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Report Title

Semiconductor Nanocrystal Photonics

ABSTRACT

Please See Attached file.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

C. B. Poitras, M. Lipson, M. A. Hahn, H. Du, and T. D. Krauss, "Photoluminescence enhancement of colloidal semiconductor quantum dots embedded in a monolithic microcavity," Appl. Phys. Lett. 82, 4032 (2003).

J. J. Peterson and T. D. Krauss, "Fluorescence Spectroscopy of Single Lead Sulfide Quantum Dots," Nano Lett. (in press, 2006).

Number of Papers published in peer-reviewed journals: 2.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Z. Yu, L. Guo, H. Du, T. Krauss and J. Silcox, "Characterization of shell material on colloidal CdSe/ZnS quantum dots," in Nanoparticles and Nanowire Building Blocks-Synthesis, Processing, Characterization and Theory, Eds: O. Glembocki, C. Hunt, C. Murray, G. Galli, Mat. Res. Soc. Symp. Proc. 818 M 6.8 (2004).

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(c) Papers presented at meetings, but not published in conference proceedings (N/A for none)

T. D. Krauss, "Enhanced Fluorescence from Semiconductor Quantum Dots in Optical Microcavities," presented at the Conference on Nanoscale Devices & System Integration, Houston, Texas (2005).

Li Guo, Xiaowei Teng, Hong Yang, Todd D. Krauss, Carl B. Poitras, and Michal Lipson, "Enhanced Energy Transfer between Colloidal Semiconductor Quantum Dots in an Optical Microcavity," poster presented at the Fall 2005 Meeting of the Materials Research Society, Boston, Massachusetts (2005).

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(d) Manuscripts

L. Guo, X. Teng, H. Yang, T. D. Krauss, C. B. Poitras, and M. Lipson, "Energy transfer between colloidal semiconductor quantum dots in an optical microcavity," (submitted, 2006).

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Li Guo (0.75)

Jeffrey Peterson (0.25)

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PI: Todd D. Krauss

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Semiconductor Nanocrystal Photonics

Abstract:

The overall objective of the project is to take advantage of the unique photon density of states of periodic structures to enhance the energy transfer between two sizes of semiconductor nanocrystals placed inside a planar optical microcavity. We have fabricated thin films of two sized CdSe nanocrystals with controllable thickness. These films show efficient energy transfer from the smaller to the larger nanocrystals as measured by steady state and time resolved fluorescence. We have successfully deposited these films in the middle of single-mode, planar optical microcavities and measured spectrally narrow optical emission from the cavity. We have also measured increased fluorescence in the cavity by a factor of 13 from the larger nanocrystals (relative to free space) due to the combination of energy transfer processes and enhancement from the cavity. Finally, we have succeeded in fabricating highly fluorescent and size-tunable PbS nanocrystals and detecting their fluorescence on the single particle level. Studies of PbS and PbSe nanocrystals are especially interesting and important because they provide an alternative NC material that can emit throughout the technologically important near-infrared region. Preliminary results coupling PbSe NC fluorescence into near infrared optical cavities and waveguides have also been achieved.

Scientific Progress and Accomplishments

Nanocrystal Photonics

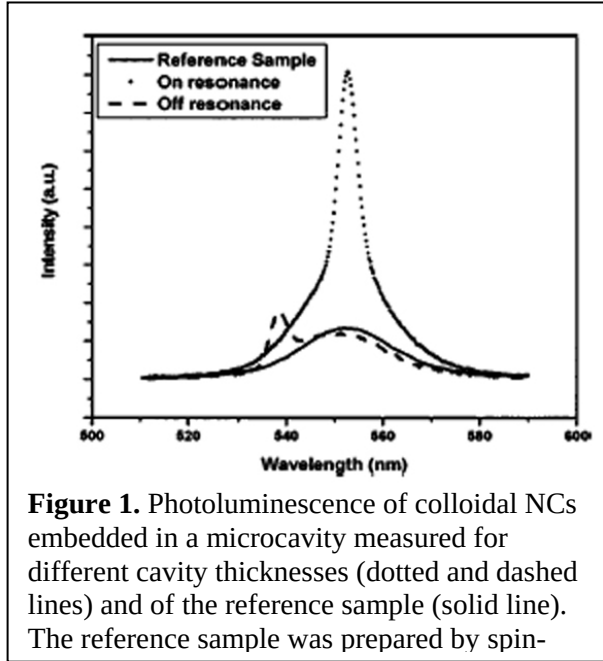
It is well known that energy transfer from one material (donor) to another material (acceptor) can take place non-radiatively through a resonant dipole-dipole interaction (RDDI) when the two materials are separated by a distance much less than the optical wavelength. However, the effect of optical microcavity induced changes in the RDDI (i.e. on the energy transfer rate) is much less clear, and convincing arguments have been presented on both sides of the issue. We are addressing the important and long standing fundamental question of whether an optical microcavity can affect the RDDI, which we have explored through studies of energy transfer between colloidal CdSe nanocrystals.

