

ELECTRO- AND PHOTO-LUMINESCENCE STUDIES OF CdS NANOCRYSTALS PREPARED BY ORGENOMETALLIC PRECURSOR

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The optical and electrical properties of semiconductor nanoparticles are strongly dependent on their size. Here we report the size dependence of photo- and electro luminescence of CdS nanocrystals prepared by single source organometallic precursor. The precursor was prepared by dissolving CdCl₂, thiourea and NaOH in ethanol. The mixed solution was kept at 60°C and samples were extracted at different reaction times. The samples were characterized by transmission electron microscopy and x-ray diffraction. For shorter reaction time small CdS nanocrystals are obtained, which exhibit blue- shift in absorption edge. In PL spectra one peak is observed at 528 nm. peak may be attributed to shallow bound excitons. Electroluminescence (EL) studies show that the light emission starts at some threshold voltage and increases rapidly with increasing applied voltage. It is seen that smaller CdS crystals give electroluminescence of higher brightness starting at lower threshold voltage. It seems that the EL in CdS nanoparticles arises due to the high electric field, in which band bending causes release of trapped electrons and their subsequent recombination with holes give rise to the light emissions.

(Received

Keywords: CdS nanocrystals; Photoluminescence; Electroluminescence.

1. Introduction

Nanostructured materials have been the subject of intense study for last several years, due to their size dependence physical and chemical properties below a critical size- characteristic of the material. Surface atoms have different environment and therefore exhibit different characteristics. Nanoparticle have a large number of surface atoms compared to the bulk, therefore, the characteristics of surface atoms have more contribution towards their properties. Due to finite size of the nanocrystals the continuous energy band of the bulk crystal transforms into a series of discrete states resulting in widening of the effective band gap. Blue shift in the optical absorption spectra, size dependent luminescence, enhanced oscillator strength and nonlinear optical effect is some of the interesting properties exhibited by these nanocrystals.

Semiconductor nanoparticles have been extensively investigated during the last decade, due to their unique properties and application in diverse area such as solar cell, display panel and new devices like single electron transistor and so on[1-3]. Among these, CdS is a widely used substance with many advanced technological application. It is a direct band gap material of energy band gap 2.42 eV at 300 K. For nanoparticles, the size and surface effect are both important [4]. By controlling these, it is possible to design materials of required optical, magnetic, elastic and chemical properties. The synthesis of highly monodispersed CdS nanocrystals via size restricting growth modes, eg: by adding surface capping organic materials to the solution has opened the way towards tunable light emitting devices and low voltage display. One of the highly cited methods for making CdS or CdSe quantum dots is organometallic precursor. Well defined molecules

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containing both the group II element and the group VI element as a single source precursor can be decomposed to produce II-VI quantum dots [5-6].

Though there are many reports on luminescence of CdS nanoparticles, but a few have studied electroluminescence in these [7-9]. In the present work CdS nanocrystals of different sizes have been synthesized by organometallic precursor and their photoluminescence as well as electroluminescence have been investigated. This research could also provide important information about the trap emission in CdS nanoparticles and dependence of electroluminescence on the applying voltage.

2. Experimental

Thermolysis of single source organometallic precursor is very simple and low cost method for high quality nanoparticles. Single source containing cadmium and sulfur precursor is thermally unstable and decompose to CdS nanocrystals. The growth of CdS crystals has been restricted by the reaction time. All the chemicals used were of analytical grade and they were used as received without further purification. All the experiments were conducted under air atmosphere. The CdS nanocrystals of various sizes were prepared by single source organometallic precursor in noncoordinating solvent ethanol [10]. The precursor solution A was prepared by dissolving 36 mg cadmium chloride ($\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$) and 12 mg of thiourea $[(\text{NH}_2)_2\text{CS}]$ in 30 ml ethanol at 60°C in water bath under magnetic stirring. Another solution B was prepared by dissolving 10 mg sodium hydroxide (NaOH) in 10 ml ethanol. Now the solution B was added into solution A. The mixed solution was kept at 60°C under magnetic stirring. In the beginning a white solution was obtained, which gradually become transparent and the colour changed from white to green yellow. The solution samples were extracted from the mixture solution at different reaction times, centrifuged and washed with ethanol and then with acetone, and dried to obtain nanocrystalline CdS powder. Five different samples CdS I, CdS II, CdS III, CdS IV and CdS V were prepared with 20, 30, 60, 80 and 90 min reaction time, respectively.

