All-Liquid Photonic Microcavity Stabilized by Quantum Dots

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Optical microcavities have been utilized for laser resonators,[1−4] biological/chemical sensors,[5] compact microphotonic devices,[6] and cavity quantum electrodynamics,[7] owing to their high optical quality factors (Q-factors) and small optical mode volumes (V) that lead to an enhanced light−matter interaction.[8] The most fascinating features of spherical microcavities are the spectrally narrow whispering-gallery resonances that are caused by a total internal reflection of light along the periphery of the spherical surfaces.[8,9] Recently, it was demonstrated that whispering-gallery modes (WGMs) in spherical microcavities can lead to signal enhancement in both fluorescence and Raman spectroscopy.[9] However, to obtain high-Q WGMs a high refractive index contrast [$\Delta = (n_{surrounding} - n_{sphere})/n_{surrounding}$] of the microsphere compared to the surrounding liquid is required.

The Q-factor of these WGMs depends strongly on the surface roughness of the interface between the resonator and the ambient medium. Solid dielectric microspheres that have a very high surface quality and low surface roughness are, in general, difficult to synthesize. Liquid microdroplets can provide an alternative route for obtaining WGMs with high Q-factors. Hossein-Zadeh et al. demonstrated that millimeter-scale water droplets in an index-matching liquid can provide relatively high-Q cavities due to the extremely low surface roughness between the two liquid phases.[10] Only if the liquid microdroplets can maintain their size and spherical shape, even in a liquid phase, can they form the stable and high-Q WGM resonators. To that end, the interfacial tension between two immiscible liquids is critical for maintaining the spherical shape and a smooth interface. However, liquid microdroplets are easily deformed by gravitational or other external forces since the microdroplets require a solid support to avoid the necessity of any levitation.[11] Otherwise, the uncontrollable floating of the microdroplets would reduce their usefulness for many applications. Therefore, stabilizing the shape of high refractive index contrast liquid droplets in the liquid phase and obtaining simultaneously a high Q-factor continue to be important challenges.[10]

Here, we present two distinct methods for fabricating highly stable toluene microcavities in water by stabilizing the toluene microdroplet (interface between toluene microdroplets and surrounding water) by using CdSe/ZnS quantum dots (QDs). We demonstrate that high Q-factors for the WGMs close to the theoretical limit can be obtained with these QD-stabilized toluene microcavities.

Our "all-liquid" approach has several advantages compared to previously reported methods for generating microdroplets in air.[12] Although liquid microdroplets in air can have extremely high Q-factors due to a high refractive index contrast, they also easily

evaporate in the air and can be utilized only for short times. In our approach, however, the liquid surrounding the microcavities provides the droplet resonator with a much longer lifetime and an additional damping force against its mechanical vibrations and enhances the mechanical stability of the resonator compared with its counterparts suspended in air.[10] Next, the droplets in the all-liquid phase are quite stable, thereby avoiding complex trapping methods (e.g., quadrupole traps[13]). Finally, a large number of the microdroplets can be easily produced in a short time without any need of a microdroplet generator. Highly stable and high-Q WGM resonators would have the potential of being developed into all-liquid lasing devices in the future since the microdroplets in the liquid phase can be easily manipulated at the microscale (e.g., positioning the microdroplets in microfluidic devices).

The microdroplets need to be physically stabilized such that different droplets do not merge with each other to form larger droplets.[14,15] Recently, semiconductor nanocolloidal CdSe/ZnS quantum dots (QDs) have attracted interest as active gain materials for micro- and nanooptic devices,[12,16,17] and they can also be utilized to stabilize liquid microdroplets in a liquid phase.[18]

For our demonstration we use toluene microdroplets (refractive index of toluene, $n_{toluene} = 1.496$) which are generated in water (refractive index of water, $n_{water} = 1.33$). The QDs that cover the toluene microdroplet may also contribute to the higher effective refractive index of the microdroplet. Thus, the refractive index contrast (Δ) of the microdroplet is believed to be slightly greater than 0.11. Previously, it was shown that hydrophobic QDs in toluene could stabilize water microdroplets dispersed in toluene.[18,19] However, these QDs cannot form a stable toluene-in-water emulsion without any QD surface modification. For the hexadecylamine (HDA)-capped QDs, this can be explained by the reduced interfacial tension between QDs and toluene compared to the tension between QDs and water.

