Low-Temperature Synthesis of Highly Efficient, Deep-Red Zn-Cu-In-Se/ZnSe Fluorescence Quantum Dots

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We report a facile synthesis method on CuInSe₂ (CISE)-based quantum dots (QDs) by using tri-*n*-octylphosphine selenium (TOPSe) as selenide precursor, with assistance of oleylamine (OAm) and *n*-dodecanethiol (DDT). We demonstrate that the OAm and DDT jointly contribute to the formation of the low-temperature-decomposable metal-sulfide clusters, and promote the QD nucleation at relatively low temperature range of 180–200°C. Furthermore, to improve fluorescence property, Zn-doping and ZnSe coating are simultaneously carried out. The obtained deep-red ZnCISE/ZnSe QDs possess higher quantum yield of 65% at wavelength of 670 nm, which is in the best performance range ever reported. Then, we investigate the improvement mechanism, where the sufficient Zn replacement of In sites is the crucial factor. This modified core-shell structure provides two benefits, on the one hand, the enhancement on intrinsic defect-related

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recombination, and the other hand, the improved core-shell interface that reduces the nonradiative recombination.

Keywords: Quantum dots; deep-red ZnCuInSe; ZnCuInSe/ZnSe; low-temperature synthesis.

1. Introduction

Ternary I–III–VI group semiconductor quantum dots (QDs), such as CuInS₂ (CIS), CuInSe₂ (CISE) and AgInS₂ (AIS), have attracted widespread attention because they are the ideal substitutes for the non-environmentally friendly cadmium- and plumbum-based QDs.^{1,2} Although these low-toxic QDs are very promising in the field of light-emitting diode,^{3–5} solid-state lighting⁶ and bioimaging,^{7–9} one of the biggest challenges that hampers their application is to improve the photoluminescence quantum yields (PLQYs). In recent years, the PLQY of CIS-based QDs has been improved by various approaches.^{10–12} Once zinc sulfide is coated on these CIS QDs, however, the bandgap tuning capacity is greatly influenced by Zn diffusion into the host matrix that only efficient emission from green to orange-red (generally from 540 nm to 620 nm) could be achieved.^{13–15} To obtain red and deep-red fluorescence emission, CISE-based QDs is getting more and more attention since its emission covers the range from visible to near-infrared depending on the size and composition.^{7,16,17}

Inspired by above motivation, the synthesis of CISE QDs has extensively been studied. For instance, small nonstoichiometric CISE QDs with QY of 20% using bis(trimethylsilyl) selenide as precursor obtained at 280–360°C were first reported by Allen *et al.*¹⁶ Cassette *et al.*⁷ have prepared CISE QDs with CuCl and InCl₃ as metal cation precursors and Selenourea as selenium source with a simple one-pot synthetic route. After the growth of a ZnS shell onto these QDs, their PLQY increased up to 40–50% at 800 nm. Park *et al.*¹⁸ have synthesized CuIn_xSe_y QDs by the reaction of CuI, InI₃, and bis(trimethylsilyl) selenide ((TMS)₂Se) in trioctylphosphine oxide (TOPO) and hexadecylamine (HDA) at 270°C. After ZnS coating, a PLQY of ~60% has achieved for this CuIn_xSe_y/ZnS QDs. Yarema *et al.*¹⁷ reported a colloidal synthesis of CISE QDs based on a silylamide-promoted approach, which was carried out at 285–320°C.

The luminescence efficiency improved to 50–60% by overcoating ZnS or ZnSe shells.

Despite the rapid progress, the conventional synthesis of CISE-based QDs should be further improved due to the use of explosive and toxic selenide precursor. Besides, the CISE QDs synthesis usually proceeds at high temperature, which may result from the low reactivity of metal-selenide intermediates. Recently, Zhong *et al.*¹⁹ reported a simple synthetic method by using TBPSe and DDT as chalcogenide precursor at a moderate reaction temperature (200°C). But, the obtained CISE/ZnS QDs have a relatively low PLQY of 10–26%. More efforts should be made to further optimize this meaningful synthesis strategy.

