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Colloidal particles as liquid dispersion stabilizer: Pickering emulsions and materials thereof

*Émulsions de Pickering stabilisées par des particules colloïdales et matériaux dérivés*

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ARTICLE INFO

Article history:

Available online 18 October 2014

Keywords:

Pickering emulsions
Particle adsorption
Limited coalescence
Stimuli-responsive

Mots-clés:

Émulsions de Pickering
Adsorption de particules
Coalescence limitée
Stimulable

ABSTRACT

Solid stabilized emulsions, also referred to as Pickering emulsions, are very diverse owing to the large variety of available colloidal particles from naturally occurring to synthesized ones, from hard to very deformable ones and from spheres to more complex shaped particles. Here we illustrate this variety and, despite this huge diversity, we aim at highlighting the common features. We discuss next the remaining open questions that, in our point of view, should sustain special efforts in the future and we illustrate elaboration of original materials based on Pickering emulsions.

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R É S U M É

Les émulsions stabilisées par des particules colloïdales, aussi appelées émulsions de Pickering, présentent une très grande diversité résultant de la grande variété de particules actuellement disponibles. Des particules d'origine naturelle ou synthétique, des particules sphériques rigides, de formes irrégulières ou très déformables peuvent toutes stabiliser des émulsions. Nous proposons dans cet article d'illustrer cette diversité, mais aussi de mettre en exergue leurs propriétés communes. Nous identifions les questions, qui, à notre avis, restent encore sans réponse et qui mériteraient que la communauté consacre des efforts supplémentaires dans un proche futur. Nous donnons des exemples de matériaux originaux élaborés à partir d'émulsions de Pickering.

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1. Introduction

Emulsions are metastable colloids made of two immiscible fluids, like oil and water, one being dispersed in the other as droplets [1]. These out-of-thermodynamic equilibrium systems are usually kinetically stabilized by surface active species. When the stabilizers are particles the emulsions are referred to as Pickering emulsions following the name of one of the

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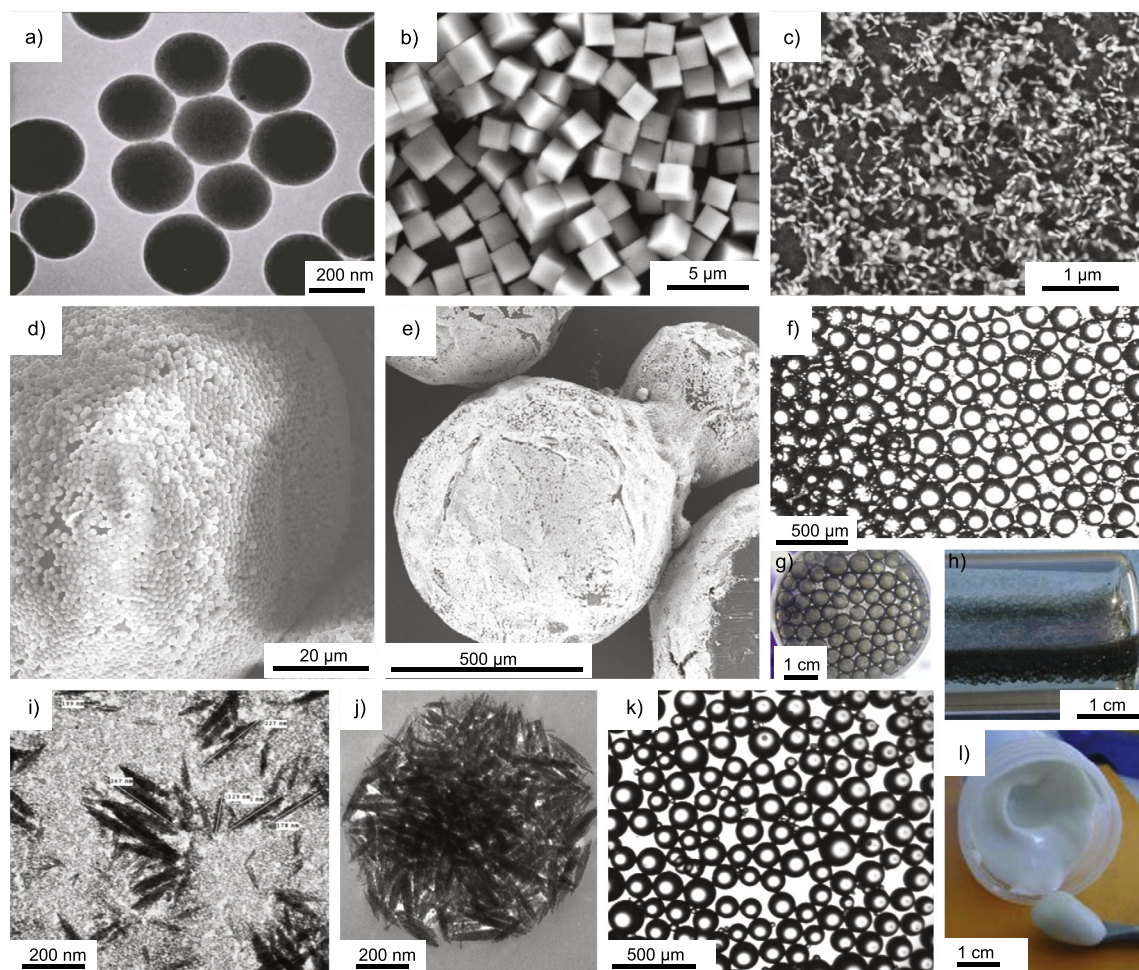


Fig. 1. (Color online.) Overview of diverse particles able to stabilize emulsions. Electronic microscopy images of (a) silica particles obtained from Stöber synthesis, image adapted from [19], (b) neighborite cubes synthesized following the synthesis described in [20], (c) peanut-like iron oxide particles using the synthesis described in [21], (d) a drop of emulsion covered by spherical silica particles like the one reported in (a), (e) a drop of emulsion covered by neighborite cubes from Fig. 1b, (f) an optical microscopy picture of an emulsion stabilized by the peanut particles, (g) macroscopic image of a water-in-dodecane emulsion stabilized by multi wall carbon nanotubes (MWCNT), (h) and (k) macroscopic and microscopic images of dodecane-in-water emulsions stabilized by oxidized MWCNT, (i) and (j) electronic microscopy images of hematites and drops stabilized thereof respectively, (i) example of an unctuous texture of a Pickering emulsion.

pioneering researchers in this field [2]. Pickering emulsions are hence known for a long time but, after the preliminary description by Ramsden [3] and Pickering, they have fallen into oblivion. They regained interest only at the end of the 1990s beginning of the 2000s, likely due to a large development of particle chemistry at that time and to a general context promoting the questioning of classical surfactant and the diversification of stabilizing agents. Then Pickering emulsions have considerably developed both in academic (about 150 publications per year in the last five years) and industrial fields; mainly in cosmetics, phytosanitary products, printing, detergency, laundry, home care, adhesives and nuclear decontamination. An exhaustive review of Pickering emulsions falls out of the scope of the present paper because, due to the very large and constantly rising amount of literature dedicated to Pickering emulsions, such a review would immediately become obsolete at publishing. The aim of the present paper is rather to discuss some of the important concepts in order to contribute to widespread the knowledge in such systems while stressing the main difficulties that should be overcome to increase both the understanding of Pickering emulsions and their use. Indeed, when employed as-made, they possess a strong potential in fields as diverse as food, cosmetics, pharmaceuticals, emulsion-based catalysis while, when combined with chemistry, they offer strong insights in materials science highlighting the fields of insulation, heterogeneous catalysis, energy conversion, hydrogen storage and so forth.

