Synthesis, structural and optical characterisation of cadmium sulphide nanoparticles

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Cadmium sulphide nanoparticles of uniform size have been synthesized at room temperature via wet chemical precipitation method using cadmium chloride and sodium sulphide with methanol as capping agent. The microstructure and morphology of the synthesized CdS nanoparticles have been characterized by X-ray diffraction and scanning electron microscopy analysis. XRD pattern reveals that as-synthesized CdS nanoparticles exhibit both sphalerite and wurtzite phases. The size of the particles calculated by Debye Scherrer formula according to the XRD spectra has been found to be about 13-17 nm. X-ray peak broadening analysis has been used to calculate the crystalline size and lattice strain by the Williamson-Hall (W-H) plot. The optical properties of the sample have been studied by UV-Visible and photoluminescence spectroscopy. The existence of blue shift in UV-visible spectroscopy reveals the quantum confinement effect of CdS nanoparticles. The photoluminescence spectrum shows two broad bands centered at 422 and 538 nm.

Keywords: CdS nanoparticles, X-ray diffraction, Optical properties, HRSEM, Quantum confinement, Microstrain

1 Introduction
Recent investigations in nanotechnology reveal that nanometer-sized inorganic semiconductor compounds have attracted considerable attention due to their novel size-dependent characteristics, different physico-chemical and optoelectronic properties, compared with the corresponding bulk counterparts1-3. These classes of nanoparticles exhibit the size dependant properties such as blue shift of absorption onset, change of electrochemical potential of band edge and enhancement of photo catalytic activities4. Semiconductor nanocrystals displaying interesting electronic and optical properties have attributed to the quantum confinement effect and the large surface to volume ratio of atoms are having both the fundamental and technological interest. In particular chalcogenides such as CdS, with a direct band gap of 2.43 eV at room temperature, is one of the most important semiconductor and has given considerable attention by the researchers and scientist for potential applications in the future opto-electronic, nanodevices and biological labeling due to the tunable electronic band gap depending on the size and shape of nanocrystals. A great interest has been shown in cadmium sulphide (CdS) because of the availability of discrete energy levels, tunable bandgap, size dependant optical properties and well developed synthetic protocols, good chemical stability and easy preparation techniques5. Hence, the major thrust is concentrated towards the technological applications of CdS nanoparticles, ranging from microelectronics to non-linear optics, optoelectronics, catalysis, optical windows for solar cell and photo-electrochemistry6-12.

Currently there has been an increasing demand to explore the optoelectronic applications of CdS semiconductor in the frontier areas such as photo-electrocatalysis, biotechnology and communication among which the optoelectronic properties of CdS nanomaterials are strongly influenced by their morphologies and structures. Hence, it is very important to establish the simple and mild methods to achieve the controlled synthesis of isolated inorganic semiconductor nanostructures belonging to this category. Cadmium sulphide is a well-known semiconductor that can be prepared either by chemical or physical methods. Several methods have been developed to synthesize CdS in nanophase with different morphologies and structures such as nanocrystals, quasi-nanospheres, nanorods, nanowhiskers, nanowires, nanobelts and nanotubes etc13,14. In the present work, a simple aqueous chemical method for the preparation of cadmium sulphide nanoparticles with comparable size is reported and fine nanoparticles of very low size
distribution is obtained successfully. The synthesized CdS nanoparticles were characterized by X-ray diffraction (XRD), high resolution scanning electron microscopy (HRSEM) analysis, UV-visible spectra and photoluminescence study. The size of the as-prepared sample was calculated by Debye-Scherrer formula from the XRD spectra which was found to be of the order of 13-17 nm.

2 Experimental Details

2.1 Synthesis
CdS nanoparticles were synthesized by wet chemical method at room temperature using analar grade sodium sulphide, \( \text{Na}_2\text{S.9H}_2\text{O} \) as the source for \( \text{S}^2- \) ions and cadmium chloride as the source for \( \text{Cd}^{2+} \) ions with methanol as the capping agent.

In the synthesis procedure, 0.1 M of \( \text{NaOH} \) was prepared in 20 ml of deionised water and this solution was slowly added to 2.5 ml of methanol which acted as a capping agent. The prepared solution was then placed in ultrasonication bath for 1 h and the freshly prepared solution of \( \text{Na}_2\text{S} \) was mixed drop by drop into the above solution using vigorous stirring. In the resulting solution, 0.1 M of \( \text{CdCl}_2 \) was added by continuous stirring, which gave a yellowish solution. The selective precipitation of the final solution was carried out using acetone as non-solvent and centrifuged. The precipitate collected from centrifugation was dried at 60\(^\circ\)C for few hours to obtain the powdered CdS nanoparticles of fine size. The dried CdS nanopowder was subjected to the characterization of XRD, HRSEM, UV-visible spectra and photoluminescence studies.

