

## CdS, CdSe 나노결정의 형성 및 특성분석

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### Formation and Characterization of CdS and CdSe nanocrystals

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### INTRODUCTION

Cadmium chalcogenide nanocrystals are of great interest for both fundamental research and industrial applications due to the ability of tuning the optical properties by simply varying their size owing to the quantum confinement effect [1-4]. To attain these ends, it is of primary importance to develop low-cost, green, fast, and safe methods for synthesis of semiconductor nanocrystals with desired quality.

During the past decade, study on the synthesis of semiconductor nanocrystals have been intensively conducted, including the single molecule precursor methods [5], the homogeneous phase precipitation [6], the reverse micelle technique [7], and the colloidal solution methods [8, 9]. The colloidal methods developed by *Murray et al.* [8] in 1993, which involved the reaction of Cd(CH<sub>3</sub>)<sub>2</sub> with a Se precursor in TOPO (trioctylphosphine oxide), have the ability to produce large quantities of nanocrystals with both nearly monodisperse size and shape. *Peng et al.* [10,11] used noncoordinating solvents such as 1-octadecene instead of coordinating solvents such as trioctylphosphine oxide and this method has been extensively studied recently. In general, trialkylphosphine-based synthesis is achieved by injection of room temperature organometallic precursors into a well-stirred, hot organic solvent, which is usually carried out at temperature >300 °C, and the control of reaction temperature is necessary to separate the nucleation from the growth.

However, the injection-based synthetic method is not suitable for large-scale, industrial purpose. In this industrial case, the rapid injection of precursors and the control of nucleation and growth temperature are very difficult to achieve. Herein, we report the development of a non-trialkylphosphine-based precursor, Cd-oleylamine complex, elemental S and Se powder, for the preparation of CdS and CdSe nanocrystals respectively.

### EXPERIMENTAL SECTION

The synthetic methods used in the present experiments were similar to *Joo et al.* [12] and that of *Murry et al.* [8] reported previously. Synthesis was conducted under an ambient condition for a reality with an industrial large-scale. A typical synthetic procedure is as follows and the detailed conditions are given in Table 1.

**Synthesis of CdS Nanocrystals.** CdCl<sub>2</sub> (2 mmol, 0.366 g) was added to 20 mL of oleylamine at room temperature and the resulting solution was heated to 120 °C, forming a homogeneous and clear solution. Elemental sulfur (1 mmol, 0.032 g) was dissolved in 10 mL of oleylamine, and the resulting sulfur solution was swiftly injected into the Cd-oleylamine complex solution at 120 °C. The temperature of resulting mixture was maintained at 120 °C and the mixture was stirred vigorously at that temperature until the desired size of nanocrystals was formed. After the size of CdS nanocrystals

reached to a desired one, which is monitored by UV/Vis spectroscopy, the reaction mixture was cooled to 60 °C and cold n-hexane (30 mL) was added in order to remove unreacted Cd-oleylamine complex. Ethanol (50 mL) was added in order to cause the CdS nanocrystals to be precipitated. The precipitate was retrieved by centrifugation, producing yellow colored CdS nanocrystals. The final precipitate was vacuum-dried and obtained as a powder.

**Synthesis of CdSe Nanocrystals.** Elemental Se powder (1 mmol, 0.079 g) was added to Cd-oleylamine complex solution, which was prepared by reacting CdCl<sub>2</sub> (6 mmol, 0.366 g) and 15 mL of oleylamine with vigorous stirring at 140 °C. The color change from green to dark red occurred within a few minutes after injecting the elemental Se powder, indicating that nuclei were generated by the thermal decomposition of the Cd-oleylamine complex. The resulting solution was maintained at 140 °C. The reaction mixture was cooled to 60 °C and cold n-hexane (30 mL) was added in order to remove unreacted Cd-oleylamine complex. Ethanol (50 mL) was added in order to cause the CdSe nanocrystals to be precipitated. The precipitate was retrieved by centrifugation.

## **RESULTS AND DISCUSSION**

Figure 1 illustrates UV/vis absorption spectra of CdS and CdSe nanocrystals prepared under different monomer concentrations. The absorptions of CdS and CdSe nanocrystals are shifted from their 512, 716 nm bulk band gap, respectively, which show the effect of quantum confinement. The nucleation occurs within the first minute and crystals are continuously growing during reaction period. We have prepared different sized nearly monodisperse CdS and CdSe nanocrystals with the first absorption peaks of these particle ranging from 380 to 430 nm and 420 to 620 nm, respectively. When monomer concentration was relatively low, CdS quantum dots were formed (Figure 1a and 2a). On the other hand, CdS nanorods were formed at high monomer concentration (Figure 1b and 2b). Compared with both absorption spectra of dots and rods, their position of first absorption peak are similar at a same reaction time, which means that the first absorption peak of CdS nanocrystals is influenced by their diameter and not shape [13].

Structural analysis was conducted using transmission electron microscopy (TEM) and X-ray diffraction (XRD). We observed that the CdS nanocrystals obtained by the present method have a both zinc blende and wurtzite structure at very low temperature of about 120 °C. In addition, zinc blende structure exists about 15% through a TEM analysis (Figure 3b) and a comparison between relative intensities of the (110) and (103) diffraction. This structural assignment is consistent with the TEM observation (Figure 3).

