

# Synthesis of cadmium selenide nanoparticles by wet chemical method

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## ABSTRACT

Nanotechnology deals with various structures of matter having dimensions of the order of a billionth ( $1 \times 10^{-9}$ ) of a meter. In recent years nanotechnology has become one of the most important and exciting forefront fields in physics, chemistry, engineering and biology. Particles which are smaller than the characteristic lengths associated with particular phenomena often display new chemistry and physics, leading to new behavior which depends on the size. So, for example, the electronic structure, conductivity, reactivity, melting temperature and mechanical properties have all been observed to change when particles become smaller than a critical size. Nanotechnology is expected to enable environmentally friendly mass production at low cost. It is also expected that nanotechnology will prove to be useful in the development of light and strong materials, biomedical materials pharmaceutical materials and multifunctional intelligent materials. Many important nanostructures are composed of the group IV elements Si or Ge, type III-V semiconducting compounds such as Ga As, or type II-VI semiconducting materials such as CdS, CdSe, so these semiconductors materials will be used to illustrate some of the bulk properties that become modified with incorporation into nano-structures.

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## Introduction

### Experimental Section

#### Preparation of thiol stabilized CdSe using Se (IV) precursor

Taking 0.045 g of cadmium chloride ( $\text{CdCl}_2$ ) (1mM) was dissolved in 250 ml of millipore water in the presence of 0.01 M of Mercaptoacetic acid and pH of the solution was adjusted to 7.4 using 0.1M NaOH. The reaction mixture was discharged into a beaker. Now taking 0.065g of Sodium Selenite ( $\text{Na}_2\text{SeO}_3$ ) (1mM) dissolved into 250 ml of millipore water in the presence of 0.01 M of Mercaptoacetic acid. An equal volume of the prepared two solutions are mixed together and the final pH of the solution was adjusted to 7.4.

Then the mixture was stirred for 2 hours at room temperature. The appearance of an orange yellow in color solution is due to the formation of thiocarboxylic acid protected CdSe nanoparticles. After the completion of the reaction, the thiocarboxylic acid protected CdSe nanoparticles was precipitated out by the drop wise addition of 2-propanal and resulting orange yellow color precipitate was obtained. Fine powders of thiocarboxylic acid stabilized CdSe nanoparticles was filtered and dried. Thiol stabilized CdSe nanoparticles were synthesized by varying the mole ratio of Cd or Se and pH of the solution. In the present work, the mole ratio of Cd and Se was chosen as 1:1, 1:2, 2:1 at the pH 7.4 and 11.2.

## Results and discussion

### XRD Analysis

X-ray diffraction studies were carried out for all samples of various mole ratio between Cd and Se, such as 1:1 at pH=7.4, pH=11.2 and 1:2 at pH=7.4, pH=11.2.

Diffraction peaks for the system of CdSe synthesized with mole ratio 1:1 at pH=7.4 are  $2\theta = 43.69^\circ, 49.21^\circ, 51.01^\circ, 72.54^\circ$  which corresponds to the (2 2 0), (1 1 3), (3 1 1), and (3 3 2) plane reflections of cubic CdSe respectively with the cell parameter  $a = b = c = 6.077 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ . The position of the reflection peaks

match with the cubic CdSe. The diffraction peaks for the system of CdSe synthesized with mole ratio 1:2 at pH=7.4 are  $2\theta = 23.23^\circ, 29.17^\circ, 43.62^\circ, 51.18^\circ, 72.55^\circ$  which corresponds to the (0 1 0), (1 0 1), (1 1 1), (2 0 1), and (2 1 2) plane reflections of hexagonal CdSe respectively, with the cell parameter  $a = b = 4.299 \text{ \AA}$ ,  $c = 7.010 \text{ \AA}$ ,  $\alpha = \beta = 90^\circ, \gamma = 120^\circ$ .

The position of the reflection peaks match with the hexagonal CdSe. The cubic modification has found to be more preferable for the mercaptoacetic acid capped CdSe nanoparticles than the hexagonal phase.

The structural confirmation was done by XRD. The spectral transmittance in the UV-Visible region was analyzed by the UV-Visible Spectrophotometer. The Fluorescence and the FTIR studies were also done.

