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Introduction

II–VI compound colloidal quantum dots (CQDs), or semiconductor nanocrystals, have advanced from being laboratory curiosities to technologically viable, competitive materials in full-color solid-state displays, as evidenced by the articles in this issue as well as from recent literature.¹–¹⁰ These successes beg the question of the possibility to further expand the role of CQDs to other optical device technologies. In this article, we examine their status across the visible spectrum as possible candidates for active devices such as lasers. Beyond the requirements for current display materials, additional challenges for CQD lasers rapidly emerge, including fundamental physics questions (e.g., the nature of excited electronic states) and practical considerations (e.g., robustness of the material to withstand high excitation levels). While significant research into the physics of optical gain in II–VI CQDs has been investigated actively for more than a decade,¹¹–¹⁴ we show in this review how recent developments may have advanced the landscape to gauge the technological feasibility of a single-material-based laser across the red, green, and blue (RGB) wavelengths. If eventually realized, such devices could replace existing (and ubiquitous) visible semiconductor lasers, fabricated from epitaxially grown single crystals, which presently typically require three different materials to cover the visible wavelengths (such as InGaN, GaAsP, InGaAs), each with distinct materials science and device architectures.¹⁵–¹⁷ The green spectral region is especially difficult to access by either III-nitride or III-phosphides and still carries the appellation “valley of death.”¹⁶–¹⁸

In the following, we first examine key material requirements for a CQD laser, focusing specifically on the benefits of very densely packed solid CQD thin films. We then address fundamental questions regarding the physics of optical gain and stimulated emission from photoexcited cadmium selenide-based II–VI CQDs. We point out some of the fundamental inhibiting mechanisms that only recently appear to have become surmountable, to enable electron–hole excitation (injection) levels that are practical and reasonable. Finally, early proof-of-concept demonstrations of stimulated emission and lasing in the RGB are illustrated, with some emphasis on recent advances in the authors’ laboratories.¹⁹

Material considerations for potential colloidal quantum dot lasers

Any candidate material for a laser must possess superior intrinsic optical properties. In addition to the obvious requirements of high radiative quantum efficiency and suitable electronic structure, other attributes such as optical homogeneity, suitability to adapt to an optical resonator for optical feedback, plus a host of other material demands¹⁵,²¹ place a high bar to entry for a new material. In recent years, striking progress has been made to increase the radiative efficiency of II–VI CQDs.
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well beyond 90% across the visible regime, both in a solution form and, more importantly, in the preservation of such high quantum efficiency in a solid host matrix. 28 Challenges remain in the display context, including robustness against temperature, and blue CQD materials can benefit from further basic development. However, the synthesis of CQDs is still based largely on an empirical approach, whereby “secret” recipes seem to vary a good deal across various commercial and academic organizations.

While some of the fundamental physics of the electronic nature of optical gain in wide-bandgap semiconductor CQDs are addressed later, we note that numerous examples of optical gain demonstration and insightful theoretical model concepts in various preparations involving CQDs (e.g., CdSe/ZnS) have appeared in the literature, ranging from sophisticated experiments both for CQDs in solution to those with CQDs embedded in a solid host. 14,21–26 One important solid form for compact CQD laser media is a highly densely packed, self-assembled, thin solid film, from a fundamental physics and practical optical points of view.

Most of the work to date in exploring processes of stimulated emission (mainly through amplified spontaneous emission, ASE) in solid form has accessed this densely packed CQD regime. Good reasons for this “avoidance” include early experiments that showed how the total radiative efficiency in such multilayer CQD preparations is typically very low as electronic or (near-field) dipolar coupling (Förster resonance energy transfer, FRET) between nearest neighbor CQDs and creates spatially extended pathways for energy transfer across populations, whereby nonradiative defects (e.g., in a certain fraction of the population) can rapidly deplete potential luminescence. 27,28

We have re-examined the question of dense multilayer CdSe-based core–shell CQDs—now with a strategy of specific design of the core–shell composition and dimensions and, importantly, the choice of the aromatic monolayer organic ligands. 29 The role of the ligands, in combination with Zn0.5 Cd0.5 S thin shells, has enabled the generation of RGB CQDs in non-polar solutions without (the usual) aggregation in room ambience. Importantly, the high packing density (near the theoretical limit) also produces optically highly homogeneous material (no internal light scattering losses)—a key requirement for a lasing medium.

