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Optimization of the recipe for the synthesis of CuInS$_2$/ZnS nanocrystals supported by mechanistic considerations

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Abstract: CuInS$_2$/ZnS (CIS/ZnS) quantum dots (QDs) with high photoluminescence (PL) were synthesized via a facile solvothermal approach. Gaussian deconvolution of PL spectra, transmission electron microscopy, and time-resolved PL spectroscopies were used to characterize the emission properties of the prepared CIS and CIS/ZnS QDs. It was found that the growth of ZnS can reduce the surface defect acting as traps to minimize donor-acceptor emissions, and the contribution of band to donor/acceptor transition becomes a dominating emission with the increase of shell growth time. The blue shift of PL emission wavelength of CIS/ZnS QDs underwent two steps: the dramatic blue shift originated from the decreased fraction donor-acceptor transition due to the reduction of surface defects at the beginning and the subsequently mild blue-shift with the time from the interdiffusion of CIS and ZnS. The effect of trioctylphosphine (TOP) and dodecanethiol (DDT) as ligands during shell growth on the optical properties of QDs were investigated and compared. The PL quantum yield (QY) of CIS core affects the final value of CIS/ZnS QDs, and the higher PL QY is achieved while using CIS core with higher PL QY. Based on the selected ligand DDT, the reaction parameters, such as CIS core reaction time, shell growth time, and Zn/Cu feed molar ratio, were further optimized. CIS/ZnS QDs with high PL QY can be obtained with a Zn/Cu feed molar ratio larger than 4, shell growth time of 30 to 90 min, and shell growth temperature 220$^\circ$C–240$^\circ$C, and the maximum value was up to about 80% by adjusting the above-mentioned parameters.

Keywords: core/shell; CuInS$_2$; ligands; process optimization; quantum dots.

1 Introduction

In the past decade, types II-VI and IV-VI semiconductor nanocrystals (so-called quantum dots, abbreviated as QDs) such as CdSe, CdTe, and PbSe and their alloys have been intensively studied due to their appealing optical properties such as narrow emission bands, emission wavelength tunability with size, and photostability [1]. They have promising applications in solar cells [2–4], heat electrical application [5], light-emitting diodes (LED) [6, 7], sensors [8], fluorescent probes [9, 10], biolabeling [11], anticontroling [12], etc. However, the intrinsic toxicity of QDs containing heavy metals (e.g. Cd, Pb, Se, and Te) awoke environmental and healthcare concerns. Recently, many researchers turned their attention to the type I-III-VI semiconductor nanocrystals, in particular, CuInS$_2$ (CIS), which is presently the most attractive and lesser toxic alternative combination [13]. CIS is direct band-gap ternary semiconductor with low toxicity, high optical absorption coefficients ($10^5$ cm$^{-1}$) [14], and high photochemical stability [15].

Several independent approaches for CIS synthesis were reported, for example, solvothermal synthesis [16], single-source precursor routes [17], and hot injection techniques [18, 19]. An overview of the chemical synthesis methods for CIS or ternary compounds has been published by Kolny-Olesiak and Weller and Aldakov et al. [20, 21]. All of them produce high-quality CIS QDs in terms of monodispersity, crystallinity, and high photoluminescence (PL) efficiency. Recently, Tian et al. [22] developed a cost-efficient continuous process for the synthesis of core CIS based on microreaction technology, and the obtained maximum PL quantum yield (QY) was
about 28%. However, the PL QY of pure CIS nanoparticles is still far from commercial applications. To improve the PL QYs of CIS nanoparticles, ZnS is typically used as a shell to decrease CIS surface defects that can trap exciton, thus inducing a nonradiation transition. Several methods aiming at the growth of ZnS shell were developed, and the process parameters such as reaction time of CIS core, shell growth time, Cu/In feed ratio, Zn/Cu feed ratio, and types of shell were studied and optimized to improve the PL QY of QDs [22–26]. Different types of ligands were used in the synthesis of CIS/ZnS QDs by several groups. For examples, the group of Reiss [23] used 1-dodecanethiol (DDT) and dimethylformamide (DMF) as ligands in the growth of ZnS shell, and the maximum PL QY was obtained at a core reaction time of 20 min (at 230°C) and shell growth time of 30 min. Li et al. improved the PL QY of CIS selecting CdS and ZnS as shell and using zinc stearate (cadmium oleate) with S-trietylphosphine (TOP) for shell growth, and the PL QYs of up to 67% CIS/ZnS and 86% CIS/CdS QDs were obtained by optimizing the shell growth time [24]. Li et al. used DDT and paraffin liquid as ligands for ZnS shell growth at 260°C and obtained CIS/ZnS QDs that exhibited the maximum PL QY of about 81% [25]. The researches on the Cu/In ratio for adjusting PL emission wavelength and PL QY were also studied by different groups [26–28]. Hua et al. studied the effect of Cu/In feed ratio to PL emission wavelength and PL QYs of CIS/ZnS using oleic acid (OA) as ligands during ZnS shell growth. The PL emission wavelength showed the blue-shift properties with the decrease of Cu/In ratio (from 1 to 1/9), and the PL QY of CIS/ZnS was up to 40% at a Cu/In ratio of 1/6 [26]. Chuang et al. varied the Cu/In ratio to adjust the PL emission wavelength and QY of CIS core and synthesized CIS/ZnS QDs using DDT as ligands during ZnS shell growth, and the maximum PL QY can be obtained up to 81% at a Cu/In ratio of 1/2 [27]. As seen from the above literature review, the PL QYs of CIS/ZnS QDs seem to be sensitive to ligands aside from the mentioned parameters.

