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Sustainable food-grade Pickering emulsions stabilized by plant-based particles

Anwesha Sarkar* and Eric Dickinson

Food Colloids and Bioprocessing Group, School of Food Science and Nutrition,

University of Leeds, UK

*E-mail: A.Sarkar@leeds.ac.uk

Abstract

This review summarizes the major advances that have occurred over the last 5 years in the use of plant-based colloidal particles for the stabilization of oil-in-water and water-in-oil emulsions. We consider the characteristics of polysaccharide-based particles, protein-based particles, and organic crystals (flavonoids) with respect to their particle size, degree of aggregation, anisotropy, hydrophobicity, and electrical charge. Specific effects of processing on particle functionality are identified. Special emphasis is directed towards the issue of correctly defining the stabilization mechanism in order to distinguish those cases where the particles are acting as genuine Pickering stabilizers, through direct monolayer adsorption at the liquid–liquid interface, from those cases where the particles are predominantly behaving as 'structuring agents' between droplets without necessarily adsorbing at the interface, *e.g.* in many so-called high internal phase Pickering emulsions (HIPPEs). Finally, we consider the outlook for future research activity in the field of Pickering emulsions for food applications.

Keywords: Pickering emulsion; microgel; cellulose; prolamin; flavonoid; particle shape

Introduction

Dispersions of liquid emulsion droplets or gas bubbles stabilized by colloidal particles (*via* the Pickering stabilization mechanism) are highly resilient towards coalescence and Ostwald ripening as compared with conventional dispersions stabilized by surfactants or polymers. This behaviour is attributed to the large detachment energy (ΔG_d) associated with dislodging spherical colloidal particles from the fluid–fluid interface [1–4] once they have become located there:

$$\Delta G_{\mathrm{d,sphere}} = \gamma_{\alpha\beta}\pi r^2(1-|cos\,\theta|)^2 \qquad . \qquad (1)$$

In equation (1), r is the radius of the spherical colloidal particle, $\gamma_{\alpha\beta}$ is the surface free energy or fluid–fluid interfacial tension (*i.e.*, γ_ow for oil–water, γ_wo for water–oil, γ_ww for water–water, γ_aw for air–water, γ_ao for air–oil), and θ is the equilibrium three-phase contact angle reflecting the partial wetting of the particles by the two fluids. Noteworthy that equation (1) is only valid for spherical particles. Solving equation (1) for a typical spherical colloidal particle with a radius of $r \approx 300$ nm, even with a low wettability ($\theta \approx 30°$) and using $\gamma_\mathrm{ow} \approx 50$ mN m^{-1} for the interfacial tension, leads to a calculated value of $\Delta G_\mathrm{d} \approx 10^4\ k_\mathrm{B}T$ (where k_B is Boltzmann's constant and T is the absolute temperature). Moreover, for $\theta \approx 90°$, corresponding to the particle surface being equally wetted by both phases, each particle can be said to be irreversibly trapped at the fluid–fluid interface ($\Delta G_\mathrm{d} \approx 10^6\ k_\mathrm{B}T$) [1,2•]. This situation confers outstanding stability to the liquid droplets, in contrast to conventional emulsions, where individual low-molecular-weight surfactant species (with $\Delta G_\mathrm{d} < 10\ k_\mathrm{B}T$) tend to exchange rapidly and reversibly between the interface and the bulk phase(s) [5].

Due to their distinctive characteristics, particle-stabilized systems have for many years intrigued both experimental and theoretical colloid scientists [1,2•]. Originally the research domain was dominated by studies of inorganic particles, with silica particles the 'gold-standard' Pickering stabilizer [6], resulting in fundamental insights into the basic principles of Pickering emulsion stabilization. In more recent years, however, we have entered the 'neo-Pickering era' of colloid science [7•] as a consequence of a paradigm shift in emphasis from the limited realm of simple inorganic materials to a broad landscape embracing many different kinds of nanoparticles and microparticles of biological origin. In particular, due to an increasing global demand for sustainable materials, there has developed a strong impetus for the exploration and investigation of clean-label, natural, biopolymeric particles that are suitable for use in food, agrochemicals, personal care, and healthcare. In all these applications, ingredient biocompatibility is increasingly regarded as a non-negotiable attribute. From the perspective of a member of the food colloids community, one is therefore not surprised to observe the exponential growth of research output numbers in the area of food-grade Pickering emulsions [8–12].

In response to the rising demands of sustainability, and also the growing consumer interest in veganism, there is renewed enthusiasm for studying the functionality of different kinds of plant-based particles. In the case of plant structural proteins, it has to be said that many colloid scientists have traditionally been discouraged from studying them in model dispersed systems due to their poor aqueous solubility arising from the complex quaternary structure, and their strong tendency for self-aggregation and association with other metabolites such as polyphenols in the natural state [13,14]. On the other hand, the low level of solubility of plant proteins in both aqueous media and edible oils is now likely to be considered as a valued functional attribute by researchers working on Pickering systems. Included amongst the most popular classes of materials used for making plant-based Pickering emulsions are prolamine-based particles (especially zein [15]), soy protein particles/aggregates [16], globular proteins behaving as soft nanoparticles [17•], and thermo-sheared protein microgel particles/aggregates [13,18••]. In addition to protein particles, the list of plant-based Pickering stabilizers also includes insoluble polysaccharide particles possessing semi-crystalline structures over mesoscopic length scales (cellulose

[19], starch [20]), as well as some secondary metabolites in the form of organic crystals (flavonoids [21•]).

The present article focuses on the Pickering stabilization of oil-in-water (O/W) and water-in-water (W/O) emulsions. Some other types of Pickering dispersions such as aerated systems and water-in-water emulsions are considered to be beyond the scope of this article as they been recently reviewed elsewhere [7•,22–24]. The comprehensive survey of bio-derived particles by Lam and co-workers [25•] covering the relevant literature up until 2014 provides the main springboard for our current article, which is devoted to the most significant new work that has emerged over the last 5 years. We direct our attention here on how the effectiveness of the Pickering stabilization mechanism depends on particle size, shape, and wettability, and on how particle characteristics are affected by processing operations during and after the extraction of the biological material from its natural origin. Many of the plant-derived particles that are ubiquitous in nature are non-spherical. So we discuss the influence of shape anisotropy on the estimated desorption energy of these particles and hence on their expected effectiveness in emulsion stabilization. We also highlight the importance in mechanistic terms of distinguishing between studies of *fully adsorbing* plant-based particles, which can create stable liquid-like emulsions with classical Pickering stabilizing layers, and the large body of recent work involving bio-derived particles acting predominantly as *non-adsorbing* ‘structuring agents’, notably in the gel-like emulsified systems known as ‘high internal phase Pickering emulsions’ (HIPPEs). Finally, we mention a few scientific issues and technological challenges that need to be addressed in order to optimize the successful exploitation of plant-based Pickering stabilizers in the food and allied soft matter industries.

