

Ultrafast photophysics in Mn-doped semiconductor quantum dots for optoelectronic application

Meng, Jie

Publication date: 2021

Document Version Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA): Meng, J. (2021). *Ultrafast photophysics in Mn-doped semiconductor quantum dots for optoelectronic application.* DTU Chemistry.

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.

- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.



Ultrafast photophysics in Mn-doped semiconductor quantum dots for optoelectronic application

Jie Meng

Ph.D. Thesis Department of Chemistry Technical University of Denmark August 2021

Ultrafast photophysics in Mn-doped semiconductor quantum dots for optoelectronic application

Ph.D. Thesis

August 31st, 2021

Jie Meng

jmen@kemi.dtu.dk

Department of Chemistry

Technical University of Denmark

Main supervisor

Senior Researcher: Kaibo Zheng

Department of Chemistry

Technical University of Denmark

Co-supervisors

Associate Professor: Susanne Mossin

Department of Energy Conversion and Storage

Technical University of Denmark

Senior researcher: Sophie E. Canton

Deutsches Elektronen Synchrotron (DESY)

Preface and acknowledgment

This dissertation is submitted to Technical University of Denmark (DTU) for the degree of Doctor of Philosophy (Ph.D.). The project was mainly carried out in Department of Chemistry, DTU under the supervision of Senior researcher Kaibo Zheng. Also, I would like to acknowledge the support from the project financial support from China Scholarship Council.

Firstly, I would like to express my sincere appreciation to my supervisor, Kaibo Zheng for the discussion in experimental design, results and manuscript revision. Kaibo is always patient in my whole PhD project and help me a lot in ultrafast spectroscopies. Thanks for the support from the Tönu Pullerits for the ultrafast spectroscopy discussion and Sophie E. Canton for the project discussion. Every travel for the beamline, Hamburg or Tokyo, I realize this world and life is beautiful and amazing. Also, thanks for the EPR experiment from the support from Susanne Mossin, ultrafast experiments from Mohamed and DFT calculation from Zhenyun Lan and Ivano E. Castelli in my Mn doped project.

Secondly, many thanks to my colleagues or friends from the DTU chemistry and Lund University. The supports from DTU chemistry, IT, workshop and other measurements, are really helpful so that I could put my full energy in my own project. The friends from our group and Nanochemistry are all so kind and the story in each person reminds me to cherish my life and this world. The life or every experiments in Division of chemical physics from Lund University is really unforgettable. Every friend and their stories are so interesting. I believe I will never forget the sofa in kitchen in Division of Chemical physics, Lund University. It ever accompanied my overnight experiments several times and one Christmas Eve.

The last part is to my family, my girlfriend and me. Thank you so much for your trust, support and encouragement all the time. Thanks for my happy and anxiety, expectation and disappointment, pain and thinking, which are valuable wealth in my life. I love this world, and where there is life, there is hope.

Jie Meng

August 2021, Lyngby Denmark.

Contributions during PhD project

The thesis is mainly based on the following papers.

I. Modulating Charge-Carrier Dynamics in Mn-Doped All-Inorganic Halide Perovskite Quantum Dots through the Doping-Induced Deep Trap States (Chapter 3)

Jie Meng, Zhenyun Lan, Mohamed Abdellah, Bin Yang, Susanne Mossin, Mingli Liang, Maria Naumova, Qi Shi, Sol Laura Gutierrez Alvarez, Yang Liu, Weihua Lin, Ivano E. Castelli, Sophie E. Canton, Tönu Pullerits, and Kaibo Zheng*

J. Phys. Chem. Lett. 2020, 11, 9, 3705-3711

II. Tailoring the Hot Carrier Cooling by Transition Metal Doping in All-inorganic Lead Halide Perovskite Nanocrystals (Chapter 4)

Jie Meng, Zhenyun Lan, Weihua Lin, Maria Naumova, Mingli Liang, Xianshao Zou, Qian Zhao, Huifang Geng, Ivano E. Castelli, Sophie E. Canton, Tönu Pullerits, and Kaibo Zheng*

Submitted

My contribution to the papers

My works (chapter 3-4) in this thesis mainly focus on the sample synthesis, structural characterizations, spectroscopies experiments and analysis, manuscript.

Other Publications not included in this thesis

 Meng, J.; Lan, Z.; Castelli, I. E.; Zheng, K. Atomic-Scale Observation of Oxygen Vacancy-Induced Step Reconstruction in WO₃ 2021, 125, 8456–8460.

(2) Lan, Z.; <u>Meng, J.</u>; Zheng, K.; Castelli, I. E. Exploring the Intrinsic Point Defects in Cesium Copper Halides. J. Phys. Chem. C 2021, 125, 1592–1598.

(3) Hattori, Y.; Gutiérrez Álvarez, S.; <u>Meng, J.</u>; Zheng, K.; Sá, J. Role of the Metal Oxide Electron Acceptor on Gold–Plasmon Hot-Carrier Dynamics and Its Implication to Photocatalysis and Photovoltaics. ACS Appl. Nano Mater. 2021, 4, 2052-2060.

(4) Gao, Q.; <u>Meng, J.</u>; Yang, Y.; Lin, Q.; Lu, Y.; Wei, X.; Li, J.; Han, G.; Zhang, Z. Zirconium Doping in Calcium Titanate Perovskite Oxides with Surface Nanostep Structure for Promoting Photocatalytic Hydrogen Evolution. Appl. Surf. Sci. 2021, 542, 148544.

(5) Hattori, Y.; <u>Meng, J.</u>; Zheng, K.; Meier de Andrade, A.; Kullgren, J.; Broqvist, P.; Nordlander, P.; Sá, J. Phonon-Assisted Hot Carrier Generation in Plasmonic Semiconductor Systems. Nano Lett. 2021, 21, 1083–1089.

(6) Cao, Y.; Guo, L.; Dan, M.; Doronkin, D. E.; Han, C.; Rao, Z.; Liu, Y.; <u>Meng, J.</u>; Huang, Z.; Zheng, K.; et al. Modulating Electron Density of Vacancy Site by Single Au Atom for Effective CO₂ Photoreduction. Nat. Commun. 2021, 12, 1–10.

(7) Liu, Y.; Zhou, Y.; Yu, S.; Xie, Z.; Chen, Y.; Zheng, K.; Mossin, S.; Lin, W.; <u>Meng, J.</u>;
Pullerits, T.; et al. Defect State Assisted Z-Scheme Charge Recombination in Bi₂O₂CO₃/Graphene Quantum Dot Composites For Photocatalytic Oxidation of NO. ACS Appl. Nano Mater. 2020, 3, 772–781.

(8) Cao, H.; Zheng, Z.; <u>Meng, J.</u>; Xiao, X.; Norby, P.; Mossin, S. Examining the Effects of Nitrogen-Doped Carbon Coating on Zinc Vanadate Nanoflowers towards High Performance Lithium Anode. Electrochim. Acta 2020, 356, 136791.

(9) Liang, M.; Lin, W.; Lan, Z.; <u>Meng, J.</u>; Zhao, Q.; Zou, X.; Castelli, I. E.; Pullerits, T.;
 Canton, S. E.; Zheng, K. Electronic Structure and Trap States of Two-Dimensional

Ruddlesden–Popper Perovskites with the Relaxed Goldschmidt Tolerance Factor. ACS Appl. Electron. Mater. 2020, 2, 1402–1412.

(10) van Turnhout, L.; Hattori, Y.; <u>Meng, J.</u>; Zheng, K.; Sá, J. Direct Observation of a Plasmon-Induced Hot Electron Flow in a Multimetallic Nanostructure. Nano Lett. 2020, 20, 8220–8228.

(11) Tang, Y.; Gomez, L.; Lesage, A.; Marino, E.; Kodger, T. E.; Meijer, J.-M.; Kolpakov,
P.; <u>Meng, J.</u>; Zheng, K.; Gregorkiewicz, T.; et al. Highly Stable Perovskite Supercrystals
via Oil-in-Oil Templating. Nano Lett. 2020, 20, 5997–6004.

(12) Lin, Q.; Guan, W.; Zhou, J.; <u>Meng, J.</u>; Huang, W.; Chen, T.; Gao, Q.; Wei, X.; Zeng,
Y.; Li, J.; et al. Ni–Li Anti-Site Defect Induced Intragranular Cracking in Ni-Rich Layer-Structured Cathode. Nano Energy 2020, 76, 105021.