The samples were examined by TEM and XRD at Inter University Consortium (IUC) Indore. The TEM images were obtained using Techani 20 G² electron microscope. The X-ray diffraction patterns of powder samples were recorded by Philips X ray diffractometer with irradiation from $K\alpha$ line of copper ($\lambda=1.5406 \text{ \AA}$). The ultraviolet- visible absorption spectra of powder sample were recorded by a Perkin Elmer λ -12 spectrometer. The photoluminescence spectra of the samples were carried out by a Perkin Elmer LS-55 fluorescence Spectrometer.

The cells for electroluminescence (EL) investigations were fabricated by depositing emissive layer of DMSO dispersed CdS nanoparticles on SnO_2 coated conducting glass plate. The conducting glass plates were prepared by depositing a layer of SnO_2 over heated glass plates using chemical vapour deposition technique. A thin mica sheet having small window of $2 \times 2 \text{ mm}^2$ was fixed over emissive layer of CdS nanoparticles. An aluminium electrode was used as another electrode.. For electroluminescence studies A.C.voltage of various frequencies was applied at conducting glass plate and aluminium electrodes using EL power supply along with audio frequency generator. EL brightness at different voltages and frequencies was measured by a photomultiplier tube connected to a picoammeter. EL spectra were obtained with the help of grating monochromator and photomultiplier tube.

3. Results and discussion

Fig. 1 (a) shows a typical TEM image of CdS III samples. It indicates nearly spherical CdS nanocrystals. The average crystal-sizes obtained by TEM for various samples are given in column III of Table 1. Fig. 1(b) shows the selected area electron diffraction (ED) pattern of the sample. It is seen that the close packed plane is perpendicular to the field of view. These ED patterns clearly indicate the development of lattice ordering in the CdS nanocrystals.

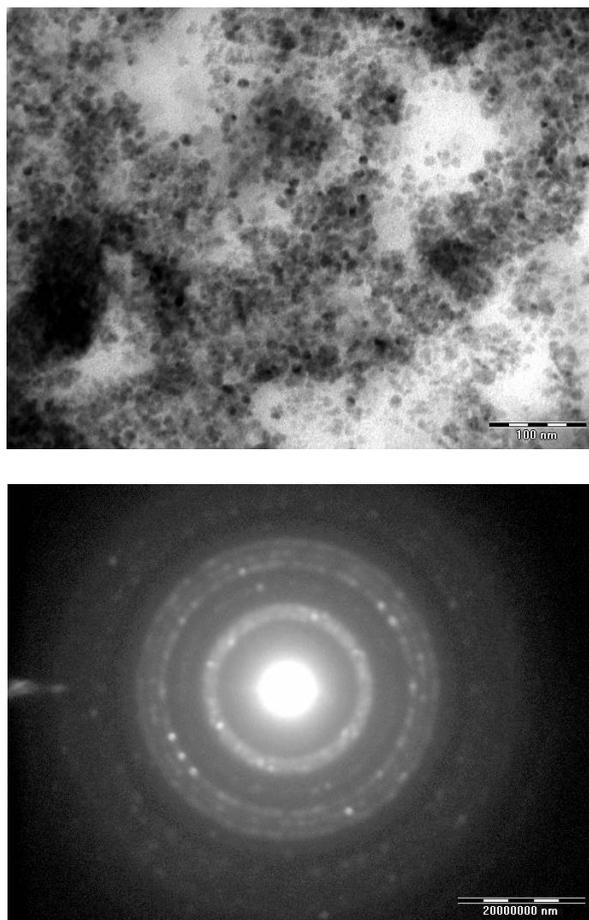


Fig. 1 (a) TEM Image of CdS II Samples Nanoparticles Fig. 1(b) ED pattern of CdS II Samples Nanoparticles.

