Two-Photon Absorption and Multi-Exciton Generation in Lead Salt Quantum Dots

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ABSTRACT

Understanding the nonlinear optical processes in semiconductor nanostructures leads to possible applications in areas including laser amplifiers, optical switches, and solar cells. Here we present a study of the frequency degenerate two-photon absorption (2PA) spectrum of a series of PbS and PbSe quantum dots (QDs). The influence of the quantum confinement is analyzed using a four-band model which considers the mixing of valence and conduction bands. In contrast to our observations of CdSe QDs, the present results point to an increase of the 2PA cross-section (normalized by the QD volume) as the quantum dot size is made smaller. This is explained by the symmetry between the valence and conduction bands which allows the density of states to remain high even for small QDs. A study of the ultrafast carrier dynamics of the PbS quantum dots is also presented. Through nondegenerate femtosecond pump-probe experiments we show evidence of multi-exciton generation with quantum yield (number of excitons generated per absorbed photon) up to 170% for excitation with $\hbar\omega > 3\ E_g$ (where E_g is the bandgap energy).

Keywords: Semiconductor quantum dots, two-photon absorption, nonlinear optics, nonlinear spectroscopy, ultrafast spectroscopy, multi-exciton generation.

1. INTRODUCTION

The nonlinear optical properties of semiconductor quantum dots (QDs) have been the subject of interest for many research groups for the last decade. The possibility of modifying their optical properties by controlling their size distribution makes them promising for applications in several new technologies such as optical communications[1], laser amplifiers[2,3], 3D imaging[4,5] and solar cells.[6,7]

The quantum confinement strongly affects the electronic structure of semiconductors going from a continuum distribution of states in the bulk, to a system with discrete energy levels and blue shifted bandgap in QDs. Lead salt semiconductors are of special interest due to their narrow bandgap and small effective masses, allowing for a strong

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confinement regime for relatively large QDs. Also, due to the small effective masses, the QDs bandgap, and consequently the fluorescence band, can be tuned from the NIR (~ 2000 nm) down to ~ 600 nm by changing the QDs sizes[8].

There is relatively little previous work on the nonlinear absorptive properties of lead salt QDs. We previously showed that in the case of CdSe and CdTe QDs the quantum confinement leads to a decrease of the overall 2PA even if the QD volume is taken into account.[9] That reduction is explained by the quantum confinement induced decrease of the density of states, and by the asymmetric band structure of CdSe and CdTe. The peculiar band structure of PbS is expected to result in a different trend for the 2PA.

In this paper we discuss the size dependence of the 2PA in PbS QDs and explain, based on a four-band envelop function model,[10] the similarities and differences as compared to CdSe QDs. We will also discuss the multi-exciton generation in these nanomaterials which could make them promising for solar cell applications.

2. EXPERIMENTAL

2.1 Sample preparation

Our PbS nanocrystals[8] were synthesized using a solution based organometallic route previously described in Ref. [11].

