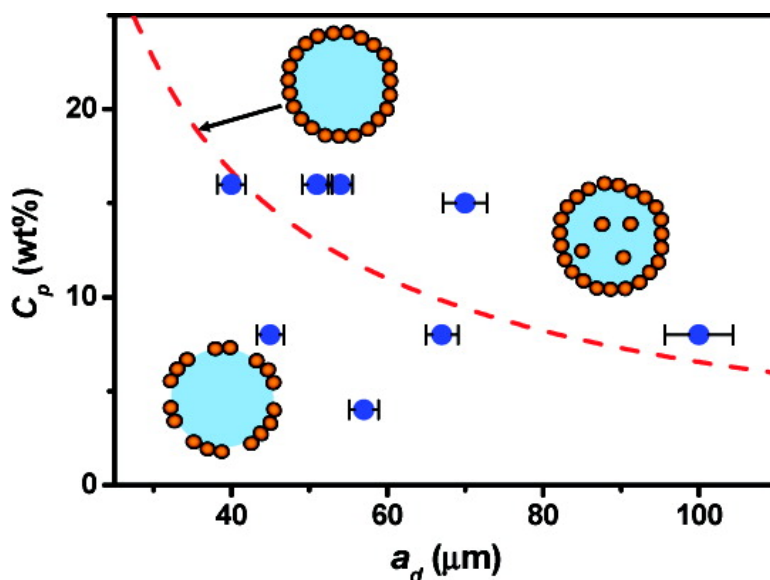## Communication

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An "Inside-Out" Microfluidic Approach to Monodisperse Emulsions Stabilized by Solid Particles

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Particle-stabilized emulsions (Pickering emulsions) have recently seen a surge in interest, owing to their extremely high stability against coalescence and a broad range of applications in the fabrication of functional materials, for example, hollow permeable structures,[1] foams,[2,3] and hybrid supracolloidal assemblies.[4−6] Adsorption of colloidal particles to liquid−liquid interfaces occurs when they are not completely wetted by any of the phases. The attachment of a particle of radius a_p to a water−oil interface is governed by a reduction of surface energy, $E = \pi a_p^2 \gamma (1 - |\cos \theta|)^2$, where γ is the interfacial tension between the two liquid phases and θ is the contact angle of the particle at the fluid interface.[7−10]

Pickering emulsions are generated by injection methods or by the shearing of a mixture of two immiscible fluids with the solid particles present in excess, that is, in an amount that is significantly larger than is required for the complete coverage and stabilization of the droplets. Lower particle concentrations result in droplet coalescence[11] whereas an excess of particles in the system leads to their undesired loss and in principle, can affect the properties of the material derived from the Pickering emulsions.

For a particular system, the concentration of particles required for the efficient stabilization of droplets depends on many factors, including the ratio between the dimensions of droplets and particles, and the number of particles.[9] Current methods for producing particle-coated emulsions generate droplets with a broad distribution of sizes, which complicates the rationalization of the amount of particles introduced in the system. Recently, microfluidic emulsification has provided a means for the formation of highly monodisperse droplets.[12,13] Furthermore, Subramaniam et al.[14] have shown that the deposition of microbeads from the continuous phase to the bubble-liquid interface is greatly assisted by hydrodynamic flow.

Herein, we describe a microfluidic "inside-out" approach to the generation of monodisperse water-*in*-oil and oil-*in*-water Pickering emulsions, as well as the supracolloidal polymer microspheres. Our strategy has the following new features: the microfluidic emulsification of a dispersion of colloidal particles in the *particle-free* continuous phase and a rationalized, based on geometric considerations, approach to controlling the coverage of the droplets with a layer of solid particles.

Emulsification was conducted in a microfluidic flow-focusing droplet generator.[13] A dispersion of 3.5 μm-diameter poly(divinyl-benzene-methacrylic acid) (poly(DVB-MAA)) particles in the water−ethanol (85/15 v/v) mixture was emulsified in hexadecane. The value of θ between the polymer film derived from the particles and the water−ethanol mixture was $82.2 \pm 2.1°$. Upon the

formation of droplets with polydispersity below 5%, the microbeads rapidly migrated from the interior of the droplets to the droplet surface.

Since the diameter of the particles used in the present work was significantly smaller than the diameter of the droplets, the surface coverage of the droplets, δ, was estimated as $\delta = A_p/A_d = C_p \rho_d a_d / (4\rho_p a_p)$ (eq 1), where A_d and A_p are the surface area of the droplet and the area of the droplet coated with particles, respectively; ρ_d is the density of the droplet phase, and C_p and ρ_p are the concentration and the density of particles, respectively.

