

High-brightness and Monodisperse Quaternary CuInZnS@ZnS Quantum Dots with Tunable and Long-lived Emission

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Abstract: As an essential candidate for environment-friendly luminescent quantum dots (QDs), CuInS-based QDs have attracted more attention in recent years. However, several drawbacks still hamper their industrial applications, such as lower photoluminescence quantum yield (PLQY), complex synthetic pathways, uncontrollable emission spectra, and insufficient photostability. In this study, CuInZnS@ZnS core/shell QDs was prepared *via* a one-pot/three-step synthetic scheme with accurate and tunable control of PL spectra. Then their ensemble spectroscopic properties during nucleation formation, alloying, and ZnS shell growth processes were systematically investigated. PL peaks of these QDs can be precisely manipulated from 530 to 850 nm by controlling the stoichiometric ratio of Cu/In, Zn²⁺ doping and ZnS shell growth. In particular, CuInZnS@ZnS QDs possess a significantly long emission lifetime (up to 750 ns), high PLQY (up to 85%), and excellent crystallinity. Their spectroscopic evolution is well validated by Cu-deficient related intragap emission model. By controlling the stoichiometric ratio of Cu/In, two distinct Cu-deficient related emission pathways are established based on the differing oxidation states of Cu defects. Therefore, this work provides deeper insights for fabricating high luminescent ternary or quaternary-alloyed QDs.

Key words: quantum dot; CuInS; alloying; core/shell; ensemble spectroscopic; Cu-deficient related emission

Colloidal semiconductor QDs have recently attracted broad attention for wide applications in biological analysis^[1-4], solar concentrators^[5-6], solar cells^[7-8], photocatalysis^[9], and information display^[10-11] because of their size-dependent and unique optical properties. In the past three decades, more attention has been devoted to II-VI compounds such as CdSe, CdTe, and CdS QDs, including their synthesis methodologies and characterizations^[12-15]. However, Cd- or Pb-based QDs have a doubtful future because of their high toxicity. In contrast, III-V compounds (especially InP QDs) are generally referred to as environmental QDs because the constituting elements are more friendly than Cd, Pb, and Hg. Significant progress has been made to improve the optical properties of InP QDs during the past decades. However, the expensive and highly flammable organic

phosphorus sources (such as tris(trimethylsilyl)phosphine) greatly limit their large-scale preparation and application. Recently, more researchers have tuned attention to ternary nontoxic I-III-VI compounds such as CuInS and CuInSe QDs^[16-21]. One of the most studied I-III-VI nanocrystals is CuInS QDs, which features a size-tunable photoluminescence in the range of visible to near-infrared light. Previous studies have proved that the size, elemental stoichiometry, morphology, and crystal symmetry are known to influence the optical properties of CuInS QDs^[18, 22-24]. Therefore, it is of great interest to further explore a simpler and more efficient synthetic route to achieve control of these vital parameters and obtain high quality QDs. This study aims to develop an efficient approach toward fabricating high luminescent CuInS-based QDs, systematically explore nonstoichiometry

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effects of cationic precursors on ensemble spectroscopic evolution of CuInZnS@ZnS QDs, and develop a universal method for obtaining Cd-free QDs with high PLQY, excellent crystallinity, and photostability.

1 Experimental

Experimental section is shown in the Supporting Materials.

2 Results and discussion

2.1 Optical properties of CuInS QDs, CuInZnS QDs, and CuInZnS@ZnS QDs

CuInZnS@ZnS core/shell QDs were prepared *via* a one-pot/three-steps strategy (Fig. 1(a))^[25]. CuInS QDs were performed through thermal decomposition of the mixture of copper (I) iodide, indium (III) acetate, and 1-dodecanethiol (DDT) at 215 °C (Fig. S1). Herein, CuInS QDs with four stoichiometric ratios of Cu : In (1 : 1, 1 : 2, 1 : 4, and 1 : 6) were synthesized by controlling the amount of In(Ac)₃ with a fixed dosage of DDT (10 mL) and CuI (0.1 mmol). Without purification step of the CuInS QDs, zinc stearate was directly added into the

CuInS QDs crude solution and kept at 200 °C for further fabricating CuInZnS alloyed QDs. At last, ZnS shell growth was implemented by the continuous injection of both shell precursor solutions into the CuInZnS QDs solution by a syringe pump for obtaining the CuInZnS@ZnS QDs (detailed information is available in Supporting Materials).

During the growth of CuInS QDs, aliquots were taken from the reaction solution to monitor the reaction process of core QDs, and representative digital photographs for the temporal evolution of CuInS QDs under daylight and UV light were demonstrated (Fig. S2). During the synthesis process, a progressive color change in the reaction solution was observed from yellow to orange, red, and finally crimson, indicating subsequent nucleation growth of CuInS QDs. Meanwhile, octanethiol (OT) was also used as a sulfur source for fabricating CuInS QDs, and these QDs showed brighter photoluminescence than those with DDT for growth of 30 min (Fig. S3), which proves short-chain OT has higher reaction reactivity than DDT.

Fig. S4 shows the time evolution of PL emission spectra of CuInS QDs synthesized with varying molar stoichiometric ratios of Cu : In (the temperature is 200 °C). Under the experimental conditions, CuInS QDs (the stoichiometric ratios of Cu : In are 1 : 2, 1 : 4, and

