Transient absorption spectroscopy of InP/ZnSe QDs

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Quantum dots are a promising material under intense study for the past 17 years - since it was discovered that they can provide optical gain. A core/shell colloidal quantum dot (InP/ZnSe) was studied with transient absorption spectroscopy. In the end, no gain was shown but there is hope for future studies ending with a different result.

I. INTRODUCTION

Quantum dots (QDs) are a special type of semiconductor material with sizes ~10 nm. They were first discovered in the 1980s with pioneering work done at, now defunct, Bell labs in 1982 [1]. By now, they have found a broad range of applications, from commercially available TVs [2] to microspectrometers [3].

A. Tunable band gap

While bulk semiconductors have a fixed band gap at a certain temperature, the band gap of a particular quantum dot corresponds to its size due to the effects of quantum confinement; the charge carriers adjust their energy spectrum according to particle size [4] (Fig.1).

A simple model that can be used for describing the size-tunable energy spectrum is the model of a particle in a spherical "box"; for a spherical quantum dot the energy is given by:

$$E_n \approx \frac{\hbar^2 \pi^2 n^2}{2 m_{eh} R^2}, \tag{1}$$

where R is the radius of the quantum dot, n is the nth root of the spherical Bessel equation of the first kind and $\frac{1}{m_{eh}} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$, m_e^* and m_h^* being effective electron and hole masses. One can see now that by synthesizing quantum dots of different sizes the band gap changes accordingly (R^{-2}). By "tuning" the size/band gap, one can obtain different optical properties.

B. Auger recombination

When an energetic photon gets absorbed by an electron in the valence band, the electron "jumps" to the conduction band, a hole left in its wake, creating an electron-hole pair. The electron and the hole "cool" down to the band edge states through radiative processes, such as (stimulated) emission of photons, and/or nonradiative ones, such as carrier trapping and Auger recombination, creating a bound electron-hole pair called an exciton. Auger recombination is a nonradiative process where an exciton collides with a charge carrier and transfers its energy and momentum to the carrier, "kicking" it into higher energy states, from which the carrier cools down through interactions with lattice vibrations (phonons), losing energy through heat rather than photon emission.

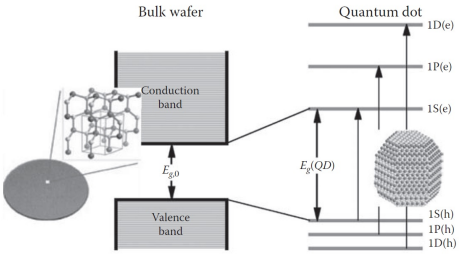

Figure 1. The energy spectrum of a bulk semiconductor (left) and of a QD (right) [5].

In quantum dots, due to small size, excitons have a greater interaction energy than in bulk materials, so that multiexcitonic states can be created, contributing to Auger recombination. The higher the number of excitons in a multiexcitonic state, the shorter the lifetime of the process, meaning single excitons have lifetimes on the order of nanoseconds or more and biexcitons lifetimes are on the order of a hundred picoseconds or less (i. e. [6]). The lifetimes scale linearly with volume [7].

C. Optical gain

When light enters a material with a certain intensity at a certain wavelength λ and then comes out with a higher

intensity at the same wavelength, one speaks of optical gain. This is also called light amplification. In quantum dots, the creation of (multi)excitons changes the absorption spectrum by changing the occupancy of the energy levels and by changing the energy levels themselves [8] (Fig. 2).

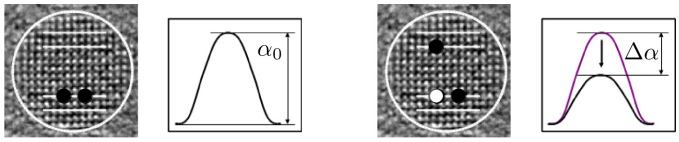

Figure 2. Absorption spectra before and after excitation [8].