2. What kind of particles?

The first necessary condition to produce Pickering emulsions is the particle double affinity for both phases: particles require to be wetted by the two liquids. In the case this condition is not fulfilled, particles will remain dispersed in either

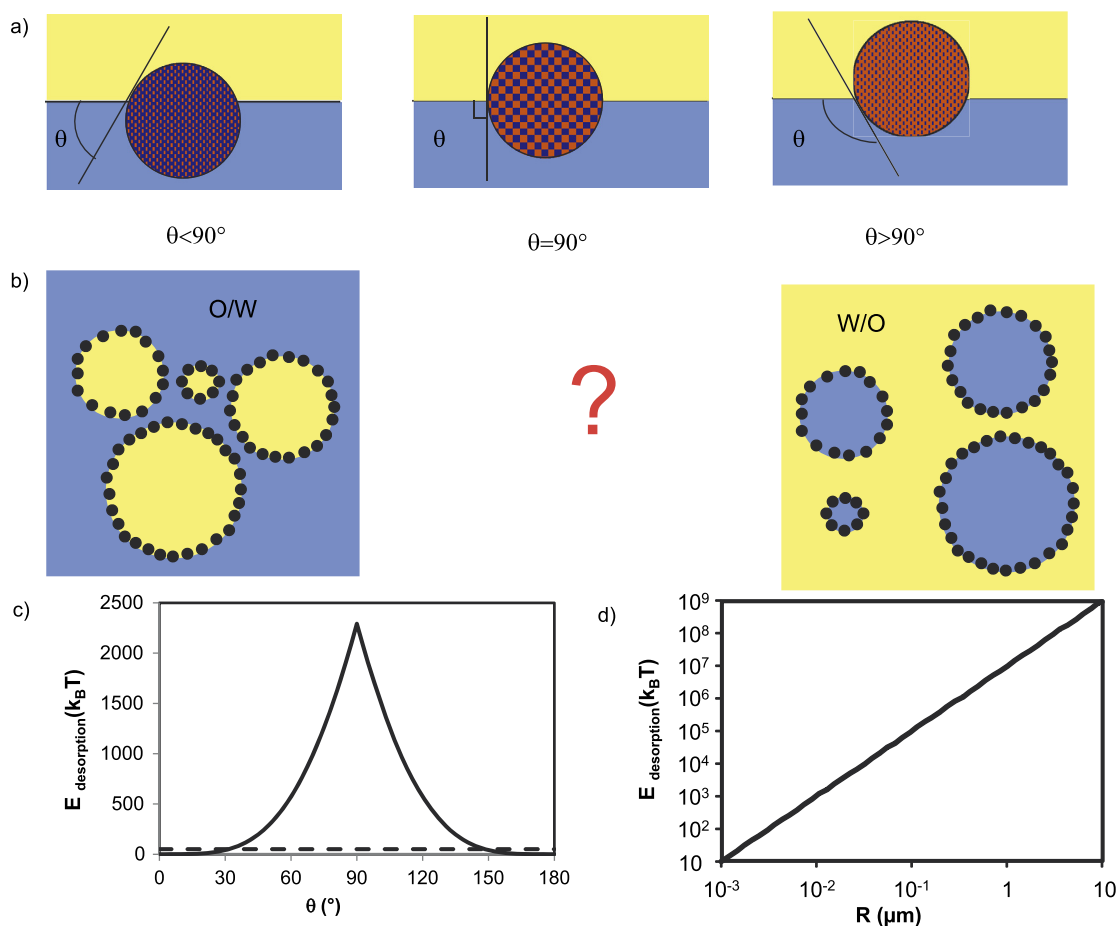


Fig. 2. (Color online.) Adsorption of particles at an oil–water interface. (a) Definition of the contact angle θ taking values lower (resp. higher) than 90° for preferred hydrophilic (resp. lipophilic) particles and (b) the corresponding expected emulsion type: direct O/W when $\theta < 90^\circ$ and reverse W/O when $\theta > 90^\circ$. For well-balanced particles, the contact angle is equal to 90° , but the type of emulsion is not elucidated. (c)–(d) Energy needed to detach a particle from the interface and to disperse it into its preferable wetting liquid as a function of (c) the contact angle and (d) the particle radius R . The dashed line in Fig. 2c corresponds to the thermal energy $k_B T$.

phase. A first important issue concerns the adsorption of particles at the oil–water interface and whether there exists an adsorption barrier. From the literature, the general answer is ambiguous. For charged particles, a unanimous trend can be drawn, particles should overcome an adsorption energy barrier [4–6], and the presence of salt allows lowering the barrier leading to particle coagulation at the drop’s surface. However, in other cases, generally for no or poorly charged particles that spontaneously aggregate in the dispersion, particles require to be better dispersed by ultra-sonication, for example. Therefore, unlike a persistent preconceived and widespread idea, previous flocculation or aggregation of particles is not always beneficial for interfacial adsorption. Another view consists in considering the possibility that line tension acting around adsorbed particles could have an effect on particle adsorption [7–10]. A thermodynamic approach allows then an estimation of the free adsorption energy. In all cases, the description of particle adsorption remains insufficient because it applies only to specific cases like charged or small particles and it cannot be generalized to the large variety of particles able to stabilize emulsions. Until now all attempts to anticipate the particle ability to adsorb at a given interface knowing the particle surface chemistry has been unsuccessful. Indeed, there is no simple criterion to design *a priori* an emulsion. Therefore a complete theory describing the particle adsorption at the interface taking into account the proportions of the two immiscible liquids, the size and shape of the particle as well as its surface chemistry remains a challenge for the coming years.

Particles reported in the literature able to stabilize emulsions are very diverse and grow in number every year. They have various chemical surface functions as they may arise from organic or inorganic chemistry, they are naturally occurring like clays [11], talc, spores [12], yeasts [13], viruses [14]... or synthesized with a high control of their size and surface chemistry as lattices or silica particles obtained from a Stöber-like method. They often exhibit spherical geometries, but they may have regular but non-spherical shapes as neighborite cubes [15], carbon nanotubes, ribbons, peanuts or irregular shapes [16] when stemming from a less controlled process as fumed silica or when resulting from aggregates [17,18]. Examples of particles we synthesized following protocols described in literature and emulsion stabilized thereof are given in

