JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 7, July 2007, p. 2200 - 2204

Hyper Rayleigh Scattering in CdS nanoparticles grown in PPS polymer

J. W. DADGE, K. G. KANADE[a], B. B.KALE[b], D. P.AMALNERKAR[b], R. C.AIYER[*]
Department of Physics, Laser Laboratory, University of Pune, Pune-411007. India
[a]Department of Chemistry, Mahatma Phule College, Pimpri, Pune-411017.India
[b]Center for Materials for Electronics Technology (C-MET), Pune-411008. India

---

The CdS nanoclusters synthesized by a novel polymer-inorganic solid state reaction of CdI_2 and Cd $(NO_3)_2$ $4H_2O$ with polyphenylsulphide (PPS) giving average sizes of 20 and 32 nm respectively, were studied for coherent second harmonic generation (SHG) in different organic media. Significant enhancement in SHG intensity of CdS nanoparticles in Toluene is observed due to its highest refractive index. The particles having 32 nm size were further studied for HRS to determine their β value is found to be 1.84×10^{-25} esu which is one order of magnitude higher than that reported for CdS particles.

(Received November 30, 2006; accepted June 27, 2007)

Keywords: Nonlinear optics; hyperpolarizability; nanoparticles

---

1. Introduction

The Hyper Rayleigh Scattering is a nonlinear incoherent second order light scattering, which is used for studying the second order nonlinear optical (NLO) properties of molecules or nanoparticles in solution [1]. The generation of HRS is due to the fluctuations of the density or orientation of molecules or nanoparticles, which instantaneously break the centrosymmetry of isotropic media and create conditions of net frequency doubling. The problem with the experimental determination of the second order NLO polarizability, β, lies in the fact that centrosymmetric structures of individual molecules with a nonzero microscopic hyperpolarizability, which do not possess a macroscopic second order NLO susceptibility B. Therefore, the first measurements of B were performed on crystals without centrosymmetry, Langmuir-Blodgett films and poled polymers [1,2]. However, the Kurtz powder method generates substantial amount of second harmonic powder efficiency data [3]. Compared to the conventional technique of electric field induced second harmonic generation (EFISHG) [1] the HRS method offers advantages. In particular, it can be performed in a liquid phase without applying an electric field for alignment. Consequently, HRS has been successfully used to determine β value of CdS nanoparticles. Semiconductor or metal nanoparticles exhibit interesting optical properties due to the confinement of the electronic wave functions, the drastically changing surface to volume ratio and their surface conditions [4].

The quantum dots (QD) have generated lot of research in the recent years because they possess properties intermediate between the bulk materials and atoms or molecules. The physical properties of semiconductor nanoclusters are usually dominated by spatial confinement of excitations, which determines non-linear optical effects from polarizable excited states. Second order optical nonlinearities in the metal and semiconducting quantum dots is used as a surface probe [5].

In this paper to the best of our knowledge the first example of CdS quantum dots grown in PPS polymer gives higher value of β and coherent SHG than pure CdS quantum dots [6]. These nanoparticles are synthesized by a polymer-inorganic solid state reaction route for the in situ generation of nanochalcogenide semiconductor in the network of polymer which itself acts as a chalcogen source.

2. Experimental

The CdS nanocrystallites are synthesized by reacting CdI_2 and $CdNO_3$ independently with engineering thermoplastic polyphenylene sulphide (PPS). In case of PPS:$Cd(NO_3)_2$ $4H_2O$ (1:1 molar ratio) scheme, the X-ray diffractogram (Fig. 1,a) reveals the formation of mainly hexagonal CdS with size 32 nm and an occurrence of extraneous phase as indicated by diffraction peaks corresponding to d values 2.6820Å, 2.3270 Å and 1.1701 Å.. In case of PPS:CdI_2 (1:1 molar ratio) scheme, X-ray diffractogram (Fig. 1 (b) reveals occurrence of mixed phases (cubic and hexagonal) of CdS as well as hexagonal phase of CdI_2. The prominent diffraction peaks at 2.10 Å and 1.70 Å are associated with cubic/hexagonal CdS and hexagonal CdI_2. Figure 2 (a) shows a representative TEM photograph of CdS nanoparticles. In the case of PPS:CdI_2 scheme, the nearly spherical and irregular shaped dark black regions are nanosized CdS nanoparticles as evidenced by selective area diffraction pattern associated with these spots (Figure 2 (b). It also reveals the occurrence of cubic CdS which in total agreement with the XRD. The selective area diffraction pattern rings evidently indicate the polycrystalline nature of the product whereas the spots imply the single crystalline nature of the product. Thus, it can be inferred that the as formed CdS nanocrystallites are randomly positioned between polycrystalline and single crystalline lattices. We can see that the polymer forms a ribboned or flaked network (Fig. 2 (a) within which CdS nanocrystallites are embedded. The particle size is observed to be 12 nm from TEM measurements.

