EFFECT OF CU^{2+} DOPING ON STRUCTURAL AND OPTICAL PROPERTIES OF CDS NANOPARTICLES

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Abstract:
Nanocrystalline pure and Cu^{2+} doped (CdS) with different concentration were synthesized via chemical co-precipitation route. Cadmium acetate, sodium sulphide and copper (II) acetate were used as a source of cadmium, sulphur and copper respectively while DMF is used as stabilizing agent and catalyst. The prepared samples were analyzed through (XRD), (TEM), UV-Vis spectroscopy, EDAX and FTIR. XRD studies reveals that the prepared CdS and Cu^{2+} doped CdS samples found to be of cubic structure and the particle size estimated to be about 2.5 to 5 nm. TEM micrograph also reveals the particle size in nano range. The effect of Cu^{2+} doping concentration on the optical properties of CdS:Cu nanoparticles has been investigated using UV-Visible absorption spectroscopy. The optical band gap of the samples is found to be decreasing with doping concentration. FTIR spectroscopy is used to identify the functional groups present in the samples. The elemental analysis by EDAX confirms that the prepared sample contains the appropriate weight percentages of cadmium, sulphur and copper in the reaction compound.

Keywords: CdS:Cu nanoparticles, XRD, TEM, optical band gap FTIR and EDAX.

1. INTRODUCTION:

Research on semiconductor nanocrystals has increased extensively during the past two decades because of their exciting novel optical, electrical, structural, catalytic properties and its variety of applications. Decrease in the particle size shows dramatic change in the optical and electronic properties due to the size quantization effect [1-3]. Now a days the study of doped semiconductor nanocrystals have attracted great attention in many research groups due to their wide range of applications in various fields of science and technology as well as to obtain basic information of impurity states and to examine their potential technological applications in various light emitting devices [4-5]. CdS is an important II-VI group n-type semiconducting material with a direct band gap of 2.42 eV at room temperature. It has numerous applications for solar cell, LEDs, photoconductors, gas sensor, detectors for laser and infrared, photo resistance, nonlinear optical devices, luminescence devices, biological sensors and so on [6-9]. Various synthesis methods have been reported by many researchers and scientific communities for the synthesis of nanostructured CdS and doped with transition metals such as sol-gel technique, sonochemical method, chemical vapour deposition, electro deposition, electrochemical method, spray pyrolysis technique, thermal decomposition of precursors and other chemicals techniques and so on [10-12]. The present paper is focused on the preparation, structural and optical characterization of Cu^{2+} doped CdS nanoparticles by simple chemical precipitation technique. The prepared samples were characterized by XRD, TEM, EDAX, UV-Visible Spectrometer and FTIR.

2. MATERIALS AND METHODS

2.1 Experimental:

Pure CdS and CdS:Cu samples were prepared using cadmium acetate [$(CH_3COO)_2$ Cd, $2H_2O$] (extra pure Loba Chemie), copper (II) acetate [$(CH_3COO)_2$ Cu, H_2O] (Merck) and sodium sulphide [Na_2S, H_2O] (extra pure Loba chemie) as the starting materials. DMF $(CH_3)_2NC(O)H$ (Merck) is used as stabilizing agent and catalyst. All the chemicals used in the present investigation were of analytical reagent (AR)

grade and used as received without further purification. The deionised water was used throughout the experiment as solvent for all the solutions referred in this investigation.

CdS:Cu powder samples were synthesized by chemical route using their acetate salts. 0.1 M cadmium acetate [Cd^{2+}] solution is made by dissolving cadmium acetate in 100 ml double distilled water and 0.1 M sodium sulphide [S^{2-}] is also made in 100 ml double distilled water. Then 2, 5, 10 and 15 at % copper (II) acetate [$(CH_3COO)_2$ Cu, H_2O] is simply added to cadmium acetate solution and stir continuously to mix the solution. Then specific amount of DMF is added in the mixture and stir for 20 minutes. Then 100 ml sodium sulphide solution is added in the mixture drop by drop with constant stirring for 3 hours. This results in dark green solution. This solution is kept overnight to form the precipitate. Latter on it was centrifuged several times with deionised water and acetone to eliminate the un-reacted molecules. The obtained precipitate was filtered, dried in vacuum oven at 60^0 for 8 hours. The samples then crushed in to fine powder and then collected in a sample bottle for the characterizations.

