PRAMANA
— journal of
physics

© Indian Academy of Sciences

Vol. 82, No. 2
February 2014
pp. 327–330

Observation of two-photon absorption at UV radiation in ZnS quantum dots

MANAJIT CHATTOPADHYAY[1], PATHIK KUMBHAKAR[1,*] and UDIT CHATTERJEE[2]

[1]Nanoscience Laboratory, Department of Physics, National Institute of Technology, Durgapur 713 209, India
[2]Laser Laboratory, Department of Physics, Burdwan University, Burdwan 713 104, India
*Corresponding author. E-mail: kumbhakarp@yahoo.com; pathik.kumbhakar@phy.nitdgp.ac.in

DOI: 10.1007/s12043-014-0685-x; ***e*Publication:** 12 February 2014

Abstract. Research studies on quantum dots (QDs) of semiconductor materials are of potential interest in present days having promising applications in different optoelectronic devices. Among other materials, ZnS is a direct bandgap semiconductor material having a wide bandgap of 3.6 eV for its cubic phase at room temperature and it shows excellent optical properties. However, here the nonlinear optical (NLO) properties of chemically synthesized ZnS QDs of average size of ∼1.5 nm have been reported which are measured by using an indigenously developed Z-scan technique. The pump radiation is 355 nm which is the third harmonic of the Q-switched Nd:YAG laser radiation having pulsed duration of 10 ns with the repetition rate of 10 Hz. The measured experimental data have been analysed by using analytical models and two-photon absorption coefficients of the ZnS QDs at 355 nm have been extracted.

Keywords. Nonlinear optical properties; quantum dots; Z-scan.

PACS Nos 42.65.–k; 78.67.Bf

Research interest has witnessed an exponential growth in recent times to find highly potential multiphoton active materials [1–10]. Quantum dots (QDs) of zinc sulphide (ZnS) and Mn^{2+}-doped ZnS (ZnS:Mn) have been found to be potential materials due to their visible photoluminescence and enhanced nonlinear optical (NLO) properties [3–6]. There are some previous reports on the multiphoton absorption properties of ZnS and ZnS:Mn QDs, viz. two-photon absorption (2PA) has been reported by Zheng *et al* [5] at 532 nm radiation with picosecond laser radiation in 0.5% Mn^{2+}-doped ZnS QDs. Also, some enhancement in 2PA have been reported in ZnSe/ZnS core/shell and ZnS quantum structures at 806 nm and 532 nm laser pulses, respectively [8]. NLO properties of ZnS in the ultraviolet (UV) wavelength region have not been investigated extensively. However, in this work we have presented our observation of 2PA in undoped ZnS QDs at 355 nm

