



Original Article

Detection of Luminescence Centers in Cu-doped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ Quantum Dots by Synchronous Luminescence Spectroscopy

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Abstract: The identification of luminescence centers in Cu-doped ternary CdZnS quantum dots (QDs) remains challenging because the broad visible emission generally arises from multiple overlapping radiative transitions, making peak assignment highly dependent on indirect evidence. In this work, the luminescence mechanism of Cu-doped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QDs synthesized by a colloidal method was systematically investigated by combining X-ray diffraction (XRD), UV-Vis absorption, photoluminescence (PL), and synchronous luminescence (SL) spectroscopy. XRD showed a zinc-blende CdZnS alloy structure with no detectable secondary crystalline phase, while the first excitonic absorption yielded an optical band gap of 3.172 eV. The PL spectrum exhibits a narrow band-edge emission at 403 nm together with an intense broad visible emission centered at 554 nm. Unlike conventional PL, SL spectroscopy resolves the broad emission into three spectroscopically distinct bands centered at approximately 445, 488 and 503 nm, providing additional spectroscopic constraints for identifying the corresponding radiative transitions. Based on the complementary structural and spectroscopic evidence obtained in this work together with previously reported first-principles defect calculations and Cu-related luminescence mechanisms in ZnS-based materials, a semi-quantitative, evidence-integrated energy-level model is proposed to consistently interpret the observed emissions in terms of Cu-related acceptor states and intrinsic donor/acceptor defect states within the CdZnS alloy lattice. The present approach demonstrates that integrating SL with

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conventional structural and optical characterization provides a more reliable approach for identifying the dominant radiative recombination pathways in Cu-doped semiconductor QDs than assignment based solely on emission wavelengths.

Keywords: Cu-doped CdZnS quantum dots; synchronous luminescence spectroscopy; luminescence centers; defect-related emission; radiative recombination.

1. Introduction

In recent years, transition metal-doped II-VI semiconductor nanocrystals (NCs) are being extensively researched, thanks to their superior optical properties in comparison to their undoped counterparts, including their tunable emission wavelength via impurities [1-3], comparatively longer excited state lifetime [4], and large Stokes shift [5] leading to reduced self-absorption [6]. These advantages have created opportunities for the use of transition metal-doped NCs in the display and light-emitting devices [7, 8], photovoltaic applications [9, 10], photocatalytic applications [11], as well as biomedical sensing and imaging [12].

Transition-metal-doped semiconductor NCs can provide efficient visible emissions [13-16]. In Cu-doped $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ NCs' dopant-related emission has generally been interpreted as radiative recombination involving Cu-related acceptor states, although the exact microscopic transition may depend on the host composition, particle size and defect configuration [17,18]. Consequently, the emission wavelength can be tuned within a wide range ($\sim 400 - 680$ nm) by varying the size and Cd/Zn content ratio of the host NC [19]. In general, photoluminescence (PL) spectra of Cu-doped $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ NCs are characterized by an emission peak at short wavelength caused by near band edge exciton and a broad emission band at longer wavelengths related to surface dangling bonds and intrinsic defects such as sulfur vacancies (V_S), Zn/Cd interstitials ($\text{I}_\text{Zn}/\text{I}_\text{Cd}$), Zn/Cd vacancies ($\text{V}_\text{Zn}/\text{V}_\text{Cd}$) [20-22], and the Cu^{2+} acceptor state (T_2) [17, 18, 20, 23]. These defects introduce localized electronic states within the band gap, thereby governing the radiative recombination pathways and optical properties of the doped NCs. As of the time of writing, several luminescence mechanisms have been proposed for undoped [21, 22, 24] and Cu-doped [20, 23] $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ host NCs.

As the donor or acceptor levels may be very close in energy, PL spectra of semiconductor NCs are usually featureless with significant peak broadening, causing difficulties in the differentiation of luminescence centers using conventional PL spectroscopy. Synchronous luminescence (SL) spectroscopy is a viable technique for analyzing materials with overlapped emission and/or excitation spectra, owing to its selectivity, spectral resolution, and reduction of interference due to light scattering [25]. As known, PL spectroscopy involves scanning the emission wavelength (λ_emiss) of the sample under photoexcitation at a chosen wavelength (λ_exc). The PL excitation spectrum is collected by changing λ_exc , while the emission is recorded at a constant λ_emiss . Differently from PL emission and excitation spectroscopy, SL measurements are performed by synchronously varying λ_exc and λ_emiss at a constant difference $\Delta\lambda = \lambda_\text{emiss} - \lambda_\text{exc}$ [26, 27]. This technique has been successfully applied to investigate properties of inorganic materials such as the size dependency of CdTe QDs [28], as well as to study luminescence centers of SrTiO_3 [29], CaTiO_3 [30], anatase and rutile TiO_2 [31, 32]. Previous work has demonstrated the applicability of SL spectroscopy to undoped colloidal $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ nanocrystals [22]. To the best of our knowledge, however, its application to Cu-doped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ quantum dots (QDs) has not yet been reported.

