

## **Development of CdS, ZnS Quantum Dots and their Core/Shell Structures by wet chemical method**

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### **Abstract**

Due to the unique optical properties like size-tunable emission color, narrow emission peak, and high luminescence efficiency semiconductor quantum dots (QDs) are emerging candidates for various applications. Size-controlled zinc sulfide (ZnS) and cadmium sulfide (CdS) quantum dots and their core/shell structures with varying concentration of capping agent were prepared using wet chemical methods. The obtained particles were characterized by XRD, UV/VIS, PL, FTIR and TEM. Corresponding broadening in XRD peaks reveals the reduction in particle size with uniform size distribution in the range particles of 2-10 nm. Optical absorption studies show that the absorption edge shifts due to quantum confinement towards the blue region as the capping agent concentration is increased indicating that effective band gap energy increases with decreasing particle size. Photoluminescence spectroscopy was used to study the luminescence enhancement on the basis of quantum confinement, composition and structure of QDs. The surface characterization of the quantum dots has been performed by FTIR spectroscopy. O-H, N-H and C-O groups were present on the surface of QDs which are functional groups that can easily attach with bio-molecules. Transmission electron microscopy has been performed as the best proof for the particle size and particle size distribution.

**Keywords:** Quantum dots, Core/shell structures, Photoluminescence, FTIR

## 1. Introduction

Semiconductor quantum dots of II-VI group elements have attracted special attention to research community due to their fascinating optical and electronic properties. Zinc sulphide (ZnS) and cadmium sulphide (CdS) are II-VI semiconductors with direct band gap of 3.68 eV, 2.42 eV respectively in bulk form. ZnS and CdS quantum dots were synthesized by wet chemical method which is very easy, economic and effective route to synthesis quantum dots. The chemical synthesis has the advantages of producing size-controlled nanoparticles. Particle size must be less than twice of Bohr radii of exciton as quantum confinement regime is limited to that size. The tunability of the properties of nanoparticles by controlling their size may provide an advantage in formulating new materials with optimized properties for various applications. Most of the physical or chemical properties exhibited by these nanoparticles are due to their crystallite size. We describe here the synthesis and characterisation of 2-Mercaptoethanol capped ZnS and CdS QDs and their core/shell structures by wet chemical method. CdS/ZnS core-shell structure formed by capping of a CdS core, with a thin ZnS shell. The formation of ZnS shell can greatly passivate the core surface to protect it from oxidation and prevent CdS leaching into the surrounding medium and also improve the photoluminescence yield and photo-stability [1-6]. The novel CdS/ZnS quantum dots are biocompatible due to the use of 2-Mercaptoethanol as stabiliser, which uses the thiol group to bind to the Zn ions on the surface of core-shell QDs. There have been various studies that used 2-Mercapto as capping agent to produce QDs. They were used in biological applications and for nonlinear optical materials. The present study is aimed to synthesize nanoparticles of ZnS, CdS with their core/shell structures and studied their structural, optical, luminescence, surface chemistry properties and size distribution using X-ray diffraction (XRD), UV-Vis spectroscopy, photoluminescence spectroscopy (PL), Fourier transform

infrared spectroscopy (FTIR) and Transmission electron microscopy (TEM) respectively to verify the formation of ZnS, CdS and core/shell quantum dots.

## **2. Experimental**

### **2.1. Synthesis of CdS Q-Dots**

Cadmium sulphide Q-Dots were synthesized using wet chemical route at 35°C temperature. The starting materials for the synthesis of CdS nanoparticles were cadmium chloride (Merck) as cadmium source, ammonium chloride (Merck); and thiourea (Merck) as sulphur source and distilled water as solvent. All chemicals were of analytical grade products and used without further purification. The reaction matrix employed in our study consisted of AR grade CdCl<sub>2</sub>, NH<sub>4</sub>Cl and thiourea in 1:1.5:3 molar ratios. The reaction matrix was prepared in two parts. Typical synthesis, cadmium chloride and ammonium sulphate was mixed in 50 ml of distilled water. Ammonia was added to it until the formation of clear metallic complexes. The pH was kept at 8.5. Then thiourea was added into 50 ml of prepared solution and continuously stirred for 5 hours. Immediately (5%) 2-mercaptoethanol was added as a surfactant to control the particle size of CdS QDs.

