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Study of Non Linear optical properties of Fe doped CdSe nanoparticles

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ABSTRACT

Fe doped CdSe nanoparticles were synthesized by Co-Precipitation method. Optical, Structural, Morphological studies were carried out by UV-Vis spectroscopy, Fluorescence spectroscopy, FTIR and Scanning Electron Microscopy (SEM). Inecrease in band gap, fluorescence quenching and red shift of fluorescence peak position was observed with increasing dopant (Fe) concentration in CdSe. Absorption spectra of undoped CdSe, Fe doped CdSe QDs exhibits a blue shift as compared to the bulk CdSe which indicates clearly the quantum confinement effect. The nonlinear optical parameters viz. nonlinear absorption coefficient (β), nonlinear refractive index (n_2) and third order nonlinear susceptibilities (χ^3) of quantum dots have been estimated using second harmonic of Nd:YAG laser. The study predicts that CdSe:Fe quantum dots exhibits strong non linearity as compared to core CdSe nanoparticles.

Keywords: Co-Precipitation, fluorescence quenching, nonlinear absorption coefficient, nonlinear refractive index, susceptibility

INTRODUCTION

Nanosized semiconductor materials have gained much attention in this decade owing to their structural, optical and physical properties which are different from those of their bulk counterparts. CdSe is one among the II-VI semiconductors with wide band gap (1.74 eV) at room temperature and Bohr exciton radius ≈ 5.6 nm[2]. Pure and doped semiconductor QDs are extensively investigate to obtain basic knowledge on impurity states in QDs and to examine their potential applications in novel optical devices.[1] By doping with an impurity element fine band gap tuning can be achieved which modifies various properties of nanoparticles[3]. The study of nonlinear optical properties of pure and doped semiconductor QDs, with large third order nonlinear susceptibility are of great interest, due to their possible application in future high-capacity communication networks, optoelectronics and photonic devices[4]. We have synthesized Fe doped CdSe nanoparticles using thioglycolic acid as a capping agent by co precipitation method, and characterize them by FTIR, SEM, UV-VIS and Fluorescence Spectroscopy. Investigation of their nonlinear optical properties such as nonlinear absorption, refraction coefficients and $\chi^{(3)}$ have been done with the help of Z-scan experimental setup using a Nd:YAG laser (at 532 nm).

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EXPERIMENTAL DETAILS

Materials

Cadmium dihydrate $CdCl_2 2H_2O$, Selenium Powder, Sodium Borohydride ($NaBH_4$) thioglycolic acid (TGA) and Ferric chloride have been purchased from Hi Media. HPLC grade water with resistivity of 18MΩ $cm^{-1}$was used for the preparation of aqueous solutions.

Instrumentation

UV–visible absorption spectra were recorded on a Varian UV–vis spectrophotometer (Cary 5000). Fluorescence emission spectra were collected on Varian fluorescence spectrophotometer (Cary Eclipse Varian 3315), where an excitation wavelength of 400 nm was used for all the measurements reported here. The morphology of QDs was determined using scanning electron microscope (SEM) (Microtech semtrac mini). The nonlinear optical properties of QDs in deionized water were measured using Nd:YAG (Quanta System, HYL-101) laser at ~532nm wavelength.

Synthesis of QDs

Cadmium acetate of molar concentration 0.05M was dissolved in 40ml ultra pure deionized water and stirred vigorously for 1 hour with constant heating at 60-70^0 C. Ferric chloride were added to cadmium acetate solution (1% by weight) under vigorous magnetic stirring, followed by addition of 0.5ml TGA to obtain the milky white solution. After 30 min under same conditions 40ml NaHSe solution of optimum molarity was added quickly to obtain colored solution. NaHSe solution was prepared by adding Sodium Borohydride and Se powder in 4 mL distilled water in the ratio 4:1. The reacting system was cooled to 0ºC, in dark. To discharge the pressure from the hydrogen gas, resulting

during the reaction a small outlet connected to the flask was kept open. The precipitates were collected and centrifuged to separate quantum dots from the reaction medium, washed repeatedly with ethanol followed by distilled water to remove impurities and then further characterization were carried out. QDs so obtained were stored at 4°C to prevent the agglomeration.[5]

