Interfacial Assembly

DOI: 10.1002/ange.201106665

Nanoparticle-Stabilized Double Emulsions and Compressed Droplets**

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Emulsion droplets can be stabilized against coalescence by many types of interfacially active species, including proteins, small-molecule surfactants, polymers, nanoparticles and microparticles. When the fluid–fluid interface of an oil-in-water (o/w), or water-in-oil (w/o), emulsion is stabilized by adsorption of particles at the interface, a "Pickering emulsion" is obtained in which the particles occupy the fluid–fluid interface and prevent, or retard, droplet coalescence. Pioneering work of Ramsden[1] and Pickering[2] on paraffin/water emulsions containing solid particles, such as iron oxide, silicon dioxide, barium sulfate, and kaolin clays demonstrated the critically important role of particles in such interfacial stabilization. Theoretical treatment of nanoparticle-stabilized droplet structures, reported for example by Pieranski[3] and Binks,[4–6] describe the reduction of the overall surface energy of the system due to nanoparticle interfacial segregation as a function of particle size and the relative interfacial energies of the system (oil–water, oil–particle, and water–particle).

The tendency of particles to localize to oil–water interfaces opens opportunities to fabricate new materials based on the individual and collective properties of the particles, including: 1) the optical properties derived from colloidal crystallization,[7,8] 2) self-assembled conducting structures,[9,10] and 3) encapsulation and release technologies.[11,12] For example, Weitz and co-workers reported the oil–water interfacial assembly of polystyrene microspheres into hexagonally packed capsule structures termed "colloidosomes."[13] For nanoparticles, the energy holding each particle at the fluid–fluid interface is smaller than that for microscale objects; nonetheless, there have been numerous reports of nanoparticle-stabilized emulsion droplets, in which the droplets are stable for hours, days, or longer. CdSe QDs,[14,15] Au NPs,[16–18] Fe_3O_4 NPs,[19] "Janus" nanoparticles[20] and plant-derived virus particles[21] all prove amenable to stabilizing fluid–fluid interfaces of different types. Moreover, embedding functional ligands on nanoparticle surfaces provides access to further droplet stabilization through chemical cross-linking of the ligands, thereby converting these dynamic self-assembled systems into robust structures.[22]

Double-emulsion droplets, whether water-in-oil-in-water (w/o/w), or oil-in-water-in-oil (o/w/o), are attractive for providing a means to control release from the inner phase to the outer phase, while effectively shielding the interior phase from the continuous phase. Double emulsions can be prepared by a one- or two-step emulsification process, in the presence of a relatively hydrophilic surfactant that stabilizes o/w droplets, and a relatively hydrophobic surfactant that stabilizes the w/o interfaces.[23] Such emulsions have been generated during phase inversion processes, that is, when the continuous phase of the immiscible liquid–liquid dispersion becomes the dispersed phase. We note that early work on double emulsions, reported by Seifriz and co-workers, examined systems involving reversible emulsions of petroleum oil and aqueous casein,[24] where addition of barium hydroxide to an initially unemulsified oil/water mixture led to formation of double (and multiple) emulsions.

Stabilization of double emulsions by particulates, rather than traditional surfactants, remains a largely unexplored route. Binks and co-workers[25] observed double emulsions while studying reversible (o/w) systems stabilized with fumed silica particles of intermediate hydrophilicity (i.e., using partially hydrophobized silica), where the energy of adsorption of the particles to the fluid–fluid interface exceeds thermal energy $k_B T$. Thus, the particles are not easily removed from the interface, enabling formation of stable double-emulsion droplets. However, this approach requires careful control over particle wetting characteristics to achieve stabilization of both o/w and w/o interfaces, and did not give fine control over droplet size.

Here, we exploit the simultaneous interfacial adsorption of independently functionalized semiconductor and metallic nanoparticles to give stable w/o/w and o/w/o double-emulsion structures. To our knowledge, this represents the first example of double emulsions stabilized exclusively by two different types of nanoparticles. The use of two different particulate stabilizers, where the interfacial activity and properties of each can be chosen independently, provides a general route to particle-stabilized double emulsions, and integrates into the droplets the optical and electronic properties inherent to the nanoparticles. In addition to polydisperse droplets formed

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[**] This work was supported by the National Science Foundation Materials Research and Engineering Center (MRSEC) on Polymers at UMass Amherst (DMR-0820506, C.M. and I.K.), the Department of Energy (DOE) award DE-FG02-04ER45126 (J.K.), and the Energy Frontier Research Center funded by the DOE Office of Basic Energy Sciences, under Award No. DE-SC0001087 (E.L. and R.H.).