To achieve QD-stabilized toluene microdroplets in water, two different methods for the surface ligand-exchange of the hydrophobic HDA-capped CdSe/ZnS QDs are available, both based on a method reported by Lee et al.[20] The first method uses a partial ligand-exchange of QDs to obtain partially hydrophilic QDs that can be located at the toluene−water interface. The ligand-exchange level of the hydrophobic QDs with hydrophilic 3-mercaptopropionic acid (MPA) molecules was controlled by varying both the reaction time and the amount of MPA. After the ligand-exchange, the modified QDs were dissolved in 90 μL of DI water and the aqueous solution was sonicated with 10 μL of toluene. If the HDA ligands of the QDs would be completely exchanged by MPA, the majority of the QDs would have to be located completely in the aqueous phase rather than at the interface between the toluene droplet and the water.

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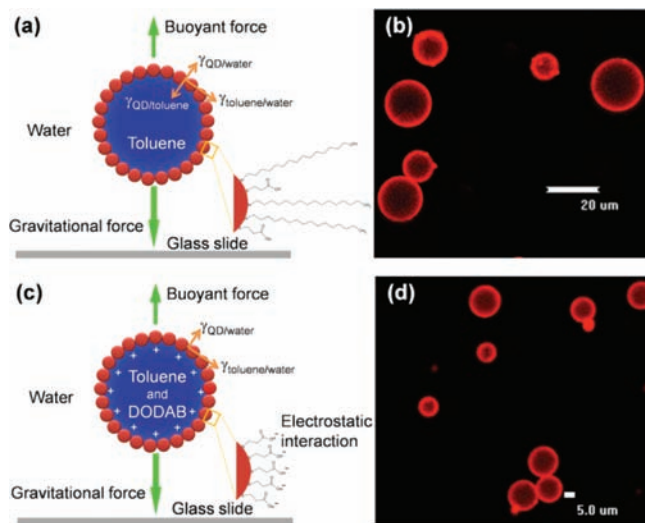§ Lawrence Berkeley National Laboratory.

Figure 2. (a) PL spectra of ligand-exchanged QDs (method 1 and method 2) and a WGM (a 23-μm-sized microdroplet with QDs modified by method 1), which were excited at 405 nm. (b) Bright field image of WGM microdroplets together with a scheme of the photoluminescence measurement setup.

Figure 3. Size dependence of Q-factors and losses (method 1 and method 2). (a) Q-factors from PL spectra with various sizes of microdroplets. (b) Mode distance at maximum wavelength with various sizes of microdroplets.

Figure 1. Scheme of microdroplet structures. Cross-sectional views of a QD-stabilized microdroplet and forces affecting its stability for (a) method 1 and (c) method 2. Corresponding confocal microscope images of QD-stabilized microdroplets (c) method 1 and (d) method 2. Although QDs might introduce some surface roughness of the microdroplets, a relatively homogeneous interface between two liquids can still be preserved even in the presence of QDs.

The second method is based on the assembly of completely carboxylated (ligand-exchanged) QDs in water onto the outer surface of positively charged toluene microdroplets with dimethyldioctadecylammonium bromide (DODAB). For this method, completely ligand-exchanged QDs with MPA in 90 μL of DI water (pH 9) were used to provide the QDs with strongly negative charges. Finally, a solution containing the QDs was sonicated with 10 μL of the positively charged toluene solution. It is important to adjust the amount of both negative and positive charges by optimizing the concentrations of negatively charged QDs in water and positively charged DODAB ions in toluene. Otherwise, the microdroplets can be completely deformed resulting in changed Q-factors of the WGMs.