The ratio between the change of absorption ($\Delta\alpha$) and the "ground-state" absorption (α_0)

$$\frac{\Delta\alpha}{\alpha_0} = -\frac{g_v + g_c}{g_v g_c} N_{ex}, \tag{2}$$

defines whether we have any gain ($\frac{\Delta\alpha}{\alpha_0} < -1$) or not. This can be measured with transient absorption spectroscopy (TAS), a method that is used to observe ultrafast processes, comprising of a "pump" beam, which excites the sample, and a "probe" beam, which is then used to observe the change in absorption. From eq. (2), once can see that the greater number of excitons created per quantum dot, the greater the gain. Eventually, this can lead to laser construction if nonradiative losses can be diminished.

II. EXPERIMENTAL SETUP

A. Sample preparation

The quantum dots that were used in these experiments were synthesized in the *Physics and Chemistry of Nanocrystals* group, Ghent University, by Dorian DuPont. They are core/shell structures, meaning that one compound is used as the nucleus around which a "blanket" of another compound is grown (Fig. 3). In this case, the core is made of InP with a radius of 3.2 nm, while the shell is made ZnSe with a radius of 14 nm and the quantum dots are dispersed in toluene so that a colloidal solution is obtained. The sizes were determined with TEM imaging.

B. α_0 spectrum

The colloidal solution was then diluted so that the α_0 spectrum can be measured and then loaded into a 2 mm thick transparent cuvette (Fig. 4). The cuvette was then placed in a PerkinElmer Lambda 950 UV/VIS spectrometer and a spectrum was obtained in the proprietary PerkinElmer software (Fig. 5)

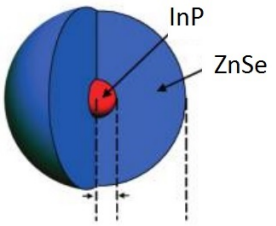

Figure 3. A depiction of a core/shell QD. Modified from [10].

Figure 4. The sample and the chemicals needed for preparing it for spectrometry.

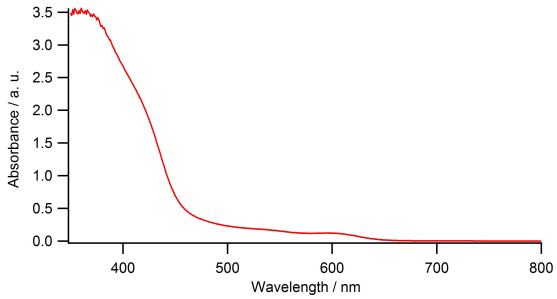

Figure 5. A usual spectrum obtained by the PerkinElmer Lambda 950.

C. Transient absorption

The cuvette was then placed in the transient absorption spectroscopy setup. The seed laser used was Spectra-Physics' Mai Tai SP ultrafast laser combined with the Spectra-Physics Empower diode-pumped pulsed green laser acting as the pump for the amplifier. Both lasers were fed to the Spectra-Physics Spitfire Ace Ti:sapphire amplifier which then produces 800 nm 180 fs pulses at a frequency of 1 kHz. This beam is used as the pump for TAS.

A greater part of the pump beam is reflected with a beam splitter to a Spectra Physics' Topas optical parametric amplifier. This device is able to change the wavelength of the beam to 520 nm (which is around 2.38eV - near the InP core band gap). The pump beam was then lead through a neutral density filter (ND) with which the power level of the pump beam could be attenuated. For measuring the power level, a Thorlabs PM100A Compact

powermeter was used while all light sources were shut off. After the ND, the pump beam went through a 500kHz chopper and then finally hit the sample.

A smaller part of the original Spitfire Ace beam continues to the delay stage. This will be the probe. The delay stage is computer-controlled, allowing for precise delays (~100 fs) between the pump and the probe arrivals to the sample so that $\Delta\alpha$ can be measured at different time delays. The probe then continued to a CaF_2 crystal which changes the probe beam's frequency in such a way that white light hits the sample. Most of the probe's original wavelength was not converted to white light so a 800 nm notch-filter was used to get rid of more than 90% of the 800 nm wavelength (Fig. 6).

