

# Blue- and red-shifting amplified spontaneous emission of CdSe/CdS core/shell colloidal quantum dots

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**Abstract:** We report blue- and red-shifting amplified spontaneous emission of CdSe/CdS quantum dots, controlled by varying core/shell dimensions and modifying exciton-exciton interactions, with low optical gain threshold of two-photon absorption pumping.

**OCIS codes:** (190.4180) Multiphoton processes; (160.4236) Nanomaterials; (160.2540) Fluorescent and luminescent materials.

With their size tunable optical and electronic properties, colloidal quantum dots (CQDs) are highly attractive for lasing applications. Owing to strong quantum confinement effect in CQDs, the density of charge carriers contributing to band-edge emission processes is higher compared to their bulk counterparts; therefore, lower optical gain thresholds should be expected using CQD-based lasers. Having a discrete molecular energy level, CQD-based lasers should ideally offer better temperature insensitivity for lasing. Also, CQDs exhibiting narrower emission behavior while having a broad absorption spectrum are highly desired for optical gain studies. As a result of all these appealing properties, lasers with lower lasing thresholds, improved temperature stabilities and narrower emission bandwidths can be in principle obtained using CQDs [1]. However, increased Auger recombination processes in CQDs hinder the targeted optical gain performance. To address this issue, optical gain performances of different sizes, shapes and types of CQDs with single photon optical pumping have been extensively studied and recently low threshold lasers employing CQDs with single photon excitation have been shown [2]. On the other hand, although CQDs are considered to be very good two-photon sensitizers [3], optical gain from CQDs based on the two-photon absorption (TPA) mechanism has not been demonstrated to date.

TPA is an important mechanism for CQD-based lasers because it offers great advantages including lowering the risk of photo-damage to the sample when compared with the single photon optical pumping [3]. Furthermore, a wide variety of high power semiconductor laser sources operating in the infrared region to pump the active medium makes TPA mechanism highly attractive for CQD-based lasers. In this study, to achieve high optical gain performance utilizing the TPA mechanism, we studied optical gain performance of CdSe/CdS core/shell CQDs. Here we demonstrated for the first time both blue- and red-shifting amplified spontaneous emission (ASE) from the same core/shell material combination of CdSe/CdS with respect to their spontaneous emission by changing the core/shell dimensions of CQDs to engineer repulsive vs. attractive nature of their exciton-exciton interactions, which are responsible for the spectral positioning of the ASE peak.

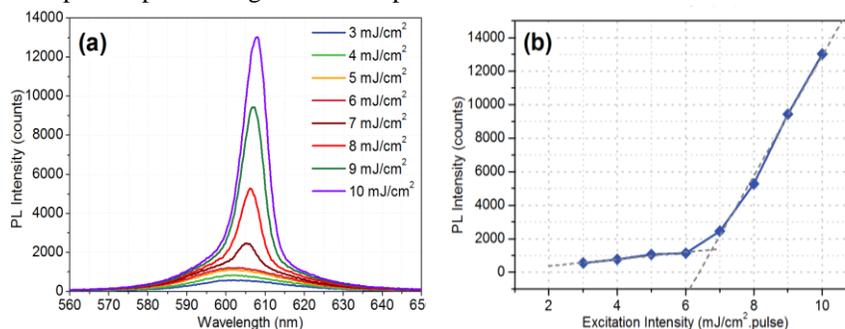


Fig. 1. (a) Photoluminescence (PL) spectra of 3.2 monolayer (ML) CdSe/CdS core/shell CQDs with different excitation intensities, and (b) excitation pulse intensity dependence of the optical intensity at the wavelength of ASE peak [6].

