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# Molecular insight into intrinsic-trap-mediated emission from atomically precise copper-based chalcogenide models†

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Luminescent Cu-doped semiconductor nanocrystals have long played a pivotal role in the advancement of lighting and display technologies. The luminescence observed in colloidal copper-based I-III-VI nanocrystals is attributed to defect emission arising from donor-acceptor pair recombination of excited charge carriers. However, a detailed atomic-level exploration of how distinct chemical components precisely influence the defect position has remained challenging, primarily due to inherent local structural imprecision of the traditional I-III-VI nanocrystals. In this study, we have prepared a set of copper-containing I-III-VI metal chalcogenide nanoclusters, 1-CulnS, 1-CuGaS, and 2-CuGaS, serving as unique models to address the aforementioned issues. Interestingly, despite possessing an identical crystalline structure, 1-CuInS and 1-CuGaS exhibit significantly different photoluminescence behaviors. For comparsion, 1-CuGaS and 2-CuGaS, which share the same second building units but differ in structural configuration, demonstrate similar luminescence performance. More importantly, we found that the green emission observed in 1-CulnS likely stems from the radiative recombination of electrons migrating from shallow delocalized traps to copper-localized holes. In contrast, the red emission observed in both 1-CuGaS and 2-CuGaS is presumably due to the recombination of electrons originating from deeply localized traps with copper-localized holes. This disparity in trap sites appears to be highly dependent on the presence of trivalent metal ions (In<sup>3+</sup> and Ga<sup>3+</sup>) within the clusters, and the hypothesis is further substantiated through photoluminescence characterization of 1-CulnGaS containing both In<sup>3+</sup> and Ga<sup>3+</sup> ions simultaneously. Furthermore, we have explored the impact of introducing Cd ions into 1-CuinS, which can alter the position of shallow delocalized traps and thereby fine-tune the luminescence properties. Our findings shed light on the intricate interplay of chemical composition and defect states in coppercontaining I-III-VI nanoclusters, offering valuable insights into the optoelectronic properties of copperbased semiconductor nanocrystals.

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# Introduction

Metal chalcogenide semiconductor nanocrystals, also referred to as quantum dots (QDs), have captivated the scientific and technological community over the past few decades due to their intriguing photoluminescence (PL) properties. Among these, copper-based I–III–VI nanocrystals have garnered particular interest, attributable to their photophysical characteristics, such as optically activated copper midgap states, tuneable photoluminescence (PL) behavior across the visible and near-infrared (NIR) spectral range, and a composition free from toxic elements such as Cd or Pb, having them promising substitutes for most II–VI and IV–VI nanocrystals. Consequently, these nanocrystals hold potential applications in light-emitting diodes, nonlinear optics, and biomedical labeling. 11-14 In this regard, extensive research efforts have

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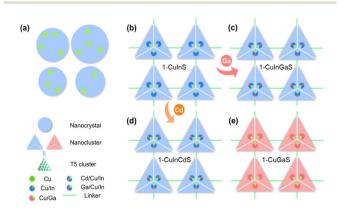
<sup>†</sup> Electronic supplementary information (ESI) available: Experimental details, physical measurements, and additional figures and tables. CCDC 2062543 for 1-CuInS, 2062544 for 1-CuGaS and 2062545 for 2-CuGaS. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d3qi02132g

been dedicated to unfolding the luminescence mechanisms and investigating the factors that influence the properties of copper-based I-III-VI nanocrystals, with the aim of enhancing their optoelectronic performance and further applications.

Research Article

In general, the luminescence observed in copper-based I-III-VI nanocrystals serves as a quintessential example of the donor-acceptor pair (DAP) emission mechanism, which is related to the recombination of excitons, where electrons located in inherent defect sites situated below the conduction band act as donor states, and holes trapped in Cu vacancy  $(V_{Ci})$ . <sup>2,6,15,16</sup> Previous efforts have demonstrated that both the composition and surface structure of these nanocrystals play a crucial role in determining the location and types of intrinsic defects, exerting a significant influence on the emission performance. 15,17,18 However, despite special emphasis has been placed on understanding the defect-induced luminescence of I-III-VI nanocrystals, the correlations between chemical components and defect positions have yet to be systematically explored, primarily due to the inherent uncertainties of the atomic position in typical I-III-VI nanocrystals. Furthermore, the size inhomogeneity of QDs also presents challenges in elucidating the mechanism behind defectmediated emission.

