Synthesis and Spectroscopic Characterization of Cdse Nanoparticles for Photovoltaic Applications

P Sanjay\textsuperscript{1}, K Deepa\textsuperscript{2}, J Madhavan\textsuperscript{2} and S Senthil\textsuperscript{1}

\textsuperscript{1}Department of Physics, Government Arts College For Men (Autonomous), Nandanam, Chennai - 35, Tamil Nadu, India.
\textsuperscript{2}Department of Physics, Loyola College, Chennai - 34, Tamil Nadu, India.
Email: ssatoms@yahoo.co.in

Abstract. Cadmium selenide nanoparticle [CdSe] is an important chemical substance gaining great importance and widely used as an additive in the production of various, industrial products like rubber, cosmetics, catalyst, optical materials solar cells etc. CdSe being a wide band gap material and with better lattice matching properties made it suitable option for solar cell applications, the CdSe nano rods are synthesized by a simple solvothermal method at the morphology, phase and the optical properties of Cdse nano particles are studied using powder X-ray diffraction [XRD], High resolution transmission electron microscope [HRTEM], UV-visible absorption spectroscopy, and Photoluminescence [PL] Spectroscopy, the HRTEM images confirm the formation of CdSe nano rods. The presence of elements was confirmed by Fourier transform infrared spectroscopy [FTIR], energy dispersive X-ray spectroscopy [EDAX], SEM images showed the morphology of the samples.

1. Introduction
Nowadays nano structured material research is a rapidly growing field of science, where the efforts of chemists, physicists, materials scientists and recently biologist and engineers have merged. Inorganic semiconductor nano crystals have exhibited interesting and novel size – dependent physical properties, which greatly differ from those of the corresponding bulk materials. For example, semiconductor nano crystals show blue shifts in both optical absorption and emission spectra with the decrease of nano crystal size due to quantum confinement effect [1]. The size and shape of inorganic nano materials are well known to have an important influence on their widely varying electrical and optical properties [2], which are important in various applications such as catalysis, optoelectronics, luminescent materials, lossing materials, solar cells, light emitting diodes and biomedical imaging. As one of the most important II – VI group semiconductors and nanocrystalline wurtzite structured Cadmium selenide (Eg = 1.74 eV) has attracted great interest in their various promising optoelectronic application owing to its excellent optical conductivity, such as photoelectron – chemical cells, photoconductors. One dimensional semiconductor nanocrystals having unique structural, optical and electrical properties have been considered as structural
unit for modern electronic devices sensors, photonics materials. Several synthesis routes have been employed for production nanorods and nanowires [3-4].

This include template directed method, vapor phase approach, vapor liquid solid growth, sol-gel technique, solvothermal synthesis, solution phase growth based on capping agents. Sonochemical, radiolytic method among others reported. Therefore, the need to develop different methodologies for synthesis of nano materials is inevitable in synthetic chemistry. Among the II – VI semiconducting nano materials, Cds and CdSe are widely synthesized, because of their high crystallites size dependent features of photoluminescence and absorption [5] and great deal of work has been done to characterize Cds and CdSe nano crystals. In the ongoing research on “bottom – up” approach to produce nano particles, the hydrothermal method is turning out to be the most feasible as well as versatile approach. From the environmental perspective, solvothermal method are more environmentally benign them many other synthesis method [6]. The investigation on the role of hydrazine hydrates as the reducing agent proves that it not only controls the morphology of the nano particles but also provides stability to the CdSe nano rods by preventing the oxidation of nano particles due to its reducing capacity [7], the as - prepared nano particles have characterized structurally and optically using powder X-ray diffraction, UV-visible spectroscopy, photoluminescence, Fourier transform infrared spectroscopy (FTIR), High resolution transmission electron microscopy (HRTEM), etc. studies.

