



Microstructure analysis of chemically synthesized wurtzite-type CdS nanocrystals

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Abstract. Microstructure of chemically synthesized wurtzite-type CdS nanocrystals have been investigated by X-ray diffraction (XRD) peak profile analysis by applying different forms of Williamson–Hall (WH) method viz., uniform deformation model (UDM), uniform stress deformation model (USDM) and uniform deformation energy density model (UEDDM), and transmission electron microscope (TEM) observations. The WH methods show the average crystallite size to be about 10 nm. Strain, stress and energy density of the nanocrystals are found to be 1.18×10^{-2} , 0.43 GPa and 2.27 kJ m^{-3} , respectively. High-resolution TEM (HRTEM) results show the nanocrystals to be in spherical shape with an average crystallite size of 10 nm, thereby complementing the size estimation by WH methods. Further, HRTEM observations reveal the presence of edge dislocations and twin boundaries within the nanocrystals.

Keywords. Nanocrystals; chemical synthesis; X-ray scattering; crystal structure.

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1. Introduction

CdS is a group II–VI semiconductor with a direct band gap of 2.42 eV and is a promising material for application in optoelectronic devices in its nanocrystalline form [1–3]. CdS generally occurs in cubic (sphalerite), hexagonal (wurtzite), or their mixed crystalline phases at room temperature [4–9]. Transformation from hexagonal to cubic as well as from cubic to hexagonal structures can occur by applying suitable temperature and pressure [10–12]. Properties of CdS have been reported to depend on the crystal structure i.e., whether it is cubic, hexagonal or a mixture of both. Wei *et al* studied the structure stability and carrier localization of CdS in both cubic and hexagonal structures by band-structure calculation, where they found that the band gap and valence band maximum of hexagonal CdS are more than those of cubic CdS, which can significantly affect the transport properties of the device in a mixed cubic/hexagonal system [13]. Hexagonal CdS nanoparticles have much better photocatalytic activity for degradation of methylene blue [14] and better

hydrogen production activity for water photolysis [15] compared to cubic one. On the other hand, Y Yu *et al* reported that cubic CdS has a better photocatalytic activity for degradation of rhodamine B as compared to hexagonal and mixed cubic–hexagonal phases [16]. Therefore, controlled synthesis of CdS nanocrystals in cubic and hexagonal structures is very important.

A perfect crystal would extend to infinity if periodicity of arrangement of atoms is maintained exactly everywhere. However, real crystals are not perfect because of their finite size and presence of strain. Generally, materials with crystallite size in the range 1–100 nm are known as nanocrystalline (NC) materials. When crystallite sizes of materials are in the nanoregime, their properties are different/modified. For example, when crystallite sizes of semiconductors become comparable or smaller than their exciton Bohr radius, which are usually a few nanometres, their optical properties become size-dependent [17]. Further, NC materials are characterized by the presence of large volume fraction of atoms in the grain boundaries and contain more lattice strain as compared to their coarse-grained counterparts [18]. Other than structure and size of the nanocrystals, lattice strain plays an important role in determining their properties. Optical and electronic properties of semiconductor nanocrystals can be tuned by lattice strain [19,20], and catalytic properties of Pd nanocrystals can be changed by strain [21]. In order to understand the various physical, chemical or mechanical properties of nanocrystals, different structural aspects must be considered and therefore proper estimation of structural parameters such as crystallite size, lattice strain, stress, energy density etc. are important. In recent years, considerable amount of research work has been reported on the structural properties of semiconductor nanocrystals like ZnO [22–24], ZnS [25], PbS [26], Si [27], NiO [28] etc. However, a detailed analysis of the structural properties of CdS nanocrystals, especially in hexagonal form, is lacking in the literature.

