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Biocompatible off-stoichiometric copper indium sulfide quantum dots with tunable near-infrared emission *via* aqueous based synthesis[†]

Mingxia Jiao, ம a Xiaodan Huang, ^b Linzheng Ma, ^a Yun Li, ^a Peisen Zhang, ^b Xiaojun Wei, ^b Lihong Jing, ம *^b Xiliang Luo, ம *^a Andrey L. Rogach ^b ^c and Mingyuan Gao ^b

The present study reports an aqueous synthesis approach towards off-stoichiometric copper indium sulfide quantum dots with emissions in the near-infrared spectral range. The photoluminescence properties of the dots, and in particular the appearance of dual emission at high Cu deficiency, were studied with temperature-dependent steady-state and transient photoluminescence spectroscopy.

Copper indium sulfide (CIS) quantum dots (QDs), as representative ternary I–III–VI nanocrystals, have been widely explored due to their potential applications in optoelectronics and biomedical imaging, as they possess a direct band gap ($E_{g,bulk} = 1.5 \text{ eV}$) and tunable fluorescence ranging from the visible to near-infrared (NIR) spectral region.^{1–5} CIS QDs exhibit a large optical absorption coefficient ($\alpha > 10^5 \text{ cm}^{-1}$), high photostability, a large Stokes shift, and high photoluminescence quantum yield (PL QY) upon appropriate shell coating.^{6–8} Moreover, being free of toxic elements such as Cd or Pb makes CIS QDs a promising alternative to majority of II–VI and IV–VI QDs, and thus particularly suitable for *in vivo* applications.⁹ These advantages have drawn a significant amount of research into the wet-chemical synthesis of CIS QDs with desired optical properties.^{10–16}

The optical properties of ternary CIS QDs not only depend on the particle size, but are also closely related to the chemical composition of colloidal QDs. The Cu/In molar ratio has been demonstrated to have a great impact on the PL properties of CIS QDs.^{12,17–20} For example, Uehara *et al.* tuned the CIS QD composition from CuInS₂ to CuIn₃S₅ by adjusting the concentration of the

† Electronic supplementary information (ESI) available: (1) Experimental details, (2) characterization of the QDs, and (3) PL decay-fitting data. See DOI: 10.1039/c9cc07674c

Cu precursor, which resulted in nearly unchanged particle size but blue shifts of the absorption edge and emission peak as well.¹⁷ Zhong and coworkers reported that by varying the Cu/In ratio from 0.3 to 1.6, the PL peak of the CIS QDs shifted from 650 nm to 760 nm with its full width at half maximum (FWHM) maintained at around 120 nm, and the highest QY was obtained by adjusting the molar ratio of Cu/In to 0.7.¹² Specifically, they proposed a "donor-acceptor pair" (DAP) recombination mechanism for the composition-dependent emission whose PL QY is largely governed by defect concentration.^{12,21} An alternative carrier recombination between a quantized electron state and a defectrelated hole state was also proposed.15,21 However, there remains lack of a systematic study on the degree of Cu deficiency and the related off-stoichiometry effects on the optical properties of CIS ODs. The intrinsic defects in ternary CIS systems are generally considered as the dominant sources of recombination channels for charge carriers.^{21,22} On the other hand, most of the reported CIS QDs were prepared through thermal decomposition of metal precursors in the non-aqueous phase,^{10,14} so the resulting hydrophobic particles are not compatible with biological systems before further surface modification. Therefore, it is necessary to develop synthetic methods for achieving water-soluble CIS QDs with tunable PL in the near-infrared range.

Following our previous studies on preparation and *in vivo* imaging applications of $CuInS_2$ nanocrystals,^{9,23} herein we report an aqueous synthesis of biocompatible CIS QDs. By adjusting the Cu/In molar ratio from 0.025 to 0.33, the off-stoichiometry effects especially in terms of Cu-deficiency on the PL properties were investigated by steady-state and transient spectroscopy in combination with structural and compositional analysis on the resulting nanocrystals. By coating CIS particles with ZnS, highly stable, low cytotoxic, and strongly luminescent CIS/ZnS QDs were obtained.