In this aspect, metal chalcogenide supertetrahedral nanoclusters (Tn, n indicates the number of metal layers along the edge of the tetrahedron) with precisely defined compositions and uniform sizes could serve as excellent model system to solve the above issue (Scheme 1). 19-29 In previous study, Mnrelated emission have been studied in detail in Mn based II-III-VI supertetrahedral nanoclusters. For instance, our investigations have delved into the role of dipole-dipole interactions directed by Mn-Mn distances in controlling Mn-related emissions through the examination of three structurally welldefined Mn-based II-III-VI supertetrahedral nanoclusters (MCOF-5, MCOF-6, and MCOF-7).<sup>30</sup> In contrast, there has been a relative scarcity of investigation into the luminescence



Scheme 1 (a) Cu-based classical I-III-VI nanocrystals with imprecise sites of Cu ions and inhomogeneous particle sizes. Copper-based chalcogenide supertetrahedral nanoclusters including (b) 1-CuInS, (c) 1-CulnGaS, (d) 1-CulnCdS, and (e) 1/2-CuGaS with relatively precise sites of Cu ions and homogeneous cluster size.

mechanism of copper-related emission from Cu-based I-III-VI supertetrahedral nanoclusters.31-34

Herein, a series of copper-based I-III-VI metal chalcogenides (1-CuInS, 1-CuGaS, and 2-CuGaS) were synthesized and their photoluminescence behaviors were found strongly depend on the specific components present. Specifically, both 1-CuInS and 1-CuGaS are constructed by the assembly of supertetrahedral T5-Cu<sub>5</sub>M<sub>30</sub>S<sub>56</sub> clusters which are linked by [MSb<sub>4</sub>S<sub>10</sub>] units (M = In for 1-CuInS and M = Ga for 1-CuGaS). In contrast, 2-CuGaS adopts the same second building units (SBUs) as 1-CuGaS but utilizes [SbS<sub>3</sub>] units as linkers. Interestingly, at room temperature, 1-CuInS emits green luminescence, whereas 1-CuGaS and 2-CuGaS only emit red luminescence at low temperatures. Temperature-dependent PL and PL decay dynamics analysis indicated that the green emission originates from shallow delocalized traps while the red emission arises from deep localized traps, and both resulting in radiative recombination with Cu vacancy acceptor. Additionally, the emission of 1-CuInS could be finely tuned through doping cadmium ions in the parent clusters due to the modulating of the position of the shallow delocalized traps.

# Results and discussion

# Synthesis and characterization of 1-CuInS, 1-CuGaS, and 2-CuGaS

Crystalline samples discussed here were synthesized via a similar solvothermal method with different types of protonated organic amines as templates (see the ESI† for more details). Their crystalline structures were determined by singlecrystal X-ray diffraction (SCXRD), and compositions were further confirmed by energy dispersive X-ray spectroscopy (EDS) and elemental analysis (EA) (Fig. S1-S3†). In addition, the phase purity and thermal stability of the as-synthesized samples were characterized by powder X-ray diffraction (PXRD) (Fig. S4–S6†) and thermal gravimetric analysis (TGA) (Fig. S7– S9†), respectively. Furthermore, X-ray photoelectron spectroscopy (XPS) confirmed that Cu atoms in all the three structures were monovalent (Fig. S10†).

SCXRD analysis indicates that 1-CuInS and 1-CuGaS crystallize in the same space group tetragonal  $I4_1/a$  with very similar unit cell parameters while 2-CuGaS crystallizes in the hexagonal space group  $P6_3/m$  (Table S1†). The structures of **1-CuInS** and 1-CuGaS are isomorphic, characterized by the assembly of supertetrahedral T5-Cu<sub>5</sub>M<sub>30</sub>S<sub>56</sub> clusters linked by [MSb<sub>4</sub>S<sub>10</sub>] units (M = In for 1-CuInS and M = Ga for 1-CuGaS) (Fig. 1a and b). At the center of the linker is the tetrahedral  $[MS_4]$  unit, which is further connected with four trigonal-pyramidal [SbS<sub>3</sub>] units through corner sulfurs, resulting in the formation of a  $[MSb_4S_{10}]$  unit with windmill shape when viewed along the c axis (Fig. S11†). Each [MSb<sub>4</sub>S<sub>10</sub>] unit joins for four T5-Cu<sub>5</sub>M<sub>30</sub>S<sub>56</sub> cluster through corner-shared μ-S<sup>2-</sup> and vice versa, creating a double-interpenetrated framework with diamond topology (Fig. S12a, S12b, and S13a†). For 2-CuGaS, it pos-

