Ultralow Threshold One-Photon- and Two-Photon-Pumped Optical Gain Media of Blue-Emitting Colloidal Quantum Dot Films

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Ⓢ *Supporting Information*

ABSTRACT: Colloidal quantum dots (QDs) offer advantageous properties as an optical gain media for lasers. Optical gain in the QDs has been shown in the whole visible spectrum, yet it has been intrinsically challenging to realize efficient amplified spontaneous emission (ASE) and lasing in the blue region of the visible spectrum. Here, we synthesize large-sized core/gradient shell CdZnS/ZnS QDs as an efficient optical gain media in the blue spectral range. In this Letter, we demonstrate for the first time that two-photon-absorption-pumped ASE from the blue-emitting QD is achievable with a threshold as low as 6 mJ/cm^2. Utilizing these QDs, we also report one-photon-absorption-pumped ASE at an ultralow threshold of ~60 μJ/cm^2, which is comparable to the state-of-the-art red-emitting QD-based gain media. This one-photon-pumped ASE threshold is an order of magnitude better than that of the previously reported best blue-emitting QD-based gain media.

Two photon pumped amplified spontaneous emission in blue quantum dots

SECTION: Physical Processes in Nanomaterials and Nanostructures
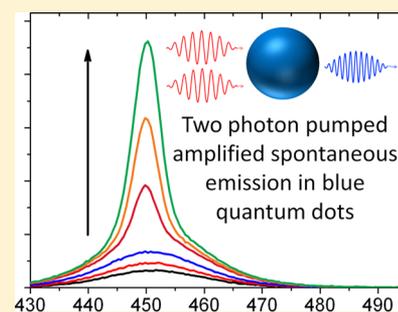
Colloidal quantum dots (QDs) are favorable light-emitting materials owing to their size, shape, and composition tailorable optical properties,[1,2] which make them promising light-emitting materials for light-emitting diodes[3] and lasers.[4−8] QD-based optical gain media represent an important field of study because their emission spectrum is easily tunable and full color lasing is possible with potentially high gain, which make them competitive against other gain media such as organic materials or other quantum-confined structures.[8−10] Recently, full color lasing was successfully demonstrated in the QD-based gain media by one-photon absorption (1PA) pumping.[8] Also, two-photon absorption pumping (2PA) was shown to be an alternative route for the excitation of the QD-based optical gain media for frequency up-converted lasing.[11−17] However, for the blue region of the visible spectrum, optical gain performance of the QD-based gain media has been severely limited as compared to the other color-emitting QDs (i.e., green, yellow and red). Up to this date, several reports demonstrated amplified spontaneous emission (ASE) in the blue region only with 1PA pumping.[6,8,18,19] The first demonstration of the ASE in the blue region was achieved only at cryogenic temperatures.[18] Later, Bawendi et al. demonstrated the first room-temperature ASE and laser by blue-emitting QDs.[6] To the best of our knowledge, the lowest ASE threshold for the blue-emitting QDs was shown to be 800 μJ/cm^2.[8] Additionally, 2PA-pumped ASE of blue-emitting QDs was not possible before. This poor optical gain performance of the blue-emitting QDs is probably due to their small size, where strong nonradiative

Auger recombination (AR) is expected to dominate and create ample losses. In addition, it was demonstrated that the optical gain threshold is size-independent provided that the hot exciton surface trapping is minimized.[20−23] In addition, the small size of these QDs had restrained the 2PA cross section, preventing achieving 2PA-pumped optical gain.