The type and concentration of the ligands have an important impact on not only optical properties but also morphology. CIS or CIS/ZnS QDs with spherical, triangle, rod-like, hexagonal, and spindle shapes were synthesized using different ligands such as TOP, oleylamine (OLA), DDT, DMF, OA, and tri-octylphosphine oxide (TOPO) [22–32]. Until now, the PL QYs of CIS/ZnS in the reach stage have been up to more than 80% [24, 25, 27, 33]. Castro et al. [17] reported a difference in the PL QY of two orders of magnitudes when applying different ligands. The strong effect on the optical properties has been assigned to the large number of defects on the surface of nanocrystals that provide a source of defects or unpassivated sites where nonradiative recombination takes place. Even the same type of ligands with different chain length or group numbers would impact the result. Michalska et al. [29] synthesized CuInZnS_{2+x} QDs with amines (OLA, dioctylamine, dodecylamine, and octadecylamine) as ligands during ZnS shell introduction. The PL emission wavelength can be adjusted from 590 to 690 nm by changing amines, reaction temperature, and time. The maximum PL QY of about 70% of CuInZnS_{2+x} was achieved using dioctylamine, and the PL QY of 22% with pyramidal shape was achieved using OLA. The effect of ligands with different types on the optical properties of CIS/ZnS was not compared in detail. Therefore, systematic studies on the effect of parameters and optimization would be necessary to improve the PL QY of nanoparticles for the preparation of future large-scale production.

Unlike traditional II-VI group QDs, CIS nanoparticles exhibit broad bandwidth [full-width at half-maximum (FWHM)] of emission and have no obvious band edge absorption [16, 17]. Furthermore, the PL peak wavelength of CIS/ZnS has a blue shift compared to CIS QDs [23, 24, 34]. The resulting optical properties of CIS QDs were defined as defect emissions [17, 35]. The PL emission of CIS/ZnS was studied by several groups as different explanations: Kraatz et al. suggested indium-copper antisite (In\(\cdot\cdot\cdot\)) to valance band emission [36], Nam et al. explained that the PL emissions originated from two aspects: In\(\cdot\cdot\cdot\) to copper vacancy (V\(\cdot\cdot\cdot\)) combination and conduction band to V\(\cdot\cdot\cdot\) [37]. Hua et al. studied the PL properties using steady-state and time-resolved PL spectroscopy analysis and found that the recombination of intrinsic defects inside QDs including donor-acceptor emission and a quantized conduction band to defects are the main contribution [26]. In addition, the PL blue-shift property of CIS/ZnS had been discussed by several groups and explained that Cu\(^{+}\)/In\(^{x-}\) and Zn\(^{+}\) cation exchange induced the reduction of CIS core size during the growth of ZnS shell [18, 25], CIS surface reconstruction [23], etching of the plain core materials [24], or the interdiffusion of CIS and ZnS [34, 35]. Therefore, the physical model of PL mechanism for CIS and CIS/ZnS core/shell QDs deserves further discussion, and the purpose is to better understand the emission nature of QDs to serve as a guide to optimize the recipe or process in achieving the desired quality such as defined PL wavelength and high PL QY.

In the present work, a facile and scalable method for synthesizing CIS/ZnS QDs using DDT and TOP as ligands during ZnS shell growth was developed. The PL emission
mechanism of CIS and CIS/ZnS was investigated based on the deconvolution of PL spectra by Gaussian function, transmission electron microscopy (TEM), and energy levels and transitions of CIS QDs. The effect of different ligands on the improvement of PL QY of QDs were investigated, and the effects of core reaction time, shell growth time and temperature, and the Zn/Cu feed molar ratio to optical properties of the CIS/ZnS QDs were systematically studied based on selected DDT ligands. Based on the analysis of the reaction mechanism and the optimization of reaction conditions, the suitable operational condition and the methodology for further improving PL QY of samples were put forward. Different from other reports summarized in the reference list, which usually address the relationships between the structure of the nanoparticles and the optical properties, this paper is focused on the research of the effect of different types of ligands on CIS/ZnS growth and the development of the operational characteristics as basis for large-scale production. The information concerning the extensive characterization of the developed material is presented in the supporting papers [38, 39].

2 Materials and methods

2.1 Chemicals

Zinc acetate (99.9%) and zinc diethyl dithiocarbamate (ZDC) were purchased from Tokyo Chemical Industry Co., Ltd. Copper(I) acetate (CuOAc; 99%) and indium acetate [In(OAc)₃; 99.99%] were purchased from ABCR. ZDC (99.9%) was purchased from Tokyo. DDT (97%) was purchased from Acros. Octadecene (ODE; 90%) and TOP (90%) were purchased from Alfa. The chemicals were directly used without further purification.