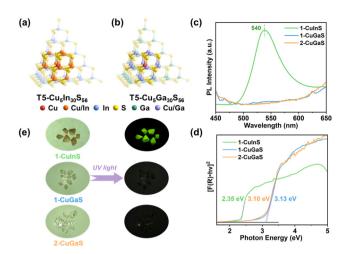


Fig. 1 (a) Supertetrahedral [Cu<sub>5</sub>In<sub>30</sub>S<sub>56</sub>] cluster in 1-CuInS. (b) Supertetrahedral [Cu<sub>5</sub>Ga<sub>30</sub>S<sub>56</sub>] clusters in 1-CuGaS. (c) RT PL spectra of 1-CulnS, 1-CuGaS, and 2-CuGaS. (d) Tauc plots of 1-CulnS, 1-CuGaS, and 2-CuGaS derived from UV-Vis DRS. (e) The optical images of pristine crystals with and without irradiation of an UV lamp.

sesses the same second building units (SBUs) as 1-CuGaS but with different linkers (Fig. 1b). Each [SbS<sub>3</sub>] linker in 2-CuGaS bridges three T5-Cu<sub>5</sub>Ga<sub>30</sub>S<sub>56</sub> clusters and each T5-Cu<sub>5</sub>Ga<sub>30</sub>S<sub>56</sub> connects to four neighboring clusters by four [SbS<sub>3</sub>] units, which give rise to a two-dimensional honeycomb (hcb) net (Fig. S12c and S13b†).

Interestingly, despite bearing similar supertetrahedral T5-Cu<sub>5</sub>M<sub>30</sub>S<sub>56</sub> units, the three crystalline samples exhibit distinct photoluminescence properties. As illustrated in Fig. 1c, 1-CuInS displayed a strong green emission peak at 540 nm with a broad full width at half-maximum (fwhm) of 0.242 eV under excitation of 420 nm at room-temperature (RT). However, the luminescence of 1-CuGaS and 2-CuGaS was negligible at RT (Fig. 1e). The observation of green emission in 1-CuInS is reminiscent of the so-called copper "green" ("G-Cu") luminescence in many Cu<sup>+</sup>-doped semiconductors with different compositions.35 In addition, the UV-Vis diffuse-reflectance spectra of the three samples were measured. As indicated in Fig. 1d, 1-CuInS, 1-CuGaS and 2-CuGaS were semiconductors, and their corresponding band gaps were detected to be 2.35 eV, 3.13 eV, and 3.10 eV, respectively. Ultraviolet photoemission spectroscopy (UPS) measurements revealed that they had a similar valence band position (5.14 eV for 1-CuInS; 5.10 eV for 1-CuGaS, and 4.97 eV for 2-CuGaS) (Fig. S14a†). Notably, 1-CuInS and 1-CuGaS displayed conspicuously different photoluminescence performances although they possessed identical frameworks and with different chemical compositions in the T5 SBUs. Conversely, 1-CuGaS and 2-CuGaS with the same SBUs both exhibited no emission at RT. These findings have spurred our interest for further research.

