



# Fluorescence and Nonlinear Optics of PbS Quantum Dots Dispersed in Toluene

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**Abstract:** The absorption fluorescence spectra of three sizes of Lead Sulfide PbS quantum dots have been investigated. The NMR spectrum reveals the absence of any residuals of the original chemicals used in the syntheses of quantum dots or any other contaminants. Optical absorption spectra are characterized by a large blue shift as the size of the quantum dot decrease. Identical effect was observed for diluted solutions of quantum dots. The fluorescence emission spectra were found to grow linearly with applied excitation power. The data were found to be conforming to the band structure of the material. The variation of the emission peak and half width at half maximum with excitation power were discussed. Z-scan technique was used to investigate nonlinear optical properties of PbS quantum dots. The calculated nonlinear index of refraction and nonlinear absorption coefficient suggest strong self action behaviors.

**Keywords:** PbS quantum dots, fluorescence, nonlinear index of refraction, nonlinear absorption coefficient.

## 1. Introduction

Semiconductor quantum dots emerge as a serious candidate material for a large scale of applications, particularly in photonics and optoelectronics. Some interesting properties of these materials include fluorescence [1], electroluminescence [2], and nonlinear optics [3]. Lead-salts quantum dots (QDs) exhibit a strong confinement regime for both electrons and holes. Therefore, nonlinear optical properties are expected to be greatly enhanced in quantum dots made from these semiconductors. Modulating the size of QDs gives rise to a spectacular change in the band gap energy that strongly influence the electronic, fluorescence, optical, thermal and redox properties of the nanostructured material. These attributes were the subject of intensive research work leading to their use in a wide range of applications including quantum computing and information processing [4], LEDs [5], solar cells [6], single electron transistors [7], and laser devices [8].

Lead Sulfide PbS is an IV-VI lead-salt semiconductor with a bulk gap of 0.41 eV [9] with an absorption onset at 3024 nm, and a nanocrystal exciton Bohr radius of 18 nm [10]. The size effect in PbS QDs

can have a drastic effect on the band gap of the material that could be driven from 0.41 eV in the bulk up to 2.3 eV in the nanostructured regime [11]. Therefore, PbS QDs exhibit a strong confinement regime resulting in quantized electronic energy levels. This behavior is the source of new emerging physical phenomena such as bottleneck [12, 13], efficient charge carrier multiplication [14, 15], Coulomb [16] and spin blockade [17]. Creation of multi excited states in QDs upon absorption of a single high energy photon [12] generated an intense research work because of its potential application in the development of high efficiency solar cells. The synthesis methods of lead-salt QDs have witnessed in the past few years a dramatic improvement, resulting in an accurate control of their size distribution, and consequently on the range of their energy gap distribution. Thus, QDs can be made to have emission spectra covering all the spectral range from the visible to the near infrared region [18, 19]. Telecommunication wavelengths correspond to QDs size-quantized transition in the IR region of the spectrum [20]. Therefore, IV-VI compounds, such as lead sulfides, are desirable in telecommunication applications. Moreover, due to quantum confinement

effect in semiconductor nanocrystals, nonlinear optical properties are enhanced. This encouraged investigations of the third-order susceptibility  $\chi^{(3)}$  to design self action photonic devices.

In this paper we investigate the properties of the fluorescence emission spectra of PbS quantum dots dispersed in toluene with different radii corresponding to emissions in the near infrared region of the spectrum. Also, a preliminary study of the nonlinear optical behavior of PbS quantum dots dispersed in toluene has been carried out.

## 2. Experimental

In this study we used three different sizes of quantum dots dispersed in toluene corresponding to emissions in the near infrared region of the spectrum. These quantum dots samples have been purchased from Evident Technologies. The purity of the toluene quantum dot system was verified by NMR measurements. To perform these measurements, a small amount of the QDs solution is dissolved in deuterated solvent. In our case we used deuterated chloroform ( $\text{CdCl}_3$ ) to run the sample. So there was no hydrogen in the solvent as it was replaced by deuterium. The only hydrogen is then originating from toluene (3 aliphatic and 5 aromatic), as depicted in Figure (1). The peak at 0.00 ppm is for the TMS reference. The appearance of the only toluene originated peaks indicates the absence of any contamination that could influence the fluorescence spectra. Samples of different concentrations were prepared by diluting the original solution with an appropriate amount of solvent. The fluorescence properties of QDs were investigated using argon ion laser (514 nm) as the excitation source. The QDs spectra were studied as a function of the excitation power and the concentration of QDs in toluene. Finally, preliminary study of the nonlinear optical behavior of PbS quantum dots dispersed in toluene has been carried out.

