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Synthesis of CdS Nanoparticles by Chemical Co-precipitation Method and its Comparative Analysis of Particle Size via Structural and Optical characterization

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ABSTRACT

In this study, CdS Nanoparticles (NPs) have been prepared successfully by chemical co-precipitation method, using cadmium acetate and sodium sulphide as precursors. A comparative study of average particle size calculated by Scherrer Plot, Uniform Deformation Model (UDM), Dynamic Light Scattering (DLS) analysis and Brus Model has been done here. The structural and optical behaviour of synthesized samples were investigated via X-ray diffraction (XRD), DLS and UV–Visible Spectroscopy. The XRD spectra of the prepared CdS NPs revealed the crystalline phase having cubic structure. The average particles size has been studied via Debye Scherrer equation and Scherrer Plot. For the theoretical calculations of particle size along with the induced lattice strain, considering the broadening effect of lattice strain, Williamson-Hall analysis was employed. Assuming the lattice strain to be isotropic in nature, UDM was applied for calculation. The particles size distribution profile in terms of volume as well as intensity was recorded using DLS analysis in ethanol medium at room temperature. Besides this, the energy bandgap was obtained by applying Tauc model in the recorded absorption spectra and he obtained value of bandgap was used in Brus model for estimating the average particle size.

Introduction

Nano-engineered semiconductors have attained significant popularity and still are the major subject of investigation over the past few decades [1-2]. The appreciable structural and optical behaviour of these semiconductors arises due to the quantum confinement effect and their size in nanometer range which is different from their conventional bulk crystals [3-4]. In view of the novel properties, this kind of materials have potential application in luminescent devices, quantum dot laser, solar energy converters, super capacitor, optoelectronics, photocatalytic devices, chemical sensors, field effect transistors, etc [5-8].

CdS is an interesting binary Chalcogenide material, which is most widely studied among II-VI n-type semiconductors. Due to its wide energy bandgap of 2.42 eV at room temperature, it is considered as an important and promising material for the optoelectronic application like solar cell, laser, photodiode, light emitting diode, photo detectors, etc [9-10]. CdS as a semiconductor provides a variety of advantages like fabulous chemical stability, bandgap tunability, favourable electronic and optical properties and easy synthesis process [11]. Due to the ease of preparation, CdS has been mainly explored in the form of nanoparticles imparting versatile properties to it. There are a range of methods for the synthesis of CdS nanoparticles such as chemical co-precipitation method, spray pyrolysis, sol-gel method, microwave assisted method, Thermolysis, hydrothermal method and photochemical method [12-16]. Among these chemical co-precipitation method is one of the most convenient, fast and green approach for the synthesis of CdS nanoparticles [11].

In presented study, we have synthesized CdS nanoparticles via chemical co-precipitation method using cadmium acetate and sodium sulphide as precursors. Furthermore, we investigated the average particle size via Scherrer formula. Assuming the isotropic nature of strain, the strain analysis was done via UDM plot using the broadening of XRD spectra. Besides this, DLS analysis and Brus Equation calculation were done to estimate the average particles size distribution along with energy bandgap of CdS nanoparticles. In addition, this study gives the information regarding the size dependent lattice strain and the band gap.

Experimental Method

Reagents and Materials Used:

All the chemicals reagents used for the synthesis of CdS nanoparticles were of analytical grade and used directly without further purification. Cadmium acetate ($Cd(CH_3COO)_2.2H_2O$), sodium sulphide (Na_2S), ethanol, acetone, hydrochloric acid and nitric acid were purchased from Merck. Deionized water was used for preparing a range of molar solution. To ensure the absence of contaminations, all the glasswares were treated with a mixture of concentrated nitric acid and hydrochloric acid, and washed thoroughly prior the initiation of synthesis.