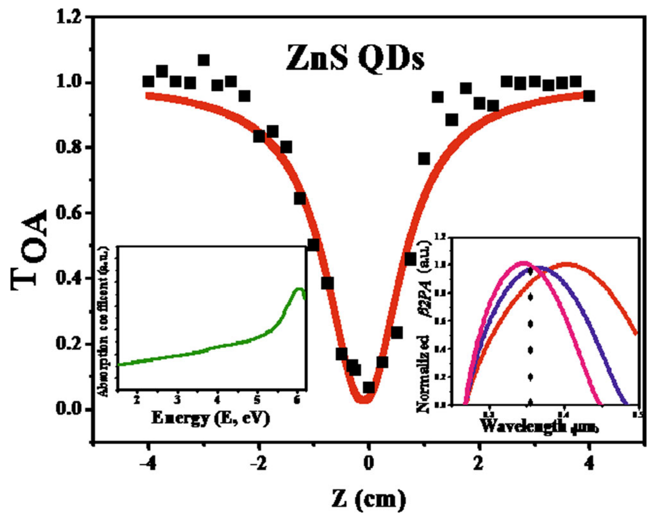

Figure 1. Normalized transmittance curves for OA Z-scan at 355 nm incident laser radiations for ZnS QDs sample at 27.4 GW/cm^2 peak intensity. Symbols are experimental points. The solid curve is the theoretically fitted one with 2PA processes in thick media. Left inset shows UV–visible absorption characteristics of ZnS sample dispersed in methanol [6]. Right inset shows the wavelength dispersion of the normalized 2PA coefficients for bulk semiconductor considering 2PA scaling rule as reported by Sheik-Bahae *et al* [10]. Red, blue, and magenta curves correspond to the normalized 2PA coefficients calculated by taking the band-gap values as 4, 5.2, and 6 eV, respectively [10]. It has been found that the normalized 2PA shows a peak at 355 nm for $E_g = 5.2$ eV (this is shown by a vertical line).

UV radiation. The sample used in this work is freshly prepared by following the chemical precipitation method as elaborated in [6]. UV–visible absorption characteristic of the sample, measured by a spectrophotometer (Hitachi U-3010) are shown as the left inset of figure 1 [6]. The average particle size (radius) as obtained from X-ray diffraction (XRD) measurements is ∼1.5 nm [6] and a standard Z-scan experimental set-up is used [6,10]. However, in the present experiment, the third harmonic radiation generated at 355 nm (10 ns, 10 Hz rep. rate) has been used as the excitation source. This third harmonic UV radiation from a Q-switched Nd:YAG laser having 10 ns pulse duration and 10 Hz repetition rate is allowed to pass through a quartz lens of 7.5 cm focal length and then focussed on the sample (ZnS nanopowder dispersed in methanol and kept in a quartz cuvette of 2 mm path length (L)). This satisfies the thick sample condition ($L > n_0 z_0$) [9], where n_0 and z_0 are the refractive index of the sample and the confocal parameter of the used Z-scan system respectively [9].

In the present experiment, for thick sample condition, the on-axis normalized open aperture (OA) transmittance (T_{OA}) can be written as [9],

$$T_{\mathrm{OA}} = [1 + 0.5Q_0 \left[\tan^{-1}(Z^N + l) - \tan^{-1}(Z^N)\right]^{-1}, \quad (1)$$

where $Z^N = z/n_0 z_0, l = L/n_0 z_0, Q_0 = q_0[1 + \tanh(l/2) \times \{(3\varphi_0/10) + (\varphi_0^2/8)\}]$, $q_0 = \beta_{2\mathrm{PA}} I_0 n_0 z_0$, and $\varphi_0 = 2\pi\gamma n_0 z_0/\lambda$. Here, I_0 is the on-axis peak irradiance at focus in W/cm^2, and β_{2PA} and γ are the 2PA coefficient and nonlinear refraction coefficient of the sample, respectively [9]. Here λ is the wavelength of the used radiation. Figure 1 shows our experimentally and theoretically fitted OA Z-scan transmission traces for ZnS QDs sample measured with the maximum intensity of 27.4 GW/cm^2. Here, symbols are experimental points and the solid curve is the theoretically fitted one using eq. (1). From figure 1 it is obvious that the theoretical curve obtained by considering 2PA shows excellent fittings to the experimental data.

