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Transition from CdSe Nanoparticles to CdSe nanorods with Growth Time

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ABSTRACT

A simple chemical reduction route is followed to grow the CdSe nano structured materials at room temperature (30 ^{0}C). The growth time is kept 3 hours, 8 hours and 12 hours respectively to synthesize the material. The samples are characterized structurally, optically. The surface morphology of the samples are also studied. The result supports the formation of nanoparticle at 3 hours growth time. With the increase of growth time the nanoparticle structure changes to nanorod and is very prominent at 12 hours growth time. An increase in bandgap is also observed for the sample at higher growth times.

***Keywords*:** Nanoparticles, Nanorods, Structural Properties, Surface Morphology, Bandgap.

1. Introduction

Semiconductor quantum dots are the building blocks of numerous optoelectronic applications like Light Emitting Diode (LED), solar cells, photo detector, biosensors, high density magnetic information storage etc due to their peculiar role played by quantum confinement effect[1-8]. The nano-scale modification of the bulk semiconductors and its morphological study opens the window for the researchers to get control over its size dependent optical and electrical properties [9-12]. The properties of the semiconducting nanostructured materials prepared by different synthesis techniques are critically depends upon the preparation process and growth kinetics like inert atmosphere, growth temperature, growth time and the physical properties of capping agents. CdSenano crystals (Gr II -VI) are synthesized because of its bandgap lies in the visible range and its potential use as photo a node in photoelectrochemical (PEC). There are many methods [13] to synthesize CdSenano crystals. The methods are not cost effective and the used precursors may cause environmental hazards. Some synthesis processes also need a very high temperature which may oxidize the material [14-17]. Hence a simple chemical reduction route is preferred [18-25]. The present study is focused to synthesize the CdSe nanostructure materials in different growth time. The morphological study is done using Field Emission Scanning Electron Microscopy (FESEM). The structural and optical characterization is done using transmission electron

microscopy (TEM), X-ray diffraction (XRD), UV-VIS absorption spectra and photoluminescence (PL) technique respectively.

2. Experimental

Anhydrous Cadmium Chloride ($CdCl_2$) selenium powder (Se) and sodium borohydride ($NaBH_4$) are used for the synthesis of CdSe nanostructure materials. Ethylenediamine (EN, NH2CH2CH2NH2) is used as a capping agent. $NaBH_4$is taken to initiate the reaction at room temperature (30 ^{0}C). For the synthesis of CdSe, the amounts of $CdCl_2$, Se and $NaBH_4$ are 532 mg, 208 mg and 500 mg respectively. Magnetic stirrer is used to grow the three different sets of samples and the stirring is continued for 3 hours, 8 hours and 12 hours at a particular speed. The powder X-ray diffraction (XRD) pattern of CdSe samples are recorded by a X-ray diffractometer (miniflexII, desktop-X-ray diffractometer) using Cu-kα radiation. For TEM and TED measurements, the grown samples are dispersed in ethanol by ultrasonification. A small drop of dispersed CdSe samples are taken on three different thin carbon film supported on the copper grid andkept for some time for drying. The Transmission Electron Micrograph of the as-prepared samples are taken using a JEOL-JEM- 200 transmission electron microscope operating at 200 kV. SAED pattern and EDX analyses of the said nanostructured materials are alsoperformed.Optical absorption measurements of the dispersed samples are studied using a Shimadzu Pharmaspec 1700 UV–VIS. Photoluminescence spectra of the same samples are obtained using a Hitachi F-7000 FL Spectrophotometer.Field Emission Scanning Electron Microscopy (FESEM) of CdSe nanostructured materials are also done using Agilent 5500 for its morphological characterization.

3. Results and discussions

The XRDpattern of the of the as-prepared CdSe nanostructures synthesized at different growth times are observed.The diffraction peaks mostly shows the hexagonal phase of the materials grown at different stirring time. The peaks are identified comparing with ICDD data. The nanoparticles formed are of CdSe which is confirmed.

X-ray diffraction pattern of blackish-red powder of CdSe nanoparticles, obtained by chemical reduction method, are shown in Figure 1.

