Using Colloidal Quantum Shells as a Novel Gain Medium for Integrated Visible Lasers

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Colloidal quantum dots (QDs) are heavily investigated for their applications in light emission such as light emitting diodes and, more challenging, lasers. This is due to their appealing processing conditions, compared to e.g. epitaxy, resulting in lowering cost. They can also be patterned and their optical properties can be tuned. Using quantum confined Cd-based QDs, several groups have shown light amplification and ensuing lasing action in the red part of the spectrum. Although impressive milestones were achieved, there is to date no single material that can provide the demanding combination of gain metrics to be truly competitive with existing epitaxial growth approaches. In this work, we take a look at a new geometry of nanocrystals, the so-called "Quantum Shells". Rather than placing the material with the smallest bandgap in the core, it's placed as the outer shell, confining carriers to the shell rather than the nanocrystal's center. We show that these unique materials display impressive gain metrics for red emitters. Using these novel gain materials, we demonstrate lasing in the red (580 - 660 nm) both with pulsed and quasi-CW optical excitation. These lasers are made using a Photonic Crystal Surface Emitting Laser (PCSEL) type cavity.

Introduction

Ever since the groundbreaking discovery of optical gain in CdSe-based Colloidal Nanocrystals in the year 2000[1], the pursuit of more efficient solution-processable gain materials has resulted in the development of a vast library encompassing a diverse range of atomic structures, elemental compositions, and geometric configurations. Through deliberate modifications to the system, achieved either by incorporating semiconductor shell(s) to enhance charge separation from the surface, or by changing the geometry to fundamentally reshape the underlying physical mechanism for optical gain, better materials for various applications are now available. This can be seen in working opto-electronic devices with room-temperature continuously operated Amplified Spontaneous Emission (ASE) on integrated devices[2].

Exploring the criteria that make a solution-processable material valuable in a non-linear optical device remains a topic of ongoing discussion within the community. We can categorize these materials based on three non-linear optical material parameters: the inverted-sate (or "gain"-) lifetime τ_G, the threshold carrier density n_{th} and the material gain coefficient g_i. These are reported for a variety of materials in the library, where for each metric there are superior materials: type II Quantum Dots (QDs) and electron-doped systems, with record low n_{th} but limited g_i; 2D nanoplatelets[3], with record g_i but sub-nanosecond τ_G; and the family of core/shell CdSe/CdS-based QDs which offer a compromise solution on the three fronts, driven mainly by small bi-exciton redshifts of less than 10 meV[4]. While these results are impressive, instead of having a material that

combines good values for each metric, a compromise is made, as there is an intrinsic interplay between specifically g_i and τ_G for QDs. Opting for extended gain lifetimes over material gain constrains the potential power output. An interesting observation that can be made is that in recent years, there has been more and more interest into nanocrystals with larger and larger active volumes. Recently, work has been published showing that going beyond the bohr diameter and using so-called "bulk nanocrystals" shows impressive gain metrics, specifically for the material gain, in combination with multiple nanoseconds gain lifetimes[5].

Here, we expand upon one novel material platform in the library, the CdSe/CdS Quantum Shell (QS)[6,7]. This material consists of multiple shells, where contrary to typical QDs, the material possessing the smallest band gap (CdSe) is located not within the core, but rather in the initial shell. The core and the outer shell consist of a material with a larger band gap (CdS), and the whole structure is encapsulated with a ZnS shell. We start studying this material by conducting Transient Absorption (TA) Spectroscopy to check for optical gain, which highlights a promising material candidate for lasing applications. To validate these resasing is demonstrated on an integrated Silicon Nitride (SiNx) on Silicon Oxide (SiOx) platform. A Photonic Crystal (PhC)-type cavity is used[8], similar to previous demonstrations of solution-processible based materials. Lasing action is shown over a wide spectral region (580-660 nm), with comparable thresholds in literature on solution-processible materials.

Transient Absorption Spectroscopy

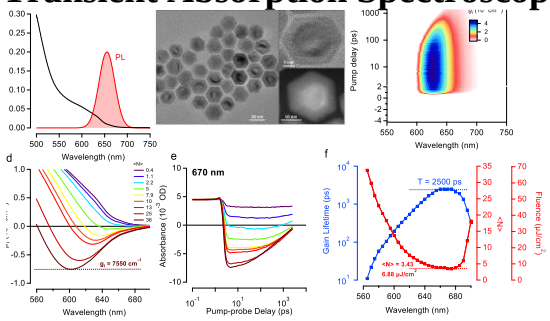

Figure 1: Linear characterization and Transient Absorption Spectroscopy of Colloidal Quantum Shells.