### **2.2. Synthesis of ZnS Q-Dots**

The process for preparing Zinc sulphide Q-Dots were similar as to CdS QDs using solution growth wet chemical method at 35°C temperature. The reaction matrix employed in our study consisted of AR grade ZnSO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and thiourea in 1:1.5:1.5 molar ratios. Zinc sulphate dehydrate, and ammonium sulphate was mixed in 50 ml of distilled water. Ammonia was added to it until the formation of clear metallic complexes. The pH was kept at 9.5. Then thiourea was dissolved in 50ml of prepared solution. After that a 5% solution of 2-mercaptoethanol was added in solution for passivation then continuously stirred for 5 hours. Centrifuged (3500 RPM, 10 min) prepared sample of ZnS and washed several times with distilled water.

### 2.3. Synthesis of CdS/ZnS core-shell structure

CdS/ZnS core-shell structure was synthesized by seed growth method. The reaction matrix employed in our study consisted of AR grade  $\text{ZnSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$  and thiourea in 1:1.5:1.5 molar ratios. Zinc sulphate dehydrate, and ammonium sulphate were mixed in 50 ml of distilled water. Ammonia was added to it until the formation of clear metallic complexes. The pH was kept at 9.5. After this processes prepared CdS solution was added (2.5 ml) of as mentioned in CdS synthesis as above. Then thiourea was dissolving in 50 ml of prepared solution. After that a 5% solution of 2-mercaptoethanaol was added in solution for passivation then continuously stirred for 5 hours. When the reaction was completed, purify the CdS/ZnS core-shell nanocrystals.

### 2.4. Characterization techniques

In order to study the different properties of the prepared quantum dots we have characterized the samples using various techniques. Structural analysis has been performed using XRD, and the XRD patterns were recorded in a Shimadzu powder x-ray diffractometer using Cu  $\text{K}\alpha 1$  radiation. The optical properties were studied by PerkinElmer Lambda2 UV-Vis spectrophotometer and absorbance spectra were recorded. Photoluminescence (PL) emission spectra of the samples were recorded by a computer controlled rationing luminescence spectrophotometer LS55 (Perkin-Elmer Instruments, UK) with  $\lambda$  accuracy=  $\pm 1.0$  nm and  $\lambda$  reproducibility=  $\pm 0.5$  nm. A tunable 20 kW pulse  $< 10$   $\mu\text{s}$  from a Xenon discharge lamp was used as the excitation source for recording photoluminescence emission spectra. A gated photo multiplier tube was used as a detector. Prior to the PL experiments signal-to-noise ratio was adjusted to 500:1, using the Raman band of water with excitation at 220 nm. The surface chemistry of the quantum dots has been studied using FTIR (Perkin-Elmer LS50).

Transmission electron microscopy has been performed as the finest proof for the particle size and particle size distribution.

### 3.1. Structural Analysis

Figure 1 presents the XRD patterns of pure CdS QDs and 2-Mercaptoethanol capped CdS Quantum dots. From the XRD analysis it is found that the crystal structure of all samples of CdS is cubic/ wurtzite. The prominent peaks (110), (002), (200) and (201) were indexed to the wurtzite structure. It is well known that broadening of these peaks is due to the reduction of the crystallite size. The average sizes of CdS quantum dots are in the range from 2 to 4.3 nm, which was obtained from the width of the (002) peak using the Scherrer's formula. It is important to note that the 2-Mercaptoethanol capping provides the smallest grain size (2.0 nm). The diameter of the quantum dots (d) has been calculated using Scherrer's formula

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where  $\lambda$  is the wavelength of the x-rays used,  $\beta$  the full width at half maximum of the 100% XRD peak, and  $\theta$  the Bragg angle.

