carboxylated silica particles dispersed in the water phase are surface functionalized from the oil phase by a mixture of amine-terminated polydimethylsiloxane (PDMS-NH2) with two different molecular weights (schematic in i). ii and iii) Confocal micrographs of bijels formed by homogenization of water, carboxylated silica nanoparticles, and either a single or a combination of two different molecular weights of the in-situ hydrophobizer, PDMS-NH2. Adapted with permission from ref 133. Copyright 2017 Springer Nature.

the phase separation process (Figure 10a, bottom right). As the phase separation coarsens, more nanoparticles attach to the interface until the interface is jammed by them, arresting the spinodal structure. Electron micrographs of an STrIPS bijel fiber are shown in Figure 10b, making visible the jamming of silica nanoparticles surface-modified by CTAB at the diethylphthalate (DEP) and water interface. By tuning the particle concentration, the in situ surface hydrophobizer concentration, and the initial ternary composition, features with sizes down to the submicron scale are possible (Figure 10c).

Another advantage of particle in situ modification for STrIPS bijels is that the initial nanoparticle surface characteristics can be restored after consolidation of the interfacially jammed emulsion. Haase et al. replaced DEP in the previous ternary mixture with a hydrophobic monomer (hexanediol diacrylate) and added a corresponding photoinitiator (2-hydroxy-2-methylpropiophenone) to enable the fabrication of polymerizable, STrIPS bijels.[2] By extruding this mixture into an continuous phase through a coaxial nozzle with an internal aqueous bore fluid, hollow fiber membranes were mass-produced after irradiation with UV light (Figure 11a, left and bottom). Planar membranes were also producible with this technique, by submerging a substrate wetted by the polymerizable, ternary mixture into an aqueous bath (Figure 11a, right). After washing these polymerized materials with ethanol, their nanoparticle-decorated surface returned to the initial hydrophilic state. Treating the membrane with zwitterionic silanes introduced biofouling resistance, with pore sizes in the nanometer range. These small pore sizes enabled the filtering of gold nanoparticles with diameters down to 20 nm.

The interface is shapeable into biphasic, interconnected channels not only through spinodal phase separation, but also by shearing the interface under carefully chosen conditions. Cai et al. fabricated these channels by shearing the interfaces of fluids of increased viscosities via a multistep homogenization procedure.[132] First, an aqueous solution of glycerol, fluorescently labeled silica particles, and CTAB is slowly mixed with silicone oil (1:1 by mass mixture of 10 000 and 50 cSt), forming multiple emulsions in a silicone oil, continuous phase. The in situ hydrophobizer concentration must be tuned for neutral particle wettability of either phase for multiple emulsions to be stabilized. These emulsions are then mixed rapidly, shearing them to the extent that the emulsions are broken and reconnect into tortuous fluid passages, forming a bijel. The resultant bijel is shown in Figure 11b.

Huang et al. also formed bijels via homogenization, but this time by combining in situ modifiers with different molecular weights.[133] The neutral wettability of the carboxylated nanoparticles is adjustable by combining different polymeric in situ modifiers of PDMS-NH_2. With low-molecular-weight PDMS-NH_2 (1000 g/mol) in toluene, either o/w or w/o emulsions were formed, while higher-molecular-weight PDMS-NH_2 (3000 g/mol) in toluene formed only w/o emulsions, suggesting that the size of the PDMS polymer chain resulted in a preferred interfacial curvature. Mixing together low- and various high-molecular-weight functional polymers, bijels with diverse channel sizes can be generated (Figure 11c).

Bijels are typically too fragile for direct applications. Through microfluidic in situ mechanical testing, Haase et al. showed that the tensile strengths of STrIPS bijels range from hundreds to thousands of pascals (comparable to calcium cross-linked alginate hydrogels).[134] However, most recently, Di Vitantonio et al. have introduced a technique to reinforce bijels.[7] They made bijels resistant to mechanical stresses and prevented detachment of nanoparticles from the oil/water interface by chemically fusing the interfacial nanoparticles. Within the reinforced bijel, a homogeneously catalyzed biphasic chemical reaction was realized.