In this work, we developed CdZnS/ZnS having both a large size and gradient shell with a mean size in the range of 8−10 nm. These QDs have emission in the blue region of 440−460 nm. We demonstrate high-efficiency 1PA- and 2PA-pumped ASE employing these QDs as the optical gain media. The 1PA-pumped ASE threshold is as low as 60 μJ/cm^2, which represents more than an order of magnitude enhancement as compared to that of the blue-emitting QDs, as reported before. In addition, we report for the first time that 2PA-pumped ASE of blue-emitting QDs is viable, and we achieve an ASE threshold of 6 mJ/cm^2, which is comparable to that of the 2PA-pumped large-size red-emitting QDs. These substantially reduced optical gain thresholds are attributed to the large size of the QDs along with the gradient shell of the QDs, which helps to suppress the nonradiative AR.[24,25]

Blue-emitting CdZnS/ZnS QDs are synthesized using the slightly modified recipe from the literature.[26] Formation of the
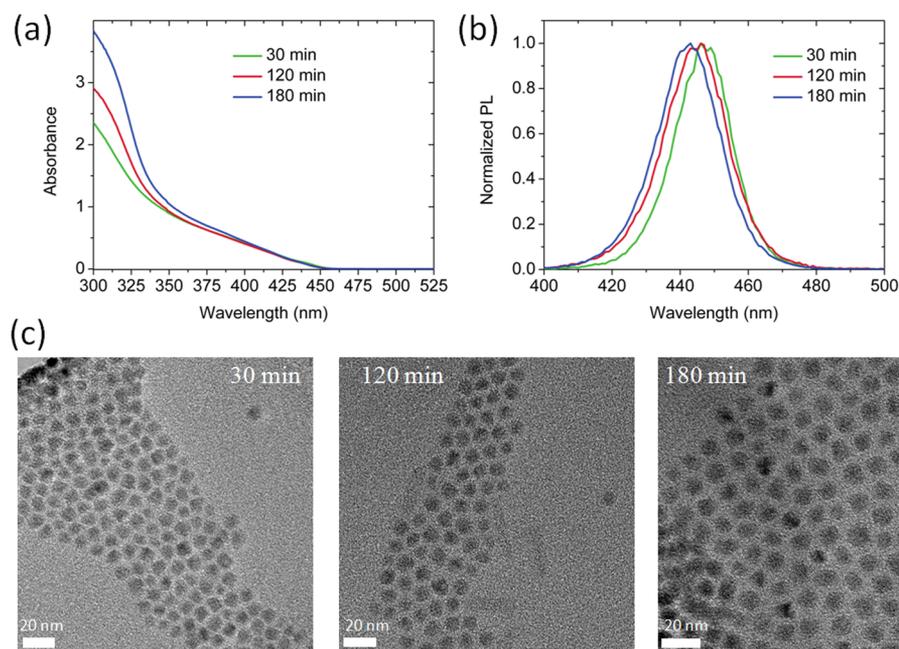
Figure 1. (a) Absorbance and (b) PL of the blue-emitting CdZnS/ZnS QDs having different shell growth times. (c) TEM images of the different duration shell-grown QDs: 30, 120, and 180 min.
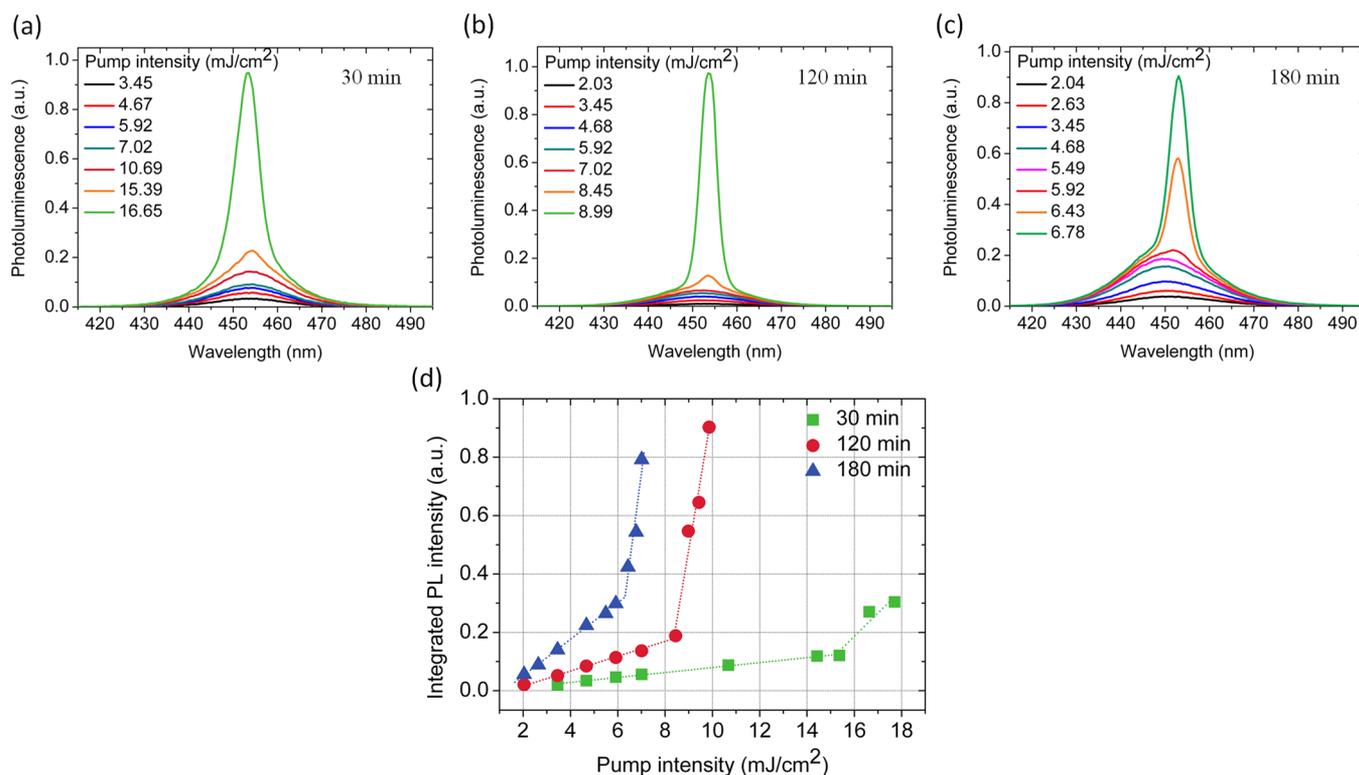