## 3. Electronic Structure

The electronic structure is indispensable tool to understand the electronic and optical behavior of almost all nanomaterials. The most relevant information we can extract from the electronic structure model are the energies and wavefunctions of the lowest excited exciton states and their coupling to optical phonons. Many theoretical studies of the electronic structure of PbS quantum dots have been advanced. The most notable ones are the parabolic effective mass model [21], the hyperbolic-band approximation [22], and the tight-binding type

calculation [23]. These models turn out to be inadequate for lead-salt QDs because they neglect the nonparabolic band nature of these materials, or they are incapable to calculate the energies of higher exciton states, or they are studied only for certain range of QDs radii. The most reliable model for lead-salts is the four-band envelop function [9]. This model is based on a realistic non parabolic and anisotropic band structure. The PbS crystalline structure has direct band gaps at four equivalent L points in the Brillouin zone [9]. The bottom of the conduction band exhibits  $L_6^-$  symmetry in the double group notation, and the top of the valence band exhibits  $L_6^+$  symmetry [24].

## 4. Absorption Spectra

Figure (2) shows typical absorption spectra of PbS QDs dispersed in toluene for three different concentrations. The absorption spectra were measured using the UV-Vis-NIR Shimadzu UV-3600 dual beam spectrophotometer. The spectrum is characterized by discrete absorption peak as signature of quantum confinement effect. The absorption spectra of diluted solutions (2mg/ml and 1mg/ml) decreases dramatically for a dilution coefficient of 5 or more, and the absorption spectrum becomes broader and is shifted to shorter wavelengths. The total absorbance increases almost linearly for small changes in concentration, and saturates for concentrations exceeding 10 gm/lm, as shown in Figure (3). Figure (4) depicts the absorption spectra for three different sizes of QDs. For the 5 nm QDs size (radius), the absorption peak is centered at 1325 nm. As the radius of the QDs decreases, the absorption spectrum is blue shifted. For the 3.2 nm QDs radius, the absorption peak occurs at about 980 nm, and when the radius is decreased further to 2.4 nm the absorption peak shifts to 775 nm. Thus, small variation in the size of the QDs translates into large variations in the allowed energies and the absorption and emission wavelengths. This is the signature of strongly confined environment. In bulk semiconductors, the distribution of the electronic states density is continuous. In these materials, conduction electrons can move around freely, and accordingly they exhibit continuous energy spectrum, and a density of allowed states that increases as the square root of energy. However when electrons are confined to a small region of space, their energy spectrum becomes discrete, and their energy gap increases, and is now dominated by the quantum confinement effect. The isolated absorption peaks at room temperature are evidence of the narrow distribution of QDs sizes. The band diagram of lead-salts is characterized by four equivalent valleys, and the absorption spectra of QDs

made of these materials arise from dipole transitions between quantum-confined electron and hole states in the conduction and valence bands.

### 5. Fluorescence of PbS QDs

The fluorescence emission peak is bell-shaped (Gaussian), and occurs at a slightly longer wavelength than the lowest exciton energy peak marking the absorption onset. This energy separation, or Stoke shift, is typically of the order of 120 nm for 2.4 nm size QDs. Figure (5) shows the intensities of the fluorescence emission spectra of PbS QDs at different excitation power. The emission peak occurs approximately at 900 nm. The energy band diagram of PbS has four L valleys [9]. The origin of the emission spectra is strictly linked to the band structure of the material. Phonon-assisted transitions can occur between different valleys. In this process indirect transitions involve excitons made up of an electron and a hole pertaining to different L valleys. The associated transition between the electrons and holes states will be shifted by the phonon energy. Furthermore, the Coulomb interaction between electrons and holes has the effect of lowering the overall energy levels. One has to note that the study of indirect exciton states resulting from inter-valley scattering in QDs is quite complicated. The difficulty arise from the fact that indirect transition from the valence band at a given L point to the conduction band at another L point, mediated by the X-point phonon in bulk material, is now modified by the quantum confinement in QDs [25]. Phonon confinement gives rise to new phonon modes, and thus modifies the electron-phonon coupling. The effect of these interactions is to mix direct and indirect excitons states in two different valleys. It was shown that the magnitude of these many-body perturbations is negligible in lead-salt QDs [9]. Therefore, coulomb attraction, exchange interaction, and inter-valley scattering effects are negligible as compared to the confinement energy. The edge states of the conduction and valence bands are normally coupled. This coupling is essential for the optical properties of narrow band gap materials such as PbS, and it provides an accurate description of exciton states in QDs.

