1. Introduction

Recently, semiconducting quantum dots (QDs) have attracted many attentions for their various applications to light-emitting displays (LED) and biomarkers for detecting cancers or viruses, since QDs of CuCl$_2$ and CdS were firstly synthesized \[1, 2\]. The bandgap energies of QDs could be controlled by changing the crystal sizes, thus photoluminescent light color can be varied from blue to red due to their quantum confinement. In this study, we focused on the control of bandgap energy of quantum dots by changing the Zn/(In+Zn) ratio in the In(Zn)P core. Zinc incorporation can change the photoluminescent light colors of green, yellow, orange, and red. Diluting a solution of as-synthesized QDs by more than 100 times did not show any quenching effects by the Förster resonance energy transfer phenomenon between neighboring QDs.

Keywords: InP; quantum dot; QLED; core/shell; FRET

2. Experiment

2.1. Chemicals

For the synthesis of In(Zn)P QD cores, indium(III) acetate
(In(Ac)₃, 99.99 %, Sigma Aldrich, USA) and zinc acetate (Zn(Ac)₂, 99.99 %, Sigma Aldrich, USA) were purchased from Sigma Aldrich and trioctylamine was purchased from Daejung Chemical. (TOA, 99 %, Daejung, Korea) The source of phosphine was tris(trimethylsilyl)phosphine. (ca. 10 % in Hexane, (TMS)₃P; TCI Tokyo, Japan)

The capping agent for QDs was oleic acid (OA, 90 %, Sigma Aldrich, USA) and lauric acid (LA, 98%, Sigma Aldrich, USA) and palmitic acid. (LA, 98%, Sigma Aldrich, USA) For the formation of shell, ZnSe, selenium (Se, 99.99 %, Sigma Aldrich) and trioctylphosphine (TOP, 90 %, Sigma Aldrich) were purchased from Sigma Aldrich. For ZnS shell, sulfur (S, 99.98 %, Sigma Aldrich) was used. The organic solvents for the dispersion of QDs were 1-octadecene (ODE, 90 %, Sigma Aldrich, USA) and toluene (99.8 %, Sigma Aldrich), hexane (95 %, Sigma Aldrich) and chloroform (99 %, Duksan chemical, Korea). For the purification, acetone (99.8 %, Daejung) and methyl alcohol (99.5 %, Daejung) were used.

2.2. Synthesis of In(Zn)P@ZnSe@ZnS QDs

2.2.1 The synthesis of In(Zn)P core

The precursor chemicals of In(Zn)P cores were In(Ac)₃, (TMS)₃P, Zn(Ac)₂. In a 100 mL 3-neck flask, 1.2 mmol of Zn(Ac)₂ was dissolved in 2.4 mmol of OA and 10mL of ODE and degassed at 120 °C for 1 h (~500 mTorr). The reactant solution was observed to be clear. It was cooled to R∙T under N₂ and then 0.6 mmol of In(Ac)₃ and 1.8mmol of LA were added. In this experiment, we varied In/(In+Zn) ratio from 0.33 to 1 by changing Zn(Ac)₂ to In(Ac)₃ molar ratio as shown in Table 1. The reactant was degassed at 120 °C for 1 h again (~500 mTorr). After that, 0.4mmol (TMS)₃P precursor that was dissolved in 10 mL TOP was injected after heating up to 150 °C under N₂. The temperature was heated to 240°C and the heating mantle was removed to cool down to below 100 °C, rapidly. The reactant was transferred into two 50 mL conical tubes and 25 mL of acetone was added into each tube for purification. The reactant solution was centrifuged at 9,000 rpm for 5 m and the supernatant was discarded and the precipitate was taken and 25 mL of acetone was added and centrifuged at 9,000 rpm for 5 m. The purification was performed three times. Finally, the precipitate of In(Zn)P QD core was suspended in 2 mL toluene.