For this purpose, we report a low-temperature synthetic scheme to prepare highly efficient CISE-based QDs. In particular, the employment of OAm and DDT is favorable for the formation of metal-sulfide intermediates. This kind of metal-sulfide intermediate could easily decompose and promote the formation of CISE-based QDs at temperature as low as 180°C. Besides, we carried out Zn-doping to elaborately modify surface structure of the CISE core and investigated the improvement mechanism. The sufficient In replacement by Zn has proved to be beneficial to the PLQY improvement. An improved PLQY of ~65% at emission wavelength of 670 nm has been achieved, compared with that (695 nm) of CISE/ZnSe QDs.

2. Experimental

2.1. Chemicals

Copper iodide (Aldrich, 99.95%), indium(III) acetate (Aldrich, 99.99%), zinc stearate (Zn(St)₂, Aldrich, Zn 10–12%), selenium (Aldrich, 200 mesh, 99.99%), oleic amine (OAm, Aldrich, 90%), *n*-dodecanethiol (DDT, Aldrich, 98%), tri-*n*-octylphosphine (TOP, Aldrich, 90%), and *l*-octadecene (ODE, Aldrich, 90%) were used as purchased and without purification.

2.2. Synthesis of CISE, ZnCISE and ZnCISE/ZnSe QDs

A typical synthesis of CISE and ZnCISE QDs was performed as follows: CuI (24 mg, 0.125 mmol), In(OAc)₃ (146 mg, 0.5 mmol) and Zn(St)₂ (79.0 mg, 0.125 mmol) (no Zn(St)₂ adding when synthesis of CISE QDs) were mixed with 5 mL of ODE, 1 mL of OAm and 0.5 mL of DDT in a 50-mL three-necked flask. The reaction mixture was degassed under vacuum for 15 min and purged with nitrogen three times. During this process, the temperature was gradually increased up to 100 °C until a clear solution was formed. After that, the solution was heated to 180 °C under nitrogen atmosphere, and 1 mL of TOPSe stock solution (made by dissolving 1 mmol of Se powder in 0.5 mL of TOP and 0.5 mL of ODE, and sonicated for 20 min) was swiftly injected into the flask and kept for 15 min at the same temperature. With the temperature increase, the color of the reaction solution gradually changed from yellowish to transparent orange, red and finally deep red. For the convenient description, the CISE QDs obtained at different times, i.e., 5 min, 10 min and 15 min were named as CISE-5 min, CISE-10 min, and CISE-15 min, respectively. The ZnCISE QDs samples obtained at different times, such as 5 min, 10 min and 15 min were named as ZnCISE-5 min, ZnCISE-10 min and ZnCISE-15 min, respectively.

Without QDs purification, 2 mmol (1.27 g) of Zn(St)₂ was added into the as-prepared ZnCISE QDs. Then, the whole solution was purged with nitrogen and degassed at 100 °C to remove any low-boiling point chemicals. Subsequently, the solution was heated for 180 °C, and 2 mL of TOPSe stock solution (made by dissolving 2 mmol of Se powder in 1 mL of TOP and 1 mL of ODE) was slowly added into the solution by drip injection for 180 min to grow the ZnSe shell. ZnCISE QDs with different coating times with ZnSe, i.e., 60 min, 120 min, 180 min were named as ZnCISE/ZnSe-60 min, ZnCISE/ZnSe-120 min, ZnCISE/ZnSe-180 min, respectively.

The prepared colloidal QDs were precipitated by addition of ethanol, and centrifuged at 8000 rpm for 5 min, the upper layer liquid was decanted, and then the isolated solid was redispersed in *n*-hexane for further analysis.