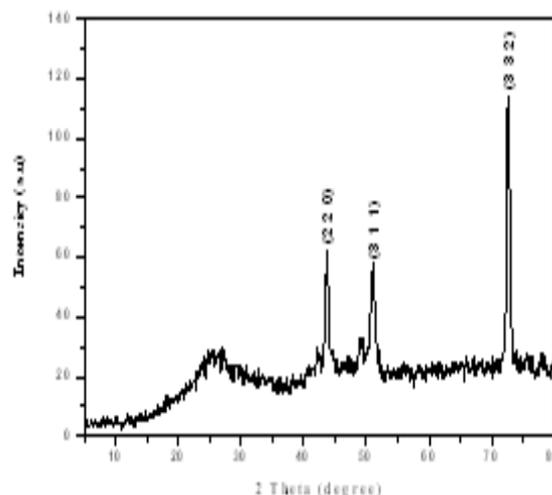


Fig.1. XRD Pattern for the synthesized CdSe with 1:1 mole ratio at pH= 11.2

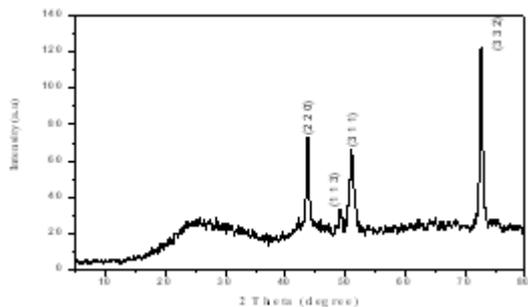


Fig.2. XRD Pattern for the CdSe synthesized with 1:1 mole ratio at pH=7.4

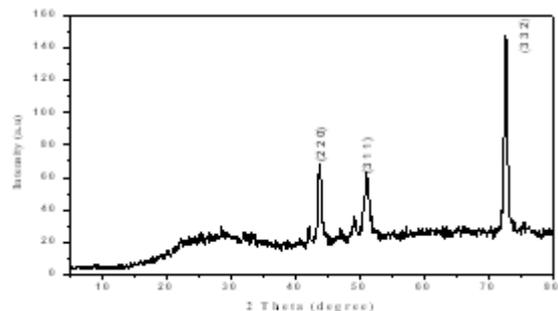


Fig.3. XRD Pattern for the CdSe synthesized with 1:2 mole ratio at pH= 11.2

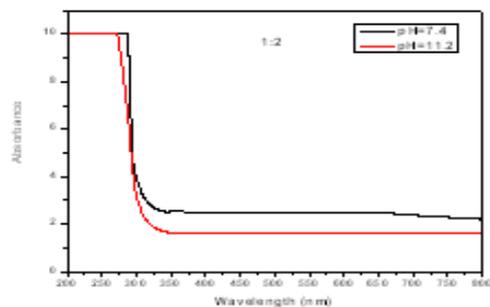


Fig.4. XRD Pattern for the CdSe synthesized with 1:2 mole ratio at pH= 7.4

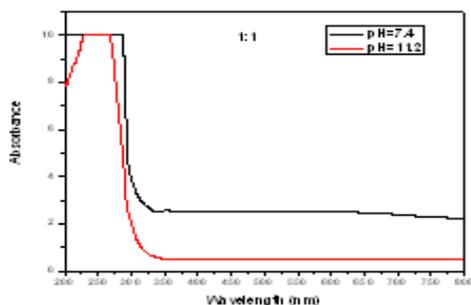


Fig.5. UV-Visible spectrum of the sample with mole ratio 1:1 at pH= 7.4& 11.2

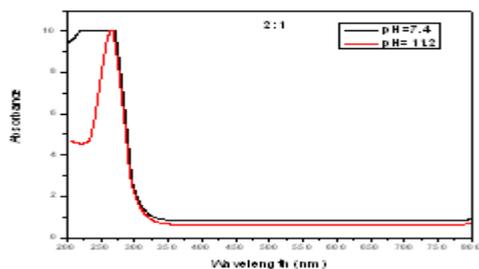


Fig. 6. UV-Visible spectrum of the sample with mole ratio 2:1 at pH= 7.4& 11.2

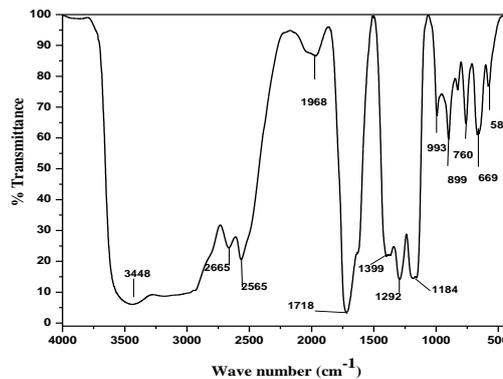


Fig. 7. FT-IR Spectrum of Mercaptoacetic acid

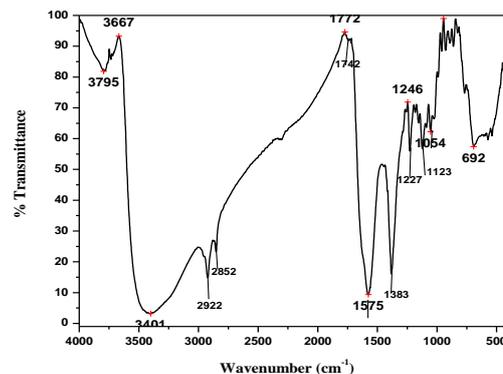


Fig. 8. FT-IR Spectrum of capped Cdse

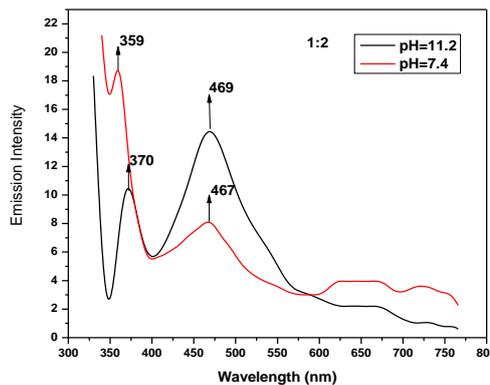


