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<td>Cuong, Dang; Joonhee, Lee; Craig, Breen; Jonathan, S. Steckel; Seth, Coe-Sullivan; Arto, Nurmikko</td>
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Supplementary Information

Red, Green, and Blue Lasing enabled by Single-Exciton Gain in Colloidal Quantum Dot Films

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Quantifying the Atomic Composition of CdSe/Zn\textsubscript{x}Cd\textsubscript{\textit{1-x}}S Core/Shell CQD Structure

We used Energy-dispersive X-ray spectroscopy (EDS) to quantify the composition of CdSe/Zn\textsubscript{x}Cd\textsubscript{\textit{1-x}}S structure.

\textbf{Figure S1:} Energy-dispersive X-ray spectroscopy analysis of the red CQD films showing all four elements of CdSe/Zn\textsubscript{x}Cd\textsubscript{\textit{1-x}}S core/shell structure.

By analyzing the EDS results (Fig. S1), the weight and atomic percentages of the individual elements in CdSe/Zn\textsubscript{x}Cd\textsubscript{\textit{1-x}}S core/shell structure are summarized in Table S1. The atomic percentage of Cd (27.20\%) is the contribution of Cd in CdSe core and Cd in Zn\textsubscript{x}Cd\textsubscript{\textit{1-x}}S shell. The
former is considered to be similar to Se percentage (7.97%); thus the latter is 19.23%. From the atomic percentage of Zn (19.92%), one can calculate: x~0.51, which agrees well with our target shell material: Zn$_{0.5}$Cd$_{0.5}$S.

**Table S1:** Weight and atomic percentages of individual elements in CdSe/ Zn$_{x}$Cd$_{1-x}$S core/shell structure.

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<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
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<td>S</td>
<td>22.40</td>
<td>44.91</td>
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<tr>
<td>Zn</td>
<td>20.26</td>
<td>19.92</td>
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<tr>
<td>Se</td>
<td>9.78</td>
<td>7.97</td>
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<tr>
<td>Cd</td>
<td>47.56</td>
<td>27.20</td>
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**CQD Films Support High Frequency Ultrasound Propagation.**

We employed a nondestructive method using ultrafast optoacoustics to test for the material continuum of our laser films from their ability to support the propagation of sound waves$^{31,32}$. The epitaxial-like CQD films (300 nm thick) were spin casted on fused silica substrate; then a 90 nm Aluminum layer was deposited atop the CQD films by electron-beam evaporation.

![Figure S2: Pump-probe experiment to study high frequency ultrasound propagation in the densely packed CQD thin films.](image)

**Figure S2:** Pump-probe experiment to study high frequency ultrasound propagation in the densely packed CQD thin films. a, The transient reflected probe-beam intensity (indicated as signal on lock-in amplifier), as a function of probe beam delay time after impulsive pump at t = 0 ps; inset, the material structure for experiment, where 90 nm thick Aluminum acousto-optic transceiver layers were deposited on 300 nm thick CQD films (spin casting the high concentration CQD solution on fused silica substrate). b, After background subtraction, the coherent oscillations appear as the telltale signal for showing the films’ ability to support > 1GHz frequency acoustic wave propagation, thus demonstrating the epitaxial-like thin film material.
The optoacoustic method works as follows: ultrashort (100 fs) laser pulses at a wavelength \( \lambda = 790 \text{ nm} \) (ultrasound generating pump beam) is sent through the substrate glass and CQD film to the Al film at incident angle of 45° (inset of Fig. S2a). The Al film absorbs the laser pulse and, through instantaneous thermal expansion (on ps time scale) acts as opto-acoustic transducer to generate a high frequency (~ 10 GHz) ultrasound impulse. This strain pulse then propagates into CQD film. The second (“probe”) laser pulse arrives at the structure at normal incidence and its transient reflection (from strain induced index of refraction change) is monitored by a photodiode (plus lock-in amplifier electronics). Fig. S2a shows the modulated probe beam reflection as a function of delay time between pump and probe pulses. The very fast electronic cooling curve after absorbing pump pulse and very fast oscillation as a result of strain pulse propagating and reflecting inside aluminum transceiver layer were subtracted from raw data\textsuperscript{32} in Fig. S2a. Fig. S2b yields the useful subtracted signal which shows transient oscillations as a result of optical interference between a probe beam reflecting from the propagating strain pulse (in CQD films) and probe reflection beams from the Al surface. Such oscillations are telltale signs of the ability of a material to support high frequency (~10 GHz) acoustic waves and characterize the propagating ultrasonic wavefronts\textsuperscript{32,33}. Here, the period of this oscillation (T~150 ps) indicates the velocity of the ultrasonic wave \( v = \lambda/2nT = 1.6 \text{ nm/ps} \) (estimated refraction index of CQD film: 1.6, at \( \lambda = 790\text{nm} \), which is slightly higher than that of water (1.5 nm/ps) or soft metal Pb (1.3 nm/ps). Although due to finite acoustic wave scattering the sound velocity cannot be compared directly with values obtained with this technique for single crystal materials (where propagation velocities are ~5-6 nm/ps), the results are important in showing that our CQD films do support ultrasonic sound propagation; hence the appellation of “epitaxial-like” thin film material.