### Temperature-dependent PL property of 1-CuInS, 1-CuGaS, and 2-CuGaS

To uncover the mechanism behind Cu-related emission, temperature-dependent PL spectra were performed on these crystalline samples. Fig. 2a displays the temperature-dependent PL spectra of 1-CuInS. Upon cooling from 308 to 68 K, the emission peak wavelength  $(\lambda_{max})$  gradually blue-shifted from 541 nm to 518 nm, accompanied by a slight reduction in the PL fwhm from 0.231 eV to 0.204 eV (Fig. 2b). Meanwhile, the maximum excitation wavelength shifted from 504 nm to 486 nm according to PLE spectra (Fig. S15a†). Furthermore, we obtained the integrated PL data in Fig. 2a to illustrate the relationship between PL intensity and temperatures, as demonstrated in Fig. 2c. As the temperature decreased, the PL intensity of 1-CuInS increased non-monotonically. The initial increase in PL intensity from 308 to 158 K was mainly due to the suppression of non-radiative recombination pathways. However, the following decrease in PL intensity from 158 to 68 K is rather anomalous. The emission peak wavelength blueshifts as the temperature decreases, ruling out the possibility of thermally activated delayed luminescence but suggesting negative thermal quenching (NTQ). NTO is an occasional phenomenon, which has been observed previously in defect emission.36 It is generally been explained by thermally activated carrier transfer from lower- to higher-energy emissive electron traps. Fig. 2d plots the energy of the Cu-related emission peak versus temperature. The orange solid line represents the fitting of these temperature-dependent peak energies to the Varshni equation:

$$E_{\rm g} = E_0 - \alpha T^2/(T+\beta)$$

where  $E_g$  is the energy gap in semiconductors,  $E_0$  represents its value at 0 K, and  $\alpha$ ,  $\beta$  are constants. The values were found  $[E_0 = 2.41 \text{ eV}, \alpha = (10.1 \pm 1.98) \times 10^{-4} \text{ eV K}^{-1}, \beta = (5.58 \pm 1.98) \times 10^{-4} \text{ eV K}^{-1}]$ 1.73) ×  $10^2$  K] with  $R^2$  equal to 0.999. The good agreement provided strong support for the associations between the copper-

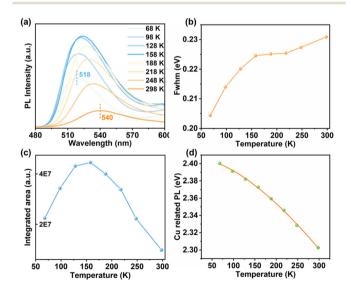


Fig. 2 Temperature-dependent PL properties of 1-CulnS: (a) PL spectra under different temperatures. (b) Fwhm of the Cu-related green emission (c) PI -integrated areas of different emission (d) Plot of the energies of PL peaks versus temperature. The orange solid line represents fits of the data to the Varshni equation.

related PL of **1-CuInS** and the shallow delocalized traps, which vary with the position of the conduction band. A similar model has been proposed for bulk ZnS: Cu,<sup>39</sup> where the green emission originates from shallow delocalised traps, and the slight red shift of this emission was correlated with the shift of the conduction band to lower energies with increasing temperature.

Unexpectedly, although 1-CuGaS and 2-CuGaS exhibited almost no emission at RT, both were able to emit Cu<sup>+</sup>-related red luminescence at lower temperatures. When cooling from 248 K to 68 K, the emission peak of 1-CuGaS gradually redshifted from 621 nm to 643 nm and the emission intensity was remarkably increased (Fig. 3a). Notably, the maximum excitation wavelength showed negligible shifts during this process (Fig. S15b†). Similarly, the temperature-dependent PLE spectra of 2-CuGaS demonstrated that the maximum excitation wavelength remained unchanged as the temperature decreased (Fig. S15c†). Also, 2-CuGaS exhibited a similar redshift of emission peak and an increase in emission intensity with decreasing temperature (Fig. 3b). It is worth noting that, in comparison to 1-CuInS, both 1-CuGaS and 2-CuGaS have larger optical band gaps and emit longer wavelength emissions, resulting in a larger Stokes shift. The redshift of the emission peak with the decrease of temperature in 1-CuGaS and 2-CuGaS suggests that the radiative recombination is less associated with shallow delocalised traps and could be explained by processes related to deeply-localized-traps. In such a situation, the excited state occupies lower vibration levels with temperature decreasing, leading to the redshift of the emission spectra.<sup>35</sup> Moreover, as depicted in Fig. 3c and d, the change of PL fwhm with temperature in 1-CuGaS and 2-CuGaS was comparable but much greater than that in 1-CuInS. In all, the emission peak of 1-CuInS shifted to higher energies with a decrease in temperature, accompanied by a slight reduction of half-widths. In contrast, the emission peaks of 1-CuGaS and 2-CuGaS

