Pickering Emulsions - A Paradigm Shift

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1. Introduction

Emulsions stabilized by solid particles are known as Pickering emulsions. Although Pickering emulsions are encountered in various natural and industrial processes such as crude oil recovery, oil separation, cosmetic preparation, and waste water treatment, the underlying phenomena are poorly understood. Recently, there is an increasing interest in Pickering emulsions because they open new avenues of emulsion stabilization.

Pickering emulsions, composed of droplets of one immiscible liquid in another liquid stabilized by solid particles, were discovered almost a century ago.[1] In addition to increasing possibilities for practical applications, Pickering emulsions also provide a new and convenient experimental model system for investigating solid particles at liquid-liquid interfaces.[2,3] The advantages of using Pickering emulsions include, (i) a Pickering emulsion generates a well-defined three-phase system that provides opportunities to evaluate the multiphase interactions of nanoparticles; (ii) a Pickering emulsion is formed by self-assembly of solid particles at the emulsion interface; thus, the self-assembled structure directly reflects the balance between attractive and repulsive forces between the particles; (iii) the confinement at the interface restricts the 3D Brownian movement, and makes it more convenient for direct visualization of particle diffusion at the 2D; (iv) easily changeable interfacial properties such as curvature, tension, and rheology.

In our work, using confocal microscopy and environmental transmission microscopy (E-TEM), we have studied the structure of self-assembled microparticles and dodecanethiol-capped silver nanoparticles at Pickering emulsion interfaces. Monodisperse polystyrene particles were found to aggregate and form small patches at the polydimethylsiloxane/water emulsion interface with local "hexagonal" order. Polystyrene particles with different sizes (1 μm and 4 μm) and, intriguingly, different wettability (hydrophobic and hydrophilic) could simultaneously aggregate to the emulsion interface and form mixtures on it. In contrast, the dodecanethiol-capped silver nanoparticles (1-5 nm) formed randomly distributed multilayers at the trichloroethylene/water interface with an inter-particle distance varying from close contact to approximately 25 nm. Our work, to the best of our knowledge, offers the first work revealing the detailed self-assembled structure of nanoparticles at a liquid/liquid interface when the size of the nanoparticles is comparable to the molecular dimension of the liquids.

Finally, we have used Pickering emulsions as a model system to investigate the particle mobility at the two-dimensional level. Remarkably, the rate of diffusion of the colloidal-sized polystyrene particles at the oil (5 cSt.)-water interface is only moderately slower than in the bulk water phase. The diffusion constant of solid particles is significantly reduced by increasing the viscosity of the oil phase. Furthermore, we successfully observed the in-situ structural formation of solid particles at the oil-water interface, which may have important implications on the stabilization and subsequent destabilization of the emulsion.

2. Experimental Section

2.1 Materials: The polydimethylsiloxane (Rhodorsil® Fluid, viscosity of 5 - 350 cSt. at 25°C) was purchased from Rhodia. Water (HPLC grade, residue after evaporation < 1 ppm) and trichloroethylene (certified A.C.S. grade) were purchased from Fisher Scientific. The interfacial tension of the oil-water, measured using a Krüss K100 Tensiometer, varied from 40.4 mN/m to 42.7 mN/m when using polydimethylsiloxane oils with different viscosities (5-350 cSt.). The microparticles are FluoSphere® fluorescent polystyrene microspheres from Molecular Probes. In our investigation, we included sulfate-treated polystyrene particles of 1.1 ± 0.026 μm and 4 ± 0.14 μm (hydrophobic, fluorescent excitation/emission wavelengths of 505/515 nm, average surface charge densities of 5.176×10^{-2} C/m^2 and 5.486×10^{-2} C/m^2, respectively) and carboxylate-treated polystyrene particles of 1 ± 0.032 μm (hydrophilic, fluorescent excitation/emission wavelengths of 540/560 nm, average surface charge density of 2.496×10^{-1} C/m^2). The density of the polystyrene particles, 1.055 g/cm^3, is fairly close to those of water and oil and minimizes the gravity effect in the experiments. The dodecanethiol-capped silver nanoparticles are synthesized and size selected following well-established wet-chemistry methods.[4,5]

2.2 Emulsion Preparation: The Pickering emulsions containing surface treated polystyrene solid particles and dodecanethiol-capped silver nanoparticles were prepared using an ultrasonic processor, Sonics VibraCell, 500 watt model.

