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# Branch-Angle Variation of CdS Nanorods with Hydrothermal Temperature

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**Abstract:**
The physical properties of nanocrystals vary with its shape, size, morphology and crysttalinity. The shape, size and crysttalinity widely vary with the growth rate of the crystal. In this paper, branched CdS nanorods are synthesized by a hydrothermal process. The hydrothermal temperature ($T_H$) is varied keeping all other parameters such as amount of salts and the surfactant amount etc intact. Noticeable changes in the branch angle (the angle between the main trunk of the nanorod and its side growth) are observed with variation of the $T_H$. For relatively lower $T_H$, the angle is lesser and at the relatively higher $T_H$, the angle is larger. HR-TEM reveals a better cryttalinity for higher $T_H$. The UV-Vis. absorption spectra, FTIR, XRD and FE-SEM are used to characterize the as grown CdS samples.

## Introduction

Physical properties of nanostructured materials depends on their shape [1], size, crysttalinity [2], morphology [3] and present of any trace amount of impurities. Among them, shape of the nanocrystals plays an important role for subtle change of the physical properties of nanocrystals [4]. Among the various properties, optical property of the nanocrystals is affected most with variation in shape [5] and crysttanity [6]. Apart from optical property, catalytic activity [7], mechanical property [8], thermal property [9] and chemical reactivity [10] also depends on the shape and crysttalinity of the nanocrystals. Consequently, nanocrystals of various shape, size, morphology and crysttalinity are synthesized by using various processes in last two decades. Among the various morphologies, branched nanocrystals [11] are widely investigated till date. Metal nanocrystals with side branches show splitting of plasmon spectra [12] due to their high aspect ratio. Emission spectrum of semiconductor nanocrystals show variations due to presence of side growths [13]. Moreover, branched nanocrystals are also widely synthesized to study their crystal growth mechanism and study of defects introduced during their synthesis process. Sutripto Majumdar et all [14] synthesized semiconductor nanocrystals by using a solution based route and investigated their growth mechanism. Growth of silver nanowires with side branches is hydrothermally synthesized and their optical property is investigated by this author [15]. In this paper, CdS nanocrystals are synthesized by using a hydrothermal process, their plausible growth mechanism is discussed and optical property is investigated. The noticeable thing is the variation of branch angle with hydrothermal temperature ($T_H$).

## Experimental details

### Chemicals and Methods

All the chemicals were used as received i.e. without further purification. 1gm of PAM (MW>5,000,000, Poole, England) is mixed with 200mL of distilled water and stirred for nearly 15 min., kept for one week to get matured and used as stock solution. 0.65gm of thiourea ($CH_4N_2S$, Merck, Mumbai, India) and 0.85gm of cadmium sulfate ($CdSO_4$, Aldrich Chemicals Company, Milwaukee, USA) solutions are taken in a beaker. Required amount of stock solutions were added to the solution containing cadmium sulfate and thiourea. The mixture is stirred for 1 h. and transferred to a teflon lined stainless steel homemade autoclave and heated at $T_H$ for 2 h in a hot air oven after filing nearly 80% of its total volume by distilled water. The yellow solution after cooling the autoclave to room temperature is centrifuged and then dried at $100^0$C for 1 h in a vacuum oven and used for characterization.

### Instruments and Specifications

The optical, morphological and microstructural properties of the as synthesized samples are investigated in detail. The phase purity and crystallite structure of the samples were characterized by powder X-Ray Diffraction (XRD) with a Rigaku (Washington, USA) diffractometer. A small amount of the CdS samples is dispersed in water by ultrasonication to measure Photoluminescence (PL) emission spectra using Fluoromax 4 (Horiba Jobin Yvon, Kyoto, Japan) with excitation wavelength at 280nm. The morphology, size and crystal structure of the CdS samples are determined by Transmission Electron Microscope (TEM, JEM 2010) and Field Emission Scanning Electron Microscope (FESEM, JSM 6700F, Tokyo, Japan).

