



Review

Pickering emulsions stabilized by colloidal surfactants: Role of solid particles



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ABSTRACT

Pickering emulsions are emulsions stabilized by colloidal surfactants, i.e. solid particles. Compared with traditional molecular surfactant-stabilized emulsions, Pickering emulsions show many advantages, such as high resistance to coalescence, long-term stability, good biocompatibility and tunable properties. In recent years, Pickering emulsions are widely applied in scientific researches and industrial applications. In this review, we focus on the influences of particle properties on Pickering emulsions, including particle amphiphilicity, concentration, size and shape, and summarize the strategies developed for the preparation of amphiphilic Janus particles. The applications of Pickering emulsions in food industry, cosmetic industry, material science, drug delivery, biomedical research and vaccine adjuvant will also be covered. Pickering emulsions are a unique system for multi-disciplinary studies and will become more and more important in the future.

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Introduction

Emulsions are systems of one phase dispersed in another immiscible phase in the form of droplets, such as water-in-oil emulsions or oil-in-water emulsions. Emulsions are generally prepared under external energy input, e.g. by means of sonication or homogenization (Prince, 2012). Emulsions are thermodynamically unstable, since smaller emulsion droplets have larger total interfacial area and thus larger total interfacial energy. Once external shearing stops, emulsion droplets tend to coalesce and revert to originally phase separated state to minimize the total interfacial area and thus the total interfacial energy (Adams et al., 2007).

To improve the emulsion stability, molecular surfactants are added in the continuous phase. Molecular surfactants are generally amphiphilic molecules consisted of both hydrophilic group and hydrophobic group. These amphiphilic molecules tend to adsorb at the water/oil interface with the hydrophilic group submerged in water and the hydrophobic group in oil, which could effectively reduce the interfacial tension (Ren et al., 2019; Rosen & Kunjappu, 2012). However, the anchoring of molecular surfactants at the interface is in a thermal equilibrium state of adsorption and desorption, since molecular surfactants could desorb from the interface driven by thermal motion; emulsions will slowly coalesce (Borwankar & Wasan, 1988). In addition, due to Ostwald ripening, small droplets with high internal pressure will become smaller while large droplets with small internal pressure will become larger (Voorhees, 1985). Under the influences of droplet coalescence and Ostwald ripening, the average droplet size of emulsions will slowly increase over time to lower its total interfacial energy, eventually leading to phase separation (Chesters, 1991; Evans & Needham, 1987), at which the total interfacial area of the system is smallest and the total interfacial energy is lowest.

Alternatively, solid particles, also called colloidal surfactants, are able to stabilize emulsions of two immiscible phases for a long period of time (Ramsden, 1903). The stable emulsions stabilized by colloidal surfactants are called Pickering emulsions (Pickering, 1907). Compared to traditional molecular surfactant-stabilized emulsions, Pickering emulsions stabilized by colloidal surfactants have many unique properties: (i) The desorption energy of colloidal surfactants from the water/oil interface is several orders of magnitude higher than the thermal energy, which results in irreversible adsorption of colloidal surfactants at the interface, contributing to excellent emulsion stability (Aveyard, Binks, & Clint, 2003; Binks, 2002; Pieranski, 1980); (ii) Colloidal surfactants could be made of biocompatible materials, showing good biocompatibility (Yang, Fu, Wei, Liang, & Binks, 2015); (iii) Colloidal surfactants could be designed to implement Pickering emulsions with diverse functions, such as pH, temperature or light-triggered responses (Tang, Quinlan, & Tam, 2015; Wei, Yu, Rui, & Wang, 2012; Hao et al., 2018). Pickering emulsions could provide a unique platform for multi-disciplinary studies and will play a more and more important role in scientific researches and industrial applications.

Here we provide a comprehensive review on Pickering emulsion systems. Three main aspects are covered: (i) Influences of particle properties, including particle amphiphilicity, concentration, size and shape, on Pickering emulsions; (ii) Preparation of amphiphilic

Janus particles, including selective surface modification, emulsion templates by microfluidics, self-assembly of block copolymer and phase separation; (iii) Applications of Pickering emulsions in food industry, cosmetic industry, material science, drug delivery and biomedical research.

Influences of particle properties on Pickering emulsions

There are many factors, which could influence the properties of Pickering emulsions, including amphiphilicity, concentration, size and shape of particles.

The surface wettability of particles generally reflects the hydrophilicity or hydrophobicity of particles and is characterized by the three-phase contact angle θ (Wang, Wang, & Lu, 2019). The contact angle θ could be determined by the Young's equation, $\cos\theta = (\gamma_{so} - \gamma_{sw})/\gamma_{ow}$, where γ_{so} is the solid/oil interfacial tension, γ_{sw} is the solid/water interfacial tension and γ_{ow} is the oil/water interfacial tension. Hydrophilic particles with contact angle $\theta < 90^\circ$ will mostly reside in the water phase, while hydrophobic particles with contact angle $\theta > 90^\circ$ will mostly reside in the oil phase, as shown in Fig. 1(a) (Binks, 2002). Correspondingly, hydrophilic particles favor the interfacial curvature of oil-in-water emulsions, while hydrophobic particles prefer the interfacial curvature of water-in-oil emulsions.

The desorption energy of spherical particles from the interface strongly depends on the surface wettability. According to the formulation (Binks & Lumsdon, 2000a), $E = \pi R^2 \gamma_{ow} (1 + \cos\theta)^2$, where E is the energy required to remove the particle from the interface, R is the radius of the spherical particle, γ_{ow} is the interfacial tension and θ is the contact angle, the anchoring strength maximizes at contact angle $\theta = 90^\circ$ under constant R and γ_{ow} , as shown in Fig. 1(b). The anchoring strength falls rapidly as contact angle θ moves away

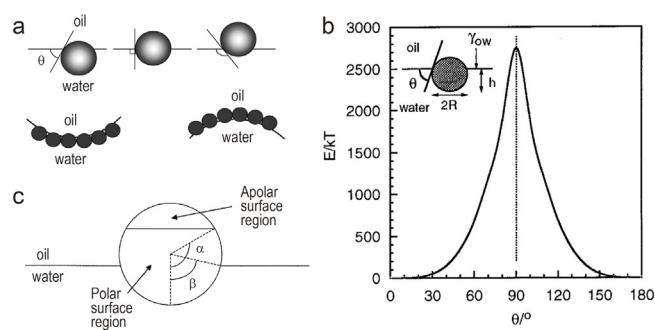


Fig. 1. Anchoring strength of spherical particles at the oil/water interface. (a) Configuration of spherical particles at the interface with contact angle $\theta < 90^\circ$, $\theta = 90^\circ$ and $\theta > 90^\circ$ and the corresponding preferred interfacial curvature. The contact angle is defined as the angle between the tangent line of oil/water interface and the tangent line of water/solid interface made at the intersection point of oil, water and solid (Binks, 2002). (b) Energy required to detach a spherical particle from the interface. The anchoring strength is maximized for particles with a contact angle of 90° (Binks & Lumsdon, 2000a). (c) Configuration of a spherical Janus particle at the oil/water interface. The relative areas of polar and apolar surfaces are parametrized by the angle α . The immersion depth of particles at the oil/water interface is parametrized by the angle β (Binks & Fletcher, 2001).

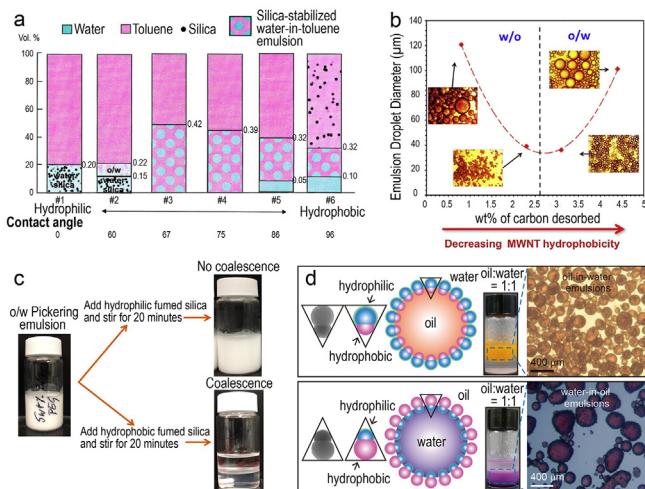


Fig. 2. Influences of particle amphiphilicity on Pickering Emulsions. (a) Toluene-in-water emulsions transition to water-in-toluene emulsions as the hydrophobicity and thus the contact angle of silica nanoparticles increase (Yan et al., 2001). (b) Dependence of emulsion type and droplet diameter on the hydrophobicity of multi-walled carbon nanotubes (MWNTs). The water-to-oil ratio is kept constant at 1 and the concentration of MWNTs in water is kept constant at 0.07 wt% (Briggs et al., 2018). (c) Oil-in-water emulsions previously stabilized by polyethylene glycol silane-modified silica nanoparticles could be destabilized by adding hydrophobic fumed silica nanoparticles, which favor water-in-oil emulsions (Griffith & Daigle, 2019). (d) When the hydrophilic bulb is larger than the hydrophobic bulb, amphiphilic dimer particles prefer to stabilize oil-in-water emulsions and vice versa. The water-to-oil ratio is kept constant at 1. The oil phase is dyed by Sudan II. The water phase is stained with Evans blue (Sun, Yang, Wang et al., 2020).

from $\theta = 90^\circ$ and the desorption energy is only 10 kT or less, when contact angle θ is below 20° or above 160° .

To maximize the anchoring strength of particles at the interface, contact angle $\theta = 90^\circ$ is preferred. Amphiphilic particles with one hydrophilic hemisphere and the other hydrophobic hemisphere, also called Janus particles, tend to have their hydrophilic hemispheres submerged in water and hydrophobic hemispheres submerged in oil, resulting in contact angle $\theta = 90^\circ$. Amphiphilic Janus particles could perform as emulsion stabilizers and greatly improve the interfacial stability. Generally, the relative surface areas of polar (hydrophilic) to apolar (hydrophobic) regions are characterized by the angle α and the immersion depth of the particle into the water phase is characterized by the angle β , as shown in Fig. 1(c) (Binks & Fletcher, 2001).

