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Supracolloidal Structures through Liquid-Liquid Interface Driven Assembly and Polymerization

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Summary: Solid particles can adhere to liquid-liquid interfaces. When emulsion droplets are stabilized in such a way one speaks of a Pickering emulsion. The supracolloidal structures formed by this interface driven assembly process can be referred to as colloidosomes. Herein we explain the concept of colloidosome formation, their deformation behavior upon evaporation of their inner phase. Moreover, we describe Pickering miniemulsion and suspension polymerization processes, both yielding armored raspberry-type core-shell composite polymer particles.

Keywords: colloids; emulsions; Pickering; polymerization; self-assembly

Manipulation of materials in order to build useful structures has always fascinated mankind. When you start from a bulk material you can shape it either by carving or etching, or via molding. These shaped objects can then be used as building blocks to subsequently form more complex materials, made via assembly of the individual parts. The preparation of the building blocks follows a *top-down* approach. This method of producing materials can become complex if the targeted object and individual building blocks become small, *i.e.* of micro- or nano-sized dimensions. Interest is small materials was initiated by a fascinating lecture given by physicist Richard Feynman in 1959 entitled "*There is plenty of room at the bottom*" in which he addressed the problem of manipulating and controlling things on a tiny scale, with the example of printing the entire 24 volumes of Encyclopedia Britannica on the head of a pin.

An alternative approach to produce miniature building blocks, is referred to as *bottom-up*, and has great potential. In this, the individual building blocks are synthesized via chemical procedures. This can be a complex task in itself, but the real challenge comes from arranging these individual components into the desired suprastructure. The latter process is referred to as assembly, and there are two ways to achieve this, either directed or spontaneous.

Our interest lies in methods of assembling nano- and micron-sized colloids into more complex supracolloidal structures. The most intuitive way of arranging these building blocks is to be able to physically move them via micromanipulation. In 1986 Ashkin *et al.* showed that light could be used to trap and move particles, a technique referred to as optical tweezers.[1] With holographic optical tweezer arrays it is possible to manipulate and order multiple particles at the same time.[2] Electric fields can be used for on-chip manipulation and assembly of colloidal particles, as recently reviewed by Velev and Bhatt.[3] Winkleman *et al.* showed that 100 μm glass microspheres could assemble into ordered arrays on patterned electrodes under the influence of an applied electric field.[4] Electrodeposition of latexes has been used for years in the coatings industry.[5] Convective flow can be used to assemble colloids into highly ordered lattices, thereby producing photonic crystals.[6] Van Blaaderen showed that uniform FCC crystals can be formed from simple gravity deposition of microspheres on an underlying perforated substrate having a

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hexagonal arrangement of particle-sized holes.[7] Capillary forces can be used to guide directed assembly of objects/colloids. Whitesides demonstrated the mesoscale assembly of hexagonal disks at the interface of water and perfluorodecalin. By altering which sides of the disks were hydrophilic or hydrophobic, control of the self-assembly process driven by capillarity was gained. This resulted in a number of different suprastructures.[8] In this manuscript we will focus on the ability of solid particles to adhere to a liquid-liquid interface.

Pickering Stabilization and Emulsions

The first person to describe that solid particles could adhere to a liquid-liquid interface thereby stabilizing emulsions was Pickering in 1907.[9] Hildebrand *et al.*[10] suggested that the reason for this was that the particles were partially wettable by the two phases involved. Moreover, they postulated that water-in-oil emulsions would be produced when the angle of contact of the interface with the solid exceeded 90°, whereas oil-in- water emulsions would form for angles lower than 90°. Pieranski demonstrated by solely taking into account interfacial tensions that micronsized polystyrene spheres at the water-air interface are in essence trapped in a surface energy well.[11]

When we take a polystyrene latex particle of 100 nm radius we can vary its z-direction with respect to a flat interface of water (phase 1) and hexadecane (phase 2) (see Figure 1).

