Synthesis and optical properties of cadmium selenide quantum dots for white light-emitting diode application

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**A B S T R A C T**

Yellow light-emitting cadmium selenide quantum dots were synthesized using one-step and two-step methods in an aqueous medium. The structural luminescent properties of these quantum dots were investigated. The obtained cadmium selenide quantum dots displayed a broad excitation band suitable for blue or near-ultraviolet light-emitting diode applications. White light-emitting diodes were fabricated by coating the cadmium selenide samples onto a 460 nm-emitting indium gallium nitride chip. Both samples exhibited good white balance. Under a 20 mA working current, the white light-emitting diode fabricated via the one-step and two-step methods showed Commission Internationale de l’Éclairage coordinates at (0.27, 0.23) and (0.27, 0.33), respectively, and a color rendering index equal to 41 and 37, respectively. The one-step approach was simpler, greener, and more effective than the two-step approach. The one-step approach can be enhanced by combining cadmium selenide quantum dots with proper phosphors.

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**1. Introduction**

White light-emitting diodes (WLEDs) for solid-state illumination have received significant attention for their better efficiency and environmental friendliness compared with conventional lighting [1,2]. One of the most commonly used methods to assemble WLEDs is to combine an InGaN blue chip with yellow light from YAG:Ce phosphor [3–5]. However, several challenges still remain in this coupled process, such as the lack of red emission, low luminescent efficiency, and low color rendering index (CRI) [6,7]. Quantum dots (QDs) have been used to replace frequently used phosphor-based materials in WLEDs because of their unique optical properties and the need for new phosphors for solid-state lighting applications [3,8,9]. QDs have advantages over conventional phosphors. First, the emission wavelength of QDs can be tuned by controlling their sizes, providing an approach to obtain tunable fluorescence [10]. Second, fewer scattering effects are observed in QDs because of their narrow size distribution compared with that of conventional inorganic phosphors [11], indicating that QDs are promising new phosphors for WLED devices.

Cadmium selenide (CdSe) QDs are important semiconductor nanomaterials that have been synthesized using various approaches, including organic [12] and aqueous methods [13].

Selenium [14], selenourca [15], and sodium selenide [16] were used as selenium sources in most of these aqueous approaches. An alternative approach to prepare CdSe QDs using selenium dioxide as the selenium source was reported in our previous publication [17]. However, the application of the obtained CdSe QDs was not investigated. In the current experiment, water-soluble thiglycolic acid (TGA)-capped CdSe QDs were synthesized using a typical two-step aqueous approach with Na2SeSO3 as a precursor and the one-step method with SeO2 as the source. A WLED device consisting of yellow CdSe QDs as color-conversion materials and a near-ultraviolet (UV) InGaN LED chip as an excitation source was obtained.

**2. Materials and methods**

CdCl2·2.5H2O (A.R.), Se powder (A.R.), Na2SO3 (A.R.), SeO2 (A.R.), NaBH4 (A.R.), and TGA (A.R.) were used to prepare CdSe QDs.

**2.1. Synthesis of CdSe QDs**

**2.1.1. One-step method**

CdCl2·2.5H2O (0.4567 g) was dissolved in 100 ml of deionized water in a 250 ml three-neck flask, and 0.3 ml TGA was added while stirring. The pH of the solution was adjusted to pH 8 with 1.0 mol L−1 NaOH solution. After several minutes, 0.0227 g NaBH4 and 0.0222 g SeO2 were added to the solution. Then, the solution was refluxed at 100 °C for 5 h.

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2.2. Two-step method

Na₂SO₃ (6.3 g) was dissolved in 100 mL of deionized water in a 250 mL three-neck flask, and 0.395 g Se powder was added while stirring. The mixture was refluxed at 80 °C for 6 h and filtered to obtain 0.0409 mol L⁻¹ Na₂SeSO₃ solution (A) [18]. CdCl₂·2.5H₂O (0.4567 g) was dissolved in 100 mL of deionized water in a 250 mL three-necked flask, and 0.3 mL NaOH solution was added while stirring. The pH was adjusted to obtain a pH range of 8–9 with 1.0 mol L⁻¹ NaOH solution to obtain the solution (B). After several minutes, 6.1 mL Na₂SeSO₃ solution (A) was added into the solution (B). Then, the mixture was refluxed at 100 °C for 5 h.