In Figure 1 the broken line shows the estimated variation in the concentration of particles required to achieve complete coverage of the droplets with varying size with a colloidal monolayer, with the assumptions that (i) all particles migrate from the droplet interior to the droplet surface and (ii) at the interface the particles form a hexagonal lattice with a packing density of 0.906. Below the line, the amount of particles is not sufficient for the complete coverage of the droplets; whereas above the line, the microbeads present in excess form a multilayer shell or remain in the droplet interior. Since the number of particles is proportional to the droplet volume ($\sim a_d^3$) and $A_d \approx a_d^2$, complete coverage of droplets with larger radii requires a lower concentration of the particles.
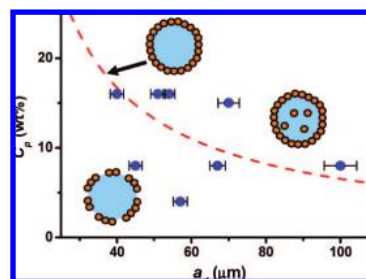

Figure 1. A diagram of the surface coverage of water-ethanol droplets with 3.5 μm-diameter poly(DVB-MAA) particles. The broken line shows the condition for the complete coverage of the droplets with the monolayer of 2D hexagonally packed particles. Filled circles show the experimental data points.

In the experiments, we controlled the surface coverage of the droplets by varying independently the value of C_p from 4 to 16 wt % and the values of a_d from 40 to 100 μm (by tuning the ratio of flow rates of the droplet-to-continuous phases.[14] Filled symbols in Figure 1 show the experimental results. Droplets with $\delta \geq 0.7$ were stable to coalescence, whereas droplets with $\delta < 0.7$ were prone to coalescence when collected at the exit of the microfluidic droplet generator. The attachment of particles from the droplet phase to the liquid−liquid interface and the formation of the close-packed crystalline shell occurred within several seconds and was assisted by the hydrodynamic flow.[14] Owing to the very rapid particle jamming at the fluid interface, at high values of C_p, we were able
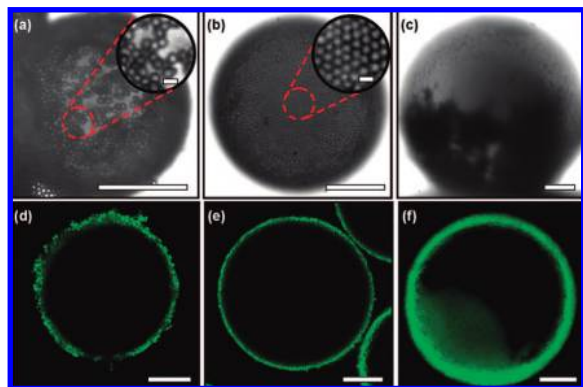
Figure 2. (a−c) Optical and (d−f) oil-immersion confocal microscopy images of the water-ethanol droplets armored with a shell of poly(DVB-MAA) particles at the not-complete (a,d) and complete (b,e) surface coverage, and at the excess of particles in the droplet interior (c,f). In panel c an excess of particles appears as the large dark region on the background of the droplet coated with a monolayer of particles. In (d−f) poly(DVB-MAA) microbeads were copolymerized with anthryl methacrylate. Confocal microscopy images show the plane located in the center of the droplets. C_p = 8 wt %. λ_{ex} = 380 nm. Scale bars in panels a−e, f are 50 and 100 μm, respectively. Scale bars in insets are 5 μm.

to produce nonspherical particle-coated droplets with the shape determined by the geometry of the microchannel (see SI).

In Figure 2 representative optical microscopy and confocal fluorescence microscopy images show that for C_p = 8 wt % and increasing droplet size, a transition occurred from the noncomplete coverage to the complete coverage, and then to the excess-of-particles regime. The noncomplete coverage of the surface of droplets with polymer particles is explicitly illustrated in Figure 2a,d. In the complete coverage regime (in agreement with the values of C_p and a_d predicted by the diagram in Figure 1) the microbeads formed a close-to-hexagonal lattice on the droplet surface (Figure 2b, inset). The precision in controlling the surface coverage of the droplets with particles can find applications in studies of colloid crystallization on curved fluid interfaces. In the excess-of-particles regime particles present in excess formed dark or bright concentrated regions in the interior of the droplets (Figure 2 panels c and f, respectively).

The "inside-out" approach was also exploited for the preparation of oil-*in*-water Pickering emulsions and the corresponding supracolloidal structures. In these experiments, the droplet phase contained a mixture of tripropylene glycol diacrylate, TPGDA, the photoinitiator 2,2-dimethoxy-2- phenyl-acetophenone (4 wt %), and poly(DVB-MAA) particles at C_p = 14 wt %. To favor the migration of the particles to the fluid interface, 10^{-4} M of NaOH were introduced in the continuous aqueous phase.[15] Following the encapsulation of the highly monodisperse TPDGA droplets with the colloidal shells, the droplets were collected at the exit of the microfluidic device and exposed to 1 min UV-irradiation (400 W, λ = 330−380 nm). Photopolymerization of TPDGA yielded large polymer microspheres armored with a shell of poly(DVB-MAA) particles. Figure 3a shows the surface of the supracolloidal microsphere produced at C_p = 14 wt % (ca. 40% higher than required to achieve δ = 0.906). The average 3.0 μm diameter of the protruded parts of the poly(DVB-MAA) particles and the mean 4.2 μm center-to-center distance between them implied that (i) a larger area of the microbead surface resided in the corresponding droplet than in the continuous phase and (ii) ca. 0.7 μm mean distance existed between the surfaces of the particles immersed in the droplet phase, similar to the earlier findings, of Horozov et al.[16]
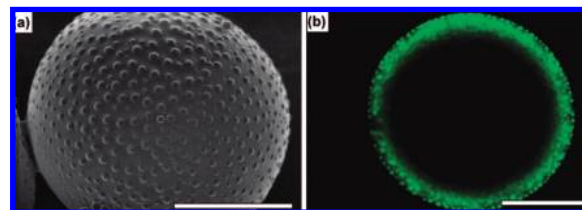

