STUDY OF STRUCTURAL, MORPHOLOGICAL AND OPTICAL PROPERTIES OF Cu AND Ni DOPED CdS NANOPARTICLES PREPARED BY MICROWAVE ASSISTED SOLVO THERMAL METHOD

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CdS is one of the important II-VI compound semiconductors having wide applications in various optoelectronic devices. It has also proved to be a promising material for solar cell and biolabeling applications. The present work reports the synthesis of undoped and transition metal (Cu and Ni) doped CdS nanoparticles. The synthesis of pure and doped CdS nanoparticles have been carried out in aqueous medium by microwave assisted solvo thermal method using cadmium acetate, nickel chloride, copper chloride and sodium sulphide as precursors. The study of structural, morphological and optical properties was done by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Photoluminescence (PL), Fourier Transform Infrared (FTIR) and UV-Visible spectroscopy. The crystal structure and morphology of the as synthesized nanoparticles have been studied by X- ray diffraction and scanning electron microscopy. The XRD spectrum confirms the crystallanity of the samples. The size of the nanocrystallites was calculated using Debye-Scherrer formula. The average crystallite size was found to be around 8 nm for undoped CdS and it was around 4.5 nm for Cu doped CdS and 4.0 nm for Ni doped CdS nanoparticles. For the determination of the different functional groups present on the surface of the synthesized nanoparticles, FTIR spectra were also recorded. The absorption spectra were recorded using UV-Visible spectrophotometer. The energy band gap of as synthesized nanoparticles was estimated using Tauc plot. The result of UV-Visible spectra shows that the band gap of doped CdS increases as compared to that of pure CdS, clearly indicating the blue shift of the bandgap values from the bulk CdS.

1. Introduction

In the recent past, the binary compound of group III-V and II-VI semiconductors have become prominent materials for the fabrication of optoelectronic devices like light photoconductive cells, photocatalytic, light emitting diodes (LEDs), laser diodes (LDs), solar cells, memory device applications, etc [1-5]. Among these, CdS is one of the most important wide gap semiconductors, because of their wide application in optoelectronics [5]. The low bandgap enables it to be used as window in solar cells [7-8]. However for such kind of application, doping of CdS with any transition metal (like Cr, Fe, Co, Ni, Cu, Zn, etc) is required [9-13]. Chalcogenide materials are of great importance due to their tunability in optical properties[14]. Among

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transition metals, Copper (Cu) and nickel (Ni) impurities behave as an acceptor in CdS, which changes its structural as well as optical properties [15-16]. There are various techniques for the synthesis of CdS nanoparticles like chemical co- precipitation, sol gel, solvothermal, spray pyrolysis, microwave assisted synthesis, etc [17-21]. CdS at nanosize has high surface energy therefore it is a difficult task to limit the growth of nanosizedCdS [22].With use of repeated heating and cooling in microwave oven the unwanted growth of CdS particles can be limited within the range of nanoparticle size [17-18, 23].

The present work has been focused on the detailed study of structural, morphological and optical properties of undoped and transition metal (Cu and Ni) doped CdS nanoparticles synthesized by Microwave Assisted Method. Further this study reveals the information regarding the size dependent bandgap of nanoparticles.

2. Experimental

2.1. Chemicals
The chemical reagents used for the synthesis of undoped and transition metal (Cu and Ni) doped CdS nanoparticles were of analytical grade and used without further purification. Deionised water was used for all dilution and sample preparation. Cadmium acetate ($Cd(CH_3COO)_2.2H_2O$), sodium sulphide ($Na_2S.xH_2O$), copper chloride ($CuCl_2$) and nickel chloride ($NiCl_2$)have been procured from Molychem and were used as precursors. For avoiding impurities during synthesis process, all the glassware were washed with acid and dried before use.

