ACS APPLIED MATERIALS & INTERFACES

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In Situ Assembly of Hydrophilic and Hydrophobic Nanoparticles at Oil−Water Interfaces as a Versatile Strategy To Form Stable Emulsions

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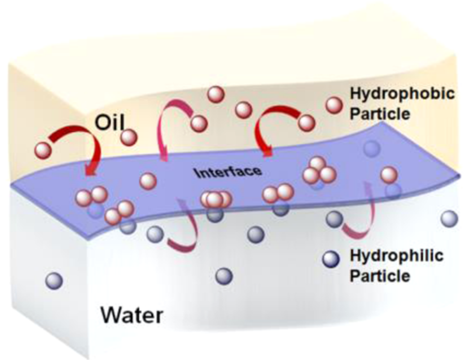
Ⓢ *Supporting Information*

ABSTRACT: We report a conceptually new strategy for forming particle-stabilized emulsions. We begin with stable, dilute suspensions of highly hydrophilic nanoparticles in water and hydrophobic nanoparticles in oil. When the two suspensions are mixed, attractive interactions between the hydrophilic and hydrophobic particles cause them to assemble at the oil−water interfaces into partially wettable or Janus-like clusters that effectively stabilize emulsions. By tuning the ratio of hydrophilic to hydrophobic particles in the clusters, both water-in-oil as well as oil-in-water emulsions can be formed. The van der Waals interaction energy between two particle types across an aqueous−organic interface provide a systematic guide to particle and liquid combinations that can form stable emulsions using our strategy, or identify when emulsions will not form. Our experiments and analysis provide a new platform for the formation of particle-stabilized emulsions and can be used to combine particles of different functionalities at emulsion droplet surfaces for generating novel materials.



KEYWORDS: *particle-stabilized emulsion, in situ particle cluster assembly, van der Waals interaction, particle aggregates*

Emulsions stabilized solely by particles located at liquid−liquid interfaces were first reported over 100 years ago by Ramsden[1] and by Pickering.[2] The energy of detachment, ΔE, for a spherical particle (aspherical particles require even greater energy/mass for detachment than spheres[3,4]) from a liquid−liquid interface into either bulk phase, is given by

$$\Delta E = \pi R^2 \gamma_{ow} (1 - |\cos\theta|)^2 \tag{1}$$

Here, R is particle radius, γ_{ow} is oil−water interfacial tension, and θ is contact angle through either phase. For a typical oil−water interfacial tension of 35 mN/m and $R = 10$ nm, $\Delta E > 500$ kT for $55° < \theta < 125°$. Particles with these contact angles are partially wettable in both phases, and would lodge preferentially and irreversibly at oil−water interfaces, helping stabilize emulsion droplets.[5,6] One consequence of this partial wettability is that these particles will have a tendency to agglomerate or form a network in whichever phase they are suspended in. Individual nanoparticles can stay suspended because their Brownian motion dominates over sedimentation. However, agglomeration often causes particles to sediment, whereas network formation results in a large increase of the zero shear viscosity,[3,7] making it difficult to mix with another low viscosity phase. Unless the particles are kinetically stabilized, sustaining a homogeneous dispersion of individual partially wettable particles requires an input of energy up to the time a second immiscible liquid is added to form an emulsion. In addition, emulsions stabilized by specific particles are sometimes desired, but this becomes difficult because of an inability to modify the particle's wettability. Alternate methods are then required. In this paper, we describe a conceptually new strategy for creating a particle-stabilized emulsion that relies on in situ assembly of fully wettable particles at liquid−liquid interfaces to create partially wettable complexes or Janus-like clusters that can stabilize emulsions. This concept can be applied to a broad range of particles, opening up the possibility of making emulsions and materials that have unique functionalities.

Control experiments are performed first. Toluene is mixed into a stable aqueous hydrophilic particle suspension, or water is mixed into a stable toluene suspension containing hydrophobic particles. The particles in water are either hydrophilically modified carbon black or spherical iron oxide, while those in toluene are either hydrophobically modified fumed or spherical silica. The particle concentrations are 0.015%w/w or 0.035%w/w, matching those used in subsequent experiments. Because the particles are either too hydrophilic or too hydrophobic to lodge at oil−water interfaces, we get the expected result that the aqueous and organic phases separate rapidly and completely after mixing, and emulsions are not

Received: July 29, 2015
Accepted: September 15, 2015
Published: September 15, 2015

DOI: 10.1021/acsami.5b06940
ACS Appl. Mater. Interfaces 2015, 7, 21010−21014

formed. This happens at all proportions of the aqueous to oil phase.