**Amplified Spontaneous Emission from Blue CQD Films**

Figure S3. Spectral analysis of edge emission in stripe excitation configuration and absorbance of the blue CQD film. The ASE threshold is clearly demonstrated by abrupt intensity increase and spectral narrow.
The ASE behavior here is similar to the green and red CQD films, so that e.g. the spectra of edge emission in blue CQD films shows clear transition from PL to ASE when increasing pumping levels (Fig. S3). The abrupt intensity increase and spectral narrow occur when excitation level exceeds the threshold of ~800 μJ/cm². The value is high (by standards of this paper) and assigned in large part to the low absorbance of blue CQD films at our fixed 400 nm pump wavelength (in comparison with that of green and red CQD films). We note that the lowest exciton absorption peak is not very clear, either, because of the complication in low energy confinement barrier of ternary shell Zn₀.₅Cd₀.₅S in this wide band gap CQD. Yet, the ability to form densely packed, optically homogenous “epitaxial-like” blue CQD films and their nature of single exciton gain have been able to produce stable ASE and laser action.

**Calculation of Average Number of Exciton per CQD**

The average number of excitons per CQD in the epitaxial-like films under spot or stripe excitation condition can be accurately obtained from the following:

\[
\frac{I_i - I_T - I_r}{f} = \langle N \rangle \frac{A T D}{V} E_p
\]

where \(I_i, I_T, I_r\) are the time integrated intensities of the incident, transmitted, and specularly reflected pump beams, respectively; \(f\) is the pump pulse repetition rate (100 kHz); \(A\) is the measured excitation area; \(T\) is the thickness of the CQD film (from SEM and ellipsometry results) and \(D\) is the film packing fraction (extrapolating as 0.5 when compared effective refractive index of CQD films, \(n=1.73\), with that of bulk CdSe, \(n=2.5\), and ZnS, \(n=2.36\)). The average volume of a single CQD (from TEM data) is denoted as \(V\), and \(E_p\) is excitation photon energy (3.1 eV). The intensity of incident, transmitted, and specularly reflected beams were continuously monitored during the experiment. Note that the \(\langle N \rangle\) calculated by this experimentally direct approach is likely to represent an upper limit. The actual value of \(\langle N \rangle\) can be smaller because finite light scattering of excitation in real experiment is not considered in equation S1. The stripe length in ASE configuration is readily measured via slit width. The accuracy of excitation area \(\langle A \rangle\) relies on the measurement of excitation stripe width in the ASE experiments or the measurement of focusing-spot diameter in spot excitation.