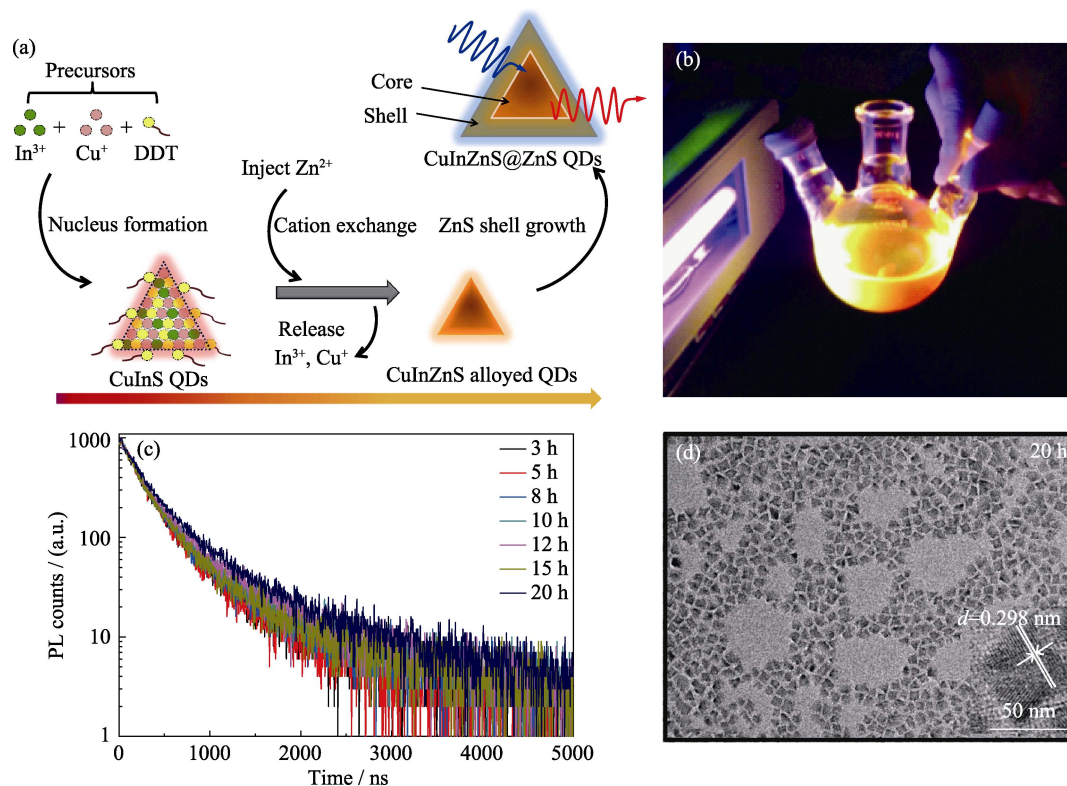


Fig. 1 Optical and morphology characterization of the CuInS-based QDs

(a) Synthetic route of the CuInS-based QDs; (b) Photograph of the CuInZnS@ZnS QDs with shell growth of 20 h (Cu : In : Zn is 1 : 2 : 3) under 365 nm showing brilliant luminescence; (c) Transient PL decays of the CuInZnS@ZnS QDs with different shell growth time (Cu : In : Zn is 1 : 2 : 3); (d) TEM images of the CuInZnS@ZnS QDs (Cu : In : Zn is 1 : 2 : 3) with shell growth of 20 h.

Colorful figures are available on website

1:6) had PL peaks in the range of 620–650 nm. Meanwhile, CuInS QDs synthesized with less In precursors (the stoichiometric ratio of Cu:In is 1:1) exhibited longer wavelength of PL peak (over 700 nm) with prolonged reaction time. These results illustrated that the reaction temperature and growth time significantly influenced the growth process of CuInS QDs due to the decomposition rate of alkylthiols. Typically, these QDs showed PL emission in the near-infrared reflection from 500 to 850 nm. Their PLQYs were in range of 1%–22%, depending on the stoichiometric ratio of cationic precursors (Table S1). Without specifically pointing out, the reaction temperature of 215 °C and reaction time of 30 min for CuInS QDs growth were chosen in the subsequent experiments, and the corresponding PL peaks located at 710, 633, 625, and 618 nm, respectively (Table S1).

Compared with CuInS QDs, the PLQY of CuInZnS alloyed QDs increased, usually in range of 13%–37% (Table S2). The final PL peaks of these alloyed QDs respectively moved to 675, 596, 590, and 581 nm (Table S2). All these CuInZnS alloyed QDs exhibited a specific blue shift of 30–40 nm compared with their original CuInS QDs. The blue shift phenomenon of the PL and UV-Vis absorption spectra of all CuInZnS alloyed QDs *versus* CuInS QDs was attributed to the surface etching of core QDs, and then the formation of an alloyed CuInZnS interfacial structure^[21, 25–28]. In this experiment, the annealing temperature (200 °C) for the cation exchange process was lower than the nucleation formation temperature of CuInS QDs (215 °C) and reported reaction temperature (usually over 230 °C)^[21–22, 28]. Therefore, the decomposition velocity of DDT significantly decreased, and the cationic exchange process may play a dominant role in this growth stage. Thus, cationic exchange of Cu⁺ and In³⁺ ions with Zn²⁺ in the formation of CuInZnS QDs also seems a pretty convincing reason for the decrease of adequate size of CuInS QDs (the ionic radii of Cu⁺, In³⁺ and Zn²⁺ are 0.096, 0.08, and 0.074 nm, respectively)^[29]. This experimental data are consistent with a conversion of CuInS QDs into quaternary structured CuInZnS QDs upon their cation exchange reaction with Zn²⁺. These results documented that CuInZnS QDs had an alloyed structure.

Fig. S5 shows the PL spectra of the CuInS QDs, CuInZnS QDs, and all CuInZnS@ZnS QDs with shell growth time of 20 h. Their corresponding UV-Vis absorption (Fig. S6) profiles display a broad shoulder rather than a sharp excitonic peak, which is attributed to the compositional off-stoichiometry and inhomogeneity at an ensemble level in case of ternary nanocrystal. The final PL emission peaks of these CuInZnS@ZnS QDs

were in the range of 610–620 nm (the stoichiometric ratio of Cu:In is 1:1) and 530–550 nm (the stoichiometric ratios of Cu:In are 1:2, 1:4, and 1:6). Finally, all these QDs exhibited a blue shift of 100–110 nm compared with their original CuInS QDs. Interestingly, the PL spectra and UV-Vis absorption of all CuInZnS@ZnS QDs demonstrate a continuous blue shift with shell growth (Fig. S7). Three situations can account for this noticeable and continuous blue shift phenomenon during shell growth. Firstly, a certain amount of zinc ion may still diffuse into the CuInZnS alloyed structure at high temperature, which enlarges the band gap of QDs and thus results in the blue-shifted PL spectra of QDs^[22, 28]. Recently, our group found a continuous element content decrease of In:Cu in the (Zn)CuInS/ZnS QDs^[25], which also can support this ion diffusion phenomenon. Secondly, In ions, especially those at the surface of CuInZnS alloyed QDs, may be partly substituted by Zn ions during the shell growth, leading to a bit of shrinkage of the CuInZnS alloyed QDs and a gradual blue shift of the PL spectra^[30]. Thirdly, the compressive lattice strain applied to CuInZnS QDs arises from the formation of inorganic shell layer with smaller lattice parameters as well as size/shape uniformity.