In the present work, CdS nanocrystals of hexagonal (wurtzite) crystal structure have been synthesized by room-temperature coprecipitation process. Literature survey reveals that suitable concentration of polyvinyl alcohol (PVA) can be used as a capping agent for obtaining hexagonal phase of CdS [29]. Hence, PVA is chosen as capping agent and the molarity of the precursors of Cd and S ions, concentration of PVA and pH of the solution are optimized for obtaining hexagonal phase of CdS. The microstructural properties of the as-synthesized hexagonal CdS nanocrystals are investigated by XRD peak profile analysis by applying different forms of WH method viz., UDM, USDM, UEDM, and TEM observations, and are reported here.

2. Experimental details

Required amount of cadmium chloride and thiourea with a molarity ratio 1 : 1 and 2% polyvinyl alcohol are dissolved in 10 ml triple distilled water separately. The solutions are mixed together and ammonium hydroxide solution is added drop by drop until the pH of the solution becomes 11. The resulting solution is kept at room temperature for 24 h and then the precipitates are filtered, washed in triple distilled water and then allowed to dry for a few days. The powders are characterized by X-ray diffractometer (D8 Advance, Bruker AXS) with CuK_α radiation and transmission electron microscope (JEM-2100, Jeol).

3. Results and discussion

3.1 XRD results and analysis

Figure 1 shows the XRD pattern of CdS nanocrystals, which is found to be in good agreement with the standard pattern of bulk CdS with hexagonal (wurtzite) crystal structure (JCPDS data file: 80-0006). The diffraction peaks are broad, indicating the formation of crystals with small crystallite size having lattice strain. Another important feature of the XRD pattern is that the (1 0 0), (0 0 2) and (1 0 1) diffraction peaks are superimposed and they have to be separated for X-ray peak profile analysis. These peaks are decomposed to individual peaks by considering Lorentzian distribution for each component peak and then by using Levenberg–Marquardt algorithm [30]. The same procedure is also applied for finding the individual contribution of the (1 1 0), (1 0 3) and (1 1 2) peaks. The decomposed peaks along with the overall fit for the (1 0 0), (0 0 2), (1 0 1), (1 1 0), (1 0 3) and (1 1 2) peaks are presented in figure 2. The (1 0 2) peak has not been considered for analysis because of its very low intensity.

Crystallite size, strain and instrumental factors contribute towards the broadening of X-ray peak profiles. Instrumental factor eliminated peak profiles can be analysed to obtain various structural parameters. If the strain contribution is neglected, the crystallite size can be estimated using the Scherrer formula [31]

$$D = \frac{0.9\lambda}{\beta \cos \theta}, \quad (1)$$

where β is the FWHM of the diffraction peaks, θ is the Bragg angle and λ is the wavelength of Cu K $_{\alpha}$ radiation (0.15406 nm). The average crystallite sizes as estimated by

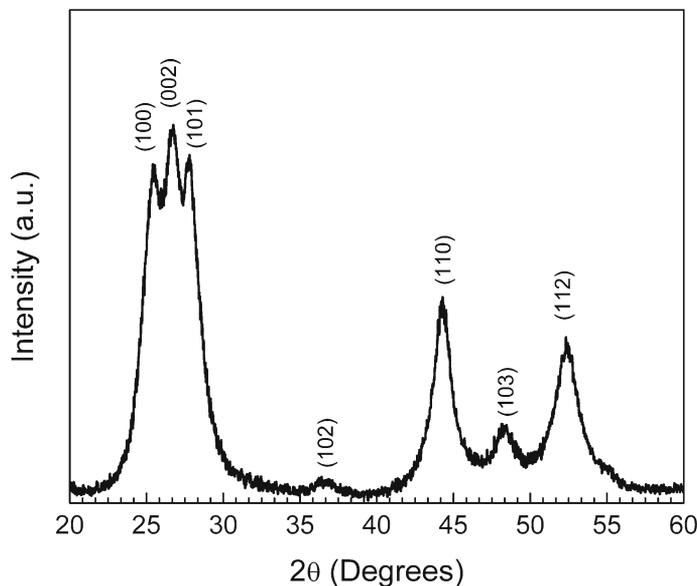


Figure 1. XRD pattern of CdS nanocrystals.