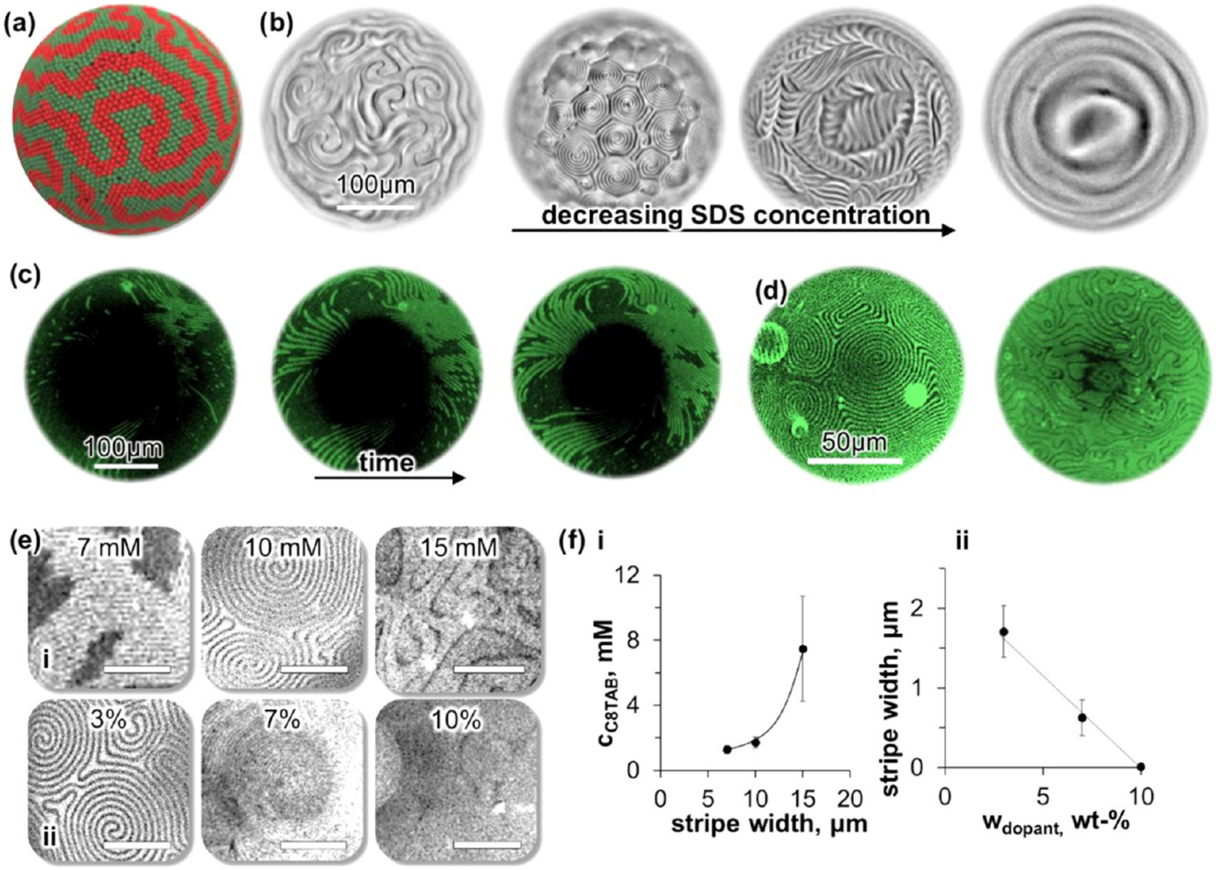

Figure 12. Liquid crystal patterned interfacial particle assemblies. (a) Simulation of a smectic liquid crystal droplet (left). The interface of the droplet has bicontinuous stripes of liquid crystal mesogens (red) and surfactant that induces homeotropic anchoring of the mesogen (green). Confocal micrograph of a cholesteric liquid crystal (right). Fluorescently labeled silica particles are in-situ surface functionalized with octyltrimethylammonium bromide, energetically driving them to the droplet surface. The liquid crystal elastic field causes the particles to segregate into stripes, as the surfactants did in simulations (left). Adapted with permission from ref 143. Copyright 2012 Springer Nature. (b) The periodicity of the nanoparticle assemblies are tunable by varying the in-situ modifier concentration (i & c, top) or by varying the amount of chiral dopant mixed into the liquid crystal (ii & c, bottom). Adapted from ref 23 with permission of American Physical Society. (c) Submicron stripes are obtainable by the latter method. All scale bars are 25 μm. Adapted from ref 23 with permission of the American Association for the Advancement of Science.

Bijels bring together the three-phase contact angle in determining interfacial curvature, seen with phase-inverting emulsions, and the kinetic arresting of interfaces from nanoparticle jamming, seen with nonspherical emulsions, resulting in innovative materials with promise for use in industrial applications. The most auspicious characteristic of the systems highlighted is the wide range of nanoparticle materials that can stabilize the interface. This is a direct consequence of the versatility imbued by in situ surface modification, opening up bijels as avenues for continuously flowing, biphasic catalysis.

