

Communication

A Blue-Light-Emitting 3 nm-Sized CsPbBr₃ Perovskite Quantum Dot with ZnBr₂ Synthesized by Room-Temperature Supersaturated Recrystallization

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Abstract: Recently, tuning the green emission of CsPbBr₃ quantum dots (QDs) to blue through quantum size and confinement effects has received considerable attention due to its remarkable photophysical properties. However, the synthesis of such a blue-emitting QD has been challenging. Herein, supersaturated recrystallization was successfully implemented at room temperature to synthesize a broadband blue-emitting ZnBr₂-doped CsPbBr₃ QD with an average size of ~3 nm covering the blue spectrum. The structural and optical properties of CsPbBr₃ QDs demonstrated that QD particle size may decrease by accommodating ZnBr₂ dopants into the perovskite precursor solution. Energy-dispersive spectroscopy confirmed the presence of zinc ions with the QDs. This work provides a new strategy for synthesizing strongly quantum-confined QD materials for photonic devices such as light-emitting diodes and lighting.

Keywords: quantum dot; halide perovskite; CsPbBr₃; blue light emitting; quantum confinement; supersaturated recrystallization; nanocrystal



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1. Introduction

All-inorganic lead halide perovskite CsPbX₃ (X = Cl, Br, and I) nanocrystals (NCs) have attracted considerable attention from researchers as a potential optoelectronic material to be used in light-emitting diodes (LEDs) and lighting [1–3]. Their outstanding potential mainly stems from their high photoluminescence quantum yields (PLQYs), a narrow full width at half maximum (FWHM), tunable band gap (ranging from ultraviolet to near-infrared), low trap-state density, and low-cost solution processability [4–7]. Recently, a green- or red-band emission with near-unity PLQYs has been demonstrated [8–10]. However, the development of blue-band emission with high PLQYs remains challenging [5,11–14].

Normally, a mixed halide perovskite such as CsPbCl_xBr_{3–x} can cover the entire blue spectrum [15,16]. However, this approach is constrained by lattice mismatch, phase segregation, and chlorine vacancies [17–19]. Specifically, the Cl vacancies are responsible for deep defects and the low PLQYs [13,17,19]. On the other hand, CsPbBr₃ has a stable structure with fewer crystal defects due to its well-fitted atomic radii [19]. However, the instability of the perovskites to photon, thermal, moisture, and operational challenges is

still a bottleneck for the commercialization of perovskite QD-based devices. The instability problem is more pronounced for Cl-based QDs due to defects as well as the intrinsic distortion of the $[\text{PbCl}_6]^{4-}$ octahedron [20], opening the channel for the degradation of materials. Moreover, mixed $\text{CsPbCl}_x\text{Br}_{3-x}$ perovskites are prone to both phase segregation and spectral instability [21]. To overcome these drawbacks, in situ and/or post-treatment Cl defect passivation has been investigated using versatile ligands. However, excess ligands may impede the charge-transport properties of the perovskite QDs [22]. As a result, many researchers have examined pure bromine CsPbBr_3 QDs as a source for blue emission by substituting Pb^{2+} with a similar-sized metal cation considering Goldschmidt's tolerance factor, $t = (r_A + r_X) / [\sqrt{2} \cdot (r_B + r_X)]$, with $0.813 \leq t \leq 1.107$ for structural stability, where r_A , r_B , and r_X are the radius of A cation, B cation, and X anion in the ABX_3 perovskite structure, respectively [23]. For example, the blue shift of optical spectra was demonstrated by partially replacing Pb^{2+} with a divalent cation (Cd^{2+} , Zn^{2+} , Sn^{2+} , Cu^{2+}) and a trivalent cation (Al^{3+} , Sb^{3+}) [11,24–26]. Here, the blue shift is attributed to the lattice contraction as these ions possess a smaller ionic radius than Pb^{2+} . As a result, the Pb–Br bond becomes shorter and increases interaction between Pb and Br orbitals, which is responsible for the blue shift [11,24–29]. Besides emission, the dopant metallic cation can enhance the stability of the CsPbBr_3 not only by increasing the defect formation energy but also passivating the defect state of the QDs [26–30].

The other strategy is controlling the quantum size of CsPbBr_3 NCs in a quantum-confinement regime [28,29]. The two most common synthesis methods, i.e., hot injection (HI) and supersaturation recrystallization (SR), usually afford CsPbBr_3 QDs with a size of greater than 7 nm, resulting in green light emission. Hence, different techniques have been employed to control the CsPbBr_3 QDs in strong confinement regimes like ligand composition engineering (oleic acid/oleylamine ratio change) [31], hydrogen bromide (HBr) acid etching-driven ligand exchange [32], synthesis under thermodynamic equilibrium environment [9,33], and the two-step SR technique [34]. Importantly, to date, most of the blue-emitting CsPbBr_3 QD synthesis has been based on the typical HI method, which requires a high-temperature injection as well as an inert gas environment, limiting its practical application due to energy and material cost.

In this work, we synthesized a blue light-emitting ZnBr_2 -doped CsPbBr_3 QD using the SR method at room temperature (without any inert gas but under ambient conditions). This approach is initiated by the principle of the size-dependent stoichiometry of Br^- in CsPbBr_3 QDs (higher Br^- contents in the smaller QDs) and the equilibrium between the QDs and colloidal dispersion medium [33,35]. The ~3 nm-sized QDs were obtained by adding a controlled amount of ZnBr_2 into the perovskite precursor solution, resulting in a broadband blue emission.

2. Materials and Methods

2.1. Materials

Cesium bromide (CsBr, 99.9%, Sigma-Aldrich, Darmstadt, Germany), lead (II) bromide (PbBr_2 , 99%, Sigma-Aldrich, Darmstadt, Germany), zinc bromide (ZnBr_2 , 99.9%, anhydrous, Nice, Kochi, India), oleic acid (OA, 98%, Sigma-Aldrich, Darmstadt, Germany), oleylamine (OAm, technical grade 70%, Sigma-Aldrich, Darmstadt, Germany), *N,N*-dimethylformamide (DMF, 99%, AR chemicals, Delhi, India), toluene (99%, AR chemicals, Delhi, India), and ethyl acetate (99%, AR chemicals, Delhi, India) were used as received without further purification.