a) Synthesis of undopedCdS nanoparticles

For the synthesis of undoped CdS nanoparticles, 225 ml of 0.2 M solution of Cadmium acetate ($Cd(CH_3COOH)_2.2H2O$) and 450 ml of 0.1 M sodium sulphide were prepared and combined stoichiometrically. The solution was further diluted with deionize water and hence stirred magnetically for 45 minutes to make homogeneous solution at room temperature. After stirring, the obtained solution was put under the microwave process at 25 % duty cycle (which means the sample was microwave irradiated for 20 seconds and then put on rest for the next 60 seconds) About 13 to 14 cycles took place for the formation of nanoparticles. The obtained yellowish colloidal solution was filtered and washed suitably several times. The obtained filtrate was dried in oven for 12 hours at 60°C to obtain the fine powder of undopedCdS nanoparticles.

b) Synthesis of Cu and Ni doped CdS nanoparticles

For the synthesis of Cu doped CdS nanoparticles, 225 ml of 0.2 M cadmium acetate solution was mixed with 45 ml of 0.2 M copper chloride. The solution was stirred on a magnetic stirrer at 650 rpm at room temperature until a homogeneous solution was obtained. Then, 450 ml of 0.1M sodium sulfide was added drop wise to the above mixture. Thereafter the solution was put under microwave oven and the process was repeated as performed in the synthesis of pure CdS. It took around 22 cycles for the synthesis of Cu doped CdS nanoparticles. The obtained greenish brown colloidal solution was filtered and washed suitably several times. The obtained filtrate was dried in oven for 12 hours at 60° C to obtain the fine powder of Cu doped CdS nanoparticles.

Similarly, for the synthesis of Ni doped CdS nanoparticles 225 ml of 0.2 M cadmium acetate solution was mixed with 48 ml of 0.2M nickel chloride. After stirring around 30 minutes, 450 ml of 0.1M sodium sulfide was added drop wise to the above mixture. The above mentioned microwave process was repeated to obtain the yellowish brown voluminous precipitate of Ni doped CdS nanoparticles.

2.2. Characterization techniques
Following techniques were used for the characterization of the as synthesized nanoparticles. The X-ray diffraction (XRD) spectra of the powder samples were recorded from 20° to 80° using X-ray diffractometer (RIGAKU) with a Cu k_α radiation (λ=1.5418 Å). The crystallite size was calculated using Debye-Scherer formula at the full width half maximum of XRD peaks. The morphology of the nanoparticles was studied using scanning electron microscope (SEM; JEOL-JSM-6390 LV). UV-visible (RAYLEIGH UV 2601) absorption spectra, Photoluminescence (SHIMADZU-RF-5301PC), and FTIR (SHIMADZU-IR-Prestige 21) spectra

of the samples were recorded at room temperature for investigating the optical properties of the synthesized samples.

3. Result and discussion

3.1. XRD studies

The structural properties of the as synthesized undoped and doped CdS nanoparticles have been studied by XRD analysis. The X-ray diffraction spectra of the prepared nanoparticles are shown in Fig. 1(a-c). The major peaks in the spectrum of pure CdS nanoparticles have been observed at 2θ equals 27^0, 44.5^0 and 52^0. The XRD pattern reveals that the prepared nanoparticles have three main diffraction features corresponding to (111), (220) and (311) planes. The obtained XRD pattern of the nanocrystals was well matched with the standard cubic CdS (JCPDS Card No. 10 - 454). The nanosize of the prepared particles of undoped and transition metal (Cu and Ni) doped CdS has been clearly indicated by the broadening of the diffraction peaks. No major change in the peak position of Cu and Ni doped CdS with respect to that of undopedCdS has been observed.The average crystallite size has been calculated at the full width half maximum (FWHM) of the diffraction peaks using Debye-Scherer equation:

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

where, k is particle shape factor (taken as 0.9), λ is the X-ray wavelength (1.5418 Å), β is FWHM value and θ is the angle of diffraction. The average crystallite size of undoped, Cu doped and Ni doped CdS was found to be around 8 nm,4.5 nm and 4 nm respectively.The inter planer spacing d can be calculated using Bragg's law:

$$n\lambda = 2d \sin\theta \tag{2}$$

In the above equation (2), n is the order of diffraction, λ is the X-ray wavelength (1.5418 Å), d is the inter planer spacing and θ is the angle of diffraction. The values of d were found to be slightly decreased from 0.345 nm (for undopedCdS) to 0.327 nm and 0.336 nm for Cu and Ni doped CdS respectively. This may be due to the smaller ionic radius of Ni (0.72 Å) and Cu (0.73 Å) as compared to the ionic radius of Cadmium (0.97 Å).

