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Research on the photoluminescence properties of Cu²⁺-doped perovskite CsPbCl₃ quantum dots†

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CsPbX₃ (X = Cl, Br, and I) quantum dots (QDs) and Cu²⁺-doped CsPbCl₃ QDs with different Cu-to-Pb molar ratios were synthesized *via* a solvent-based thermal synthesis method. The photoluminescence (PL) properties of these Cu²⁺-doped CsPbCl₃ QDs were also investigated in this study. The results showed that with the increase in the Cl⁻ concentration the surface defects of CsPb(Cl/Br)₃ QDs increased, which resulted in an increase in the non-radiative recombination of excitons and weakened the PL intensity. Moreover, Cu²⁺-doped CsPbCl₃ QDs maintained the cubic crystal structure of the initial phases. Owing to the doping of Cu²⁺ ions, the surface defects of CsPbCl₃ QDs were effectively eliminated, which facilitated the excitonic recombination *via* a radiative pathway. The PL quantum yields (PLQYs) of Cu²⁺-doped CsPbCl₃ QDs were increased to 51%, showing great photostability. From the results, it is believed that Cu:CsPbCl₃ QDs can be widely used in optoelectronic devices.

1 Introduction

All-inorganic cesium lead halide (CsPbX₃, X = Cl, Br, and I) quantum dots (QDs) have outstanding physical and chemical properties, such as an adjustable photoluminescence in the visible light range (400–700 nm), narrow emission line width, high fluorescence quantum yields, tolerant point defects and good grain boundaries.^{1–7} These characteristics endow the perovskite quantum dots (PQDs) with a promising potential for the applications in optoelectronic devices such as photovoltaics,^{8–15} light-emitting diodes (LEDs)^{16–21} and lasers.^{22–27} Hence, PQDs have aroused widespread research interest. The luminescence color of PQDs can be controlled by either composition or size modulation, and the halogen anion exchange has proven to be an effective strategy to tune the band gap of PQDs instead of destroying the size and crystal structure of its parent nanocrystals.²⁸

In addition, the host lattice of CsPbX₃ QDs is doped with the transition metal elements to replace a part of the Pb²⁺ ions, which can improve the optical performance.^{29–31} However, the practical applications of PQDs in some optoelectronic devices is restricted due to the presence of surface defects, poor stability, and easy oxidation. The elements of Cu and Mn are two representative transition metal elements doped in nanocrystals to improve their optical performance. Mn-doped QDs have stable and high PLQYs (above 50%).^{32,33} Since the emission of doped QDs is considered to be derived from the ⁴T₁–⁶A₁ transition of Mn²⁺, the emission

wavelength is between 580 nm and 600 nm, and the respective luminous color is orange-yellow, which confines their applications. However, compared with Mn-doping, the emission wavelength of the Cu element can be tuned in the visible–near infrared region according to the composition of the main quantum dots.

Srivastava *et al.*³⁴ prepared Cu:ZnS/Zn_{1–x}Cd_xS QDs with PLQYs of 38%. The PLQYs of Cu:ZnInS/ZnS QDs prepared by Yuan *et al.*³⁵ exceeded 40%. The PLQYs of Cu-doped CdS QDs prepared by Stouwdam *et al.*³⁶ exceeded 50%. The Cu:SnO₂ QDs prepared by Babu *et al.*³⁷ showed a strong absorption in the visible light region. Bi *et al.*³⁸ prepared CsPb_{1–x}Cu_xX₃ QDs (X = Br and Br/Cl) by doping Cu ions into CsPbX₃ QDs, which improved their optical characteristics and thermal stability. These results illustrate that Cu²⁺ ions doped into QDs can effectively improve the fluorescence emission efficiency. Herein, we prepared Cu:CsPbCl₃ QDs by doping Cu²⁺ into CsPbCl₃ QDs, which eliminated the surface defects. We explained the enhancement mechanism of PLQYs from excitonic recombination *via* new radiative pathways. The PLQYs of Cu:CsPbCl₃ QDs increased to 51%, exhibiting excellent photostability.

In this study, the synthesis strategy of Cu:CsPbCl₃ QDs is depicted in Fig. 1. The rationale is that the metals of CsCO₃, PbCl₂ and CuCl₂ were used as raw materials, which were mixed mechanically at high temperatures. Then, Cu replaced a part of Pb for the synthesis of nanocrystals *via* a solvent-based, thermal synthesis method.