Despite the considerable number of studies on Cu-doped II-VI semiconductor QDs, the microscopic origin of the broad visible emission in Cu-doped CdZnS QDs remains under debate because different defect-related transitions may produce emission bands in similar spectral regions. Consequently,

assignments based solely on emission wavelengths often remain ambiguous, particularly when the conventional PL spectrum consists of several overlapping radiative components [33, 34].

In the present work, Cu-doped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QDs were synthesized by a colloidal method, and their structural and optical properties were systematically investigated using X-ray diffraction (XRD), UV-Vis absorption, PL, and SL spectroscopy. Unlike conventional PL measurements, SL spectroscopy provides an additional spectroscopic dimension by simultaneously correlating excitation and emission processes, thereby enabling overlapping emission components to be experimentally separated. By integrating the structural information obtained from XRD with the electronic constraints derived from UV-Vis absorption and the complementary spectroscopic evidence obtained from PL and SL, a semi-quantitative, evidence-integrated energy-level model is developed to identify the most probable radiative recombination pathways responsible for the observed visible emission. This multi-constraint strategy provides a more reliable and physically self-consistent interpretation of the luminescence mechanism than assignment based solely on previously reported emission wavelengths or any single published luminescence model [33-35].

2. Experimental

2.1. Chemicals

Initial chemicals, including zinc stearate ($\text{Zn}(\text{St})_2$, 98%), cadmium oxide (CdO , 99.99%, powder), sulfur (S, 99.98%, flour), copper chloride ($\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$, 99%), 1-octadecene (ODE, 90%), stearic acid (SA, 90%), and tetramethylammonium hydroxide pentahydrate (TMAH, 97%), were purchased from Aldrich and used as received without further purification.

2.2. Synthesis of Cu-doped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ Quantum Dots

S, Cd, Zn and Cu precursor solutions were prepared for synthesizing the Cu-doped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QDs. The S precursor was obtained by stirring a mixture of S (1 mmol) and ODE (24 mmol) at 100 °C for 60 min. 0.3 mmol of CdO , 1.4 mmol of SA, and 60 mmol of ODE were added into a three-neck flask and heated up to 280 °C for 60 min to obtain the clear Cd precursor. The Zn solution was prepared by dissolving 0.7 mmol of $\text{Zn}(\text{St})_2$ in a mixture of SA (0.036 mmol) and ODE (60 mmol) at 180 °C for 60 min. With the specified amounts of Cd and Zn precursors, the elements' contents in the synthesized QDs will be approximately 0.3 and 0.7, respectively [36]. The Cu precursor was prepared using CuCl_2 , TMAH and methanol. The amount of Cu precursor used was calculated to produce Cu-doped QDs with a dopant content of $n_{\text{Cu}}/(n_{\text{Cd}} + n_{\text{Zn}}) \approx 1\%$.

To prepare uniformly alloyed $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QDs doped with Cu throughout their volumes, the S precursor solution was first quickly injected into a reaction flask containing half of the prepared Zn and Cd precursors and all of the Cu precursor preheated to 280 °C. This is followed by the alternate injection of small amounts of the remaining Zn and Cd precursor solutions, forming alternating thin Cu-doped Zn- and Cd-rich layers in the QDs. This process is expected to promote alloy homogenization through thermally activated self-diffusion of metal ions, resulting from the preparation's high temperature (280 °C) and long duration (270 min). Both the precursor solutions and QDs were prepared under pure nitrogen flow.

The obtained crude solution was mixed with isopropanol with a solution-to-isopropanol volume ratio of 1/3. The QDs were then collected from this mixture by centrifugation at 15000 rpm for 3 min. Part of the purified product in powder form was used to investigate the QDs' crystal structure, while the remaining portion was dispersed in toluene to evaluate their morphology, size, UV-Vis absorption and PL characteristics.