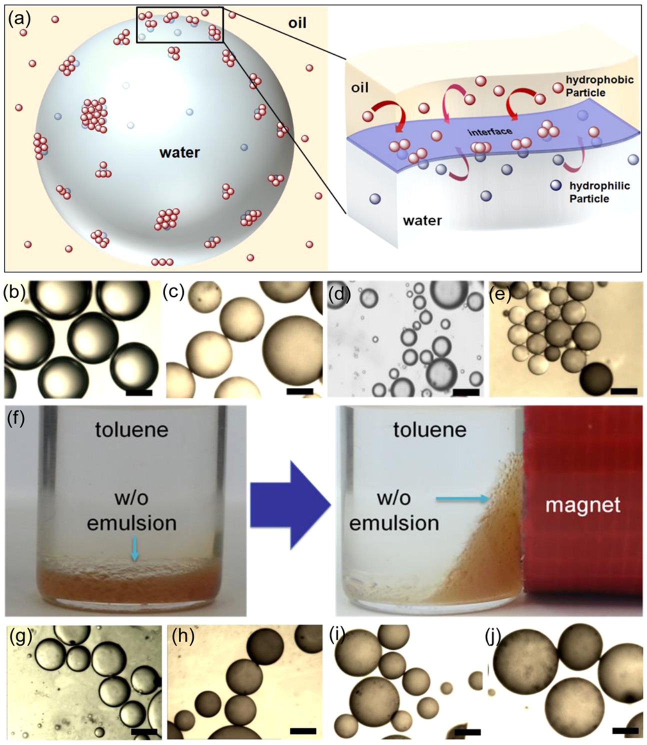


Figure 1. (a) Illustration of emulsion stabilization by fully hydrophilic and fully hydrophobic particles forming clusters at the oil—water interface. (b) Water—in—toluene emulsion formed by mixing a hydrophilic 0.015%w/w CB suspension in water with a 0.015%w/w hydrophobic fumed silica suspension in toluene, at a 3:7 volume ratio; (c) toluene-in-water emulsion formed by these particles when the aqueous suspension to toluene suspension volume ratio is 7:3. Emulsions stabilized by spherical hydrophilic iron oxide particles and spherical hydrophobic silica particles; the suspension concentrations are 0.015% w/w. (d) Water in-toluene emulsion when the volume ratio of aqueous suspension to toluene suspension is 3:7; (e) toluene-in-water emulsion formed when that suspension volume ratio is 7:3; (f) the emulsion formed in d under the influence of a magnetic field. Emulsions formed by mixing equal volumes of aqueous and toluene suspensions. (g) Water-in-toluene emulsion formed by mixing 0.015% w/w of hydrophilic carbon black in water with 0.035%w/w hydrophobic fumed silica in toluene; (h) toluene-in-water emulsion formed by mixing a 0.035% w/w hydrophilic carbon black suspension in water and 0.015% w/w hydrophobic fumed silica suspension in toluene; (i) a water-in-toluene emulsion formed when a 0.015% w/w hydrophilic spherical iron oxide particle suspension is mixed with a 0.035% w/w hydrophobic spherical silica suspension in toluene. (j) a toluene-in-water emulsion formed when a 0.035% w/w hydrophilic iron oxide suspension is mixed with a 0.015% w/w hydrophobic silica suspension in toluene. Scale bars are 100 μm.