The TEM images of the samples shows that with the increase of growth time CdSe changes its shape from nanoparticles to nanorods. At 3 hours growth time the TEM image clearly shows the formation of nanoparticles of size 5-8 nm. At lower growth time particles are assembled but as the growth time increases the particles are trying to assemble at a particular direction giving rise to the appearance of nanorod like structures. At 8 hours growth time, the TEM images shows that the formation of nanorod from nanoparticles is just began, whereas for 12 hours growth time, it completely changes to nanorod shape. It is also observed that each nanorods are seems to be composed of a number of nanoparticles stacking along its length.This is possible due to Ostwald ripening in which larger nanorods may formed in exchange of smaller nanoparticles with a particular alignment along its length. The average size of the nanorods are determined from TEM to be 350-375 nm in length and 20-25 nm in diameter and is shown in Figure 2.

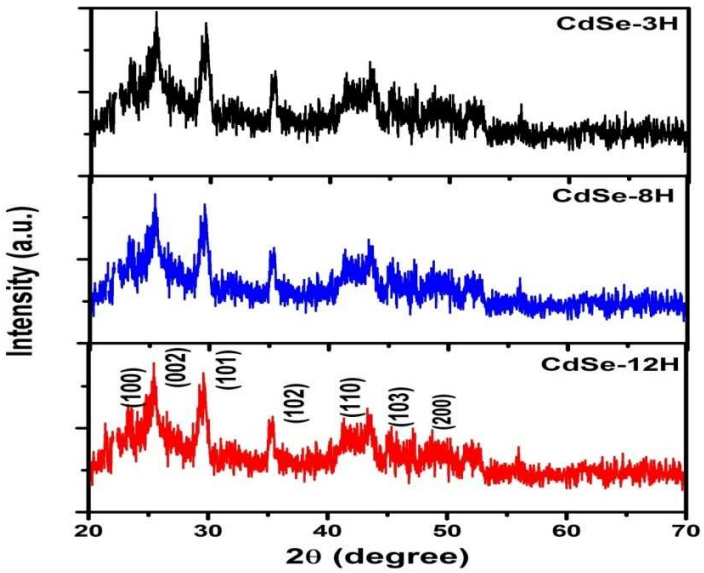

Figure 1: X-Ray Diffraction pattern of the CdSe nanostructured materials synthesized with different growth time.

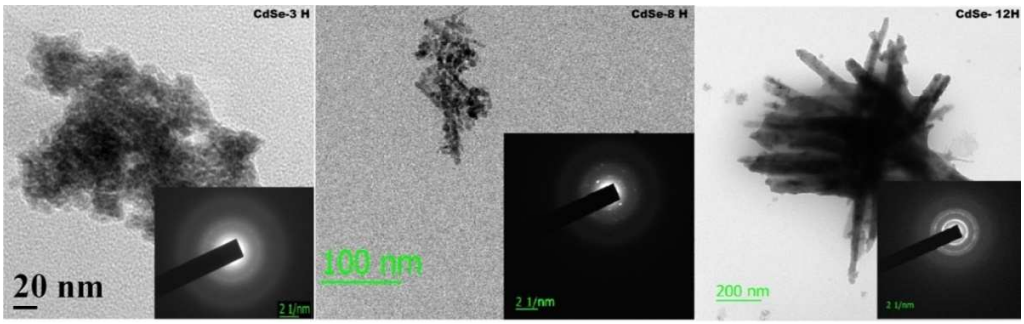

Figure 2: TEM image of the CdSe nanostructured materials synthesized with different growth time and its corresponding SAED pattern (at its inset).

The Selected area electron diffraction (SAED) pattern indicates that crystallinity is good for lower growth time. The FESEM of the CdSe nanostructures reveals the surface morphology of the materials and is shown in Figure 3. It is clearly seen that at 3 hours growth time the surface of the synthesized CdSe nanoparticles are polycrystalline in nature and the particles exhibits spherical granules like structures. Sample synthesized with growth time 8 hours is also polycrystalline in nature but the spherical granules are trying to align lengthwise which is possibly due to Ostwald ripening and at 12 hours

growth time the surface morphology totally changes from 3 hours grown samples and nanorods are observed which is supported by Figure 2.