The sample morphology is shown in Figure 1. It consists of a 8.5 nm CdS core, followed by a 1.9 nm CdSe shell. After additional CdS/ZnS shelling, the total particles are 21-22 nm, consisting of an additional CdS shell and a 1 nm thick ZnS shell, found through a TEM analysis Figure 1b. The resulting material emits around 660 nm, with a Quantum Yield close to 100%. It is very similar to the material used in the work of Harankahage et al.[7]

We studied the optical gain by means of femtosecond Transient Absorption (TA). A 110 fs pulse is used to excite a QS dispersion to create electron-hole pairs, using off-resonant excitation at 515 nm (2.4 eV). After the initial pump pulse, a second short but broadband probe pulse is injected into the sample. By measuring the difference in transmission when the QS sample is excited or not, a change in absorption ΔA can be measured. In succession changing the delay between the pump and the probe, ΔA can be measured as a function of time. Adding the linear absorption A_0 to the measured ΔA and checking where this signal becomes negative, yields a gain map as shown in Figure 1c. This map shows for what wavelengths there is optical gain, how strong it is, and how long the optical gain persists in this system. By varying the excitation power, multiple of these maps can be measured to find the gain threshold.

In Figure 1d, the absorption spectrum is shown for a 3 ps pump-probe delay for multiple excitation densities, showing a gain window stretching from 550 to 680 nm at high powers. Interestingly, there does not seem to be any sort of saturation of the gain. In Figure 1e, the absorption is shown at 670 nm, near the band gap, from which the gain lifetime can be found. Here, we see gain that extends the limitation of our TA setup, reaching up to 2.5 ns. Finally, in Figure 1f, the found gain lifetime (blue), and the threshold (red) are plotted together, showing the inversely proportional relationship between these two parameters. Ultimately, the QSs show an impressive combination of strong material gain, with record long gain lifetimes, outcompeting both colloidal QDs (both in gain magnitude and gain lifetime) and QWs (in gain lifetime).

Demonstrating Lasing with Photonic Crystal based Lasers

The resonating wavelength within a cavity follows Bragg's Law, defined as $m \cdot \lambda_{Bragg} = 2n_{eff}\Lambda$, where m denotes the order of diffraction, λ_{Bragg} is the resonant wavelength, n_{eff} is the effective refractive index in the structure, and Λ is the period of the grating. A second order grating was used to achieve surface emission, typically referred to as a "Photonic Crystal Surface Emitting Laser" (PCSEL). In this study, gratings were designed with a square lattice, featuring periods spanning from 320 to 460 nm at 5 nm intervals. This range was determined based on an estimate of the effective index, ensuring a comprehensive scope.

Laterally, the devices are 600x600 periods. A schematic of a device is shown in Figure 2a. They are designed with a duty cycle of 60%, defined as the ratio between the side of the hole and the total period. SEM images in Figure 2b,c show a device with a period of 395 nm. The top view shows that the different QSs can be clearly resolved despite the oxide cladding. From the cross-section it can furthermore be seen that the sidewalls are very rough, and that the SiNx is nearly etched fully through. Moreover, a duty cycle of around 70% is found, indicating an overexposure or over etching is occurring.

Next, we use the same ultrafast laser used in the TA spectroscopy to study the lasing. An example of a measurement where spectra are measured as a function of excitation power is illustrated in Figure 2b, for a period of 385 nm, showing lasing at 637.5 nm. The inset graph depicts peak counts as a function of fluency, revealing distinct threshold behavior, with a measured threshold of 35.8 µJ/cm2. Devices exhibited lasing across periods ranging from 335 nm to 405 nm, corresponding to resonant wavelengths spanning 580 to 660 nm, as shown in Figure 2e. Figure 2f illustrates device thresholds in red, revealing the lowest threshold within the range of 640-660 nm, measured at 15.9 µJ/cm2. This study shows low threshold and broadband lasing from the QSs.

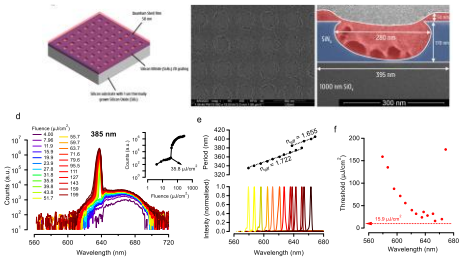

Figure 2: Lasing with Colloidal Quantum Shells through Photonic Crystal Surface Emitting Lasers

Conclusions

In this study we investigated the optical gain in Colloidal Quantum Shells. Our findings not only confirm the long gain lifetimes previously observed[6], but also unveil their high material gain, surpassing benchmarks set by colloidal Quantum Dots[2]. Validity is demonstrated by making lasers on an integrated SiNx/SiOx based platform, PCSEL type cavity. Lasing is achieved with femtosecond excitation, showcasing competitive thresholds of 15.9 µJ/cm^2. This exciting first look into utilizing colloidal QSs in integrated devices not only highlights their potential but also positions them as promising candidates for more intricate and practical applications.

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