Preparation of CdS Nanoparticles:

The CdS nanoparticles were prepared using chemical co-precipitation method. In a typical experiment, molar solution of cadmium acetate and sodium sulphide is prepared using the deionized water. The molar solution of cadmium acetate is kept on a magnetic stirrer for

continuous stirring at 700 rpm at room temperature. The molar solution of sodium sulphide is loaded in a clean burette whose nozzle is fixed just above the conical flask containing the cadmium acetate solution. After the continuous stirring of cadmium acetate solution for 20 minutes, sodium sulphide solution was added to the cadmium acetate in a dropwise manner which takes almost 1 hour. The precipitates start forming as soon as the drop of sodium sulphide falls into the cadmium acetate. The chemical reaction taking place is shown by the equation below:

$$Cd(CH_3COO)_2 + Na_2S \longrightarrow CdS + 2CH_3COONa \quad (1)$$

The whole yellowish colloidal solution containing the precipitates is kept on the stirrer for 6 hours at the temperature of 70° C. The obtained solution is washed several times using ultracentrifuge at 5000 rpm with plenty of ethanol for the removal of other salts present in it. The final obtained residue is dried for 2 hours at 60°C to get the fine powder CdS nanoparticles.

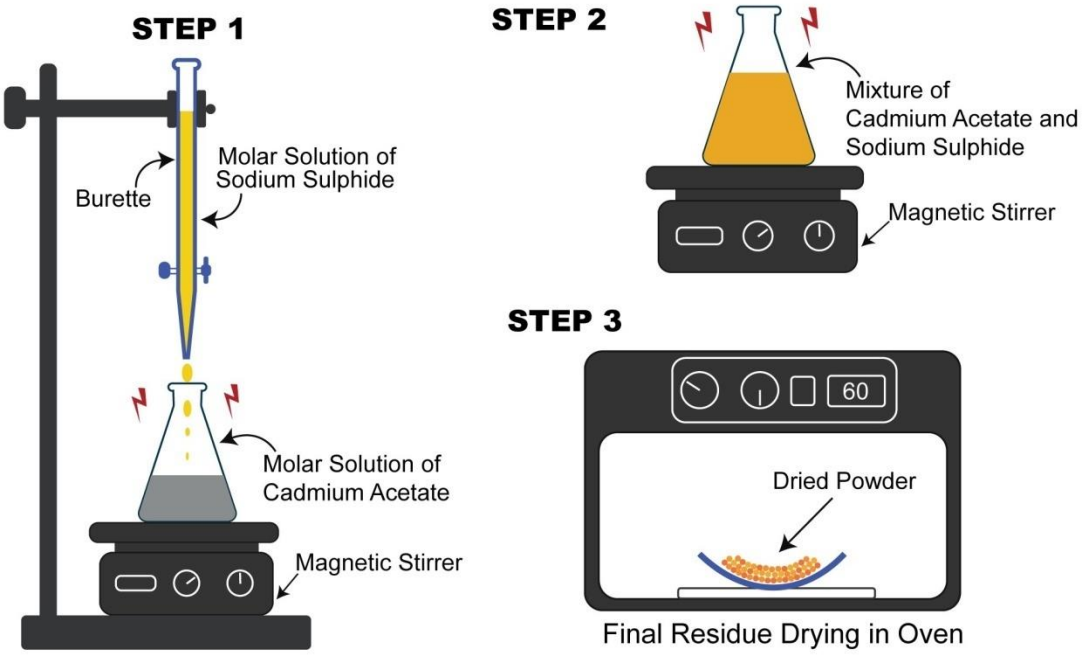

Figure 1. Steps involved during the synthesis of CdS nanoparticles via chemical co-precipitation method

Characterization Techniques:

For the structural and optical characterization of the prepared CdS nanoparticles; X-Ray Diffraction, Dynamic Light Scattering and UV-Visible Spectroscopy were performed.

Structural Characterization: The X-ray diffractometer (RIGAKU) with copper target emitting Cu K_α radiation (wavelength=1.54 Å) was used to record the diffraction pattern in the 2θ range 20° to 60° at room temperature. The intrinsic structural behaviour of the synthesized CdS nanoparticles has been examined through powder x-ray diffraction technique. The

recorded XRD spectrum of the sample gives the intrinsic crystallographic information like crystallinity, phase, grain size, interplanar spacing, lattice parameters, etc.
The interplanar spacing between the atomic layers was calculated using Bragg's law, mathematically expressed as