Figure (6) shows the spectra of the original solution and two diluted samples. The emission is quenched and blue shifted, and thus it follows the same trend as the absorption spectra.

The emission intensity for various excitation power is depicted in Figure (7). The intensity grows linearly with excitation power. As the excitation power increases, agitation of the toluene solution becomes more prominent. This process may lead to more QDs

exposed to the beam of excitation source per unit time. Ultimately, we expect saturation to occur at certain high excitation power, or equivalently more rapid saturation at low concentration of QDs per unit volume, as shown in the same figure for diluted samples.

We studied the position of the peak wavelength in terms of the pumping power for three different concentrations, as illustrated in Figure (8). The position of the emission peak is randomly distributed in a very small range of wavelengths and does not follow a specific trend within the experimental error. An interesting property of the emission spectra is that the peak emission wavelength was found to be independent of the excitation power for all studied concentrations.

Figure (9) shows the variation of full width at half maximum (FWHM) for various excitation power. The FWHM increases systematically for the original sample from 90 nm to 100 nm for a change of excitation power from 1 mW to 10 mW. At lower concentrations, the spectra is broader and follow the same trend as the original solution. A possible source of this broadening may originate from thermal effect arising from collision between QDs. However, this mechanism is far from being operative in samples of diluted concentrations. The specifications of the quantum dots announce 5% tolerance in size. Therefore, the distribution of QDs sizes may have an effect, but it remains limited. Another possible source of broadening is the toluene solution itself. A similar behavior was observed in laser dyes.

### 6. Nonlinear optics of PbS QDs

Nonlinear optical behavior of PbS QDs has been investigated using the Z-scan technique (26, 27). The Z-scan technique is considered to be relatively simple way to determine both nonlinear absorption coefficients and nonlinear refractive indices for a wide variety of interesting advanced materials. Both the nonlinear index of refraction and absorption coefficient were calculated by measuring the transmission of a focused Argon laser beam of wavelength 514 nm on a 2-mm thick quartz cuvette. Figure (10) shows self-focusing action at very low excitation power of 0.5 mW. The enhancement of optical nonlinearity is mainly due to high degree of excitons confinement within quantum dots. The degree of confinement is dependent on QD size. It has been found that the third order susceptibility  $\chi^{(3)}$  of polymers is enhanced when QDs is embedded in the polymer (28).

Figure (11) presents variations of both the nonlinear index of refraction and nonlinear absorption coefficient as a function of excitation power. The row data have

been analyzed following the procedures and theoretical base presented in (26, 27). For excitation power levels higher than 1 mW, formation of diffraction fringes (see Figure 12) and self fanning dominate the transmittance spectrum shown in Figure (10). Also, the effect of QDs concentration, size, and excitation wavelength resulted in interesting nonlinear self actions that are investigated and analyzed in another article. Finally, using beam probe method revealed encouraging findings on low threshold all optical switching devices such as inverter, AND, and NOR gates. The results of this investigation will be published.

### 7. Conclusion

The absorption and fluorescence spectra of PbS quantum dots dispersed in toluene were investigated for various concentrations. The absorption spectra are characterized by a pronounced peak at 1324 nm for solutions containing 5 nm QDs. A blue shift of the absorption spectra was obtained for smaller dimensions of QDs. Reducing the QDs concentration results in quenching the absorption bands and shifting them to higher energies. The fluorescence spectra exhibit a Gaussian shape and increases linearly with applied excitation power. The spectral emission was discussed in terms of the band structure of the material. The linearity of the variation of the fluorescence bands with excitation power was explained in terms of exposed QDs to the laser beam as the agitation of the toluene solution becomes more prominent at higher excitation power. No significant shift in the emission peak was observed despite changing the QDs concentrations. A broadening of the spectral emission band was observed. The various possible mechanisms or sources of this broadening were discussed. Self action due to the third order susceptibility showed remarkable values of both nonlinear index of refraction and absorption coefficient signifying that PbS QDs as an excellent medium for many photonic devices such as optical limiting and all-optical logic gates .