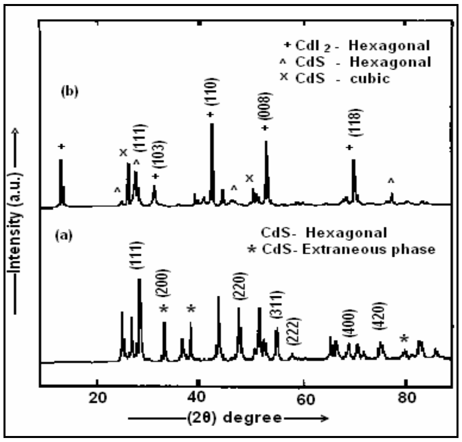
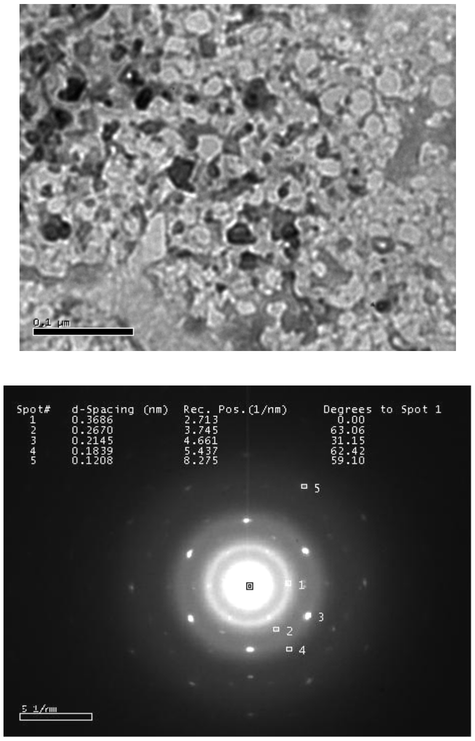


Fig. 1. (a) XRD pattern of CdS nanoparticles obtained from PPS:Cd $(NO_3)_2$ $4H_2O$ for the size 32nm. (b) XRD pattern of CdS nanoparticles obtained from PPS:CdI_2 for the size 20 nm.



```
Spot#   d-Spacing (nm)  Rec. Pos.(1/nm)     Degrees to Spot 1
  1     0.3686          2.713                  0.00
  2     0.2670          3.745                 63.06
  3     0.2145          4.661                 31.15
  4     0.1839          5.437                 62.42
  5     0.1208          8.275                 59.10
```

Fig. 2 (a) and (b) TEM image and selective area diffraction pattern of CdS nanoparticles respectively.

The schematics of the experimental setup for coherent SHG and HRS measurement is shown in Fig. 3. which consists of a Q-switched Nd:YAG laser (λ = 1064 nm) of 1 to 100 mJ pulse energy, 1 Hz repetition rate and 20 ns pulse width [7-10]. The laser radiation was filtered by a 1064 nm pass filter (Melles Griot) to minimize the background intensity. For coherent SHG the laser beam was focused on a 10 x 10 x 1 mm^3 borosilicate cuvette using a lens (focal length 14cm). The cuvette contains nanoparticles in the colloidal form. The signal generated in the visible range was detected through a monochromator with a photomultiplier tube after passing through a 1064 nm stop filter and a 530 nm pass filter and measured on a fast storage oscilloscope (THS 730A). The pulse width of fundamental beam and 2ω beam was found to be the same confirming the second harmonic generation measured on FND-100 with appropriate filters and the coherence was confirmed by using a polarizer. The coherent SHG measurements of CdS nanopaticles were carried out for 20 nm and 32 nm sizes in different organic solvents. All the solvents were prechecked by the same experimental setup for SHG. None of the solvents showed SHG; as the solvents have no absorption between 300 to 1200 nm. In this case powder urea was used as the reference sample.