Liquid Crystals. We have thus far reviewed several methods of shaping the interface ranging from electric fields and printing to phase separation and shearing, with length scales ranging from many centimeters, down to submicron. With all of the methods discussed thus far, the nanoparticle wetting is tuned, in situ, to achieve the desired interfacial curvature and to jam the interface. Nanoparticle assemblies kinetically arrest the interface, preventing the system from evolving toward equilibrium. Yet, often in materials development, it is desirable for the system features themselves to be reconfigurable, at the micron or submicron scale. One external field that can shape and reshape nanoparticle assemblies from adjusting the interface is a liquid crystalline, elastic field.

Liquid crystals are phases of matter where the constituents are rodlike. They are able to flow, while resisting certain deformations, making the material an elastic fluid. For a nematic liquid crystal, the centers of mass of the rodlike molecules are randomly ordered in space, yet the rods point in a preferential direction, with elastic energy costs associated with orientations away from this direction. Furthermore, since liquid crystals are fluid, they are easily confined, such as into films and droplets. Tuning the boundary conditions of liquid crystals by chemically driving the molecules to align either perpendicular (homeotropic) or parallel (planar) to the interface often gives rise to a wealth of patterns, from the system reconciling surface and bulk energies.

Both particles and molecular surfactants have previously been found to organize at the interface.[135−141] The hydrocarbon tails of molecular surfactants interdigitate with liquid crystal molecules, causing them to be homeotropically anchored to the interface.[136] Surfactant-laden regions of homeotropic anchoring form domains, phase separating from regions with planar anchoring, mediated by the nematic elasticity. However, since particles are typically larger than

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molecules, their organization at the interface can differ. Particles organize around regions of disorder called defects and, when they are larger than 1 μm, can create defects themselves, increasing interparticle repulsion that is mediated by the elastic field.[135,139] Defects are well organized because of the geometry and topology of a given set of boundary conditions, facilitating the fabrication of patchy particles with designed, chemical heterogeneity.[137,138]

However, there are drawbacks in relying solely on defects to order particles. Defects cannot pattern large regions of the interface because of the high elastic cost associated with them, and the particle densities of such systems are low.[137,138] Exploiting regions of differing liquid crystal anchoring, as was done for molecular surfactants, allows for higher densities of patterned particle assemblies at the interface, for larger chemical patches.[23,139−141]

By using in situ surface modification, nanoparticles can be altered to be highly interfacially active using the same surfactants that create domains of homeotropic anchoring at the interface.[23] This approach facilitates high densities of nanoparticles at the interface and allows for nanoparticles that, at the right solution conditions, can mimic the behavior of molecular surfactants.

Furthermore, by utilizing a layered liquid crystal instead of a nematic, such as a smectic or a cholesteric liquid crystal, the bulk elastic energy can be in greater competition with the surface energy, giving rise to domains with well-defined shapes, such as interfacial stripes of alternating homeotropic and planar anchoring domains (Figure 12a).[23,142,143]

Cholesteric liquid crystals can be made from nematics by the introduction of a chiral dopant, resulting in a helical structure as the ground state of the system.[142] Tran et al. demonstrated that diverse surface patterns on cholesteric liquid crystal droplets composed of 4-cyano-4′-pentylbiphenyl doped with (*S*)-4-cyano-4-(2-methylbutyl)biphenyl can be obtained by surfactant-mediated anchoring control.[142] Figure 12b depicts the resulting patterns when the concentration of surfactant sodium dodecyl sulfate (SDS) in the surrounding water phase is varied.

Tran further developed this concept to pattern in situ surface-functionalized nanoparticles on the cholesteric liquid crystal/water interface. The data in Figure 12c show a time series of the diffusion-controlled deposition of fluorescently labeled, silica nanoparticles, made surface active by octyltrimethylammonium bromide (OTAB), on cholesteric liquid crystal emulsions. Figure 12d reveals possible final patterns obtained with the fluorescent nanoparticles.

The patterned nanoparticle assemblies are tunable from both interfacial and bulk approaches. The size of the domains with homeotropic anchoring at the interface can be reconfigured by higher amounts of surfactant adsorbed at the interface with increasing in situ modifier concentrations (Figure 12e-i,f-i). The in situ modifier plays a dual role in this system. It acts to change the liquid crystal anchoring at the emulsion interface, altering the emulsion stripe patterning. It also changes the particle wettability to render the particles hydrophobic, driving them to the interface, while moderating particle aggregation. ζ potential measurements suggest that, at the solution conditions where the nanoparticle patterning best follows the underlying elastic field, the in situ modifier forms a slight double layer at the particle surface, similar to the double phase-inverting systems discussed previously. The head groups of the in situ modifier structure themselves to face outward from the particle surface to increase the interparticle, electrostatic repulsion. The nanoparticle assemblies are then more flexible and can be easily shaped by the underlying elastic field.