2.2 Synthesis of CIS QDs

The synthesis procedure was derived from the Zhong et al. method for CIS QD synthesis [16]. CuOAc (0.60 mmol) and In(OAc)₃ (0.60 mmol) were mixed with 15 ml ODE and 1.5 ml DDT in a 100 ml three-necked flask under N₂ atmosphere. The mixture was degassed for 30 min by magnetic stirring and then heated to the reaction temperature of 240°C with a rate of 19–20 K/min. After keeping the mixture at the reaction temperature for 1–180 min, the heating source was removed and the CIS solution was formed. CIS QDs were precipitated by adding three equivalents of acetone/isopropanol (1:4, v/v) mixture and stirred for 3 h and then centrifuged at 9000 rpm for 20 min. The obtained CIS core QDs were redispersed in toluene. Such precipitation/dispersion cycle was repeated at least twice to eliminate unreacted reactants, by-products, excess ligand, and solvent ODE. The CuOAc and In(OAc)₃, feed molar ratio (Cu/In feed molar ratio) was fixed at 1 in all experiments.

2.3 Synthesis of CIS/ZnS QDs

The Zn precursor solution was prepared by dissolving a certain amount of zinc acetate in the mixture of 3 ml of ligands (DDT or TOP) and 6 ml ODE. The zinc acetate and CuOAc feed molar ratio (Zn/Cu feed molar ratio) was adjusted from 1 to 8. Then, the ZnS precursor solution was rapidly added into the above CIS solution without any purification step. The shell growth temperature was in the range of 220°C–240°C. The samples were syringed out at the expected shell growth time. The purification of CIS/ZnS QDs was carried out in the same way as described for CIS core QDs. Whereas TOP was selected as ligand, ZDC was used as Zn and S source. The ZDC and CuOAc feed molar ratio was 4.

2.4 Characterization

The UV-visible absorption spectrum of CIS core and CIS/ZnS QDs was measured using a UV-visible spectrophotometer (Varian, USA). The sample was diluted to toluene until the absorption value of the QDs was about 0.05 at 485 nm. The PL spectrum of the QDs was measured using a spectrofluorometer (Cary Eclipse, Varian) at an excitation wavelength of 485 nm. The PL QYs of the QDs were determined by comparing their integrated emissions to that of the standard dye of rhodamine B with a known PL QY of 97% in ethanol solution. The PL lifetime was studied with time-resolved PL excited at 440 nm pulses at a 500 kHz repetition rate and detected with a time-correlated single-photon counting system. The shape and size of the samples were observed using TEM (CM20, Philips).

3 Results and discussion

3.1 Synthesis of CIS core particles

The amount of Cu/In ratio could change the band gap of CIS. The wider band-gap was found in more Cu-deficient CIS QDs, which has been already discussed [27, 28]. In the present study, the Cu/In feed molar ratio was fixed at one in CIS and later CIS/ZnS synthesis according to stoichiometry. Depending on the reaction time, the Cu/In molar ratio of particles could differ from the feed molar ratio, which has been discussed and published by us in another paper and would not be discussed again here [38]. The absorption and emission spectra of CIS QDs that were excited at 485 nm are presented in Figure 1A and B. These QDs were synthesized at 240°C and syringed at different reaction times. The broad absorption spectra had no obvious exciton band and absorption for wavelengths longer than 350 nm. The emission spectra were bell shaped, with the peaks that had a maximum intensity at wavelengths ranging between 650 and 710 nm. The wavelength of the maximum PL intensity and its value strongly depend on reaction time. This
dependency has been quantitatively evaluated in Figure 1C. PL QY exhibits a clear maximum of about 6% for the synthesis time of 60 min. Obviously, there is a need for a further improvement of the synthesis of core nanoparticles, as higher yields have been reported, usually up to 10% [18, 23, 34], but also extraordinary high values of 28% [22]. The wavelength of this maximum amounted to about 654 nm (i.e. CIS core particles emitted at maximum with the red color). Up to the point of the maximum QY, the corresponding wavelength was almost constant but increased strongly for synthesis times above 60 min. Similar dependence (i.e. shift of the emission spectra to longer wavelengths with growing synthesis time) has been reported for CIS QDs, also when applying other recipes [16, 23]. This dependency has been explained by the growing size and reduced confinement effect. During the precipitation of CIS QDs, large amounts of unsaturated and dangling bonds (so-called defects) were formed on the surface of the nanoparticles. In turn, electron and hole can be trapped in these defects. Therefore, only a small fraction energy was converted to photon emission during the electron and hole recombination, but most of them are consumed as nonradiation transition. In consequence, in general, the QY of CIS QDs is quite low. However, this explanation is not sufficient to explain the maximum QY, which has been observed also in other studies [23]. Obviously, there are two effects that have to be taken into account. Primarily, the QY is increasing because, with the increasing time, the defects in the lattice that were generated in the precipitation phase could be healed and the density of the defects on the surface was reduced with the growth of particle size. Therefore, the faction of nonradiation transition was reduced. On the contrary, at long reaction times, the thermal decomposition of ligands becomes a problem. The additional defects generated from the decomposition products increased the nonradiation recombination again. This agrees with the interpretation by Klimov et al. that low PL QY with competitive nonradiative pathways is related to surface states [40].

To get a better understanding of the effect of the reaction time on the quality of QDs, the PL spectra were deconvoluted. Because the spectra were unsymmetrical, it has been assumed that there were at least two sources of emission. To identify them, each spectrum was fitted with Gaussian functions. Different from other studies [23], where three characteristic wavelengths were identified (660, 713, and 806 nm), two functions were sufficient to get a good description of the spectra (Figure 2). This result indicates that there are two dominating mechanisms of the emission. Take CIS samples synthesized at 60 min, for example, the left peak with the dominating wavelength of about 640 nm and the right peak with the wavelength of about 690 nm. To clarify the attribution of each emission, the emission of CIS QDs was investigated. The particle size (±standard deviation) of CIS QDs was about 3.6±0.4 nm as shown in Figure 3. The size-dependent band gap of samples can be calculated according to the finite-depth-well effective mass approximation model calculation [41, 42]. The band gap is about 2 eV (620 nm), which is not obviously fitting the PL wavelength.