2.3. Characterization

TEM images of the Cu-doped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QD samples were recorded using the Jeol JEM 1010 microscope. XRD patterns were obtained using the Siemens D5005 X-ray diffractometer with a $\text{Cu K}\alpha$ radiation source having a wavelength of $\lambda = 1.5406 \text{ \AA}$. The QDs' UV-Vis absorption spectra were measured using the Jasco 670 spectrometer. Their PL spectra were obtained with the Horiba Fluorolog FL3-22 spectrometer in the Front Face (FF) geometry equipped with dual monochromator gratings on the excitation and emission paths. To eliminate the effects of photoexcitation intensity fluctuations, spectral intensities were recorded as the ratio between the emission intensity S and the reference intensity R of the excitation beam. The PL emission spectrum was obtained with excitation and emission slits at 5 nm. SL measurements were also performed with the Fluorolog FL3-22 spectrometer in FF geometry, with the excitation and emission slits set at 5 nm. Similarly to the above, S/R ratios were recorded in the spectra. In these measurements, the $\Delta\lambda$ parameter was varied in 10 nm increments. The QDs' size was determined using the ImageJ software, and their first UV-Vis peak position was obtained at the absorption spectrum's second derivative's minimum.

3. Results and Discussion

Figure 1 shows the TEM image of the Cu-doped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QDs, which exhibit a nearly spherical morphology with an average diameter of approximately 4.5 nm and a relatively narrow size distribution, as shown in the inset.

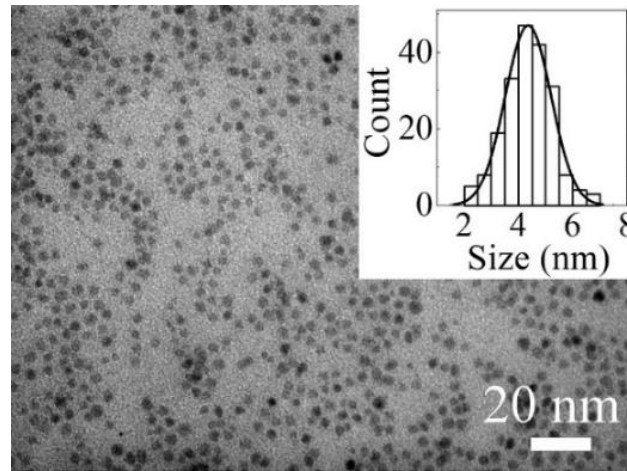


Figure 1. TEM image and size distribution of Cu-doped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QDs.

Figure 2(a) shows that the diffraction pattern can be indexed to the zinc blende (ZB) structure, with the three diffraction peaks centred at 28.0° , 46.8° and 55.3° , corresponding to the (111), (220) and (311) crystallographic planes, respectively. Cu incorporation into semiconductor NCs has been reported for ZB structures [37]. Using the Bragg diffraction equation $2d_{(111)} \sin \theta = n\lambda$ ($n = 1$) and the relationship between lattice constant a and distance between (111) crystal planes $d_{(111)}$ of ZB structures $a = \sqrt{3} \times d_{(111)}$, the Cu-doped ZB- $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QDs' lattice constant was calculated to be 0.5513 nm. Vegard's law on the linear relationship between lattice constants and bulk materials' contents is known to have been widely applied for ternary and quaternary semiconductor nanocrystals [38, 39]. For the $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ solid

solution, the lattice constant a is linearly dependent on the content x according to the following expression [20, 40]:

$$a_{\text{Cd}_x\text{Zn}_{1-x}\text{S}} = xa_{\text{CdS}} + (1-x)a_{\text{ZnS}} \quad (1)$$

where $a_{\text{Cd}_x\text{Zn}_{1-x}\text{S}}$, a_{CdS} , and a_{ZnS} are lattice constants of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$, CdS, and ZnS, respectively. In this work, Vegard's law was used as an indirect criterion to evaluate the alloying behaviour of the prepared Cu-doped ZB- $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QDs. Figure 2(b) shows that the measured lattice constant (0.5513 nm) is very close to the Vegard-law value (0.553 nm for $x = 0.3$), with a deviation of only approximately 0.3%. Although this agreement does not by itself prove complete compositional homogeneity, it is consistent with the formation of a well-alloyed $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ host lattice.