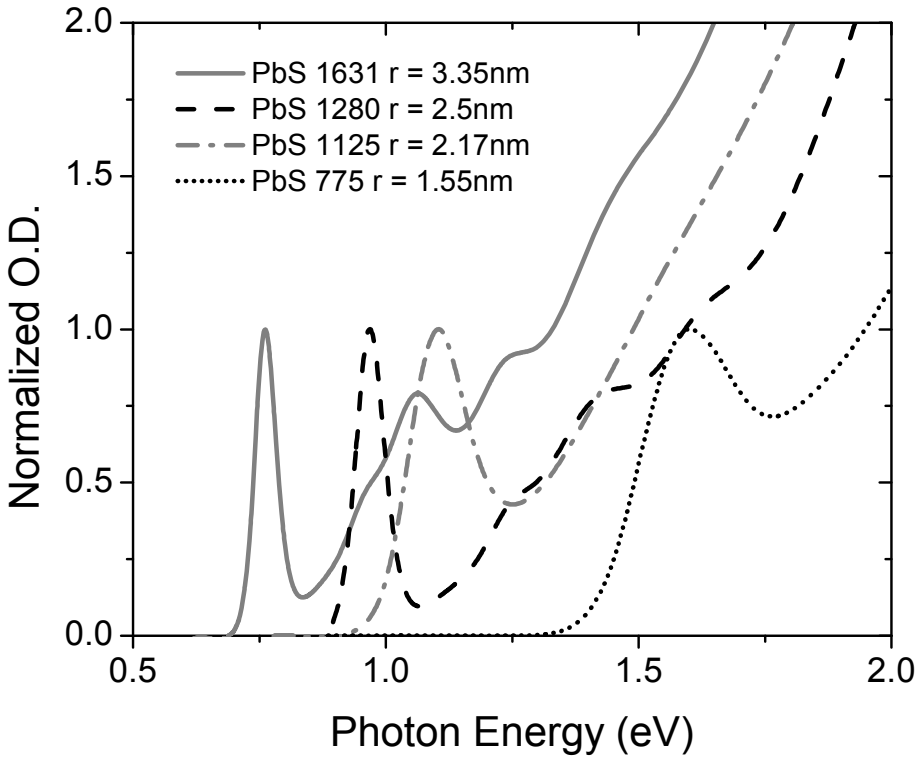


Figure 1 Linear absorption of the series of PbS QDs investigated here.

PbO is mixed with oleic acid and octadecene and heated under heavy stirring to create a lead oleate precursor. The sulfur source (Hexamethyldisilathiane mixed with octadecene in a nitrogen glove box) is injected into the flask with the lead precursor under argon in a Shlenk line, after which the solution is removed from the heat. Reaction is then quenched with acetone. The PbS oleate capped nanocrystals are isolated from any side products by precipitating with acetone and redispersing in toluene repeatedly. The final nanocrystals are redispersed in toluene for measurements. The size of the nanocrystals is controlled via variation of precursor concentration, injection temperature, and growth time. Figure 1 shows the linear absorption spectra of the series of PbS QDs studied here.

2.2 Experimental Setups

The nonlinear optical spectroscopy is performed using a femtosecond laser system which consists of a Ti:sapphire regenerative amplifier (Clark – MXR 2010) operating at 1 kHz and delivering 2 mJ per pulse at 780 nm and 140 fs. The Ti:sapphire amplifier pumps two OPG/OPA's (Light Conversion, TOPAS-800) which can be independently tuned from 300 nm to 2.6 μm with pulsewidth from 120-150 fs. The pulsewidth is measured either by interferometric autocorrelation or using a GRENOUILLE (Newport, UPM-50-105).

The frequency degenerate 2PA spectroscopy is performed by two experimental methods, open aperture Z-Scan[12] and two-photon excited fluorescence (2PF)[13]. The 2PF is a fast technique to obtain the 2PA spectrum; however, in order to obtain the 2PA cross-section values, it is necessary to use reference samples (Rhodamine 6G, for example[13]) with known 2PA cross section and fluorescence quantum yield. On the other hand, the open aperture Z-scan allows for an absolutely calibrated measurement of the 2PA coefficient of the sample, and it is necessary only to know the QD's concentration in the solution to be able to extract the 2PA cross section. Due to limitations of our 2PF system, we are able to characterize only samples with fluorescence peaks shorter than 800 nm. So, for most of the samples investigated here, the 2PA spectroscopy was done with Z-scans. In order to check the Z-scan setup and determine the focal spot size, we measure the nonlinear refraction of CS_2 with closed aperture Z-scan[12], and the 2PA of bulk semiconductors such as CdTe and GaSb.

The ultrafast dynamics is measured using a nondegenerate pump-probe setup with the probe beam a femtosecond white-light continuum. For this experiment, the output of one of the TOPAS is set to 1300 nm and is used to pump a calcium fluoride plate, generating the subpicosecond white-light continuum used as the probe. The pump wavelength is selected from the second OPA. To ensure that the probe beam goes through the sample under the same pump condition, the probe spot size is made ~ 10 x smaller than that of the pump. The multi-exciton generation study is done by analyzing the transient absorption of the first absorption peak (1S -1S transition) as a function of the pump wavelength[14].