2 Experimental section

2.1 Materials and chemicals

Cs₂CO₃ (Macklin, 99%), PbCl₂ (Aladdin, 98%), PbBr₂ (Macklin, 99%), PbI₂ (Aladdin, 99%), 1-octadecene (ODE, Aladdin, 90%),

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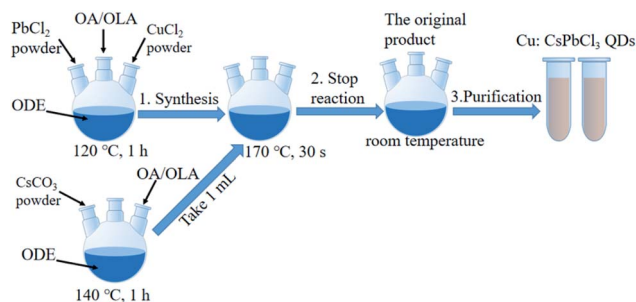


Fig. 1 Schematic of the synthesis of Cu:CsPbCl₃ QDs.

oleic acid (OA, Aladdin, 90%), oleylamine (OLA, Aladdin, 80–90%), CuCl₂ (Jinshan, 99%), and *n*-hexane (Fuyu, 98%) were purchased. All chemicals were used without any further purification.

2.2 Preparation of the Cs-oleate solution

2.5 mL OA, 30 mL ODE and Cs₂CO₃ (0.8 g, 2.5 mmol) powder were put into a 100 mL three-neck flask at 140 °C for 1 h under magnetic stirring until the Cs₂CO₃ powder completely dissolved and the solution became transparent.

2.3 Synthesis of CsPbX₃ QDs

1.5 mL OA, 1.5 mL OLA and 15 mL ODE, and 0.15 g, 0.54 mmol PbCl₂, 0.2 g, 0.54 mmol PbBr₂, 0.25 g, 0.54 mmol PbI₂, PbCl₂/PbBr₂ with specific molar ratios were loaded into a 100 mL three-necked flask and heated at 120 °C for 1 h to obtain CsPbCl₃ QDs, CsPbBr₃ QDs, CsPbI₃ QDs, CsPb(Cl/Br)₃ QDs, respectively. After the reaction temperature was increased to 170 °C, the Cs-oleate solution (1 mL) was quickly injected for reacting and after 30 s, the solution was cooled to room temperature in an ice bath.

2.4 Synthesis of Cu:CsPbCl₃ QDs

We prepared Cu:CsPbCl₃ QDs with the molar ratios of CuCl₂ and PbCl₂ of 0.1 : 1, 0.3 : 1, 0.5 : 1, 0.9 : 1, and 1.7 : 1. The typical synthetic procedure of Cu:CsPbCl₃ QDs with the Cu-to-Pb molar ratio of 0.9 : 1 as follows: 1.5 mL OA, 1.5 mL OLA, 15 mL ODE, PbCl₂ (0.097 g, 0.35 mmol) and CuCl₂ (0.053 g, 0.31 mmol) powders were loaded in a 100 mL three-neck flask heated to 120 °C for 1 h. The reaction temperature was increased to 170 °C, and the Cs-oleate solution (1 mL) was quickly injected, and after 30 s, the reaction was cooled to room temperature on an ice bath.

2.5 Purification

CsPbX₃ and Cu:CsPbCl₃ QDs were extracted from the original product *via* centrifugation at 8000 rpm for 5 min, and the precipitate was taken out. The resulting precipitates were dispersed in *n*-hexane at room temperature and were centrifuged for 5 min at a speed of 6000 rpm; the supernatant was taken, and this process was repeated twice to get CsPbX₃ and Cu:CsPbCl₃ QDs. Then, they were kept aside for 24 h in a freezer, and were taken out again for centrifugal purification, obtaining a clear colloidal CsPbX₃ and Cu:CsPbCl₃ QDs.