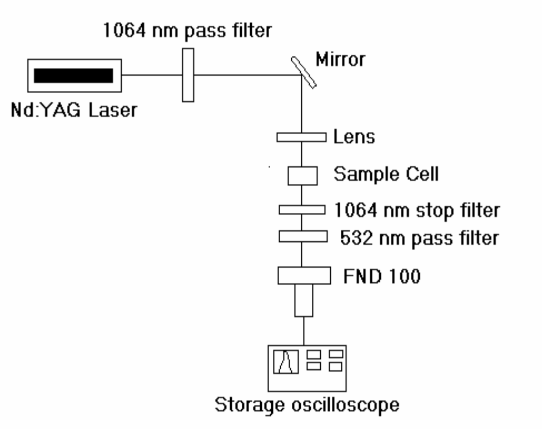


Fig. 3. Experimental setup for HRS and SHG.

The HRS measurements of CdS nanoparticles with size of 32 nm was carried out in Methanol by the methods described in [11-14]. The laser beam was focused on a 10 x 10 x 45 mm^3 quartz cuvette using a lens (Focal length 14 cm) containing the nanocrystallites in the colloidal form. The HRS signal generated was focused onto a detector (FND 100) after passing through a 532 nm pass filter (Melles Griot). The detector was placed at right angle to the fundamental beam. The HRS signal was measured using a Tecktronix fast storage oscilloscope (THS 730A).

3. Results and discussion

The coherent SHG measurements of CdS nanopaticles were carried out for 20 nm and 32 nm sizes in different organic solvents is shown in Fig. 4 and 5 respectively. The observed coherent SHG in present case can arise mainly due to two factors. First, bulk like effect due to asymmetry in the structure of CdS nanoparticles. The observed wurtzite lattice in the present case implies the lack of inversion symmetry [15] and second factor originating from the surface. Since a substantial number of atoms reside on the surface for nanoparticles, the contribution to SHG from the surface is always non zero because of highly asymmetric electronic charge distribution around surface atoms.

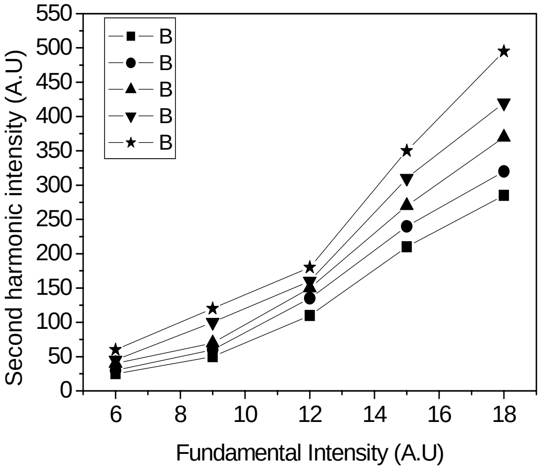


Fig. 4. SHG of 20 nm size CdS nanoparticles in different organic media.

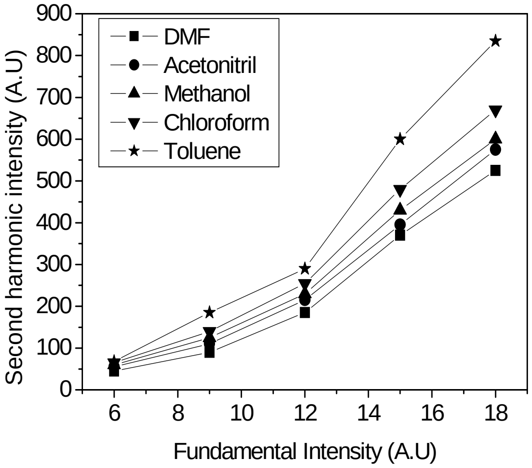


Fig. 5. SHG of 32 nm size CdS nanoparticles in different organic media.

The second harmonic signal increases with increase in cluster size (i.e. 20nm and 32nm) as a function of incident energy in different organic solvents. This could be explained as follows. The quadratic susceptibility of a centrosymmetric system is equal to zero in the dipole approximation. Therefore even small distortions breaking the inversion symmetry of the particles lead to a noticeable enhancement of second order optical response due to the appearance of non zero dipole quadratic susceptibility [16]. Therefore in more realistic approach to study quadratic optical effects in nanometer size particles the fluctuations of the particle shape should be taken into account. Increase in second harmonic intensity for 32 nm size nanoparticles than 20 nm size nanoparticles is may due to the number of particles seen by the beam, which results in increase in the second harmonic intensity. Present results show much higher intensity of SHG in toluene than that in methanol, chloroform, acetonitrile, and DMF (Dimethylformamide). Inorganic semiconductors usually possess large refractive indices. When they are embedded in media with lower refractive indices such as solvents, a boundary is established by the difference in refractive indices. When illuminated by laser light, the local electric field experienced by the nanoparticles can be enhanced compared to the incident field because of the presence of this boundary. The local field can also arise from the dipole-dipole interaction between the clusters and surrounding medium. In the case of toluene the refractive index is highest amongst the solvent used for measurements. The field experienced inside the nanoparticles will be larger giving rise to a higher SHG intensity. It is expected that in DMF and acetonitrile the SHG signal to be higher than that in methanol. On the contrary it is observed to offer the least SHG intensity from CdS nanocrystallites in DMF. This can occur only if there is direct interaction of the polar solvents with the surface.