The value of lattice constant (a) can be calculated from the obtained value of d, by using the given relation:

$$d = a/(h^2 + k^2 + l^2)^{1/2} \tag{3}$$

The volume of the unit cell is calculated from the value of lattice constant, by using the relation:

$$V = a^3 \tag{4}$$

where 'a' is the lattice constant of the unit cell. The calculated values of crystallite size, inter planer spacing, lattice constants and volume of the unit cell is shown in the Table 1.

Table 1. Variation of crystallite size (D), Interplanar spacing (d), Lattice constant (a) and volume of Unit cell (a^3) of undoped, Cu doped and Ni doped CdS nanoparticles.

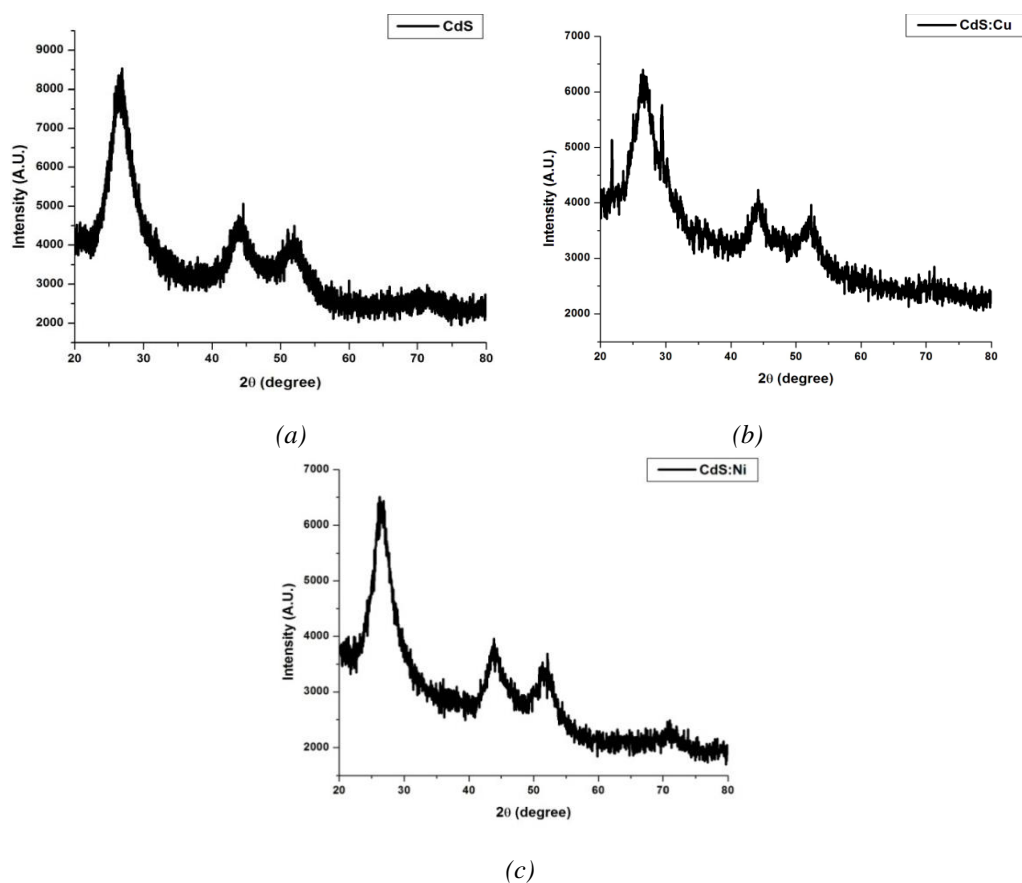| Compound	Crystallite Size 'D' (nm)	Interplanar Spacing 'd'(Å)	Lattice Constant 'a'(Å)	Volume of unit cell 'a³' (nm)³
CdS	8	3.45	5.97	0.212
CdS:Cu	4.5	3.27	5.66	0.181
CdS:Ni	4.0	3.36	5.82	0.197