2.3 Characterization Techniques: A confocal laser scanning microscope, Olympus FV 300, was used to obtain detailed information on the assembled solid arrays, the mobility, and in-situ structural formation of solid particles at the polydimethylsiloxane-water interface under ambient conditions (with a typical temperature of 22 °C). The possible effect of droplet rotation and fluctuation has been carefully addressed.[3] Also, we used the sequential scanning technique to differentiate the simultaneously assembled sulfate- and carboxylate-treated polystyrene particles, by exciting one fluorescent species at a time. We performed post-image analysis using ImageJ® from NIH Image.

Pickering emulsions containing dodecanethiol-capped silver nanoparticles were imaged using both a laser scanning confocal microscope and an environmental transmission electron microscope (E-TEM), the Tecnai-20 FEG with upgraded environmental capability. Since this was the first time that the E-TEM technique is used to image nanoparticles in a liquid medium, the experimental procedure is described briefly: a small droplet of the Pickering emulsion was placed on a thin carbon film (in a well) supported by a copper grid, sealed with another thin carbon film, and quickly transferred to the microscope column. The droplet was kept from drying by making the observation under 2-4 Torr of water vapor pressure. The effect of the electron beam on drying was reduced by recording images quickly and operating the microscope at low magnifications and low beam currents. The focused droplets remain good for imaging for 10-15 minutes.

3. Results and Discussion

3.1 Self-assembly of Microparticles

Figure 1 shows a three-dimensional (3D) fluorescent image of a stationary droplet of a polydimethylsiloxane (oil)-in-water Pickering emulsion containing sulfate-treated (hydrophobic) polystyrene particles. The oil-water interface is only partially covered with solid particles, although there are excess particles in the water phase. At the oil-water interface, the particles form small patches with local hexagonal order; these domains were separated by other particle-free domains.[6] Because of the relatively low surface concentration of the solid particles (~ 0.46) at the oil-water interface, the aggregation of particles and formation of islands are likely due to the diffusion-limited cluster aggregation (DLCA), which is analogous to colloidal suspensions.[7] However, it is intriguing to observe the local "hexagonal" order within the clusters and from the force-distance profiles, the electrostatic repulsion is responsible for this ordering.[6]

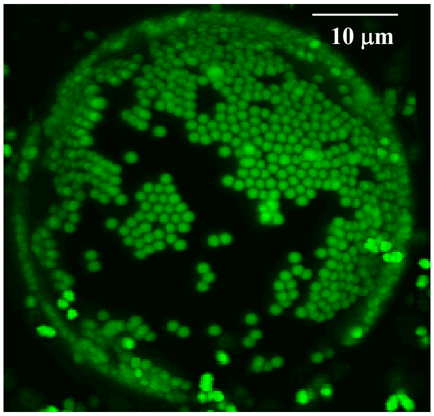

Figure 1. A fluorescent 3D image of a PDMS-in-water Pickering emulsion droplet.

Pickering emulsions also provide a new template for heterogeneous self-assembly of solids.[6] Figure 2 shows a mixture of the sulfate-treated polystyrene particles with different sizes (1 μm and 4 μm in diameter) simultaneously assembled at the oil-water interface from the equal bulk concentration of 0.15% by weight of each particle type in the liquid phase. It appears that the inclusion of 4 micron solid particles

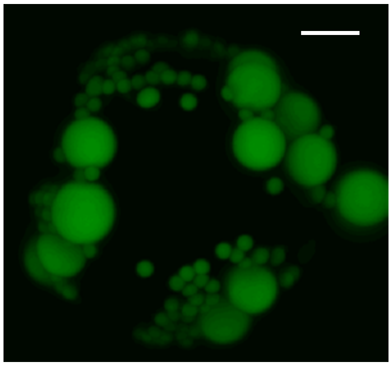

Figure 2. Heterogeneous Self-assembly of particles with diameters of 1 μm and 4μm at the oil-water interface. The scale bar is 5 μm.