Amphiphilicity of particles

The hydrophilicity or hydrophobicity of particles could influence the anchoring strength of particles at the interface, the stability of particle-stabilized emulsions and the emulsion type, as shown in Fig. 2(a) (Yan, Gray, & Masliyah, 2001). When the particles are hydrophilic, they tend to disperse in the water phase and stabilize oil-in-water emulsions. When the particles are hydrophobic, they tend to disperse in the oil phase and stabilize water-in-oil emulsions. Only particles with intermediate hydrophobicity show the best performances in producing stable water-in-oil emulsions. Rod-like multi-walled carbon nanotubes (MWNTs) with varying hydrophobicity show similar behaviors. As the hydrophobicity of MWNTs gradually decreases, the emulsion type changes from water-in-oil emulsion to oil-in-water emulsion, while the droplet size decreases first and then increases, as shown in Fig. 2(b) (Briggs et al., 2018). Since MWNTs with a moderate hydrophobicity have a stronger adsorption at the oil/water interface, they are able to prevent droplets from coalescing, leading to smaller droplets. Interestingly, oil-in-water emulsions previously

stabilized by hydrophilic fumed silica nanoparticles could be destabilized by the addition of hydrophobic fumed silica nanoparticles, as shown in Fig. 2(c) (Griffith & Daigle, 2019); the results suggest that the change of the average hydrophobicity of mixed particles with different hydrophobicity could also cause the emulsion type to reverse (Binks & Lumsdon, 2000b). By adjusting the ratio of hydrophilic to hydrophobic bulbs of amphiphilic dimer particles, the average hydrophobicity of dimer particles could be tuned and oil-in-water or water-in-oil emulsions could be obtained depending on the average hydrophobicity, as shown in Fig. 2(d) (Sun, Yang, Wang et al., 2020). When the hydrophilic bulb is larger than the hydrophobic bulb, amphiphilic dimer particles prefer to stabilize oil-in-water emulsions. When the hydrophilic bulb is smaller than the hydrophobic bulb, amphiphilic dimer particles better fit at the interface of water-in-oil emulsions.

Concentration of particles

Concentration of particles in the continuous phase is an important factor, which could influence the stability of Pickering emulsions. For molecular surfactants, to achieve a good performance in stabilizing emulsions, the concentration of molecular surfactants in the continuous phase needs to be above critical micelle concentration (CMC), above which molecular surfactants aggregate to form micelles. Above CMC, adsorption of molecular surfactants on the droplet surface will reach a maximum value and the interfacial tension of droplets will drop to a minimum value, even though molecular surfactants are in thermal equilibrium of adsorption and desorption.

Solid particles served as colloidal surfactants are different from molecular surfactants. Because of the irreversible adsorption of solid particles on the droplet surface, solid particles in the continuous phase will first cover the droplet surface. When further increasing the particle concentration, excess particles will form a network structure around each droplet, thus further improving the emulsion stability and leading to an increase in the viscosity of the emulsion system. For example, toluene-in-water emulsions stabilized by different concentrations of silanized fumed silica nanoparticles are demonstrated and modeled in Fig. 3(a) (Juarez & Whitby, 2012). At low particle concentration, emulsions are unstable as droplets are partially covered by silica nanoparticles and there are barely excess nanoparticles in the continuous phase. As the concentration of nanoparticles increases, aggregates of excess nanoparticles in the continuous phase change from compact flocs to loose networks, keeping droplets well separated from each other.

The influences of particle concentration on Pickering emulsions mainly include three aspects: particle density on the droplet surface, droplet size and viscosity of the emulsion system. Generally, particle density on the droplet surface will increase until the droplets are fully covered by particles as the particle concentration increases, while the droplet size will decrease until it reaches a minimum value as the particle concentration increases, as shown in Fig. 3(b). For a system with a fixed oil-to-water ratio, the total surface area of droplets increases as the droplet size decreases. Therefore, as the particle concentration increases, the total surface area that could be fully covered by particles increases and thus the droplet size could decrease until it reaches a minimum value, which is limited by shearing. Further increase in the particle concentration will lead to excess particles in the continuous phase, which may form multi-layer adsorption on the droplet surface or may aggregate to form a cementitious network structure, leading to the appearance of emulsion gels (Ardity, Whitby, Binks, Schmitt, & Leal-Calderon, 2003; Aveyard et al., 2003; Binks & Whitby, 2004; Binks, Philip, & Rodrigues, 2005; Chen et al., 2018; Wiley, 1954).

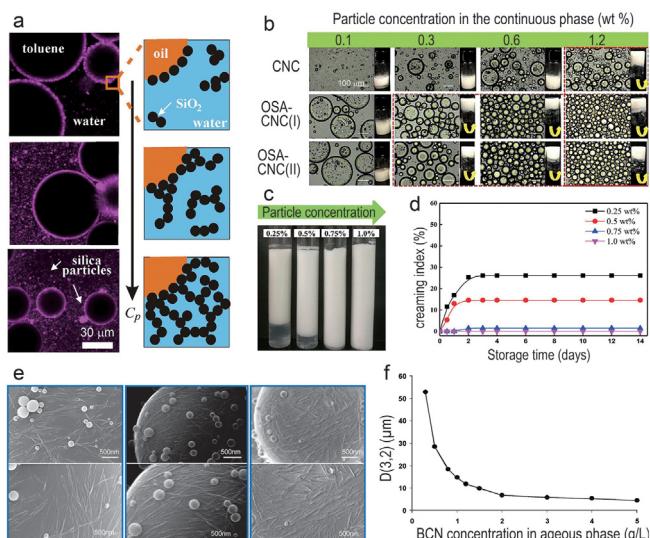


Fig. 3. Influences of particle concentration on Pickering Emulsions. (a) Fluorescent confocal microscope images and schematic illustrations of emulsions stabilized by 0.5 wt%, 0.8 wt% and 1.0 wt% fluorescent particles (from top to bottom) (Juarez & Whitby, 2012). (b) Optical microscope and visual images of high internal phase emulsions (HIPEs) ($\phi = 0.8$) stabilized by unmodified and OSA-modified cellulose nanocrystals (CNCs) with particle concentration varying from 0.1 wt% to 1.2 wt% (Chen et al., 2018). (c) Visual image of Pickering emulsions with an oil-to-water ratio of $\phi = 0.3$ stabilized by nanoparticles derived from insoluble soybean polysaccharides with particle concentration varying from 0.25 wt% to 1.0 wt% and (d) the evolution of their creaming index over time (T. Yang et al., 2019). (e) SEM images of polystyrene particles prepared by polymerizing styrene droplets stabilized by bacterial cellulose nanocrystals (BCN) with concentration = 0.5 g/L, 1 g/L and 5 g/L (from left to right) and (f) dependence of surface mean diameter $D(3,2)$ of hexadecane-in-water emulsions ($\phi = 0.3$) on BCN concentration (Kalashnikova et al., 2011).

Pickering emulsions stabilized by different types of colloidal surfactants generally show a similar dependence on the particle concentration. For example, insoluble soy polysaccharide nanoparticles (ISPNs) prepared via a facile sonication process are demonstrated to perform as outstanding stabilizers for oil-in-water Pickering emulsions, as shown in Fig. 3(c) and (d) (Yang, Liu, Li, & Tang, 2019). When the ISPN concentration increases from 0.25 wt% to 1.0 wt%, the creaming index, which is the ratio of water height to emulsion height, shows an increase in the emulsion stability over time, suggesting the formation of a gel-like network.

Pickering emulsions stabilized by non-spherical colloidal surfactants, such as bacterial cellulose nanocrystals (BCNs), show similar dependence on particle concentration; the droplet size decreases to a plateau value of diameter $\sim 4.2 \mu\text{m}$, as the BCN concentration increases, as shown in Fig. 3(e) and f (Kalashnikova, Bizot, Cathala, & Capron, 2011).

Size of particles

The size of particles mainly influences the mobility of particles in the continuous phase and the curvature of Pickering emulsions. According to Einstein's formula (Einstein, 1905), $D = \frac{kT}{6\pi\mu a}$, where D is the diffusion coefficient, k is the Boltzmann constant, T is the absolute temperature, μ is the liquid viscosity and a is the particle radius, smaller nanoparticles have a larger diffusion coefficient and thus are expected to adsorb onto the droplet surface more rapidly (Lin, Skaff, Emrick, Dinsmore, & Russell, 2003).

Generally, droplet size increases as particle size increases; this is because large particles are not able to fit the large curvature of small droplets. According to the formula (Kralchevsky, Ivanov, Ananthapadmanabhan, & Lips, 2005), $ks = \frac{1}{2}\sigma a^2 \left(\frac{3}{4}\lambda \sin^4 \theta + 5\cos^2 \theta - \frac{7}{8} \right)$, where ks is the bending elas-

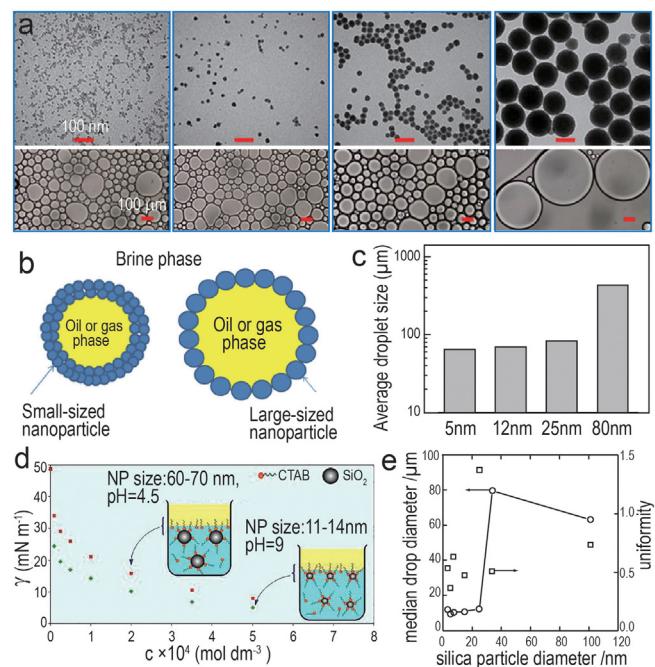


Fig. 4. Influences of particle size on Pickering Emulsions. (a) TEM and optical images of Pickering emulsions stabilized by silica nanoparticles with particle size of 5 nm, 12 nm, 25 nm and 80 nm (from left to right). (b) Schematics showing oil or gas emulsions in brine stabilized by nanoparticles of small size or large size. (c) Dependence of average droplet size of Pickering emulsions on particle size (Kim et al., 2016). (d) Dependence of interfacial tension of kerosene in water on silica nanoparticle size and CTAB surfactant concentration (Saien & Fadaei, 2018). (e) Median drop diameter (circles) and uniformity (squares) of heptane-in-water emulsions ($\phi = 0.2$) at pH = 9.5 stabilized by 2 wt% silica particles and 2×10^{-4} M DTAB as a function of the silica particle diameter (Binks & Whitby, 2005).

ticity of droplet surface, σ is the interfacial tension, a is the particle radius, $\lambda = \frac{\pi}{2\sqrt{3}}$ is a constant and θ is the particle contact angle, the bending elasticity, which describes the resistance to bending, of a closely packed particle monolayer is proportional to the square of particle radius and thus droplet size increases as particle size increases.