2.6 Characterization and spectral analysis

PL spectra were obtained on a Cary Eclipse-G9800A Fluorescence Spectrophotometer from Agilent Technologies. UV-Visible (UV-Vis) spectroscopy was performed using a UV-2700 UV-Vis Spectrophotometer from Shimadzu. The doping concentrations of Cu²⁺ were monitored by an Agilent inductively coupled plasma-optical emission spectrometer 730 (ICP-OES730). Dried powdered samples of QDs were acid-digested and then diluted prior to measurements. The crystal structures were characterized on a Jeol-2100f transmission electron microscope (TEM) at 200 kV. TEM specimens were prepared by directly drying a drop of a dilute *n*-hexane solution of PQDs on the surface of a carbon-coated copper grid. Energy dispersive X-ray (EDX) measurements were performed using X-max 80 from Oxford Instruments. X-ray photoelectron spectroscopy (XPS) characterizations were conducted on a Thermo Scientific ESCALAB 250Xi spectrometer using a monochromatic Al K α radiation source (200 W), where the sample were prepared directly by drying a drop of dilute *n*-hexane solution of PQDs onto an Si wafer. X-ray diffraction (XRD) measurements were performed by a Rigaku SmartLab XG X-ray diffractometer. XRD specimens were prepared by directly drying a drop of the dilute *n*-hexane solution of PQDs onto a glass slide. The room temperature PLQYs of PQDs were calculated by comparing the integrated emission of the PQD samples in an *n*-hexane solution with that of rhodamine 6G with the PLQYs of 95% in ethanol with identical optical density. Fourier transform infrared (FTIR) spectrum was obtained using a VERTEX70 Spectrometer from Bruker.

3 Results and discussions

3.1 The PL and UV-Vis absorption spectra of CsPbX₃ QDs

The PL and UV-Vis absorption spectra of CsPbX₃ QDs are shown in Fig. 2a and b. The PL intensity of CsPbCl₃ QDs was much lower than that of CsPbBr₃ and CsPbI₃ QDs. Owing to the surface of perovskite CsPbCl₃ QDs have a serious local trap states,³⁹ which produced non-radiative recombination and resulted in a weak PL intensity. The peaks of excitonic absorption from CsPbCl₃, CsPbBr₃ and CsPbI₃ QDs were located at 395 nm, 469 nm and 676 nm, respectively. The red shift in the absorption peaks was caused by the weak binding ability of the halogen element.

In order to observe the PL spectra of PQDs mixed with halogen elements, we prepared a series of CsPb(Cl/Br)₃ QDs mixed with different Cl-to-Br molar ratios. The PL spectra and UV-Vis absorption spectra of these QDs are shown in Fig. 2c and d, respectively. The PL intensity of CsPb(Cl/Br)₃ QDs decreased gradually with the increase in the Cl⁻ ion concentrations, and the peaks of exciton emission were blue-shifted. There were Pb-Cl ion vacancies on the surface of CsPbCl₃ QDs, which seriously reduced its PL efficiency.³² This illustrated that as the concentration of Cl⁻ ions increased, the number of Pb-Cl ion vacancies on the surface also increased. This led to the non-radiative recombination of QD excitons and reduced the PL intensity of CsPb(Cl/Br)₃ QDs. The peak of excitonic absorption was also blue-shifted with the increase in Cl⁻ ion concentrations. The divalent Cu²⁺ in the transition metal series has a smaller ionic