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through sequential emulsification by shaking, we show that these nanoparticle-stabilized w/o/w double emulsions can be formed using a glass microcapillary fluidic device, greatly improving control over droplet size. These droplets, in turn, give rise to interesting honeycomb and foam-like structures upon solvent evaporation, where the nanoparticles line the structures in a wire or mesh-like fashion. We emphasize that such unique structures are generated using simple emulsification and evaporation processes, rather than any writing or patterning technique for nanoparticle deposition.

We begin with the preparation of nanoparticle-stabilized double emulsions, using tetra(ethylene glycol) (TEG) functionalized Au NPs that are known to stabilize o/w droplets,[11] and CdSe QDs that are known to stabilize w/o droplets when the QDs are functionalized with their native alkyl (i.e., phosphine oxide and phosphonic acid) ligands.[8] Interestingly, we found that double emulsions containing CdSe QDs and Au NPs were obtained easily, albeit crudely, after shaking oil/water/NP/QD solutions by hand in a two-step procedure. For example, as shown in Figure 1a, to obtain an o/w/o double

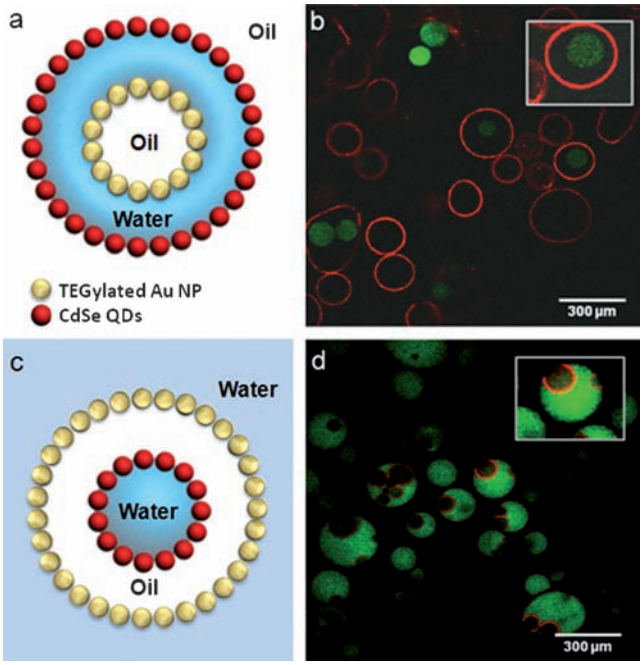

Figure 1. Schematic representations and fluorescence confocal microscopy images of NP-stabilized double emulsions: a,b) o/w/o double-emulsion droplets, and c,d) w/o/w double-emulsion droplets. The red fluorescence is from the CdSe QDs, and the green fluorescence is from Coumarin 153.

emulsion, first 0.1 mL of 1,2,4-trichlorobenzene (TCB), the minor oil phase, was added to 0.9 mL of an aqueous phase containing 5 mg mL^{-1} Au NPs. Vigorous shaking gave an oil-in-water single emulsion stabilized by the Au NPs. These droplets were then utilized as the minor aqueous phase, and added to a 1 mg mL^{-1} toluene solution of CdSe QDs. Shaking this mixture (by hand) gave the desired o/w/o double emulsion, as confirmed by optical and confocal fluorescence microscopy. As seen in Figure 1a, different types of emulsion droplets were obtained, including those containing one or more inner droplets mixed with single-emulsion structures. The size of the double-emulsion droplets varied widely, from 150–250 μm for the outer droplets, and 60–170 μm for the inner droplets. Notably, in the double emulsions, the size of the inner droplets remained consistent with the o/w single emulsions used in their formation, suggesting that the second emulsification step does little to disrupt the initial interfacial NP assembly, though some exchange of NPs between interfaces is not ruled out. Using CdSe QDs enhances structural characterization, enabling droplet imaging by fluorescence confocal microscopy to confirm their presence and location within the double-emulsion structure. Since the TEG-functionalized Au NPs are not fluorescent, Coumarin 153 was added to the TCB oil phase to visualize the Au NP stabilized droplet. Coumarin 153 is convenient for its fluorescence emission at 530 nm, distinct from the CdSe QD emission, allowing easy differentiation between the aqueous and oil phases. Figure 1b shows a fluorescence confocal microscopy cross-section of a sampling of these droplets, in which the red fluorescence is indicative of the CdSe QDs as the outer encapsulating phase, and the green fluorescence is from Coumarin 153, held in the oil-filled inner droplets by the stabilizing TEGylated Au NPs.