In a detailed study of emulsions of DI water or NaCl solution in cyclohexane stabilized by hydrophobic polystyrene particles (Binks & Lumson, 2001), the average droplet diameter increases with the increase in the particle size. A formula, $r_e = 4\Phi_w r_p / \Phi_p$, where r_e is the droplet radius, r_p is the particle radius, Φ_w is the volume fraction of water phase and Φ_p is the volume fraction of particles, is proposed, where the drop radius is a linear function of the particle radius under constant Φ_w and Φ_p .

Experiments using four different sizes of silica nanoparticles are carried out to investigate the influences of particle size on Pickering emulsions, as shown in Fig. 4(a–c) (Kim, Worthen, Johnston, Dicarlo, & Huh, 2016). In the four experiments, 5 mL decane is ultrasonicated in 5 mL water with 0.5 wt% silica nanoparticles. The size of nanoparticles has little effect on the contact angle of nanoparticles at the interface, as the contact angle of nanoparticles at the interface are determined by solid/oil, solid/water and oil/water interfacial tensions, but mainly influences the droplet size. As the nanoparticle size increases from 5 nm to 80 nm, the average droplet size increases from $64 \mu\text{m}$ to $432 \mu\text{m}$.

In systems with both colloidal surfactants (silica nanoparticles) and molecular surfactants (CTAB), the interfacial tension of kerosene in water decreases as the size of silica nanoparticles decreases or as the concentration of CTAB increases, as shown in Fig. 4(d) (Saien & Fadaei, 2018). Similarly, for droplets of heptane in water with 2 wt% silica particles and 2×10^{-4} M DTAB at pH

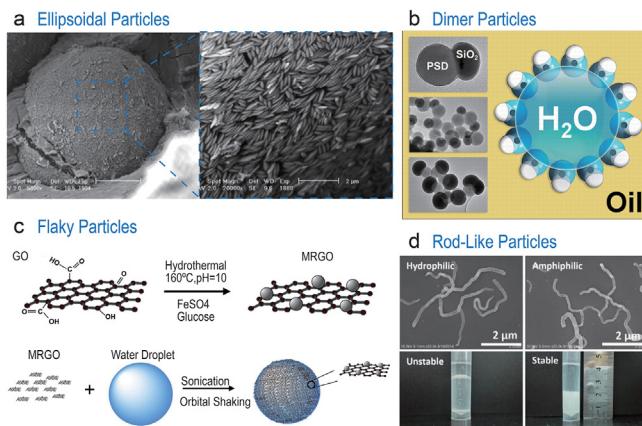


Fig. 5. Various shapes of particles developed as colloidal surfactants. (a) Ellipsoidal Particles. Cryo-SEM image of a water droplet covered by ellipsoidal polystyrene particles (aspect ratio ~4.3) (Madivala et al., 2009). (b) Dimer particles. Water-in-oil emulsions stabilized by amphiphilic snowman-like dimer particles (Passas-Lagos & Schuth, 2015). (c) Flaky particles. Synthesis of magnetically responsive reduced graphene oxides (RGOs) and preparation of Pickering emulsions stabilized by them (Lin et al., 2015). (d) Rod-like particles. Water-in-oil Pickering emulsions stabilized by amphiphilic silica nanowires (Yan et al., 2015).

= 9.5, the median drop diameter increases as the silica particle diameter increases, as shown in Fig. 4(e) (Binks & Whitby, 2005). However, the surface area of silica particles also increases as the diameter increases, thus leading to a decrease in the adsorption density of DTAB surfactants on the particle surface, which may cause a decrease in the median drop diameter when the silica particle diameter is larger.

Shape of particles

Spherical particles are the most widely studied colloidal surfactants and they mainly include three types: (i) inorganic spherical particles, such as silica particle (Zhao et al., 2018), titanium dioxide (Zhang, Bai, Guo, & Meng, 2015), magnetic Fe₃O₄ particle (Lin, Zhang, Li, & Deng, 2016; Yang et al., 2017; Zhou et al., 2011) and calcium carbonate (Zhu, Lu, Gao, Cui, & Binks, 2013); (ii) organic spherical particles, such as polystyrene (He, Ge, Liu, Zhou, & Zhang, 2007) and chitosan (Wei, Wang, Zou, Liu, & Tong, 2012); (iii) biogenic particles, such as starch granule (Rayner, Sjoo, Timgren, & Dejmek, 2012; Song et al., 2015; Timgren, Rayner, Sjoo, & Dejmek, 2011; Ye et al., 2017), kafirin particle (Xiao, Wang, Gonzalez, & Huang, 2016), zein protein (de Folter, van Ruijven, & Velikov, 2012), pea protein isolate (Liang & Tang, 2014), soy protein isolate (Liu & Tang, 2013), whey protein isolate (Wu et al., 2015) and lactoferrin protein (David-Birman, Mackie, & Lesmes, 2013; Shimoni, Levi, Tal, & Lesmes, 2013). The developments of scientific researches have broadened the diversity of colloidal surfactants, such as ellipsoidal particle, dimer particle, flaky particle and rod-like particle (Ortiz, Pochat-Bohatier, Cambedouzou, Bechelany, & Miele, 2020).

When spherical polystyrene particles are imbedded in a PVA matrix and unidirectional stretched, spherical particles undergo plastic deformation and change to prolate ellipsoidal particles. Polystyrene particles with an average aspect ratio (AR) of 1.0, 3.0, 3.7 and 4.3 are thus prepared. In systems with a decane-to-water ratio = 1:1 and 1 wt% hydrophobic polystyrene particles, spherical particles with AR = 1.0 could not stabilize any emulsions. In contrast, ellipsoidal particles with AR = 3.0, 3.7 and 4.3 are able to form stable water-in-oil emulsions and the droplet surface is fairly densely packed by monolayers of ellipsoidal particles, as shown in Fig. 5(a) (Madivala, Vandebril, Fransaer, & Vermant, 2009). Surface rheology on planar monolayers of ellipsoidal particles demonstrates that the magnitude of the interfacial viscoelastic property

strongly depends on the aspect ratio of ellipsoidal particles at a given surface coverage.

Dimer particles generally consist of two distinct bulbs and may show dumbbell-like, snowman-like or mushroom-like shape, depending on the size of the two bulbs. For example, magnetic amphiphilic dimer particles with one hydrophobic bulb of poly(styrene-co-divinylbenzene) and the other hydrophilic bulb of silica, could successfully stabilize emulsions of water in oil, as shown in Fig. 5(b) (Passas-Lagos & Schuth, 2015). Amphiphilic dimer particles are superior in tuning the curvature of emulsions and thus determining the emulsion type by adjusting the aspect ratio of hydrophilic bulb to hydrophobic bulb. In systems with a fixed water-to-oil ratio = 1:1 and particle concentration of 48 mg/mL, oil-in-water emulsions are achieved when the aspect ratio of hydrophilic bulb to hydrophobic bulb equals 1.5, while water-in-oil emulsions are obtained when the aspect ratio of hydrophilic bulb to hydrophobic bulb equals 0.65 (Sun, Yang, Wang et al., 2020).

Flaky particles are basically two dimensional, same as 2D interface, and are good colloidal surfactants for Pickering Emulsions. Flaky particles, such as laponite clays (Ashby & Binks, 2000), layered double hydroxides (Yang et al., 2006) and graphene oxides (McCoy, Pottage, & Tabor, 2014), have been prepared and investigated. Because flaky particles generally have surface charges, their performances in emulsion formation and stabilization are strongly influenced by electrolytes and pH values. The addition of electrolytes or the change of pH values could reduce the zeta potential of flaky particles, making it easier for flaky particles to adsorb onto the interface and aggregate into a network and thus facilitating the formation and stabilization of emulsions. Recently, hydrophobic magnetic reduced graphene oxides (MRGOs) decorated with 10 nm Fe₃O₄ nanoparticles have been prepared, which show good performances in stabilizing water-in-dodecane emulsions, as shown in Fig. 5(c) (Lin, Yang, Petit, & Lee, 2015).

Rod-like particles, such as carbon nanotubes (Chen, Liu, Liu, Bang, & Kim, 2011), CdSe nanorods (He, Zhang et al., 2007), cellulose nanocrystals (Kalashnikova, Bizot, Bertoncini, Cathala, & Capron, 2013; Zoppe, Venditti, & Rojas, 2012) and silica nanowires (Yan et al., 2015), have successfully been prepared and applied as colloidal surfactants for emulsion stabilization. The performances of Pickering emulsions stabilized by rod-like particles depend on the length, diameter, rigidity and amphiphilicity of rod-like particles. For example, hydrophilic silica nanowires with length ~5 μm and diameter ~225 nm dispersed in the water phase could not form stable emulsions, while amphiphilic silica nanowires with length ~5 μm and diameter ~225 nm dispersed in the oil phase are able to form stable water-in-oil emulsions, as shown in Fig. 5(d) (Yan et al., 2015). If the hydrophilic silica nanowires dispersed in the water phase are long enough, for example length ~10 μm and diameter ~225 nm, they are able to stabilize oil-in-water emulsions for 4 months.

Preparation of amphiphilic Janus particles

Amphiphilic Janus particles with one hydrophilic hemisphere and the other hydrophobic hemisphere tend to have their hydrophilic hemispheres submerged in water and hydrophobic hemispheres submerged in oil, thus maximizing the anchoring strength of particles at the interface and greatly improving the emulsion stability. Therefore, amphiphilic Janus particles are excellent emulsion stabilizers and various strategies have been developed to prepare the particles, including selective surface modification, emulsion templates by microfluidics, self-assembly of block copolymer and phase separation.

Selective surface modification

Selective surface modification is an important method of preparing amphiphilic particles. It uses 2D planes or 3D emulsions to partially mask the particle surface and chemically modify the exposed particle surface, making the two surfaces with different chemical properties. Selective surface modification could be divided into 2D plane mask method and 3D emulsion mask method. In 2D plane mask method, silica nanoparticles are embedded in a polymer film through an amideation reaction with the active esters submerged in the polymer film. The bottom areas of silica nanoparticles are thus protected by the polymer film and the top exposed areas could selectively be modified to contain gold nanoparticles via electrostatic interactions, forming anisotropic Janus nanoparticles, as shown in Fig. 6(a) (McConnell, Kraeutler, Yang, & Composto, 2010). To increase the mask area, silica nanoparticles could partially be embedded in electrospun PMMA/P4VP nanofibers and selectively grafted with functional groups on the exposed surfaces, achieving Janus nanoparticles after dissolving the nanofibers (Ho, Chen, Shie, Lin, & Kuo, 2008).

