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Investigation on the structural and morphological behaviour of CdSe nanoparticles by hydrothermal method

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ABSTRACT

One dimensional semiconductor nanorods of CdSe were successfully synthesized by solvothermal method using hydrazine hydrate (HH) and ethylenediamine tetraacetic acid (EDTA) as complexing agents. The average diameter of nanorods was found to be around 30 nm and 40 nm from XRD analysis. Thus there is a strong blue-shift in the absorption spectra for both the samples HH and EDTA capped CdSe, indicating that particles must be smaller than the exciton Bohr radius. The emission peak (PL) observed at 560 and 562 nm is attributed to the recombination of charge carriers on the surface of the nanorods.

INTRODUCTION

Cadmium selenide is an interesting member of the II-VI semiconductor family, having suitable band gap (1.74 eV at 300k) to match the maximum of solar spectrum and also high photosensitivity. During the past decade, one-dimensional (1D) and quasi 1-D nanostructure has become an important object of material research owing to their unique chemical and physical properties [1]. While most of the work has been focussed on single crystal, studies on one dimensional nanostructure have been scarcely reported [2] due to the difficulties associated with their preparations. In fact, nanoparticle assemblies provide direct bridges between nanometer scale object and the macro scale world, with increasing attention being paid to these unique structures. CdSe nanocrystalline semiconductors have attracted great interest over the past years because their properties and applications such as light-emitting diodes, lasers, holographic optical memories, photonic band-gap crystals, ultrafast photonic switches, and biomedical tags for fluoroimmuno assays, nanosensors and biological imaging [3,4].

Different methods have been employed to synthesize metal-chalcogenide. Ma and co-workers [5] have synthesized nanoribbon structure of Wurtzite CdSe with saw-shaped teeth on one side. Cumberland and co-workers [6] prepared a series of materials (CdSe, ZnSe nanoparticles) by single-source precursor methodology based on the introduction of an inorganic metal-chalcogenides cluster into an alkyl amine solvent. Hydrothermal method is feasible and versatile to synthesize nanomaterials. Yang et al [7] have successfully synthesized several chalcogenide nanorods via solvothermal routes. In recent years, the hydrothermal/solvothermal method is stranding towards an ambient condition, such as low temperature, low pressure, additives and so on. Several attempts have been made to choose optimal additives to control the morphology and size dependent effectively.

This manuscript deals with the synthesis of CdSe nanorods/nanoflower like morphology with uniform shapes and excellent monodispersity by hydrothermal/solvothermal method. The products were demonstrated to be in hexagonal phase. The reactions were carried out under ambient condition and the reproducibility was high and of good quality. The as prepared nanoparticles were characterized structurally and optically using powder X-ray diffraction, scanning electron microscopy (SEM), UV-Vis absorption and photoluminescence (PL) analysis.

MATERIALS AND METHODS

2.1 Synthesis of CdSe

Cadmium nitrate $Cd(NO_3)_2.4H_2O$ (0.01 mol) and Sodium Selenide Na_2SeO_3 (0.005mol) were used as a starting precursor for Cd and Se source respectively. Hydrazine hydrate ($N_2H_4.H_2O$) and EDTA were used as complexing agents. EDTA was used as chelating ligands in addition to the synthesis procedure described earlier [8]. The ratio of Cd: Se is 2:1.

$$2Cd(NO_3)_2 + 2Na_2SeO_3 + 3N_2H_4 \xrightarrow{180°C,\ NH_3.H_2O} 2CdSe\downarrow + 3N_2\uparrow + 4NaNO_3 + 6H_2O$$

Finally, the dark red product was collected by centrifugation. This product was washed with deionized water and absolute ethanol several times and dried at 80°C.