2.2 Physical measurements
The X-ray diffraction (XRD) patterns for cadmium sulphide samples were recorded on a Schimadzu Labx X-ray powder diffractometer with \( \text{CuK}\alpha \) radiation (\( \lambda =1.5406\text{Å} \)) with 20 ranging from 10\(^\circ\) to 90\(^\circ\) at the scanning speed of 10\(^\circ\) per minute. The surface morphology of the CdS nanoparticles was analyzed using SEM images using a FEI Quanta FEG 200-High resolution scanning electron microscope operating at 30 kV. The optoelectronic properties have been studied by ultraviolet-visible absorption spectra in the range 200-1000 nm using VARIAN CARRY 5E Model spectrophotometer and LS 55 Perkin Elmer spectrophotometer was used for recording the photoluminescence spectra of CdS nanoparticles with 310 nm as the excitation wavelength.

3 Results and Discussion

3.1 X-ray diffraction and structure determination
The powder X-ray diffraction (XRD) pattern recorded for the as-prepared CdS nanoparticles is shown in Fig. 1. In general, XRD pattern provides the information about the crystalline phase of the nanoparticles as well as the crystallite size. The sharp and well defined intense peaks in the recorded pattern reveal the high orientation and confinement of the as-prepared CdS nanoparticles. The peaks at 20 values 24.1\(^\circ\), 28.6\(^\circ\) and 48.8\(^\circ\) corresponding to (100), (101) and (103) planes are well agreed with the hexagonal phase of CdS (JCPDS 80-006). Also the main peak at 30.36\(^\circ\) corresponds to (200) plane which is in agreement with the cubic phase of standard CdS (JCPDS 80-0019). CdS has been reported to exhibit both the hexagonal and cubic phases in the nanosize regime\(^{15-17} \). However, in many cases the exact phases could not be resolved due to the similarity of the cubic and hexagonal peaks and the broad peaks that appear confirm the existence of CdS in nano phase. The other intense diffraction peaks in the pattern may be arising from the impurity phases.

Experimental results also suggest that the broadening which occurs for the small crystallites differs from the broadening due to strain. Hence, from the XRD pattern, the full width half maximum (FWHM) can be expressed as a linear sum of FWHM of size, FWHM of strain and FWHM of instrumental\(^{18} \):

\[
\beta_{\text{tot}} = \beta_{\text{size}} + \beta_{\text{strain}} + \beta_{\text{instrumental}} \quad \ldots(1)
\]

Here the instrumental broadening \( \beta_{\text{inst}} \) was corrected corresponding to each diffraction peak and fitted with a Lorentzian profile.

![Fig. 1 — XRD pattern of CdS nanoparticles](image-url)
The grain size of the nanocrystalline CdS was calculated from the Scherrer’s equation as:

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  

where \( \lambda \) → Wavelength of copper K\( \alpha \) line (1.5406 Å).  
\( \theta \) → The angle between the incident beam and the reflection lattice planes.  
\( \beta \) → Full width half maximum of the peak.  
\( D \) → Average particle size (nm).

The average crystallite size as estimated from Eq. (2) was found to be about 13-17 nm. It is obvious that the size calculated out from XRD results is much smaller than those observed from SEM images. The exact reason is that the XRD method measures the property of the crystalline grains and not the size of the aggregated particles.

Generally, local distortion of the lattice generates strain in the lattice and its contribution to peak broadening is known as strain broadening. By considering the strain to be uniform in all crystallographic directions and the isotropic nature of the crystal, the strain broadening can be written as:

\[ \varepsilon = \frac{\beta_{\text{size}}}{4\tan \theta} \]  

Substituting the values for \( \beta_{\text{size}} \) and \( \beta_{\text{strain}} \) in Eq. (1)

\[ \beta_{\text{hkl}} = K \frac{\lambda}{D} \cos \theta + 4\varepsilon \tan \theta \]  

By rearranging Eq. (3), we get:

\[ \beta_{\text{hkl}} \cos \theta = K \frac{\lambda}{D} + 4\varepsilon \sin \theta \]  

where the microstrain parameter is \( \varepsilon = \Delta D_{\text{hkl}} / D_{\text{hkl}} \)

A graph drawn with 4\( \sin \theta \) along the X-axis and \( \beta_{\text{hkl}} \cos \theta \) along the Y-axis for the as-prepared CdS nanoparticles is shown in Fig. 2. From the linear fit to the data plot, the particle size has been estimated by the Y-intercept and the strain was calculated from the slope of the graph. It is observed that the particle size calculated from the Scherrer’s equation (13-17 nm) has closely agreed with the particle size estimated from the W-H plot (20 nm). The microstrain evaluated from the slope of the graph is found to be 0.00728. The less values of microstrain indicate strain free and narrow size of the nanoclusters.