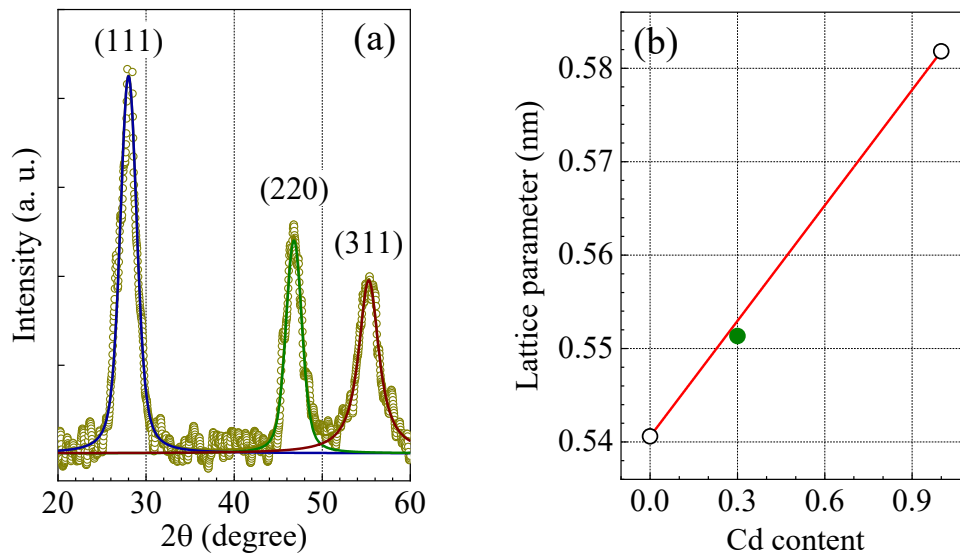


Figure 2. (a) XRD pattern of Cu-doped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QDs, and (b) evaluation of alloying behaviour based on Vegard's law. Unfilled dots in Figure 2(b) denote lattice parameters taken from Joint Committee on Powder Diffraction Standards (JCPDS) cards N5-566 and N10-454 for ZnS and CdS, respectively.

UV-Vis absorption and PL spectra of the Cu-doped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QDs are illustrated in Figure 3(a). The QDs' optical band gap energy is 3.172 eV. The Bohr radius of excitons in bulk $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ ranges from 2.2 to 3.0 nm as x varies from 0 to 1 [41]. As presented above, the Cu-doped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QDs have an average diameter of 4.5 nm (Figure 1). Therefore, their optical band gap energy $E_g^{\text{Cd}_x\text{Zn}_{1-x}\text{S}}$ mostly depends on x and can be approximated using the following expression for bulk materials [20, 42, 43]:

$$E_g^{\text{Cd}_x\text{Zn}_{1-x}\text{S}} = xE_g^{\text{CdS}} + (1-x)E_g^{\text{ZnS}} - bx(1-x) \quad (2)$$

where E_g^{CdS} and E_g^{ZnS} are optical band gap energies of bulk CdS (2.5 eV [44]) and bulk ZnS (3.7 eV [44]), respectively, and b is a size-independent optical bowing constant (which is 0.61 eV for $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ QDs [42, 45]). The dependency of the optical band gap energy in undoped $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ QDs on x is shown by the solid line in Figure 3(b). The experimental band gap energy value of 3.172 eV of Cu-doped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QDs (shown by the green dot in Figure 3(b)) is extremely close to the theoretical value of 3.21 eV determined with expression (2) at $x = 0.3$. Therefore, the close agreement between the

experimental and theoretical band-gap energies suggests that 1% Cu incorporation causes only a slight perturbation of the host electronic structure.

As mentioned above, the radiative recombination process of Cu-doped $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ QDs is governed by not only exciton recombination but also the presence of Cu dopant and native defects. Together with the QD surface states, Cu-related acceptor states and intrinsic donor/acceptor defect states in the band gap create a broad emission band. As can be seen in Figure 3(a), the QDs' PL spectrum is characterized by an emission peak at 403 nm and a high-intensity broad luminescence band centred at approximately 554 nm, with full widths at half maximum of 17 nm and 115 nm, respectively. The spectral band at 554 nm is asymmetric, indicating that it may be a superposition of multiple peaks. It should be noted that the 554 nm band is featureless, making reliable peak assignment by conventional spectral deconvolution inherently uncertain.