Properties of plant-based Pickering particles

Figure 1 shows images of various kinds of plant-based particles of different sizes (from hundreds of nanometres to a few micrometres), with variable extents of aggregation, and possessing diverse shapes (spherical, polygonal, rod-like, fibrils, with/without sharp facets). All of these particles have been used to make Pickering emulsions during the last 5 years.

It is evident from equation (1) that particle size plays a pivotal role in the Pickering stabilization mechanism: the detachment energy ΔG_d scales with r^2 in the case of spherical particles of radius r (**Figure 2a**). However, many plant-based particles are non-spherical (**Figure 1**). Hence the influence of particle shape on interfacial orientation and packing would seem likely to be important for understanding the properties of Pickering emulsions.

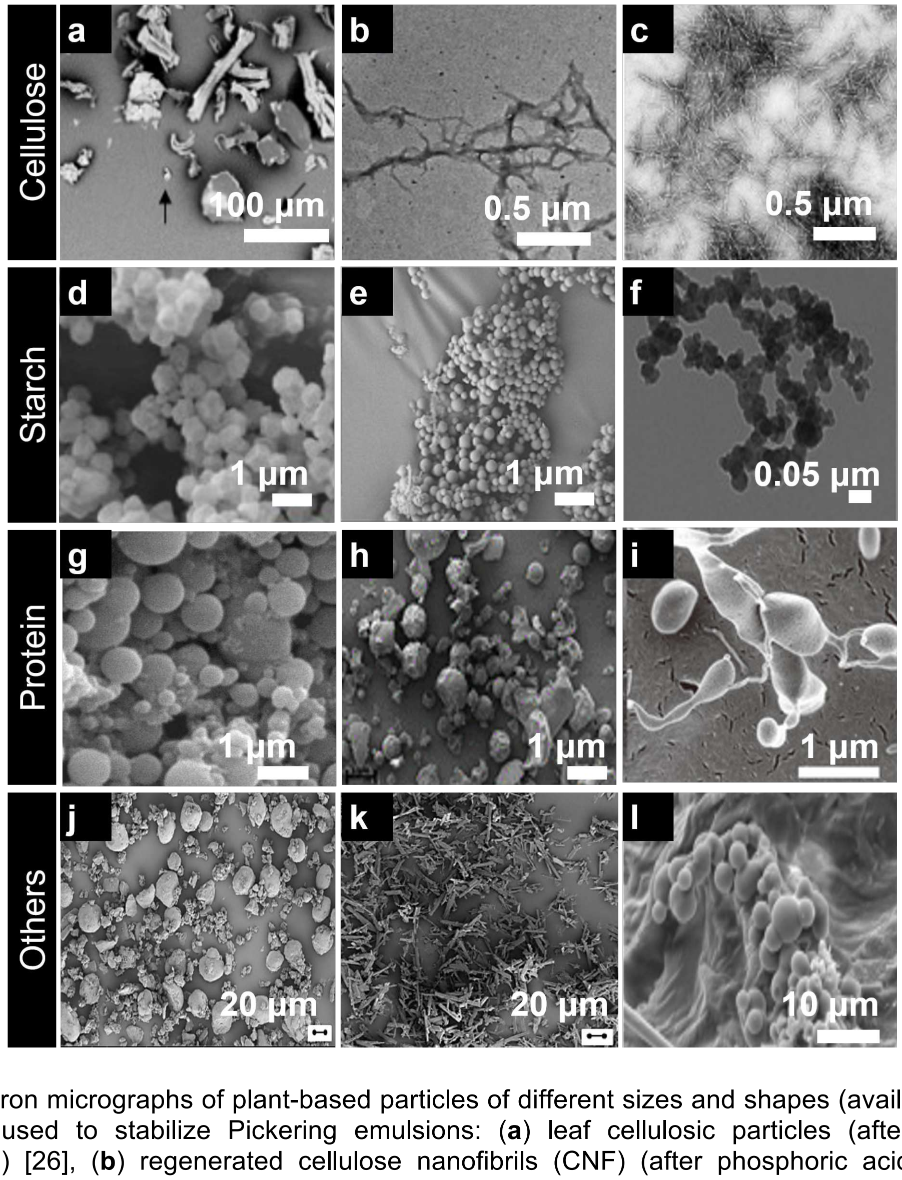

Figure 1. Electron micrographs of plant-based particles of different sizes and shapes (available from nature or processed) used to stabilize Pickering emulsions: (**a**) leaf cellulosic particles (after high pressure homogenization) [26], (**b**) regenerated cellulose nanofibrils (CNF) (after phosphoric acid treatment and homogenization) [27], (**c**) cellulose nanocrystals (CNC) modified with OSA [28•], (**d**) OSA-modified quinoa starch granules [29], (**e**) starch nanoparticles obtained by dissolution in DMSO followed by ethanol precipitation [30], (**f**) starch nanoparticles obtained by gelation and mechanical shearing followed by ethanol precipitation [31••,32], (**g**) zein particles after antisolvent precipitation with ethanol followed by ultrasonication [33], (**h**) quinoa protein nanoparticles obtained by ultrasonication [34], (**i**) peanut microgel particles (from homogenization of protein hydrogel obtained by transglutaminase crosslinking to create microgel particles followed by alkaline pH treatment) [66•], (**j**) curcumin crystals [21•], (**k**) quercetin crystals [21•], and (**l**) coffee

particles (after drying, ball-milling and hydrothermal processing) [36•]. (Reproduced with permissions from Elsevier (images **a–b, d–g**), American Chemical Society (image **h**), Wiley (image **i)** and MDPI Company (image **l**). Images **c**, **j** and **k** were produced at the University of Leeds).