(13) Guo, R.; Zhang, L.; <u>Meng, J.</u>; Liu, A.; Yuan, J.; Zheng, K.; Tian, J. Exploiting Flexible Memristors Based on Solution-Processed Colloidal CuInSe₂ Nanocrystals. Adv. Electron. Mater. 2020, 6, 2000035.

(14) Naumova, M. A.; Kalinko, A.; Wong, J. W. L.; Alvarez Gutierrez, S.; <u>Meng, J.</u>; Liang, M.; Abdellah, M.; Geng, H.; Lin, W.; Kubicek, K.; et al. Exploring the Light-Induced Dynamics in Solvated Metallogrid Complexes with Femtosecond Pulses across the Electromagnetic Spectrum. J. Chem. Phys. 2020, 152, 214301.

(15) Nguyen, T. L. T.; Gascón Nicolás, A.; Edvinsson, T.; <u>Meng, J.</u>; Zheng, K.; Abdellah,
M.; Sá, J. Molecular Linking Selectivity on Self-Assembled Metal-Semiconductor Nano-Hybrid Systems. Nanomaterials 2020, 10, 1378.

(16) Naumova, M. A.; Kalinko, A.; Wong, J. W. L.; Abdellah, M.; Geng, H.; Domenichini,
E.; Meng, J.; Gutierrez, S. A.; Mante, P. A.; Lin, W.; et al. Revealing Hot and Long-Lived Metastable Spin States in the Photoinduced Switching of Solvated Metallogrid Complexes with Femtosecond Optical and X-Ray Spectroscopies. J. Phys. Chem. Lett. 2020, 11, 2133– 2141.

(17) Li, C.; Rahaman, A.; Lin, W.; Mourad, H.; <u>Meng, J.</u>; Honarfar, A.; Abdellah, M.; Guo, M.; Richmond, M. G.; Zheng, K.; et al. Electron Transfer Mediated by Iron Carbonyl Clusters Enhance Light-Driven Hydrogen Evolution in Water by Quantum Dots. ChemSusChem 2020, 13, 3252–3260.

(18) Pei, J.; <u>Meng, J.</u>; Wu, S.; Lin, Q.; Wei, X.; Li, J.; Zhang, Z. Effects of Ca/Ti Ratio on Morphology Control and Photocatalytic Activity of CaTiO₃/Ca(OH)₂ Composite Photocatalyst. Mater. Lett. 2020, 276, 128229.

(19) Guo, R.; <u>Meng, J.</u>; Lin, W.; Liu, A.; Pullerits, T.; Zheng, K.; Tian, J. Manganese Doped Eco-Friendly CuInSe₂ Colloidal Quantum Dots for Boosting near-Infrared Photodetection Performance. Chem. Eng. J. 2020, 403, 126452.

(20) Hattori, Y.; Abdellah, M.; <u>Meng, J.</u>; Zheng, K.; Sá, J. Simultaneous Hot Electron and Hole Injection upon Excitation of Gold Surface Plasmon. J. Phys. Chem. Lett. 2019, 10, 3140–3146.

Abstract

Recent years witnessed a substantial improvement of solar cell technologies with the power conversion efficiencies of a variety of devices that can approach the thermodynamic limits (Shockley–Queisser Limit). However, in order to finally overcome the Shockley–Queisser Limit (~33% for a standard cell with bandgap 1.4 eV), any process that will induce the loss of harvested photon energy should be well prevented. On the one hand, defects trapping of the excited charge carriers in the photovoltaic materials will result in non-radiative recombination and reduce the quantum efficiency of solar cells. On the other hand, rapid photo-generated hot-carrier cooling is another primary channel for heat loss. The reduced defects concentration and diminished HCs cooling in solar absorbers are, therefore, critical features for realizing highly efficient solar cells to break the Shockley–Queisser Limit. Quantum dots (QDs) are among such promising candidates in solar cells as the size-tunable optical properties can be utilized for materials engineering to achieve the above objectives.

Meanwhile, the emerging metal ions doping in colloidal QDs raises new opportunities to overcome SQ limitations. Such doping states could modulate not only the electronic structures but also the phonon structures of the QDs. If the electronic structure and phonon structure can be well-tailored by the doping in QDs, we can expect enhanced efficiency for QDs solar cells. The main objective of the thesis is thereby to seek the feasibility of photophysical modulation on QDs by transition metal doping.

In the first work of the thesis, we studied the influence of the Mn dopant on the photoinduced charge carrier dynamics in Mn-doped CsPbCl₃ perovskite QDs by steady-state and time-resolved spectroscopies. We found the Mn-doping not only adds extra electronic states in the QDs, but also significantly modulates the defect state of the materials. The energy levels of those possible defect states were thoroughly analyzed using Density Functional Theory (DFT) calculations. As the Mn concentration increases, the exciton photoluminescence quantum yield (PLQY) decreases and the Mn dopant emission QY first increases and then decreases. The experiments and calculations reveal that Mn^{2+} doping qualitatively changes the type of defects from antisites Pb_{Cs} (undoped) to interstitials Cl_i (doped). The competition between exciton to Mn/dopant energy transfer and defect trapping at early timescale (< 100 ps) determines the final PLQY of the CsPbCl₃ QDs. In the second work, we study hot carriers (HCs) relaxation dynamics in Mn-doped LHPs CsPbI₃ nanocrystals (NCs) combining femtosecond transient absorption spectroscopy and DFT calculations with a particular focus on the influence of Mn-doping on the electronic and phononic structures. We demonstrate that Mn^{2+} doping 1) enlarges the LO-acoustic phonon bandgap, 2) enhances the electron-LO phonon coupling strength, and 3) adds HCs relaxation pathways (LO is longitudinal optical mode). The first two factors are associated with the local distortion after Mn^{2+} replacement of Pb^{2+} in the lattice, while the third effect is attributed to the location of Mn orbitals within the bands of LHPs. The spectroscopic study shows that the HCs cooling process is decelerated after doping under band-edge excitation due to the dominant effect of enlarged LO-acoustic phonon bandgap. When the excitation photon energy is much larger than the optical bandgap and the Mn^{2+} transition gap, the doping accelerates the cooling rate owing to the dominant effect of enhanced carrier-phonon coupling and relaxation pathways. The enhanced electronphonon coupling and efficient thermalization of HCs at high energy together with delayed heat dissipation after thermalization with HCs at low energy are optimal for the HCSC application. Our results establish a straightforward methodology to control the HCs dynamics by doping.

Abstract-Danish

De seneste år har været vidne til en væsentlig forbedring af solcelleteknologier med effektomdannelseseffektiviteten af en række forskellige enheder, der kan nærme sig de termodynamiske grænser (Shockley–Queisser Limit). For endelig at overvinde Shockley–Queisser -grænsen (\approx 33% for en standardcelle med båndgap 1,4 eV), bør enhver proces, der fremkalder tab af høstet fotonenergi, da varme, godt forhindres. På den ene side vil defekter, der fælder de ophidsede ladningsbærere i de fotovoltaiske materialer, resultere i ikke-strålende rekombination og reducere solcellers kvanteeffektivitet. På den anden side er hurtig fotogenereret hot-carrier-køling en anden primær kanal til varmetab. Den reducerede defektkoncentration og formindskede HC'ers afkøling i solabsorbere er derfor kritiske træk for at realisere meget effektive solceller for at bryde Shockley–Queisser - grænsen. Quantum dots (QDs) er blandt sådanne lovende kandidater i solceller, da de størrelsesindstillelige optiske egenskaber kan bruges til materialeteknik for at nå ovenstående mål.

I mellemtiden skaber de nye metalioner, der doping i kolloide QD'er, nye muligheder for at overvinde SQ-begrænsninger. Sådanne dopingtilstande kunne modulere ikke kun de elektroniske strukturer, men også phononstrukturer i QD'erne. Hvis den elektroniske struktur og fononstrukturen kan skræddersyes godt ved doping i QD'er, kan vi forvente forbedret effektivitet for QD'ers solceller. Specialets hovedformål er derved at søge gennemførligheden af fotofysisk modulering på QD'er ved overgangsmetaldoping.