Compared with 2D plane mask method, 3D emulsion mask method, which selectively modifies the particle surfaces inside the droplet and outside the droplet, has larger mask area and thus higher productivity. For example, silica nanoparticles anchored at the interface of water-in-oil emulsions could selectively be modified via atom transfer radical polymerization (ATRP) with hydrophilic and hydrophobic polymers on the inner and outer surfaces, respectively, forming amphiphilic Janus particles, as shown in Fig. 6(b) (Liu, Wei, Qu, & Yang, 2008). Fused silica nanoparticles could also be fixed at the frozen interface of wax-in-water emulsions with their surfaces exposed in water chemically modified with ammonia-propylsilane, thus achieving Janus particles after dissolving the wax in chloroform (Hong, Jiang, & Granick, 2006). To obtain aspherical Janus particles, the surfaces of silica nanoparticles exposed in water could chemically be etched by using NH₄F; different shapes of Janus particles, such as mushroom, bonnet, dumbbell and flower, could thus be prepared by changing the degree of etching (Liu, Zhang, Liu, Qu, & Yang, 2009).

Emulsion templates by microfluidics

Microfluidics is advantageous to prepare single and multiple emulsions with tunable size, chemical composition and hierarchical structure, which could be used as templates to prepare Janus particles with tunable properties (Peng, Wang et al., 2020; Wang, Sun, & Chen, 2020; Shi, Yan, Wang, Feng, & Chen, 2020). To prepare Janus particles, single emulsions with two inner phases or double emulsions are generally used as templates (Ge, Huang, Xu, Chen, & Luo, 2016; Wang et al., 2013; Chen et al., 2017). For example, one stream of isobornyl acrylate monomer containing titanium dioxide (white stream) and the other stream containing carbon black (black stream) are co-injected into a microfluidic device through two inlets as the inner phases, which are co-sheared into Janus droplets by the continuous water phase containing polyvinyl alcohol. Due to low Reynolds number, Janus droplets with distinct black bulb and white bulb could be polymerized by UV irradiation before the two bulbs mix with each other, forming Janus particles, as shown in Fig. 6(c) (Nisisako, Torii, Takahashi, & Takizawa, 2006). Janus particles with one PLA bulb and the other PCL bulb could also be prepared using Janus emulsions as templates upon solvent evaporation (Ekanem, Zhang, & Vladisavljevic, 2017). In addition to spherical particles, disc-like (Shepherd et al., 2006), rod-like (Dendukuri, Pregibon, Collins, Hatton, & Doyle, 2006) and wedge-like (Dendukuri, Hatton, & Doyle, 2007) Janus particles could be prepared by confining Janus droplets in microchannels of different geometric shape before UV polymerization.

Janus particles could also be prepared using double emulsions as templates. By tuning the interfacial tensions, double emulsion droplets could transition to Janus droplets. For example, monodisperse water-in-oil-in-water double emulsions are prepared using a glass capillary microfluidic device. By adjusting the concentration of molecular surfactants in the outer continuous water phase, the interfacial tensions of the double emulsion droplets could be tailored and double emulsion droplets could transition to Janus droplets driven by energy minimization (Wang et al., 2013).

Self-assembly of block copolymer

Block copolymers, which consist of blocks of different polymers in a single chain, could self-assemble into molecular aggregates or supramolecular structures by virtue of weak interactions, such as hydrogen bonding, van der Waals force and electrostatic interaction (Deng et al., 2020). The composition and morphology of Janus particles prepared by molecular self-assembly can precisely be regulated by pre-designing the composition and structure of block copolymers.

PS-b-PI-b-PtBMA (SIT) triblock copolymers are designed to synthesize Janus particles consisted of a cross-linked PI core surrounded by PS and PMAA hemispheres, as shown in Fig. 6(d) (Schroder et al., 2016). The SIT triblock copolymers are dissolved in THF and dialyzed in a mixture of acetone and isopropanol (volume ratio of acetone:isopropanol = 60:40) to form multicompartment micelles via self-assembly. The PI blocks are then cross-linked by UV-initiated radical polymerization to obtain SIT Janus nanoparticles, which consist of a cross-linked PI core surrounded by PS and PtBMA hemispheres. To make one hemisphere hydrophilic, PtBMA hemispheres are hydrolyzed to form PMAA hemispheres by acid-catalyzed elimination of isobutene. In addition to Janus particles, various shapes could be achieved by the self-assembly of block copolymers; polystyrene-polybutadiene-polymethylmethacrylate (SBM) triblock copolymers are shown to self-assemble into complex Janus nanostructures, including Janus ring, Janus cylinder, Janus plate and perforated Janus plate (Steinhaus, Chakroun et al., 2019; Steinhaus, Srivastva, Nikoubashman, & Gröschel, 2019).

Phase separation

Generally, two polymers with distinct properties are immiscible with each other. However, they could be mixed in a co-solvent or in the form of monomer. When the co-solvent evaporates or the monomers are polymerized into polymers, they phase separate. Therefore, Janus particles could be prepared based on phase separation and the methods include polymerization-induced phase separation, seeded emulsion polymerization and solvent evaporation-induced phase separation.

In polymerization-induced phase separation, polystyrene particles serve as the seed particles and are fully swollen with ethylene imine monomers; upon the addition of initiators, ethylene imine monomers start to polymerize into polyethylene imine, which phase separates from polystyrene, forming amphiphilic dumbbell-like Janus particles with one hydrophilic polystyrene bulb and the other hydrophobic polyethylene imine bulb, as shown in Fig. 6(e) (Kim, Larsen, & Weitz, 2006). Similarly, PAN/PS Janus particles could also be prepared based on polymerization-induced phase separation (Zhang et al., 2010).

Seeded emulsion polymerization also use polymer particles as seed particles. However, instead of swelling seed particles, free radiation reaction of monomers take place on the surface of seed particles, thus forming Janus particles (Kaewsaneha, Bitar, Tangboriboonrat, Polpanich, & Elaissari, 2014; Yu, Sun, Liang, Jiang, & Yang, 2019).

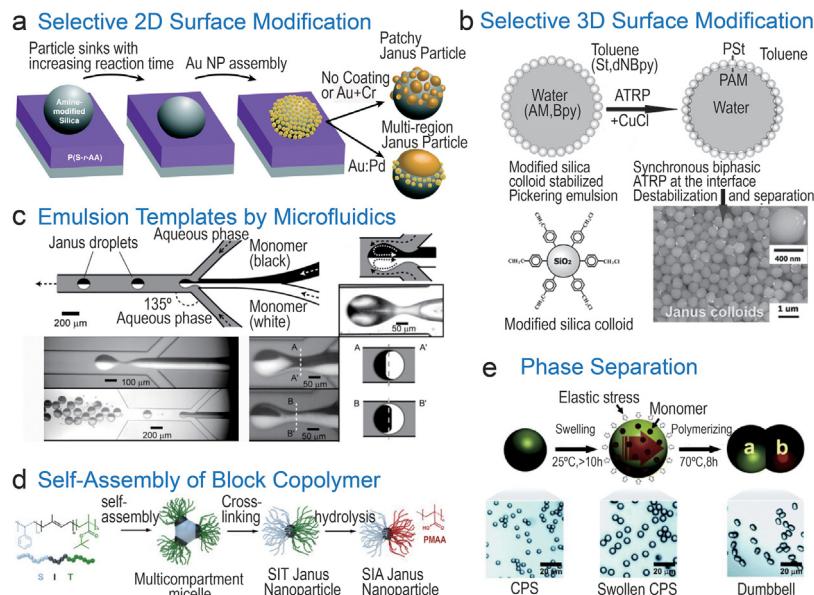


Fig. 6. Various strategies developed for the preparation of amphiphilic Janus particles. (a) Selective 2D surface modification using 2D film as mask (McConnell et al., 2010); (b) Selective 3D surface modification using 3D emulsion as mask (B. Liu et al., 2008); (c) Emulsion templates by microfluidics (Nisisako et al., 2006); (d) Self-assembly of block copolymer (Schroder et al., 2016); (e) Polymerization-induced phase separation (Kim et al., 2006).

In solvent evaporation-induced phase separation, two immiscible polymers co-dissolved in a solvent thermodynamically phase separate upon solvent evaporation (Sun, Wu et al., 2020; Kong, Jin et al., 2019; Kong, Chen et al., 2019). For example, PMMA and PS are co-dissolved in toluene and then the solution is emulsified into droplets in an aqueous phase. Upon the evaporation of toluene, PMMA and PS phase separate, forming PMMA/PS Janus particles (Tanaka, Nakatsuru, Kagari, Saito, & Okubo, 2008).

Applications of Pickering emulsions

Food industry

Pickering emulsions are widely used in food, such as milk, ice cream, butter, margarine and beverage. The particles used in food are mainly biogenic particles, such as fat crystals (2013, Frasch-Melnik, Norton, & Spyropoulos, 2010; Rousseau, 2000), starch particles (Chivero, Gohtani, Yoshii, & Nakamura, 2016; Yano et al., 2017) and zein proteins (Gao et al., 2014). Particle-stabilized Pickering emulsions are stable against droplet coalescence, showing long-term stability. The use of Pickering emulsions in food is also beneficial to achieve uniform texture, good taste, low fat and low calorie. For example, to reduce the fat content in chocolate without affecting the taste and improve the product stability, stable water-in-oil Pickering emulsions, which are fruit juice dispersed in molten chocolate stabilized by chitosan and silica particles, are developed, as shown in Fig. 7(a) (Skelhon, Grossiord, Morgan, & Bon, 2012).

Cosmetic industry

Emulsion is an indispensable formulation in cosmetics. Emulsions stabilized by traditional molecular surfactants have disadvantages of skin irritation and greasy feeling. Pickering emulsions, in which colloidal surfactants replace molecular surfactants, have demonstrated applications in cosmetics with good skin sensation, low skin irritation and high product stability (Sun, Yang, Eggersdorfer et al., 2020). Sunscreen is a typical product using Pickering emulsions. Titanium dioxide (TiO_2) and zinc oxide (ZnO) nanoparticles are two typical sun blockers and have very good

skin compatibility (Kent, Aldous, & Blake, 2010). The nanoparticles could also perform as colloidal surfactants, stabilizing Pickering emulsions, as shown in Fig. 7(b) (Marto et al., 2016). An innovative Pickering emulsion-based sunscreen formulation, including TiO_2 , ZnO and aluminum starch octenylsuccinate, is developed, which shows very good skin compatibility and waterproof performance. The dermal delivery of cosmetic products using Pickering emulsions without any molecular surfactants are also proved to increase the skin penetration depth (Simovic, Ghouchi-Eskandar, & Prestidge, 2011).

