

# Mild synthesis of ultra-small CdSe quantum dots in ethylenediamine solution

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## Abstract

Ultra-small CdSe quantum dots (QDs) were synthesized by using reducing agent in ethylenediamine solution at mild temperature. Various reaction conditions of different precursor concentration, reaction temperature, and reducing agent were applied for the synthesis control of CdSe QDs. The control experiments resulted in two distinctively different sizes of ultra-small CdSe QDs of which the existing ratio was governed by the reaction factors of temperature and precursor concentration.

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**Keywords:** CdSe; Quantum dot; Mild temperature; Ultra-small; Ethylenediamine

## 1. Introduction

Semiconductor quantum dots (QDs) of low dimension have attracted great attentions due to their potential applications such as light emitting diodes [1–3], solar cells [4], catalysts [5], biological labels [6,7], lasing media [8,9], and opto-electronics [10]. Many studies have revealed novel properties for the semiconductor QDs, which were much different from those of the bulk systems. Such novel properties of the QDs are generally known to be resulted from size quantization of semiconductor QDs and large surface to volume ratio compared with the bulk materials [11,12].

Particularly, CdSe semiconductor has often been investigated due to its well-known physical properties and potentially controllable band-gap energy in full visible spectral range [2]. Most of CdSe QDs has been synthesized by using organometallic precursors in standard airless condition at relatively high temperatures (250–500 °C) [13,14]. Recently, a few studies were tried to prepare the CdSe QDs at mild conditions around room temperature [15,16]. However, they resulted in the nanostructures with

larger particle size than 6 nm which is in weak quantum confinement regime.

In this study, although the synthetic conditions were selected at lower temperatures than 100 °C, the CdSe QDs could still be obtained in ultra-small size regime, and the size distribution of the synthesized CdSe QDs was varied with the synthetic factors. The resulting CdSe QDs were characterized with UV–Vis absorption, X-ray diffraction (XRD), and high-resolution transmission electron microscopic (HRTEM) imaging.

## 2. Experimental

### 2.1. Preparation of CdSe QDs

Ethylenediamine (EDA) which formed complexes with QDs [17,18] was used as a stabilizer of the CdSe QDs. The preparation of the CdSe QDs was conducted in EDA solution on the different conditions of precursor concentration, temperature, and reducing agent.

For preparation of the CdSe QDs, Cd(NO<sub>3</sub>)<sub>2</sub> (0.5 mmol, 0.154 g) was added into 20 ml EDA and, subsequently, elemental selenium (0.5 mmol, 0.0395 g) was added into the EDA solution containing cadmium(II) nitrate. Excess

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$\text{NaBH}_4$  (8 mmol) was further added into the solution and stirred for 5 h at room temperature (RT). The preparation of the CdSe QDs was also conducted with higher precursor concentrations (1 and 5 mmol) of both the  $\text{Cd}(\text{NO}_3)_2$  and elemental selenium in EDA solution at RT. In order to study the dependence of reducing agent and reaction temperature, the solution containing 0.5 mmol of  $\text{Cd}(\text{NO}_3)_2$  and selenium was subjected to the different reducing agent of  $\text{KBH}_4$  at RT, and two different temperatures of 50 and 80 °C were applied for the reactions which have the precursor concentrations of 0.5 mmol and the excess  $\text{NaBH}_4$ .

## 2.2. Characterization

Absorption spectra of the ultra-small CdSe QDs were measured with an UV–Vis spectrophotometer (Shimadzu, UV-160A). Structural information of the CdSe QDs was studied by using an X-ray diffractometer (MAC Science, M03XHF<sup>22</sup>) with Cu-K $\alpha$  radiation ( $\lambda=1.54056 \text{ \AA}$ ). Images of the CdSe QDs were obtained with a HRTEM (JEOL, 3010) that was operated at 200 kV. In order to study the structural information and particle morphology, the products in the EDA solution were centrifuged and the precipitates were repeatedly washed with ethanol and dried overnight in an oven at 40 °C. The final products were applied for the XRD and HRTEM measurements.