Figure 2. Pump-intensity-dependent PL of (a) 30, (b) 120, and (c) 180 min shell-grown CdZnS/ZnS QDs under 2PA pumping. (d) Luminescence versus pump intensity curve of the 30, 120, and 180 min shell-grown QDs with 2PA pumping.

core and growth of the shell is carried out in a single-step synthesis. Sulfur injection is performed two times. With the first injection of the sulfur precursor, nucleation of CdZnS cores is achieved. Then, with the dropwise injection of the second sulfur precursor at later times, the shell growth is initiated. In this work, we study three different QD samples, which have the same CdZnS core but a varying duration for the shell growth (i.e., 30, 120, and 180 min), resulting in different shell thickness

and overall size (i.e., increasing size as the shell growth duration is increased). The absorption and the photoluminescence (PL) spectra of the QDs are shown in Figure 1a and b. The emission of the QDs in solution is located at ~443−448 nm. There is a slight blue shift of the spontenous emission peak as the shell growth duration is increased from 30 to 180 min, which is an indication of the alloying and interdiffusion of Zn into the core/shell interface. The size of the QDs is investigated by
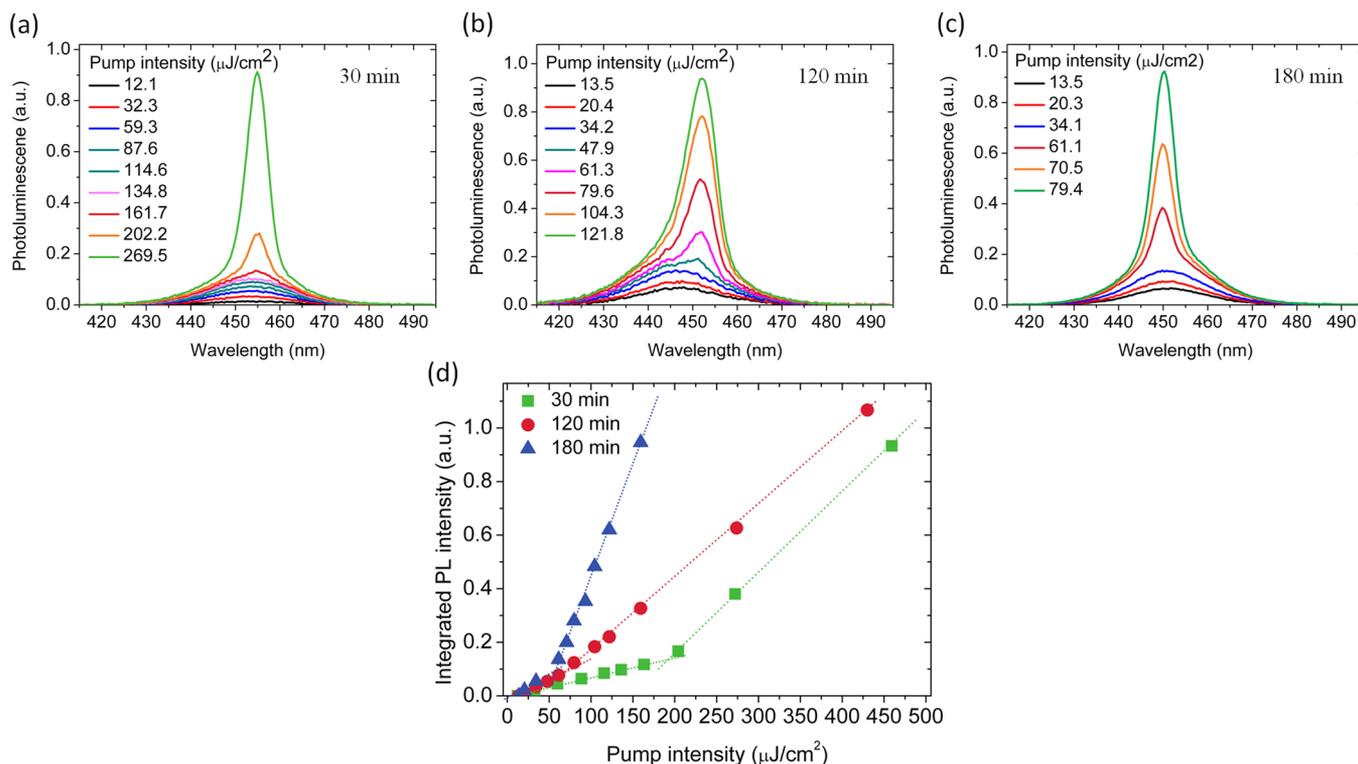
Figure 3. Pump-intensity-dependent PL of (a) 30, (b) 120, and (c) 180 min shell-grown CdZnS/ZnS QDs under 1PA pumping. (d) Luminescence versus pump intensity curve of the 180 min shell-grown QDs with 1PA pumping.

transmission electron microscopy (TEM). The analysis of the ensemble measurements reveals sizes of 8.36, 9.15, and 10.01 nm with a variance of 1 nm for the 30, 120, and 180 min shell-grown QDs, respectively.