(a)

(b)

(c)

Fig. XRD spectra of nanoparticles:
a) undoped CdS; , b) doped CdS with Cu; c)doped CdS with Ni
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3.2. SEM studies

The surface morphology of undopedand transition metal (Cu and Ni) doped CdS nanoparticles have been studied using SEM. Fig. 2 (a-c) shows SEM micrograph of the prepared undoped and doped CdS nanoparticles. As clearly seen from the figure, the synthesized nanocrystals have smooth surface and seems to be spherical in shape and highly aggregated which may be due to the absence of capping agent in the prepared solution. The obtained SEM images indicate considerable amount of change in morphology and porosity of the prepared CdS samples on doping.
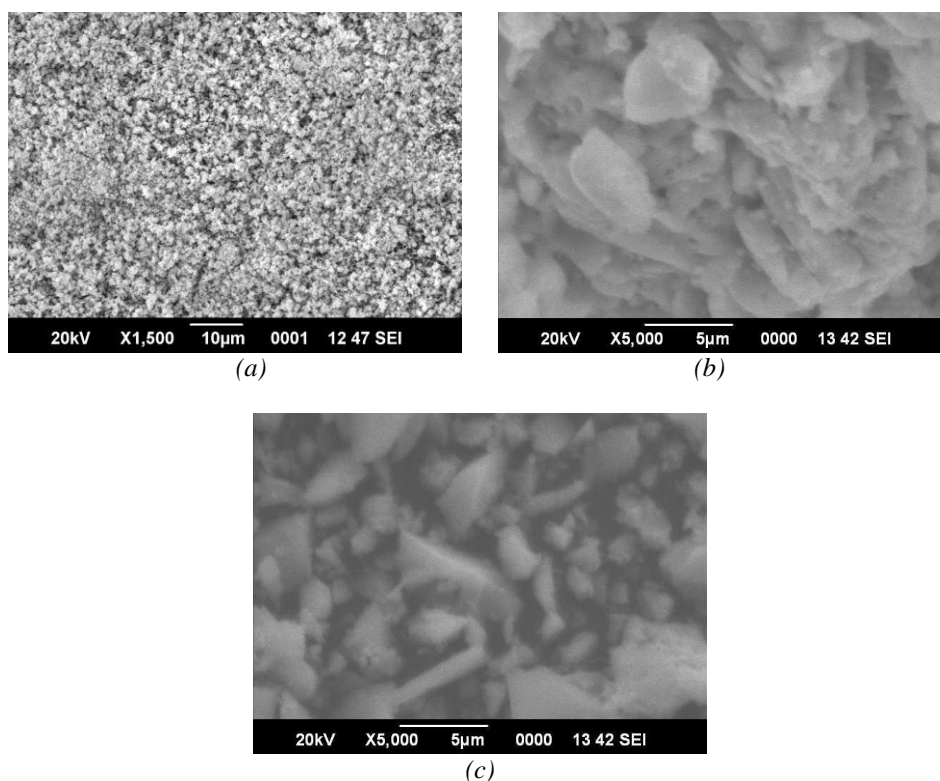
(a)

(b)

(c)

Fig. 2. SEM image of nanoparticles:
a) undoped CdS; , b) doped CdS with Cui; c)doped CdS with Ni