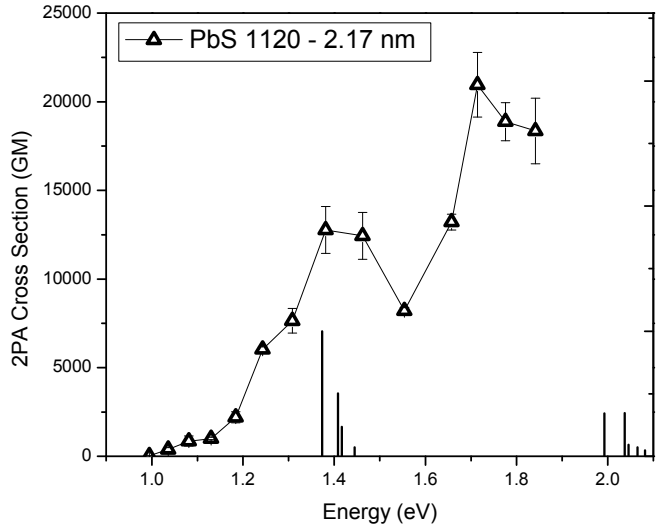
In order to analyze the experimental results it is extremely important to know the QD's concentration and the one-photon absorption cross section. We estimate these two values for all the samples using the empirical method proposed by Cadermatiri et.al.[15] and considering the integrated cross section under the first absorption peak.

3. EXPERIMENTAL RESULTS

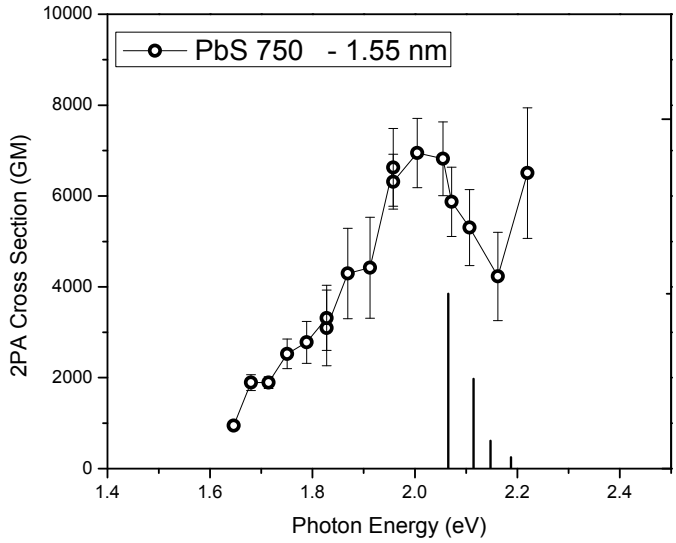
3.1 Two-Photon Absorption

Figure 2 shows the two-photon absorption spectrum of two different sizes of PbS QDs, 2.17 nm and 1.55 nm (sizes estimated from Kang and Wise[10], based on the position of the first 1PA transition), as measured via open aperture Z-scan. The experimental results are plotted together with two-photon allowed transitions as predicted from a four-band envelope function[10]. The results show that the 2PA cross section (expressed in GM = 10^{-50} cm^4s^{-1}) at the first allowed 2PA peak, increases from 6900 GM to 12700 GM as the QD's size goes from 1.55 nm to 2.17 nm. This result is similar

to that previously observed for CdSe QDs[9]. It is clear from Fig. 2 that the model used here does not well predict the position of the first 2PA allowed transition for the smaller QDs. This model, which considers the bulk band structure and adds confinement as an infinite potential barrier, is expected to fail for such small QD's, where tight binding approaches would be more appropriated.



a)

