Synthesis and characterization of CdS nanoparticles by chemical growth technique

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Semiconductor nanoparticles are very attractive & interesting objects for scientific research of strongly confinement effects & tailoring of band gap. Semiconductor nanocrystallites will dominate in future generation of electronic devices and growth of science and technology. Among the various materials used for fabrication, cadmium sulphide (CdS) nanoparticles have drawn much attention because of its potential application and variety of methods of its preparation.. The most important information to be obtained from growth analysis concerns the sizes, the size distribution, stoichiometry, structure and the interface configuration of the nanocrystals. Formations of nanoparticles have been characterized using various sophisticated instruments like double beam spectrophotometer, X-Ray diffraction (XRD) and Transmission Electron Microscope (TEM). Surface morphology & composition have been observed by SEM, Atomic Force Microscope (AFM) and XRF technique. Formation of bonds was examined by FTIR. Determination of size and composition observed from various characterization techniques have shown that nanoparticles size is less than 6 nm.

1. Introduction

Semiconductor nanocrystalline material (such as quantum dots) is of great current interest [1-3]. The electronic and optoelectronic properties of nanoparticles are well understood. Yet there is an interest in this system due to the size controlled band gap from quantum confinement. As the size of nanocrystallite is decreased, quantum confinement of charge carriers causes a blue shift of absorption. The size dependence of physical and optical properties of nanocrystal have been studied in high quality samples. CdS quantum dots embedded in polymer matrices have been widely investigated. In earlier studies most workers used a controlled colloid precipitation method to synthesise the CdS nanoparticles.10 CdS dots made in aqueous solution at room temperature result in relatively low quantum yields due to insufficient crystallization of their surfaces.

Apart from highly expensive and complex method, like MBE, chemical solution also provides nanoparticles as efficient as grown by MBE. CdS nanoparticles embedded in Polymer matrix have been subject of many theoretical and experimental investigations [3] Quantum dots are semiconducting inorganic nanocrystallites with critical dimensions smaller than the Bohr radius of the material in question. They have great potential in electronic devices, because of their unique nonlinear optical and luminescence properties [5–7]. Nanoparticles of II–VI semiconductors can be formed, without much difficulty, using a chemical route. Moreover, almost all these II–VI semiconductors are direct-bandgap materials and allow manipulation of properties by controlling the stoichiometry

The incorporation of quantum dots into monodisperse polymer microbeads can give materials with reproducible properties, which can be used in applications such as: optical coding, biological assays, optical data storage and sensing. [8-9] In this present article, we report the synthesis of CdS Quantum particle by using chemical bath technique. PVOH is used as a capping material. The sample structures were analyzed by UV-VIS spectrophotometer, XRD & TEM. Surface morphology and composition have been observed by SEM, AFM, EDS and XRF technique. Formation of bonds was examined by FTIR.

2. Experimental

5 wt% solution of polyvinyl alcohol (PVOH), $CdCl_2$ was added with various concentration (2,3,4 wt%) under a high stirring rate (200 rpm). Aromatic solids like PVA, being good solute to multiple phase system and it provides uniform gaps that are very close to each other and distributes in the form of array The constant temperature 70^0C for 3 hours was maintained. The sample under preparation was kept for 12 hours for complete dissolution to get a transparent solution. To this solution 2 wt% Na_2S was added till the whole solution turns into yellow colour. The CdS nano particle containing PVOH were caste over glass slides to produce thin film form. The chemical reaction occurs as follows

$$\longrightarrow \quad CdCl_2 + Na_2S \quad CdS + 2NaCl \qquad (1)$$

The size of the quantum dots formed depends on the number of cadmium ions exchanged and hence on the concentration of the cadmium chloride solution. Changing the temperature of the solution, amount of polymer stabilizer, pH of the whole solution and controlling the stirring time of the solution controlled the size nano particles.

X-ray powder diffractograms (XRD) of the samples are taken on a Philips X'Pert Pro diffractometer. operating at 40 kV-30mA The radiation source used was CuKα (λ =1.542 Å) and a Nickel filter was used to block K_β. Radiations. Optical absorption spectra of the samples are recorded using (HITACHI-U3210) double beam spectrophotometer in the range 800–200 nm. SEM observations of the CdS nanocrystals were performed by using (model LEO 1430VP). TEM observations of the CdS thin films were performed by using (model JEOL JEM-100cx) transmission electron microscope, operating at 400 kV accelerating voltage The AFM measurements were performed in contact mode in air by using a molecular imaging microscope (model PICO Scan 2500). The composition of the samples were analyzed by Energy Dispersive X-ray Spectroscopy (EDX) attached with SEM and X-ray Fluorescence Spectroscopy (XRF)(PW1480 of Philips, Holland).