Initially, we placed colloidal CdSe nanocrystals (NCs) inside a 1-D optical microcavity and studied the enhancement of the spontaneous emission from the NCs. This project was in collaboration with Michal Lipson in the Department of Electrical and Computer Engineering at Cornell University, who fabricated the cavities used in the experiment. The optical cavity was composed of a half-wavelength thick SiO₂ layer sandwiched between two distributed Bragg reflectors (DBRs). The colloidal NC suspension was spun-coat into a 95-nm thick layer in the center of the cavity and then the other layers forming the top DBR were finally deposited.

Our major findings were:

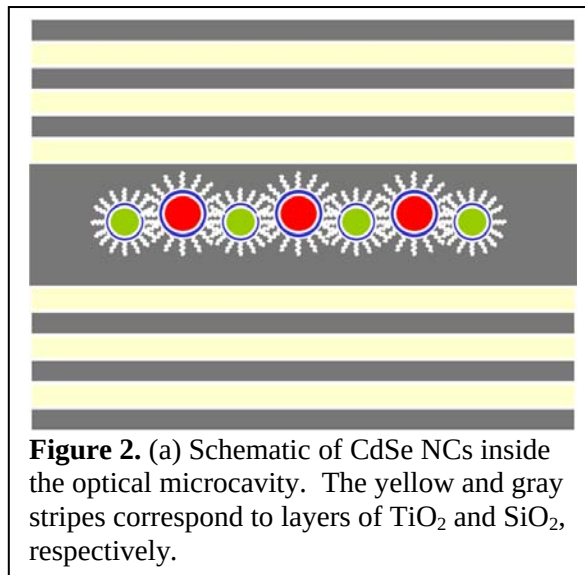
- 1) When embedded in the cavity, the spontaneous emission of the NCs is enhanced by a factor of 2.7 (See Figure 1) compared to a reference structure. The theoretical value for the integrated enhancement is 4.5, in good agreement with our measured value.
- 2) There was also a strong amplification by one order of magnitude in the absorption of the CdSe NCs due to the cavity effect.

The major significance of these findings was that we demonstrated for the first time an enhancement of the spontaneous emission (i.e. fluorescence) of a colloidal NC when placed inside an optical microcavity.



As can be seen in Figure 1, a major problem with our initial fabrication strategy was that the fluorescence from a significant number of NCs was not coupled to the cavity, causing the broad "pedestal" below the narrow cavity emission feature. We improved upon our initial device fabrication strategy by forming a monolayer of NCs in the cavity through Langmuir-Blodgett techniques (Figure 2). In this manner, a single monolayer of NCs was all coupled to the single mode of the cavity when the free space emission wavelength of the NC was resonant with the cavity. When not resonant with the cavity mode, no emission from the NCs was observed.

We found that our new NC deposition strategy also improved the performance of the device significantly. When the NC free space fluorescence maximum was in resonance with the cavity mode, the emission from the NC was enhanced



by a factor of 4.8 compared to free space (Figure 3), whereas before we had only a factor of 2.7 improvement. Also, the full width at half maximum (FWHM) of the NC fluorescence spectrum narrowed considerably from 33 nm to 5.5 nm for the NCs inside the microcavity. The narrow luminescence line width (5.5 nm) is also very close to the FWHM of the cavity mode (4 nm) as measured with transmission spectroscopy, due to coupling between the cavity mode and the NC emission.

For a mixed sized NC monolayer placed inside the same 1-D optical cavity, consisting of a 4:3 molar ratio of smaller (emission maximum at 550 nm) to larger (emission maximum at 625 nm) NCs, the spectrally integrated fluorescence of the

larger NCs (per NC) was greater by a factor of 2.7 ± 0.4 compared to the film consisting of purely large NCs (when the free space fluorescence maximum of the larger NCs is in resonance with the cavity mode). The increase in the fluorescence intensity for the mixed NC layer compared to the purely large NC layer is clearly due to energy transfer from the smaller NCs to the larger NCs. Further, efficient coupling of the smaller NCs (in the mixed film) to the optical cavity prevented their fluorescence from leaving the cavity (Figure 3). 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 a over a 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.