The final solution of CuInZnS@ZnS QDs with growth time of 20 h was uniform and transparent and showed bright luminescence under UV lamp (Fig. 1(b)). Fig. S8 demonstrates that the CuInZnS@ZnS QDs with 1:2 stoichiometric ratio of Cu:In show a higher PLQY of about 85% with shell growth time of 9 and 10 h (PL peak at about 550 nm), but PLQY of 60%–70% was more routinely achieved when growth time was over 5 h. Normally, the photostability and PLQY of binary or ternary NCs could be greatly improved by covering higher band-gap materials. CuInS and ZnS have a small lattice mismatch of only about 2%, much less than the CdSe/CdS and CuInSe/ZnS system (the lattice mismatch is about 4% and 7%)^[31], which minimizes the lattice strain between core and shell during the formation of core/shell heterostructure^[18, 32–33]. With prolonged reflux time, the generated defects in the ZnS shell may be the source of new nonradiative recombination sites, which caused the decline of PL emission quality with thicker ZnS shell. Similarly, variations of PLQY were found in the other different stoichiometric ratios of Cu:In (the stoichiometric ratios of Cu:In are 1:1, 1:4, and 1:6).

The PL decay curves of QDs were well-fitted by a sum of two exponentials, and two time constants were derived. The slow time component was associated with an internal defect-related emission, and the fast time component was probably correlated to primary nonradiative recombination associated with surface-related

traps^[17, 21, 27]. For CuInS QDs, the PL lifetimes were 264 (65), 270 (71), 293 (86), and 299 (95) ns, respectively (Table S1). This result demonstrated that the internal defect-related emission process was highly promoted by the large Cu deficiency, which was consistent with the improved PL intensity and the formation of defect-ordered structure by the large Cu deficiency in CuInS QDs. Very interestingly, the quaternary CuInZnS QDs had similar PL lifetimes, and the data were 277 (102), 284 (101), 284 (110), and 282 (112) ns, respectively (Fig. S9, Table S2). This data indicated that, although the stoichiometric ratio of Cu : In had a strong influence on the PLQY of the CuInZnS QDs, it had less significant effect on the emission lifetimes of these alloyed QDs in this work.

The CuInZnS@ZnS QDs exhibited size-dependent fluorescence lifetime, which gradually increased with shell growth (Fig. 1(c)). The fluorescence lifetime of CuInZnS@ZnS QDs (the stoichiometric ratio of Cu : In is 1 : 2) with shell growth time of 20 h was 755 (231) ns (Table S3). Meanwhile, the PL lifetimes of CuInZnS@ZnS QDs synthesized with Cu : In stoichiometric ratio of 1 : 4 were over 500 ns with different growth times (Fig. S10, Table S4). To the best of our knowledge, this was probably the longest lifetime in the Type-I structured CuInS/ZnS QDs system in those reported literature^[17-18, 21, 26, 34]. The origin of long lifetime is different from quasi-Type II structured CuInS/CdS core/shell nanorod system since electron is delocalized into CdS shell materials^[35]. These long lifetimes, which probably originate from relatively slow but smooth ZnS shell growth and CuInZnS alloying process, were well beneficial for time-resolution fluorescent analysis and imaging.

2.2 TEM characterization of QDs

Fig. S11 shows the resulting CuInS QDs (the stoichiometric ratio of Cu : In is 1 : 2) exhibited pyramidal shapes, and the sizes were typically (2.0 ± 0.5) nm. Such a size distribution was usually an inherent phenomenon in the non-injection-based synthetic route and can be partially attributed to a continuous and slow release of the S^{2-} ion from DDT throughout the reaction. Noticeable improvements in the uniformity of size and shape inhomogeneity of the CuInZnS alloyed QDs were obtained after zinc stearate etching, as confirmed by HR-TEM (Fig. S12). These alloyed QDs appeared to be nearly pyramidal in shape and fairly monodisperse, exhibiting an average size of (1.7 ± 0.5) nm for Cu : In stoichiometric ratio of 1 : 2. Continuous lattice fringes could be clearly observed, indicating the high crystallinity of these QDs (Fig. S12). The average sizes of the CuInZnS@ZnS QDs with shell growth of 5 and 20 h were (2.9 ± 0.5) nm and (6.8 ± 0.6) nm (the stoichiometric

ratio of Cu : In : Zn is 1 : 2 : 3), which showed a size increase with the continuous introduction of shell precursors (Fig. 1(d), Fig. S13, and Fig. S14). These QDs also revealed a pyramidal shape and showed quite monodisperse in size. The HR-TEM image of the corresponding QDs is shown in the inset of Fig. 1(d), where the lattice fringe $d=0.298$ nm corresponds to the (200) lattice plane of zinc ZnS. The formation of core/shell structure was further confirmed by XRD patterns (Fig. S15). Such thick ZnS shell can be precisely obtained with the fewest crystalline defects due to the significantly closer lattice parameters of the two materials, by comparison with the CdSe/ZnS system in which only a few ZnS monolayers can be epitaxially grown^[25, 31-32].

Usually, predictable control of size and shape requires that the reaction temperature remains stable throughout the entire precursor's injection. According to our experiment, the injection of precursor solutions was performed slowly enough not to significantly perturb the reaction temperature. The slow growth rate of QDs in these experimental conditions (with a whole reaction time of 20 h) was different from the rapid growth of CdSe/CdS synthetic system^[13, 36-37]. During the growth process, the typical pyramidal shape is consistently observed at all sizes. This further proved that the one-pot/three-step synthetic scheme was beneficial for obtaining high-quality I-III-VI QDs, and the slow growth process enabled easy selection of a specified QD size.

2.3 Cu/In ratio and shell passivation effect on PL properties

Fig. S7 and Fig. S8 show that as the Cu/In ratio gradually changes from 1 : 1 to 1 : 6, the amount of PL blue-shift and the enhancement of PLQY from core-only QDs to core/shell QDs are varied. The PL emission mechanism of this phenomenon is well explained in the recent report from Klimov *et al.*^[38] The observed ensemble optical phenomenon in this systematic spectroscopic study can be validated by the Cu-deficient related intragap emission model they proposed with a bit of modification, as shown in Fig. 2.

