# Selective Synthesis of Wurtzite CdSe Nanorods and Zinc Blend CdSe Nanoparticals through Solvothermal Routes

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By simply changing the reactants' composition, highly crystallized wurtzite CdSe nanorods and zinc blend CdSe nanoparticles were separately fabricated through a convenient solvothermal route with the reaction of cadmium nitrate ($Cd(NO_3)_2 \cdot 4H_2O$), hydrazine hydrate ($N_2H_4 \cdot H_2O$), and Se in ethylenediamine at 140 °C.

During the past decade, II–VI family nanoscaled semiconductors have attracted considerable interest owing to their fundamental optical and electronic properties.[1–3] Among them, CdSe nanocrystals have been especially investigated because of their wide potential application in solar cells, photovoltaic devices, biological labeling, and so on.[4–6] Since phase and shape are found to have distinct effect on their properties,[7] great attention has been paid to the control the morphology and strucure of CdSe nanocrystals.[8–12] However, most of the conventional synthesic strategies can only supply CdSe nanocrystals with unitary morphology and phase, and reports on getting CdSe nanocrystals with tunable morphologies and phases are still quite rare. Herein, we report a selective solvothermal route through which the morphology and structure of CdSe nanocrystals can both be controlled by simply changing the reactants' compositions at a low temperature (140 °C).

$Cd(NO_3)_2 \cdot 4H_2O$, $N_2H_4 \cdot H_2O$, and Se were selected as reactants and the reaction took place in ethylenediamine (en). The chemical reaction can be formulated as

$$2Cd^{2+} + N_2H_4 \cdot H_2O + 2Se + 4OH^- \\ \rightarrow 2CdSe\downarrow + N_2\uparrow + 5H_2O$$

In a typical procedure, 3.08 g (0.01 mol) of analytical grade $Cd(NO_3)_2 \cdot 4H_2O$ was put into a glass beaker filled with 50 mL of en. The mixture was stirred for 5 min at room temperature to form a clear solution and then placed into a Teflon-lined stainless steel autoclave. After 0.7896 g (0.01 mol) of Se powder and 0.05 mol of $N_2H_4 \cdot H_2O$ were added, the autoclave was maintained at 140 °C for 10 h and then allowed to cool to room temperature. The resulting dark brown precipitate was filtered, subsequently washed with distilled water and absolute ethanol, and allowed to dry at 60 °C in air. The whole process, which was to prepare wurtzite CdSe nanorods, can be easily adjusted to synthesize zinc blend CdSe nanoparticles by simply changing the amount of Se to 1.5792 g (0.02 mol).

The phase purity of the products was examined by X-ray diffraction (XRD) with a Rigaku D/max-rA X-ray diffractometer with Cu K$\alpha$ radiation ($\lambda = 1.5418$ Å). All the patterns in Figure 1a can be readily indexed to a hexagonal CdSe wurtzite structure with lattice constants $a = 0.4299$ and $c = 0.701$ nm (JSPDS 8-461), while those in Figure 1b correspond to a zinc blend structure with lattice constants $a = 0.6077$ nm (JSPDS 19-191). No characteristic peaks of impurities could be found, indicating that pure wurtzite and zinc blend CdSe could be obtained, respectively.

Transmission electron microscopy (TEM) images were taken with a Hitachi model H-600-2 transmission electron microscope using an accelerating voltage of 100 kV. As shown in Figures 2a and 2b all the wurtzite CdSe products display rodlike morphology with diameters of 10–15 nm and lengths of about 100 nm, while all the zinc blend CdSe samples are composed of nanoparticles with average size of about 100 nm. It can be seen that the nanoparticles have regular faces and most of them

