RESONANT Z-SCAN MEASUREMENT OF NON-LINEAR PROPERTIES OF COLLOIDAL LEAD SULFIDE QUANTUM DOTS

Ivan SKURLOV, Evgenia PONOMAREVA, Sergey PUTILIN, Aleksei POPOV, Aliaksei DUBAVIK, Anton TSYPKIN, Aleksandr LITVIN

ITMO University, Saint-Petersburg, Russian Federation, ivan.skurlov.23@gmail.com

Abstract

Studying the nonlinearities in the resonant mode one may face thermo-optical effects due to sample overheating, occurring upon exposure to high-frequency repetition rate probing pulse. If present, thermo-optical contribution to the refractive index are extremely hard to separate from the electronic contribution. In order to obtain purely electronic non-linear change in refractive index and to avoid thermal effects we modify classic Z-scan method to operate with low probing laser pulse repetition rate of 1 Hz. In our work, we present results of a Z-scan measured non-linear refraction coefficient of colloidal PbS QDs of different sizes free from thermal contribution. Our measured values of nonlinear refractive index is in order of 10^{-16} cm^2/W and independent on the QD concentration in the solution.

Keywords: Nanocrystals, quantum dots, lead sulfide, z-scan, non-linear refraction

1. INTRODUCTION

Due to low energy bandgap, high absorption coefficient in near infrared region, size-tunable properties and suitability for wet processing, colloidal lead sulfide (PbS) quantum dots (QD) are widely studied material for applications in the near-infrared region [1]. This, combined with potentially high resonant non-linear optical response [2] and tunable non-linear absorption and reflection, make PbS QDs possible alternative material for use in the non-linear optics.

Common technique to study optical nonlinearities was introduced in 1990 by Sheik-Bahae et. al. [3] and ever since providing the simple and sensitive way to measure absolute values of nonlinear refraction and absorption coefficient of thin samples.

Previous Z-scan studies on the third-order nonlinear susceptibility of PbS quantum dots report either saturable [4] or mostly multiphoton absorption [5-7]. The common issue lies in the varying values of the nonlinear refractive index from different authors, e.g. $-(10\div60)\ 10^{-12}$ cm^2/W in C_2Cl_4 [6], or $-8.2\cdot10^{-16}$ cm^2/W in toluene, $-2.3\cdot10^{-15}$ cm^2/W in hexane, $-1.2\cdot10^{-15}$ cm^2/W in CCl_4 [8]. Mentioned problems arising from differences in the sample preparation method and, more important, in the origins of nonlinearity measured. We can split nonlinear contributions to one, reflecting purely nonlinear electron response (with response time of 10^{-15} - 10^{-10} s) to the applied electromagnetic field, and thermal (with response time of 10^{-8} s or more), arising when absorbed excitation energy is converted to heat due to thermo-optical coefficient dn/dT is higher than zero. Which in turn leads to thermal lensing effect, changing the resulting z-scan trace, thus acting as a parasite source of nonlinearity if one have to determine the electronic nonlinearity.

There is a way to reduce, if not entirely remove, thermal counterpart from the result. Electronic and thermal nonlinearity response time are different in magnitude by a few orders, so utilizing ultra-fast optical pulses can reduce the thermal counterpart. Although, using high repetition rate pulsed lasers can lead to formation of steady-state temperature profile hence accumulating thermal lens effect [9] so it is necessary to increase the time spacing between pulses to a minimum of $t_c = w^2/4D$, where D is thermal diffusion coefficient and w - beam diameter). Commonly used polar solvents have D in order of 10^{-3} cm^2/s thus the maximum repetition rate is in order of tens of kHz for typical z-scan setup. In our work, we demonstrate that the absence of the

thermal counterpart to the nonlinear refractive index of PbS QD changes the behavior of the nonlinear refraction coefficient.