Z-scan technique

The schematic diagram of Z-scan experiment setup used to measure the non linear refractive index and TPA of the QDs is shown in Fig. 1. The Z- scan has been performed using second harmonic of Nd:YAG laser at wavelength (λ=532nm) with Gaussian beam having 10 Hz repetition rate and pulse width of 5ns and maximum 200mJ per pulse energy. The laser beam was focused by using a convex lens with focal length of 20 cm. The samples have been translated along the z direction and the transmitted intensity has been detected using silicon photo detector (Thorlabs, DET-110). The output has been recorded by digital storage oscilloscope (Tektronix, TDS-2024). An aperture of 4mm has been employed to capture on axis fluence. The calculated beam waist (w_0) is 32.45µm which gives Rayleigh range z_0 equal to using the relation $z_0 = k\, w_0^2/2$ where $k=2\pi/\lambda$ is a wave vector. A typical peak power density was ~ 0.761×10^{12} W/cm^2. In this technique, the sample is scanned along the optical axis in the focal region of the laser beam.

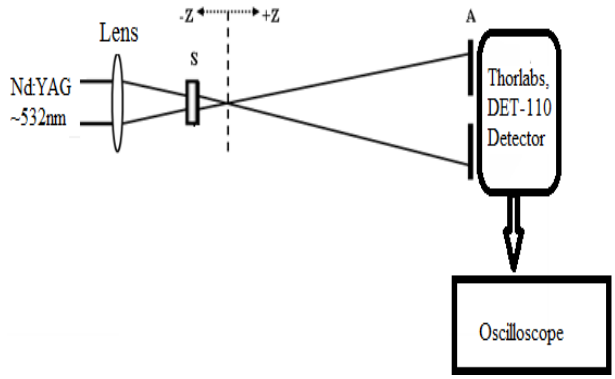

Figure 1 Z-scan Experimental set up

RESULTS AND DISCUSSION

SEM Measurements

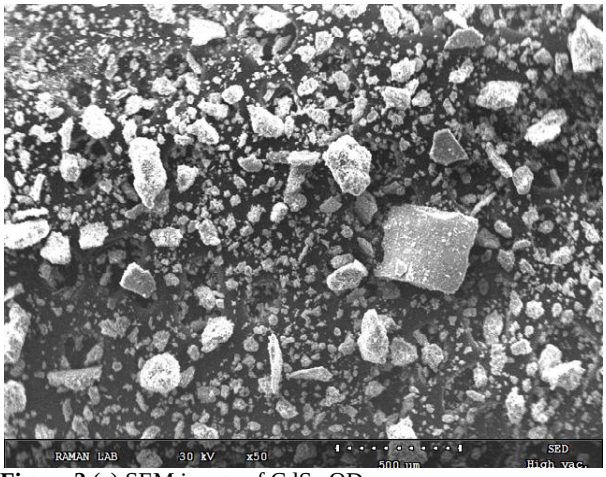

Figure 2 (a) SEM image of CdSe QDs

SEM images shows that QDs are spherical in shape.

FTIR Analysis

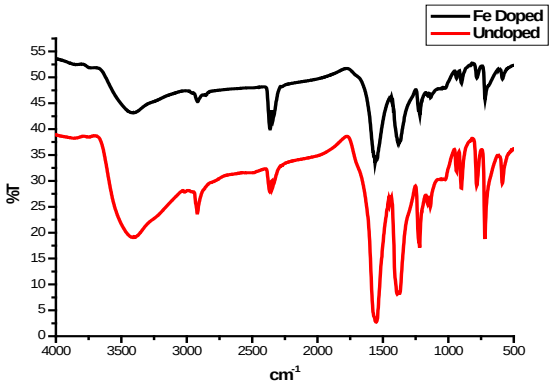

Figure 2 (b) FTIR spectra of CdSe and Fe doped CdSe QDs

To investigate the interaction between TGA and CdSe QDs, the FTIR spectrum was recorded for QDs. A broad absorption band nearly at 3464 cm^{-1} is assigned to O–H vibration of the absorbed H_2O. An absorption band due to S–H vibration at 2560cm^{-1} is absent. The characteristic absorption band of C=O vibration shifts from 1700 cm^{-1} to 1572cm^{-1}. Band at 1396 cm^{-1} is due to stretching vibration of C-OH bond in the carboxyl group of TGA. The absorbed band at 1126 cm^{-1} corresponds to C-O vibration. Band at 722cm^{-1} is assigned to Cd-Se bond which becomes weaker and weaker with increased concentration of dopant. These results strongly suggest that the thiol groups of TGA coordinate with Cd^{+2} ions on the QDs surface, and the hydrophilic hydroxyl groups face outward, making QDs water-soluble.[6]

