Size-Controlled Synthesis and Characterization of CdS, ZnS Quantum Dots and their Core/Shell Structures for Bio Based Applications

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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. QDs are therefore investigated towards their applications in light-emitting devices (QLEDs), solar cells, and for bio-imaging purposes. QDs made from compounds like Cds, ZnS or CdS/ZnS were studied because of their facilities and reliable synthesis. 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. It is observed that particle size decreases with increasing capping agent concentration. Optical absorption studies show that the absorption edge shifts towards the blue region as the capping agent concentration is increased indicating that effective band gap energy increases with decreasing particle size. Quantum confinement was observed for all theses particle types as the size of the particles were reduced and produce blue shifted absorption edge at and around 240 nm using UV/VIS absorption spectroscopy. 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 finest 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 3.68eV, 2.42 eV respectively in bulk form. ZnS and CdS quantum dots are 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. Chemical precipitation in the presence of capping agents, reaction in micro emulsions, sol gel reaction and auto combustion are commonly used techniques for synthesis of 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-Mercaptoethenol capped Zinc Sulphide (ZnS) and Cadmium Sulphide (CdS) quantum dots and their core/shell structures by wet chemical method. CdS/ZnS core-shell structure formed by capping of an emissive semiconductor CdS core, with a thin ZnS shell. ZnS has a wider band gap than CdS, which allows the epitaxial growth of a thin ZnS layer outside the CdS core. 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-Mercaptoethenaol 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 properties, 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^{o}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 sources and distilled water as solvent. All chemicals were analytical grade products and used without further purification. The reaction matrix employed in our study consisted of AR grade $CdCl_2$, NH_4Cl 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-mercaptoethenaol was used 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 QD's using solution growth wet chemical method at 35^{o}C temperature. The reaction matrix employed in our study consisted of AR grade $ZnSO_4$, $(NH_4)_2SO_4$ 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-mercaptoethenaol 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 $ZnSO_4$, $(NH_4)_2SO_4$ 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 (2.5ml) 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-mercaptoethenaol 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 Kα1 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 λ accuracy= ±1.0 nm and λ reproducibility= ±0.5 nm. A tunable 20 kW pulse <10 μs 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-Mercaptoethenol 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 (111), (100), (200) and (311) were indexed to the cubic/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 (111) peak using the Scherrer's formula. It is important to note that the 2-Mercaptoethenol capping provides the smallest grain size (2.0 nm). The diameter of the quantum dots (d) has been calculated using Scherrer's formula

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

where λ is the wavelength of the x-rays used, β the full width at half maximum of the 100% XRD peak, and θ the Bragg angle.

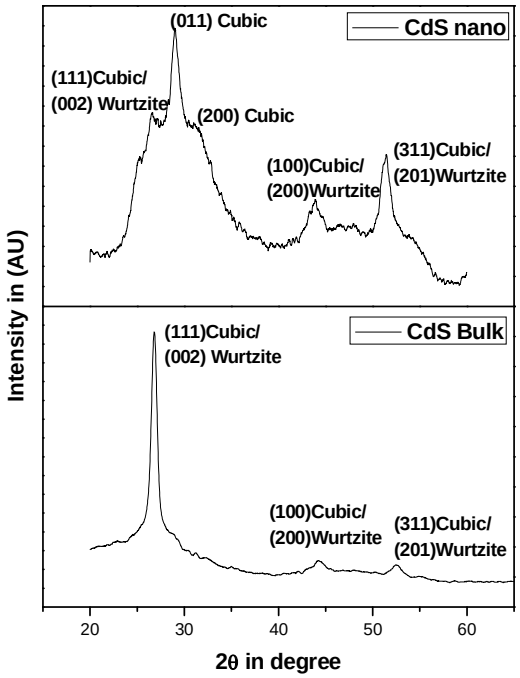


Figure 1. XRD of bulk CdS and 2-mercaptoethanol capped CdS quantum dots.

