Understanding the mechanisms behind optical gain in bulk solution processible semiconductors

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ABSTRACT

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 talk, we take a look at material properties of CdS/Se nanocrystals in the regime of vanishing quantum confinement, so-called 'bulk nanocrystals'. We show that these unique materials display disruptive optical gain metrics in the green optical region. Indeed, while showing similar gain thresholds compared to state-of-the-art QD materials, the gain window (440-600 nm, 640-750 nm), amplitude (up to 50.000/cm) and gain lifetime (up to 3 ns) vastly outpace other solution processible materials.

These results, while very impressive, are also puzzling. In the solution processible community a material system without quantum confinement does not exactly inspire confidence to have good emission metrics. We attempt to explain the physics behind these huge gain coefficients, by using a bulk semiconductor model which includes a strong band-gap renormalization effect, and argue why going to a bulk semiconductor can be advantageous compared to confined systems for making integrated lasers.

Keywords: Transient Absorption Spectroscopy, Optical Gain, Bohr Radius, Bulk Physics, Solution Processible Semiconductor, CdS, CdS, Band Gap Renormalisation

1. INTRODUCTION

Since the year 2000, Colloidal Nanocrystals (NCs) have been under investigation for their potential as an optical gain material[1]. Transient Absorption (TA) spectroscopy has emerged as a commonly employed technique for this investigation. Our focus lies on exploring "bulk nanocrystals" (BNCs)[2], materials that have surpassed the confines of strong confinement due to a radius exceeding the Bohr radius. Remarkably, these materials, particularly CdS BNCs, exhibit gain metrics that significantly surpass the current benchmarks for solution-processable semiconductors, reaching up to 50.000/cm. Moreover, they showcase a cutting-edge gain lifetime of up to 3 ns, coupled with a competitive gain threshold. In this study, we utilize TA spectroscopy to showcase these impressive gain metrics, incorporating CdSe BNCs as well. The underlying physics of this optical gain are elucidated through a bulk semiconductor model.

2. TRANSIENT ABSORPTION SPECTROSCOPY

In TA spectroscopy, we initiate the process with an ultrashort narrowband excitation pulse (110 fs) to stimulate a sample consisting of NCs dispersed in a solvent. A certain time later, a broadband probe pulse is injected into the sample. By gauging the absorbance of the sample under both excited and unexcited conditions, we can discern the alteration in absorbance resulting from the excitation. This process is repeated for various delays between the pump and probe, enabling the determination of the change in absorption concerning the pump-probe delay and wavelength, as illustrated in Figure 1a. The observed change in absorption (ΔA) is integrated with the linear absorbance (A_0) to derive the non-linear absorbance ($A = \Delta A + A_0$). When this absorbance assumes a negative value, indicating more light emission than absorption, optical gain is present in the sample ($g = -A$). Normalizing to volume[3], we define intrinsic absorbance and intrinsic gain, facilitating the comparison of different NCs through the intrinsic gain map – illustrated in Figure 1b.

Slices of these maps at a three-second pump-probe delay are showcased in Figure 1c (CdS) and 1d (CdSe) for various excitation powers, both excited off-resonance (400 nm for CdS, 515 nm for CdSe). CdS exhibits optical gain of up to 50.000/cm, surpassing other known colloidal NCs[4]. Meanwhile, CdSe, experiencing a red shift compared to regular CdSe-based QDs due to the absence of strong confinement, presents more modest gain magnitudes, peaking at 6.000/cm— still outperforming confined NCs. The carrier decay dynamics for both materials are depicted in Figure 1e (CdS) and 1f (CdSe), highlighting the up to 3 ns gain lifetime for CdS and up to 2 ns for CdSe. This establishes CdS as the state-of-the-art optical material for the green region and introduces CdSe as a novel material for the red.
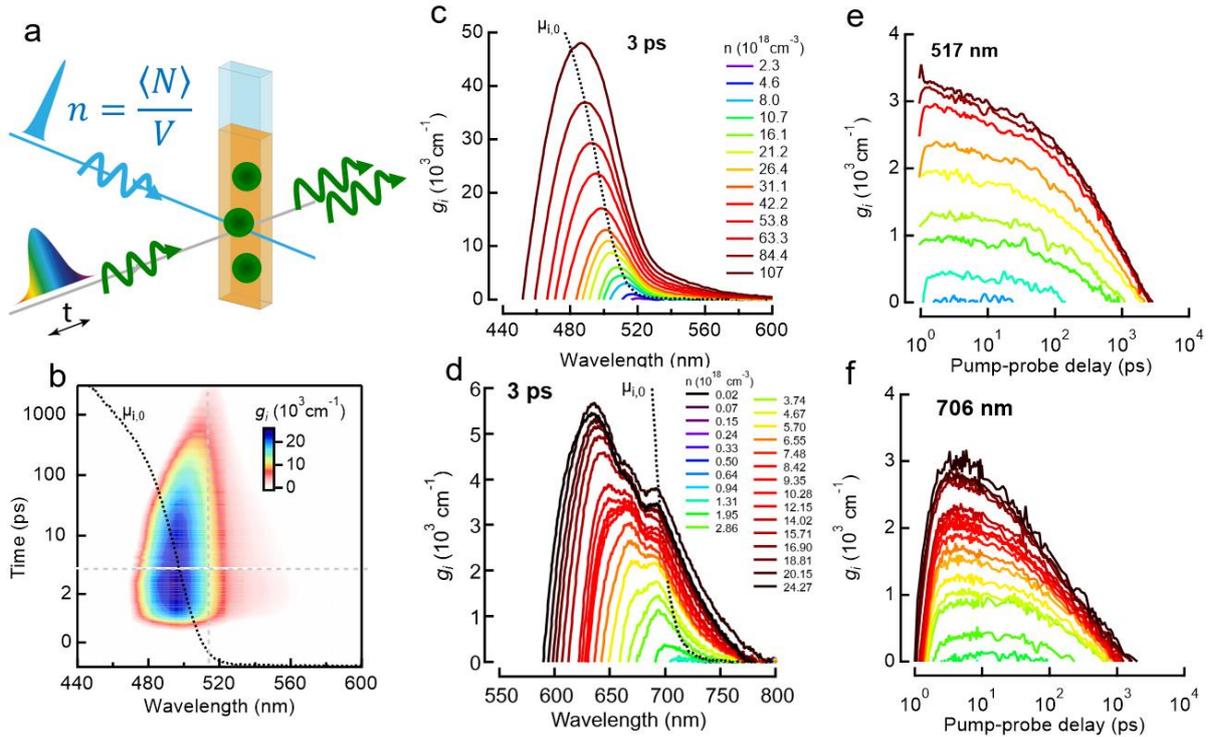