2.2.2 The synthesis of In(Zn)P@ZnSe@ZnS core/shell

The inner shell of In(Zn)P@ZnSe QDs was formed by dissolving Se in TOP specified below. 2.4 mmol of Zn(Ac)₂ in 4.8 mmol of OA and 10mL TOP was added and degassed at 120 °C for 1 h (~500 mTorr). The reaction temperature was raised to 180 °C under N₂, 2 mL of In(Zn)P cores synthesized previously were injected into the reaction solution and 0.72 mmol of SeTOP (in 10mL TOP) was added dropwise while raising the temperature to 320 °C and reacted for 1 h. Then, for the formation of the first outer shell of ZnS, that is, the final formation of In(Zn)P@ZnSe@ZnS core/shell, 0.8 mmol of STOP (in 10mL) were injected and reacted at 320 °C for 1h. For the formation of the second outer shell of ZnS, the reactant was cooled down to 280 °C, and 1.7 mmol of STOP (in 10mL) was injected into the reaction solution and reacted at 280 °C for 40 m. The reactant was cooled down to R∙T and centrifuged by chloroform and methanol. The experimental procedure for the synthesis of In(Zn)P@ZnSe@ZnS was shown in Fig. 1.

2.3. Characterization

UV–Vis Absorption Spectroscopy and PL emission spectra
Steady-state absorption spectra of the QD samples diluted by 1 to 3,200 times were recorded by using a UV/vis spectrometer (V670, Jasco, Japan). Steady-state PL of QDs in toluene was measured by using a fluorescence spectrophotometer (HR4000, Ocean Optics, USA) excited by 425 nm blue LED light. The sample preparation of the QDs for the transmission electron microscopy (TEM) observation was conducted by putting the

<table>
<thead>
<tr>
<th>Samples</th>
<th>In(Zn)P core</th>
<th>ZnSe shell</th>
<th>ZnS shell</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In</td>
<td>Zn</td>
<td>In/(In+Zn)</td>
</tr>
<tr>
<td>#1</td>
<td>1</td>
<td>2</td>
<td>0.33</td>
</tr>
<tr>
<td>#2</td>
<td>1</td>
<td>1</td>
<td>0.50</td>
</tr>
<tr>
<td>#3</td>
<td>2</td>
<td>1</td>
<td>0.67</td>
</tr>
<tr>
<td>#4</td>
<td>4</td>
<td>1</td>
<td>0.80</td>
</tr>
<tr>
<td>#5</td>
<td>1</td>
<td>0</td>
<td>1.0</td>
</tr>
</tbody>
</table>
3. Results

Photoluminescence spectra of In(Zn)P@ZnSe@ZnS with 0.33 of In/(In+Zn) was shown in Fig. 2(a). The synthesized QDs showed the low PL peak intensity less than 10,000 cps. However, the dilution up to 25 times the intensity increase is slow and it increased very largely up to 50,000 cps for 100 times of dilution and saturated up to 800 times and then began to decrease up to 17,000 cps for 3,200 times of dilution. The wavelength of the emitted light of QDs with no dilution was 590 nm
and decreased to 553 nm for 100 times of dilution and then did not show any change. As shown in Fig. 2 (a), the light color of the sample was green. When the contents of In/(In+Zn) was 0.5, that is, 1:1 molar ratio of In to Zn, as shown in Fig. 3, the PL intensity increased very small up to 50 times of dilution, and then increased very largely up to 50,000 cps for 100 and 200 times of dilution. After that, it decreased to 15,000 cps for 3,200 times of dilution. The wavelength of the samples decreased from 605 nm for no dilution to 566 nm for 3,200 times of dilution. The light color of the sample with 200 times of dilution was greenish yellow color, equivalent to the wavelength of 560 nm. The increase of indium contents to 0.67 of In/(In+Zn) ratio increased the emission light wavelength to 605 nm for 200 times of diluted sample. The light color under 420 nm UV light illumination was red as shown in Fig. 4. The PL intensity variations with dilution quantities showed the almost sample trend. There is a small increase of PL intensity for 25 times of dilution and then increased greatly up to 200 times of dilution and began to decrease for greater than 800 times of dilution. As shown in Fig. 5, the more increase of indium ratio to 0.8 decreased the wavelength of emitted light to 580 nm, yellow light. The PL intensity increased slightly to 2,500 cps for 100 times of dilution and then increase greatly for 200 to 1,600 times of dilution and began to decrease for greater than 1,600 times of dilution. The PL spectra of In(Zn)P@ZnSe@ZnS with 1 of In/(In+Zn) was shown in Fig. 6. This QD sample without zinc showed the red-
light emission with 613 nm of wavelength. The emitted light wavelength without dilution was 640 nm and decreased gradually to 613 nm for more than 200 times of dilution.