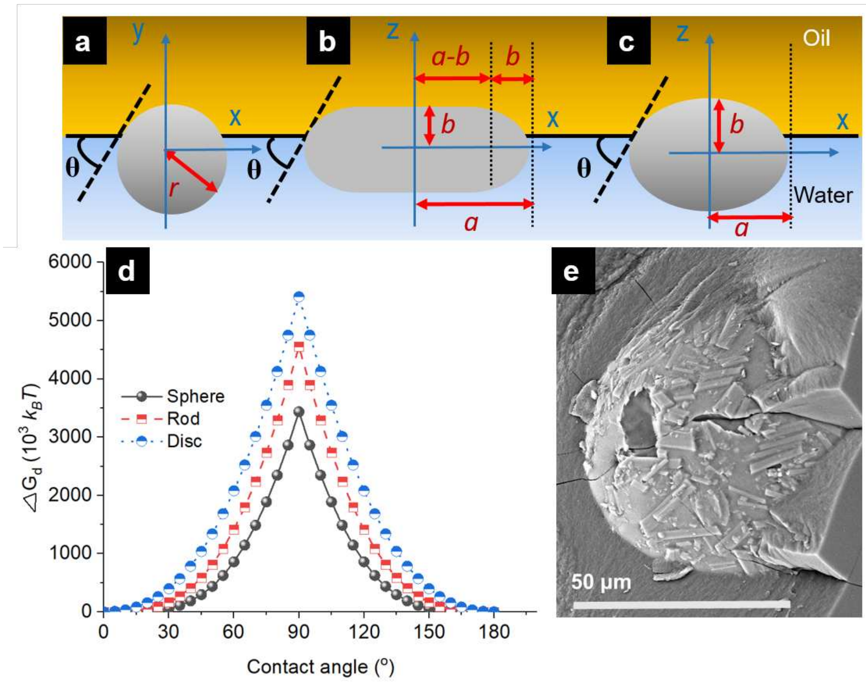

Figure 2. Cross sections of (**a**) a spherical particle, (**b**) a rod-like particle (with hemispherical ends) and (**c**) a rounded disc-like particle attached to the oil–water interface in a planar orientation with contact angle in the range 0 < θ < 90°. Here r is the sphere radius and a and b are long and short semi-axes of the rod-like and disc-like particles. (**d)** Calculated detachment energies of the particles, for constant particle volume, r = 300 nm, aspect ratio (a/b) = 2.5, and $\gamma_{ow} \approx 50$ mN m^{-1}. (**e**) Cryo-scanning electron micrograph, imaged at University of Leeds, showing the planar conformation of rod-shaped quercetin crystals at the surface of a water droplet in a W/O Pickering emulsion.

The value of ΔG_d for anisotropic particles is dependent on at least two characteristic length scales. For rod-shaped (**Figure 2b**) and disc-shaped particles (**Figure 2c**), the lengths of both the long and the short axes need to be taken into account. The detachment energy for rod-shaped particles with 0 ≤ θ ≤ 90° can be calculated from [2•]:

$$\Delta G_{\mathrm{d,rod,w}} = \gamma_{\mathrm{ow}}\pi b^2(1-\cos\theta)^2\left[1+\frac{4(a/b-1)(\sin\theta-\theta\cos\theta)}{\pi(1-\cos\theta)^2}\right] \quad . \qquad (2)$$

Here a and b are dimensions of long and short semi-axes, respectively. The parameter b can be expressed in terms of r and the aspect ratio (a/b) as $b = r[1+((3/2)\{(a/b)-1\}]^{-1/3}$ assuming that the particle volume is kept constant, *i.e.* set equal to that of the equivalent sphere. For a Pickering W/O emulsion with 90° ≤ θ ≤ 180° equation (2) is replaced by [2•]:

$$\Delta G_{\mathrm{d,rod,o}} = \Delta G_{\mathrm{d,rod,w}} + 4\gamma_{\mathrm{ow}}\pi b^2 \cos\theta \left(\frac{a}{b}\right) \quad . \tag{3}$$

For disc-shaped particles ΔG_{d} is given by equations (4) and (5) for $0 \le \theta \le 90°$ and $90° \le \theta \le 180°$, respectively [2•]:

$$\Delta G_{\mathrm{d,disc,w}} = \gamma_{\mathrm{ow}}\pi b^2 (1-\cos\theta)^2 \left[1 + \frac{\left({}^{a}/_{b}-1\right)^2}{1-\cos\theta} + \frac{2(a/b-1)(\sin\theta - \theta\cos\theta)}{(1-\cos\theta)^2}\right] \quad , \tag{4}$$

$$\Delta G_{\mathrm{d,disc,o}} = \Delta G_{\mathrm{d,disc,w}} + 2\gamma_{\mathrm{ow}}\pi b^2 \cos\theta \left[\left(\frac{a}{b}-1\right)^2 + \pi\left(\frac{a}{b}-1\right) + 2\right] \quad . \tag{5}$$

Again, under conditions of equivalent particle volume, the disc dimension *b* may be expressed in terms of *r* and the aspect ratio (*a*/*b*) as

$$b = r\left[\frac{3\left({}^{a}/_{b}-1\right)^2}{2} + \frac{3\pi\left({}^{a}/_{b}-1\right)}{4} + 1\right]^{-1/3} . \tag{6}$$

On comparing the cross-sectional areas at the interface for these three kinds of particles, we can observe that the inequality condition $\Delta G_{\mathrm{d,disc}} > \Delta G_{\mathrm{d,rod}} > \Delta G_{\mathrm{d,sphere}}$ is satisfied for any value of the contact angle lying between 0 and 180° (**Figure 2d**). This seems to suggest that anisotropic particles of plant origin, such as rod-shaped cellulose nanocrystals (CNC) [28•] (**Figure 1**), are able to generate even stronger forms of physical attachment to liquid interfaces than are the equivalent spherical entities.