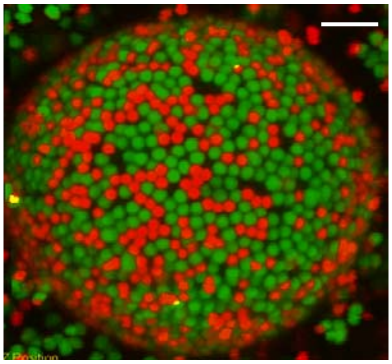

Figure 3. Simultaneously self-assembly of hydrophobic (green) and hydrophilic (red) particles with diameters of 1 μm. The scale bar is 5 μm.

destroys the ordered packing. The wettability of solid particles in Pickering emulsions has been reported as a key controlling factor, with hydrophilic particles tending to stabilize oil-in-water Pickering emulsions and hydrophobic particles tending to stabilize water-in-oil Pickering emulsions.[8,9] In a most intriguing result, Figure 3 shows the sequential scanning result of a three-dimensional (3D) fluorescent image of an polydimethylsiloxane (oil)-in-water Pickering emulsion droplet containing both hydrophobic (in green) and hydrophilic (in red) polystyrene particles of 1 micron. We hypothesize that this is due to the amphiphilic nature of the oil-water interface.

3.2 Self-assembly of Nanoparticles

Figure 4a shows a differential interference contrast (DIC) image of a trichloroethylene-in-water Pickering emulsion containing dodecanethiol-capped silver nanoparticles (1-5 nm) observed by the confocal microscope.[10] The wide droplet size distribution is evident and it is worthwhile to note that the image is in focus and the blur of the emulsion droplet edges is due to the resolution limit of the confocal

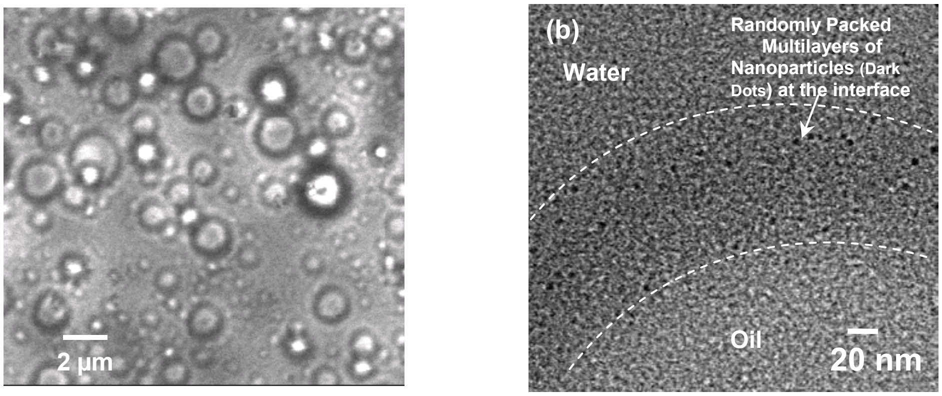

Figure 4. A trichloroethylene-in-water Pickering emulsion containing dodecanethiol -capped silver nanoparticles (1-5 nm) imaged using (a) confocal microscopy in the differential interference contrast mode and (b) E-TEM, showing details at the interface.

microscope. This limitation was overcome by using an environmental transmission electron microscope (E-TEM), which allows the imaging of hydrated materials in their natural states with a high resolution.[11] A portion of a droplet is shown in Figure 4b (a color print may be needed to illustrate effect), where the interface is abundant with nanoparticles which form randomly distributed multilayers. Possible explanations for the multilayers are the variable inter-particle distance (0-25 nm) between the nanoparticles, suggesting an imbalance of attractive and repulsive forces, and a "large" interface (~ 85 nm) compared to the size of the nanoparticles.[10]

3.3 Mobility and In-situ Aggregation of Microparticles

Figure 5 plots the mean square displacement, $<r^2>$, as a function of time $<t>$ for a single charged polystyrene particle at the oil (5 cSt.)-water interface as well as for a charged polystyrene particle dispersed in water.[4] Displacement was recorded every second. The mean square displacement was calculated by following the movement of the particles in each frame. The insert in Figure 5b is the trajectory of particle movement. The ambient diffusion constant, calculated from the particle dispersed in water and from $<r^2> = 4Dt$ (although the particle was moving three-dimensionally, we only recorded the two-dimensional trajectories), is 2.8×10^{-9} $\mathrm{cm^2/s}$. This value is reasonably close to the value, 4.4×10^{-9} $\mathrm{cm^2/s}$ calculated from the Stoke-Einstein

