

Photoluminescence enhancement of colloidal quantum dots embedded in a monolithic microcavity

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We demonstrate an enhancement of the spontaneous emission from colloidal CdSe quantum dots embedded in a half-wavelength one-dimensional cavity. When embedded in the cavity, the emission of the quantum dots is enhanced by a factor of 2.7. We also show a strong amplification by one order of magnitude in the absorption of the CdSe quantum dots due to the cavity effect. © 2003 American Institute of Physics. [DOI: 10.1063/1.1581007]

Periodic photonic structures¹ can confine and enhance the electromagnetic field by orders of magnitude. Many properties have been predicted for structures such as microcavities and photonic crystals, including the ability to enhance and inhibit light emission. However, most demonstrations of enhancement and inhibition of spontaneous emission rely on the construction of the photonic structure on the substrate of the active layer itself, which limits the application to a specific set of materials. Examples include self-assembled quantum dots (QDs) in photonic crystals,^{2,3} single QDs embedded in pillar microcavities⁴ and epitaxially grown quantum wells in planar microcavities.⁵ In the case of self-assembled QDs, the nature of the growth technique also makes it difficult to control the number of QDs interacting with the optical field.

In this letter, we report the study of CdSe colloidal QDs in a microcavity formed between two distributed Bragg reflectors (DBRs). Colloidal semiconductor QDs are inorganic particles, typically a few nanometers in size. They are intensely fluorescent, and have a very high absorption cross section compared with other visible fluorophores such as organic dyes.^{6,7} The size dependence of the optical and electronic properties of semiconductor nanoparticles render them promising materials for photonics applications such as organic-inorganic hybrid solar cells,⁸ white-light lasers and energy converters,⁹⁻¹² and tunable sources of infrared radiation.¹³ The embedment of colloidal QDs in photonic structures opens the possibility of endowing optoelectronic properties to a wide variety of intrinsically inactive materials such as silicon and oxides.

Colloidal semiconductor QDs have a number of advantages over other semiconductor nanostructures with regard to their implementation as active layers in photonic cavities. For example, in contrast to self-assembled QDs, the surface density of colloidal semiconductor QDs can be easily controlled. Appropriate chemical functionalization of their surfaces allows colloidal QDs to be incorporated in a variety of materials, useful for hybridlike structures. Finally, the ability to dilute colloidal QDs to low surface densities can lead to

the exciting possibility of single QD interactions with the photonic states.

Several attempts to incorporate colloidal QDs in photonic structures have been made, including QDs embedded in poly(methylmethacrylate) spheres,¹⁴ polystyrene microspheres,¹⁵ one-dimensional microcavities,^{16,17} and opal photonic crystals.¹⁸⁻²⁰ However, enhancement of the spontaneous emission has not yet been shown, mainly because of the large size of the structures compared to the visible emission wavelength of the QDs. Here, we demonstrate the enhancement of the spontaneous emission of colloidal QDs embedded in a one-dimensional cavity.

CdSe QDs were synthesized in coordinating solvents using variations of the methods developed by Murray *et al.*²¹ and Qu *et al.*²² The QD core diameter was 2.8 nm as determined from optical absorption spectroscopy. CdSe QD cores were further capped with a semiconductor shell (ZnS) according to literature methods.^{23,24} The cavity is composed of a half-wavelength thick SiO₂ layer sandwiched between two DBRs. Each DBR consists of six periods (12 layers) of TiO₂-SiO₂, quarter-wavelength thick layers. rf sputtering was used for SiO₂ and reactive dc sputtering was used for the TiO₂ layers. The last layer deposited on top of the first DBR established the first half of the $\lambda/2$ cavity. The colloidal QD suspension was spun coat into a 95 nm thick layer in the center of the cavity on that last SiO₂ film. The second half of the SiO₂ cavity and the other layers forming the top DBR were finally deposited. The entire structure was deposited in a wedged manner to obtain a continuum of Fabry-Perot resonances that are position determined (approximately 4 nm/mm) across the cavity sample. A reference sample was prepared by spin coating QDs with the same thickness on a glass slide and capping them with a sputtered 75 nm thick layer of SiO₂.