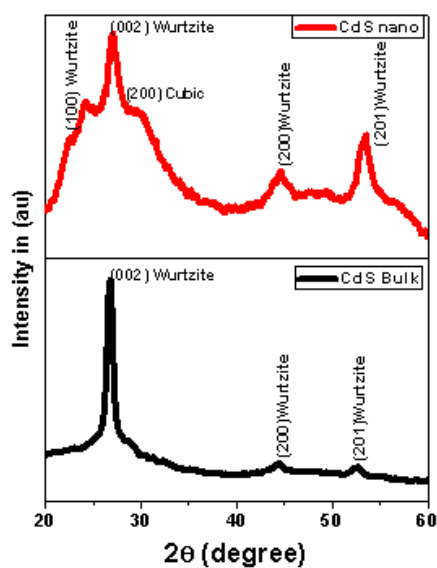
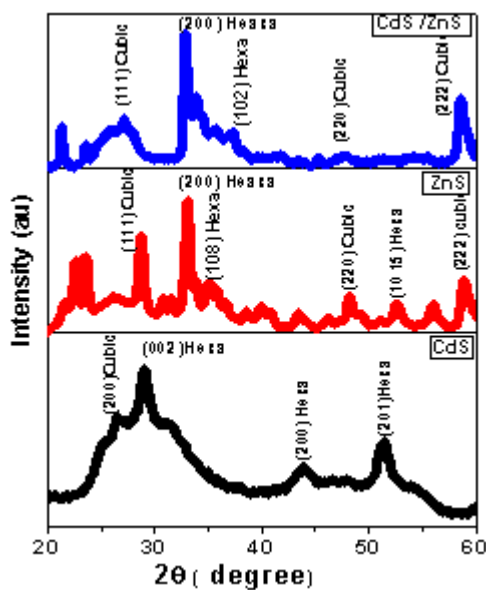


Figure1. XRD of bulk CdS and 2-mercaptoethanol capped CdS quantum dots.

In figure 2 The XRD traces shows about CdS, ZnS and CdS/ZnS that were synthesized by solution growth method. In first trace prominent peaks (002), (200) and (201) were indexed to the hexagonal structure of CdS quantum dots. The XRD peaks are found to be broad indicating size of the grains of the CdS sample is reducing. The average grain size of the sample is determined to be 2- 2 .26 from the full width at half maximum of the most intense peak making use of the Scherrer's equation.

In second trace the prepared zinc sulphate was found crystalline having wurtzite type structure. The wurtzite type structure was confirmed from the agreement of  $2\theta$ . The most prominent peak is oriented in (002), (200) and (201) direction. The average particle sizes were measured using Debye Scherer formula and were found to lies in the range 4 - 4.5 nm. XRD characterization also shows a clear broadening with a (2 $\theta$ ) peak around 48.40 in ZnS nanoparticles attributing the formation of quantum dots.

In 3<sup>rd</sup> trace x-ray diffraction pattern of core/shell structure (CdS/ZnS) has been shown. In this trace most prominent peaks are similar as ZnS QDs i.e (002) direction along with the other reflections at (200) and (201) planes. These peaks show that ZnS present at the outer surface in the form of a shell and size controlled the cabinet. The average particle size of CdS/ZnS core/ shell was measured using Debye Scherrer formula and was found to lie in the range 5- 5.40 nm. CdS quantum dots have maximum strain i.e 1.78, ZnS quantum dots have minimum strain and core shell structure have strain in between CdS, ZnS i.e 1.06. According to XRD both CdS and ZnS peaks were present in the core shell structure so that core shell structure shows intermediate strain value.



**Figure 2. XRD spectra of 2-Mercaptoethanol capped CdS, ZnS and CdS/ZnS quantum dots.**

**Table 1: FWHM, Intensity, Phase assignment, Lattice constant and Particle size of 2-Mercaptoethanol capped CdS, ZnS and CdS/ZnS QD's at room temperature.**