2.2 Characterization of CdS:Cu nanoparticles:

The structural investigation of CdS and CdS:Cu nanoparticles were carried out using X-ray powder diffractometer (Model: D-8 Advance) with CuKα radiation (λ = 0.15406 nm) scanning 2θ in the range 10^0- 90^0. The X-rays were produced using sealed tube and the wavelength of X-ray was 0.1541 nm. The X-rays were detected using a fast counting detector based on Silicon strip technology (Bruker Lynx Eye detector). The morphology of the nanoparticles was characterized by transmission electron microscopy (TEM) using model Tecnai 20 G^2 (FEI) makes under 200 KV. UV-Vis absorption spectrum was recorded using Jasco spectrometer, (Model name: V-770, Serial No. A013161801 for the wavelength range 200-800 nm. EDAX spectra were recorded using Model JEOL JSM 5600. FTIR spectra were recorded using Bruker, Germany. Model: Vertex 70 with resolution 0.5 cm^{-1}.

Results and Discussion

2.1 X-ray Diffraction:

The structural characterization of the undoped and doped CdS samples with different doping concentration of Cu^{2+} ions has been carried out by X-ray diffraction technique using CuKα radiation. The XRD pattern of all samples of CdS(Pure) and CdS:Cu doped with different concentration of cu (2, 5, 10 & 15 at %) is represented in figure-1. The XRD pattern of CdS and CdS:Cu samples indicates three distinct diffraction peaks at three different angles 2θ = 26.68^0, 43.57^0 and 52.06^0 corresponding to reflections from (111), (220) and (311) crystal planes respectively which exhibits cubic crystal structure of CdS and is well matched with **JCPDS card file no. (80-0019).** The addition of Cu^{2+} dopant to CdS does not create any change in the CdS matrix.

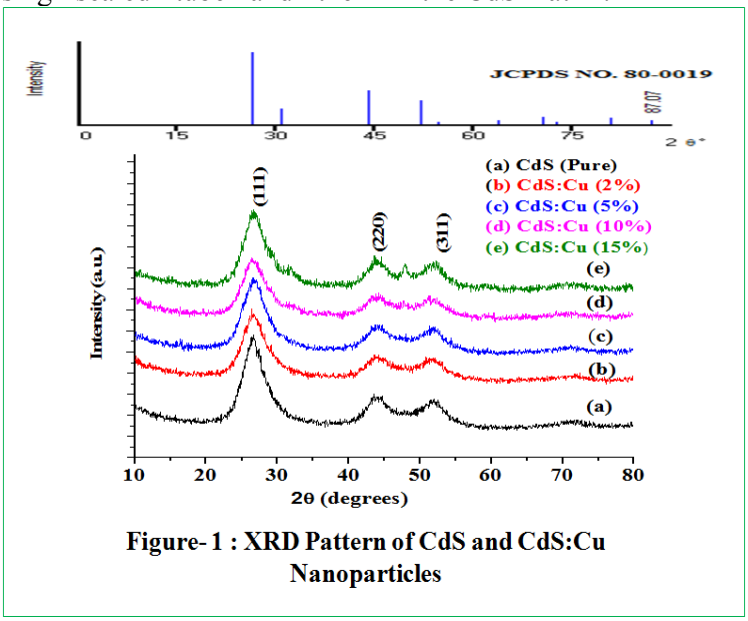

Figure- 1 : XRD Pattern of CdS and CdS:Cu Nanoparticles

The diffraction peaks as obtained in the XRD spectra are significantly broadened with Cu^{2+} incorporation which reveals the decrease in particle size. The peak broadening in the diffraction pattern indicates the formation of the particles in nano range. The intense and the sharp

peaks reveal the good crystallinity of the materials. In addition the relative intensities of (111), (220) and (311) diffraction are observed to be vary in Cu^{2+} doped CdS nanoparticles. It could be due to replacement of Cd^{2+} by Cu^{2+} at different lattice sites of CdS.