Physics of CQD optical gain: On biexciton and single exciton state

While the improvement of radiative properties of II–VI CQDs in the visible portion of the spectrum have steadily improved over the years to reach competitive levels with inorganic phosphors for instance, accessing and understanding their electronic states that might yield optical gain (amplification) has been a challenge. The significant variations in material quality and constructs (core–shell compositions and sizes plus multiple choices for organic ligands) have not helped. Nonetheless, based on experiment and theory, physical models by researchers such as Efros, Klimov, Bawendi, and many others have converged on the idea of biexciton states being the predominant and most common excitation responsible for gain in Type I CQDs. 11,22–24,30–34

A biexciton state corresponds to two electron–hole pairs occupying a given CQD as a consequence of initial excitation (most commonly by optical pumping at photon energies above the fundamental excitonic energy gap). Ideally, such a four-particle state is population inverted with respect to the single exciton (two-particle state), by definition. (A single

Figure 1. Structural characteristics of individual colloidal quantum dots (CQDs) and their spin-cast densely packed films. (a–b) Transmission electron microscope (TEM) image of a CQD cluster displaying finite shape anisotropy and a well-defined lattice of crystalline structure. (c) Scanning electron microscopy (SEM) image of a dense solid CQD film cross-section. The small grains are metallic (Au–Pd) grains used as SEM imaging dielectric materials. 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 \( n_{\text{CQD}} = 2.5; n_{\text{R,R,S}} = 2.36 \)). (d) Atomic force microscopy shows a smooth CQD closely packed film surface; the root mean square (RMS) and peak-to-peak surface roughness were ~2 nm and ~15 nm (\(<\lambda\)), respectively, for an area of 1 \( \mu \text{m}^2 \). (e) A crack of a thicker CQD film on an \( n\)-Silicon substrate reminiscent of the cleavage or breakage by strain in crystalline epitaxial films. Reprinted with permission from Reference 29. © 2012 Nature Publishing Group.
exciton represents occupancy of one electron–hole pair per CQD). For crystallographically perfect single CQD, where the combination of electron and hole “particle-in-the-box” confinement energies and their Coulomb interaction define near atomic-like series of sharp energy levels, optical gain cannot ensue with a single exciton, as the processes of photon absorption and emission exactly cancel each other out in probability (as seen in the simplified schematic of Figure 2a).11 One way around this upper limit of optical transparency has been to propose a Type II CQD structure,12,35 where either by choice of specific core–shell compounds/compositions or by an applied electrostatic field, the conduction and valence band lineups create an energetic minimum for the electron (e.g., in the CQD core), while the hole is energetically and thus spatially separated in the outer shell layer. The transient Stark effect, the induced effect by an electrical field on the first exciton state,12 induces a large energy offset of the biexciton state from the single exciton state (Figure 2b), breaking the balance between emission and absorption of a single exciton CQD, and therefore enabling single exciton gain (Figure 2c).

While the obvious advantage of single exciton gain is its long lifetime (up to a nanoseconds order as opposed to picoseconds in a biexciton gain mechanism—inset of Figure 3a), the penalty for such a spatially indirect conduction-valence band transition is a significant reduction in the optical oscillator strength (which is prime currency for a laser). As a result, the ASE thresholds for these Type II CQD films are still at unpractical levels (Figure 3b), typically about 2 mJ/cm² using ultrafast optical pump sources.

