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Optical Gain with Colloidal Quantum Dots: From material photo-physics to integrated devices

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Colloidal quantum dots (QDs) have emerged as a most attractive optical gain medium in recent years. They offer a broad gain spectrum that can be readily adjusted by exploiting size-dependent quantum confinement, a specific choice of QD material or the judicious formation of heterostructured core/shell QDs. Together with their suitability for solution-based processing, this makes them a most versatile gain medium for photonic integrated circuits. CdSe/CdS core/shell QDs in particular have shown amplified spontaneous emission (ASE) and lasing under femtosecond and nanosecond pumping. However, to fully assess their potential for micro- and nanophotonics, a quantitative understanding of their gain characteristics is needed. Here, we show that the material gain of colloidal QDs can be determined through ultrafast transient absorption measurements on QD-dispersions, which is a key parameter for the design and optimization of future QD-based amplifiers and microlasers.

Introduction

Colloidal quantum dots (QDs) offer a number of unique properties that make them ideal as light emitters in integrated photonics. Due to size quantization, they have a bandgap and a concomitant emission wavelength that can be readily tuned by their dimensions. Moreover, being provided as solution-based dispersions, they can be readily incorporated into dielectric host materials and different photonic structures, including waveguides, microcavities and photonic crystals by straightforward solution-based processing methods. This combination of tunable electronic energies and versatile processing makes them ideal building blocks for integrated optical devices [1].

Various QDs have shown optical gain, mostly under femtosecond optical pumping [2]. Their integration within dielectric host materials to make optically pumped solid-state QD-lasers is a subject of intense research addressed by various groups. One approach, compatible with C-MOS processing and amenable to photonic integration is their embedding in SiNx/QD/SiNx layered stacks. As shown recently, SiNx waveguides and microdisks, thus functionalized with CdSe/CdS core/shell QDs, can show amplified spontaneous emission (ASE) [3] and lasing [4] under pulsed optical excitation. One of the difficulties in designing such devices is that the conditions where stimulated emission can overcome optical losses in the device and yield net gain are not well known. This requires a framework in which the material gain of colloidal QDs is (1) properly defined, (2) measurable and (3) can be linked to the modal gain of QD-based devices. Here, we extend the concept of the intrinsic absorption coefficient as a QD material property to an intrinsic gain coefficient or QD material gain. Furthermore, we show that the material gain can be measured using pump-probe transient absorption spectroscopy and we demonstrate that it predicts the experimental modal gain of SiNx/QD/SiNx waveguides. We conclude that the QD material gain, defined as the intrinsic gain coefficient, is a most useful quantity to assess the optical gain characteristics of different colloidal QDs in view of their application in optical amplifiers and lasers.

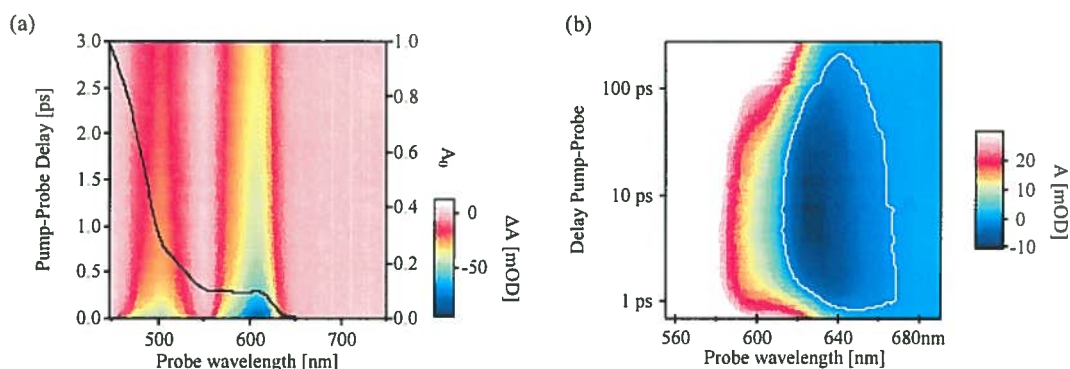


Figure 1 (a) 2D-spectrum from a TAS measurement on 9 nm diameter core/shell CdSe/CdS CQDs (pulse energy $95 \mu\text{J}/\text{cm}^2$). The black curve corresponds to A_0 , which is the absorption spectrum of the unpumped sample. (b) Corresponding 2D-map of A as function of probe wavelength and delay time, $A < 0$ corresponds to gain, $A = 0$ is indicated by a white line.