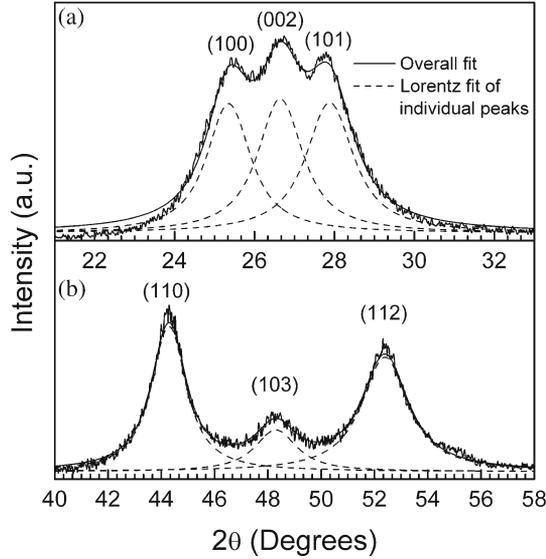


Figure 2. Decomposed XRD peaks of CdS nanocrystals.

Scherrer formula for (1 0 0), (0 0 2), (1 0 1), (1 1 0), (1 0 3) and (1 1 2) peaks are found to be 12, 13, 10, 11, 9 and 11 nm respectively. If the contribution of strain is taken into account and considering strain to be uniform in all crystallographic directions, the classical Williamson–Hall (WH) equation takes the form [22–24,32]

$$\beta \cos \theta = \frac{0.9\lambda}{D} + 4e \sin \theta, \quad (2)$$

where e is the strain. This method of calculation of crystallite size and strain is also known as uniform deformation model (UDM) form of WH method [22]. All the X-ray diffraction peaks in figure 2 are used to construct a plot between $\beta \cos \theta$ and $4 \sin \theta$ (presented in figure 3). The crystallite size and strain calculated from the intercept and the slope are found to be 10 nm and 1.18×10^{-2} respectively. WH method can be modified by considering induced stress to be uniform in all crystallographic directions, known as uniform stress deformation model (USDM) as [22–24]

$$\beta \cos \theta = \frac{0.9\lambda}{D} + \frac{4 \sin \theta \sigma}{E_{hkl}}, \quad (3)$$

where σ is the stress and E_{hkl} is the Young’s modulus. E_{hkl} is related to their elastic compliances s_{ij} for hexagonal crystals as [22]

$$E_{hkl} = \frac{\left[h^2 + \frac{(h+2k)^2}{3} + \left(\frac{a}{c}l\right)^2 \right]^2}{s_{11} \left[h^2 + \frac{(h+2k)^2}{3} \right]^2 + s_{33} \left(\frac{a}{c}l\right)^4 + (2s_{13} + s_{44}) \left\{ h^2 + \frac{(h+2k)^2}{3} \right\} \left(\frac{a}{c}l\right)^2}. \quad (4)$$