I afhandlingens første arbejde studerede vi indflydelsen af Mn dopant på den fotoinducerede ladningsbærerdynamik i Mn-dopede CsPbCl₃ perovskite QD'er ved steady-state og tidsopløste spektroskopier. Vi fandt, at Mn-doping ikke kun tilføjer ekstra elektroniske tilstande i QD'erne, men modulerer også materialernes defekttilstand markant. Energiniveauerne for de mulige defekttilstande blev grundigt analyseret ved hjælp af DFT -beregninger (Density Functional Theory). Når Mn -koncentrationen stiger, falder exciton -fotoluminescens -kvanteudbyttet (PLQY), og Mn -dopantemissionen QY stiger først og falder derefter. Eksperimenterne og beregningerne afslører, at Mn²⁺ doping kvalitativt ændrer typen af defekter fra antisites PbC'er (udoped) til interstitials Cli (dopet). Konkurrencen mellem exciton til Mn/dopant energioverførsel og defektopsamling i tidligt tidsrum (<100 ps) bestemmer den endelige PLQY af CsPbCl₃ QD'erne. I det andet arbejde studerer vi hot carriers (HCs) afspændingsdynamik i Mn-dopede LHP'er CsPbI3 nanokrystaller (NC'er), der kombinerer femtosekund-transient absorptionsspektroskopi og DFT-beregninger med særlig fokus på påvirkning af Mndoping på de elektroniske og fononiske strukturer. Vi demonstrerer, at Mn^{2+} doping 1) forstørrer LO-akustisk fononbåndgap, 2) forbedrer elektron-LO-fononkoblingsstyrken og 3) tilføjer HCs-afslapningsveje (LO er optisk i længderetningen). De to første faktorer er forbundet med den lokale forvrængning efter Mn²⁺ udskiftning af Pb²⁺ i gitteret, mens den tredje effekt tilskrives placeringen af Mn orbitaler inden for LHP'ernes bånd. Den spektroskopiske undersøgelse viser, at HCs-køleprocessen bremses efter doping under båndkant-excitation på grund af den dominerende effekt af forstørret LO-akustisk fononbåndgap. Når excitationsfotenergien er meget større end den optiske båndgab og Mn²⁺ -gabet, accelererer dopingen kølehastigheden på grund af den dominerende effekt af forbedret bærer-fononkobling og afslapningsveje. Den forbedrede elektron-phononkobling og effektiv termisering af HC'er ved høj energi sammen med forsinket varmeafledning efter termalisering med HC'er ved lav energi er optimale til HCSCapplikationen. Vores resultater etablerer en ligetil metode til at kontrollere HC's dynamik ved doping.

Abbreviations

CB(M) : Conduction band (minimum)	PVs : Photovoltaics		
DFT : Density functional theory	PQDs : Perovskite QDs		
DT : Deep trap	QDs : Quantum dots		
DOS: Density of state	SE: stimulated emission		
EPR: Electron paramagnetic	ST: shallow trap		
resonance	SQ limit : Shockley–Queisser limit		
ET: Energy transfer	TA: Transient absorption		
GSB: Ground state bleach	T _c : Carrier temperature		
HCs: Hot carriers	TCSPC: Time-correlated single		
HCSC: Hot carrier solar cell	photon counting		
ICP-MS: Inductively coupled	TEM: Transmission electron		
plasma mass spectrometry	microscopy		
LA: Longitudinal acoustic	T _L : Lattice temperature		
LHPs: Lead halide perovskites	TO: Transverse optical		
LO: Longitudinal optical	TRPL: Transient		
NC(s): Nanocrystal(s)	photoluminescence		
NOPA: Non-linear optical	XA(S): X-ray absorption		
parametric amplifier	spectroscopy		
ODE : 1-Octadecene	XPS : X-ray photoelectron		
OA: Oleic acid	spectroscopy		
OAm : Oleylamine	UV: ultraviolet		
PIA: Photoinduced absorption	UV-vis: Ultraviolet-visible		
PLQY: Photouminescence quantum	VB(M): Valence band (maximum)		
yield			

Contents

Preface and acknowledgment	III
Contributions during PhD project	IV
Other Publications not included in this thesis	V
Abstract	VIII
Abstract-Danish	X
Abbreviations	XII
Chapter 1 Introduction	1
1.1 Theoretical background	1
1.1.1 Excited-state dynamics in the molecular system	1
1.1.2 Excited-state dynamics in semiconductors	3
1.1.3 Hot carriers cooling	6
1.1.4 Phonon and carrier-phonon coupling	8
1.1.5 Determining factors for the HC cooling dynamics	10
1.2 Transition metal doping in LHPs QDs	11
1.2.1 Lead halide perovskites (LHPs)	11
1.2.2 Quantum confinement and Quantum dots (QDs)	13
1.2.3 Mn doping in semiconductor QDs	14
1.3 Defects and trap states in LHPs	16
1.4 Outline of the thesis	18
References	20
Chapter 2 Methodology	
2.1 Steady-state and ultrafast spectroscopies	28
2.1.1 Steady-state UV-vis absorption spectroscopy	28
2.1.2 Steady-state photoluminescence spectroscopy	

2.1.3 Transient absorption spectroscopy (TA)	31
2.1.4 Time-correlated single photon counting (TCSPC)	34
2.2 Structural characterizations	35
2.2.1 X-ray photoelectron spectroscopy (XPS)	35
2.2.2 Transmission electron microscopy (TEM)	36
2.2.3 Electron paramagnetic resonance (EPR)	37
2.2.4 Inductively coupled plasma mass spectrometry (ICP-MS)	38
2.2.5 X-ray absorption spectroscopy (XAS)	38
2.3 Synthesis of Mn-doped QDs	39
References	40
Chapter 3 Charge-carrier dynamics in Mn-doped CsPbCl ₃ QDs4	
Chapter 4 Hot carrier cooling in Mn-doped CsPbI ₃ NCs	
Chapter 5 Conclusion and perspective	121

Chapter 1 Introduction

This chapter briefly introduces the background and development of doped perovskite QDs and their photophysical processes. In the first part, some basic photophysical fundamentals related to this thesis are introduced. These processes are the critical physical process determining the conversion efficiencies for solar cells to overcome the Shockley–Queisser limit (SQ limit) at about 33%. Then, I also talk about the materials, i.e. Mn doped lead halide perovskite QDs, to be targeted in this thesis. Also, trap states will also be discussed. Finally, the outline of this thesis is presented. The introduction in this chapter will be the starting point for the understanding of the following chapters.

1.1 Theoretical background

Due to its sustainability, abundance, and cleanness, utilizing solar energy has been the subject of intense efforts during the past decade.^{1,2} Earth's annual available solar energy capacity is about a hundred times the energy that entire global fossil fuel resources reserve.³ Therefore, research topics on solar energy capture and conversions, including photovoltaics (PVs), photoluminescence (PL), photosynthesis and so on, have attracted much attention.^{4,5} Since the conversion efficiency of an optoelectronic devices is mainly dependent on photophysical behaviors, characterization and interpretation of those behaviors are vital for device engineering.⁶ In the following section, some fundamental photophysical processes relevant to solar energy conversion will be introduced.