$$n\lambda = 2d\sin\theta \quad (2)$$

Where n is the order of diffraction, d is the inter planar spacing between the atomic layers, λ is the wavelength of incident x-ray beam (1.54 Å) and θ is the diffraction angle. The lattice parameters of the sample were easily calculated. The angles between the edges along x, y and z- axis is 90° since the structure is cubic and the value of lattice constant is a=b=c, i.e. only single parameter is required to be calculated via equation below:

$$d = a/(h^2 + k^2 + l^2)^{1/2} \quad (3)$$

On substituting the obtained value of lattice constant (a), the volume of the unit cell was also calculated. Beside these, the average grain size and intrinsic strain of the CdS nanoparticles was obtained through the Scherrer method and adjusted Williamson Hall models like Uniform Deformation Model, assuming the crystals to be isotropic in nature.

Scherrer Method:

The peaks of the obtained x-ray diffractogram appeared to be broadened in the nanocrystal due to three major factors: crystalline size effects, intrinsic strain effects and the instrumental broadening. To obtain accuracy in the calculations, the effect of instrumental broadening is subtracted from the experimentally observed XRD peaks using silicon as a standard material. The average grain size or particle size (D) was determined by using Debye Scherrer equation

$$D = \frac{K\lambda}{\beta\cos\theta} \quad (4)$$

Where k represents the shape factor (0.9), β is the full width at half maxima in radian, θ and λ have their usual meanings. The value of particle size from Scherrer equation was found to be 4.2 nm. On rearranging the above equation we get

$$\cos\theta = \frac{K\lambda}{D} \cdot \frac{1}{\beta} \quad (5)$$

The plotted graph $1/\beta$ versus $\cos\theta$ as shown in figure 3 is known as Scherrer plot. The slope of the graph taken in modulus is used for calculating the value of average particles size (D), which was found to be 4.4 nm. The other essential structural parameters like dislocation density and stacking fault were calculated through the following equations:

$$\text{Dislocation density, } \delta = 1/D^2 \quad (6)$$

$$\text{Stacking Fault, } SF = [(2\pi^2/45(3\tan\theta)^{1/2}]\beta \quad (7)$$

Williamson Hall Analysis:

The Scherrer equation only accounts the broadening effect of the spectra due to crystallite size and does not include the intrinsic strain effect created within the lattice by stacking fault, point defect, grain boundary, etc. There are several ways for calculating the intrinsic strain along with the particle size simultaneously. Williamson Hall method is one of the easiest and simplified methods. W-H method states that the total broadening of the diffraction peak is given by the sum of the broadening due to size and broadening due to strain-induced in the nanocrystal, which is written as

$$\beta_{\text{Total}} = \beta_{\text{size}} + \beta_{\text{strain}} \tag{8}$$

Where β_{size} represents the broadening due to size, also written as β_D and β_{strain} represents the broadening due to strain. By using modified W-H equations such as UDM, UDSM and UDEDM the particle size and strain values can be calculated. In the present work, we have focussed on Uniform Deformation Model (UDM) only.

Uniform Deformation Model:

The Uniform Deformation Model (UDM) accounts the isotropic nature of the intrinsic strain induced within the crystal lattice due to various imperfections. This intrinsic strain is responsible for the surplus physical broadening of the XRD pattern apart from the crystalline size effect and can be mathematically expressed in the form of equation

$$\beta_{\text{strain}} = 4\varepsilon \tan\theta \tag{9}$$

Where, the strain induced in the sample is represented by ε, peak broadening is represented by β_{strain}. On rearranging the above equation, the strain induced due to crystal defect and imperfection can be written as,

$$\varepsilon = \frac{\beta_{\text{hkl}}}{4\tan\theta} \tag{10}$$

Where β_{hkl} represents the total sum of broadening (FWHM) due to size as well as strain at a particular hkl peak value, can be expressed as,

$$\beta_{\text{hkl}} = \beta_{\text{size}} + \beta_{\text{strain}} \tag{11}$$

From equation (x), the Scherrer equation can be rearranged as,

$$\beta_{\text{size}} = \frac{K\lambda}{D}.\frac{1}{\cos\theta} \tag{12}$$

Substituting the equation (2) and (5) in equation (4) and multiplying with (cos θ) both sides, we get

$$\beta_{\text{hkl}}.\cos\theta = \frac{K\lambda}{D} + 4\varepsilon.\sin\theta \tag{13}$$

The above equation (13) is Williamson Hall equation representing the uniform deformation model (UDM) in which the induced strain of the crystal is assumed to be isotropic in nature.