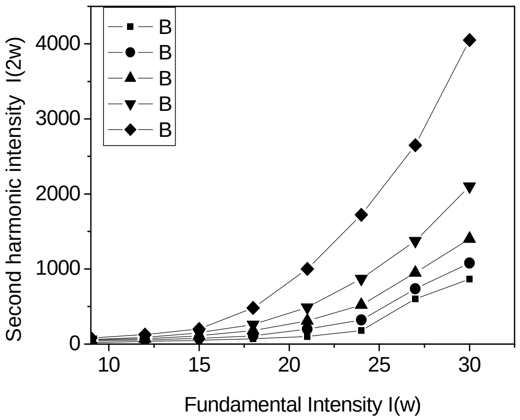


Fig. 6. Incoherent SHG in methanol for CdS nanoparticles.

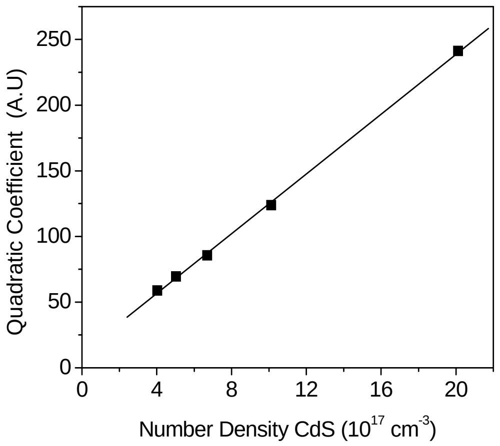


Fig. 7. Quadratic Coefficient $GB^2 = G\,[N_{solvent}\,\beta^2_{solvent} + N_{solute}\,\beta^2_{solute}]$, *obtained from the curves in fig.6 vs.* N_{solute}, *the number density of CdS nanoparticles in methanol.*

The incoherent harmonic signal, known as the Hyper Rayleigh signal, scattered by the solution in the right angle direction to the fundamental incident beam has been detected from a monodispersed solution of nanoparticles.

A quadratic dependence of the HRS signal $I^{2\omega}$ on the incident light intensity I^{ω} is always observed, according to $I^{2\omega} = GB^2\,(I^{\omega})^2$, where G is a proportionality constant containing geometrical and electronic factors. For a two component system,

$$B^2 = N_{solvent}\,\beta^2_{solvent} + N_{solute}\,\beta^2_{solute} \qquad (1)$$

The low concentration of solute molecules does not significantly change the number density $N_{solvent}$ of the solvent molecules. Measurements at different number densities of the solute then shows a linear dependence of GB^2 on N_{solute}. From the intercept and the slope, β_{solute} is calculated [17-19], when $\beta_{solvent}$ is known, or vice versa. Since no external field has been applied for directing the dipoles, the local field correction factor at zero frequency is eliminated. The local field correction factors are needed at optical frequencies, which can be estimated by the standard methods [2]. The internal reference method (IRM) eliminates the need for local field correction factors. These factors are divided out by calibrating and measuring in nearly the same local field as long as the number density of the solute molecules present does not significantly change the refractive index of the solution.

To ascertain that the results of our measurements are consistent with the accepted data, we have calibrated our experiment by using paranitroaniline (p-NA) dissolved in methanol as the sample. The obtained value of β of p-NA to be 9.1 X 10^{-30} esu, which was in satisfactory agreement with the literature value [20]. The quadratic dependence of the observed HRS signal $I^{2\omega}$ on incident intensity I^{ω} is illustrated in Figure 6 for 32 nm size CdS nanoparticles in methanol. The expected linear dependence of the retrieved value for the quadratic coefficient GB^2 on the number density N_{solute} is shown in Figure.7. The hyperpolarizability of a single CdS nanoparticle was obtained, provided the hyperpolarizability of a methanol molecule is known, which is $\beta_{solvent} = 0.69 \times 10^{-30}$ esu [21]. We were able to deduce the method of extracting accurate values for β_{solute} by the IRM. The obtained value for CdS nanoparticle is $\beta_{CdS} = 1.84 \times 10^{-25}$ esu, which is one order of magnitude higher than that reported for CdS particles 1.45 x 10^{-26} esu [6].