The combined UV-Vis absorption and PL results provide two important constraints for interpreting the luminescence mechanism. First, the excellent agreement between the experimental optical band gap (3.172 eV) and the theoretical value predicted for $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ indicates that the electronic structure is primarily governed by the alloy composition, while 1% Cu incorporation induces only a slight perturbation of the host band structure rather than introducing a separate electronic phase. This behaviour is consistent with previous theoretical studies showing that dilute Cu incorporation mainly introduces localized Cu-related acceptor states without substantially modifying the host band structure [34]. Second, although the near-band-edge emission at 403 nm is clearly resolved, the visible emission appears as a single broad asymmetric band with a much larger spectral width, indicating that multiple radiative recombination channels contribute simultaneously to the observed luminescence. Consequently, conventional steady-state PL spectroscopy alone cannot unambiguously distinguish the individual defect-related transitions because several intrinsic and Cu-related recombination channels may contribute within the same spectral region. This limitation motivates the use of complementary spectroscopic analysis to resolve the overlapping emission components [33, 34].

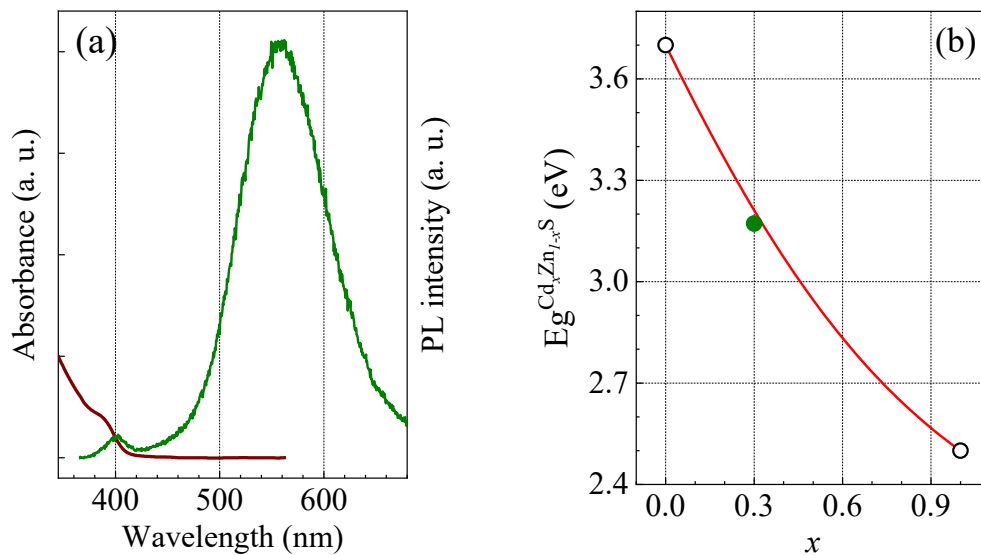


Figure 3. (a) UV-Vis and PL spectra of Cu-doped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QDs, and (b) comparison of their experimental optical band gap energy (shown by the green dot) against theoretical values (red curve).

To resolve the individual luminescence components associated with the Cu dopant and native defects, SL measurements with different $\Delta\lambda$ parameters were performed on the Cu-doped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QD sample. As can be seen in Figure 4(a), the SL spectra exhibit four well-defined peaks (A-D) superimposed on a broad background attributed to surface-state emission. Whereas the peak A remains essentially unchanged, peaks B-D gradually shift towards longer wavelengths as $\Delta\lambda$ is increased, as demonstrated by the dashed lines. As the $\Delta\lambda$ parameter's value increases, the intensities of the SL peaks first increase to their maxima and then decrease with further increases in $\Delta\lambda$ (Figures 4(a) and 4(b)). Peaks A, B, C and D have the maximum intensities at 403, 445, 488 and 503 nm when $\Delta\lambda = 10, 120, 80$ and 120 nm, respectively. The peak positions corresponding to the maximum SL intensities are therefore taken as the characteristic emission energies of the dominant radiative recombination channels in Cu-doped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QDs. These experimentally determined emission energies constitute one of the principal spectroscopic constraints for constructing the semi-quantitative energy-level model discussed below. The corresponding transition energies are 3.077, 2.786, 2.541 and 2.465 eV for peaks A, B, C and D, respectively.