3.2 High resolution scanning electron microscopy

The HRSEM images obtained for the CdS nanoparticles at higher magnification are shown in Fig. 3. It is observed that the images exhibit uniform orientation of the CdS nanoparticles without any inclusion. The images also confirm that the nanocluster consists of a high density of CdS nanoparticles with lengths varying from 500 nm to 1 \( \mu \)m with average particle size around 13-17 nm.

3.3 UV-visible spectroscopic analysis

The optical absorption spectrum of CdS nanoparticles recorded between 200 to 1000 nm is shown in Fig. 4.
It is observed from the spectrum that the absorption onset edge is found to be at the lower wavelength corresponding to 241 nm indicating the blue shift in absorption edge. The blue shift of light absorption confirms the quantum confinement effect in the prepared nanosample and is highly agreed with the result of direct band gap semiconductor nanocrystals reported for potential applications. The shift of the optical absorption towards lower wavelength also reveals the decreasing size of the nanoparticles. Owing to the direct band gap of the material, the absorption coefficient \( \alpha \) obeys the following relation for high photon energies \( h\nu \):

\[
\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} 
\]

where \( E_g \) is the optical band gap of the material and \( A \) is a constant of the material.

The plot showing the variation of \( (a\nu^2) \) versus \( h\nu \) is shown in Fig. 5. From the profile, the value of \( E_g \) is evaluated by the extrapolation of the linear part of the variation of \((a\nu^2)\) along \( Y \) axis. The band gap determined for the present investigation is found to be 4.17 eV. Comparing this with the band gap of bulk CdS reveals an enhancement of optical band gap around 1.64 eV, which clearly indicates the nanophase and quantized nature of the prepared CdS sample. As a consequence of wide band gap, the prepared CdS nanoparticles have large transmittance in the visible region which is an important parameter for extending the applications of CdS towards optoelectronic and semiconductor devices.

Also it is evident that for CdS like nanoparticles, the relation between the mean size of the grains and the onset absorption wavelength is related by Henglein’s empirical formula:

\[
2R_{CdS} (\text{nm}) = 0.1/0.1338 - 0.0002345\lambda_e \quad \cdots (6)
\]

where \( \lambda_e \) is the wavelength of absorption onset. The calculated size of CdS nanoparticles by Henglein’s formula is also closely agreed with the size calculated from the XRD pattern using Scherrer’s formula.

### 3.4 Photoluminescence spectral studies

Photoluminescence is a measure of photo absorption in direct band gap material, from which the light emission of the material of a particular wavelength can be determined. To investigate the luminescence property of the as-synthesized CdS nanoparticles, the PL spectra have been performed. The photoluminescence spectrum recorded in the wavelength range 200-800 nm is shown in Fig. 6. It is observed that the photoluminescence spectrum consists of two broad bands centered at 422 nm and 538 nm. Usually for semiconductor nanocrystals, two emission peaks can be observed due to the exciton and the trapped luminescence, among which the exciton emission peak is sharp and the trapped emission is broad.

The green emission band at 538 nm was associated with the emission due to electronic transition from the conduction band to an acceptor level due to interstitial sulphur ions \( (I_s) \). However,
the blue emission in the spectrum confirms the blue shift towards the absorption edge.

4 Conclusions

Good quality CdS nanoparticles of size ranging from 13-17 nm have been successfully synthesized by chemical precipitation method followed by heat treatment. The prepared CdS nanoparticles have been characterized by XRD, HRSEM, UV-visible spectra and photoluminescence studies. XRD pattern of the CdS nanoparticles reveals the presence of both cubic and hexagonal phases. The size of the CdS nanoparticles estimated from the W-H analysis and Henglein’s empirical formula are found to be in good agreement with that of the average particle size calculated from the Scherrer’s equation. SEM micrographs show uniform orientation of low dimensional CdS nanoclusters without any inclusion. The UV-visible absorption spectrum reveals the blue shift in absorption edge and the high quantum confinement of nanoparticles. The PL spectrum of CdS nanoparticles confirms the blue shift of wavelength, the present exciton and trapped luminescence. The shift of wavelength from violet to yellow in the higher photonic region of PL spectrum reveals that CdS nanomaterial can be used as a blue laser for tunable frequencies. Owing to the uniform orientation of nanoclusters with high optical properties the prepared CdS nanoparticles by wet chemical method can be effectively used for potential applications towards optoelectronics and semiconductor devices.

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