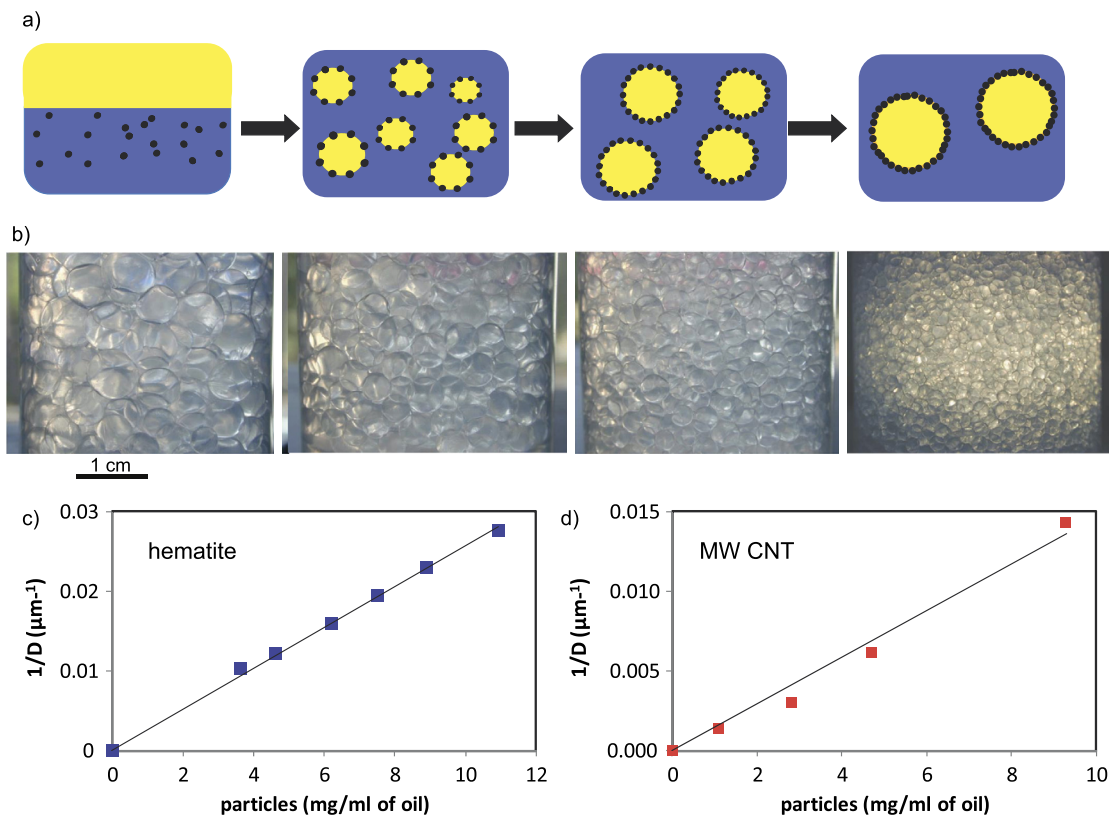


Fig. 3. (Color online.) Limited coalescence occurring in Pickering emulsions. (a) Scheme of the limited coalescence process operating for strongly adsorbed particles and in the particle poor regime. The amount of interface created by stirring exceeds the area particles are able to stabilize so that coalescence takes place until it is stopped by the adsorbed particles. This final state depends on the amount of particles and on their packing at the interface. (b) Final state of emulsions obtained by limited coalescence for various amounts of particles keeping all other parameters fixed (oil/water ratio, energy input) Adapted from [17]. (c)–(d) Examples of limited coalescence obtained with shape anisotropic particles: (c) inverse drop diameter as a function of hematite particles amount, and (d) inverse drop diameter as a function of the amount of multi wall oxidized carbon nanotubes (MWCNT). The linear relationship evidences the limited coalescence process.

Fig. 1. We can non-exhaustively list silica particles [19] (Fig. 1a and d), neighborite cubes [20] (Fig. 1b and e), peanut- [16] (Fig. 1c and f) or needle-like (Fig. 1i and j) shaped iron oxide particles [21]. Most often, these particles are hard solids, non-deformable, but recently a real craze rose for soft deformable particles as microgels due to their high versatility [22,23]. It is worth noticing that the microgels have been shown to spontaneously adsorb at the interface and to adopt either flattened or compressed conformations giving rise to tunable emulsion properties.

A large proportion of native particles are unable to adsorb at the interface so that they have to be modified in order to acquire the required double wettability. For example, silanol groups may be grafted onto silica particles to confer them higher hydrophobicity or hydrophobic latex can gain hydrophilicity by grafting sulfate or acrylic acid groups [17,24]. Also carbon nanotubes may become suitable for interfacial adsorption [25–27]. For our part, we used multi wall carbon nanotubes (MWCNT) either raw (for stabilizing W/O) or oxidized by a HNO_3 treatment (for O/W emulsions) (see Fig. 1g and h and Fig. 3d). An adequate chemical treatment also transformed cellulose nanocrystals into efficient emulsion stabilizers [28–30]. The high potential in food or cosmetic applications boosted the development of succinate modified starches [31,32]. As just described, particle functionalization often results from grafting, but it may also be obtained by a physicochemical adsorption of surfactant onto the particle surface. Indeed mixtures of particles with very low amounts of surfactants have been used for a long time to stabilize emulsions [33]. In this case, due to the very low surfactant concentration (lower than a hundredth of the critical micellar concentration), the surfactant alone is unable to stabilize the oil–water interface and only the synergy between particle and surfactant allows the targeted effect. The most efficient systems are given by charged particles and the oppositely charged surfactants so that the surfactant head adsorb electrostatically onto the particle surface and the lipophilic chains confer some hydrophobicity to the initially highly hydrophilic particles [33]. As evidenced, the surfactant amount should be small enough to avoid competitive adsorption at the interface as well as the formation of multilayers at the particle surface.

Proteins are known to efficiently stabilize emulsions and also to adapt their conformation to external stimuli as pH, temperature i.e. to be submitted to denaturation. By these two treatments, some proteins form aggregates exhibiting the

same stabilizing properties than particles. Therefore processed proteins could also be considered as Pickering emulsions stabilizers [34–38].

The particle double affinity or more precisely, its hydrophilic/lipophilic balance is determined and quantified by the contact angle defined as the angle, through the aqueous phase, between the tangent to the particle and the interface (Fig. 2a). For spherical model particles that adsorb individually, the contact angle is unambiguously defined, but it loses its signification for aggregates, for irregularly shaped particles or for soft particles that deform at the interface. Nevertheless it remains a useful parameter for many studied systems. Even if simple to define, its experimental determination is a real challenge. Various methods have been proposed in the literature: we can mention indirect methods, such as for example ellipsometry [39,40] and reflectometry [41,42] techniques or the recording of the pressure/area isotherm in a Langmuir trough [43–45] that measures global properties of model particle-laden interfaces and deduces the average contact angle from educated hypotheses and models. Direct methods as atomic force microscopy (AFM) [46,47] and interferometry [48,49] also provided alternative ways enabling the contact angle measurement of individual particles to be measured. Recently, a seducing method has been also proposed by Isa et al. [50,51] based on the freeze-fracture of an interface, the subsequent shadow-casting by a unidirectional metal deposition at a known oblique angle, and the determination of the shadow length by cryo-SEM visualization. This technique offers accurate measurements over a wide range of particles sizes (from several microns down to 10 nm). Among all the possible methods, it is worth highlighting the gel trapping technique (GTT) first proposed by Paunov [52], it consists in immobilizing the particle at the desired interface by gelling the aqueous phase, then by replacing the oil phase with a polymerizable oil and to remove the obtained film before observing the particles embedded in the oily film either by SEM or by AFM techniques. These two latter methods are the most reliable ones as they really give the angle at the real interface.

Despite their large variety in terms of shape and chemical nature, all these particles have in common their ability to adsorb, spontaneously or not, at the interface and to kinetically stabilize emulsions.