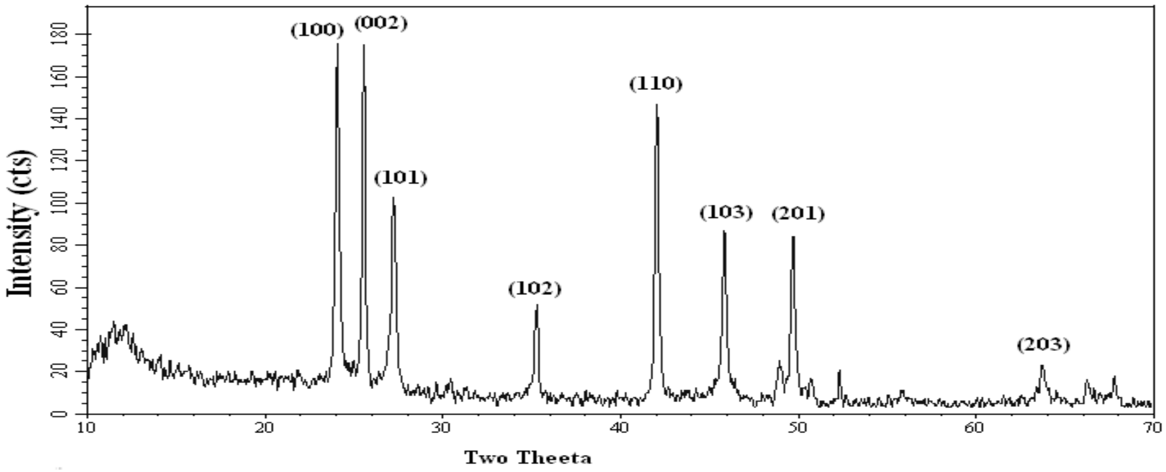
2.2 Characterization

The obtained powder was characterized by X-ray diffraction with CuK_α radiation (λ=1.5481nm), the 2θ range used was from 10 to 70° at a scanning rate 0.02 deg/sec. The UV-Visible spectrum was recorded using double beam CARY 5E UV-VIS-NIR SPECTRO PHOTOMETER. The photoluminescence study was done on the CdSe nanoparticles using JOBIN YVON FLUROLOG-3-11 SPECTRO FLUROMETER. A 450 W xenon lamp was used as the excitation source and a photomultiplier tube (PMT) with a resolution of 0.2 nm acted as the detector. For Scanning Electron Microscopy (SEM), The Quanta 200 FEG analytical was used. Samples for microscope observation were prepared by putting a pinch of the powder sample dispersed in methanol and subsequent drying in vacuum.