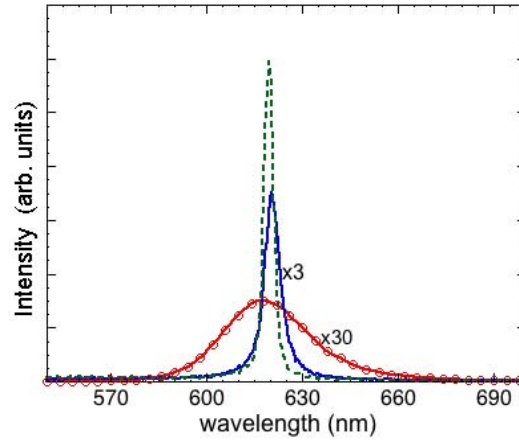


Figure 3. Normalized fluorescence spectra from monolayers of CdSe/ZnS NCs. The red, blue, and green lines correspond to large NCs in free space, large NCs the optical cavity, and mixed sized NCs in the optical cavity. The spectrum of large NCs in free space is scaled by a factor of 30, and the spectrum of large NCs in the microcavity is scaled by a factor of 3.

More experiments are needed to clarify whether the optical cavity is having an effect on the energy transfer process. The free-space mixed NC monolayer has fluorescence intensity enhancement per large NC of 2.2, due to the energy transfer from the smaller to larger NCs. Inside the optical cavity this identically prepared monolayer has an enhancement of 2.7, which is 20% larger than the mixed layer in free space. On the other hand our estimates of the errors in each of these enhancement values suggest that the enhancement is barely statistically significant. Further and more convincing support could come from measurements of the fluorescence lifetime of the donor and/or acceptor NC. However, we were unfortunately not able to obtain fluorescence lifetimes from the cavity samples since our time-resolved fluorescence apparatus has been inoperative for over 18 months.

For our energy transfer studies our major findings were:

- 1) Discovered that efficient coupling of a single monolayer of CdSe NC to the single mode of a 1-D optical microcavity could enhance the NC fluorescence intensity by a factor of 5.
- 2) For a NC film containing two-sized NCs inside the same optical cavity, the fluorescence of the larger NCs was further enhanced by a factor of 2.7 due to Förster energy transfer processes.

3) When the cavity mode is resonant with the acceptor NC fluorescence emission maximum, donor NC emission is completely suppressed, providing a narrow spectral output.

PbS and PbSe Nanocrystals

Part of the interest in studying energy transfer in optical cavities is to discover novel physical phenomena that will enable the next generation of lasers, optical amplifiers, displays, etc. Given the massive investment in optoelectronics at wavelengths important to the telecommunications industry, it is clear that such novel photonics devices based on semiconductor NCs will have significantly more impact if they can operate in the near infrared (NIR) between 1300 and 1550 nm. Unfortunately, an understanding of the optical properties of NCs that emit in the NIR is just beginning to take shape since high quality NCs were just synthesized in the last couple of years. To that end, we have synthesized and studied the optical properties of PbS and PbSe NCs down to the single particle level.

A series of PbS and PbSe NC absorption spectra as a function of NC size is shown in Figure 4. Most sizes of NCs exhibit multiple exciton peaks in their absorption spectra, and the onset of absorption is shifted substantially to the blue of the bulk band gap. From the absorption spectra we estimate a size distribution of 5 - 10%. Room-temperature fluorescence is bright and dominated by band edge recombination. The spectral bandwidth of the fluorescence is comparable to that of the absorption peaks, which suggests that the bandwidth is a consequence of the particle-size distribution. Fluorescence from deep traps, typically observed as weak, broad, and highly Stokes-shifted emission, was never observed.