The above equations (2–5) are valid for the planar orientation, *i.e.* the 'side-on' state with the major axis parallel to the oil–water interface [38]. The planar orientation is the most energetically favourable state for many, if not most, kinds of anisotropic particles [39] when solely the interfacial energy is taken into account. This predicted behaviour has been confirmed by experimental observations in our laboratory [21•] for rod-like polyphenol crystals (composed of quercetin) (**Figure 1**) exhibiting a side-on orientation at the curved water–oil interface of a W/O emulsion (**Figure 2e)**. Computational modelling at the atomistic scale indicates that hydrated quercetin molecules favour the planar interfacial conformation because it allows them to pack more efficiently through non-polar π–π stacking interactions and hydrogen bonding with water molecules located within the quercetin hydrate crystal lattice [40]. Similarly, for rod-shaped cellulose nanocrystals (CNC), the small-angle neutron scattering (SANS) experiments of Cherhal and co-workers [41••] have revealed that the CNC crystals become oriented at the interface with the lateral dimension present in a monolayer of thickness 7 or 18 nm, depending on the particle surface chemistry, *i.e.* sulfated or desulfated, respectively. A useful rule of thumb is that the particle orientation having the minimum free energy is the one for which the particle distorts the interface the most, *i.e.* the one in which the particle make the largest ‘hole’ in the interface [38]. Under such circumstances, attractive capillary forces (corresponding to energies of several million times $k_B T$) become especially relevant when there is overlap between the interfacial distortions created by neighbouring anisotropic particles [38, 42]. The resulting clustering of the anisotropic particles at the interface results in a higher particle packing efficiency and an enhancement in the effectiveness of the steric stabilization of the emulsion droplets.

Besides particle shape, the detailed surface chemistry of the particles further affects their orientation at the interface. The associated phenomenon of ‘patchy wetting’ can have an influence on the effective value of ΔG_d [38]. For instance, the elegant work of Blanco and co-workers [43•] has shown that, for the case of organic–inorganic patchy Pickering particles, where the water-insoluble protein zein was used to modify the wettability of hydrophilic silica particles, an optimal degree of stabilization was surprisingly achieved with only partial coverage of zein on the silica surface, instead of full coverage. Furthermore, in the case of CNC, the lateral crystalline plane of the particle has been demonstrated [41••] to interact with the oil–water interface through the CH-groups of the CNC and the alkyl chains of the hydrocarbon oil (*n*-hexadecane) without necessarily causing any deformation of the liquid interface at the nanoscale or the creation of ‘holes’ due to poor wettability of the CNC surface by the oil phase. With the notable exception of this definitive work on CNC particles [41••,44], it would appear that most of the rigorous experimental work carried out so far on anisotropic particles at liquid interfaces has been limited to inorganic materials.

Polysaccharide-based particles

In the formulation of conventional O/W emulsions, a few polysaccharide ingredients such as gum arabic and pectin are considered to be highly effective as both emulsifiers and emulsion stabilizers because their macromolecular species contain surface-active proteinaceous residues or hydrophobic side-chains [45]. But these specific molecular factors are strictly applicable to soluble hydrocolloids; the emulsification behaviour of insoluble polysaccharides is governed by different considerations. In practice, the role of carbohydrate polymers in Pickering stabilization is dominated by two kinds of insoluble biopolymers that are widely abundant in nature: cellulose (**Figure 1a-c**) and starch (**Figure 1d-f**). Today these two plant-based materials monopolize the polysaccharide-based nanoparticle domain within the Pickering emulsion landscape (**Table 1**). In mesoscopic structural terms, the functionality of these two materials can be largely attributed to the presence of alternating amorphous and nanocrystalline domains. This structural attribute can be exploited in various ways to create nanocrystals under suitable chemical processing conditions (*e.g.*, solvent treatment, acidic pyrolysis) [46–48].

Research on cellulosic particles has recently acquired significant momentum owing to the availability of off-the-shelf commercial supplies of CNC. Depending on the commercial source and the chemical treatment, these particles possess a variable high aspect ratio ranging from 16:1 to 35:1 [49] together with a net negative charge across a wide range of pH values as a consequence of the sulfate groups introduced during acidic treatment. The sulfated CNCs are poorly wetted by the oil phase [41••], resulting in low contact angle θ and consequently a reduced value of ΔG_d (see **Figure 2d**). A recent surface pressure study has revealed [44] that ΔG_d diminishes to a great extent in the presence of polar oils, which is consistent with separate observations on emulsions [50] where stability was impeded for polar oils stabilized by CNCs as compared with non-polar oils. Recent work by Du Le and co-workers in our laboratory [28•] has shown that hydrophilic sulfated CNCs with a diameter of 2–4 nm and a long axis of 40–100 nm (**Figure 1c**) do not adsorb effectively at the oil–water interface unless the surface is esterified with octenyl succinic anhydride (OSA). The chemical modification was observed to raise the static water contact angle from 56° to 80.2° thereby allowing the particles to act as effective Pickering stabilizers for O/W emulsions with outstanding stability over several months [28•,51].

Table 1. Overview of different types of plant-based materials used to stabilize O/W and W/O Pickering emulsions, categorized in two different droplet size ranges, based on reports published during the last 5 years.

O/W Emulsions				
Type of Pickering particles*		**Droplet size**		**References**
		<1–10 µm	**10–100 µm**	
Polysaccharide-based particles	Cellulose nanocrystals/ nanofibres or amorphous cellulose	🟩		28•,41••,50,52
			🟩	51,53–56
	Starch particles/granules		🟩	29–31••,35,37•,57
Protein-based particles	Zein particles/complexes		🟩	33,58-60
	Prolamin-rich protein particles other than zein	🟩		33
			🟩	33,61–64
	Globulin-rich (soy, peanut, pea protein particles and microgels	🟩		18••,65,66•,67
			🟩	68–71
Other particles	Protein–polysaccharide self-assembled complex particles derived from biomass	🟩		72,73
	Food waste lignin-based particles		🟩	36•
	Oleosomes		🟩	74•
	Polyphenol particles		🟩	53•
W/O Emulsions				
Polysaccharide-based particles	Cellulose nanocrystals/ nanofibres		🟩	53,75,76
	Starch particles		🟩	77,78
Protein-based particles	Zein particles		🟩	79
Other particles	Food waste-derived lignin particles		🟩	36•
	Oleosomes		🟩	74•
	Polyphenol particles		🟩	21•,53,80••,81•

* The Pickering particles in many of these studies have been modified chemically or physically, and some are complexed with other molecular species such as soluble biopolymers or plant secondary metabolites.

