Colloidal-Quantum-Dot Ring Lasers with Active Color Control

Boris le Feber, Ferry Prins, Eva De Leo, Freddy T. Rabouw, and David J. Norris

Optical Materials Engineering Laboratory, Department of Mechanical and Process Engineering, ETH Zurich, 8092 Zurich, Switzerland

Supporting Information

ABSTRACT: To improve the photophysical performance of colloidal quantum dots for laser applications, sophisticated core/shell geometries have been developed. Typically, a wider bandgap semiconductor is added as a shell to enhance the gain from the quantum-dot core. This shell is designed to electronically isolate the core, funnel excitons to it, and reduce nonradiative Auger recombination. However, the shell could also potentially provide a secondary source of gain, leading to further versatility in these materials. Here we develop high-quality quantum-dot ring lasers that not only exhibit lasing from both the core and the shell but also the ability to switch between them. We fabricate ring resonators (with quality factors up to ∼2500) consisting only of CdSe/CdS/ZnS core/shell/shell quantum dots using a simple template-stripping process. We then examine lasing as a function of the optical excitation power and ring radius. In resonators with quality factors >1000, excitons in the CdSe cores lead to red lasing with thresholds at ∼25 μJ/cm². With increasing power, green lasing from the CdS shell emerges (>100 μJ/cm²) and then the red lasing begins to disappear (>250 μJ/cm²). We present a rate-equation model that can explain this color switching as a competition between exciton localization into the core and stimulated emission from excitons in the shell. Moreover, by lowering the quality factor of the cavity we can engineer the device to exhibit only green lasing. The mechanism demonstrated here provides a potential route toward color-switchable quantum-dot lasers.

KEYWORDS: Quantum-dot lasers, core/shell nanocrystals, giant-shell nanocrystals, colloidal quantum dots, template stripping, ultrafast switching

Nanoscale semiconductors, such as nanocrystals, nanowires, and monolayers, provide useful new gain media for lasers. Among these, spherical nanocrystals, known as colloidal quantum dots (QDs), are arguably the most developed material. QDs can now be grown from a variety of semiconductors with good control of size and shape. Due to their solution processability and size-tunable optical transitions, they offer a versatile gain material for use throughout the visible and infrared spectrum. In the presence of optical feedback, these materials can enable lasing from single excitons, low-threshold amplification, and even spasing.

These developments have been possible because of improvements in the gain properties of QDs. Specifically, nanocrystals are now routinely coated with shells of a wider-bandgap material. When these core/shell particles are excited by photons with energies above the bandgap of the shell, the shell effectively acts as an antenna that absorbs light and channels excitons to the core on a picosecond time scale (Figure 1a). Because such structures suppress nonradiative Auger recombination, core/shell systems have led to some of the lowest reported lasing thresholds. In addition, the relaxation of the photoexcited carriers from the wider bandgap shell to the core can give rise to new effects. For example, in specific QD geometries, green (amplified) spontaneous emission from a CdS shell was shown to dominate radiation from a CdSe core under strong excitation.

Here, our goal is to exploit the competition between direct emission from the shell and relaxation into the core in a high-quality QD laser. Specifically, we examine whether it can lead to active color control, in which the output wavelength of the laser changes with excitation power. We find that such “color switching” of the device is possible. That is, we show that thick-shell QDs can switch from lasing from the core (around 610 nm) to lasing from the shell (as short as 500 nm). Furthermore, by lowering the cavity quality factor, we can engineer the cavity to lase only at the shell wavelength. Finally, we develop a rate-equation model and use it to identify the competing processes that give rise to the color-switching behavior of our QD lasers.

For such experiments, we require high-quality optical cavities to provide the critical feedback upon which device performance depends. Surprisingly, despite the vast number of studies on the optimization of QD gain, the influence of the cavity on QD-laser processes remains mostly unexplored. Many studies exploit simple fabrication methods that provide limited control over the cavity geometry. For example, it is common to use random or “coffee-stain” cavities. It would be better to employ a fabrication approach that allows multiple well-defined micron-scale QD resonators on a single chip. We develop such a method to investigate active color control of core/shell QD
lasers. More generally, this approach also allows the study of how cavity design impacts laser performance.