3. Pickering emulsions

Once adequately functionalized, particles are adsorbed at an oil–water or air–water interface, it is unanimously admitted that they should overcome a high-energy barrier to be removed. This feature can indeed be easily demonstrated by the resistance of emulsions to several washing cycles consisting in replacing the continuous phase by a stabilizer-free phase. In opposition to surfactants, no sharing equilibrium exists between adsorbed and dispersed particles. For spherical individual particles, and based on simple thermodynamic considerations taking into account the surface energies in the various phases, the energy needed to desorb a particle from the interface and to suspend it in its preferred suspending phase is given by:

$$E_{\text{desorption}} = \gamma_{\text{o/w}} \pi R^2 (1 - |\cos \theta|)^2 \quad (1)$$

where $\gamma_{\text{o/w}}$ is the interfacial tension of the pristine oil–water interface, θ is the contact angle and R the particle radius (see Fig. 2). This expression shows that, as long as $30^\circ < \theta < 150^\circ$, the anchoring energy of particles is large compared to the thermal energy $k_B T$, even for nanometric particles. The quadratic dependence of energy with particle size shows that emulsions are better stabilized by large particles. It is worth noticing the singular point for well equilibrated particles ($\theta = 90^\circ$) corresponding to a maximal desorption energy. It could then be concluded that such situation lead to the optimum stability [53]. As a consequence, the formulator could tend to seek for such particles. However on a practical point of view, there is no convincing experiment demonstrating this optimum. On the contrary, well balanced particles may lead to unstable emulsions, likely because the previous expression only takes into account contact energies and other effects as anti-foaming or irregular surface lines... are omitted in the description [54]. Until now, as syntheses do not allow a perfect control of the particle size, shape, chemical surface, the homogeneity is not sufficient enough to conclude on this point. Nevertheless there is a good consensus over the quasi-irreversible particle anchoring and the absence of particle exchange. This is at the origin of peculiar properties of Pickering emulsions.

Numerous studies aimed at establishing the correlation between the preferred wettability of particles and the type of emulsion (direct O/W or reverse W/O). Bancroft's rule establishing that a colloid preferentially dispersed in water (in oil respectively) stabilizes preferentially a direct (a reverse respectively) emulsion is generally valid [55]. This rule, termed in a general context by Bancroft, who was aware of Pickering's work, is better known for surfactants. Later, this rule has been sharpened for particles and an empirical correlation between the contact angle and the type of emulsions has been made. It is known as Finkle's rule: the emulsion type (O/W or W/O) is mainly determined by the relative particle wettability in both liquids, characterized by θ [56]. The most wetting liquid becomes the continuous phase, i.e. for equal volumes of the two immiscible fluids, if the particles are relatively hydrophilic with $\theta < 90^\circ$, an O/W emulsion is preferentially obtained (while a W/O emulsion is preferentially obtained for relatively lipophilic particles characterized by $\theta > 90^\circ$). This feature is illustrated in Fig. 2b.

For surfactant-stabilized emulsions, the empirical Bancroft's rule has been explained either with the spontaneous curvature of the surfactant or using energy arguments. Similarly some attempts have been made to explain Finkle's rule. Even if convincing, some exceptions have been reported in the literature, showing that the deep reason is not fully understood yet.

Due to the strong particle anchoring, emulsions may be produced, exploiting the limited coalescence phenomenon that occurs in a stabilizer poor regime (Fig. 3). Indeed, in the case of complete and irreversible particle adsorption, emulsification

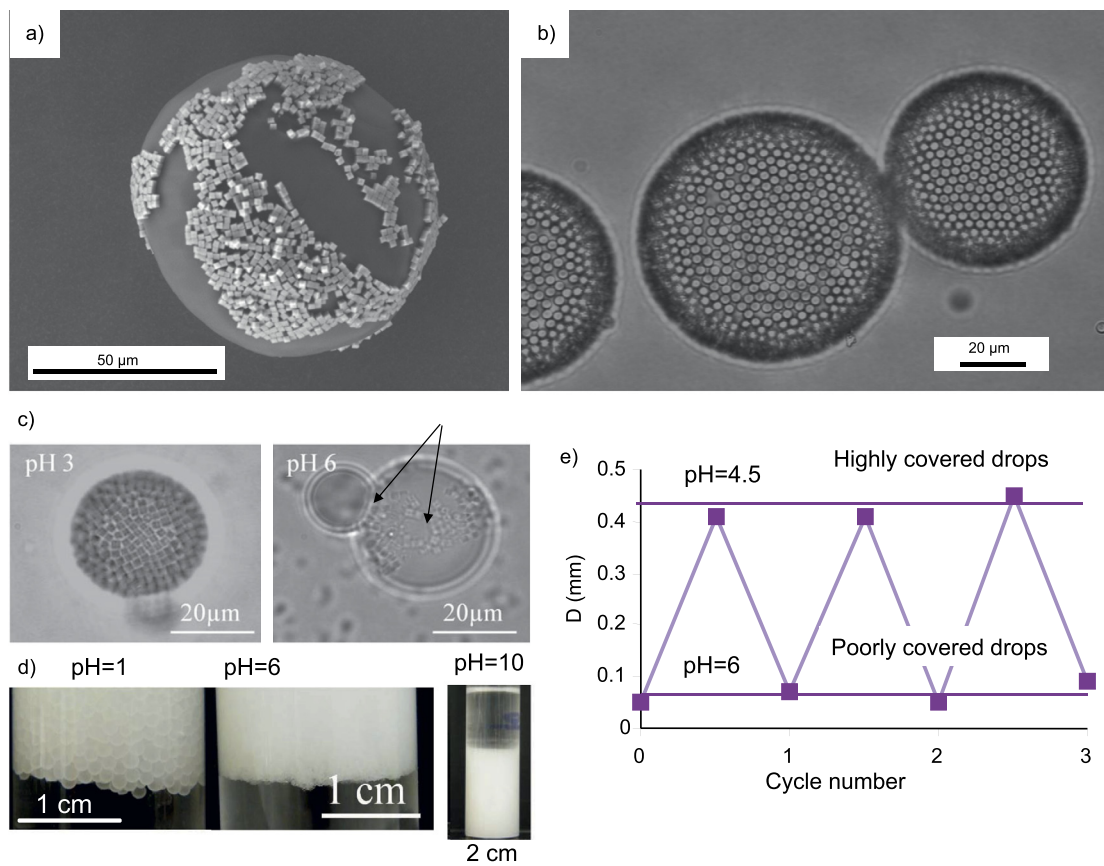


Fig. 4. (Color online.) pH-stimulable Pickering emulsions with two kinetically stable coverage states. Isolated drops stabilized by charged (a) neighborite cubes at pH = 6 (SEM picture), (b) core-shell latex@polyacid particles at pH = 6 (optical microscopy picture), (c) microscopy image of a highly covered hexadecane drop stabilized by neighborite cubes at pH = 3 and of a poorly covered hexadecane drop stabilized by neighborite cubes highlighting the existence of crowns (see arrows) at contact with other drops, (d) macroscopic aspect of the three states of emulsion depending on the pH adapted from [54], and (e) cyclability between the two states for silica particles adapted from [24].

