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Surface-emitting red, green, and blue colloidal quantum dot distributed feedback lasers

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Abstract: We demonstrate surface emitting distributed feedback (DFB) lasers across the red, green, and blue from densely packed colloidal quantum dot (CQD) films. The solid CQD films were deposited on periodic grating patterns to enable 2nd-order DFB lasing action at mere 120, 280, and 330 μJ/cm² of optical pumping energy densities for red, green, and blue DFB lasers, respectively. The lasers operated in single mode operation with less than 1 nm of full-width-half-maximum. We measured far-field patterns showing high degree of spatial beam coherence. Specifically, by taking advantage of single exciton optical gain regime from our engineered CQDs, we can significantly suppress the Auger recombination to reduce lasing threshold and achieve quasi-steady state, optically pumped operation.

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References and links


1. Introduction

Following in the footsteps of fundamental studies of quantum confinement effect in low dimensional semiconductors [1–3], colloidal II-VI compound quantum dots (CQDs) in the visible have become an appealing candidate for the next generation of luminescent materials for displays whether as advanced phosphors [4, 5] or light-emitting diodes (LEDs) [6–8]. The chemically synthesized CQDs are solution-processed semiconductor nanocrystal materials and their fabrication process into e.g. an RGB phosphor is fairly straightforward. State-of-the-art CQDs exhibit small size dispersion (less than 5%), high crystalline structure quality and effective surface passivation [9] so that their photoluminescence quantum yield can reach near unity with high color purity.

Given such assets of CQDs, research has also focused on the possibility of their use as laser media. Two factors, one fundamental and the other practical have presented obstacles. On the fundamental side, and overriding their favorable light-emitting properties, CQDs suffer from non-radiative multiexcitonic Auger recombination process under typical high excitation conditions for optical amplification or lasing. The efficiency of the Auger process is greatly enhanced in quantum dots so that this inelastic electron-electron scattering can be much stronger than electron-photon coupling [10]. Consequently, ultra-short pulsed (sub-picosecond) optical excitation sources have been employed to study optical amplification, circumventing the ~100 ps non-radiative decay channel [11, 12]. We will not review this issue here except to note that to suppress the Auger recombination, various types of quantum dot structures have been proposed and investigated including type-II heterostructure core-shell CQDs [12] and quantum rods structures [13]. By first engineering specific type-I CQDs and then assembling them in very densely packed thin films, we have shown how access becomes possible to a single-exciton gain regime whereby both Auger effects and optical pumping thresholds for stimulated emission are greatly reduced [11].

In this paper, we focus on creating proof-of-concept for practical laser device structures in the red, green, and blue without changing material composition, by embedding the CQD gain media within distributed feedback (DFB) resonator structures. We demonstrate such RGB surface-emitting second-order DFB lasers [11, 14–18] while achieving single cavity mode operation with well-defined spatially coherent output beams and good efficiency. In the
optical pumping experiments a compact solid-state laser was used as the excitation source, with pulse widths exceeding the Auger decay time, and thus in contrast with much of the previous ultrashort pulse laser work in the literature.

2. Dense CQD thin films and optical properties

The type-I CdSe/ZnCdS core/shell CQDs used in this study were fabricated by high-temperature organometallic synthesis [19]. The diameters of CdSe core varied between 2.5~4.2 nm to tune the principal excitonic absorption and emission resonance wavelengths across the visible, from which gain and lasing was to be extracted. As part of the construct a 1 nm-thick ternary shell was grown to reduce strain and create a proper core/shell bandgap difference for confinement of the electrons and holes. The cadmium composition in the ternary shell gives maximum alloy potential fluctuations, which may help in spatial localization of exciton wavefunction as shown in bulk single II-VI crystals [20]. Finally, monolayer scale hydrophobic aromatic ligands were added for surface passivation. These engineered type-I CQDs were realized at extremely high concentrations (~150 mg/ml) in Toluene without aggregation, yet were able to reach an approximately 80% photoluminescence-measured quantum yield. Such concentrated solutions were then spin-cast on quartz substrates to form self-assembled, densely packed solid thin films [11]. The films were 200-300 nm in thickness with an effective refractive index between $n = 1.65-1.8$ across the RGB samples determined by ellipsometry. Calculating from the refractive indices for the bulk materials, and without accounting for the organic ligand, we obtained for the packing density of the films about a value of ~50% which is remarkably high when compared to the maximum case of identical hard spheres (~74%). Very importantly, the surfaces of the RGB films were optically smooth, indicating surface flatness of $\lambda / 30$ and root-mean-square (RMS) surface roughness of 2 nm analyzed by atomic force microscopy [11].

