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SYNTHESIS, STRUCTURAL AND OPTICAL STUDY OF CDS NANOPARTICLES DOPED WITH DIFFERENT CONCENTRATION OF Cu

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Semiconductor nanoparticles have received much interest for their optical and electronic properties. CdS nanoparticles have been synthesized by chemical synthesis method using EDTA as a capping agent. Different concentration of Cu is doped in CdS nanoparticles during synthesis. X-ray diffraction (XRD) measurements showed that the nanoparticles have the structure of cubic phase. The broadening of XRD patterns indicates that the prepared samples are nanostructured. The optical absorption of the CdS nanoparticles is studied in the range of 200-800 *nm. The optical properties of CdS nano particle were investigated by the UV-Vis absorption spectroscopy and Photoluminescence. The band gap of CdS nano particles has been determined.*

Keywords: *NANOPARTICLES, X-RAY DIFFRACTION, ABSORPTION SPECTROSCOPY, PHOTOLUMINISCENCE, BAND GAP.*

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1. INTRODUCTION

Nanoparticles have attracted great interest in recent years because of their unique chemical, physical, optical, electrical and transport properties which are different from those of either the bulk materials or single atoms. Due to the vast surface area, all nanostructured materials posses a huge surface energy and thus, are thermodynamically unstable or metastable. One of the great challenges in fabrication and processing of nanomaterials is to overcome the surface energy and to prevent the nanomaterials from growth in size driven by the reduction of overall surface energy. Due to high surface energy of the nanoparticles, they are extremely reactive and most systems without protection or passivation of their surfaces undergo aggregation. Organic stabilizers are usually used to prevent nanoparticles from aggregation by capping their surfaces [1]. The potential applications of semiconductors in optical switching, single charge memories, single electron transistors, etc are most investigated. The physiochemical properties of semiconductors are greatly affected by the consequences of low dimensionality when the radius of the particle is comparable to the Bohr radius of the exciton versus the bulk material. Modification in the electronic levels occurred very strongly due to the limited number of atoms in the particles [2]. In undoped II-VI semiconductors such as CdS, CdTe, CdSe and ZnS, the band gap is engineered by controlling the crystal size, leading to a tunable band edge emission. By doping the nanoparticles with luminescent activators, the excitation can be tuned by quantum size effect while the activator related emission is largely unchanged [3].

Various effort have been made by the researchers to dope transition metal ions in nanomaterials. P.H. Borse et al. [4] have reported the luminescence quenching in ZnS nanoparticles due to Fe and Ni doping. They found that the blue light emission in ZnS nanoparticles could be completely quenched when doped with iron and nickel.

Nowadays the combination of semiconductor NCs with the polymer matrix has received much attention due to their nonlinear optical properties. The polymer prevents particles from agglomeration and provided a stable medium [5].

2. EXPERIMENTAL

Nanoparticles of CdS and CdS:Cu have been prepared by chemical precipitation method. All the chemicals were of analytical grade and were used without further purification. The percentage of cu doping is from 1 wt % to 5 wt %. The samples are given numbers as sample No. 1 for the pure CdS, sample No. 2 for 1 wt % Cu doped CdS and respectively. The particles separated by filtration and centrifugation, and then dried in vacuum decicator for two days.

The wide angle X-ray diffraction pattern of the samples were obtained using Bragg- Brentanno geometry on P analytical X'pert Pro diffractometer in 2θ range of 15-80° with CuK_α radiation source ($\lambda = 1.5406$ Å). The X-ray tube was operated at 45 kV and 40 mA. UV-visible spectrum of the nanoparticels dispersed in alcohol is recorded using Shimadzu Cary Model 5000 spectrophotometer in the wavelength range 200-800 nm. The PL is recorded using Shimadzu PL.

3. RESULTS AND DISCUSSION

3.1 Structural properties

Fig. 1 shows the X-ray diffraction pattern of the CdS nanoparticle and Cu doped CdS nanoparticles (up to 4 wt %) with different concentration. The XRD peaks are found to be very broad indicating very fine size of the grains of the sample.

Three diffraction peaks appearing for all the samples at 2θ values of about 26.67, 43.73 and 51.95 correspond to the (111), (220) and (311) planes of cubic phase of CdS. The addition of Cu to CdS nanoparticles does not create any change in the CdS matrix. The XRD data was refined by removing the broadening due to instrumental and non uniform stain present in the lattice. The average grain size of the sample is determined to be ~ 2.3 nm from the full width at half maximum of the most intense peak making use of the Scherrer equation.

$$D = 0.9\lambda/\beta \cos\theta, \qquad (1)$$

where λ is the wavelength of the X-ray radiation, β is the FWHM in radians of the XRD peak and θ is the angle of diffraction. Average particle size calculated from XRD has been shown in Table 1.

