Stabilization of Pickering emulsions with oppositely charged latex particles: influence of various parameters and particle arrangement around droplets

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Abstract: In this study we explore the fundamental aspects of Pickering emulsions stabilized by oppositely charged particles. Using oppositely charged latex particles as a model system, Pickering emulsions with good long term stability can be obtained without the need for any electrolyte. The effects of parameters like oil to water ratio, mixed particle composition and pH on emulsion type and stability are explored and linked to the behavior of the aqueous particle dispersion prior to emulsification. The particle composition is found to affect the formation of emulsions, *viz*. stable emulsions were obtained close to a particle number ratio of 1:1 and no emulsion was formed with either positive or negatively charged particles alone. The emulsions in particle mixtures exhibited phase inversion from oil-in-water to water-in-oil beyond an oil volume fraction of 0.8. Morphological features of emulsion droplets in terms of particle arrangement on the droplets are discussed.

Introduction

Since the discovery of particle-stabilized emulsions by Ramsden[1] and Pickering[2] more than a century ago, a great deal of progress has been made both in terms of conceptual understanding of the underlying mechanisms and experimental realization of applying these ideas to a wide range of technological applications like food[3], pharmaceutical[4], drug delivery[5], porous materials[6] and encapsulation[7]. Pickering emulsions thus serve as a platform technology for several industrial applications.

In recent years emulsion stabilization using oppositely charged species, *e.g.* particle-particle, particle-surfactant or biopolymer-polyelectrolyte to stabilize emulsions and to tune their rheological properties, has attracted attention. One of the first studies on these lines was made by Abend *et al.*[8] They demonstrated that, using oppositely charged plate-like clay nanoparticles, paraffin oil-in-water (o/w) emulsions can be stabilized without the use of electrolyte or surfactant. Guzey and McClements[9] reported on the influence of using oppositely charged biopolymers on the properties of oil-in-water (o/w) emulsions relevant in food applications. Binks *et al.*[10] stabilized o/w emulsions using oppositely charged silica and alumina-coated silica nanoparticles. Mao and McClements[11] used oppositely charged starch-coated and protein-coated fat droplets in water to tune the rheological properties of their emulsions. Nallamilli *et al.*[12] employed oppositely charged polystyrene latex particles to stabilize water-in-oil (w/o) emulsions. In this context, it is worth mentioning the work of Liu *et al.*[13] who used oppositely charged polymer microgel particles to stabilize separately two populations of o/w emulsion drops which, upon mixing, did not coalesce. The difference between this work and that presented here is that the microgel particles when present alone (anionic or cationic) stabilise emulsions whereas the latex particles do not. Synergism in the combination of oppositely charged nanoparticles and surfactant was also demonstrated with respect to emulsion formation and stability[14].

The second and more recently understood aspect is the charge on particle surfaces. Several authors reported that particles which are highly charged cannot stabilize emulsions when used alone.[15] However, when a small amount of electrolyte was added to the particle dispersion in water, they were then capable of stabilising emulsions. This phenomenon was explained by the image charge effect. A charged particle trying to approach an oil-water interface from a high permittivity medium (water, 80) to a low permittivity medium (oil, 2) will experience a repulsive image charge in oil whose magnitude depends on the charge on the particle. In general the image charge barrier to particle adsorption is a net result of both particle charge-image charge and particle charge–interface charge, *i.e.* classical double layer interaction. When the interface is already populated with particles, repulsion between the approaching particles and the particles which are already adsorbed will also contribute to the overall barrier. It is clear that when electrolyte is added to the water phase containing particles the charge on the particles is screened and thus the repulsive image charge barrier is reduced thus enabling the particles to enter the interface and stabilize emulsions. With this understanding it is important to note that both the hydrophobicity and the charge of particles play a crucial role in determining the ability of particles to stabilize an emulsion and dictate the type of emulsion thus obtained.

The majority of the literature published on Pickering emulsion research so far is concerned with the use of a single type of particle. The use of a mixture of oppositely charged particles (OCP) has received very little attention.[8,10,12] The reasons for undertaking the present study are: (i) to extend the basic understanding of the formation and stability of emulsions formed by OCP, (ii) to use a new material model system, *viz*. latex particles, which is widely used as a model in colloid research, (iii) to extend the previous work to systems containing both sub-micron and micron size particles and (iv) to understand the structural aspects of emulsion droplets formed by OCP and their possible uses. We present an experimental investigation into the nature of Pickering emulsions formed from oppositely charged polystyrene latex particles. A range of parameter space is explored including the number ratio of oppositely charged particles (here referred to as composition), the oil:water ratio and aqueous phase pH. These parameters were found to affect the formation and type of the emulsion, the droplet size and the emulsion morphology. For the first time we also study the arrangement of particles on droplet surfaces within these emulsions using optical microscopy.

Experimental

Materials

Positively charged and negatively charged monodisperse surfactant-free polystyrene latex particles functionalized by amidine and sulphate groups respectively were purchased from Invitrogen, (Oregon, USA). The particles are supplied as an aqueous suspension at 8 w/v%. The diameters of the positively charged particles were either 0.5 μm or 2.2 μm and those of the negatively charged particles were 0.5 μm, 3.0 μm or 9.0 μm. Carboxyl-functionalized silica particles (powder) of diameter 4.0 μm were purchased from Fibre Optic Centre Inc. (Massachusetts, USA). Carboxyl-functionalized polymer-based (benzene-ethenyl homopolymer) magnetite particles (ProMag^{TM}) of diameter 3.0 μm were purchased from Polysciences Inc. (USA). Further details of all particles are given in Table S1 of Supporting Information. Hexadecyltrimethoxysilane (HDMS) was purchased from Sigma Aldrich (Bangalore, India) and n-decane (>99%, AR grade) was obtained from Spectrochem (Mumbai, India). Decane was treated with alumina to remove polar impurities. Deionised water from a Milli-Q system (Millipore) was used for all experiments. Its resistivity was > 18.2 MΩ cm.