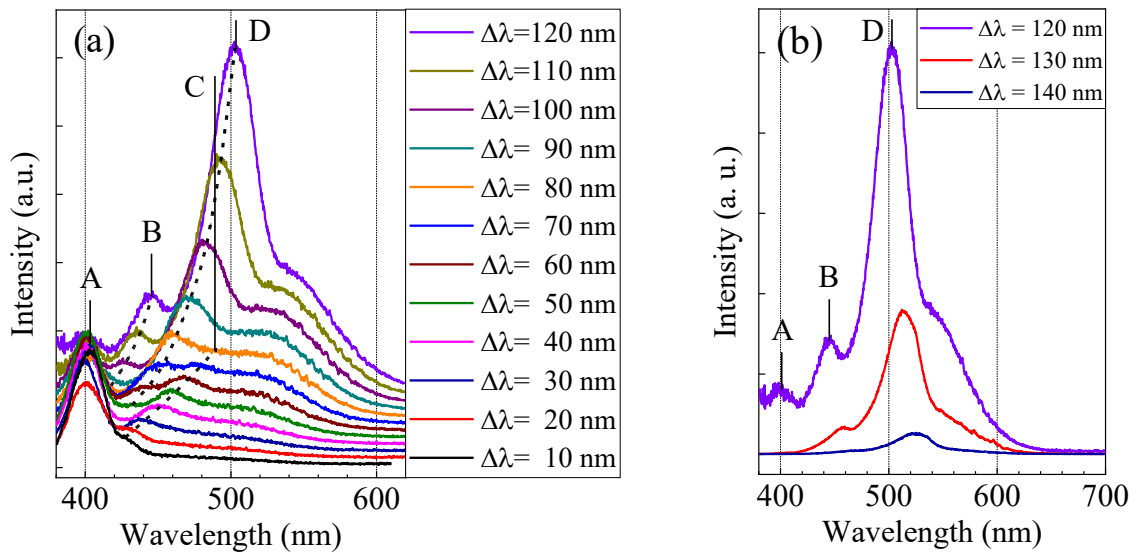


Figure 4. SL spectra at $\Delta\lambda$ parameters of (a) 10 - 120 nm, and (b) 120 - 140 nm. SL spectra in Figure 4(a) have been vertically shifted for clarity.

The peak A reaches its maximum intensity under excitation at wavelength $\lambda_{\text{exc}} = \lambda_{\text{emiss}} - \Delta\lambda = 403 \text{ nm} - 10 \text{ nm} = 393 \text{ nm}$ (3.155 eV). Similarly, the maximum intensities of peaks B, C and D are obtained under excitation at wavelengths 325 nm (3.815 eV), 408 nm (3.039 eV), and 383 nm (3.237 eV), respectively. The corresponding $\Delta\lambda$ values together with the excitation and emission energies of these peaks are listed in Table 1.

Table 1. $\Delta\lambda$ parameters and the corresponding excitation and emission energies of SL peaks.

Peak	$\Delta\lambda$ (nm)	Exc. Energy (eV)	Emiss. Energy (eV)
A	10	3.155	3.077
B	120	3.815	2.786
C	80	3.039	2.541
D	120	3.237	2.465

Since the energy position of the peak A (3.077 eV) is close to the optical band gap energy (3.172 eV), the peak is attributed to near-band-edge emission. As presented, the broad luminescence bands at long wavelengths of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ host NCs usually contain emissions from not only surface states but also luminescence centers such as V_S , $V_{\text{Zn}}/V_{\text{Cd}}$ and $I_{\text{Zn}}/I_{\text{Cd}}$. Therefore, it is probable that the SL peaks of the Cu-doped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QDs in the 420 - 650 nm range (Figure 4) relate to the Cu dopant and lattice defects.

The combination of PL and SL spectroscopy provides considerably stronger evidence for identifying the radiative recombination channels than conventional PL analysis alone. Whereas the PL spectrum reveals only a broad visible emission band, the SL spectra successfully resolve this band into three independent emission components centred at approximately 445, 488 and 503 nm, each exhibiting a distinct excitation–emission offset ($\Delta\lambda$). These different SL responses demonstrate that the visible luminescence does not originate from a single defect center but instead consists of multiple radiative recombination channels associated with different defect-related electronic states. When combined with the single-phase ZB crystal structure confirmed by XRD and the optical band gap determined from the UV-Vis absorption spectrum, the PL and SL results provide substantially stronger experimental constraints for constructing the luminescence mechanism than emission wavelengths alone [33-35].