2.3. Characterization

Photoluminescence spectra, absolute PLQY and decay dynamic were measured by FLS980

fluorescence spectrometer from Edinburgh Instruments Ltd at an excitation wavelength of 450 nm. Optical absorption spectra were recorded on a Perkin-Elmer Lambda 750 spectrophotometer. The chemical compositions of the QDs were measured by inductive coupling plasma atomic emission spectrometry (ICP-AES). XRD measurements were performed on an X'Pert PRO system operated at 40 KeV and 40 mA with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). High-resolution transmission electron microscope (HRTEM) images were obtained by a JEOL-2100F TEM.

3. Results and Discussion

3.1. Modified core synthesis

Experimental and theoretical results presume that the formation of I–III–VI groups QDs is achieved by a thermo-decomposition process.^{20–22} Therefore, one of the prerequisites for successful CISE QDs synthesis is the formation of metal-based intermediates.¹⁷ To obtain such reactant, DDT and OAm are employed in our synthesis system, which jointly contribute to generate abundant Cu-In-(S-R)_x-(NH₂-R)_y clusters in 100 °C, as shown in the synthesis route of Fig. 1. This differs from the protocol reported in the literature where the oleic acid (OA) was commonly used.¹⁹ Actually, in our previous study, we have found that the OAm rather than OA is more efficient to dissolve In(Ac)₃ and thereby readily to form the desired clusters.²³ Moreover, the DDT is another critical reactant to obtain metal-sulfide intermediates. These intermediates are more easy to decompose at low temperature, in comparison to the metal-silylamide

Fig. 1. Synthesis route of the CISE and ZnCISE/ZnSe QDs.

Fig. 2. XRD patterns of CISE and ZnCISE cores prepared with different reaction times.

counterpart that is prepared using lithium bis(trimethylsilyl)amide.¹⁷ Under such optimized conditions, the QD nucleation takes place at lower temperature of 180°C in our work, compared with

the conventional schemes that commonly proceed at 200–360°C.^{7,16–19}

Although DDT is employed to obtain metal-sulfide intermediates, CISE rather than CIS or CISES constitute the QDs nucleus. This is because S is less reactive than Se, and combined with the self-purification function of the QDs nucleation, the S atoms are hard to incorporate into CISE. This can be verified by XRD measurement, as presented in Fig. 2. For the standard tetragonal CIS (JCPDS 85-1575), the diffraction peaks from (112), (204)/(220), and (116)/(312) crystal planes center at 27.9°, 46.3°, and 54.7°, respectively. However, the XRD pattern of the CISE-15 min QDs shows that the corresponding peaks locate at $2\theta = 26.7^\circ$, 44.3° and 52.4° , which are in good accordance with those of tetragonal CISE (JCPDS 40-1487). No obvious diffraction angle shift toward CIS is observed, suggesting DDT has few effects on the formation of CISE QDs.

We should highlight that the metal cation proportion in CISE has great influence on the

Fig. 3. UV-Vis absorption and PL emission spectra for the CISE (a,b) and ZnCISE (c,d) QDs obtained from different reaction times.

luminescence properties. In general, stoichiometric CISE QDs have moderate PL properties, while In-rich CISE phases usually possess the highest PLQY. Yet, we presume that the fluorescence performance of In-rich CISE could be further improved by Zn-doping method, similar to the results in Zn-doped CIS QDs.^{15,24} Therefore, we herein have further developed and improved ZnCISE QDs synthesis route. The XRD pattern of ZnCISE core QDs is shown in Fig. 2. It can be seen that the ZnCISE QDs still retains the tetragonal structure despite of the incorporation of Zn atoms. As reaction time increases from 5 min to 15 min, the diffraction peaks slightly shift toward large angle. This can be attributed to the sufficient In sites replacement by Zn atoms, as proved in the following section. Regardless of the Zn-to-Cu/In composition, these core samples exhibit tetragonal structure, ruling out the occurrence of impurity phase.

