Structural, Optical, Morphological, and Dielectric Properties of CdSe Nanoparticles by Hydrothermal Method

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Abstract— Nano crystalline samples of cadmium Selenide were prepared by hydrothermal method. The morphological, structural, and optical properties of prepared samples were characterized by TEM and High-resolution transmission electron microscopy [HRTEM], X-ray diffraction [XRD], and UV-Vis absorption spectroscopy studies. The low resolution TEM images confirm the formation of the CdSe nanorods and also the agglomeration of Nanoparticles. The crystalline size of the synthesized CdSe Nanoparticles was calculated from XRD pattern and it was also confirmed through HRTEM. The broadened XRD peaks revealed that the formation of nanorods with Wurtzite structure. From the photoluminescence studies, enhanced near-band-edge blue shift confirms. The dielectric properties of CdSe nanoparticles were studied at room temperature.

Index Terms— CdSe nanorods, XRD, UV-Vis, HRTEM, Dielectric studies.

1 INTRODUCTION

Semiconductor nano crystals have attracted impressive attention, because of their novel optical and electronic properties [1]. Varying the size of the particle and changes in the degree of confinement of the electron and affects the electronic structure of the solid in particular band edges, which are tunable with particle size. One of the most important II – VI group semiconductors and nano crystalline Wurtzite structured Cadmium Selenide has attracted great interest in their various promising optoelectronic applications owing to its excellent optical conductivity such as photoelectron – chemicals, photoconductors , thin film transistor [2-4]. Blue shift in the band gap of this material, with decreasing grain size has led to many applied investigations.

Many strategies have been utilized to prepare 1-D nano structural materials, where wet chemical method is considered as a practical and effective method for the synthesis of 1-D nano materials because it is more convenient and facile to be compared with most physical methods and need little expensive equipment by which CdSe nanorods, nanowires and nanotubes have been prepared successfully. Recently, many wet chemical methods have been applied to synthesize CdSe, and most noticeable two method are colloidal method [5-7] and hydrothermal or solvothermal technique [8, 9].

Among various synthetic methods, templating against existing nanostructures offers a very powerful means to increase the compositional diversity of materials or to generate nanostructures that might be difficult or impossible to be synthesized directly. Hydrothermal synthesis is becoming popular for environmental reason, since water is used as reaction solvent than organics. This method has been widely used to prepare nanostructures due to its simplicity, high efficiency and low cost.The investigationon the role of hydrazine hydrate as the reducing agent proves that it not only controls the morphology of the nanoparticles but also provides stability to the CdSe nanorods by preventing the oxidation of nanoparticles due to its reducing capability [10, 11]. The use of $NH_3.H_2O$ not only increases the opportunity to form rod – like morphology, but also provides a relatively clean reaction environment [12]. The prepared samples were characterized structurally and optically using powder X – ray diffraction, UV-visible spectroscopy, photoluminescence, TEM, High Resolution Transmission Electron Microscopy (HRTEM) and Dielectric studies.

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2 EXPERIMENTAL PROCEDURE

2.1 Synthesis of CdSe nanoparticles

All the chemicals were used of highest purity analytical grade, Cadmium nitrate ($Cd(NO_3)_2$ $4H_2O$, Merck 99%) and Sodium selenite (Na_2SeO_3, Merck 90%), no need to undergo any post treatment after the reactions with excess of ($N_2H_4.H_2O$) and ammonia (NH_3 H_2O).

During the synthesis, the molar ratio of $Cd(NO_3)_2$ $4H_2O$ and Na_2SeO_3 was kept at 2:1. Cadmium nitrate $Cd(NO_3)_2$ $4H_2O$ (0.01 mol) was dissolved in 10 ml of Milli Q – water and then $NH_3.H_2O$ 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_2SeO_3 (0.005 mol) was stirred for 5 min with 15 ml of hydrazine hydrate (N_2H_4 H_2O) 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 capacity. The pH of the solution was found to be 11 before heating. The autoclave was sealed and heated at 180°C for a reaction time of 4 hr. After the completion of the reaction, the autoclave was allowed to cool upto

room temperature. Finally, the deep dark red product was collected, washed repeatedly with Milli Q – water, ethanol and then dried at 80°C.