Literature information [17, 20, 21, 43–47] on the different mechanisms of emissions can be compiled into the comprehensive emission model presented in Figure 4. As shown in Figure 4, besides excitonic emission [1(a), 1(b) and (2)], defects such as atom vacancy (V_Cu′·), V_in′′·, V_in′′′·), indium or copper interstitial (In_i·, Cu_i·), and indium-copper antisite (Cu_in″·, In_cu″·) can also generate emission through the recombination with band (conduction or valence band) or between defects. These can be assigned as defect-related emissions. Based on the energy level difference to conduction or valence band, the PL emission wavelength with different energy levels of CIS QDs synthesized at 240°C for 60 min was calculated and summarized in Table 1. By comparing the wavelength at
640 nm and the wavelengths calculated for the different energy levels, it seems that this peak was in the range of the bound excitonic emission (633–635 nm) or band to donor/acceptor emission (631–689 nm). Considering that the FWHM is comparably broad (about 95 nm) and that excitonic emissions are seldom observed in QDs with a high number of defects [43], it can be postulated that this peak can be associated to band to donor/acceptor emission [energy level of 3(a–d)]. Correspondingly, the peak with the dominating wavelength of 690 nm represents the donor-acceptor emission [energy level of 4(a–d)]. In addition to both peaks, a slight red shift can be observed. However, the most intriguing is the strong change of the intensity ratio (left peak/right peak) as a function of the reaction time; for example, when the synthesis time increased from 30 to 120 min, the intensity ratio decreased from 0.97 to 0.23. The changing tendency of intensity ratio of two peaks proved that the donor-acceptor emission had an increasing contribution with the increase of reaction time. In total, it can be concluded that the emission of CIS QDs is mainly from band to donor/acceptor emission and donor-acceptor emission, and the donor-acceptor emission is the main contributor for materials synthesized at a long reaction time (>60 min). This observation is aligned with the result published by Castro et al. who also postulated that the donor-acceptor emission was a dominating mechanism for CIS QDs [17].

### 3.2 Shell synthesis

To improve the QY, the surface of CIS nanoparticles is usually coated with ZnS shell, which has a wider band and can confine both electrons and holes in the core. CIS/ZnS QDs were synthesized at 240°C for 60 min for core and at 220°C. A Zn/Cu feed molar ratio of 8 was selected as an initial study to ensure enough ZnS thickness for reducing the surface defects of CIS core, which would be studied and discussed later. The absorption and PL spectra of obtained samples are presented in Figure 5.
In agreement with previous reports, ZnS shell improved the intensity of absorption and emission [23–39]. The dependence of the PL intensity was no more monotonic; for example, it exhibited a maximum at the synthesis time of about 60 min with improved QY of 65.5%. Contrary to the dependence reported for core synthesis, the increased reaction time during the shell growth was accompanied by a blue shift. Furthermore, the emission bandwidth was not significantly narrowed. The broad FWHM and blue-shift properties of CIS/ZnS PL emission were different from the reported narrow FWHM and red-shift properties of CdSe and CdS QDs because of excitonic emissions [9, 48, 49].

Similar to core particles for the CIS/ZnS ones, a Gaussian deconvolution of the PL intensity spectra has been performed (Figure 6). It is interesting that the

Table 1: PL emission and their assignments of CIS QDs calculated based on energy levels.

<table>
<thead>
<tr>
<th>Emission types</th>
<th>Transition</th>
<th>Energy level</th>
<th>E_g/MeV</th>
<th>E_m/MeV</th>
<th>λ/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free exciton emission</td>
<td>Free exciton emission</td>
<td>(1a)</td>
<td>2000</td>
<td>1998</td>
<td>621</td>
</tr>
<tr>
<td>Free exciton emission</td>
<td>Free exciton emission</td>
<td>(1b)</td>
<td>2000</td>
<td>1980</td>
<td>626</td>
</tr>
<tr>
<td>Bound exciton emission</td>
<td>Bound exciton emission</td>
<td>(2)</td>
<td>2000</td>
<td>1958–1954</td>
<td>633–635</td>
</tr>
<tr>
<td>Band to donor/acceptor emission</td>
<td>V^− to valence band</td>
<td>(3a)</td>
<td>2000</td>
<td>1965</td>
<td>631</td>
</tr>
<tr>
<td>Conduction band to V^−−−</td>
<td>(3b)</td>
<td>2000</td>
<td>1850</td>
<td>670</td>
<td></td>
</tr>
<tr>
<td>Conduction band to V^−−− or Cu^+</td>
<td>(3c)</td>
<td>2000</td>
<td>1800</td>
<td>689</td>
<td></td>
</tr>
<tr>
<td>In^−−− or In^−−− to V^−−−</td>
<td>(3d)</td>
<td>2000</td>
<td>1922</td>
<td>645</td>
<td></td>
</tr>
<tr>
<td>Donor-acceptor pair</td>
<td>V^−−− to V^−−−</td>
<td>(4a)</td>
<td>2000</td>
<td>1815</td>
<td>683</td>
</tr>
<tr>
<td>V^−−− to V^−−− or Cu^+</td>
<td>(4b)</td>
<td>2000</td>
<td>1765</td>
<td>703</td>
<td></td>
</tr>
<tr>
<td>In^−−− or In^−−− to V^−−−</td>
<td>(4c)</td>
<td>2000</td>
<td>1772</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>In^−−− or In^−−− to V^−−− or Cu^+</td>
<td>(4d)</td>
<td>2000</td>
<td>1722</td>
<td>720</td>
<td></td>
</tr>
<tr>
<td>Deep donor-deep acceptor</td>
<td>Cu^−−− to V^−−−</td>
<td>(5)</td>
<td>2000</td>
<td>1394</td>
<td>890</td>
</tr>
</tbody>
</table>