3. Results and discussion

As the size and presence of impurity cause dramatic changes in the properties of semiconductor nanostructure, it is therefore essential to characterize the sample after formation of nanoparticle. The samples are subjected to different characterization technique as described bellow.

XRD observation In order to identify the structure and phase, the diffraction patterns of as prepared sample were taken by Philips X'Pert Pro diffractometer operating at 40 kV-30 mA.
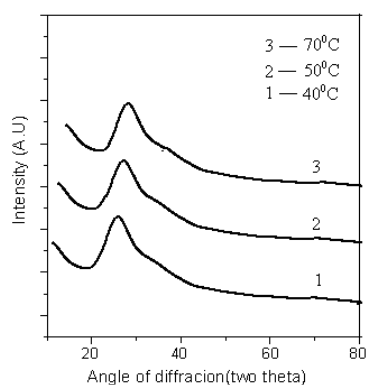

Fig. 1. XRD pattern of CdS nanoparticle at different synthesis temperature.

Fig.1 shows the XRD spectra of CdS nanostructure at different temperature of whole solution. A broad peak at $2\theta = 26.7, 26.9, 27$ in samples 1, 2 and 3 shows the formation of CdS nanocrystallites, clearly suggesting small crystallite size of cubic phase. X-ray peak intensities

are weak and broad compared to bulk counterpart suggesting the crystalline sizes are small. Besides the single phase in nano CdS, the X-ray peaks shifted to higher diffraction angle with decreasing crystalline size suggesting lattice contraction. The lattice contraction is expected to occur because of higher surface to volume ratio [10]. Besides a predominantly cubic phase some separate peak also identified, which may be CdO. As the XRD patterns were recorded in ambient condition the phase of CdO is not surprising. The average grain sizes of the crystallite are calculated by using Sherrer formula [11].

$$D_{hkl} = K \lambda / w \cos\theta) \tag{2}$$

w being FWHM and θ is the Braggs angle and K= 0.89 for spherical shape(confirmed by TEM). From Fig. 1, it is observed that, as the temperature increases from 40^0C to 70^0C, the particle size decreases. Above the 70^0C no XRD traces are recorded. As the temperature increases the value of pH decreases and due to the common ion effect the rate of reaction becomes very slow and particles formation becomes large. The calculated size is found between 4.8-7.3 nm. The optimum range of temperature is found between (50^0C-70^0C).

Optical observation The optical properties of semiconducting material mainly depend upon band gap. Bulk CdS semiconductor is a direct band gap (E_g=2.42 eV at 300K). The nature of band gap was obtained by plotting $(\alpha h\nu)^2$ vs hν using the relation

$$\alpha h\nu = const (h\nu - E_g)^n \tag{3}$$

For direct transition n=1/2 and for indirect transition n=2. The value of α is obtained from α =2.3026(A/ t) where A is absorption and t is the film thickness. Thickness of sample is measured by Gravimetric method [11] using high precision electronic balanced. According to Gravimetric method the film thickness can be calculated as

$$Thickness (t) = M/\rho a \tag{4}$$

where M= mass of the deposited film, ρ= density of CdS and a= area of film. From XRD the density of CdS is found 4.87 g/cm^3.
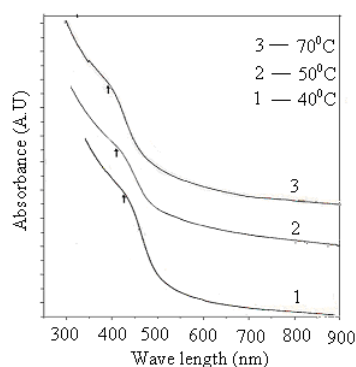

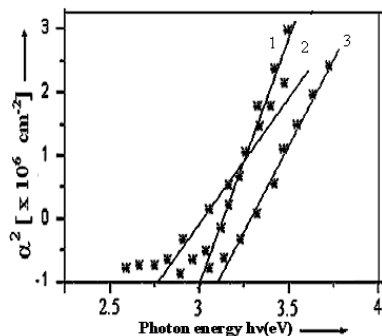*Fig. 2. Absorption spectra of CdS nano particles at different synthesis temperature.*

Fig. 3. α^2 versus hν showing the band gap energy.

Fig. 2 shows the absorbance spectra and Fig. 3 determination of band gap from equation 3. The optical absorbance of CdS films were recorded at the room temperature using double beam automated spectrophotometers (HITACHI-U3210). The spectrum has shown absorption maximum at 380 nm, which is expected to be 1S-1S quantum particle as suggested by Brus [12]. We have calculated the blue shift energy (514 to 420 nm) with respect to bulk. A hyperbolic band model as proposed [6] has been used to explain the change of energy gap as a function of particle size. The equation derived for radius of particle is given by

$$E^2_{gn} = [\ E^2_{gb} + 2\hbar^2 E_{gb}(\pi/R)^2 \ / \ m^*].   \quad (5)$$

where m^* is the effective mass of the specimen, E_{gb} is bulk band gap and E_{gn} is the band gap in strong absorption edge. The average particle size is calculated and found to be between 5 to 9 nm, which is not same in accordance with size obtained by TEM observations and Deby Sherer formula. From the absorption spectra it is observed that due to the confinement of holes and electrons, the lowest energy of optical transition from valence band to conduction band increases, resulting in the increase in effective band gap and as a result in decrease of particle size.