In its perfect crystal model, the biexciton state for “automatic” optical gain via the biexciton-to-single exciton electronic transition requires elevated levels of external excitation in an ensemble of CQDs, with an additional significant cost for the wide bandgap CQDs in the visible regime. This cost occurs due to a highly efficient non-radiative recombination channel by the so-called Auger recombination. The Auger process represents the loss of a quantum of (useful) energy via an inelastic electron–hole collision within the multi-exciton entity, with a typical decay time constant on the order of a few tens to a few hundreds of ps.21,26,36–39 This is much faster than the typical single exciton radiative decay time constant in a CdSe-based CQD on the order of 10 ns by spontaneous emission. As a consequence, while much insightful spectroscopy of the biexciton gain characteristics has been accomplished in the past decade, these experiments have used intense ultrashort pulse lasers (100 fs) to create the picosecond temporal window needed for study of this gain and associated ASE—before the onset of the Auger recombination (inset of Figure 3a). A gain media, whose excitation (and duration) requires femtosecond lasers, is unattractive for a practical semiconductor laser device.

On the other hand, when effects due to the deviation from perfect quantum dots are taken into account and manipulated in specific ways, optical gain from single exciton states can be obtained in Type I CQDs, largely unencumbered by the Auger process. In addition to avoiding the Auger process, a big payoff ensues from a laser device point of view, due to the lower excitation level that is now needed to reach optical gain and amplification. Access to the single exciton regime appears to be quite feasible via a combination of finite CQD size/shape/compositional disorder as well as the impact of the organic dielectric outermost cladding/barrier layers, all of which contribute to a finite exciton density of states tail in the low

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**Figure 2.** Simplified view of excitonic energy states in a single colloidal quantum dot (CQD). Em. and Abs. indicate emission and absorption, respectively. (a) A single exciton creates optical transparency in Type I CQD. (b) With the presence of a transient Stark effect, the biexciton energy is higher than the single exciton state, creating optical gain with only one exciton. (c) On average, the occupancy of an exciton per CQD to create optical transparency in Type II CQD ensembles is 2/3. (d) A finite Stokes shift in engineered Type I CQD creates radiatively emissive states, which are energetically below the maximum probability of photon absorption, enabling the single exciton gain. Reprinted with permission from Reference 12. © 2007 Nature Publishing Group.
energy side of the principal $n=1$ single exciton absorption peak (a delta function in a perfect crystal CQD). Thus, following absorption at the $n=1$ exciton resonance (or at higher energies above the effective bandgap), the Coulombically interacting single exciton can relax to these low-energy density of states tails through a combination of excitonic scattering and acoustic phonon interaction, then finally recombine with one-photon emission (as illustrated in the simplified schematic of Figure 2d).

In terms of (display regime) CQD optical properties, this well-known energetic separation between the spectral peak positions of the $n=1$ absorption and luminescence (spontaneous emission), are known as the “Stokes shift” (not to be confused with the Raman effect). Depending on the CQD material, the Stokes shift can vary widely from a few meVs to hundreds of meVs. The origin of the “Stokes shift” here may involve interactions in the dense thin films, unlike conditions with solution-based colloidal preparations. The conditions for photo or electrical excitation in the “display regime” are typically so low ($<N>$ less than one, where $<N>$ is the average occupancy of the electron–hole pair per CQD) that virtually no biexcitons are created.

Recently, using the previously described densely packed and specifically configured CdSe-core/Zn$_{0.5}$Cd$_{0.5}$S-shell thin films as the material test bed, we have exploited the Stokes shift as a means of accessing the single exciton regime also for strong optical gain. The magnitude of the Stokes shift must be precisely optimized by CQD engineering for the overlap between radiative emission and absorption resonances; this reduces absorption losses for the emitted photons, which are on the lower energy tail of the $n=1$ single exciton absorption peak.

Figure 4a shows an example of the spectral overlap between absorption and spontaneous emission, which is comparable to the half width at half maximum of the emission spectrum. The Stokes shift must not be too large, since sufficient excitonic density of states must be available for optimum condition for net gain. In the time domain, and by using ultrafast spectroscopic techniques, the transient details of optical gain creation are illustrated in Figure 4b, in which the total transient absorption coefficient was measured as a sum of linear
and differential absorption at 2 ps after ultrashort pulsed excitation. Many such transient experiments have been conducted while focusing on the biexciton dynamics and competition with Auger processes, but this regime of excitation was largely bypassed. The optimum Stokes shift enables the single exciton gain in solid CQD films, with the gain threshold as low as \(<N> = 0.5\) (i.e., well within the single exciton gain regime).