Material science

Pickering emulsions consisted of one phase dispersed in the other phase are good templates for preparing porous functional materials with large surface area (Na et al., 2019; Qin et al., 2020; Yang, Xu, Shu, Wang, & Ge, 2020). For example, porous polymers with high permeability and porosity could be synthesized by directly polymerizing the continuous oil phase of water-in-oil Pickering emulsions by heating (Ikem, Menner, Horozov, & Bismarck, 2010). Similarly, highly porous and electrically conductive polymers could be prepared in one step using carbon nanotube-stabilized Pickering emulsions as templates, in which the continuous oil phase is polymerized at an elevated temperature (Menner, Verdejo, Shaffer, & Bismarck, 2007).

In addition to directly polymerizing the continuous phase of Pickering emulsions, porous scaffolds could also be prepared by solvent evaporation; as solvent in the continuous phase gradually evaporates, polymers dissolved in the solvent precipitate to form porous scaffolds. For example, porous poly(lactide-co-glycolide) (PLGA) scaffolds are prepared using Pickering emulsions stabilized by poly(L-lactic acid)-grafted hydroxyapatite (g-HAp) nanoparticles by solvent evaporation for drug release, as shown in Fig. 7(c) (Hu, Gu et al., 2014). The scaffold morphology, pore structure and mechanical property could be adjusted by changing the concentration of g-HAp nanoparticles or the volume fraction of the dispersed phase. When loaded with anti-inflammatory drug in the scaffolds, ibuprofen, the release rate of ibuprofen could be tuned by the concentration of g-HAp nanoparticles. Similarly, porous poly(L-lactic

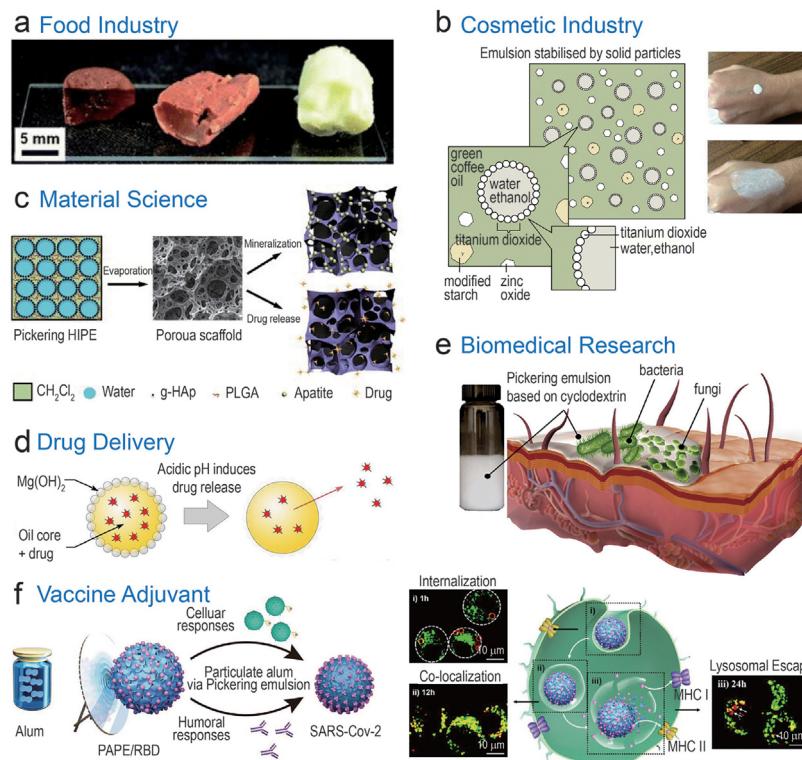


Fig. 7. Applications of Pickering emulsions in food industry, cosmetic industry, material science, drug delivery, biomedical research and vaccine adjuvant. (a) Images of dark (left), milk (middle) and white (right) chocolates prepared using Pickering emulsions of cranberry juice in cocoa butter (Skelhorn et al., 2012). (b) Creams for UV protection prepared by particle-stabilized water-in-oil Pickering emulsions (Marto et al., 2016). (c) Porous scaffolds prepared using Pickering emulsions as templates for drug delivery (Hu, Gu et al., 2014). (d) pH-triggered release of drugs encapsulated in Mg(OH)_2 -nanoparticle-stabilized Pickering emulsions (Sy et al., 2018). (e) Pickering emulsions based on cyclodextrins for sustained release of antifungal econazole derivatives (Leclercq & Nardello-Rataj, 2016). (f) Particulate alum via Pickering emulsion (PAPE) as an enhanced COVID-19 vaccine adjuvant. PAPE stimulates the cellular uptake and cross-presentation of antigens for enhanced humoral and cellular responses. RBD and lysosomes are labeled by Cy5 (red) and Lysotracker Green TM DND-99 (green), respectively (Peng, Cao et al., 2020). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

acid) (PLLA) scaffolds are fabricated by solvent evaporation (Hu, Zou, Chen, Tong, & Wang, 2014).

Drug delivery

Pickering emulsions are stabilized by particles at the water/oil interface and the particle layer at the interface is much thicker than the molecular layer in emulsions stabilized by molecular surfactants, resulting in better sustained release for drug delivery. Therefore, active substances could be encapsulated in Pickering emulsions to control their release kinetics and improve their bioavailability (Xia et al., 2018; Casamonti et al., 2019; Wu, Yang, Li, Feng, & Weitz, 2020).

Hydrophobic drugs could be encapsulated in Mg(OH)_2 nanoparticle-stabilized oil-in-water Pickering nanoemulsions, as shown in Fig. 7(d) (Sy et al., 2018). Since Mg(OH)_2 nanoparticles could be dissolved in acidic media, drugs could be released more easily from the Pickering emulsions under acidic condition, showing a pH-dependent release for drug delivery. Various particles, including silica nanoparticles (Tikekar, Pan, & Nitin, 2013), cellulose nanocrystals (Low et al., 2019), chitosan nanoparticles (Shah et al., 2016), protein nanogels (Araiza-Calahorra & Sarkar, 2019) and starch granules (Marefati, Bertrand, Sjoo, Dejmek, & Rayner, 2017), have been used as stabilizers in Pickering emulsions for drug delivery.

While oil-in-water Pickering emulsions are suitable delivery vehicles for hydrophobic drugs, water-in-oil Pickering emulsions could be used to deliver hydrophilic drugs. For example, a water-soluble chemotherapeutic drug for liver tumors, oxaliplatin, is

encapsulated in water-in-oil Pickering emulsions stabilized by biodegradable polylactic-co-glycolic acid (PLGA) nanoparticles (Deschamps et al., 2018). While oxaliplatin encapsulated in molecular surfactant-stabilized emulsions is almost completely released within 24 h, the total amount of oxaliplatin released from colloidal surfactant-stabilized Pickering emulsions after one month is only about 72%.

Biomedical research

Pickering emulsions are also widely applied in biomedical research (Song et al., 2019; Yang, Dong et al., 2020; Wu et al., 2021). Pickering emulsions without molecular surfactants have a high skin permeability, a high skin penetration depth and thus a strong adsorption capacity (Frelichowska, Bolzinger, Valour, et al., 2009); drugs loaded in Pickering emulsions can quickly pass through the corneum and then enter the dermis and subcutaneous tissues, preventing the skin from further infection and promoting its recovery ((Frelichowska, Bolzinger, Pelletier, Valour, & Chevalier, 2009)). For example, biocompatible cyclodextrins are used as emulsion stabilizers to formulate bactericidal Pickering emulsions containing econazole nitrate for topical applications. The antifungal and antibacterial tests show that the formulation is able to inhibit fungus and bacterial growth, as shown in Fig. 7(e) (Leclercq & Nardello-Rataj, 2016). In addition to cyclodextrin, silica (Frelichowska, Bolzinger, Pelletier et al., 2009; Salerno et al., 2016) and chitosan particles (Asfour, Elmotasem, Mostafa, & Salama, 2017) have also been explored as emulsion stabilizers for topical applications.

Vaccine adjuvant

Recent outbreak of COVID-19 is a global challenge. Squalene-in-water Pickering emulsions stabilized by alum microgels are developed as an enhanced COVID-19 vaccine adjuvant, as shown in Fig. 7(f) (Peng, Cao et al., 2020). Particulate alum via Pickering emulsion (PAPE) could stimulate the cellular uptake and cross-presentation of antigens for enhanced humoral and cellular responses, offering potential insights for the development of a safe and efficient COVID-19 vaccine adjuvant. During the initial stage, PAPE is co-internalized and transported through early endosomes. After 12 h of co-incubation, the cargo is concentrated within the endosomes. During this process, PAPE, which contains surface-packed alum, experiences enhanced protonation within the acidic endosomes, which might stimulate the rapid inflow of H⁺ and boost the rupture of the lysosomes, releasing the antigens into the cytoplasm for potent cellular immune responses.

Conclusion

Solid particles adsorb strongly at the water/oil interface and could perform as colloidal surfactants for the stabilization of Pickering emulsions. Due to the diverse morphologies, tunable properties and designable functions of colloidal surfactants, Pickering emulsions have high resistance to coalescence, long-term stability, good biocompatibility and tunable properties, continuously expanding their applications in scientific researches and industrial applications.

In this paper, we provide a comprehensive review on Pickering emulsion systems. Three main aspects are covered: (i) Influences of particle properties on Pickering Emulsions, including particle amphiphilicity, concentration, size and shape; (ii) Preparation of amphiphilic Janus particles, including selective surface modification, emulsion templates by microfluidics, self-assembly of block copolymer and phase separation; (iii) Applications of Pickering emulsions in food industry, cosmetic industry, material science, drug delivery, biomedical research and vaccine adjuvant.

With the increasing interest in Pickering emulsions, the search for new biocompatible colloidal surfactants as effective stabilizers for Pickering emulsions is still a challenge. Innovation of new technologies for the high-throughput preparation of colloidal surfactants using a versatile and green method is also required to meet the requirements of industrial applications. The applications of Pickering emulsions in the fields related to human health and medical therapy need to be further explored and will become more and more important in the future.

Conflict of interest

All authors declare that no conflict of interest exists.