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### REFERENCES

[1] Byung-Ryool Hyun, Yu-Wu. Zhong, Adam C. Bartnik, Liangfeng Sun, Hector D. Abruña, Frank W. Wise,

Jason D. Goodreau, James R. Matthews , Thomas M. Leslie , and Nicholas F. Borrelli , ACS Nano, , 2 (11), 2206–2212, (2008).

- [2] [Bakueva, L.](#), [Hines, M. A.](#), [Chang, T.-W. F.](#), [Tzolov, M.](#), [Scholes, G. D.](#), and [Sargent, E. H.](#), Appl. Phys. Lett. **82**, 2895 - 2897, (2003).
- [3] Wundke K., Potting S., Auxier J., Schullzgen A., Peyghambarian, N. and Borrelli, N. F., Appl. Phys. Lett. **76**, 10, (2000).
- [4] Petta, J. R., Johnson, A. C., Taylor, J. M., Laird, E. A., Yacobi, A., Lukin, M. D., Marcus, C. M., Hanson, M. P., Gossard, A. C., Science, 309, 2180, (2005).
- [5] Luther, J. M., Law, M., Beard, M. C., Song, Q., Reese, M. O., Ellingson, R. J., Nozik, A. J. Nano Lett., 8(10), 3488-3492, (2008).
- [6] Gur, I., Fromer, N. A., Alivisatos, A. P., J. Phys. Chem. B, 110 (50), 25543-25546,, (2006).
- [7] [David L. Klein](#), [Richard Roth](#), [Andrew K.L. Lim](#), [A. Paul Alivisatos](#), [Paul L. McEuen](#), Nature, **389**, 699 (1997)
- [8] Robel, I., Subramanian, V. Kuno, M., Kamat, P. V., J. Am. Chem. Soc., 128(7), 2385-2393, (2006).
- [9] Inuk Kang and Frank W. Wise, J. Opt. Soci. of America (JOSA) B, **14**, Issue 7, 1632-1646 (1997).
- [10] Borrelli, N. F. and Luong, J. C., Proc. SPIE 866, 104, (1987).
- [12] Nozik, A., J. Ann. Rev. Phys. Chem., **52**, 193, (2001).
- [13] Harbold, J. M., Du, H., Krauss, T. D., Cho, K. S., Murray, C. B., and Wise, F. W., Phys. Rev. B, **72**, 195312, (2005).
- [14] Ellington, R. J., Beard, M. C., Johnson, J. C., Yu, P., Micic, O. I., Nozik, A. J., Shabaev, A., Efros, A. L., nano Lett., **5**, 865, (2005).
- [15] Schaller, R. D., Klimov, V. I., Phys. Rev. Lett., **92**, 186601, (2004).
- [16] Schler, R., Ihn, T., Ruh, E., Ensslin, K., Tews, M., Pfannkuche, D., Driscoll, D., Gossard, A., Phys. Rev. Lett., **94**, 206805, (2005).
- [17] Koppens, F. H. L., Folk, J. A., Elzerman, J. M., Hanson, R., Willems van Beveren, L. H., Vink, I. T., Tranitz, H. P., Wegscheider, W., Kouwenhoven, L. P., Vandersypen, M. K., Science, **309**, 1346, (2005).
- [18] Wang. N. Herron, J. Phys. Chem. 92, 4988, (1988)