1.1.1 Excited-state dynamics in the molecular system

After absorbing phonons, the photoactive materials can be excited from their ground state to excited state where species like excitons or charge carriers are generated.⁷ The excitedstate dynamics of a photoactive system manifest the ultrafast generation, transfer as well as the decay of those excited species.⁸ We can first obtain a basic overview of such processes in a relatively simple molecular system where a well-known Jablonski Diagram is commonly used for demonstration.⁹ The Jablonski Diagram is named to memorize the pioneering contributions of Polish physicist Aleksander Jablonski.¹⁰ The Jablonski diagram is known as a powerful tool to visualize the possible transitions after photoexcitation in molecular system, as shown in Figure 1.1. The blue arrows represent the absorption process. In this process, a molecule will be excited from its ground state to higher excited state after optical absorption with a timescale of about 10⁻¹⁵ s, which is the fastest transition in the Jablonski diagram. After absorbing a photon, the molecules will be promoted from the lowest vibrational level of the ground state S_0 to one of the vibrational levels of the singlet excited states (S₁, S₂,...). It is not possible to directly excite molecules from the ground state to the triplet excited states $(T_1, T_2,...)$ because of the conservation of angular momentum.¹¹ The excess vibrational energy will be lost to surrounding molecules (intermolecular) or within the same molecule (intramolecular) until reaching the lowest vibrational level of the excited state. This process is called vibration relaxation (Process 2) and occurs very rapidly with timescale of $10^{.12} - 10^{.10}$ s, which could outcompete all other transitions.¹² The internal conversion immediately followed by vibrational relaxation (Process 3, the purple arrows) will also happen for the molecules from a higher singlet electronic state to a lower singlet electronic state on a timescale of $10^{.11}$ to $10^{.9}$ s.¹³ Because the rate of internal conversion is in inverse ratio to the energy gap between the two electronic states, a wider states electronic gap will show a slower internal conversion rate, which will be in competition with other transition process like intersystem crossing.¹⁴

The radiative transition from the $S_1 \rightarrow S_0$ with photon emission after the rapid vibrational relaxation and internal conversion processes is called fluorescence (Process 4, green arrows) in Figure 1.1, which occurs within a timescale of 10^{-10} to 10^{-7} s.¹⁵ The fluorescence process happens from the lowest vibrational levels of the first electronic excited singlet states to the singlet ground states. This energy loss follows Kasha's Rule where photon emission (fluorescence or phosphorescence) occurs in appreciable yield only from the lowest excited state of a given multiplicity. The Stokes-Shift will occur that the wavelength of fluorescence is longer than that of the absorption.¹⁶ Phosphorescence is a forbidden transition in principle while is weakly allowed by spin-orbit coupling. Consequently, the lifetime of phosphorescence is much longer than that of fluorescence in the range of 10^{-6} to 10 s.^{17} The transition from the S₁ to the T₁ state is called intersystem crossing (process 5), which is marked by the yellow-colored arrows. This transition could be weakly allowed is because of spin-orbit coupling between the spin angular momentum and the orbital angular momentum.¹⁸ After intersystem crossing, the molecules will immediately undergo vibrational relaxation to the ground vibrational level of T₁ because this state is non-equilibrium and will eventually lost their energy to the ground state.



Figure 1.1 The typical Jablonski diagram with the possible radiative and non-radiative transitions processes. The black solid lines are energy levels. The transitions between different energy levels are marked by different colors. S_0 represents the singlet ground state of the molecules. S_n (like $S_1, S_2...$) is the nth excited singlet state. T_1 represents the first excited triplet state and T_n is the nth excited triplet state.

1.1.2 Excited-state dynamics in semiconductors

Compared with the molecular system, the excited-state dynamics in semiconductors are usually more complicated since their energy band structure are more complex instead of discrete energy levels.¹⁹ The electronic structures of the semiconductors are dominated not only by the compositions of the compounds but also by their dimensions and morphological features. Therefore, there are some distinctions between molecular systems and semiconductors systems. As shown in Figure 1.2, when samples are excited by a photon with energy higher than the band gap energy, an electron will be excited into the conduction band (CB) after absorption, and leave a hole in the valence band (VB). The excited electrons and holes in a higher excited state with excess energy are also called hot carriers (HCs).²⁰ These hot carriers dissipate excess energy through carrier-carrier and carrier-phonon interactions and reach the equilibrium temperature of the lattice, thereby relaxing to the band-edge state, which is called hot carrier cooling (HCs cooling).²¹ Due to Coulomb's interaction, excitons can also be formed by electrons and holes.²² Electrons and holes located at the band edge of the semiconductors can undergo radiative or nonradiative decay through electron-hole recombination. However, if there are sub-band gap states due to defects or surface dangling bonds, photo-excited charge carriers can be trapped at these states on a time scale faster than radiative recombination.²³ The trapped carriers can recombine radiatively or non-radiatively. Trap emission by radiative recombination is red-shifted relative to the band-edge emission. For different trap states, the lifetime of the trap state in semiconductors ranges from tens of picoseconds to nanoseconds or longer.24



Figure 1.2 Schematic diagram of the carrier relaxation in semiconductor. The long solid line with an upward arrow represents photo-excitation. The curves with downward

arrows indicate different relaxation processes: (1) electron relaxation or hot carrier cooling in the CB, (2) falling into shallow trap (ST) states and deep trap (DT) states and further from ST to DP, (3) band edge carrier recombination, (4) electron-hole recombination, (5) exciton-exciton annihilation.

The excited-state dynamics of semiconductors are also highly dominated by the excitation concentration.²⁵ As discussed above, the photophysical processes of photo-excited species are mainly composed of two parts: the initial HCs relaxation and subsequent recombination that occur on a timescale of femtoseconds to microseconds. The absorption of phonons possessing energy higher than the band gap will generate electron-hole pairs. The non-thermal distributed carriers will thermalize by Maxwell-Boltzmann distribution within t < 100 fs, then cool to the lattice temperature through carrier-phonon coupling. This process is called HCs cooling.²⁶ After that, the relaxed charge carriers at the band edge of the semiconductors will undergo transfer and then recombination processes to finally reach the ground state. In this section, we will focus on such charge carrier densities subsequently to the hot carrier cooling as shown in Figure 1.3.

In the past decade, lead halide perovskites (LHPs) have been regarded as one of the most promising materials in optoelectronic devices.²⁷ Perovskite represents a type of crystal structure with the chemical formula ABX₃, where A and B are cations, and X is an anion. In LHPs, the X positions are halogen anion. A high optical absorption coefficient, a long charge carrier diffusion length and suppressed recombination rate make them promising in the application of solar cells or luminescence devices.²⁸ In our work (Chapter 3), the charge carrier recombination dynamics of Mn-doped LHPs were studied. Therefore, various photophysical processes and charge carrier recombination rates in CH₃NH₃PbI₃ over a range of photoexcited carrier densities from the reported literature were used as an example.

At low fluence with carrier densities $n_0 < 10^{17}$ cm⁻³, monomolecular processes including geminate recombination and trap-assisted recombination are inefficient with low firstorder recombination coefficients.²⁹ Due to the low exciton binding energy (E_B $\leq k_B$ T) of perovskite halides, free carriers are the intrinsic charge carriers at room temperature. The splitting time of excitons to free carrier at ambient conditions was estimated to be ~20 *fs* reported by Ghosh *et al.*^{30,31} The time scales of geminate recombination are typically on tens to hundreds of $ps.^{32}$ Because the charge carrier requires the opposite charge to be in the vicinity of the trap in order to recombine, the radiative trap-assisted recombination shows a relatively long timescale, which is less probable at low charge carrier densities.

At an intermediate carrier density $n_0 \approx 10^{17}-10^{18}$ cm⁻³, multiparticle effects like nongeminate recombination (bimolecular) become more probable. Nongeminate recombination originates from the bimolecular recombination and their recombination constants are approximately 4 orders lower than the Langevin rates, which is determined by assuming free carrier annihilation.^{29,33}

At high charge carrier density $n_0 > 10^{18}$ cm⁻³, amplified spontaneous emission and Auger recombination are dominant recombination processes. Auger recombination involves three particles where the lost energy from the electron-hole recombination will transfer to another electrons or holes. Then these electrons or holes will be excited to higher energy states rather than recombinating directly.³⁴



Figure 1.3 Excitation dependent photophysical processes in CH₃NH₃PbI₃. Reproduced with permission from ref. 25.²⁵

1.1.3 Hot carriers cooling

For solar cells, fast HCs cooling is a major loss channel in suppressing their conversion efficiency.²⁶ When the semiconductors excited by photons with energies much higher than the band gap energy ($hv > E_g$), the excited electrons or holes will show excess energies above the band gap and their temperature will be higher than the lattice temperature (Tc > TL). Therefore, these hot species are termed "hot carriers".³⁵ However, these hot carriers will lose their excess energies to phonons through carrier-phonon scattering within hundreds of femtoseconds, making hot carriers extraction extremely challenging.³⁶ The schematic evolution of the carrier distributions with time after photon excitation is shown in Figure 1.4.³⁷ Firstly, the excited carriers will be generated after absorbing the photons with high energies (process 1), the excited carriers will thermalize quickly by a carrier-carrier interactions and this process, called carrier thermalization (process 2), normally occurs within 100 fs. The consequence is that hot carriers will approximately be distribute as a Maxwell-Boltzmann with Tc >> TL. Then, the thermalized hot carriers will start to equilibrate with the phonon mainly through inelastic carrier-phonon interactions and this process is known as "hot carriers cooling (HCs cooling)" (process 3-4). Generally, HCs cooling (process 3) occurs within 1 ps till the excess energies are less than the LO phonon energy. Afterward, the emitted LO phonons followed by electron-LO-phonon scattering will decay into the acoustic phonons (process 4). The excess energy will be further lost via decay of acoustic phonon emissions. Finally, the cooled carriers will recombine and the timescale of this process usually occurs in nanosecond. Therefore, the phonons play a critical role in controlling the HCs cooling process.²¹

The hot carrier solar cell (HCSC) is regarded as a solar energy converter that collects the excess energy to excite electrons or holes to generate direct current.³⁷ Unlike traditional solar cells, HCSC maintains the number of HCs. Therefore, the excess carrier energy above the edges of each energy band helps to achieve higher conversion efficiency than traditional solar cell. The conversion efficiency of traditional batteries is limited to 33% by the Shockley-Queisser limitation of a single-junction solar cells (SCs). According to theoretical calculation, the conversion efficiency of the HCSC could reach 66%.³⁸

An ideal HCSC will absorb a wide range of photon energy and extract most of the energy, providing very high efficiency by collecting the HCs before they thermalize to the band edge.³⁹ Therefore, an important characteristic of a HCSC is to be collected when the hot

carriers are still at high energy ("hot"), thereby allowing a higher voltage to be obtained from the solar cell.⁴⁰ However, achieving an efficient HCs extraction with all the excess energy to be harvested is extremely challenging. Previous studies attributed the bottleneck to the suppression of HCs extraction through faster HCs cooling to the edge of the band, and looking for materials with a slow HCs cooling rate to ensure that HCs is injected into the electrode in a hot state.^{36,41–43} However, from our understanding, the excess energy of HCs will still be lost in the energy-selective electrode. Therefore, the optimal kinetics of HCSC should initiate the effective establishment of the abovementioned thermal quasi-equilibrium, in which the excess energy of HCs is converted into heated cold carriers. Subsequently, this quasi-equilibrium state should be long-lived to promote the extraction of HCs.



Figure 1.4 Schematic diagram of the charge carrier distribution and the processes of HCs cooling in semiconductors. Reproduced with permission from ref. 37.³⁷

1.1.4 Phonon and carrier-phonon coupling

Many solid materials, including metal or inorganic materials, consist of atoms arranged in a periodic lattice called crystals. Theoretically, the atoms in a crystal will locate at the position with lowest energy or equilibrium state at a temperature of absolute zero. When thermal energy is posed to the crystal, the atoms in the lattice confined by the electric forces will stretch or compress a bit within the limitation of vibrations to a higher energy configuration. The excess energy is kept in the crystal to support the compression and stretching of the atoms. This quasi-particle of the lattice vibration is called the phonon. If two neighboring atoms move in the same direction, this vibration mode is acoustic phonons. If they are displaced in opposite directions, this is called an optical phonon. In addition, two vibration modes can be classified concerning their energy dispersion. If we simulate the oscillation of the atoms in a one-dimension by the chain of the two balls with the masses M_1 and M_2 , the dispersion of a linear chain can be seen the following:⁴⁴

$$\omega_{+}^{2}(k) = \beta \left(\frac{1}{M_{1}} + \frac{1}{M_{2}}\right) + \beta \sqrt{\left(\frac{1}{M_{1}} + \frac{1}{M_{2}}\right)^{2} - \frac{4sin^{2}\frac{ka}{2}}{M_{1}M_{2}}}$$
(1.1)

$$\omega_{-}^{2}(k) = \beta \left(\frac{1}{M_{1}} + \frac{1}{M_{2}}\right) - \beta \sqrt{\left(\frac{1}{M_{1}} + \frac{1}{M_{2}}\right)^{2} - \frac{4sin^{2}\frac{ka}{2}}{M_{1}M_{2}}}$$
(1.2)

where β is spring constant, $\mathbf{k} = \frac{2\pi}{\lambda}$ is the wave vector of the vibration related to its wavelength. The plus sign in equation 1.1 results in the so-called *optical* mode, and the minus sign in equation 1.2 to the *acoustic* mode. In addition to the acoustic and optical, the phonon can also be classified by considering the direction of atomic displacement with respect to the wavevector \mathbf{k} . The phonons can be regarded as longitudinal phonons or transverse phonons if the displacement direction is parallel or perpendicular to \mathbf{k} , respectively. The number of phonon modes is determined by the number of atoms, N, in the unit cell. We find three acoustic (specifically one longitudinal acoustic (LA) and two transverse acoustic (TA)) modes, originating from the three degrees of freedom of an atom. The number of optical modes is 3N - 3, where TO mode is transverse optical mode and LO is longitudinal optical modes.⁴⁵

In order to discuss the electron-phonon coupling in periodic crystals, the Fröhlich Hamiltonian will be introduced firstly. It describes the lattice motion and the coupling between carriers and the lattice.

$$H = H_{carrier} + H_{lattice} + H_{coupling}$$
(1.3)

In this equation, $H_{coupling}$ describes the coupling of charge carrier and phonon. There are two general types of interaction. One is the interaction via the short-range deformation potential, which locally perturbs the lattice and changes the electronic band structures. The other is the long-range polar-optical interaction and it is dominant in the polar semiconductor, like lead halide perovskites. In these polar semiconductors, energy loss through carrier-phonon coupling mainly occurs through the Fröhlich interaction by LO phonons. ⁴⁶ Following the carrier-phonon interaction, the optical phonons will further decay into acoustic phonons through several channels. The first one is the Klemens mechanism where one optical phonon will decay into two acoustic phonons: $E_{LO} \rightarrow E_{LA} + E_{LA}$. The energy of two decayed acoustic phonons are 1/2 E_0 and equal to each other, but with antiparallel momentum. With a large phononic band gap with $E_{A,max} < 1/2E_{O,min}$, the Klemens mechanism will be suppressed.⁴⁷ The next important decay channel is the Ridley mechanism, where an LO phonon will decay into one TO phonon mode and one LA phonon mode with low energy: $E_{LO} \rightarrow E_{TO} + E_{LA}$ at a zone-center.⁴⁸ Vallée–Bogani channel is another similar process, where a LO mode decays into a lower LO phonon from the same branch and an acoustic mode: $E_{LO} \rightarrow E_{TO} + E_{LA}$.⁴⁹ This mechanism is dominant in phonon decay of the case of GaAs. Finally, an optical phonon decays into two transverse optical phonons of a lower branch: $E_{LO} \rightarrow E_{TO} + E_{TO}$. This channel is very common for hexagonal materials in wurtzite structure, called Barman–Srivastava, where a small splitting of these modes would reduce the efficiency of this channel (Figure 1.5).⁵⁰



Figure 1.5 Schematic diagram of (a) phonon dispersion and (b) major decay routes for LO phonons. Reproduced with permission from ref. 37.

1.1.5 Determining factors for the HCs cooling dynamics

The above-mentioned HCs cooling dynamics are all highly structural related, and some of them are even interactive with each other. In the following, we summarize the most critical factors:

1) Phononic band gap: When the injection level for the carriers is high, the relaxation rate of the non-equilibrium carrier-phonon interaction will decrease. This phenomenon is called hot phonon bottleneck.⁵¹ In order to efficiently block the Klemens channel for LO phonon decay, the phononic band gap between LO and LA ($\hbar\omega_{\text{LO-min}} - \hbar\omega_{\text{LA-max}}$) must be much larger than the maximum energy $\hbar\omega_{\text{LA}}$ ($\hbar\omega_{\text{LA-max}}$) of LA (i.e., $\hbar\omega_{\text{LO-min}} - \hbar\omega_{\text{LA-max}}$) $\hbar\omega_{\text{LA-max}}$), thus contributing to the formation of hot-phonon bottleneck and nonequilibrium phonon population.^{36,52,53} So, HCSC requires an enlarged phononic band gap to suppress the phonon decay as well as HCs relaxation through phonon vibration.