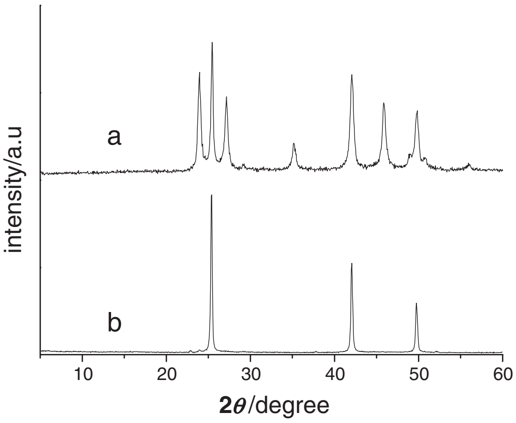

**Figure 1.** XRD patterns of the as-prepared (a) wurtrite CdSe and (b) zinc blend CdSe nanocrystals.

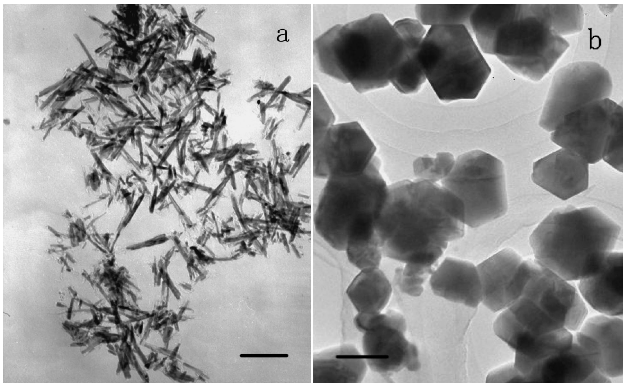

**Figure 2.** TEM images of the as-prepared (a) wurtrite CdSe nanorods (b) zinc blend CdSe nanoparticles (bar = 100 nm).

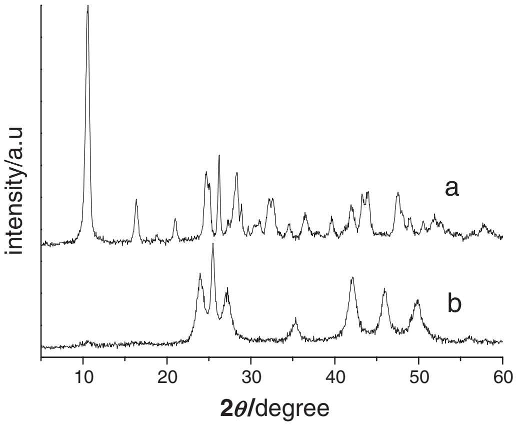

**Figure 3.** XRD patterns of: (a) CdSe•0.5en obtained at 100 °C regardless of the Cd:Se raito and (b) wurtzite CdSe products obtained after hydrothermal treatment of the precursor at 120 °C for 10 h.

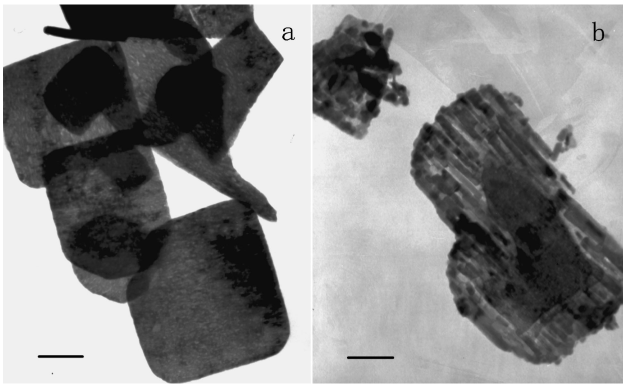

**Figure 4.** TEM images of (a) CdSe•0.5en nanosheets obtained at 100 °C regardless of the Cd:Se raito and (b) hexagonal CdSe products obtained after hydrothermal treatment of CdSe•0.5en at 120 °C (bar = 100 nm).

display a hexahedron-like shape. It's obvious that in our system, not only phase, but also morphology of the CdSe nanocrystals can be conveniently controlled.

It has been reported that the reactant concentration can affect the growth of crystals under proper conditions,[13] so we believe that the change of the concentration of $Se^{2-}$ ions is the key to the control of the morphology and structure. As well known, wurtzite structure is a high-temperature stable phase for CdSe which normally cannot be obtained at a temperature as low as 140 °C. In the present situation, however, when Cd:Se ratio is 1:1, as has been investigated by Li et al.,[14,15] en molecules intercalate into the CdSe inorganic framework to form a layered precursor with the structural formula CdSe•0.5en, which then break into wurtzite CdSe nanorods by releasing en. In this process, en is the crucial factor for the formation of the wurtzite structure and rodlike morphology. When Cd:Se ratio is 1:2, we suppose that since $Se^{2-}$ ions are excessive in the system and the interaction between $Se^{2-}$ and $Cd^{2+}$ is obviously much stronger than that between en and $Cd^{2+}$, en molecules cannot incorporate with $Cd^{2+}$ as usual. As a result, zinc blend structure, which is the low-temperature stable phase of CdSe and should essentially form at 140 °C, can be obtained. Accordingly, the morphology of the CdSe product also changes.

It is noteworthy that temperature was also found to play an important role in the reaction and only when the temperature was higher than 140 °C, could the control on the phase and morphology of the CdSe products be established. When the reaction was carried out at 100 °C, the layered precursor CdSe•0.5en could always be detected regardless of the Cd:Se ratio (see XRD patterns shown in Figure 3a and TEM image given in Figure 4a) and only wurtzite CdSe products could be obtained after post-hydrothermal treatment of the precursor. (XRD patterns are shown in Figure 3b and TEM image is shown in Figure 4b) We deduce that when temperature is lower than 140 °C, even if Se is excessive, the rate of the reaction between Se and $N_2H_4 \cdot H_2O$ is not fast enough to supply excessive $Se^{2-}$ ions. Thus, en can favorably interact with $Cd^{2+}$ ions, leading to final CdSe products with wurtzite structure and rodlike morphology.

In summary, not only the structure, but also the morphology of CdSe nanocrystals has been successfully tuned by simply changing the reactants' compositions. This method can surely be used to synthesize other II–VI family nanoscaled semiconductors and this may have wide potential applications because of its simple apparatus and low reaction temperature.

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