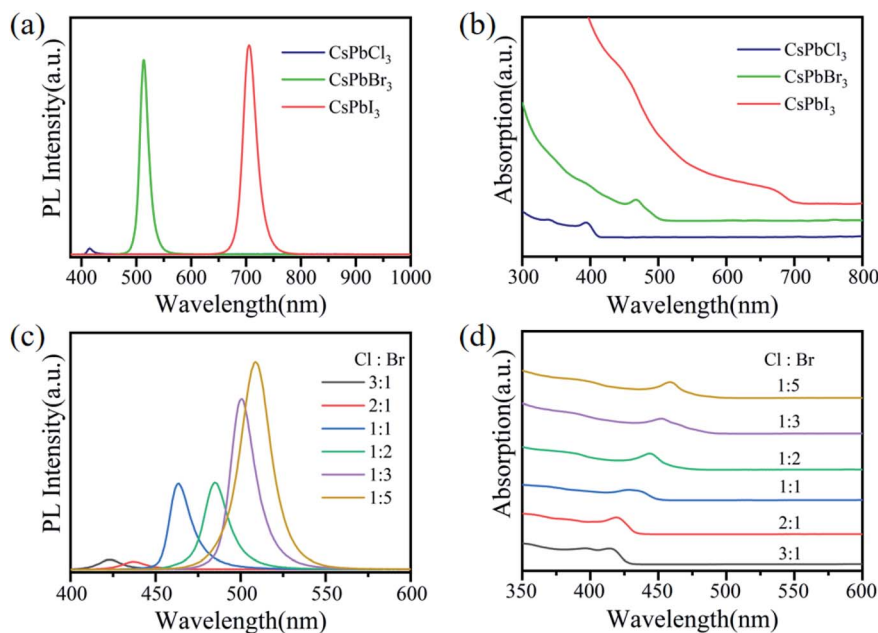


Fig. 2 (a) The PL spectra of CsPbX₃ QDs. (b) Absorption spectra of CsPbX₃ QDs. (c) The PL spectra of CsPb(Cl/Br)₃ QDs with different Cl-to-Br molar ratios. (d) UV-Vis absorption spectra of CsPb(Cl/Br)₃ QDs with different Cl-to-Br molar ratios.

radius (73 pm) and can be used as a good doping element to eliminate the surface defects of the quantum dots.

To eliminate the surface defects of CsPbCl₃ QDs for improving its fluorescence emission efficiency and photostability, we further doped the divalent metal Cu²⁺ ion in the CsPbCl₃ QDs to increase the proportion of copper ions.

3.2 TEM images

In order to illustrate the effects of Cu²⁺-doped on the surface structure of CsPbCl₃ QDs, the TEM images of undoped and Cu²⁺-doped CsPbCl₃ QDs are shown in Fig. 3a and b. The

structural morphologies of Cu²⁺-doped CsPbCl₃ QDs were of cubic crystal structure as CsPbCl₃ QDs. These are in line with the crystal phase of PQDs prepared under the conditions of high temperature synthesis and QD surface effects.^{16,40} Fig. 3c and d show their HRTEM images with clear lattice fringes. As measured from their crystal plane spacings of 0.283 nm and 0.280 nm, it was found that they corresponded to (002) lattice plane of CsPbCl₃ QDs. These results indicate that Cu²⁺-doped CsPbCl₃ QDs maintain the crystal structure of the initial phases and shrink the surface lattice spacing, improving the crystallinity of QDs.

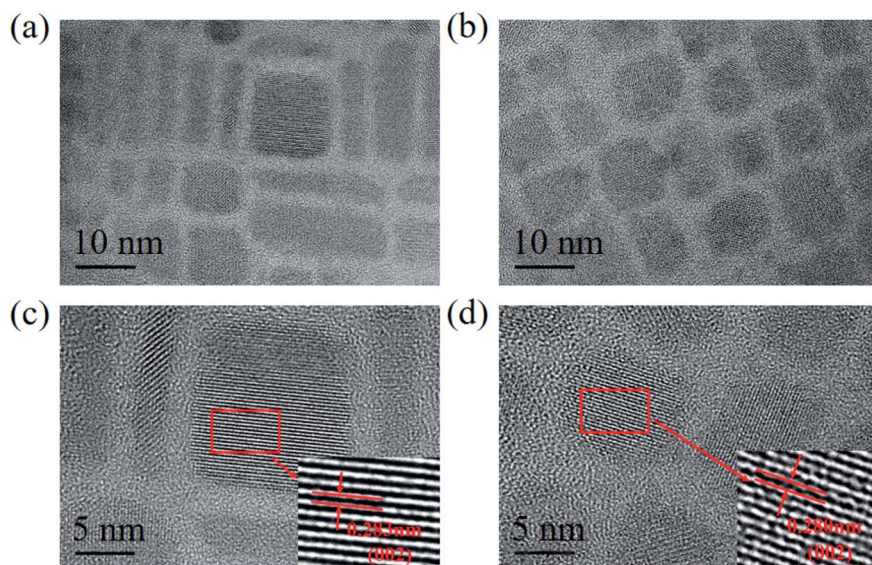


Fig. 3 (a) TEM images of CsPbCl₃ QDs. (b) TEM images of Cu²⁺-doped CsPbCl₃ QDs with the Cu-to-Pb molar ratio of 0.9 : 1. (c) HRTEM micrograph of CsPbCl₃ QDs. (d) HRTEM micrograph of Cu²⁺-doped CsPbCl₃ QDs with the Cu-to-Pb molar ratio of 0.9 : 1.