The optical properties were explored using Dynamic Light Scattering (Zetasizer Nano ZSP, Malvern Instruments) and UV-Visible spectroscopy (RAYLEIGH UV 2601). DLS was used to determine graphical profile of particle size distribution. The UV-Visible spectroscopy was carried out to investigate the optical behaviour of CdS nanoparticles. The absorption spectrum of the powder sample was recorded using spectrometer in the wavelength range 200-800 nm at room temperature. The energy bandgap of the sample was calculated using Tauc Model which is expressed in the form of equation

$$\alpha h\nu = A\,(h\nu - Eg)^{n} \tag{14}$$

Where hv is the incident photon energy, α is the absorption coeficient, Eg is the difference between the energy levels conduction and valence band i.e. the energy bandgap and A is taken as a constant. The power n depends on the nature of electronic transition responsible for optical absorption and its value is taken to be 1/2 for this case i.e. direct allowed transition.

The obtained value of energy bandgap from Tauc model could be utilized here to describe the particles size of the sample using Brus model. The model is based on the quantum mechanical approximation of effective mass which is mathematically described by equation.

$$Eg_{(nano)} = Eg_{(Bulk)} + \frac{h^2}{2r^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{3.6\,e^2}{4\pi\varepsilon r} \tag{15}$$

The model describes the relationship between the bandgap of nanomaterials ($Eg_{(nano)}$), bandgap of bulk materials ($Eg_{(Bulk)}$), diameter of the particle denoted by r, Planck's constant (h), effective mass of the electron (m_e^*) and hole (m_h^*). The following values of the parameters were considered for the calculation: $Eg_{(nano)}$ = 3.90 eV (from Tauc plot), $Eg_{(Bulk)}$ = 2.42 eV (for bulk CdS), h = $6.626*10^{-34}$Js, m_e^* = 0.19 m_e, m_h^* = 0.8 m_e, m_e = $9.1*10^{-31}$ kg, e = $1.6*10^{-19}$ C and $\varepsilon/\varepsilon_0$ = 5.7.

Result and Discussion

XRD Analysis:

Figure 2 illustrates the typical X-ray diffractogram of CdS nanoparticles recorded in the range of 20° to 60° at room temperature. The diffractogram revealed the three major peaks at 2θ = 26.7°, 44.2° and 51.9°, clearly indicating the sample was crystallized in cubic CdS structure (JCPDS Card No. 10-454). These peaks corresponds to (111), (220) and (311) crystal plane respectively. The broader peaks appeared on the diffractogram confirms the nanoscale ranged particles formation. This broadening could be also occurred due to the instrumental broadening effect. In this case the instrumental broadening effect is assumed to be negligible and not accounted in the calculations.

