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

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Colloidal quantum dots (CQDs) exhibit efficient photoluminescence with widely tunable bandgaps, owing to quantum confinement effects¹. They are emerging as an appealing complement to epitaxial semiconductor laser materials which are ubiquitous and technologically mature, but unable to cover the full visible spectrum (red, green, and blue - RGB)². However, the requirement of high CQD packing density and the complication by nonradiative multi-excitonic Auger recombination have been obstacles for advancing colloidal CQD laser development³⁻⁹. Here we engineer CdSe/ZnCdS core/shell CQDs with aromatic ligands to demonstrate single-exciton gain in RGB densely packed CQD films. Consequently, the threshold of amplified spontaneous emission (ASE) is reached at very low energy densities of 90 $\mu\text{J}/\text{cm}^2$, more than one order of magnitude improvement from reported values⁹⁻¹². Leveraging this nanocomposite gain, we have produced the first

colloidal-quantum-dot vertical-cavity surface-emitting lasers (CQD-VCSEL). Our results realize a significant step toward full-colour single-material lasers.

CdSe-based CQDs are widely applied from fluorescent bio-labels¹³ to prototype light-emitting diodes^{14,15}. However, their use as gain media for lasers has been challenged by both practical and fundamental obstacles. One key challenge is realization of high-performance optical gain medium, wherein each individual CQD preserves its quantum size effect and high quantum efficiency and a dense assembly of CQDs offers a homogeneous optical continuum. For ideal spherical type-I CQDs, requirement for light amplification is that the ensemble averaged number of exciton per CQD is greater than unity, $\langle N \rangle > 1$, signifying an exact balance between absorption and stimulated emission for ensemble averaged single exciton occupancy per CQD. This condition is referred to as biexciton gain^{4-11,16-19}. When adding the electronic structure and inclusion of biexciton states¹⁷⁻¹⁹, the gain threshold will be closer to $\langle N \rangle \sim 1.5$ whereupon a fundamental complication comes from enhanced non-radiative multiexciton (Auger) recombination in nanometer size systems^{7-9,20}. The Auger process, for example in CdSe-based CQDs ($\tau_{\text{Auger}} \sim 100$ ps), is two orders faster than photoluminescence (PL) decay, severely hindering the dynamic buildup of population inversion. Quantum rod structures were investigated to reduce Auger processes²¹ but this also dilutes joint electronic density of states thereby reducing interband oscillator strength. Elsewhere, for type-II CQDs in which electrons and holes are likewise separately confined, a positive biexciton binding energy shifts the absorption spectrum of single exciton CQDs off their emission. This biexciton level shifting enables single-exciton gain where the Auger process is inhibited^{12,22,23}. However, apart from

challenges in type-II CQD synthesis²⁴, a decrease in interband optical oscillator strength significantly reduces the optical gain and PL rate. Here we demonstrate single exciton gain in type-I CQDs as a powerful solution to achieve high optical performance of CQDs towards full colour CQD semiconductor lasers.

Our RGB type-I CdSe/Zn_{0.5}Cd_{0.5}S core/shell CQDs were prepared by high temperature organometallic synthesis²⁵ with nominal CdSe core diameters of 4.2 nm, 3.2 nm, and 2.5 nm, respectively. A thin (1 nm) ternary shell with large Cd-fraction Zn_{0.5}Cd_{0.5}S (supplemental Fig. S1 and Table S1) reduces strain and creates a moderate core-shell bandgap difference (~1.3 eV in bulk-equivalent materials). The Cd composition provides maximum alloy potential fluctuations which in single II-VI crystals lead to spatial localization of exciton wave-functions²⁶. The TEM images (Fig. 1a, b) show well-defined crystallinity with anisotropic particle shapes. The distinct ‘pyramidal-like’ shape together with moderate core-shell bandgap difference and maximum alloy potential fluctuation of the Zn_{0.5}Cd_{0.5}S shell modify the electronic states from those of the ideal spherical CQDs (e.g. by removing valence band degeneracies) which have been the staple for theoretical models. For example, shape-engineered CdSe/CdS sphere/rod nanostructures have been used to study altered carrier confinement on excitonic interactions²⁷ in which the distinct separation between absorption and PL spectra then enabled optical gain with threshold $\langle N \rangle = 0.95$, lower than theoretical value for ideal spherical CQDs.

We achieved a quantum yield (QY) exceeding 80% at exceptionally high concentrations in starting solution (148 mg/ml) for subsequent spin-cast self-assembled CQD films (Fig. 1c). The CQD films exhibit optically smooth surfaces (Fig. 1d), known to be provided by robustly hydrophobic ligands²⁸. Effective refractive index of the films is $n = 1.73$, with very low

background scattering, suggesting a packing density of about 50% (supplemental Eq. S1), strikingly high when considering the theoretical limit for identical spheres: $\pi/\sqrt{18} \sim 74\%$. The mechanical continuity and cohesiveness of the films were validated by observing GHz ultrasound propagation (supplemental Fig. S2). Under low speed spinning conditions, we could even create well-defined cracks (Fig. 1e), reminiscent of cleavage by built-in strain of single crystal epitaxial thin films.