The observed NLO properties are endorsed only to the semiconductor QDs sample and the quartz cuvette filled with methanol did not show any NLO properties at this wavelength. The value of intrinsic 2PA coefficient (β_{2PA}^{Int}) of the used sample is calculated using the relation $\beta_{2PA}^{Int} = \left[\beta_{2PA}(n_0^{soln})^2\right] / \left[(n_0^{QDs})^2 f(\pounds)^4\right]$, the details of which have already been given in [3]. The obtained value of 2PA coefficient (β_{2PA}^{Int}) is given against values from other literature in table 1. The value of incident photon energy (E_p) is $\sim$3.5 eV and the band-gap energy (E_g) of the ZnS QDs sample is $\sim$5.16 eV which satisfies the condition $2E_p > E_g$. It clearly shows the dominance of 2PA in the present experiment [4,5]. In another calculation, using the dispersion scaling rule given by Sheik-Bahae *et al* [10], it has been found from inset (right) of figure 1 that at the used wavelength of 355 nm, the normalized 2PA is maximum (peak) when the band gap of the material and the wavelength of the photon energies are taken as 5.2 eV and $\sim$3.5 eV, respectively. In figure 1, red, blue, and magenta curves showing the variation of the normalized 2PA coefficients calculated by taking the different values of bandgaps as 4, 5.2 and 6 eV, respectively. At $E_g = 5.2$ eV, the blue curve shows the maximum (peak) normalized 2PA at 355 nm, whereas the other curves (i.e. for different band gaps) show the deviation of peak maxima from 355 nm, indicating the higher probability of occurrence of 2PA at 355 nm at the band-gap energy (E_g) of 5.2 eV. So a suitable choice of the band gap of semiconductor as well as the corresponding wavelength is the best combination for obtaining large 2PA. The average particle size of 1.5 nm of the used QDs being less than the exciton Bohr radius of 2.2 nm of bulk ZnS, the huge enhancement in 2PA coefficient is attributed to the quantum confinement effects as well as to the large surface-to-volume ratio of the QDs.

In summary, we have presented here, 10^5 times enhanced 2PA coefficient in ZnS QDs over that of bulk ZnS at 355 nm by Z-scan technique [7]. This huge enhancement in 2PA in the studied sample is attributed to the quantum confinement effects. As the particle size is reduced below the exciton Bohr radius of the material, there is concentration

Table 1. 2PA coefficient measured in ZnS QDs at 355 nm wavelength at 27.4 GW/cm^2 intensity.

Sample	β^{Int} (cm/GW)	
	This work	Literature data
ZnS QDs	3.8×10^5	1^a, 1.18^b, 1 ± 0.3^c

[a]Bulk ZnS at 610 nm [7].
[b]ZnS QDs at 532 nm [5].
[c]ZnS QDs at 795 nm [8].

of oscillator strength into just a few transitions and this leads to the enhancement in the nonlinearity of the material. Moreover, the productive combination of the experimental parameters, such as the incident photon energy and the band gap of the used samples, provided the highest probability for achieving 2PA in the investigated samples. The present observation of enhanced nonlinear absorption of the undoped ZnS sample at 355 nm, combined with our previous observations at 532 and 1064 nm [3,6] showed that this QD is excellent to be used in optoelectronic and biophotonic devices [2–6].

Acknowledgements

Authors are grateful to DST (Grant No. SR/FTP/PS-67/2008), Govt. of India, for the partial financial support.

References

[1] S M Oak, K S Bindra, R Chari and K C Rustagi, *J. Opt. Soc. Am.* **10**, 613 (1993)
[2] B Gu, Y X Fan, J Chem, H T Wang, J He and W Ji, *J. Appl. Phy.* **102**, 083101 (2007)
[3] M Chattopadhyay, P Kumbhakar, R Sarkar and A K Mitra, *Appl. Phys. Lett.* **95**, 163115 (2009)
[4] R A Ganeev, *J. Opt. A: Pure Appl. Opt.* **7**, 717 (2005)
[5] J J Zheng, G L Zhang, Y X Guo, X Y Wang, W J Chen, X S Zhang and Y L Hua, *Chin. Phys. Lett.* **23**, 3097 (2006)
[6] M Chattopadhyay, P Kumbhakar, C S Tiwary, R Sarkar, A K Mitra and U Chatterjee, *J. Appl. Phys.* **105**, 024313 (2009)
[7] T D Krauss and F W Wise, *Appl. Phys. Lett.* **65**, 1793 (1994)
[8] A D Lad, P P Kiran, D More, G R Kumar and S Mahamuni, *Appl. Phys. Lett* **92**, 034126 (2008)
[9] W P Zang, J G Tian, Z B Liu, W Y Zhou, F Song and C P Zhang, *J. Opt. Soc. Am. B* **21**, 63 (2004)
[10] M Sheik-Bahae, D C Hutchings, D J Hagan and E W Van Stryland, *IEEE J. Quantum Electron* **27**, 1296 (1991)