## 3. Results and discussion

Absorption spectra for the CdSe QDs prepared from EDA solutions are shown in Fig. 1. The CdSe QDs

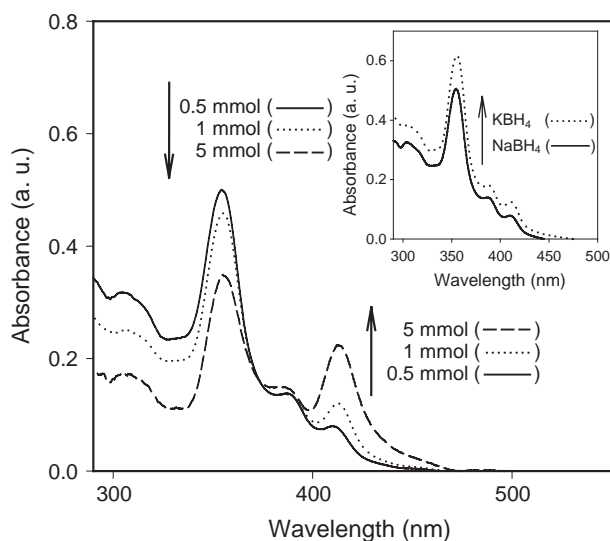


Fig. 1. Absorption spectra of the CdSe QDs with an isobestic point around 370 nm, which were prepared with the precursor concentrations of 0.5 (solid line), 1 (dotted line), and 5 mmol (dashed line). Inset shows the absorption spectra of the CdSe QDs prepared by using  $\text{NaBH}_4$  (solid line) and  $\text{KBH}_4$  (dotted line).

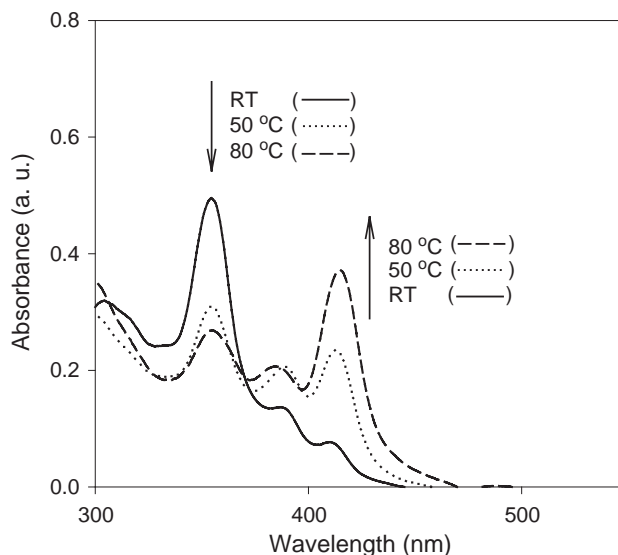


Fig. 2. Absorption spectra of the CdSe QDs prepared at RT (solid line), 50 °C (dotted line), and 80 °C (dashed line). As the reaction temperature increases, the intensities of two absorption peaks at 385 and 410 nm increase while the two strong absorption peaks at 310 and 355 nm decrease.

prepared from the solution containing  $\text{Cd}(\text{NO}_3)_2$  (0.5 mmol) and elemental selenium (0.5 mmol) show two strong absorption peaks at 310 and 355 nm along with two weak absorption shoulders at longer wavelength region. The two strong absorption peaks imply the lowest electronic transitions which correlate to the  $1\text{S}(e)-2\text{S}_{3/2}(h)$  and  $1\text{S}(e)-1\text{S}_{3/2}(h)$  of CdSe QDs, respectively, as reported in the literatures [19–21]. The CdSe QDs prepared at the higher precursor concentrations show interesting spectral changes with an isobestic point around 370 nm, depending on the precursor concentrations from 0.5 to 5 mmol (Fig. 1).

As the both precursor concentrations increase, the two weak absorption shoulders (at 385 and 410 nm) gradually increase while the two strong absorption peaks (at 310 and 355 nm) decrease. When different reducing agent ( $\text{KBH}_4$ ) is applied to the reaction, it is shown that the absorption spectrum of the produced CdSe QDs is little changed compared with the absorption spectrum of the CdSe QDs prepared by using  $\text{NaBH}_4$  (inset of Fig. 1).