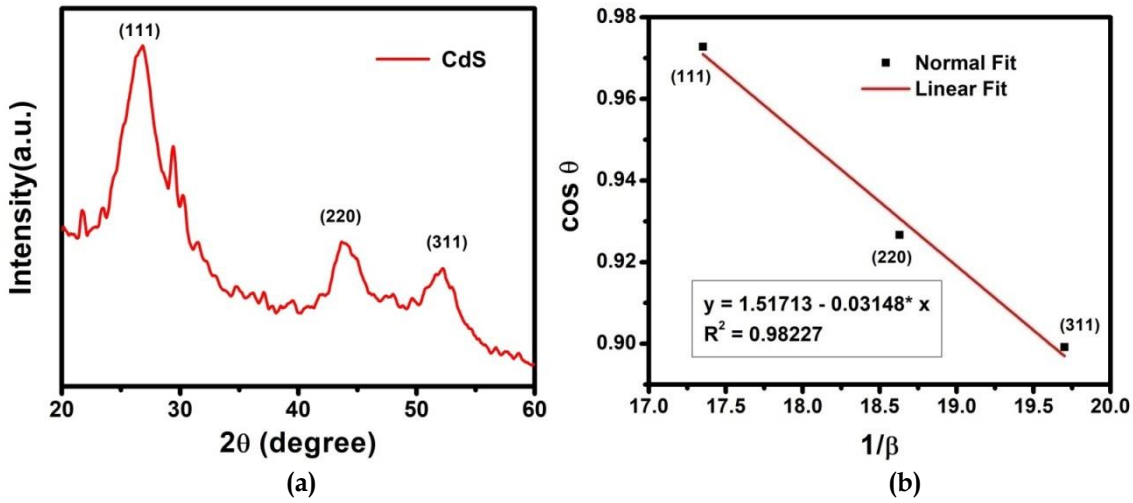

Figure 2. (a) XRD spectra from 20<2θ<60 and (b) Scherrer Plot of CdS nanoparticles.

The average crystallite size of the particle was found to be 2.76 nm from the Scherrer equation as stated in equation (4). The value of the interplanar spacing is approximately calculated using Bragg's law and found to be 3.33 Å. The other parameters like lattice constant, volume of unit cell, dislocation density and stacking fault were calculated from equation (3), (6) and (7) respectively.

Table 1. The summary of the important structural parameter of CdS nanoparticles.

Compound	Avg. crystallite size(nm)	Interplanar Spacing 'd'(Å)	Lattice Constant 'a'(Å)	Volume of unit cell 'a³' (Å)³	Dislocation Density (10^{17} lines/m³)	Stacking Fault
CdS	2.76	3.33	5.76	191.87	1.31	0.0298

The equation (13) indicates the straight line equation (y = mx + c) analogy in which y is $\beta_{hkl}.\cos\theta$, slope m is ε, x is $4sin\theta$ and intercept is Kλ/D. Figure 3 shows the UDM plot of 4sinθ along the x-axis versus βcosθ along the y-axis. The linear fit of the data provided intercept and slope values, which was further used for calculating the average crystallite size and the strain ε respectively. The strain induced in the lattice is mainly due to the lattice expansion or contraction due to quantum confinement effects. These confinements are responsible for the distortion of the atomic arrangements compared to the bulk counterpart, creating the defects and deformation, hence intrinsic lattice strain is induced. The average crystallite size was found to be 2.1 nm. The negative slope indicates the lattice contraction which creates lattice strain of 1.235 $*10^{-2}$.

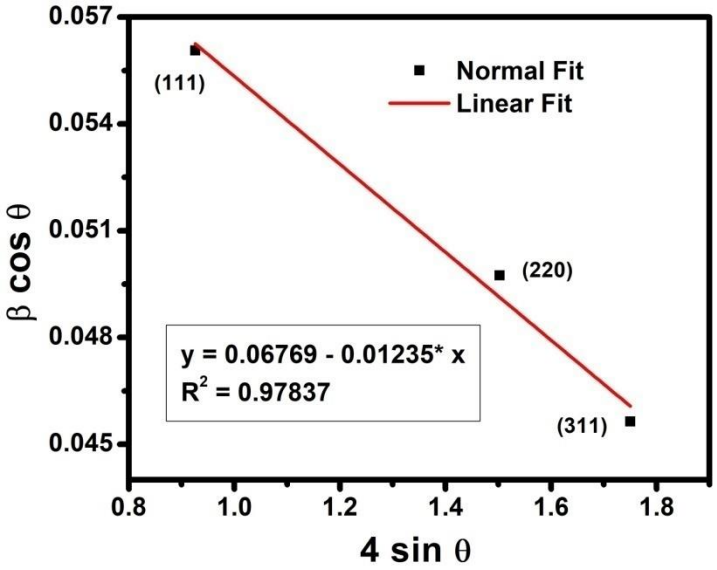

Figure 3. Uniform Deformation Model (UDM) plot.