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References

- Adams, F., Walstra, P., Brooks, B., Richmond, H., Zerfa, M., Bibette, J., et al. (2007). *Modern aspects of emulsion science*. Royal Society of Chemistry.
- Araiza-Calahorra, A., & Sarkar, A. (2019). Pickering emulsion stabilized by protein nanogel particles for delivery of curcumin: Effects of pH and ionic strength on curcumin retention. *Food Structure*, 21, Article 100113.
- Ardity, S., Whitby, C. P., Binks, B. P., Schmitt, V., & Leal-Calderon, F. (2003). Some general features of limited coalescence in solid-stabilized emulsions. *European Physical Journal E*, 11, 273–281.
- Asfour, M. H., Elmotasem, H., Mostafa, D. M., & Salama, A. A. A. (2017). Chitosan based Pickering emulsion as promising approach for topical application of rutin in a solubilized form intended for wound healing: In vitro and in vivo study. *International Journal of Pharmaceutics*, 534, 325–338.
- Ashby, N. P., & Binks, B. P. (2000). Pickering emulsions stabilised by Laponite clay particles. *Physical Chemistry Chemical Physics*, 2, 5640–5646.
- Aveyard, R., Binks, B. P., & Clint, J. H. (2003). Emulsions stabilised solely by colloidal particles. *Advances in Colloid and Interface Science*, 100, 503–546.
- Binks, B. P. (2002). Particles as surfactants – Similarities and differences. *Current Opinion in Colloid & Interface Science*, 7, 21–41.
- Binks, B. P., & Fletcher, P. D. I. (2001). Particles adsorbed at the oil-water interface: A theoretical comparison between spheres of uniform wettability and "Janus" particles. *Langmuir*, 17, 4708–4710.
- Binks, B. P., & Lumsdon, S. O. (2001). Pickering emulsions stabilized by monodisperse latex particles: Effects of particle size. *Langmuir*, 17, 4540–4547.
- Binks, B. P., & Lumsdon, S. O. (2000a). Influence of particle wettability on the type and stability of surfactant-free emulsions. *Langmuir*, 16, 8622–8631.
- Binks, B. P., & Lumsdon, S. O. (2000b). Transitional phase inversion of solid-stabilized emulsions using particle mixtures. *Langmuir*, 16, 3748–3756.
- Binks, B. P., & Whitby, C. P. (2004). Silica particle-stabilized emulsions of silicone oil and water: Aspects of emulsification. *Langmuir*, 20, 1130–1137.
- Binks, B. P., & Whitby, C. P. (2005). Nanoparticle silica-stabilised oil-in-water emulsions: Improving emulsion stability. *Colloids and Surfaces A—Physicochemical and Engineering Aspects*, 253, 105–115.
- Binks, B. P., Philip, J., & Rodrigues, J. A. (2005). Inversion of silica-stabilized emulsions induced by particle concentration. *Langmuir*, 21, 3296–3302.
- Borwankar, R. P., & Wasan, D. T. (1988). Equilibrium and dynamics of adsorption of surfactants at fluid-fluid interfaces. *Chemical Engineering Science*, 43, 1323–1337.
- Briggs, N., Raman, A. K. Y., Barrett, L., Brown, C., Li, B., Leavitt, D., et al. (2018). Stable pickering emulsions using multi-walled carbon nanotubes of varying wettability. *Colloids and Surfaces A—Physicochemical and Engineering Aspects*, 537, 227–235.
- Casamonti, M., Risaliti, L., Vanti, G., Piazzini, V., Bergonzi, M. C., & Bilia, A. R. (2019). Andrographolide loaded in micro-and nano-formulations: Improved bioavailability, target-tissue distribution, and efficacy of the "king of bitters". *Engineering*, 5, 69–75.
- Chen, D., Amstad, E., Zhao, C. X., Cai, L. H., Fan, J., Chen, Q. S., et al. (2017). Biocompatible amphiphilic hydrogel-solid dimer particles as colloidal surfactants. *ACS Nano*, 11, 11978–11985.
- Chen, Q. H., Zheng, J., Xu, Y. T., Yin, S. W., Liu, F., & Tang, C. H. (2018). Surface modification improves fabrication of pickering high internal phase emulsions stabilized by cellulose nanocrystals. *Food Hydrocolloids*, 75, 125–130.
- Chen, W., Liu, X., Liu, Y., Bang, Y., & Kim, H. I. (2011). Preparation of O/W Pickering emulsion with oxygen plasma treated carbon nanotubes as surfactants. *Journal of Industrial and Engineering Chemistry*, 17, 455–460.
- Chesters, A. K. (1991). The modeling of coalescence processes in fluid liquid dispersions – A review of current understanding. *Chemical Engineering Research & Design*, 69, 259–270.
- Chivero, P., Gohtani, S., Yoshii, H., & Nakamura, A. (2016). Assessment of soy soluble polysaccharide, gum arabic and OSA-Starch as emulsifiers for mayonnaise-like emulsions. *LWT—Food Science and Technology*, 69, 59–66.
- David-Birman, T., Mackie, A., & Lesmes, U. (2013). Impact of dietary fibers on the properties and proteolytic digestibility of lactoferrin nano-particles. *Food Hydrocolloids*, 31, 33–41.
- de Folter, J. W. J., van Ruijven, M. W. M., & Velikov, K. P. (2012). Oil-in-water Pickering emulsions stabilized by colloidal particles from the water-insoluble protein zein. *Soft Matter*, 8, 6807–6815.
- Dendukuri, D., Hatton, T. A., & Doyle, P. S. (2007). Synthesis and self-assembly of amphiphilic polymeric microparticles. *Langmuir*, 23, 4669–4674.
- Dendukuri, D., Pregibon, D. C., Collins, J., Hatton, T. A., & Doyle, P. S. (2006). Continuous-flow lithography for high-throughput microparticle synthesis. *Nature Materials*, 5, 365–369.
- Deng, Y. W., Chen, H., Tao, X. F., Treput, S., Ling, J., & Li, M. H. (2020). Synthesis and self-assembly of poly(ethylene glycol)-block-poly(N-3-(methylthio)propyl glycine) and their oxidation-sensitive polymersomes. *Chinese Chemical Letters*, 31, 1931–1935.
- Deschamps, F., Harris, K. R., Moine, L., Li, W. G., Tselikas, L., Isoardo, T., et al. (2018). Pickering-emulsion for liver trans-arterial chemo-embolization with oxaliplatin. *Cardiovascular and Interventional Radiology*, 41, 781–788.
- Einstein, A. (1905). On the motion of small particles suspended in liquids at rest required by the molecular-kinetic theory of heat. *Annalen der physik*, 17, 549–560.
- Ekanem, E. E., Zhang, Z. L., & Vladislavljevic, G. T. (2017). Facile production of biodegradable bipolymer patchy and patchy Janus particles with controlled morphology by microfluidic routes. *Langmuir*, 33, 8476–8482.
- Evans, E., & Needham, D. (1987). Physical-properties of surfactant bilayer-membranes – Thermal transitions, elasticity, rigidity, cohesion, and colloidal interactions. *Journal of Physical Chemistry*, 91, 4219–4228.