From full width at half maximum (FWHM) of the most intense peak, the average crystalline size for all the samples has been estimated using Debye-Scherer's formula [13,14]:

$$D = \frac{0.9\,\lambda}{\beta\,cos\theta}$$

Where $\lambda = 0.1541$ nm is the wavelength of X-ray diffraction, β is the FWHM in radian of the most intense XRD peak and θ is the angle of diffraction. The grain size of the prepared samples determined using XRD found to be in the range of 2.5 - 5 nm.

The lattice parameter **'a'** for CdS and CdS:Cu nanoparticles is calculated using equation

$$\mathbf{a} = \frac{\lambda}{2\,sin\theta} \times \sqrt{h^2 + k^2 + l^2}\ \text{Å}$$

The d-spacing for cubic system for $2\theta_{(111)}$ is calculated by using equation

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}\ \text{Å}$$ and

The microstrain calculated using equation $\varepsilon = \frac{\beta\,cos\theta}{4}$ [15] are listed in table-1

Table-1 : The structural parameters of undoped and Cu doped CdS samples.

Samples	Peak position $2\theta_{(111)}$ (degrees)	FWHM **β** (degrees)	**a=** $\frac{\lambda}{2\,sin\theta}\sqrt{h^2+k^2+l^2}$ **(Å)**	Microstrain $\varepsilon = \frac{\beta\,cos\theta}{4}$	d = $\frac{a}{\sqrt{h^2+k^2+l^2}}$ **(A^0) (for $2\theta_{(111)}$)**
CdS (Pure)	26.6849	1.59735	5.8077	0.3568	3.3530
CdS:Cu (2%)	26.7349	1.74556	5.855	0.3897	3.3803
CdS:Cu (5%)	26.6349	1.86952	5.8332	0.4178	3.3677
CdS:Cu (10%)	26.4851	2.35368	5.8471	0.5267	3.3757
CdS:Cu (15%)	26.6849	2.27095	5.7762	0.5073	3.2521

2.2 Transmission Electron Microscopy (TEM):

The Transmission Electron Microscope (TEM) image imparts the information pertaining to the surface morphology via grain size, shapes, grain boundary and their uniformity. The TEM micrograph with SAED pattern for pure and doped CdS samples are given in figure-2(a) and 2(c). The TEM images shows that the surface morphologies are in the form of assemblies of nanoparticles which forms crystalline aggregates uniformly distributed over the entire surface and the particles are very narrow and spherical shaped.

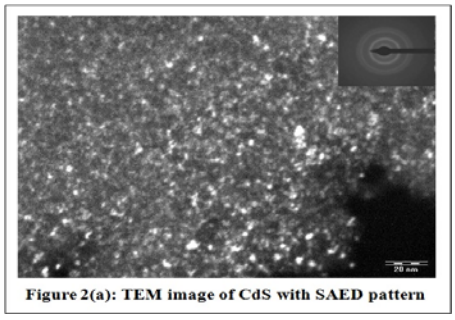

Figure 2(a): TEM image of CdS with SAED pattern

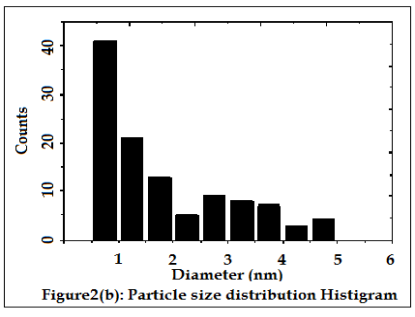

Figure2(b): Particle size distribution Histigram

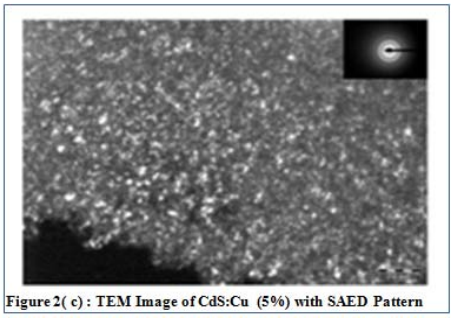

Figure 2(c) : TEM Image of CdS:Cu (5%) with SAED Pattern

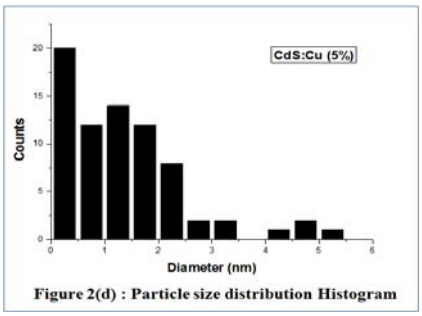

Figure 2(d) : Particle size distribution Histogram

The particle size distribution histograms for pure and Cu doped CdS are given in figure-2(b) and 2(d). The average particle size of the CdS and CdS:Cu nanoparticles from TEM is found to be about 4.2 nm.