The dynamics of optical gain in CQD films were studied in pulsed stripe photoexcitation experiments, Fig. 2a. Emission from the film edge with increasing pump power exhibits a clear transition from PL to stimulated emission (here observed as ASE) by an abrupt increase in output intensity and spectral narrow (Fig. 2b-e). Fig. 2c displays the ASE thresholds for CQD films of $90 \mu\text{J}/\text{cm}^2$, $145 \mu\text{J}/\text{cm}^2$ and $800 \mu\text{J}/\text{cm}^2$ in RGB colours, respectively. The values for red and green films represent an improvement of more than one order of magnitude from commonly reported values ($> 1 \text{ mJ}/\text{cm}^2$) for similar colours in both type-I⁹⁻¹¹ and type-II¹² CQDs. The ASE for deep blue CQD films is demonstrated here for the first time (supplemental Fig. S3) though at higher threshold, mainly due to the reduced absorption at the 400 nm pump wavelength of this high bandgap CQD. Indeed, accounting for these pumping thresholds and the measured packing density (supplemental Fig. S4, and equation S1), we can quantify: $\langle N \rangle \approx 0.80, 0.76$ and 0.73 for ASE thresholds of the three RGB CQD films, respectively. These values are distinctly below theoretical values for biexciton gain in homogeneously broadened spherical type-I CQDs⁴: $\langle N \rangle=1$, and only slightly above that of single-exciton gain in ideal type-II CQDs¹²: $\langle N \rangle=2/3$.

The lowest exciton absorption peaks ($1S_e - 1S_h$ transition) in Fig. 2d, e show well-defined Gaussian shapes, distinctly blue-shifted with respect to PL. This Stokes shift reduces the self-

absorption of emitted photons - thereby lowering the ASE threshold. Spectrally, the ASE emerges from the absorption edge tail, slightly on red side of PL, reflecting the optimal wavelength at which the gross optical gain and finite self-absorption are balanced, a phenomenon seen e.g. with green-blue II-VI semiconductor quantum well lasers²⁹ as well as organic dye gain media³⁰.

The transient spectra of the ASE in Fig. 3a show that the spectrally narrow, red-shifted ASE only occurs at very fast time scales (0-40 ps) after impulsive excitation. In the subsequent time window (300-640 ps), the broader PL is the dominant emission. Under small diameter (22 μm) circular “spot” excitation geometry (Fig. 3b) where short optical path length prevents ASE, PL at high excitation level ($>$ ASE threshold) shows two identifiable decay rates. The slower rate is similar to single-exciton decay in the low excitation regime, $T_1 \sim 14.2$ ns, comparable to that of CQD solution (~ 15.8 ns). These measurements suggest that our CQDs retain approximately 90% of their QY when transferred from solution into densely packed films. The faster rate was resolved by a streak camera (Fig. 3c): $T_2 \approx 126$ ps (red) and 101 ps (green), consistent with rates of Auger recombination for respective CQD size^{5,7,20}. However, only a small fraction of emission energy was released at this faster rate whereby single-exciton emission dominates the radiative process. Fig. 3c also shows very fast ASE decay in comparison to the “Auger-dictated” PL component. The measurement is limited by streak camera resolution of 16 ps. Employing variable stripe length (VSL) method⁶, we showed that the edge emission intensity reaches saturation with the excitation stripe length exceeding 1.1 mm (supplemental Fig. S6), corresponding to a photon travel time of ~ 6 ps in a CQD film. This radiative gain depletion time implies highly proficient stimulated emission which is more than an order of magnitude faster than the Auger recombination. The VSL method also gave us an estimate of the modal gain as

$95 \pm 10 \text{ cm}^{-1}$ (red CQD film at $120 \text{ } \mu\text{J}/\text{cm}^2$) and $60 \pm 10 \text{ cm}^{-1}$ (green CQD film at $155 \text{ } \mu\text{J}/\text{cm}^2$) at the ASE peak. These net gain coefficients are comparable to those in other reports^{4,6} - but here achieved at much lower pumping levels.