In the case of starch, a common approach is to use native starch granules as Pickering microparticles following hydrophobic modification with OSA [29,35]. Emulsions stabilized by such starch granules exhibit excellent long-term stability, as illustrated by the absence of any detected droplet coalescence in O/W emulsions stabilized by OSA-treated quinoa starch granules (volume fraction 0.1) during quiescent storage for a period of some 8 years [37•]. However, starch granules are typically rather large in size (> 1 μm) (**Figure 1d**), which means that the resulting Pickering emulsions tend to be extremely coarse (average droplet size >> 10 μm). To facilitate the making of finer emulsions, an alternative approach is to chemically disrupt the starch granules and then reassemble them as a smaller starch nanoparticles. One such method [30] brings about starch dissolution by exposing the granules to dimethylsulfoxide (DMSO) followed by ethanol-induced precipitation. The DMSO solvent disrupts the inter- and intra-molecular hydrogen bonding, destroying the crystalline structure of the granule [82], and hence allowing subsequent precipitation of the starch polymers in ethanol to form spherical starch nanoparticles (size 10–400 nm, V-type crystallinity) (**Figure 1e**). A greener approach is to avoid the DMSO dissolution step altogether through heat-induced starch gelatinization followed by high-shear mechanical agitation and subsequent ethanol precipitation into nanoparticles [31••,32] (**Figure 1f**). This latter innovative method [31••] has not only enabled the creation of OSA-free starch nanoparticles from three different sources (corn, tapioca, sweet potato) ranging in diameter from 100 to 220 nm, but it has also resulted in Pickering particles of enhanced surface hydrophobicity with near-optimum static water contact angles of 84.3°, 89.1°, and 94.8°, respectively. Based on measurements of the three-phase contact angle and the oil–water interfacial tension, the estimated value of ΔG_d for starch-based nanoparticles (size 100–300 nm) at the *n*-hexane-water interface has been estimated to be from three to five orders of magnitude larger than that for macromolecular OSA-modified starch [83].

Protein-based particles

Plant-based proteins are largely storage proteins located in the endosperms of cereal seeds or cotyledons of legume seeds. They can be conveniently classified into water-soluble albumins, salt-soluble globulins, alcohol-soluble prolamins, and acid/alkali-soluble glutelins [84,85]. The technologically seminal work of creating prolamine-rich zein particles from corn *via* anti-solvent precipitation was carried out in 2012 by Folter and co-workers [86]. The preparation of Pickering emulsions using these particles sparked many exciting researches into the utilization of water-insoluble biopolymer-based particles. While zein from corn still occupies a major share of protein-based nanoparticle research (**Table 1**), the boundary of activity has recently progressed towards the creation of Pickering particles from other prolamine-rich cereals such as sorghum, barley and wheat, thereby generating colloidal particles composed of kafirin [61], hodein, secalin [33] and gliadin [63]. In order to reduce the particle size of these Pickering stabilizers to submicron dimensions, ultrasonication has emerged as a promising method of disrupting unwanted particle–particle aggregation. Use of this processing treatment has facilitated the preparation of nanoparticles of zein (**Figure 1g**), hodein and secalin [33], as well as quinoa protein nanoparticles with hydrodynamic diameters in the range 100–200 nm (**Figure 1h**), hence enabling the formation of Pickering emulsions with droplets smaller than 10 μm.

A wide range of physical and biochemical treatments, involving heating, enzymes, pH change, divalent cations and shearing, either alone or in combination, has been exploited to create Pickering nanoparticles or microgels from globulin-type plant proteins derived from soy [69, 70], peanut [66•] and pea [18••,65]. For example, in our laboratory a procedure involving heat-triggered gelation *via* the sulfhydryl–disulfide interchange reaction followed by controlled shearing has been exploited [18••] to create hairy pea protein microgel particles ranging in hydrodynamic diameter from 200 to 400 nm. Although calculated interaction potentials had suggested that such protein microgel particles should become aggregated at higher ionic strengths (≥ 50 mM NaCl), the theoretical predictions of instability were not validated experimentally by dynamic light scattering data. A dominant repulsive contribution from steric hindrance was postulated for the first time in the interparticle interactions of these hairy plant-protein based microgels [18••] — this stabilization mechanism may be regarded as analogous to the steric forces involved in the stabilization of casein micelles by hairy layers of *κ*-casein [87]. In an alternative enzymatic cross-linking approach, the combination of transglutaminase-induced gelation and shearing has been employed [66•] to convert peanut protein into spherical Pickering microgel particles of diameter 40–150 nm (**Figure1i**). Depending on pH, these microgel particles were found to exhibit variable extents of aggregation and different values of the three-phase contact angle in the range 75°–132°.

The self-assembly of proteins and polysaccharides from alternative sources such as jack fruit [72] and mucilages [73] *via* photocatalysis [72] or electrostatic interactions (pH adjustment) [73] has enabled the fabrication of new varieties of plant-based Pickering nanoparticles (**Table 1**). Further such studies can be expected in the near future given the significant knowledge base that already exists on electrostatic protein–polysaccharide complexes and heteroprotein coacervates [88-90] which is surely now ripe for technical exploitation through the creation of new kinds of soft biopolymer-based particles for emulsion stabilization.

Polyphenol crystals and other entities

Plants are highly efficient in synthesizing secondary metabolites. The most commonly studied are the polyphenolic crystals, such curcumin, quercetin, rutin and naringin, all of which have been recently recognized as effective Pickering stabilizers [21•,53] (**Table 1**), following the original pioneering work on flavonoid Pickering stabilization by Luo and co-workers in 2011 [91]. We have demonstrated [21•] that water-insoluble polyphenol crystals such as polyhedral curcumin (log P = 3.29) (**Figure 1j**) and rod-shaped quercetin (log P = 2.16) (**Figure 1k**) are effective as W/O Pickering stabilizers (where P is the partitioning coefficient of the molecular species between *n*-octanol and water). Without any additional physical or chemical treatments, these nature-derived polyphenol crystals give rise to estimated detachment energies of at least $10^5\ k_B T$ for both curcumin (θ = 116°) and quercetin (θ = 79°), thereby indicating the effective stabilization of W/O emulsion droplets. Adsorbed layers of quercetin crystals at the oil–water interface have been found to exhibit much higher values of the surface shear viscosity and stronger interparticle interfacial interactions as compared with curcumin crystals [21•,81]. This is consistent with the larger aspect ratio of the rod-shaped quercetin crystals (**Figure 1k**) which implies a larger predicted value of ΔG_d (see **Figure 2b, d-e**) and also a more efficient state of interfacial packing between the anisotropic particles, through the role of capillary forces as discussed above.