Optical Measurements

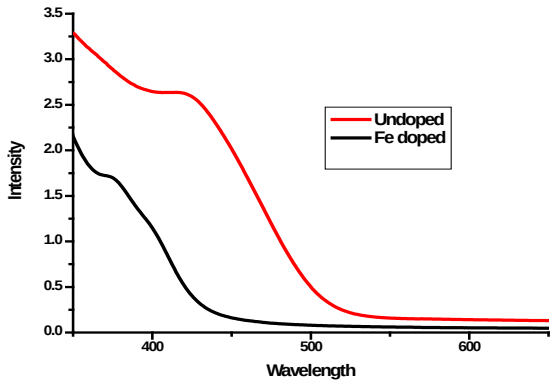

Figure 3(a) Absorbance spectra of CdSe and Fe doped CdSe QDs

Figure 3(a) shows the absorption spectra of pure and Fe doped CdSe nanoparticles. The absorption spectra of pure as well as Fe doped CdSe nanoparticles show a clear blue shift in absorption edge as compared to their bulk counterpart. Quantum confinement of an electron-hole pair (exciton) may be responsible for the observed blue shift in the absorption spectra.

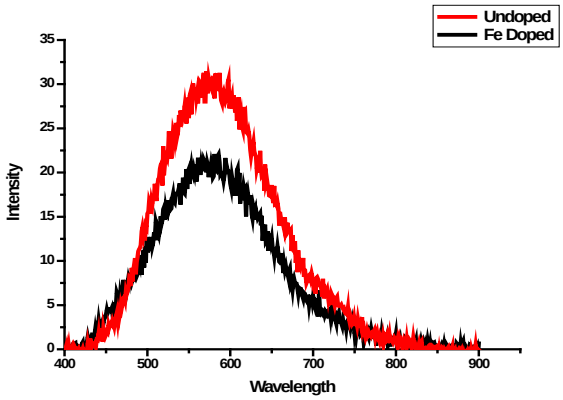

Figure 3 (b) Emission spectra of CdSe and Fe doped CdSe QDs

Figure 3(b) shows the room temperature PL spectra of Fe-doped CdSe nanoparticles. The emission peak centred at 570nm which is shifted to 590nm due o incorporation of Fe ions. Fe dopant occupies the Cd lattice site and behaves as a trap site for charge carriers[7].

Optical Band gap of QDs have been calculated from tauc's plot and found to be to be 2.44 eV & 2.62 eV for CdSe and CdSe:Fe QDs respectively. This blue shift of the band gap in comparison with bulk one (1.74 eV) takes place because of the quantum confinement effects.

The particle size of QDs was determined using Brus equation based on Effective mass approximation formula[8] (EMA).

$$E_g = E_{bulk} + \frac{h^2}{8R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.786e^2}{4\pi\epsilon_0\epsilon_r R} \qquad (1)$$

Where, E_g= band gap energy of quantum dot, E_{bulk} = band gap energy of bulk semiconductor, R = radius of quantum dot, m_e^*= effective mass of excited electron, m_h^*= effective mass of excited hole, h= Planck's constant. Calculated particle size was nm 4.1 & 3.5nm for CdSe and CdSe:Fe QDs.

The linear refractive index of QDs is given as[9]

$$n_{0\ CdSe\ (QDs)} = \sqrt{1 + \frac{(\varepsilon_{bulk} - 1)}{1 + \left(\frac{0.75}{D}\right)^{1.2}}} \qquad (2)$$

Where, ε_{bulk} = 6.2 is the dielectric constant of bulk CdSe and D is the average diameter of QDs in units of nm[10].

