

## One-Pot Synthesis of CdSe Quantum Dots Using Selenium Dioxide as a Selenium Source in Aqueous Solution

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A novel technology has been developed for the synthesis of thioglycolic acid (TGA)-capped CdSe quantum dots (QDs) in aqueous medium. The reaction was carried out in air atmosphere with one-pot by using SeO<sub>2</sub> to replace Se or Na<sub>2</sub>Se. The technological parameters including refluxing time, pH values and molar ratios of selenium to cadmium had significant influence on the luminescence properties of CdSe QDs. Furthermore, the obtained QDs were characterized by fluorescent spectroscopy, X-ray powder diffraction (XRD) and transmission electron microscopy (TEM), respectively. The results demonstrated that the CdSe QDs were of zinc-blended crystal structure in a sphere-like shape.

**Key Words** : Cadmium selenium, Nanocrystalline materials, Selenium dioxide, Luminescence

### Introduction

Because of their unique optical and electrical properties, CdSe QDs have gained increasing attention in the fields of chemical analysis,<sup>1</sup> biolabeling,<sup>2</sup> and solar cell,<sup>3</sup> etc. Up to now, two successful routes have been reported for the synthesis of CdSe QDs, one is organometallic synthesis based on the high-temperature thermolysis of the precursors,<sup>4</sup> and another is synthesis in aqueous medium using thiols as stabilizing agents.<sup>5</sup> In most of the aqueous route, either Se powder<sup>6-8</sup> or Na<sub>2</sub>Se lump<sup>9</sup> is utilized as the selenium sources. When Se powder is used as a source of selenium, it must first be reduced by NaBH<sub>4</sub> to produce NaHSe precursor at lower temperature, or reacted with Na<sub>2</sub>SO<sub>3</sub> at 100 °C to produce Na<sub>2</sub>SeSO<sub>3</sub>. However, NaHSe and Na<sub>2</sub>SeSO<sub>3</sub> are instable, which should be prepared immediately before using. Even though the moisture-sensitive Na<sub>2</sub>Se as an alternative selenium source can also be used for preparing CdSe QDs, it is toxic, expensive and instable. Therefore, it is very necessary to hunt for a novel selenium source for the synthesis of CdSe QDs.

In previous study, sodium selenite<sup>10</sup> has been used to synthesize CdSe QDs, these QDs were not thiol-capped, and the luminescence and controllable size of such CdSe QDs have not been reported. Compared with sodium selenite, selenium dioxide is stable, cheap and less toxic. In this manuscript, we describe a simple one-pot synthetic route for preparing CdSe QDs in an aqueous solution. Here Se powder or Na<sub>2</sub>Se lump was replaced by an air-stable and inexpensive selenium source, SeO<sub>2</sub>, which was reduced by NaBH<sub>4</sub> in ambient conditions to generate Se<sup>2-</sup> ions. Thus the reaction could be carried out with a single procedure. The effects of refluxing time, initial pH values and molar ratios of selenium to cadmium on the luminescence properties of CdSe QDs were investigated systematically. To the best of our knowledge, this is the first time for the use of selenium dioxide as

selenium source to synthesizing CdSe QDs in an aqueous medium. Compared with Se powder and Na<sub>2</sub>Se lump route, the new SeO<sub>2</sub> route is an environment-friendly and low-cost synthesis route, which is suited for large-scale synthesis.

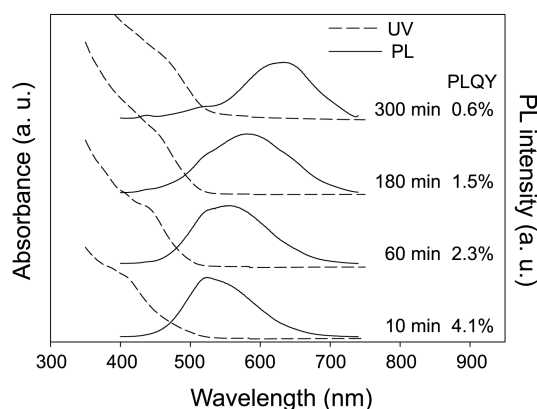
### Experimental

In a typical procedure, 0.4567 g (2 mmol) CdCl<sub>2</sub>·2.5H<sub>2</sub>O was dissolved in 100 mL of deionized water in a 250-mL three-neck flask, and 0.5 mL thioglycolic acid (TGA) was added while stirring. The solution was adjusted to pH 11.0 with 1.0 mol·L<sup>-1</sup> NaOH solution. After several minutes, excess NaBH<sub>4</sub> (0.1 g) and 0.111 g (1 mmol) SeO<sub>2</sub> was added successively into the above solution. The solution was then refluxed at 100 °C for different time to control the size of the CdSe QDs.