In the case of bare QD with Cu/In ratio close to stoichiometric, there are two trap bands associated with surface defects shown in Fig. 2(a). One is near the conduction band (CB) edge (T_c), and the other is near the valence band (VB) edge (T_v). After excitation, the hot electron can recombine with the hole located at Cu^+ intragap state radiatively, while the hot electron and hole can also be trapped at surface defect sites. The competition among the three channels significantly decreased the PLQY. When Cu/In ratio decreases in Cu-deficient QDs, the hole trap associated with surface defects is diminished (T_{free} in Fig. 2(b) indicates a region

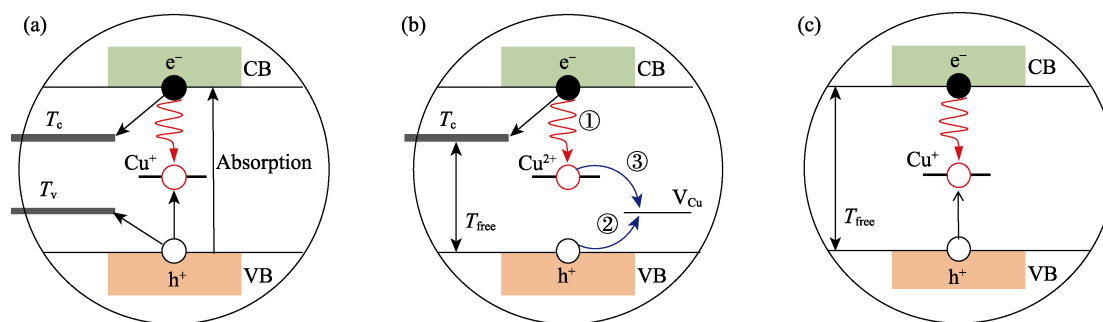


Fig. 2 Schematic depictions of relaxation processes in stoichiometric CuInS QDs (a), Cu-deficient CuInS QDs (b), and Cu-deficient CuInZnS@ZnS core/shell QDs (c)

(a) Photon absorption is mainly due to the VB to CB transition. For the CuInS QDs with Cu/In ratio close to stoichiometric, the PL emission was due to radiative recombination of the CB electron with the hole existing in the intragap Cu^+ state.

(b) For the Cu-deficient CuInS QDs, there are three main processes. Process ①: a hole existing in the ground state forms Cu^{2+} defect, and it can directly recombine with the CB electron. Process ②: the recombination process was slow with the lifetime lasting hundreds of nanoseconds. To dominate the PL emission, another Cu vacancy trap (noted as V_{Cu}) quickly captured the photogenerated hole from the VB state, and formed a charge-compensated pair with the Cu^{2+} defect. Process ③: the trapped hole at V_{Cu} center radiatively recombined with the electron and finished the whole recombination process. (c) For the Cu-deficient core/shell QDs, the diffusion of Zn^{2+} ions occupied and decreased the V_{Cu} intragap states, and the thick ZnS shell eliminated the electron trap bands associated with the CB. The recombination of hot electron at CB edge and hole located at the intragap state (Cu^+) dominated the PL decay process.

without defects), while two intragap states (Cu^{2+} and Cu vacancy, V_{Cu}) are formed. Since the effective mass of an electron is much smaller than that of the hole, the de-trapping rate of the electron is faster and has a weaker effect on the radiative rate compared to that of the hole. The Cu-deficient QDs should potentially have higher PLQY maxima. The data in Fig. S8 also shows the QDs with Cu/In of 1 : 6 have lower PLQY after growing a shell compared to the ones with Cu/In of 1 : 4. This is probably associated with the complexities of Cu^+/Cu^{2+} charge transfer and relative V_{Cu} per QD volume, which will not be explained here.

In order to improve QDs stability and PL performance, the ZnS shell was deposited on CuInS cores accompanied by Zn/Cu exchange through Zn diffusion. Fig. 2(c) shows that in Cu-deficient core/shell QDs, V_{Cu} at the intragap are filled by diffused Zn^{2+} and electron trap bands associated with CB are fully eliminated with high-quality ZnS passivation. Therefore, the main radiative PL decay channel is the recombination of hot electrons at the CB edge and the hole located at the intragap state (Cu^+). This model explains well single-exponential fitted PL decay curves and longer PL decay times with thick shell growth (Table S3, shell reaction time of 8–12 h). Noting that moderate shell thickness is quite essential to obtain optimal PLQY since the lattice strain significantly increases with thick shell deposition, and the strain accumulated at the interface will cause defects after exceeding certain threshold. Similar cases can be found in the CdSe-based core/shell QDs system^[39–41].

3 Conclusions

In summary, off-stoichiometric CuInZnS@ZnS core/shell QDs with high PLQY (up to 85%), long PL lifetime (up to 755 ns), and excellent crystallinity were prepared *via* a one-pot/three-step approach. The prepared CuInZnS@ZnS QDs show a continuous blue shift during the growth of CuInZnS QDs and CuInZnS@ZnS QDs, which is attributed to the continuous and ongoing cation exchange (diffusion) process during their alloying and shell growth processes. The QDs size firstly decreases during the alloying process and then gradually increases with the introduction of ZnS shell. The observed phenomena are well explained by the Cu-deficient related intragap emission model. Therefore, this work provides deep insights concerning the spectroscopic evolution for fabricating multi-component QDs and a promising route for further synthesis of ternary or quaternary-alloyed QDs.

Supporting Materials

Supporting Materials related to this article can be found at <https://doi.org/10.15541/jim20240426>.

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具有可调谐和长寿命荧光发射的高亮度、 单分散四元 CuInZnS@ZnS 量子点

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摘 要: 作为环境友好型发光量子点(QDs)的重要替代材料, CuInS 基核/壳量子点近年来受到越来越多的关注。然而, 这类量子点的一些缺点仍然阻碍了它们的工业化应用, 比如较低的光致发光量子产率(PLQY)、复杂的合成途径、发射光谱易失去控制、光稳定性不足等。本研究通过一锅/三步法合成策略成功制备了 CuInZnS@ZnS 核/壳量子点, 并精确调控其荧光发射光谱, 然后系统研究了 CuInZnS@ZnS 量子点在晶核形成、合金化和 ZnS 壳层生长过程中的集体光谱特性。通过控制 Cu/In 元素的化学计量比、Zn²⁺掺杂以及 ZnS 壳层生长, 实现了量子点荧光发射峰在 530~850 nm 范围内的精准调控。CuInZnS@ZnS 量子点具有明显的长荧光发射寿命(长达 750 ns)、高 PLQY(高达 85%)和优异的结晶度。基于 Cu 缺陷相关的分子内定域能级发射模型阐释了集体光谱演变规律。通过控制 Cu/In 元素的化学计量比, 并且基于 Cu 缺陷的不同氧化态, 提出了两种不同的 Cu 缺陷相关发射途径。本工作为制备高荧光效率的三元或四元合金量子点提供了更深入的见解。

关 键 词: 量子点; 铜铟硫; 合金; 核壳; 集体光谱; Cu 缺陷发光

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Supporting information:

High-brightness and Monodisperse Quaternary CuInZnS@ZnS Quantum Dots with Tunable and Long-lived Emission

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S1 Experimental Section

S1.1 Materials and reagents

The following chemicals were used as received. Technical grade (90%) 1-octadecene (ODE), copper (I) iodide (CuI, 99.999%), indium acetate (In(Ac)₃, 99.99%), zinc stearate (10%–12% Zn basis), oleic acid (90%), trioctylphosphine (TOP, 90%, technical grade), and 1-dodecanethiol (DDT, ≥ 98%) were purchased from Sigma-Aldrich and used as-received. Nanocrystal growth was carried out under argon using Schlenk Line techniques. Air-sensitive reagents were prepared in a nitrogen-filled glovebox.