Figure 5: (A) Absorption, (B) PL spectra, and (C) PL QY and emission wavelength evolution of CIS/ZnS QDs.

CIS core was synthesized at 240°C for 60 min, and the growth of ZnS shell was synthesized at 220°C and a Zn/Cu feed molar ratio of 8.

In agreement with previous reports, ZnS shell improved the intensity of absorption and emission [23–39]. The dependence of the PL intensity was no more monotonic; for example, it exhibited a maximum at the synthesis time of about 60 min with improved QY of 65.5%. Contrary to the dependence reported for core synthesis, the increased reaction time during the shell growth was accompanied by a blue shift. Furthermore, the emission bandwidth was not significantly narrowed. The broad FWHM and blue-shift properties of CIS/ZnS PL emission were different from the reported narrow FWHM and red-shift properties of CdSe and CdS QDs because of excitonic emissions [9, 48, 49].

Similar to core particles for the CIS/ZnS ones, a Gaussian deconvolution of the PL intensity spectra has been performed (Figure 6). It is interesting that the
donor-acceptor emission peak that was dominating in core particles was strongly suppressed after the shell synthesis step, that is, it had a minor effect on the spectrum after 5 min of the shell synthesis and disappeared completely after 15 min. This indicated a high-quality material, as other researchers reported a two peak distribution also for the coated nanoparticles [23]. In addition to the left peak, a blue shift can be observed (see Table 2). The PL emission intensity increased significantly and the distribution of the PL intensity of core/shell nanoparticles could be well described with one Gaussian function, which indicated that the traps of \( V_{\text{In}}^- \), \( V_{\text{Cu/In}}^- \), \( \text{In}^- \) and \( \text{In Cu}^- \) were passivated by ZnS; therefore, the faction of donor-acceptor emission and nonradiative transition was significantly reduced, and band to donor/acceptor emission became a dominating mechanism for CIS/ZnS nanoparticles. The similar result was also published by Li et al. who studied the emission of CIS/ZnS QDs through time-resolved spectroscopic analysis [23, 24, 26]. They postulated that the dominating mechanism involves the transition from a conduction band to a defect (surface defect or internal defect).

### 3.3 Blue-shift effect

In Figure 5, the continuous blue-shift as a function of the reaction time in the shell growth phase could be observed. This phenomenon has been also reported by other researchers [22–26]. This effect seems to be specific for ZnS shell because, for the overcoating with CdS, a red shift has been reported [24]. To get a better understanding of this effect, additional studies have been performed. Figure 6 shows the emission wavelength of CIS/ZnS QDs prepared at different shell growth temperatures and Zn/Cu feed molar ratios. The CIS/ZnS QDs used for this analysis were synthesized according to the recipe described in the experimental section, but ZDC was used as a starting material for zinc and sulfur. Because ZDC can decompose at comparable low temperature (at above 150°C) [50], the interdiffusion of core and shell should not occur at such low temperature. Figure 7 shows that at the beginning of shell growth the PL emission wavelength undergoes a dramatic blue-shift. For example, at a shell growth temperature of 150°C and a Zn/Cu feed molar ratio of 2, the PL emission wavelength had a blue shift about 20 nm from 657 to 637 nm at 5 min and then was kept constant. When the Zn/Cu feed molar ratio was increased to 8, the same dependence was observed. The total blue-shift of the PL emission wavelength was about 36 nm, which is larger than that of the samples prepared at a Zn/Cu feed molar ratio of 2, that is, the blue shift increased with the growing Zn/Cu feed molar ratio. Similar dependence (i.e. a steep decrease of the wavelength in the first few minutes) has been observed at all temperatures. The main reason for the blue shift at the first few minutes is most likely due to the passivation of the surface defects. The passivation by means of ZnS reduced the fraction of donor-acceptor emission with a lower energy level; therefore, the band to donor/acceptor emission with a higher energy level became dominating. Therefore, the fast blue-shift was observed.