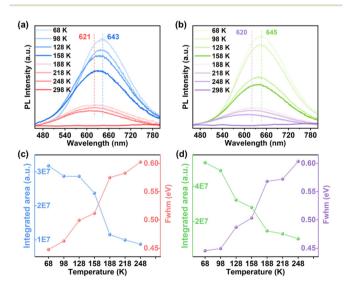


Fig. 3 Temperature-dependent PL spectra of (a) 1-CuGaS and (b) 2-CuGaS. PL-integrated areas and fwhm of (c) 1-CuGaS and (d) 2-CuGaS at different temperatures.

shifted towards lower energies as the temperature decreased and half-widths of the spectra reduced significantly. Such differences in PL properties have been documented in cases involving different traps inducing copper-related emissions in Cu-based QDs. More importantly, it is reasonable to conclude that the position of trap sites is closely related to the local surroundings (In<sup>3+</sup> and Ga<sup>3+</sup> ions) rather than the structural patterning modes of these structures.

## PL decay dynamics of 1-CuInS, 1-CuGaS and 2-CuGaS

To investigate the origin of the green and red emissions in more detail, temperature-dependent excited-state lifetime of 1-CuInS, 1-CuGaS, and 2-CuGaS were also recorded. As the temperature decreased, the PL decay time of 1-CuInS increased from 128 ns at 298 K to 7.2 µs at 68 K, which was ascribed to the decrement of non-radiative pathways (Fig. 4a and b; Tables S2 and S3†). In comparison, 1-CuGaS and 2-CuGaS exhibited significantly longer decay lifetimes. These values reached approximately 158 µs for 1-CuGaS and 214 µs for 2-CuGaS at 68 K (Fig. 4c, d, and S16; Tables S4 and S5†). Normally, the lifetime of band edge emission in various semiconductor nanocrystals falls in the range of one to a few tens of nanoseconds, which is not the case in the present work. These indicate that the emission of all the three samples is expected to originate from dopant related channels, similar to many Cudoped nanocrystals.41 In addition, the literature suggests that the formation of long-lived photogenerated states in copperdoped nanocrystals, lasting from tens to hundreds of microseconds, is presumably associated with carrier localization at deep localised traps.<sup>35</sup> Wherein, the shallow-delocalized traps of 1-CuInS and the deep-localized traps of 1-CuGaS and 2-CuGaS could also be reasonably explained. Furthermore, the gradual decrease in the average lifetime of both crystals with

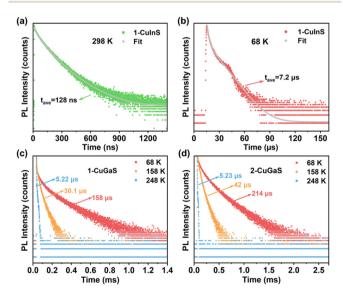


Fig. 4 PL decay curves of 1-CulnS measured at (a) 298 K and (b) 68 K. Temperature-dependent PL decay curves of (c) 1-CuGaS and (d) 2-CuGaS

increasing temperature can be attributed to the increased occurrence of non-radiative pathways.

### Optical band gap and PL property of 1-CuInGaS

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Based on the above results, trivalent metal ions (In<sup>3+</sup> and Ga<sup>3+</sup>) have indeed influence on the position of trap sites, further regulating the PL performance. To validate this hypothesis, we intentionally introduced Ga ions into 1-CuInS and obtained 1-CuInGaS. PXRD analysis confirmed the successful incorporation of Ga3+ ions into 1-CuInGaS, causing a slight shift in peak position due to the partial replacement of In<sup>3+</sup> by Ga ions (Fig. S17†). EDS data indicated that the ratio of Ga to In is about 1:2 in a SBU (Fig. S18†). As illustrated in Fig. 5a, 1-CuInGaS has a band gap of 2.48 eV, which falls between the values of 1-CuInS and 1-CuGaS. Interestingly, under excitation of 450 nm at RT, 1-CuInGaS exhibited dual emissions in a high-energy band (530 nm) and low-energy band (684 nm) (Fig. S19†). Notably, the high-energy band showed a blue-shift tendency with decreasing temperature, while the low-energy band displayed a red-shift tendency (Fig. 5b and S20†). Furthermore, the decay lifetime of low-energy band was much longer than that of high-energy band at both 68 K and 298 K (Fig. 5c and d; Tables S6 and S7†). In this case, the highenergy band emission in 1-CuInGaS may result from the In<sup>3+</sup> induced shallow-delocalized-traps to copper-localized hole transitions, while the low-energy band emission can be ascribed to the Ga3+ mediated deep-localized-traps to copperlocalized hole transitions.