Fig. 9. Fluorescence spectrum of CdSe nanoparticles with mole ratio 1:2 at pH= 7.4 & 11.2

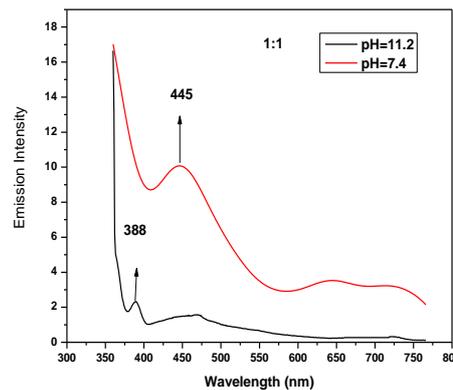
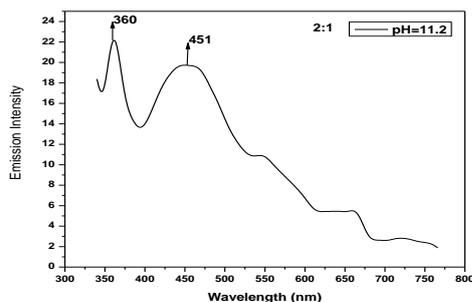


Fig. 10. Fluorescence spectrum of CdSe nanoparticles with mole ratio 1:1 at pH= 7.4& 11.2



**Fig.11. Fluorescence spectrum of CdSe nanoparticles with mole ratio 2:1 at pH= 11.2**

#### UV-Visible Absorption Studies

The change in absorbance spectrum depending on the mole ratio of the Cd and Se ions, and the effect of pH was analyzed. The absorption edge lies at 340nm for the mole ratio of 1:1 at pH=7.4 and for the mole ratio of 1:1 at pH=11.2 the absorption edge lies at 350nm, which is a pronounced shift from 712 nm of the bulk CdSe band gap. For the mole ratio of 1:2 at pH=7.4 the absorption edge lies at 343 nm and for the mole ratio of 1:2 at pH=11.2 the absorption edge lies at 358nm. For the mole ratio of 2:1 at pH=7.4 the absorption edge lies at 355 nm and for the mole ratio of 2:1 at pH=11.2 the absorption edge lies at 359nm.