Methods

(a) Zeta potential and size of particle mixtures

Glass vials used in this study were silanized using HDMS. About 250 μL of HDMS was added to a glass vial and spread along the interior surfaces. After 30 min., excess HDMS was removed and the vials were rinsed thoroughly with deionised water. This treatment was used because amidine particles are known to interact with negative charges on the surface of glass and flocculate to some extent over time. In order to determine the size and charge of heteroaggregates of oppositely charged particles (OCP) in water prior to emulsification, OCP of polystyrene with diameter 0.5 μm were mixed in varying proportions. The mixed dispersions were allowed to settle for 48 hours at 25 °C. After 48 hours the vials were gently shaken before measuring the zeta potential and size of the aggregates. In this experiment, the total particle concentration was kept constant at 0.1 w/v % (~ 1.45×10^{10} particles per mL). The number fraction of positive particles in water, ϕ_p (hereafter referred to as "composition"), was varied from 0 (only negative particles) to 1 (only positive particles). The size of particle aggregates and their zeta potentials were measured with a particle size analyser (Horiba SZ-100, Japan) and Partica instrument (Horiba LA 950 V2, Japan) respectively. Samples were diluted to 0.05 w/v% before making measurements and 3-5 readings per sample were recorded. Depending on the size of the aggregates, either the Smoluchowski or Debye-Hückel approximations were used to convert measured electrophoretic mobilities to zeta potentials.

(b) Emulsion preparation and characterization

Emulsions were prepared in 5 mL glass vials treated with HDMS. The total volume of the oil plus water phase was fixed at 4 mL. OCP of the desired compositions were initially mixed in water. The required volume of decane was added and the mixture was emulsified with a vortex mixer (Remi laboratory instruments, India) at 2500 rpm for 2 min. In all experiments the emulsion type was determined using the drop test. To visualize the emulsion droplets and estimate their size distributions, about 20 μL of emulsion sample was placed on a clean glass slide and images were acquired using an inverted microscope (Leica DMI3000B, Germany) equipped with 10x, 20x and 63x objectives. Images were analysed manually with ImageJ software to acquire diameters of about 100 droplets in each sample. Photographs of glass vials were acquired using a Sony cyber shot at 12 megapixel resolution and the heights of the oil, emulsion and water phases were measured using ImageJ software. A pre-measured vial (diameter 1.1 cm) is used for calibration of the image scale. Emulsions were prepared and stored at 25 °C.

Results and Discussion

(i) Size and charge of aggregates in aqueous phase

In order to understand the nature of the particle aggregates formed in the water phase before emulsification, oppositely charged polystyrene particles of diameter 0.5 μm were mixed at different compositions ranging from purely negative to purely positive particles. In these experiments, the total particle concentration was fixed at 0.1 w/v% corresponding to ~ 1.45×10^{10} particles per mL of water phase. Figure 1 shows the glass vials of aqueous suspensions of OCP mixed at different compositions taken initially and after 48 hours. Aggregation leading to particle sedimentation was observed for ϕ_p values between 0.3 and 0.7, partial aggregation occurred at ϕ_p = 0.2 and 0.8 and no aggregation was observed at ϕ_p = 0 and 1 after 48 hr. Results of a similar experiment with oppositely charged particles of size 2.2 μm (+) and 3.0 μm (-) are given in Figures S1 (stability), S2 (zeta potentials) and S3 (sizes) of Supporting Information. Figure 2 shows the mean diameter and zeta potential of discrete particles of one type and aggregates of particle mixtures at different compositions (ϕ_P). The key observation here is that the aggregate size varies with composition, *i.e.* large aggregates of low zeta potential are observed at compositions close to $\phi_P = 0.5$ whereas small but highly charged aggregates are observed at extreme compositions. The zeta potential of the aggregates changes sign at intermediate values of ϕ_P. When particles are mixed in equal proportions almost all the particles go into the formation of aggregates thus yielding large aggregates (single cluster-forming regime).[16] However, when they are mixed at compositions where one of the particle types is deficient in the system, aggregation proceeds to a certain extent but further aggregation is limited by the availability of particles in the minority, thus leading to finite-sized aggregates (stable cluster-forming regime).[16] These finite-sized aggregates are saturated by particles in the majority and are thus charged.

(ii) Effect of composition on emulsions at fixed oil:water ratio

In understanding the properties of emulsions with OCP, one of the key variables is the composition of the OCP. Figure 3 shows the effect of varying the composition of OCP on the formation of emulsions at a fixed oil:water volume ratio of 1:1 and for a fixed total number of particles. No emulsion formation is possible at both limiting compositions, *viz.* $\phi_P = 0$ and 1. This is due to the fact that highly charged particles, be it positive or negative, face repulsive image charges as they diffuse towards the oil-water interface. Progressively, as ϕ_P increases, o/w emulsions can be formed. Emulsion formation was observed for compositions $0.1 < \phi_P < 0.9$. The volume of stable emulsion phase one hour after their preparation is found to be maximum at values of ϕ_p between 0.3 and 0.5 as shown in Figure S4 of Supporting Information. Emulsions were very stable to coalescence with negligible change in volume for more than a year. Another noticeable observation is that the water phase following emulsion creaming at intermediate compositions is much clearer compared to that at extremes of composition. These observations can be explained in the following way. Charged particles of one type alone as in the limiting cases cannot stabilize emulsions due to the image charge effect. However when OCP are mixed they form aggregates of reduced or near zero charge. These aggregates face no repulsive image charge barrier and can stabilize an emulsion. If we assume that the volume of oil emulsified depends on the number of neutral aggregates then maximum extent of emulsion formation should occur at intermediate compositions since maximum aggregation occurs here. On the other hand, at extreme compositions, since one type of particle will limit the formation of aggregates, there will be few aggregates and a large excess of charged particles remaining in water thus reducing the extent of emulsification. This is observed precisely in Figure 3, with the water phase being more turbid due to excess particles towards extreme compositions and clearer at intermediate compositions. Thus particle aggregates rather than individual charged particles themselves determine the formation of an emulsion in systems with OCP. An important point worth noting in this context is that frequently in the literature on Pickering emulsions a small amount of electrolyte like NaCl is added to screen the charge on the particles and thus facilitate their stabilisation of emulsions. In emulsions with OCP this is achieved by using the particles themselves without the need for electrolyte. Thus, this method in principle will be useful in industrial and biomedical applications where addition of extraneous agents is undesirable.