2) LO phonon energy: The energy loss rate of HCs via carrier-LO phonon interaction can be expressed with the following equation when the hot phonon bottleneck is absent.^{26,54}

$$P = \frac{m^{1/2}e^2}{\pi\varepsilon_0\hbar^2} \left(\frac{\hbar\omega_{L0}}{2}\right)^{3/2} \left[\frac{1}{\varepsilon_{opt}} - \frac{1}{\varepsilon_{stat}}\right]$$
(1.4)

where ε_{Opt} and $\varepsilon_{\text{Stat}}$ are the optical and static dielectric constants, respectively. For a given energy loss of HCs, smaller $\hbar\omega_{\text{LO}}$ means more phonons are required, and HCs cooling rate will slow down. Therefore, the low LO phonon energies will have two advantages for HCSC. The first benefit is that there are many phonons emitted before HCs cool to the band edge. The second benefit is further LO emission could lead to phonon re-absorption.

3) Carrier effective mass: According to the above Equation (1.4), a lighter effective mass for carriers will also contribute to less efficient HCs relaxation. Thus, substitution with other elements for a small effective mass is an advantage for designing HCSC absorbers.

4) Quantum confinement: Quantum confinement could easily alter band gap as a result of size variation. Quantum confinement could be a positive feature to prolong HCs lifetimes. For example, hot phonon bottleneck in QDs is often considered to be the results of the discrete electron density of states (DOS).⁵⁵ Neil et. al. report that the separate energy levels in the FASnI₃ nanocrystals will slow down the HCs cooling by two orders of magnitude at low injected carrier densities.⁵⁶ While some works put forward opposite opinion, they think the contribution of quantum confinement in suppressing the HCs cooling could be ignored. For example, no suppression of HCs cooling is observed through altering the size of CsPbBr₃ nanocrystals from Ivan et al.'s work.⁵⁷

1.2 Transition metal doping in LHPs QDs

1.2.1 Lead halide Perovskites (LHPs)

The term perovskite was first used in 1893 for the CaTiO₃ mineral and it is named to memorize the mineralogist Lev Alekseyevich von Perovski.⁵⁸ Besides perovskite oxides, the perovskites can also describe oxynitrides, chlorides, nitrides, fluorides and so on.⁵⁹ The LHPs, as one of perovskite halides, have attracted much attention in photovoltaics, light-emitting diodes, photodetectors and solar fuels, due to their excellent optical absorption, long diffusion length, tunable band structures long carrier lifetimes and high quantum efficiencies.⁶⁰ In 2009, the LHPs were first utilized as an optical absorber applied in solar cells by Miyasaka.⁶¹ To date, the power conversion efficiency (PCE) of inorganic-organic hybrid perovskite-based solar cells has reached 25.5%, which is comparable with that of silicon-based solar cells.⁶²



Figure 1.6 (a) Schematic representation and (b) tolerance factors of the typical LHPSs ABX₃ crystal structure of halide perovskites. Reproduced with permission from ref. 63.⁶³

The general chemical formula for LHPs compounds can be expressed as ABX₃. In this formula, A represents a monovalent cation, like MA⁺ (methylammonium), FA⁺ (formamidinium), and Cs⁺ (cesium), etc.), and B represents a divalent metal cation (Pb²⁺,

Sn²⁺, etc.), and X represents occupied by halides (Cl⁻, Br⁻, and I⁻) (Figure 1.6a).⁶⁴ Generally, LHPs are sensitive to environment. They may undergo phase degradation under the change of temperature, humidity, gas, and solvents conditions.⁶⁵ To evaluate the structural stability of perovskite, tolerance factors t have been used as follows.⁶⁶

$$t = \frac{(R_A + R_X)}{\sqrt{2} (R_B + R_X)}$$
(1.5)

Here R_A , R_B , and R_X are the ionic radius of A, B, and X, respectively. The tolerance factors for typical perovskite halide materials are shown in Figure 1.6b. When $0.9 \le t \le 1$, perovskites tend to be formed with cubic structure. When $0.71 \le t \le 0.9$, the distortion can be found in perovskite structure. Because the tolerance factor covers a range in halide perovskites, doping by other transition metal elements to replace the Pb atoms are structurally feasible (Figure 1.6).⁶⁷



1.2.2 Quantum confinement and Quantum dots (QDs)

Figure 1.7 (a) The solar radiation spectrum and inset is size-dependent photoluminescence of QDs. (b) Schematic images of quantum confinement. Reproduced with permission from ref. $71.^{71}$

The quantum confinement effect describes electrons in terms of energy level, potential well, VB, CB, and E_g . When the particle size is reduced to be comparable with the wavelength of the electrons, the quantum confinement effect is observed. The band gap is increased when the particle size is reduced. In the case of nanocrystals with the diameter of approx. 2-10 nm, compared with bulk semiconductors, various fluorescence colors could be used to reflect small differences in particle size due to the quantum size effect.⁶⁸

QDs, a colloidal nanocrystal (size range $\sim 1-20$ mm) have attracted much attention over the past decades due to their unconventional physical and chemical properties compared with their bulk counterparts. In QDs, the quantum confinement is greatly obvious as the particle size is comparable to the wavelength of the electron. In a strong confinement scenario, when the particle size of QDs is smaller than the exciton Bohr radius, as the energy level splits, the band gap will increase (Figure 1.7).⁶⁹

Such quantum confinement effect allows us to design and synthesize QDs with controllable shapes, structures and even chemical compositions to precisely adjust the energy of optical transitions and discrete electronic energy states. In the past years, various high-quality colloidal QDs, including bare and core-shell QDs, strong absorption ability, size-tunable optical properties, high photoluminescence quantum yield (PLQY) and good light stability, have been achieved through various well-controlled synthesis methods. Recent studies have shown that QDs have shown great potential in recycle and renewable energy applications, such as photovoltaic devices, photocatalysts, luminescence, etc., in addressing the environmental pollution and energy crisis.⁷⁰

1.2.3 Mn doping in semiconductor QDs

Doping strategy has been demonstrated as an effective approach to modulate the electronic properties of semiconductors while retaining their intrinsic crystalline structure. During the doping process, a small amount of impurities introduced into the lattice can drastically tune the electronic structure.⁷² For photoactive semiconductors, transition metal Mn is a perfect dopant because doping Mn (II) in wide band gap semiconductors could introduce stable d orbitals within the band gap which can act as acceptors to accommodate the excitation from the hosts by energy transfer. The transferred charge carriers are long-lived at those triplet states which is beneficial for optoelectronic application. They can also undergo triplet emission with large stokes shift and extremely long lifetime.⁷³

The Mn doping in QDs was earlier reported with a ZnS host, gradually this topic was extended to other complex nanostructures.⁷⁴ Recent developments on Mn doping in LHPs nanocrystals have also been widely investigated.⁷⁵ LHPs nanocrystals have higher absorption coefficients and narrower emission peaks and the similar ion radius between Mn^{2+} (0.97 Å) and Pb²⁺ (1.19 Å) ensures the stable incorporation of Mn^{2+} into perovskite lattice.⁷⁶



Figure 1.8 Proposed energy level diagram for Mn²⁺ doped LHPs with the emitting center of Mn²⁺ as a free-ion state and in a crystal field of cubic symmetry in the relative to energy band structure of LHP. Reproduced with permission from ref. 77.⁷⁷

In Mn doped QDs, the carriers excitation from the host QDs can be transferred to the Mn dopants via an energy transfer process.⁷⁸ Such transfer efficiency is determined by the energy alignment between the dopant Mn ⁴T₁ and ⁶A₁ states and the intrinsic band structure of the QDs.⁷⁶ When the halide ions (X⁻) are changed from Cl⁻ to Br⁻ to I⁻, the exciton to dopant energy transfer becomes less efficient due to the lower energy of the QD band edge than the Mn states.⁷⁷ Generally, the energy levels of Mn²⁺ can be expressed by the Tanabe-Sugano diagram. This energy levels are largely related to the crystal field environment because the radiation transition of Mn²⁺ results from the outermost electrons from the 3d⁵ state.⁷⁹ As shown in Figure 1.8, the spin-orbit coupling ⁴G and ⁴D degenerate energy levels of the Mn²⁺ free ion state will split into ⁴T₁ (⁴G), ⁴T₂ (⁴G), ⁴E, ⁴A₁ (⁴G) and ⁴T₂ (⁴D).⁸⁰ From the PL spectrum, the orange emission due to the Mn^{2+:} 4^T1 \rightarrow

 ${}^{6}A_{1}$ transition can be observed in CsPbCl₃ implying that the ground state ${}^{6}A_{1}$ and the excited state ⁴T₁ of Mn²⁺ are within the band gap or between CBM and VBM.⁸¹ As shown in Figure 1.8, some of the excited states of Mn²⁺ may overlap with CB of perovskite QDs (PQD) after increasing the Br/Cl ratio. It is worth noting that the relationship between the exciton emission of PQDs and dopant emission of $Mn^{2+} d \rightarrow d$ are in mutual competition. If we increase the Mn²⁺ concentration in the host, the energy transfer from PQD to Mn^{2+} dopants will be promoted and the result is Mn^{2+} emission will be obvious. This phenomenon is common in the pure CsPbCl₃, which is also discussed in our work (Chapter 3). The anion exchange of Cl-to-Br will significantly reduce the dopant emission of Mn²⁺ relative to intrinsic emission from pure CsPbCl₃ to CsPb(Cl/Br)₃. In other words, in high Br/Cl ratio, exciton emission will be dominant compared to the Mn^{2+} emission. The anion exchange from Cl to Br will result in band gap reduction, which will make CB close to the $Mn^{2+:4}T_1(4G)$ state, and some of electrons in the ${}^{4}T_1({}^{4}G)$ state could return to CB through deactivation. Therefore, it is important to maintain the balance between Mn²⁺ emission energy states and CB/VB positions by appropriately replacing Cl⁻ with Br⁻ in Mn²⁺ doped LHPs system (Figure 1.8).

1.3 Defects and trap states in LHPs

In crystals, any deviation from the periodic order of the crystal lattice will result in defects. Most of the photophysical parameters, including the mobility and recombination rates of charge carrier will be greatly affected by these defects. Therefore, a good understanding of the structures of defects and their influence on the photophysical features of the materials is vital for the device application.⁸² In general, the non-periodic local structure will introduce disorder into the periodic crystal structures. Such localized electronic states induced by the defects (also called trap states) usually reside within the band gap of the semicondutors with lower energy compared with the excited charge carriers, providing pathways to trap photo-excited charge carriers. Depending on the energy difference (ΔE) between the band edges (CBM/VBM) and the defect levels, the trap states can be divided into shallow traps ($\Delta E \leq k_{\rm B}T$) and deep traps ($\Delta E > k_{\rm B}T$) where $k_{\rm B}$ is the Boltzmann constant and T represents temperature, respectively. Typically, charge carriers restricted in shallow trap states can be easily detraped back into the excited states, while deep traps hinder the detrapping and the trapped charge carriers will be

bonded at the defect sites before they directly relax to the ground states. On the other hands, defects states can also locate within the CB or VB of the semiconductor, which are then incapable of trapping carriers.²³

The defects in LHPs, like other semiconductors, can be classified by intrinsic defects and extrinsic defects.⁸³ Extrinsic defects refer to the impurities with atomic elements different from host composition, for instance, the dopant in the doping. Kröger–Vink notations are commonly used in intrinsic (or native) point defects, for example, label VM, Mi, Ms identify as vacancy defects, interstitial defects and substitution defects, respectively.⁸⁴ For instance, for CsPbBr₃, the Br vacancy can be labeled as V_{Br}, the Br_i represent the Br atoms located in the interstitial sites and lead occupying a Bromide site yields an anti-site label of Pb_{Br} (Figure 1.9). When the formation energy of a defect is negative, it is thermodynamically advantageous for the formation of this defect in the semiconductor spontaneously. The formation energy depends on the atomic chemical potential and the electron chemical potential.⁸⁵ The former is related to the concentration and activity of the reactants, and the later factor is related to the Fermi level. Therefore, the defect structure (types or concentration) will change significantly under different synthesis conditions, such as reaction temperatures, concentrations, solvents, precursors and so on. The traditional method of studying defects in specific materials is to theoretically calculate their formation energy. In order to study the materials containing defects systematically, each defect in different charge states will be considered. The most stable charge state of defect is the lowest formation energy from calculation while it may vary according to the value of the Fermi level. If there is a transition of the Fermi level within the band gap, the charge carriers can interact with this energy level. Therefore, Density Functional theory (DFT) calculation is currently the most accepted method for investigating the origin of point defects.⁸⁶ The defects and their formation energies in perovskites halide were substantially investigated using DFT.

There are some reports about defects and trap states in LHPs. It was found that CsPbBr₃ has a high degree of defect tolerance in its electronic structure. Most inherent defects cause shallow transition energy levels. Only a few defects will show deep transition energy levels while their formation energy is high. ⁸⁷ Furthermore, it is reported that Ni doping in CsPbCl₃ could be used to eliminate the halide vacancy defects and increase short-range order. From DFT calculations, it is revealed that Ni doping will not only increase defect formation energy, but also avoid to introduce deep trap states within the

band gap, thus contributing to near-unity PLQY.⁸⁸ Besides, from the alkaline metals doping investigation, it is found that Ca²⁺ and Sr²⁺ ions exist on/close to the surface of nanocrystals could form a passivation layer. This passivation layer could suppress the formation of vacancy defects, thereby inhibiting non-radiative recombination pathways in NCs.⁸⁹



Figure 1.9 Schematic diagram of defects in LHPs. (a) Various types of defects in LHPs: i) perfect perovskite crystals, vacancies like ii) V_A , iii) V_X , iv) V_B , interstitials v) A_i , vi) X_i , vii) B_i , viii) impurity interstitial, anti-sites: ix) A_B , x) A_X , xi) X_B , xii) X_A , xiii) B_A , xiv) B_X , xv) lattice dislocations, xvi) grain boundary defects, xvii) Schottky defect, xviii) Frenkel defect, xix) substitution with external impurities. (b) The schematic images of LHPs with surface defects and ligands. Reproduced with permission from ref. 90.⁹⁰

1.4 Outline of the thesis

This thesis contains five chapters. It is outlined as follow:

Chapter 1-Introduction

It starts with the background of basic photophysics in molecular and inorganic materials. Some photophysical concepts and phenomena related to our work were introduced, like carrier recombination, hot carriers, carrier-phonon coupling and so on. Afterward, the materials to be investigated of LHPs and corresponding defects were discussed. The main purpose of this part is to supply the background and discussion for the following chapter.

Chapter 2-Methodology

In this chapter, the details of ultrafast spectroscopies and equipment for materials characterization used in the thesis work are introduced.

Chapter 3- Charge-carrier dynamics in Mn-doped CsPbCl₃ QDs

The correlation between structure and photo-induced charge carrier dynamics in Mn^{2+} doping in CsPbCl₃ perovskite QDs (one of the benchmark samples nowadays for efficient dopant emission) with different doping levels was discussed.

Chapter 4- Hot carrier cooling in Mn-doped CsPbI3 QDs

The effect of transition metal (Mn²⁺) doping of lead halide perovskites in their HC cooling dynamics was investigated through both ultrafast laser spectroscopy and DFT calculation. We found the HCs cooling rate is modified by the Mn doping, but the trend is excitation energy-dependent.

Chapter 5- Conclusion and perspective

Main conclusions from chapters 3-4 and perspective are presented.