The absorbance spectra of the QDs with different In/(In+Zn) ratio diluted at 200 times and their corresponding PL spectra were shown in Fig 7 (a) and (b), and the photographs of QDs with 0.33, 0.5, 0.67, 0.8 and 1 of In/(In+Zn) ratio under 420 nm of UV illumination were shown in Fig. 7 (c). The absorbance peak appeared at 523 nm for 0.33 ratio, 573 nm for 0.5, 587 nm for 0.67, 536 nm for 0.8 and 470 nm for 1 In/(In+Zn) ratio. The corresponding PL emission peaks were 553, 569, 624, 581, and 612 nm, respectively. The colors of the QDs were green, yellow, red, orange, and dark red, respectively. First absorption peak wavelengths, absorbances, band edge energy ($E_{QD}$), volume of QDs ($V_{QD}$), molar extinction coefficients ($\varepsilon$), and molar concentrations (C) of QD samples were summarized in Table 2. As In/(In+Zn) ratio less than 0.67, the QDs showed the green or yellow colors at PL peak range between 550-570 nm, and their absorbance peaks increased from 535 nm for 0.33 ratio to 587 nm for 0.67 nm. For more than 0.67 ratio, PL peaks showed red color with more than 600 nm (except 581 nm for 0.8 of the ratio) and their absorbance peak decreased from 587 nm to 470 nm. (Fig. 7 (c)) As mentioned in the introduction section, Kirkwood et al [25] specifically studied of Zn location in InP.
The concentration of InP@ZnSe@ZnS QDs is determined by the absorbance of where \( L_{QD} \) is the average nanocrystal edge length, \( E_{QD} \) is the energy of band edge transition, \( E_b \) is the calculated size of 7.3 nm. However, the calculated QD crystal size is considered to be 8.65 nm. As shown in table 2, the QD crystal sizes were 7.30 nm for 0.33 of In/(In+Zn) ratio, 6.75 nm for 0.5, and the largest value of 11.14 nm for 0.67 of the ratio, and decreased to 6.85 nm for 0.8 and 4.3 nm for 1. The QD crystal size for 0.33 by TEM observation is about 10 nm, which is a little greater than the calculated size of 7.3 nm. However, the calculated QD crystal size

### 4. Discussion

#### 4.1. Size and volume of QDs

We can calculate the size of QD nanocrystals by using the following formula [26].

\[
L_{QD} = \left( \frac{C}{E_{QD} - E_b} \right)^{1/\alpha}.
\]

where \( L_{QD} \) is the average nanocrystal edge length, \( E_{QD} \) is the energy of band edge transition, \( E_b \) is the bulk band gap of InP (1.35 eV), and \( C \) and \( \alpha \) are empirically derived fitting parameters (4.25 and 0.96, respectively for a tetrahedral-shaped InP QD nanocrystal). Reference 2 assumed the particles were in almost spherical shape (Fig. 7 (d) and Fig. 8).

As shown in Table 2, the QD crystal sizes were 7.30 nm for 0.33 of In/(In+Zn) ratio, 6.75 nm for 0.5, and the largest value of 11.14 nm for 0.67 of the ratio, and decreased to 6.85 nm for 0.8 and 4.3 nm for 1. The QD crystal size for 0.33 by TEM observation is about 10 nm, which is a little greater than the calculated size of 7.3 nm. However, the calculated QD crystal size...
is considered to be 8.65 ± 1.35 nm (standard error) (Fig. 8).

4.2. Absorptivity ($\ell_i$) and molar concentration of QDs

The concentration of InP@ZnSe@ZnS QDs is determined by the absorbance of UV–Vis spectroscopy. The intrinsic absorption coefficient of a QD material, $\mu_i$, is size-independent at sufficiently short wavelengths. The absorbance ($A$) of QDs can be expressed as the Beer-Lambert equation, $A = e c l$, where $e$ is a molar attenuation (or extinction) coefficient (M$^{-1}$cm$^{-1}$), $c$ is a molar concentration (M) of QDs, and $l$ is an optical path length of cuvette (in meter scale). The absorbance of A is also expressed as $A = \ln \frac{I_0}{I}$, where $I_0$ is an intensity of incident light and $I$ is that of transmitted light. The absorbance can be shown as $A = \frac{\mu_i f l}{\ln 10}$, where $f$ is a volume fraction of QDs. $\mu_i$ is related to the wavelength ($\lambda$)-dependent optical constants, including the real ($n$) and imaginary ($k$) parts of the refractive index of ZnSe and the local field factor $|f_{LF}|$, as well as the refractive index of the surrounding medium ($n_i$) [26].