Particle Size Analysis using Dynamic light scattering (DLS):

Dynamic light scattering (DLS) also known as Quasi Elastic Light Scattering (QELS) is an ideal technique used to estimate the hydrodynamic particle size of samples like gold nanoparticles, protein molecules, etc within the range of nanoscale. This technique is based on the phenomenon of light scattered from a solution or suspension, undergoing some definite changes in their intensity which ultimately helps to ascertain the size of particles that scatter the light. The average hydrodynamic diameter of the as synthesized CdS nanoparticles was measured via DLS (Zetasizer Nano, Malvern) in ethanol medium at 25° C.

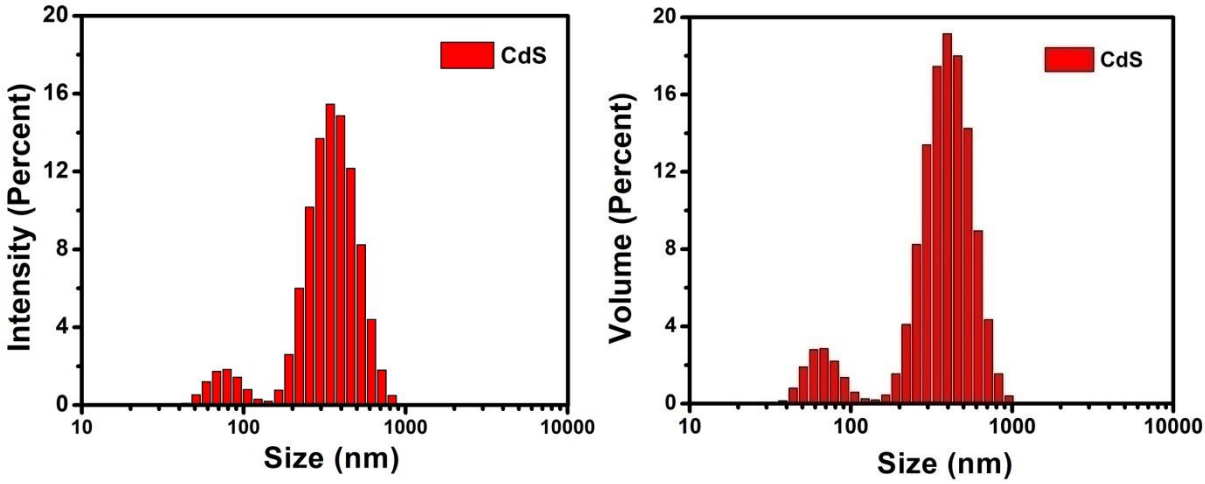

Figure 4. DLS histogram showing particles size distribution in terms of Intensity and volume of the particles.

Prior the measurement was taken; the sample was first uniformly dispersed in ethanol using ultrasonication for 20 minutes. The obtained dispersed solution was poured in quartz

microcuvette and three measurements were taken from which the average result was recorded. Figure 5 illustrates the average hydrodynamic particle size distribution of the sample with respect to (a) Intensity and (b) Volume. The scales in the x-axis are choosen to be logarithmic whereas the y-axis scales are kept linear. The most of the particle size from figure 5 is obtained to be in the range of 300-400 nm whereas few particles are in the range of 40-90 nm. These obtained values of particle size are very high as compared to those obtained from Scherrer and UDM plot. This may due to the agglomeration and surface solvation. Besides this, DLS measurements assume the spherical shape symmetry of the particles irrespective of the morphologies which also considers the ions and molecules attached to its surface.

UV-Visible Spectroscopy

Figure 6 (a) illustrates the absorption spectra of CdS nanoparticles which shows the single broader peak near 370 nm wavelength. It is clearly seen that this characteristic peak of CdS nanoparticles in the quantum size range is showing blue shift of the with respect to the bulk CdS. The quantum confinement effects in the CdS nanoparticles are probably liable for this blue shift. The bandgap of the CdS nanoparticle was obtained by extrapolation of the graph of $(\alpha h\nu)^2$ versus $h\nu$ (using equation 14) to its x-axis as shown in figure 6(b). The value of bandgap was found to be 3.90 eV. This increment in the value of bandgap of CdS nanoparticles as compared to the bulk CdS (2.42 eV) is clearly showing the shift in the blue region.