## Results and Discussion

**Figure 1(A)** shows the X-ray Diffraction (XRD) pattern of sample heated at $160^0$C. The diffraction pattern can be indexed to CdS (JCPDS file no. 42-1411). The gradual appearance of (102) and (103) planes at $36.76^0$ and $48.05^0$ (2θ) in XRD spectra is the indication of formation of CdS hexagonal wurtzite structures [16]. No characteristic peaks from impurities, such as elemental 'Cd' or other phase of CdS or oxides are detected. **Figure 1(B)** represents FTIR spectra of CdS and PAM. The peak at 1660cm$^{-1}$ is red shifted to 1640cm$^{-1}$ indicating presence of PAM on the surface of as grown nanocrystals [17]. The presence of PAM on the sample surface also confirms that the growth of CdS nanostructures is controlled by presence of PAM in the hydrosol.

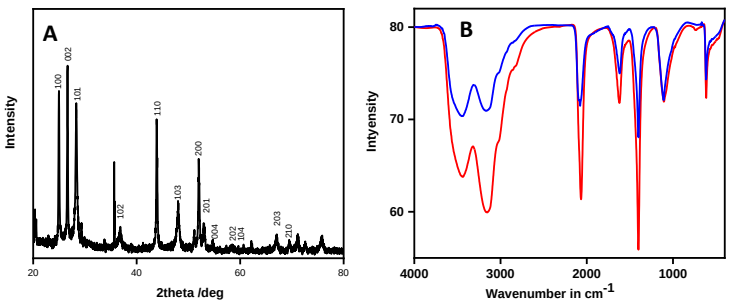


**Figure 1:** (A) XRD pattern of the CdS Nanorods (B) FTIR spectra of CdS @PAM

**Figure 2 (A)** absorption spectra shows weak peak at 380nm indicating formation of very small particles. However, if $T_H$ is increased; then the hump shifts to higher wavelengths due to formation of relatively larger size nanocrystals. The spectra becomes very broad and covers nearly all the regions due to formation of micron size nanocrystals as reported earlier by Mahdi et al [18]. **Figure 2 (B)** shows Photoluminescence (PL) spectra of CdS heated at different $T_H$. The PL spectra of the CdS sample heated at $160^0$C shows a high energy sharp emission peak at 424nm. However, if $T_H$ is increased to $180^0$C, another broad low energy peak arises at 550nm indicating presence of different surface states. The two peaks at 424nm (2.9eV) and 550nm (2.25eV) are assigned to band edge and deep trap emission respectively [19]. The position of band edge emission totally depends on the particles size and the peak at 424nm indicates that at $180^0$C, the nucleation centers grow in size to form quantum dots of CdS, which originates this band emission at 424nm and is blue shifted compared to its bulk (2.42eV) counterpart due to quantum confinement [20]. However, with increasing $T_H$ these quantum dots gradually grow in relatively large structures which contain 'S' defects at the surface resulting the second peak at 550nm [21]. It is seen that at higher $T_H$ the intensity of the second peak increases at the expense of the first peak.