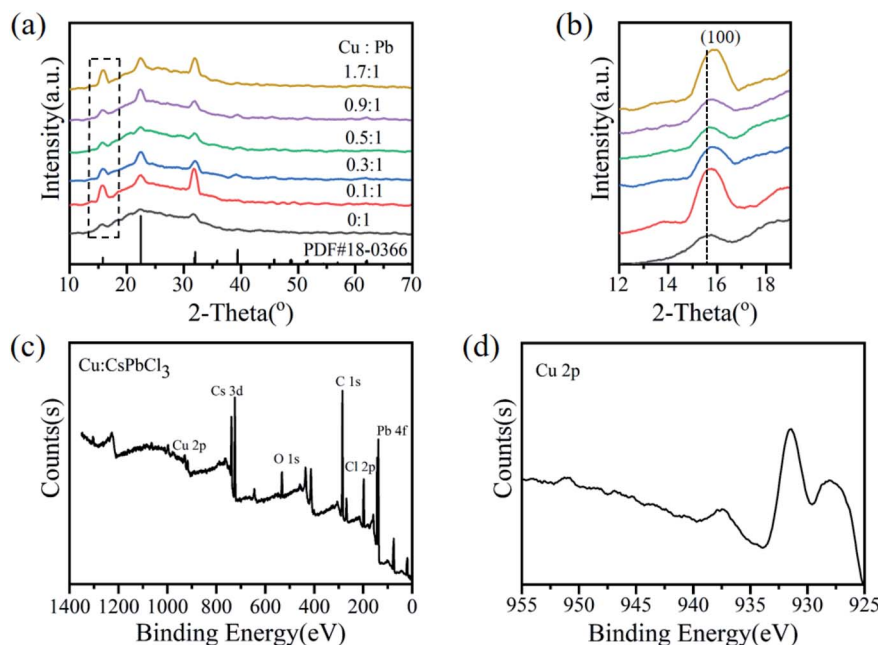


Fig. 4 (a) XRD patterns of Cu^{2+} -doped CsPbCl_3 QDs with different Cu-to-Pb molar ratios. (b) Enlarged the XRD patterns of the 2-theta degree. (c) XPS spectrum of $\text{Cu}:\text{CsPbCl}_3$ with the Cu-to-Pb molar ratio of 0.9 : 1. (d) The high-resolution XPS spectrum of Cu 2p.

3.3 XRD, XPS and EDX spectra

The typical XRD patterns further confirmed that the $\text{Cu}:\text{CsPbCl}_3$ QDs prepared by different Cu-to-Pb molar ratios retained the same crystalline structure of tetragonal CsPbCl_3 QDs, as shown in Fig. 4a. The diffraction characteristic peaks of undoped and Cu^{2+} -doped CsPbCl_3 QDs are similar, which correspond to the standard XRD spectra of CsPbCl_3 QDs (PDF #18-0366). The peak positions of (100) moved to higher 2-theta degree values (shown

in Fig. 4b) with the increase in the Cu^{2+} ion concentrations, which indicate that the lattice contraction and the lattice parameters became smaller.³⁸ These results show that some of the larger Pb^{2+} (119 pm) ions in CsPbCl_3 QDs were replaced by smaller Cu^{2+} (73 pm) ions. The doping concentrations of Cu ions were measured *via* ICP-OES (Table S1†). When Cu^{2+} -doped CsPbCl_3 QDs with the Cu-to-Pb molar ratio of 0.9 : 1, its PLQYs reached 51%. Also, the doping concentration of Cu ions relative