In this work, we synthesized CdSe/CdS core/shell CQDs having better structural and optical properties compared to more commonly used CdSe/ZnS CQDs. These CdSe/CdS CQDs were synthesized via a modified recipe available

in the literature [4]. With a CdSe core having a diameter of 2.2-2.4 nm and 2.4-3.2 monolayer (ML) CdS shell, a near unity quantum yield (>90%) was observed. In addition, TPA cross-section of 3.2 ML CdSe/CdS CQDs was measured to be ca. 44600 GM using the open-aperture Z-scan method. This is a very high TPA cross-section value when compared to the alternatives of CdSe/CdS CQDs such as organic molecules or other CQDs of similar sizes. For optical gain measurements, highly concentrated and closely packed films of CdSe/CdS CQDs were prepared by drop-casting on quartz substrates. The samples were pumped with 45 fs laser pulses with 1 kHz repetition rate at the optical wavelength of 800 nm. As it can be seen from Figure 1, when the excitation intensity exceeded the optical gain threshold value of  $6.5\text{ mJ/cm}^2$ , red-shifted ASE was observed with a narrower emission behavior having full-width-at-half-maximum (FWHM) of ca. 6 nm. This optical gain threshold is very low, compared to other CQDs of similar sizes considering the fact that there is no loss compensation mechanism in the sample.

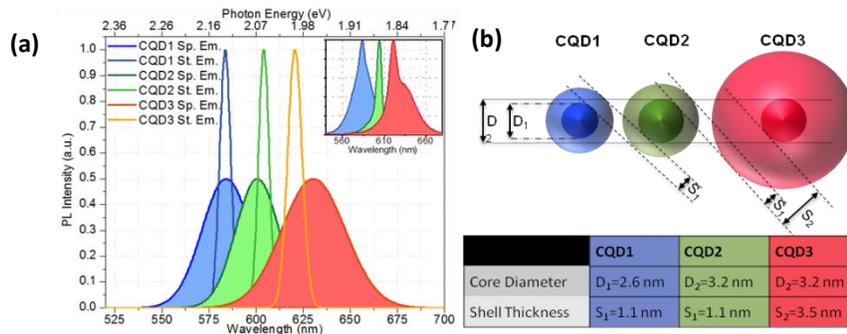


Fig. 2. (a) Normalized decomposed ASE and spontaneous emission spectra of three different CdSe/CdS core/shell CQDs under intense two-photon excitation conditions. The inset shows the original experimental PL spectra. (b) Schematics illustrating three different CdSe/CdS core/shell CQDs (drawn proportional to their real sizes along with their core diameters and shell thicknesses) [6].

Here, we showed that the peak position of ASE originating from the biexciton emission can be tuned to be either blue-shifting or red-shifting with respect to the spontaneous emission peak. This is achieved through exciton-exciton interaction engineering by changing the core diameter and shell thickness. In CdSe/CdS CQDs, unlike the case for holes, owing to low energy barrier for electrons to be confined in the core, electron and hole wave functions are partially separated, which can be conveniently adjusted with varying the core diameter and shell thickness. In other words, while Type-I behavior was observed for CdSe/CdS core/shell CQDs having a larger core, quasi Type-II behavior was observed for CQDs having a smaller core [5]. Therefore, to investigate the ASE peak shifting, we designed and synthesized three different CdSe/CdS CQDs having different core diameters and shell thicknesses. Although CQD1 and CQD2 have the same shell thickness, owing to the larger core diameter of CQD2, a red-shifted ASE peak was observed for CQD2, which is expected for CQDs having Type-I like behavior. On the other hand, for CQD3 having the same core diameter with CQD2, as a result of the thicker CdS shell, a blue-shifted ASE peak was observed, which is consistent with the behavior of quasi Type-II CQDs. Furthermore, we also verified the experimentally observed shifting of the ASE peak with respect to their spontaneous emission spectra by using parameterized quantum mechanical simulations of the electronic structure of the CdSe/CdS CQDs.

In conclusion, we showed that CdSe/CdS CQDs are good candidates for lasing applications with two-photon optical pumping. They exhibited very high two-photon absorption cross-section ( $\sigma_2=44600\text{ GM}$ ), which is highly desirable for achieving lower lasing thresholds. Moreover, by changing the core diameter and shell thickness, for the first time, we tuned the ASE peak with respect to the spontaneous emission spectrum via exciton engineering. To control the ASE shift, varying the core/shell dimensions basically modifies the repulsive vs. attractive nature of exciton-exciton interactions. These CQDs yield the minimum optical gain threshold of  $\sim 6.5\text{ mJ/cm}^2$ , which is low compared to those of CQDs having similar sizes. Furthermore, based on our quantum mechanical simulations, we obtained strong agreement between the experimental and numerical results. These results indicate the two-photon absorption, with the ability to control the ASE peak shift, is very promising for CQD lasing.

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