results in producing a large excess of oil–water interface compared to the amount that can be covered by the solid particles. When the agitation is stopped, the partially unprotected droplets coalesce, thus reducing the total amount of oil–water interface. Since the particles are irreversibly adsorbed, the coalescence process stops as soon as the oil–water interface is sufficiently covered [17,57,58]. The resulting emulsions exhibit a drop diameter that is controlled by the mass of particles and their packing at the interface. Assuming that all the particles are adsorbed at the oil–water interface, from simple geometrical considerations, the final drop diameter D is given by:

$$\frac{1}{D} = \frac{m_p}{6C\rho_p V_d} \frac{a_p}{v_p} \quad (2)$$

where m_p is the mass of particles, ρ_p is the particle density, V_d is the volume of the dispersed phase and C is the surface coverage, i.e. the fraction of the droplet interfacial area covered by the particles. The particle geometry is taken into account through the a_p/v_p ratio, where a_p is the particle area projected on the interface (corresponding to the surfactant area per polar head) and v_p the particle volume. For spherical particles, a_p is the equatorial surface so that the ratio is equal to $3/(2d_p)$, where d_p is the particle diameter. The covering parameter C characterizes the packing density of the particles at the interface. For example, for hexagonally-closed packed monodisperse spherical particles, C , is equal to 0.9. If C is lower than 0.9, it means that particles are loosely packed, whereas a value of C larger than 0.9 reflects the presence of particle multilayers or aggregates. For a given system, C can take a value of the order of 0.9 or larger, depending on the initial aggregation state of the dispersed particles and on the energy input during emulsification. Eq. (2) is valid for spherical particles, but the linear relationship between the final drop size and the initial amount of particles is preserved for non-spherical particles [29]. Two examples of limited coalescence revealed by the linearity for non-spherical particles are given in Fig. 3c and d with the needles and the MWCNT reported in Fig. 1. In both cases, oil-in-water emulsions are obtained. Limited coalescence is therefore a very general and an easy way to control the final drop size, even in turbulent flow conditions, with an optimal use of the particles. Moreover this process is easily scalable for industrial applications.

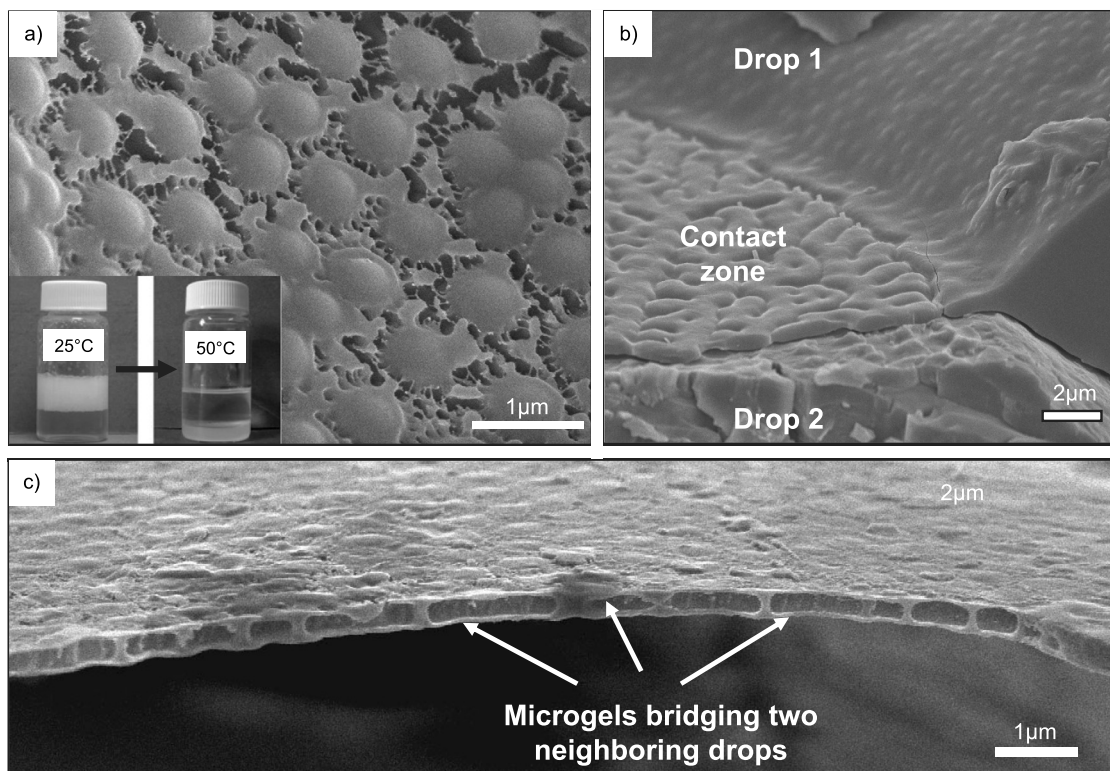


Fig. 5. Temperature-stimulable Pickering emulsions stabilized by microgels. CryoSEM images showing the (a) flattening of microgels at the alkane–water interface of emulsion drops. The microgels adopt a fried egg-like morphology due to their core-shell structure inherent to the synthesis—the insert shows the thermo-sensitivity of emulsions—, (b) the contact zone between two adjacent drops, and (c) the film separating two drops after light sublimation. Adapted from [72] and [62].

Usually coalescence is arrested by the steric repulsion of adsorbed particles, but in some other cases drops are poorly covered by charged particles. At model interfaces or on the surface of W/O drops, charged particles can assemble as colloidal crystals that may prevent the drop from coalescence [59,60]. For O/W emulsions, no crystal could be observed and particles are inhomogeneously distributed at the interface [15,24,54] (Fig. 4). In that case, dipolar interactions may be at the origin of the formation of crowns or patches that involve only few particles [54]. Even such low amounts of particles are efficient for emulsion stabilization because they are localized in the contact zones between drops. Despite their stability at rest, such emulsions remain fragile against compression when the contact surface is increased [54]. As a consequence, emulsions can be destroyed by a mechanical stress. Such emulsions, obtained with all kinds of charged particles, composed of poorly covered drops are still insufficiently understood and this constitutes another challenge.

Such dipolar interactions between particles disappear as soon as particles are neutral or if their charges are screened by the addition of salt. Drops are then densely covered and coalescence is arrested by steric hindrance. Capillary interactions between particles can develop at the interface or bad solvent effect may lead to strong attractive interactions between adsorbed particles, resulting in solid interfaces. Arditty, *via* two methods, based on emulsion compression or drop fragmentation, showed that the drop surfaces exhibited a plastic behavior characterized by a high 2D yield stress that has to be overcome to deform and break the interface [61]. Such techniques are indirect and it should be within reach in the future to develop direct 2D characterization methods to determine the mechanical behavior of drop surface equivalently to the 2D rheology operating at model interfaces.

The very high stability of Pickering emulsions seems to result from both the high energy required to desorb individual particles from the interface and from the strong attractive interactions between adsorbed particles, another obstacle that should be overcome to destabilize Pickering emulsions.

It is worth noticing here that the particle shape may also alter the high emulsion stability. For example, adsorbed needles as those reported in Fig. 1 confer good stability at rest; however, emulsions are unstable under flow likely because needles may pierce the interfaces and provoke coalescence when flow promotes contact between drops.