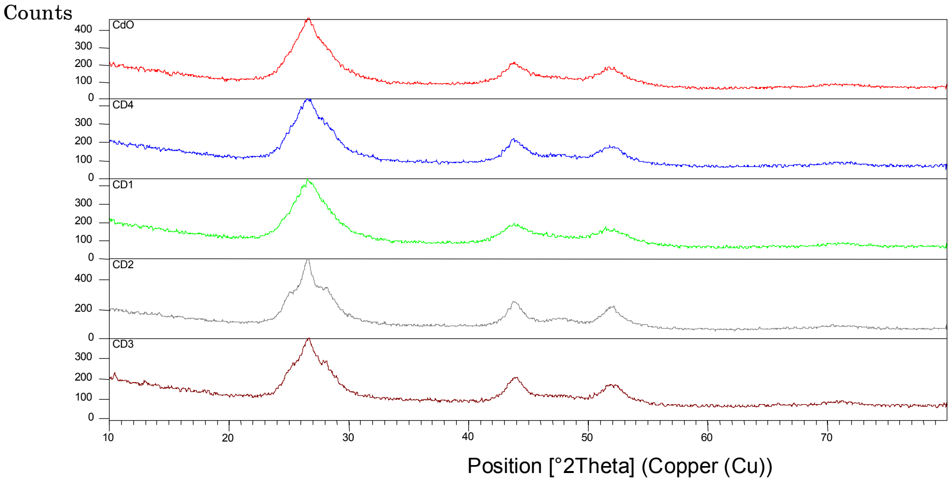

Fig. 1 *– XRD pattern of samples*

Table 1 *– Values of particle sizes of all the sample through XRD*

Sample	Particle Size through XRD (nm)
Sample no.1	2.3
Sample no.2	5.6
Sample no.3	3.0
Sample no.4	2.5
Sample no.5	3.1

3.2 Optical measurements

3.2.1 UV-VIS

The UV-visible absorption spectroscopy has been used to monitor the optical properties of nano-sized particles. The absorption spectrum of the nanoparticles of CdS with doping of different concentration of Cu is shown in Fig. 2. The absorbance versus wavelength traces for all samples have been recorded in the range 300-700 nm. The absorption, which corresponds to electron excitation from the valence band to conduction band, can be used to determine the nature and value of the optical band gap. The relation between the absorption coefficients (α) and the incident photon energy ($h\nu$) can be written as [6],

$$(\alpha h\nu) = A\ (h\nu - E_g)^n \tag{2}$$

where A is a constant and E_g is the band gap of the material and exponent n depends on the type of transition. For direct allowed $n = 1/2$, indirect allowed transition, $n = 2$, and for direct forbidden, $n = 3/2$.The spectrum exhibits well-defined absorption features (peaks) from 475 nm to 495 nm respectively for all the samples, which is considerably blue-shifted relative to the peak absorption of bulk CdS indicating quantum size effect [7, 8].

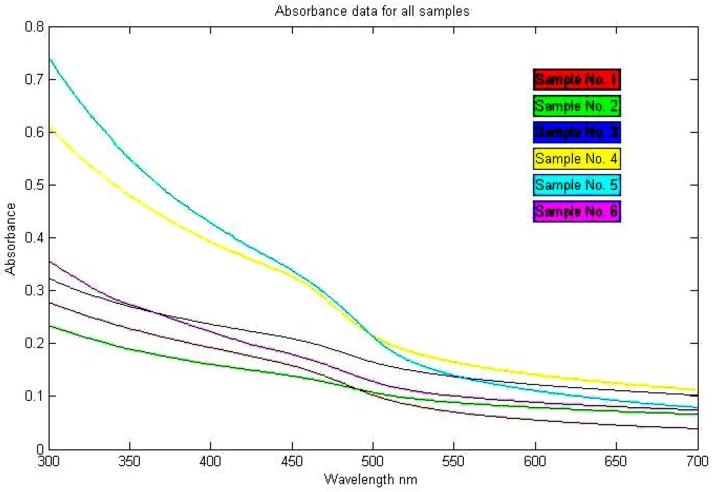

Fig. 2 *– Absorption spectra of all samples*

To measure the energy band gap from the absorption spectra a graph $(\alpha h\nu)^2$ versus $h\nu$ is plotted (Fig. 3) The absorption edge shifts towards the lower value of wavelength (higher energy) with a increase in concentration of Cu. It is clear that band gap increase with doping concentration slightly. The trend of observed band gap variation after doping in present study is similar to that reported earlier [9, 10]. In our system, it is postulated that the number and rate of nucleation is increased with Cu^{2+} doping concentration because of lesser solubility of CuS, which produces relatively small particle leading to quantum confinement effect.