2.3 UV-Visible Absorption Spectra:

UV-Visible absorption spectroscopy is an effective tool to monitor the optical behaviour of the semiconducting nanomaterials. Hence UV-Visible absorption spectroscopy has been employed to study the optical properties of nano sized particles. The optical absorption behaviour of CdS and CdS:Cu samples is represented in Figure-3(a). The material of the present study is of direct band gap nature. The bulk band gap of CdS is 2.42 eV as reported by earlier workers. The optical band gap is related to the absorbance and the photon energy by the following Tauc relation [16-17].

$$(\alpha h\nu)^{1/n} = A\,(h\nu - E_g)$$

Where 'α' is absorption coefficient, 'A' is constant related to the effective masses associated with the bands, 'hν' is the energy of photon and 'E_g' is the band gap of material. The exponent n depends on the type of transition. For direct allowed transition n = ½, indirect allowed transition n = 2, direct forbidden transition n = 3/2, indirect forbidden transition n = 3. To determine the possible transitions, $(\alpha h\nu)^2$ Vs hν is plotted and corresponding band gap were evaluated by extrapolating the linear portion of the curve on hν axis. The direct band gap value of CdS sample have been obtained from $(\alpha h\nu)^2$ Vs hν plot as shown in figure-3(b). The absorption edge shifts towards lower wavelength (higher energy) side with the addition of Cu^{2+} doping concentration. It is observed that the band gap reduces slightly with the incorporation of doping concentration which results in the increased conductivity of the material [18]. The average particle size of CdS and CdS:Cu samples were estimated using following Brus equation [19, 20]

$$E_{g\,(nano)} = E_{g\,(bulk)} + \frac{h^2}{8\,R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8\,e^2}{4\pi\epsilon_0\,\varepsilon_r}$$

Where $E_{g(nano)}$ = band gap of nanoparticles, $E_{g(bulk)}$ = 2.42 eV, m_e^* = 0.21 m_e is the effective mass of electron, m_h^* = 0.8 m_e is the effective mass of hole, m_e is the free electron mass and R is the particle radius, ε_r is the dielectric constant and ϵ_0 is the permittivity of free space. The first term in above equation indicates the confinement effect and the second term is the coulomb term. The second term is small due to strong confinement and can be neglected [21]. The crystalline size and the optical band gap estimated from UV-Visible absorption spectra for CdS and CdS:Cu samples are given in table-2.

Table-2: Optical band gap and crystalline size of CdS and CdS:Cu samples.

Samples	Band gap (eV)	Crystalline size (nm)
CdS	4.5	2.6
CdS:Cu (5%)	4.4	2.64
CdS:Cu (10%)	4.33	2.7
CdS:Cu (15%)	4.28	2.74

In the present study, it has been observed that the optical band gap decreases with the increase in doping concentration. Similar decrease in the band gap have also been reported by P. Reys et al in Cu doped CdS [7] , S. Kumar et al in Ni

doped CdS [22] and S. Salimian et al in Mn doped CdS [23]

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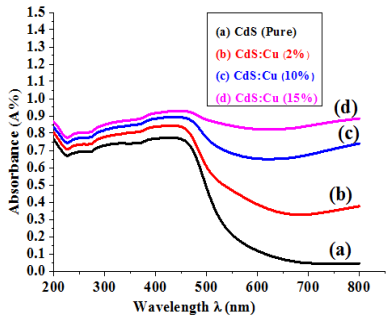