Fig. S4a sketches the setup where a sharp blade edge was aligned parallel to the stripe while the blade was moved across the stripe (z-direction), and the transmitted beam was captured by a calibrated average power meter. After measuring the power as a function of blade position (z-position), the first derivative of this quantity, representing the beam intensity profile, was fitted into a Gaussian function (Fig. S4b) to find the full-width at half maximum (FWHM) of the stripe. Then the blade was moved along the lens axis (X direction) to measure the waist and also depth of focus of the excitation (Fig. S4c). The measurement yielded a stripe width at the waist as 10.5 μm, in very good agreement with estimated size (9.67 μm) when focusing an ideal input
Gaussian beam ($\lambda=400$nm and 2 mm diameter) by a 38 mm focal length lens. An 8 cm focal length lens used for spot excitation focuses the similar laser beam into a spot of 22 $\mu$m in diameter, the value which was measured by a very similar method.

Figure S4: Stripe width measurements. a, A sketch of the experiment setup with a movable blade to scan along and across the focused excitation beam; a power meter was used to measure transmission intensity of the beam after the blade. b, The measured intensity as function of blade position (z-axis) whereby its first derivative yields the beam profile. c, The focused beam width as a function of blade position (x-axis).

Identification of the Lowest Exciton State from Absorbance Measurements

Figure S5: Analysis of CQD film absorbance. a, The raw absorbance of a ‘green’ CQD film with the visible lowest exciton state near 535nm and the superposed ‘interpolating background curve’ (in red). b, After subtraction of the interpolating function, revealing several Gaussian absorption peaks.
We employed an interpolation technique applied to raw absorbance data from the thin films to generate a smooth background baseline in the full absorbance spectrum as in Fig. S5a. By this physically realistic approach, the excitonic resonances (as distinct peaks) can be isolated by subtracting this background from the raw absorbance spectrum. The subtracted data suggests three distinct peaks in Fig. S5b. However, while the lowest exciton state corresponding unambiguously to the $1S_e-1S_h$ transition is clearly resolved and procedurally stable as displayed in Fig. 2d and 2e of this letter, the other higher photon energy peaks are very sensitive to details of the interpolating technique (and not relevant to the main theme of the article).

**Modal Gain of Epitaxial-Like CQD Films.**

![Figure S6. The edge emission intensities as functions of stripe length in green and red CQD films.](image)

The measurements show the optical gain behaviors before reaching the saturation at the stripe length greater than 1.1 mm. The pumping levels are 120 μJ/cm² and 155 μJ/cm² for red and green CQD films, respectively.

Using variable stripe length method, we measured the edge emission ASE intensity as a function of stripe length for both green and red CQD films (Fig. S6). The ASE intensities increase with stripe length increase as optical gain behaviors before reaching the saturation at the stripe length greater than 1.1 mm. The modal gains at the ASE peaks are estimated as 95±10 cm⁻¹ and 60±10 cm⁻¹ for red and green CQD films at 120 μJ/cm² and 155 μJ/cm² pumping level, respectively. The intensity saturation occurs at the stripe length exceeding 1.1 mm, implying that the gain depletion time of 6 ps, the travel time for a photon in these CQD films (refractive index of 1.7).

**A Model for Spontaneous Emission of Multiexciton Quantum Dots**

In our spontaneous emission model, the number of emitted photons per CQD is given by:

$$I(N) = P(1)\beta_1 + P(2)(\beta_1 + \beta_2) + P(3)(\beta_1 + \beta_2 + \beta_3) + \cdots$$
where \( \langle N \rangle \) is average exciton per CQD, \( \beta_i \) is the quantum efficiency of the \( i^{th} \) exciton, \( n \) is the number of exciton in a CQD, and \( P(n) \) is Poisson distribution of \( n \) in the ensemble. \( \beta_1 \) is 0.8 (quantum yield at low excitation level - single exciton state). If there are two excitons in a CQD, the “extra” one has two possibilities to recombine: non-radiative Auger recombination (rate: \( T_2^{-1} \)) and spontaneous recombination (rate: \( T_1^{-1} \)). Thus the biexciton quantum efficiency is \( \beta_2 = \beta_1 * \frac{T_1^{-1}}{T_1^{-1} + T_2^{-1}} \), which is very small in our CQD films (0.007 and 0.005 for red and green respectively).