Background

The absorption coefficient of a composite material consisting of QDs dispersed in a non-absorbing medium can be seen as the product of the QD volume fraction f (defined as the ratio between the total QD volume and the sample volume) and the intrinsic absorption coefficient μ_i of the QDs:

$$\mu = \mu_i \times f \quad (1)$$

Defined according to eq (1), μ_i is the absorption coefficient of a fictitious QD dispersion that has a QD volume fraction of 1. In principle, size quantization makes μ_i a function of the wavelength and the size of the QDs. However, it was found that μ_i becomes size-independent at short wavelengths, with an experimental value closely matching the value predicted by Maxwell-Garnett theory based on the bulk dielectric function of the QD material. [5] Hence, using μ_i at such a reference wavelength, a μ_i spectrum can be readily obtained as a normalized absorbance spectrum $A(\lambda)$, regardless of the QD volume fraction:

$$\mu_i(\lambda) = \frac{A(\lambda)}{A(\lambda_{ref})} \mu_i(\lambda_{ref}) \quad (2)$$

Optical Gain in Transient Absorption Spectroscopy

Transient absorption spectroscopy (TA) is a pump-probe technique where a sample is pumped with ultrashort laser pulses after which the change in absorption ΔA is measured by a time-delayed white-light pulse. Figure 1a shows as an example the transient absorption map, showing ΔA as a function of probe wavelength and pump-probe delay, when a CdSe/CdS QD dispersion is pumped using 110 fs pump pulses at 520 nm and a 1 kHz repetition rate. The most striking feature is a reduced absorption or bleach ($\Delta A < 0$) at around 620 nm due to state filling of the band-gap transition of the CdSe core. Adding the absorbance spectrum A_0 of unexcited QDs, shown in black in Figure 1a, to ΔA yields at every delay time the actual absorbance A of the photoexcited

dispersion. The concomitant map of this so-called non-linear absorbance A is shown in Figure 1b. Here, positive regions reflect a situation where probe light is still absorbed by the photo-excited sample. A negative A , on the other hand, implies that probe light is amplified, i.e., the sample is in a population-inverted state. Clearly, such a state is present, for the given pump intensity at around 620 nm, for the first 100 ps after the pump pulse.

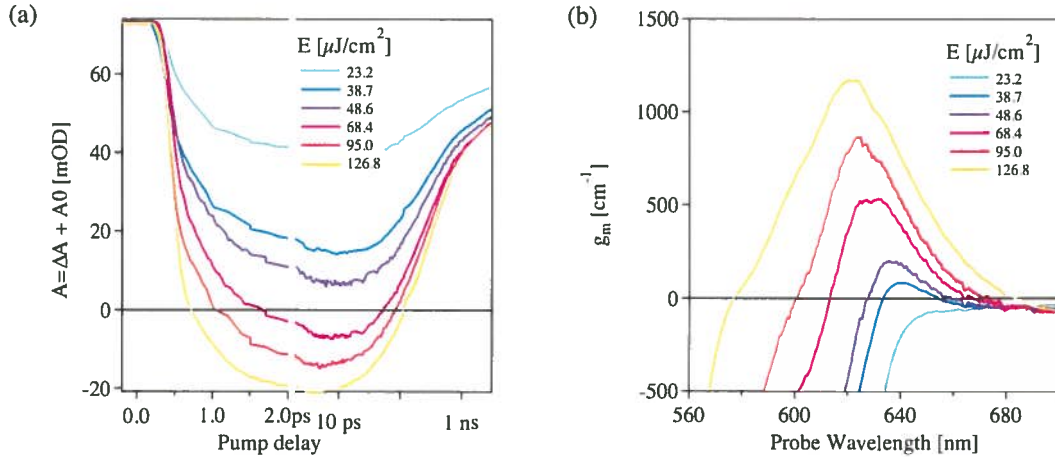


Figure 2 (a) Time slices for different pump pulse energies at fixed probe wavelength 620 nm. (b) Corresponding material gain spectra with different pump pulse energies at a fixed delay of 4 ps.