We compare the optical properties of the core QDs synthesized without/with Zn-doping by UV-Vis absorption and PL spectra, as shown in Fig. 3. The optical bandgaps E_g of QDs is calculated according to an empirical formula $Ah\nu = \sqrt{h\nu - E_g}$, by plotting $(Ah\nu)^2$ as a function of $h\nu$. Among them A is the absorbance, $h\nu$ is the photon energy.²³ The E_g of QDs is estimated by extrapolating a straight line to the x axis and is listed in Table 1. Obviously, the E_g of CISE QDs enlarges due to this Zn-doping. For instance, the measured E_g of ZnCISE-5 min QDs is 2.20 eV, larger than that of 2.16 eV for the CISE-5 min counterpart [see Figs. 3(a) and 3(c)]. With reaction time prolonged to 30 min, the E_g of ZnCISE and CISE QDs decreases to 1.88 eV and 1.82 eV. PL spectra evolution exhibits similar tendency, but the emission of blue-shift is more conspicuous when reaction time increases to 30 min (834 $\rightarrow$ 791 nm), compared with their emission wavelengths at 5 min reaction time (694 $\rightarrow$ 686 nm). This can be attributed to the sufficient In displacements by Zn atoms. Representative ICP measurement results are

presented in Table 1. The CISE-15 min has a characteristic of Cu:In:Zn = 1:5.29:0. In contrast, this ratio becomes 1:3.64:0.19 when Zn-doping is implemented, suggesting In rather than Cu sites which are substantially replaced by Zn atoms.

To further study, the influence of Zn-doping on core structure, TEM measurement is carried out. In Fig. 4, the TEM images and the corresponding size distribution diagrams of the CISE-5 min, CISE-15 min, ZnCISE-5 min and ZnCISE-15 min QDs are compared. From size distribution diagrams, we can find that Zn-doping leads to a slower growth of the QDs, since the average diameter is significantly reduced (2.4 nm versus 2.1 nm for 5 min and 2.8 nm versus 2.6 nm for 15 min). Additionally, high-resolved TEM images reveal that Zn incorporation reduces the lattice constant of the matrix material. For example, the measured distance for (112) plane, $d_{(112)}$ is 0.33 nm for CISE-15 min, but it decreases to 0.31 nm after Zn-doping. This evidence strongly indicates In but not Cu site is mainly replaced by Zn atoms, as concluded above, because the atomic radius between Zn and Cu is nearly equal (0.137 nm versus 0.128 nm).

Herein, we underline that, based on our modified synthesis protocol, the nucleation temperature could further lower to 160°C. More importantly, this low-temperature synthesis also works in nucleation of Zn-doping QDs, as proved by PL spectra in Fig. 5(a). To our best knowledge, this temperature is in the lowest range among studies on CISE synthesis. The main effect of reaction temperature lies in determining the growth rate of core QDs. For instance, redshift (from 619 nm to 769 nm) occurs in PL spectra when synthesis proceeded at higher temperature, which suggests that the QDs grow faster according to empirical theory on the size-dependent quantum confinement effect [shown in Figs 5(a) and 5(b)].^{25,26} As shown in Fig. 5(c), ZnCISE QDs can nucleate at 160°C. But considering the poor qualities of the obtained QDs at this

Table 1. Summary parameters in term of grain size, bandgap, composition ratio, PL decays and QY for CISE, ZnCISE and ZnCISE/ZnSe QDs.

