Band gap engineering on CdS quantum dots through dual doping of Zn$^{2+}$ and of Ni$^{2+}$ ions

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Abstract. The CdS Quantum dots (QDs) have been synthesized without using any capping agent via a co-precipitation chemical route. The structural and optical investigations of the Ni$^{2+}$-doped Cd$_{0.9}$Zn$_{0.1}$S QDs have been made. XRD patterns revealed that the synthesized QDs exhibit cubic structure and the particle size was measured ~ 2 nm. EDX spectra showed that the existence of cadmium, zinc, sulphide, and nickel in the synthesized samples. FTIR spectra verified the vibrational peaks related to available molecules of elements in the samples. The absorbance rate of Ni$^{2+}$-doped Cd$_{0.9}$Zn$_{0.1}$S QDs doped was more than Cd$_{0.9}$Zn$_{0.1}$S QDs in the visible region. The introduction of Ni$^{2+}$ ions into CdZnS QDs improved the optical transmittance in the visible spectrum and the band gap was blue-shifted for Ni = 6 at.\% composition. The quantum confinement effect played an effective role in the band gap tailoring of CdS QDs via particle size tuning mechanism.

1. Introduction
The semiconductor industries are proliferating more due to its fantastic structural, electrical, electronic, optical, photocatalytic and magnetic behaviours [1]. The semiconductors are highly attracted in the development of modern technology because of their potential applications in diverse areas [2]. Quantum dots (QDs) are playing a vital role in exploring innovations in optical engineering, especially in labelling, imaging, and display devices manufacturing. The CdS is identified as an optimum QDs and it is one of the semiconductors in the II-VI group. These materials are utilized in optoelectronic device fabrication for producing remarkable achievements [3]. Additional energy states creation observed near the absorption edge in nickel-doped CdS QDs [4]. The fabrication of CdS by the co-precipitation method is when we compare with other methods [5]. The CdS crystal is identified as a best material for the preparation of semiconducting materials through transition metal (TM) doping. Zn (at.10\%) doped CdS QDs exhibited better optical properties and hence Zn composition was limited as 10\% here [6]. The dopant and co-dopant materials were helpful to tune the optical structural properties of CdS QDs. The usage of capping agent will increase the particle size, hence we avoided it to know the original size of synthesized particles. We have made an attempt in this work to observe the collective properties of Zn and Ni on CdS QDs In the present work, Ni$^{2+}$, Zn$^{2+}$ dual doped
CdS QDs were prepared by the co-precipitation technique under Ar atmosphere. The structural, morphological, and optical behaviours of CdS QDs were analyzed.

2. Experimental section

Ni\textsuperscript{2+}-doped Cd\textsubscript{0.9}Zn\textsubscript{0.1}S QDs (Ni = 0% to 6%) QDs have been synthesized via co-precipitation method. The Cadmium acetate (Cd(CH\textsubscript{3}COOH)\textsubscript{2}·2H\textsubscript{2}O), Nickel acetate (Ni(CH\textsubscript{3}COO)\textsubscript{2}·2H\textsubscript{2}O), zinc acetate (Zn(CH\textsubscript{3}COO)\textsubscript{2}·2H\textsubscript{2}O), and sodium sulfide (Na\textsubscript{2}S) were taken as the source materials. These chemicals belong to AR grade and purchased from Merck Ltd. Cadmium acetate, zinc acetate, nickel acetate and sodium sulfide were taken as per the stoichiometry target ratio and dissolved in 50 ml DI water. The chemical solution was added dropwise in a common beaker under constant stirring at the stirring rate 600 rpm. The aqueous ammonia solution was used to stabilize the pH value of the solution. The final solution was kept in a continuous stirring for 4 h. Once the reaction was completed, a brownish precipitate was deposited. The brownish white precipitate was filtered out using Whatman filter paper and washed using DI water and methanol to eliminate any impurities. The wet precipitate was kept in a microwave oven at the temperature of 80°C for 7 h for drying. Finally, nanopowders were obtained by grounded the dried sample thoroughly using agar mortar. This procedure was repeated for several times to get Ni\textsuperscript{2+}-doped Cd\textsubscript{0.9}Zn\textsubscript{0.1}S QDs (Ni = 0% to 6%) QDs.