3 Results & Discussion

3.1 XRD studies

The structural properties of the prepared nanoparticles were studied using X – ray diffraction. Fig.1 shows the XRD pattern of CdSe nanoparticles. From the XRD analysis the peaks were found to be very sharp and narrow at (100) (002) (101) and (110) (103) (112) planes. All the peaks correspond to the Wurtzite phase of CdSe the lattice parameter values a, b and c have been calculated and are found to be a = 4.218 A° b = 4.218 A° and c = 6.887 A° which are in good agreement with the JCPDS 77 – 2307. The presence of small and broad peaks in the X – ray diffractogram reveals that the formation of nanoparticles. The average size of particles has been obtained from the X – ray diffraction pattern using the Scherrer formula, $D = 0.89\lambda/\beta\cos\theta$, where D is the grain size, β is the full width at half maximum (FWHM) and λ is the wavelength of X - ray (1.5466 A°). The obtained average particle size of the prepared CdSe nanorods is 35 nm.

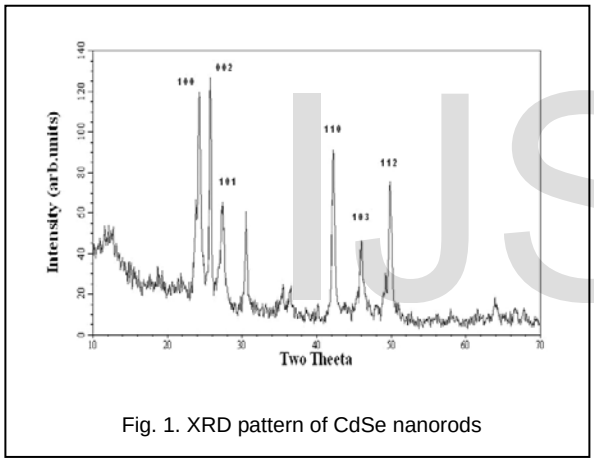


Fig. 1. XRD pattern of CdSe nanorods

3.2 Optical analysis

In order to determine the band gap of CdSe nanoparticles the optical properties of the nano materials depend on the size and shape of the particles. UV – Visible absorption spectrum of CdSe nanorods is shown in Fig. 2. The absorption edge of CdSe nanorods is 645 nm. The excitonic absorptions are very sharp. The absorption edge of CdSe nanorods at 645nm to be blue shifted. The blue shift of the absorption curves is a reduction of the band gap energy.

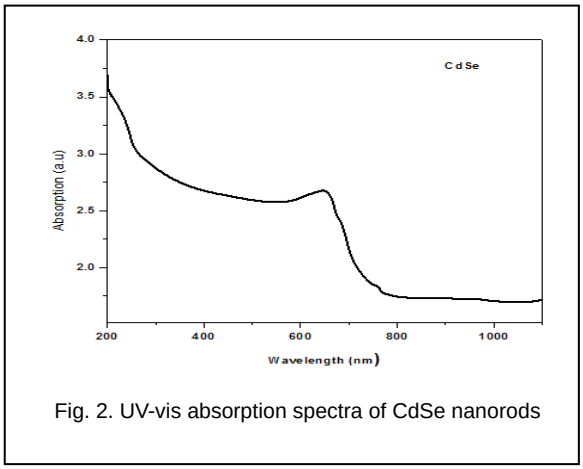
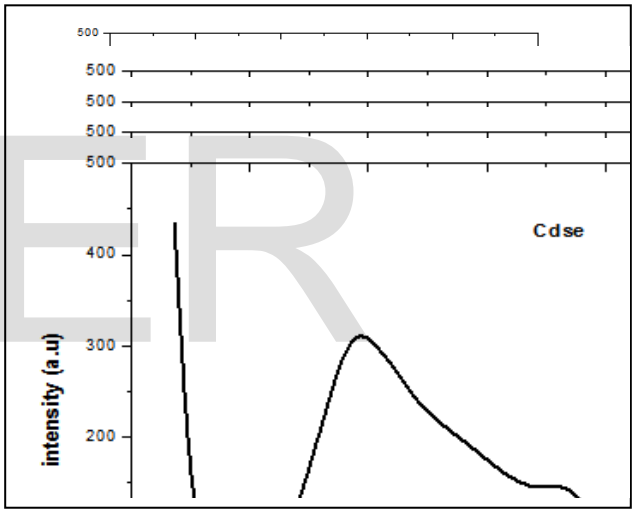


Fig. 2. UV-vis absorption spectra of CdSe nanorods

The band gap energy of the material is calculated using the formula, Eg = $h\frac{c}{\lambda} \times 6.2415 \times 10^{18}$ eV, Where h = Planks constant = 6.626×10^{-34} Js, C = Speed of light = 3.0×10^{8} m/s, λ = Cut-off wavelength = 645×10^{-9} m. The calculated band gap energy of the CdSe nanorods is 1.9235 eV.