2.2. Synthesis of ZnBr_2 - CsPbBr_3 QDs

The ZnBr_2 was prepared by the SR method at room temperature [36]. Under magnetic stirring, 0.4 mmol CsBr, 0.4 mmol PbBr_2 , 1 mL OA, and 0.5 mL OAm were dissolved in 10 mL of DMF for 2 h as a source of Cs, Pb, and Br. Under the same conditions, 2.5 mmol ZnBr_2 was dissolved in 5 mL of DMF for 2 h. Then, 0 and 200 μL of a ZnBr_2 solution and 1 mL of the perovskite precursor ($\text{PbBr}_2/\text{CsBr}$) solution were simultaneously injected into

10 mL of toluene under vigorous magnetic stirring. The synthesized QDs were centrifuged at 3500 rpm for 5 min. Then, the QD dispersion mixed with 5 mL ethyl acetate was centrifuged at 9000 rpm for 10 min. Finally, the precipitated QDs were used for further characterization after re-dispersing in toluene acting as an antisolvent.

2.3. Characterization

The morphology and size of the as-prepared QDs were measured by high-resolution transmission electron microscopy (HR-TEM, JEOL JEM-2100, Peabody, MA, USA). Elemental analysis was carried out by energy-dispersive spectroscopy (EDS, Oxford INCA energy TEM 250, High Wycombe, UK). X-ray diffraction (XRD) patterns were obtained using Cu K α radiation (bench-top X-ray diffractometer of Rigaku Mini-Flex 600, Kyoto, Japan). The absorption and steady-state photoluminescence (PL) spectra were obtained using ultraviolet–visible (UV–vis) spectrometry (UV-2600, Shimadzu, Kyoto, Japan), and a PL spectrophotometer (RF-6000, Shimadzu, Kyoto, Japan), respectively. Time-resolved PL (TRPL) decay was obtained by the Fluorolog 3 TCSPC spectrofluorometer (Horiba, Irvine, CA, USA).

2.4. Computational Methods

The electronic band structures of the $3 \times 3 \times 3$ CsPbBr₃ supercells without or with zinc doping were calculated using Cambridge Serial Total Energy Package (CASTEP, Materials Studio 2017, Vélizy-Villacoublay, France). General gradient approximation (GGA) with perdue–burke–ernzerhof (PBE) exchange–correlation functional was used to calculate both geometry optimization and the electronic properties of the materials [37]. The Monkhorst pack grid of $3 \times 3 \times 3$ size was constructed for k-points in the Brillouin zone. The energy of 1.0×10^{-5} eV/atom, force of 0.02 eV/Å, maximum displacement of 4×10^{-4} Å, and maximum stress of 0.04 GPa were used for geometry optimization.

3. Results and Discussion

Figure 1 shows the schematic explanation of the supersaturated recrystallization process for the synthesis of CsPbBr₃ QDs. As shown in Figure 1a, when a green-light-emitting CsPbBr₃ QD was synthesized, the perovskite colloidal dispersion was transparent yellow. On the other hand, when a blue-light-emitting CsPbBr₃ QD was prepared, that was partially cloudy without any yellowish color, implying that the QD size might be very small with a strong quantum size and confinement effect in nanoscale. The desired amount of ZnBr₂ as described in the experimental section was employed to reduce the size of CsPbBr₃ QDs in nanoscale. This approach is consistent with the literature reports [33,35], in which ZnBr₂ was a source of excess Br[−] ions to adjust the size of CsPbBr₃ QDs. Smaller QDs have a larger surface area requiring sufficient amounts of surface ligands and/or Lewis base Br[−] ions.

The CsPbBr₃ QDs without/with ZnBr₂ dopant were synthesized by SR under ambient conditions [38]. Figure 2 shows the XRD patterns of the CsPbBr₃ drop-cast films [38–41], corresponding to the cubic phase of CsPbBr₃ [40]. Please note that CsPbBr₃ shows polymorphism depending on temperature, like orthorhombic (≤ 88 °C), tetragonal ($88 \leq T \leq 130$ °C), and cubic (≥ 130 °C) [38–41]. However, in the case of nanoscale crystals, the cubic phase was frequently observed in comparison to the orthorhombic, indicating the metastable state of QDs, i.e., kinetically metastable or stable but thermodynamically unstable. The XRD patterns for ZnBr₂-doped CsPbBr₃ drop-cast film display more orientational order compared to the pristine CsPbBr₃ film without ZnBr₂ doping. Importantly, the same XRD patterns indicate that the zinc-ion doping into the CsPbBr₃ NCs does not affect the crystal structure of this perovskite crystal. This observation is consistent with the literature reports confirming that the zinc ion maintains a crystal phase of CsPbBr₃ [42,43]. However, the presence of a lot of small XRD peaks indicates that the orientational order is very small in the drop-cast CsPbBr₃ thin films composed of polydisperse nanoparticles. In this work, any post-annealing process, co-solvent addition, and antisolvent dispensing (so-called

solvent engineering) were not employed, which should affect the crystal orientation during film formation via the intermediate phase of the perovskite precursors. Importantly, nanocrystals have a high surface energy and weakly bound surface ligands in the case of oleic acid, which may allow a further aggregation of QD particles in order to decrease free energies during thin-film drying processing, indicating a meta-stability of QDs. However, further detail could be addressed in our future work regarding the phase transformation and stability of nanoscale QDs.