In figure 2 The XRD traces shows about CdS, ZnS and CdS/Zns that were synthesised by solution growth method.In first trace prominent peaks (111), (100), (200) and (311) were indexed to the cubic structure of CdS quantum dots. The XRD peaks are found to be broad indicating size of the grains of the CdS sample reducing. The average grain size of the sample is determined to be 2 to 4.3 nm nm 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 are crystalline having wurtzite type structure. The wurtzite type structure was confirmed from the agreement of 2θ. The most prominent peak is oriented in (200) direction along with the other reflections at (111) and (222)

planes. The average particle sizes were measured using Debye Scherer formula and were found to lie in the range 2–3 nm. XRD characterization also shows a clear broadening with a (2θ) peak around 48.40 in ZnS nanoparticles attributing the formation of quantum dots. In 3rd trace we shows X-ray difraction pattern of core shell structure (CdS/ZnS). In this trace most prominent peaks are similar as ZnS QD's i.e (200) direction along with the other reflections at (111) and (222) 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 sizes Cds/ZnS core shell was measured using Debye Scherrer formula and was found to lie in the range 2 – 3.27 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 peeks were present in the core shell structure so that core shell structure shows intermediate strain value.

3.2. Optical Studies

The UV-Visible spectra of the as-prepared CdS, ZnS and CdS/ZnS nanoparticles are shown in the figure 5. It shows strong absorption edges around 265, 242 and 214 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 as presented in the Figure 3.

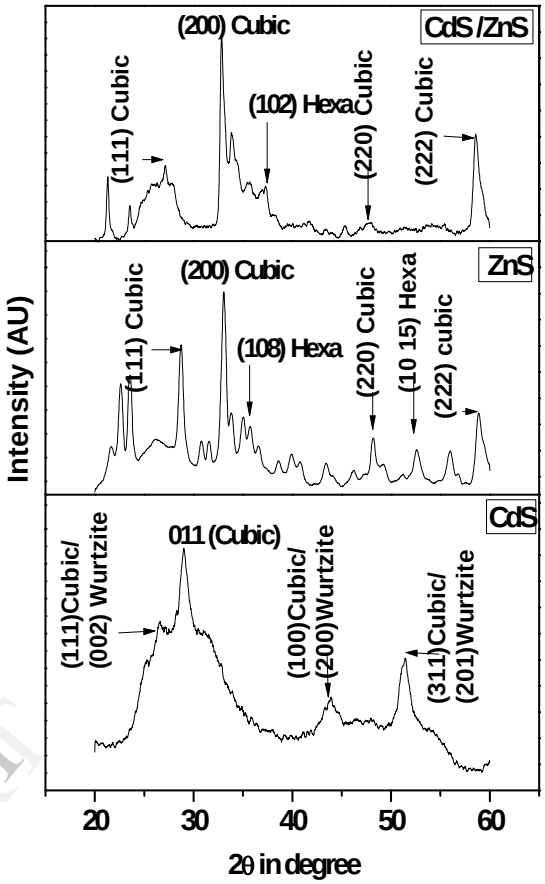


Figure 2. XRD of 2-Mercaptoethanol capped CdS, ZnS and CdS/ZnS quantum dots.

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.

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.

Sam.	2θ (degree)	d (Å)		FWHM (degree)	Intensity	(hkl)	Phase assignment	Particle size (D)	Lattice constant (Å)	Lattice Mismatch (%)	Strain
		Obs.	Stand.								
CdS	28.98	1.77	1.77	1.32	55	(111)	cubic	2.26 nm	a = 3	2.45	1.78
ZnS	28.71	2.06	1.75	3.92	22	(220)	Cubic	3.71 nm	a = 5.8	0.4	1.06
CdS/ ZnS	33.82	1.67	1.68	2.08	10	(222)	Cubic, Hexa	3.27 nm	a = 5. 7 a = 3.8 c =30.8	0.3 0.5 1.2	0.48

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

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

where h= planck's constant and *E* = energy band gap of the semiconducting nanoparticles in the optical spectra. Average blue shift of 2.3ev, 1.0eV 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.