For the CdSe QDs prepared at elevated temperatures, the resulting absorption spectra present the similar spectral changes with the spectral changes of the CdSe QDs which are prepared with the increased precursor concentrations as shown in Fig. 2. Since the chemical environment is similarly preserved in the reaction condition with the case of the increased precursor concentration, the largely enhanced two peaks centered at 385 and 410 nm are also responsible for the electronic transitions of the CdSe QDs. Previously, the similar spectral overlap was observed in semiconductor QDs with multiple size distribution [22]. Therefore, all the absorption peaks of 385 and 410 nm for the CdSe QDs prepared at the higher temperature and precursor concen-

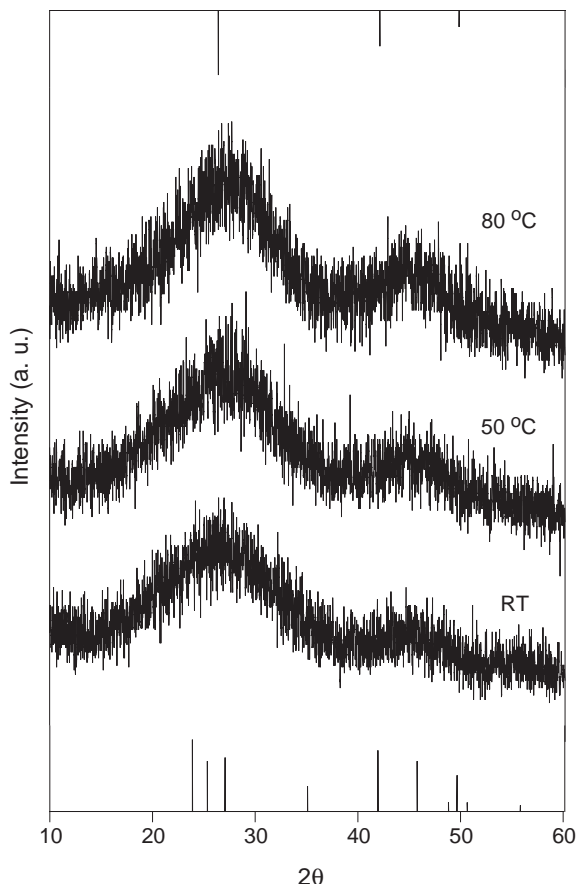


Fig. 3. XRD patterns of the CdSe QDs prepared at the different reaction temperature. Reference diffraction patterns are shown for the bulk CdSe with cubic (upper) and wurtzite (lower) structures.

tration are considered to be due to the respective two lowest electronic transitions of  $1S(e)-2S_{3/2}(h)$  and  $1S(e)-1S_{3/2}(h)$  for the CdSe QDs with larger particle size [19–21]. In this

case, although the higher series of electronic transitions such as  $1S(e)-3S_{1/2}(h)$  and  $1P(e)-1P_{3/2}(h)$  for the CdSe QDs with larger particle size may be somewhat overlapped with the lowest electronic transitions of  $1S(e)-2S_{3/2}(h)$  and  $1S(e)-1S_{3/2}(h)$  for the CdSe QDs with smaller particle size, the characteristic isobestic pattern can be clearly observed in the electronic absorption spectra. Depending on the reaction factors, such interesting spectral changes with an isobestic point lead us to suggest that the CdSe QDs may have two major different particle sizes rather than a broad distribution composed of multi-sized particles. In cluster chemistry, combination of several tens of atoms yields a stable nanostructure with a defined cluster size which is referred as ‘magic number’ [23]. The CdSe clusters with a defined size were also suggested by theoretical calculations [24,25].

The XRD patterns of the CdSe QDs prepared at the different temperatures are shown in Fig. 3. The obtained XRD patterns show broad diffraction peaks. Generally, QD systems have diffractive uncertainties originating from the small particle size and the strain, which results in diffraction peaks broadening [22,26]. Although the observed diffraction peaks have the diffractive uncertainties, the diffraction peaks for the CdSe QDs are approximately positioned at the diffraction pattern for the cubic (JCPDS Card No. 19-0191) or the wurtzite (JCPDS Card No. 08-459) structure of the bulk CdSe. As the reaction temperature increases, the diffraction peak of the CdSe QDs centered at  $26.5^\circ$  in  $2\theta$  is slightly narrowed from  $13^\circ$  to  $11^\circ$  in full-width at half maximum, which implies slightly larger particle size of the obtained CdSe QDs at the higher reaction temperature.