Figure 1a shows the proposed in situ assembly route for hydrophilic and hydrophobic particles at oil—water interfaces to form partially wettable or Janus-like clusters that can stabilize emulsions. The average wettability of particle aggregates will determine whether an oil-in-water or a water-in-oil emulsion is formed.[3] For a given set of particles, this can be tuned by varying the proportion of hydrophobic to hydrophilic particles assembling at the interface into a local aggregate. If the particle concentrations in each of the suspensions are fixed, the volume ratio of the suspensions will directly impact the hydrophobic/hydrophilic balance of the particle clusters. We performed experiments using this rationale. Figure 1b shows optical micrographs of a water-in-toluene emulsion formed by mixing a 0.015%w/w carbon black suspension in water with a 0.015%w/w fumed silica suspension in toluene at a volume ratio of 3:7. When this volume ratio is changed to 7:3, a toluene-in-water emulsion is formed, shown in Figure 1c. To demonstrate the versatility of this technique, we have used 10 nm spherical iron oxide particles suspended in water at 0.015%w/w and 80 nm hydrophobically modified spherical silica particles suspended in toluene at 0.015%w/w, and formed a water-in-toluene emulsion when these are mixed at a 3:7 volume ratio, as shown in Figure 1d. When the volume ratio of the aqueous to the oil phase is changed to 7:3 for this set of suspensions, a toluene-in-water emulsion is formed, shown in Figure 1e. In Figure 1f, we show that emulsion droplets stabilized by iron oxide and silica can be mobilized using magnets.

To eliminate the possibility that it is only the volume ratio of water to oil that determines the type of emulsion formed, we mixed aqueous- and toluene-based suspensions at equal volumes, but the particle concentrations in each suspension were changed to either 0.015% w/w or 0.035% w/w, resulting in net hydrophilic to hydrophobic particle mass ratios of either 3:7 or 7:3. Both fractal and spherical particle suspensions were examined. A water-in-oil emulsion is formed when the proportion of the hydrophobic particles is larger (Figure 1g, i), whereas an oil in-water emulsion is formed when that proportion is lower (Figure 1h, j). All the emulsions shown in Figure 1 remain stable for several months.

We note here that a conversion of mass ratios to net particle volume ratios, using the densities of the particles, will still result in the dominance of one of the types of particles in the aggregate as their proportions are changed from 3:7 to 7:3.

Figure 2a shows a cryo-SEM image of a toluene drop stabilized by hydrophobic fumed silica and hydrophilic carbon black particles. The fracture plane is magnified in Figure 2b. The layer of fumed silica particles is visible in the bottom left, while the CB particles covering the fumed silica layer is visible on the upper right. The CB and fumed silica particles bind at the toluene-water interface to form Janus-like clusters that stabilize the emulsion. Figure 2c is a cryo-SEM image of an oil drop stabilized by 80 nm spherical hydrophobic silica and 10 nm spherical hydrophilic iron oxide particles. Figure 2d is a magnified image showing silica and iron oxide particles forming clusters at the oil—water interface. Both these entities can successfully stabilize emulsions.

Emulsions formed by mixing equal volumes of carbon black and fumed silica suspensions with either 3:7 or 7:3 ratios of particle concentrations are deposited on a TEM grid, and the particles at the toluene-water interfaces are imaged. Figure 2e, f shows aggregates that have a proportion of CB to fumed silica that agrees qualitatively with their concentrations in the suspensions.

We provide a rationale for these experimental observations next. Following previous work,[8−12] we obtain an expression for the van der Waals energy of interaction between two particles through two immiscible liquids. As the distance between particles becomes small compared to the particle dimensions, we ignore particle curvature, and model the system as two semi-infinite flat plates interacting across two immiscible liquids, shown in the inset of Figure 3a. The van der Waals energy/area U of a particle P1 in a medium M1 interacting with a particle