- [19] Iwan Moreels, Kris Lambert, Dries Smeets, David De Muynck, Tom Nollet, José Martins, Frank Vanhaecke, Andre Vantomme, Christophe Delerue, Guy Allan, and Zeger Hens, published on line by american chemical Society, 3, no. 10, 3023-3030, (2009).
- [20] Harrison, M. T., Kershaw, S. V., Burt, M. G., Rogach, A. L., Kornowski, A., Eychmüller, A., and Weller, H., Pure Appl. Chem., **72**, no. 1-2, 295-307, (2000).
- [21] Efros, Al. L., and Efros, A. L., Sov. Phys. Semicond. 16, 772-775, (1982).
- [22] Wang, Y., Suna, A., Mahler, W., and Kasowski, R., J. Chem. Phys. **87**, 7315-7322, (1987).
- [23] Kane, R. S., Cohen, R. E. and Silbey, R., J. Phys. Chem, **100**, 7928-7932 (1996)
- [24] Nimtz, G., and Schlicht, B., "narrow-gap lead salts", in "Narrow-Gap Semiconductors", Höhler, ed. Springer-Verlag, Berlin, 1-117, (1983).
- [25] [Francesco Masia](#), [Wolfgang Langbein](#), [Iwan Moreels](#), [Zeger Hens](#), and [Paola Borri](#), Phys. Rev. B 83, 201309(R), (2011).
- [26] M. S. Bahae, A. A. Said, and E. W. van Stryland, Opt. Lett. **14**, 955 (1989).
- [27] M. Sheik-Bahae, A. A. Said, T. H. Wei, et al., IEEE. J. Quantum Electron. 26, 760 (1990).
- [28] Du et al. Synthesis, characterization, and nonlinear optical properties of hybridized CdS-Polyesterene nanocomposites. Chem. Mater., 14, 4473-4479, (2002).

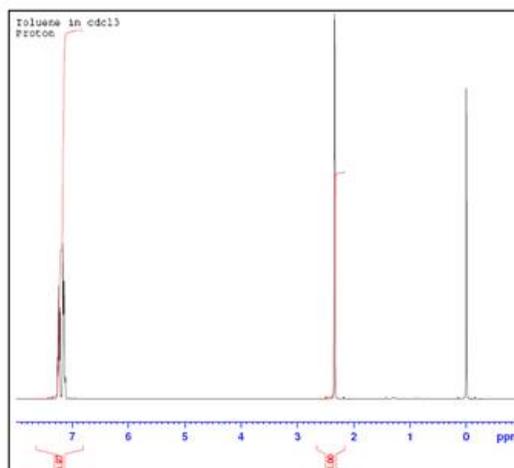


Figure 1: NMR spectra of PdS quantum dots in toluene solution.

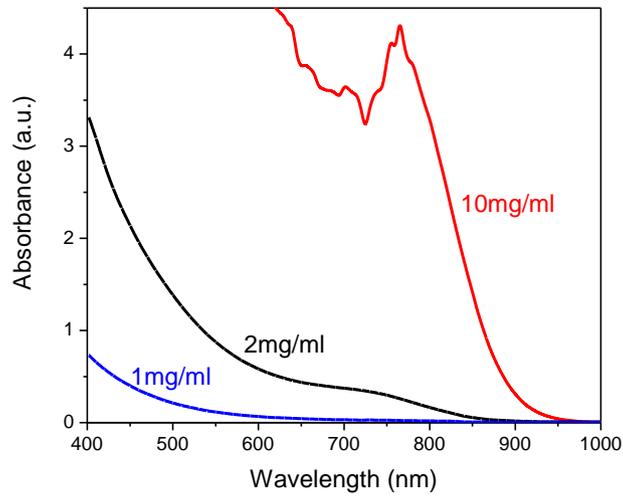


Figure 2: Absorbance of 2.4 nm QDs size at different concentrations.

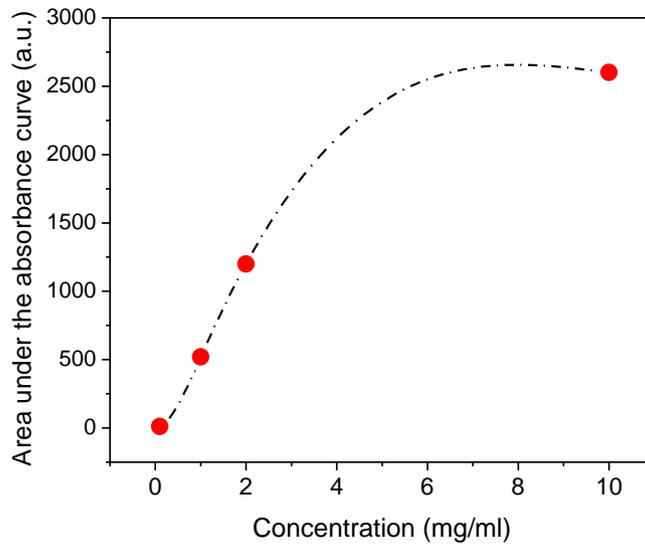


Figure 3: Calculated area under absorbance curves at different concentrations of 2.4 nm QDs size.