Quantitatively, the number of excitons per CQD, n , can be taken as a Poisson distribution^{10,11,20}: $P(n) = \frac{\langle N \rangle^n e^{-\langle N \rangle}}{n!}$. In time resolved PL, the fast decay is contributed by CQDs with multiexciton: $P(n > 1)$ and the slow decay is contributed by all excited CQDs: $P(n > 0)$. The ratio between these two contributions is experimentally given (Fig. 3b for red CQD film at $100 \text{ } \mu\text{J}/\text{cm}^2$) as 0.39, which corresponds to $\langle N \rangle = 0.92$. Therefore, at the ASE threshold level ($90 \text{ } \mu\text{J}/\text{cm}^2$), we have $\langle N \rangle = 0.83$, very good agreement with above direct measurement $\langle N \rangle = 0.80$. One also can see the small but finite loss by Auger process even at single exciton gain threshold $\langle N \rangle = 0.80$ as $P(n > 1) \sim 19\%$. The loss would be highly detrimental if higher excitation levels are required, as with other reported ASE thresholds⁹⁻¹¹. By contrast, in our densely packed CQD films, the ASE process is so fast ($\sim 6 \text{ ps}$) as to readily overcome this Auger loss. With increasing excitation levels in spot excitation, we see directly how Auger loss decreases quantum efficiency (Fig. 3d). Experimental results for both green and red CQD films agree very well with our theoretical model (supplemental Eq. S3). Specifically, excitation levels at the ASE thresholds (in Fig. 2) fall within the *linear regime* of this PL model, confirming the nature of single-exciton emission in these excited CQDs. Therefore, ASE in these films must originate from single exciton gain.

Given their demanding gain/loss criteria, VCSELs are among the most challenging device configurations for any optical gain material. Here we demonstrate the first optically pumped CQD-VCSELs (Fig. 4a). The supplemental video and Fig. 4b, c show two CQD-VCSELs lasing

with well-defined spatial coherence (beams) in the red and green, respectively. Below threshold pumping level, the PL spectra in Fig 4d shows Fabry-Perot microcavity modes. Above threshold, sharp laser lines appeared in the CQD gain spectrum coincident with the cavity modes and emergence of a spatially coherent beam. The inset of Fig. 4d shows the single mode green CQD-VCSEL at shorter cavity length. The lasing onset in Fig. 4e shows the pumping threshold for red CQD-VCSEL as $\approx 60 \mu\text{J}/\text{cm}^2$. Because of the very low DBR reflectivity at the 400 nm pump wavelength ($R < 5\%$), we can assume a single pass of the pump beam through the CQD layer. This indicates that the threshold for this CQD-VCSEL corresponds to exciton occupancy as low as $\langle N \rangle = 0.53$, showing how low loss resonators reduce stimulated emission thresholds, closer to the fundamental “intrinsic” single exciton limit. The overall efficiency of the red CQD-VCSEL is 0.4% at excitation energy density of $140 \mu\text{J}/\text{cm}^2$, and lasting few minutes before fading out as commonly seen in other conventional VCSELs without any heat sinking. The performance can be vastly improved with device optimization.

In conclusion, very low thresholds of ASE across RGB spectrum and the first CQD-VCSELs were enabled by single-exciton gain in type-I CQD films. The single exciton gain was confirmed by four independent experimental results: direct absorption measurement, multiexciton contribution via time resolved PL, linear dependence of PL intensity on excitation energy at threshold levels, and very low CQD-VCSEL threshold. Our demonstration of overcoming the Auger barrier for stimulated emission in these CQD materials is successful with a compact, sub-nanosecond pulsed diode laser as a pumping source (supplemental Fig. S8). This emphasizes the profound benefits of single exciton gain towards producing practical CQD lasers, namely that stimulated emission is achievable even on a time scale which exceeds the Auger time constant.

Methods

The effective refractive index of CQD films was measured by ellipsometry technique at a wavelength of 632.8 nm (He-Ne laser). All the experiments in this work were performed at room temperature and under ambient conditions. The ultra-fast impulsive laser excitation source was a frequency-doubled amplified titanium-sapphire pulsed laser (Coherent Reg A Model 9000, 400 nm wavelength, 100 fs pulse width, 100 kHz repetition rate). While impractical in any real devices, such a source is advantageous for the investigative work which we report. As shown in supplemental Fig. S8, much longer pump laser pulses (sub-nanosecond) could likewise be used to elicit stimulated emission. We employed time correlated single photon counting system and streak camera for the transient spectroscopy experiments at two different time scales.

For fabricating the high reflectivity DBRs, 8 pairs of quarter-wavelength thick $\text{SiO}_2/\text{TiO}_2$ layers for the red CQD-VCSELs were deposited on flat fused silica substrate by Argon ion sputtering. For green CQD-VCSELs, we used dielectric mirrors from CVI Melles Griot. A narrow stripe of 30- μm -thick SU-8 was placed at one edge of a DBR to create a finite wedge for a prior built-in thickness variation of the final cavity. A drop of highly concentrated CQD solution was placed atop this DBR, and then a complete CQD-VCSEL structure was made by placing the second DBR on top. CQD solution was mildly squeezed and dried between these two DBRs which form a Fabry-Perot cavity. We note that the density of self-assembled CQD wedge inside cavity could be improved to the level of quality of the spin-casted epitaxial-like CQD films for higher CQD-VCSEL performance.