(iii) Effect of oil:water ratio on emulsion type and stability

Polystyrene latex particles are partially hydrophobic when adsorbed at the decane-water interface.[17] The contact angles of amidine polystyrene particles and sulphate polystyrene particles are around 103.1 ± 4.0° and 116.1 ± 12.3° respectively,[17] measured through the water phase. The sulphate stabilized latex particles possessing charged surface groups are known to stabilize w/o emulsions, despite originating in the water phase.[18] This is generally called anti-Bancroft type behaviour. As shown in Figure 3, the preferred emulsion type for a 1:1 mixture of OCP and an equal oil:water ratio is o/w. However, as shown in Figure 4, when the volume fraction of oil phase ϕ_o was increased to 0.8 and beyond, the system spontaneously phase inverted *via* catastrophic inversion from o/w to w/o emulsions. Since the total number of particles ($\sim 1.16 \times 10^{11}$ in the total volume of oil + water) and their composition ($\phi_p = 0.5$) are kept constant in the experiment, the only parameter that could affect the emulsion type is the oil:water ratio. The stability to coalescence of o/w emulsions decreases approaching the phase inversion. An increase in droplet diameter ranging from 105 μm ± 30 μm at $\phi_o = 0.05$ to as large as 350 μm ± 50 μm at $\phi_o = 0.4$ is observed. Thus the average droplet size is found to increase towards phase inversion. Optical microscopy images of emulsions shown in Figure 4 are given in Figure S5 of Supporting Information. The w/o emulsions after phase inversion however are stable to coalescence but experience sedimentation. These observations leads us to conclude that emulsions containing mixtures of OCP also exhibit catastrophic phase inversion beyond a certain o:w ratio allowing both emulsion types to be formed in the same chemical system. The result could be different if a different mixture of OCP is used, *e.g.* where one particle type is partially hydrophilic and the other partially hydrophobic. This possibility is not explored in the present study.

(iv) Effect of composition on droplet size for w/o and o/w emulsions

Droplet size is an important parameter in emulsion science. Its magnitude plays a crucial role in many emulsion formulations as it affects various aspects like stability[19] and rheological properties[20]. In Pickering emulsions, the droplet diameter is shown to be inversely proportional to the particle concentration in the emulsifier-poor regime. This is given by the well-known limited coalescence model.[21,22] Since OCP are shown to form both o/w as well as w/o emulsions at extreme oil:water ratios, two complementary experiments were designed to explore the effect of composition on droplet size in both these cases. In experiments shown in Figure 5 and Figure 7, a fixed total number of particles (~1.16×10^{11} corresponding to 4 w/v% in Figure 5 and 0.2 w/v% in Figure 7) was taken and the volume fraction of oil phase was fixed at 0.95 and 0.05 respectively. The composition ϕ_p of the particles was systematically varied from 0 to 1. In Figure 5, although the total particle concentration is fixed, there is a significant difference in the water droplet size of these w/o emulsions. Fine emulsion droplets are formed at intermediate compositions compared with the larger droplets at extremes of composition. The size distributions of w/o emulsion droplets are given in Figure 6. This result shows that unlike single particle systems where drop size depends only on total particle concentration, in systems of OCP it also depends on the composition ϕ_p. Thus, by using OCPs, one can in principle tune the droplet size by altering the number ratio of OCP *viz*. composition. This gives us a new handle on the control of droplet size apart from particle concentration known in conventional Pickering emulsions.

This phenomenon can be qualitatively explained in the following way. As mentioned earlier, OCP form aggregates in the water phase prior to emulsification. Only these aggregates will participate in the emulsification process due to their low charge and low image charge barrier in becoming adsorbed at the droplet interface. More effective aggregate formation occurs at intermediate compositions whereas at extreme compositions very few aggregates can form leaving a large excess of charged particles. Since these aggregates are the effective particle emulsifier, the minimum drop size should occur at intermediate concentrations and large drop size should occur as one moves towards extreme compositions as observed in Figures 5 and 6. The droplet diameters range from approximately 50 μm at intermediate compositions to large droplets approaching 1 mm at extremes of composition and several non-spherical droplets can also be observed. If both particle types are identical in all respects apart from charge type, we expect maximum aggregate formation and thus the smallest droplet size to occur at $\phi_p = 0.5$, as observed in Figure 5. It is evident from Figure 2 that this is where the size of the aggregates is the largest. The minimum in the drop size is due to the fact that the maximum number of particles is available for emulsification thus allowing the stabilisation of maximum oil-water interfacial area. A detailed discussion of the phenomenology of such systems is made in our recent work[12] where a model that extends the known limited coalescence model to such OCP systems is proposed. In this model we consider particle aggregates to be the effective emulsifiers rather than individual particles and re-derive the limited coalescence model taking into account parameters like composition and aggregate size. The estimated drop sizes using this modified model match reasonably well with the experimentally observed ones. This approach gives us two independent levers on controlling droplet sizes in Pickering emulsions *viz*. total particle concentration and composition.

Figure 7 shows a complementary experiment to that in Figure 5, where the volume fraction of oil is now only 0.05 and all emulsions formed are o/w. Emulsion formation was observed only at compositions $0.1 \leq \phi_p \leq 0.8$. It is also observed that the subnatant water phase after creaming at intermediate compositions is clearer compared to that for extremes of composition, demonstrating that irrespective of the oil:water ratio the particle composition plays a central role in determining the ability of the system to stabilize an emulsion. The major inference from the results presented in Figures 5 and 7 is that emulsion type is affected by the bias of the oil:water ratio whereas the formation of an emulsion and droplet size in both cases is affected by the composition of the particle mixture in the system. Irrespective of the volume fraction of oil, no emulsion is formed at extreme compositions, *i.e.* with pure amidine or sulphate particles, and all particles remain in the water phase even after intense agitation. This lends support to the concept of an image charge barrier to charged particles in the formation of emulsions. Figure 8 shows the microscopy images of the o/w emulsions photographed in Figure 7. The size distribution of these droplets is given in Figure S6 of Supporting Information. A similar trend of droplet size with composition as observed with w/o emulsions is also observed here, where smaller droplets are formed at intermediate compositions and larger drops at extreme compositions. It is worth noting however that the w/o emulsion droplets of Figure 5 were rather discrete and free flowing whereas those of the o/w emulsions of Figure 8 were flocculated to some extent. Macroscopically the latter had a gel-like appearance and consistency. The reason for this difference might be that in w/o emulsions no particles were present in the continuous oil phase and all the particles were present at water droplet interfaces or dispersed within the water phase of the droplets. Here there is no possibility to form any network-like structure of particles which would result in an increase in the viscosity of the oil phase. By contrast, in o/w emulsions, excess particles if any were present in the continuous water phase where they could form a network increasing the effective viscosity of the water phase trapping oil droplets within thus giving a gel-like consistency.