A recent study [74] suggests Pickering stabilization by plant natural oil bodies, *i.e.*, sunflower oleosomes with or without defatting (**Table 1**). Such a mechanistic interpretation is certainly plausible, but the lack of wettability information for these architecturally complex oil bodies (containing a range of proteins and phospholipids) with respect to either of the fluid phases, together with the absence of detailed structural information at the droplet surface, makes it difficult to be convinced whether these particles do generate *true* Pickering emulsions.

The issue of food waste valorization provides another motivation for the study of particle functionality. For instance, it has been demonstrated that spent coffee particles (**Figure 1l**) can behave as spherical Pickering particles following hydrothermal treatment (250 °C for 1 h) using an approach derived from the bioenergy field [36•]. The hydrothermal treatment apparently induces a relocation of the hydrophobic lignin component of the cell walls from inside the particles to the outer surface. This structural change increases the surface hydrophobicity of the coffee particles, thereby enabling them to stabilize Pickering emulsions [36•]. One may assume that a substantial proportion of the lignocellulosic materials and plant cells which are common by-products of the food industry could in principle be converted into colloidal particles by utilizing current colloid science knowledge and employing suitable physical and chemical treatments. The exploitation of such technical developments could lead to the opening up of an almost untapped field of new opportunity for future plant-based Pickering particle research.

Pickering O/W and W/O emulsions

Figures 3 summarizes the wide range of (a) O/W emulsions and (b) W/O emulsions that has characterized scientific work on Pickering stabilization published over the last 5 years. Investigators have focused more attention on water-continuous Pickering emulsions rather than on the alternative oil-continuous ones. This apparent bias does not necessarily reflect the comparative needs of the food industry. More likely it is reflection of the long-standing greater emphasis by researchers on the stability of O/W emulsion systems, and perhaps also simply the lower ready availability of convenient particles that are preferentially wetted by polar food oil phases. One may note that, through the controlled variation of suitable chemical and physical treatments, several kinds of plant-based particles (zein particles, cellulose nanocrystals/fibres, starch particles, polyphenol crystals) can be made to satisfy the requirements of both O/W and W/O stabilization (**Figure 3**). In addition, a few studies have reported the ability to stabilize both O/W and W/O emulsions using particles having the same physical treatment [36•,53,74]. While such a capability does seem more likely with Pickering particles than with adsorbed surfactants or polymers, we are inclined to the view that any designation of dual-purpose functionality needs to be treated with a little caution in the absence of convincing confirmatory data on the long-term stability of these emulsions, including the susceptibility to shear-induced phase inversion.

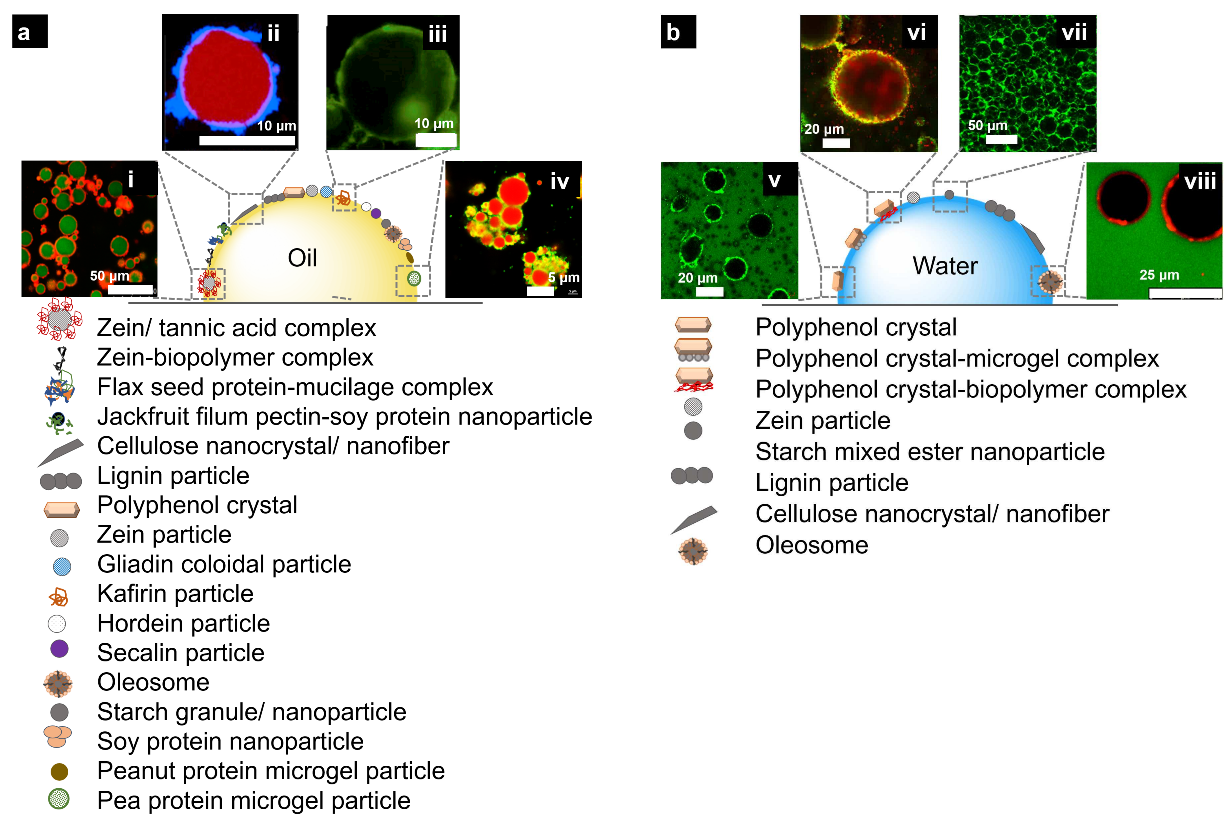

Figure 3. Schematic representation of (**a**) Pickering O/W emulsions and (**b**) Pickering W/O emulsions stabilized by a variety of modified plant-based particles. The images show confocal micrographs of oil droplets stabilized by (**i**) zein–tannic acid complex [60], (**ii**) cellulose nanocrystals [28•], (**iii**) kafirin nanoparticles [61], and (**iv**) pea protein microgel particles [18••]; and water droplets stabilized by (**v**) curcumin crystals [21•], (**vi**) quercetin crystal–protein complex [81•], (**vii**) starch particles [77], and (**viii**) sunflower oleosomes [74]. (Micrographs are reproduced with the permission of American Chemical Society (image **i**), Elsevier (images **ii**, **iii** and **vii**), and Royal Society of Chemistry (image **viii**). Images **iv–vi** were produced at the University of Leeds).