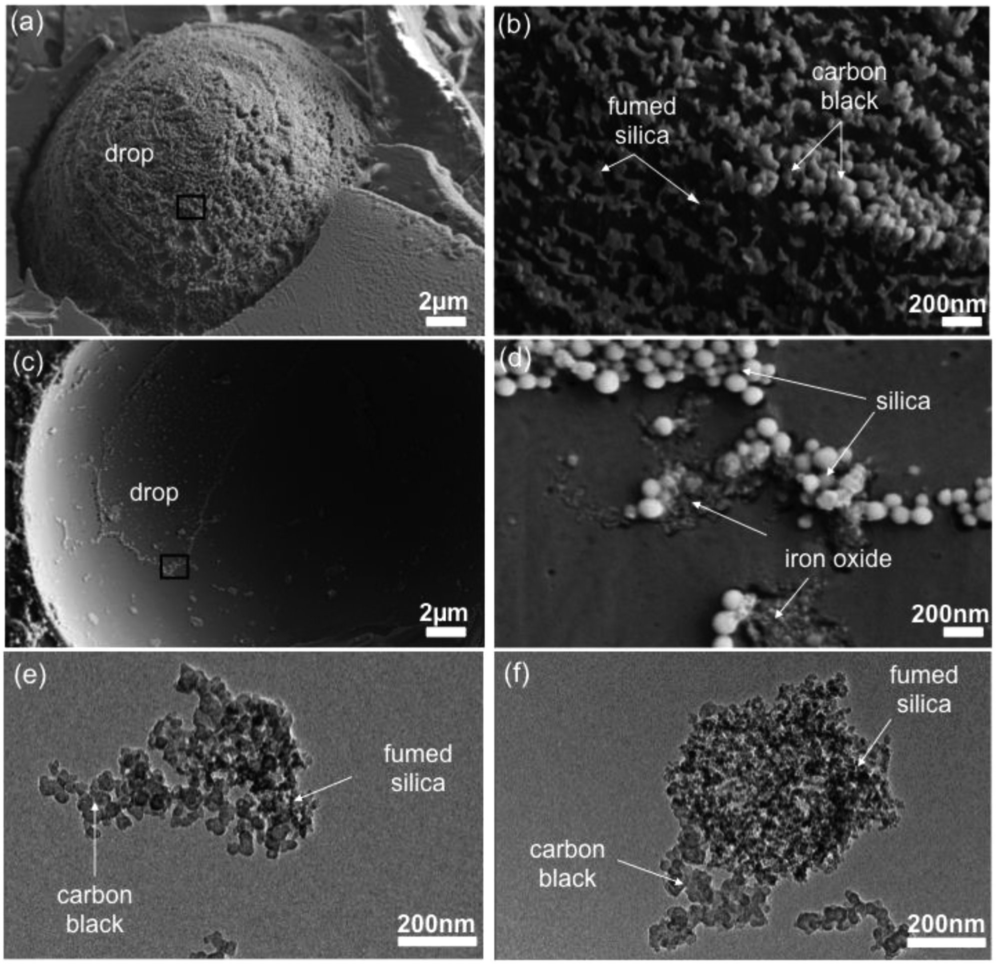


Figure 2. Cryo SEM images of (a) a toluene drop stabilized by carbon black (CB) and fumed silica particles; (b) the region identified by the black rectangle in a is magnified. A Janus-like cluster is visible; the CB particles are on top of the fumed silica particles. (c) Toluene drop with spherical silica–spherical iron oxide particles at the interface; (d) the region marked by the black rectangle in c is magnified. The toluene–water interface shows silica–iron oxide clusters. TEM images of carbon black- fumed silica aggregates formed by mixing suspensions, depositing the resulting emulsion on a grid, then imaging from the "interface" region of a drop. The fumed silica has smaller primary particles, and appears darker than the CB particles. (e) Larger proportion of CB is visible in the aggregate when equal volumes of 0.035%w/w CB and 0.015%w/w fumed silica suspensions are mixed; (f) smaller proportion of CB in the aggregate when the suspensions had 0.015% w/w CB and 0.035% w/w fumed silica.