3.3 Photoluminescence spectroscopy

The PL spectra of the CdSe nanorods were recorded at excitation wavelength of 400 nm at room temperature. The obtained spectrum is shown in Fig. 3. Sharp peaks were observed at 610 and 724 nm in the spectrum. The sharp peak at 724 nm confirms the blue shift of the bulk Wurtzite CdSe. The strong PL intensity ascertains the good crystalline quality of the synthesized nanorods. The PL absorption spectra study supports the view that the nanoparticles are predominantly nanorods with uniform size distribution.

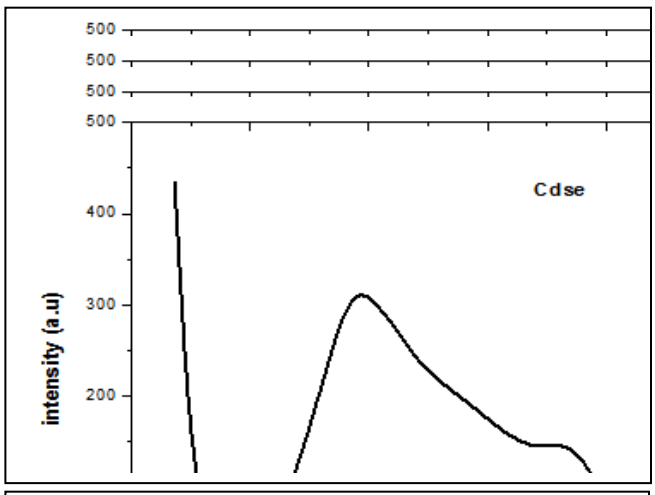


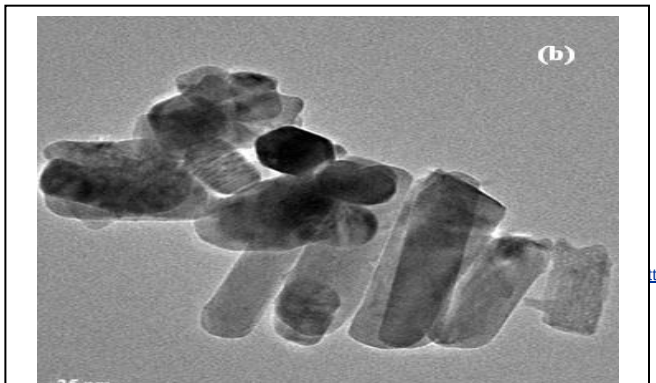
3.4. TEM and HRTEM analysis

TEM allows the direct imaging of nanoparticles and provides authentic information on the distribution, size and morphology of the nanocrystallites. The low magnification TEM images of sCdSe shown in Figure. 4 a, b confirm the uniform size and shape distribution of CdSe nanorods. The influence of hydrazine hydrate to control the morphology of CdSe nanorods has been reported by few research groups (Lifei Xi *et al.,* 2008, Peng *et al.,* 2002). In the reverse micelle assisted hydrothermal method, hydrazine hydrate was used as both reducing and templating agent, and its presence was found to favour the formation of rod-like structure (Lifei xi et al 2008) and it is further reported that the use of increased quantity (10 ml) of hydrazine hydrate resulted in poor quality rods. Similarly, Peng *et al* .,(2002) have used 10 ml of hydrazine hydrate in the hydrothermal method and obtained NRs of length more than 200 nm, but these nanorods were seen to possess significant numbers of stacking faults and such similar stacking faults were also observed in the case of CdSe long rods synthesized by Manna *et al.,* (2000). However, in the present work, we have

used an increased quantity of 15 ml of hydrazine hydrate and still managed to get CdSe nanorods of good crystalline nature, this is possibly due to the increased reaction time of 4 h, when compared to the reaction time of 2 h used in the earlier work (Peng *et al*.,2002). It is observed from the TEM images (Figure.4 a, b) that the CdSe nanorods synthesized in this work are in good shape with less pronounced stacking faults, with their measured values of mean diameter and length 25 nm and 82 nm respectively.

However, this result is different from the estimated particle size of 35 nm, obtained with XRD data. This could be attributed to the reason that in low resolution TEM measurement, which may not differentiate particles in clustered, aggregated or coalesced form unless special preparation technique or high-resolution TEM is used, where as XRD measures planes of single crystals and gives an average size of individual particles (Klug et al 1954). Though the majority of the CdSe nanoparticles possess rod-like morphology, few particles with spherical shape are also seen in agglomerated condition (Figure. 4b). High resolution transmission electron microscope (HRTEM) is an important research tool for the study of the structure of individual CdSe nano rods. The HRTEM image (Figure 4c) shows the lattice fringes of CdSe nanocrystallites corresponding to (002) lattice planes of the wurtzite (hexagonal) structure. This lattice plane can be indexed with the wurtzite (hexagonal) structure of CdSe and the calculated interplanar distance is around 0.357 nm. The formation of individual nanorods of CdSe with narrow size distribution is evident from the HRTEM images, Figure 4 c shows the lattice fringes of a single nanorod and the clearly visible lattice plane endorses the formation of well crystallized single crystal CdSe nano rods. The same trend is clearly observed in the selected area electron diffraction (SAED) pattern of CdSe in Figure.4d where, the hexagonal bright spots are clearly visible and it can also be indexed to the wurtzite phase.