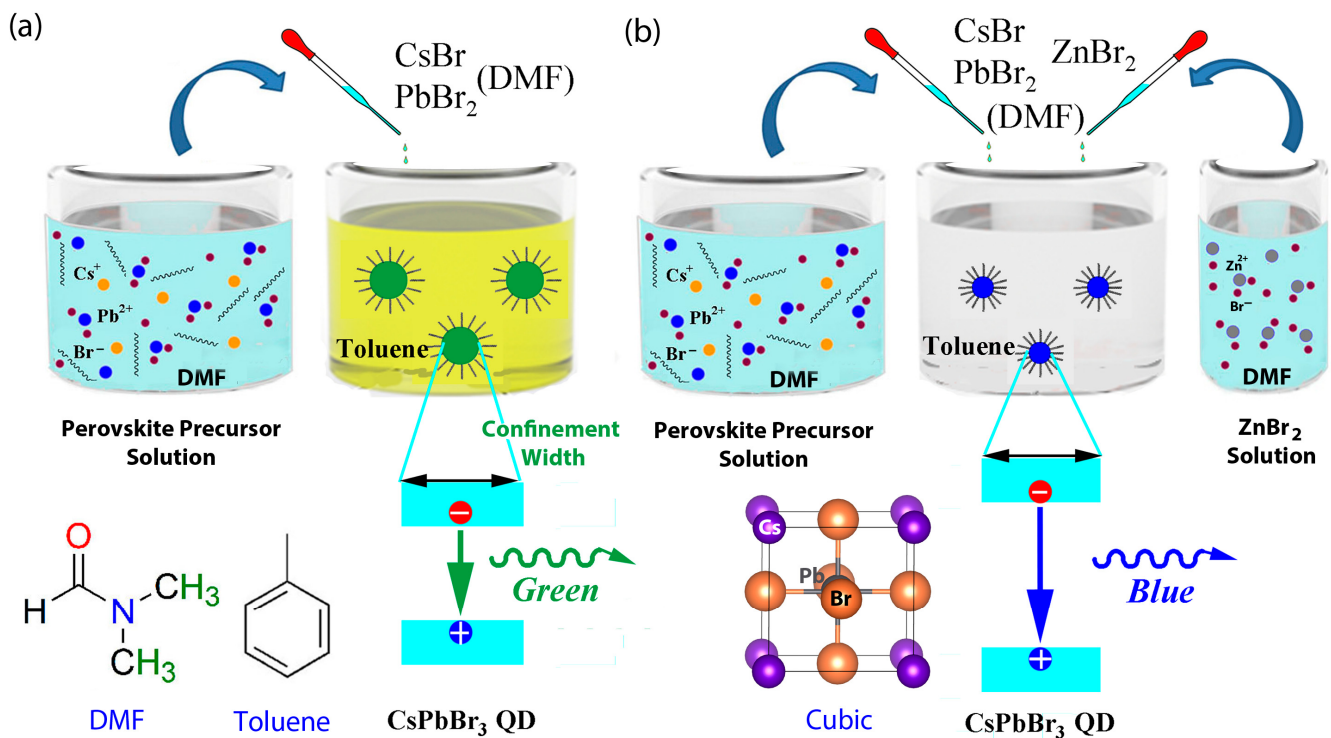


Figure 1. Schematic explanation of supersaturated recrystallization (SR): (a) CsPbBr₃ QD as a green light emitter, and the chemical structures of DMF and toluene. (b) CsPbBr₃ QD as a blue-light emitter, and the cubic structure of CsPbBr₃.

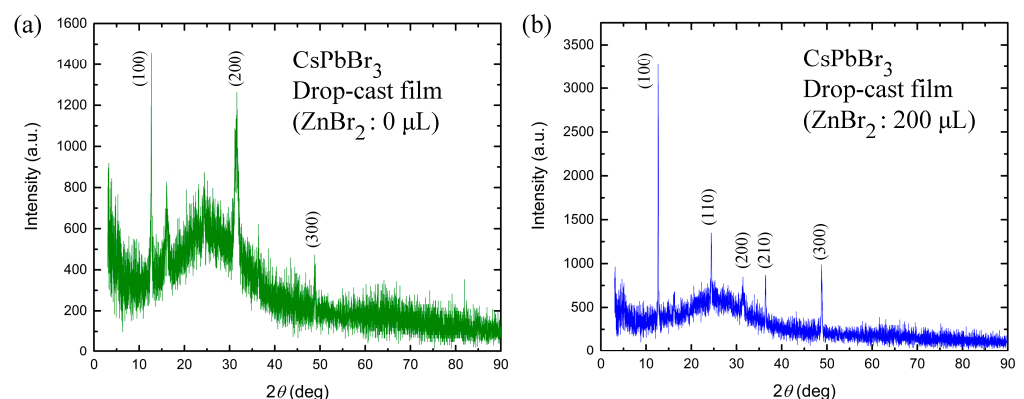


Figure 2. XRD patterns of CsPbBr₃ drop-cast thin films (a) without ZnBr₂ and (b) with ZnBr₂ doping at room temperature.

Figure 3 shows the EDS spectra for CsPbBr₃ QDs. As shown in Figure 3, when ZnBr₂ was incorporated into the perovskite precursor solution, the synthesized CsPbBr₃ QDs exhibited the presence of the zinc element (see Figure 3b). Importantly, the zinc ions can stay with CsPbBr₃ QDs in two possibilities, i.e., substitutional (e.g., substitution of Pb²⁺ ions), and interstitial substitution in the bulk and/or surface of CsPbBr₃ QDs. The exact

location is out of scope in the current study. However, based on literature reports [23], the zinc ions are known to stay in the CsPbBr_3 crystal structure by partially substituting the Pb^{2+} ions in the bromide plumbate [29].

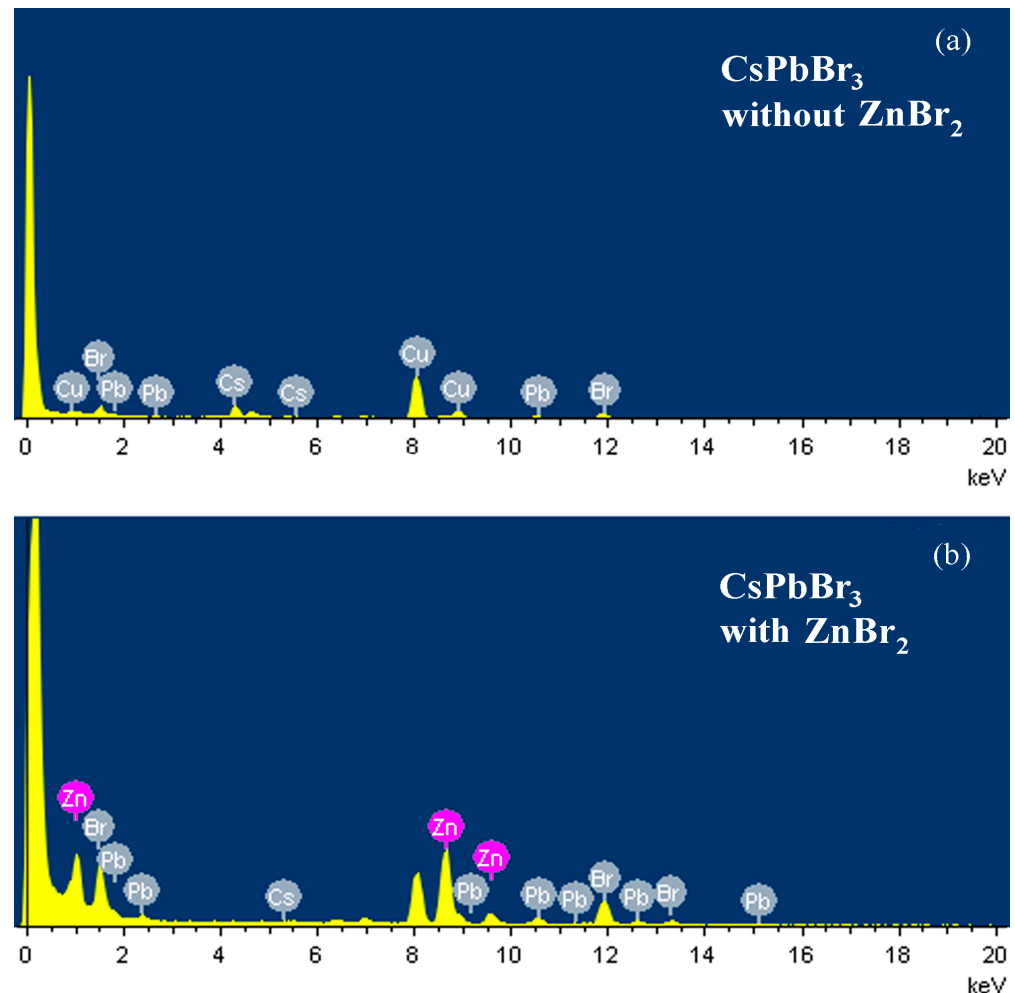


Figure 3. The EDS spectra for CsPbBr_3 QDs (a) without ZnBr_2 and (b) with 200 μL ZnBr_2 doping.