It is known that the HRS method relies upon random density fluctuations to create condition compatible with net frequency doubled. For each scatterer in solution, a substantial requirement for the finite HRS is the presence of noncentrosymmtric structure. The CdS nanoparticles studied here have hexagonal structure. As reported, surface termination of the crystalline lattice creates a condition of noncentrosymmetry, which contributes to the large β values [6, 22]. The literature [5] also indicated that the electron distribution around the surface atoms is inherently highly noncentrosymmetric. Moreover an important feature of nanoscale particles is the enhanced ratio of the surface atoms to volume atoms. This shows that nanoparticles surface atoms play an important role in the contribution to the HRS signal.

4. Conclusions

In conclusion, using the HRS technique, large second order NLO response of the CdS nanoparticles grown in PPS polymer was exhibited. The CdS β_{CdS} 1.84×10^{-25} esu in methanol is calculated. These predict considerable potential of CdS nanoparticles in NLO applications. CdS nanoparticles for two sizes exhibit SHG in different media.

References

[1] K. Clays, Persoons A, Phy. Rev. Lett. **66,** 2980 (1991).
[2] D. J. Williams, Angew Chem.Int.Ed. Engl. **23,** 690 (1984).
[3] J. R. Nicoud, R. J. Twieg, Nonlinear Optical Properties of Organic Molecules and Crystals (Orlando, FL, Academic) **2**, 221 (1987).
[4] X. Wang, Y. Zhang, F. U. Degang, L. U. Zuhong, C. U. I. Yiping, Proc. SPIE. **3899**, 384 (1999).
[5] M. Jacobsohn, U. Banin, J. Phys. Chem.B. **104**, 1 (2000).
[6] Y. Zhang, X. Wang, D. F. Lu, Journal of Physics and Chemistry of Solids **62,** 903 (2001).
[7] Q. Song, C. Wan, C. K. Johnson J. Phys. Chem. **98**, 1999 (1994).
[8] H. Wang, E. C. Y. Yan, E. Borguet, K. B. Eisenthal Chem. Phys. Lett. **259**, 15 (1996).

[9] S. Pethkar, J. A. Dharmadhikari, A. A. Athawale, R. C. Aiyer, K. Vijayamohanan, J. Phys. Chem. B **105**, 5110 (2001).
[10] M. L. Sandrock, C. D. Pibel, F. M. Geiger, C. A. Fross (Jr), J. Phy. Chem. B **103**, 2668 (1999).
[11] W. Terhune, P. D. Maker, C. M. Savage, Phys. Rev. Lett. **14**, 681 (1965).
[12] M. H. Rouillat, I. R. Antoine, E. Benichou, P. F. Brevet, Analytical. Sciences. **17** (Suppl), i235 (2001).
[13] P. Galletto, P. F. Brevet, H. H. Girault, R. Antoine, M. Broyer, Chem. Comm. 581 (1999).
[14] C. X. Zhang, Y. Zhang, X. Wang, Z. M. Tang, Z. H. Lu, Analytical Biochemistry **320**, 136 (2003).
[15] Q. Zhengping, Yi Xie, Yingjie Zhu, Q.Yitai, J. Mater. Chem. **9**, 1001 (1999).
[16] O. A. Aktsipetrov, P.V. Elyutin, A. A. Nikulin, E. A. Ostrovskaya Phys. Rev. B **51** 17591 (1995).
[17] S. Shin, M. Ishigame, J. Chem. Phys. **89**, 1892 (1988).
[18] S. Kielich, J. R. Lalanne, F. B. Martin, Phys. Rev. Lett. **26,** 1295 (1971).
[19] M. C. Flipse, R. D. Jonge, R. H. Woudenberg, A. W. Marsman, C. A. Van Walree, L. W. Jenneskens Chem. Phys. Lett. **245,** 297 (1995).
[20] M. A. Pauley, H. W. Guan, C. H. Wang, K.Y. J Alex, J. Chem. Phys. **104,** 7821 (1996).
[21] R. L. Sutherland, Handbook of Nonlinear Optics (New-York: Marcel Dekker) p-256, 1996.
[22] K. Clays, E. Hendrickx, M. Trient, A. Persoons J. Mol. Liq. **67,** 133 (1995).

---

[*] Corresponding author: jagdish@physics.unipune.ernet.in