$$\mu_i = \frac{2\pi}{n_A l_0} |f_{LF}|^2 2n_QD k_{QD},$$

$$|f_{LF}|^2 = \frac{9n_i^4}{(n^2-k^2+2n^2)^2+4(nk)^2)}.$$

Comparing to Beer-Lambert’s law, the molar extinction coefficient, $e$, from this intrinsic absorption coefficient is expressed as following equation.

$$e = \frac{N_A V_{QD}}{1000ln10} (f_{InP}\mu_{InP} + f_{ZnSe}\mu_{ZnSe}),$$

where $N_A$ is the Avogadro number, $V_{QD}$ is the average volume of the In(Zn)P@ZnSe@ZnS QDs, and $\mu_{InP}$ is $8.5 \times 10^4$ cm$^{-1}$ at 413 nm and $\mu_{ZnSe}$ is the intrinsic absorption coefficient of ZnSe.

**Fig. 8.** Scanning electron microscopy and energy-dispersive X-ray spectroscopy mapping images of In(Zn)P@ZnSe@ZnS QDs.
Table 3. Photoluminescence wavelengths and intensities, FWHM and absorbance of In(Zn)P@ZnSe@ZnS QDs with varying molar ratios of In/(In+Zn).

<table>
<thead>
<tr>
<th>Samples</th>
<th>In/(In+Zn)</th>
<th>Molar ratio</th>
<th>PL peak</th>
<th>Intensity</th>
<th>FWHM</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td></td>
<td>0.33</td>
<td>553</td>
<td>55,751</td>
<td>43</td>
<td>0.1857</td>
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<tr>
<td></td>
<td></td>
<td>571</td>
<td>36,179</td>
<td>45</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>559</td>
<td>57,611</td>
<td>44</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mean (95%, k = 2)</td>
<td>561 ± 23</td>
<td>49,847 ± 29,494</td>
<td>44 ± 2.5</td>
<td>0.0926</td>
<td></td>
</tr>
<tr>
<td>#2</td>
<td></td>
<td>0.5</td>
<td>569</td>
<td>50,782</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>560</td>
<td>13,441</td>
<td>42</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>551</td>
<td>28,507</td>
<td>49</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mean (95%, k = 2)</td>
<td>560 ± 22</td>
<td>30,910 ± 46,667</td>
<td>48 ± 13</td>
<td>0.2097</td>
<td></td>
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<tr>
<td>#3</td>
<td></td>
<td>0.67</td>
<td>574</td>
<td>19,663</td>
<td>41</td>
<td>0.2097</td>
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<tr>
<td></td>
<td></td>
<td>600</td>
<td>54,083</td>
<td>56</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>624</td>
<td>47,526</td>
<td>66</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Mean (95%, k = 2)</td>
<td>599 ± 62</td>
<td>40,424 ± 45,400</td>
<td>54 ± 31</td>
<td>0.3101</td>
<td></td>
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<tr>
<td>#4</td>
<td></td>
<td>0.8</td>
<td>556</td>
<td>22,435</td>
<td>53</td>
<td>0.3101</td>
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<tr>
<td></td>
<td></td>
<td>579</td>
<td>22,402</td>
<td>49</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mean (95%, k = 2)</td>
<td>568 ± 146</td>
<td>22,418 ± 210</td>
<td>51 ± 25</td>
<td>1.15844</td>
<td></td>
</tr>
<tr>
<td>#5</td>
<td></td>
<td>1</td>
<td>612</td>
<td>17,704</td>
<td>43</td>
<td>1.15844</td>
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<tr>
<td></td>
<td></td>
<td>601</td>
<td>15,998</td>
<td>47</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mean (95%, k = 2)</td>
<td>607 ± 70</td>
<td>16,851 ± 10,838</td>
<td>45 ± 25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

QD, quantum dot.