Figure 4 shows the HR-TEM images of CsPbBr_3 QDs (Figure 4a,b) without ZnBr_2 and (Figure 4c,d) with ZnBr_2 doping, respectively. Figure 4a revealed that the shape of the pristine CsPbBr_3 QDs is cuboidal [44,45] with an average edge length of (~ 22 nm), whereas that of the ZnBr_2 -doped CsPbBr_3 QDs is very small, ~ 3 nm (Figure 4d). This TEM image demonstrates that adding the appropriate amount of ZnBr_2 dopants into the perovskite precursor solution may allow control of the size of CsPbBr_3 in the strong quantum-confinement regime, affording the blue emission in the below.

Figure 5 shows the size distribution of CsPbBr_3 QDs based on the aforementioned HR-TEM images. The pristine CsPbBr_3 QDs exhibit an average QD size of ~ 22 nm. However, the range is somewhat broad, from ~ 7 nm to ~ 50 nm, indicating the polydispersity of nanoparticles in this SR method at room temperature, although the chosen conditions (OA and OAm ratio) should affect this QD size and distribution. Importantly, when ZnBr_2 was employed as a dopant for CsPbBr_3 QDs, the QD size is in the range of ~ 1.5 to ~ 5.5 nm, with the average size of ~ 3 nm, guaranteeing the quantum size and confinement effect, a blue-light emission in this study.

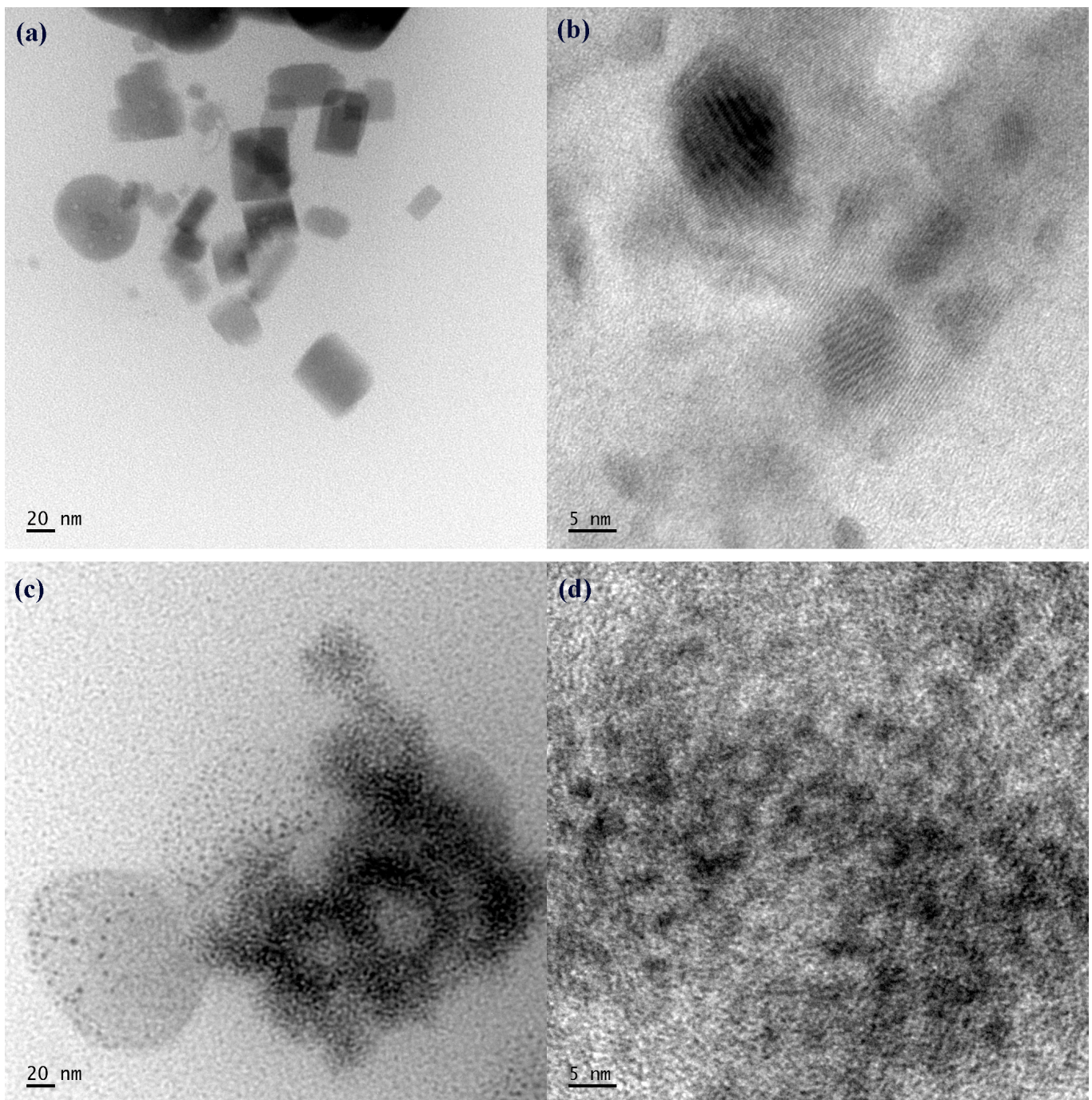


Figure 4. HR-TEM images of CsPbBr₃ QDs: (a,b) without ZnBr₂. (c,d) with 200 μ L ZnBr₂ doping.