If a CQD has more than two excitons, the non-radiative Auger process will become even more likely and thus further decrease the quantum efficiency. The system will emit mostly like biexciton CQDs. In other words, \( \beta_{i>2} \) are irrelevant and the equation S2 becomes:

\[
I(\langle N \rangle) = [1 - P(0)]\beta_1 + [1 - P(0) - P(1)]\beta_2 \quad (S3)
\]

The equation S3 is represented as a theoretical model line in Fig. 3d. The model agrees very well with experimental results for both green and red CQD films.

CQD-VCSEL: Testing for Spatial Coherence

Figure S7: Red CQD-VCSEL in operation without a long pass filter to show the spontaneous emission and the laser beam as well as the coaxial unabsorbed, focused pump laser beam (white spot on the screen). a, Below threshold. b, Above threshold excitation.

To further highlight the well-defined spatial coherence, Fig. S7 shows close-up photographic images in the experiment when the long pass filter was removed. The image on the target screen is a composition of the residual transmission from the excitation beam (\( \lambda = 400 \) nm, blue, though appearing white in the pictures due to CCD saturation) and emission from CQD-VCSEL. When the pumping level is below threshold, spontaneous emission from CQD-VCSEL illuminates the
target screen weakly and almost uniformly (Fig. S7a). By contrast, when pump level exceeds the threshold (Fig. S7b), a red laser beam from CQD-VCSEL emerges as a spatially well defined and centered with respect to the transmitted pumping beam.

**Sub-nanosecond Amplified Spontaneous Emission**

While the use of an ultrashort (sub-picosecond) pulse laser is useful for the key research goals into the excitonic origins of RGB stimulated emission in the dense CQD films as well as demonstrating the CQD-VCSELs, such a laser source is impractical for compact device applications such as RGB projector displays. Towards this end we here briefly mention current work where a compact solid state laser (532 nm, 270 ps (FWHM) pulse width, 1 kHz repetition rate – PowerChip laser from Teem Photonics) has been employed to achieve robust ASE of our red thin solid CQD films – relying and exploiting the operation in the single exciton gain regime.

![Figure S8: ASE of the red CQD film pumping by a compact 1 kHz repetition rate sub-nanosecond pulsed 532 nm laser. a, Intensity of edge emission as a function of pump energy density per pulse. b, Transient ASE at two different pumping energy density, time referenced to the pumping laser.](image)

Fig. S8a shows the intensity of edge emission as a function of pump pulse energy density. The ASE occurs when the pumping is greater than 720 μJ/cm². In contrast with ultrashort (sub-picosecond) pulsed excitation, the possible competition from the Auger decay process (for finite amount of CQDs with multiexciton state) in this “quasi-steady-state” pumping pulse could be significant. Rate equations are necessary to solve for average number of exciton per CQD: \( \langle N \rangle \). The model rate equations were also considered with the absorption of red CQD film at 532 nm (reduced from that at 400 nm by factor of 5.1), we find that at the ASE threshold (720 μJ/cm²), the average number of exciton per CQD at maximum is \( \langle N \rangle = 0.86 \), again in very good agreement with \( \langle N \rangle = 0.80 \) when using ultrashort pulse laser.
To focus on the tell-tale time dynamics, the time resolved ASE (Fig. 8b) was measured by a fast photodiode (25 GHz) and a digital sampling oscilloscope (50 GHz). The pulse width of ASE output is seen to increase with pumping level so as to finally reach the duration of the pump laser pulse width which in turn is more than twice of Auger time constant for this CQD system. This result directly shows quasi-CW ASE from red CQD film without the inhibition by the Auger process and invites further device development.

Video Clip S1: Red Colloidal Quantum Dot Vertical Cavity Surface Emitting Laser (CQD-VCSEL). First, the clip sketches a simplified introduction to the CQD-VCSEL experimental geometry. Second, a short video demo of CQD-VCSEL in real-time lab operation, with the pump laser intensity controlled/adjusted continuously. The clip shows the threshold crossing twice in succession while the attenuator disk is turned back and forth. Third, the CQD-VCSEL beam allowing transmission also of the coaxial pump laser light (blue; here as a white spot due to camera saturation) shows the overlap of the spatially coherent pump and the VCSEL beams.

References: