

Enhanced Luminescent Performance via Passivation of Surface Undercoordinated Pb Atoms in a CsPbBr₃ Microplate

Yizhi Zhu, Linlin Shi, Heng Guo, Jinping Chen, Junfeng Lu, Weian Wang, Zhangsheng Xu, Naiwei Gao, Xun Han, Zhengchun Peng,* Qiannan Cui, Chunxiang Xu,* and Caofeng Pan*

Perovskite materials are widely used in the fields of luminescence and light energy conversion with the advantages of low cost and outstanding optoelectronic properties. However, abundant surface lattice defects heavily affect the performances of perovskite optoelectronic devices. Here, by treating surface defects with oleylamine molecules in situ, the surface trap states are significantly decreased in a CsPbBr₃ microplate, enabling photoluminescence intensity and carrier lifetimes to be dramatically enhanced and prolonged, respectively. These interesting phenomena can be attributed to the binding of undercoordinated Pb atoms with N atoms on the surface of perovskite microplate. The strong binding energy of lead-halogen bonds inhibits the photodegraded reactions of the crystal, leading to the significant improvement of luminescent stability for the microplate correspondingly. The results not only provide experimental guidance for passivating lattice defects but also pave the way for improving the efficiency of wide materials and optoelectronic devices.

1. Introduction

Due to low fabrication cost and excellent optoelectronic performances, solution-processable lead halide perovskites have been extensively applied in the fields of solar cells,^[1–6] photodetectors,^[7–10]

transistors,^[11–13] and so on. So far, the energy conversion efficiency of perovskite solar cells has exceeded 25%,^[14–16] superior to polycrystalline silicon solar cells, but this value is still far below the theoretical efficiency limit. In addition, benefiting from outstanding luminescent properties and tunable emission wavelengths,^[17] perovskite has also attracted great attention in luminescence applications, such as light-emitting diodes (LEDs)^[18–20] and optically pumped lasers.^[21–24] Although perovskite materials have achieved above remarkable progress in the application of optoelectronic devices,^[25–30] the efficiency of these devices still needs to be further improved and optimized urgently, to match the practical application.^[31–37]

Solution-processed perovskite tends to form abundant lattice defects because of low crystal nucleus formation

energy.^[38,39] The existence of abundant surface lattice defects plays a vital role in the performances of perovskite optoelectronic devices.^[31,32,40–42] First of all, lattice defects can cause carriers trap states in momentum space,^[43] and the formed trap states will heavily dissipate the energies of photocarriers

Y. Zhu, N. Gao, Z. Peng, C. Pan
College of Physics and Optoelectronic Engineering
Shenzhen University
Shenzhen 518060, P. R. China
E-mail: zcpeng@szu.edu.cn; cfpan@binn.cas.cn


Y. Zhu, Z. Xu, C. Pan
CAS Center for Excellence in Nanoscience
Beijing Key Laboratory of Micro-nano Energy and Sensor
Beijing Institute of Nanoenergy and Nanosystems
Chinese Academy of Sciences
Beijing 101400, P. R. China

L. Shi
College of Physics and Optoelectronics
Key Lab of Advanced Transducers and Intelligent Control System of
Ministry of Education
Taiyuan University of Technology
Taiyuan 030024, P. R. China

H. Guo, J. Chen, W. Wang, Q. Cui, C. Xu
State Key Laboratory of Bioelectronics
School of Biological Science and Medical Engineering
Southeast University
Nanjing 210096, P. R. China
E-mail: xcseu@seu.edu.cn

J. Lu
College of Science
Nanjing University of Aeronautics and Astronautics
Nanjing 211106, P. R. China

X. Han
College of Mechatronics and Control Engineering
Shenzhen University
Shenzhen 518060, P. R. China

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adom.202202428>.

DOI: 10.1002/adom.202202428

into heat through a non-radiative recombination process.^[40,44] It is a serious problem that hinders the performance of perovskites-based optoelectronic devices.^[32,39] The other serious problem is that the crystal structures of perovskites can be decomposed by water, oxygen, and heating.^[45,46] Previous works have shown that surface lattice defects in perovskite can deeply affect crystal stability and hinder the device's service lifespan by accelerating the photodegraded reactions mediated with H₂O and O₂.^[47,48] Therefore, surface lattice defects are one of the essential factors that restrict the performance of perovskite optoelectronic devices.

In this paper, aiming to improve luminescent performances and reduce non-radiative energy loss, OLA molecules are employed to passivate surface lattice defects of the CsPbBr₃ microplates. Results have shown that OLA molecules can effectively decrease surface trap states via passivating under-coordinated Pb²⁺ ions. Thus, both the PL intensity and the carrier's lifetime of OLA-CsPbBr₃ are enhanced and prolonged compared with pure CsPbBr₃ microplate. In addition, the luminescent stability of the microplates is also significantly improved after passivating the undercoordinated Pb atoms by OLA molecules. Our results are significant for an extensive range of high-efficiency perovskite materials and devices.

2. Results and Discussion

2.1. Experimental Design and Structural Analysis

First, an optical system has been built by connecting a PL spectrometer and a streak camera (see Figure 1a) to investigate

the luminescent performance of a perovskite microcrystal. A 400 nm laser beam is adopted as the excitation source, which is focused on a CsPbBr₃ microplate by an objective lens with an NA of 0.4. The emitted PL from the microplate is split into two beams by a beam splitter. One beam is recorded with a spectrometer for PL analysis, and the other one is sent to a streak camera for carrier dynamics measurement. By successfully constructing this optical measurement system, we can precisely investigate the PL and TRPL of a perovskite microplate. The experimental design for surface passivation of a CsPbBr₃ microplate is depicted in Figure 1b. As presented in Figure 1b, we attempt to passivate surface lattice defects with OLA molecules and a microplate ultimately achieves excellent luminescent performance. Moreover, the structure and morphology of solution-fabricated microplates are measured with X-ray diffractometry (XRD) and scanning electron microscopy (SEM) equipped with an energy dispersive spectroscopy (EDS), respectively, as shown in Figure 1c–e. The synthesized CsPbBr₃ microplates demonstrate a smooth surface and sharp edges with a square shape, indicating excellent crystalline quality. In addition, Cs, Pb, and Br elements are uniformly distributed on the crystal surface. It indicates that we have successfully fabricated high-quality CsPbBr₃ microplates by the solution-synthesized method.

2.2. Trap Density and Exciton Dynamics

Next, a series of steady micro-PL spectra on a 200 nm thick CsPbBr₃ microplate is measured to quantitatively estimate trap density (The details of the thickness of CsPbBr₃ microplates can be seen in the Supporting Information). Figure 2a shows

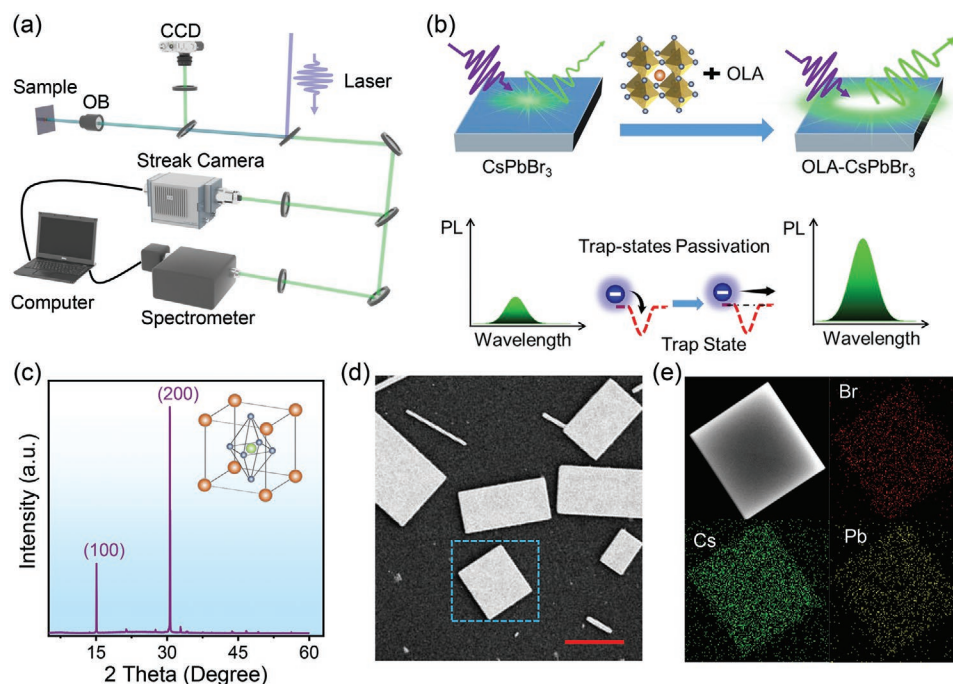


Figure 1. Testing setup, experimental design, and structural measurement of the CsPbBr₃ microplates. a) The optical path for measuring PL and time-resolved photoluminescence (TRPL) spectra emitted from a CsPbBr₃ microplate. b) A schematic diagram for surface passivation design. c) The XRD pattern of the as-synthesized CsPbBr₃ microplates. The inset shows the crystal structure of CsPbBr₃. d) An SEM image of solution-synthesized CsPbBr₃ microplates with a scale bar of 10 μm. e) The elemental mapping of Cs, Pb, and Br for a microplate.

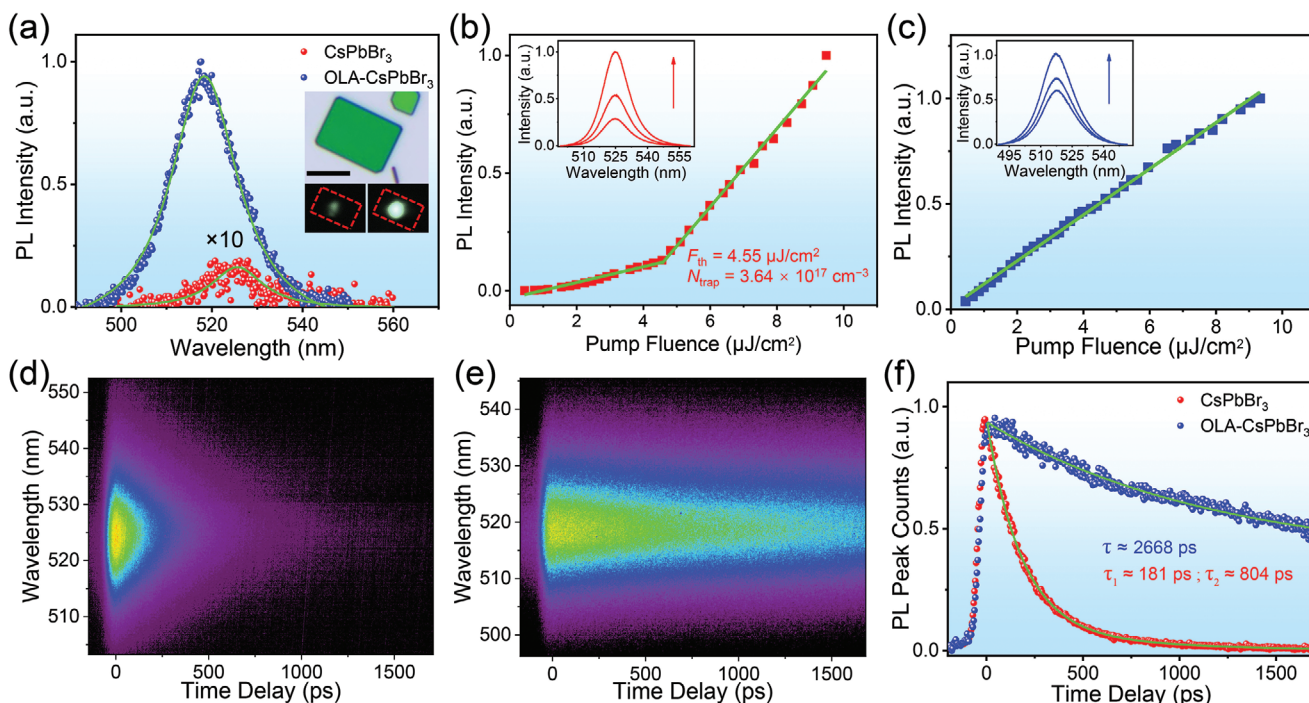


Figure 2. The measurement of micro-PL and micro-TRPL spectra for a CsPbBr₃ microplate in situ. a) Steady PL spectra for a CsPbBr₃ microplate with and without OLA molecules. Corresponding insets show bright and dark fields of optical images of the CsPbBr₃ microplate with 10 μm scale bars. Excitation fluence of a 400 nm femtosecond laser beam is fixed at 0.44 μJ cm⁻². PL intensity as a function of pump fluence is presented for b) CsPbBr₃ and c) OLA-CsPbBr₃ microplate. Solid lines are linear fittings. Insets are the three typical PL spectra for the two samples. Typical TRPL spectra for d) CsPbBr₃ and e) OLA-CsPbBr₃ microplate, and f) temporal decay of PL intensity at PL peak extracted from (d) and (e) when excitation fluence is fixed at 3.82 μJ cm⁻². The green lines in (f) for CsPbBr₃ and OLA-CsPbBr₃ are bi-exponential and exponential fittings, respectively.

the PL spectra of the CsPbBr₃ microplate with and without OLA molecules. It shows that the PL intensity of OLA-CsPbBr₃ is remarkably enhanced by about 70-folds than the pure CsPbBr₃ microplate. Inset in Figure 2a is the bright field optical image of the microplate, it shows a greenish CsPbBr₃ microplate with a length of about 10 μm. And it is clear that under the excitation of the 400 nm laser, much higher luminescence radiation is observed by a charge-coupled device (CCD) when OLA molecules are employed on the CsPbBr₃ microplate, which agrees well with PL enhancement results as shown in Figure 2a. It suggests that OLA molecules can effectively improve the luminescence performances of CsPbBr₃. Moreover, we can find that the fitted PL peak of OLA-CsPbBr₃ is located at 518.28 nm, exhibiting an obvious blueshift of 6.96 nm compared with pure CsPbBr₃ (525.24 nm) recorded by a Princeton Instrument Spectrometer (Supporting Information). Therefore, we can infer that there is a stronger interaction between CsPbBr₃ and OLA molecules.

To reveal this conjecture, we carefully performed pump power-dependent steady micro-PL of the CsPbBr₃ microplate with and without OLA molecules treatment. Figure 2b presents the PL intensity of CsPbBr₃ as a function of pump fluences, and pump fluences of red-solid spectra in the inset are 3.60, 4.55, and 5.80 μJ cm⁻². It indicates that the PL intensity exhibit two linear growth trends with a threshold of 4.55 μJ cm⁻². Based on a trap-filling model,^[39,40,49] the photogenerated band-edge excitons can be captured by trap states when the pump fluence is low. After trap states are filled, a large number of excess

excitons at the band-edge will emit PL by the path of radiative recombination. Thus, the quantum efficiency and PL intensity are suddenly increased. Figure 2b shows the threshold obtained by fitting the scatter plot through two linear functions which can be approximately adopted to calculate the average trap density. Therefore, when the pump fluence threshold is 4.55 μJ cm⁻², the trap density of the CsPbBr₃ microplate can be estimated to be 3.64 × 10¹⁷ cm⁻³ (Supporting Information). The PL intensity of CsPbBr₃ as a function of pump fluences is shown in Figure 2c and pump fluences of blue-solid spectra in the inset are 3.60, 4.66, and 5.95 μJ cm⁻². It is noticed that the trap density of OLA-CsPbBr₃ is significantly decreased, approaching the ideal defect-free conditions, as indicated by Figure 2c. These results prove that the OLA molecules can effectively passivate surface lattice defects on the CsPbBr₃ microplate.

Then, the micro-TRPLs of the microplate before and after surface passivating treatment with OLA are measured by a streak camera to further elaborate exciton dynamics. TRPL spectra of OLA-CsPbBr₃ present a significantly longer tail along the temporal axial than the pure CsPbBr₃, as shown in Figure 2d,e. It shows that OLA-CsPbBr₃ possesses a longer PL lifetime compared with pure CsPbBr₃. To better understand exciton dynamics in CsPbBr₃, temporal dynamics of PL peaks are extracted from Figure 2d,e, as plotted in Figure 2f. For a pure CsPbBr₃ microplate, indicated by the red sphere, we fit

this PL peak with a bi-exponential function: $I = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}}$, where A_1 (A_2) is constants, τ_1 and τ_2 are fast and slow PL decay

components, respectively. The fitted A_1 and A_2 are 0.87 and 0.09, and τ_1 and τ_2 are about 181 and 804 ps, respectively. Furthermore, the average PL lifetime of the CsPbBr₃ is 377 ps calculated by $\tau_{avg} = (A_1\tau_1^2 + A_2\tau_2^2) / (A_1\tau_1 + A_2\tau_2)$. Previous works have reported that fast (τ_1) and slow (τ_2) PL decay components are intrinsically originated from the exciton recombination process in the surface and bulk regions of a CsPbBr₃ microplate with inhomogeneous trap densities.^[39,50] Thus, we can safely estimate the proportion of PL emission in the surface region is about 68.5%, which is calculated by $A_1\tau_1 / (A_1\tau_1 + A_2\tau_2)$. Since OLA-CsPbBr₃ exhibits defect-free properties as shown in Figure 2c, we empirically interpreted the PL_t peak of OLA-CsPbBr₃ with an exponential function: $I = Ae^{-t/\tau}$. It exhibited that the fitted τ of OLA-CsPbBr₃ equals 2668 ps as seen in Figure 2f. It concludes that the PL lifetime of OLA-CsPbBr₃ is ≈ 7 times longer than the pure CsPbBr₃, indicating an excellent surface passivation effect, which agrees well with the results in Figure 2b,c. In addition, it is observed that the temporal-integrated PL spectrum (0–1700 ps, temporally recorded by an Optronics Streak Camera and see the Supporting Information) of OLA-CsPbBr₃ is blueshifted by 5.66 nm compared with the pure CsPbBr₃. This result is satisfactorily consistent with Figure S1 (Supporting Information) by a measurement error of 1 nm, confirming the high quality of our steady PL and TRPL measurements.

From PL and TRPL results, two spectroscopic features can be summarized: 1) PL intensity is remarkably enhanced while defects are efficiently passivated by OLA molecules. 2) Benefiting from the decrease of trap states, the PL lifetime of OLA-CsPbBr₃ is prolonged significantly. Based on these features, we proposed a schematic illustration to interpret carrier dynamics in the CsPbBr₃-based microplate. As depicted in Figure 3a, abundant surface lattice defects in a pure CsPbBr₃ microplate can generate carrier trap states in momentum space, leading

to the capture of free carriers by defects and the dissipation of energy into heat during their paths of energy relaxations. Thus, the microplate presents poor PL performance and a rather short PL lifetime caused by heavy surface recombinations. When OLA is introduced on the surface of the microplate, trap states are significantly reduced because of the passivation of surface defects with OLA molecules, as shown in Figure 3b. Since the passivation of OLA molecules decreases the surface recombination of carriers, PL performance and carrier lifetime of OLA-CsPbBr₃ are enhanced and prolonged respectively. It indicates that OLA molecules can effectively decrease surface recombination by passivating surface trap states of the perovskite.

2.3. Surface Elemental Analysis

According to the exciton dynamics results, it can be inferred that OLA molecules can passivate the lattice defects on the surface of pure CsPbBr₃ microplate. Since the N atom exists at the amine head of OLA molecule, we can expect that the passivation mechanism of the OLA molecule is similar to that of Lewis bases where lone pair of electrons hang outside to N atoms. So the lone pair can bind with an undercoordinated Pb atom at the surface of perovskite to passivate the lattice defects, as shown in Figure 4a. To further elucidate the passivation mechanism, the XPS spectra of OLA, pure CsPbBr₃, and OLA-CsPbBr₃ are measured, respectively, as shown in Figure 4b. The peaks of Cs, Pb, and Br elements are observed from both pure CsPbBr₃ and OLA-CsPbBr₃ microplates, while the N element is detected at the surface of OLA-CsPbBr₃, suggesting that the OLA molecules are successfully bonded to the surface of pure CsPbBr₃ microplates. XPS high-resolution spectra of Cs 3d, Br 3d, and Pb 4f on pure CsPbBr₃ and OLA-CsPbBr₃ are extracted and presented in Figure 4c–e, respectively. It can be seen that

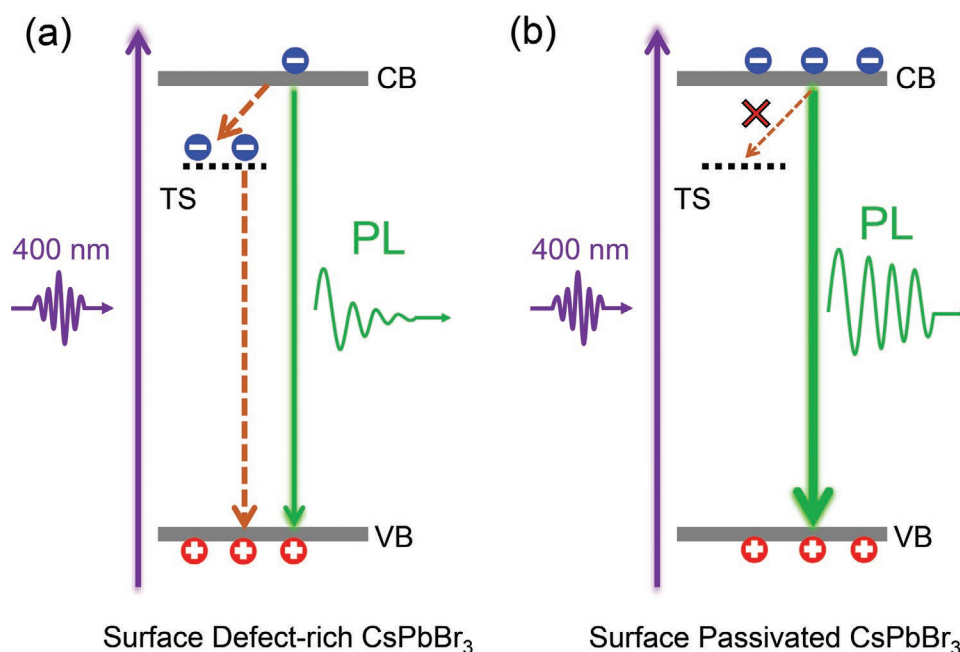


Figure 3. Schematic illustration of trap-state-mediated carrier dynamics. Photogenerated carrier relaxation process in a) a pure CsPbBr₃ and b) surface passivated CsPbBr₃ microplate.

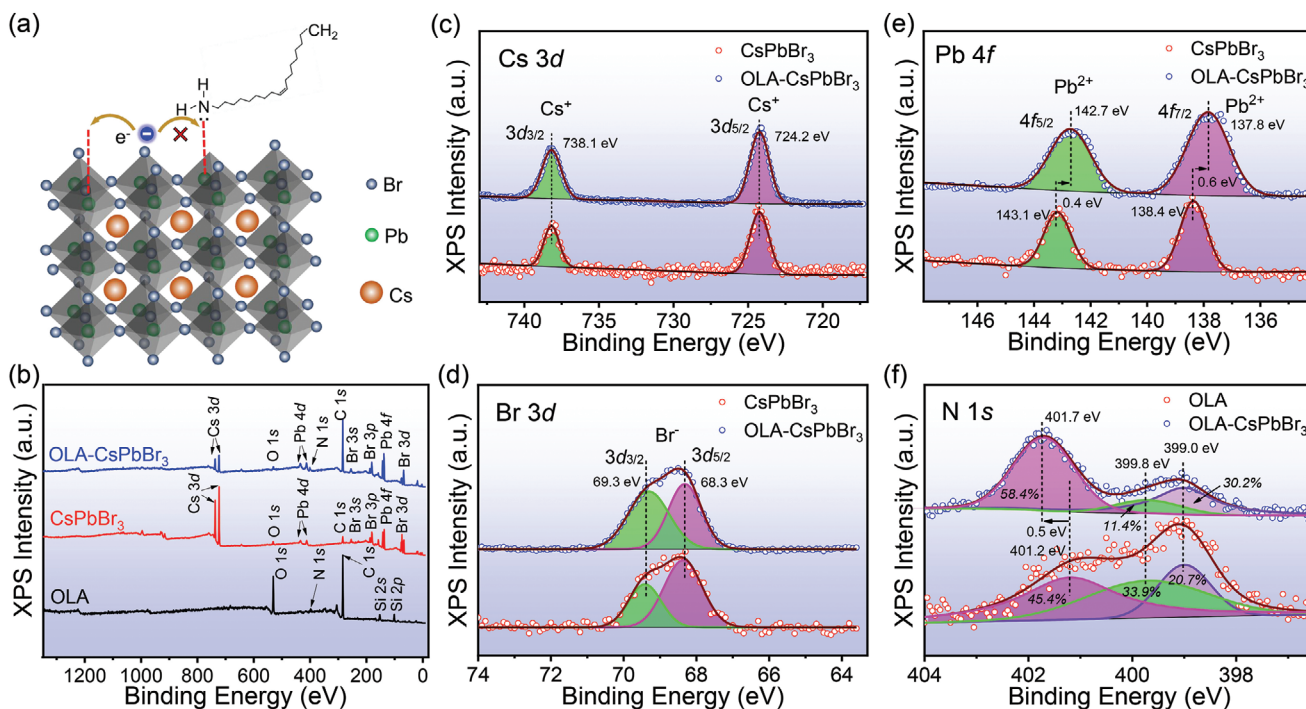


Figure 4. XPS survey and high-resolution spectra. a) The possible passivation mechanism between OLA molecules and pure CsPbBr₃ microplate. b) XPS survey spectra of OLA, pure CsPbBr₃, and OLA-CsPbBr₃. High-resolution XPS c) Cs 3d, d) Br 3d, and e) Pb 4f of pure CsPbBr₃ and OLA-CsPbBr₃. f) High-resolution XPS N 1s of OLA and OLA-CsPbBr₃.

the binding energy of Cs 3d and Br 3d in OLA-CsPbBr₃ have no shift compared with pure CsPbBr₃. However, XPS peaks of Pb 4f_{7/2} and 4f_{5/2} are shifted toward the lower binding energy region by 0.6 and 0.4 eV after OLA passivating, respectively. It suggests that the undercoordinated Pb atom can bond with OLA, and receive electrons from OLA molecules.

To further reveal the passivation mechanism, we measured the XPS high-resolution spectra of N in OLA and OLA-CsPbBr₃, respectively. As shown in Figure 4f, the binding energies of N for pure chemical OLA are located at 401.2, 399.8, and 399.0 eV, corresponding to the lone pair of N atom,^[51,52] -NH₂^[53,54] and N-O^[55,56] bond, respectively. The N-O bond is likely to be caused by oxidation of the amine head during the measurement. However, the binding energies of N in OLA-CsPbBr₃ are located at 401.7, 399.8, and 399.0 eV, respectively. Compared with pure OLA molecules, the peak of NH₃⁺ is shifted to a high binding energy region by 0.5 eV on the surface of OLA-CsPbBr₃ microplates, and its ratio increases from 45.4% to 58.4%. It further reveals that the N atom in OLA interacts with surface defects on perovskite by donating electrons. Combined with the results in Figure 4e,f, we can safely conclude that the passivation mechanism of OLA-CsPbBr₃ is that the undercoordinated Pb atom on pure CsPbBr₃ can be bonded with the N atom of OLA molecule. These experimental results are consistent with the expected possible passivation mechanism as shown in Figure 4a. It has been reported that surface lattice defects of pure CsPbBr₃ mainly include undercoordinated bonds, such as Pb²⁺ and Br⁻ ions.^[57] Lewis acids and Lewis bases can specifically passivate the undercoordinated Pb²⁺, Br⁻, and other chemical bonds, respectively.^[57,58] Since the structure of OLA

molecules is like Lewis bases, the lone pair on the terminal N atom can bind to the Pb²⁺ bond with a lead-halogen bond,^[59,60] ultimately passivate the surface defects of perovskite crystals. It is to be mentioned that our results are consistent with the previously reported passivation mechanism of Lewis bases.

Based on the XPS high-resolution spectra, the XPS valence band spectra of pure CsPbBr₃ and OLA-CsPbBr₃ are measured to investigate the interfacial optoelectric properties of the perovskite crystals. As indicated in Figure 5a,b, the top of valence band for OLA-CsPbBr₃ is shifted to a lower binding energy region by $\Delta E = 1.21 - 1.08 = 0.13$ eV compared with pure CsPbBr₃. The optical absorption spectra of pure CsPbBr₃ and OLA-CsPbBr₃ are shown in Figure 5c. It indicates that their optical absorption band edges are overlapped well and with a value equal to 2.37 eV. Therefore, we can draw the energy level diagram of pure CsPbBr₃ and OLA-CsPbBr₃ based on the above results, as shown in Figure 5d. It can be seen that the energy level diagram of OLA-CsPbBr₃ changes slightly than the pure CsPbBr₃ crystal. This evidence further suggests that the OLA molecules can influence the surface of perovskite by modifying the interfacial physical properties.

2.4. Luminescence Stability

To further investigate the luminescent stability of perovskite, we also measured the PL performance of pure CsPbBr₃ microplate before and after passivation. Figure 6a shows the time-dependent PL intensities of a pure CsPbBr₃ microplate excited by a 405 nm continuous laser beam with a fluence of 2.442×10^3 mJ cm⁻².

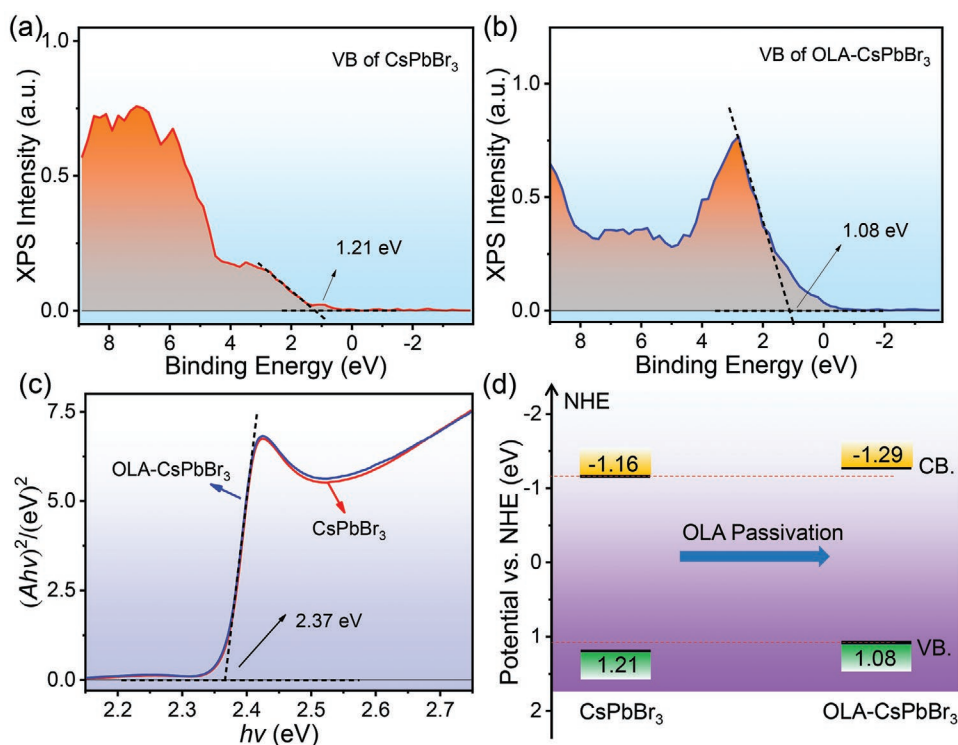
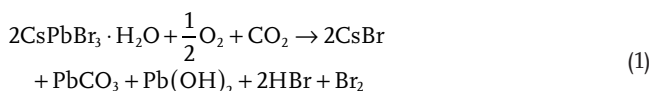


Figure 5. XPS valence band spectra of a) pure CsPbBr₃ and b) OLA-CsPbBr₃. c) Absorbance of pure CsPbBr₃ and OLA-CsPbBr₃. d) Energy level diagram of pure CsPbBr₃ and OLA-CsPbBr₃.

As shown in Figure 6a, the pure CsPbBr₃ microcrystal exhibits poor luminescent performance and stability. However, with the passivation of undercoordinated Pb atoms at surface of the pure CsPbBr₃ microplate by OLA, the performance of luminescent stability for OLA-CsPbBr₃ significantly enhanced, as indicated in Figure 6b. It shows that the luminescence stability of perovskite can be significantly improved through the passivation of undercoordinated Pb atoms with OLA molecules. As reported in the literature, the photodegraded reactions of CsPbBr₃ crystals under light illumination in an atmospheric environment are expressed as follows:^[47,48,61]



To begin, an H₂O molecule can be absorbed by an active site (such as surface lattice defect, etc.) to form CsPbBr₃•H₂O.^[47,48] Subsequently, photodegraded reactions can be switched on with CO₂ and O₂ molecules under light illumination. Because the reaction destroys the structure of perovskite crystals, the luminescent performance of CsPbBr₃ microcrystal decrease gradually.

Combined with the above results and analysis, we obtained the possible mechanism for the improvement of the luminescence stability of perovskite with OLA molecules, as presented in Figure 6c. It has been reported that,^[62] the O atom of H₂O molecule is preferred to bond with a Pb²⁺ undercoordinated

bond at the perovskite surface with a bond length of 2.53 Å and a binding energy of 808 meV. Since large numbers of undercoordinated Pb²⁺ bonds offer adsorption sites for H₂O molecules, structural degradation of perovskite can be accelerated by photodegraded reactions. However, when the crystal was coated with OLA molecules, the undercoordinated Pb²⁺ bonds can be passivated by a lone pair of N atoms in OLA molecules. The binding energy of the Pb atom to OLA is 874 meV,^[61] which is much higher than the H₂O molecule (808 meV). We noticed that room-temperature thermal energy is about 26 meV ($k_B T$, $T = 300$ K). However, the H₂O molecule is still not enough to destroy the binding energy of lead-halogen bond between the N atom and Pb atom when it accepts the thermal energy ($k_B T$) at room temperature. Therefore, OLA molecules can not only passivate abundant undercoordinated Pb²⁺ bonds but also inhibit photodegradation reactions and enhance the luminescence stability of perovskite crystals.

3. Conclusion

To conclude, in this work, OLA molecules were employed to passivate the surface defects of pure CsPbBr₃ microplate and improved its luminescent performance. With the similar passivation mechanism of Lewis bases, OLA molecules can effectively passivate the uncoordinated Pb²⁺ chemical bonds at the surface of perovskite. Hence, the PL intensity and PL lifetime were enhanced significantly with the decrease of surface trap states. In addition, the luminescence stability of OLA-CsPbBr₃ was improved remarkably by inhibiting photodegradation

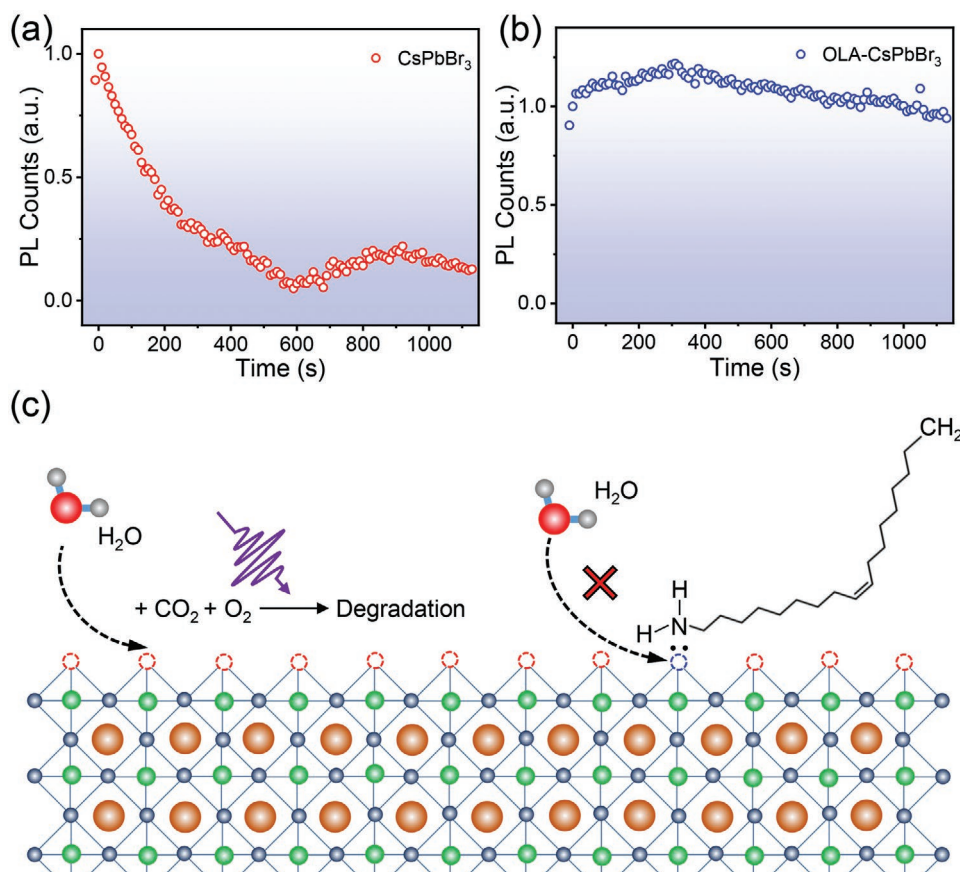


Figure 6. Luminescent stability for a) pure CsPbBr₃ and b) OLA-CsPbBr₃. The excitation source is a 405 nm continuous laser beam and the fluence is fixed at $2.44 \times 10^3 \text{ mJ cm}^{-2}$. c) The possible photodegradation mechanism for OLA molecules at the surface of pure CsPbBr₃ microplate.

reactions with H₂O molecules. Our results not only deepen the understanding of the surface passivation mechanism but also can be applied to a wide range of luminescent materials and devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors thank the support of the Shenzhen Science and Technology Program (Grant No. KQTD20170810105439418), National Natural Science Foundation of China (62204157, U20A20166, 52192610, 61704024, 62205235, 61805015, 52125205, and 61804011), a national key R&D project from the Minister of Science and Technology, China (2021YFB3200302 and 2021YFB3200304), National Science Foundation of Beijing Municipality (Z180011), and the Fundamental Research Funds for the Central Universities.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

defects passivation, luminescent performance, perovskite microplates, photodegraded reaction, undercoordinated Pb atoms

Received: October 14, 2022

Revised: December 24, 2022

Published online:

- [1] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.* **2009**, *131*, 6050.
- [2] H. Zhou, Q. Chen, G. Li, S. Luo, T.-b. Song, H.-S. Duan, Z. Hong, J. You, Y. Liu, Y. Yang, *Science* **2014**, *345*, 542.
- [3] M. Saliba, T. Matsui, K. Domanski, J.-Y. Seo, A. Ummadisingu, S. M. Zakeeruddin, J.-P. Correa-Baena, W. R. Tress, A. Abate, A. Hagfeldt, M. Gratzel, *Science* **2016**, *354*, 206.
- [4] J. Y. Kim, J. W. Lee, H. S. Jung, H. Shin, N. G. Park, *Chem. Rev.* **2020**, *120*, 7867.
- [5] L. Hu, Q. Zhao, S. Huang, J. Zheng, X. Guan, R. Patterson, J. Kim, L. Shi, C.-H. Lin, Q. Lei, D. Chu, W. Tao, S. Cheong, R. D. Tilley, A. W. Y. Ho-Baillie, J. M. Luther, J. Yuan, T. Wu, *Nat. Commun.* **2021**, *12*, 466.

- [6] M. De Bastiani, A. J. Mirabelli, Y. Hou, F. Gota, E. Aydin, T. G. Allen, J. Troughton, A. S. Subbiah, F. H. Isikgor, J. Liu, L. Xu, B. Chen, E. Van Kerschaver, D. Baran, B. Fraboni, M. F. Salvador, U. W. Paetzold, E. H. Sargent, S. De Wolf, *Nat. Energy* **2021**, *6*, 167.
- [7] L. Shi, K. Chen, A. Zhai, G. Li, M. Fan, Y. Hao, F. Zhu, H. Zhang, Y. Cui, *Laser Photonics Rev.* **2021**, *15*, 2000401.
- [8] W. Tian, H. Zhou, L. Li, *Small* **2017**, *13*, 1702107.
- [9] H.-P. Wang, S. Li, X. Liu, Z. Shi, X. Fang, J.-H. He, *Adv. Mater.* **2021**, *33*, 2003309.
- [10] D. Liu, B.-B. Yu, M. Liao, Z. Jin, L. Zhou, X. Zhang, F. Wang, H. He, T. Gatti, Z. He, *ACS Appl. Mater. Interfaces* **2020**, *12*, 30530.
- [11] Y. Zou, F. Li, C. Zhao, J. Xing, Z. Yu, W. Yu, C. Guo, *Adv. Opt. Mater.* **2019**, *7*, 1900676.
- [12] J. W. Ward, H. L. Smith, A. Zeidell, P. J. Diemer, S. R. Baker, H. Lee, M. M. Payne, J. E. Anthony, M. Guthold, O. D. Jurchescu, *ACS Appl. Mater. Interfaces* **2017**, *9*, 18120.
- [13] H. Sun, T. Lei, W. Tian, F. Cao, J. Xiong, L. Li, *Small* **2017**, *13*, 1701042.
- [14] J. J. Yoo, G. Seo, M. R. Chua, T. G. Park, Y. Lu, F. Rotermund, Y.-K. Kim, C. S. Moon, N. J. Jeon, J.-P. Correa-Baena, V. Bulovic, S. S. Shin, M. G. Bawendi, J. Seo, *Nature* **2021**, *590*, 587.
- [15] J. Jeong, M. Kim, J. Seo, H. Lu, P. Ahlawat, A. Mishra, Y. Yang, M. A. Hope, F. T. Eickemeyer, M. Kim, Y. J. Yoon, I. W. Choi, B. P. Darwich, S. J. Choi, Y. Jo, J. H. Lee, B. Walker, S. M. Zakeeruddin, L. Emsley, U. Rothlisberger, A. Hagfeldt, D. S. Kim, M. Graetzel, J. Y. Kim, *Nature* **2021**, *592*, 381.
- [16] E. Lamanna, F. Matteocci, E. Calabrò, L. Serenelli, E. Salza, L. Martini, F. Menchini, M. Izzi, A. Agresti, S. Pescetelli, S. Bellani, A. E. Del Rio Castillo, F. Bonaccorso, M. Tucci, A. Di Carlo, *Joule* **2020**, *4*, 865.
- [17] B. R. Sutherland, E. H. Sargent, *Nat. Photonics* **2016**, *10*, 295.
- [18] Y. J. Yoon, Y. S. Shin, H. Jang, J. G. Son, J. W. Kim, C. B. Park, D. Yuk, J. Seo, G. H. Kim, J. Y. Kim, *Nano Lett.* **2021**, *21*, 3473.
- [19] S.-J. Woo, J. S. Kim, T.-W. Lee, *Nat. Photonics* **2021**, *15*, 630.
- [20] G. Pacchioni, *Nat. Rev. Mater.* **2021**, *6*, 108.
- [21] H. Yu, X. Xu, H. Liu, Y. Wan, X. Cheng, J. Chen, Y. Ye, L. Dai, *ACS Nano* **2020**, *14*, 552.
- [22] K. Wang, S. Wang, S. Xiao, Q. Song, *Adv. Opt. Mater.* **2018**, *6*, 1800278.
- [23] G. Li, T. Che, X. Ji, S. Liu, Y. Hao, Y. Cui, S. Liu, *Adv. Funct. Mater.* **2019**, *29*, 1805553.
- [24] S. W. Eaton, M. Lai, N. A. Gibson, A. B. Wong, L. Dou, J. Ma, L. W. Wang, S. R. Leone, P. Yang, *Proc. Natl. Acad. Sci. USA* **2016**, *113*, 1993.
- [25] T. C. Sum, N. Mathews, *Energy Environ. Sci.* **2014**, *7*, 2518.
- [26] L. Chouhan, S. Ghimire, C. Subrahmanyam, T. Miyasaka, V. Biju, *Chem. Soc. Rev.* **2020**, *49*, 2869.
- [27] H. Chen, S. Xiang, W. Li, H. Liu, L. Zhu, S. Yang, *Sol. RRL* **2018**, *2*, 1700188.
- [28] Q. Zhang, S. Zuo, P. Chen, C. Pan, *Infomat* **2021**, *3*, 987.
- [29] C. Wang, R. Ma, D. Peng, X. Liu, J. Li, B. Jin, A. Shan, Y. Fu, L. Dong, W. Gao, Z. L. Wang, C. Pan, *Infomat* **2021**, *3*, 1272.
- [30] J. Li, Z. Yuan, X. Han, C. Wang, Z. Huo, Q. Lu, M. Xiong, X. Ma, W. Gao, C. Pan, *Small Sci.* **2022**, *2*, 2100083.
- [31] T. A. S. Doherty, A. J. Winchester, S. Macpherson, D. N. Johnstone, V. Pareek, E. M. Tennyson, S. Kosar, F. U. Kosasih, M. Anaya, M. Abdi-Jalebi, Z. Andaji-Garmaroudi, E. L. Wong, J. Madoe, Y. H. Chiang, J. S. Park, Y. K. Jung, C. E. Petoukhoff, G. Divitini, M. K. L. Man, C. Ducati, A. Walsh, P. A. Midgley, K. M. Dani, S. D. Stranks, *Nature* **2020**, *580*, 360.
- [32] Z. Ni, C. Bao, Y. Liu, Q. Jiang, W.-Q. Wu, S. Chen, X. Dai, B. Chen, B. Hartweg, Z. Yu, Z. Holman, J. Huang, *Science* **2020**, *367*, 1352.
- [33] X. Han, Z. Xu, W. Wu, X. Liu, P. Yan, C. Pan, *Small Struct.* **2020**, *1*, 2000029.
- [34] J. Ren, W. Zhang, Y. Wang, Y. Wang, J. Zhou, L. Dai, M. Xu, *Infomat* **2019**, *1*, 396.
- [35] Y. Lu, X. Qu, W. Zhao, Y. Ren, W. Si, W. Wang, Q. Wang, W. Huang, X. Dong, *Research* **2020**, *2020*, 2038560.
- [36] G. Ge, W. Yuan, W. Zhao, Y. Lu, Y. Zhang, W. Wang, P. Chen, W. Huang, W. Si, X. Dong, *J. Mater. Chem. A* **2019**, *7*, 5949.
- [37] G. Ge, Y. Lu, X. Qu, W. Zhao, Y. Ren, W. Wang, Q. Wang, W. Huang, X. Dong, *ACS Nano* **2020**, *14*, 218.
- [38] A. Walsh, D. O. Scanlon, S. Chen, X. G. Gong, S.-H. Wei, *Angew. Chem., Int. Ed.* **2015**, *54*, 1791.
- [39] J. Kang, L. W. Wang, *J. Phys. Chem. Lett.* **2017**, *8*, 489.
- [40] Q. Jiang, Y. Zhao, X. Zhang, X. Yang, Y. Chen, Z. Chu, Q. Ye, X. Li, Z. Yin, J. You, *Nat. Photonics* **2019**, *13*, 460.
- [41] Y. Zhu, Q. Cui, J. Chen, F. Chen, Z. Shi, X. Zhao, C. Xu, *ACS Appl. Mater. Interfaces* **2021**, *13*, 6820.
- [42] Y. Zhu, H. Guo, Q. Cui, J. Chen, Z. Li, J. Lu, T. Lu, Z. Peng, C. Xu, C. Pan, *Laser Photonics Rev.* **2023**, *17*, 2200497.
- [43] H. Jin, E. Debroye, M. Keshavarz, I. G. Scheblykin, M. B. J. Roeflaers, J. Hofkens, J. A. Steele, *Mater. Horiz.* **2020**, *7*, 397.
- [44] M. Zhou, W. Wang, J. Lu, Z. Ni, *Nano Res.* **2020**, *14*, 29.
- [45] D. Zhang, Y. Fu, H. Zhan, C. Zhao, X. Gao, C. Qin, L. Wang, *Light Sci Appl* **2022**, *11*, 69.
- [46] D. J. Slotcavage, H. I. Karunadasa, M. D. McGehee, *ACS Energy Lett.* **2016**, *1*, 1199.
- [47] Y. Ouyang, L. Shi, Q. Li, J. Wang, *Small Methods* **2019**, *3*, 1900154.
- [48] Y. Ouyang, Y. Li, P. Zhu, Q. Li, Y. Gao, J. Tong, L. Shi, Q. Zhou, C. Ling, Q. Chen, Z. Deng, H. Tan, W. Deng, J. Wang, *J. Mater. Chem. A* **2019**, *7*, 2275.
- [49] G. Xing, N. Mathews, S. S. Lim, N. Yantara, X. Liu, D. Sabba, M. Gratzel, S. Mhaisalkar, T. C. Sum, *Nat. Mater.* **2014**, *13*, 476.
- [50] Y. Zhu, J. Chen, Q. Cui, H. Guo, Z. Li, Z. Shi, C. Xu, *Nano Res.* **2021**, *14*, 4288.
- [51] D. Meroni, L. Lo Presti, G. Di Liberto, M. Ceotto, R. G. Acres, K. C. Prince, R. Bellani, G. Soliveri, S. Arduzone, *J. Phys. Chem. C* **2017**, *121*, 430.
- [52] A. Zakhtser, A. Naitabdi, R. Benbalagh, F. Rochet, C. Salzemann, C. Petit, S. Giorgio, *ACS Nano* **2021**, *15*, 4018.
- [53] J. Yu, M. Guan, F. Li, Z. Zhang, C. Wang, C. Shu, H. Wei, X.-E. Zhang, *Chem. Commun.* **2012**, *48*, 11011.
- [54] S. Liu, Z. Duan, C. He, X. Xu, T. Li, Y. Li, X. Li, Y. Wang, L. Xu, *RSC Adv.* **2018**, *8*, 8026.
- [55] T. Huang, S. Mao, G. Zhou, Z. Zhang, Z. Wen, X. Huang, S. Ci, J. Chen, *Nanoscale* **2015**, *7*, 1301.
- [56] K. Xu, E. T. Vickers, L. Rao, S. A. Lindley, A. L. C. Allen, B. Luo, X. Li, J. Z. Zhang, *Chemistry* **2019**, *25*, 5014.
- [57] B. Chen, P. N. Rudd, S. Yang, Y. Yuan, J. Huang, *Chem. Soc. Rev.* **2019**, *48*, 3842.
- [58] Y. Li, H. Wu, W. Qi, X. Zhou, J. Li, J. Cheng, Y. Zhao, Y. Li, X. Zhang, *Nano Energy* **2020**, *77*, 105237.
- [59] N. K. Noel, A. Abate, S. D. Stranks, E. S. Parrott, V. M. Burlakov, A. Goriely, H. J. Snaith, *ACS Nano* **2014**, *8*, 9815.
- [60] G. Wu, R. Liang, M. Ge, G. Sun, Y. Zhang, G. Xing, *Adv. Mater.* **2022**, *34*, 2105635.
- [61] J. Li, L. Wang, X. Yuan, B. Bo, H. Li, J. Zhao, X. Gao, *Mater. Res. Bull.* **2018**, *102*, 86.
- [62] B. Akbali, G. Topcu, T. Guner, M. Ozcan, M. M. Demir, H. Sahin, *Phys. Rev. Mater.* **2018**, *2*, 034601.