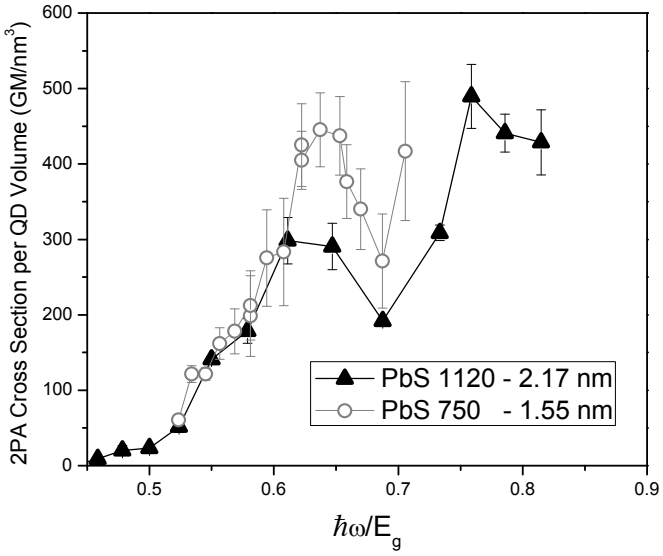


b)

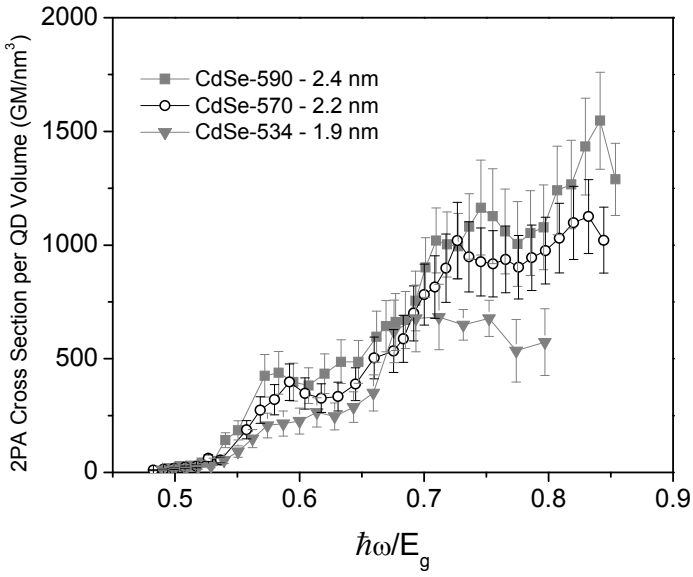
Figure 2 Two-photon absorption spectra for two sizes of PbS QDs. The solid lines are the 2PA transitions predicted by the four band envelope function model[10].

A better way to compare the magnitude of the 2PA cross section for different sizes is taking into account the volume of the QD. Figure 3 shows the 2PA normalized by the QD volume for the PbS QDs (a) and, as previously reported,[9] for

CdSe QDs (b). One can see the different trend for the two different QD systems. While for the CdSe QDs the quantum confinement reduces the 2PA cross section per unit volume, the quantum confinement enhances the 2PA for PbS nanoparticles. For both systems the quantum confinement enhances the 2PA oscillator strength for a single transition; however, the reduction of the overall 2PA observed in CdSe QDs is explained by the decrease of the density of states. The peculiar band structure of PbS, which has symmetric valence and conduction bands, confines the possible 2PA transitions to a small spectral range so that the reduction of the density of states is smaller than in CdSe QDs.



a)



b)

Figure 3 2PA per unit volume of different QDs. For the PbS QDs (a) the confinement leads to enhancement of the 2PA while for the CdSe (b) the same causes the reduction of the 2PA

The quantum confinement induced 2PA enhancement in PbS QDs may be interesting for applications considering that it is possible to reach 2PA cross sections > 10,000 GM for wavelengths around the telecommunication window (see Fig. 2).

