

Controlling crystal growth orientation and crystallinity of cadmium sulfide nanocrystals in aqueous phase by using cationic surfactant†

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Dispersed CdS single crystals were obtained *via* a hydrothermal method by using cetyltrimethylammonium bromide (CTAB) as a surfactant. The strong interaction between the cationic head group of CTAB and the (001) plane of CdS hexagonal crystals results in a single-crystalline growth along the [100] direction.

In recent years, semiconductor nanocrystals have attracted much attention due to their many potential applications. The formation of nanocrystals with controlled size, shape, and crystallinity is very important in various applications. As one of the most important II–VI semiconductors, cadmium sulfide with band gap energy of 2.42 eV in the visible region has been widely used for photoelectric conversion solar cells, photocatalysts, light emitting diodes, and thin film transistors.^{1–5}

Various methods have been reported for the synthesis of CdS in the nanoscale such as chemical vapor deposition process, thermal decomposition, solvothermal and hydrothermal process.^{6–9} These studies showed the efforts to control crystallinity, size and morphology of CdS nanocrystals with all kinds of shapes including rods, tetrapods, hexagons, cubes and pyramids. For example, Kar *et al.* obtained CdS nanoribbons through the vapor transport method.¹⁰ Regev's group synthesized CdS nanowires using mesoporous silica as a template.¹¹ Qingqing *et al.* reported on synthesis of dendritic CdS nanocrystals by hydrothermal treatment.¹² However, these studies mostly reported on the aggregated form of CdS crystals. It is well known that controlling of size, morphology and crystalline structure of a material in nanoscale is very important in determining the physicochemical properties. To the best of our knowledge, it is difficult to synthesize CdS single nanocrystals with high dispersibility in water even when surfactants are used to decrease agglomeration. Most of the dispersed CdS single crystals are synthesized in diverse micelles, organic solvents or at severe conditions.^{13–15} Hence, the method producing dispersive and crystalline CdS single crystals in the aqueous phase would have important applications because it provides hydrophilic crystals and is environmentally friendly. In this paper, we report a facile method to synthesize high crystalline CdS nanocrystals with

the aid of CTAB molecules acting as a capping agent. The strong interaction of CTAB with other metal sulfides have been already reported in the literature, but few works studied cadmium sulfide.^{16–18} Here we present the effect of CTAB on the crystalline growth direction of CdS single crystals.

The CdS single-crystalline nanoparticles were synthesized by simply dissolving thioacetamide (TAA) in an aqueous solution of CdCl₂. The reaction solution was then treated under hydrothermal condition at 200 °C (experimental details are given in the ESI†). The crystalline structure of the as-synthesized products was characterized by X-ray diffraction (XRD). The XRD pattern of the product (Fig. 1a) matches well with the hexagonal CdS crystal structure (JPCDS, card no. PDF #01-080-0006 in blue colour). The scanning electron microscopy (SEM) (Fig. 1b) and transmission electron microscopy (TEM) (Fig. 1c) images reveal that the CdS nanocrystals are well dispersed with an average size of around 50 nm. High-resolution TEM images of CdS nanocrystals (Fig. 1d) were also taken which show {100} closed-pack planes of hexagonal structure with lattice spacing *d* of around 3.57 Å. Fig. 2 presents high-resolution TEM images and respective fast Fourier transform

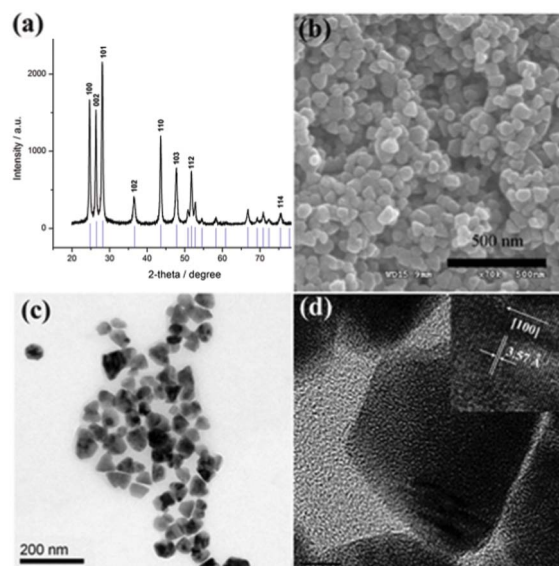


Fig. 1 (a) XRD pattern, (b) SEM image, (c) TEM image and (d) HR-TEM image of CdS sample prepared at 200 °C with CTAB.