We study the optical gain performance of the solid films of the QDs that are spin-coated on quartz substrates at a high concentration (50−60 mg/mL in hexane). As the pump source, we utilize a Spectra Physics−Spitfire Pro XP regenerative amplifier having a 120 fs pulse width at 800 nm with 1 kHz repetition rate. Using a cylindirical lens (20 cm focus), we excite the samples with a stripe geometry. Pump-intensity-dependent PL is measured via collection of the emitted photons along the stripe using a fiber coupled to a spectrometer (Maya2000 Pro). For the case of 2PA-pumped films, pump-intensity-dependent PLs are shown for 30, 120, and 180 min shell-grown CdZnS/ZnS QDs in Figure 2a−c, respectively. At low pump intensities, spontenous emission dominates the PL spectra of the QDs that have full width at half-maxima (fwhm) of 20 nm for the 30 min QDs and 22 nm for the 120 and 180 min QDs. As the pump intensity is further increased, the PL spectrum starts to narrow down with an emerging ASE peak having a fwhm of ~4.5−6.5 nm. For the 30 min shell-grown QDs, the position of the ASE peak is almost at the same position as the spontaneous emission peak. For the 120 and 180 min shell-grown QDs, ASE is red-shifted by 2 and 2.3 nm as compared to the spontaneous emission PL peak of the QDs, respectively. Figure 2d demonstrates the integrated PL intensity versus pump intensity for the three different QDs having different shell thicknesses. The thresholds for 2PA-pumped ASE are 6.25, 8.44, and 15.45 mJ/cm^2 for the 180, 120, and 30 min shell-grown QDs, respectively. Thus, we achieve a frequency upconverted stimulated emission in the QDs that has emission in the blue region of the visible spectrum. The

ASE threshold is comparable to the best-reported threshold for the red-emitting QDs and even better than that of the green-emitting QDs.[12,13,17] The decrease of the ASE threshold as the shell thickness is increased is attributed to the increasing size of the QDs that both increase the 2PA cross section and also reduce the nonradiative AR together with the enhanced alloying of the core/shell interface.[24,26,27] It was shown that QDs having a soft interface at the core−shell interface, that is, the gradient shell, have great contribution to the suppression of AR when compared to that for QDs having abrupt interfaces at the core−shell interace.[24] With the combination of larger size and a gradient shell, suppressed AR and superior optical gain performances have been demonstrated from CdSe/CdS core/shell QDs.[17,28] However, these types of QDs could be made to emit only in the red spectral range. Previously, it was not possible to achieve blue-emitting QDs from the gradient shell QDs (see Supporting Information for the depth profile study of the QDs using X-ray photoelectron spectroscopy revealing the gradient structure).

1PA-pumped ASE of these blue-emitting QDs is also investigated by frequency doubling the pump source using a nonlinear BBO crystal and filtering out the residual 800 nm. Here, 180 min shell-grown QDs again exhibit the best ASE performance. Figure 3a−c depicts the pump-intensity-dependent PL curves for the 30, 120, and 180 min shell-grown QDs, respectively. Interestingly, for the 180 min shell-grown QDs, the ASE peak emerges almost at the spontenous emission peak of the QDs (~450 nm), whereas the ASE of the same QDs was achieved ~2.3 nm red-shifted for the case of 2PA pumping. This could be attributed to the fact that 2PA pumping may cause extra heating that could red shift the emission. Another possibility is that the gain type might be altered from biexiton gain to single-exciton gain.[8,9] Also, the ASE peak can move
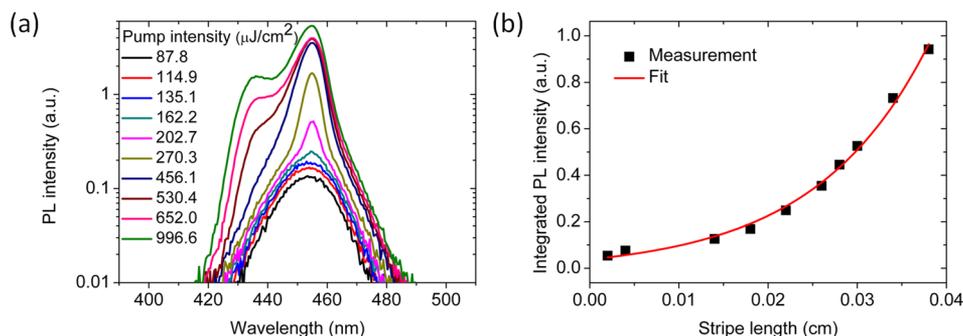
Figure 4. (a) PL intensity of the 30 min shell-grown QDs under 1PA pumping as a function of pump intensity. At higher pump intensities, higher-order multiexcitonic ASE is observed in addiation to the regular ASE. (b) Variable stripe length measurement of the gain coefficient of the 180 min shell grown QDs pumped by 1PA.