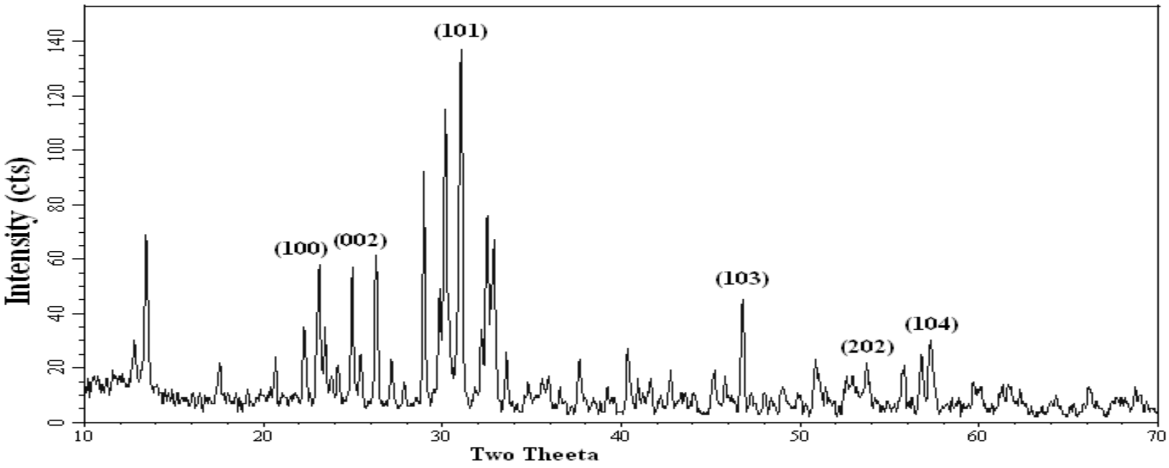
RESULTS AND DISCUSSION

3.1 XRD structural analysis

The Fig. 1 (a & b) shows the powder XRD pattern of CdSe in Wurtzite hexagonal obtained using $N_2H_4.H_2O$ and EDTA surfactant. From the XRD pattern, it is clear from the broadening of diffraction peaks of that the particles crystallize at nanoscale regime. The intensity of the peaks indicates that the CdSe nanoparticles are of high crystalline and there is no trace of cubic phase. All the diffraction peaks are indexed to hexagonal structure with lattice constant values of a=4.218Å, b=4.21Å and c=6.887Å (JCPDS 77-2307). The peaks (1 0 0), (0 0 2), (1 0 1), and (1 0 3) are corresponding to the hexagonal phase. Usually, the (1 0 1) diffraction peak in hexagonal CdSe is strong and narrow, which may be ascribed to the preferential growth along (1 0 1) plane of CdSe crystallites. From the experimental results, the average grain size of CdSe nanoparticles was calculated from the Debye-Sherer formula and the average diameters of the as grown CdSe calculated from the XRD pattern are 30 and 40 nm for HH and EDTA capped CdSe respectively.



(a)



(b)

Fig. 1 Powder X- Ray diffraction pattern of CdSe nanoparticles

3.2 SEM analysis

The SEM micrographs of CdSe with different magnification at room temperature are shown in Figs. 2 (a & b). The HH capped CdSe nanorods were observed at different magnification level at 5 µm. Interestingly, Fig. 2 shows the agglomeration free nanorods. The ligand HH plays a major role in controlling the particle shape and size [8]. In this synthetic route, the formation of 1D cadmium selenide nanocrystals indicated (scheme-1) that the nucleation and growth were well controlled. The solvent hydrazine hydrate (HH) and ammonia ($NH_3.H_2O$) play an important role in the growth of as-formed cadmium selenide nanorods. The solvent molecule is a bidentate ligand HH. It can react with metal ion to form relatively stable metal complex [9]. It is well known that $Cd^{2+,}$ Ni^{2+}, and Cu^{+} could form tetradentate complex with N,N'-bidentate ligand. Bi^{3+}, Sn^{4+} and Pb^{2+} can also combine with N,N'-bidentate ligand to produce relatively tetradentate stable complex. It can be concluded that the solvent hydrazine hydrate may act as a bidentate ligand to form a relatively stable Cd^{2+} complex. When the loss of hydrazine is faster, selenide molecules will agglomerate together and condense as rod shaped crystals. Therefore, in the synthesis of metal selenide 1D nanostructure, several factors, such as the reaction temperature and time of heating, should be considered.

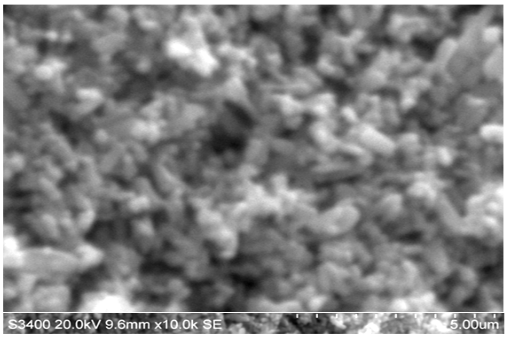
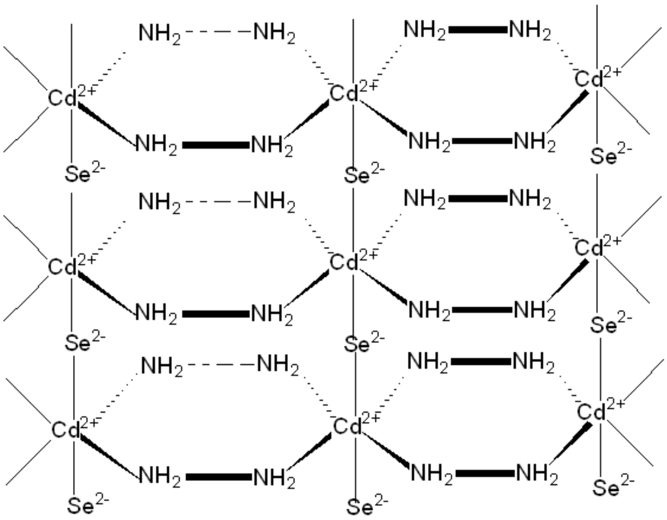