TEM studies   The nanostructures observed using TEM prepared at optimum growth temperature is shown in Figure 4. Almost non-dispersed, individual nanoparticles were identified as bulk dot in TEM micrograph. It is to be noted that the TEM photograph patterns were recorded using a selected area observations and the particle sizes were determined in higher magnification ($\sim 2 \times 10^5$).
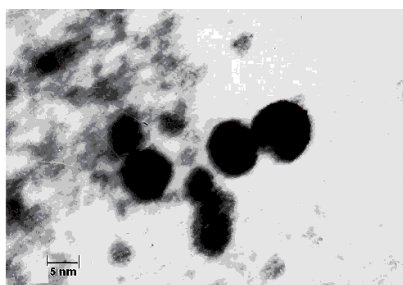

Fig. 4. TEM image of CdS nanoparticle at temperature 70⁰C.

AFM studies   Fig. 5 and Fig. 6 shows AFM the images of CdS films with various growth temperatures. The surface of CdS films exhibited uniformity in temperature range 60^0 to 70^0C. It indicated that there would be more defects existing higher temperature growth condition films with varying grain size and orientation distributions.

Temperature bellow 60^0C films are observed to have smaller grains, non-uniform grain size and random orientation with poor degree of crystallinity. As the growth temperature of films decreases during deposition, the deeper layers of atoms are subjected to stronger interatomic forces and form a compact structure, whereas for thin films the atoms near the surface are subjected to a weaker interatomic force and thus form a spongy loose packed structure. The variation of the surface roughness was observed at different temperatures. The drastic change in surface roughness is in conformity with the analysis of the growth of the film.
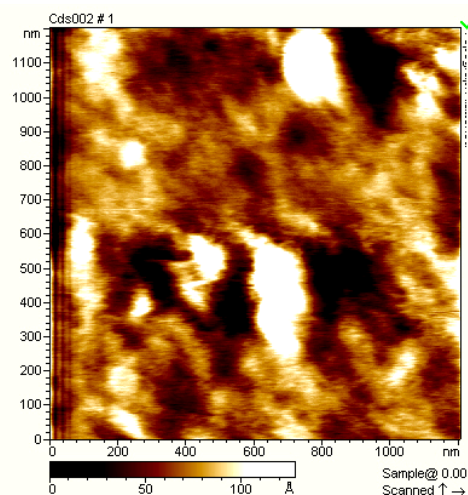
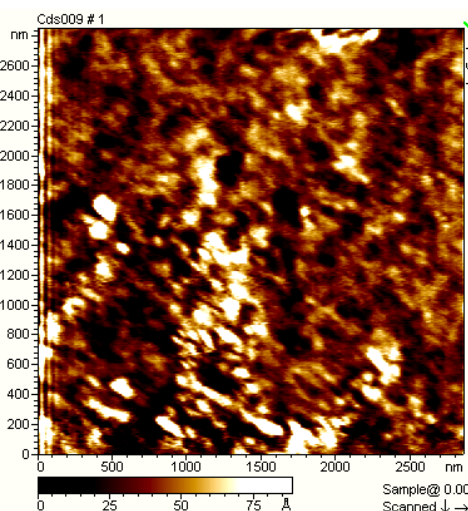

Fig. 5. AFM image of CdS nanoparticlet at temperature 40⁰C.

Fig. 6. AFM image of CdS nanoparticle at temperature 70⁰C.

SEM studies. Observations of the CdS nanocrystals grown at different temperature were performed by using SEM (model model LEO 1430VP). Figure7 shows the surface morphology of a nanocomposite prepared at temperature 70^0C with PVA: CdCl$_2$=5:4 and at pH=2. The picture shows the particles are not completely spherical in shape. The size obtain from other characterization was different with SEM observation. The discrepancy associated with nano-CdS samples could be the non-spherical geometry of nanoparticles and SEM also reveal with grains and topographical observations [13].
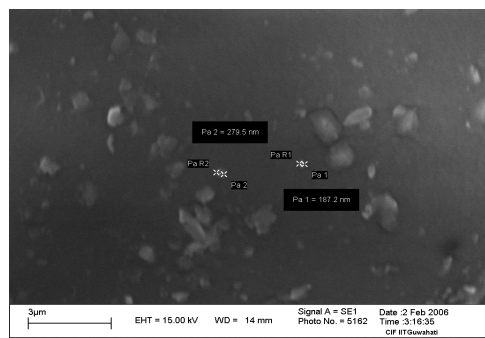

Fig. 7. SFM image of CdS nanoparticle at temperature 70^0C.