Figure 2a represents non-linear absorbance traces obtained on the same sample at a fixed probe wavelength of 620 nm at different pump pulse energies. It can be seen that a minimum pulse energy is needed to reach population inversion. However, once pump energies are sufficiently high, population inversion can be reached within 1 ps after pumping and can last up to 80 ps. Fitting the relaxation of the transient absorbance A to a single exponential, yields a decay rate of 4 ns^{-1} .

Using eq 3, the non-linear absorbance as plotted in Figs 1b-2a can be rescaled into an intrinsic gain coefficient. This number yields the gain a QD material with a volume fraction $f = 1$ would have under the same conditions of optical pumping and multiplying it with the actual volume fraction yields the gain of any QD sample. Hence, our rephrasing of the intrinsic gain coefficient as the material gain g_m . Figure 2a represents g_m spectra of CdSe/CdS QDs studied here at a fixed delay of 4 ps. Especially at high pulse energy, a broad gain band develops with g_m reaching values of 1000 cm^{-1} and more.

Integrated devices

We exemplify the qualities of g_m as a design parameter using the case of QD-doped SiN_x waveguides, where we compare g_m with the modal gain obtained from a classical variable stripe length experiment. [3] The aforementioned QDs were integrated in a SiN_x/QD/SiN_x stack, which are etched to form 5 μm wide waveguides of varying lengths. Pumping these with the same 110 fs pulses at a pump intensity corresponding to about twice the threshold power for ASE (see Figure 3c), yields an exponentially increasing light output for waveguides 200-400 μm long (see Figure 3a). Fitting the distance-dependent light intensity to $I = A_0(e^{g_l l} - 1)/g$ [6] yields a modal gain of 100-120 cm^{-1} . This modal gain can be seen as the product of the material gain, the QD

volume fraction in the film and the overlap between the optical mode and the QD layer. Estimates of both quantities obtained through refractive index measurement and optical simulations amount to 50% and 23%, respectively. In combination with the peak material gain of 750 cm^{-1} under the given pump intensity (see fig 3d), this indeed yields a modal gain of $\approx 90 \text{ cm}^{-1}$, a number in close agreement with the experimental value.

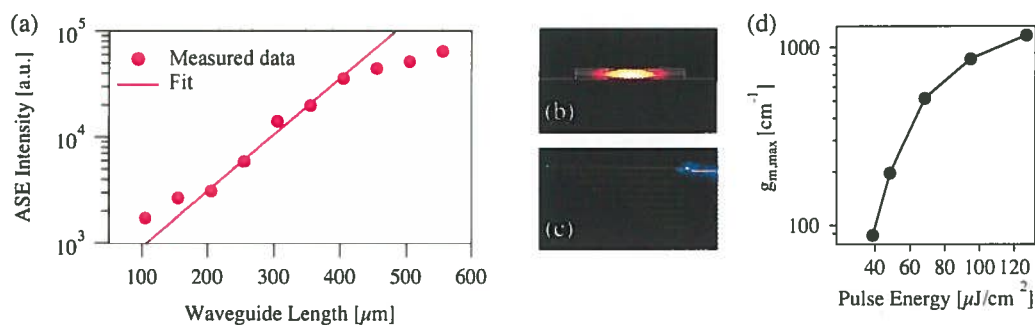


Figure 3 (a) ASE intensity versus the length of the waveguide at an excitation level of $\approx 2 P_{\text{ASE}}$. (b) Cross-section of waveguide and its mode profile. (c) Microscope picture of the emitting waveguide and the multimode fiber. (d) The peak material gain (from fig 2b) as a function of pulse energy. For a pulse energy of $\approx 80 \mu\text{J}/\text{cm}^2$, which is about $\approx 2 P_{\text{ASE}}$, we find a max g_m of $\approx 750 \text{ cm}^{-1}$

Conclusion

We have introduced the interpretation of the intrinsic gain coefficient of dispersed colloidal QDs as their material gain. As such, the material gain of colloidal QDs can be readily obtained from a normalization of their non-linear absorbance as measured using transient absorption spectroscopy. Studying gain in SiNx/QD/SiNx strip waveguides, we show that the experimental modal gain can be interpreted as the product of the material gain of the QDs, their volume fraction and the overlap between the optical mode and the QD layer. This indicates that this material gain is a most useful characteristic of colloidal QDs, that makes possible a comparison between different QDs as gain medium and the design and simulation of QD-based amplifiers and lasers.

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