Photoluminescence measurements at room temperature were performed using the 457.9 nm line of an argon laser for optical excitation, with an intensity of 0.14 W/cm². A spot size of approximately 1 mm in diameter averaged out any spatial inhomogeneities arising from the spin-coating process. 2 mm apertures in the optical path ensured that the measurements were taken from light emitted solely perpen-

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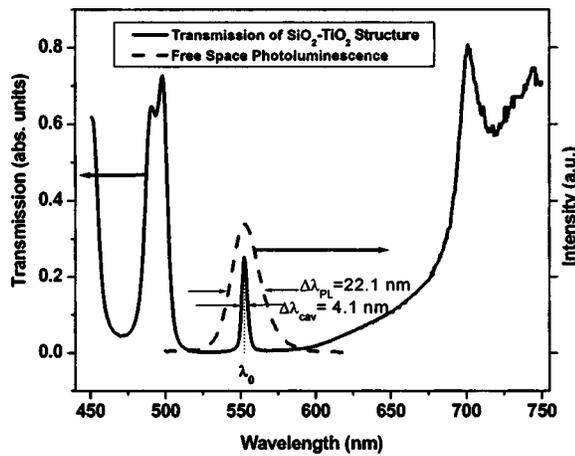


FIG. 1. Measured transmission of the monolithic Fabry-Perot microcavity embedded with QDs. Superimposed is the free space photoluminescence spectrum of the reference sample.

dicular to the structure in order to avoid light collection from adjacent cavity resonances.

Figure 1 shows the transmission spectrum of the structure at a position on the cavity sample surface corresponding to a cavity mode at $\lambda_0=552.7$ nm. Also shown in Fig. 1 is the photoluminescence spectrum from the reference sample whose emission maximum corresponds to the cavity resonance. The quality factor $Q=\lambda_0/\Delta\lambda$ of the cavity is 135. The observed lower transmission at the cavity mode is attributed to the absorption of the QD layer at the emission wavelength.³

The QD absorption at the emission wavelength is enhanced due to the cavity effect. The magnitude of this enhancement was obtained by fitting calculated transmission spectra to the measured spectra, for different cavity resonances using the transfer matrix method.²⁵ From the curve fits of the theoretical spectra and the experimental transmission spectra between 530 and 580 nm, the cavity thickness and the layer extinction coefficient of the QDs as a function of wavelength were determined. Indices of refraction of 1.46 and 2.1 for SiO₂ and TiO₂, respectively, were used for the calculations. The QD layer was modeled with a real index of $n_r=2.8$ (determined using ellipsometry). Note that the relatively high index for the QD layer may originate from the fact that the wavelength used for the ellipsometric measurements was close to an electronic resonance of the QDs.

Figure 2(a) shows the transmission of three different cavity resonances along with the fitted theoretical data. In Fig. 2(b), the absorption obtained from the fitted spectra is shown for the cavity structure together with the absorption of the reference sample. The absorption at the emission wavelength is amplified by an order of magnitude due to the light confinement in the cavity. Similar enhancement of absorption was previously shown for embedded quantum wells in microcavities.²⁶ In the case of colloidal QDs, the absorption enhancement is especially strong due to the significant free space absorption at the emission wavelength. Unfortunately, significant enhancement of the absorption limits the effective Q that can be achieved since the electric-field in a strongly absorbing system is weaker relative to one that has no absorption. This limitation on the Q is important in systems where the emission linewidth approaches that of the cavity

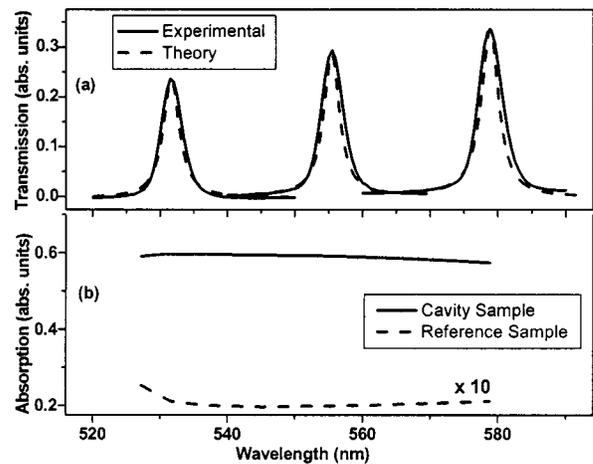


FIG. 2. (a) Experimental and theoretical transmission spectra for three different cavity resonances. (b) Calculated absorption of the cavity and reference samples as a function of wavelength.

linewidth, where the coupling to the cavity is strongly dependent on the cavity Q , such as for example a single QD in a cavity.