(v) Combined effect of pH and composition on emulsions

Figure 9 demonstrates the combined effect of both pH and composition on the stability of o/w emulsions stabilised by polystyrene latex particles. In this experiment a total of 49 samples were prepared corresponding to a pH of the water phase ranging from 2 to 12 and compositions ϕ_p ranging from 0 to 1. The oil:water ratio is kept at 1:1 by volume. In each case the heights of the supernatant oil phase (h_{oil}), emulsion phase ($h_{emulsion}$) and subnatant water phase (h_{water}) were measured from the photographs one hour after preparation and the fraction of each phase with respect to the total height (h_{total}) was calculated. Figures 9(a), 9(b) and 9(c) represent the fraction of supernatant oil, emulsion and subnatant water phase respectively. The contour plots shown are plotted from a smooth interpolation of experimentally measured values from 49 samples. Systems containing sulphate polystyrene particles alone (ϕ_p = 0) are rather insensitive to pH over the entire range (Figure S8) and did not yield emulsions at any pH whereas those containing amidine polystyrene particles alone (ϕ_p = 1) yielded stable emulsions only at a high pH of 12 but not at low pH. The reason for this difference is that sulphate latex particles are charged at all pH values whereas amidine latex particles are amphoteric (pK ≈ 10-11), see Figure S8. The charge on the latter particles is positive at low pH values but as pH increases the charge on the particles comes close to zero at high pH values.[23] Thus at high pH these amidine latex particles flocculate and are capable of stabilizing emulsions alone. At intermediate compositions irrespective of pH o/w emulsions were obtained. However the volume fraction of emulsion phase varied as shown in Figure 9(b). This indicates that aggregates of low charge (near electroneutral) or zero charge facilitate adsorption of particles to the interface and hence promote emulsion stabilization.

(vi) Particle arrangement on emulsion droplet interfaces

In this section we briefly discuss the arrangement of particles on the interfaces of stable emulsion droplets containing OCP. Since the literature on the use of OCP to stabilize emulsions is very scant, to the best of our knowledge the present work attempts to yield information on interfacial particle arrangement using OCP for the first time. As shown in Figure 10 and Figure S7, monolayer-like and close packed arrangement of particles on water drop surfaces in oil is observed with particle combinations of two or more types. In this figure, the surfaces of w/o emulsion drops stabilized by (a) a mixture of partially hydrophobic latex particles, (b) magnetic and non-magnetic particles and (c) a mixture of partially hydrophobic latex and partially hydrophilic silica particles are shown. When a mixture of partially hydrophobic and partially hydrophilic particles form w/o emulsions, the emulsion drops appear to be stabilized by a layer of particles that appear segregated across the interface. In Figure 10(c) it is observed that silica particles (white) being hydrophilic are more into the water phase and polystyrene particles (slight black) being hydrophobic are protruding outward into the oil phase, *i.e*. seen sitting above the silica particle layer. This statement is based on observations using the optical microscope in that when the drop surface was bought into focus, latex particles being on the top first came into focus followed by silica particles. It can also be seen that the silica particles are repulsive with each other whereas the latex particles are less repulsive and form small clusters. The emulsion drop shown in Figure 10(b) obtained using magnetic and non-magnetic particles opens opportunities for the fabrication of field-responsive emulsions. Figure 10(d) shows a further extension of this strategy to obtain multi-particle-stabilized Pickering emulsions using a combination of three types of particle. Figure 10 illustrates the formation of particle-stabilized emulsions using OCP of different sizes and wettability. Although we have not studied emulsions containing all these mixtures in detail, those formed at optimum ϕ_p were stable to coalescence for over a year, even in mixtures containing relatively large particles (9 μm).

Bright field optical microscopy used to image the microstructure of the drop surface at the length scale of single particles (Figure 10) clearly demonstrates the presence of reasonably close-packed layers of particles on drop surfaces. Since particle aggregates are present in the aqueous phase prior to emulsification, this leads us to conclude that structural rearrangements occur as the aggregates reach the drop surface. In the absence of such structural changes, one would expect particle aggregates residing at the oil-water interface. It was also argued previously by one of us that the wetting of the aggregates may differ from that of individual particles leading to emulsification when oppositely charged particles are used.[10] The authors in that study concluded that low surface charge and a sufficiently hydrophobic nature of the aggregates formed due to heteroaggregation facilitating the formation of particle-stabilized emulsions. The attachment and rearrangement of particle aggregates is a complex process involving several steps including aggregate formation in bulk, diffusion/convective transport of these aggregates to newly formed droplet surfaces during emulsification, shear-induced breakage of these aggregates during emulsification and finally rearrangement of aggregates once attached to the interface. It also involves several forces *viz*. attractive columbic forces leading to particle aggregation in bulk water and image charge and capillary forces as the aggregates approach and finally enter the interface. The transport and attachment of aggregates pre-existing in the water phase to the oil-water interface and further rearrangement that occur at the interface is a very fast process. As it occurs during turbulent emulsification process, it is difficult to visualize such processes in-situ. However, we use the following argument based on adsorption energy to show that such rearrangements are energetically feasible.

Consider a large single rigid particle (of the same size as a particle aggregate), there can be no further vertical movement as the particle adsorption is irreversible and the interfacial position of the particle is determined by its contact angle. However, aggregates as those formed by mixing OCPs being a collection of smaller particles held together by electrostatic forces has a possibility to reconfigure itself in such a way that the overall adsorption energy (more specifically, free energy) is minimized. From our previous work[12], the radius of a spherical aggregate containing x smaller particles each of radius a is given by

$$\Rightarrow \mathrm{R}_{\mathrm{X}}^{agg} = \mathrm{a}\sqrt[3]{\mathrm{X}(1+\rho)} \qquad (1)$$

where R_X^{agg} is the radius of the aggregate, ρ is the voidage of particles in an aggregate, typical value is 0.26 for hexagonal close packing of spherical particles. Similarly, the cross-sectional area of such an aggregate (area that it replaces when it sits at the interface) is

$$\mathrm{A}_{\mathrm{X}}^{agg} = \pi \mathrm{a}^2[\mathrm{X}(1+\rho)]^{\frac{2}{3}} \qquad (2)$$

Thermodynamically, adsorption free energy is directly proportional to area that particles/aggregates replace by sitting at the interface. Here we should ask the following question: is it more favorable for the aggregate to remain as a sphere and remain at the interface or is it more favorable if it gets deformed/flattened as much as possible until all the particles spread out as a monolayer? This can be answered by comparing the adsorption free energies of aggregate and individual particles.