The absorption and photoluminescence spectra were measured using a UV-2102 spectrometer and a RF-5301 fluorescence spectrometer, respectively. Estimates of PLQY were obtained by comparing the integrated emission from Rhodamine6G (QY = 95%) in ethanol and that of CdSe QDs dispersed in double deionized water. X-ray powder diffraction were taken on a D/MAX 2500V diffractometer equipped with Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm). The morphology measurement was performed using an H-7650 transmission electron microscopy.

### Results and Discussion

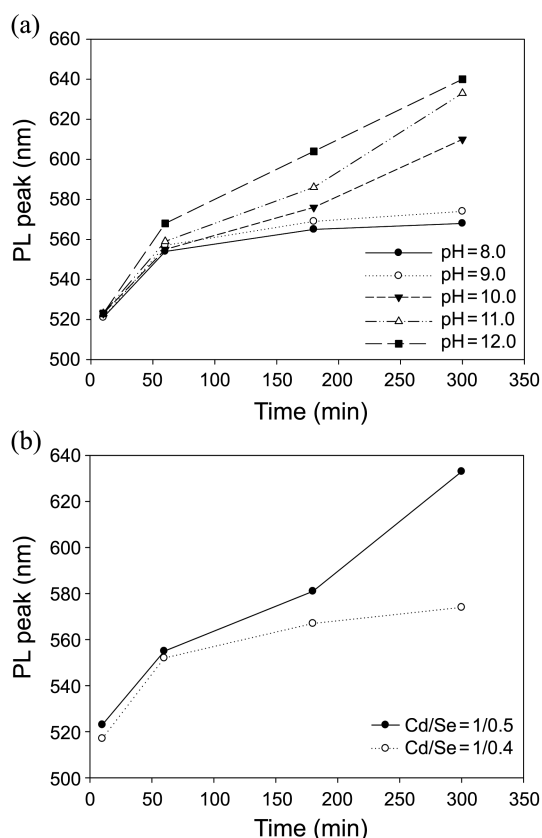
Figure 1 shows typical absorption and PL spectra of a size series of CdSe QDs. The spectra were measured on as-prepared CdSe solutions which were taken from the refluxing reaction mixture at different intervals of time and diluted with water. For all samples, the absorption onset appeared at around 510 nm, blue-shifting 206 nm compared with bulk CdSe (716 nm),<sup>11</sup> which was caused by quantum confine-



**Figure 1.** Temporal evolution of absorption (dashed line) and PL spectra (solid line) of CdSe QDs.

ment effect. The strong blue-shifting indicated that the particle size was very small. After 10 min refluxing, an excitonic absorption peak of CdSe QDs appeared at 410 nm, which shifted to longer wavelengths with increasing of reflux time. It can be seen, in all cases, the excitonic absorption peaks were not very distinct, indicating the formation of CdSe QDs with wider size distribution. As described in Figure 1, the CdSe QDs exhibited very broad PL bands attributed to defect-related emission,<sup>12,13</sup> which also shifted toward longer wavelength with the increase of reflux time. The reason for the generation of defect-related emission may be that the extremely small diameter has a very high surface-to-volume ratio, and the high-density dangling bonds and trap sites on the surface is easy to be formed and difficult to be passivated. The PLQY of the four samples was calculated to be 4.1%, 2.3%, 1.5% and 0.6%, respectively, using Rhodamine 6G as reference, which can almost be comparable to the CdSe QDs prepared by an organometallic route.<sup>14</sup>

In preparation, the initial pH values was adjusted to 8.0, 9.0, 10.0, 11.0 and 12.0, respectively, we investigated the influence of various initial pH values on the optical properties of CdSe QDs. It can be seen in Figure 2(a), at the start of reflux, the initial pH values almost had no influence on the PL peak of QDs, after refluxed for 60 min, the PL peak of CdSe increased with the increase of initial pH value. In comparison with the CdSe QDs obtained at pH = 8.0 or 9.0, the CdSe QDs formed at pH  $\geq$  10.0 have a longer PL peak. According to the theory of acid-base equilibrium, the initial pH value of original solution determines the dissociation state of TGA and the coordination between TGA and Cd<sup>2+</sup> ion. The dissociation constants of TGA are  $pK_{a1} = 3.48$  (carboxyl) and  $pK_{a2} = 10.11$  (thiol).<sup>15</sup> When pH < 3.48, the precursor solution was milk-like, no cadmium thiol complexes occurred. With pH enhancement, complexation formed gradually. At pH > 10.11 in precursor solution, the concentration of  $\text{SCH}_2\text{COO}^-$  is higher than that of  $\text{HSCH}_2\text{COO}^-$ , the overwhelming majority of TGA coordinate with Cd<sup>2+</sup> ion to form Cd<sup>2+</sup>-TGA complexes. Thus, at higher pH, more CdSe nuclear are formed, resulting in the acceleration of the QDs growth and the corresponding red