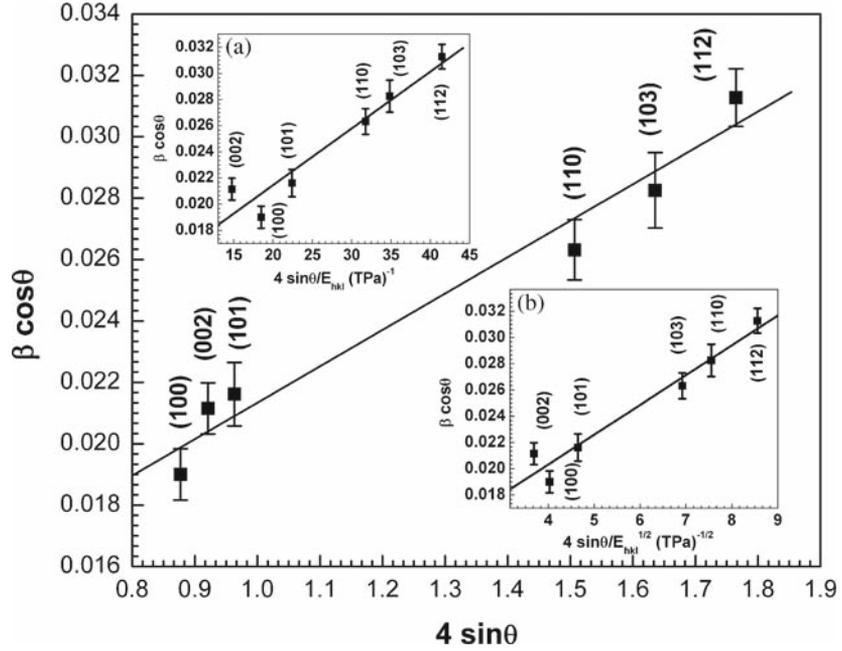


Figure 3. WH plot for CdS nanocrystals, UDM, inset (a) modified form of WH plot, USDM, inset (b) modified form of WH plot, UEDM.

Again S_{ij} is related to elastic stiffness constants c_{ij} as [33]

$$s_{11} = \frac{c_{11}c_{33} - c_{13}^2}{(c_{11} - c_{12})(c_{11}c_{33} + c_{12}c_{33} - 2c_{13}^2)} \quad (5)$$

$$s_{12} = \frac{c_{13}^2 - c_{12}c_{33}}{(c_{11} - c_{12})(c_{11}c_{33} + c_{12}c_{33} - 2c_{13}^2)} \quad (6)$$

$$s_{13} = \frac{-c_{13}}{c_{11}c_{33} + c_{12}c_{33} - 2c_{13}^2} \quad (7)$$

$$s_{33} = \frac{c_{11} + c_{12}}{c_{11}c_{33} + c_{12}c_{33} - 2c_{13}^2} \quad (8)$$

$$s_{44} = \frac{1}{c_{44}}. \quad (9)$$

The c_{ij} values of CdS hexagonal crystals are $c_{11} = 84.32$, $c_{12} = 52.12$, $c_{13} = 46.38$, $c_{33} = 93.97$, $c_{44} = 14.89$ in the unit of 10^9 Nm^{-2} [34]. The elastic compliances are calculated using eqs (5)–(9) and are found to be $s_{11} = 2.108$, $s_{12} = -1.001$, $s_{13} = -0.544$, $s_{33} = 1.602$, $s_{44} = 6.716$ in unit of $10^{-11} \text{ m}^2 \text{ N}^{-1}$. The lattice parameters a and c and thereby a/c of CdS nanocrystals are calculated from the (1 0 0) and (0 0 2) peaks and

Table 1. Young's modulus of bulk and nanocrystals of CdS.

Crystallographic direction	Young's modulus (GPa)	
	Bulk CdS (wurtzite)	CdS nanocrystal (wurtzite)
(1 0 0)	47.44	47.44
(0 0 2)	62.42	62.42
(1 0 1)	42.98	43.04
(1 0 2)	43.18	43.08
(1 1 0)	47.44	47.44
(1 0 3)	46.93	46.71
(1 1 2)	42.53	42.58

are found to be 0.4016 nm, 0.6635 nm and 0.6053 respectively. Lattice parameters a , c and a/c of bulk CdS are 0.4121 nm, 0.6682 nm and 0.6167 respectively (JCPDS data file: 80-0006). Thus, the a/c ratio of CdS nanocrystals is slightly low as compared to its bulk form. The Young's modulus along different crystallographic directions of CdS in both nanocrystal and bulk form are calculated from eq. (4) using the elastic compliances and the a/c ratio, and are presented in table 1. Young's modulus is found to differ slightly in the CdS nanocrystals as compared to bulk in certain crystallographic directions which arises because of the changed a/c ratio. A plot is constructed using eq. (3) and is presented in the inset of figure 3. The crystallite size and stress are calculated from the plot and are found to be 11 nm and 0.43 GPa, respectively. There are reports on the formation of CdS nanocrystals of pure hexagonal phase at a high pressure of 1 GPa [5]. Therefore, high internal stress of 0.43 GPa in the presently investigated CdS may be related to the observed hexagonal phase. Another modified form of WH method known as uniform deformation energy density model (UDEDM) takes into account the influence of stress energy on diffraction peaks and can be expressed as [22–24]