At these solution conditions, the periodicity of the cholesteric, and consequently, the periodicity of the stripes, are also adjustable by varying the chiral dopant concentration of the liquid crystal bulk (Figure 12e-ii,f-ii). With increasing chiral dopant, the stripe widths decrease. Nanoparticle-filled stripes with widths down to the submicron, optically relevant length scales are feasible, allowing for possible applications within optical devices.[23]

Moreover, since the nanoparticles are introduced from the surrounding aqueous phase, instead of through the liquid crystal bulk, the particle assemblies are guaranteed to be located at the interface, with greater chemical accessibility. Tran et al. demonstrated this by physically cross-linking the assemblies of silica particles with the addition of lanthanum chloride to the surrounding phase. The nanoparticle stripes then remained intact, even after large perturbations of the underlying elastic field.

Using liquid crystals to organize nanoparticles that have been surface-modified by surfactants, in situ, harnesses the dual role of the surfactant as both particle wettability modifiers and liquid crystal anchoring cues. The myriad of patterns possible within various liquid crystalline phases open up a wider array of blueprints for nanoparticle assemblies that are shapeable postprocessing, with designable, submicron-sized features.

■ CONCLUSIONS

In situ techniques that drive the interfacial assembly of particles have been widely employed in an extensive range of soft materials and applications, as covered within this review. We envision the field of directed self-assembly expanding with the use of in situ techniques in the following ways:

The use of short amphiphiles to modify particle wettability has allowed for high particle densities to stabilize emulsions as templates for macroporous materials. The materials produced with these in situ techniques have been demonstrated to be 3D printable,[3,26] and therefore, industrially viable. With the use of biocompatible particles and modifiers, such as cellulose nanocrystals,[52] macroporous materials formed by particle-stabilized emulsions could be further developed and implemented as biocompatible foams and as hierarchical frames for tissue growth.

The components of capsules and colloidosomes could also be imparted with additional properties to be actuatable with external fields. For instance, multifunctional, submicron colloidosomes, stabilized by fluorescently labeled silica and iron oxide, have been fabricated by Bollhorst et al., resulting in capsules that are responsive to magnetic fields.[6] More varied nanoparticle types, such as conductive particles, could also be introduced as emulsion stabilizers for manipulation with an electric field. Furthermore, time- and spatially varying electromagnetic fields can be applied to distort droplet shapes[78] while also rearranging particles at the interface to form even more complex assemblies and nonspherical emulsions.

These actuatable particles can be further applied to the study of stimuli-responsive films. Liquid mirrors have recently been developed by Montelongo et al., by assembling stimuli-responsive, gold nanoparticles with in situ promotion.[5] However, the switching times are on the scale of hours, limiting the use of this system in devices. A possible route to enhance the assembling/disassembling times could be the use of external fields or convective shear flows. For instance, core—shell gold nanoparticles with iron oxide cores would allow for use of an external magnetic field, while still maintaining the nanoplasmonic properties of the film. The nanoparticle shapes could additionally be varied to further structure the interfacial particle assemblies by imparting anisotropic plasmonic responses. Moreover, altering the particle shape could vary the possible interfacial particle packings. Consequently, more dense packings with higher reflectivity and stronger external field responses could be obtained.

Furthermore, in situ promotion techniques for interfaces that are stable even without the attachment of particles has potential for greater control over the interfacial particle assembly and aggregation behavior. For instance, the in situ patterning of nanoparticles at the interface of liquid crystals could access a greater number of patterns by separating the two roles of the amphiphile as particle wettability modifier and as anchoring adjuster.[23] By using in situ promotion instead of in situ modification methods, patterns that require planar anchoring can also be exploited for particle assembly, while maintaining high particle densities.

Finally, the intricate liquid networks that are obtained within bijels can be harnessed for tissue engineering, separation membranes, and for cross-flow biphasic catalysis. Ultrafiltration for bijel-templated, hollow fiber membranes was demonstrated.[2] Future work could be focused on further enhancing the selectivity of these membranes toward nanofiltration. Moreover, the flexibility of in situ modifications also allows for the fabrication of membranes with catalytic nanoparticles, showing potentials as self-cleaning membranes or membrane reactors. The reinforcement of STrIPS bijels by Di Vitantonio et al. was a crucial step to realize biphasic catalysis in these systems.[7] To fully realize cross-flow, biphasic catalysis within bijels, they need to be developed with and stabilized by catalyst particles, and approaches for realizing continuous flow in bijels still require implementation.

The methods outlined in this paper exploit the synergistic interactions of components within the system to not only tune assembly structures but also function with external means of shaping the interface. By varying particle compositions and particle shapes, even more interactions of interfacial particles with external fields are attainable. With dynamic control of both the particle interfacial behavior and the interfacial geometry with in situ techniques and external fields, materials with feature sizes that range from the many centimeters to the submicron scale are realizable, broadening the possibilities of soft material design via directed self-assembly.

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