![Fig. 1. Absorption and photoluminescence spectra from densely packed solid red, green, and blue CQD films at room temperature.](image)

Figure 1 shows the absorption and spontaneous emission spectra of the red, green, and blue CQD films at room temperature. The red and green CQD films display very well-defined, spectrally isolated lowest exciton absorption peaks (up to $n = 3$ for the red CQD), whereas these features are weak in the blue CQD films. In all cases, the emission peaks are moderately red-shifted from their lowest exciton absorption peaks (“Stokes shift”).

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Importantly, the magnitude of the Stokes shifts in each of the RGB CQD films was comparable to the half of the full-width-half-maximum (FWHM) of their spontaneous emission. We have found empirically that this approximate relationship is optimal for achieving low threshold stimulated emission from the lowest exciton resonance while reducing the associated self-absorption of emitted photons.

3. Design and fabrication of the RGB colloidal QD thin film DFB laser

![Diagram](image)

Fig. 2. The procedure of the green and blue DFB grating fabrication. a-e, 170 nm-thick layer of PMMA was spin-coated on quartz, then soft-baked at 180 °C for 180 sec. Then, as a charge-dissipation layer for the electron beams, a thin Cr film (less than 10 nm) was evaporated above the PMMA (a). The PMMA resist was developed after removing the Cr film by wet etching process (b). A 30 nm-thick Cr layer was deposited on the patterned PMMA (c). Lift-off process of the PMMA in acetone resulted in a periodic Cr hard-mask pattern (d). Finally, a grating pattern with groove depth of 75 nm was formed by ICP-RIE process (e). Reference SEM image of the cross-sectional view of red DFB gratings fabricated by holographic lithography (f-g), SEM image of the bare blue DFB grating by electron beam lithography (h) and with closed-packed quantum dot films via spin-casting (i). In (i), the CQD film at the cleaved edge is lifted thereby offering a retracted quasi-3D view of the grating and the film, respectively. Scale bars are 500 nm.

Second-order DFB configuration was chosen as the common laser resonator substrate for the red, green, and blue devices, respectively, to provide optical feedback through Bragg scattering. The DFB lasers, ubiquitous in today’s optical communication, have the advantage of relatively simple lithographic fabrication and good optical confinement of the oscillating mode both of which are attributes for low threshold operation [21]. Specifically, for the second-order DFB laser, the corrugated grating structure provides for in-plane distributed feedback and perpendicular output coupling from the grating plane via second- and first-order diffractions, respectively. The emission wavelength, \( \lambda_{\text{Bragg}} \), is governed by the Bragg relation \( \lambda_{\text{Bragg}} = 2n_{\text{eff}} \Lambda / p \), where \( n_{\text{eff}} \) is the effective refractive index of the waveguide, \( \Lambda \) is the pitch of the grating, and \( p \) is the grating order. We used the ellipsometrically measured refractive indices and the wavelengths of the amplified spontaneous edge emission (ASE) of stripe geometry excited planar red, green, and blue CQD films (Fig. 2) as a means to target the desired pitches of the gratings as 360 ± 5 nm (red), 330 ± 5 nm (green), and 270 ± 5 nm (blue) according to the Bragg relation and anticipated gain spectral linewidth.