2. Experimental Procedure

All the chemicals used were of analytical grade and were of highest purity, Cadmium nitrate (Cd(NO$_3$)$_2$ 4H$_2$O, Merck 99%) and Sodium selenite (Na$_2$SeO$_3$, Merck 90%), no need to undergo any post treatment after the reactions with excess of (N$_2$H$_4$H$_2$O) and ammonia (NH$_3$ H$_2$O). During the synthesis, the molar ratio of Cd(NO$_3$)$_2$ 4H$_2$O and Na$_2$SeO$_3$ was kept 2:1. Cadmium nitrate Cd(NO$_3$)$_2$ 4H$_2$O (0.01 mol) was dissolved in 10 ml of Milli Q – water and then NH$_3$H$_2$O was slowly added into the solution, which initially led to the formation of white precipitate, however, with further addition of ammonia, a clear solution was formed. This indicates the conversion of Cd$^{2+}$ into Cd(NH$_3$)$_4$$^{2+}$. The Se source, Na$_2$SeO$_3$ (0.005 mol) was stirred for 5 mins with 15 ml of hydrazine hydrate (N$_2$H$_4$H$_2$O) and it was mixed with the previously prepared solution (Cd source), this resulted in colorless and transparent solution. The final solution was transferred into Teflon – coated autoclave and then filled with Milli Q – water up to 70% of filling. The pH of the solution was found to be 11 before heating. The autoclave was selected and heated at 180°C for a reaction time of 4 hr. After the completion of the reaction, the autoclave was allowed to return to room temperature. Finally, the deep dark red product was collected, washed repeatedly with Milli Q – water, ethanol and then dried at 80°C.

The prepared CdSe nanopowder was characterized by X – ray diffraction (XRD). Measurements were carried out at room temperature by using Siemens X – ray diffraction D500 with CuK$_{\alpha}$. The UV – visible absorption spectrum of the sample was recorded in the range 190 – 1200 nm, Photoluminescence (PL), Scanning Electron Microscope (SEM) was used to examine the surface morphology of samples. The energy dispersive - ray (EDAX) technique was used to determine their elemental compositions. The FTIR spectroscopic measurement is carried out to study the chemical groups present in the sample. The high resolution transmission electron microscopy was done with a JEOL JEM 3010 microscope. The sample for HRTEM analysis was prepared by dissolving the cds e nanoparticles with few drops of dilute methanol.
3. Results and Discussion

3.1. XRD analysis
The powder XRD result for CdSe nanoparticle is shown in figure 1. All the reflection peaks can be indexed to wurzite phase of CdSe. From the XRD pattern, it is clear from the broadening of diffraction peaks of that the particles crystallize at nano scale region. The intensity of the peaks indicates that the CdSe nano particles are of high crystalline and there is no trace of cubic phase. The products are pure in phases with the calculated lattice constant, $a = 4.218 \text{ Å}$, $b = 4.218 \text{ Å}$, $c = 6.887 \text{ Å}$, which are in good agreement with the values given in literature (JCPDS 77 – 2307). The average grain size ($D$) of CdSe is calculated by the Debye – Scherrer formula, $D = \frac{0.89 \lambda}{\beta \cos \theta}$, where, $\lambda$ is the wavelength of CuK$_\alpha$ line, $\beta$ is full width at half maximum and $\theta$ is the diffraction angle. From the XRD analysis the average particle size of the nano rods was estimated at 35nm.

![Figure 1. XRD pattern of CdSe nanoparticles.](image)

3.2. UV – Vis Spectroscopy
The optical properties were observed by UV – Vis spectroscopy. The UV – Vis absorption spectroscopy of CdSe nano structural material was measured and shown in figure 2, in the wavelength range 200 – 1200 nm the absorption was measured at room temperature. The absorption edge of CdSe narrowed at 244 nm to be blue shifted the blue shift of the absorption curve results in a reduction of the band gap energy.
3.3. Photoluminescence Spectroscopy (PL)

Figure 3 shows the photoluminescence spectra of the prepared CdSe nano rods. The influence of the width of the CdSe nano rods/nano shows on the shifting behavior in the photoluminescence spectrum has been reported by few researchers [8,9]. The photoluminescence emission spectra of the CdSe nano rods excited at a wavelength of 600 – 720 nm. The sharp peak observed at 642 nm confirms a blue shift compared with bulk wurtzite CdSe which may result which may result from the quantum size effect. The strong PL intensity attains good crystalline quality of the synthesize nano rods.

Figure 3. Photoluminescence spectra of CdSe nanoparticles.
3.4. SEM analysis
The surface morphology of the prepared CdSe sample was studied using Scanning Electron Microscope. The SEM micrographs of the CdSe with different magnification at room temperature are shown in Figure 4. The CdSe nano rods were observed at different magnification level at 50 nm. The solvents hydrazine and ammonia (NH₃H₂O) play an important role in the growth of as – formed cadmium selenide nano rods. When the loss of hydrazine is faster, selenide molecules will agglomerate together and condense as rod shaped crystals. The SEM investigation of all the nano CdSe samples reveals that the crystallites are nanometer in size.