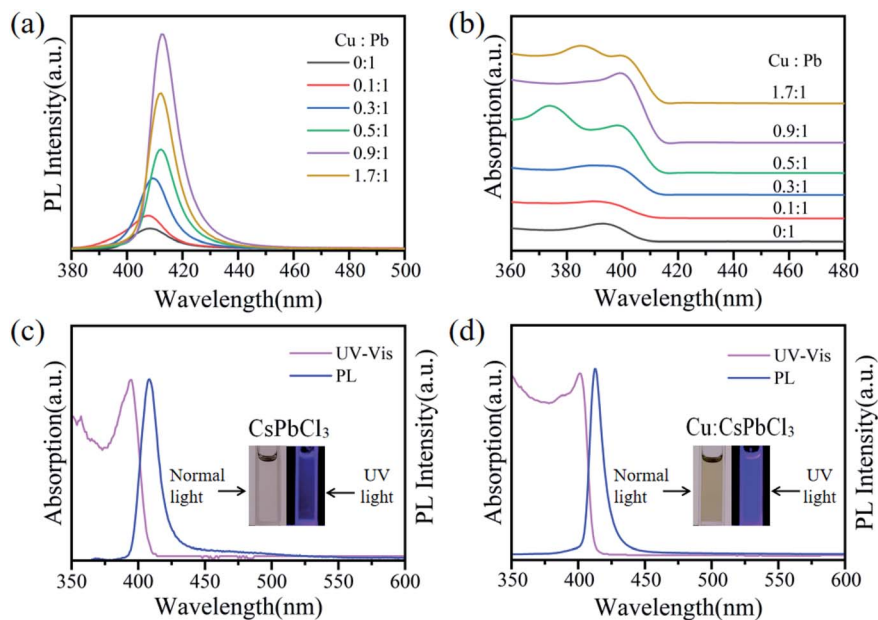


Fig. 5 (a) PL spectra of Cu^{2+} -doped CsPbCl_3 QDs with different Cu-to-Pb molar ratios. (b) UV-Vis absorption spectra of Cu^{2+} -doped CsPbCl_3 QDs with different Cu-to-Pb molar ratios. (c) UV-Vis absorption and PL spectra of CsPbCl_3 QDs. (d) UV-Vis absorption and PL spectra of Cu^{2+} -doped CsPbCl_3 QDs with the Cu-to-Pb molar ratio of 0.9 : 1; the insets show photographs under normal light and 365 nm excitation.

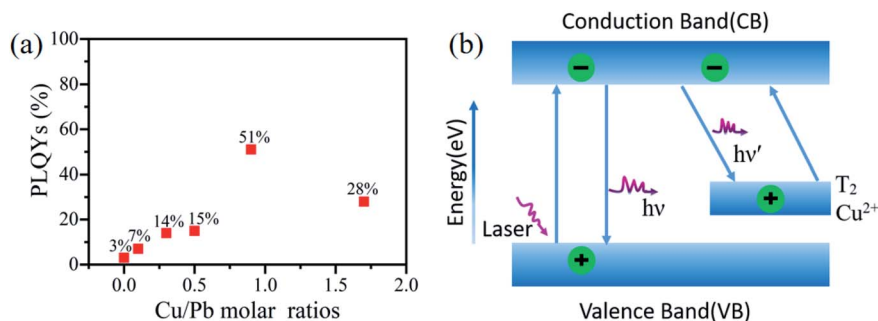


Fig. 6 (a) PLQYs of Cu^{2+} -doped CsPbCl_3 QDs with different Cu-to-Pb molar ratios. (b) Schematic showing the pathways of radiative recombination of the introduction of Cu^{2+} states within the host band gap.

to Pb ions was 2.32%. The EDX spectrum of Cu^{2+} -doped CsPbCl_3 QDs with the Cu-to-Pb molar ratio of 0.9 : 1 is shown in Fig. S1a,† the presence of Pb, Cs, Cu and Cl elements were observed. The XPS spectrum of Cu: CsPbCl_3 QDs with the Cu-to-Pb molar ratio of 0.9 : 1 is shown in Fig. 4c, which exhibited XPS peaks of Cu 2p, Cs 3d, Pb 4f, Cl 2p, C 1s and O 1s. Furthermore, the high-resolution XPS spectra (Fig. 4d) reveal that the binding energy (BE) is 931.5 eV for Cu 2p_{3/2}, and the BE peak at 937.5 eV is the characteristic Cu^{2+} shake-up satellite peak.⁴¹ In addition, the BE at 738.4 eV and 724.4 eV are for Cs 3d_{3/2} and Cs 3d_{5/2}, 143.1 eV and 138.2 eV for Pb 4f_{5/2} and Pb 4f_{7/2}, 199.4 eV and 197.8 eV for Cl 2p_{1/2} and Cl 2p_{3/2}, respectively, as shown in Fig. S1b–d.† These results suggest that Cu^{2+} was successfully doped into CsPbCl_3 QDs.