The optical properties of CsPbBr₃ without and with ZnBr₂ doping are summarized in Figure 6. As indicated above, the size of ZnBr₂-doped CsPbBr₃ QDs was about 3 nm, which is much less than the Bohr exciton radius of ~ 7 nm [14]. The very small size of the quantum dot was responsible for the significant blue shift of absorption and emission peaks (Figure 6c) due to the quantum-confinement effect. Moreover, the blue shift might be assisted by the lattice internal stress, owing to the zinc-ion doping in the perovskite NCs. As shown in Figure 6c, the absorption peaks in the UV-vis absorption spectra were detected at 396.5 nm, 375.0 nm, and 356.0 nm, respectively. The absorption peak of 396.5 nm is attributed to the transition from Br(4p) to Pb(6p) orbitals, whereas the 375.0 nm corresponds to the transition from Pb(6s) to the Pb(6p) orbitals [46]. The PL spectra are composed of

multiple peaks in the deep blue spectrum region, and Figure 6d shows the multiple fitted PL data. The peaks are at 470.5, 459.1, 432.4, and 409.2 nm, respectively. The broadband emission and multiple-peak emission are attributed to the polydispersity of QD's spatial size (see Figure 5b) [47]. The Stokes shift and the FWHM of peak 4 are 12.7 nm and 17.0 nm, respectively. This small value of Stokes shift and FWHM implies that the peak of 4 results from the band-edge radiation in the form of free excitons [46]. However, the other peaks have larger Stokes shifts (more than 35.9 nm) and FWHMs (more than 24.6 nm). This phenomenon may take place due to the electron–phonon coupling, which is responsible for the increment of Stokes shift.

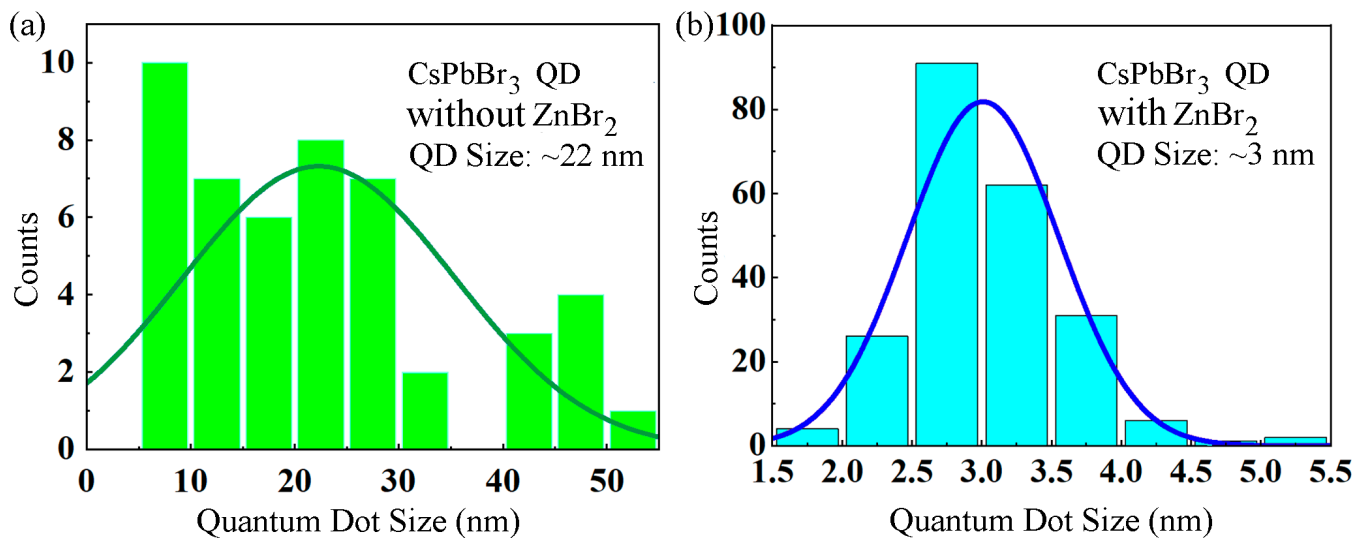


Figure 5. Size distribution of CsPbBr₃ QD (a) without ZnBr₂ and (b) with 200 µL ZnBr₂ doping.

Figure 7 shows the determination of optical band gaps of CsPbBr₃ QDs and ZnBr₂-doped CsPbBr₃ QDs based on the Tauc model. From the UV–Vis absorption spectra, the bandgap was quantified by extrapolating the straight-line portion of the Tauc plot of $(\alpha h\nu)^2$ vs. $h\nu$, in which h is Plank's constant, ν is frequency of incident photons, and α is absorption coefficient [48]. Resultantly, the bandgap is 2.30 eV for the pure CsPbBr₃ and 3.02 eV for ZnBr₂-doped CsPbBr₃, respectively.

To demonstrate the defect densities and size effects of the CsPbBr₃ QDs, the TRPL decay spectra were analyzed. The PL decay curve, as shown in Figure 8, can be well fitted with a bi-exponential function Equation (1) [49].

$$A(t) = A_0 + A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (1)$$

where A_0 represents a constant and A_1 and A_2 are the weights of multiple exponential functions constants, whereas τ_1 and τ_2 indicate short and long lifetimes originating from the excitonic radiative recombination and the trap-assisted nonradiative recombination, respectively. The average lifetime (τ_{ave}) was calculated using Equation (2) and the fitting parameters are shown in Table 1. Figure 8 and Table 1 show that the lifetime is shorter for smaller-size QDs (ZnBr₂-doped CsPbBr₃ QDs). A longer lifetime is due to longer exciton (charge) diffusion length before its recombination (radiative and nonradiative). It is rational for the smaller-size QDs to have a shorter lifetime [32,50,51] because smaller-size QDs have a higher surface area-to-volume ratio, resulting in high defect density and faster charge recombination. Here, it is noteworthy that any crystals with grain and grain boundaries (including small nanocrystals) are metastable (or unstable) compared to the bulk single crystals, because the surface energy is high enough, indicating that the phase

transformation could be undergone by lowering energy to reach the equilibrium state, although the kinetics is unknown.