Figure 3. SEM (a) and confocal fluorescence microscopy (b) images of poly(TPGDA) particles armored with poly(DVB-MAA) particles. C_p = 14 wt %. Scale bars are 40 μm in panel a and 60 μm in panel b.

Inspection of the colloidal shell using confocal microscopy revealed that poly(DVB-MAA) particles formed a multilayer on the surface of the microspheres (Figure 3b), due to the long-range attraction between the microparticles in the TPGDA medium, with no particles in the microsphere interior.

In summary, we have demonstrated a new approach to the preparation of particle-encapsulated droplets, which has (i) a high efficiency and a minimized waste of particles, due to their introduction in the droplet phase, rather than in the continuous medium; (ii) a narrow size distribution of droplets, which provides a route for easier analysis of the dynamics of formation and buckling of Pickering emulsions, and colloid crystallization on curved fluid interfaces; (iii) the ease of the control over the coverage of droplets with particles by manipulating the concentration of particles or the flow rates of the liquids. With respect to the microfluidic preparation of Pickering emulsions, the "inside-out" approach allowed us to minimize the fouling of the microchannels and provided direct visualization of the process of droplet encapsulation. We envisage that the proposed approach will open a route to the preparation of colloidal materials with complex structural hierarchy.

Supporting Information Available: Geometry of the droplet generator, materials, synthesis of polymer beads, images of the Pickering emulsions, the values of wetting angles. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Dinsmore, A. D.; F., H. M.; Nikolaides, M. G.; Marquez, M.; Bausch, A. R.; Weitz, D. A. *Science* **2002**, *298*, 1006–1009.
(2) Binks, B. P; Murakami, R. *Nat. Mater.* **2006**, *5*, 865–869.
(3) Colver, P. J.; Bon, S. A. F. *Chem. Mater.* **2007**, *19*, 1537–1539.
(4) Lin, Y.; Skaff, H.; Boeker, A.; Dinsmore, A. D.; Emrick, T.; Russell, T. P. *J. Am. Chem. Soc.* **2003**, *125*, 12690–12691.
(5) Arumugam, P.; Patra, D.; Samanta, B.; Agasti, S. S.; Subramani, C.; Rotello, V. M. *J. Am. Chem. Soc.* **2008**, *130*, 10046–10047.
(6) Chen, T.; Colver, P. J.; Bon, S. A. F. *Adv. Mater.* **2007**, *19*, 2286–2289.
(7) (a) Ramsden, W. *Proc. R. Soc.* **1903**, *72*, 156–164. (b) Pickering, S. U. *J. Chem. Soc., Trans.* **1907**, *91*, 2001–2021.
(8) Zeng, C.; Bissig, H.; Dinsmore, D. *Solid State Commun.* **2006**, *139*, 547–556.
(9) Aveyard, R.; Binks, B. P.; Clint, J. H. *Adv. Colloid Interface Sci.* **2003**, *100−102*, 503–546.
(10) Studart, A. R.; Gonzenbach, R. T.; Akartuna, I.; Tervoort, E.; Gauckler, L. J. *J. Mater. Chem.* **2007**, *17*, 3283–3289.
(11) Wiley, R. M. *J. Colloid Sci.* **1954**, *9*, 427–437.
(12) Thorsen, T.; Roberts, R. W.; Arnold, F. H.; Quake, S. R. *Phys. Rev. Lett.* **2001**, *86*, 4163–4166.
(13) Anna, S. L.; Bontoux, N.; Stone, H. A. *Appl. Phys. Lett.* **2003**, *82*, 364–366.
(14) (a) Subramaniam, A. B.; Manouk, A.; Stone, H. A. *Nat. Mater.* **2005**, *4*, 553–556. (b) Tice, J. D.; Song, H.; Lyon, A. D.; Ismagilov, R. F. *Langmuir* **2003**, *19*, 9127–9133.
(15) Leunissen, M. E.; van Blaaderen, A.; Hollingsworth, A. D.; Sullivan, M. T.; Chaikin, P. M. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 2585–2590.
(16) Horozov, T. S.; Aveyard, R.; Binks, B. P.; Clint, J. H. *Langmuir* **2005**, *21*, 7405–7412.

JA807764M