The particles position with respect to the interface and relative to the centre of the sphere can be expressed as a dimensionless number, z_0:

$$z_0 = \frac{z}{R}$$

The following energy contributions can be derived when taking into account the three interfacial tensions, σ_{P1}, σ_{P2} and σ_{21} and the respective areas (See Figure 1):

$$\begin{aligned} E_{P1} &= \sigma_{P1} 2\pi R^2 (1 + z_0) \\ E_{P2} &= \sigma_{P2} 2\pi R^2 (1 - z_0) \\ E_{21} &= -\sigma_{21} \pi R^2 (1 - z_0^2) \end{aligned}$$

Taking the sum of these provides the total energy the system experiences, made dimensionless by taking its ratio with the thermal energy k_BT:

$$\begin{aligned} E_0 &= \frac{E_{P1} + E_{P2} + E_{21}}{k_B T} \\ &= \left[\frac{\pi R^2 \sigma_{21}}{k_B T}\right] \\ &\quad \times [z_0^2 + 2(a-b)z_0 + 2a + 2b - 1] \end{aligned}$$

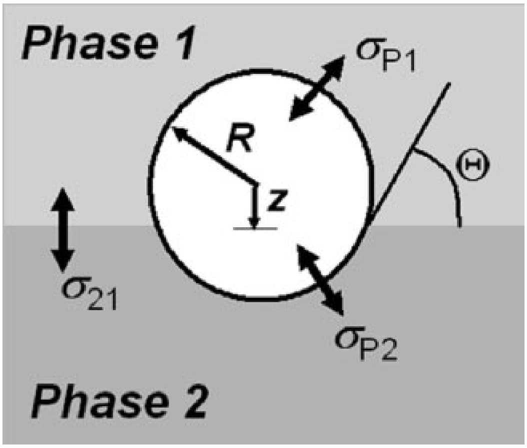

Figure 1.
Model for sphere sitting on flat interface based on capillary forces.

with a and b being:

$$a = \frac{\sigma_{P1}}{\sigma_{21}} \quad b = \frac{\sigma_{P2}}{\sigma_{21}}$$

As can be observed the result is a simple quadratic expression giving a parabola with a minimum energy for a certain value of z_0. This will be the equilibrium position for the particle:

$$\frac{dE_0}{dz_0} = 2z_0 + 2(a-b) = 0$$
$$z_0^{\min} = b - a$$

When $z_0^{\min}$ has a value larger or equal than 1, the particle will be completely in phase 1 (water). For values lower or equal than -1, the particle will be completely in phase 2 (hexadecane). Only for values of $z_0^{\min}$ in between -1 and 1, the particle will adhere to the interface.

Imagine the particle adheres to the interface and we would like to pull it off. The energy it will take to remove the particle from the interface and re-enter it into either phase 1 (water) or phase 2 (hexadecane) can be calculated from:

$$\Delta E_1 = E_0(z_0 = 1) - E_0(z_0 = b - a)$$
$$\Delta E_2 = E_0(z_0 = -1) - E_0(z_0 = b - a)$$

For our polystyrene sphere with a radius 100 nm realistic values for the three interfacial tensions, σ_{P1}, σ_{P2} and σ_{21} are 32, 14.6 and 53.5 mJ m^{-2} respectively. The results are shown in Figure 2.

From Figure 2 it can be seen that the particle is more submerged into phase 2, which is the hexadecane phase. This is logical as the interfacial tension between the polystyrene and hexadecane, *i.e.* $\sigma_{P2} =$ 14.6 mJ m^{-2} is lower than the interfacial tension between polystyrene and water, i.e. $\sigma_{P1} = 32$ mJ m^{-2}. The energy barriers enter the particle into either bulk phase have values in the order of $10^5 k_BT$, which means that the particle is essentially irreversibly trapped at the interface and cannot leave via simple Brownian motion. This means that we can use a liquid-liquid, or a liquid-air, interface as a tool to assemble colloidal building blocks. Based on the above one can imagine that emulsions stabilized by