As an example of potential applications in optical communications , multi-photon absorption can be used to reduce amplitude noise on optical signals.[16] For a purely N-photon absorbing medium, the irradiance propagating through the material is given by,

$$\frac{dI}{dz} = -\alpha_N I^N,$$

where N is a positive integer and α_N is the N-photon absorption coefficient. This has the plane wave solution,

$$\left[\frac{I_{in}}{I_{out}}\right]^{N-1} = 1 + (N-1)\alpha_N L I_{in}^{N-1}, \quad \text{for N} > 1.$$

Where I_{in} and I_{out} are the input and output irradiances, respectively ,and L is the material thickness. We may rewrite this as,

$$T^{1-N} = 1 + Q_N,$$

where T is the transmittance and $Q_N = (N-1)\alpha_N L I_{in}^N$. Now if I_{in} and I_{out} are considered as input and output signals, and a small amplitude notice of δI_{in} ia added to the input, then the output noise is given by,

$$\delta I_{out} = \delta I_{in} \frac{dI_{out}}{dI_{in}}.$$

Hence if the input and output signal-to-noise ratios are $I_{in}/\delta I_{in}$ and $I_{out}/\delta I_{out}$, the improvement, R, in signal-to-noise ratio affected by the multiphoton absorber is given by,

$$R = \frac{I_{out}/\delta I_{out}}{I_{in}/\delta I_{in}} = T\frac{dI_{in}}{dI_{out}} = T^{1-N}.$$

Therefore assuming a transmittance of 0.5, the increase in signal to noise ratio for a 2-photn absorber is 2, whine for a 3-photon absorber, the increase would be 4, and so on.

Here we demonstrate a two-photon absorption based regulator for optical power fluctuations using the PbS QDs as the 2PA medium. Figure 4 shows the results measured with a sample of PbS QDs with 2PA peak at 1550 nm using 140 fs.

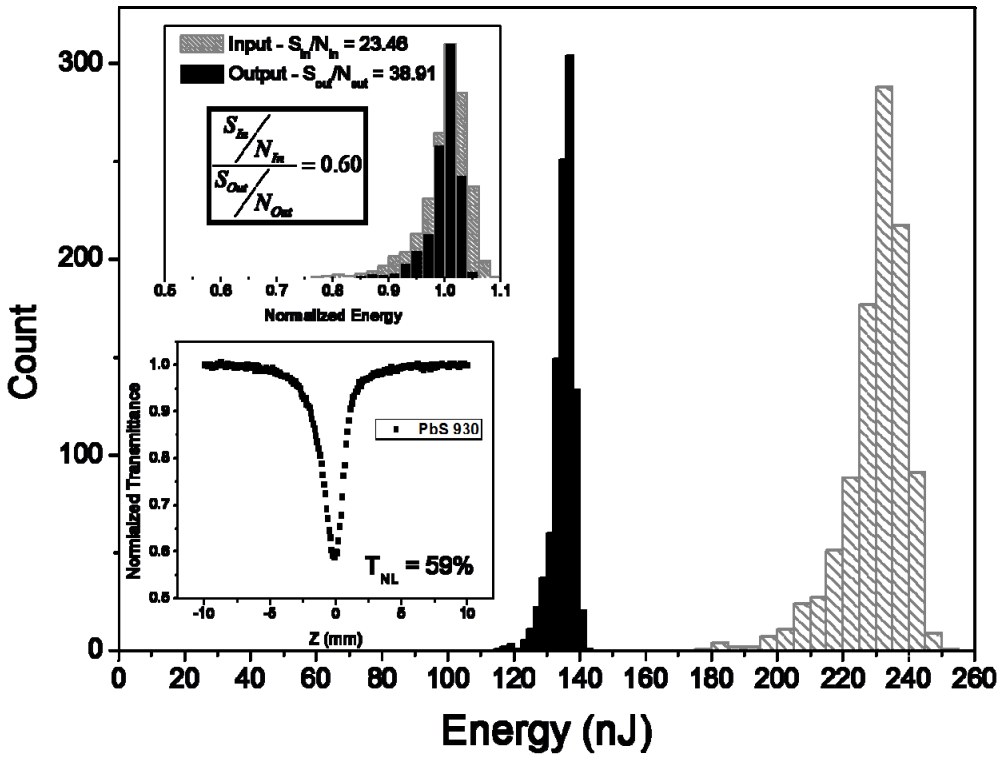


Figure 4 Optical power noise reduction using PbS QDs. The input energy is shown on the shaded area and the full area shows the output. The signal-to-noise improvement is R = 1.66 times when the transmittance is 59%