However, at higher temperatures and high Zn/Cu feed molar ratios, the changes were not completed in the first 5 min. As the temperature was increased to 180°C, the shell growth rate increased and induced an even larger blue-shift of PL emission peak at the same growth time (i.e. the PL emission wavelength went through a fast decrease from 657 to 617 nm at 5 min) and then gradually decreased to 593 nm after 90 min. The total blue-shift of the emission peak was about 64 nm and by almost 300% compared to that measured at 150°C. Obviously, at these conditions, not only surface passivation happened but also other processes have been activated. The most probable condition is the diffusion of Zn toward the core of QDs and reaction with the material of core. When Zn atoms gradually diffused to CIS core, it led to the decrease of core size, which

<table>
<thead>
<tr>
<th>Shell growth time</th>
<th>Peak wavelength (nm)</th>
<th>Peak intensity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Left peak</td>
<td>Right peak</td>
</tr>
<tr>
<td>5 min</td>
<td>623</td>
<td>704</td>
</tr>
<tr>
<td>10 min</td>
<td>620</td>
<td>706</td>
</tr>
<tr>
<td>15 min</td>
<td>617</td>
<td>–</td>
</tr>
<tr>
<td>60 min</td>
<td>594</td>
<td>–</td>
</tr>
</tbody>
</table>

Figure 7: Temporal evolution of the PL wavelength of CIS/ZnS QDs at different reaction conditions. CIS QDs were prepared at 240°C for 60 min; CIS/ZnS QDs were prepared at different shell growth temperatures and Zn/Cu feed molar ratios.
induced an additional blue-shift. This interdiffusion between core and shell was also proven by us through another analysis such as inductively coupled plasma-optical emission spectroscopy and X-ray photoelectron spectroscopy [38]. This mechanism has been also postulated by other researchers [18, 25, 34, 35]. In summary, the blue shift of CIS/ZnS PL emission wavelength is the contribution of surface passivation by ZnS and CIS core size reduction due to the interdiffusion of CIS and ZnS.

### 3.4 PL dynamics

The PL dynamics of the CIS QDs before and after ZnS shell growth further proved our deduction on the emission nature of CIS and CIS/ZnS QDs. Figure 8 shows that the temporal decay of the samples showed biexponential function. The decay curves were fitted accordingly with \( I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \), wherein \( \tau_1 \) and \( \tau_2 \) are slow decay and fast decay and \( A_1 \) and \( A_2 \) are decay component accordingly. The average PL lifetime of nanoparticles can be calculated according to equation: \( \tau_{\text{average}} = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1 + A_2 \tau_2) \) [51]. The PL relaxations of the samples could be decomposed into fast and slow decay components. Table 3 records the data from TRPL. It seems to be a characteristic feature of the CIS nanoparticles that single exponential fitting does not work [24, 52]. The fast decay component was with a time constant \( \tau_1 = 16 \) ns and contributed 18.2% to the whole emission profile in CIS QDs. The slow decay component was with a time constant \( \tau_2 = 115.5 \) ns and contributed 81.8% to the emission. After growth with ZnS, the fast decay component was suppressed and had a constant 23 ns with a contribution of 4.4% to the emission, whereas the slow decay had a constant 169 ns with a contribution of 95.6% to the PL emission. The decay times of both spectral components were very long compared to that of the excitonic transition, which rules out the assignment of these bands to originate from the exciton-related emissions [52]. The suppression of fast decay and improvement of PL efficiency suggests the decrease of the number of defects. The fast decay was assigned to nonradiation transition that was largely eliminated by ZnS growth and so can be associated with a surface state. The other slow decay was dominated after ZnS growth, meaning that it originated from band to donor/acceptor or donor-acceptor emission [24, 53]. Both time constants determined in this study for the fast and slow decays as well as the time scale of the decay agree well with other studies [24, 52, 53].

### 3.5 Effect of ligands

In the published papers, the CIS and CIS/ZnS QDs with high PL QY were easily achieved while DDT was introduced into the system [23, 25, 26]. The result was different from other QDs such as CdSe, CdS, and InP using TOP, amine, and OA as ligands. Here, TOP was also introduced as a ligand during ZnS shell growth to compare the result to that of DDT. CIS core was synthesized at 240°C and 60 min, and ZnS shell growth was conducted at 200°C with a Zn/Cu feed molar ratio of 4. The ligand concentration was 13% (according to the volume ratio in total solution). The PL emission wavelength and PL QY of CIS/ZnS QDs are presented in Figure 9. The PL emission wavelength of samples shifted to shorter wavelengths with the shell growth time using either DDT or TOP. While TOP was used as a ligand, the PL emission wavelength of samples decreased from 657 to 557 nm at the time of 120 min, a total blue-shift of about 100 nm. However, while DDT was used, the PL emission wavelength had a total blue-shift of about 40 nm at the same shell growth time. This result differed from the measurements of Castro et al. who have not observed any significant effect of the ligands on the characteristic wavelengths [17]. The difference of blue shift is possibly due to the different particle growth rates with various ligands. Typically, the nanoparticles are in a thermal dynamic metastable state in the process of growth; the bonding of ligands and nanocrystalline is a dynamic equilibrium of adsorption and desorption, in which the adsorption of ligand can avoid the agglomeration of nanoparticles as
a result of van der Waals force; and the dynamic desorption of ligands on the surface of crystalline can get the monomer from the solution for growth [54]. During the growth of ZnS shell, the interaction ability of DDT and particles is relatively stronger, resulting in a slower shell growth rate. The PL emission wavelength decreased and then was kept constant at the longer shell growth time due to the moderating effect of DDT. TOP and ZDC can form a complex at low temperature, which increased the activity of the precursor, and the shell growth rate was faster. At the end, the larger thickness of ZnS shell induced the more PL blue-shift.