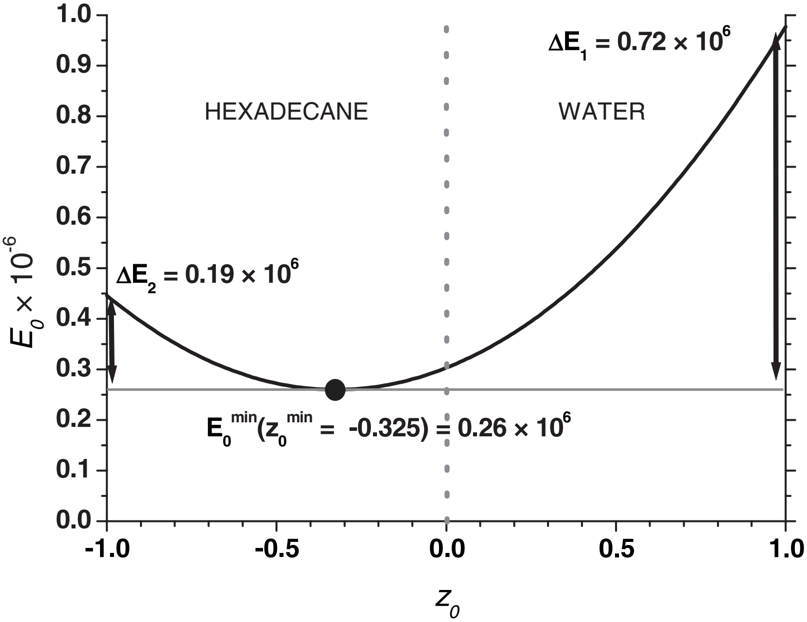

Figure 2.
Energy profile of a spherical polystyrene particle with a radius of 100 nm at a flat water-hexadecane interface.

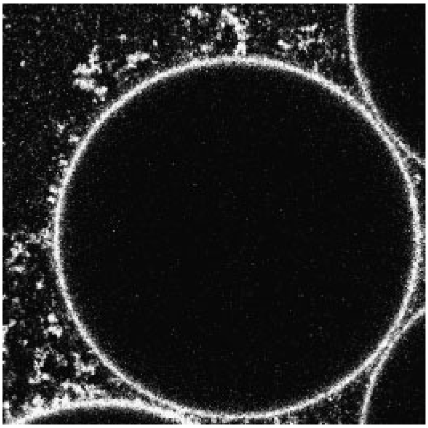

Figure 3.

Confocal *z*-slice of fluorescent poly(methyl methacrylate) microgels of 220 nm in diameter adhering to the surface of a hexadecane droplet of 180 μm in diameter dispersed in water.

solids, often referred to as Pickering emulsions, are of great stability.[12]

We prepared fluorescent hostasol-tagged microgels of poly(methyl methacrylate) and studied their ability to adhere at the interface of a hexadecane emulsion droplet dispersed in water. When the surface charge of the particles was low, in practice this means absolute values for the ζ-potential of less than 30 mV, stable Pickering emulsions could be formed.

Figure 3 displays a *z*-slice of a confocal microscope image of the system described above. We can clearly see that the latex is colloidally unstable, because of its low surface charge. Individual particles and flocks adhere clearly to the interface and are not able to cross into the hexadecane droplet.

An interesting innovation recently is the development of responsive Pickering stabilizers. Upon an external trigger, *e.g.* pH or magnetic field, a stable Pickering emulsion can be broken. Fujii *et al.* demonstrated that pH responsive hybrid microgels could be used as reversible Pickering stabilizers.[13] Fuller *et al.*[14] prepared solid-stabilized emulsions using paramagnetic carbonyl iron particles at an oil-water interface that can undergo macroscopic phase separation upon application of an external magnetic field.

Supracolloidal Structures through Liquid-Liquid Interface Driven Assembly: Colloidosomes

Pioneering work by Velev *et al.*[15,16] showed that hollow structures could be built via assembly of polystyrene latex on the interface of emulsion droplets. These structures, created by fully covering emulsion droplets with colloidal building blocks, were named *colloidosomes* by Dinsmore and coworkers.[17] Since then, a variety of building blocks of different chemical nature and dimensional scale have been used to create self-assembled structures, mainly using emulsion droplets as templates.[18–28]

Colloidosomes are permeable supracolloidal structures. Interstitial spaces will be present and their size will be dependent on the geometry of the colloidal building blocks used, their packing density, and presence of dislocations. This means that the inner liquid phase can diffuse out. We looked at this by manufacturing a giant colloidosome with a shell of crosslinked poly(divinylbenzene) microspheres, and observing its behavior upon evaporation of the inner water phase (See Figure 4).