Fig. 2a SEM micrograph of HH capped CdSe nanorods at 5 µm



Scheme -1

Fig. 2b shows the typical SEM image of CdSe nanocrystals prepared with EDTA. Here EDTA was used as a solvent as well as capping ligand. Fig. 2b confirms the nano-flakes like morphology which plays an important role in nano-engineering devices. The influence of EDTA over the growth of CdSe nanocrystallites and the various other factors which contributes to the development of CdSe nanostructure is investigated.

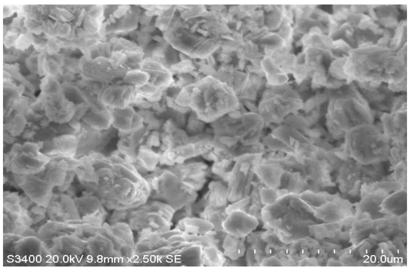
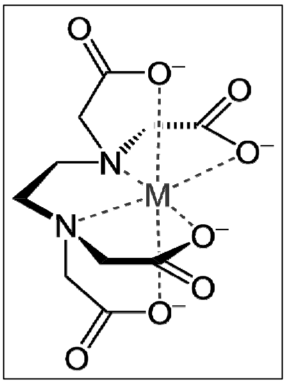


Fig. 2b. SEM micrograph of EDTA capped CdSe nanorods at 20 µm

The efforts have been made to synthesize CdSe nanostructures using ethylenediamine tetraacetic acid (EDTA) as the chelating complex under mild hydrothermal conditions, resulting in a hydrolysis. This could be attributed to the fact that EDTA being a highly polar medium, ultimately influences the non-polar medium of toluene to get polarized and thus encouraging controlled hydrolysis. The introduction of EDTA ensures the formation of hexadentate chelated CdSe-EDTA complex and the formation of stable molecular precursors. EDTA is a weak acid which can act as a hexadentate ligand (scheme – 2), structure of ethylenediamine tetraacetic acid (EDTA)) coordinating to a metal ion simultaneously through six donor sites (Malik et al 2001). In doing so, it engulfs the metal ion, forming an extremely stable complex.