Both methods are illustrated in Figure 1 for the QD-stabilized toluene microdroplets in water, where the buoyant and the gravitational forces, the surface tension, and electrostatic interaction (only in method 2) determine the stability of the droplets. In the case the microdroplets would not be stabilized by QDs, the QDs would be located either in water or in toluene. However, Figure 1 shows a strong emission of PL from the surface of the droplets, a clear signature that the QDs are located at the toluene/water interface. The abundance of the QDs at the microdroplet interface leads to a gravitational force that is larger than the buoyant force, resulting in a precipitation of the microdroplets onto the glass slide carrier. Hence, the microdroplets slightly touch the glass slide surface and may be deformed by the gravitational force. Such a deformation can be minimized by the buoyant force, due to the lower density of toluene ($\rho_{toluene}$ = 0.867 g/mL) compared to that of water (ρ_{water} = 1.0 g/mL). Although all of these forces affect the generated microdroplets, the remarkable stability of the microdroplets can eliminate the necessity of any levitation to keep the shape of the microdroplets almost perfectly spherical. Typical confocal microscope images of the QD-stabilized toluene microdroplets prepared by both methods are shown in Figure 1.

For efficiently manipulating the light−matter interaction with localized optical modes, such as WGMs in spherical resonators, small mode volumes, and high Q-factors are highly desired. Therefore, smaller droplets could provide a stronger interaction,
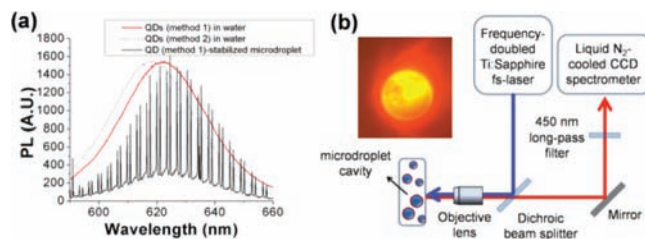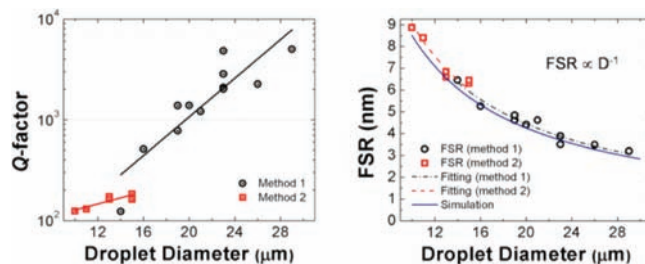
since the mode volume of the WGMs corresponds to the size of the QD-stabilized microdroplets if the Q-factor can be maintained at the same level. We found that, for our first stabilization method, the sizes of the microdroplets were, in general, larger (up to ∼60 μm) than those for the second method (up to ∼20 μm). This seems to be due to the lack of electrostatic interaction in method 1, which resulted in slower diffusion of the QDs in the water onto the interface of toluene microdroplets. The slower diffusion of QDs in method 1 was macroscopically observed, even though the concentration of QDs in method 1 was five times larger than that in method 2.

The stabilization of microdroplets with QDs opens the opportunity to directly observe the WGMs by simply measuring the QDs' photoluminescence (PL) spectrum of the QDs on the surface of the microdroplets. Since the QDs have direct contact with the microdroplets, their PL will be preferentially emitted directly into the WGM of the droplet cavity. At the same time, the light of the WGMs can be scattered by the QDs to the far-field, where it can easily be detected. A typical PL spectrum of a QD-stabilized microcavity is shown in Figure 2a, where a spectral comb of narrow PL lines is clearly observable. The PL lines appear in pairs of two lines with one line related to a transverse electric (TE) and the other to a transverse magnetic (TM) mode. The spectral line width of these modes is directly correlated with the total optical loss for the WGMs in the microdroplet.[21] Hence, the Q-factor can be determined directly from the line width of the PL peaks for liquid microcavities in the "liquid phase" (Figure 2b).