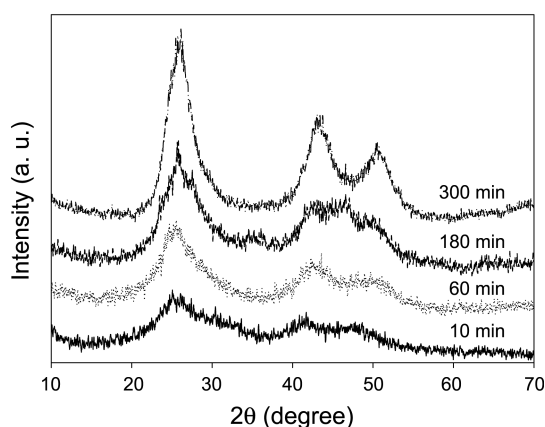


**Figure 2.** PL peaks of CdSe QDs with (a) different initial pH value and (b) various Cd/Se molar ratios.

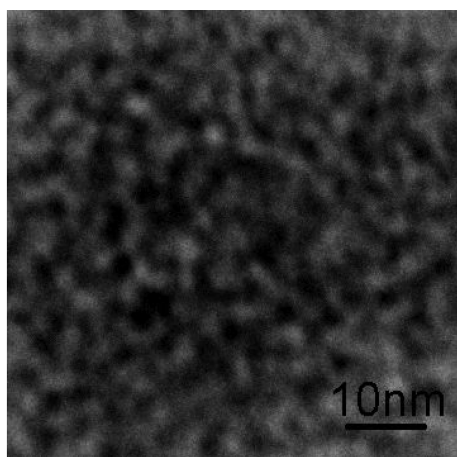
shift of the PL peak.

The research<sup>16</sup> disclosed that the molar ratio between Cd and Se played a major role in determining nucleation and growth of CdSe QDs. In preparation, the Cd/Se molar ratio was varied from 1:0.67 to 1:0.4 with fixed TGA concentration and pH value, we investigated the influence of various Cd/Se molar ratios on the optical properties of CdSe QDs. When the ratio was 1:0.67, red turbid would appear with prolonged heating, and the PL peak of products almost had no change. As can be seen in Figure 2(b), with the commonly adopted ratio at 1:0.5, the PL peak of QDs gradually shifted to longer wavelength with reflux time ranging from 10 min (523 nm) to 300 min (633 nm). While with the ratio at 1:0.4, after refluxed for 60 min, the PL peak position had only small change of several nanometers. Obviously, the location of PL peak can be turned by changing the Cd/Se molar ratios of the precursor solution. Compared with the CdSe QDs obtained with two other Cd/Se molar ratios, the CdSe QDs prepared at Cd/Se molar ratio 1:0.5 have a broad PL peak cover range.

The crystallinity and structure of CdSe QDs were demonstrated by the XRD patterns as revealed in Figure 3. XRD patterns of CdSe samples exhibit three peaks that can be assigned to (111), (220), and (311) diffractions corresponding to cubic zinc-blende structure. This is often the observed phase of CdSe prepared in aqueous solution.<sup>17-19</sup> These peaks are broadened due to finite crystalline size. The



**Figure 3.** XRD patterns of CdSe QDs prepared at different reflux time.



**Figure 4.** TEM image of CdSe QDs.

particle size can be calculated according to Scherrer's equation<sup>20</sup>:

$$L = \frac{0.9\lambda}{B\cos\theta}$$

where  $L$  is the coherence length,  $\lambda$  is the X-ray wavelength (0.15406 nm in this study),  $B$  is the full width at half maximum of respective diffraction peak, and  $\theta$  is the angle of diffraction for (111) plane. In the case of small crystallites,  $L = 3/4D$ , where  $D$  is the average diameter of QDs. Based on the reflection peak at  $2\theta$  of 25.3, an average diameter of the four samples is calculated as 1.5, 1.8, 2.6 and 3.0 nm, respectively.

A typical TEM image is shown in Figure 4. According to the TEM image, the CdSe QDs appear as spherical particles with the size of about 2-3 nm, which is in accord with the result of the XRD analysis.

## Conclusions

A novel and simple technology for preparing CdSe QDs using  $\text{SeO}_2$  as selenium source has been described. The advantages of the method are as following: firstly, the preparation condition is mild, and the procedure is simple; secondly, it is a cheap and green route for synthesis of CdSe QDs; thirdly, this method may be extended for the preparation of other selenide or telluride QDs such as ZnSe, CdTe, and so on.

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