S1.2 Synthesis of CuInS QDs

For a typical synthesis of CuInS QDs^[25], 0.1 mmol CuI powder, 0.4 mmol In(Ac)₃, and 10 mL 1-dodecanethiol (DDT) were mixed in a 50 mL three-neck flask. The round-bottom flask was first put under vacuum and heated to 80 °C while stirring, backfilled with Ar. Under argon flux, the temperature was heated to about 215 °C. Upon heating up, the reaction mixture became transparent and colorless at around 160 °C, and it started to change color from 190 °C, turning from yellow, to red and dark red at 215 °C, which indicated the nucleation and growth of CuInS QDs. In order to synthesize CuInS QDs with different stoichiometric ratios of cationic precursors (that is, with a ratio of copper to indium lower than one), the amounts of CuI (0.1 mmol) and DDT (10 mL) were held fixed, while the quantity of In precursor was adjusted (0.1 mmol, 0.2 mmol, 0.4 mmol, and 0.6 mmol).

S1.3 Synthesis of CuInZnS alloyed QDs

Without intermediate purification step of the CuInS QDs, the CuInS QDs solution was degassed at 120 °C for 30 min. The zinc stearate solution (0.3 mmol zinc stearate dissolved in 4 mL ODE and 1 mL TOP) was dropwise added by a syringe pump within 30 min to the

CuInS QDs solution at 120 °C. Then, the temperature was heated to about 200 °C and maintained for 90 min before cooling to 120 °C^[17, 25].

S1.4 Synthesis of CuInZnS@ZnS core/shell QDs

The CuInZnS alloyed QDs solution was degassed at 120 °C under vacuum for 60 min, and then the temperature was heated to 220 °C under argon flux, and a solution of zinc and sulfur mixed precursors (20 mL of a 0.1 mol/L solution of zinc stearate in 5 mL oleic acid, 5 mL DDT, and 10 mL ODE) were injected by a syringe pump at a rate of 2 mL/h. The aliquots were taken out at a certain time for further measurements. The entire growth process was monitored by ultraviolet-visible (UV-Vis) and photoluminescence spectra. After the injection of precursors, the reaction solution was stirred for an additional 60 min of refluxing process at 220 °C, then the heating vessel was allowed to naturally cool to room temperature.

S1.5 Materials characterization

UV-Vis absorption and PL emission spectra of CuInS-based QDs were obtained by a UV/Vis-3501 spectrophotometer and an F-380 spectrometer (Tianjin Gangdong SCI & Tech. Development Co., Ltd., China). HRTEM images were recorded on a JEM-2100 (JEOL Ltd., Japan) with an accelerating voltage of 200 kV. Time-resolved fluorescence spectra were measured *via* the time-correlated single-photon counting (TCSPC) method using an FLS920 steady state and lifetime fluorescence spectrometer (Edinburgh Instruments, UK). The relatively PLQY of various QDs samples were comparatively studied by taking Rhodamine 6G (R6G) as a reference fluorescent dye with the known QY (95%) and comparing the integrated fluorescence intensity of the solutions, both recording exciting samples having the same absorbance (< 0.1 au in order to minimize possible reabsorption effects). The PLQY of the as-prepared QDs were calculated using the following equation:

$$QY_{\text{sample}} = QY_{\text{R6G}} \times (\text{grad}_{\text{sample}}/\text{grad}_{\text{R6G}}) \times (n_{\text{sample}}/n_{\text{R6G}}).$$
Where grad stands for the gradient (slope) of the plot of

the integrated fluorescence intensity vs absorbance, and n stands for the refractive index of the solvent (1.36 for

ethanol, 1.37 for hexane, and 1.50 for toluene). The excitation wavelength was set at 450 nm.

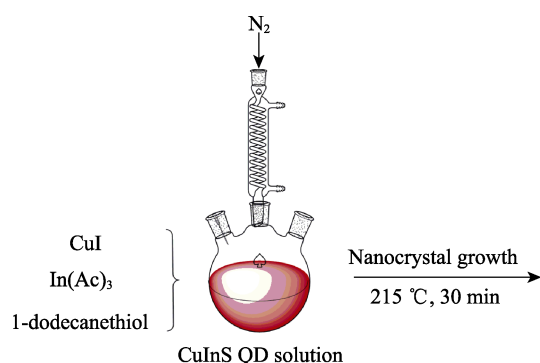


Fig. S1 Synthetic equipment of the CuInS-based QDs

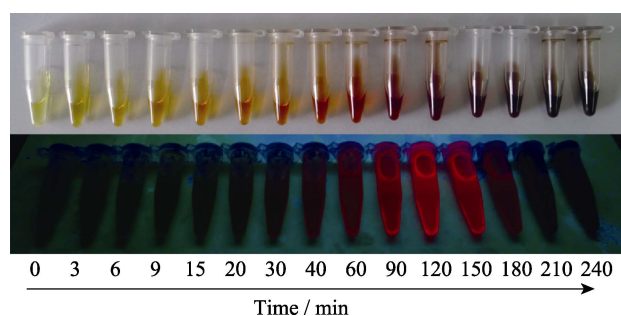


Fig. S2 Digital photographs of CuInS QDs in a typical nucleation growth process under daylight lamp and UV lamp (365 nm)

DDT was chosen as the sulfur source, surface ligand, and solvent. The reaction temperature was 200 °C