Sizes of plant-based particles lie mainly in the range from hundreds of nanometres to several micrometres (**Figure 1**). Consequently the droplet sizes in most Pickering emulsions made from plant-based particles are reported to be the range 10–100 µm (**Table 1**). One should be aware that the quoted colloidal stability of O/W Pickering emulsions usually refers to the long-term coalescence stability, *i.e.*, the resilience towards oiling off over several months. If they are *true* Pickering emulsions, the individual oil droplets in even such coarse emulsions should be highly resistant to coalescence and Ostwald ripening. But the rapid creaming of such large oil droplets under gravity is inevitable unless the oil volume fraction is extremely high or the rheology of the continuous phase is controlled using a hydrocolloid thickening agent. The apparent belief of some current investigators of particle-stabilized emulsions that the best way to stabilize an emulsion is to convert it into a gel neglects the important fact that many food applications require the formation of an O/W emulsion system possessing the rheological and sensory character of a low-viscosity Newtonian liquid. In order to successfully achieve the objective of preparing fine liquid-like Pickering emulsions (droplet size ~ 1 μm) with satisfactory long-term creaming stability, it will clearly be necessary for researchers to develop improved techniques of fabrication of plant-based nanoparticles of reduced average size (~100 nm).

Besides the study of model systems stabilized by individual types of particles, there has been an upsurge in activity on the design of Pickering emulsions stabilized by plant-based particles in combination with other surface-active species. Examples include protein nanoparticle–secondary metabolite complexes [68,92,93] (**Figure 3a-i**), particle–biopolymer complexes [58,59,62,81•] (**Figure 3b-vi**), and polyphenol crystal–protein microgel complexes [80••] obtained via covalent conjugation and electrostatic interactions (**Figures 3a-ii–iv**, **3b-v,vii–viii**). Often such complexation with a natural surface-active species such as a protein [51,80••,81•] leads to a favourable modification of the particle surface, resulting in stronger particle attachment at the oil–water interface and enhanced emulsion stability without the requirement for additional chemical modification (*e.g.* with OSA). In our laboratory, the generation of stable Pickering W/O emulsions has been accomplished through the interfacial complexation of polyphenol crystals with soluble proteins [81•] or protein-based microgels [80••]. The underlying stabilization mechanism has been inferred from a combination of surface shear rheology and Langmuir trough experiments: the hydrophobic polyphenol particles (quercetin or curcumin crystals) adsorb from the oil phase and the hydrophilic protein or proteinaceous microgel particles adsorb from the water phase. This combination of ingredients provides what might be described as a dual Pickering stabilization mechanism — most notably in the case of the polyphenol crystal–microgel system (**Figure 3b-vi**). The mixed formulation allows the water volume fraction to be raised from 5 wt% [21•] in the absence of the proteinaceous component to 20 wt% in its presence [80••,81•], highlighting the practical significance of the occurrence of synergistic particle–particle or particle–biopolymer complexation at the particle-laden oil–water interface.

In many of the studies mentioned above, the long-term stability of the Pickering emulsion is enhanced by particle network formation within the continuous phase (**Figure 4**). This colloidal structuring inhibits (or retards) the various instability processes of liquid drainage, sedimentation (W/O systems), and cream layer formation (O/W systems). For instance, in our own study of modified CNC-stabilized O/W emulsions (**Figure 3a-ii**) [28•], elastic gel-like behaviour (storage modulus *G*' >> loss modulus *G*'') was observed at moderately high ionic strengths (≥ 20 mM NaCl). This was postulated to be associated with the networking of the rod-shaped CNCs in the bulk aqueous phase, with van der Waals forces dominating the attractive interparticle interactions and the CNC-rich phase forming 'a space-filling isotropic gel' [94]. In other words, one may argue that the role of CNC as a 'structuring agent' in the bulk phase is at least as relevant as the adsorbed Pickering monolayer to the observed long-term stability behaviour of the emulsion (**Figure 4**). Similar kinds of bulk-phase gelation behaviour have also been reported with zein–tannin complexes [60] and gliadin particles [64]. In fact, in studies where the emulsion properties have not been explored in depth, and where the main focus is on the creation of emulsion gels with the particles forming a network in the continuous phase [65,67,71], it seems debatable as to whether the constituent particles are actually functioning as Pickering stabilizers at all. That is to say, the particle-based ingredient may simply be acting as network-forming 'structuring agent', somehow entrapping the aggregated emulsion droplets within the bulk phase and hence inhibiting long-term instability (**Figure 4**). One possible way to test for *true* Pickering stabilization in these gel-like O/W emulsion samples would be to subject them to extensive dilution and shearing, and then to investigate the coalescence stability of the diluted and sheared emulsions after prolonged storage.