Pickering emulsions were often thought to exhibit a curdled milk aspect detrimental to applications. This aspect directly results from strong attractive interactions between drops. Such drop adhesion can result from particles that tend to aggregate even in the dispersed state or from bridging between drops. This bridging phenomenon has been particularly evidenced in emulsions stabilized by deformable organic particles [62]. However, due to the large variety of systems and possible interactions, the aspect as well as the flow properties of emulsions can adopt the whole behavior spectrum from

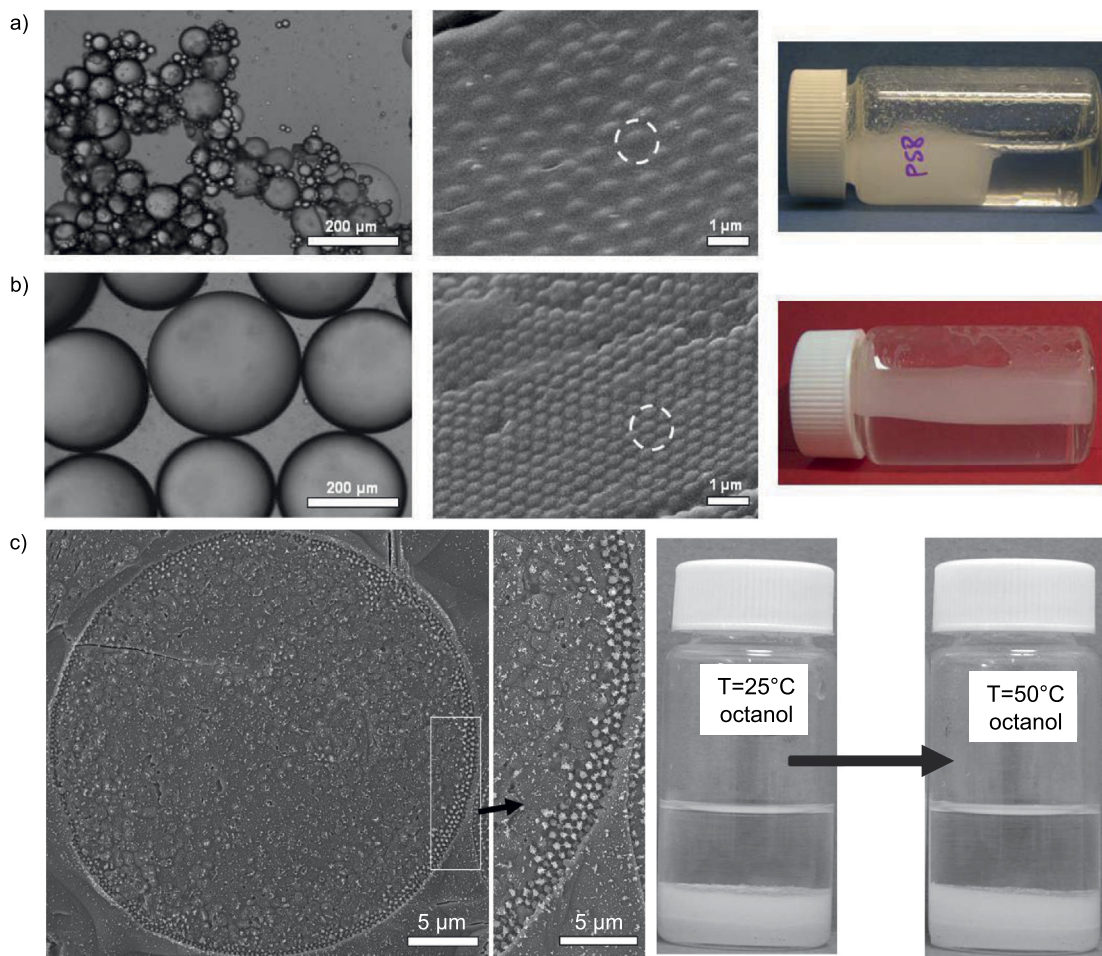


Fig. 6. (Color online.) Direct and reverse microgel-stabilized emulsions. The type and properties of emulsions may be tuned by the emulsification temperature: (a) emulsification at room temperature, (b) emulsification above the VPTT followed by a temperature quench—the microgel packing is much denser than previously—, (c) reverse water-in-octanol emulsion, the temperature sensitivity is lost. Adapted from [72] and [75].

purely liquid to highly solid through the unctuous cream, as can be seen in Fig. 11. It is therefore of utmost importance to control interactions between drops.

As for classical emulsions, for non-interacting drops, emulsions acquire elasticity above the random close packing volume fraction ($\phi = 0.635$) which can be accounted for by Mason or Princen's laws provided that the interfacial tension governing the drop deformability (equal to the half Laplace pressure in surfactant-stabilized emulsions) is replaced by the adequate surface rheology, i.e. by the 2D yield stress for solid drop surface. For non-dispersed drops, elasticity arises already in more diluted conditions and the emulsions behave as conventional colloidal gels describable by a power law [63]. Then adhesion is either detrimental or, on the contrary, beneficial when, for example unctuousness is wished, even at low expensive oil content. It is therefore of utmost importance to know how to control and tune the interactions between drops.

To sum up, stability and flow properties in Pickering emulsions result from a set of parameters: anchoring energy, interactions between adsorbed particles as well as interactions between drops mediated by the particles.

4. Stimuli-sensitive Pickering emulsions

Pickering emulsions are appreciated for their high stability very favorable for long time storage; however their main drawback also originates from their outstanding stability as, in many applications, it is necessary to destabilize on demand the emulsion. This is the case for any application for which provoked release is required or, as for catalysis, the particles should be re-usable and cycled. In the case of water treatment, phase separation between water and oil is mandatory and water has to be cleaned from the surfactant. Using Pickering emulsions, breakable on demand, would simplify the phase separation and provided that particles are large enough, they would sediment and become recoverable, leaving the water clean and avoiding further treatment. It is therefore especially interesting to design emulsions able to be destabilized on demand after a long storage period without alteration.

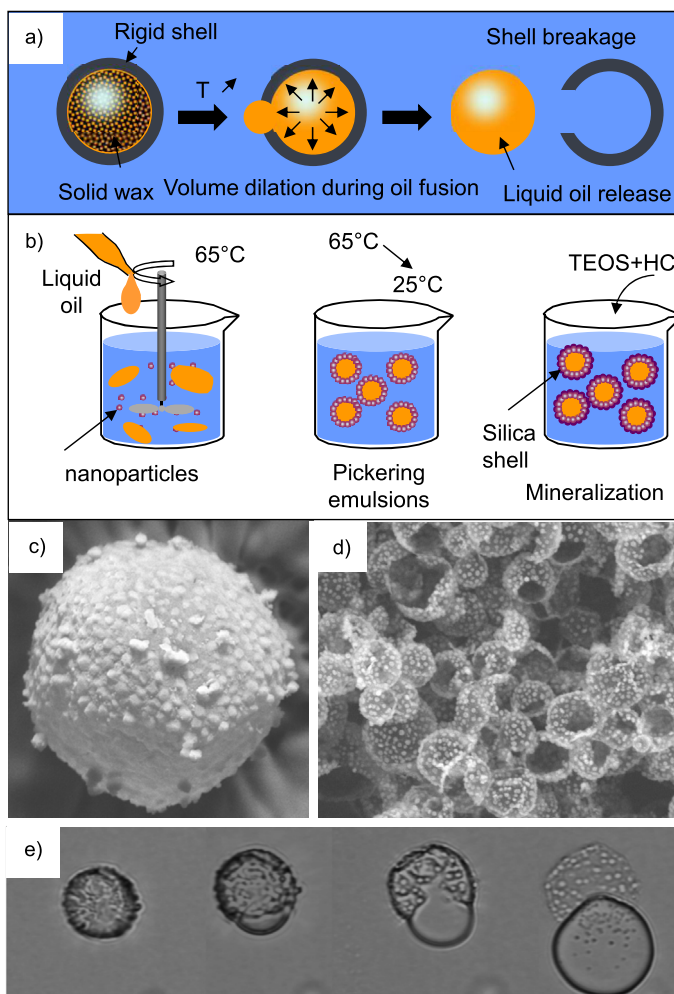


Fig. 7. (Color online.) Thermo-sensitive capsules combining Pickering emulsion and sol/gel chemistry. Schemes depicting (a) the proposed concept and (b) the elaboration principle. SEM images of the obtained capsules (c) before and (d) after heating. This shows the oil release that is even better evidenced by (e) optical microscopy observation under heating. Adapted from [76].