With respect to the PL QY of CIS/ZnS QDs, PL QY could be increased up to almost 55% at a shell growth time of 120 min while using DDT as a ligand; the effect of the prolonged time of the shell synthesis is significantly smaller while using TOP as a ligand (i.e. PL QY increased to 35% at the same time). During the ZnS growth in the presence of ligands, the ligand as an organic layer was coated on the surface of nanoparticle. This organic layer will influence the absorption and PL properties of QDs. The ligands can effectively reduce the number surface defects of the ZnS layer but also can generate a possible nonradiative relaxation as a hole receptor [55, 56]. In the synthesis of CIS/ZnS using TOP, the PL QY of CIS/ZnS is impacted by two factors. On the one hand, the growth of ZnS shell reduced the number of defects on the crystal surface defects and improved the PL intensity, which has been already discussed; on the other hand, TOP representing a hole receptor on the surface of the particles promoted nonradiative relaxation and caused the decrease of PL intensity. Therefore, the improvement of the PL QYs of CIS/ZnS was limited using TOP [39, 55, 56]. The chain length of ligands is also one of the factors to affect PL improvement. Michalska et al. synthesized CIS core with DDT and CuInZn$_{2+x}$S$_{2+y}$ QDs with amines during ZnS shell growth. The reaction rate varied depending on the chain length of amines besides other parameters [29]. It means the optimization of the same type of ligands with different chain lengths (such as octanethiol, iso-octylthiol, tetradecanethiol, hexadecanethiol, and octadecanethiol aside from DDT). Based on the results, DDT was selected as a ligand for the further process parameter optimization to improve the PL QY of samples.

### 3.6 Effect of temperature in the shell growth

The increase of temperature affects the rate of decomposition of the zinc precursor. Therefore, similar dependencies as observed for the reaction time could be expected. However, the effect of temperature as the measure to reduce the reaction time is important with respect to the synthesis in flow. In Figure 10, when increasing the temperature from 200°C to 220°C to 240°C, the time to reach the maximum PL QY was shortened 180 min to 60 and 30 min correspondingly. The positive effect of the increased temperature was similar to the one of the longer reaction time, that is, at a higher temperature and at the same time, a thicker ZnS shell was formed, thereby greatly reducing...
the surface defects of core CIS and nonradiative transition probabilities. The larger blue-shift (about 100 nm) of the CIS/ZnS sample prepared at 240°C also proved our results of core size shrinking and surface passivation of particles. However, at a higher temperature, the PL QY dependence on the synthesis time passed through a maximum. The decrease of the PL QY after maximum is probably coursed through the continuous decomposition of ligands, which introduced new defects on the surface. Therefore, depending on the temperature, the optimized shell growth time should be considered. Similar dependences have been reported also by Park and Kim [18]. However, their study was limited to 230°C; therefore, the maximum PL QY was not achieved.

3.7 Effect of Zn/Cu feed molar ratio

The Zn/Cu feed molar ratio from 1 to 8 was selected to investigate the effect of Zn amount to PL QY and the PL emission wavelength. CIS core was synthesized at 240°C for 60 min. The shell growth was kept constant at 220°C. The changes of QY and PL emission wavelength with different Zn/Cu feed molar ratios are shown in Figure 11. The result showed that, at the same shell growth time, the obtained samples had higher PL QYs and a larger blue-shift with the increase of Zn/Cu feed molar ratio. This is because a higher Zn precursor concentration has a higher growth rate, and the difference of PL emission wavelength of CIS and CIS/ZnS QDs was growing with the increase of Zn/Cu feed molar ratio at the same shell growth time. The total blue-shifts of CIS and CIS/ZnS emission wavelength within 180 min were about 38 and 61 nm at Zn/Cu feed molar ratios of 1 and 8, where the 23 nm difference is because a higher Zn amount has a larger effect on core size decrease due to the interdiffusion between ZnS and CIS QDs.

3.8 Effect of CIS core reaction time

The synthesized CIS core had different PL QY values with the change of reaction time. The PL QY of CIS core also influences the final PL QY and emission wavelength of the formed CIS/ZnS samples. CIS QDs were synthesized at 30, 60, 90, and 120 min (so-called Core-30 min, Core-60 min, Core-90 min, and Core-120 min), and the corresponding PL QYs are 4%, 6.8%, 4.3%, and 1.4% as shown in Figure 12A. The growth of ZnS shell was conducted at 240°C with a Zn/Cu feed molar ratio of 4. The obtained CIS/ZnS QDs had the maximum PL QYs of 51%, 80%, 54%, and 27% using CIS core from 30, 60, 90, and 120 min. Compared to CIS core, the maximum PL QY of CIS/ZnS QDs can be improved more than 10 times. The PL QY changing tendency of CIS core and CIS/ZnS QDs are the same, which indicated

![Figure 11](image1.png)

**Figure 11:** (A) PL QY, and (B) emission wavelength evolution of CIS/ZnS QDs prepared with different Zn/Cu feed molar ratios. CIS was synthesized at 240°C for 60 min, and the shell growth temperature is 220°C.

![Figure 12](image2.png)

**Figure 12:** (A) PL QY of CIS and CIS/ZnS QDs and (B) PL wavelength of CIS/ZnS QDs prepared with CIS core reaction times of 30, 60, 90, and 120 min.
that CIS core with high QY can help achieve a higher PL QY of the final product. Although the wavelength of QDs varied during the changes of shell growth time, the total blue-shift was typically <60 nm (as shown in Figure 12B). Therefore, to broaden the PL emission range, the changes of core size can be considered. For example, the PL QY of CIS/ZnS at emission of 654 nm using CIS-120 min is about 27%, which is higher than 6.8% of CIS-60 min at the same emission wavelength.