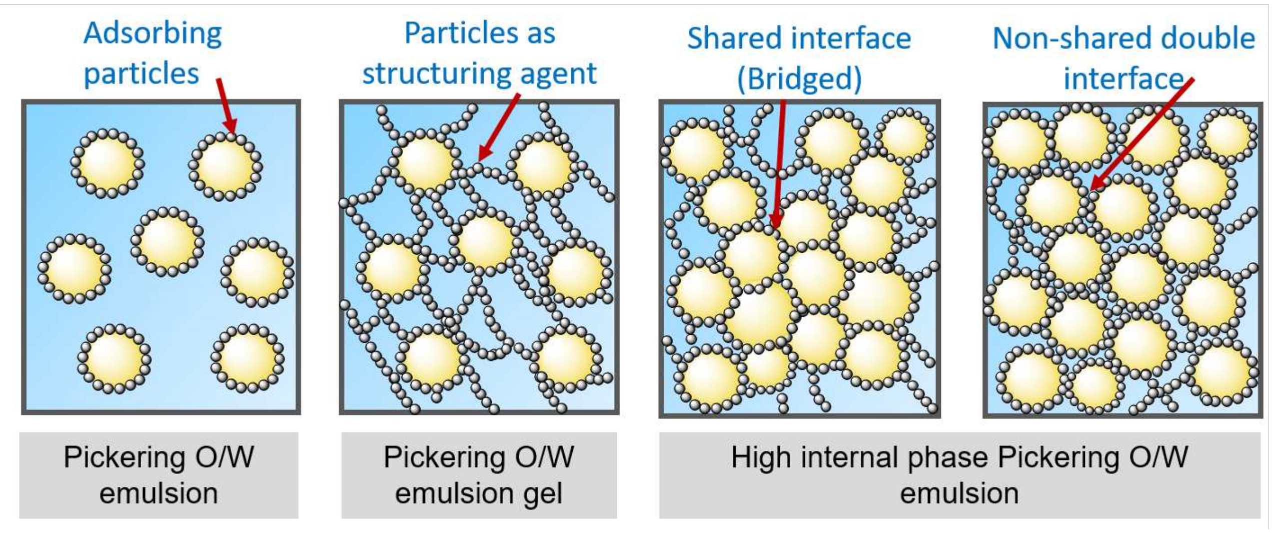

Figure 4. Schematic representations of Pickering emulsions and emulsion gels containing particles as structuring agents in the continuous phase and high internal phase Pickering emulsions (HIPPEs) with either a single shared interface between the neighbouring droplets or a non-shared double interface.

An active ongoing area of emulsion research involves the creation of high internal phase Pickering emulsions (HIPPEs) (volume fraction ≥ 0.74) that can be used as structural templates in the design of high-value porous materials [95]. In order to fabricate conventional surfactant-stabilized high internal phase O/W emulsions, the surfactant load is normally required to be very high (*i.e.* 5–50 wt% in the continuous phase) [96]. On the other hand, just a small quantity of particle-based emulsifying agent (say, ~1 wt%) is sometimes sufficient to stabilize a large concentration of oil droplets. This is because the resulting stability is provided not only by the protective layers of adsorbed particles but also by the aggregated network of interacting particles in the small gaps between the particle-coated droplets. As illustrated in **Figure 4**, there are two distinct types of idealized structures for high-volume-fraction O/W systems stabilized by plant-based Pickering particles: one is where the particles really do form a continuous Pickering-stabilized monolayer around each of the dispersed oil droplets [51], and the other is where many of the adsorbed particles are shared between adjacent droplets in a single-particle bridging configuration. In practice, these two idealized structural arrangements will tend coexist in many real HIPPE systems.

There has recently been a substantial growth in the number of publications reporting the bridged Pickering stabilization of high-volume-fraction emulsions stabilized by plant-based materials [17••,63,71,78,97]. Most of these emulsions are of the O/W type. However, one recent paper reports the use of a hydrophobically modified starch ingredient to stabilize a W/O emulsion possessing a dispersed aqueous phase content of up to 95 wt% [78•]. The stabilization mechanism in this type of study is not fully clear because of uncertainty as to whether the starch used is predominantly present in the form of soluble polymers or dispersed particles. Moreover, even if the system contains starch particles, we pose the question as to whether such a system should be properly be described as a Pickering emulsion in the classical sense, or whether it is being effectively stabilized through immobilization of droplets in a continuous network of starch stabilizer molecules forming a jammed structure of close-packed particulate entities acting as colloidal 'structuring agents'. Unfortunately, in many such HIPPE studies, the shear stability of the concentrated emulsion over the period of storage is not reported. The provision of such experimental information, preferably under conditions of both small and large strains, might assist in establishing the relative contribution of the particles to the network-induced stabilization of the overall structure as compared with the contribution to emulsion stabilization from the coverage of individual droplets by discrete interfacial monolayers.

Future outlook

It is clear that the topic of Pickering stabilization by plant-based particles has attracted strong research attention over the last half decade. This activity has been stimulated by the ready availability of a few off-the-shelf ingredients such as cellulose nanocrystals, polyphenol crystals, and nature-derived insoluble prolamin-based particles, as well as by the study of laboratory-synthesized plant protein-based microgels. Although much work still remains to be done, it is encouraging to observe the gradual emergence of plant-derived particle ingredients that are highly effective in stabilizing oil-continuous systems. The use of such plant-based sustainable emulsifying agents may ultimately enable the partial or complete replacement of the ubiquitous lipophilic surfactant polyglycerol polyricinoleate (PGPR, E476) in the formulation of model food-grade W/O and W/O/W emulsion systems.

From a fundamental research perspective, plant-based materials still present various challenges in terms of optimization of functionality through the manipulation of particle size, wettability, shape anisotropy, aggregation and surface chemistry. Understanding at a greater depth how to control these factors will surely keep experimental and theoretical colloid scientists occupied over the coming years. In order to develop the 'just-right' toolbox for the future manufacturing of sustainable Pickering emulsions on the commercial scale, it seems important to get better understanding of the underlying mechanism: in particular, what is the relative importance of interfacial stabilization by adsorbing particles acting as true Pickering stabilizers *versus* the bulk stabilizing contribution from these same particles acting as 'structuring agents'?

Looking ahead, one may assume that the exploitation of Pickering emulsions for encapsulation and delivery of bioactive compounds will remain an important area of research activity [7•], as well as the issue of how the gastrointestinal digestibility of Pickering food emulsions is influenced by the composition and structure of the interfacial layers [3•]. Furthermore, with a view to assisting the industry in formulating sustainable food emulsions offering improved sensorial pleasure, one may anticipate that the topics of oral tribology and sensory perception [98] will receive an increasing level of attention from investigators of plant-derived particle-stabilized emulsions.

Conflicts of interests

The authors declare no competing financial interest.

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Special interest (•) or Outstanding interest (••)

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