

Energy transfer between colloidal semiconductor nanocrystals in an optical microcavity

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The authors have studied nonradiative energy transfer between semiconductor nanocrystals (NCs) placed in a Fabry-Pérot microcavity. The spectrally integrated fluorescence from a monolayer of single sized NCs in the cavity is enhanced by a factor of 4.8 compared to free space. For a monolayer of mixed sized NCs, the acceptor NC fluorescence intensity is enhanced by an additional factor of 2.7 due to energy transfer processes. When the cavity mode is resonant with the acceptor NC fluorescence emission maximum, donor NC emission is completely suppressed, providing a narrow spectral output. © 2006 American Institute of Physics. [DOI: 10.1063/1.2335632]

Due to their size-dependent optical and electronic properties,¹ high brightness, and photostability, semiconductor nanocrystals (NCs) have demonstrated great potential for novel photonics applications.²⁻⁴ Further, the use of inter-NC energy transfer to enhance the performance of integrated NC-phonic systems is also expected to take on increasing importance in a similar manner to what has taken place for all-organic devices.⁵ Indeed, nonradiative energy transfer involving semiconductor NCs has been studied in nanocrystal assemblies⁶ and nanocrystal-organic dye systems,⁷ with applications in biological sensing⁸ and nanophotonics.⁹

Several attempts to modify the luminescence of semiconductor nanocrystals using photonic structures have been described, including NCs embedded in polymer spheres,^{10,11} one-dimensional (1D) optical microcavities,^{7,12} and opal photonic crystals.¹³⁻¹⁵ Whereas cavity-induced enhancement of the spontaneous emission of colloidal NCs was recently demonstrated,¹² the study of the nonradiative energy transfer process between two sized colloidal semiconductor NCs in an optical microcavity has not been reported.

In this letter we present studies of energy transfer between semiconductor NCs placed in Fabry-Pérot (1D) microcavities. The spectrally integrated fluorescence from a monolayer of single sized NCs is enhanced by a factor of 4.8 compared to free space, due to an enhanced electric field inside the cavity. For a monolayer containing two different sized NCs, nonradiative energy transfer enhances the fluorescence of the (larger) acceptor NCs by an additional factor of 2.7. A pure and narrow spectral output results when the cavity mode is in resonant with the acceptor NCs due to suppression of the (smaller) donor NC emission.

CdSe NCs capped with a ZnS shell were synthesized according to published methods.¹⁶⁻¹⁹ Figure 1 shows absorption and fluorescence spectra of the two sized NCs used in this study. The CdSe NC diameters for the small and large NCs are 3.6 and 4.6 nm, respectively, determined from ab-

sorption spectroscopy.^{19,20} Fluorescence quantum yields of the smaller and larger NCs (after capping with ZnS) were 27% and 10%, respectively, relative to Rhodamine 590 and Rhodamine 640, respectively. NCs were photoexcited with the 514 nm line from an argon ion laser, since that wavelength is outside the high-reflectivity band of the microcavity.

The optical microcavity structure was formed between two distributed Bragg reflectors (DBRs), as shown in the inset of Fig. 1. Each DBR consisted of six periods of quarter-wavelength thick alternating TiO₂-SiO₂ layers. Rf and reactive dc sputtering were used to deposit the SiO₂ and TiO₂, respectively. To form the NC monolayer on the substrate (consisting of a SiO₂ spacer layer and one DBR), standard Langmuir-Blodgett techniques were followed. After drying, more SiO₂ and the second DBR were deposited to complete the cavity. A reference sample consisting of a monolayer of NCs on a glass slide was similarly prepared but capped with a layer of 75 nm thick SiO₂.

Spectral overlap between the donor emission and the acceptor absorption determines the relative strength of resonant

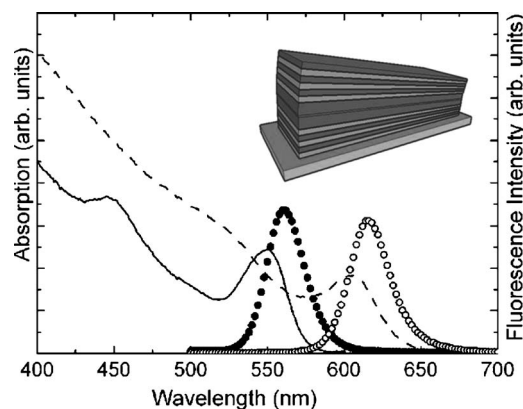


FIG. 1. Absorption and emission spectra of CdSe/ZnS NCs: solid line is the absorption spectrum of small NCs, solid circles are the emission spectrum of small NCs, dashed line is the absorption spectrum of large NCs, and open circles are the emission spectrum of large NCs. The inset is a cartoon corresponding to a cross section of the device.