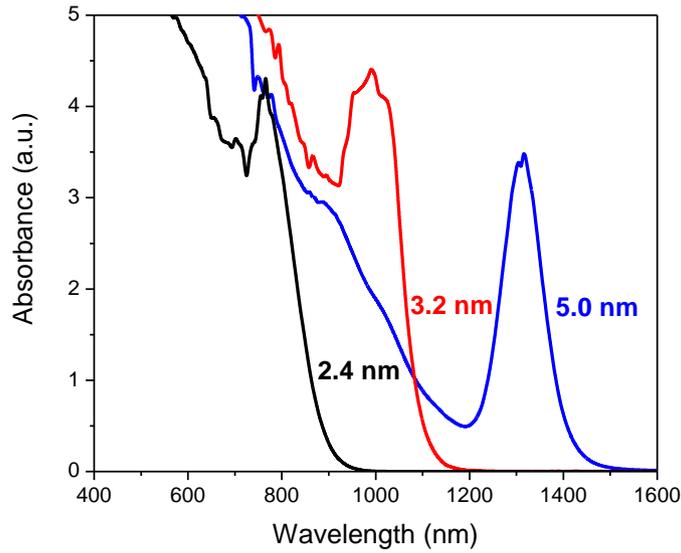


Figure 4: Absorbance of QDs of different sizes having the same concentration of 10 mg/ml.

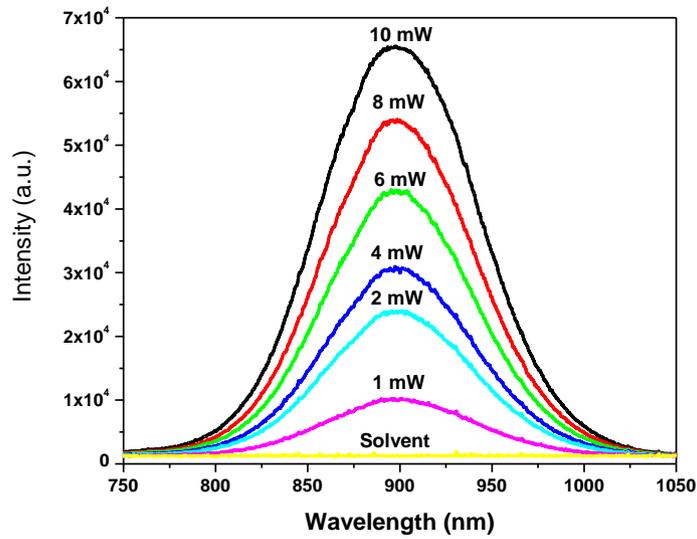


Figure 5: Fluorescence spectra of 2.4 nm QDs size with concentration of 10mg/ml at different excitation power using argon ion laser operating at 514.5 nm.

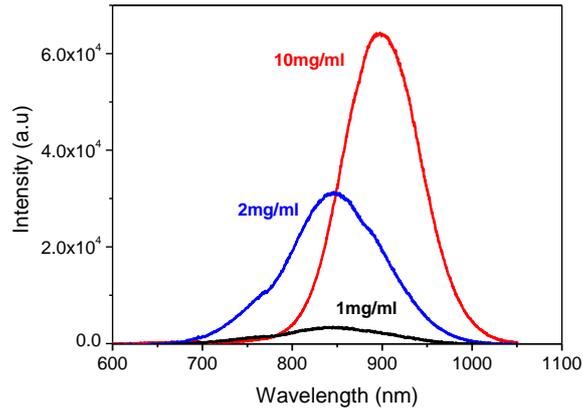


Figure 6: Fluorescence spectra of 2.4 nm QDs at different concentrations excited with a 10 mW argon ion laser operating at 514.5 nm.