3.2 Multi-Exciton Generation.

Multi-exciton generation was investigated with a transient absorption experiment fixing the probe wavelength at the first absorption peak. Figure 5 shows the carrier multiplication efficiency as a function of the energy of the pumping photon. The average number of photons absorbed per QD is kept below ~ 0.25 so, assuming a Poisson distribution, less than 10% of the QDs would have absorbed more than 1 photon.

In Figure 5 we compare the experimental results for 2.5 nm PbS QDs with data and theory for bulk PbS.[17] The results show that the multi-exciton generation threshold is much lower for the QD than for bulk. Also, an efficiency of ~170 % is observed for QDs excited with photon energy of 3.7 E_g.

Recent papers have been discussing the influence of QD photo-ionization on the transient absorption experiments possibly leading to erroneous results. McGuire et. al.[14] have shown that by stirring the QD sample, avoiding cumulative processes, the multi-exciton generation efficiency decreases drastically in PbSe QDs. In order to address this problem, we run our experiment at different laser repetition rates (lower repetition rates would decrease any cumulative effects). No difference in the carrier multiplication efficiency is observed.

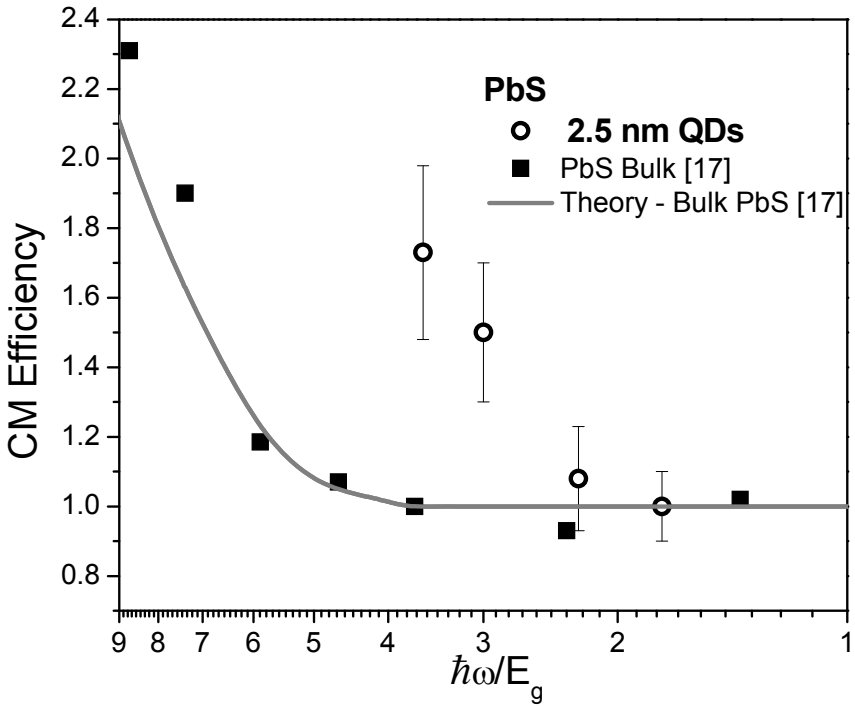


Figure 5 Comparison of the multi-exciton generation in a 2.5 nm QD and bulk PbS[17]

The results shown in Figure 5 are promising for potential application in high efficient solar cells.

4. CONCLUSIONS

We have studied the two-photon absorption and the multi-carrier generation in PbS QDs. The experimental results show that the 2PA cross section per QD volume increases as the QD is made smaller, which is an opposite trend of that previously observed for CdSe QDs.[9] The multi-exciton generation results show higher efficiency if compared to bulk PbS and a much lower photon energy threshold. The characteristics presented here make PbS QDs promising for applications in optical devices, such as optical power stabilizers and solar cells.

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