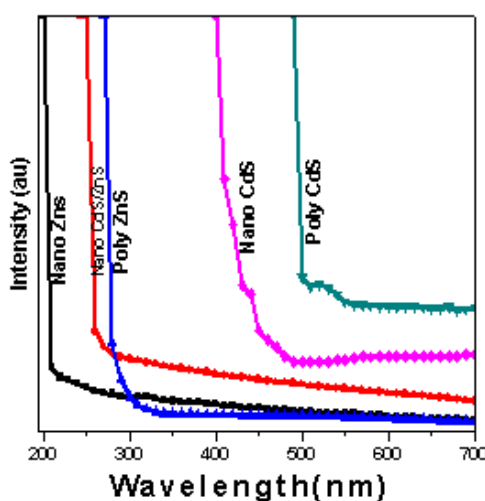
Sam.	2θ (degree)	d (Å)		FWHM (degree)	Intensity	(hkl)	Phase assignment	Particle size (D) nm	Lattice constant (Å)	Lattice Mismatch (%)	Strain
		Obs.	Std.								
CdS	28.98	1.77	1.77	1.32	55	(111)	Hexa	2.26	a = 3.8 c = 6.4	2.45 0.6	1.78 0.63
ZnS	33.02	2.06	1.75	3.92	22	(220)	Hexa	4.11	a = 5.8 c = 31.2	0.4 0.00	1.06 0.00
CdS/ ZnS	33.82	1.67	1.68	2.08	10	(222)	Hexa	5.32	a = 3.8 c = 30.8	0.5 1.2	0.48 1.02

### 3.2. Optical Studies

The UV-Visible spectra of the as-prepared CdS, ZnS and CdS/ZnS nanoparticles are shown in the figure 3. It shows strong absorption edges around 500, 250 and 285 nm for CdS, ZnS and CdS/ ZnS QDs respectively. A large blue shift has been observed in CdS and ZnS QDs with respect to their bulk absorptions. Corresponding absorption edges due to the transition between the electronic state in the conduction band and hole state in the valance band are tabulated in Table 2. The energy band gap for CdS, ZnS and CdS/ZnS QDs have been calculated from the corresponding absorption edges using the second derivative of the absorption spectra and using the formula

$$E_{ev} = hc / \lambda \quad (2)$$

where  $h$ = Planck's constant and  $E$  = energy band gap of the semiconducting nanoparticles in the optical spectra. Average blue shift of 1.0 eV is observed in the as prepared CdS, ZnS nanostructure respectively as compared to their bulk counterparts attributing the blue shift in band gap energy. This continuous blue shift shows that quantum confinement occurred in the prepared quantum dots and effectiveness of capping agent to obtain controlled size of quantum dots.



**Figure 3: Absorption spectrum of the Poly and 2-mercaptoethanol capped CdS, ZnS, CdS/ZnS QDs.**



The absorption edge of the core/shell structure is lies between CdS, ZnS quantum dots because surface to volume ratio in core/shell is more than CdS but less than ZnS . So discreteness of energy levels of core/shell lies between CdS, ZnS according to this fact edge of core shell structure is at accurate position.

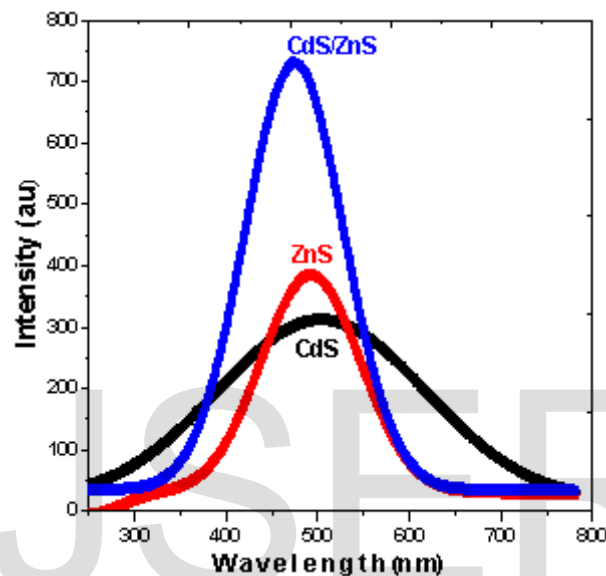
**Table 2: Band gap increment in CdS, ZnS, CdS/ZnS quantum dots due to quantum confinement.**

Sample	Absorption edge	Band gap in eV	Increment in band gap eV
CdS Poly	550	2.42	----
ZnS Poly	350	3.54	----
CdS Nano	500	2.48	0.06
ZnS Nano	250	4.96	1.42
CdS/ZnS Nano	285	4.35	0.81