Scheme-2

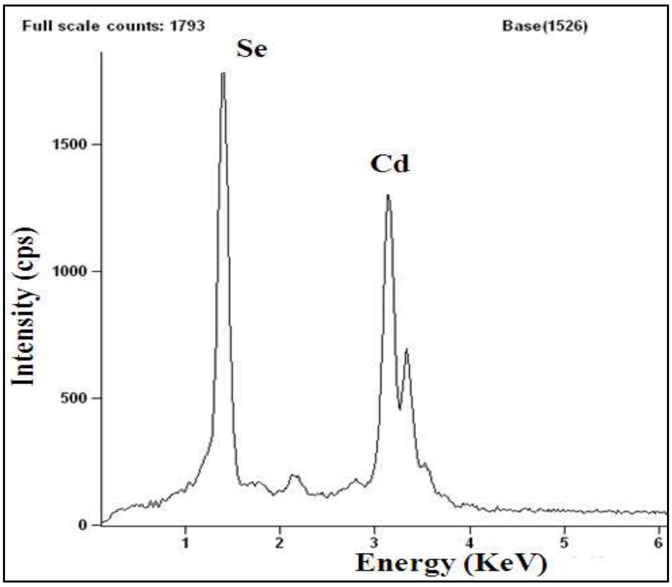


Figure 4. EDA Spectrum of CdSe Nanoparticles

Table-1: Elemental analysis data of CdSe

Element line	Net Counts	Net counts Error	Weight %	Atom %	Formula
Se	3587	+/- 72	48.86	57.63	Se
Se	24510	+/- 176	---	---	
Cd	29410	+/- 201	51.14	42.37	Cd
Cd	4218	+/- 84	---	---	
Total			100.00	100.00	

3.3 Energy dispersive X-ray analysis (EDAX)

EDAX is an important technique to analyze the composition of elements quantitatively and to solve the chemical identity of metals. It is inferred from the result of the EDAX spectrum (Fig. 4) obtained for nanoparticles prepared using different surfactants that the samples are composed of only Cd and Se and are exactly CdSe nanoparticles and no trace of other elements is observed. Though, two different capping ligands were employed, all peaks confirm only Cd and Se metals are present. From the Fig. 4, it is clear that the samples are generally cadmium rich even though a relatively higher concentration of selenium was used. From the EDAX and XRD analyses, it is clear that the obtained products are pure cadmium selenide in wurtzite hexagonal phase.

3.4 Optical absorption study

Figure.5 shows UV-Vis absorption spectra show excitonic peaks at 532 nm and 560 nm for EDTA and HH capped CdSe nanocrystals respectively. For bulk CdSe, direct band gap is 1.74 eV. An absorption peak for CdSe is therefore expected at ~716 nm. Thus there is a strong blue-shift in the absorption spectra for both the samples HH and EDTA capped CdSe, indicating that particles must be smaller than the exciton Bohr radius [11].

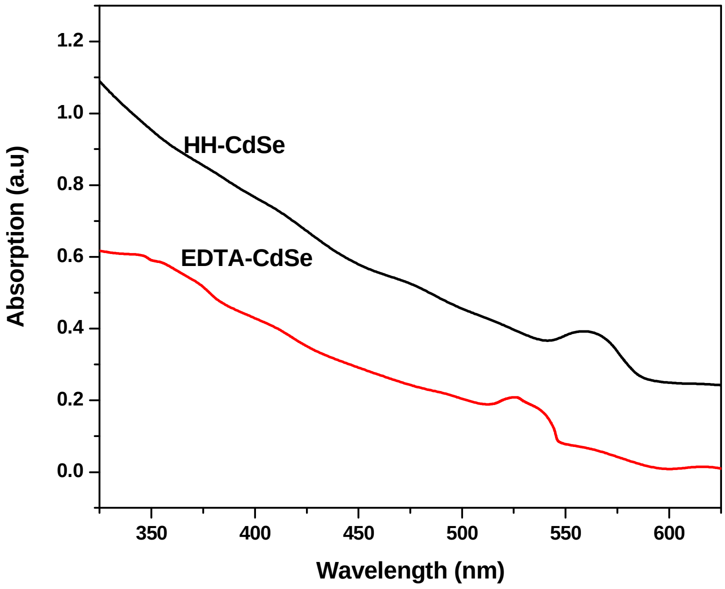


Fig. 5 UV-Vis-NIR absorption spectra of CdSe Nanoparticles

In CdSe nanocrystals, the highest occupied molecular orbital (HOMO) originates from Se 4p atomic orbital's, and the lowest unoccupied molecular orbital (LUMO) from Cd 5s atomic orbitals. Those electronic slates are strongly dependent on the size (the degree of confinement). Because increasing the aspect ratio only reduces confinement along the *c*-direction, some energy levels are sensitive to the length of the NR much more than others, and level crossing occurs. For HOMO levels, the levels consisting of a Se 4p component are more dependent on the length, by increasing the nanorods length; the energy levels converge into several energy levels. This is a transition from zero-dimension confinement (0D) to one dimensional (1D), where a continuous band forms along the *c*-axis. For this reason, more versatile nanoelectronic and optical devices, which combine the advantage of 0D and 1D confinement, can potentially be made using quantum NRs as building blocks [11].