2. METHODS

Lead sulfide quantum dots (sizes ranging from 3.4 nm to 5.2 nm) were synthesized according to [10]. To remove excess of organic ligands QD were precipitated by acetone and then redispersed in the non-polar solvent. For power, concentration and size dependent measurements we chose hexane as a solvent for its lowest non-linear response (n_2 in order of 10^{-17} cm^2/W) among other common non-polar solvents (such as toluene, chloroform and tetrachloromethane). Absorption coefficient was calculated from the absorption spectra measured with Shimadzu UV3600 UV-VIS-NIR spectrophotometer. To measure the nonlinear refractive index we used standard z-scan setup with femtosecond Ti:sapphire laser (Avesta) with center wavelength 800 nm, pulse width >35 fs, acting as an excitation light source. In order to get rid of the thermal counterpart of the refractive index we lowered the pulse repetition rate to 1 Hz. Z-scan layout is schematically shown in **Figure 1.**

Typical open aperture Z-scan trace of pure hexane and colloidal QD solution are shown in the **Figure 2**. Presuming the additivity of nonlinear indexes of the QDs and the solvent we can subtract z-scan curve of the solvent to obtain the z-scan trace, attributed only to QDs [11]. n_2 values were calculated using formula (1) from [3]

$$n_2 = \frac{\Delta T}{0.406} \cdot \frac{\lambda}{2\pi I_{in} L_\alpha} \cdot \frac{\sqrt{2}}{(1-S)^{0.25}}, \quad (1)$$

here ΔT is the difference between the normalized peak and valley transmittance; I_{in} - light intensity within the sample; $L_\alpha = \left(1 - e^{-\alpha L}\right) / \alpha$ - effective length, where α is the linear absorption coefficient and *L* - sample thickness; λ - wavelength of light, S - aperture.

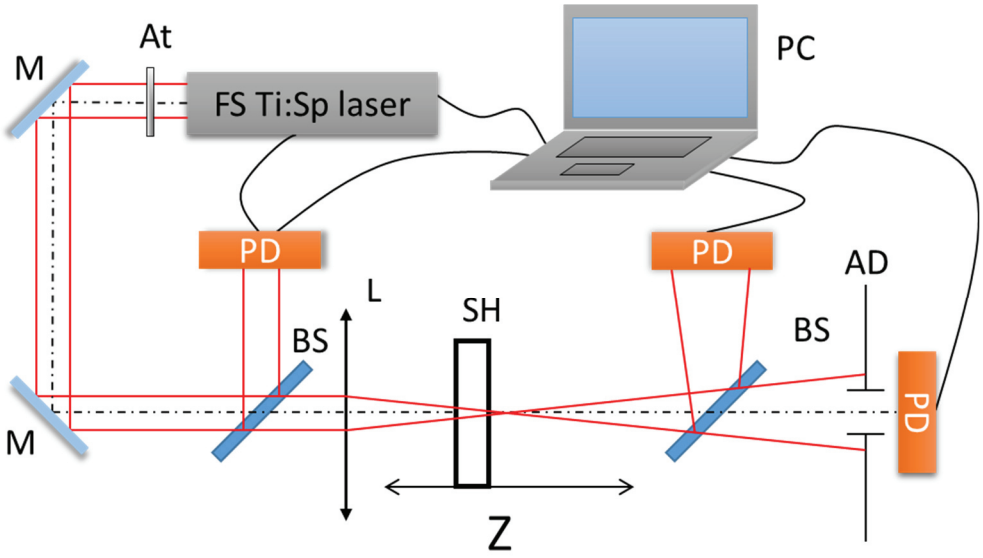

Figure 1 Scheme of the z-scan setup: **At** - laser output power attenuator, **M** - mirrors, **PD** - photodetectors; **BS** - beam splitters; **L** - condensing lens (f = 20 cm), **SH** - sample holder on a positioning table, **AD** - aperture diaphragm

3. RESULTS AND DISCUSSION

First, we have performed Z-scan measurement using the described setup with a pulse repetition rate of 70 MHz, MHz repetition rates are commonly used in works, studying PbS QD with z-scan technique [4-7]. Z-scan measurements were performed for the 4.5 nm QD colloidal solutions with different concentrations ranging from $3 \cdot 10^{-6}$ M to $14 \cdot 10^{-6}$ M.·The calculated n_2 values are $-(25 \div 90)\ 10^{-12}$ cm²/W and close to the values reported in the literature [5-7]. Negative sign of the nonlinear refraction index indicates the self-defocusing process. From **Figure 2(a)** it is clearly seen that non-linear refractive index changes linearly with the concentration.