$$\tau_{ave} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \quad (2)$$

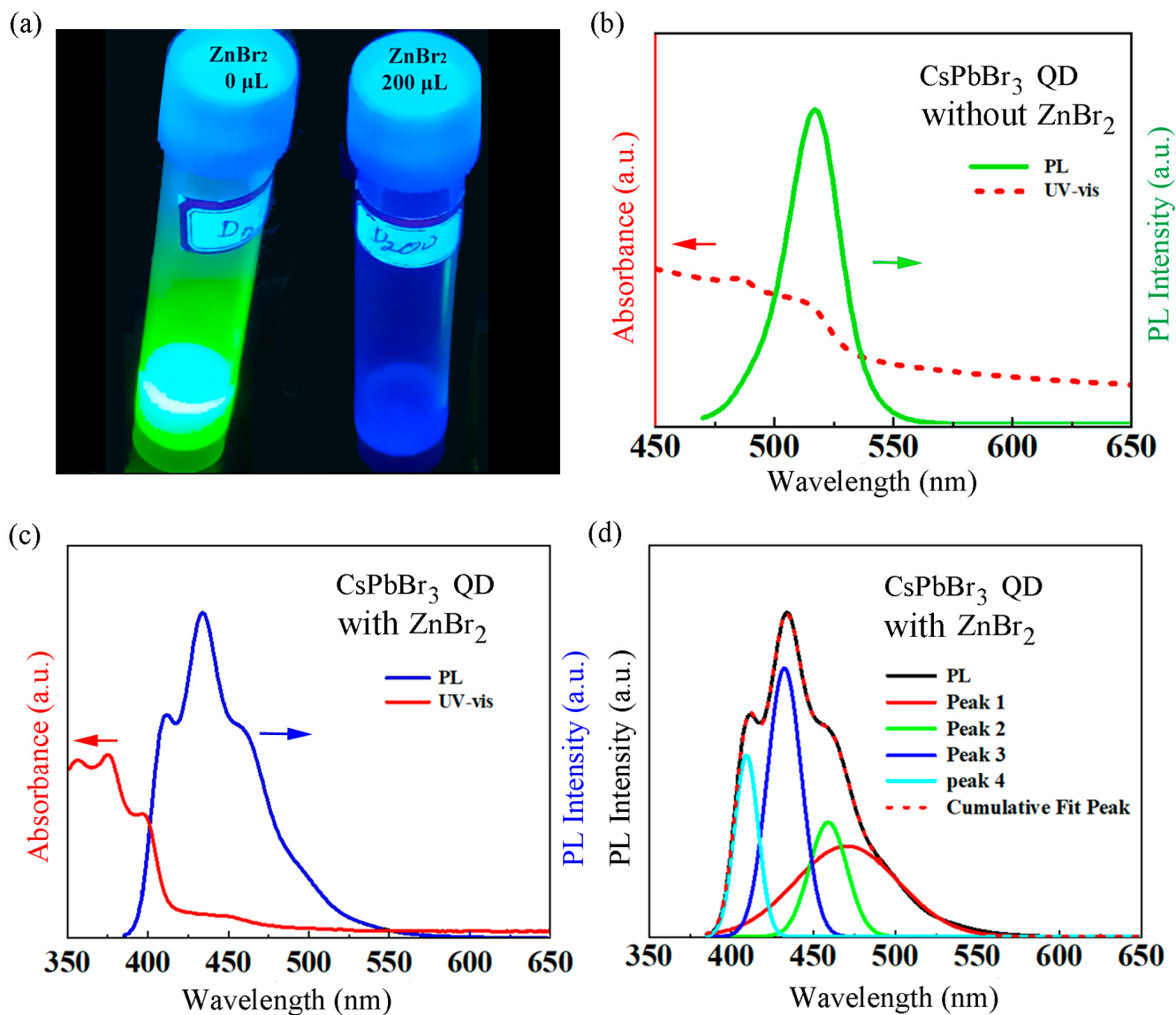


Figure 6. (a) Photograph of CsPbBr₃, without and with ZnBr₂ doping under UV-lamp ($\lambda = 365$ nm) illumination. (b) UV-vis absorption and PL emission spectra of CsPbBr₃ without ZnBr₂ doping. (c) UV-vis absorption and PL emission spectra of CsPbBr₃ QDs with ZnBr₂ doping. (d) Multiple PL peak fitting for the PL emission spectra of CsPbBr₃ QDs with ZnBr₂ doping.

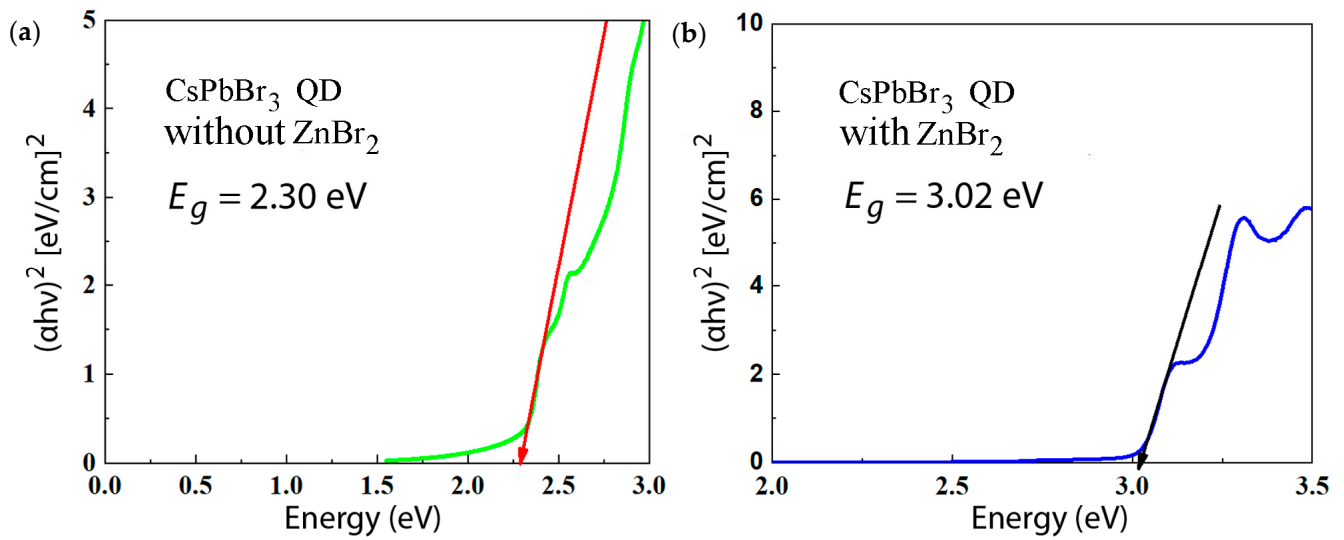


Figure 7. Determination of bandgap based on the Tauc model. (a) CsPbBr₃ without ZnBr₂: $E_g = 2.30$ eV, and (b) CsPbBr₃ with ZnBr₂: $E_g = 3.02$ eV.