The top left image in Figure 4 displays a fresh water droplet with a diameter of *ca.* 5 mm covered with crosslinked poly(divinylbenzene) microspheres on a glass microscope slide. The microspheres were made via precipitation polymerization in acetonitrile-toluene based on a recipe from Li and Stover.[29] The colloidosome deviates from a spherical shape and appears oval. The reason is that gravity cannot be neglected on this large colloidosome filled with water. Water normally spreads on a glass slide. In the present case, however, the shell of poly(divinylbenzene) microspheres prevents this and a large ‘‘contact angle’’ is observed. This cannot be explained exclusively by the hydrophobicity of the microspheres. The raspberry-type morphology of the giant colloidosome creating a surface roughness and the mechanical properties of the colloidal shell play also their part. The series of images follows the deformation process of the colloidosome upon evaporation of its inner water-phase. The second

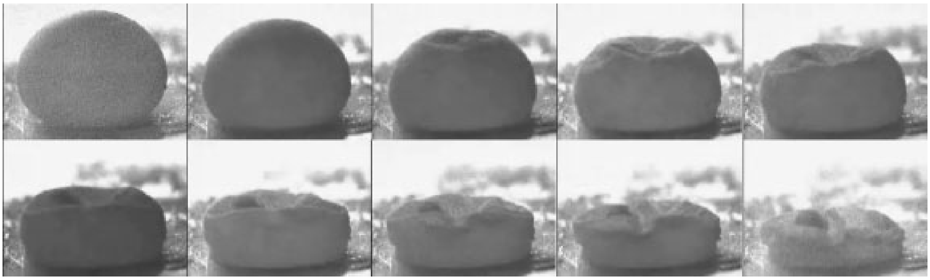

Figure 4.
Series of microscopic images following the deformation process of a giant 5 mm colloidosome made from crosslinked poly(divinylbenzene) microspheres upon evaporation of its inner water-phase in air. The colloidosome is placed on a glass slide.

image clearly shows shrinkage of the supracolloidal structure. This basically means that its total surface area is reduced, causing an increased packing density of the microspheres. Upon further evaporation, however, a point is reached at which the system jams. A maximum for the packing density of the microspheres is reached. Particles of this size are irreversibly adhered to the interface. This means that the total surface area of the droplet can no longer decrease. The only alternative for the droplet is to change its surface-to-volume ratio, which means it has to deform. This process is commonly referred to as buckling.[30] The overall drying process took approximately 3 h.

Pickering Miniemulsion and Suspension Polymerization

One of our research interests is to combine the formation of supracolloidal structures through liquid-liquid interface driven assembly with conventional heterogeneous polymerization techniques, such as (mini)-emulsion and suspension polymerization. Pioneering work in this area was done by Hohenstein[31,32] and Wiley[33] who described in essence Pickering suspension polymerizations.

We looked at the design of new routes towards polymer-clay composites and supracolloidal materials made thereof. We recently reported the first Pickering miniemulsion polymerization, in which we used Laponite clay as stabilizer.[24] Laponite RD is a synthetic trioctahedric hectorite clay, composed of two tetrahedral silica sheets and a central octahedral magnesia sheet. Its chemical formula can be expressed as $[Si_8(Mg_{5.45}Li_{0.4})O_{20}(OH)_4]Na_{0.7}$, and it has a density of 2570 kg m^{-3}. The disks have an overall negative charge with the rim being amphoteric. In water Laponite RD can be dispersed as individual disk-shaped colloids with a lateral diameter of *ca.* 25–35 nm and approximately 1 nm in thickness. Its dimensions mean that we are able to produce Pickering emulsions of hydrophobic monomers in water with submicron particle size distributions. In other words we make submicron colloidosomes composed of Laponite clay pellets and filled with monomer. The latter we can polymerize via radical polymerization to yield latex particles armored with Laponite-clay pellets.