3.4 The PL and UV-Vis absorption spectra of Cu: CsPbCl_3 QDs

Fig. 5a depicts the PL spectra of Cu^{2+} -doped CsPbCl_3 QDs with different Cu-to-Pb molar ratios. It is observed that as the Cu^{2+} ion concentration increased, the PL intensity of Cu^{2+} -doped CsPbCl_3 QDs also increased and then gradually decreased. Their emission peaks display a redshift from 408 nm to 412 nm. When the Cu-to-Pb molar ratio reached 1.7 : 1, the PL intensity of Cu: CsPbCl_3 QDs weakened. This indicates that excessive doping of Cu^{2+} ions form a non-radiative relaxation channel in CsPbCl_3 QDs leads to the decrease in the PL intensity. It can be observed from the Urbach tails in the UV-Vis absorption spectra shown in Fig. 5b that the absorption edge of doped Cu^{2+} ions was steeper than that of undoped QDs, which confirmed that the system was disordered or the defects were reduced.^{42,43} This is consistent with the enhancement of the PL intensity of excitonic emission. In the case mentioned above, the redshifts of the PL and absorption spectra of Cu^{2+} -doped CsPbCl_3 QDs are caused by the recombination of electrons in the conduction band of the host material and holes in the Cu^{2+} T₂ state.^{34,44,45} These results confirmed that doping Cu^{2+} with an ionic radius of 73 pm forms Cu–Cl ion pairs to fill the Pb–Cl ion vacancies, effectively eliminating the non-radiative recombination of excitons, which enhanced the PL intensity of CsPbCl_3 QDs.

Fig. 5c and d show the UV absorption and PL spectra of undoped and Cu^{2+} -doped CsPbCl_3 QDs with the Cu-to-Pb molar ratio of 0.9 : 1, respectively. As shown in the both figures, the full width at half maxima (FWHM) of the PL spectra of Cu^{2+} -

doped was narrower (12 nm) than that of the undoped CsPbCl_3 QDs (16 nm), which illustrated that the size distribution of the PQD nanoparticles and homogeneity of the morphology were improved. From the photographs of these solutions under 365 nm excitation, the blue-violet light emitted by Cu^{2+} -doped under the excitation of the laser was obviously brighter than the undoped CsPbCl_3 QDs. Fig. 6a shows the PLQYs of Cu^{2+} -doped CsPbCl_3 QDs with numerous molar ratios of Cu-to-Pb (0 : 1, 0.1 : 1, 0.3 : 1, 0.5 : 1, 0.9 : 1 and 1.7 : 1), increasing from 3% to 51%.

3.5 The mechanism model of enhanced PL

According to the above-mentioned results, the mechanism model of enhanced PL of Cu: CsPbCl_3 QDs is shown in Fig. 6b. Under the excitation of 365 nm laser, the CsPbCl_3 QD host absorbs energy and emits a 408 nm blue-violet light *via* the radiative recombination of excitons between the valence band (VB) and the conduction band (CB). Due to the presence of defect trap states, the non-radiative recombination pathway of excitons leads to energy loss. Hence, Cu^{2+} is introduced to recombine the excitons with a new radiation pathway. A part of the electrons in the conduction band of the CsPbCl_3 host are transferred to the Cu^{2+} T₂ state and recombined with the holes in this energy state, forming a new excitonic recombination pathway.^{46,47} It leads to the red-shift in the PL emission peak. Furthermore, the Cu^{2+} T₂ states absorb energy and then pump the electrons to transition to the conduction band of the host. The energy transfer of the photoinduced excitons from the CsPbCl_3 QD host to the Cu^{2+} T₂ state, which promotes the

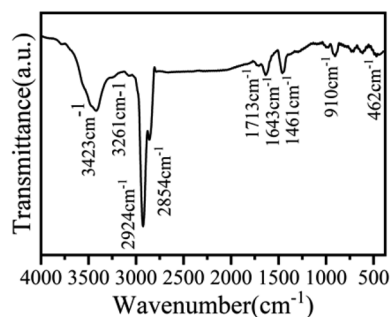


Fig. 7 FTIR spectrum of Cu: CsPbCl_3 QDs with Cu-to-Pb molar ratio of 0.9 : 1.