2.3. Characterization

The products were characterized via X-ray diffraction (XRD) using a Rigaku D/max-2500 X-ray diffractometer with CuKα radiation (λ = 1.54056 Å). Fourier transform infrared spectroscopy (FTIR) was conducted using a Shimadzu UV–vis spectrophotometer (Japan). Morphology was observed with transmission electron microscopy (TEM) using a JEM-21100F transmission electron microscope. The UV–visible (UV–vis) absorption spectra were determined using a Shimadzu UV–2501PC spectrophotometer (Japan). Excitation and emission spectra were obtained via a Shimadzu RF-5301PC fluorescence spectrophotometer (Japan) using the Xe lamp as excitation source. LED parameters were measured on an EVERFINE PMS-80 UV–vis–IR spectrophotometer.

2.4. Fabrication of WLED

A blue InGaN chip was used as the excitation source and the yellow-emitting CdSe QDs were used as nanophosphors to fabricate WLEDs. The 460 nm-emitting InGaN chip was coated with CdSe QDs mixed with AB silicone. Then, the solvent was dried off. Transparent epoxy materials were placed over the CdSe QD-InGaN chip to solidify and form a semimide shape. The structure of WLEDs and the photographs of their lighting are illustrated in Fig. 1.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of CdSe QDs synthesized via the one-step and two-step methods are shown in Fig. 2(a) and (b), respectively. The three typical distinct peaks at 2θ = 25.4, 42.0, and 49.7 can be found in the two patterns, indicating that the zinc-blended structures have peaks corresponding to (1 1 1), (2 2 0), and (3 1 1) reflections, respectively. The XRD peaks of CdSe are consistent with the data given by JCPDS card 88-2346, which is often the observed CdSe phase in aqueous solution [19,20]. The XRD peaks of CdSe QDs (Fig. 2) are comparatively wider than those of the bulk materials because of their finite crystallite size. The particle size was estimated from the XRD pattern by determining the full width at half maximum (FWHM) of the characteristic peak (1 1 1). The following Debye–Scherrer equation [21] was used in determining the nanoparticle (spherical particle) radius:

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

where L is the coherence length, λ is the X-ray wavelength (0.15406 nm in the current study), B is the FWHM of the respective diffraction peak, and θ is the angle of diffraction for the (1 1 1) plane. For small crystallites, L = 3/4D, where D is the average QD diameter. Based on the reflection peak at 2θ = 25.4, the corresponding diameters of the CdSe samples synthesized via the one-step and two-step methods are calculated at 1.82 and 1.40 nm, respectively.

3.2. FTIR results and characterization of high resolution transmission electron microscopy (HRTEM)

The absorption band corresponding to the S–H vibration observed at 2560 cm⁻¹ was absent in both FTIR spectra (Fig. 3(a)), indicating that the thiol groups are bound to the surface of the Cd²⁺ site through the Cd–SR bonds. This condition also revealed that CdSe is capped with TGA.

TEM and HRTEM images of the CdSe QDs are shown in Fig. 3(b) and (c), respectively. The as-synthesized CdSe QDs have an estimated average diameter of approximately 3 nm. The particles of CdSe QDs prepared using the two-step method are smaller than those of CdSe QDs synthesized using the one-step method. From the HRTEM images, the space lattice can be observed from the QD surface, indicating the efficient crystallization of QDs. The lattice spacing was 0.350 nm for one-step method and 0.351 nm for two-step method, corresponding to atomic planes along the [1 1 1] lattice plane direction of the cubic CdSe [22].
The radius of the nanoparticles obtained by XRD resulted from the size calculated by diffraction methods corresponding to the magnitude of the coherent crystal regions. Thus, the size obtained by diffraction cannot always correspond to the sizes measured by other techniques [23, 24].

3.3. Optical analysis

The typical optical absorption spectra, photoluminescence (PL) emission, and excitation band of the CdSe QDs fabricated using the one-step and two-step methods are shown in Fig. 4(a) and (b). The PL emission band excited at 365 nm by the CdSe fabricated via the one-step and two-step methods have peaks at 572 and 537 nm, respectively. The broad PL spectra (ranging from 400 nm to 700 nm) of the CdSe QDs correspond to the defect-related emission [9, 25]. Defect-related emissions result from extremely small diameters, extremely high surface-to-volume ratio, high-density dangling bonds, and trap sites on the surface that are easily formed and difficult to passivate. Small emission band peaks are shown in Fig. 4(a). Several beads transform to large grains because of the Ostwald ripening effect. The grains are accompanied by a small peak based on the quantum size effect [26]. The corresponding excitation band of the prepared CdSe QDs is broad, with the ability to absorb light efficiently in the UV or blue range, confirming their potential as phosphors for WLED application.