Research in the field of Pickering emulsions has considerably evolved towards such stimutable emulsions, that is to say when an external lever allows triggering destabilization. This sensitivity is most often given by the particles' sensitivity. Examples are given by magnetic particles for which the application of a controlled field allows either handling the emulsions or tearing the particles from the interface [64]. In this paper, more than hundred stabilizing–destabilizing cycles have been applied without modification of the drop size, showing the perfect cycling ability and strong application possibilities of such systems. Another example is given by particles bearing groups, ionizable through the pH, like amines or carboxylic functions. Such particles are then pH and salt sensitive and emulsions stabilized thereof can cyclically be destabilized and reformulated [15,24,65,66] (Fig. 4). Depending on the chemical function of the particle surface, emulsions can phase separate at high or low pH. A good control of the particle chemistry allows finely tuning the switching pH.

Sensitivity to temperature is often given by use of *N*-isopropylacrylamide (NIPAM) a well-known thermally sensitive monomer. It is often the main component of microgels obtained by precipitation polymerization. Such microgels have shown their ability to adsorb at interfaces in various conformations. Because the polymer exhibits a Lower Critical Solubilization Temperature (LCST), the resulting microgels collapse above the so called Volume Phase Transition Temperature (VPTT) and swell below. For pure pNIPAM, the microgel VPTT is about 32°C that makes it a widely studied system. The VPTT can be tuned by the appropriate choice of co-monomer during synthesis. NIPAM suspended in a Pickering emulsion stabilized by silica particles may also be polymerized by UV radiation to form a hybrid shell with the silica nanoparticles [67]. Multi-stimuli responsiveness can be conferred to emulsions by adding a pH sensitive co-monomer during the microgel synthesis for example [68–70] or the use of magnetic nanoparticles combined with the temperature sensitive monomer [71] in the hybrid shell. As for hard particles, microgel-stabilized emulsions may also be produced by limited coalescence. For non-polar oils, direct emulsions are obtained, stabilized by deformable particles that flatten at the interface in a fried-egg like structure [72] (Fig. 5). Adhesion and microgel packing may be tuned through process or formulation parameters, modifying

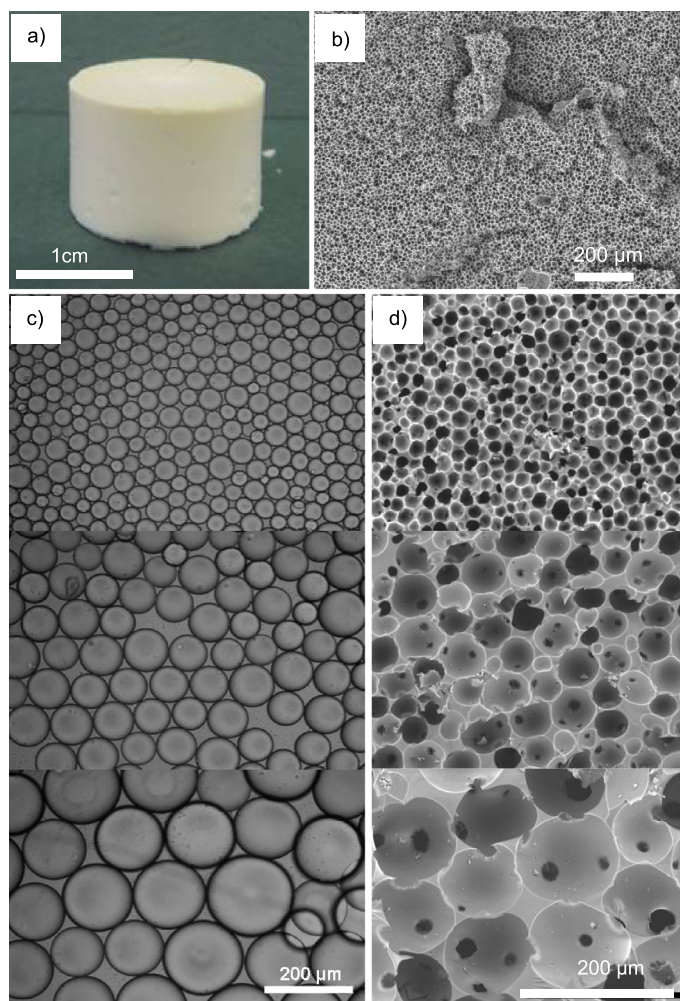


Fig. 8. (Color online.) Solid foams obtained from Pickering emulsion combined to sol/gel chemistry noted SiPHIPE. (a) Picture of the monolith and (b) zoom in the material via SEM. Limited coalescence allows tuning (c) the drop size of the initial emulsion and (d) consequently the void size of the final solid foam. Adapted from [87].

again the final emulsion properties [23,62,73,74] (Fig. 5). In the presence of polar oils, reverse anti-Finkle emulsions are obtained, stabilized by multilayers of non-flattened microgels. Emulsion drops are well dispersed and flow easily but, due to an oil uptake, the temperature sensitivity is lost [75] (Fig. 6).

Thermal sensitivity can alternatively results from the emulsion core rather than from the shell (Fig. 7 and following paragraph).

Stimulable emulsions consist in new model systems to improve the fundamental understanding of destabilizing mechanisms, but also open a large field to design smart materials.

5. Materials based on Pickering emulsions

In addition to stimuable systems interesting by themselves, Pickering emulsions can serve as templates or intermediaries for various kinds of materials. The aim of this paragraph is just to list few illustrative examples.

5.1. Thermo-sensitive core-shell capsules

Combining Pickering emulsions and sol-gel chemistry allows designing capsules able to deliver their content thanks to a provoked rupture of the shell (Fig. 7). The principle relies on the production of a Pickering wax-in-water emulsion. After emulsification at a temperature above the melting point of the wax, the drops solidify during cooling down and are surrounded, in a second step by a solid and fragile shell obtained by mineralization. Such a feature can be realized using a crystallizable oil exhibiting a volume expansion when melting, combined by a rigid non-deformable and breakable shell. Upon heating, the oil melts inducing a volume expansion not bearable with the shell that breaks, leading to a release of the