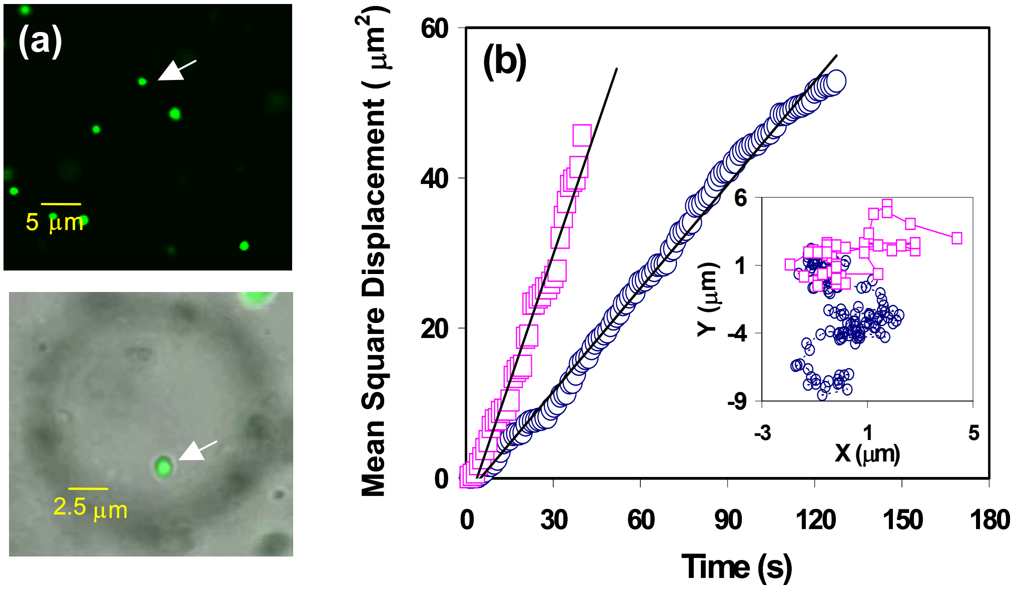

Figure 5. A fluorescent image (top) of polystyrene particle dispersed in water and an overlay of a fluorescent image and a differential interference contrast image (bottom) of a polystyrene particle at the oil-water interface; the arrows point to the particles analyzed in part b, (b) Mean square displacement of the particle dispersed in (water squares) and particle at the oil/water interface (circles). The solid lines represent the linear regression lines. The insert is the trajectory of particle movement; the time between each point is 1 second. The initial positions were set to be at (0,0).

relationship, D = kT/6$\pi\eta$a, where k is the Boltzman constant, η is the viscosity of the medium, and a is the radius of the particle. The comparable values support the hypothesis of the applicability of the Stoke-Einstein relationship to electrically charged particles.[13] In addition to the dispersed particle in water, we also quantified the diffusion for the single particle at the oil-water interface in Figure 1. Remarkably, the ambient diffusion constant of the particle at the oil-water interface ($D_{\text{at oil-water interface}} = 1.1 \times 10^{-9}$ cm^2/s) is only moderately smaller compared to that in the bulk. This suggests that the Brownian motion of charged solid particles at the two-dimensional oil-water interface is surprisingly fast.

We have changed the viscosity of the oil phase and found that it has a significant influence on the diffusion of charged solid particles at the oil-water interface, as shown in Figure 6.[3] The ambient diffusion constant drops rapidly from 1.1×10^{-9} cm^2/s to 2.1×10^{-11} cm^2/s by increasing the viscosity of the oil phase to 350 cSt. By comparing with the values calculated from the Stoke-Einstein relationship (the dashed line in Figure 6) if the particles were dispersed in the bulk oil phase, our work suggests that the hindrance of the diffusivity at the liquid-liquid interface is significantly influenced by the characteristics of the phase with higher viscosity. We performed experiments on both the oil-in-water type and water-in-oil type Pickering emulsions; the emulsion type seems to have a minor influence on particle diffusion in these systems.