Fig. 4 shows the HRTEM images of the CdSe QDs. From the image of the CdSe QDs prepared at RT, which have the strong electronic absorption at  $\sim 355$  nm (assigned to  $1S(e)-1S_{3/2}(h)$  transition), the averaged particle diameter is

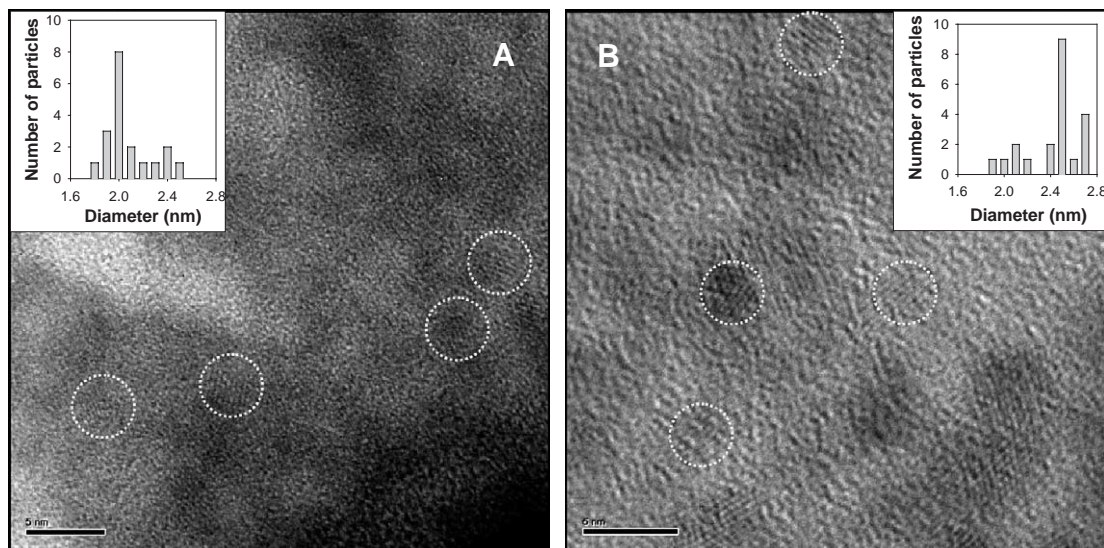


Fig. 4. HRTEM images and size distributions of CdSe QDs prepared at RT (A) and  $80^\circ\text{C}$  (B). The distinct CdSe QDs are clearly shown within the dotted circles. Reference bar is 5 nm.

estimated to be approximately 2.0 nm. On the other hand, the averaged particle diameter for the CdSe QDs prepared at the higher reaction temperature of 80 °C is estimated to be approximately 2.5 nm, of which absorption spectrum have the strong electronic absorption at ~410 nm (assigned to 1S(e)–1S<sub>3/2</sub>(h) transition). The estimated averaged particle sizes of ~2.0 and ~2.5 nm are comparable to the particle sizes of 2.0 and 2.2 nm for the CdSe QDs calculated by the effective-mass approximation based on the lowest electronic transitions [27]. Furthermore, the existence of lattice fringes on the observed HRTEM images confirms the crystallinity of the ultra-small CdSe QDs, and energy dispersive X-ray analysis proves the elemental existence of Cd and Se with the ratio of 1.0:1.2, respectively. From the HRTEM images, it is shown that the prepared CdSe QDs consist of the two major particle diameters (approximately 2.0 and 2.5 nm) and the ratio of the two particle sizes varies, depending on the precursor concentration and the reaction temperature.

#### 4. Conclusions

The CdSe QDs with ultra-small size were successfully prepared by chemical reduction process even at mild temperatures lower than 100 °C under the various synthetic conditions such as precursor concentration, reducing agent, and reaction temperature. In this study, the chelation of the EDA molecules effectively stabilizes the prepared ultra-small CdSe QDs in our synthetic conditions, and the resulting CdSe QDs distinctively have two major particle diameters (approximately 2.0 and 2.5 nm) of which the existing size ratio is governed by the reaction conditions of the precursor concentration and the reaction temperature.

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