In a typical experiment 0.510 g of Laponite XLG clay was dispersed in 100 mL of deionized water. This was subsequently sonicated whilst stirring using a Branson digital 450 W sonifier for 1 min, after which 0.583 g of NaCl was added. Sonication was continued for another 3 minutes, each with a 30 s interval. Next a mixture of 2.627 g of styrene, 0.127 g of hexadecane and 0.05 g of V-65 non-ionic radical initiator, was added. The mixture was sonified for 6 min, again with 30 s intervals after each minute of sonication time. This yielded a stable Pickering miniemulsion which was subsequently poly-

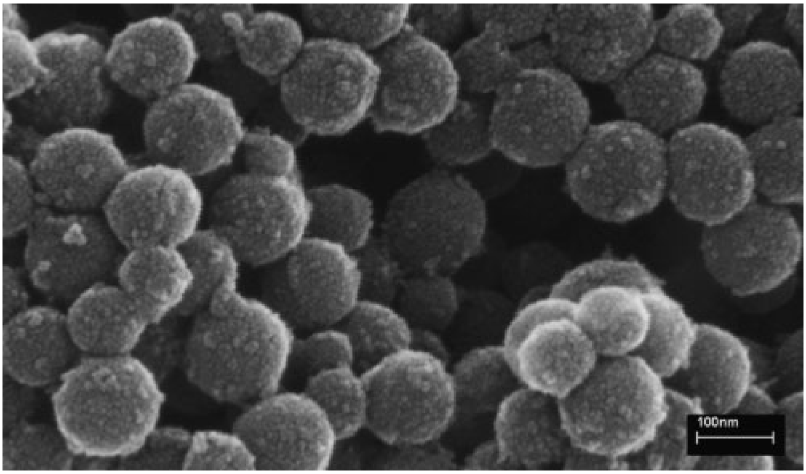

Figure 5.
Laponite clay armored polystyrene latex particles made via Pickering miniemulsion polymerization.

merized at 51 °C overnight. Dynamic light scattering showed an average particle size of 173 nm, with a polydispersity of 0.07. FEG-SEM analysis clearly shows the presence of the Laponite clay pellets at the surface of the latex particles, as displayed in Figure 5.

We are able to control the particle size of our armored latexes and to vary the monomer composition. An interesting feature is that upon film formation these latexes undergo limited polymer-polymer interdiffusion. Basically the armored shell of Laponite pellets partially prevents the polymer from flowing and mixing, as clearly can be observed from Figure 6, showing a composite polystyrene-clay film formed at 230 °C.

When we use inorganic nanoparticles of approximately 200 nm in diameter we can generate a micronsized Pickering emulsion

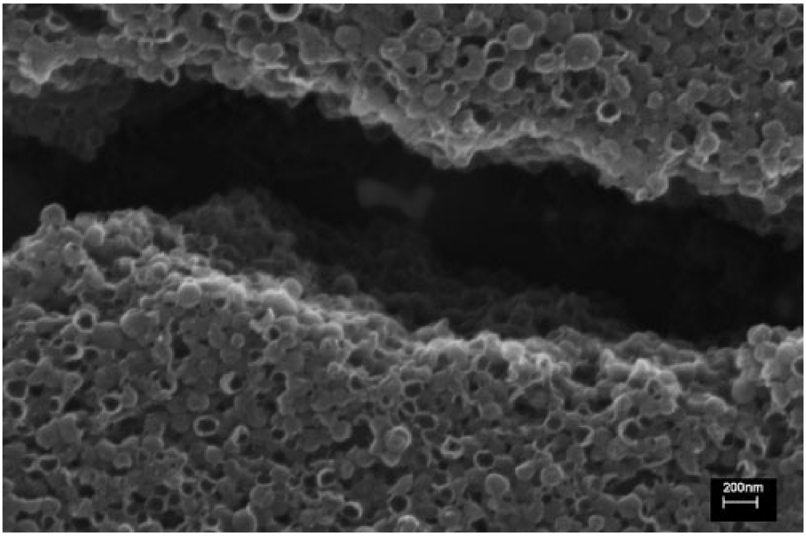

Figure 6.
Laponite-polystyrene composite produced via film formation of armored polystyrene latexes made via Pickering miniemulsion polymerization.