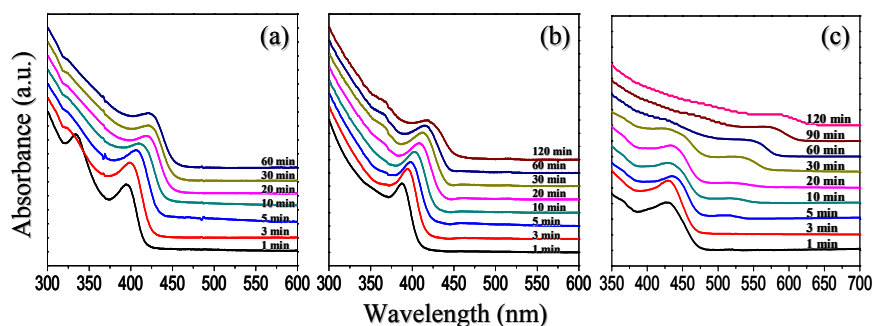
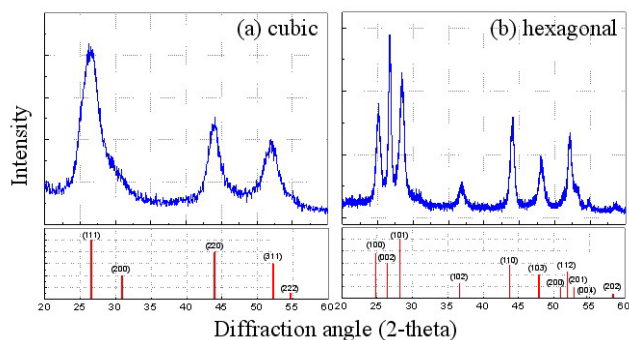
Figure 4 shows the powder XRD patterns of CdSe nanocrystals. Both zinc blende and wurtzite lattice structures are observed, respectively. The zinc blende structure was produced in the case of a low monomer concentration. In contrast, wurtzite phase of CdSe was obtained at a high monomer concentration and diffraction pattern are shown in Figure 4b.

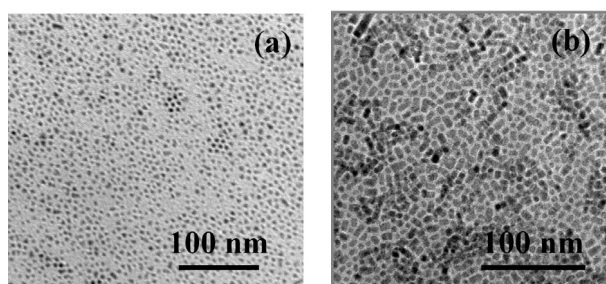
## **CONCLUSIONS**

The nucleation and crystal growth process of highly crystalline and nearly monodisperse CdS and CdSe nanocrystals were assessed. In this method, the structure of seed crystal and growth process is affected by the monomer concentration and initial precursor ratio. Quantum-sized CdS and CdSe nanocrystals with spherical and rod shapes were synthesized through a non-trialkylphosphine-based method. Also, wurtzite structure of CdS and CdSe nanocrystals as well as zinc blende was obtained at low temperature of 120 °C and 140 °C, respectively. Furthermore, this greener and mild synthetic method will offer the opportunity of industrial large-scale synthesis of II-VI semiconductor nanocrystals.

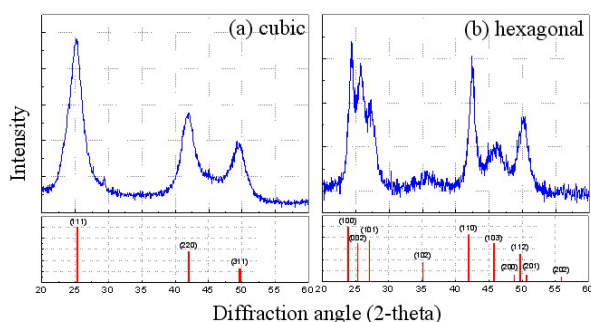
**Table 1.** Experimental conditions of as-prepared CdS and CdSe nanocrystal.

CdCl <sub>2</sub> (mmol) /oleylamine (mL)	S (mmol) /oleylamine (mL)	total oleylamine (mL)	# of experiment
2/20	1/10	30	Exp.1
2/30	1/15	45	Exp.2
1/30	2/15	45	Exp.3
CdCl <sub>2</sub> (mmol) /oleylamine (mL)	Se (mmol)	total oleylamine (mL)	# of experiment
2/20	1/10	30	Exp.4
4/20	1/10	30	Exp.5
2/30	1/15	45	Exp.6

**Figure 1.** Temporal evolution of the UV/vis absorption of a growth reaction of CdS and CdSe nanocrystals at room temperature: (a) CdS quantum dots prepared with condition of Exp. 3; (b) CdS nanorods prepared with condition of Exp. 1; (c) CdSe quantum dots prepared with condition of Exp. 2.**Figure 2.** XRD patterns of the CdS nanocrystals: (a) CdS quantum dots prepared with condition of Exp. 3; (b) CdS nanorods prepared with condition of Exp. 1. The standard diffraction peak positions and relative intensity of bulk zinc blende and wurtzite CdS are indicated respectively.



**Figure 3.** Low-resolution TEM images of CdS nanocrystals: (a) CdS prepared with condition of Exp. 3; (b) CdS prepared with condition of Exp. 1.



**Figure 4.** XRD patterns of the CdSe nanocrystals: (a) CdSe quantum dots prepared with condition of Exp. 6; (b) CdSe quantum nanorods prepared with condition of Exp. 4. The standard diffraction peak positions and relative intensity of bulk zinc blende and wurtzite CdSe are indicated respectively.

### **ACKNOWLEDGEMENT**

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