For an aggregate, free energy of adsorption

$$\Delta E_{agg} = \gamma_{ow}[A_X^{agg}] = \gamma_{ow}[\pi a^2[(1+\rho)X]^{\frac{2}{3}}] \qquad (3)$$

where γ_{ow} is the interfacial tension of the oil-water interface. If all the x particles were to spread out as a monolayer the free energy change will be

$$\Delta E_X = X\gamma_{ow}\pi a^2 \qquad (4)$$

It can be seen that for any value of x > 2, $\Delta E_X > \Delta E_X^{agg}$. Therefore from a thermodynamic view point, this suggests that once at the interface it is much more favorable for particle in an aggregate to spread out as monolayer (and contribute more towards the lowering of free energy) than to stay as an aggregate. Though the experimental validation of above mentioned arguments is difficult at this point, results of the experiments presented in Figure 10 and Figure S7 help us in exploring the possibility of using them as templates for the fabrication of colloidal superstructures like colloidosomes of specific structure and functionality. We plan to study particle arrangement around droplets using different coloured particles of opposite charge using confocal laser scanning microscopy to understand this aspect more explicitly.

Conclusions

We have demonstrated that mixtures of OCP of polystyrene latex give rise to stable emulsions and offer a good control on the emulsion properties. The size of emulsion drops can be tuned by varying the mixing ratio of the OCP, and the surface morphology (texture) of the emulsion surface can be tuned by using particles of different sizes and different functionality. An inversion of the type of emulsion is observed when the oil:water ratio is progressively changed. Using OCP, Pickering emulsions are stabilized by a close-packed monolayer of particles at the oil-water interface formed due to rearrangement of aggregates of oppositely charged particles formed initially in water. The structure of OCP-stabilized emulsions depends on the interactions between the charged particles and the size and shape of the aggregates. The use of oppositely charged particles in this context seems to be quite general and is expected to work with a multitude of particle combinations. This flexibility can be exploited to create emulsions and their material derivatives for potential applications in diverse fields ranging from material science, biology, agriculture and pharmaceuticals. This approach of using OCP as a lever in controlling the surface morphology of droplets/colloidosomes will prove to be particularly useful in designing heterogeneous/designer colloidal macrostructures.

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ASSOCIATED CONTENT

Supporting Information. Characterization details of particles used in this study, heteroaggregation, size and zeta potential of mixtures of 2.2 μm and 3 μm particle mixtures, graph representing volume fraction of emulsion phase, representative microscopy images of emulsion droplets formed during phase inversion experiment, droplet size distributions of o/w emulsions and surface morphology of emulsion droplets, zeta potentials of amidine and sulphate particles. This material is available free of charge *via* the Internet at http://pubs.acs.org.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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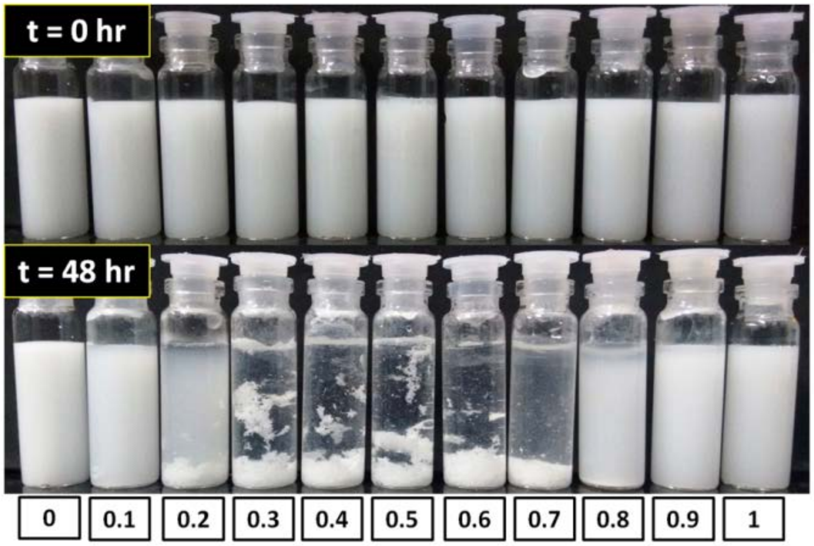


Figure 1. Aggregation of aqueous dispersions of oppositely charged polystyrene latex particles (diameter 0.5 μm) mixed at various compositions, ϕ_p (given), initially and after 48 hr. The total concentration of particles was 0.1 w/v% (≈ 1.45×10^{10} particles/mL) and pH = 7.

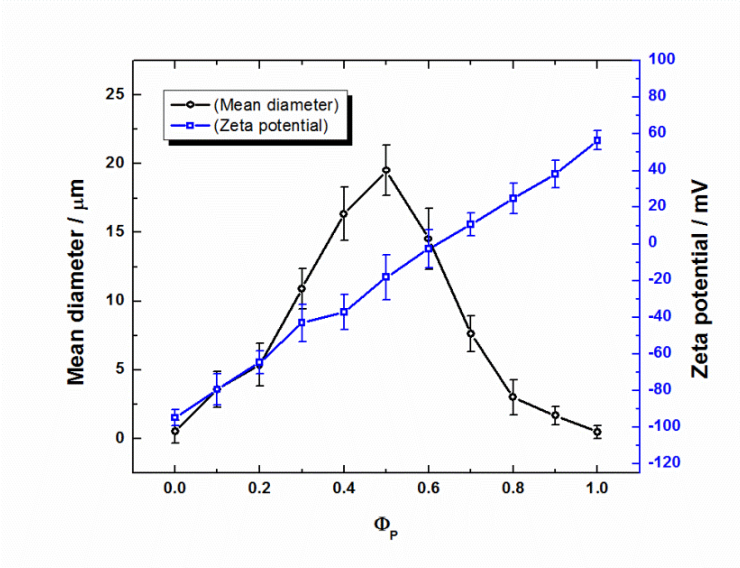


Figure 2. Mean diameter (circles) and zeta potential (squares) of aqueous mixtures of oppositely charged polystyrene latex particles (diameter 0.5 μm) 48 hr after preparation at 25 °C. Aggregates formed at intermediate compositions have relatively low charge compared with aggregates at extreme compositions. Larger aggregates were observed at intermediate compositions compared to extreme compositions, pH = 7.