Additional experiments demonstrated an inherent versatility to the CdSe QD and Au NP combination for preparing double-emulsion structures, as w/o/w double emulsions were also formed readily. This was done by first forming single w/o droplets (in toluene) stabilized with CdSe QDs, then adding this emulsion as the minor phase to a solution of Au NPs in water. As seen in the fluorescence confocal micrograph of Figure 1d, in this case the CdSe QDs reside at the interface of the inner droplet, often as multiple droplets contained inside Au NP-covered toluene droplets.

The NP-stabilized droplets described thus far are otherwise surfactant free, lacking the small-molecule or polymeric surfactants typically required to generate emulsion droplets. Rather, the NPs themselves function as surfactants, while simultaneously bringing the properties of the semiconductor and metallic particles into the droplet structures. Pendant drop tensiometry provides evidence for the surfactancy of these particles. The interfacial tension of TCB/water, measured by the pendant drop technique to be approximately 45 mN m^{-1}, was reduced to 22 mN m^{-1} in the presence of Au NPs, and 29 mN m^{-1} in the presence of CdSe QDs.

We next sought to refine the structures of the NP-stabilized double-emulsion droplets using microfluidic techniques. A glass capillary device combining both co-flow and flow focusing was used to form w/o/w double-emulsion droplets,[26] as shown in Figure 2a. The innermost aqueous phase was deionized water, while the middle oil phase consisted of 2 mg mL^{-1} CdSe QDs in TCB (with 1 vol% Coumarin 153 added to facilitate characterization by fluorescence microscopy), and the outer phase consisted of 5 mg mL^{-1} Au NPs in water. The size of outer droplets is controlled by the size of the exit capillary orifice, with larger openings yielding larger droplets, and the relative flow rates and viscosities of the outermost and middle fluid phases (higher flow rates and higher viscosities of the outer phase

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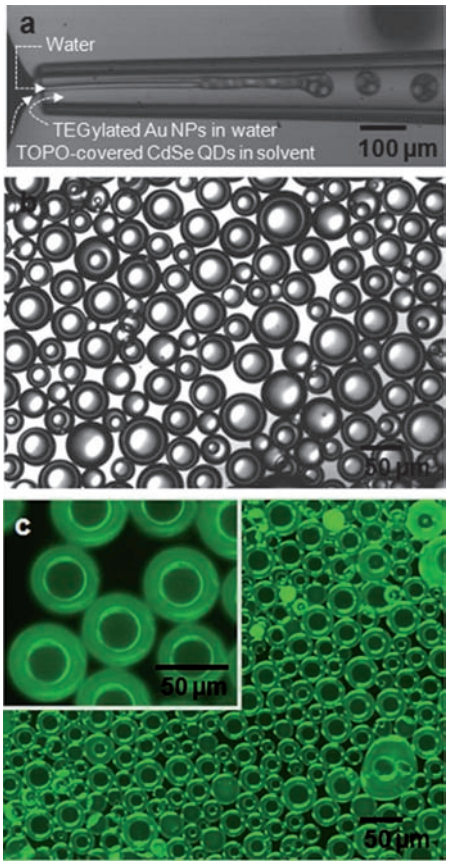

Figure 2. a) Formation of NP/QD-stabilized double emulsion in a microcapillary device with a flow-focusing geometry. b) Optical and c) fluorescence microscopy images of w/o/w double emulsions stabilized by Au NPs and CdSe QDs.

yield smaller droplets). The number and sizes of internal droplets are determined by similar considerations of the inlet capillary nozzle and the relative rates and viscosities of the middle and inner phases. Typical resulting w/o/w emulsion droplets are shown in the optical and fluorescence images of Figure 2. As seen in Figure 2c, fluorescence emission from Coumarin 153 in the oil phase unambiguously establishes the structure of these droplets as w/o/w double emulsions, while the enhanced fluorescence intensity at the interface between the inner and middle phases arises from the presence of CdSe QDs (ca. 6 nm). In this experiment, the outer droplet diameter is seen to range from 17 to 40 μm, representing a substantial improvement in droplet uniformity relative to the double emulsions formed simply by shaking. Moreover, the flow-focusing technique produced samples in which nearly every oil droplet contained a single internal water droplet. However, achieving a precise size uniformity of these droplets, in the absence of traditional polymeric surfactants, proved non-trivial. We speculate that this reflects slower kinetics associated with interfacial adsorption of the nanoparticles, providing more time for droplet coalescence to occur in the microfluidic device prior to achieving sufficient NP coverage for droplet stabilization.