In detail, the water-soluble CIS QDs were synthesized by refluxing the aqueous solution containing $CuCl_2$, $InCl_3$, and Na_2S in the presence of L-glutathione (GSH) and sodium citrate (SC) as surface ligands at pH 6.0. Because GSH bearing a thiol group as a soft Lewis base prefers to pair with soft Lewis acid Cu^+ , while sodium citrate acid as a hard Lewis base prefers to

^a Key Laboratory of Optic-electric Sensing and Analytical Chemistry for Life Science, MOE, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Zhengzhou Road 53, Qingdao 266042, China. E-mail: xiliangluo@qust.edu.cn

^b Key Laboratory of Colloid, Interface and Chemical Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Bei Yi Jie 2, Zhong Guan Cun, Beijing 100190, China. E-mail: jinglh@iccas.ac.cn

^c Department of Materials Science and Engineering, and Centre for Functional Photonics (CFP), City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong SAR



Fig. 1 Absorption and PL spectra of CIS QDs obtained at different Cu/In molar ratios.

bind with hard Lewis acid In³⁺, they were selected to properly regulate the reactivities of Cu⁺ and In³⁺. Highly reactive Na₂S was chosen as the sulfur source to enable the preparation of CIS QDs at a relatively low temperature.¹⁸ The PL properties of CIS QDs are known to be strongly dependent on the crystal composition. Therefore, for tuning the PL, the Cu/In molar ratio in CIS QDs was gradually changed by adjusting their feeding molar ratio from 0.025 to 0.33. As confirmed by the elemental analysis as shown in Table S1 and Fig. S1 (ESI†), the Cu/In molar ratio in the obtained CIS QDs was quite consistent with the feeding ratio, therefore, the Cu/In ratio used in the following discussion was referred to as the feeding ratio. It is worth mentioning that the Cu/In molar ratio of Cu-deficient CIS QDs synthesized in this work is far beyond the range reported in previous reports.^{12,18,19} Fig. 1 presents the absorption and PL spectra of a series of QDs with different Cu/In molar ratios. The absorption progressively shifts to lower energies against the Cu/In ratio, with the exciton absorption peak being broadened and absorption onset extended to the near-infrared (NIR) region, accompanied by a gradual red-shift of PL emission. A dual-emission appeared, with a high-energy emission shoulder at 560 nm and a low-energy emission peaking at around 670 nm, for QDs with a Cu/In ratio of 0.025. This made the QD solution exhibit an orange fluorescence under UV irradiation as shown in Fig. S2 (ESI⁺). Along with the increase of Cu content, the intensity of the emissive shoulder at 560 nm is weakened but unchanged in position (Table S2, ESI⁺), while the low-energy emission gradually red-shifted. Meanwhile, the PL QY of CIS QDs firstly increased and reached the maximum of 4.2% for samples with a Cu/In ratio of 0.10 and then decreased (Fig. S3 and Table S2, ESI[†]). The high-energy emission disappeared when the Cu/In molar ratio reached 0.20, leaving a single emission peaking at 720 nm. Upon further increasing the Cu/In molar ratio above 0.33, e.g., 0.50 and 1.0, no PL was observed, and the UV-Vis absorption spectra (Fig. S4, ESI[†]) displayed an increased NIR absorption for the sample with a Cu/In ratio of 1.0.

To investigate the structural variations of the QDs synthesized with different Cu/In molar ratios, X-ray diffraction (XRD)



Fig. 2 (a) Powder X-ray diffraction (XRD) patterns of CIS QDs with different Cu/In ratios together with line patterns for tetragonal CIS (pink line, JCPDS 65-2732) and cubic In_2S_3 (black line, JCPDS 32-0456), and (b) TEM images of CIS QDs with different Cu/In ratios. The scale bars correspond to 10 nm. The inset shows the HRTEM image of CIS QDs with a Cu/In ratio of 0.33.

measurements were performed (Fig. 2a). The XRD patterns of powder samples with the Cu/In ratio from 0.33 to 0.10 match well with the tetragonal chalcopyrite phase of CIS (JCPDS card no. 65-2732).¹² However, for the samples with a Cu/In ratio of 0.050 and 0.025, the FWHM of the diffraction peaks became broader, and peaks shifted to higher angles. The broadening of the diffraction peaks can collectively be attributed to the decreased crystallinity and distorted lattice of QDs at relatively higher defect concentrations, while the peak shift reveals that the crystal phase approaches cubic In₂S₃ (JCPDS card no. 32-0456) for CIS QDs with a Cu/In ratio of 0.025. The TEM images of CIS QDs (Fig. 2b) show that they possess nearly unchanged particle size irrespective of the Cu/In molar ratio, as further illustrated by the statistical size histograms in Fig. S5 (ESI⁺). The HRTEM image of the QDs with a Cu/In ratio of 0.33 (inset of Fig. 2b) further confirms the tetragonal chalcopyrite crystal structure with an observed lattice spacing of 0.243 nm which is well consistent with the lattice spacing (0.242 nm) of the (211) plane of the corresponding bulk material.¹²