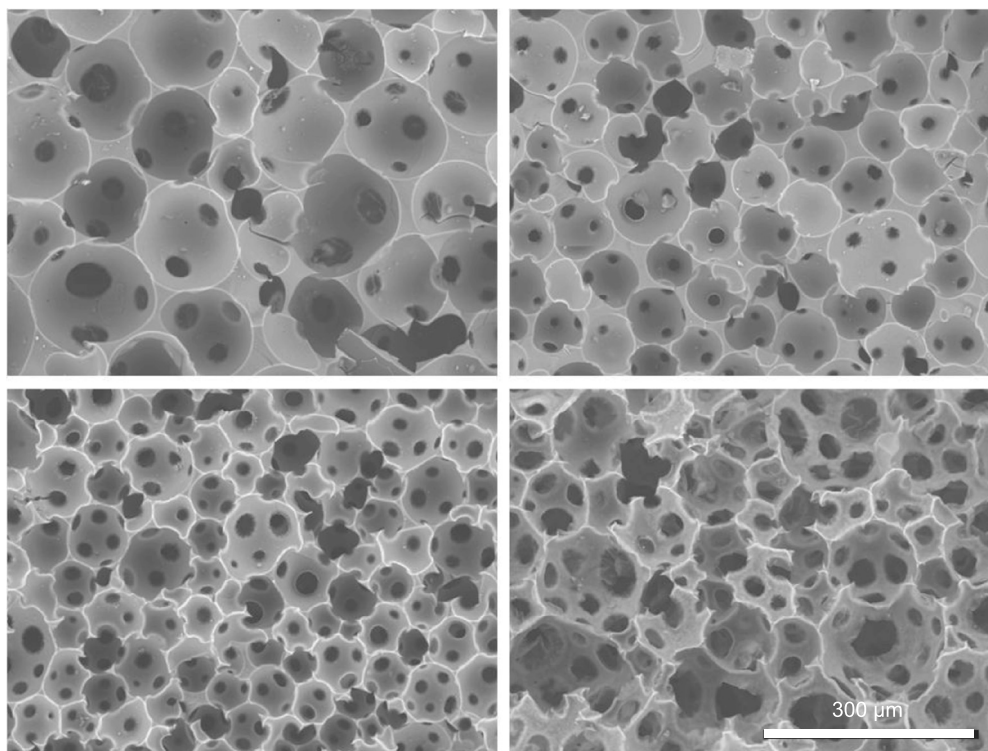


Fig. 9. Solid foams based on Pickering emulsions and sol/gel chemistry. At constant void size, the foam density and hence the window size may be tuned by varying the dispersed phase volume fraction of the initial emulsion. Adapted from [87].

content. The concept developed for simple O/W Pickering emulsions [76,77] can be extended to double O/W/O and W/O/W Pickering emulsions [78–81], allowing co-encapsulation of hydrophilic or lipophilic drugs.

5.2. From biliquid foams to solid foams

A second example is given by the elaboration of solid foams from concentrated emulsions also called biliquid foams or high internal phase emulsions (HIPE). The strategy consists in solidifying the continuous phase of an emulsion composed of more than 64% of dispersed phase that corresponds to the random close packing [82–85]. Above this volume fraction, all the drops are in contact and the resulting monolith exhibits a so-called open porosity. Solidification may be obtained by the organic polymerization of the continuous phase or by its mineralization. Concentrated emulsions act then as soft template toward organic or inorganic foams morphosyntheses. Final inorganic or hybridized foams are outstanding candidates toward diverse enhanced applications as metallic- or enzymatic-based heterogeneous catalysis, photonic materials, while when employed as hard templates for the generation of carbonaceous foams, the field of energy conversion is reached with success with the elaboration of electrochemical capacitors, electrodes for Li-ion batteries, enzymatic biofuel cell electrodes and so forth [86]. Considering the aforementioned foams, whatever their chemical nature, silica, hybrid organic–inorganic or carbonaceous, main advanced properties are emerging from the convection-driven mass transport occurring with the macroscopic voids. As such, it is a challenge of offering a good monodisperse character of both the macroscopic void diameters as well as their junction windows. The use of Pickering emulsions presents the multiple advantages of easily controlling both the initial drop size with narrow drop size distributions and the dispersed volume fraction and to access to drops with large sizes (Fig. 8). Such solid foams have been referred to as Si PHIPE for Silica Pickering-based High Internal Phase Emulsion [87]. The final void size is a function of the initial drop size and the contraction rate during drying and sintering (Fig. 8). Volume contraction decreases when the number of particle layers adsorbed at the initial oil–water interface is increased, the latter parameter being tunable with the stirring energy, for example during emulsification. In addition to the void size, the size of the junction windows that connect adjacent macroscopic voids is of utmost importance as it governs the convective mass transport within the solid-state foams. The junction size can be triggered at constant initial drop size by the dispersed phase volume fraction (Fig. 9). Additionally, both parameters, that is to say void diameters and connecting windows can be tuned independently, offering thus a strong versatility toward the foams morphology. These Si PHIPE based foams can be further employed as hard templates for the design of carbonaceous foams, for biofuel cell application, with the advantage of tuning on demand the macroscopic mass transport [88].

5.3. Pickering emulsions as a tool to design Janus particles

Pickering emulsions have also shown their interest for the elaboration of spherical particles with regioselective surface chemical modifications also called Janus particles. The strategy consists in adsorbing the particles to be modified at the interface of a wax-in-water emulsion. Due to the large amount of interface, the use of a Pickering emulsions has the advantage to allow the production of large quantities of particles compared to a Langmuir model film. The emulsion is prepared at a temperature higher than the wax melting temperature and then cooled down to solidify the drops. Once at the interface, the particles are embedded in the wax and unable to tumble, the immobilized end cap emerging toward the aqueous phase can then be modified by chemical grafting [89,90].

Such particles are promising to develop materials with complex shape and properties [91–94]. For example, spherical beads presenting a chemical surface segregation could be used either as dual-functionalized devices or as building blocks for supra-particle assemblies. They also exhibit an interest as particular surfactants if one hemisphere is hydrophilic and the other one hydrophobic [95]. Indeed they are thought to adsorb with a higher energy than particles with an isotropic chemistry [96–98].

6. Possible future of Pickering emulsions

On a fundamental point of view, we think that theoretical and/or experimental efforts should be devoted to a better understanding of particle adsorption at the interface as well as interactions between adsorbed charged particles at the same or at opposite interfaces. Indeed some fundamental questions remain still unanswered: what is the origin of the adsorption barrier and in what conditions is this barrier suppressed? What happens for well-balanced particles, are the emulsions the most stable according to the maximum energy or do the two phases separate? The domain of existence for drops very poorly covered is still intriguing and deserves special attention.

On a more applied point of view, there is no doubt that Pickering emulsions will develop. However, some difficulties should be overcome. Are particles and specially nanoparticles toxic for the manufacturer until they are dispersed in a solvent? What is the size limit to avoid toxicity, and consequently is aggregation a favorable factor? This societal question is nowadays the most controversial and the one able to put a brake on the development of Pickering emulsion by limiting the possible stabilizers. Another drawback arises for organic particles that often contain residual impurities themselves able to adsorb at interfaces and stabilize emulsions. At the laboratory scale, these impurities are removed either by [centrifugation removal of supernatant/redispersion in pure solvent] cycles: a method difficult to transfer at the industrial scale or by filtration easier to scale up. Once cleaned, do the particles deliver some non-covalently bounded oligomers that could alter the emulsion stability? Also real products are usually complex systems made of numerous components (surfactant, mineral charges as pigments, perfume or drugs, preservatives, alcohol...) that may exhibit a surface activity. To avoid competitive adsorption, the process can be adapted by first introducing the particles as desired stabilizers. If the particles are sufficiently trapped at the interface, the addition of other species should have no impact. The process becomes therefore of even higher importance than with surfactant-stabilized emulsions.

Despite possible obstacles, many applications based on particle-stabilized emulsions are being and will be developed in the future.

Acknowledgements

The authors would like to thank Serge Ravaine and Jean-François Dechézelles for their help in synthesizing the neighborite cubes and Jean-Paul Salvétat for providing and functionalizing carbon nanotubes.

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