

SPIN COATING OF HIGHLY LUMINESCENT Cu DOPED CdS NANORODS AND THEIR OPTICAL STRUCTURAL CHARACTERIZATIONS

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Copper doped CdS nanorods were synthesized using spin coating of gel. The gel was formed by new ultra sonicated sol gel route. Fine green and blue colored particles were appeared and filtered for characterization. The samples were analyzed by XRD, SEM, FTIR, Optical transmission and Photoluminescence studies. X ray diffractograms show single broad peak of (101) for undoped CdS. Intensity of this peak increases with increase in Copper doping concentration. Large numbers of islands were observed for undoped CdS. On increasing Cu doping these islands grow as more and more particles bind together and start to re assemble in ordered rodlike structures. Decrease in bandgap and increase in PL with increasing copper concentration make these structures suitable for tunable optoelectronic devices.

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1. Introduction

In recent years, semiconductor nanostructures such as nanoparticles, nanorods, nanotubes and nanowires have received enormous attention because of their novel physicochemical properties, which are more superior to the conventional organic fluorescence materials [1-3]. Due to their wide range of applications, the development of semiconductor nanocomposites presents new challenges and opportunities for future technologies [4-5]. Much attention has been given to II-VI nanocrystals because of their potential applications in electroluminescent and photovoltaic devices [6]. Cadmium sulphide is a brilliant II-VI wide band gap semiconducting material with direct band gap of 2.4eV at room temperature with many notable physical and chemical properties. CdS has promising applications in various technical fields including non-linear optical devices, cathode ray tube, gas sensor, microstrip detectors for laser and infrared and so on [7-8]. Recently doping in semiconductor nanocrystals has attracted much attention due to their advantages of improving emission activity and increasing thermal & photochemical stability. It modifies the properties of semiconductors [9]. However, until now, very few Copper doped CdS nanocrystals synthesis have been reported. It has been reported that even with very small quantity of Cu dopants have ability to tune the band gap of CdS nanocrystals. It forms deep trap levels and act as luminescence centers to make them suitable for wide range of applications such as light emitting displays and optical sensors [10-11]. Visible light emission of various colors with long term stability can be achieved by Cu:CdS [12-13]. The synthesis of CdS nanostructures through sol-gel method involves processing at relatively lower temperature as compared to other methods like hydrothermal synthesis, microwave synthesis, evaporation method and vapor phase synthesis [14-16]. This method is less complicated and has relatively low cost. Sol gel process deals with, chemical reaction in solution at nanometer scale. It can be used to make semiconductor nanostructures of different composition, size and shape suitable for various optoelectronic devices.

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Here, in the paper we have presented the influence of Cu dopant concentration on the crystal structure and the optical properties of Cu: CdS nanoparticles synthesized by ultrasonicated chemical sol-gel method.

2. Experimental

Undoped and Cu doped CdS nanostructures were synthesized by ultrasonicated sol gel route. All the chemicals were of analytical grade supplied by Ranbaxy. The sol was prepared by continuous ultrasonication of mixture of ethylene glycol, ethanol, acetic acid in the ratio 1:2:1 as solvent and Cadmium chloride (CdCl_2) & thiourea as the precursors of Cd and S respectively at 50°C temperature for 3 hours. For Cu doping Cupreous chloride was added slowly. The solution was kept for another ultrasonic agitation for next 5 hours. Finally the sol was kept for another 24 hours for aging. Fine green and blue colored particles were appeared and filtered for characterization. APEX spin coater NXG with speed of 3000-7000 rpm was used to prepare the thin film on the glass substrate. The sample was annealed 300°C for two hours. The samples were analyzed by XRD, SEM, FTIR, optical transmission and Photoluminescence studies. The X ray diffractograms were obtained in the 2θ range from 20 to 80° with Cu $K\alpha$ radiation of wavelength 1.546 \AA using XPERT-PRO XRD, SEM micrographs were obtained using SEM- Zeiss EVO-40 EP, FTIR spectra in the range 400 cm^{-1} - 4000 cm^{-1} using KBr pallet method in Perkin Elmer Spectrum two, transmission spectra were obtained using Perkin Elmer Lambda 25, in the range 200 to 800 nm. PL spectra was obtained using Perkin Elmer LS55.