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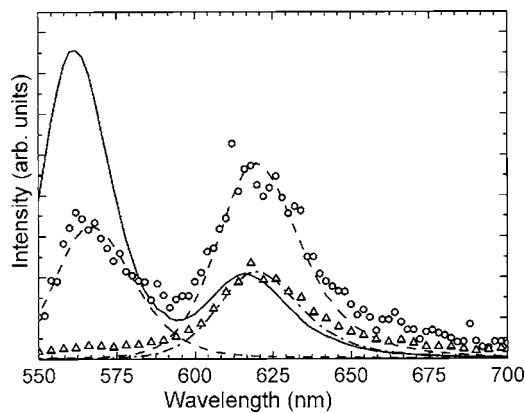


FIG. 2. Fluorescence spectra in free space from a colloidal suspension of mixed sized NCs (solid line), a single monolayer of mixed sized NCs (open circles), and a monolayer of large NCs (open triangles). The dashed and dashed-dot lines are Gaussian fits indicating the contributions of each sized NC to the mixed and large NC fluorescence spectra, respectively.

dipole-dipole interactions.²¹ Accordingly, for a given spectral overlap, a critical donor-acceptor distance R_0 can be defined as the distance when the rate of energy transfer (k_{ET}) equals the sum of all other radiative (k_r) and nonradiative (k_{nr}) rates. Figure 1 shows the spectral overlap between the fluorescence and absorption from the 3.6 nm (donor) and 4.6 nm diameter (acceptor) NCs. From the donor-acceptor spectral overlap, the critical distance R_0 can be calculated according to²²

$$R_0 = 9.78 \times 10^3 [\kappa^2 n^{-4} Q_D J(\lambda)]^{1/6}, \quad (1)$$

where κ^2 is the relative orientation of the donor and acceptor and is equal to 2/3 here; n is the refractive index of the NC monolayer; Q_D is the luminescence quantum yield (QY) of the donor; and $J(\lambda)$ is the spectral overlap. For the NC monolayer, we use an effective index of refraction $n=2.0$ based on the volume fraction of CdSe in such a layer (i.e., we include the volume of the organic ligand), where the NC index of refraction is identical to that of bulk CdSe ($n=2.6$), and the organic cap (trioctylphosphine) has $n=1.47$. We calculate $R_0=5.8$ nm, which agrees with earlier calculations for similarly sized NCs.⁶ The expected energy transfer efficiency E is given by²²

$$E = mR_0^6 / (mR_0^6 + R_{DA}^6), \quad (2)$$

where m is the number of acceptors per donor (3/4) and R_{DA} is the actual donor-acceptor distance. Given the diameters of the CdSe core NCs and the thickness of the ZnS shell (0.45 nm),²³ and assuming a separation of 1.1 nm due to the organic surface capping molecule,⁶ we calculated 6.1 nm for R_{DA} and an energy transfer efficiency of 36%.

The fluorescence spectrum from a colloidal suspension of small and large CdSe/ZnS NCs with a molar ratio of 4:3 is shown in Fig. 2. Also shown in Fig. 2 is the fluorescence from the same suspension cast into a single monolayer. Relative to the colloidal suspension, in the thin NC film the smaller NC fluorescence intensity is decreased while that from the larger NCs is increased. For comparison, the fluorescence spectrum of a monolayer of purely large NCs is also shown in Fig. 2. This spectrum is normalized such that it represents fluorescence from the same number of large NCs as the spectrum from the mixed NC monolayer. Fitting the fluorescence data in Fig. 2 with a sum of two Gaussian functions, each centered at the fluorescence maxima of the

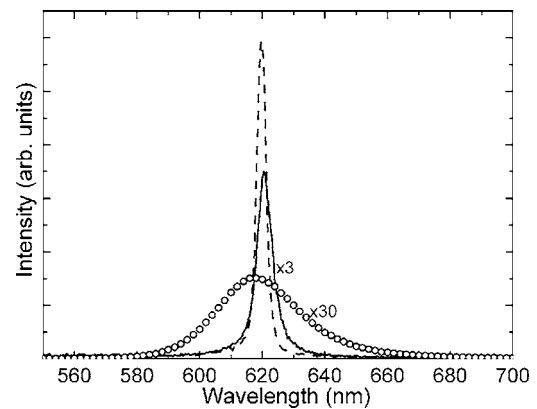


FIG. 3. Normalized fluorescence spectra measured from monolayers of CdSe/ZnS NCs. The open circle, solid line, and dashed line correspond to a monolayer of large NCs in free space, large NCs in the optical cavity, and mixed sized NCs in the optical cavity, respectively. The spectrum of the large NC monolayer in free space is scaled by 30, and the spectrum of the large NC monolayer in the microcavity is scaled by a factor of 3.

smaller and larger NCs, allows for a quantitative determination of the contribution of each sized NC to the mixed NC fluorescence spectrum and thus a determination of the relative increase in fluorescence intensity (per large NC) in the mixed size NC films. We determine that the relative integrated emission is increased by a factor of 2.0 ± 0.3 for the mixed NC film compared to the purely large NC film. Also, fluorescence lifetime measurements (data not shown) show that the lifetime of the smaller (larger) NCs is decreased (increased) in the mixed sized film relative to a monolayer of just small (large) NCs. An increase in the fluorescence lifetime of the acceptor NC coupled with a decrease in the lifetime of a donor NC suggests that the observed increase in fluorescence intensity of the larger NCs in the mixed sized NC monolayer results from nonradiative energy transfer processes.