3.3. FTIR studies

For the investigation of vibrational and functional groups present in the prepared samples, FTIR measurement of the undoped and transition metal (Cu and Ni) doped CdS nanoparticles have been studied inthe wavenumber range of 4000-500 cm^{-1} at room temperature. Figure 3(a-c) illustrates the FTIR spectrum of undoped, Cu doped and Ni doped CdS nanoparticles. The broad and weak absorption band around 3400-3600 cm^{-1} is assigned to the presence of OH stretching vibration of water molecules and moisture present in the prepared sample. The absorption peak around 2800-2900 cm^{-1} is assigned to C-H stretching. The small and weak peak around 1550 cm^{-1} is due to the presence of H-O-H bending vibration of water molecules. The medium strong band positions in the range of 1000-1150 cm^{-1} are possibly due to stretching vibrations of sulphate group. The sharp peak around 615- 625 cm^{-1} corresponds to Cd-S stretching. The Cd-S bond is found to be shifted from 617 cm^{-1} for undoped CdS to 621 cm^{-1} for Cu doped CdS. There is no major shift in Cd-S bond after Ni is doped. Cu and Ni incorporation as well as size effect may be responsible for the shift in the frequency when compared with undoped Cd-S bond.
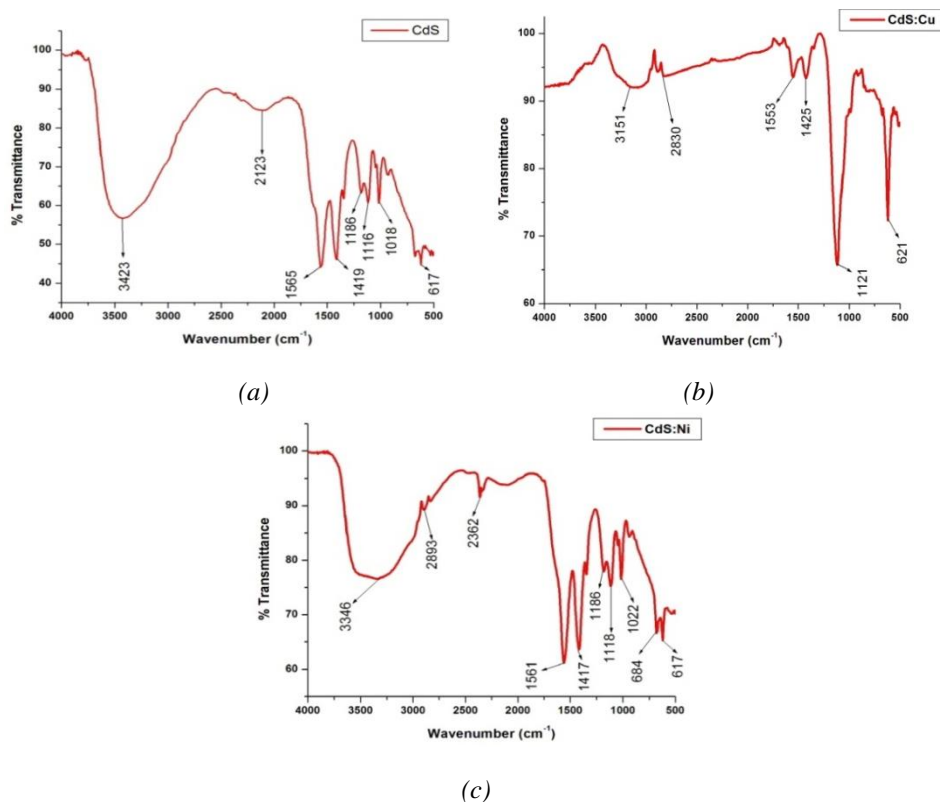
(a)

(b)

(c)

Fig. 3. FTIR spectra of nanoparticles:
a) undoped CdS; , b) doped CdS with Cu; c)doped CdS with Ni