Table 1. Size of CdS nanoparticles by various techniques.

| S. No. | Reaction time (in min) | Size by TEM (in nm) | Size by XRD (in nm) | Absorption Edge (in nm) | Size by abs. Edge (in nm) |
|--------|------------------------|---------------------|---------------------|-------------------------|---------------------------|
| I | 20 | 5 | 7 | 470 | 5.7 |
| II | 30 | - | - | 480 | 6.6 |
| III | 60 | 7 | 9 | 490 | 8 |
| IV | 80 | 9 | - | - | - |
| V | 90 | - | 12 | 500 | 11 |

The XRD patterns of CdS samples are shown in Fig. 2. From the figure it can be seen that the XRD pattern of CdS can be consistently indexed on the basis of the hexagonal, wurtzite structure [11] with lattice constant $a = 4.121$, $c = 6.682$, in which the six prominent peaks at 2θ values of 24.4° , 26.7° , 28.4° , 44° , 47.8° and 51.9° angles corresponds to the reflections at (100), (002), (101), (220) (103) and (112) planes. The weak peak due to (102) plane was also observed. The XRD patterns exhibit hexagonal structure with similar peaks.

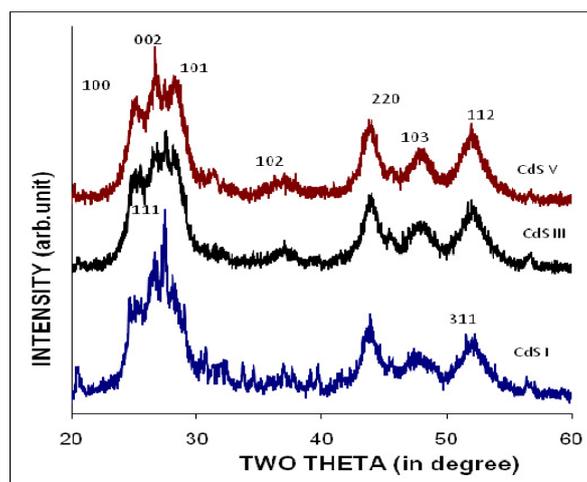


Fig. 2 XRD patterns of CdS nanocrystals

XRD studies indicated that the particle size is reduced with decreasing reaction time period. It is known that the XRD peaks intensity decreases and width increases with decreasing crystalline size. The broadening of XRD peaks can be qualitatively expressed by Debye Scherrer's formula [12].

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where D is average crystal size, λ is wavelength of X-rays used. β is the full width at half maxima (FWHM) of the XRD peak, θ is Bragg angle and K is the shape factor, which has the value close to unity. The average crystal size was computed from the broadening of peak at $2\theta = 44^\circ$ corresponding to (220) plane using equation (1) and it is given in column IV of Table 1. Banerjee et al [13] have also reported XRD of CdS nanoparticles. They have found that small CdS nanocrystals are cubic in nature. The structure transform from cubic to hexagonal phase as the crystal size increases.

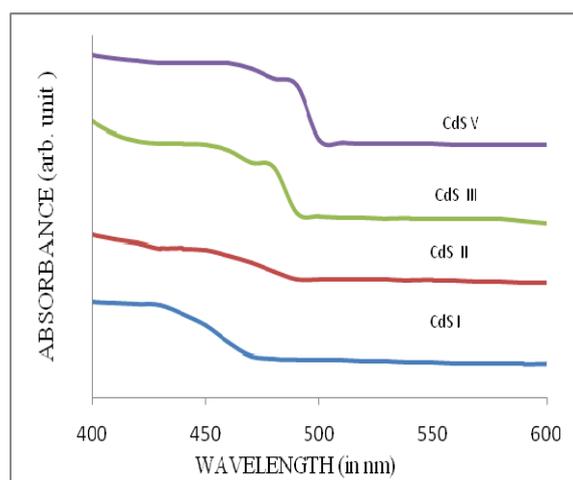


Fig. 3 Absorption Spectra of CdS nanocrystals.