To fabricate high-quality resonators, we use QD template stripping, a simple technique that enables the fabrication of structured QD surfaces. We extend this approach to the fabrication of micron-scale laser cavities (see Figure 1b). In brief (see Supporting Information for details), we use electron-beam lithography and reactive-ion etching to create an array of circular rings (~500 nm deep) on a silicon (Si) template (step I, Figure 1b). The Si template is then coated with a dense alkane-terminated self-assembled monolayer to reduce the surface energy of the template and later facilitate the release of our structured QD surfaces (see Supporting Information for more details). After this treatment, we spin-coat 12 nm diameter CdSe/CdS/ZnS core/shell/shell QDs (see the inset of Figure 1a) on top of the template (step II, Figure 1b). This fills the rings and covers the Si surface with a smooth layer of QDs. To improve the confinement of the cavity modes in the final device, we remove excess QDs on top of the Si template using adhesive tape, leaving behind only the QDs inside the rings (step III, Figure 1b). We then attach a glass slide to the back of the QDs with an ultraviolet-light-curable epoxy in between. This allows us to strip off the QDs from the Si template using mechanical cleavage (step IV, Figure 1b). The final structure is an array of QD rings on a transparent backing (step V, Figure 1b).

This fabrication approach produces ring cavities with high yield. The structural quality of these rings is confirmed via scanning electron microscopy (Figure 1c) as well as fluorescence microscopy (see below). Using atomic force microscopy (AFM), we measured a root-mean-squared surface roughness as low as 4.2 nm. This indicates that we obtain cavities with high surface quality and reduced scattering losses, even though the structure consists only of QDs.

In general, the relevant photon-loss mechanisms in QD ring cavities will be leakage, QD absorption, and scattering by defects. Leakage is an intrinsic loss mechanism for ring resonators that increases with decreasing ring radius. Reabsorption of red emission by the CdSe QD cores is reduced due to the large volume fraction of the resonator occupied by the wide-bandgap CdS/ZnS shell materials, which are transparent to red light. Finally, scattering by (surface)

Figure 1. Fabrication of quantum-dot (QD) ring resonators. (a) Normalized absorption (ABS) and photoluminescence (PL) spectra of the thick-shell CdSe/CdS/ZnS core/shell/shell QDs. The inset of the figure shows a sketch of the QD geometry, which consists of a 3.2 nm diameter CdSe core (red), a 12 monolayer CdS shell (green), and a 2 monolayer ZnS shell (blue). The CdS/ZnS interface is partially alloyed. When an exciton is created in the shell, the hole (black circle) localizes rapidly (in ~1 ps) to the core while the electron is more delocalized. (b) Schematic overview of the fabrication process. The steps I–V are discussed in the text. Dark gray indicates the Si template, orange indicates the quantum dots, purple indicates the adhesive tape, and blue indicates the epoxy glue. (c) Scanning electron micrographs of a QD ring resonator. The ring diameter and width are 5 μm and 500 nm, respectively.

Figure 2. Optical characterization of QD ring resonators. (a) Leakage spectra for rings with radii (R) from 0.5 to 5.0 μm. (b) Q factors obtained via a Lorentzian fit to the narrowest peaks in the leakage spectra shown in (a). The inset shows a fit (black line) of two closely spaced Lorentzian peaks (blue lines) in the spectrum (thick gray line) from 637 to 639 nm for a ring with a radius of 6 μm.
defects limits the maximum attainable photon lifetime in the cavity. This is reduced by our high-quality fabrication. Losses in our resonators can be quantified in terms of the quality factor, $Q = \omega/\Delta \omega = \omega \tau_c/2$, where $\omega$ is the angular frequency of the light, $\Delta \omega$ is the full width at half-maximum (fwhm) of the cavity resonance, and $\tau_c$ is the cavity decay time. To measure $Q$, we used the photoluminescence of the QDs as a built-in source to couple light into the cavity. That is, we focused a weak excitation laser on the ring and collected the leakage radiation from another spot on the ring, sufficiently far from the excitation to avoid direct luminescence. The spectra collected for rings with radii ranging from 0.5 to 7.0 μm are shown in Figure 2a. They exhibit a broad background peak with sharper features riding on top. The broad background is due to spontaneous free-space emission of the QDs in the detection volume. The sharper features are caused by leakage (i.e., scattering of photons) from cavity modes. The line width of each peak depends on the $Q$ of the corresponding cavity mode with broader peaks signifying lower $Q$’s. For all ring radii, we observe broader resonances at shorter wavelengths. We attribute this to increased reabsorption losses (see Figure 1a) and increased scattering losses.38 Hence, the sharpest peaks and highest $Q$’s occur at longer wavelengths. By fitting Lorentzian line shapes to the sharpest peaks in the spectrum of each resonator, we find that the cavity $Q$ ranges from 484 (corresponding to $\tau_c = 2$ ps) at a ring radius of 1 μm to 2443 ($\tau_c = 10$ ps) at 7 μm (Figure 2b). We note that this maximum $Q$ is almost 1 order of magnitude larger than typical $Q$’s reported for QD resonators.39 Thus, the long cavity lifetimes and tunability of the QD ring resonators make them an interesting candidate for laser studies.