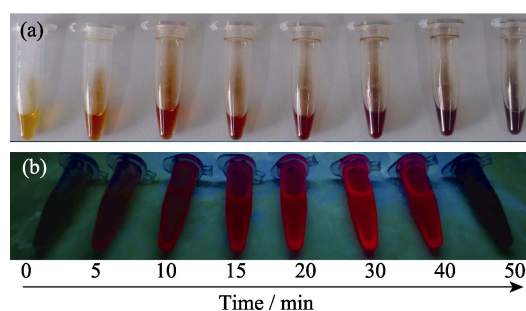


Fig. S3 Digital photographs of CuInS QDs in a typical nucleation growth process under daylight lamp and UV lamp (320 nm)

Octanethiol was chosen as the sulfur source, surface ligand, and solvent. The reaction temperature was 200 °C

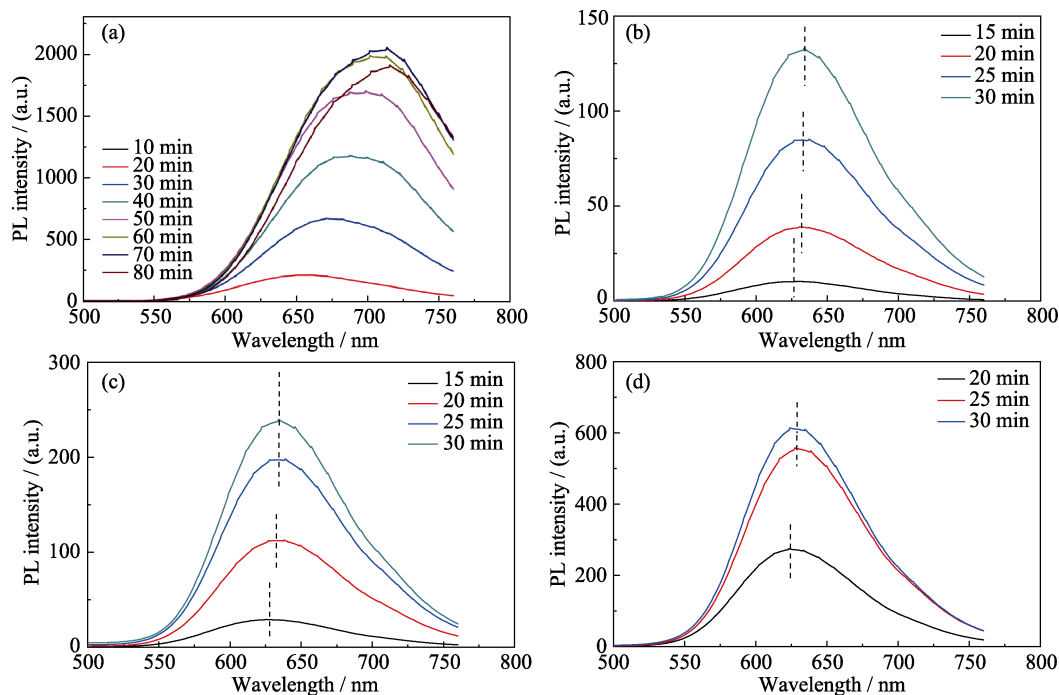


Fig. S4 Temporal evolution of PL emission spectra of CuInS QDs synthesized with different molar stoichiometric ratios of Cu : In precursors

(a-d) stand for 1 : 1, 1 : 2, 1 : 4, and 1 : 6. DDT was chosen as the sulfur source. The aliquots of QDs samples for the PL intensity test were fixed. PL spectra were recorded with excitation at 450 nm

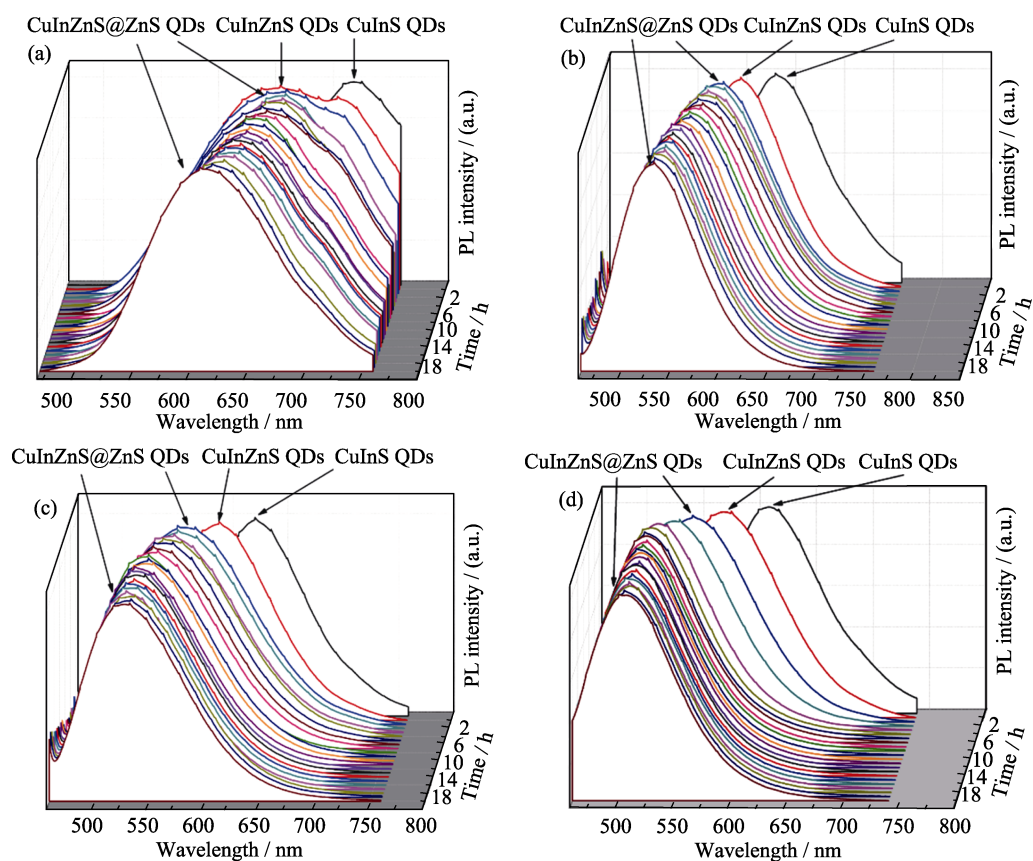


Fig. S5 Temporal evolution of PL spectra of CuInS QDs, CuInZnS QDs, and CuInZnS@ZnS QDs with different growth time (a-d) stand for the stoichiometric ratio of Cu : In at 1 : 1, 1 : 2, 1 : 4, and 1 : 6. PL spectra were recorded with excitation at 450 nm