The absorption edge of the core shell structure are lies between CdS, ZnS quantum dots because surface to volume ratio in core shell in more than of CdS but less than two 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 in Figure 3.

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

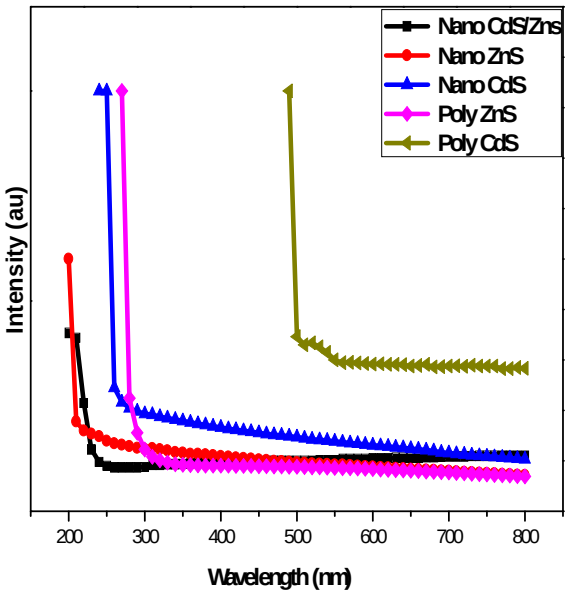


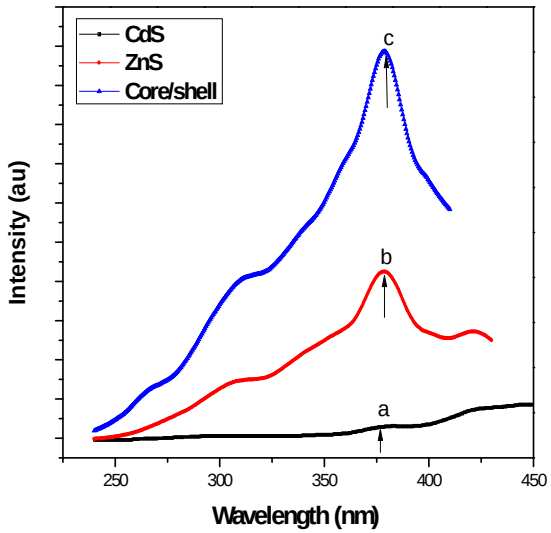
Table 2: Band gap increment in CdS, ZnS, CdS/ZnS quantum dots due to quantum confinement.

Sample	Absorption edge	Original Band gap in eV	Band gap in eV	Increment in band gap eV
CdS Poly	508	2.44	-	
ZnS Poly	302	4.10	-	
CdS Nano	265	2.44	4.7	2.3
ZnS Nano	242	4.10	5.1	1.0
CdS/ZnS Nano	214	-	5.8	

3.3. Photo Luminescence

The room–temperature photoluminescence spectra of as-prepared CdS, ZnS, CdS/ZnS quantum dots were shown in figure 6 (a, b and c). All the samples were excited at 220 nm. The obtained results show that the 2- Mercaptoethenol having an excellent capping efficiency because dangling bonds are effectively passivated in Cds and ZnS samples. The emission spectra of ZnS QDs (fig 6b) is having comparatively 10 fold enhancement from CdS (fig 6a) 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 5 shows the schematic diagram for CdS/ZnS core/shell structure.



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

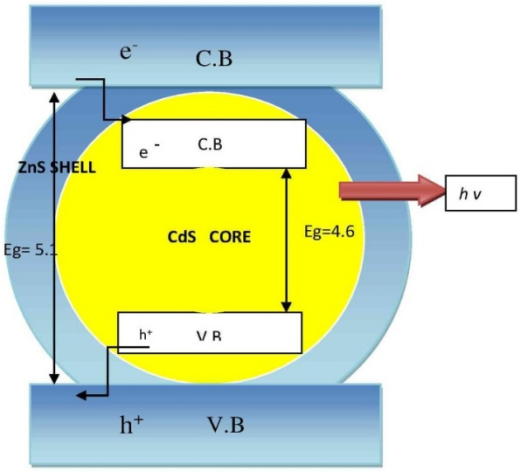


Figure 5. Schematic diagram of Core/Shell structure.