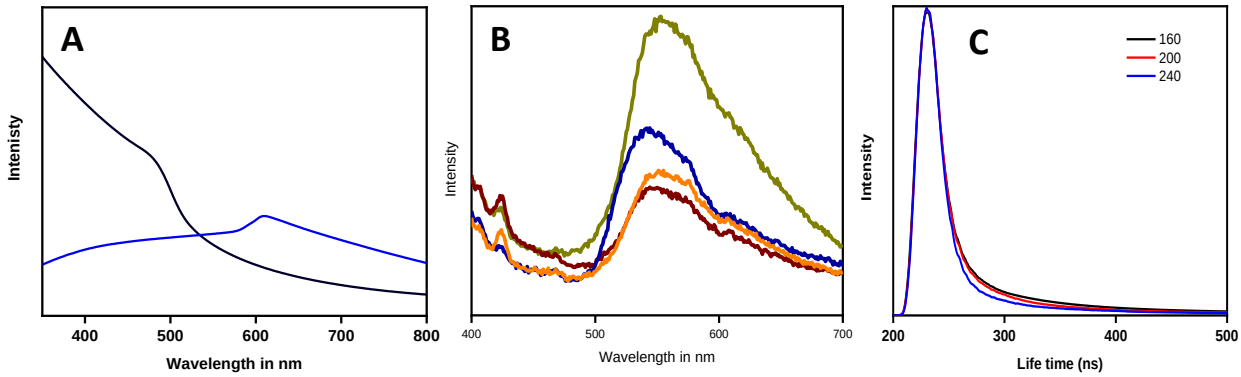


**Figure 2:** (A) Absorption spectra of CdS (B) Emission spectra of CdS (C) TCSPC of the CdS nanorods

$240^0$C, the band to band emission nearly disappears and intensity of the second peak increases to the highest value indicating formation of maximum surface defects. The increase in defect states with $T_H$ is calculated from the TCSPC as shown in **Figure 2(c)**. This indicates that at this temperature the growth process is completed and the PL peak is dominated mainly by the 'S' defects, which will be understood clearly during discussion of the growth mechanism of CdS nanostructures. Apart from increase in intensity a small red shift of the deep trap emission (~19nm) is also noticed which is due to interaction of PAM with CdS nanocrystals.

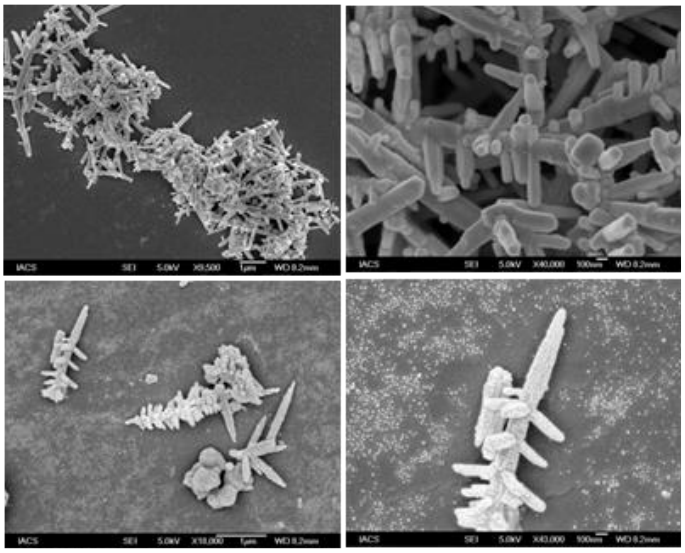

**Figure 3:** (A), (B), (C) & (D) FE-SEM images of the CdS nanorods with branch at different $T_H$

To investigate the variation of the CdS tip angle with hydrothermal temperature ($T_H$) four samples are fabricated with $T_H$ $180^0$C (S1), $200^0$C (S2), $220^0$C (S3) and $240^0$C (S3). FESEM images in **Figures 3(A), (B), (C)** and **(D)** shows the CdS nanorods with nanotips. Tip angles for the samples S1, S2, S3 and S4 is $60^0$, $66^0$, $70^0$ and $78^0$ respectively. The gradual increase of the tip angle is clearly seen. However, increase of the tip angle is assigned to higher rate of growth at relatively higher $T_H$. At relatively lower $T_H$, the growth rate being slow, crystals tend to grow spherical which is favorable shape due to its minimum surface energy [22]. But, as the $T_H$, increased the PAM in the solvent releases larger amount of ammonia gas increasing the inside pressure of the container. At this high temperature and pressure nanocrystals grow fast [23]. This fast growth of nanocrystals leads to increased tip angle.