Considering isolated QDs in colloidal solution, change the concentration leads only to change in the absorption. However, absorption change is taken into account in the calculations of n_2 via absorption-dependent effective length L_{eff} in equation (1). Thus, purely electronic nonlinear refractive index should remain constant. High absorption in the resonant (i.e. above-bandgap) excitation mode leads to the diffusion heating of the colloidal sample and consequent formation of the thermal lens, altering the n_2 values. Long-term thermal diffusion arises when sample cannot return to the equilibrium temperature because the time spacing between pulses are shorter than $t_c = w^2/4D$, where D is thermal diffusion coefficient and w - beam diameter, for most z-scan setups t_c>40 μs [9]. Hence, to get rid of the thermal diffusion (and thermal lens) it is necessary to reduce pulse repetition rate lower than few kilohertz.

Lowering the pulse repetition rate, we observed that n_2 concentration dependence vanishes when the repetition rate approaches ~10 Hz, and are completely gone at 1 Hz in the concentration range $2 \cdot 10^{-7}$ M to $3 \cdot 10^{-5}$ M, see **Figure 2(b)**. Resulting n_2 values are still negative, but significantly changed from $\sim 10^{-12}$ cm²/W to $\sim 10^{-16}$ cm²/W. Hence, we assume that colloidal QD n_2 concentration dependence indicates the presence of the thermal lens effect. To prove that our results obtained from equation (1) are correct, we have performed z-scan measurements with four different pulse powers (pulse repetition rate 1 Hz). Results for 4.5 nm diameter QD colloidal solution (concentration $1.1 \cdot 10^{-5}$ M) are shown on **Figure 2(c)**. As it can be seen, n_2 values are independent from the intensity in the range of 110-235 GW/cm².

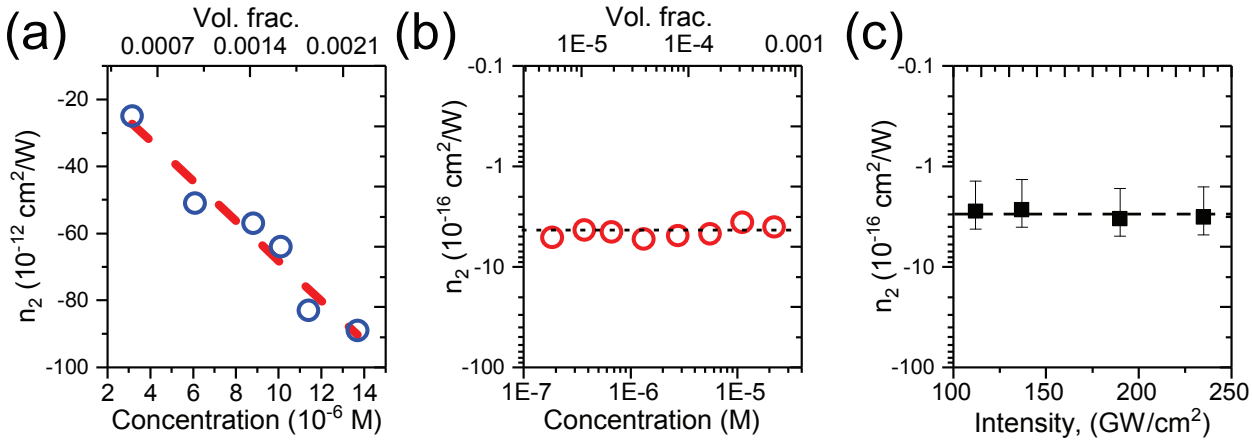

Figure 2 (a) n_2 dependence on QD (d = 4.5 nm) concentration pulse repetition rate - 70 MHz;
(b) n_2 dependence on QD (d = 4.5 nm) concentration (or volume fraction) pulse repetition rate - 1 Hz;
(c) n_2 dependence on input power I_{in} for lead sulfide QDs (d = 4.5 nm)