3.4. FTIR analysis:

2-mercaptoethanol capped CdS, ZnS, CdS/ZnS quantum dots were examined by recording their FTIR spectra in the range 4500–100 cm^{-1} (Fig. 6). The broad peak at 2120, 1383 cm^{-1} and the weak peak at 1614 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 cm^{-1} corresponds to (O-H) alcohols and 1119 cm^{-1} shows (C-N) amines along with two small peaks at 1626 cm^{-1} for (N-H) amines and 1401 cm^{-1} for O-H means carboxylic acid in ZnS samples, similar peaks occured 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.

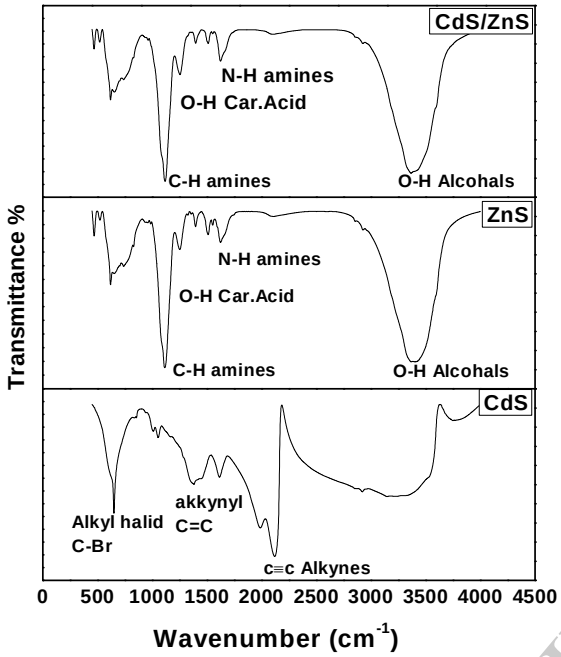


Figure.6. FTIR spectra of Capped CdS, ZnS, CdS/ZnS quantum dots with their functional groups.

3.5. Transmission electron microscopy

Transmission electron microscopy has been performed to ensure about the particle size and to check the effectiveness of cappent and the result for CdS QDs is presented in figure 7. TEM image of the CdS QDs shows highly monodispersed nanoparticles with average sizes of 4–5 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.

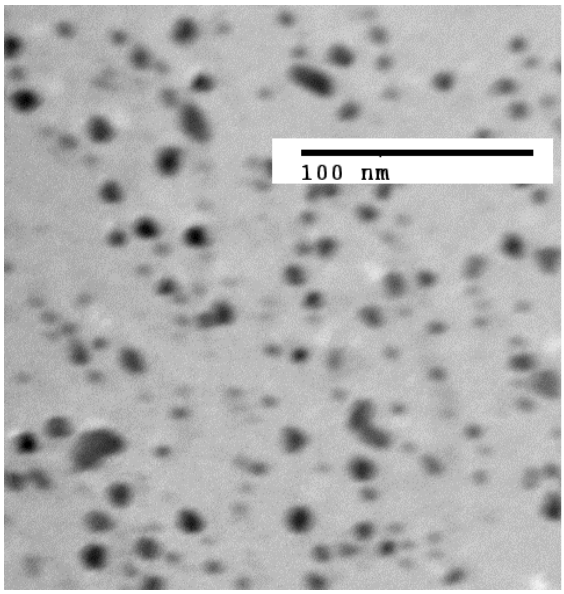


Figure 7. TEM image of Capped CdS QD's.

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 XRDn 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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