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Synthesis of CdS: Cu Nanorods For Application In Photonic Devices

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ABSTRACT :

In our present work undoped CdS and Cu doped CdS thin films were deposited on glass substrate by chemical bath method. XRD analysis of the as-prepared sample indicated CdS:Cu nanorods to be mixture of two phases namely hexagonal and cubic. It has been observed that one particular plane (100) has preferentially grown as the maximum intense peak whereas the other two planes (101) and (102) have diminished intensities indicating the highly oriented growth of the particles. TEM image of CdS: Cu nanostructure shows the garland like nanorod structures that consist of the mixture of cubic and hexagonal particles. Hexagonal particles confirm the hexagonal phase of the CdS. Some particles dispersed in hexagonal form are weakly agglomerated. The size of the hexagonal structure is in the range of 75-100nm. The TEM image of the undoped CdS reveals the similar hexagonal structure of those CdS nanoparticles. The UV_VIS spectra of Cu doped CdS show the red shift of quantum confinement over undoped CdS. The additional long wavelength absorptions shows that copper can exists as different types of impurities such as replacing host Cd in its lattice site as well as interstitials within the crystal lattice.

Keywords – CdS:Cu, Nanorods, Nanoparticles, TEM.

1. INTRODUCTION:

Synthesis and characterization of discrete nanostructure is of significant importance because of their fundamental role in basic research and technological application [4]. Nanostructures of metal sulfide semiconductor such as CdS, ZnS and CuS etc have aroused much attention in recent years due to their unique electronic and optical properties and potential applications. [1-5]. It is reported that metal doping on such semiconductor results the formation of the different types of nanostructures with novel properties[5] and increase surface to volume ratio in nanoparticles enhances surface and interface effects resulting in novel phenomena [4-5]. Furthermore luminescence characteristic of metal doping CdS nanocrystals differ markedly from those of the bulk CdS [11].

CdS is one of the important electronic materials which has a potential to use in the fabrication of various electronic devices such solar cell, photo sensor and electronic display screen [9]. It has band gap 2.4eV and thereby have a tendency to nanostructure if it synthesis in proper matrix [8]. Although many researchers have synthesized CdS nanostructure in thin films as well as colloidal powder, yet there has large scope in studying the doping effect on the optical properties of this material. The problem of doping is yet to be solved. The effects of external and internal doping in the synthesis as well as the physics of doping pattern are yet to be understood. Hence more experimental findings are desirable for modulating future device oriented optical properties. The chemical growth is quite easy and inexpensive for the synthesis compared to the other method. Keeping the above aspects, an experimental work on the chemical synthesis of CdS and Cu doped CdS has been taken to study their structural and optical properties.

2. SYNTHESIS: MATERIALS AND METHODS:

The simple chemical both deposition (CBD) method was employed to deposit Cu doped CdS thin films on to glass substrates. The undoped CdS deposition was carried out in a matrix solution of equivolume and equimolar $CdSO_4$ and thiourea in an alkaline medium. The solution of $CdSO_4$ (0.5M) was prepared by dissolving $CdSO_4$ in deionised water. An aqueous solution of 3% weight of poly-vinyl alcohol (PVA) was prepared with constant stirring at constant room temperature and kept overnight prior to the deposition. The PVA solution was mixed with $CdSO_4$ solution under constant stirring to form a well dispersed PVA capped Cd^{2+}ion solution. Ammonia solution was added slowly to the above matrix solution to form the metallic complex. The P^H was adjusted between 10 and 12. The thiourea as S^{2-} ion source was then added to the metallic complex solution drop by drop to form colloidal solution of CdS nanoparticles. For Cu doping, $CuSO_4$ solution of 0.005M was mixed with the host $CdSO_4$ (0.5M) solution prior to deposition and similar steps were followed to have final CdS:Cu matrix solution. Commercially available glass slides were cleaned through boiling in chromic acid, rinsed with distilled

water and dried in air. The glass slides were dipped in the final matrix solution for 48-56 hours to cast thin films.

