

## STRUCTURAL AND OPTICAL PROPERTIES OF PURE AND Mg DOPED CdSe NANOPARTICLES SYNTHESISED BY MICROWAVE ASSISTED METHOD

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Nanoparticles (NPs) of CdSe, a II-VI binary chalcogenide and Mg doped CdSe nanoparticles have been prepared by Microwave assisted method at room temperature. CdSe nanoparticles have size-dependent photo-luminescence properties and promising applications in light emitting devices and anti-reflecting coating. The synthesis of pure and Mg doped CdSe nanoparticles was performed using cadmium chloride (CdCl<sub>2</sub>), Selenium (Se) powder, Magnesium (Mg) powder with the presence of Deionized water, Ethylene glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>) and Hydrazine hydrate (N<sub>2</sub>H<sub>4</sub>). The synthesized nanoparticles were characterized for their structural, optical and morphological properties using XRD, TEM, FTIR and UV-visible absorption spectroscopy. The particle size was calculated from XRD image using Debye-Scherrer formula and the average diameter of CdSe and Mg doped CdSe nanoparticles was found to be around 13 nm and 18 nm. The absorption spectra obtained by UV-visible absorption spectroscopy was taken from 200 – 800 nm. The optical band gap of nanoparticles was calculated by Tauc equation and was 3.88 eV and 3.70 eV respectively for pure and Mg doped CdSe nanoparticles. Doping Mg is a simple way to control the light emission wavelength because of assumed blue shift in absorption spectra.

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### 1. Introduction

In recent years, nanomaterials have been widely used in many areas such as medicine, food industry, lighting, surface modifications [1-3]. The growth of nanotechnology has brought scientists to a new generation; many breakthroughs have been invented when studying nanoscience. As nanomaterials have many useful functions and diverse properties, they can differ considerably from their bulk counterparts. The large surface-to-volume ratio influences optical and surface properties of semiconductor nanomaterials. Different properties such as size, shape, and surface characteristics will result in different applications, including sensing, electronics, photonics, energy conversion, biomedical and others. Some basic concepts of nanomaterials have been discussed in brief, particularly on synthesis of nanomaterials such as quantum dots with their properties and applications. The most evident manifestation of properties is the optical light emission in the blue–red spectral region characterized by a blue shift at smaller crystallite dimensions. Such properties construct semiconducting nanostructures suitable for several kinds of applications, from anti reflecting coatings [4] to biomolecular detection [5] and light emitting devices [6]. Semiconductors and their compounds found a wide range of application in recent scientific and technological aspect. In the past decade, II–VI semiconductor nanoparticles attracted much attention because of their size-dependent (and thus tuneable) photo- and electro-luminescence properties and promising applications in optoelectronics. Among the family of II–VI semiconductors, ZnS [7-9], CdS [10,11], ZnO [12], CdSe [13-17], CdTe [18] and other chalcogenide glasses [19] are the foremost candidates due to their favourable electronic and optical

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properties for wide optoelectronic applications such as light-emitting devices, optical devices, solar cells, laser diodes, Nano-sensing and biomedical imaging.

In particular CdSe quantum dot (QD) is an important II–VI semiconductor with a wide optical band gap, making it a very attractive material for optical applications, especially in nano-crystalline form [20-23]. Colloidal CdSe quantum dots are one of the most well-known photonic materials in nanotechnology for the last several years [24, 25]. They show almost full visible-range light emission by size variation. CdSe can have two different crystal structures cubic zinc blende and hexagonal wurtzite and a direct band structure. CdSe quantum dots of appropriate size can have an absorption edge and emission peak anywhere in the visible spectrum. Woo-Chul Kwak et al [26] have reported that Mg doped CdSe nanocrystals showed apparent blueshifts both in the UV–visible absorbance and photoluminescence (PL) emission spectra. Also, the PL intensity of the Mg-doped nanocrystals was even slightly higher than that of the pure CdSe. In this study we successfully synthesized CdSe and Mg doped CdSe by microwave assisted method. Further structural, morphological and optical properties of the undoped CdSe and Mg doped CdSe have been studied.

## 2. Experimental

### 2.1. Synthesis of CdSe nanoparticles-

The materials used for synthesis of CdSe NPs were Cadmium Chloride ( $\text{CdCl}_2$ ), Selenium powder (Se), hydrazine Hydrate ( $\text{N}_2\text{H}_4$ ) and Ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ). All the materials taken were highly purified and were used without further purification. For CdSe NPs synthesis, aqueous solution of Cadmium Chloride ( $\text{CdCl}_2$ ) (0.0218 M) and Selenium (Se) (0.0253 M) were mixed. Then Hydrazine Hydrate (18.18 ml) was added to the mixture which acts as reducing agent by reducing Se to  $\text{Se}^{2-}$ . The resulting mixture then turned white. Now Ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ) (54.54ml) was added to it and then the solution was kept on the Magnetic stirrer for an hour. Further the solution was microwaved with a power of 900W for duration of about 9 minutes with a duty cycle (D) of 25% to get precipitate of dark grey colored CdSe nanoparticles. Then the CdSe nanoparticles were filtered and allowed to dry at  $60^\circ\text{C}$  in an oven for the next 4 hours. Finally powdered form of CdSe was obtained after complete drying.