Figure 3. Effect of composition (ϕ_p) of OCP on formation of decane-in-water (1:1) emulsions one hour after preparation. Residual emulsions were stable for more than 1 year. Cationic and anionic polystyrene latex particles of diameter 0.5 μm were mixed at a total particle concentration of 0.4 w/v% ($\approx 5.8\times10^{10}$ particles per mL of water phase). Emulsions were only observed at intermediate compositions ($0.1 < \phi_p < 0.9$) with no emulsion formed at extreme compositions. Some coalesced or non-emulsified oil is present above emulsions at intermediate ϕ_p. pH = 7.

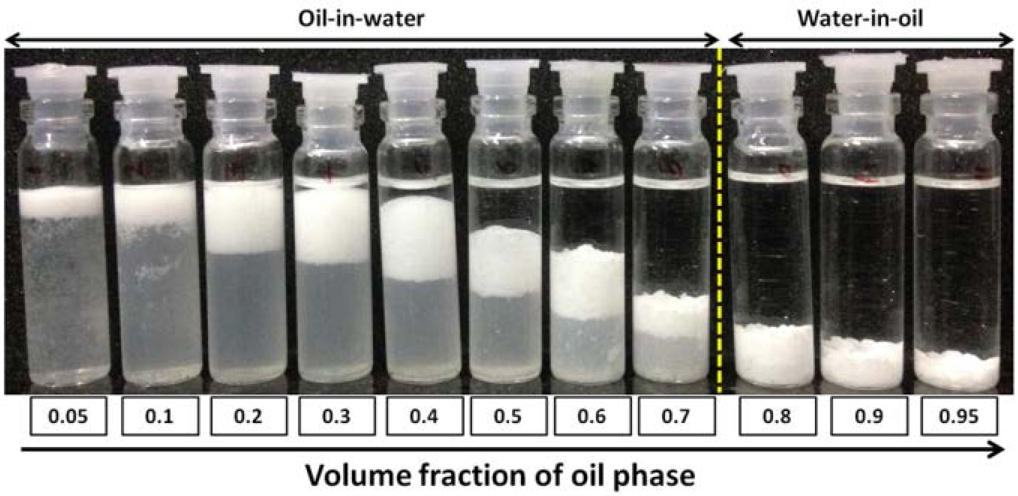


Figure 4. Effect of oil:water ratio on the type and appearance of decane-water emulsions stabilized by OCP of polystyrene latex particles of diameter 0.5 μm mixed in a 1:1 ratio ($\phi_p = 0.5$) at a fixed total particle number of ≈ 1.16×10^{11}. Catastrophic phase inversion occurs for a volume fraction of oil ≥ 0.8, pH = 7.

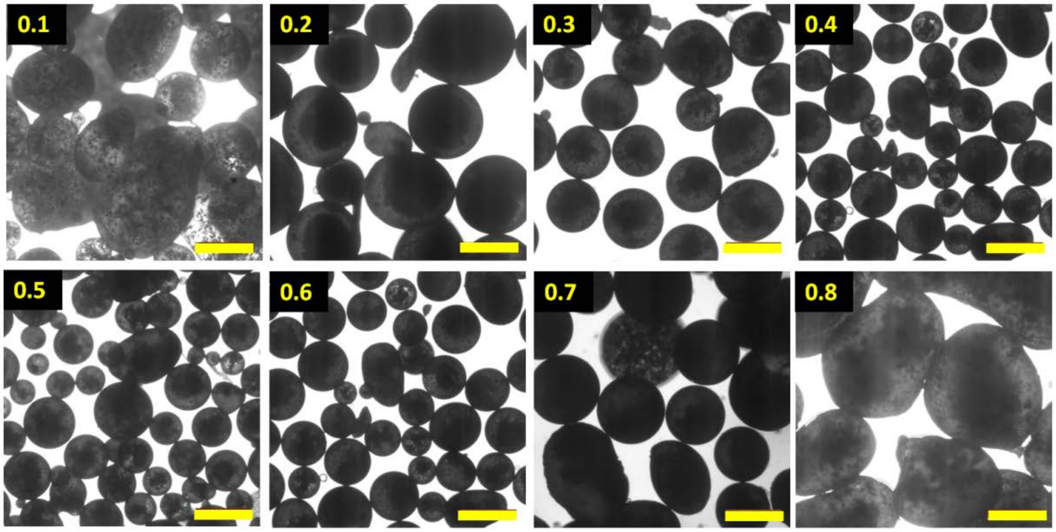


Figure 5. Optical microscopy images of w/o emulsion droplets formed at various compositions, ϕ_p (given) for emulsions prepared with ϕ_o = 0.95 and stabilized by OCP of polystyrene latex particles of diameter 0.5 μm and total particle concentration being 5.8x10^{11} per mL of aqueous phase, pH = 7. Droplets look rather dark as the drop interior contains excess latex particles that did not participate in emulsification. Scale bar = 200 μm. A systematic change in droplet size can be observed ranging from small at intermediate compositions to large droplets at extreme compositions.

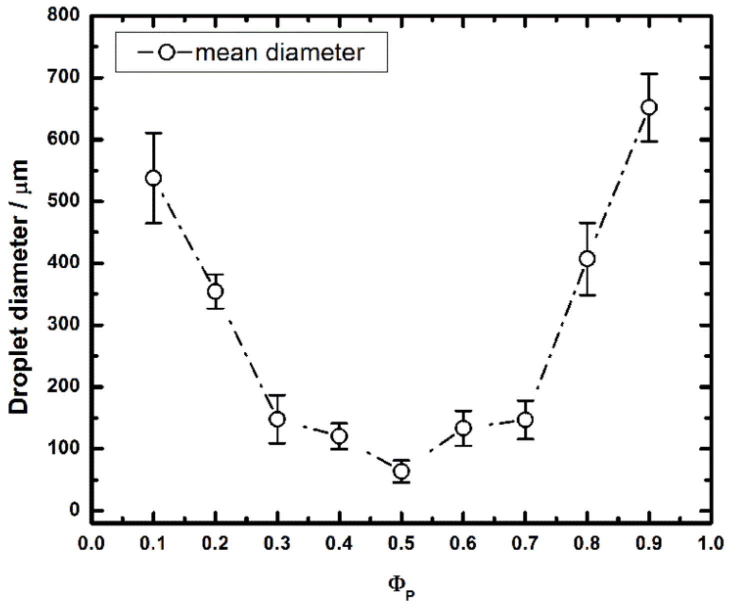


Figure 6. Variation of average droplet diameter of w/o emulsions shown in Figure 5 with ϕ_p. Error bars represent standard deviation.