The optical absorption spectra for the samples are shown in Fig. 3. CdS is a direct band gap material, which has the band gap energy ~ 2.42 eV. From the figure it is clear that the absorption edge for all the samples is blue shifted as compared to that of bulk CdS. For CdS V sample, the absorption edge is nearly equal to that of the bulk CdS. The blue-shift in the absorption edge

indicates increase in effective band of the samples. The shift in absorption bands can be understood as the longer the reaction time, the lesser cadmium ion rich surface, and therefore, the bigger the particle in solution. The increase in band gap in nanoparticles due to quantum confinement has the quantitative form [14].

$$\Delta E_g \equiv E_g(\text{ncno}) - E_g(\text{bulk}) = \frac{h^2}{8MR^2} \quad (2)$$

where h is Planck's constant, R is the radius of the particle and M is the effective mass of the system. Equation (2) can be used to estimate size of the particle taking proper value of M and increase in band gap obtained from blue shift in absorption edge. For hexagonal CdS, $M=1.919 \times 10^{-31}$ Kg [13]. The absorption edge for samples and their particle size from equation (2) are shown in column V and VI of Table 1. The red shifting in absorption edge by increasing reaction time reveal that the size of the CdS nanoparticles was increased; this is in good agreement with XRD and TEM, observation.

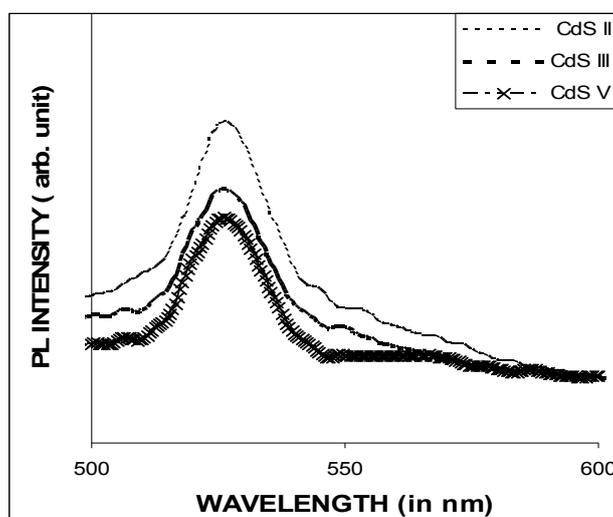


Fig. 4. PL Spectra of CdS nanocrystals

Photoluminescence (PL) studies provide information of different energy states available between valence and conduction bands responsible for radiative recombination. Figure 4 shows PL spectra of various CdS samples. Photoluminescence excited by 390 nm. In the PL spectra of CdS nanocrystals, band edge luminescence was not detected. One PL peaks has been observed, at 528 nm. This peak can be attributed to the second ionization states of sulfur vacancy (V_s^+ / V_s^{2+}) [15]. Compareli et al and Zang et al [16-17] have also reported a weak broad emission peak at $\lambda = 540$ nm which is attributed to recombination via surface localized states. This peak becomes much more intense with smaller reaction time period. In the case of the larger CdS cluster, the Stokes shifted luminescence are attributed to mid gap states [18]. These indicate a larger Franck-Condon displacement in the excited states. These results indicate that the preparation method is not sufficiently effective for removing surface defects of CdS. The reduction of luminescence intensity with increasing reaction time period is interpreted as due to removal of sulfur anion vacancies. The observation that the nature of emitting states change as the cluster size decreases, as the cluster size decreases the, increased band gap makes certain defect states energetically accessible, i.e, the number of surface states increased, therefore increasing luminescence intensity with shorter reaction time.