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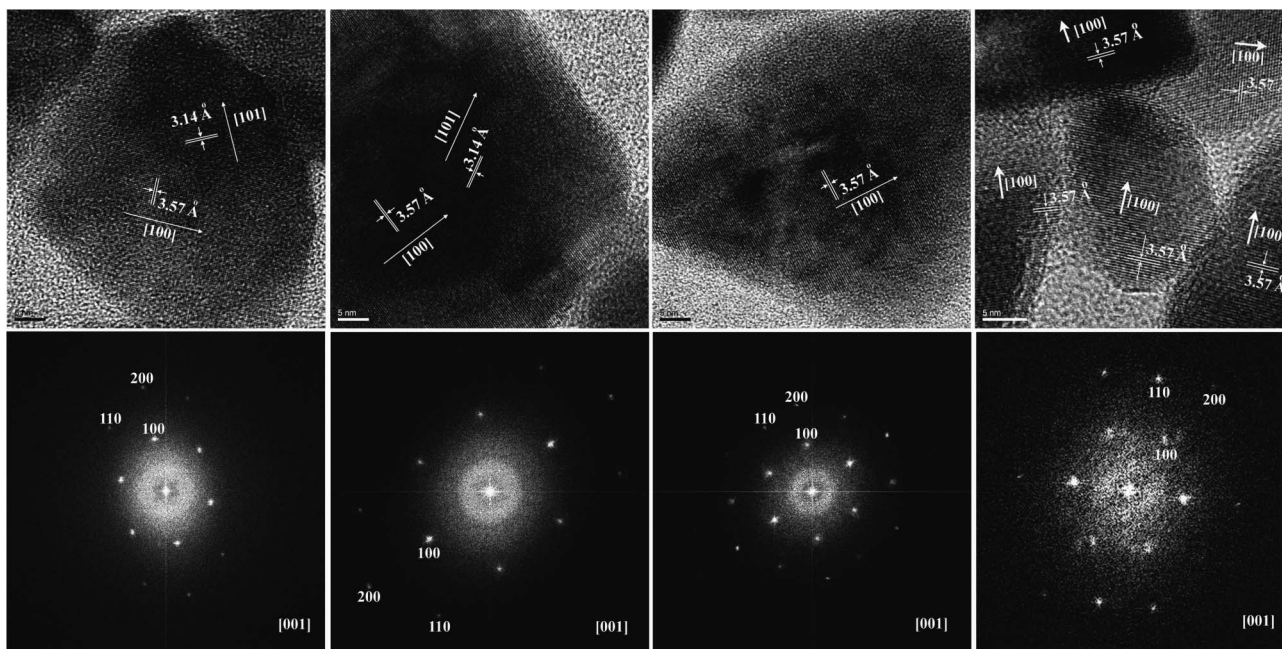


Fig. 2 High-resolution TEM images and FFT patterns of CdS particles prepared at 200 °C with CTAB.

(FFT) patterns (below) of randomly selected CdS nanocrystals prepared with CTAB. The FFT patterns are similar for all nanocrystals and well-defined spots are clearly observed. This confirms all that particles are single-crystalline. The spots matched well with the 100, 110, and 200 planes of the hexagonal CdS crystal structure.¹³ Both FFT patterns were taken along the [001] zone axis directions. This is the preferential alignment of the crystal axis as we can obtain similar FFT patterns from many other nanocrystals. Both particles have the {100} or {101} close-packed planes of hexagonal CdS structure. The hexagonal CdS unit cell is shown in Fig. 3. The {001} plane can be divided into two types: {001}_{Cd} planes which have positive charge with only Cd atoms and {001}_S planes which have negative charge with only S atoms. The {100} planes with both Cd and S atoms (1 : 1) are uncharged

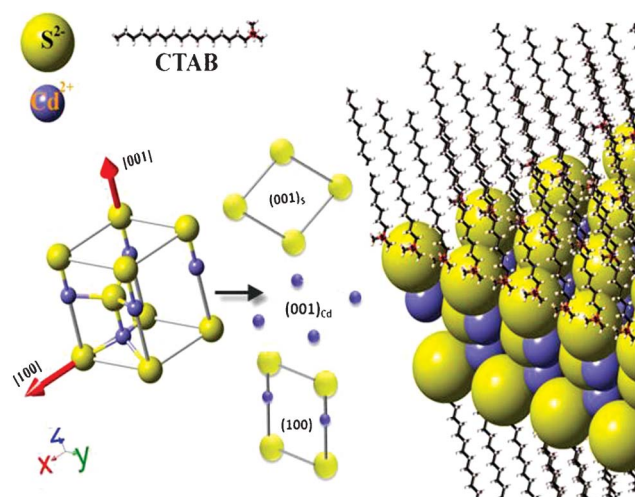


Fig. 3 Illustration of hexagonal CdS unit cell with the exposed (001)_S in the presence of CTAB.