spectrally based upon surface trapping and/or multiexciton effects.[17,21] For the 30 and 120 min QDs, we achieved the ASE peak red-shifted as compared to their spontenous emission peaks with a fwhm of 6−9 nm. Figure 3d shows the integrated emission intensity versus pump intensity curves for the three different QDs. The thresholds of the ASE for 1PA pumping are 58.9, 74, and 193.5 $\mu J/cm^2$ for the 180, 120, and 30 min shell grown QDs, respectively. The 1PA ASE threshold achieved for the 180 min QDs represents an order of magnitude better result than the previously reported best threshold for the blue-emitting QDs, which was ∼800 $\mu J/cm^2$.[8] The 1PA ASE threshold of our blue QDs is comparable to that of the state-of-the art green- and red-emitting QD-based gain media.[8] Recently, using similar QDs, record efficiency electrolumines-cent light-emitting diodes were shown, where the enhanced performance was attributed to the suppression of the nonradiative AR processes and inter-QD nonradiative energy transfer.[26]

Furthermore, we investigate the emission of our QDs at increased pump intensities to understand the suppression of the nonradiative AR. Surprisingly, we observe higher-order multi-excitonic ASE for the first time using blue-emitting QDs.[29] This type of higher-order ASE could be only shown previously for red-emitting core/shell QDs,[30] dot-in-rod, and tetrapod-like nanocrystals.[31] Figure 4a shows the pump intensity (1PA-pumped) dependent PL of the 30 min shell-grown QDs. As the pump intensity is below the ASE threshold, we observe the spontenous emission of the QDs. After surprassing the ASE threshold (∼200 $\mu J/cm^2$), the ASE peak emerges and starts to dominate the PL spectra. At further increased pump intensity (530 $\mu J/cm^2$), which is 2.5-fold greater than the ASE threshold, we observe the onset of a new emission peak at the higher-energy side of the spontaneous emission peak (110 meV blue-shifted as compared to the spontaneous emission peak). At further increased pump intensities, this newly emerging peak increases at a faster rate than the regular ASE peak. We attribute this newly emerging higher-energy peak to the ASE resulting from higher-order excitonic states ($1P_e$−$1P_{3/2}$) in these QDs. This observation of higher-order excitonic ASE supports the existence of the long-lived multiexitons, which is a clear indication of the suppressed nonradiative AR. Otherwise, higher-order excitons would not be sustained in these QDs. This type of multiexcitonic ASE could not be observed for the blue-emitting QDs before. Finally, we measure the gain coefficient of our blue-emitting QDs, as shown in Figure 4b by applying the variable stripe length method. The integrated PL intensity of the 180 min shell-grown QDs is shown in

Figure 4b for varying stripe length (VSL).[32] The VSL data is fitted according to ref 33. The gain coefficient turns out to be up to 78 cm^{-1}. This value is comparable to the highest reported gain coefficient of 150 cm^{-1} for the red-emitting QDs.[34]

As a summary, we synthesize and study optical gain performance of CdZnS/ZnS QDs having both large size and a gradient shell that emits in the blue spectral region. For the first time, 2PA-pumped ASE is shown with a threshold as low as ∼6 mJ/cm^2 for the blue-emitting QDs. Furthermore, these QDs exhibited the best-reported 1PA-pumped ASE perform-ance with a threshold down to 60 $\mu J/cm^2$ and gain coefficient up to ∼80 cm^{-1}. These QDs will be expected to be promising optical gain media for blue-emitting QD-based lasers.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Details of a depth profile study of the quantum dots using X-ray photoelectron spectroscopy. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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