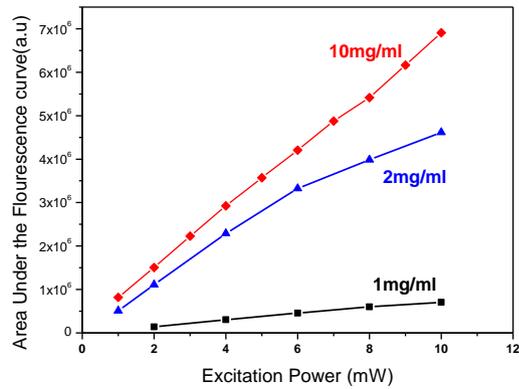


Figure 7: Intensity expressed as the area under fluorescence spectral band of 2.4 nm QDs at different excitation power.

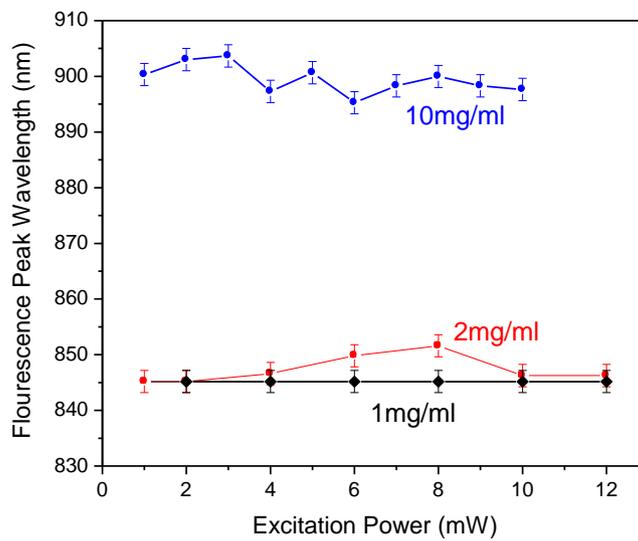


Figure 8: Fluorescence peak wavelength variations of 2.4 nm QDs as a function of excitation power for three different concentrations.

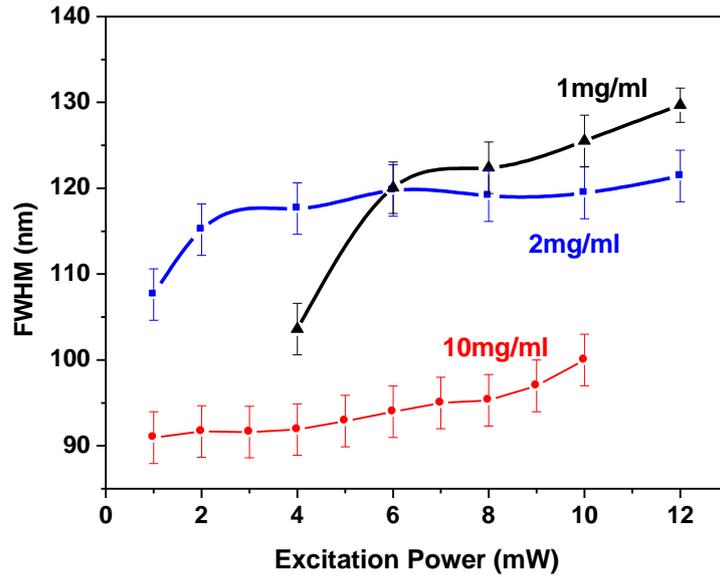


Figure 9: FWHM of fluorescence spectral band of 2.4 nm QDs at different excitation power.