InP at 413 nm. We adopted $5.0 \times 10^4 \text{ cm}^{-1}$ (theoretical value) of $\mu_{\text{InP}}$ at 420 nm, $f_{\text{InP}}$ and $f_{\text{ZnSe}}$ is volume fractions of InP and ZnSe of core/shell components of QDs, where the values $f_{\text{InP}}$ and $f_{\text{ZnSe}}$ were adopted as 0.037 and 0.963, respectively in the...
reference [4]. The molar extinction coefficient of QDs were in the range of 2.25–9.70 × 10^6 M^−1 cm^−1 and the molar concentration were between 20 and 137 nM. The concentrations were of the diluted QDs by 200 times, and so the as-synthesized molar concentration was calculated to be between 4-27 μM.

4.3. Förster Resonance Energy Transfer (FRET) effects of QDs

Fluorescence resonance energy transfer (originally Förster resonance energy transfer; FRET) is energy transfer from donor to acceptor, In(Zn)P@ZnSe@ZnS QDs fluorophore and oleic acid in this paper. The FRET efficiency (E) depends on many physical parameters such as (1) the distance between the donor and the acceptor, (2) the spectral overlap of the donor emission spectrum, and (3) the relative orientation of the donor emission dipole moment. In this study, the acceptor of oleic acid is not a fluorophore and so it plays only as an energy transfer path for the donor the QDs to lipid organics. The rate of energy transfer (k_FET), can be expressed like the following equation.

\[ k_{FET} = \left( \frac{R_0^6}{r} \right) \frac{1}{\tau_D} \]

where \( k_{FET} \) is the Förster distance of this pair of donor and acceptor, \( \tau_D \) is the donor’s fluorescence lifetime in the absence of the acceptor, \( R_0 \) being the Förster distance of this pair of donor and acceptor, i.e. the distance at which the energy transfer efficiency is 50% and \( r \) is the distance between donor and acceptor [27].

\[
R_0^6 = \frac{9000 \ln(10) Q_D k^2}{128 \pi^5 n^4 N_A} \int_0^\infty F_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda / \int_0^\infty F_D(\lambda) d\lambda
\]

\[
R_0^6 = 8.79 \times 10^{-28} n^{-4} Q_D k^2 f(\lambda) cm^6
\]

where \( Q_D \) is the fluorescence quantum yield of the donor in the absence of the acceptor, \( k^2 \) is the dipole orientation factor, \( n \) is the refractive index of the medium, \( N_A \) is the Avogadro constant, \( \epsilon_A(\lambda) \) is the acceptor molar extinction coefficient, and \( f(\lambda) \) is the spectral overlap integral calculated as

\[
\int_0^\infty F_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda / \int_0^\infty F_D(\lambda) d\lambda
\]

Here, we use hexane as a medium with refractive index 1.33 and \( Q_D \) is 0.4 and \( \epsilon_A(\lambda) \) is 1.14x10^4 mol^−1 cm^−1, the wavelength of In(Zn)P@ZnSe@ZnS emission is 540 nm, then we obtained \( R_0 \) as 47.6 nm. The molar concentration of QDs calculated by Beer-Lambert law was about 5 μM, that is, 5 nmol/mL. It means that the number of QDs was 3.0 × 10^15 ea/mL and the average distance between neighboring QDs is calculated as about 70 nm. In our study, the quenching effect by FRET appeared at less than 100 dilution, 50 nM, where the neighboring distance is 7 μm, as shown in Fig. 9.

5. Conclusions

In our study, we discussed effects of the ratio of In/(In+Zn) to the PL and UV-Vis. absorption properties of In(Zn)P@ZnSe@ZnS QDs. The PL light of the QDs with the ratio of more than 2/3 indium is red color and the PL lights of the QDs with less than 2/3 of In ratio show green and yellow colors. The brightest red PL properties of the QDs can be obtained for 2/3 ratio of In/(In+Zn) with the largest crystal size. The FRET quenching effects of the QDs suppress the PL intensities with less than \( R_0 \) 70 nm calculated FRET equation. The dilution of QDs solution by more than 100 times with about 50 nmol/mL does not show FRET phenomenon with the distance of 7 μm between the neighboring QDs.

Conflict of Interest Declaration

The authors declare no competing financial interests or personal relationships.

Author Information


Acknowledgments

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References