For the red “reference” DFB laser the grating structure was fabricated by holographic lithography on quartz substrate [12]. A thin film (5 nm) of chromium (Cr), acting as a hard
mask for the subsequent etching process, was deposited first on the quartz substrate and photoresist grating patterns were transferred on it [22, 23]. The grooves were formed by inductively-coupled-plasma reactive-ion-etching (ICP-RIE) with designed etch depth of 75 nm. By contrast, and due to practical limitation in resolution of the holographic interference lithography technique, we deployed electron-beam lithography (EBL) process to fabricate the smaller pitch grating patterns for both the green and the blue DFB lasers. This fabrication procedure is illustrated in Figs. 2(a)–2(e). Spin-cast and baked poly(methyl methacrylate) (PMMA) layer on quartz substrate was exposed by electron beams (30 kV of accelerating voltage and 0.17 nA of electron beam current) to form the desired periodic grating pattern. The ICP-RIE process was carried out with the same recipe which had been established for the red DFB grating fabrication. Scanning electron microscope (SEM) images of the grating in cross-section view are shown in Figs. 2(f)–2(h). Finally, after controlled spin-casting of the red, green, and blue CQD ultrahigh concentration solutions on their designed grating structures, we were able to achieve in each case a complete filling of the grating grooves followed by self-planarization of the QD films with optically smooth top surfaces Fig. 2(i) shows this outcome for the blue DFB structure where upon cleaving, the QD film immediately adjacent to the cleaved edge was lifted thereby offering a recessed quasi-3D view of the grating and the film, respectively. The overall grating areas were 200 × 200 µm².

4. Results and discussion

A compact solid state laser (pulse duration of $\tau_{\text{exc}} = 400$ ps; repetition rate of 1 kHz) at 532 nm (for red) and 355 nm (for green and blue) of second- and third-harmonics from a Nd:YAG source was used to optically pump the CQD DFB lasers. We underscore that the pump pulses were thus longer than the typical non-radiative Auger decay time constants of $\approx 100$ ps for biexciton and multiexciton processes which have dominated the literature on optical gain experiments in II-VI CQDs that use ultrashort pulsed excitation [10, 12]. The excitation was focused by a cylindrical lens to form an approximately 20 µm wide stripe excitation onto the CQD films, first onto planar films to acquire the ASE reference characteristics, and then onto the DFB structures along the full 200 µm length of the gratings. We varied the pitch of the gratings to tune the output emission wavelength of the CQD DFB lasers with a fixed groove depth of 75 nm. These parameters were chosen for being close to optimizing a low lasing threshold as indicated in our previous results with red CQDs [18]. A summary of the RGB emission in terms of spectral characteristics is shown in Fig. 3(a). At low pumping level, the devices emitted typical Gaussian-shaped photoluminescence (PL) signals. At a well-defined threshold for each color, the onset of stimulated emission was unambiguous from the linewidth narrowing. Figure 3(a) also includes the ASE spectra from corresponding planar films (edge emission) which we used to optimize the DFB laser operation by tuning the dominant grating mode into spectral coincidence from varying the effective index of refraction of the CQD films. Specifically, to match the DFB lasing with the ASE emission, we prepared a series of samples where the thickness of the CQD films ranged between 150 nm and 300 nm to fine tune the effective refractive indices of the CQD films on the corrugated grating structures. By varying the thickness of CQD films, we were able to observe spectral shifts of the lasing peaks, further verifying the dominance of DFB-induced optical feedback through the CQD gain media.

The lasing outputs exhibited a very narrow linewidth (FWHM < 1 nm, below the limit of our spectrometer resolution), indicating an evident single-mode operation. Figures 3(b)–3(d) show the output intensities from the RGB CQD DFB lasers as a function of input energy density per pump pulse, showing evident threshold behaviors. The micrographs in the insets visually show a significant increase in the output intensity of the stripe when the pumping level is above the threshold for all three colors. The threshold pumping energy densities were measured as 120, 280, and 330 µJ/cm² for the red, green, and blue CQD DFB lasers, respectively.
Fig. 3. (a) Spectral characteristics of the RGB DFB lasers. Solid lines represent the single mode output laser beams emerging from spontaneous emission perpendicular to the device surfaces just above threshold. Edge emission ASE spectra (dashed lines) acquired in separate experiments on planar CQD films is superposed to indicated the wavelengths for presumed maximum gain in the red, green, and blue, respectively. (b)-(d) Input-Output characteristics of the three lasers highlighting the threshold regime (lines connecting data points are guide to the eye). Insets show the far-field patterns perpendicular to the DFB plane, underscoring the spatial coherence in the laser emission (whose beam geometry reflects the narrow 20 µm stripe of excitation along a 200 µm length of the gratings).