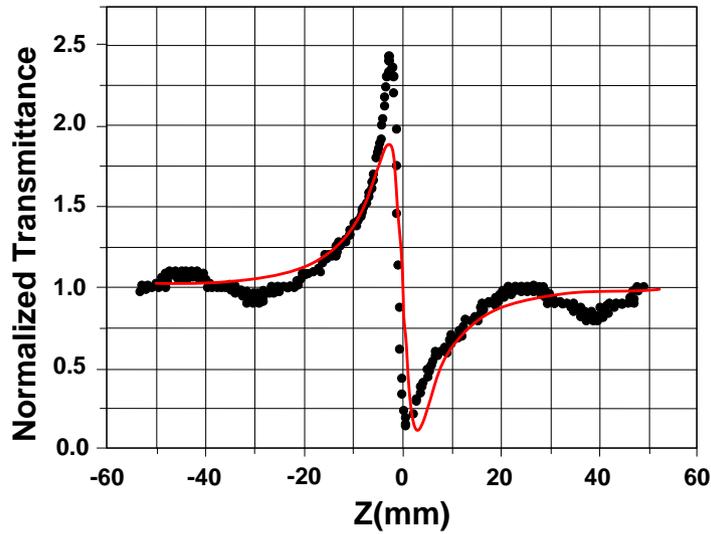


Figure 10: Closed-aperture Z-scan of QDs cell showing self-focusing action in the 2.4 nm QDs size excited with 0.5 mW Ar<sup>+</sup> laser Gaussian beam at 514 nm .

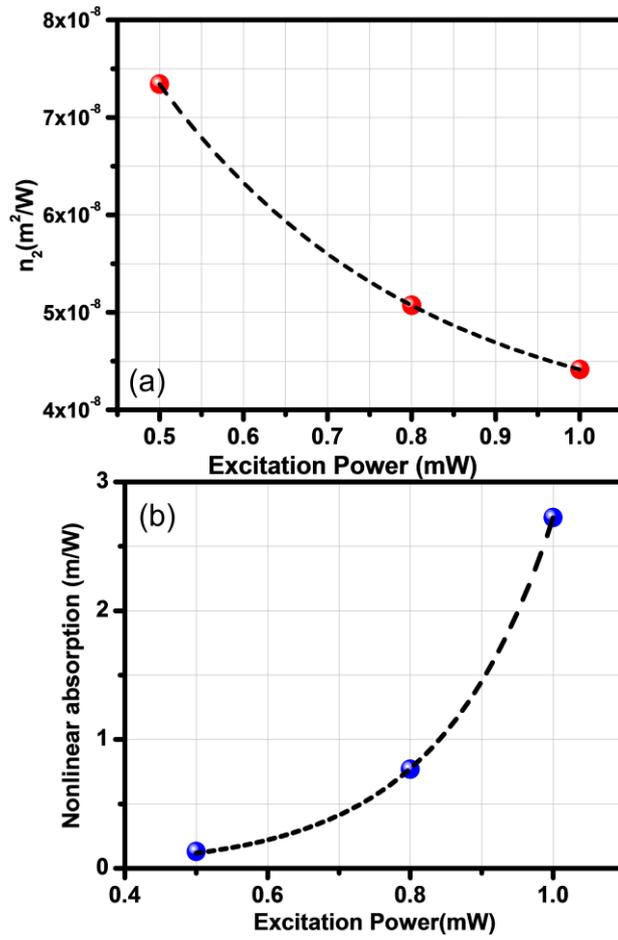


Figure 11: Variation of (a) nonlinear index of refraction and (b) nonlinear absorption coefficient of 2.4 nm QDs size sample as function of excitation power from  $\text{Ar}^+$  laser beam at 514 nm.

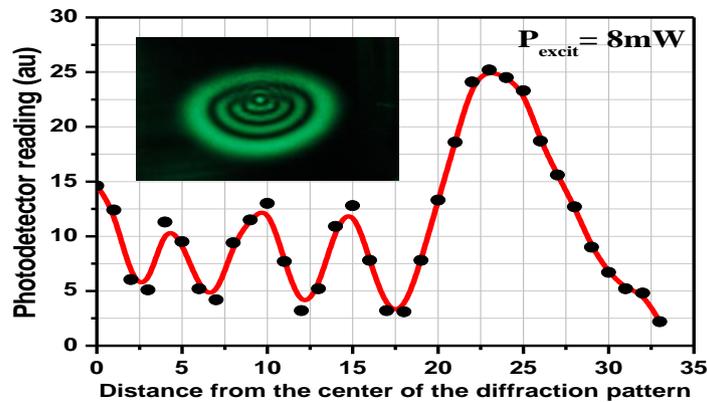


Figure 12: Typical photograph of the diffraction rings formed due to nonlinear diffraction by 2.4 nm QDs sample pumped with 8 mW  $\text{Ar}^+$  laser beam at 514 nm. A small area photodiode scanned power distribution across the rings starting from the center the distance is in mm.