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Author Contributions: C.D. designed the research, performed the experiments and analyzed the all results; J.L. performed the green CQD-VCSEL and analyzed the results; C.B. and J.S.S. synthesized the nanocrystal CQDs; S.C-S. participated in analysis of the results; A.N. contributed to all aspects of the work ; C.D., J.L. and A.N. co-wrote the manuscript.

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Figure 1: Structural characteristics of CQDs and their spin-cast closely packed films. **a**, Transmission electron microscope (TEM) image of a red CQD cluster displaying finite shape anisotropy. **b**, High resolution TEM of a single red CQD demonstrating a well-defined lattice of crystalline structure. **c**, Angled cross-sectional view of CQD film on fused silica under scanning electron microscopy. The small grains in the image are due to 15 nm thick metallic (Au-Pd) coating to reduce charging effects and image distortion. The films are 250 nm thick with an effective refractive index of 1.73, indicating a packing density of 50% (extrapolated from the refractive indices of bulk materials ($n_{\text{CdSe}} = 2.5$; $n_{\text{ZnS}} = 2.36$)). **d**, Morphology of a smooth CQD film surface analyzed by atomic force microscopy. For an area of $1 \mu\text{m}^2$, the RMS and peak-to-peak surface roughness were ~ 2 nm and ~ 15 nm ($\ll \lambda$), respectively. **e**, A thicker CQD film on n-Silicon substrate showing the presence of a crack reminiscent of cleavage or breakage by strain in crystalline epitaxial films.

Figure 2: Edge emission in stripe excitation geometry over a range of pumping levels. **a**, Experimental configuration with a cylindrical lens focusing ultrashort (100 fs) pulse laser excitation at a fixed wavelength of $\lambda = 400$ nm as a stripe on a CQD film; a slit for precise stripe length control. **b**, Plan view photographs of emission from excited stripes of RGB CQD films, respectively; stripe length and width are 1 mm and 10.5 μm , respectively (supplemental Fig. S4). The RGB bright spots at the film edges seen above threshold levels are clear visual evidence of ASE. **c**, Edge emission as function of pump energy density for RGB CQD films, with arrows indicating the ASE energy density thresholds of 90 $\mu\text{J}/\text{cm}^2$, 145 $\mu\text{J}/\text{cm}^2$ and 800 $\mu\text{J}/\text{cm}^2$, respectively. **d**, **e**, Spectral analysis of edge emission, together with absorption peaks of the

lowest exciton state for red and green CQD films. The lowest exciton absorption peaks were isolated from full spectrum absorbance results (supplemental Fig. S5). Additionally, the full-width at half maximum (FWHM) of the spectral peaks narrows from 28 nm to 7 nm for these red and green CQD films

Figure 3: Dynamics of CQD light emission from epitaxial-like thin films under various excitation conditions. **a**, Spectral analysis of the edge emission in stripe excitation for red CQD film, integrating for two different time windows: 0 - 40 ps and 300-640 ps after impulsive pumping. **b**, PL decay of the red CQD in small round “spot” excitation geometry at different preparations. The spot diameter is 22 μm , whose gain length is incapable of supporting ASE. The two exponential decay rate fitting is for CQD film at 100 $\mu\text{J}/\text{cm}^2$ excitation. **c**, High temporal resolution of the fast PL and the ASE decays in the spot and stripe excitation geometries, respectively. Excitation levels are above ASE thresholds for each CQD film. **d**, Spontaneous emission intensity of CQD film as a function of excitation level represented as an

average number of generated excitons per CQD, compared with our theoretical model – see Supplemental Eq. S2 and S3. The arrows show the excitation levels corresponding to the ASE thresholds.

Figure 4: Optically pumped CQD-VCSELs in the red and green. **a**, A schematic of vertically pump CQD-VCSEL with long pass filter to remove any residual pump excitation beam. CQD gain media is placed inside a wedge cavity for a variable cavity length. The wedge angle is 1.2×10^{-3} radians, and two distributed Bragg reflectors (DBRs) have reflectivity higher than 99%. **b**, **c**, Photographic images of red and green CQD-VCSELs showing spatially well-defined output beams which are collinear with the pump beam (supplemental Fig. S7). **d**, Spectra from a red CQD-VCSEL structure below and above threshold. **Inset**, Single mode lasing for a green CQD-VCSEL from a shorter cavity. From the linewidth of laser emission, the quality factor of cavity was estimated about 1300. **e**, Emergence of laser modes from spontaneous emission in a CQD-VCSEL when increasing pump power.