Energy Dispersive X-ray Spectroscopy (EDX) and X-ray Fluorescence Spectroscopy (XRF). Fig. 8 shows the composition of the CdS nanocrystalline thin film with the help of Energy Dispersive X-ray Spectroscopy (EDX.).
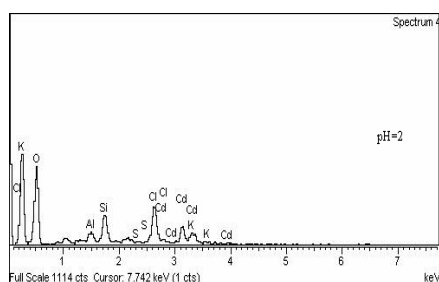

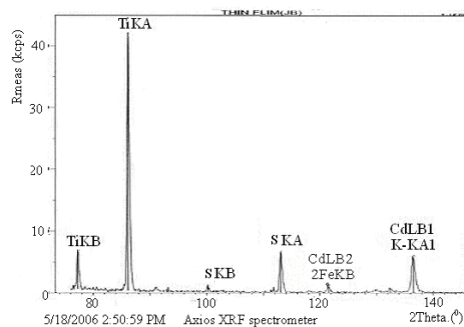*Fig. 8. EDX spectrum of CdS nanoparticle at temperature 70^0C.*

Fig. 9. XRF spectrum of CdS nanoparticle at temperature 70^0C.

Fig. 9 shows the composition of the CdS sample with the help of X-ray Fluorescence Spectroscopy (XRF) Both Fig. 8 and Fig. 9 shows the clear peaks of Cd and S, but some additional peaks are also present. Si peak is due to the amorphous glass substrate (Silica SiO$_2$). It was also observed that sample contains higher percent of cadmium (Cd) and less percent of sulfur (S) compared to cadmium. Peak of oxygen is also present which indicates presences of CdO as the sample were kept in ambient condition. Peak due to CdO was also observed in XRD spectrum [15]. The compositional analysis shows the presence of both cadmium and sulfur and indicates the excess of Cd, thus our samples are expected to be n type [14].

Infrared, Spectral Properties. Infrared spectra CdS crystallite doped polyvinyl (PVA) were taken between the ranges of 400 to 4000 cm^{-1} for CdS at temperature 70^0C. Fig. 10 shows the infrared spectra of doped samples.
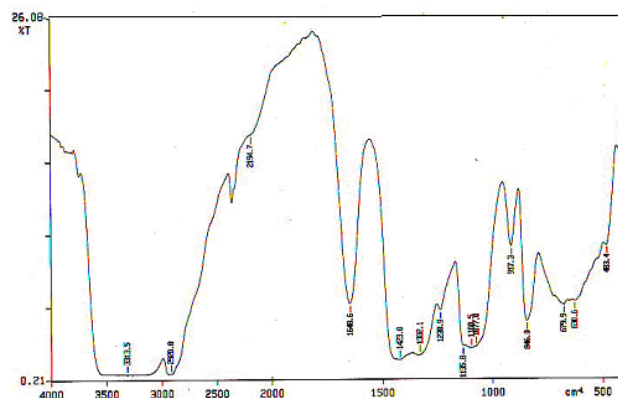

Fig. 10. FTIR spectrum of CdS nanoparticle at temperature 70^0.

Y. Badr etal [16] has reported the infrared spectral properties of PVA matrix. The medium strong band at 679 cm^{-1} and 813 cm^{-1} has been assigned as Cd-S band. There was no change in the peak positions of matrix with doping of CdS in the PVA network. This means that the CdS crystallites formed in the pores of PVA networks without disturbing the continuous three-dimensional network of the matrix. Both are independent in their chemical behavior. The main purpose of the PVA network is to provide the nanopores in which the CdS crystallites grow to nanometer size.

4. Conclusions

CdS nanoparticle of different crystallite sizes have been synthesized by chemical growth techniques. The particle size is controlled by stirring rate, temperature of the solution and time of stirring. The samples were characterized by XRD, UV-VIS spectrophotometer, SEM, TEM, AFM, EDX, XRF and FTIR and show formation of CdS quantum dots having size between 4-7nm. The sizes of nanoparticle obtained from various observations are

found to be between 3 to 7 nm. The optimum temperature for minimum size is found to be 70^0C and PVA: $CdCl_2$ ratio is found to 5:3 in our observations.

Acknowledgements

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