### Optical band gap and PL property of 1-CuInCdS@n

With the influence of trap sites on the Cu-related emission in mind, we attempted to introduce cadmium ions to adjust the

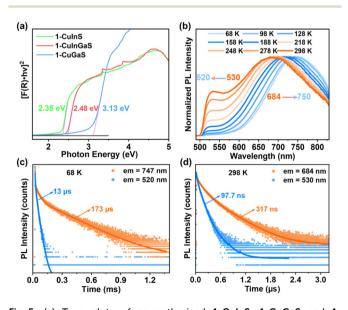


Fig. 5 (a) Tauc plots of as-synthesized 1-CulnS, 1-CuGaS and 1-CulnGaS. (b) Normalized temperature-dependent PL spectra of 1-CulnGaS. PL decay curves of the dual emission of 1-CulnGaS at (c) 68 K and (d) 298 K.

wavelength of the Cu related emission. This led to the synthesis of a series of Cd-substituted samples denoted as 1-**CuInCdS**(a)n (n = 1-4). It is noted that as n increases, the ratio of Cu to Cd in these as-synthesized samples gradually increases, as illustrated by EDS measurements (Fig. S21 and Table S8†). However, cadmium ions were failed to be introduced in 1-CuGaS and 2-CuGaS, possibly due to the large mismatch of the atomic radius of Ga and Cd ions. PXRD analysis confirmed that 1-CuInCdS@n had the same crystalline configuration with 1-CuInS (Fig. 6a). Furthermore, UV-Vis DRS of 1-CuInCdS@n were also investigated, which indicated that the addition of Cd ions to 1-CuInS indeed led to a decrease in the position of the shallow delocalized trap sites. This decrease became more pronounced with the increase of Cu content in 1-CuInCdS@n (Fig. 6b). Worth of noting is that they all exhibited the same valence band position, as confirmed by UPS (Fig. S14b†). Therefore, the shift of shallow delocalized trap sites was caused by the alteration of the conduction band position. As disclosed in Fig. 6c, 1-CuInCdS@n all exhibited a redshift in PL emission compared to that of 1-CuInS, with emission peaks at 605, 613, 624 and 633 nm, respectively, corresponding to n = 1, 2, 3,and 4. This trend in the PL performance is consistent with the red-shift of the shallow delocalized trap sites. Moreover, the temperature-dependent PLE and PL spectra of 1-CuInCdS@2 and 1-CuInCdS@4 were investigated, which showed a similar blue-shifted tendency as that of 1-CuInS as the temperature decreased (Fig. 6d, S22, S23, and S24†). This phenomenon further illustrated that 1-CuInS and 1-CuInCdS@n had similar luminescence excitation and emission processes. PL decay dynamics of 1-CuInCdS@n were also measured at 298 K (Fig. 6e and S25, and Table S2†) and at 68 K (Fig. 6f and Table S3†). All these data supported that **1-CuInS** and **1-CuInCdS**@*n* possess the same decay process. Based on the above results, we can conclude that the introduction of Cd into the framework of 1-CuInS resulted in the redshift of the shallow-delocalized trap sites along with the emission peak.

### Possible mechanism of exciton recombination

According to the above observations and previous studies, the possible mechanism of exciton recombination is depicted in Scheme 2. After absorption of light, the photo-generated electron and photo-generated hole are distributed in the conduction band (CB) and the valence band (VB), respectively. The process of radiative transition initially involves the capture of a hole from VB to the filled higher potential Cu(1) d-state, forming a transient Cu<sup>2+</sup> species that contains a vacancy in the d-shell. The transient Cu<sup>2+</sup> state has two different energy states, T2 and E,16,39,42-48 and both can accept an excited electron, which may associated with the broadening of the corresponding emission spectra. Subsequently, the green emission observed in 1-CuInS may be assigned to the recombination of an electron in the shallow-delocalized traps with a hole in the Cu d-state. In the case of 1-CuGaS and 2-CuGaS, the red emission probably attributes to exciton transition from the deep-