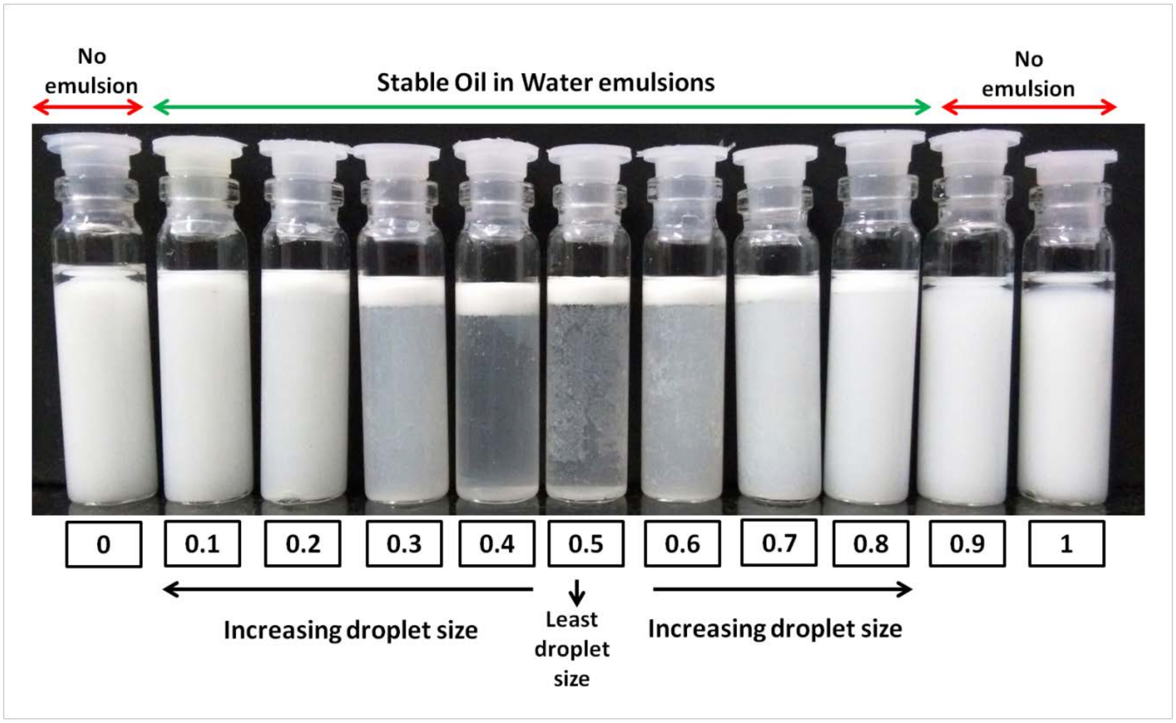


Figure 7. Effect of composition (ϕ_p) of OCP of polystyrene latex particles of diameter 0.5 μm on appearance of o/w emulsions soon after preparation. ϕ_o = 0.05 and total particle concentration = 0.2 w/v% of water phase, pH = 7.

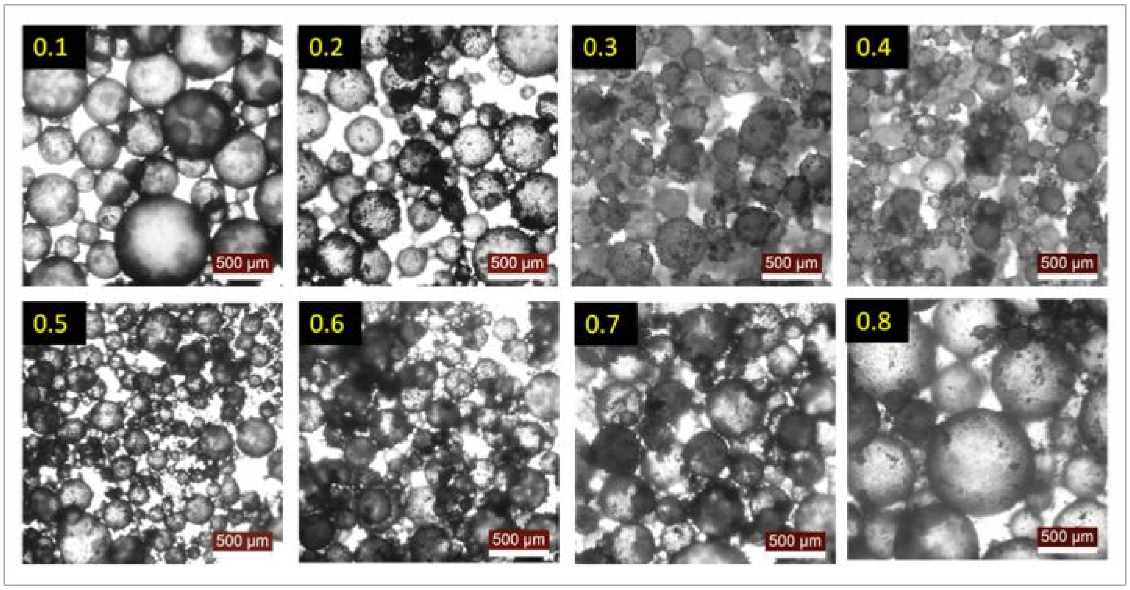
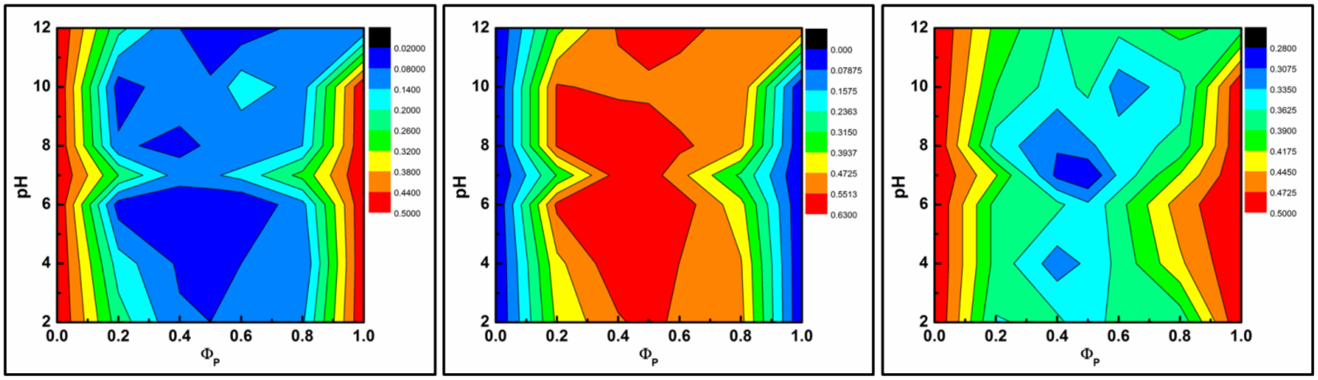