3. CHARACTERIZATION:

These thin films were taken for XRD study and the solutions were used for optical as well as TEM studies. The structural investigation of CdS and CdS:Cu was carried out using X-ray powder diffractometer (Model: Seifert XRD 3003 T/T) with CuK_α radiation (λ =0.15406nm) scanning 2θ in the range 20^0-80^0. The morphology of the nanoparticles were characterized by transmission electron microscope (TEM) [Model: JEOL JEM 100CX-II] operated with an acceleration potential of 100 kV. The UV-Visible absorption of the samples was recorded using an automated spectrometer (Model: HITACI 113210) in the wavelength range 200nm - 800nm.

4. EXPERIMENTAL RESULTS AND DISCUSSION:

4.1. XRD STUDY:

The X-ray diffraction (XRD) of nanocrystallines CdS and of CdS doped with Cu^{2+} are shown in the figure – 1(a) and 1(b) respectively. Analysis of the XRD indicated CdS nanorods to be mixture of two phases namely hexagonal and cubic [6, 8]. Considerable broadening is evident from the XRD data [6]. It has been observed that one particular plane (100) has preferentially grown as the maximum intense peaks whereas the other two planes (101) and (102) have diminished intensities attributing one dimensional growth of CdS nanostructures [6]. For Cu doped CdS, Cu and Cu related phases are not detected which implies the homogeneity of compound. F. Atay *et al* reported that the reasons of such undetection are the little amount of Cu in the thin films and the sensitivity of the XRD [8]. However the low amount of dopant concentration is enough to bring noval optical properties [5, 6, 11]. The crystalline size of the as-synthesised Cu doped CdS nanostructures have been calculated using the Scherer equation from FWHM values of the peak corresponding to (200) with a 2θ =30.15^0 and is around 9 nm. Similarly the estimation of crystalline size of CdS nanostructure is around 4nm indicating the formation of quantum dots particles.

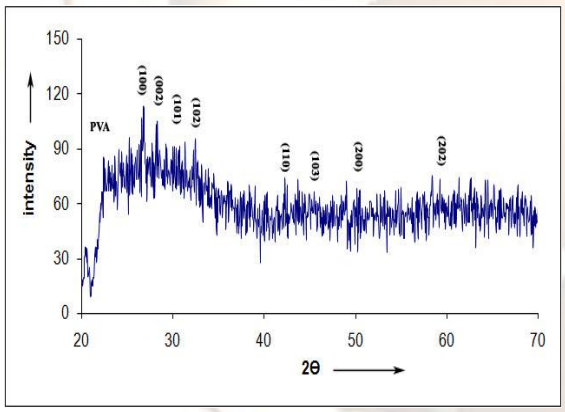

Fig 1(a). XRD of CdS (0.5M)PVA .

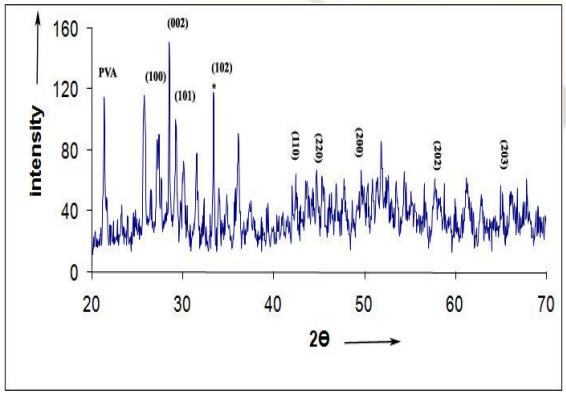

Fig 1.(b). XRD of CdS;Cu (0.1M) PVA

4.2 TEM STUDY:

The figure 2(a) representing TEM (Transmission Electron Microscope) image of CdS nanostructure shows the hexagonal type particles which confirm the hexagonal phase of the CdS. It can be seen that CdS particle are well dispersed in hexagonal form [9]. Some particles are weakly agglomerated due to the large amount of particles presented.