3. Results and discussion

Fig. 1 shows the X-ray diffractograms of undoped and Cu doped CdS nanostructures grown by ultrasonic sol-gel method dispersed on glass substrates. Broad peak of (101) hexagonal wurzite phase (JCPDS 41-1049) is observed for undoped CdS intensity of which increases with increase in Copper doping. High background peak due to amorphous substrate might occur for very thin layers of CdS.

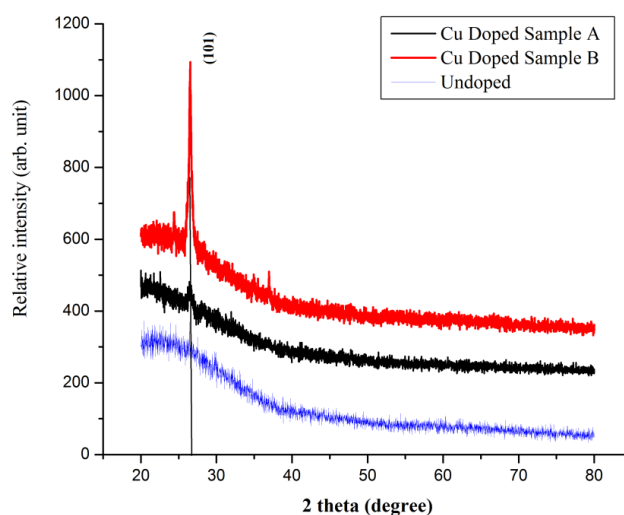


Fig.1. X-ray diffractograms of Undoped and Cu doped CdS nanostructures.

Fig. 2 shows the SEM micrographs of undoped and doped CdS nanostructures. Undoped CdS particles are randomly oriented as large number of islands are observed in Fig. 2(a). Undoped structures are generally hexagonal shape with random size. On doping with copper agglomeration

starts and these islands grow as more and more particles bind together. On further doping it start to reassemble in ordered rodlike structure. Very long rods are observed in SEM micrographs.

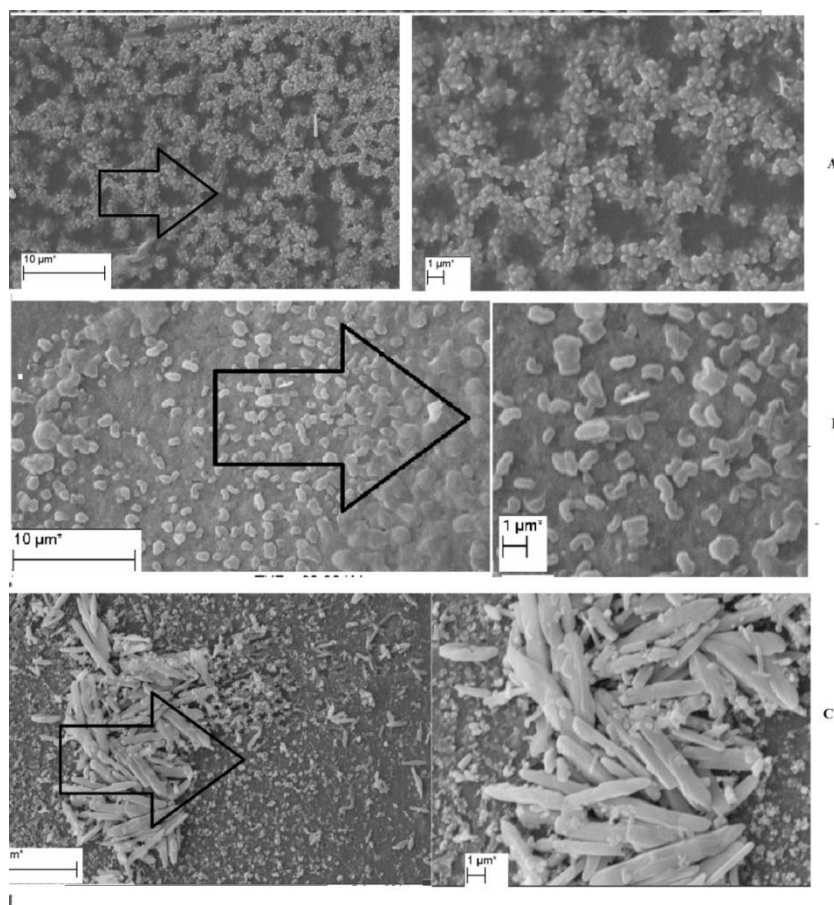


Fig. 2. SEM micrographs of (a) undoped CdS, (b) & (c) Cu Doped CdS with increasing concentration.