To achieve the population inversion required for lasing, we illuminated the entire ring with ultrafast laser pulses at 405 nm (see Supporting Information). The cavity spectra show several striking features as a function of pulse energy (Figure 3a,b). To describe this behavior, we divide the spectra into four regimes labeled I through IV in Figure 3. Below the lasing threshold of 22 μJ/cm², they show only spontaneous emission (regime I). The photoluminescence decay traces at these pulse powers (Figure 3c) are multiexponential, indicating a contribution of biexciton emission that decays on a 100–1000 ps time scale because of rapid Auger recombination (see also Figure S1 in the Supporting Information). Indeed, a significant biexciton population is expected in the QDs just below threshold, which we estimate (see Supporting Information) to occur at an average exciton occupancy per QD of $\langle N \rangle = 1.6$ (see $\langle N \rangle$ axis in Figure 3a). Above threshold (regime II), a series of sharp laser peaks near 610 nm appear in the emission spectrum in
combination with very fast (<100 ps) components in the decay curve due to stimulated emission. With a further increase of excitation power, the intensity of these laser peaks and the amplitude of the fast decay component continue to grow, until the red lasing begins to saturate at around 80 μJ/cm² ($\langle N \rangle = 8.4$) of new green lasing peaks near 530 nm. Then, at even higher pulse powers (regime III), the red lasing peaks and the fast decay components begin to disappear. The green lasing peaks grow in intensity, and eventually dominate the device output (regime IV). Real-color images recorded with a commercial digital camera (Figure 3d) reveal that the appearance of the ring completely changes in the transition from red spontaneous emission (regime I) to red (II), orange (III), and green (IV) lasing.

These results demonstrate that color switching is possible in lasers made from core/shell QDs. This color switching is dependent on the cavity radius and thereby the cavity loss rate. Figure 4, which plots the red and green emission as a function of excitation power, shows that red lasing occurs only for ring radii of 2.5 μm or larger, corresponding to $Q_s$ above 950. The thresholds are typically 30–40 μJ/cm². In contrast, green lasing emerges for all radii at an excitation power of ~400 μJ/cm². The green stimulated emission is even able to overcome cavity losses at a radius of 0.5 μm, where the $Q_s$ were so low that we could not observe a clear resonance in the leakage spectra at low excitation powers (see Figure 2a).

We now analyze the origin of the color switching. We hypothesize that it arises due to a competition between stimulated emission from the shell and charge-carrier transfer from the CdS/ZnS shell to the core. Nonresonant excitation (in our experiments at 405 nm) generates electron–hole pairs primarily in the CdS/ZnS shell because of its large volume compared to the core. Charge carriers rapidly cool to band-edge levels in the shell via the bulk-like density of states. Subsequently, charge-carrier transfer from the shell to the core occurs on a picosecond time scale depending on the details of the core/shell geometry. The resulting “core-localized” excitons consist of a tightly confined hole and an electron that is partially delocalized into the shell, as set by the quasi-type-II band structure of our QDs.

At the lower excitation powers in our experiments (20–200 μJ/cm² in Figure 3a), excitons generated in the CdS shell transfer to the CdSe core on a picosecond time scale and create population inversion in the core, leading to red lasing. For similar QD architectures, excitation powers of a few 100 μJ/cm² give rise to green amplified spontaneous emission. We propose that in our system at excitation powers >200 μJ/cm² (see Figure 3a), green stimulated emission by excitons in the shell occurs on a subpicosecond time scale, outpacing exciton transfer into the core. Consequently, at these powers the population of core excitons never reaches inversion and red lasing does not occur. This explains why the red lasing disappears as the green lasing emerges. Furthermore, this picture explains the orange color in Figure 3d. In this intermediate regime, the excitation power yields a stimulated-emission rate from the shell similar to the exciton-transfer rate to the core, and simultaneous green and red lasing is observed.