Sample	Size (nm)	E_g (eV)	Cu:In:Zn	τ_1 (ns)	B_1 (%)	τ_2 (ns)	B_2 (%)	τ_3 (ns)	B_3 (%)	τ_{avg} (ns)	QY (%)
CISE-15 min	2.8	1.98	1:5.29:0	24.4	8.8	100.2	44.3	245.2	47.0	202.5	6.5
ZnCISE-15 min	2.4	2.04	1:3.64:0.19	21.5	12.9	88.9	46.0	250.4	41.1	183.5	10.1
CISE/ZnSe-120 min	3.3	2.07	1:8.63:5.07	31.0	4.9	129.2	49.8	281.1	45.3	228.0	43.3
ZnCISE/ZnSe-120 min	3.0	2.09	1:5.77:9.15	36.9	4.1	148.4	67.3	342.7	28.6	242.9	65.0

Fig. 4. TEM images and corresponding size distribution diagrams of the CISE-5 min (a), CISE-15 min (b), ZnCISE-5 min (c) and ZnCISE-15 min QDs (d).

time, 180°C was considered as the optimal nucleation reaction temperature. Although Zn-doping leads to a slight blue shift of the PL, we still readily acquire deep-red emission window from 686 nm to 791 nm, as demonstrated in Fig. 3(d).

Besides, PL properties especially in terms of QY are greatly improved due to this Zn-doping. The highest QY for ZnCISE has reached 10.1%, with an increment of 3.6% compared with the pure CISE QDs [Fig. 5(c)].

Fig. 5. (a) PL spectra evolution of CISE and ZnCISE synthesized at different temperatures. (b) Emission wavelength and (c) QY of the QDs as a function of reaction temperature.

3.2. ZnCISE/ZnSe core-shell QDs and PL mechanism

In order to achieve target of high PLQY, we also prepare the ZnCISE/ZnSe core-shell QDs. UV-Vis absorption and PL spectra of ZnCISE/ZnSe QDs are shown in Figs. 6(a) and 6(b). Obvious blue-shift is observed when coating time increases from 60 min to 180 min. Consequently, the QY of QDs greatly enhances due to the effective surface passivation, as can be seen from the inserted photo in Fig. 6(b). We also compare CISE/ZnSe-120 min QDs with this ZnCISE/ZnSe-120 min QDs. As shown in Table 1, the emission wavelengths of CISE/ZnSe and ZnCISE/ZnSe QDs are 695 nm and 670 nm, with corresponding QY of 43.3% and 65.0%, respectively. This result highlights again the advantage of Zn-doping in high performance CISE-based QDs.

Typical XRD pattern of ZnCISE/ZnSe-120 min is presented in Fig. 6(c). The diffraction peaks are located at 27.2° , 45.1° , and 53.6° , respectively. This peak assembly is also consistent with pattern from (111), (220), and (331) crystal planes of zinc-blende ZnSe, indicating the successful ZnSe coating on ZnCISE QDs. TEM image of ZnCISE/ZnSe-120 min QDs is shown in Fig. 6(d). The average diameter of these spherical particles is 3.0 ± 0.2 nm. The measured $d_{(112)}$ reduces from 0.31 nm to 0.28 nm, which mainly stems from the further Zn diffusion into the core QDs during ZnSe coating process. To further evaluate the stability of the QDs, we tested the PLQY change of ZnCISE/ZnSe-120 min QDs during one week. The results are shown in Fig. 7. The QDs still maintain the original 95% PLQY after one week.

Fig. 6. (a) UV-Vis absorption and (b) PL spectra of ZnCISE/ZnSe QDs. (c) XRD pattern of ZnCISE/ZnSe QDs. (d) TEM image of the ZnCISE/ZnSe-120 min QDs and the corresponding size distribution diagrams.

Fig. 7. The variation of PLQY of ZnClSe/ZnSe-120 min QDs during one week.