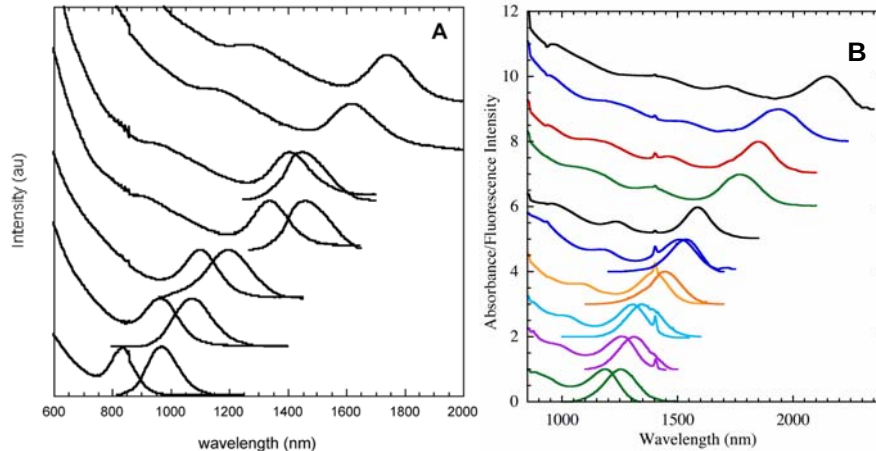


Figure 4. Absorption and fluorescence spectra for a series of different sized (a) PbS and (b) PbSe NCs ranging in diameter from ~ 3 to ~ 8 nm from left to right. The feature at 1400 nm in (b) is due to trioctylphosphine. Measured quantum yields ranged from 12 to 81%.

We have also performed preliminary studies of the fluorescence from single PbS NCs. In samples prepared at ultra-low NC concentrations, we observed isolated areas of relatively bright intensity (“hot spots”), which correspond to fluorescence from individual NCs (Figure 5). As expected, the fluorescence spectra of single PbS NCs are narrower than the ensemble (Figure 5). However, the average FWHM is huge (100 ± 30 meV), which is unexpected, since in NCs of II-VI and III-V materials there is not a huge homogeneous contribution to the fluorescence line width at 300 K. Whereas the line shape of the ensemble shows no structure, line shapes of single PbS NC spectra surprisingly can exhibit an asymmetry or shoulder (Figure 6).

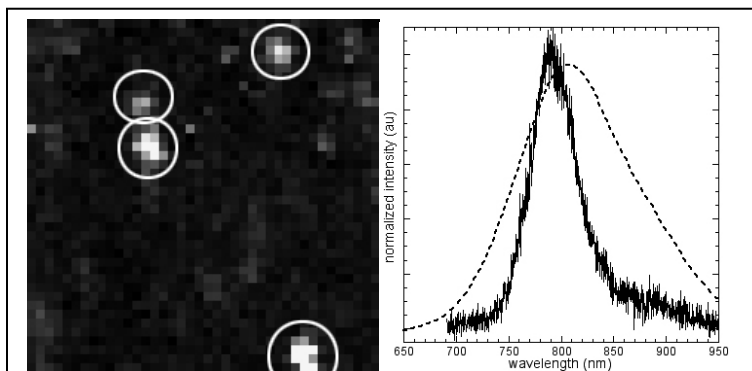


Figure 5. (Left) Fluorescence image of single PbS NCs ($10\ \mu\text{m} \times 10\ \mu\text{m}$) with a spatial resolution of $\sim 500\ \text{nm}$. (Right) Fluorescence spectra of a single PbS NC (solid) and the ensemble (dashed). The FWHM of the single and ensemble PbS NC spectra are $85\ \text{meV}$ and $240\ \text{meV}$, respectively.

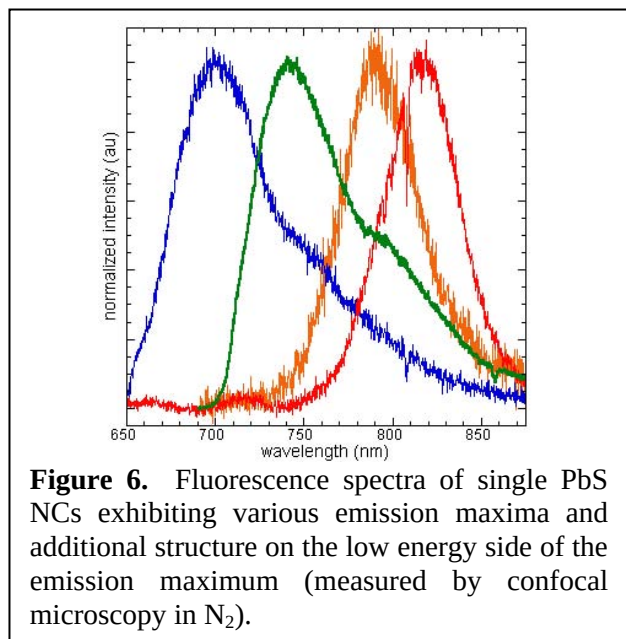


Figure 6. Fluorescence spectra of single PbS NCs exhibiting various emission maxima and additional structure on the low energy side of the emission maximum (measured by confocal microscopy in N_2).