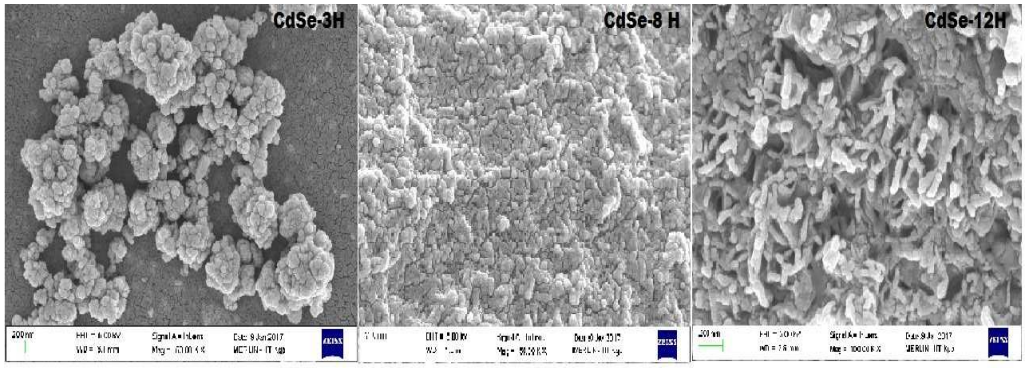

Figure 3: SEM images of the CdSe nanostructured materials with growth time 3 hours, 8 hours and 12 hours respectively.

The EDS analysis of the CdSe nanostructured materials are also performed and is shown in Figure 4. Atomic weight percentage of Se & Cd for the as-prepared samples are nearly to its stoichiometric ratio for different growth time.

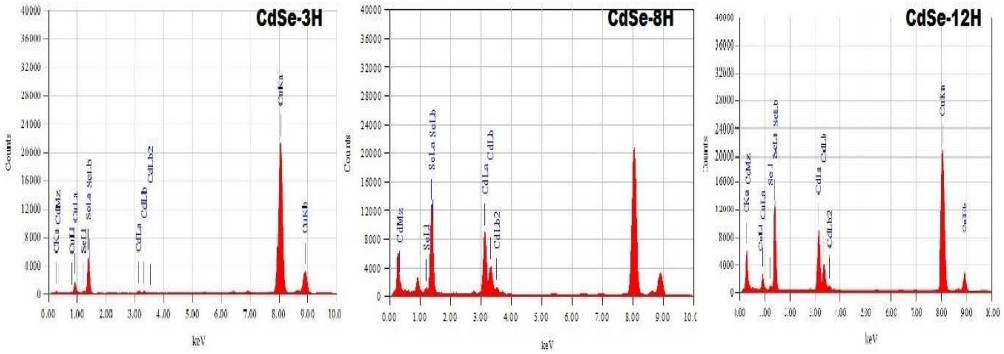

Figure 4: EDS analysis of the CdSe nanostructured materials for growth time of 3 hours, 8 hours and 12 hours.

Figure 5 displays the variation of optical absorbance with wavelength of the as-prepared nanostructured materials synthesized at 3 hours, 8 hours and 12 hours growth time.

Figure 6 shows the plot of $(\alpha h\nu)^2$ vs. energy ($h\nu$) to determine the bandgap of the samples using the relation $(\alpha h\nu) = C\,(h\nu - \Delta E_g)^{1/2}$. The bandgap calculated for the CdSe nanostructures grown at 3 hours, 8 hours, and 12 hours are 2.01 eV, 2.49 eV and 2.52 eV respectively. The increase in bandgap with the growth times is in well agreement with the quantum confinement of the nanocrystalline. The Photoluminescence spectrum (PL) of the CdSe nanostructured materials synthesized at different growth time are shown in Figure 7. From the figure it is clear that there is a peak shift towards the higher energy with the increase of growth time which supports the photo-absorption behavior of the material shown in figure 7. PL peak width increases with the increase of growth time

which is due to shape transition from nanoparticles to nanorod.The variation of particle size and its corresponding measurements are shown in Table 1.

Growth time of CdSe nanostructure (hours)	Shape Transition of CdSe nanostructure	Average size of the CdSe nanostructure	Bandgap (eV)
3	Nanoparticles	5-8 nm	2.01
8	Nanoparticles and Nanorod(mixed)	50-75 nm in length and 10-25 nm diameter	2.49
12	Nanorods (mostly)	350-375 nm in length and 20-25 nm diameter	2.52

Table 1: Summarization table of the as-prepared CdSe nanostructured materials.