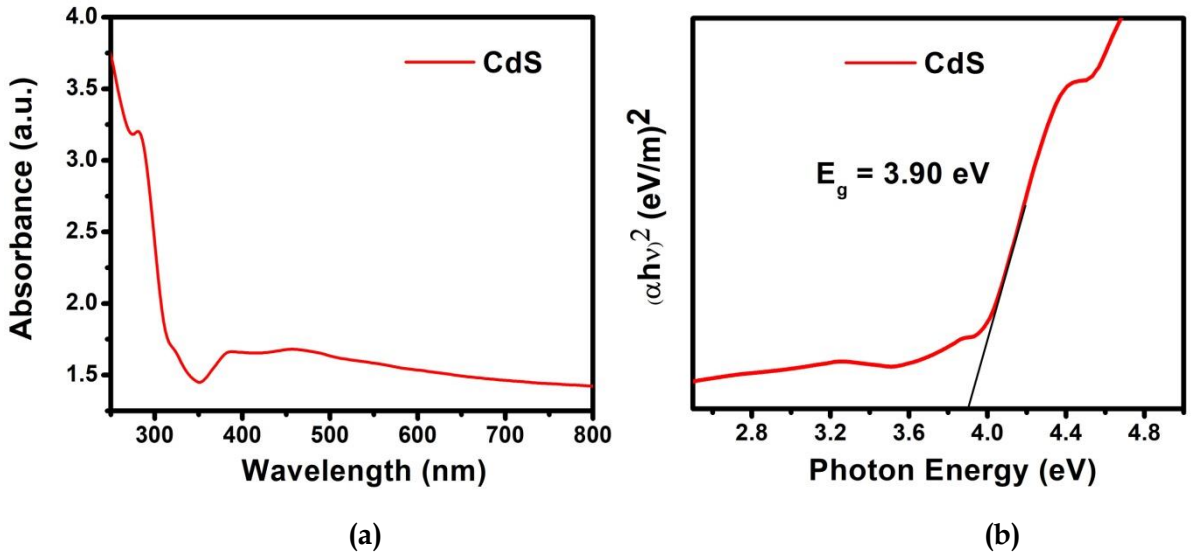

Figure 5. (a) Absorption spectra and (b) energy bandgap of CdS nanoparticles.

For estimating the particle size from the obtained bandgap of CdS nanoparticles, the required values of the various parameters were put in equation (15) i.e. Brus equation. It was found that contribution from the last term of right hand side of the equation (15) is of the order of 10^{-20} J which is negligibly small. The calculated value of the particle size of the as synthesized CdS nanoparticles from Brus equation was found to be 2.60 nm, which is in close agreement

to that obtained through XRD analysis. The table 2 shows the comparison of the average particles size of CdS nanoparticles obtained through various techniques.

Table 2. Average particles size estimated via UV Visible analysis (Brus Equation), DLS analysis and XRD Analysis (Scherrer Plot and UDM Plot) and DLS analysis.

Sample	Bandgap (eV)	Avg. Particle Size from Brus Equation (nm)	Avg. Particle Size from DLS analysis (nm)	Avg. Crystallite Size from Scherrer Plot (nm)	Avg. Crystallite Size from UDM Plot (nm)
CdS	3.90	2.60	40-400	4.4	2.1

Conclusion

It is concluded from this work that pristine CdS nanoparticles were successfully prepared using chemical co-precipitation method, which was further investigated via XRD, DLS and UV Visible spectroscopy for the comparative study of particles size analysis along with lattice strain and energy bandgap calculation. The value of energy bandgap of sample, estimated using Tauc equation was found to be 3.90 eV. This obtained value of bandgap was used for calculating the particle size using Brus equation and was found to be 2.60 nm. Besides this the particles size distribution was studied from DLS analysis, which provided the range of particles size from 30-300 nm. The average crystallite size and lattice strain has been evaluated through the peak broadening analysis via Scherrer plot and Uniform Deformation Model. Finally, Scherrer plot, UDM plot and Brus equation shows that the distribution of the average particle size are nearly similar, which is highly accurate and lies in the range 2.6–4.5 nm. DLS is not very effective methods for particle size analysis as the range of the particles size distribution is broader.