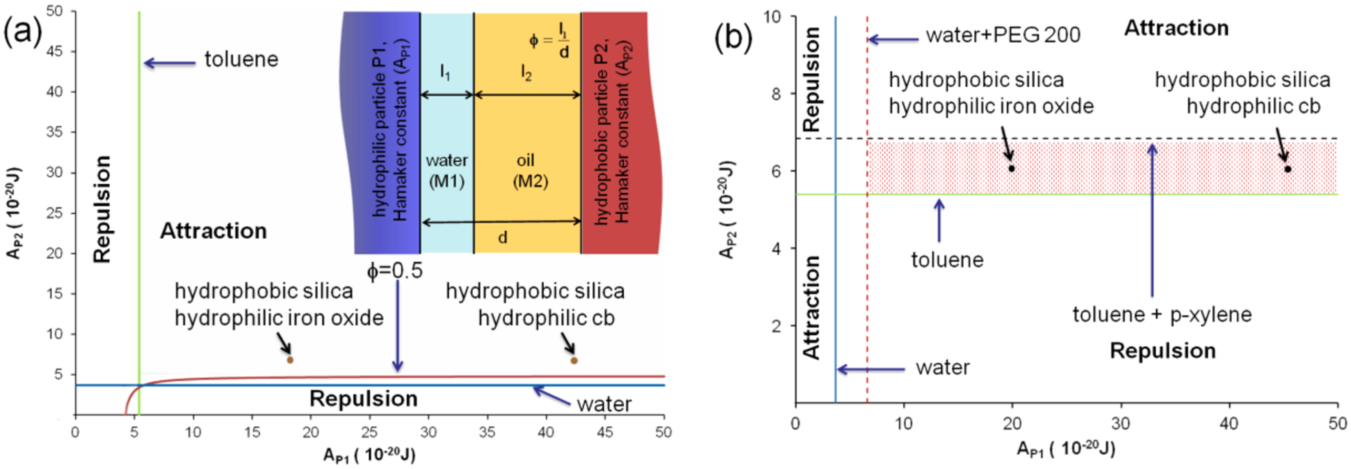


Figure 3. Range of Hamaker constants of particles P1 and P2 that will show attractive and repulsive interactions across water–toluene interfaces. (a) Locus of $U = 0$ for only water as the medium, only toluene as the medium and for $\phi = 0.5$. The Hamaker constants of the particles used in our experiments are shown. These particles will interact attractively across the water–toluene interfaces. (b) Locus of $U = 0$ for water, toluene, water +80% w/w PEG 200 and toluene +90% w/w *p*-xylene as the two immiscible media, for $\phi = 0$ and $\phi = 1$. When particle Hamaker constants lie in the shaded region, the interparticle interactions are repulsive.

P2 in medium M2 across a M1−M2 interface can be approximated by

$$-U = \frac{1}{12\pi(\Phi d)^2}(A_{P1}^{1/2} - A_{M1}^{1/2})(A_{M2}^{1/2} - A_{M1}^{1/2}) + \frac{1}{12\pi(1-\Phi)^2 d^2}(A_{P2}^{1/2} - A_{M2}^{1/2})(A_{M1}^{1/2} - A_{M2}^{1/2}) + \frac{1}{12\pi d^2}(A_{P1}^{1/2} - A_{M1}^{1/2})(A_{P2}^{1/2} - A_{M2}^{1/2}) \qquad (2)$$

where A_i is the Hamaker constant of material 'i', d is the distance between the two particles, and ϕ is the fraction of the distance d occupied by M1. $U < 0$ implies attractive interactions between P1 and P2. In our experiments, P1 is either hydrophilically modified carbon black ($A_{\text{carbon black}} = 4.7 \times 10^{-19}$ J,[8,13]) or iron oxide ($A_{\text{iron oxide}} = 2.1 \times 10^{-19}$ J[8]), whereas P2 is hydrophobically modified silica ($A_{\text{silica}} = 6.2 \times 10^{-20}$ J,[14]). We chose water as M1 ($A_{\text{water}} = 3.7 \times 10^{-20}$ J,[8,14]). Toluene is selected as M2 because it has a Hamaker constant in the high range for oils ($A_{\text{toluene}} = 5.4 \times 10^{-20}$ J,[14]), and can dissolve *p*-xylene, a high Hamaker constant solute ($A_{p\text{-xylene}} = 7.0 \times 10^{-20}$ J,[8]). We note that the surface layer on each type of particle, that modifies its wettability, will modulate the interparticle interaction energy, but that effect is small compared to the energy of interaction between P1 and P2.[8] The energy of interaction, U, calculated from eq 2, at an interparticle separation distance of 0.1 nm, or contact, $U \approx -30$ kT/nm^2. Thus, there is a significant attractive van der Waals interparticle interaction energy under these conditions.