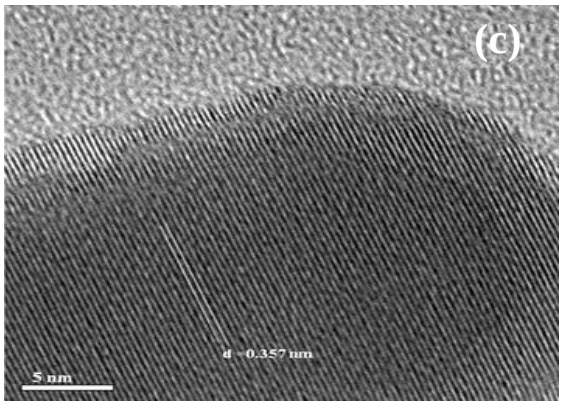
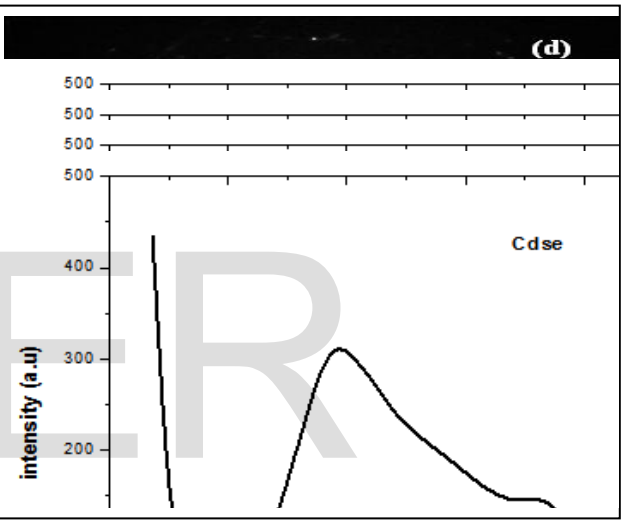