The 445 nm emission is most reasonably attributed to radiative recombination from the intrinsic sulfur-vacancy-related donor state to the valence band (VB). This assignment is supported by several independent observations. First, its emission energy is considerably lower than the optical band gap, excluding near-band-edge recombination. Second, its excitation behaviour differs significantly from those of both the 488 and 503 nm emissions, indicating that it originates from an independent radiative recombination channel. Third, first-principles calculations reported for ZnS- and CdS-based semiconductors consistently identify sulfur-vacancy-related states as one of the dominant intrinsic donor states, although their exact energies are influenced by alloy composition, local atomic configuration and defect charge state. Since neither X-ray photoelectron spectroscopy (XPS) nor electron paramagnetic resonance (EPR) measurements are available in the present work, the present assignment should therefore be regarded as the most probable electronic state associated with sulfur vacancies rather than an unequivocal identification of isolated sulfur-vacancy defects. This interpretation provides the most physically self-consistent explanation of the experimentally observed PL and SL characteristics [33, 34, 46].

The 488 nm emission exhibits excitation characteristics distinctly different from those of the 445 nm band, indicating another intrinsic radiative recombination channel. Considering both its emission energy and the defect energetics reported for ZnS- and CdS-based semiconductors, this emission is therefore tentatively attributed to intrinsic donor–acceptor pair recombination between Cd/Zn interstitial donor states and Cd/Zn-vacancy acceptor states. Such intrinsic donor–acceptor recombination is energetically consistent with the intermediate emission energy and naturally explains the different $\Delta\lambda$ values observed in the SL spectra. Consequently, the 445 and 488 nm emissions are interpreted as two different intrinsic radiative recombination processes rather than different manifestations of the same defect center [34, 35, 47].

The lowest-energy emission at 503 nm is closely associated with Cu incorporation. Compared with the undoped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QDs, Cu doping remarkably enhances the visible emission while preserving the ZB crystal structure, indicating that Cu primarily introduces an additional Cu^{2+} acceptor state that enables a new radiative recombination pathway rather than altering the host crystal structure. Based on this observation together with previous studies on Cu-doped ZnS-based semiconductors and first-principles defect calculations, the 503 nm emission is therefore attributed to radiative recombination between the intrinsic sulfur-vacancy-related donor state and the Cu^{2+} acceptor state (T_2). Although the microscopic Cu charge state cannot be directly verified without XPS or EPR measurements, this assignment consistently explains the enhanced green emission, the large integrated intensity ratio

between the visible and near-band-edge emissions, and the characteristic excitation behaviour revealed by the SL spectra [33, 34].

Therefore, the visible luminescence of Cu-doped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QDs is interpreted as three physically distinct radiative recombination channels. The 445 nm emission is attributed to radiative recombination from the intrinsic sulfur-vacancy-related donor state to the VB, the 488 nm emission is tentatively attributed to intrinsic donor-acceptor pair recombination between Cd/Zn interstitial donor states and Cd/Zn-vacancy acceptor states, whereas the 503 nm emission is attributed to Cu-assisted recombination between the intrinsic sulfur-vacancy-related donor state and the Cu^{2+} acceptor state. This evidence-integrated interpretation simultaneously satisfies all experimental constraints obtained from XRD, UV-Vis absorption, PL and SL spectroscopy and remains fully consistent with the defect physics reported for related ZnS- and CdS-based semiconductors. More importantly, the present evidence-supported interpretation helps reduce the ambiguity commonly encountered in assigning defect-related emissions in Cu-doped II-VI semiconductor QDs by integrating the complementary PL and SL evidence obtained in this work with first-principles defect calculations and established Cu-related luminescence mechanisms [33-35, 47].