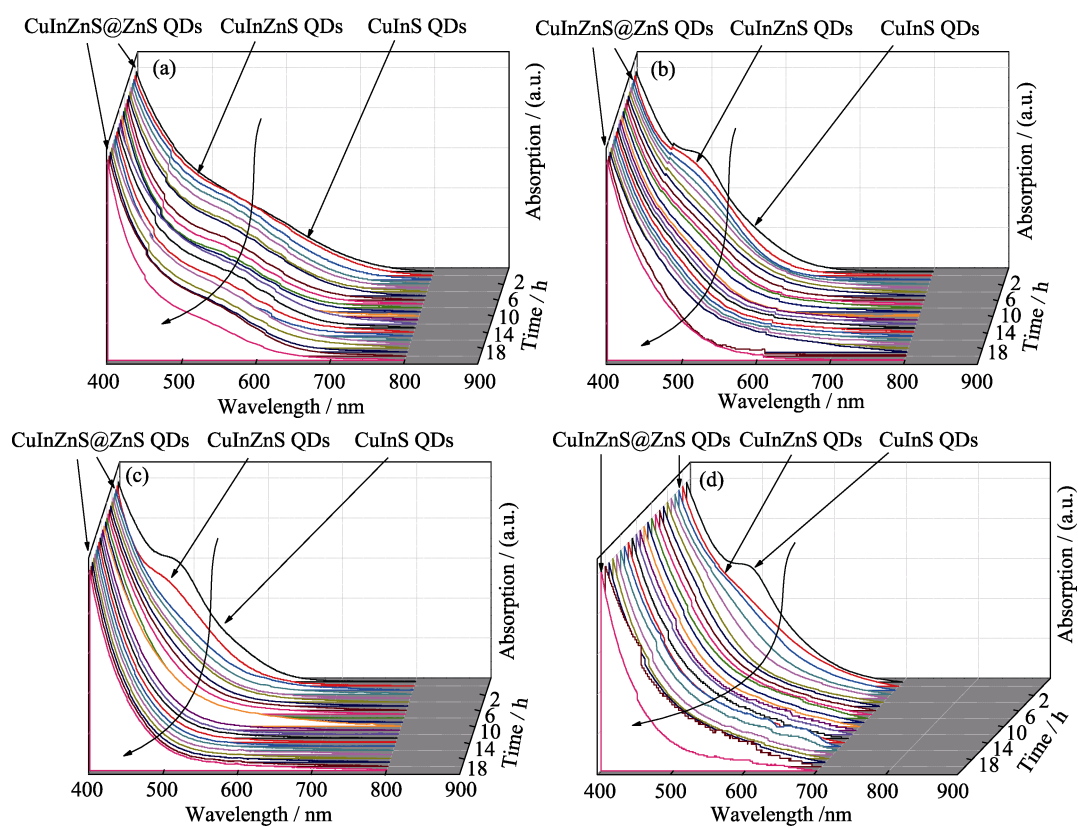


Fig. S6 Temporal evolution of UV-Vis absorption spectra of CuInS QDs, CuInZnS QDs, CuInZnS@ZnS QDs synthesized with different molar stoichiometric ratios of Cu : In precursors (a-d) stand for the stoichiometric ratio of Cu : In at 1 : 1, 1 : 2, 1 : 4, and 1 : 6. The absorption shoulder/onset is more blue-shifted with less Cu/In ratio

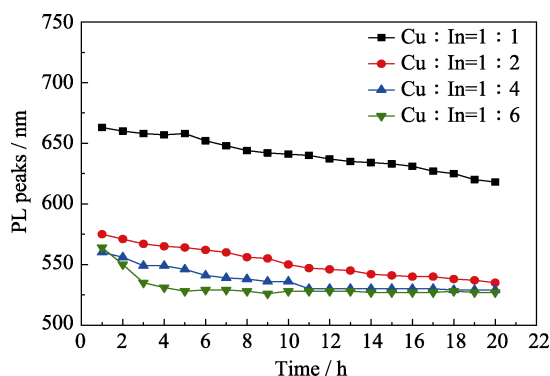


Fig. S7 Temporal evolution of PL central emission peaks for CuInZnS@ZnS QDs with different shell growth time

The stoichiometric ratios of Cu : In are 1 : 1, 1 : 2, 1 : 4, and 1 : 6

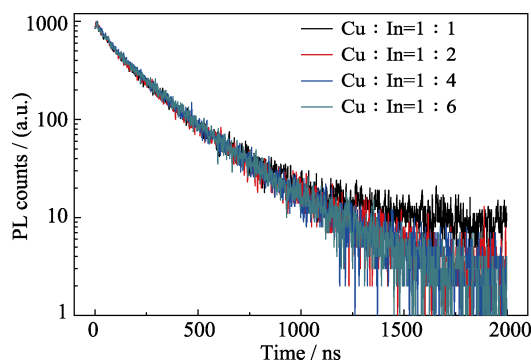


Fig. S9 Representative transient PL decays for CuInZnS QDs

The stoichiometric ratios of Cu : In are 1 : 1, 1 : 2, 1 : 4, and 1 : 6

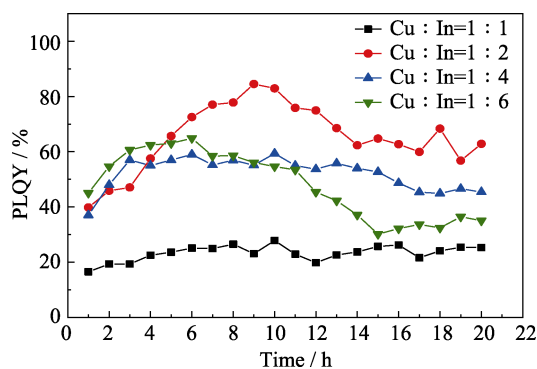


Fig. S8 Temporal evolution of PLQY for CuInZnS@ZnS QDs with different shell growth time

The stoichiometric ratios of Cu : In are 1 : 1, 1 : 2, 1 : 4, and 1 : 6

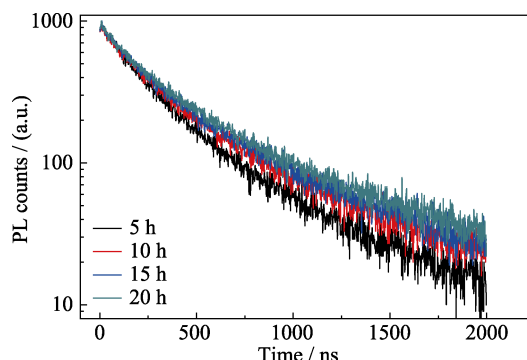


Fig. S10 Representative transient PL decays of CuInZnS@ZnS QDs with different ZnS shell growth time