The typical UV–vis absorption spectra of the two samples (Fig. 4, dashed line) showed that the first excitation absorption peak is at 434.2 nm and 380.0 nm for the CdSe QDs synthesized using the one-step (Fig. 4(a)) and two-step methods (Fig. 4(b)), respectively. These peaks correspond to diameters of 1.83 and 1.37 nm, respectively, calculated using the following empirical formula [27]:

\[
D = 1.6122 \times 10^{-9} \times \lambda^4 - 2.6575 \times 10^{-6} \times \lambda^3 + 1.6242 \times 10^{-3} \times \lambda^2 - 0.4277 \times \lambda + 41.57.
\]
where \( D \) (nm) is the size of a given CdSe sample and \( \lambda \) (nm) is the wavelength of the first excitonic absorption peak of the corresponding sample.

### 3.4. The characterization of the fabricated WLED

Two types of WLEDS were fabricated, namely, WLED i and WLED ii, which were the CdSe synthesized via the one-step and two-step methods, respectively (Table 1). The electroluminescence spectra of the original 460 nm-emitting InGaN chip (triangle), WLED i (circle), and WLED ii (square) under a 20 mA forward bias at room temperature are shown in Fig. 5(a). The blue emission band at 462 nm is attributed to the emission of the InGaN chip. The broad band from 500 nm to 750 nm is caused by the absorption of the coated CdSe QDs. Bright white light from the LEDs was observed via the LED test.

The corresponding Commission Internationale de l’Éclairage (CIE) chromaticity coordinates of the original 462 nm-emitting InGaN chip, WLED i, and WLED ii are shown in Fig. 5(b). The CIE coordinates of the InGaN/QD WLED i and ii are \((0.27, 0.23)\) and \((0.27, 0.33)\), respectively. The CIE coordinates of the two samples are all in the white area, confirming their potential as phosphors for WLED applications. The CRI of WLED i is 41, a value higher than that of WLED ii (37). However, low CRI are still observed for WLED applications because of the lack of several emitting particles and a narrower spectral band. For the QD WLEDS in our work, yellow-emitting CdSe QDs are directly coated onto the InGaN chip. Blue light is emitted by the InGaN chip through electron-hole recombination in the p-n junctions. Electron-hole pairs are indirectly injected into the CdSe QDs, resulting in an energy transfer. The CdSe QDs convert some of the blue LED light to yellow light, whereas the rest of the blue light mixes with the yellow light to give the appearance of white light [28,29]. However, when the heating time increases, the QD particle grows and the emission peak of QDs shift to a longer wavelength due to the quantum confinement effect [27]. By comparing products produced at a given reaction time and not necessarily the quality of nanocrystals produced, the LED results are expected to be at par with the two-step method. The one-step method is simpler, greener, and more effective than the two-step method, so the former can be enhanced by combining CdSe QDs with the proper phosphors. The one-step method can also be enhanced by blending two or more kinds of CdSe with different sizes because of its suitability for large-scale CdSe synthesis.

### Table 1

<table>
<thead>
<tr>
<th>No.</th>
<th>LED name</th>
<th>Chip</th>
<th>Synthesis method of CdSe</th>
<th>CIE-1931 coordinate</th>
<th>CRI</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>InGaN chip</td>
<td>460 nm InGaN</td>
<td>–</td>
<td>((x=0.14, y=0.05))</td>
<td>–</td>
</tr>
<tr>
<td>b</td>
<td>White LED i</td>
<td>460 nm InGaN</td>
<td>One-step</td>
<td>((x=0.27, y=0.23))</td>
<td>41</td>
</tr>
<tr>
<td>c</td>
<td>White LED ii</td>
<td>460 nm InGaN</td>
<td>Two-level</td>
<td>((x=0.27, y=0.33))</td>
<td>37</td>
</tr>
</tbody>
</table>

Fig. 4. The typical optical absorption spectra (dashed line), PL emission spectra (solid line), and excitation spectra (dotted line) of CdSe synthesized via the one-step method (a) and two-step process (b).

Fig. 5. EL spectra (a) of the as-fabricated LEDs (InGaN chip [solid line], WLED i [dashed line], and WLED ii [dotted line]) and the corresponding CIE coordinates of the three types of LEDs (b).
4. Conclusions

CdSe QDs were prepared in an aqueous medium. Upon excitation with 365 nm UV light, the synthesized CdSe QDs via the one-step and two-step methods showed strong yellow-emission lines with peaks at approximately 572 and 537 nm, respectively. WLEDs fabricated using InGaN chips and the CdSe QDs prepared using the two aforementioned methods exhibited CIE coordinates of (0.27, 0.23) and (0.27, 0.33) and CRI of 41 and 37, respectively. Fabricated WLED using the synthesized CdSe via the one-step method is potentially useful in illumination and display applications.

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References