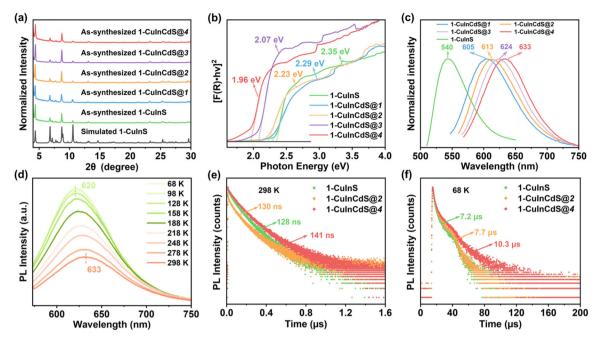
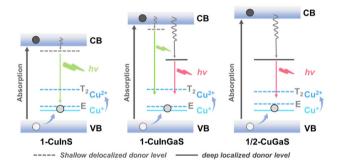


Fig. 6 (a) PXRD of simulated 1-CulnS and as-synthesized 1-CulnS and 1-CulnCdS@n samples. (b) Tauc plots of as-synthesized 1-CulnS and 1-CulnCdS@n. (c) RT PL spectra of as-synthesized 1-CulnS and 1-CulnCdS@n. (d) Temperature-dependent PL spectra of 1-CulnCdS@4. PL decay curve of as-synthesized 1-CulnS and 1-CulnCdS@n with excitation of 390 nm at (e) 298 K and (f) 68 K.



Scheme 2 Proposed energy level diagram for 1-CulnS, 1-CulnGaS and 1/2-CuGaS. (VB: valence band, CB: conduction band).

localized defect state to the Cu d-state, which can be supported by the blueshift of the maximum emission wavelength with the increasing temperature and the relative longer luminescence lifetime. Furthermore, in 1-CuInGaS, both trap sites existed simultaneously, as confirmed by the presence of green and red dual emissions. In addition, when Cd ions were introduced in 1-CuInS, they lead to a downshift of shallow defects due to the reduction of the conduction band energy, resulting in the redshift of the emission peak of 1-CuInCdS@n (Fig. S26†).

# Conclusion

In summary, we for the first time systematically studied the influence of the composition-determined defect position on

the luminescence in the copper-based I-III-VI metal chalcogenide nanoclusters. Three I-III-VI metal chalcogenides (1-CuInS, 1-CuGaS, and 2-CuGaS) with precise structures were selected as unique models to explore the inherent regulation mechanism of the Cu<sup>+</sup>-related PL emission. Interestingly, 1-CuInS and 1-CuGaS with the same framework structure exhibited a large disparity in PL performance, while 1-CuGaS and 2-CuGaS possessing the same metal components showed similar PL property. Systematic studies shows that the green luminescence of 1-CuInS stemmed from radiative recombination of electrons from shallow-delocalized traps to copper-localized hole and the red emission of 1-CuGaS and 2-CuGaS originated from radiative recombination of electrons from deep localized traps to copper-localized hole. It can conclude that the position of the traps was highly dependent on the surrounding trivalent In<sup>3+</sup> and Ga<sup>3+</sup> in the clusters, where the presence of In3+ ions will induce the formation of shallow defects and the presence of Ga3+ ions will produce deep defects. The deduction was further confirmed by dual emission properties of the 1-CuInGaS with both In<sup>3+</sup> and Ga<sup>3+</sup> ions. Moreover, by introducing different contents of Cd ions into the 1-CuInS, we also realized the regulation of luminescence from green emission to red emission. This work sheds light on understanding of the chemical components and defect positions relationship and the mechanism of Cu<sup>+</sup>-related emission, which will stimulate further regulation of the optoelectronic properties of Cu-based nanoclusters or even nanocrystals and exploration of their potential applications.

# **Author contributions**

Tao Wu and Shang-Fu Yuan: funding acquisition, project administration, resources, writing - reviewing, editing and supervision. Dong-Sheng Li: funding acquisition. Rui Zhou: funding acquisition. Yi-Lei Xu and Yayun Ding: conceptualization, data curation, formal analysis, investigation, methodology, writing - reviewing and editing. Lin-Mei Zhang, Hao Ma, Jia-Xing Liu and Jiaxu Zhang: formal analysis.

# Conflicts of interest

There are no conflicts to declare.

# Acknowledgements

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