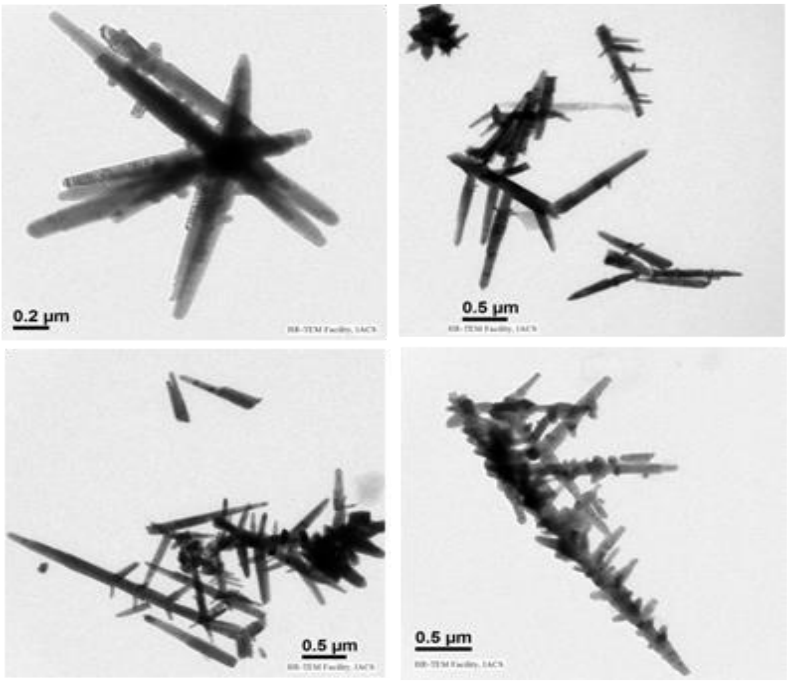


**Figure 4:** (A), (B), (C) & (D) TEM images of the CdS nanorods at different $T_H$

**Figure 4 (A), (B), (C)** and **(D)** demonstrates the TEM images of S1, S2, S3 and S4 respectively. From, HRTEM image it is clearly visible that the samples are single crysttaline in nature and the variation of tip angle with $T_H$ is prominent. HR-TEM images of the samples S1, S2, S3 and S4 are shown in the **Figure 5 (A), (B), (C) and (D)** respectively.

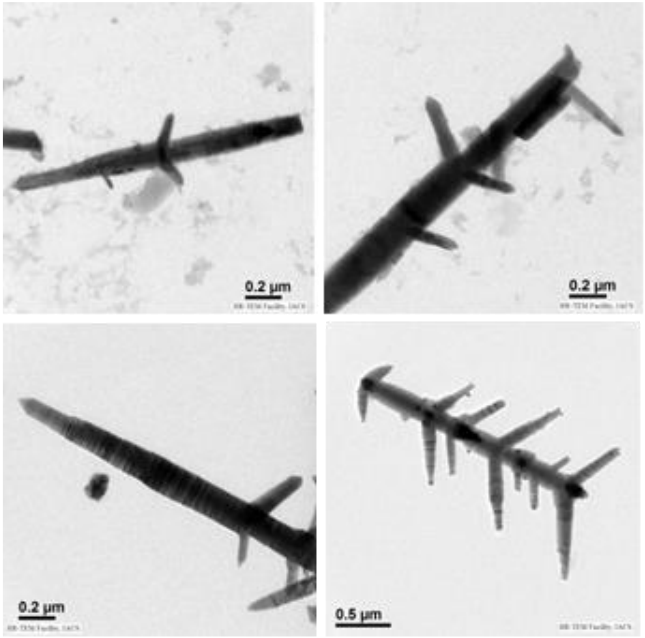


**Figure 5:** (A), (B), (C) & (D) HR-TEM images showing the branch angle clearly

## Conclusion

The variation of branch angle of the CdS nanorods suggests that the branch angle increases with increases of $T_H$. At higher $T_H$, the solubility of the salts is increased and faster mass transfer happens due to higher motion of the liquid inside the container. Consequently, some specific crystal planes get favors at this relatively higher thermo dynamical conditions and the planes begins to growth in that particular direction forming nanords with side growths. The defects on the naorods acts as nascent nucleation centers and the branches start to grow.

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