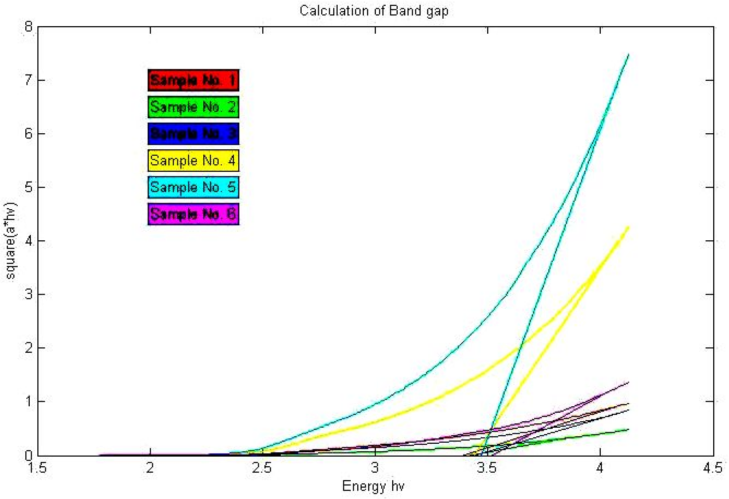

Fig. 3 *– Band gap curve*

Particle size shown in Table 1 is calculated by Brus Equation which is given as

$$E = E_g + \mathrm{h}^2/8R^2[1/m_e^* + 1/m_h^*]1.8e^2/4\ \Omega\ \varepsilon_0\varepsilon_\mathrm{a}R - \\ - 0.124e^4\ /h(4\Omega\varepsilon_0\varepsilon_\mathrm{a})^2\ [1/m_e^* + 1/m_h^*]^{-1} \tag{3}$$

where E is the onset of absorption of the sample, E_g is the bulk band gap, R is the radius of the particle, m_e^*, m_h^* are the reduced masses of the conduction band electron and valence band hole in units of the electron mass m_0, ε_0 is the vacuum permittivity and ε_a is the high-frequency dielectric constant.

***Table 2** – Band gap values and corresponding particle size for different samples*

Sample Id	Sample Details	Band Gap(eV)	Particle Size (nm)
Sample No. 1	CdS Pure	3.38	1.22
Sample No. 2	CdS:Cu 1%	3.40	1.21
Sample No. 3	CdS:Cu 2%	3.43	1.20
Sample No. 4	CdS:Cu 3%	3.44	1.19
Sample No. 5	CdS:Cu 4%	3.47	1.17
Sample No. 6	CdS:Cu 5%	3.51	1.15

3.2.2. Photoluminescence

Photoluminescence emission spectra (at 300 K) of all the samples excited at 300 nm has been shown in Fig. 4. Sample No. 1 shows a peak centered at 600 nm. The broad emission centered at 600 nm is attributed to carrier recombination at surface states. It could be due to either sulphur vacancies or cadmium vacancies depending on the availability of the cations or anions [11]. This broad emission centered at 600 nm is due to cadmium vacancies at the surface of sample No 1.This is to be Red emission while as the concentration of Cu increases in the material, blue shifting has been observed.

Sample No. 2 and 3 are showing emission peak at 545 nm and 543 nm which is Green emission, whereas Sample No. 4 is showing at 520 nm and sample No. 5 and 6 showing at 510 nm and 508 nm respectively. The Green emission band was associated with the emission due to electronic transition from the conduction band to an acceptor level due to interstitial sulphur [12]. Red emission was observed due to the presence of sulphur vacancies [13].

4. CONCLUSION

Nanoparticles of CdS and with different doping concentration of cu are synthesized through chemical synthesis method. The crystal structure and grain size of the particles are determined using XRD. UV-Vis absorption spectrum showed a blue-shift indicating quantum confinement of charged particles. Band gap of particles increases as the concentration of Cu increases in the sample. Blue shifting in PL spectra with increase in concentration of Cu is due to electronic transition from the conduction band to an acceptor level due to interstitial sulphur.

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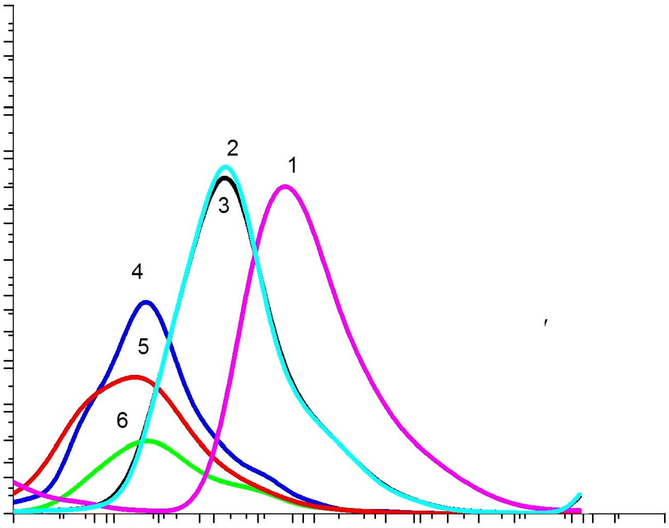

Fig. 4 *– Photoluminescence spectra of all samples*

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