Region	Intensity	Comments
500	Very weak	Cd-S bond stretching (CdS nanoparticles)
870, 890	Large sharp	S-S-S bending or C-H stretching (crystal s-s-s bond or acetone)
1040,1070	Large Sharp	C-O or S-O (acetone or sulphate)
1560	Medium Small	due to stretching vibrations of sulphate group
1600	Small	Water molecule
2800,3000	Small	
3500	Large Hump	Broad Intermolecular H-bonds (Lattice water)

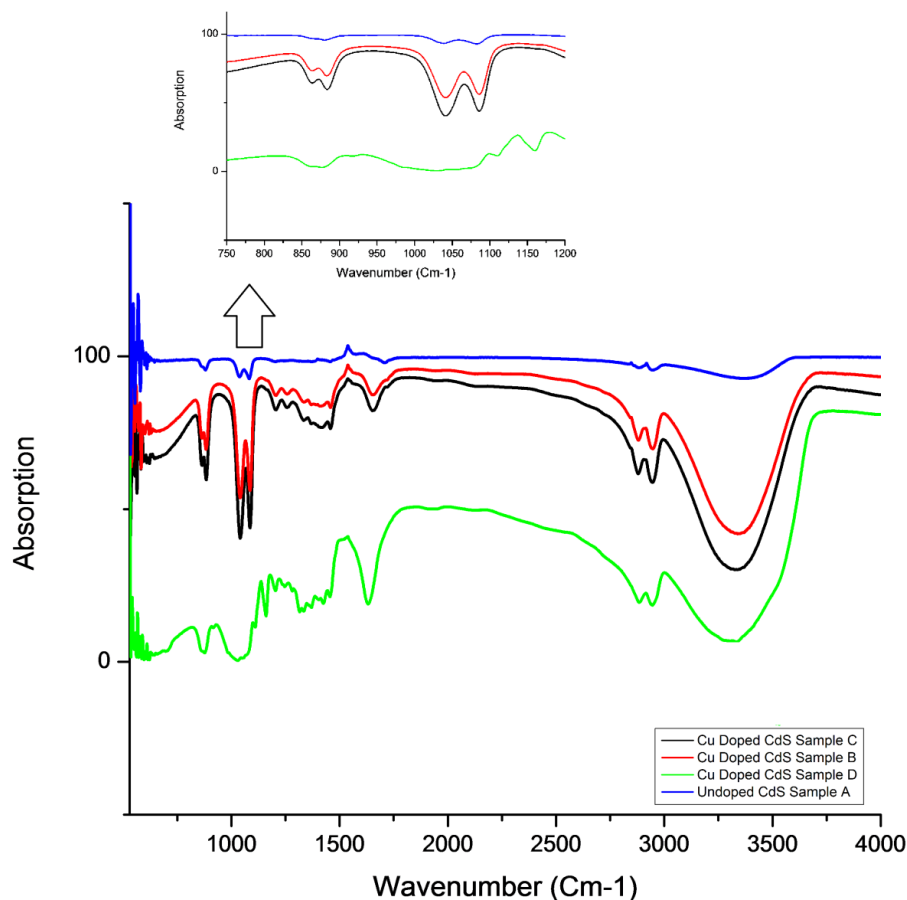


Fig. 3. FTIR Spectra for CdS nanostructures

Fourier Transform Infrared Spectroscopy FTIR spectra shown in Fig 3 obtain using Perkin Elmer Spectrum II in the range 450 cm^{-1} to 4000 cm^{-1} . The samples have been prepared with KBr medium. Absorption at 500 cm^{-1} shows presence of Cd-S bond stretching (CdS nanoparticles) which is very weak due to moisture in the sample [17]. Medium strong band positions 1560 cm^{-1} and are possibly due to stretching vibrations of sulphate group. Traces of SO peak centered at around 1070 cm^{-1} occurred in strong absorption bands [18]. Medium strong band positions 1560 cm^{-1} is possibly due to stretching vibrations of sulphate group. A large hump of absorption band is observed at 3567.66 cm^{-1} is due to O-H stretching vibration of water molecules. The presence of this hump might be due to presence of moisture in the sample. There was no change in the peak positions of matrix with doping of Cu in the CdS network. This shows that the Cu crystallites are independent in their chemical behavior, formed without disturbing the continuous three-dimensional network of the CdS. However it helps in growing rods in nanometer size.