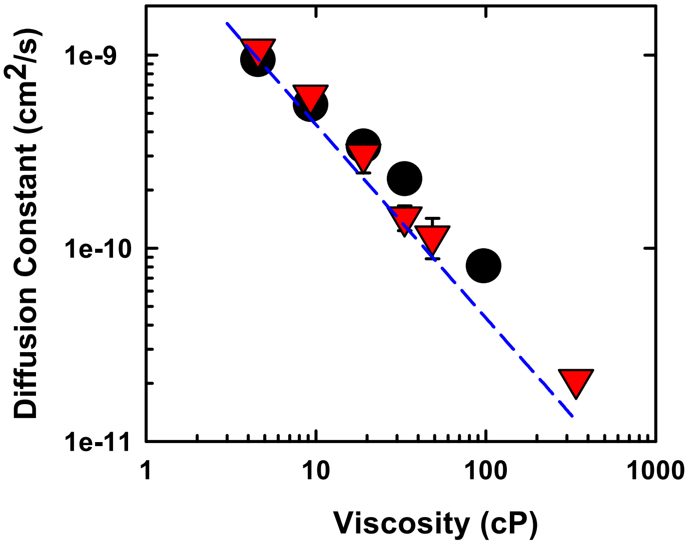

Figure 6. Effect of Polydimethylsiloxane (oil) viscosity on the diffusion constant of single polystyrene particles at the interface in oil-in-water (triangles) and water-in-oil type (circles) Pickering emulsions. The dashed line is calculated based on the Stokes-Einstein relationship if the particles were dispersed in oil phase.

Aggregation and structural formation of solid particles in two dimensions are of tremendous interest and important to various processes. Figure 7 shows an example of in-situ structural formation of polystyrene particles at the oil (20 cSt.)-water interface.[3] Since every collision of the particles at the oil-water interface leads to aggregation of particles, the observed structural formation is likely due to diffusion-limited cluster aggregation (DLCA).[7,13] Also, there was no noticeable structural change after 56 seconds. This phenomenon of in-situ structural formation may have important implications in the stabilization and subsequent destabilization of the emulsions.

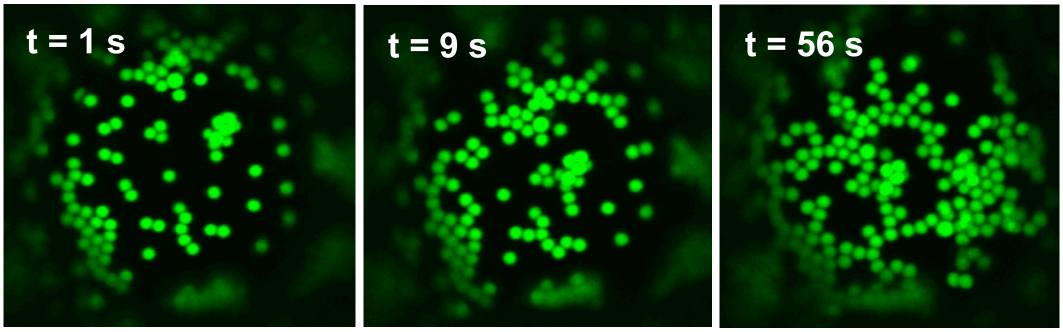

Figure 7. In-situ structural formation of polystyrene particles of 1 micron at polydimethylsiloxane (20 cSt.)-water interface. The scale bar is 4 μm.

4. Conclusions

Using confocal laser scanning microscopy, we have studied the assembly of colloidal-sized polystyrene particles and alkanethiol-capped silver nanoparticles in Pickering emulsions. The polystyrene particles, when included in the emulsions at low concentrations, were found to form small patches with local hexagonal order, separated by other particle-free domains. Also, polystyrene particles with different sizes and different wettability (hydrophobic and hydrophilic) could simultaneously aggregate to the emulsion interface. The dodecanethiol-capped silver nanoparticles (1-5 nm) at formed randomly distributed multilayers at the liquid/liquid interface, in contrast to the monolayer observed for colloidal-sized polystyrene particles. Finally, we used Pickering emulsion as a template to study the particle mobility at the two-dimensional level. The rate of diffusion of the colloidal-sized polystyrene particles at the oil (5 cSt.)-water interface is only moderately slower than in the bulk water phase. The diffusion constant of solid particles is significantly reduced by increasing the viscosity of the oil phase. In addition we successfully observed the in-situ structural formation of solid particles at the oil-water interface.

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