![SEM image of the CdSe nanoparticles.](image)

3.5. EDAX analysis

To identify the type of element in the samples Energy Dispersive X- ray Spectroscopy (EDAX) was used. The EDAX spectrum was taken using Jeol 6390LV model Scanning Electron Microscope. The EDAX spectra of the synthesized CdSe nano particles were recorded and they are displayed in figure 5. From the results it is confirmed that the elements such as Cd and Se are present in the samples.
3.6. High Resolution Transmission Electron Microscope (HRTEM)

High-resolution Transmission Electron Microscope is an important research tool for the study of the structure of individual CdSe nano rods. The formation of individual nano rods of CdSe with narrow size distribution is evident from the HRTEM images. Figure 6 shows the HRTEM images of the CdSe nano rods it confirms the uniform size and shape distribution with CdSe nano rods. The influence of hydrazine hydrate to control the morphology of CdSe nano rods has been reported by few research groups. In the present study we used an increased quantity of hydrazine hydrate and still managed to get CdSe nano rods of good crystalline nature. The average particle size of the nano rod is estimated as 35 nm.
3.7. FTIR analysis
FTIR spectroscopy is used to identify and characterize the organic species present in the CdSe nonstructural material. The FTIR spectrum was recorded in the range 400 – 4000 cm\(^{-1}\) employing Brukker model IFS 66V FTIR spectrometer. The FTIR spectrum of CdSe nano particles is shown in Fig. 7. The FTIR spectrum of the compound shows two prominent peaks at the weak band at 3730 cm\(^{-1}\) and 2926 cm\(^{-1}\) arise from C – CH\(_3\) asymmetric stretching. 2510 cm\(^{-1}\) and 2614 cm\(^{-1}\) are assigned to asymmetric and symmetric stretching vibration of C – CH\(_2\) from the methylene chain respectively. A peak at 738 cm\(^{-1}\) is due to Cd - Se band stretching. The absorption band found between 500 cm\(^{-1}\) and 700 cm\(^{-1}\) are due to the metal oxygen bonding vibrations. Thus the FTIR spectra confirm the presence of functional group and their mode of vibrations.

![FTIR spectrum of the CdSe nano particles.](image)

4. Conclusion
A CdSe nano rod was successfully synthesized by a simple hydrothermal method and easy process and with better control over the morphology and crystalline quality. The particle size and morphology are verified by powder XRD and HRTEM. The blue shift in the photoluminescence spectrum of CdSe nano rods has been confirmed by the absorption spectrum. UV-Vis spectrum shows blue shift as compared to bulk materials. FTIR analysis shows the presence of surfactant in the final product. This study opens up new avenues for research to find suitable experimental conditions and the possibilities of using different reaction mechanisms to bring out better control over the size/morphology of the semi conducting nano particles.
References

[1] Wang Q, Pan D, Jiang S, Ji X, An L and Jiang B 2006 A solvothermal route to size- and shape controlled CdSe and CdTe nanocrystals J. Cryst. Growth. 286 84-90.

[2] Ma C, Moore D F, Ding Y, Li J and Wang Z L, 2004 Nanobelt and nano saw structures of II-VI semiconductors Int. J. Nanotechnol. 1(4) 431.

[3] Duan X F, Huang Y, Cui Y, Wang J F and Lieber C M 2001 Indium phosphide nanowires as building blocks for nanoscale electronic and optoelectronic devices Nature. 409.

[4] Gates B, Wu Y, Yin Y, Yang P and Xia Y, 2001 Single-crystalline nanowires of Ag2Se can be synthesized by templating against nanowires of trigonal Se Journal of the American Chemical Society. 123 11500-11501.

[5] Ramalingam G and Madhavan J, 2011 Investigation on the structural and morphological behaviour of CdSe nanoparticles by hydrothermal method Archives of Applied Science Research, 3 (3) 217-224.

[6] Ramalingam G, Melikechi N, Dennis Christy P, Selvakumar S and Sagayaraj P 2009 Structural and optical property studies of CdSe crystalline nanorods synthesized by a solvothermal method. Journal of Crystal Growth 311 3138-3142.

[7] Riman R E, Suchanek W L and Lencka M M 2002 hydrothermal crystallization of ceramics Cristallisation hydrothermale de ceramics. Annales de Chimie Science des Matériaux 27 15-36.

[8] Yang J, Zeng J H, Yu S H, Yang L, Zhang Y H and Qian Y T, Formation process of CdS nanorods via solvothermal route Chemistry of materials. 12 3259-3263.

[9] Peng Q, Dong Y, Deng Z and Li Y 2001 Low-Temperature Elemental-Direct-Reaction Route to II–VI Semiconductor Nanocrystalline ZnSe and CdSe Inorg. Chem. 40 (16), pp 3840–3841.