Figure 3(a) : UV-Visible absorption spectra of CdS and CdS:Cu Nanoarticles

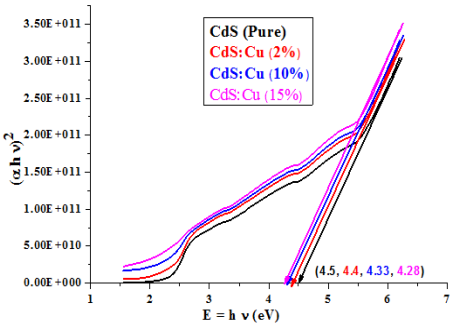

Figure 3(b) : Tauc plot of CdS:Cu nanoparticles

2.4 FTIR Analysis:

The Fourier Transform Infrared spectra of CdS and CdS:Cu nanoparticles for identifying the functional groups present in the samples are represented in figure-4. The samples have been prepared with KBr medium. A broad peak is observed in the higher energy region at 3427 cm^{-1} is assigned to O-H stretching vibration of absorbed water on the surface of the sample. A very strong peak observed at 1549 cm^{-1} is attributed to N-H deformation (Amide II band) [24]. A medium peak at 1406 cm^{-1} is due to C-N stretching (Amide III band). A strong peak at 1113 cm^{-1} occurs due to C-O stretching vibration. The peak at 615 cm^{-1} and 685 cm^{-1} which have been attributed to vibrations of Cd-S bond [25, 26].

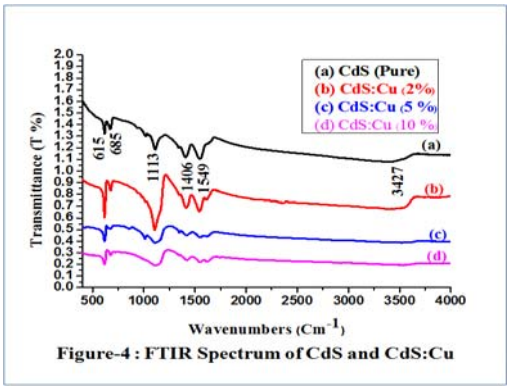

Figure-4 : FTIR Spectrum of CdS and CdS:Cu

2.5 EDAX Analysis:

Figure-5 shows the EDAX spectra of CdS:Cu (5 at %) nanoparticles which indicates the presence of Cd, S and Cu in the prepared sample. The elemental analysis by EDAX confirms that the prepared sample contains the appropriate cadmium, sulphur and copper weight percentages in the reaction compound. EDAX data shown in table-4 gives the compositions of the prepared sample in weight percentage.

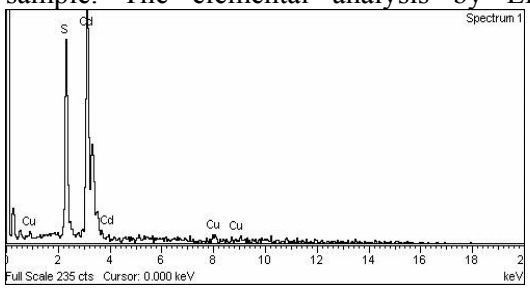

Figure-5: EDAX plot of CdS:Cu (5 at %) nanoparticles

Compound name	Element	Weight percentage %
CdS:Cu (5%)	S K	46.03
	Cu K	4.16
	Cd L	49.81
		Total = 100.00

Table-3: EDAX data of CdS:Cu (5 at %)

3. **Conclusions:**

In summary, CdS and CdS:Cu nanoparticles were synthesized successfully and ecofriendly by precipitation method. The XRD characterization reveals that the prepared samples are nanocrystalline in nature which exhibits cubic structure and the average grain size of the particles determined are in the range of 2.5 – 5 nm. The Particle size of the prepared samples is found to be decreasing with increasing Cu^{2+} doping concentration which is also confirmed by TEM micrograph. The TEM micrograph reveals the uniform distribution of fine particles, which form crystalline aggregates. The UV-Visible absorption spectrum shows that the band gap of the prepared samples decreases with increasing Cu^{2+} doping concentration. The blue shift in absorption maxima clearly indicates the quantum confinement of charged particles. FTIR analysis reveals the Cd–S stretching at 615 cm^{-1}. Compositional analysis by EDAX confirms that Cd, Cu and S are in appropriate weight percentage in the prepared sample. Thus the prepared material has a good potential to be used in optoelectronic devices [14], solar cell applications [27] etc.

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