The cuvette was loaded onto the sample holder and positioned in such a way that the probe beam is centered in the pump beam profile on the cuvette. A small magnetic bar was loaded into the cuvette which was then rotated by means of a spinning magnetic axle placed behind the lower part of the cuvette. The purpose of the spinning magnetic bar is to mix the sample solution so that the sample does not get burnt (or at least gets burnt equally in all parts of the solution).

The light emitted or passing through the sample is then reflected to an iris which serves the purpose of blocking as much of the pump light as possible. The light is then fed into an optical fiber connected to a Newport Oriel MS127i spectrograph. The data is collected by a proprietary software package.

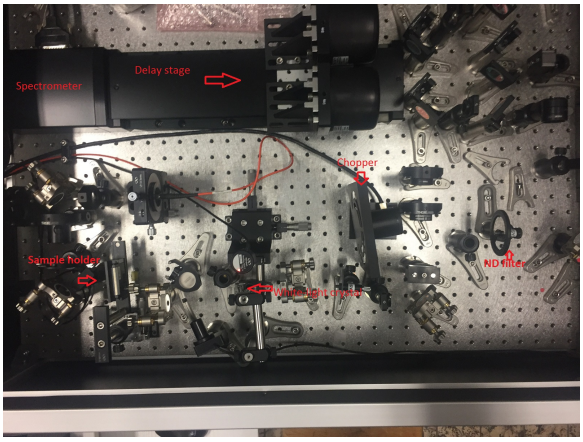

Figure 6. The delay stage, chopper, white-light crystal and sample holder

The spectrum was measured after different time delays in steps of varying size. Table 1 shows each delay and the "time-steps" after which a measurement was taken:

Delay / ps	Step / ps
3	0.04
6	0.1
10	0.5
100	5
1000	100
2000	250
2000	250

Table 1: Delay times and steps during the measurements.

A typical spectrum obtained through such measurements can be seen in Fig. 7, with time shown on the Y axis, wavelength shown on the X axis and $\Delta\alpha$ indicated by the color.

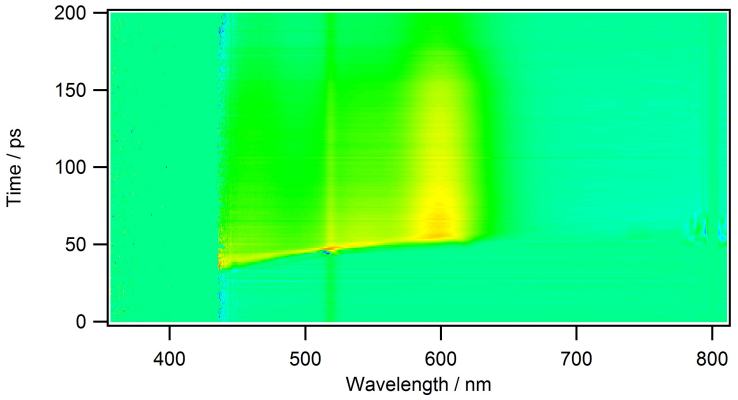

Figure 7. A typical spectrum obtained by this setup.

III. RESULTS

From the recorded spectra, one can extract the dependency of $\Delta\alpha$ on the kinetic or spectral domain with a script written by Matt Sfeir of Brookhaven National Laboratory for the Igor software package.

In Fig. 8, one can see the $\Delta\alpha$ spectra corresponding to different pump fluences in the negative absorbance half-plane and the α_0 spectrum, coloured red, in the positive absorbance half-plane, along with the sum of α_0 and $\Delta\alpha$ at the highest pump fluence (to check whether there is any gain). The dip at 520 nm in all of the $\Delta\alpha$ curves corresponds to the pump (clearly, the iris does not remove all of the pump beam).