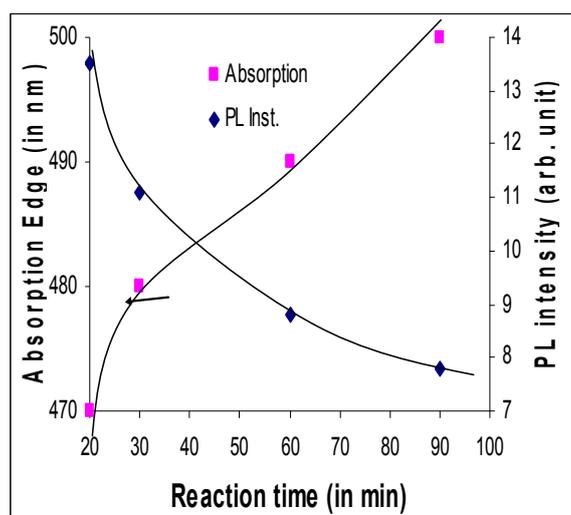


Fig. 5 Variation of absorption edge and PL intensity with reaction time.

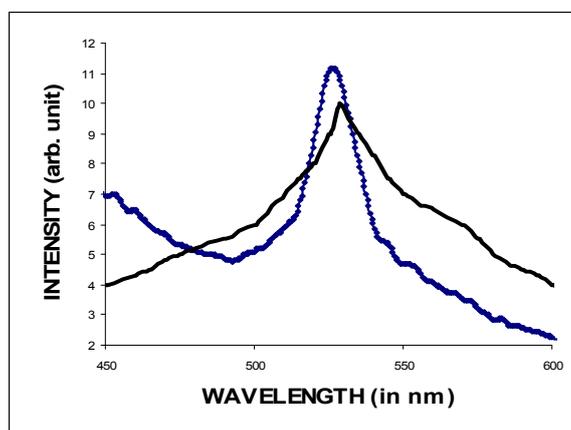


Fig. 6 EL Spectra of CdS II Samples.

The change in wavelength corresponding to the absorption edge, and variation of PL intensity of peaks with the reaction time are indicated in the Figure 5. In case of absorption edge wavelength which reveals that the growth of CdS nanoparticles. In which the larger nanocrystals grew at the expense of smaller nanoparticle whose size was below the critical size, inducing the wider size distribution of CdS nanocrystals. PL peak intensity increases with shorter reaction time. The impurity states in the CdS samples are similar to these in bulk CdS, because the size of CdS nanoparticles is larger than the exciton Bohr radius (3.6 nm) of bulk CdS.

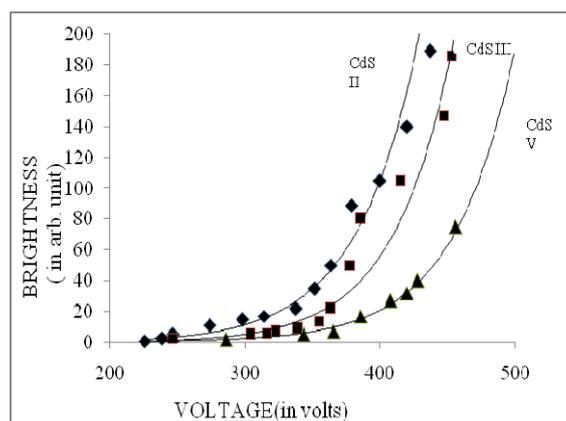


Fig. 7. Voltage Brightness curve of Curve of CdS Nanocrystals

Fig. 6 shows the electroluminescence and photoluminescence spectrum of CdS II samples. The room temperature EL Spectrum is nearly identical to the PL with same peak position. The EL is broader than the PL. This is probably due to local joule heating from the large current flux and poor thermal conductivity [19]. The correspondence between EL and PL spectra indicates that particles EL and PL from the same states. The light emission from EL cell was obtained for voltage above 200 V. Figure 7 shows EL brightness versus voltage curve for various samples. It is observed that EL starts at a threshold voltage and then increases first slowly and then rapidly with increasing voltage. The lower threshold and higher brightness have been observed for samples prepared from shorter reaction time. As voltage is increased, more electrons and holes are injected into the emission layer and their subsequent recombination increases the EL brightness. For shorter reaction time smaller CdS nanoparticles are obtained having increased oscillator strength, which improves the electron-hole radiative recombination and enhances the electroluminescence. It is observed that at higher frequencies, light emission starts at lower threshold voltages, and electroluminescence brightness increases with increasing frequency. The nature of frequency dependence of EL brightness can be understood on the basis that the emptying and detrapping of EL centers more rapidly with increase in frequency. The current-voltage characteristics of EL cells are shown in Figure 8. The linear relation between current and voltage indicates the ohmic nature.