The payoff from the single exciton gain mechanism, while maintaining the strong optical oscillation strength in Type I CQD, has enabled a record low gain threshold in our solid CQD thin films under pulsed optical pumping. For example, the gain threshold for the red CQD films (Figure 3a) is 90 \(\mu J/cm^2\)—a major improvement when compared with earlier biexciton gain literature or single exciton gain in Type II CQD (~2 mJ/cm²). By varying the excitation level, one can actually see multie exciton and single exciton dynamics emerging, as illustrated in Figure 4c. In particular, the gain after rapid quenching of the multie exciton states now persists for durations considerably longer than a nanosecond, on the order of single exciton decay. Significantly, the need for using ultrashort pulse lasers for excitation to achieve lasing is thus removed.

**Examples of red, green, and blue optically pumped CQD lasers**

The long optical gain lifetime and low excitation threshold to reach the single exciton regime in the dense CQD films have led to selected proof-of-concept laser demonstrations. The recorded low threshold RGB cavity-less lasers (ASE) were followed by the first demonstration of red and green CQD vertical cavity surface-emitting lasers (CQD-VCSELs), albeit initially with ultrashort pulsed pumps. Recently, we have demonstrated CQD distributed feedback (DFB) lasers across the full visible spectrum, RGB. In a DFB structure, an optical grating is incorporated into the laser device to provide spatially continuous optical feedback, etched into a quartz substrate. The dense solid CQD films turn out to be quite readily applicable to deposition for non-planar contours without loss of performance. By spin-casting techniques, we could deposit CQD films on the DFB gratings. As an aside, this simple process is scalable for mass production or “repainting” CQD gain media multiple times on multiple grating surfaces. A second order DFB laser structure was chosen to extract a vertical beam output and to facilitate fabrication approached by focused ion-beam lithography. A sample performance of these CQD-DFB lasers is shown in Figure 5, with close-up images (Figure 5a–f) of excitation areas below and above threshold pumping levels. We note that the ultrashort pulsed pump is no longer needed, and our pumping source is a sub-nanosecond compact diode pumped solid-state laser with pulse width much longer than the Auger time constant (i.e., entering the quasi-steady state regime) (without any thermal management for now). The spectral characteristics of some of the DFB lasers are demonstrated in Figure 5g.

Figure 5h–i demonstrates the spatial coherent outputs of the red and green CQD-DFB lasers. Spatially coherent “striped” beams were achieved in one dimension as a result of second order DFB grating configuration, after which well-collimated circular beams were achieved by using an additional cylindrical lens. The laser had output powers close to the milliwatt regime (up to 400 \(\mu W\) on average with 1 kHz repetition rate). Accounting for incomplete absorption of the pump laser light, we found an internal energy conversion efficiency (out-coming laser energy versus absorbed input energy) of 28%. Our opinion is that the optical gain with the biexciton mechanism simply cannot produce lasers with such high efficiency because of competing fast nonradiative multie exciton Auger recombination. Overall, the performance of the red CQD-DFB lasers is somewhat similar to that of the typical semiconductor laser pointer in terms of power, collimation, and efficiency.

**Summary**

While the main focus of applications to date for CQDs is their use for solid-state lighting and display applications (see other articles in this issue), we have shown that their size-dependent color tuning may also provide a means for future RGB laser applications—based on a single colloidal material base. Admittedly, the proof-of-concept and physical rationale...
behind the device demonstrations previously mentioned are only a first step toward practical lasers. For instance, the management of local heating, photochemical, and thermal stability of CQD are technologically acceptable for use as phosphor in lighting applications, but this still needs to be seriously addressed before robust, long-lifetime, optically pumped laser devices are technologically viable. Finally, while there are many challenges in direct electrical injection or excitation injection to CQD even at the level for light-emitting diodes, achieving electrical injection for a CQD laser will require a veritable quantum leap in physical ideas and material implementation.

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