### 3.3. Photo Luminescence

The room-temperature photoluminescence spectra of as-prepared CdS, ZnS, CdS/ZnS quantum dots were shown in figure 4 (a, b and c). All the samples were excited at 220 nm. The obtained results show that the 2- Mercaptoethanol having an excellent capping efficiency because dangling bonds are effectively passivated in CdS and ZnS samples. The emission spectra of ZnS QDs (fig 4b) is having comparatively 10 fold enhancement from CdS (fig 4a) because ZnS is optically transparent to the emission range, therefore there are no photon losses associated to the ZnS shell with visible light emission [10]. Interesting result of the work can be seen from the PL emission spectra that the emission intensity of capped CdS/ZnS structure is significantly high in comparison to capped CdS and ZnS nanoparticles about 3-fold increment in intensity has been achieved. This is due to core/shell nanoparticles

are excited and the photo induced charge carriers migrate to the interface and trap in the misfit dislocations. Therefore, the emissions observed can be attributed to the radiative recombination of carrier at CdS/ZnS interface. Due to these factors core shell structures gives more enhanced luminescence. With an increase in shell thickness of the CdS/ZnS core shell nanoparticles the intensity of emission peaks decreases which may due to increase of non-radiative recombination (data not shown).

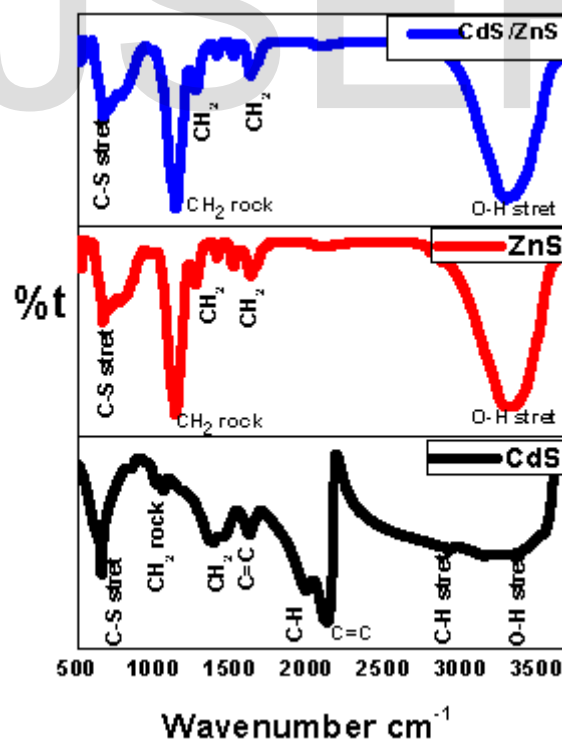


**Figure.4: Room temperature photoluminescence spectra of 2-Mercaptoethanol capped (a) CdS, (b) ZnS and (c) CdS/ZnS QD's.**

### 3.4. FTIR analysis:

2-mercaptoethanol capped CdS, ZnS, CdS/ZnS quantum dots were examined by recording their FTIR spectra in the range  $4500\text{--}100\text{ cm}^{-1}$  (Fig. 5). The broad peak at  $2120, 1383\text{ cm}^{-1}$  and the weak peak at  $1614\text{ cm}^{-1}$  were assigned to C=C, C-H characteristic vibrations in the CdS sample as marked shown in the spectra. The sharp peak at  $3365\text{ cm}^{-1}$  corresponds to (O-H) alcohols and  $1119\text{ cm}^{-1}$  shows (C-N) amines along with two small peaks at  $1626\text{ cm}^{-1}$  for (N-H) amines and  $1401\text{ cm}^{-1}$  for O-H means carboxylic acid in ZnS samples, similar peaks occurred in CdS/ZnS quantum dots. These results shows how effectively ZnS covers the