To investigate the improvement mechanism of the Zn-doping, PL dynamic measurement is performed. The PL decay curves of the ClSe and ZnClSe QDs with different reaction times were given in Fig. 8(a), which was fitted using a triple-exponential function^{27,28}

$$I(t) = B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2) + B_3 \exp(-t/\tau_3), \quad B_1 + B_2 + B_3 = 1, \quad (1)$$

where τ_1, τ_2, τ_3 represent the decay time constants, and B_1, B_2, B_3 represent the normalized amplitudes of each component. The amplitude weighted average lifetime of the entire photoluminescence decay

process was calculated using

$$\tau_{\text{avg}} = \frac{B_1 \tau_1^2 + B_2 \tau_2^2 + B_3 \tau_3^2}{B_1 \tau_1 + B_2 \tau_2 + B_3 \tau_3}, \quad (2)$$

and the fitting parameters are summarized in Table 1. Figure 8(b) depicts an empirical PL mechanism of ClSe-based QDs. The fast decay component τ_1 could be assigned to the surface state-related recombination. The medium radiative lifetime τ_2 is attributed to the intrinsic defect-related recombination. This is a transition from donor states such as In_{Cu} to the quantized valence band (VB) or the quantized conduction band (CB) to acceptor states such as $\text{Cu}_{\text{In}}, \text{V}_{\text{In}}, \text{V}_{\text{Cu}}$ etc. The τ_3 could be assigned to the donor-acceptor pair (DAP) recombination between deep defect state of Cu_{In}'' and $\text{In}_{\text{Cu}}^{\bullet\bullet}$, which usually has the longest lifetime. As can be seen in Fig. 8(a) and Table 1, the decay amplitude fractions B_1 of ZnClSe-15 min (12.9%) is larger than that of ClSe-15 min (8.8%), which indicated that ZnClSe-15 min had more surface states than ClSe-15 min. This is mainly because ZnClSe-15 min had a smaller particle size. Nevertheless, the B_2 of ZnClSe-15 min (46.0%) is larger than that of ClSe-15 min (44.3%) due to the $\text{Zn}_{\text{Cu}}^{\bullet}$ and Zn_{In}' defect states.^{12,28,29} This defect-related radiative pathway is usually desired for the ClSe-based QDs. Therefore, Zn-doping improves fluorescence property by finely modifying core structure.

From decay dynamics, we also find that the Zn-doping implemented before ZnSe coating benefits

Fig. 8. (a) PL decays for ClSe-15 min, ZnClSe-15 min and ZnClSe/ZnSe-120 min. (b) Schematic diagrams of recombination pathways observed in ZnClSe QDs including, surface defect τ_1 ; intrinsic defect-related recombination τ_2 ; and DAP recombination τ_3 .

the QY enhancement. First, the B_2 greatly increases from 49.8% to 67.3% after coating ZnSe. Second, the surface defect radiative pathway, B_1 , is reduced from 4.9% to 4.1%. Both contribute to the high QY up to 65% for ZnCISE/ZnSe-120 min QDs, which places our work among the best fluorescence performance ever reported. Here, we consider that the QY superiority for ZnCISE/ZnSe-120 min versus CISE/ZnSe-120 min origins from the improved core-shell interface. As we know, ZnSe has a 2% lattice mismatch with CISE. A lattice mismatch between core and shell materials can prevent the passivation of surface traps, which hamper the bright PL. The sufficient displacement of In/Cu atoms by Zn on QD surface before ZnSe coating, however, produces an alloy compound layer that largely eliminates this mismatch between core and shell, and thereby improves the PL property.

4. Conclusions

In this work, an OAm and DDT assisted, low-temperature synthetic scheme in preparation of ZnCISE/ZnSe QDs is reported. The employment of OAm and DDT has demonstrated as begin helpful in formation of metal-sulfide intermediates. This kind of metal-sulfide intermediate could easily decompose and promote the formation of CISE-based QDs at temperature as low as 180°C. Besides, we carried out Zn-doping to elaborately modify surface structure of the CISE core. The sufficient In replacement by Zn has proved to be beneficial for the PLQY improvement. A higher PLQY of ~65% at emission wavelength of 670 nm has been achieved, compared with that (695 nm) of CISE/ZnSe QDs. We believe this work could offer a novel but universal synthesis method that promotes the preparation especially for I–III–VI group QDs.

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