It is very important to validate a DFB laser operation by also measuring the spatial coherence of the emitted radiation as well-defined output beams. Far-field patterns from our devices are seen in Fig. 4. The patterns are vertically elongated due to the stripe geometry (200 µm-length and 20 µm-width) by the focusing cylindrical lens. They exhibit two closely spaced beams, instead of single beam. This well-known phenomenon occurs due to the interference between coherent left-and right-traveling waves in any finite length optical waveguide [21], i.e. here along the gain guided excitation stripe in the CQD films. As a result, there is always a zero intensity at the center of the stripe in the near-field which, in turn, Fourier-transforms in the far-field to a double-lobed pattern. In DFB applications requiring Gaussian fundamental transverse modes, a symmetric mode operation with single lobe can be obtained by introducing half-wave phase shift in grating structure [12] or incorporating a photonic crystal structure. Note that the angular divergence in the horizontal direction is less than 2°, which is consistent with high degree of spatial coherence.

The measured average output powers of the RGB lasers are listed in Table 1. The maximum output power from the red DFB laser was about 400 µW. We note that the device emits perpendicular output beams emerging from the surface in both opposite directions. Therefore the conversion efficiency (output power vs. absorbed power) was about 28% when considering that only 25% of the incident light was absorbed by the CQD film. Similarly, the maximum measured output power for the green and blue DFB were 40 µW and 5 µW, respectively. Since the pumping power of our third-harmonic source (355 nm) only reached 0.9 mW, the absolute output power values of the green and blue DFB lasers were not as high.
as that of the red DFB laser. Their conversion efficiencies, however were nonetheless at a satisfactory high level.

As noted, the pump pulse duration in our case was longer than the Auger time constant which is typically 100 ps in Cd-based CQDs [11, 24], placing the operation in a quasi steady-state regime from this point of view. Exciton populations under optical pumping in the CQDs follow the Poisson distribution. Even in our low excitation conditions there will be a small, if finite population of fast decaying multiexcitons in CQDs, whereas single exciton gain is assumed to be dominant process for the optical gain in our type-I CQDs [11]. Temporally, the gain follows the spontaneous emission lifetime and not the usual Auger-induced nonradiative concatenation.

Table 1. Output Characteristics of the RGB CQD DFB Lasers

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<tr>
<th>DFB Lasers</th>
<th>Excitation wavelength [nm]</th>
<th>Absorbance</th>
<th>Pump power [mW]</th>
<th>Output power [µW]</th>
<th>Efficiency [%]</th>
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<td>Red</td>
<td>532</td>
<td>0.13</td>
<td>6</td>
<td>400</td>
<td>28</td>
</tr>
<tr>
<td>Green</td>
<td>355</td>
<td>0.5</td>
<td>0.9</td>
<td>40</td>
<td>6</td>
</tr>
<tr>
<td>Blue</td>
<td>355</td>
<td>0.05</td>
<td>0.9</td>
<td>5</td>
<td>7</td>
</tr>
</tbody>
</table>

5. Conclusion

We have developed surface-emitting colloidal QD DFB optically pumped lasers which operate across the red, green and blue colors based on a single material system. The device structures employed dense, closely-packed QD films deposited on grating structures which were optimized to yield maximum performance. Highly monochromatic lasing for all three colors was achieved at low excitation thresholds and measured far-field profiles demonstrated high degree of spatial coherence in the output beams of our DFB lasers. By taking advantage of single-exciton optical gain from our engineered type-I CdSe/ZnCdS core/shell thin films, the RGB DFB lasers were optically pumped beyond the normal Auger regime into quasi-steady state operation with high conversion efficiency. To reach continuous wave operation will require strategies for heat management which were not applied here.

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