### 3.9 Final results

The learnings from the previous experiments have been used for the final optimization of the recipe to obtain QDs with a high PL QY. CIS QDs had typically PL QY lower than 10%; however, the PL QYs were significantly improved while ZnS was coated on CIS surface. Based on our previous discussion, the window of parameters for the high PL QYs of CIS/ZnS can be achieved at a Zn/Cu feed molar ratio larger than 4, shell growth time of 30 to 90 min, and CIS core and shell growth temperature of 220°C–240°C. During the improvement of PL QY of CIS/ZnS, ligands decided the possible maximum value: the maximum PL QY achieved was normally <30% while TOP was used in the system; however, DDT as ligands can dramatically improve the PL QYs of the samples. Furthermore, the initial PL QYs of CIS core limits the final maximum PL QY of the CIS/ZnS QDs with different PL emission wavelengths at fixed ligands.

To achieve the maximum PL QYs with different PL emission wavelengths, the PL QY of CIS core with a PL emission wavelength from 640 to 800 nm should be further improved. The improvement of CIS by changing the starting material, Cu/In feed ratio, or synthesis process has been already demonstrated by us [22] and other studies [26, 33, 57], which will not be discussed here. In the present study, the PL QY was about 80% with a PL emission wavelength at 583 nm using CIS core with PL QY of 6.8% in combination with a suitably chosen core reaction time and shell growth time. This is one of the highest QYs reported in the open literatures [24–26, 33]. For example, Hua et al. achieved CIS/ZnS with PL QY as high as 81% at 550 nm using CIS with PL QY of about 23% and emission wavelength of 623 nm [26]. Trizio et al. synthesized Cu-In-Zn-S (CIZS) nanocrystals based on Cu-deficient CIS core with PL QY of 23% (the PL emission wavelength was about 658 nm), and the obtained PL QY of CIZS can reach up to 80% with 590 nm [33]. In our study, similar PL QY can be achieved with even lower PL QY of CIS core while using DDT as a ligand at ZnS shell growth. The above information is also consistent with our conclusion that the PL QY of CIS would highly affect the improvement of CIS/ZnS QDs. It is reasonable to predict that the possible better results can be achieved while using CIS core with higher QY in our recipes.

With respect to the continuous synthesis of QDs, the residence time for reaction is one of the important factors to decide the equipment cost. Because the mild synthesis of CIS and CIS/ZnS QDs rely on the decomposition rate of DDT at high temperature, the direct application of the developed recipe for synthesis in continuous flow is not possible, at least not with the microchannel-based technology, which is supported by our previous studies performed in the microreactors. This differs from the many published opinions regarding the advantages of microreactor technology in typical QD synthesis within several minutes, such as CdS, CdSe, and CdSe/ZnS [48, 58]. The reason is that the typical recipes for CdS, CdSe, and CdSe/ZnS synthesis use active material S or Se powder as an anion, which can accelerate the reaction rate significantly. However, for CIS synthesis, the ligands such as OA and OLM used for coordinating S atom would limit the improvement of CIS/ZnS QDs, which is different from typical QD synthesis [58]. The PL QY will be sacrificed in the realization of continuous flow production.

### 4 Conclusions

The facile solvothermal synthesis of CIS/ZnS QDs with high PL was investigated. The results indicated that the band to donor/acceptor and donor-acceptor recombination were the main contributions to the PL emission by comparing the calculated band-gap to the PL emission wavelength of CIS QDs. Due to the large amount of defects on CIS surface, the main absorbed energy was consumed as nonradiation transition. While CIS was coated by ZnS shell, the defects acting as traps such as \( V_{\text{Cu}}^- \), \( V_{\text{In}}^- \), \( V_{\text{Cu}}'/\text{Cu}_{\text{In}}'' \), and \( \text{In}_{\text{Cu}}'' \cdot \text{Cu}_{\text{In}}'' \cdot \text{Cu}_{\text{In}}'' \) were passivated and the PL QY was improved significantly. Nonradiation transition and donor-acceptor emission were reduced significantly due to the reduction of crystal defects, whereas the band to donor/acceptor emission became a dominating emission. The blue shift of the PL emission wavelength of CIS/ZnS QDs underwent two steps: the dramatic blue-shift originated from the decreased fraction donor-acceptor transition due to the reduction of surface defects at the beginning and the subsequently mild blue-shift with the time from the interdiffusion of CIS and ZnS. TOP and DDT as an additional organic layer can reduce the surface defect beside the ZnS layer and further improve the PL
QY of CIS/ZnS; however, TOP as a hole receptor induced the nonradiation relaxation and limited the improvement of PL efficiency. DDT has significant advantages in the improvement of optical properties of QDs. The PL QY of CIS core will also affect the final PL QY of CIS/ZnS QDs; therefore, it is reasonable that the higher PL QYs can be achieved while using CIS core with higher PL QY in our recipes. Based on the selected DDT and CIS core with defined PL QY, further optimization such as shell growth temperature/time and Zn/Cu feed molar ratio to PL properties were conducted. The maximum PL QYs can be easily obtained with a Zn/Cu feed molar ratio larger than 4, shell growth time of 30 to 90 min, and shell growth temperature 220°C to 240°C. The maximum PL QY of CIS/ZnS reached up to about 80%.

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