Fig. 4.c.HRTEM image with lattice planes of CdSe nanorods



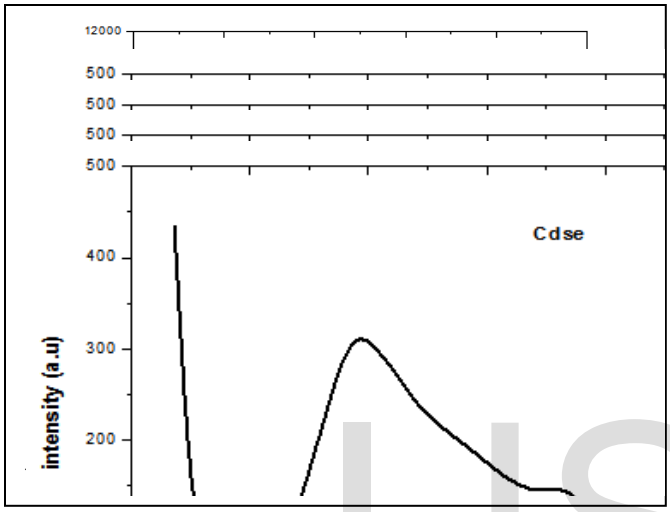
3.5 Dielectric Studies

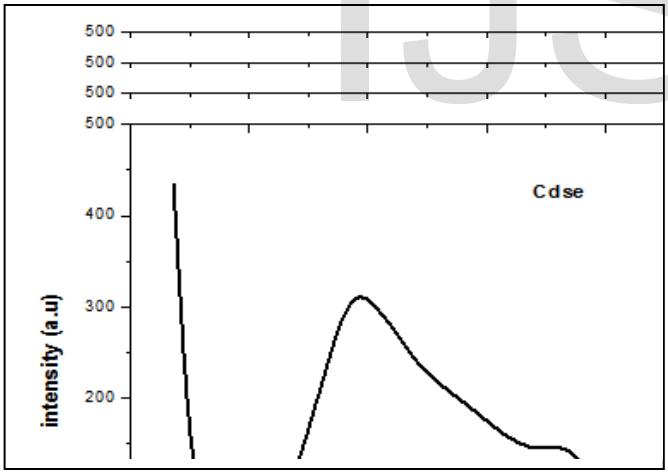
The dielectric analysis is an important tool used to know the details about the electrical properties of material at different frequencies. The dielectric properties of the CdSe nanoparticles were analyzed in frequency range 50Hz-5MHz. The imaginary and real part dielectric constant was analyzed as a function of the frequency at room temperature as shown in Fig. 5.a & b. It is observed from the dielectric constant decrease with increase in frequency. The large dielectric constant at low frequency shows the occurrence of space charge polarization arising at the grain boundary interface. The involvement of the decrease in the dielectric constant owing to electronic polarization is relatively less. The contribution to polarizability of the space charge depends on the purity of the nanoparticles.

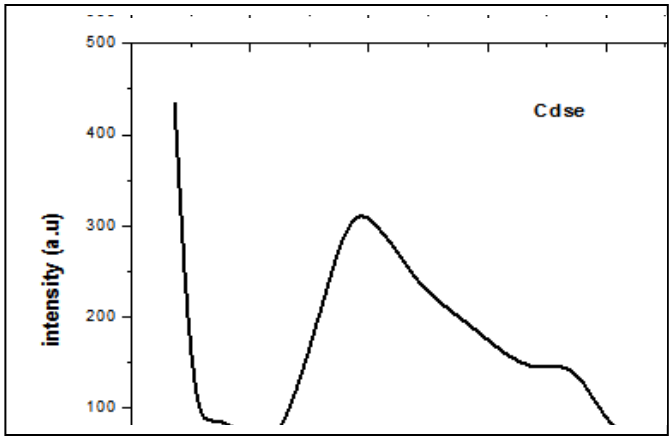
Fig.5.c. shows the variation of the dielectric loss with respect to the log f at room temperature. Dielectric loss also shows a trend similar to the one shown by dielectric constant. The dielectric loss is decrease with the increase in frequency. The dielectric loss is strongly dependent on the frequency of the applied field. The ratio of the loss or resistive current to the charging current of the sample is the loss tangent (tan δ). Also it is know that there is a strong correlation between the conduction mechanism and the dielectric constant behavior in

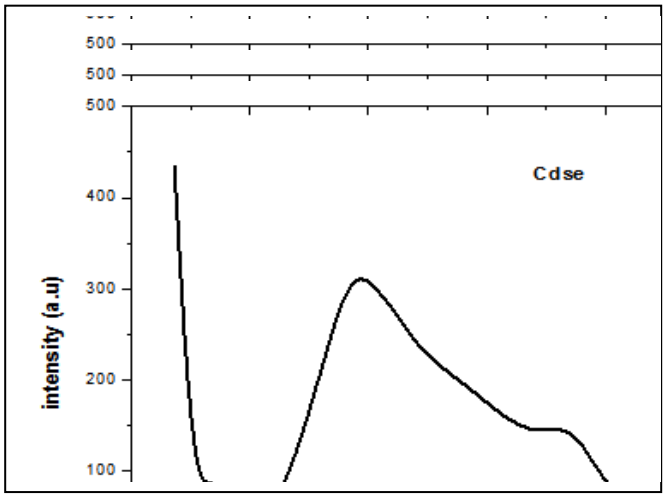
CdSe nanoparticle. It is observed that the (tan δ) shows the decreasing trend with increase in frequency which is normal behavior of any material.

Fig.5.d. shows the conductivity versus frequency plot for the CdSe nano rods. It shows that the value of conductivity is low for the lower frequencies but at higher frequencies the value of conductivity goes on increasing. This could be due to large surface scattering which results in the decreases in conductivity and also the short range intrawell hopping of charge carries between localized states of the effective number of charge carries involved decreases and thus conductivity was found to decrease.









4 Conclusion

CdSe nanoparticles have been synthesized by the hydrothermal method with better control over the morphology and crystalline quality. The particle size and morphology were verified by powder XRD and transmission electron microscopy (TEM). The blue shift in the photoluminescence spectrum of CdSe nano rods has been confirmed by the absorption spectrum. The optical properties were studied by UV-Visible spectrum and the band gap value was found to be 1.9235 eV. The dielectric constant, dielectric loss and AC electrical conductivity of CdSe nanoparticles also investigated as a function of frequency at room temperature. It indicates that the dielectric constant and dielectric loss of the materials decreases with increasing frequency. This property of the material can be used for dielectric and electronic applications. 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 nanoparticles.

5 References

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