### 2.2. Synthesis of Mg-doped CdSe nanoparticles-

Ethylene glycol and Hydrazine hydrate mixed with distilled water in the volume ratio of 7:3:1 respectively in a 200 ml capacity beaker. Now the distilled water was measured in 200 ml measuring tube for making accurate measurement of 127.3 ml. Also for ethylene glycol and hydrazine hydrate, a 100 ml measuring tube was taken for making accurate measurement of 54.6 ml and 18.1 ml respectively. Then the two beaker one containing cadmium chloride(0.0218 moles), Magnesium powder (0.5 grams) and selenium powder (2 grams) and second one containing distilled water, ethylene glycol and hydrazine hydrate mixture were mixed and stirred with a glass tube. Now the solution was put into magnetic stirrer at  $60^\circ\text{C}$  for 6 hrs. The solution resembled colour of wine red and then as the process continues it got changed into dark brown. Then the solution was Microwaved with the process as mentioned above to get precipitate of deep dark brown colour which was collected on the upper surface of the mixture. The prepared sample was filtered and left for drying. After proper drying, Mg doped CdSe nanoparticles were obtained. The chemical reaction took place in presence of mixture of Distilled water ( $\text{H}_2\text{O}$ ), Ethylene Glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ) and Hydrazine Hydrate ( $\text{N}_2\text{H}_4$ ).

The Duty Cycle for microwave process was taken to be 25%.

$$D = \frac{t_1}{t_1 + t_2} = 25\%$$

Where  $t_1 = 20$  sec (microwave time)

$t_2 = 60$  sec (relaxation time)

### 3. Result and discussions

The structural properties of the synthesized CdSe NPs and Mg-doped CdSe NPs were analyzed by recording their X-ray diffraction patterns with model Bruker AXS D8 Advance using Cu K $\alpha$  radiation having wavelength 1.5406 Å. The XRD pattern of synthesized CdSe NPs is shown in Fig 1(a). The peaks marked in figure by \* corresponds to pure phase of CdSe and rest to impure phase. The particle size was also measured by Debye-Scherrer formula which was in close agreement with one calculated by TEM image. The Debye-Scherrer formula is

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

where  $\lambda$  is wavelength of X-ray,  $\beta$  is called FWHM (Full Width at Half Maxima),  $\theta$  is the angle of diffraction. The peaks obtained in the fig.1 at  $2\theta = 23.9, 33.8, 43.6, 46.8, 49.1, 56.2, 64.4, 70.1, 71.9, 76.8$  shows pure CdSe and the other peaks obtained at  $2\theta = 15, 20, 21.5, 29.9, 31, 32.4, 62.2$  represents the impurities. The particle sizes were also measured by TEM image which was in close agreement with one calculated by Debye-Scherrer formula.