Figure 3 shows the fluorescence spectrum for a monolayer of large NCs inside the 1D optical microcavity when their free space fluorescence maximum is in resonance with the cavity mode, and also the fluorescence spectrum from a reference sample in free space. The spectrally integrated fluorescence in the forward direction (numerical aperture = 0.2) from the NCs in the cavity is enhanced by a factor of 4.8 ± 0.6 compared to the reference, and the full width at half maximum (FWHM) narrows considerably (from 33 to 5.5 nm). The luminescence linewidth is close to the FWHM of the cavity mode (4 nm), which is due to coupling between the cavity mode and the NC emission.¹²

Figure 3 also shows the fluorescence spectrum of a mixed NC monolayer consisting of a 4:3 molar ratio of small to large NCs inside the microcavity, when the fluorescence maximum of the larger NCs (620 nm) is in resonance with the cavity mode. This spectrum is normalized such that it corresponds to the same number of large NCs as would be present in a monolayer of only large NCs. Per NC, the spectrally integrated fluorescence for the mixed NC film is more intense by a factor of 2.7 ± 0.4 compared to the film consisting of purely large NCs, due to energy transfer from the smaller NCs to the larger NCs. The increase in fluorescence intensity from placing NCs in the cavity (4.8-fold) combined with the increase in intensity seen due to energy transfer (2.7-fold) results in an overall factor of 13 increase in fluorescence intensity for the mixed NC monolayer inside the

microcavity compared to a monolayer of purely large NCs in free space. Also note that we observed no fluorescence from the smaller NCs when the cavity mode is not resonant with the smaller NC fluorescence spectrum. Thus, the smaller NCs are also completely coupled to the cavity.

The microcavity modifies the NC fluorescence in several ways. First, the enhanced electric field inside the cavity causes an increase in overall NC absorption.¹² In particular, the increase in absorption by the smaller NCs causes a direct increase in emission by the larger NCs due to energy transfer. Second, the increased electric field inside the cavity also causes an intensity increase in the fluorescence from the larger NCs even with no smaller NCs present.¹² Third, the smaller NCs are prevented from radiating into cavity modes that are directed perpendicular to the cavity, although we expect that the smaller NCs can radiate into modes emitting out of the sides of the cavity.

The integrated emission enhancement Γ/Γ_0 in a 1D cavity is given by²⁴ $\Gamma/\Gamma_0 = (2F/\sqrt{2\pi})\xi$, where the finesse $F = \lambda_0 Q / (2nd)$ ($d = 310$ nm is the cavity length) and $\xi = |E_{\text{dots}}|^2 / |E_{\text{max}}|^2$. For a cavity in resonance with the large NC fluorescence, the quality factor Q in F is given by $\lambda_0 / \Delta\lambda_{\text{PL}} = 20$, since $\Delta\lambda_{\text{PL}} \gg \Delta\lambda_{\text{cav}}$ ($\Delta\lambda_{\text{PL}}$ is the NC fluorescence linewidth and $\Delta\lambda_{\text{cav}}$ is the cavity mode linewidth). The enhancement factor ξ equals the ratio of the intensity of the optical field at the NC layer to the peak value of that intensity in the cavity region. We assume $\xi \sim 1$ since the monolayer of NCs is deposited in the center of the cavity, and thus calculate $\Gamma/\Gamma_0 = 10.9$. Including energy transfer processes but neglecting the effect of the cavity on the energy transfer rate adds an additional factor of ~ 2 for a total enhancement per NC of 22, which reasonably agrees with the measured value of 13. We believe one contribution to the difference between the measured and calculated enhancements likely lies in our assumption of $\xi \sim 1$, since the NC monolayer is probably not in the exact center of the cavity. An additional contribution may come from the fact that for emitters with very high (unit) QY, the enhancement due to the microcavity is predicted to be relatively independent of the local optical mode density.²⁵ In this case, we would expect a lower experimental value than what is calculated based on a simple comparison of the optical mode densities of the microcavity and the reference.

To further increase the device output, the ratio of small NCs to large NCs could be optimized for maximum energy transfer into the larger NCs. The sizes of the donor and acceptor NCs could also be adjusted such that spectral overlap is larger and the smaller NCs could be chemically linked to the larger NCs. Finally, instead of a single layer, several multilayers of mixed NC sizes could also be used.

In summary, we have measured the optical emission characteristics from a microcavity containing monolayers of two semiconductor NC sizes. The fluorescence intensity from the larger NCs was enhanced by over a factor of 13 (per NC) compared to these NCs in free space. This substantial

enhancement arises from an increase in the electric field inside the optical cavity and from energy transfer to the larger NCs from the smaller NCs. In addition, the fluorescence from the smaller NCs is completely quenched, making the output from the optical cavity spectrally very pure. The understanding of and the ability to manipulate energy transfer between NCs inside optical cavities will positively impact future applications in nanophotonics.

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