$$\beta \cos \theta = \frac{0.9\lambda}{D} + 4 \sin \theta \left(\frac{2u}{E_{hkl}} \right)^{1/2}, \quad (10)$$

where u is the energy density. A plot is constructed according to eq. (10) and is presented in the inset of figure 3. The crystallite size and energy density are calculated and are found to be 11 nm and 2.27 kJ m^{-3} respectively. Thus, the average crystallite size of about 10 nm is shown by the different forms of WH method. Further, it is interesting to note that all the different forms of WH method show a linear behaviour as presented in figure 3 which indicates that strain, stress and energy density uniformly influence the crystals in different crystallographic directions in the presently investigated CdS nanocrystals.

3.2 TEM results and analysis

In order to further investigate the microstructural properties, TEM characterization is carried out on the CdS nanocrystals. Figure 4a shows the TEM micrograph, while figures 4b and 4c show the HRTEM micrographs of the nanocrystals. TEM micrograph shows agglomerated nanocrystals typical of polycrystalline materials. Nanocrystals of about 10 nm size having nearly spherical shape can be clearly seen from the HRTEM micrographs. One

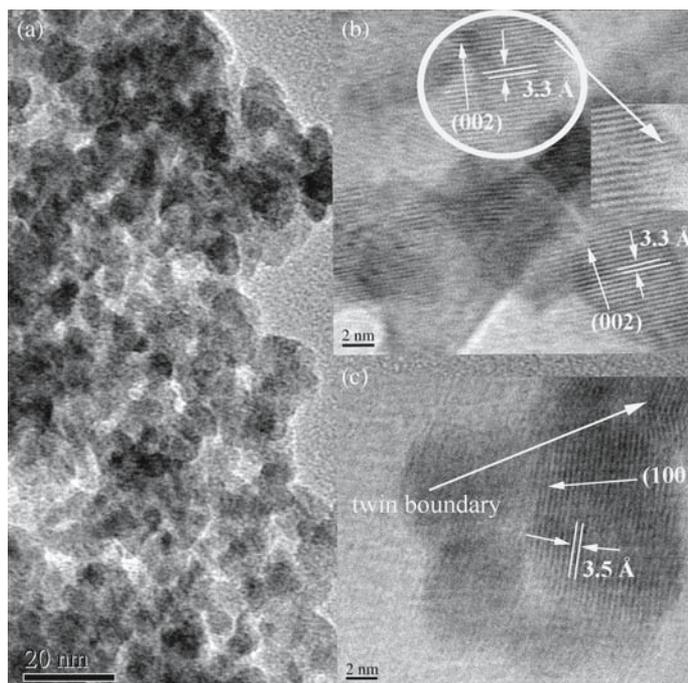


Figure 4. (a) TEM micrograph, (b) & (c) HRTEM micrographs of CdS nanocrystals.

such crystallite is shown encircled in figure 4b. HRTEM observations validate size estimation by XRD analysis by applying the WH methods. The interplanar spacings of the crystal planes which can be seen in the micrographs are evaluated. From the interplanar spacings, the crystal planes are identified and indicated in the figure. A small portion of the encircled area of figure 4b presented in magnified form shows a pure edge dislocation. A twin boundary can also be seen within the nanocrystals as shown in figure 4c. TEM observations not only complement the XRD results but also give more information on the presence of edge dislocation and twin boundary in the presently investigated CdS nanocrystals.

4. Conclusions

CdS nanocrystals of about 10 nm crystallite size having hexagonal (wurtzite) crystal structure have been synthesized by coprecipitation process. The microstructural properties are investigated by X-ray peak profile analysis, applying different forms of WH method viz. UDM, USDM and UDEDM, and TEM observations. Different forms of WH method show average crystallite size to be about 10 nm which is complemented by HRTEM observation. Strain, stress and energy density are estimated and presented. Further, HRTEM observations reveal the presence of edge dislocations and twin boundaries within the nanocrystals.

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