We found that increasing the flow rate of the inner-fluid in the microfluidic flow-focusing device led to nanoparticle-stabilized double-emulsion droplets containing multiple inner droplets, as shown in Figure 3a. These w/o/w double emulsions were composed of TEG-functionalized Au NPs at the outer interface, and CdSe QDs at the inner interface. Though the dimensions of the outer droplets were nearly uniform in size (ca. 70 μm in diameter), the inner droplets were less well-defined, reflecting a slight variation in flow rate of the inner fluid. For these experiments, toluene was chosen as the oil phase rather than TCB, allowing more rapid solvent evaporation. Following droplet formation, the samples were allowed to dry in air, during which time they showed excellent stability against coalescence with respect to both the internal droplets and the external structures. Interestingly, the stability of these toluene-based droplets was notably greater than those formed with TCB, providing opportunities for the fabrication of new types of emulsion-templated nanoparticle assemblies through removal of organic solvent. Upon evaporation of toluene, the inner droplets were compressed (Figure 3b and c), yielding planar interfaces with characteristic Plateau borders, as indicated by the yellow arrows in Figure 3d.

Complete evaporation of toluene from the middle phase yielded nanoparticle foams, that is, multi-compartment capsules in which thin walls of Au NPs and CdSe QDs separated the internal aqueous droplets from the surrounding fluid. While similar polymer-based multi-compartment vesicles have previously been formed from double-emulsion templates,[27] to our knowledge this represents the first example of such structures wherein NPs comprise the stabilizing material.

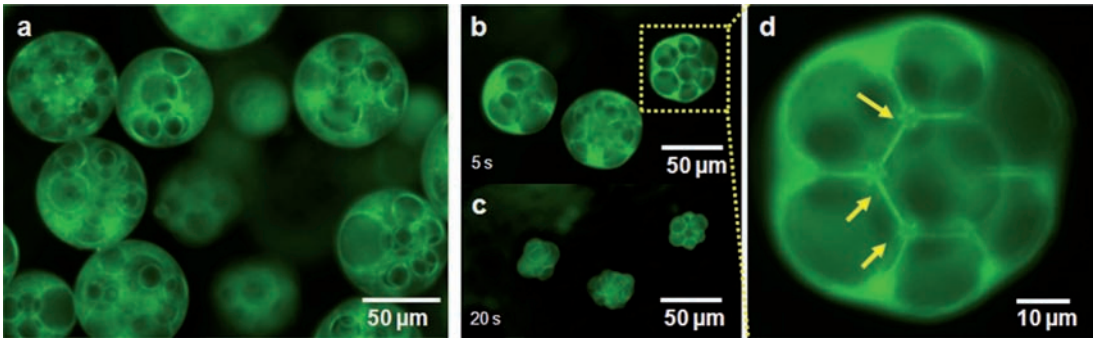

Figure 3. Fluorescence microscopy images of a) w/o/w double emulsions containing multiple inner droplets, after solvent evaporation for b) 5 s (top) and c) 20 s (bottom). d) Closer view of the compressed emulsions.

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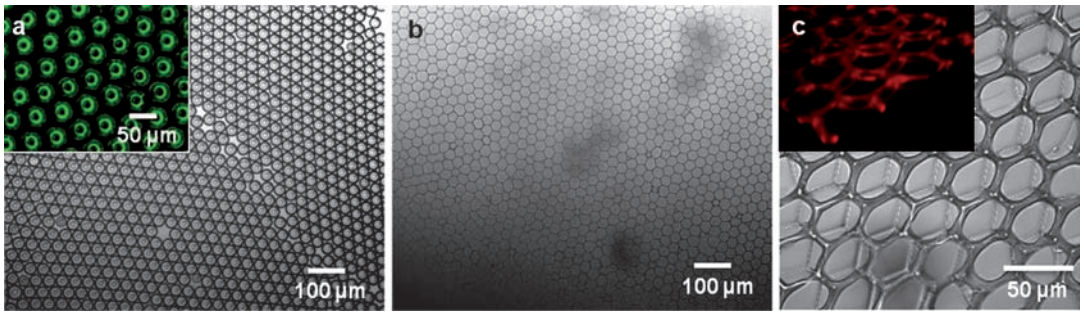

Figure 4. Optical microscopy images of a) uniform w/o/w double emulsion, formed without PVOH (inset is a fluorescence microscopy image); b,c) honeycomb structures formed upon solvent evaporation and droplet compression. The inset of (c) is a laser scanning confocal microscopy image. The fluorescence from CdSe QDs is seen as green in (a), and red in (c).