3.5 Photoluminescence (PL) study

The photoluminescence (PL) spectra of CdSe are presented in Fig. 6. Emission of two samples is around 545 and 575 nm for EDTA and HH capped nanoparticles respectively. The CdSe nanoparticle had good optical qualities and there was no emission from deep trap states at wavelengths longer than 625 nm detectable. The inhomogeneous broadening of the PL emission suggests that the nanoparticles should have a uniform size distribution. Interestingly, the emission spectra of all the samples suggest that the CdSe nanoparticles had similar size distribution as that of the HH and EDTA molecules, which implies that during the growth of the

CdSe layers, the Ostwald ripening of CdSe was effectively suppressed. The observed fluctuation of the FWHM can be attributed to the induced internal electric field at the interface of the CdSe.

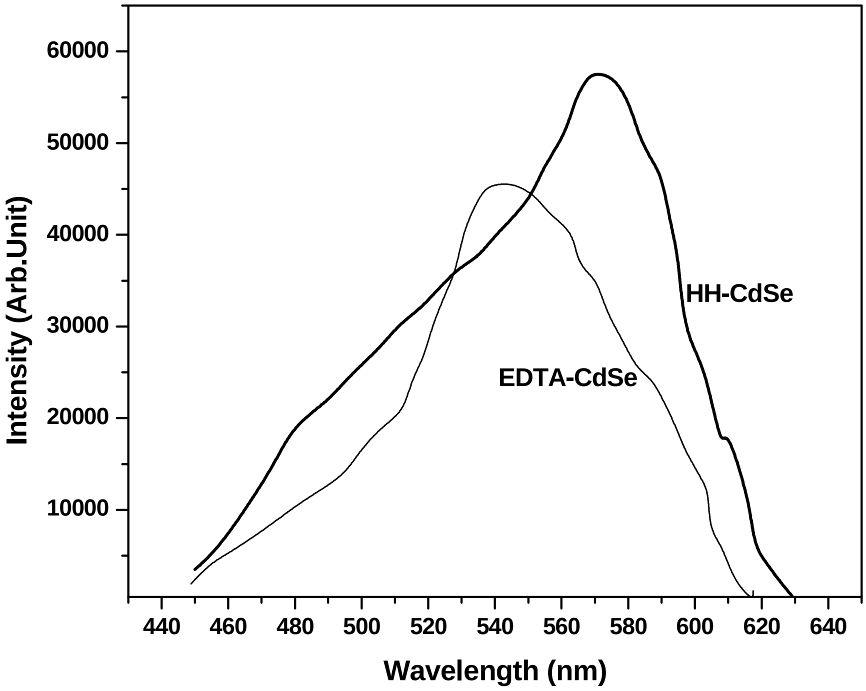


Figure 6. Photoluminescence spectra of CdSe

CONCLUSION

In summary, hexagonal CdSe nanorods have been successfully synthesized by sovothermal method at a relatively low temperature. Hydrazine hydrate and EDTA were not only acting as reduction agents but also as one of the templating agents that favour the formation of a rodlike structure. The morphologies of the as-prepared nanoparticles can be controlled by the amount reduction agent and temperature. The photoluminescence mapping of the individual nanorods shows the presence of strong PL intensity which is due to both high crystallinity and good surface states of the synthesized nanocrystals. From the above arguments, the developed CdSe nanorods have the promise for use in photonics device fabrication, solar cell and bio-medical applications.

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