To estimate QD nonlinearity size dependence we measured a set of QD with sizes ranging from d = 3.2 nm to d = 5.2 nm, with the same excitation wavelength, concentration and incident beam power. The absorption spectra of the studied batch of PbS QD solution are shown on **Figure 3(a)**. Arrow notes red shift of the QD first excitonic peak with increasing QD size, red line marks the excitation wavelength. As shown in **Figure 3(b)**, nonlinear refraction index increases (from $-0.5 \cdot 10^{-16}$ cm²/W to $-4 \cdot 10^{-16}$ cm²/W) with increasing QD size, and

consequently, reducing with increasing bandgap energy. n_2 dependence on QD radius was approximated with power function and found to be close to cubic. However, we measured only limited range of PbS QD sizes and further research has to be done to thoroughly analyze quantum confinement effect on the nonlinear properties of the QDs.

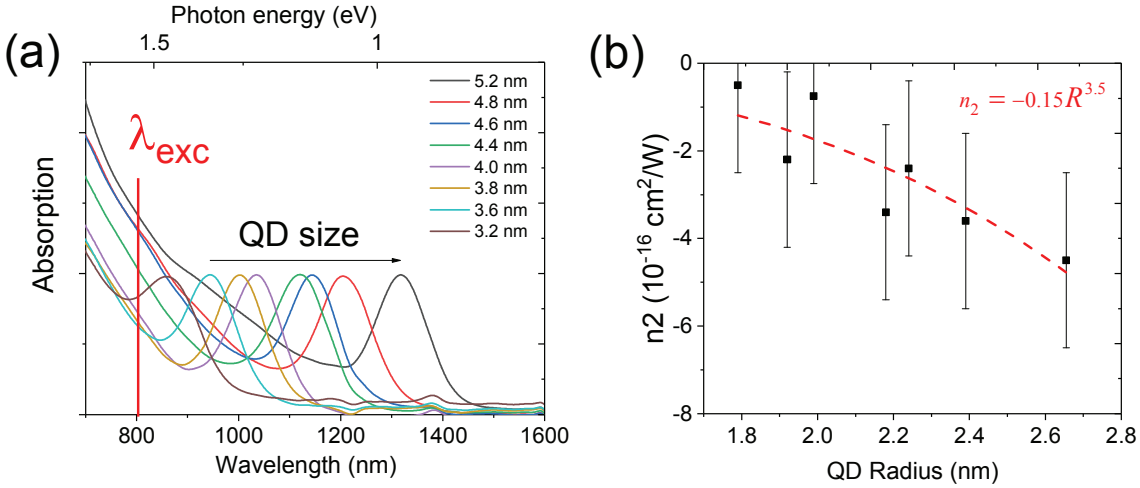

Figure 3 (a) absorption spectra for QD with different sizes, from d = 3.2 nm to d = 5.2 nm, λ_{exc} = 800 nm - excitation wavelength; **(b)** nonlinear refractive index size dependence, red dashed line stands for power function fit ($n_2 = -0.15R^{3.5}$)

4. CONCLUSION

We report that colloidal QD nonlinear refractive index concentration dependence is a sign of a thermal nonlinearity arising from the thermal lens effect. Performing z-scan measurement with low pulse repetition rate laser, thus free from thermal lens effect, we observed that nonlinear refractive index remain constant for different QD solution concentrations, and is in order of 10^{-16} cm^2/W, which is by four order lower than previously reported results. QD nonlinear refractive index are expectedly size dependent and we found it to be close to cubic dependence

ACKNOWLEDGEMENTS

This work was supported by Russian Foundation of Basic Research project № 18-32-00027.