Figure 1. Optical gain in colloidal BNCs. (a) Explanation of the Transient Absorption Experiment. (b) A Transient Absorption map, for CdS BNCs, taken at $n = 5.9 \cdot 10^{19}$ cm^3. (c) Gain spectra of CdS BNCs taken at a pump probe delay of 3 ps. (d) Same, for CdSe BNCs. (e) Decay curves at the band gap (517 nm) for CdS, and (f) CdSe, showing a gain lifetime of up to 3 ns and 2 ns, respectively.

3. UNDERSTANDING OPTICAL GAIN IN BNCS THROUGH A BULK PHYSICS MODEL

As BNCs no longer have strong confinement, a typical state-filling model to explain the optical gain[4] cannot be used. We instead switch to a more bulk physics based approach, where the quasi fermi levels are calculated based on the amount of carriers, and the absorbance is inverted for specific energy ranges

$$g_i(E, n, T) = \mu_{i,0}(E) \times [f_c(E, n, T) - f_v(E, n, T)]$$

Where f_c and f_v are the Fermi Occupation factors of the conduction and valence bands, respectively. The temperature and the carriers can be estimated from the experiment. However, this model proves inadequate to explain the optical gain, as it underestimates it. To correct, an additional parameter to include band gap renormalisation (BGR) has to be used

$$g_i(E, n, T) = \mu_{i,0}(E - \Delta_{BGR}) \times [f_c(E, n, T) - f_v(E, n, T)]$$

This addition red-shifts the absorbance spectrum before inverting. With it, the optical gain curves can be fit with excellent agreement, demonstrating that large band gap renormalisation is the driving force for the optical gain in these kind of material systems. This effect is shown in Figure 2a, where the same curve is generated both with and without the BGR effect. Figure 2b shows the fits done for various excitation powers when a 400 nm pump and 485 nm pump are used. Both figures show excellent agreement between the experiment and the model. Analysis on the CdSe BNCs is on-going, but based on theoretical assumptions that BGR scales with the exciton binding energy[5,6], we know that this is a limitation in going to similar huge gain values with this material. This theoretical model is shown in Figure 2c (black line), whereas the data is plotted in the blue and red symbols.
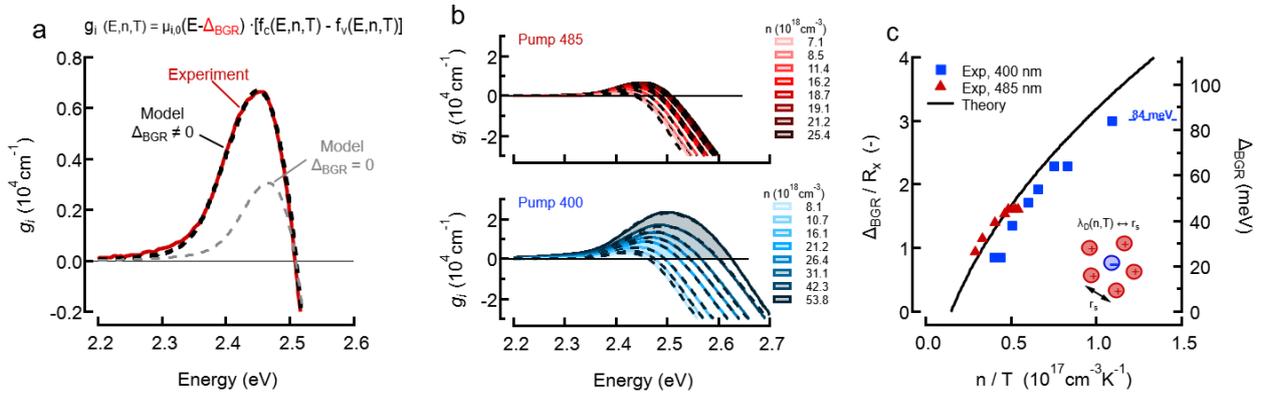

Figure 2. Modelling of optical gain in colloidal BNCs. (a) Example fit of the data, demonstrating the necessary addition of band gap renormalisation. (b) Example fits at various excitation powers for both 485 nm and 400 nm excitation. (c) Comparison between theoretical BGR values for bulk materials and the values extracted from the fitting.

4. CONCLUSION

We have shown disruptive gain metrics for BNCs, specifically ones based on CdS and CdSe. We furthermore show a physical model, based on bulk semiconductor physics, that can explain where this optical gain comes from. Our insights learn us that band gap renormalisation is the driving force for optical gain in these systems.

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