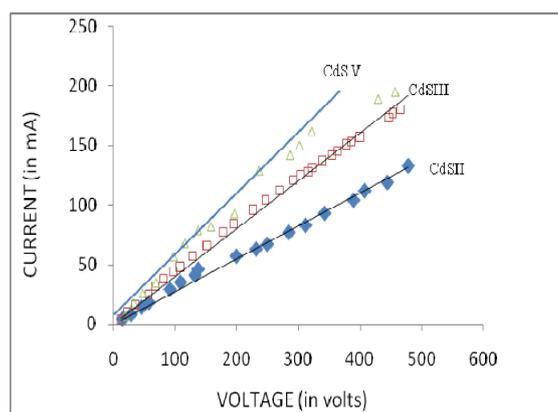


Fig. 8. Voltage Current Curve of CdS Nanocrystals

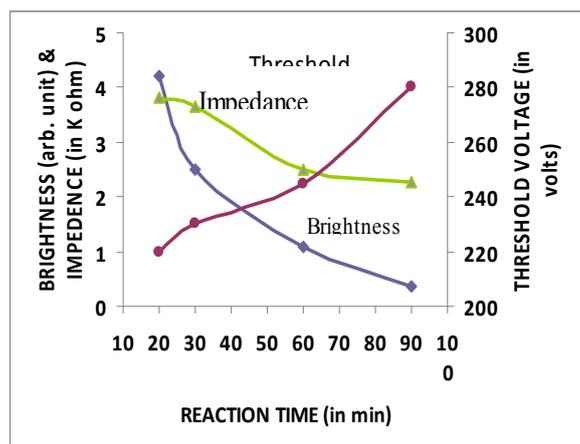


Fig. 9 Variation of Threshold Voltage and Brightness with Reaction time

The effect of reaction time on the EL brightness, threshold voltage and impedance are shown in Figure 9. It can be seen from the figure that the threshold voltage and impedance of cell increases slightly with reaction time but EL brightness is reduced sufficiently. This reveals that small particles formed by shorter reaction time give higher EL brightness at lower threshold and with lower impedance.

In fact, we have observed the high field EL in CdS nanoparticles. In this case bending of bands takes place and release of electrons from traps to the conduction bands and their subsequently recombine with the hole centers, give rise to the light emission. If electron moving in the conduction band recombines with holes in valence band, then edge emission is observed. On the other hand, if the electron moving in the conduction band recombines with the holes trapped in impurity centers, then the light emission characteristics of the defect centers are observed.

4. Conclusions

The Studies have shown that CdS nanoparticles can be prepared by single source organometallic precursor based on low temperature (60°C) thermolysis. The sizes obtained are, in general, bigger than exciton Bohr radius (3.6 nm). The size of particles increases with increasing reaction time. The sizes observed by TEM, XRD and from the blue shift in the absorption edge are nearly in agreement with each other. One PL peak is observed at 528 nm, which can be attributed to the second ionization states of sulfur vacancy (V_s^+ / V_s^{2+}). The peak becomes intense for smaller CdS nanocrystals. EL studies have shown lower threshold and higher brightness for smaller particles. Linear current–voltage characteristics have indicated ohmic nature and lower impedance in case of smaller particles. The correspondence between EL and PL spectra indicates that particles EL and PL from the same states.

Acknowledgements

Authors are thankful to Madhya Pradesh (M.P.) Council of Science & Technology, Bhopal for financial support, IUC Indore for TEM and XRD characterization of the samples and Nanophosphor laboratory, Allahabad for photoluminescence spectra.

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