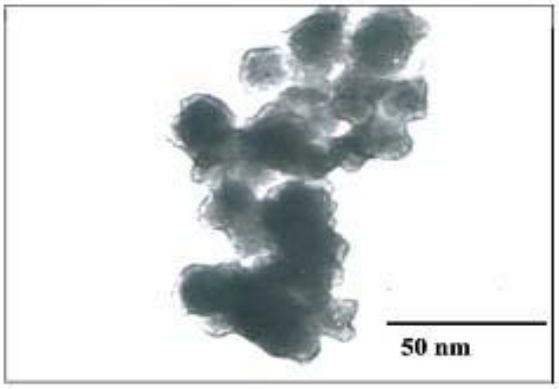

Fig. 2(a). TEM image of CdS (0.5M) PVA

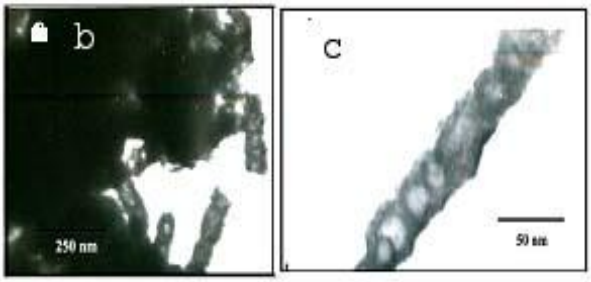

Fig. 2(b) and(C).TEM image of CdS :Cu(0.5M) nanorods

in the TEM image. The size of the hexagonal structure is in the range of 75-100nm

The figures 2(b) and 2(c) display the TEM image of Cu doped CdS nanoparticles in different magnification. In TEM image, the CdS:Cu phosphor exhibits the similar hexagonal structure of those CdS nanoparticles [15] . However, the hexagonal structure formed a garland like nanorods structures as similar to determined by other report[8]. The nanorods consist of hexagonal particles of individual size in the range of 100 to 125 nm. The figure 2(c) in higher resolution shows the formation of fine garland like nanorods structure with hexagonal arrangement of the individual particles with mixture of cubic structures. These particles are uniform with side chain agglomeration and the average width and length of garland are 55nm and 450 nm respectively. Hence the Cu doping initiated a one dimensional growth type nanostructure in CdS semiconductors [6].

4.3 UV_VISIBLE STUDY:

Fig.-3(a) and Fig.-3(b) show the UV_Visible absorption spectra of CdS and CdS:Cu respectively prepared in PVA matrix. The absorption peaks due to their transition between

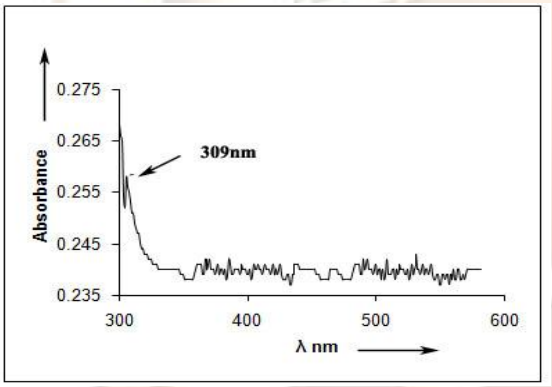

Fig.3 (a) Uv_Vis Absorption spectra of CdS (0.5) PVA.