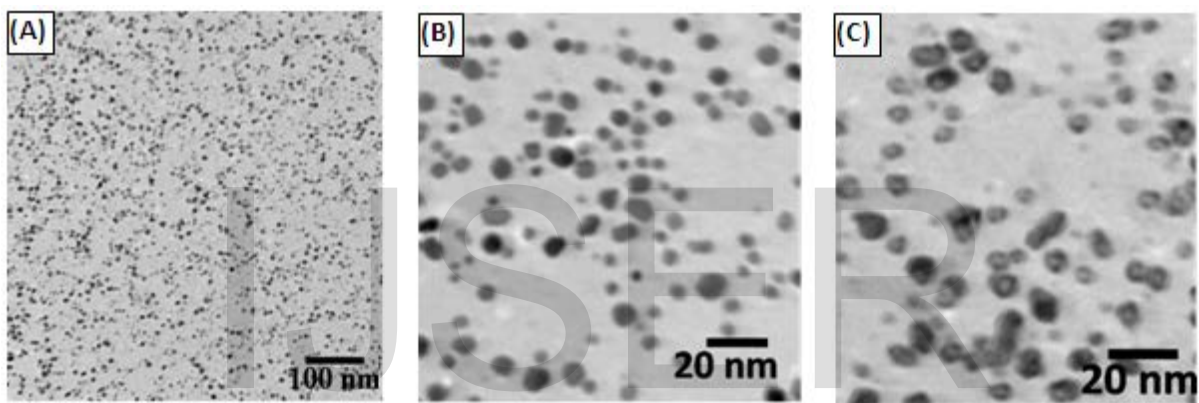
CdS core and reduce the toxicity of CdS materials as ZnS is nearly non toxic for bio molecules. The functional groups that are present on the surface of the prepared samples are easily attached with bio molecules. Generally OH (Hydroxyl), COOH (carboxylic acid) or amine functionalities are present on the bio molecules surfaces [15, 16] and similar functional groups are present in our as prepared QD's. So that prepared QD'S have compatibility to attach with bio molecule. ZnS present at the shell which is nontoxic and gives more opportunity to apply CdS/ZnS structure for bio-application like Bio imaging. Here one important point is worth mentioning that, as we have opted for aqueous medium to prepare luminescent QDs, as the results there is always hydrophilic surfaces of QDs which are directly conjugable to bio molecules. This is a plus feature of our technique as the QDs prepared by high temperature organic synthesis routes are always possessing hydrophobic surfaces and need to other additional surface processing steps before bioconjugation..



**Figure.5. FTIR spectra of Capped CdS, ZnS, CdS/ZnS quantum dots with their functional groups**

### 3.5. Transmission electron microscopy

Transmission electron microscopy has been performed to ensure about the particle size and to check the effectiveness of capping and the result have been presented in figure 6. TEM image of the CdS(A), ZnS(B) and CdS/ZnS(C) QDs show highly monodispersed nanoparticles with average sizes of 3–7 nm. It is also clear from the figure that there is no agglomeration of QDs and we can obtain either the fine solution or even powder of uniformly distributed nanoparticles for various applications. The particle size obtained from TEM is highly in accordance with the size obtained from XRD analysis.



**Figure.6. TEM image of Capped nano CdS(A), nano ZnS (B) and CdS/ZnS (C) QDs.**

### 4. Conclusion

The CdS, ZnS and CdS/ZnS their core shell structure were successfully synthesized through aqueous chemical route and their structural as well as optical properties were investigated by XRD, UV-Vis Spectroscopy, Photo luminescence spectroscopy, FTIR and TEM. XRD results indicated that lower synthesis temperature resulted in lower grain size and less strained particles. The particle sizes of CdS, ZnS and CdS/ZnS) quantum dots as determined from XRD and TEM image are in good agreement. The UV-Visible spectra show a large blue shift attributing the enhanced optical properties this size dependent blue shift of absorption edge is

attributed to the quantum size effect. PL measurement shows effectiveness of capping and core/shell structure formation as there is clear vindication of drastically enhanced luminescent efficiency. In summary, highly luminescent, nearly monodispersed cubic/wurtzite CdS, ZnS and CdS/ZnS QDs has been prepared. Core/shell semiconductor nanocrystals that were prepared by our method are low-cost, safe, and environmental friendly. The growth of the semiconductor nanocrystals can be readily controlled by the reaction temperature and time, CdS, ZnS CdS/ZnS core-shell monodispersed nanocrystals with high quantum yield and narrow PL spectra have been obtained. This method can also be applicable to synthesize the other core/shell semiconductor nanocrystals.

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