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References

[1] G. Z. Wang, W. Chen, C. H. Liang, Y. W. Wang, G. W. Meng and L. D. Zhang (2001). Preparation and characterization of CdS nanoparticles by ultrasonic irradiation, *Inorganic Chemistry Communications* 4, 208-210.

[2] A. Mercy, A. Jesper Anandhi, K. Sakthi Murugesan, R. Jayavel, R. Kanagadurai, B. Milton Boaz(2014). Synthesis, structural and property studies of Ni doped cadmium sulphide quantum dots stabilized in DETA matrix, *Journal of Alloys and Compounds* 593, 213–219.

[3] Y. Yamamoto, R.E. Slusher (1993). Optical Processes in Microcavities, *Phys. Today* 46, 66-73.

[4] A.P. Alivisatos (1996). Semiconductor Clusters, Nanocrystals, and Quantum Dots, *Science* 271, 933–937.
[5] L. Ge and J. Liu (2011). Synthesis and photocatalytic performance of novel CdS quantum dots sensitized Bi_2WO_6 photocatalysts, *Mater. Lett.* 65, 1828-1831.
[6] R.M. Ma, L. Dai, G.G. Qin (2007). High-Performance Nano-Schottky Diodes and Nano-MESFETs Made on Single CdS Nanobelts, *Nano. Lett.* 7, 868–873.
[7] C.F. Hermandez, D.J. Suh, B. Kippelen, S.R. Marder (2004). High-performance photorefractive polymers sensitized by cadmium selenide nanoparticles, *J. Appl. Phys. Lett.* 85 534–536.
[8] Jiarui Huang, Yijuan Dai, Gu Cuiping, Yufeng Sun, Jinhuai Liu (2013). Preparation of porous flower-like CuO/ZnO nanostructures and analysis of their gas-sensing property, *J. Alloys Comp.* 575, 115–122.
[9] K. P. Tiwary, F. Ali, R. K. Mishra, S. K. Choubey, K. Sharma (2020). Influence of nickel on structural and optical behaviour of cadmium sulphide nanoparticles, *Journal of Ovonic Research* 16(4), 235 – 243.
[10] Mohamed Shaban, Mona Mustafa, A.M. El Sayed (2016). Structural, optical, and photocatalytic properties of the spray deposited nanoporous CdS thin films; influence of copper doping, annealing, and deposition parameters, *Materials Science in Semiconductor Processing* 56, 329–343.
[11] R. Aruna Devi, M. Latha, S. Velumani, Goldie Oza, P. Reyes-Figueroa, M. Rohini, I. G. Becerril-Juarez, Jae-Hyeong Lee, and Junsin Yi (2015). Synthesis and Characterization of Cadmium Sulfide Nanoparticles by Chemical Precipitation Method, *Journal of Nanoscience and Nanotechnology* 15, 8434–8439.
[12] K. P. Tiwary, F. Ali, R. K. Mishra, S. Kumar, K. Sharma (2019). Study of structural, morphological and optical properties of Cu and Ni doped CdS nanoparticles prepared by microwave assisted solvo thermal method, *Digest Journal of Nanomaterials and Biostructures* 14(2), 305 – 313.
[13] Hadeel Salih Mahdi, Azra Parveen, Shraddha Agrawal, Ameer Azam (2017). Microstructural and optical properties of sol gel synthesized CdS nano particles using CTAB as a surfactant, *AIP Conference Proceedings* 1832, 050012.
[14] K.P. Tiwary, K. Sharma, Neha Bala, Firdaus Ali (2019). Microwave assisted synthesis of undoped and Cu doped CdS nanoparticles and their structural, morphological and optical characterization, *Materials Today: Proceedings* 18, 1380–1387.
[15] M. Marandi, N. Taghavinia, A. Iraji, and S. M. Mahadavi (2005). A photochemical method for controlling the size of CdS nanoparticles, *Nanotechnology* 16, 334-338.
[16] Tong, H. and Zhu, Y.J. (2006). Synthesis of CdS Nano-crystals Based on Low-Temperature Thermolysis of One Single-Source Organometallic Precursor. *Nanotechnology*, 17, 845-851.