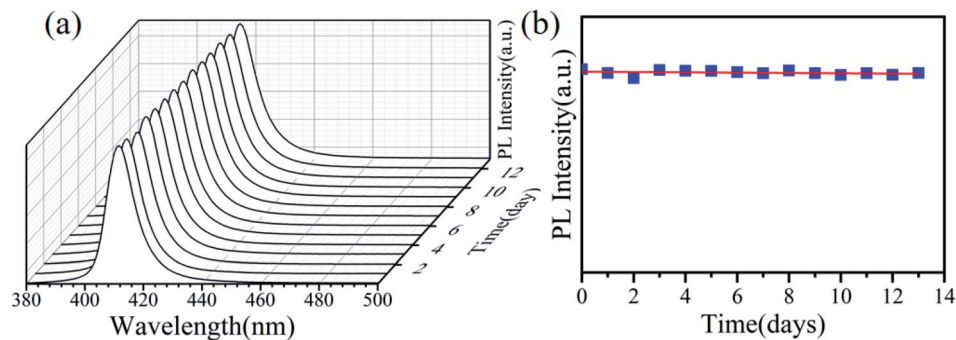


Fig. 8 PL spectra of Cu:CsPbCl₃ QDs with the Cu-to-Pb molar ratio of 0.9 : 1 over time (days): (a) the PL spectra and (b) fitting of the PL intensity.

recombination of excitons *via* the radiative pathway, reduces energy loss, and enhances the PL intensity.

3.6 FTIR analysis

Chemical components of Cu:CsPbCl₃ QDs were also analyzed. Some chemical elements can be observed in the FTIR spectrum, as shown in Fig. 7. The peaks at 3423 cm⁻¹ and 1713 cm⁻¹ are the stretching vibration peaks of the O–H and C=O bonds, which confirm that the ligand shell of PQDs contains oleic acid molecules. The peaks at 2924 cm⁻¹ and 2854 cm⁻¹ and 910 cm⁻¹ are the vibration peaks of the olefin C–H bond. A weak stretching vibration peak of the N–H bond was observed at 3261 cm⁻¹, which illustrates that the ligand shell of PQDs contains oleylamine molecules. The peak at 1643 cm⁻¹ is the stretching vibration peak of the C=C bond, while the peak at 462 cm⁻¹ is the vibration peak of the Pb–O bond, which is due to the carboxyl combines with the Pb²⁺ ions. These results show that Cu:CsPbCl₃ QDs are packaged by OA and OLA, which can combine with other materials *via* adsorption or chemical bonds.^{48–50} This is significant for the preparation of highly conductive quantum dot films for photovoltaics and LED applications. In addition, the peak at 1461 cm⁻¹ is the bending vibrations of the alkane C–H bond, which is because Cu:CsPbCl₃ QDs were dispersed in *n*-hexane.

3.7 Photostability

We further explored the photostability of Cu:CsPbCl₃ QDs, and the PL spectra of the sample with a Cu-to-Pb molar ratio of 0.9 : 1 were measured for two consecutive weeks. In Fig. 8a, the Cu:CsPbCl₃ QD PL emission slightly redshifted by 2 nm with the increase in time (days). Also, the fitting curve of the PL intensity over time is shown in Fig. 8b. It can be seen that the PL intensity increases over time and still remains relatively stable, which proved that the Cu²⁺-doped CsPbCl₃ QDs have a good photostability.

4 Conclusions

In summary, we have successfully synthesized CsPbX₃ and Cu²⁺-doped CsPbCl₃ QDs *via* a the solvent-based thermal synthesis method. The results clearly show that the PL intensity of blue-violet light-emitting CsPbX₃ QDs was much lower than that of green and red light-emitting. With the increase in the

concentration of Cl⁻ ions, the number of surface defects of CsPb(Cl/Br)₃ QDs increased, which facilitated the non-radiative recombination of excitons and weakened the PL intensity of QDs. Cu²⁺-doped facilitated the exciton recombination *via* a radiative pathway that effectively enhanced the PLQYs of CsPbCl₃ QDs from 3% to 51%, while maintaining the cubic crystal structure surface morphology. Moreover, the full width at half maxima of the PL spectra of Cu²⁺-doped CsPbCl₃ QDs was narrower than that of the undoped CsPbCl₃ QDs, which further proved that Cu²⁺-doped improves the crystallinity of CsPbCl₃ QDs and reduces surface defects. We further tested the photostability of Cu:CsPbCl₃ QDs. The sample QDs showed relatively stable PL intensity for two consecutive weeks. These results show that Cu:CsPbCl₃ QDs can be widely used in the field of optoelectronic devices.

Conflicts of interest

The authors have declared that no conflicting interests exist.

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