The QDs at the interface stabilize the microdroplet; nonetheless, the loss for the WGMs is expected to increase slightly due to the additional scattering caused by the surface roughness introduced by QDs. In the following, from the peaks in the PL spectrum, we estimated the Q-factor for microdroplets of various sizes. We found high Q-factors up to 4850 and 5100 for 23- and 29-μm-sized, QD-stabilized microdroplets, respectively (Figure 3a). We assumed that even higher values could be obtained with larger microdroplet sizes in the all-liquid phase, but these values could not be verified in the

experiment due to the limited spectral resolution ($\Delta\lambda \approx 0.11$ nm) of the spectrometer.

Assuming a perfectly smooth surface of pure toluene microdroplets in water, theoretical Q-factors of 9300 and 440 for 23- and 10-μm-diameter spheres, respectively, were calculated by finite element simulations. These Q-factors approximate a theoretical upper limit for the chosen refractive index contrast and do not include any absorption or scattering loss that would reduce the value. However, it is noted that the experimentally obtained Q-factors from the samples in the all-liquid phase are only factors of 2 to 4 smaller than the theoretical limits. Such high Q-factors have to be related either to the smooth surface of the microcavities, even in the presence of the QDs, or to the strong contribution of the QDs to a higher refractive index of the QD-stabilized microdroplet compared to pure toluene droplets in water.

To exclude the increased refractive index, we extracted the free spectral ranges (FSRs) for the microdroplet cavities from the experimentally determined WGM spectral positions (Figure 3b). Regardless of the preparation method, the FSRs of the microdroplet cavities were excellently fitted to the formula, $FSR = (\lambda^2)/(n_{eff}\pi D)$, which corresponds to the mode spacing in a circular resonator. We obtained effective refractive indices of $n_{eff} = 1.395 \pm 0.086$ and 1.371 ± 0.086 for method 1 and method 2, respectively. These values are close to the values calculated from the finite element simulations for toluene microdroplets that do not contain QDs. Hence, the effective refractive index of the pure toluene microdroplet is approximate to that of the QD-stabilized microdroplet. From our observations (high Q-factor and nearly unchanged effective index for the WGMs), we concluded that the WGMs in the QD-stabilized microcavities can experience only slightly increased scattering loss. This is perspicuous, since the size of QDs is <5.8 nm and additionally they form either a homogeneous monolayer or a submonolayer at the interface between the toluene microdroplet and water (Figure 1).

Although the surface modification of QDs was necessary to locate the QDs at the toluene–water interface, it also expedited the photoionization of the QDs, even when they were illuminated with low power laser radiation. (The excitation power level was adjusted to avoid the Auger effect.[22]) Such detrimental photoionization effects must be overcome to successfully achieve lasing in the all-liquid phase.

In conclusion, we have demonstrated two different methods for generating QD-stabilized toluene microcavities in water. These toluene microcavities provide high quality WGM microspherical resonators in the all-liquid phase. High Q-factors were size-dependently obtained from the microcavity resonators without destroying or deforming the droplets. The values are close to the theoretical, radiation-limited, Q-factor values for pure toluene microdroplets. To prove that the PL peaks corresponded to the WGMs in the QD-stabilized microdroplet, the FSR of the WGMs was compared with that of pure toluene microdroplets to prove that there was minimal scattering loss in the presence of the QDs. With our method, a large number of the droplets can be easily produced in a short time without any need for a microdroplet generator. The relatively easy fabrication scheme and the high stability make the QD-stabilized toluene microcavity resonators in the all-liquid phase a promising candidate for multiple all-liquid lasers.

Supporting Information Available: Detailed experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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