Figure 3 shows the photoluminescence spectra measured at two different positions on the cavity sample surface, corresponding to cavities in and out of resonance with the free space emission maximum of the QDs. Also shown is the photoluminescence spectrum of the reference sample. The spectrally integrated photoluminescence from the cavity structure in resonance with the free space emission line of the QDs is enhanced by a factor of 2.7 ± 0.6 compared to the photoluminescence from the reference structure. The full width at half maximum (FWHM) of the CdSe QDs photoluminescence spectrum narrows considerably from 22.1 nm to 6.6 nm when the QDs are placed inside microcavity. The narrow luminescence linewidth is very close to the FWHM of the cavity mode as measured with transmission spectroscopy (Fig. 1), and is due to the coupling between the cavity mode and the QD emission. The spectra in Fig. 3 also displays a background that corresponds to the photoluminescence spectrum of QDs in free space, in addition to the sharp cavity-mode emission. The emission at wavelengths that do not correspond to the cavity resonance indicates that some

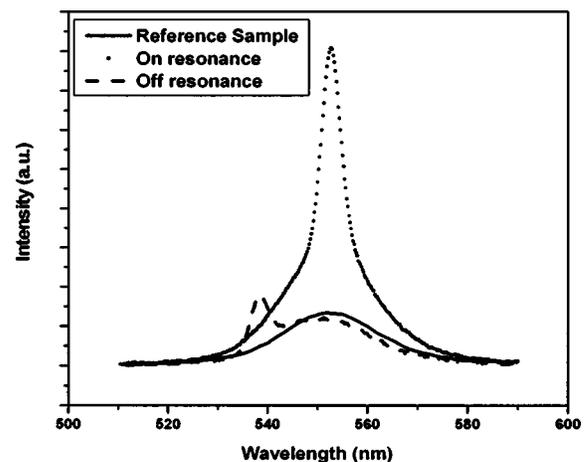


FIG. 3. Photoluminescence of colloidal QDs embedded in a microcavity measured for different cavity thicknesses (dotted and dashed lines) and of the reference sample (solid line).

QDs are not coupled to the cavity mode. Thus, these QDs may not be located inside the optical cavity, and instead may be embedded in the layers of the top DBR as a result of the sputtering process.

In a one-dimensional microcavity, the integrated emission enhancement in the direction perpendicular to the lay plane of the layers is given by²⁷

$$\frac{\Gamma}{\Gamma_0} = \frac{2F}{\sqrt{2\pi}} \xi,$$

where $\xi = |E_{\text{dots}}|^2 / |E_{\text{max}}|^2$ represents the effective intensity of the field at the QD layer relative to the peak value of that intensity in the cavity region. The finesse is given by $F = \lambda_0 Q / 2nd$. When $\Delta\lambda_{\text{PL}} \gg \Delta\lambda_{\text{cav}}$ (see Fig. 1), Q is limited to the photoluminescence quality factor ($Q = \lambda_0 / \Delta\lambda_{\text{PL}} = 25$).²⁸ The values for the average field intensity at the QDs layer E_{dots} and for the maximum field intensity at the cavity E_{max} were determined using the transfer matrix formalism resulting in a value for their ratio of 0.34. The theoretical value for the integrated enhancement Γ/Γ_0 is then 4.5. The small discrepancy between this value and the experimental value of 2.5 may be attributed to the inhomogeneity of the QDs in the cavity.

The enhancement of the QD emission indicates coupling of the QDs to the cavity mode. Similar coupling was previously observed for self-assembled semiconductor QDs.²⁹ Here, we demonstrate coupling in a colloidal QD system, allowing for the possibility of a significant control over light emission from optically inactive photonic systems. For example, structures containing colloidal QDs emitting in the technologically important near infrared^{30,31} could be fabricated in a similar manner. The coupling opens the possibility of controlling externally the intensity and lifetime of the QDs. Single QD systems could allow for the exciting possibility strong coupling to the cavity mode.³² Quantum electrodynamic effects such as the formation of dressed states are then expected, opening the door for applications such as optical computing.³³

The embedment of colloidal QDs in photonic structures holds great promise for enabling active technological breakthroughs in the area of photonics, such as the integration of monolithic light emission and modulation devices on chip. We studied the photoluminescence of colloidal semiconductor QDs embedded inside an SiO_2 - TiO_2 microcavity structure. When the cavity mode is in resonance with the photoluminescence maxima of the QDs, we measure a spectrally integrated photoluminescence enhancement of 2.5, compared to a theoretical value of 4.5. We also show amplification of the absorption of the QDs at the emission spectral range of one order of magnitude due to the cavity effect. This amplification of the absorption and emission may become an important consideration for amplifiers and lasers based on colloidal QDs.

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