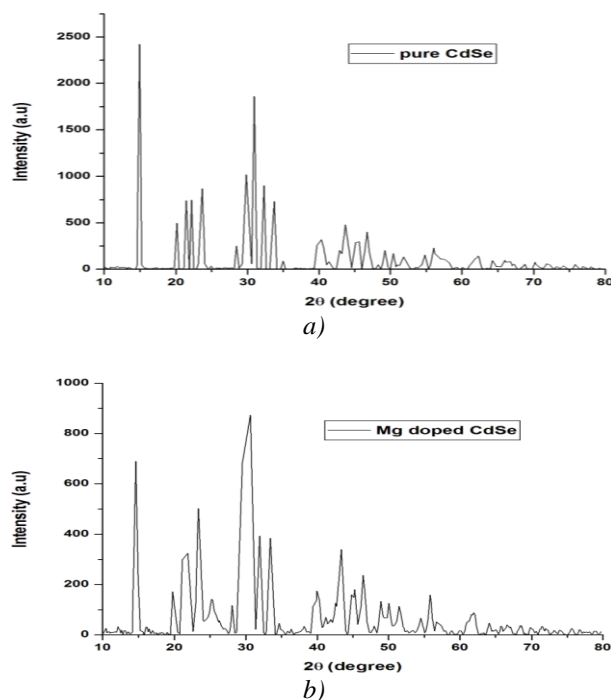


Fig.1. XRD pattern of CdSe nanoparticles: a) undoped CdSe; b) Mg-doped CdSe

The X ray diffraction pattern of Mg doped CdSe is shown in Fig 1(b). The peaks obtained in the Fig 1(b) at  $2\theta = 22.4, 33.6, 43.3, 46.6, 55.6$ , shows Mg-doped CdSe and the other peaks represent the impurities. The average particle size calculated for CdSe and Mg –doped CdSe using Debye-Scherrer formula is 13 nm and 18 nm respectively. There were observable XRD peak shifts to low  $2\theta$  angles in the Mg doped nanoparticles, indicating the crystal lattice expansion. This may be due to slightly smaller size of Mg<sup>2+</sup> ions (0.57 Å) than Cd<sup>2+</sup> ions (0.78 Å) in coordination number (CN) of 4. This could happen probably since some crystalline defects such as stacking faults can be involved during the fast growth of the nanocrystals [26].

The morphology of the as synthesized nanoparticles was analysed by HRTEM Jeol Model JEM 2100. TEM was taken to visualize the shape and size of synthesized undoped CdSe and Mg doped CdSe nanoparticles. It also confirms the nanocrystallinity of the sample. It was also observed from the image that the particles were in abundance. The average size of the CdSe and

Mg-doped CdSe nanoparticles was around 15 and 19 nm respectively, which reveals that the Mg incorporation considerably enhanced the coarsening kinetics of the CdSe nanoparticles. Transmission Electron Microscopy (TEM) images and selected area electron diffraction (SAED) patterns of the CdSe and Mg-doped CdSe nanoparticles are shown in the Fig 2(a) and Fig 2(b).

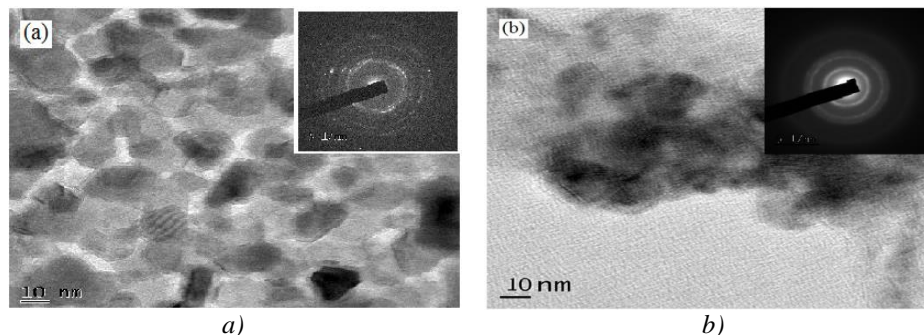


Fig 2. High-resolution electron microscopy (HRTEM) images and selected area electron diffraction (SAED) patterns CdSe nanoparticles. a) undoped CdSe; b) Mg-doped CdSe

FTIR spectrum of CdSe nanoparticles and Mg-doped CdSe nanoparticles were recorded by Thermo Nicolet, Avtar 370 model. The vibrational peak observed at 3295.79 shows N-H stretching which may be due to the presence of hydrazine hydrate. Since our sample is prepared in aqueous medium which results in O-H stretching vibrational peak at 1607.07. Further the vibrational peak at 1148.43 is attributed to C-N stretching which may be caused due to interaction of ethylene glycol and hydrazine hydrate. In Mg-doped CdSe, the vibrational peak found at 813.87 is attributed to Mg-Se interaction and the vibrational peak at 1385.01 shows the H-OH stretching [27]. Figure 3(a) and 3(b) shows the FTIR spectrum of CdSe nanoparticles and Mg-doped CdSe nanoparticles.