Whereas the simplest models predict an 8-fold degenerate ground state, the observation of structure in the single PbS NC spectra imply that that more sophisticated theoretical treatments, which include effects such as anisotropy, spin-orbit, and intervalley couplings, are required to accurately model the electronic structure of PbS NCs. Indeed, the splitting may be due to degeneracy breaking of the lowest electronic transition via coupling of equivalent L-valleys, since the average observed splitting ($120 \pm 20\ \text{meV}$) is in good agreement with a calculated value of $120\ \text{meV}$ for 2.7-nm

diameter PbS NCs. With respect to specific novel technology, such a degeneracy splitting may be prove quite advantageous. For example, optical amplification and lasing applications should benefit from reduced pumping thresholds to achieve a population inversion. On the other hand, the oscillator strength of the first transition is now spread among multiple transitions, detrimental to potential applications such as optical switching.

For our single PbS NC fluorescence studies our major findings were:

- 1) Observed of fluorescence from single PbS quantum dots (NCs) using confocal microscopy.
- 2) Single particle fluorescence linewidths averaged $100\ \text{meV}$, indicating a significant homogeneous component to the ensemble linewidth.
- 3) The splitting in the fluorescence spectrum likely is a breaking of the 8-fold degenerate ground state, which will have a significant impact on future photonics applications.

PbSe Nanocrystal Devices

Recently, we have explored the use of PbSe nanocrystals as the active elements in near-infrared (NIR) photonics devices. With regards to designing photonic structures, working in the NIR provides for many advantages in ease of fabrication, as all the sub-elements of the device can be larger. Also, working in the NIR allows for devices in a wavelength region that has

attained technological significance. In Figure 7(a) we show a 1-D optical cavity embedded in an optical waveguide designed to guide light at 1.55 μm . We have deposited PbSe NCs on top of this structure and excited the NCs at 514 nm. Preliminary fluorescence from one end of the waveguide is shown in Figure 7(b). Due to poor coupling (which we expected) between the NC fluorescence spectrum and the modes of the cavity, relatively little fluorescence is coupled into the cavity and therefore relatively little is subsequently channeled to the ends of the waveguide. However, note that what PbSe NC light that does enter the waveguide has a FWHM of ~ 10 nm, which is over an order of magnitude narrower than the FWHM of the free space spectrum. Work is in progress to adjust the NC deposition and excitation conditions such that more NC fluorescence is coupled into the device.

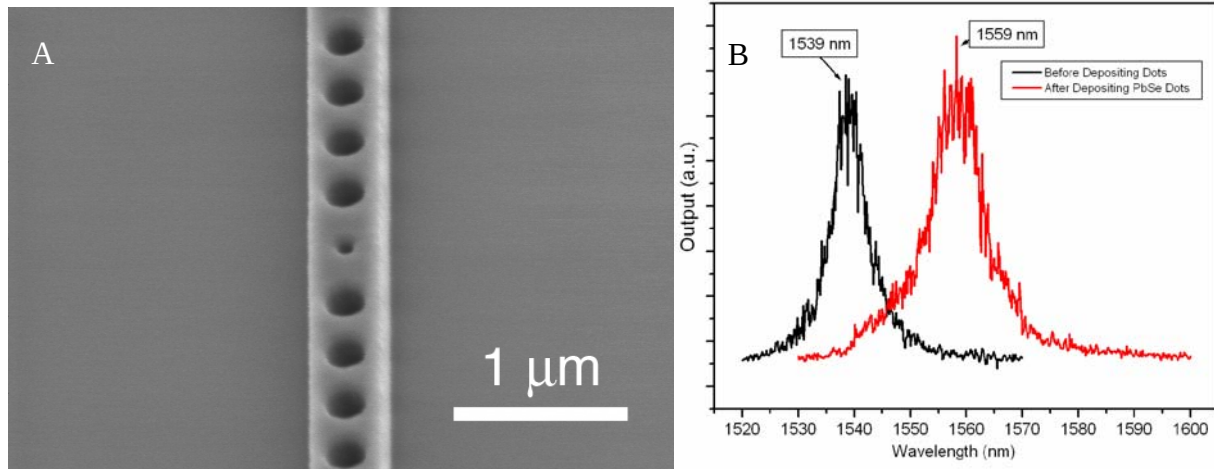


Figure 7. (a) SEM of a 1-D optical cavity embedded in a 1-D optical waveguide. Structure fabricated by Michal Lipson, Cornell University. **(b)** Optical emission out the end of the waveguide before and after PbSe NC deposition. The shift in the cavity mode is the result of a slightly different dielectric constant surrounding the device due to the PbSe layer, relative to air.