Table 1Results based on Absorption spectra

Samples	Optical band gap (eV)	Size of quantum dots (nm)	Linear refractive index(n_0)
CdSe	2.34	4.1	2.36
CdSe:Fe	2.62	3.4	2.37

Non Linear studies

The single beam Z-scan technique is used to estimate the nonlinear parameters viz. the nonlinear refractive index (n_2) and the nonlinear absorption coefficients (β). The parameter ΔTp-v has been determined as the difference between maximum and minimum transmittances.[11]

$$\Delta Tp\text{-}v = 0.406(1-S)^{0.27}|\Delta\phi| \qquad (3)$$

Here, S is the aperture transmittance and $|\Delta\phi|$ is the on axis non linear phase shift.

The nonlinear refractive index (n_2) is calculated by relation

$$n_2 = |\Delta\phi|/kI_0L_{eff} \qquad (4)$$

Here k is wave vector, I_0 is the intensity at focus, $L_{eff} = (1-e^{-\alpha L})/\alpha$ is the effective length of the sample, L is sample length, α is linear absorption coefficient.

By determining the normalized transmission difference (ΔT) in the open aperture Z-scan the nonlinear absorption coefficient (β) can be evaluated through the relation[12],

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}}$$

For non resonance excitation, real part of the third-order nonlinear susceptibility related to the nonlinear refractive index (n_2) and the imaginary part of the nonlinear optical susceptibility related to the nonlinear absorption coefficient (β)as following equations[10]

$$Re\chi^3(esu) = \frac{10^{-4}\varepsilon_0 c^2 n_0^2}{\pi} n_2(cm^2/w)$$

$$Im\chi^3(esu) = \frac{10^{-2}\varepsilon_0 c^2 n_0^2 \lambda}{4\pi^2}\beta(cm/w)$$

Where, n_o is the linear refractive index, c the velocity of light and ε_0 is the vacuum permittivity. The absolute value of third order nonlinear susceptibility (χ^3) is calculated by

$$\chi^3(esu) = \sqrt{(Re\chi^3)^2 + (Im\chi^3)^2}$$

Figure 4, 5 gives the closed-aperture and open aperture Z-scan traces of undoped and doped CdSe QDs at an intensity of 0.76TW/cm^2 for an irradiation wavelength of 532 nm. The closed-aperture curve exhibits a peak valley signature, indicating a negative value of the nonlinear refractive index n_2. It is observed that the peak valley signature of closed aperture Z-scan satisfied the condition $z \sim 1.7z_0$, thus confirming the presence of pure electronic third-order nonlinearity[13]. Peak valley signature of CA z-scan, indicates self-defocusing effect and negative non linear refractive index in QDs. Non linear refractive index changes its sign at $\hbar\omega/E_g$=0.69.[14] The optical region we studied corresponds to values of $\hbar\omega/E_g > 0.80$ so we have negative non linear refractive index. We can expect positive non linearity in these QDs at λ> 800nm.

The open aperture Z- scan curve exhibits a normalized transmittance valley, indicating the presence of reverse saturable absorption (RSA) in the QDs. Interestingly, undoped CdSe QDs show a minimum nonlinearity, while Fe doped CdSe QDs clearly exhibit a larger induced absorption behavior.

Table2: Nonlinear parameters evaluated using Z-scan experimental data

Sample	T PA coefficient (β) (cm/W)	refractive index(-n_2) (cm^2/W)	Susceptibility (χ) (esu)
CdSe	2.7×10^{-12}	8.3×10^{-17}	1.3×10^{-18}
CdSe:Fe	1.7×10^{-11}	4.7×10^{-16}	8.4×10^{-17}

Table 2 shows the values of nonlinear parameters obtained by closed and open aperture Z-scan data. The calculated nonlinear parameters (n_2, β) show fairly high values of nonlinearity at such a high intensity. Results clearly indicate that the values of nonlinear parameters are greater for Fe doped CdSe than undoped CdSe. This may be attributed to large optical band gap and its small size due to which concentration of excitons on the surface increases.

CONCLUSION

Nonlinear optical properties of CdSe and CdSe:Fe QDs have been studied in nanosecond regime using ~532nm laser sources with help of z scan technique. The nonlinear properties of CdSe:Fe QDs have been found stronger than core CdSe QDs may be due to large optical band gap and its small size due to which concentration of excitons on the surface increases. In this study we found that Fe doped QDs are best nonlinear material which can acts as a RSA based optical limiter and can be used for sensor protection applications and the development of optoelectronics and photonics devices. We have found that the doped CdSe QDs can be regarded as potential material for such applications.

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