We show lines for $U = 0$ at $\phi = 0$, corresponding to only toluene as medium, $\phi = 1$, corresponding to only water as medium, and $\phi = 0.5$ in Figure 3a, and indicate the range of particle Hamaker constants where P1 and P2 will undergo either attractive or repulsive interactions. We hypothesize that emulsions can form if the hydrophobic and hydrophilic particles interact attractively across oil−water interfaces, so that they assemble into partially wettable or Janus-like clusters. As a general rule of thumb, this will happen if both media between the particles have Hamaker constants that are either above or below that of P1 and P2. We identify points on this plot that correspond to the properties of the particles and liquids we have used in our experiments. They are all in the regions where the interparticle interaction is attractive. Such particle−liquid combinations indeed produce emulsions, as we have reported. The interparticle van der Waals energy at $d = 0.1$ nm, taken as "contact", is at least 1 order of magnitude higher than the thermal energy kT.[15] Once assembled, these particle clusters will not break up spontaneously.

If the Hamaker constants of M1 and M2 are intermediate between A_{P1} and A_{P2}, P1 and P2 would interact repulsively. In Figure 3b we show the consequence of making the aqueous phase 80% v/v PEG 200 ($A_{\text{PEG}} = 7.5 \times 10^{-20}$J[14]), and the toluene phase 90% v/v *p*-xylene,[16] raising the Hamaker constants of the aqueous and oil phases to 6.63×10^{-20} J and 6.85×10^{-20} J, respectively, above that of silica, but below that of either carbon or iron oxide. Our particles now lie in a region where the interparticle van der Waals interactions are repulsive. When 0.015% w/w or 0.035% w/w suspensions of the hydrophilic and hydrophobic particles in an 80% v/v PEG 200 solution in water and a 90% v/v *p*-xylene solution in toluene are mixed at any volume ratio, emulsion are not formed, consistent with the predictions.

Because the particles are charged under some conditions, several other interactions between particles or between particles and the oil−water interface are considered next.[17,18] The energy of repulsion between the negatively charged CB particles and the negatively charged oil−water interface at $d = 0.1$ nm is ~0.03 kT/nm^2 (eq S1), much smaller than the attractive van der Waaals energy.[19−23] Hence, electrostatic repulsion between the charged particles and the charged oil−water interface, which would retard the transport of particles to the interface, can be ignored. The interaction energy of a charged particle in an aqueous phase with its image charge in an oil phase is repulsive,[23] and is also several orders magnitude smaller than the van der Waals energy (eqs S2 and S3). The charge−induced-dipole interaction is much longer range and weaker than the van der Waals interaction,[24] as is the interaction energy of a charged particle in the oil phase with particles in the aqueous phase,[24] and thus have not been considered.

There is no added salt in the aqueous phase, so charge screening is not expected to induce lateral aggregation of particles.[25] The deformation of the oil−water interfaces by particle clusters[3] can induce lateral aggregation, but that is only a secondary effect in our experiments—the clusters must be formed first by forces that act orthogonal to the oil−water interfaces. Our experimental results and analyses strongly suggest that it is indeed interparticle van der Waals interactions between hydrophobic and hydrophilic particles that dominates the interaction between these particles and eventually determines if a partially wettable or Janus-like cluster can form to stabilize an emulsion.

In summary, we have demonstrated that when suspensions of completely hydrophilic particles in water and hydrophobic particles in toluene are mixed, attractive van der Waals interactions between these two types of particles can cause them to assemble into clusters at the oil−water interfaces that are partially wettable in both phases. These clusters are very effective at stabilizing emulsions. By tuning the proportions of each type of particle, both, water-in-oil and oil-in-water emulsions can be formed. The range of particles and liquids that will form emulsions in this way are guided by calculations of van der Waals interaction between a hydrophilic and hydrophobic particle across an oil−water interface. This strategy for forming particle-stabilized emulsions provides a versatile platform for developing new materials, with functionalities that are dictated by the types of particles forming the emulsion.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b06940.

Experimental details including preparation of emulsions and their characterization; interaction energy calculations for particles near oil−water interface (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Gulf of Mexico Research Initiative and 'a University of Rhode Island Graduate Fellowship to A.S. We gratefully acknowledge discussions on van der Waals interactions with Dr. Ashutosh Sharma.

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