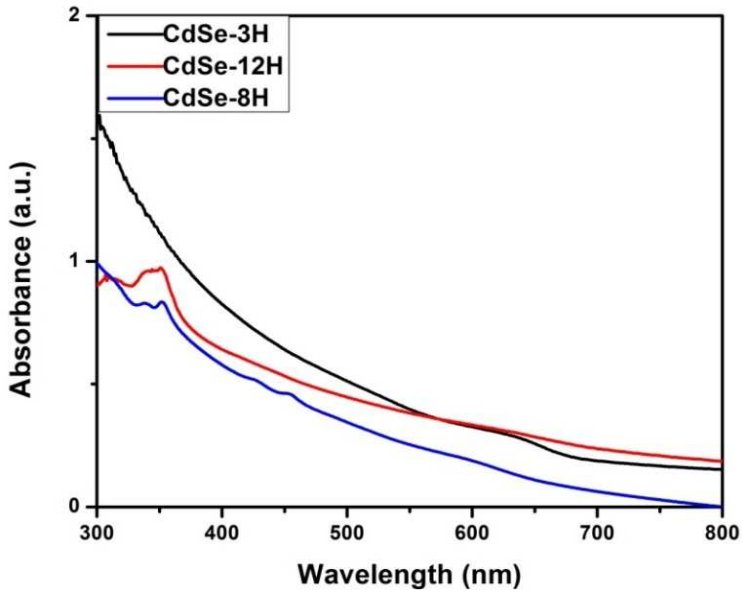

Figure 5: Plot of optical absorption spectra of the CdSe nanostructure materials synthesized with different growth time.

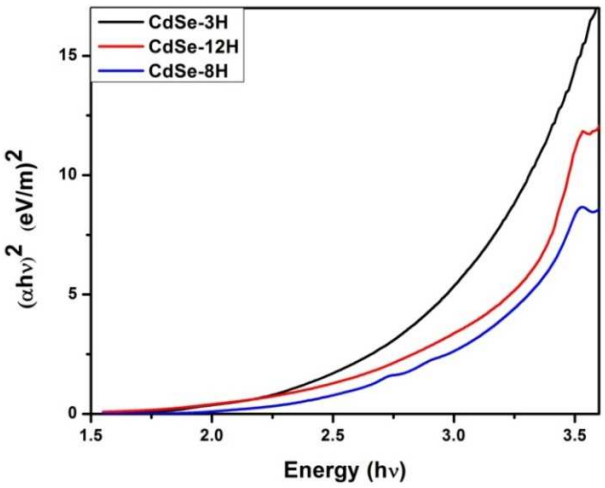

Figure 6: Plot of $(\alpha h\nu)^2$ vs. Energy ($h\nu$) for the measurement of bandgap of the CdSe nanostructures grown at different stirring time.

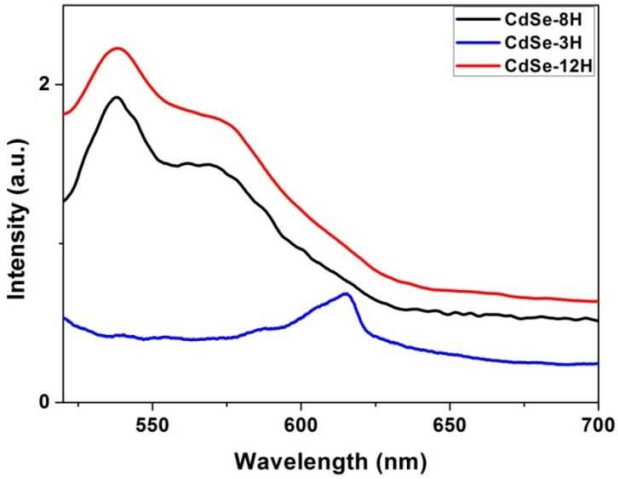

Figure 7: Photoluminescence spectra of the as prepared CdSe nanostructured materials with different growth time.

4. Conclusion

The used method to synthesize the CdSe nanostructured materials is cost effective. CdSe nanostructured materials are synthesized with different growth time. The shape of the material changes with the growth time. At lower growth time (3 hours) spherical particles are observed whereas at 12 hours growth time the spherical nanoparticles are aligned lengthwise to form nanorods. The intermediate time (8 hours) indicates the shape transition from nanoparticles to nanorods which confirms that shape of the nanostructured materials are growth time dependent. Optical absorption study shows that

with increase ofgrowth time the band gap increases and the peak shifts towards higher energy value. This clearly indicates that at higher growth time the quantum confinement is more.

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