facets. CTAB can selectively deactivate the {001} facets since its positively charged head groups can interact strongly with the negatively charged {001}_S facets rather than {100} facets. As a result, the preferable growth of the CdS crystal is dominant along the {100} direction forming 2D single crystals (as shown in Fig. 1d). Without CTAB, the growth of CdS crystals in arbitrary directions results in the formation of 3D structures. The important role of CTAB in the morphosynthesis is not only crystallographical controlling but also acting as a template to prevent the agglomeration. Fig. S1 (ESI†) shows the high-resolution TEM image of hexagonal primary crystal in the CdS sample prepared without surfactant at 200 °C. The inset shows the SEM image of the sample. As shown in the high-resolution TEM image, the crystal is 3D in structure with {002} close-packed planes along the [001] direction. The growth of wurtzite hexagonal CdS structure could be dominant along the [001] direction due to the polarized planes.¹⁴ Consequently, as shown in the XRD pattern (Fig. S2, ESI†) of a CdS sample prepared without surfactant at 200 °C, the intensity of the (002) peak is higher than the intensity of the (100) peak. In contrast, the intensity of the (002) peak is lower than the intensity of the (100) peak in the XRD pattern of CdS sample prepared with CTAB at 200 °C. This shows the dominance of [100] growth in the CdS structure when CTAB is used. Cheng *et al.* also reported 2D CdS single crystals with different growth directions without using surfactant.¹⁴ These results confirm the electrostatic interaction between CTAB and the (001)_S plane. Strong interaction of CTAB with charged facets can also slow down the growth and agglomeration of CdS crystal. Thus, well dispersed and highly crystalline CdS nanocrystals can be obtained.

For comparison, CdS nanocrystals were prepared without surfactant at 80 °C or with PVP or gelatin at 200 °C. The XRD pattern (Fig. S2, ESI†) indicates that the cubic structure is obtained at low temperature with CdS sample prepared at 80 °C. When temperature was increased to 200 °C, all peaks in the XRD patterns of the samples were matched with hexagonal structure.

The CdS particles prepared without surfactant at 200 °C also gave strong intensity peaks in the XRD pattern due to the primary crystal with a highly crystalline hexagonal structure. Dispersed CdS nanocrystals (Fig. S3 and S4, ESI†) were obtained. Fig. S5 (ESI†) shows TEM images with SAED images of CdS samples. Diffused SAED images indicate that all particles are not single crystals. The particles are clusters of many primary crystals as the mechanism of formation is illustrated in Scheme S1, ESI.† Primary single crystals are formed at the early stage of reaction. The growth of these nanocrystals accompanies the agglomeration process. The growth rate is slow at 80 °C or with the presence of polymers under hydrothermal conditions due to the slow rate of nuclei formation or surfactant barriers, respectively. Without surfactant, the growth of the CdS crystal can be dominant in hydrothermal conditions; thus, we can get hexagonal-shape crystals. These results indicate the agglomeration of CdS nanocrystals in the synthesis process without using surfactant or when PVP and gelatin were used.

Fig. S6 (ESI†) shows the optical properties of CdS samples. All spectra of CdS samples were measured in the aqueous phase, indicating the hydrophilic properties of CdS particles. UV-vis spectra (right image) show the red-shift of absorption wavelength when the particle size of the samples increases. The smallest CdS particles prepared with gelatin absorb at 475 nm while the largest particles prepared without surfactants at 200 °C show absorption at 550 nm. The results could be explained by the decrease of band gap when crystals are aggregated to bigger particles. The PL spectra of CdS crystals were defined into three peaks elsewhere.¹⁸ These peaks appear due to adjustment in the CdS crystal structure. The peaks at 465 nm and 525 nm are attributed to band-edge emissions and defects-in-distortion-lattice emissions, respectively, of CdS primary crystals. The peak at 625 nm is attributed to defects-in-self-adjustment-lattice emissions of CdS primary crystal agglomeration. This peak comes from the defects at boundaries of primary crystals in CdS particles as shown in Scheme S2, ESI.†¹⁹ Although CdS particles are different sizes, both PL spectra from (a) to (d) have the same three broad peaks. This indicates that the CdS particles are clusters of many primary crystals with different sizes. The PL spectrum of CdS sample prepared with CTAB has two peaks at 520 nm and 625 nm. These peaks are sharp and smooth. The increase of CdS particle size by using CTAB results in a decreasing of band gap energy. So, it is assumed that the high crystallinity of CdS particle structure is resulting in the red-shift of the band-edge emissions and defect-in-distortion-lattice emissions.

Consequently, the peak at 465 nm which is attributed to the band-edge emissions disappeared.

In conclusion, these results show that the growth of CdS crystals can be controlled by using surfactants which acts as passive agent of the oriented crystalline growth. This is attributed to preferable interaction between tailored surfactants and crystalline facets. With CTAB, we can obtain CdS single crystals while the growth of CdS crystals is arbitrary in the case that no surfactants or polymers are used. This method can be applied to obtain uniform single crystals with the goal of improving CdS properties.

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