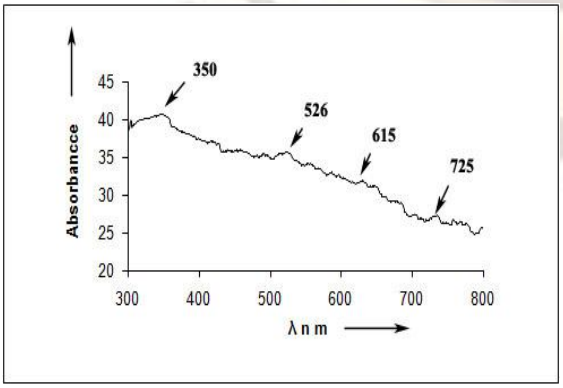

Fig. 3(b). UV_VIS absorbance Spectra of CdS:Cu (0.5M)PVA

the electronic state in the conduction band and hole state in the valence band is given in the TABLE-1. From the absorption peaks the optical energy band gap of CdS and CdS:Cu have been calculated using the formula

$$"E_{gn}=hv_{gn} = hc/\lambda_{gn"} \quad \text{..... (1)}$$

where h = plank's constant, E_{gn} = *enrgy band* gap of the semiconducting nanoparticles in the optical spectra and the calculated band gap energy are shown in the TABLE-1. Band gap energy of Cu doped CdS is decreased as compared to that of CdS nanoparticles attributing the structural and optical changes. In CdS:Cu film additional absorption lie on the long wavelength 526nm, 615nm and 725nm. This is attributed to the presence of energy levels within the forbidden gap due to Cu as different type impurities [5]. In case of doping process, depending upon the doping pattern, Cu may either replace Cd lattice site or as interstitial within the crystal lattice. Considering the band gap energy of bulk CdS as 2.34eV, large blue shift is observed in both CdS and Cu doped CdS. This indicates a clear quantum confinement in PVA capped CdS nanostructures. C. M. Janet *et al* reported that when the size of CdS nanocrystal becomes smaller then the exciton radius a remarkable quantum size effect leads to a size dependent increase in the bandgap and a blue shift in the absorption onset [6]. From these

TABLE:1. CALCULATION OF BAND ENERGY AND PARTICLES SIZES OF CdS and CdS: Cu

Samples	λ_{gn} (nm) absorption peak	E_{gn}(eV) (band gap	E_{gb} (eV) (Bulk band	ΔE_{gn} (eV) (blue shift)	Particles size D(diameter)
CdS	309	4.04	2.34	1.7	5.7
CdS: Cu	350	3.53	2.34	1.19	6.8

Calculated blue shift values (TABLE-1) theoretical size of the nanoparticles can be determined by using Effective Mass Approximation (EMA) method. The formula in EMA calculation as derived by L.E.Brus is given as [12]

$$"\Delta E_{gn} = \pi^2 h^2 /2R^2/ (1/m_e +1/m_h) -1.8e^2/\varepsilon R"$$

……..(2)

Where m_e = effective mass of the electron of the specimen, m_h = effective mass of hole of the specimen, h =6.58 x 10^{-16} eV and R = radius of the nanoparticle. The size of the particle (D) is given by D = 2R and the estimated sizes of CdS and CdS: Cu

are 5.7nm and 6.8nm (table-1) respectively which indicate quantum size effect. This increase of particle size decreases the band gap which shows a clear red shift on Cu-doping. It is reported that the increment in bandgap is approximately inversely proportional to the square of the crystal size based on the effective mass approximation [13].

5. CONCLUSION

CdS and Cu doped CdS have been synthesized successfully through chemical route and their respective sizes lie in the range of 5 nm~ 10nm which have inferred by XRD and TEM. XRD analysis of the as-prepared sample indicated CdS:Cu nanorods to be mixture of two phases namely hexagonal and cubic. The TEM image shows the formation of garland shaped CdS nanostructure. The UV_Visible study reveals large blue shift both in CdS and CdS:Cu nanoparticles indicating the strong quantum confinement. The additional long wavelength absorptions shows that copper can exists as different types of additional impurities such as replacing host Cd in its lattice site as well as interstitials within the crystal lattice. The absorption edge is red shifted with respects undoped CdS that indicate the increase of particle size from 5.7 to 6.8nm. Thus the Cu incorporated CdS nanostructure can bring morphological, structural and optical properties changes. Hence such synthesized CdS:Cu nanorods have a great potential to be used in photonic device fabrication.

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