Optimal flow focusing conditions were found to yield nearly monodisperse nanoparticle-stabilized double-emulsion droplets, as shown in Figure 4a. In this case, a 1:1 (v/v) ratio of toluene and TCB was used, yielding both excellent emulsion stability and slow solvent evaporation from droplets that settled to the fluid-substrate (glass) interface following drop-casting of the droplets onto the slide. Complete evaporation of both organic solvent and water left striking honeycomb-like structures on the substrate (Figure 4b). These correspond to hybrid nanoparticle lines templated by the hexagonally-packed arrays of compressed droplets formed during solvent evaporation. Evidently, the NP-stabilized interfaces are sufficiently robust to withstand even complete removal of both solvent phases. We note that while monodisperse NP-stabilized droplets could be obtained only over a small window of operating conditions, the use of poly(vinyl alcohol) (PVOH) as an additional stabilizing surfactant in the outer aqueous phase gave improved droplet formation with respect to size uniformity. For example, Figure 4c shows wire-like mesh structures that were obtained upon solvent evaporation from the double-emulsion droplets in which 2 wt% PVOH was present in the aqueous phase. Fluorescence microscopy reveals the presence of CdSe QDs within these hybrid polymer/NP "wires". We reiterate that such structures, potentially interesting for providing a connected and ordered array of NPs over a large area, are produced readily by use of a simple emulsification and evaporative process.

In summary, we have demonstrated that two different types of nanoparticles, Au NPs with TEG ligands and CdSe QDs with their native alkane-based ligands, can be used as surfactants to generate both o/w/o and w/o/w double-emulsion droplets. In these droplets, the o/w interface is successfully stabilized by the Au NPs, while the w/o interface is stabilized by CdSe QDs. In addition to demonstrating the facile formation of polydisperse droplets by sequential emulsification and shaking, we show that well-defined droplets can be formed using flow-focusing with a glass microcapillary device. This microcapillary technique led to the fabrication of tunable double-emulsion droplets with various size of the internal and external droplets. Remarkably, these uniform droplets give rise to a well-ordered honeycomb structure after complete solvent evaporation, where the NPs that prevent droplet merging become connected into a mesh-like structure. Extension of this approach to other NP compositions will provide a route for developing novel micro-patterned materials, which might exhibit exceptional electrical, optical, and/or catalytic properties based on NP composition and the high degree of order in materials obtained from these droplets.

Experimental Section

CdSe QDs were synthesized according to literature methods,[28] and TEGylated Au NPs were prepared following the Brust procedure.[29] The TEG-ligand for Au NPs, (1-mercaptoundec-11-yl)-tetra(ethylene glycol), was prepared by a known method.[30]

O/w/o double emulsions were formed starting with the formation of the o/w single emulsion. 0.1 mL of 3 mg mL^{-1} Coumarin 153 in TCB was added to 0.9 mL of a 5 mg mL^{-1} Au-TEG NPs solution in water. A stable emulsion was obtained after vigorous shaking. The Au-NP-coated single-emulsion droplets (0.1 mL) were then added to 0.9 mL of 1 mg mL^{-1} solution of TOPO-covered CdSe QDs in toluene. Subsequent shaking gave the w/o/w double-emulsion droplets. Similarly, w/o/w double emulsions, where the outer droplet is coated with Au NPs and the inner droplet is coated with CdSe QDs, were obtained by forming the QD-stabilized single emulsion first, then using these droplets as the oil phase with the Au NP-stabilized droplets.

A Leica TCS SP2 LCSM laser scanning confocal microscope under Ar-laser excitation (excitation at 488 nm, detection at 510–530 nm for Coumarin 153 and 590–620 nm for the QDs) was used for emulsion characterization. The samples were prepared by adding a portion of droplets to a small amount of solvent already present on a single-well glass microscope slide, and covering the glass slide with a cover-slip. A Dataphysics OCA-15 tensiometer was used in the pendant drop mode to measure the interfacial tension between water and TCB or water and toluene in the presence of nanoparticles. Glass capillary devices combining co-flow and flow focusing were prepared according to the procedure of Weitz and co-workers.[26] Each device consists of an outer square glass capillary with an inner dimension of 1 mm, within which two cylindrical glass capillaries (having outer diameters of 1 mm and inner diameters of 0.6 mm) are placed 20 to 30 μm apart. As the inner dimension of the square capillary and the outer dimension of the cylindrical capillaries are equal, coaxial alignment of the capillaries is achieved. A Zeiss Axiovert 200 inverted optical microscope was used to image the structures obtained by flow-focusing.

Received: September 20, 2011
Published online: November 23, 2011

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Keywords: emulsions · interfaces · microfluidics · nanoparticles · self-assembly

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