#### IR Spectral Studies

The adsorption of thiols on the surface of CdSe nanoparticles have been investigated by the FT-IR spectral analysis. In the FT-IR spectrum of mercaptoacetic acid, weak absorbance peak was observed for free thiol group (-SH) at 2665  $\text{cm}^{-1}$  and 2565  $\text{cm}^{-1}$  whereas the bonded thiolate do not show any peak in this region due to the adsorption of thiol on metal surface. In the free mercaptoacetic acid the  $\text{CH}_2$  band is clearly observed at 1399  $\text{cm}^{-1}$  and free carboxylic group is observed at 1718  $\text{cm}^{-1}$ .

The peak at 1292  $\text{cm}^{-1}$  shows C-O stretching vibration. In the mercaptoacetic acid capped CdSe there is no absorbance around 2600  $\text{cm}^{-1}$ , which shows that the thiols are completely adsorbed on the surface of the metal surface. The peak at 1574  $\text{cm}^{-1}$  shows the asymmetric COO- vibration for the nanoparticles and indicates that mercaptoacetic acid exists in the form of carboxylate salt.

#### Fluorescence Spectral Analysis

The fluorescence spectra of the synthesized CdSe nanoparticles were recorded using Perkin-Elmer-VS-45 spectrophotometer. The spectrum was taken using excitation wavelength of 320 nm. The less intense band around 388 nm for

the pH 11.2 and 445nm for the pH 7.4 is ascribed to the exciton emission of CdSe nanoparticles synthesized with 1:1 mole ratio Cd and Se. For the CdSe nanoparticles synthesized with 1:2 mole ratio of Cd and Se, the emission spectrum shows two bands. The less intense band around 370 nm for the pH 11.2 and 359 nm for the pH 7.4 is ascribed to the exciton emission of CdSe nanoparticles. The intense band around 469 nm is ascribed to a defect related emission and originates from the surface defects due to capping. The contribution of the defect related emission to the luminescent signal has been reduced by changing the pH. In the present case the intensity of the defect-related emission is less at the pH 7.4, and it is more pronounced at pH 11.2. Similarly for the CdSe nanoparticles synthesized with 2:1 mole ratio of Cd and Se, the emission spectrum shows two emission peaks for the pH=11.2. The less intense band around 360 nm is ascribed to the exciton emission of CdSe nanoparticles. The intense band around 451 nm is ascribed to a defect related emission and originates from the surface defects due to capping.

#### Conclusion

A detailed study of synthesis of water soluble mercaptoacetic acid capped CdSe by a single step method in aqueous medium at the pH=7.4, pH=11.2 were described. The metal to ligand ratio was then followed in the synthesis procedure, since the increase in the metal to ligand ratio leads to decrease in particle size. The effect of Cd to Se metal ratio on the particle size was studied detail for the various mole ratios such as 1:1, 1:2, 2:1 at two different pH values 7.4 and 11.2. From XRD analysis, the cubic modification has found to be more preferable for the mercaptoacetic acid capped CdSe nanoparticles than the hexagonal phase. A pronounced shift from 712 nm of the bulk CdSe band gap was observed in the UV studies. Thus water soluble thiols stabilized CdSe nanoparticles can be used directly in biological and LED applications.

#### References

- [1] Al L. Efros and Efros A.L. (1982), 'Interband Absorption of light in a Semiconductor Sphere', *Sov.Phys.-Semicond.* Vol. 16, p.772.
- [2] Alivisatos A.P. (1996 a), 'Semiconductor clusters, nanocrystals, and quantum dots', *science*. Vol. 271, pp. 933-937.
- [3] Chestony N., Harris T.D., Hull R. and Brus L.E. (1986), 'Luminescence and photo physics of cadmium sulfide semiconductor clusters: the nature of the emitting electronic state', *J. Phys. Chem.* vol. 90. No 15. PP. 3393-3399.
- [4] Krishnan R. and Frisener R.A. (1991), 'Quantum confinement effects in semiconductor clusters', *J. Chem. Phys.* Vol. 95, p, 8309.