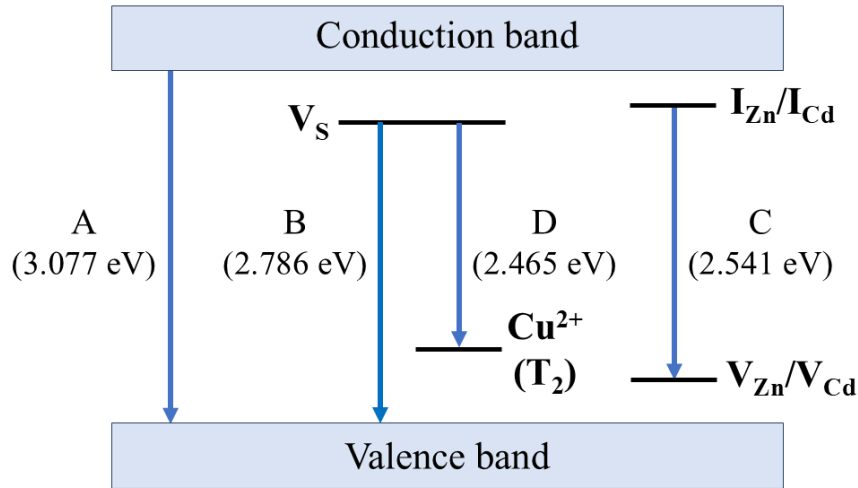


Figure 5. Semi-quantitative evidence-integrated energy-level model illustrating the proposed radiative recombination pathways in Cu-doped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QDs. The model is constructed by integrating the experimental constraints obtained from XRD, UV-Vis absorption, PL and SL spectroscopy with first-principles defect calculations and previously reported Cu-related luminescence mechanisms in ZnS- and CdS-based semiconductors. The labels V_s , $I_{\text{Zn}}/I_{\text{Cd}}$, $V_{\text{Zn}}/V_{\text{Cd}}$ and $\text{Cu}^{2+} (T_2)$ denote the corresponding defect-related electronic states associated with sulfur vacancies, Zn/Cd interstitials, Zn/Cd vacancies and Cu-related acceptor states, respectively. The energy-level positions are schematic and not to scale. Four radiative recombination channels are proposed: (i) near-band-edge recombination, (ii) radiative recombination from the intrinsic sulfur-vacancy-related donor state to the VB, (iii) tentative intrinsic donor-acceptor pair recombination between Zn/Cd interstitial donor states and Zn/Cd-vacancy acceptor states, and (iv) Cu-assisted recombination between the intrinsic sulfur-vacancy-related donor state and the Cu^{2+} acceptor state (T_2). The model represents the most probable interpretation of the luminescence mechanism that simultaneously satisfies the experimental PL and SL observations together with the currently available defect-state physics.

Based on the above analysis, a semi-quantitative evidence-integrated energy-level model is proposed, as illustrated in Figure 5. Rather than representing a direct microscopic determination of the individual defect configurations, this model integrates the experimental PL and SL constraints obtained

in the present work with previously reported defect energetics to identify the most probable radiative recombination pathways. It therefore provides a physically self-consistent framework for interpreting the visible luminescence of Cu-doped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QDs and should be regarded as an evidence-integrated interpretation rather than a unique microscopic identification of individual defects [33-35, 47].

4. Conclusion

Cu-doped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QDs with an average particle size of approximately 4.5 nm were successfully synthesized using a colloidal method. XRD analysis confirmed the formation of a single-phase ZB structure without detectable secondary phases, while the optical band gap determined from the UV-Vis absorption spectrum was 3.172 eV. PL spectroscopy revealed one near-band-edge emission at 403 nm and a broad visible emission, which was further resolved by SL spectroscopy into three distinct emission bands centred at approximately 445, 488 and 503 nm.

The combined structural and spectroscopic analyses (XRD, UV-Vis, PL and SL) provide substantially stronger experimental evidence for identifying the radiative recombination channels than conventional PL analysis alone. Based on these complementary experimental observations together with defect-state energetics reported for ZnS- and CdS-based semiconductors, the 445 nm emission is attributed to radiative recombination from the intrinsic sulfur-vacancy-related donor state to the VB, the 488 nm emission is tentatively attributed to intrinsic donor-acceptor pair recombination between Cd/Zn interstitial donor states and Cd/Zn-vacancy acceptor states, whereas the 503 nm emission is attributed to Cu-assisted recombination between the intrinsic sulfur-vacancy-related donor state and the Cu^{2+} acceptor state (T_2).

More importantly, the present study demonstrates that the broad visible luminescence of Cu-doped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QDs consists of three physically distinct radiative recombination channels rather than originating from a single defect-related emission center. By integrating structural, optical and spectroscopic evidence, a semi-quantitative evidence-integrated energy-level model has been established to describe the corresponding luminescence mechanism in a physically self-consistent manner. The proposed model provides a physically self-consistent framework for understanding the respective roles of intrinsic defect states and Cu-related acceptor states in governing the visible luminescence of Cu-doped $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ QDs and offers useful insight for the rational design of highly luminescent II-VI semiconductor nanomaterials.

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