On account of the unchanged particle size against the Cu/In ratio, the appearance of dual emission in some of the QD samples can be attributed to the influence of the Cu deficiency. The off-stoichiometry of CIS has been previously found to be correlated with PL wavelength.^{17–19,22} To shed light on the origin of the dual emission, PL excitation (PLE) spectra of the QDs were recorded at different emission wavelengths as shown in Fig. S6 (ESI[†]). When monitored at high-energy emission (560 nm), a prominent peak around 465 nm in the PLE spectra appeared, while in the low-energy emission region (>600 nm),



Fig. 3 Temperature-dependent PL spectra of the CIS QDs with a Cu/In ratio of 0.025 (a) and 0.33 (b), and normalized time-resolved PL decay curves of the CIS QDs with a Cu/In ratio of 0.025 for the high-energy emission (c) and low-energy emission (d), together with PL decay curves of the CIS QDs with Cu/In ratio of 0.33 (e).

the 465 nm peak disappeared and a new peak around 500 nm arose, which suggests that there are different optical transitions responsible for the two PL peaks. Despite the change in the composition (Cu/In ratio from 0.025 to 0.10), the 465 nm peak was observed in all PLE spectra, and the 560 nm peak remained unchanged in the emission spectra, suggesting that the highenergy emission is independent of the Cu/In ratio. Furthermore, temperature-dependent PL spectra of the QDs with a Cu/In molar ratio of 0.025 and 0.33 (i.e., the former exhibiting dual-emission while the latter showing a single emission) were recorded and are shown in Fig. 3a and b, respectively. As the temperature is decreased from 298 K to 77 K, the PL intensities of both 560 nm and 670 nm peaks (Cu/In = 0.025) remarkably increased, as shown in Fig. 3a. In contrast, the PL intensity of the QDs with a Cu/In ratio of 0.33 shows a non-monotonic behavior against temperature, which is firstly increased to a maximum at 200 K and then slightly decreased upon a decrease of temperature down to 77 K. Meanwhile, the PL peak at 746 nm is blue-shifted with the decrease of temperature. In the case of highly Cu-deficient QDs with dual emission, the high-energy transition may result from the radiative recombination of the electrons from the conduction band of the In₂S₃ dominant host to Cu⁺-localized holes, similar to Cu-doped InP reported by Gamelin and co-workers;²⁴ while the low-energy emission may arise from the radiative recombination of the electrons from the conduction band of Cu-In-S dominant dots with Cu⁺-localized holes.²⁵ This may have resulted from the fact that the former case could provide a wider energy gap between the conduction band edge and Cu⁺ level in comparison with that of the latter due to the wider band gap of In₂S₃ bulk material ($E_{\rm g} \sim 1.8 \text{ eV}$) than that of CuInS₂, thereby leading to the appearance of high-energy emission in addition to lowenergy emission. Since the band gap of In₂S₃ would not change due to the unchanged particle size, the high-energy emission peak was maintained at 560 nm for highly Cu-deficient QDs.



Fig. 4 (a) Absorption and PL spectra of CIS/ZnS QDs in water, the insets are photographs of an aqueous solution captured under ambient (left) and UV light (right), (b) temporal evolutions of the PL intensity and hydrodynamic sizes of the QDs in water and 1× PBS, and (c) cell viability of HeLa cells recorded after being incubated with the CIS/ZnS QDs.

Therefore, in the case when increasing the Cu/In ratio (*i.e.*, 0.10–0.33), the emission was evidently extended to the NIR range as the Cu–In–S components gradually dominate the dots.