The crystal structure of Ni\textsuperscript{2+}-doped Cd\textsubscript{0.9}Zn\textsubscript{0.1}S QDs (Ni = 0% to 6%) QDs were determined by powder X-ray diffraction (XRD) and diffraction peaks were recorded by using X-ray diffractometer (Make: RigaKuC/max-2500). The CuK\textalpha radiation (\(\lambda = 1.5406\ \text{Å}\)) was used for X-ray study at 40 kV and 30 mA from the range of 20 = 20˚ to 70˚. The surface morphology and elemental composition of samples were analysed using a scanning electron microscope (Model: JEOLJSM 6390) and structural characterization using transmission electron microscope(Make: PhilipXL30). The absorbance and transmittance behaviour of the QDs were determined using UV–vis spectrometer (Make: Lambda35, Make: PerkinElmer) in the wavelength range from 300 nm to 600 nm. The presence of chemical bonding in samples is studied by FTIR spectrometer (Model: PerkinElmer, Make: Spectrum RX I) in the range of 400–4000 cm\textsuperscript{-1}. All the synthesis and characterization process was done at room temperature.

3. Results and Discussion

3.1. Structural, Morphological and elemental analysis

The crystalline structure of Ni\textsuperscript{2+}-doped Cd\textsubscript{0.9}Zn\textsubscript{0.1}S QDs (Ni = 0% to 6%) as shown in Fig.1. Predominant peaks corresponding to 2θ are indexed using Miller indices as (111) (220) (311). The primary diffraction peaks value is matched well with the JCPDS card no.40-454 and confirmed that they possess a cubic zinc structure [6]. No secondary peaks were noticed in XRD spectrographs and confirmed that the dopant was successfully entered in the host crystal structure. The average crystallite size (\(D\)) of the QDs was calculated from XRD primary peaks value with the aid of Debye-Scherrer’s formula [7].

\[
D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)
\]

where \(\lambda = \) wavelength of X-ray (1.5408 Å), \(\beta = \) FWHM in radian, and \(\theta = \) angle of Bragg’s diffraction. The micro-strain (\(\varepsilon\)) produced in the crystal structure is calculated using the formula [8]

\[
\varepsilon = \frac{\beta \cos \theta}{4} \quad (2)
\]
Figure 1. (a) XRD spectra, (b) TEM picture ofCd\textsubscript{0.9}Zn\textsubscript{0.1}S:Ni (2\%) QDs (c) SAED pattern

Table 1: The FWHM value, d-value, lattice constant, average crystallite size and micro-strain of Cd\textsubscript{0.9}Zn\textsubscript{0.1}S:Ni QDs.

| Samples          | FWHM (β) (°) | d-value (Å) | lattice parameter a = b = c (Å) | Average crystallite size (D) (nm) | Micro-strain (ε) (10\textsuperscript{-3}) |
|------------------|--------------|-------------|---------------------------------|----------------------------------|-------------------------------------|
| Cd\textsubscript{0.9}Zn\textsubscript{0.1}S:0% Ni | 3.89         | 3.281       | 5.683                           | 2.10                             | 16.50                               |
| Cd\textsubscript{0.89}Zn\textsubscript{0.1}S:2% Ni  | 3.74         | 3.305       | 5.724                           | 2.24                             | 15.43                               |
| Cd\textsubscript{0.89}Zn\textsubscript{0.1}S:4% Ni  | 4.07         | 3.298       | 5.713                           | 2.06                             | 16.83                               |
| Cd\textsubscript{0.89}Zn\textsubscript{0.1}S:6% Ni  | 4.22         | 3.305       | 5.724                           | 1.98                             | 17.47                               |

The average crystallite size is found to lie in the range of 1.98 to 2.24 nm. Ni (2\%) samples have the highest size of 2.24 nm in the analysis. The observed enhancement in strain is ascertained to the changes in crystallite size and the diffraction peaks broadening was also the reason for this strain variation [9]. The particle size reduction is ascribed to the increase of micro strain due to the size effect. The X-ray diffraction patterns confirmed that the Cd–Zn–S lattice has impurity atoms on increasing the inter-planar distance ‘d’ because of the smaller ionic radius of Ni\textsuperscript{2+} (70 pm) than Cd\textsuperscript{2+} (95 pm). The charge imbalance and crystal distortion were produced when dopants are substituted into a host lattice structure.
The EDX spectra of Ni$^{2+}$-doped Cd$_{0.9}$Zn$_{0.1}$S QDs (Ni = 0% to 6%) QDs were also shown in Fig 2(a-d). The obtained peaks associated to Cd, Zn, Ni, and S were confirmed the existence of elements according to the stoichiometry ratio. The quantitative at. wt% of the elements taken are well matched with the stoichiometry ratio of the elements taken for the present investigations.