One can also plot $\Delta\alpha$ versus the pump power at different wavelengths (Fig. 9). Absorbance seems to have reached a saturation point in most curves except for those in the 590 - 610 nm spectral region. Again, this was taken at 2.5 ps.

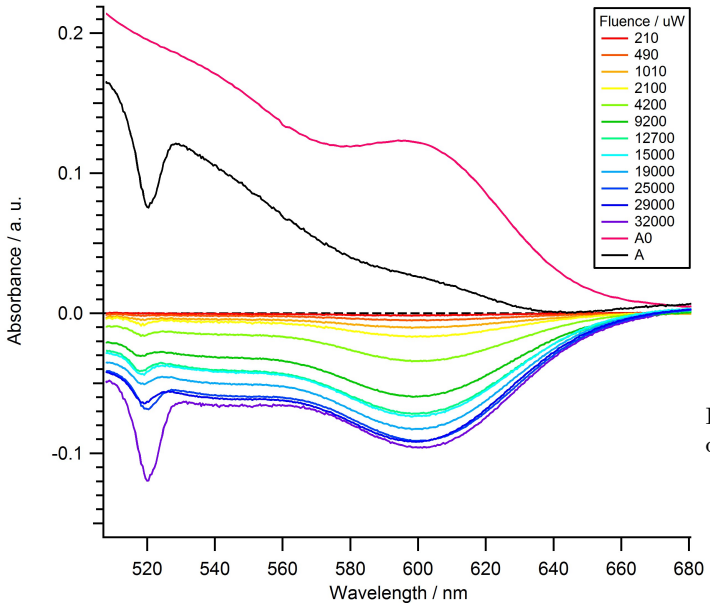

Figure 8. $\Delta\alpha$ plotted for different pump beam powers (negative), after cca. 2.5 ps, and α_0 plotted in red. The curve marked with 'A' corresponds to the sum of α_0 and the highest pump fluence $\Delta\alpha$.

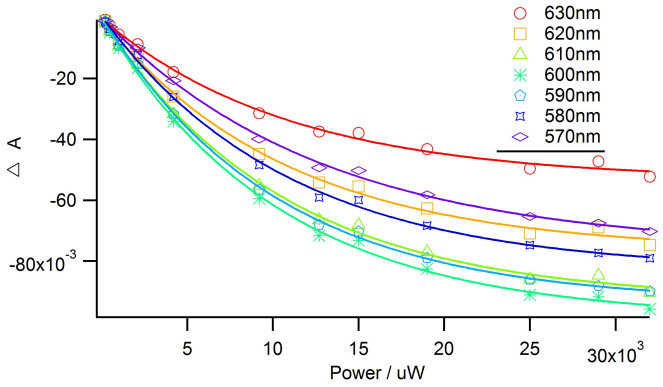

Figure 9. $\Delta\alpha$ as a function of pump beam power shown for different wavelengths, after cca. 2.5 ps. Saturation is near.

IV. CONCLUSION

InP/ZnSe core/shell quantum dots have been analyzed with transient absorption spectroscopy. The sample was pumped with a 520 nm laser, near the band gap of the core. The primary concern was whether there would be any gain so as to use them for lasing applications. Even at the highest pump fluence (32 mW), there was no gain. Indeed, from Figs. 8 and 9 one can see that the absorbance at 600 nm reaches saturation; in other words, increasing pump power will not drastically change the result.

In a lot of absorbance spectra, there is a lingering "plateau" in the higher wavelengths (680+ nm) region. This could be due to Rayleigh scattering intensified by particle aglomeration - particles sticking together and thus effectively increasing average particle size. Since the samples used were at least one year old, different results might be obtained by using "fresh" particles, thus increasing the neccesary difference between α_0 and $\Delta\alpha$.

The other way to change absorbance of the particles is to introduce an alloyed layer in between the core and the shell, with a small percentage of cadmium as in [9]. This significantly increases the multiexciton lifetime (it suppresses Auger recombination), thus intensifying $\Delta\alpha$.

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