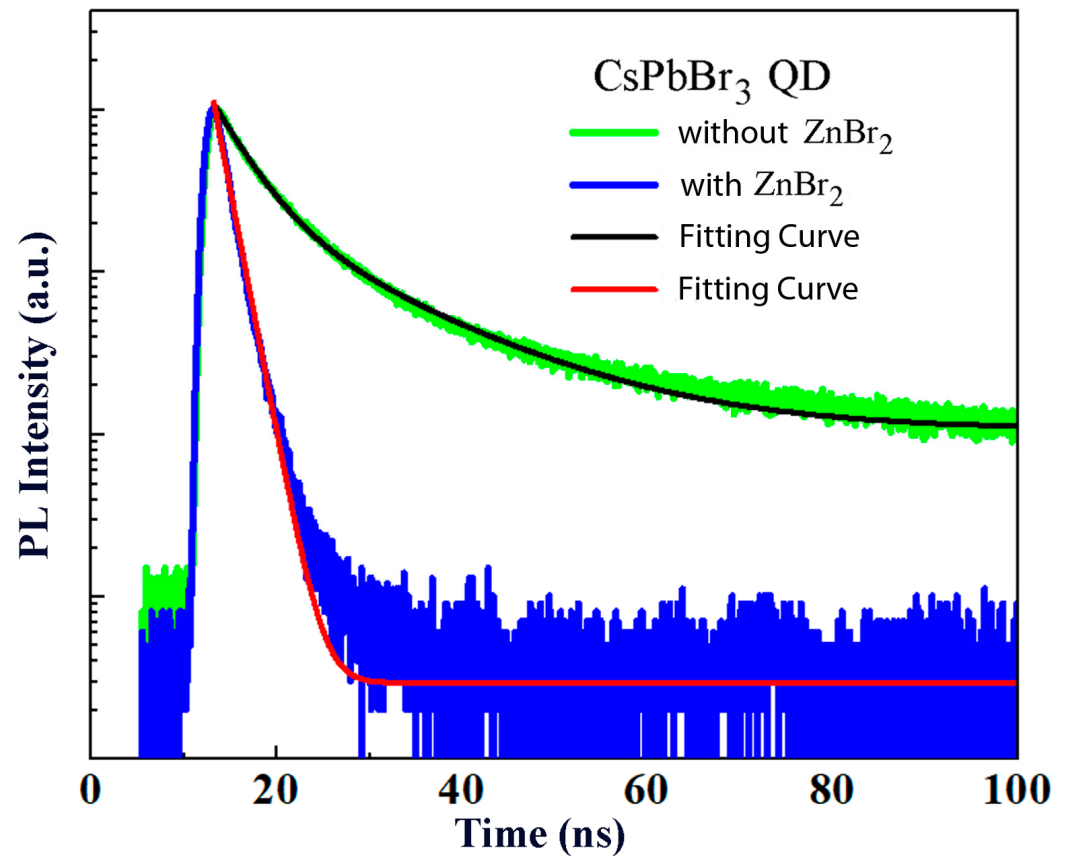


Figure 8. Time-resolved PL decay spectra of CsPbBr₃ QDs without and with ZnBr₂ doping.

Table 1. Fitted parameters of decay curve for 0 and 200 μ L ZnBr₂-doped CsPbBr₃ QDs.

Samples	A_1 (%)	τ_1 (ns)	A_2 (%)	τ_2 (ns)	τ_{ave} (ns)
CsPbBr ₃ QDs without ZnBr ₂	98.10	3.67	1.90	14.23	4.41
CsPbBr ₃ QDs with ZnBr ₂	41.29	1.45	58.71	1.45	1.45

At this moment, it is notable that when we added ZnBr_2 into the CsPbBr_3 perovskite precursor solution, the doping effect and the QD size reduction occur simultaneously. This fact indicates that it is very hard to examine a plain zinc-ion doping effect because the particle size changes simultaneously. Hence, we would like to investigate this kind of doping effect through the theoretical calculation based on the $3 \times 3 \times 3$ supercell-sized CsPbBr_3 materials as shown in Figure 9a,b. To see the inherent electronic properties of Zn^{2+} -doped CsPbBr_3 , we have calculated the electronic band structure and density of states. The PBE functional band structure of undoped and zinc-ion-doped $3 \times 3 \times 3$ CsPbBr_3 supercells are shown in Figure 9c,d, respectively. However, Ghaithan et al. noted that the PBE pseudopotentials underestimate the bandgap of lead halide perovskites [52]. In our calculation, the bandgap of undoped $3 \times 3 \times 3$ CsPbBr_3 supercells is about 2.01 eV (Figure 9c), whereas that of the doped sample was 1.72 eV (Figure 9d). Moreover, the bandgap analysis using the total density of states (DOS) shown in Figure 10a,b indicates that the bandgap decreased for the Zn^{2+} -doped CsPbBr_3 . This trend of the bandgap reduction, when Pb^{2+} was replaced by Zn^{2+} in CsPbBr_3 , is in line with Guo et al.'s results [53]. However, in the case of our experimental results, the simultaneous change in QD size upon ZnBr_2 doping makes it very difficult to examine a pure doping effect. Hence, through the size reduction from ~ 22 nm (without Zn^{2+}) to ~ 3 nm (Zn^{2+} doped), the doped sample exhibited a wider bandgap (i.e., a blue emitter) than the non-doped sample because of the apparent quantum size and confinement effects.