3.2 UV-vis absorbance, transmittance and band gap calculation

The UV–vis absorption spectra of the samples were recorded from 300 nm to 600 nm and illustrated in Fig. 4. The absorption spectra within the range of 300 nm and 375 nm as shown as inset of Fig. 3a. Two absorption peaks were obtained on Ni-doped Cd$_{0.9-x}$Zn$_{0.1}$S QDs (Ni = 2% and 4%). The absorption edge was blue-shifted and the reason for this phenomena is quantum confinement effect. The blue shift was attributed to the smaller size of Ni$^{2+}$ ions as compared to Zn$^{2+}$ or Cd$^{2+}$ ions. UV-vis transmittance spectral curves of the Cd$_{0.9}$Zn$_{0.1}$S and Ni-doped Cd$_{0.9-x}$Zn$_{0.1}$S QDs from 300 nm and 600 nm are shown in Fig. 3b. This behaviour was endorsed to the partial diffusion of Ni in CdS lattice and releasing few excess undiffused Ni$^{2+}$ ions on the surface.
Transmittance intensity decreases in the visible region and this behaviour was ascertained to the scattering of light on the uneven surfaces [36]. The suppression of transmittance is ascertained to the packing density [37]. The size effect and the defect states developed by Ni incorporation is responsible for the low transmittance curves of Ni-doped Cd$_{0.9-x}$Zn$_{0.1}$S. Band-gap values were determined using the optical absorption spectra by extending the linear portion of $(\alpha h \nu)^2$ versus $(h \nu)$ to the energy axis. Taucs’ equation is used to get band gap value [10]:

$$\alpha h \nu = A(h \nu - E_g) n$$

where $\alpha$ is the absorption coefficient and the $h \nu$ is incident photon energy.

A blue-shift has occurred in the band gap and it was ascertained to quantum confinement effect. The quantum confinement effect occurs when semiconductor QDs’ size is smaller than
the Bohr radius of excitons [11]. The larger band gap was received for the maximum concentration of Ni (6%) doped CdS QDs.

3.3 FTIR Analysis

The FTIR spectra for Ni$^{2+}$-doped Cd$_{0.9}$Zn$_{0.1}$S QDs (Ni = 0% to 6%) QDs is shown in fig.4 and assigned peaks were listed in table.2.

![Figure 4. FTIR spectra Ni$^{2+}$-doped Cd$_{0.9}$Zn$_{0.1}$S QDs (Ni = 0% to 6%)](image)

| Assignments                                | Wave number (cm$^{-1}$) |
|---------------------------------------------|-------------------------|
| O-H stretching vibration of H$_2$O          | Ni (0%) | Ni (2%) | Ni (4%) | Ni (6%) |
| C=O stretching vibration due CO$_2$         | 3338    | 3401    | 3389    | 3381    |
| H-O-H bending vibration of H$_2$O           | 2375    | 2356    | 2357    | 2358    |
| C–H bending vibration                       | 1621    | 1564    | 1565    | 1572    |
| C–O asymmetric stretching bonds             | 1405    | 1410    | 1411    | 1408    |
| Stretching mode of Cd-Zn-S [12] (doublet)   | 1018    | 1019    | 1019    | 1122    |
|                                             | 619     | 621     | 621     | 621     |
|                                             | 670     | 672     | 673     | 672     |

4. Conclusions

Ni$^{2+}$-doped Cd$_{0.9}$Zn$_{0.1}$S QDs (Ni = 0% to 6%) QDs were synthesized by the co-precipitation method.

- XRD results confirmed the cubic zinc blende structure and that the particle size of Ni-doped Cd$_{0.9}$Zn$_{0.1}$S QDs was initially increased and decreased for further increase of Ni concentration.
- EDX spectra confirmed the presence of Cd, Zn, Ni, and S as per the stoichiometry ratio in the synthesized samples.
• The large band gap value was observed for Ni (Ni = 6%) doped Zn: CdS QDs due to quantum confinement effect.
• FTIR spectra vibration modes identified the Cd-Zn-Ni-S bonds at 670 cm$^{-1}$ (Ni= 0%) was shifted to higher wavenumber side as 673 cm$^{-1}$ due to doping.
• Ni (6%) doped Zn: CdS offered a higher transmittance in UV-region, possessed wide band gap due to optimum structural property, that material can be chosen for the optical and optoelectronic device fabrication and in QLED.

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