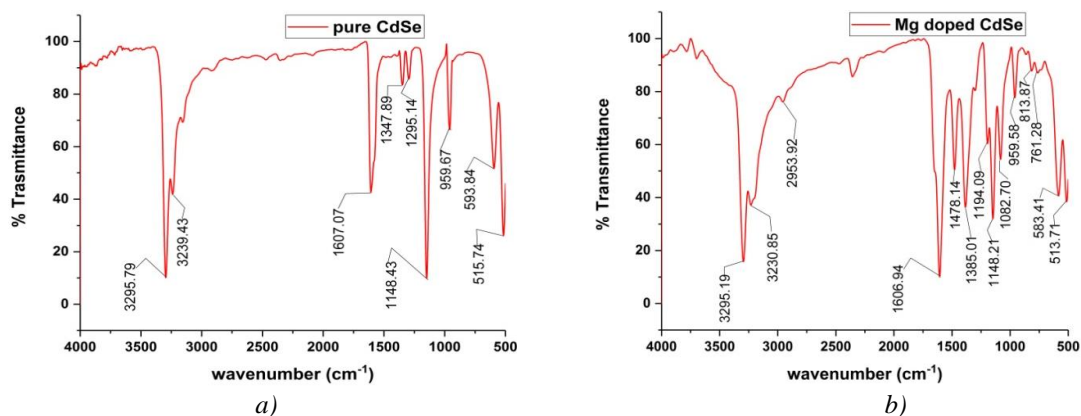


Fig. 3. FTIR spectrum of CdSe nanoparticles a) undoped CdSe; b) Mg-doped CdSe

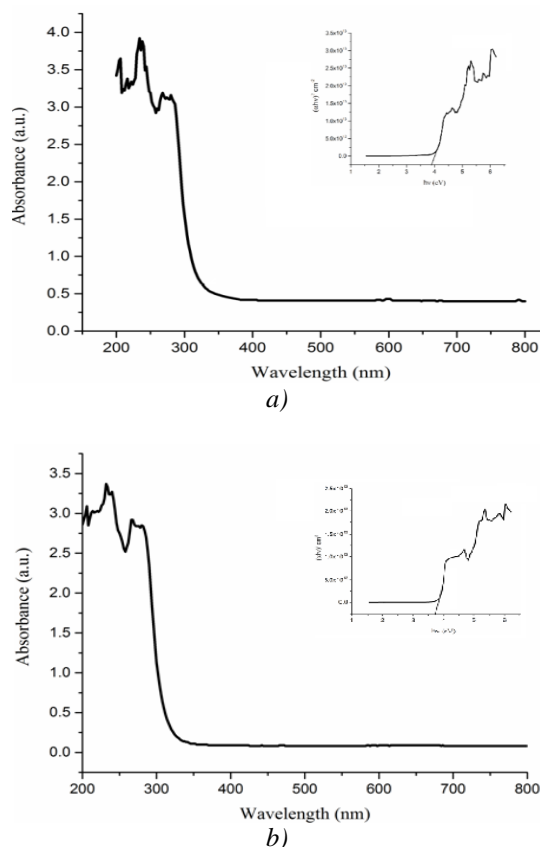


Fig. 4 UV-VIS spectrum of CdSe nanoparticles and energy band gap  
a) undoped CdSe; b) Mg-doped CdSe

The UV-visible absorption spectra of the CdSe and Mg-doped CdSe nanoparticles were obtained by the spectrometer Rayleigh UV-2601 and also the optical band gap of the material was obtained. The optical studies were carried out in the wavelength range of 200 – 800 nm as shown in Fig 4. However the characteristic absorption peaks were appeared in the wavelength range 200 - 400 nm and the peak position reflected the band gap of the nanoparticles. It was also revealed from UV- visible spectra that the absorption band was blue shifted from the bulk. The energy bandgap of the CdSe nanoparticles and Mg-doped CdSe nanoparticles were observed by plotting a graph between  $(\alpha h\nu)^2$  versus  $h\nu$  and by extrapolating the linear region of the curve to the energy axis. From absorption spectra, the optical band gap has been calculated by using Tauc relation [28].

$$\alpha h\nu = A (h\nu - E_g)^m$$

Where  $\alpha$  is the absorption coefficient, A is a constant and  $E_g$  is the direct band gap energy of the material. The value of  $m = 1/2, 2, 3, 3/2$  for direct allowed, indirect allowed, indirect forbidden, and direct forbidden transitions respectively. The present system obeys the rule of direct transition (i.e.,  $m = 1/2$ ). The Energy band gap  $E_g$  for the CdSe nanoparticles and Mg-doped CdSe nanoparticles was found to be 3.88 eV and 3.70 eV respectively. The results demonstrate that the energy band gap decreases with Mg doping in CdSe. This result may be due to the change in the size of the crystallites after doping. The absorption spectra and energy band gap of CdSe and Mg-doped CdSe nanoparticles are shown in Figure 4(a) and 4(b) respectively.

#### 4. Conclusions

In this study, we proposed microwave assisted method to realize the successful synthesis of CdSe and Mg-doped CdSe nanoparticles. The undoped CdSe nanoparticles were of size around 13 nm and Mg-doped CdSe nanoparticles were of size around 18 nm which was calculated by Debye Scherrer formula. The particle sizes were also in close agreement measured by TEM images. This Mg doping method was suggested as a simple and powerful approach to tune the energy bandgap of the CdSe nanoparticles and, in turn, to effectively control their light emission colour. The UV-visible absorption spectrum clearly shows apparent blue shifts.

The results show that doping of Mg significantly influences the particle size and optical band gap in Cd-Se. The Energy band gap  $E_g$  for the CdSe nanoparticles and Mg-doped CdSe nanoparticles was found to be 3.88 eV and 3.70 eV respectively. The results demonstrate that the energy band gap decreases with Mg doping in CdSe. This result may be due to a change in the size of the crystallites after doping.

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