Figure 8. Optical microscopy images of o/w emulsion droplets at various compositions ϕ_p (given) formed in vials shown in Figure 7. These droplets are more transparent compared to those of w/o emulsions (Figure 5) because excess particles are present outside the droplets in the continuous water phase. Scale bar = 500 μm, pH = 7.



(a) (b) (c)

Figure 9. Combined effect of pH and composition (ϕ_p) on the stability of o/w emulsions stabilized by OCP of polystyrene latex particles of diameter 0.5 µm. The oil:water ratio is 1:1 and the total particle concentration is fixed at 5.8×10^{11} particles per mL of water phase. Volume fraction (colour coded key) of (a) supernatant oil phase, (b) emulsion phase and (c) subnatant water phase 1 hr after emulsion preparation. This data was obtained by preparing 49 emulsion samples corresponding to combinations of pH (2, 4, 6, 7, 8, 10, 12) and composition ϕ_p (0, 0.2, 0.4, 0.5, 0.6, 0.8, 1). Zeta potentials of pure amidine and sulphate particles used are given in Figure S8.

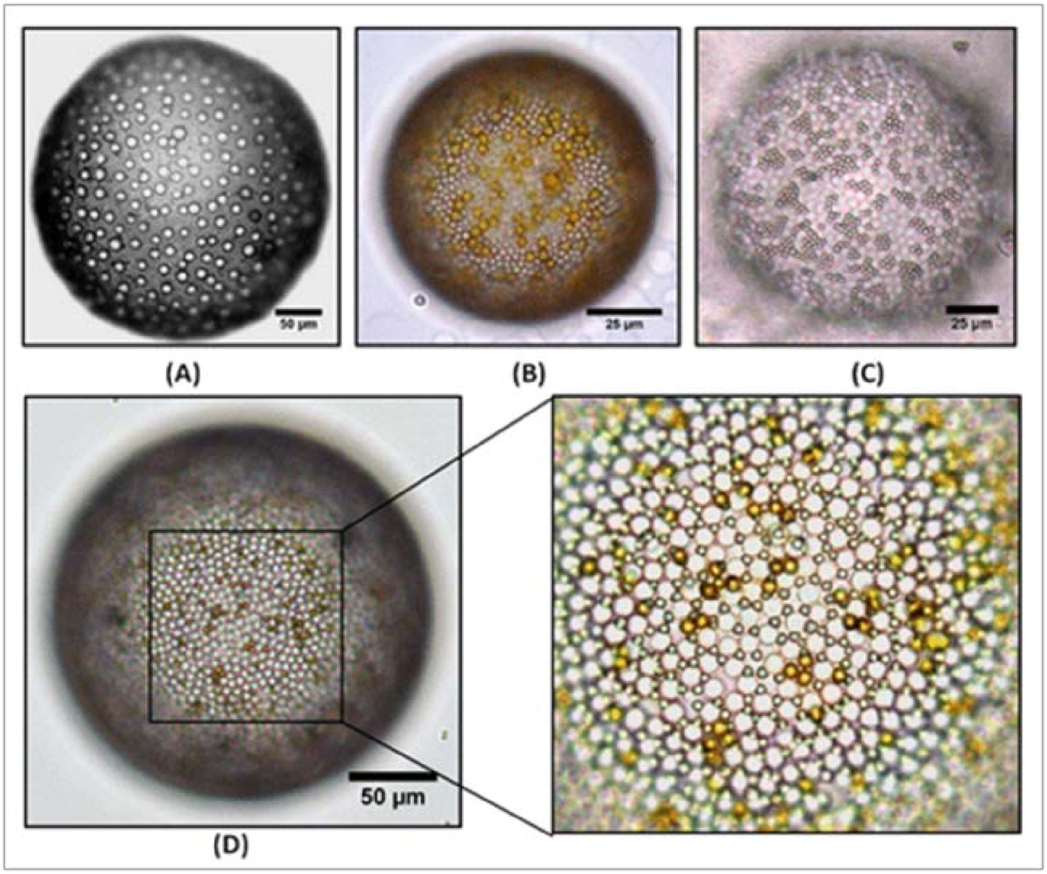


Figure 10. Bright field optical microscopy images of the surface morphology of w/o emulsion drops stabilized by different combinations of OCP. (a) 2.2 µm (+) and 9 µm (-) polystyrene-polystyrene particles, an example of partially hydrophobic–partially hydrophobic combination, (B) 2.2 µm (+) and 3 µm (-) polystyrene-magnetic polymer particles, an example of non-magnetic–magnetic combination, (C) 2.2 µm (+) and 4 µm (-) polystyrene-silica particles, an example of partially hydrophobic–partially hydrophilic combination and (D) 2.2 µm (+) polystyrene, 4 µm (-) silica and 3 µm (-) magnetic polymer particles, an example of a three component particle system with partially hydrophobic–partially hydrophilic-magnetic combination. ϕ_o = 0.9 and the ratio of positive:negative particles used is (A) 17:1, (B) 1:1, (C) 1:1 and (D) 2:1:1 respectively. In (A) the larger 9 µm particles (visible) are separated by smaller 2.2 µm particles (not so clearly visible). A magnified image of this droplet surface clearly showing the particle arrangement is given in Figure S7(e).

Table of Contents Graphic (TOC)