- Frasch-Melnik, S., Norton, I. T., & Spyropoulos, F. (2010). Fat-crystal stabilised w/o emulsions for controlled salt release. *Journal of Food Engineering*, 98, 437–442.
- Frelichowska, J., Bolzinger, M. A., Pelletier, J., Valour, J. P., & Chevalier, Y. (2009). Topical delivery of lipophilic drugs from o/w Pickering emulsions. *International Journal of Pharmaceutics*, 371, 56–63.
- Frelichowska, J., Bolzinger, M. A., Valour, J. P., Mouaziz, H., Pelletier, J., & Chevalier, Y. (2009). Pickering w/o emulsions: Drug release and topical delivery. *International Journal of Pharmaceutics*, 368, 7–15.
- Gao, Z.-M., Yang, X.-Q., Wu, N.-N., Wang, L.-J., Wang, J.-M., Guo, J., et al. (2014). Protein-based Pickering emulsion and oil gel prepared by complexes of zein colloidal particles and stearate. *Journal of Agricultural and Food Chemistry*, 62, 2672–2678.
- Ge, X. H., Huang, J. P., Xu, J. H., Chen, J., & Luo, G. S. (2016). Water-oil Janus emulsions: Microfluidic synthesis and morphology design. *Soft Matter*, 12, 3425–3430.
- Griffith, C., & Daigle, H. (2019). Destabilizing Pickering emulsions using fumed silica particles with different wettabilities. *Journal of Colloid and Interface Science*, 547, 117–126.
- Hao, Y., Liu, Y., Yang, R., Zhang, X., Liu, J., & Yang, H. (2018). A pH-responsive TiO₂-based Pickering emulsion system for in situ catalyst recycling. *Chinese Chemical Letters*, 29, 778–782.
- He, X. D., Ge, X. W., Liu, H. R., Zhou, H. X., & Zhang, Z. C. (2007). Self-assembly of latex particles at droplet interface to prepare monodisperse emulsion droplets. *Colloids and Surfaces A—Physicochemical and Engineering Aspects*, 301, 80–84.
- He, J., Zhang, Q., Gupta, S., Emrick, T., Russell, T. R., & Thiagarajan, P. (2007). Drying droplets: A window into the behavior of nanorods at interfaces. *Small*, 3, 1214–1217.
- Ho, C. C., Chen, W. S., Shie, T. Y., Lin, J. N., & Kuo, C. (2008). Novel fabrication of Janus particles from the surfaces of electrospun polymer fibers. *Langmuir*, 24, 5663–5666.
- Hong, L., Jiang, S., & Granick, S. (2006). Simple method to produce Janus colloidal particles in large quantity. *Langmuir*, 22, 9495–9499.
- Hu, Y., Gu, X., Yang, Y., Huang, J., Hu, M., Chen, W., et al. (2014). Facile fabrication of poly (l-lactic acid)-grafted hydroxyapatite/poly (lactic-co-glycolic acid) scaffolds by pickering high internal phase emulsion templates. *ACS Applied Materials & Interfaces*, 6, 17166–17175.
- Hu, Y., Zou, S., Chen, W., Tong, Z., & Wang, C. (2014). Mineralization and drug release of hydroxyapatite/poly (l-lactic acid) nanocomposite scaffolds prepared by Pickering emulsion templating. *Colloids and Surfaces B: Biointerfaces*, 122, 559–565.
- Ikem, V. O., Menner, A., Horozov, T. S., & Bismarck, A. (2010). Highly permeable macroporous polymers synthesized from pickering medium and high internal phase emulsion templates. *Advanced Materials*, 22, 3588–3592.
- Juarez, J. A., & Whitby, C. P. (2012). Oil-in-water Pickering emulsion destabilisation at low particle concentrations. *Journal of Colloid and Interface Science*, 368, 319–325.
- Kaewsaneha, C., Bitar, A., Tangboriboonrat, P., Polpanich, D., & Elaissari, A. (2014). Fluorescent-magnetic Janus particles prepared via seed emulsion polymerization. *Journal of Colloid and Interface Science*, 424, 98–103.
- Kalashnikova, I., Bizot, H., Bertoncini, P., Cathala, B., & Capron, I. (2013). Cellulosic nanorods of various aspect ratios for oil in water Pickering emulsions. *Soft Matter*, 9, 952–959.
- Kalashnikova, I., Bizot, H., Cathala, B., & Capron, I. (2011). New Pickering emulsions stabilized by bacterial cellulose nanocrystals. *Langmuir*, 27, 7471–7479.
- Kent, P., Aldous, G., & Blake, M. (2010). Titanium dioxide and zinc oxide nanoparticles in sunscreen formulations: A study of the post production particle size distribution of particles in a range of commercial emulsion variants. *Australasian Journal of Dermatology*, 51(1), A31.
- Kim, I., Worthen, A. J., Johnston, K. P., Dicarlo, D. A., & Huh, C. (2016). Size-dependent properties of silica nanoparticles for Pickering stabilization of emulsions and foams. *Journal of Nanoparticle Research*, 18, 82.
- Kim, J. W., Larsen, R. J., & Weitz, D. A. (2006). Synthesis of nonspherical colloidal particles with anisotropic properties. *Journal of the American Chemical Society*, 128, 14374–14377.
- Kong, L. L., Chen, R., Wang, X. Z., Zhao, C. X., Chen, Q. S., Hai, M. T., et al. (2019). Controlled co-precipitation of biocompatible colorant-loaded nanoparticles by microfluidics for natural color drinks. *Lab on a Chip*, 19, 2089–2095.
- Kong, L. L., Jin, X. Y., Hu, D. P., Feng, L. Y., Chen, D., & Li, H. Y. (2019). Functional delivery vehicle of organic nanoparticles in inorganic crystals. *Chinese Chemical Letters*, 30, 2351–2354.
- Kralchevsky, P., Ivanov, I., Ananthapadmanabhan, K., & Lips, A. (2005). On the thermodynamics of particle-stabilized emulsions: Curvature effects and catastrophic phase inversion. *Langmuir*, 21, 50–63.
- Leclercq, L., & Nardello-Rataj, V. (2016). Pickering emulsions based on cyclodextrins: A smart solution for antifungal azole derivatives topical delivery. *European Journal of Pharmaceutical Sciences*, 82, 126–137.
- Liang, H. N., & Tang, C. H. (2014). Pea protein exhibits a novel Pickering stabilization for oil-in-water emulsions at pH 3.0. *LWT—Food Science and Technology*, 58, 463–469.
- Lin, K. Y. A., Yang, H. T., Petit, C., & Lee, W. D. (2015). Magnetically controllable Pickering emulsion prepared by a reduced graphene oxide-iron oxide composite. *Journal of Colloid and Interface Science*, 438, 296–305.
- Lin, Y., Skaff, H., Emrick, T., Dinsmore, A. D., & Russell, T. P. (2003). Nanoparticle assembly and transport at liquid-liquid interfaces. *Science*, 299, 226–229.
- Lin, Z. Y., Zhang, Z., Li, Y. M., & Deng, Y. L. (2016). Magnetic nano-Fe₃O₄ stabilized Pickering emulsion liquid membrane for selective extraction and separation. *Chemical Engineering Journal*, 288, 305–311.
- Liu, F., & Tang, C. H. (2013). Soy protein nanoparticle aggregates as pickering stabilizers for oil-in-water emulsions. *Journal of Agricultural and Food Chemistry*, 61, 8888–8898.
- Liu, B., Wei, W., Qu, X. Z., & Yang, Z. H. (2008). Janus colloids formed by biphasic grafting at a Pickering emulsion interface. *Angewandte Chemie—International Edition*, 47, 3973–3975.
- Liu, B., Zhang, C. L., Liu, J. G., Qu, X. Z., & Yang, Z. Z. (2009). Janus non-spherical colloids by asymmetric wet-etching. *Chemical Communications*, 2009(26), 3871–3873.
- Low, L. E., Tan, L. T. H., Goh, B. H., Tey, B. T., Ong, B. H., & Tang, S. Y. (2019). Magnetic cellulose nanocrystal stabilized Pickering emulsions for enhanced bioactive release and human colon cancer therapy. *International Journal of Biological Macromolecules*, 127, 76–84.
- Madivala, B., Vandebril, S., Fransaer, J., & Vermant, J. (2009). Exploiting particle shape in solid stabilized emulsions. *Soft Matter*, 5, 1717–1727.
- Marefati, A., Bertrand, M., Sjoo, M., Dejmek, P., & Rayner, M. (2017). Storage and digestion stability of encapsulated curcumin in emulsions based on starch granule Pickering stabilization. *Food Hydrocolloids*, 63, 309–320.
- Marto, J., Gouveia, L. F., Goncalves, L., Chiari-Andreou, B. G., Isaac, V., Pinto, P., et al. (2016). Design of novel starch-based Pickering emulsions as platforms for skin photoprotection. *Journal of Photochemistry and Photobiology B—Biology*, 162, 56–64.
- McConnell, M. D., Kraeutler, M. J., Yang, S., & Composto, R. J. (2010). Patchy and multiregion Janus particles with tunable optical properties. *Nano Letters*, 10, 603–609.
- McCoy, T. M., Pottage, M. J., & Tabor, R. F. (2014). Graphene oxide-stabilized oil-in-Water emulsions: pH-Controlled dispersion and flocculation. *Journal of Physical Chemistry C*, 118, 4529–4535.
- Menner, A., Verdejo, R., Shaffer, M., & Bismarck, A. (2007). Particle-stabilized surfactant-free medium internal phase emulsions as templates for porous nanocomposite materials: Poly-pickering-foams. *Langmuir*, 23, 2398–2403.
- Na, X., Zhou, W., Li, T., Hong, D., Li, J., & Ma, G. (2019). Preparation of double-emulsion-templated microspheres with controllable porous structures by premix membrane emulsification. *Particuology*, 44, 22–27.
- Nisisako, T., Torii, T., Takahashi, T., & Takizawa, Y. (2006). Synthesis of monodisperse bicolored janus particles with electrical anisotropy using a microfluidic co-flow system. *Advanced Materials*, 18, 1152–1156.
- Ortiz, D. G., Pochat-Bohatier, C., Cambedouzou, J., Bechelany, M., & Miele, P. (2020). Current trends in pickering emulsions: Particle morphology and applications. *Engineering*, 6, 468–482.
- Passas-Lagos, E., & Schuth, F. (2015). Amphiphilic pickering emulsifiers based on mushroom-type Janus particles. *Langmuir*, 31, 7749–7757.
- Peng, S., Cao, F., Xia, Y., Gao, X. D., Dai, L., Yan, J., et al. (2020). COVID-19 vaccines: Particulate alum via pickering emulsion for an enhanced COVID-19 vaccine adjuvant (Adv. Mater. 40/2020). *Advanced Materials*, 32, Article 2070303.
- Peng, H.-Y., Wang, W., Xie, R., Ju, X.-J., Liu, Z., Faraj, Y., et al. (2020). Mesoscale regulation of droplet templates to tailor microparticle structures and functions. *Particuology*, 48, 74–87.
- Pickering, S. U. (1907). Emulsions. *Journal of the Chemical Society*, 91, 2001–2021.
- Pieranski, P. (1980). Two-dimensional interfacial colloidal crystals. *Physical Review Letters*, 45, 569–572.
- Prince, L. (2012). *Microemulsions theory and practice*. Elsevier.
- Qin, H., Zhang, H., Zhou, X. T., Gu, D. F., Li, L. X., & Kan, C. Y. (2020). Preparation and reducing-responsive property of a novel functional polyurethane nanoemulsion. *Chinese Chemical Letters*, 31, 292–294.
- Ramsden, W. (1903). Separation of solids in the surface-layers of solutions and "suspensions" (observations on surface-membranes, bubbles, emulsions, and mechanical coagulation). Preliminary account. *Proceedings of the Royal Society of London*, 72, 156–164.
- Rayner, M., Sjoo, M., Timgren, A., & Dejmek, P. (2012). Quinoa starch granules as stabilizing particles for production of Pickering emulsions. *Faraday Discussions*, 158, 139–155.
- Ren, Y., Zhang, Q., Yang, N., Xu, J., Liu, J. L., Yang, R. X., et al. (2019). Molecular dynamics simulations of surfactant adsorption at oil/water interface under shear flow. *Particuology*, 44, 36–43.
- Rosen, M. J., & Kunjappu, J. T. (2012). *Surfactants and interfacial phenomena*. John Wiley & Sons.
- Rousseau, D. (2000). Fat crystals and emulsion stability — A review. *Food Research International*, 33, 3–14.
- Rousseau, D. (2013). Trends in structuring edible emulsions with Pickering fat crystals. *Current Opinion in Colloid & Interface Science*, 18, 283–291.
- Saien, J., & Fadaei, V. (2018). The study of interfacial tension of kerosene-water under influence of CTAB surfactant and different size silica nanoparticles. *Journal of Molecular Liquids*, 255, 439–446.
- Salerno, A., Bolzinger, M. A., Rolland, P., Chevalier, Y., Josse, D., & Briancon, S. (2016). Pickering emulsions for skin decontamination. *Toxicology in Vitro*, 34, 45–54.
- Schröder, J. H., Doroshenko, M., Pirner, D., Mauer, M. E. J., Forster, B., Boyko, V., et al. (2016). Interfacial stabilization by soft Janus nanoparticles. *Polymer*, 106, 208–217.
- Shah, B. R., Li, Y., Jin, W. P., An, Y. P., He, L., Li, Z. S., et al. (2016). Preparation and optimization of Pickering emulsion stabilized by chitosan-tripolyphosphate nanoparticles for curcumin encapsulation. *Food Hydrocolloids*, 52, 369–377.