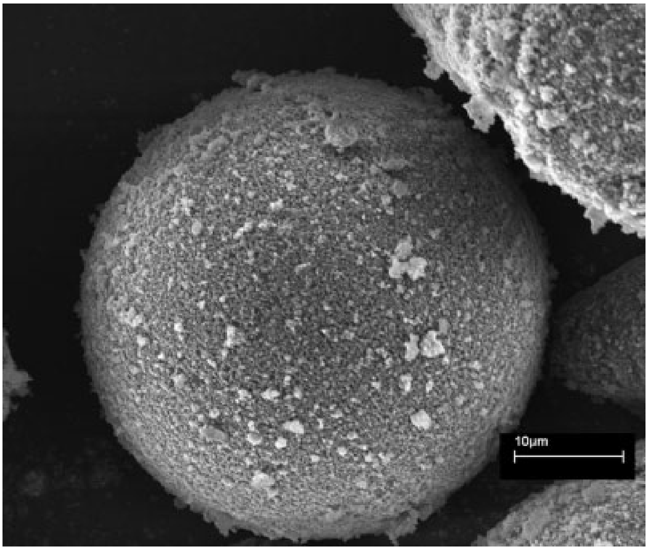

Figure 7.
Microspheres armored with a shell of inorganic nanoparticles. The composite spheres were made via Pickering suspension polymerization.

using an ultra turrax high shear mixer with droplet sized between 10–100 μm. When we use hydrophobic monomers such as styrene and divinylbenzene we can carry out a Pickering suspension polymerization. This yields polymer microspheres armored with a shell of inorganic nanoparticles. An example can be seen in Figure 7.

We recently reported the design of raspberry-shaped core-shell polymer capsules made via a Pickering suspension polymerization. Micronsized colloidosomes made from crosslinked poly(methyl methacrylate) microgels were formed and subsequently scaffolded with an interpenetrating network of which the mechanical properties could be varied (see Figure 8).[34]

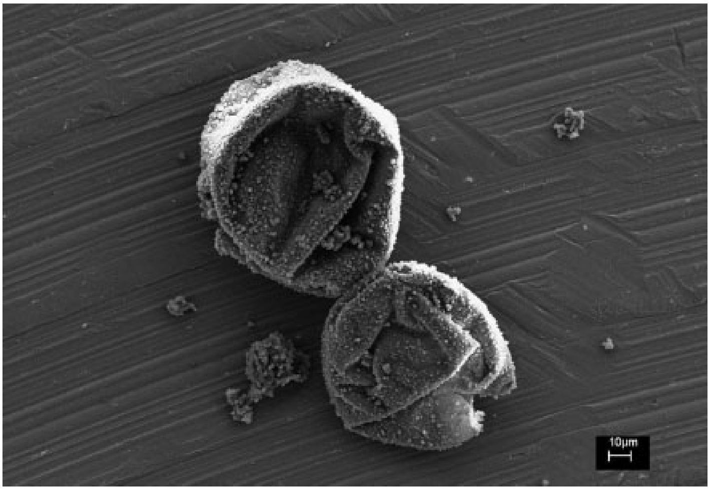

Figure 8.
Flexible raspberry core-shell polymer capsules made by using colloidosomes as polymerization vessels.[34]

Conclusions

We have shown that supracolloidal structures, referred to as colloidosomes, can be made via liquid-liquid interface driven assembly of colloidal building blocks. We demonstrated the buckling behavior of a giant colloidosome upon evaporation of its inner phase. We showed that the supracolloidal structures could be used as reaction vessels to perform miniemulsion and suspension polymerizations. We demonstrated to synthesis of exciting composite materials by using this approach.

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