Temperature-dependent time-resolved PL decays of the two QD samples with a Cu/In molar ratio of 0.025 and 0.33 were recorded and are shown in Fig. 3c-e and Fig. S7 (ESI⁺). The PL relaxation of these QDs is generally characterized by a multiexponential decay process. The best decay fits based on a threeexponential function are summarized in Table S3 (ESI[†]). For the dual-emissive QDs, the average PL lifetime recorded at 560 nm was prolonged by a factor of 13.2 as the temperature is decreased from 298 K to 77 K, i.e., 161.6 ns vs. 2140 ns (Fig. 3c). Meanwhile, the average PL lifetime for the 670 nm peak was prolonged by a factor of 5.1, *i.e.*, 485.2 ns vs. 2482 ns (Fig. 3d). The lifetime-increasing factor for the high-energy emission is more than twice that for the low-energy emission, which indicates different thermal activation processes involved in the quenching of photogenerated carriers. For the singleemissive QDs (Fig. 3e), the average lifetime for 746 nm emission is increased from 332.7 ns to 1100 ns upon changing the temperature from 298 K to 77 K, i.e., by a factor of 3.3. These results further highlight that the high-energy emission of QDs is strongly temperature-dependent, while the low-energy emission is not. Therefore, the Cu-deficiency degree in CIS QDs exhibits a strong influence on the optical transition process, which as a result can be effectively employed to regulate the NIR emission.

Towards biomedical applications, the aqueous CIS QDs obtained with a Cu/In ratio of 0.33 were further coated with the ZnS shell to enhance their emission at 746 nm. The experimental details are provided in the ESI.[†] As shown in Fig. S8 (ESI[†]), 10 min of the coating reaction already led to an improvement of the PL QY, while 2 h of shell growth resulted in a PL QY of 13.8% (inset of Fig. 4a and Fig. S8, ESI⁺), which is one order of magnitude higher than that of initial CIS cores. The PL spectrum and the corresponding absorption spectrum of the CIS/ZnS QDs are shown in Fig. 4a. Notably, during the ZnS coating process, the peak position was less blue-shifted than those previously observed,^{9,18} *i.e.*, only 6 nm occurring during initial 10 min of the coating reaction and then remaining nearly constant until the shell coating was completed, as shown in Fig. S8 (ESI[†]). On one hand, such a small blue-shift can probably be attributed to the slow diffusion of Zn²⁺ across the core-shell interface at decreased reaction temperature (80 °C) for the ZnS shell coating. On the other hand, the PL peak position became unchanged 10 min after the shell growth and the PL QY kept increasing, which strongly suggests that the late stage of the surface coating reaction is indeed dominated by ZnS growth rather than Zn²⁺ inter-diffusion. Time-resolved PL decay measurements (Fig. S9, ESI[†]) revealed that after the ZnS coating, the lifetime of the resulting core-shell QDs was prolonged from 333 ns to 448 ns. X-ray photoelectron spectroscopy (XPS) data shown in Fig. S10 (ESI[†]) also confirmed the successful ZnS coating. Long-term (over two weeks) observations show that the CIS/ZnS QDs exhibit stable PL emission, as shown in Fig. 4b and Fig. S11 (ESI⁺), apart from their excellent colloidal stability in both water and phosphate buffered saline (PBS).

The cytotoxicity of the CIS/ZnS QDs was evaluated through the 3-(4,5-dimethylthiazole-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay on the proliferation of HeLa cells. As shown in Fig. 4c, the cell viability remains above 80% even when the Cu concentration reaches 50 mM, much higher than that for the PEGylated CuInS₂@ZnS:Mn QDs reported previously.⁹ Such low cytotoxicity remarkably increases the suitability of the Cd-free CIS/ZnS QDs for *in vivo* applications.

In summary, aqueous CIS QDs with tunable NIR emission have been successfully synthesized by properly balancing the precursor reactivities. Temperature-dependent optical transitions were discussed to reveal the off-stoichiometric influence in terms of Cu-deficiency on the photoluminescence. Extremely high Cu-deficiency could increase the energy gap between the conduction band edge and Cu⁺ level, leading to the appearance of high-energy emission. However, less Cu-deficient QDs could decrease the conduction band edge energy, favoring for nearinfrared emission. Upon further coating with the ZnS shell, the fluorescence efficiency of the resulting core–shell CIS/ZnS QDs was enhanced by one order of magnitude reaching 13.8% at room temperature. The good fluorescence and colloidal stability as well as the low cytotoxicity endow the near-infrared emitting CIS/ZnS QDs with potential for *in vivo* biological studies. Our work has offered a green and effective approach for achieving biocompatible Cd-free QDs with controlled PL properties, which is highly desirable for practical applications.

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Conflicts of interest

There are no conflicts to declare.

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