Indeed, using a simple rate-equation model for the competition between stimulated emission from the shell and exciton transfer to the core (Figure 5), we can reproduce the observed color switching. We include explicitly only QD states with zero, one, or two electron–hole pairs. We assume that higher multiexciton states decay immediately through Auger recombination pathways. Importantly, our model distinguishes between excitons in the CdS shell and those in the CdSe core. This leads to six possible states for a QD, each with a different number of excitons in the core and shell, as depicted in Figure 5a. The transition rates between these states scale with the number of recombination possibilities of the carriers. To account for the strong interaction between carriers in the core, we also take the spin degeneracy of the core energy levels into account for reabsorption and stimulated emission (see Supporting Information for details).
To numerically evaluate this model, we fix the parameters that we measure (e.g., the radiative lifetime of single excitons in the core). For the remaining parameters (e.g., the exciton-localization rate) we sweep through a range of values based on the literature (see Table S1 in the Supporting Information). Within this range, our model reproduces the lasing behavior that we observe experimentally. The left plot in Figure 5b shows the predicted red and green emission intensities as a function of exciton population $\langle N \rangle$ for a high-$Q$ cavity ($Q = 1000$). In agreement with our experiments (Figure 4), red lasing begins at an exciton population of just above $\langle N \rangle = 1$ and then switches to green lasing at higher populations. Furthermore, like in experiment, the red lasing threshold is barely affected by the cavity $Q$ unless it is below a certain value. For example, if the $Q$ used in the model is below $\sim 200$, only green stimulated emission can overcome the increased cavity losses (right plot, Figure 5b). In such cavities, only green lasing is predicted, in agreement with observations.

Although the model reproduces the qualitative behavior of our devices, the exact predicted values for the thresholds and output intensities differ with experiment, presumably due to our simplifying assumptions. In particular, we limit our QDs to two excitons or fewer, while in the experiment green lasing occurs at occupations higher than $\langle N \rangle = 8$. To compensate for this difference, the model must overestimate the green (and possibly red) stimulated emission cross sections. Nonetheless, the qualitative agreement suggests that our rate-equation model captures the most important processes that are responsible for the observed color switching.

Because the relevant processes occur on ultrafast time scales, we can potentially switch the color of the QD laser at ultrafast speeds. This would require that both the build-up and ring-down of light in the cavity occur on picosecond time scales. Indeed, all of our ring cavities show cavity lifetimes (and hence ring-down times) that are less than 10 ps. Furthermore, we know that the green stimulated emission at strong excitation ($\langle N \rangle > 10$) builds up on subps time scales because we observe...
green lasing in all of our cavities. If this build up were slower, green stimulated emission would not be able to outcompete the shortest cavity decay times of ~1 ps (Figure 2). In contrast, the red (i.e., core) stimulated emission overcomes losses only for cavities with lifetimes above ~5 ps (Figure 4). We conclude that the typical build-up time for red lasing is on the order of a few picoseconds. Thus, the color should be tunable from red to green laser emission at picosecond time scales with switching speeds approaching the terahertz regime.

We have fabricated high-quality QD ring resonators that enable unique color switching between red and green laser emission. This switching occurs because green stimulated emission from the CdSe shell outpaces the exciton localization into the CdSe core. This prevents the core from reaching emission. This switching occurs because green simulated emission would not be able to outcompete the different spatial extension of the modes may have previously prevented color switching. Alternatively, in distributed Bragg reflector systems only a single resonance is present and lasing at multiple wavelengths is suppressed. In contrast, our ring lasers are well suited to the observation of the transition from red to green QD laser because of their high quality and strong modal overlap. Tuning the nonradiative Auger and charge-localization rates by optimizing the shell volume and core/shell interface geometry can aid the further development of color switching. Finally, the model that we developed can lead to the rational design of QDs with controlled radiative and nonradiative rates, as well as fast color-switchable† or white-light lasers.10,50–52 Such devices, ideally of small dimensions, can drive novel techniques for biological and chemical sensing,13 laser imaging and displays,45 and wavelength-division multiplexing.54,55

**ASSOCIATED CONTENT**

Supporting Information

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Additional details of the model and experimental methods (PDF)

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: dnorris@ethz.ch. Tel: +41 44 632 53 60.

ORCID®

Ferry Prins: 0000-0001-7605-1566

Eva De Leo: 0000-0002-9677-0274

David J. Norris: 0000-0002-3765-0678

Present Address

†Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, 28049 Madrid, Spain.

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**Notes**

The authors declare no competing financial interest.

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