- Shepherd, R. F., Conrad, J. C., Rhodes, S. K., Link, D. R., Marquez, M., Weitz, D. A., et al. (2006). Microfluidic assembly of homogeneous and janus colloid-filled hydrogel granules. *Langmuir*, *22*, 8618–8622.
- Shi, P., Yan, X. X., Wang, X. Z., Feng, L. Y., & Chen, D. (2020). One-step fabrication of biocompatible oil-core microcapsules with controlled release. *CIESC Journal*, *72*, 619–627.
- Shimoni, G., Levi, C. S., Tal, S. L., & Lesmes, U. (2013). Emulsions stabilization by lactoferrin nano-particles under in vitro digestion conditions. *Food Hydrocolloids*, *33*, 264–272.
- Simovic, S., Ghouchi-Eskandar, N., & Prestidge, C. A. (2011). Pickering emulsions for dermal delivery. *Journal of Drug Delivery Science and Technology*, *21*, 123–133.
- Skelhon, T. S., Grossiord, N., Morgan, A. R., & Bon, S. A. (2012). Quiescent water-in-oil Pickering emulsions as a route toward healthier fruit juice infused chocolate confectionary. *Journal of Materials Chemistry*, *22*, 19289–19295.
- Song, W., Das, M., Xu, Y., Si, X., Zhang, Y., Tang, Z., et al. (2019). Leveraging biomaterials for cancer immunotherapy: Targeting pattern recognition receptors. *Materials Today Nano*, *5*, Article 100029.
- Song, X. Y., Pei, Y. Q., Qiao, M. W., Ma, F. L., Ren, H. T., & Zhao, Q. Z. (2015). Preparation and characterizations of Pickering emulsions stabilized by hydrophobic starch particles. *Food Hydrocolloids*, *45*, 256–263.
- Steinhaus, A., Chakroun, R., Müllner, M., Nghiem, T.-L., Hildebrandt, M., & Gröschel, A. H. (2019). Confinement assembly of ABC triblock terpolymers for the high-yield synthesis of Janus nanorings. *ACS Nano*, *13*, 6269–6278.
- Steinhaus, A., Srivastva, D., Nikoubashman, A., & Gröschel, A. H. (2019). Janus nanostructures from ABC/B triblock terpolymer blends. *Polymers*, *11*, 1107.
- Sun, Z., Wu, B. H., Ren, Y. X., Wang, Z. Z., Zhao, C. X., Hai, M. T., et al. (2020). Diverse particle carriers prepared by co-precipitation and phase separation: Formation and applications. *ChemPlusChem*, *86*, 49–58.
- Sun, Z. Y., Yang, C. J., Eggersdorfer, M., Cui, J. C., Li, Y. W., Hai, M. T., et al. (2020). A general strategy for one-step fabrication of biocompatible microcapsules with controlled active release. *Chinese Chemical Letters*, *31*, 249–252.
- Sun, Z., Yang, C. J., Wang, F., Wu, B. H., Shao, B. Q., Li, Z. C., et al. (2020). Biocompatible and pH-responsive colloidal surfactants with tunable shape for controlled interfacial curvature. *Angewandte Chemie-International Edition*, *59*, 9365–9369.
- Sy, P. M., Anton, N., Idoux-Gillet, Y., Dieng, S. M., Messaddeq, N., Ennahar, S., et al. (2018). Pickering nano-emulsion as a nanocarrier for pH-triggered drug release. *International Journal of Pharmaceutics*, *549*, 299–305.
- Tanaka, T., Nakatsuru, R., Kagari, Y., Saito, N., & Okubo, M. (2008). Effect of molecular weight on the morphology of polystyrene/poly(methyl methacrylate) composite particles prepared by the solvent evaporation method. *Langmuir*, *24*, 12267–12271.
- Tang, J. T., Quinlan, P. J., & Tam, K. C. (2015). Stimuli-responsive Pickering emulsions: Recent advances and potential applications. *Soft Matter*, *11*, 3512–3529.
- Tikekar, R. V., Pan, Y., & Nitin, N. (2013). Fate of curcumin encapsulated in silica nanoparticle stabilized Pickering emulsion during storage and simulated digestion. *Food Research International*, *51*, 370–377.
- Timgren, A., Rayner, M., Sjoo, M., & Dejmek, P. (2011). Starch particles for food based Pickering emulsions. *11th International Congress on Engineering and Food (Icef11)*, *1*, 95–103.
- Voorhees, P. W. (1985). The theory of ostwald ripening. *Journal of Statistical Physics*, *38*, 231–252.
- Wang, K. L., Wang, G., & Lu, C. J. (2019). Particle contact angle at the oil-water interface: Effect of surface silanization. *Particuology*, *44*, 218–224.
- Wang, W., Zhang, M. J., Xie, R., Ju, X. J., Yang, C., Mou, C. L., et al. (2013). Hole-shell microparticles from controllably evolved double emulsions. *Angewandte Chemie-International Edition*, *52*, 8084–8087.
- Wang, X. Z., Sun, Z. Y., & Chen, D. (2020). Preparation of droplet suspension by microfluidic technology. *Modern Chemical Industry*, *40*, 70–79.
- Wei, Z. J., Wang, C. Y., Zou, S. W., Liu, H., & Tong, Z. (2012). Chitosan nanoparticles as particular emulsifier for preparation of novel pH-responsive Pickering emulsions and PLGA microcapsules. *Polymer*, *53*, 1229–1235.
- Wei, Z., Yu, Y., Rui, Y., & Wang, C. (2012). Alkaline lignin extracted from furfural residues for pH-responsive Pickering emulsions and their recyclable polymerization. *Green Chemistry*, *14*, 3230–3236.
- Wiley, R. M. (1954). Limited coalescence of oil droplets in coarse oil-in-water emulsions. *Journal of Colloid Science*, *9*, 427–437.
- Wu, B., Sun, Z., Wu, J., Ruan, J., Zhao, P., Liu, K., et al. (2021). Nanoparticle-stabilized oxygen microcapsules prepared by interfacial polymerization for enhanced oxygen delivery. *Angewandte Chemie International Edition*, *60*(17), 9284–9289.
- Wu, B., Yang, C., Li, B., Feng, L., & Weitz, D. A. (2020). Active encapsulation in biocompatible nanocapsules. *Small*, *16*, Article 2002716.
- Wu, J. D., Shi, M. X., Li, W., Zhao, L. H., Wang, Z., Yan, X. Z., et al. (2015). Pickering emulsions stabilized by whey protein nanoparticles prepared by thermal cross-linking. *Colloids and Surfaces B-Biointerfaces*, *127*, 96–104.
- Xia, Y., Wu, J., Wei, W., Du, Y., Wan, T., Ma, X., et al. (2018). Exploiting the pliability and lateral mobility of Pickering emulsion for enhanced vaccination. *Nature Materials*, *17*, 187–194.
- Xiao, J., Wang, X. A., Gonzalez, A. J. P., & Huang, Q. R. (2016). Kafirin nanoparticles-stabilized Pickering emulsions: Microstructure and rheological behavior. *Food Hydrocolloids*, *54*, 30–39.
- Yan, H., Zhao, B., Long, Y., Zheng, L. Q., Tung, C. H., & Song, K. (2015). New pickering emulsions stabilized by silica nanowires. *Colloids and Surfaces A—Physicochemical and Engineering Aspects*, *482*, 639–646.
- Yan, N. X., Gray, M. R., & Masliyah, J. H. (2001). On water-in-oil emulsions stabilized by fine solids. *Colloids and Surfaces A—Physicochemical and Engineering Aspects*, *193*, 97–107.
- Yang, F., Liu, S. Y., Xu, J., Lan, Q., Wei, F., & Sun, D. J. (2006). Pickering emulsions stabilized solely by layered double hydroxides particles: The effect of salt on emulsion formation and stability. *Journal of Colloid and Interface Science*, *302*, 159–169.
- Yang, H. Q., Fu, L. M., Wei, L. J., Liang, J. F., & Binks, B. P. (2015). Compartmentalization of incompatible reagents within Pickering emulsion droplets for one-pot cascade reactions. *Journal of the American Chemical Society*, *137*, 1362–1371.
- Yang, H. R., Zhang, H. X., Peng, J. X., Zhang, Y. Y., Du, G. Q., & Fang, Y. (2017). Smart magnetic ionic liquid-based Pickering emulsions stabilized by amphiphilic Fe₃O₄ nanoparticles: Highly efficient extraction systems for water purification. *Journal of Colloid and Interface Science*, *485*, 213–222.
- Yang, T., Liu, T. X., Li, X. T., & Tang, C. H. (2019). Novel nanoparticles from insoluble soybean polysaccharides of Okara as unique Pickering stabilizers for oil-in-water emulsions. *Food Hydrocolloids*, *94*, 255–267.
- Yang, J. L., Dong, Z. R., Liu, W. J., He, H. S., Fan, W. F., Lu, Y., et al. (2020). Discriminating against injectable fat emulsions with similar formulation based on water quenching fluorescent probe. *Chinese Chemical Letters*, *31*, 875–879.
- Yang, W., Xu, G., Shu, J., Wang, M., & Ge, X. (2020). Preparation and adsorption property of novel inverse-opal hierarchical porous N-doped carbon microspheres. *Chinese Chemical Letters*, *32*, 866–869.
- Yano, H., Fukui, A., Kajiwara, K., Kobayashi, I., Yoza, K., Satake, A., et al. (2017). Development of gluten-free rice bread: Pickering stabilization as a possible batter-swelling mechanism. *LWT—Food Science and Technology*, *79*, 632–639.
- Ye, F., Miao, M., Jiang, B., Campanella, O. H., Jin, Z. Y., & Zhang, T. (2017). Elucidation of stabilizing oil-in-water Pickering emulsion with different modified maize starch-based nanoparticles. *Food Chemistry*, *229*, 152–158.
- Yu, X. T., Sun, Y. J., Liang, F. X., Jiang, B. Y., & Yang, Z. Z. (2019). Triblock Janus particles by seeded emulsion polymerization. *Macromolecules*, *52*, 96–102.
- Zhang, C. L., Liu, B., Tang, C., Liu, J. G., Qu, X. Z., Li, J. L., et al. (2010). Large scale synthesis of Janus submicron sized colloids by wet etching anisotropic ones. *Chemical Communications*, *46*, 4610–4612.
- Zhang, Q., Bai, R. X., Guo, T., & Meng, T. (2015). Switchable pickering emulsions stabilized by awakened TiO₂ nanoparticle emulsifiers using UV/Dark actuation. *ACS Applied Materials & Interfaces*, *7*, 18240–18246.
- Zhao, X. Y., Yu, G. B., Li, J. C., Feng, Y. H., Zhang, L., Peng, Y., et al. (2018). Eco-friendly pickering emulsion stabilized by silica nanoparticles dispersed with high-molecular-weight amphiphilic alginate derivatives. *ACS Sustainable Chemistry & Engineering*, *6*, 4105–4114.
- Zhou, J., Qiao, X. Y., Binks, B. P., Sun, K., Bai, M. W., Li, Y. L., et al. (2011). Magnetic pickering emulsions stabilized by Fe₃O₄ nanoparticles. *Langmuir*, *27*, 3308–3316.
- Zhu, Y., Lu, L. H., Gao, J., Cui, Z. G., & Binks, B. P. (2013). Effect of trace impurities in triglyceride oils on phase inversion of Pickering emulsions stabilized by CaCO₃ nanoparticles. *Colloids and Surfaces A—Physicochemical and Engineering Aspects*, *417*, 126–132.
- Zoppe, J. O., Venditti, R. A., & Rojas, O. J. (2012). Pickering emulsions stabilized by cellulose nanocrystals grafted with thermo-responsive polymer brushes. *Journal of Colloid and Interface Science*, *369*, 202–209.