3.4. Photoluminescence (PL) studies

For the study of the luminescence properties of the prepared nanoparticles, photoluminescence spectra of the prepared samples was recorded at room temperature using Xenon light (at the excitation $\lambda = 300$ nm). Figure 4 illustrates the photoluminescence spectrum of undoped and Cu and Ni doped CdS nanostructures obtained at the excitation wavelength of 300 nm. The emission spectra are observed at 435 nm, 365 nm and 352 nm for undoped, Cu and Ni doped respectively. Blue shift emission in the prepared nanoparticles is clearly observed from the figure. The shifting of emission spectra towards left shows the enhancement of bandgap with the variation of dopant. The observed blue shift is may be due to the fact that nanoparticles exhibit quantum confinement effect.
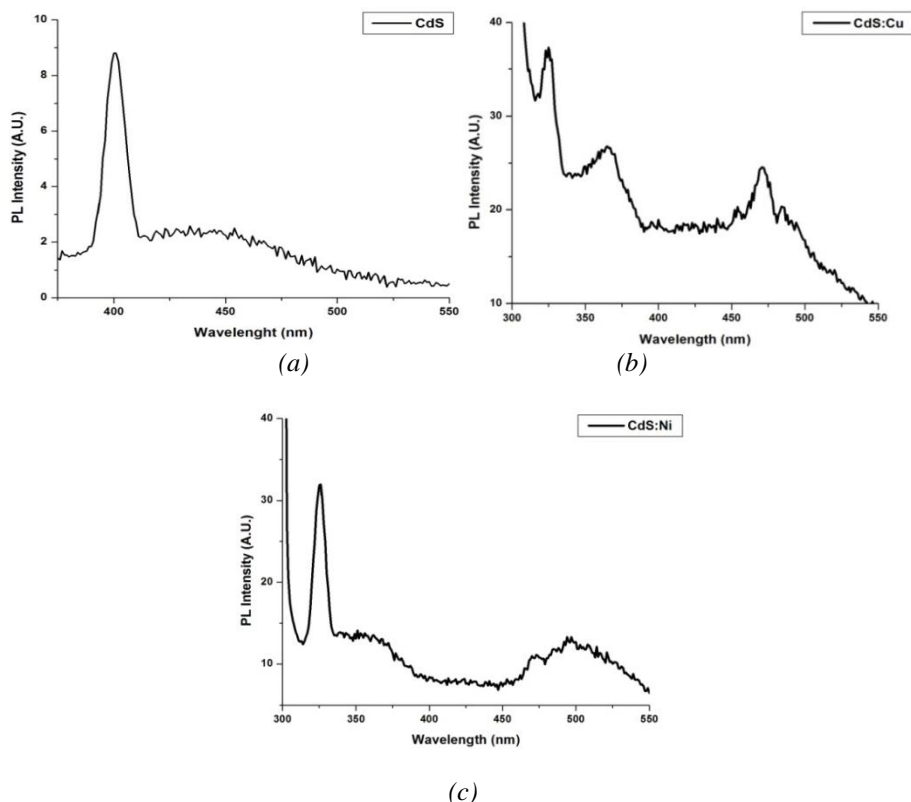
(a)

(b)

(c)

Fig. 4. PL spectra of nanoparticles:
a) undoped CdS; , b) doped CdS with Cu; c)doped CdS with Ni

3.5. UV- visible

The optical properties of the synthesized sample were investigated using UV-Visible spectrophotometer from 200 nm to 800 nm at room temperature. The optical absorption spectra of undoped and transition metal (Cu and Ni) doped CdS nanoparticles is shown in figure 5(a-c). The absorption spectra show the blue shift after doping of Ni in CdS. The optical bandgap of the prepared nanoparticles were calculated by Tauc equation, which is given by:

$$\alpha h\nu \ = \ A \, (h\nu - E_g)^n \tag{5}$$

where α is the absorbance, $h\nu$ is the the energy of incident photon, E_g is the bandgap value , A is a constant and the value of n can be 1/2, 2, 3/2 which depends on the type of transitions. In this case the value of n is taken to be ½ for direct bandgap.

And the absorption coefficient (α) is estimated by the equation given below:

$$\lambda\alpha \ = \ 4\pi k \tag{6}$$

The bandgap (E_g) has been estimated by plotting the graph of $(\alpha h\nu)^2$ versus $h\nu$ as shown in the figure. The extrapolation of the straight line of $(\alpha h\nu)^2$ to the $h\nu$ axis gives the value of the bandgap (in eV) of the prepared nanoparticles. The optical bandgap of undoped CdS is found to be 3.8 eV and for Cu and Ni doped CdS, it is found to be 4.0 eV and 3.95 eV respectively. It is cleary seen from the figure that the optical bandgap of doped CdS increases which shows a blue shift which may be due to quantum confinement effect.
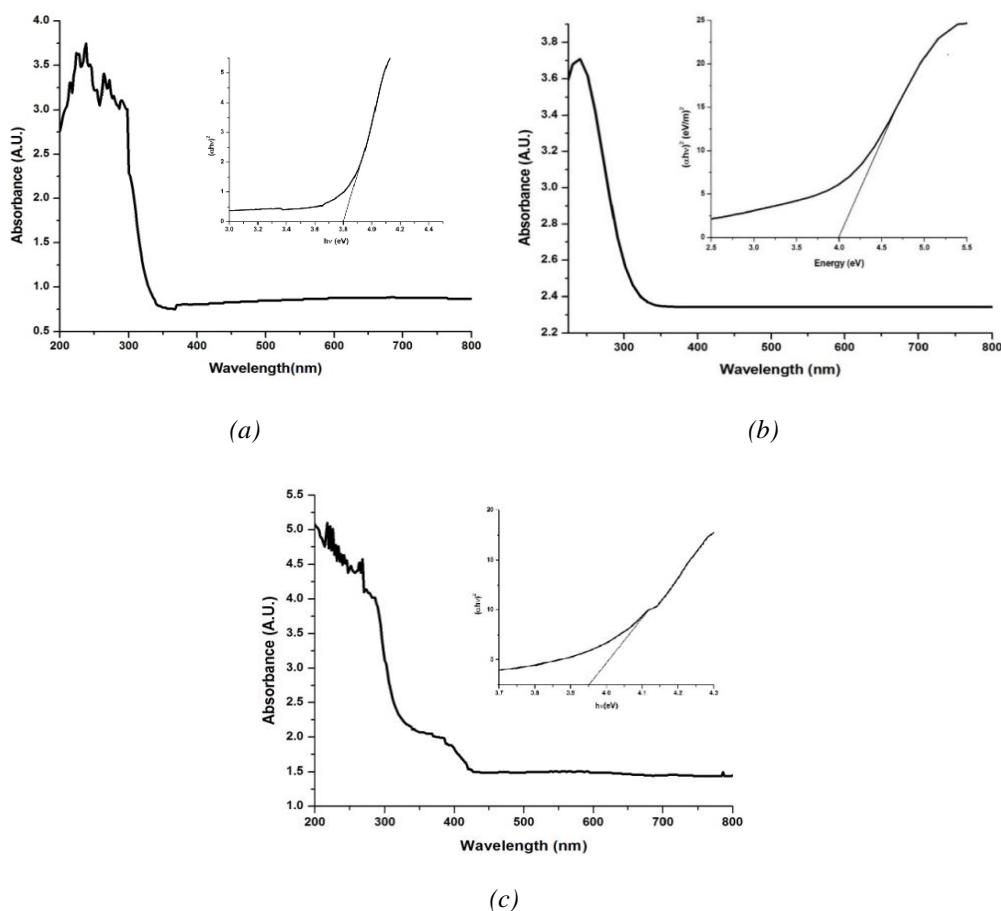
(a)

(b)

(c)

Fig. 5. Absorption spectra and energy band gap of nanoparticles:
a) undoped CdS; , b) doped CdS with Cu; c)doped CdS with Ni

4. Conclusions

Undoped, Cu and Ni doped CdS are the promising candidate for the various applications like optoelectronic devices, solar cells and many biological and biolabeling applications, which has been studied in the present work. Synthesis of undoped, Cu and Ni doped CdS nanoparticles were successfully done by microwave assisted method. The cubic structures of the prepared particles were confirmed by XRD analysis. The average crystallite size of undoped, Cu dopedand Ni doped CdS was found to be 8 nm, 4.5 nm and 4.0 nm respectively.

The SEM result shows that the particles are in nanosize and seems to be spherical and agglomerated. The various functional groups present on the surface of undoped and transition metal doped CdS nanocrystals were identified by FTIR spectra. The energy band gap was observed from UV-Visible spectra and was found to be about 3.8 eV, 4.0 eV and 3.95 eV for undoped, CU and Ni doped CdS nanoparticles respectively. UV Visible spectra show that the bandgap of CdS nanoparticles is increased after doping with the Cu and Ni.

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