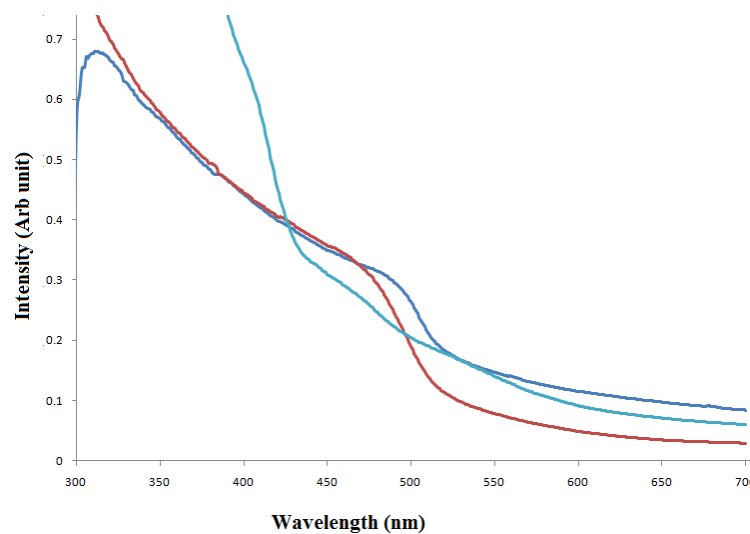


Fig. 4. Transmission spectra for undoped and Cu doped samples

Fig.4. Shows the Optical absorption spectra for CdS particles doped with Cu (in the ratios a, b, and c). Spectra exhibit good transmission in the visible region. Red shift in absorption occurs with increasing the Cu concentration. Similar kind of results already reported by sebastean (1993) and portile-morenoer (2006).

Fig. 5. Shows the normalized PL spectra for undoped and doped CdS samples. Photoluminescence property of CdS nanoparticles is very sensitive to the surface defects and size. For undoped CdS very small luminance is occurred in the range 380 nm to 480 nm. Enhancement in luminescence is observed with increasing Cu ion concentration. For higher concentration of Cu a weak peak at 300 nm is appeared along with strong peak at 580 nm. higher wavelength emission implies involvement of Cu in emission which indicates photoemission is gradually transforming from surface trap to deep dopant related emission with respect to increase in doping. Large peak is observed due to deep traps on heavy doping electron trapped by defects. Cu doped CdS nanoparticles show orange red luminescence due to efficient recombination.

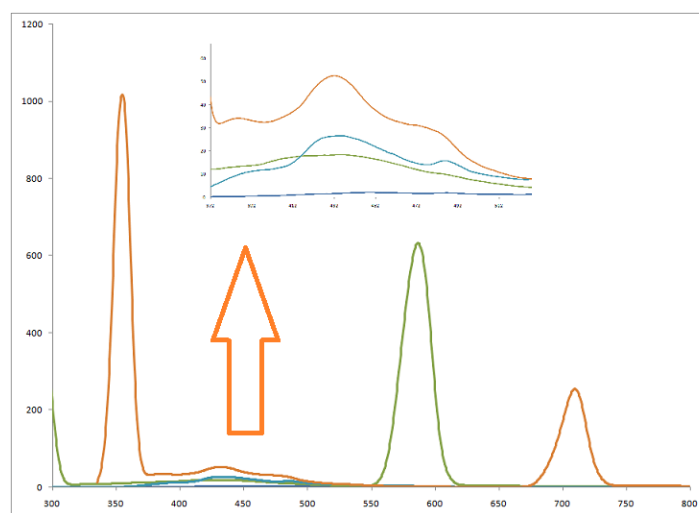


Fig. 5. Photoluminescence spectra for (a) undoped and Cu doped CdS samples

4. Conclusions

Highly luminescence Cu doped CdS rodlike nanostructures were obtained by ultrasonic sol-gel method. Broad XRD (101) peak is observed which increases with increase in Cu doping. SEM micrographs show the assembling of nanostructures in rods on increasing the concentration of copper. Samples are transparent in visible region and gives good luminescence in visible and UV region, makes them suitable for optoelectronic devices.

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