REFERENCES

[1] KERSHAW, Stephen V. SUSHA, Andrei S. and ROGACH Andrey L., Narrow bandgap colloidal metal chalcogenide quantum dots: synthetic methods, heterostructures, assemblies, electronic and infrared optical properties. *Chem. Soc. Rev.* 2013. vol. 42, no. 7, pp. 3033-3087.

[2] BANFI, GianPiero, DEGIORGIO, Vittorio and RICARD, Daniel. Nonlinear optical properties of semiconductor nanocrystals. *Adv. Phys.* 1998. vol. 47, no. 3, pp. 447-510.

[3] SHEIK-BAHAE, Mansoor, SAID, Ali A. WEI, Tai-Huei, HAGAN, David J. and VAN STRYLAND, E. W. Sensitive measurement of optical nonlinearities using a single beam. *IEEE Journal Quantum Electroics.* 1990. vol. 26, no. 4, pp. 760-769.

[4] ASUNSKIS, Daniel J.BOLOTIN, Igor L. and HANLEY, Luke. Nonlinear Optical Properties of PbS Nanocrystals Grown in Polymer Solutions. *J. Phys. Chem. C.* 2008. vol. 112, no. 26, pp. 9555-9558.

[5] OMARI, Abdoulghafar, MOREELS, Iwan, MASIA, Francesco, LANGBEIN, Wolfgang, BORRI, Paola, VAN THOURHOUT, Dries, KOCKAERT, Pascal and HENS, Zeger. Role of interband and photoinduced absorption in the nonlinear refraction and absorption of resonantly excited PbS quantum dots around 1550 nm. *Phys. Rev. B*. 2012 vol. 85, no. 11, p. 115318.

[6] KIM, Hyun S and YOON, Kyung B. Increase of 3rd-Order Nonlinear Optical Activity of PbS Quantum Dots in Zeolite Y by Increasing Cation Size. *J. Am. Chem. Soc.* 2012. vol. 134, no 5, pp. 2539-2542.

[7] WAWRZYNCZYK, Dominika, SZEREMETA, Janusz, SAMOC, Marek and NYK, Marcin. Third-Order Nonlinear Optical Properties of Infrared Emitting PbS and PbSe Quantum Dots. *J. Phys. Chem. C*. 2016. vol. 120, no. 38, pp. 21939-21945.

[8] CHENG, Hui, WANG, Yuhua, DAI, Hongwei, HAN, Jun-Bo and LI, Xianchang. Nonlinear Optical Properties of PbS Colloidal Quantum Dots Fabricated via Solvothermal Method. 2015. *J. Phys. Chem. C*. vol. 119, no. 6, pp. 3288-3292.

[9] FALCONIERI, Mauro. Thermo-optical effects in Z -scan measurements using high-repetition-rate lasers. *J. Opt. A: Pure Appl. Opt. 1999.* vol. 1, no. 6, pp. 662-667.

[10] USHAKOVA, Elena V. LITVIN, Aleksandr P. PARFENOV, Peter S. FEDOROV, Anatoly V. ARTEMYEV, Mikhail, PRUDNIKAU, Anatoly V, RUKHLENKO, Ivan D. and BARANOV, Alexander V. Anomalous size-dependent decay of low-energy luminescence from PbS quantum dots in colloidal solution. *ACS Nano*. 2012. vol. 6, no. 10, pp. 8913-8921.

[11] KHOROSHIKH, D. A. TSYPKIN, Anton N. MEL'NIK, M. V. CZINGEL, Kristian and KOKENYESI, Sandor. A study of the nonlinear refractive index in amorphous Ge-As-S layers and nanocomposites with gold nanoparticles. 2016. *Opt. Spectrosc.* 2016. vol. 121, no. 5, pp. 736-738