The stoichiometric ratio of Cu : In is 1 : 4

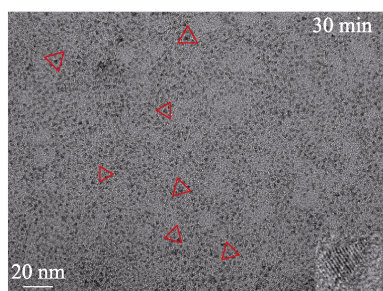


Fig. S11 TEM image of CuInS QDs (the stoichiometric ratio of Cu : In at 1 : 2) with reaction time of 30 min

The red triangle frames indicate the shapes of the CuInS QDs

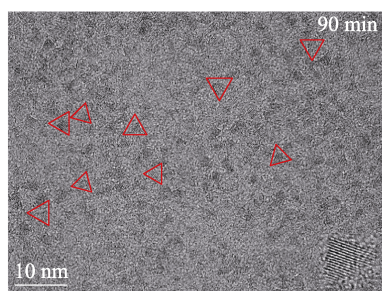


Fig. S12 TEM image of CuInZnS QDs (the stoichiometric ratio of Cu : In : Zn at 1 : 2 : 3) with Zn etching time of 90 min

The red triangle frames indicate the shapes of the CuInZnS QDs

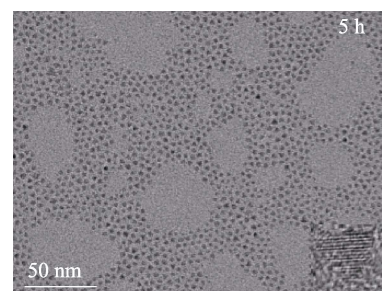


Fig. S13 TEM images of CuInZnS@ZnS QDs (the stoichiometric ratio of Cu : In : Zn at 1 : 2 : 3) with ZnS shell growth time of 5 h

The insert showing their representative high-resolution TEM images

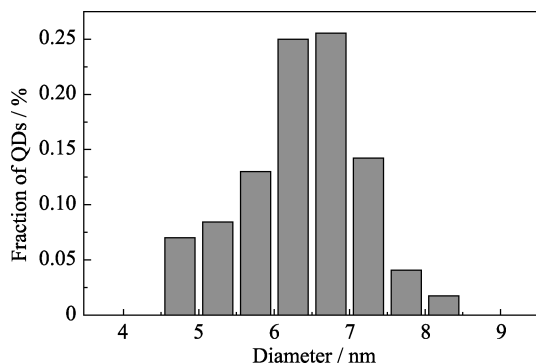


Fig. S14 Size distribution histograms for CuInZnS/ZnS QDs (Cu : In : Zn at 1 : 2 : 3) with shell growth of 20 h

To build the histograms, over 100 particles were measured

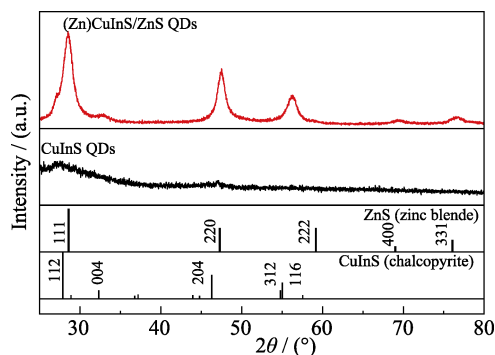


Fig. S15 XRD patterns of CuInS QDs (Cu : In stoichiometric ratio at 1 : 2) and (Zn)CuInS/ZnS QDs (Cu : In : Zn stoichiometric ratio at 1 : 2 : 3)

Table S1 Relevant parameters for CuInS QDs synthesized with different molar stoichiometric ratios of Cu : In. λ_{em} at the PL central emission peak from the QDs solution when excited at 450 nm. The amounts of DDT (10 mL) and CuI (0.1 mmol) were held fixed

Cu : In precursor	λ_{em}/nm	PLQY/%	PL decay/ns
1 : 1	710	3.3	264 (65)
1 : 2	633	8.8	270 (71)
1 : 4	625	18.9	293 (86)
1 : 6	618	21.0	299 (95)

Table S2 Relevant parameters for CuInZnS alloyed QDs synthesized with different molar stoichiometric ratios of Cu : In. λ_{em} is the PL central emission peak from the QDs solution when excited at 450 nm. The amounts of DDT (10 mL) and CuI (0.1 mmol) were held fixed

Cu : In precursor	λ_{em}/nm	PLQY/%	PL decay/ns
1 : 1	675	14.7	277 (102)
1 : 2	596	16.8	284 (101)
1 : 4	590	24.8	284 (110)
1 : 6	581	36.3	282 (112)

The crystal structure of the CuInS QDs (Cu : In stoichiometric ratio of 1 : 2) and CuInZnS@ZnS QDs (Cu : In : Zn stoichiometric ratio of 1 : 2 : 3) were characterized by XRD (Fig. S15). The peaks of the CuInS QDs at 2θ of 27.5° (112), 47.0° (204) and 54.8° ((312)/(116)) basically match with the characteristic peaks of chalcopyrite structure (JCPDS file 32-0339).

For the CuInZnS@ZnS QDs, their diffraction peaks match well with the typical zinc blende structure of cubic ZnS (JCPDS file 02-0564), implying the formation of the (Zn)CuInS/ZnS core/shell structure.

Table S3 PL lifetime of CuInZnS@ZnS QDs with the stoichiometric ratio of Cu : In at 1 : 2 after excited at 450 nm.

Shell reaction time/h	PL decay/ns
3	588 (204)
5	647 (208)
8	714 (214)
10	724 (211)
12	729 (219)
15	751 (222)
20	755 (231)

Table S4 Relevant parameters for CuInZnS@ZnS QDs with the stoichiometric ratio of Cu : In at 1 : 4, synthesized with different ZnS shell growth time. λ_{em} is the PL central emission peak from the QDs solution when excited at 450 nm. The amounts of DDT (10 mL) and CuI (0.1 mmol) were held fixed.

Shell reaction time/h	PL emission peak/nm	PLQY/%	PL decay/ns
5	546	57	509 (171)
10	536	50	530 (177)
15	531	53	558 (174)
20	530	58	549 (165)