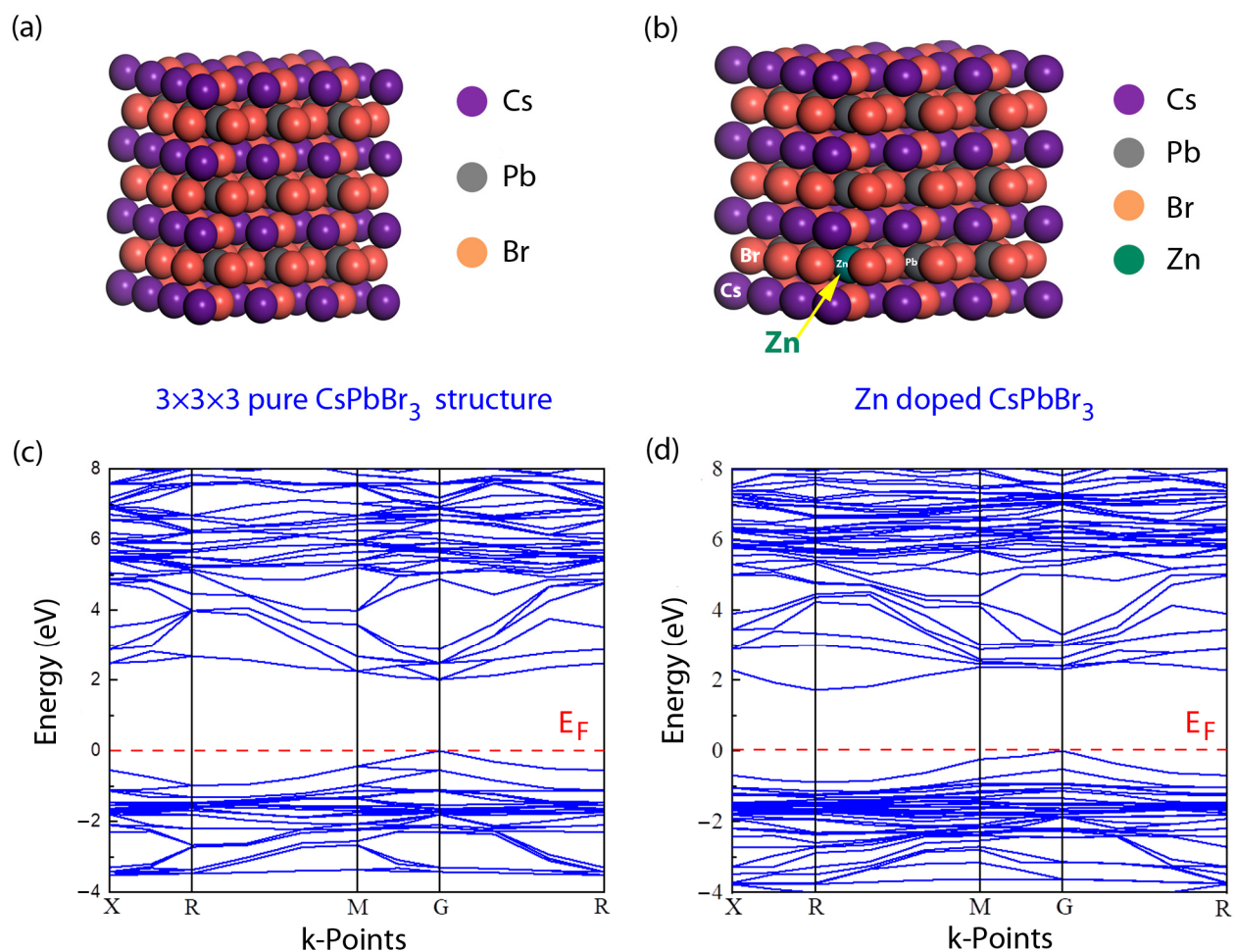


Figure 9. Supercells of (a) CsPbBr_3 without Zn doping and (b) CsPbBr_3 with Zn doping. Electronic structures of CsPbBr_3 supercells with $3 \times 3 \times 3$ size, (c) CsPbBr_3 without Zn doping and (d) CsPbBr_3 with Zn doping.

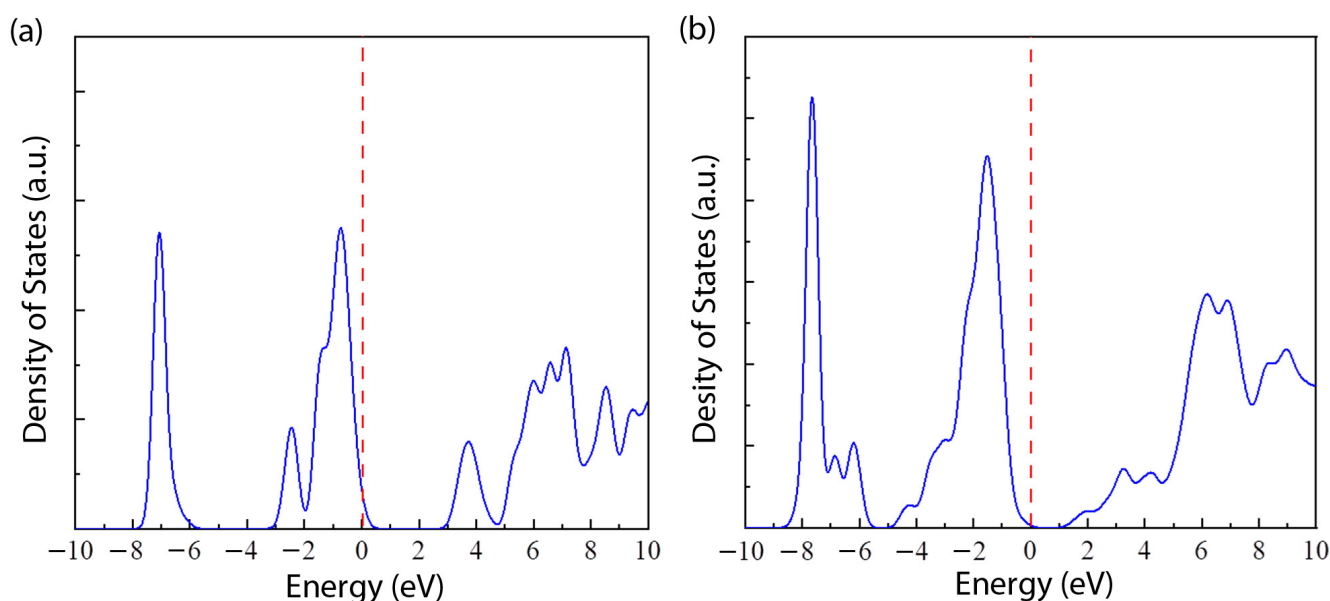


Figure 10. Density of states for (a) pure $3 \times 3 \times 3$ CsPbBr₃ and (b) Zn-doped $3 \times 3 \times 3$ CsPbBr₃.

4. Conclusions

This study demonstrates the successful synthesis of strongly quantum-confined ZnBr₂-doped CsPbBr₃ QDs under ambient conditions using the supersaturated recrystallization method. In this method, controlled amounts of ZnBr₂ were incorporated into the reaction medium to control the photophysical properties of the synthesized CsPbBr₃ QDs. As a result, 3 nm-sized blue-light-emitting CsPbBr₃ QDs were synthesized, covering the broad blue spectrum. The blue shifting of the emission spectrum is mainly attributed to the size reduction of the QDs. Our findings provide new insight into the synthesis of blue light-emitting CsPbBr₃ QDs at room temperature under ambient conditions. Future work may include the application of CsPbBr₃ QDs to photonic and optoelectronic devices including biosensors.

Author Contributions: Writing—original draft preparation, D.A.I.; writing—review and editing, J.Y.K.; conceptualization, D.A.I., M.A., D.M., A.T., S.T., F.G.A. and J.Y.K.; methodology, D.A.I., F.G.A. and J.Y.K.; formal analysis and investigation, D.A.I. and J.Y.K.; resources, S.T.; data curation, D.A.I. and F.G.A.; supervision and project administration, M.A., D.M., A.T., S.T. and J.Y.K. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The datasets used and/or analyzed during the current study are available from the corresponding author upon reasonable request.

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Conflicts of Interest: The authors declare no conflict of interest.

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