References

- Creutzig, F.; Agoston, P.; Goldschmidt, J. C.; Luderer, G.; Nemet, G.; Pietzcker, R. C. The Underestimated Potential of Solar Energy to Mitigate Climate Change. *Nat. Energy* 2017, *2*, 17140.
- (2) Gong, J.; Li, C.; Wasielewski, M. R. Advances in Solar Energy Conversion. Chem. Soc. Rev. 2019, 48, 1862–1864.
- Breeze, P. Solar Power. In *Power Generation Technologies*; Elsevier, 2019; 293– 321.
- (4) Hayat, M. B.; Ali, D.; Monyake, K. C.; Alagha, L.; Ahmed, N. Solar Energy—A Look into Power Generation, Challenges, and a Solar-Powered Future. *Int. J. Energy Res.* 2019, 43, 1049–1067.
- (5) Goetz, K. P.; Taylor, A. D.; Paulus, F.; Vaynzof, Y. Shining Light on the Photoluminescence Properties of Metal Halide Perovskites. *Adv. Funct. Mater.* 2020, 30, 1910004.
- (6) Kanemitsu, Y.; Handa, T. Photophysics of Metal Halide Perovskites: From Materials to Devices. Jpn. J. Appl. Phys. 2018, 57, 090101.
- Meschede, D. Optics, Light, and Lasers; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2017.
- Xu, J.-Y.; Tong, X.; Yu, P.; Wenya, G. E.; McGrath, T.; Fong, M. J.; Wu, J.; Wang,
 Z. M. Ultrafast Dynamics of Charge Transfer and Photochemical Reactions in Solar Energy Conversion. Adv. Sci. 2018, 5, 1800221.
- (9) Frackowiak, D. The Jablonski Diagram. J. Photochem. Photobiol. B Biol. 1988, 2, 399.
- (10) Lakowicz, J. R. Principles of Fluorescence Spectroscopy; Lakowicz, J. R., Ed.; Springer US: Boston, MA, 2006.
- (11) Sasikumar, D.; John, A. T.; Sunny, J.; Hariharan, M. Access to the Triplet Excited States of Organic Chromophores. *Chem. Soc. Rev.* 2020, 49, 6122–6140.
- (12) Omary, M. A.; Patterson, H. H. Luminescence Theory. Encycl. Spectrosc. Spectrom. 1999, 1992, 1186–1207.
- (13) Jain, A.; Blum, C.; Subramaniam, V. Fluorescence Lifetime Spectroscopy and 20

Imaging of Visible Fluorescent Proteins, First Edit.; Elsevier, 2009.

- (14) Martínez-Fernández, L.; Corral, I.; Granucci, G.; Persico, M. Competing Ultrafast Intersystem Crossing and Internal Conversion: A Time Resolved Picture for the Deactivation of 6-Thioguanine. *Chem. Sci.* 2014, *5*, 1336.
- (15) Lodge, J. P. Fluorescence Spectrophotometry. In Methods of Air Sampling and Analysis; Routledge, 2017; 187–190.
- (16) Braslavsky, S. E. Glossary of Terms Used in Photochemistry, 3rd Edition (IUPAC Recommendations 2006). Pure Appl. Chem. 2007, 79, 293–465.
- (17) Zhu, Q. In Situ Planar Optical Sensors for Sediment Diagenesis Study. In Encyclopedia of Ocean Sciences; Elsevier, 2019; 147–156.
- (18) Marian, C. M. Spin-Orbit Coupling and Intersystem Crossing in Molecules. Wiley Interdiscip. Rev. Comput. Mol. Sci. 2012, 2, 187–203.
- (19) Kittel, C.; Holcomb, D. F. Introduction to Solid State Physics. Am. J. Phys. 1967, 35, 547–548.
- (20) Shur, M. Semiconductors. In *The Electrical Engineering Handbook*; Elsevier, 2005; 153–162.
- (21) König, D.; Casalenuovo, K.; Takeda, Y.; Conibeer, G.; Guillemoles, J. F.; Patterson, R.; Huang, L. M.; Green, M. A. Hot Carrier Solar Cells: Principles, Materials and Design. *Phys. E Low-dimensional Syst. Nanostructures* **2010**, *42*, 2862–2866.
- Liang, W. Y. Physics Education Related Content Recent Citations. *Phys. Educ.* 1970, 5, 226–228.
- Jin, H.; Debroye, E.; Keshavarz, M.; Scheblykin, I. G.; Roeffaers, M. B. J.;
 Hofkens, J.; Steele, J. A. It's a Trap! On the Nature of Localised States and Charge Trapping in Lead Halide Perovskites. *Mater. Horizons* 2020, *7*, 397–410.
- (24) Schwarz, J. A.; Contescu, C. I.; Putyera, K. Dekker Encyclopedia of Nanoscience and Nanotechnology. *Choice Rev. Online* 2005, 42, 42–2552.
- (25) Sum, T. C.; Mathews, N.; Xing, G.; Lim, S. S.; Chong, W. K.; Giovanni, D.; Dewi,
 H. A. Spectral Features and Charge Dynamics of Lead Halide Perovskites:
 Origins and Interpretations. Acc. Chem. Res. 2016, 49, 294–302.
- (26) Li, M.; Fu, J.; Xu, Q.; Sum, T. C. Slow Hot-Carrier Cooling in Halide Perovskites: 21
Prospects for Hot-Carrier Solar Cells. Adv. Mater. 2019, 31, 1802486.

- (27) Song, J.; Wei, C.; Huang, Z. F.; Liu, C.; Zeng, L.; Wang, X.; Xu, Z. J. A Review on Fundamentals for Designing Oxygen Evolution Electrocatalysts. *Chemical Society Reviews*. 2020, 49, 2196-2214.
- (28) Wolff, C. M.; Caprioglio, P.; Stolterfoht, M.; Neher, D. Nonradiative Recombination in Perovskite Solar Cells: The Role of Interfaces. Adv. Mater. 2019, 31, 1902762.
- (29) Wehrenfennig, C.; Eperon, G. E.; Johnston, M. B.; Snaith, H. J.; Herz, L. M. High Charge Carrier Mobilities and Lifetimes in Organolead Trihalide Perovskites. *Adv. Mater.* 2014, 26, 1584–1589.
- (30) Ghosh, T.; Aharon, S.; Etgar, L.; Ruhman, S. Free Carrier Emergence and Onset of Electron–Phonon Coupling in Methylammonium Lead Halide Perovskite Films. J. Am. Chem. Soc. 2017, 139, 18262–18270.
- (31) Frost, J. M.; Walsh, A. What Is Moving in Hybrid Halide Perovskite Solar Cells? Acc. Chem. Res. 2016, 49, 528–535.
- (32) Kratz, S.; Torres-Alacan, J.; Urbanek, J.; Lindner, J.; Vöhringer, P. Geminate Recombination of Hydrated Electrons in Liquid-to-Supercritical Water Studied by Ultrafast Time-Resolved Spectroscopy. *Phys. Chem. Chem. Phys.* 2010, *12*, 12169-12176.
- (33) Savenije, T. J.; Ponseca Jr, C. S.; Kunneman, L.; Abdellah, M.; Zheng, K.; Tian, Y.; Zhu, Q.; Canton, S. E.; Scheblykin, I. G.; Pullerits, T. Thermally Activated Exciton Dissociation and Recombination Control the Carrier Dynamics in Organometal Halide Perovskite. J. Phys. Chem. Lett. 2014, 5, 2189–2194.
- (34) Chong, W. K.; Giovanni, D.; Sum, T.-C. Halide Perovskites Photovoltaics, Light Emitting Devices, and Beyond; John Wiley & Sons, 2018.
- (35) Conibeer, G. J.; König, D.; Green, M. A.; Guillemoles, J. F. Slowing of Carrier Cooling in Hot Carrier Solar Cells. *Thin Solid Films* **2008**, *516*, 6948–6953.
- (36) Fu, J.; Xu, Q.; Han, G.; Wu, B.; Huan, C. H. A.; Leek, M. L.; Sum, T. C. Hot Carrier Cooling Mechanisms in Halide Perovskites. *Nat. Commun.* **2017**, *8*, 1300.
- (37) Kahmann, S.; Loi, M. A. Hot Carrier Solar Cells and the Potential of Perovskites for Breaking the Shockley–Queisser Limit. J. Mater. Chem. C 2019, 7, 2471–2486.

22

- (38) Ross, R. T.; Nozik, A. J. Efficiency of Hot-Carrier Solar Energy Converters. J. Appl. Phys. 1982, 53, 3813–3818.
- (39) Conibeer, G.; Shrestha, S.; Huang, S.; Patterson, R.; Xia, H.; Feng, Y.; Zhang, P.; Gupta, N.; Tayebjee, M.; Smyth, S.; et al. Hot Carrier Solar Cell Absorber Prerequisites and Candidate Material Systems. Sol. Energy Mater. Sol. Cells 2015, 135, 124–129.
- (40) Chung, S. Hot Carrier Solar Cells: Hafnium Nitride as an Absorber Material.2017, March.
- Li, Y.; Lai, R.; Luo, X.; Liu, X.; Ding, T.; Lu, X.; Wu, K. On the Absence of a Phonon Bottleneck in Strongly Confined CsPbBr₃ Perovskite Nanocrystals. *Chem. Sci.* 2019, 10, 5983–5989.
- (42) Yang, Y.; Ostrowski, D. P.; France, R. M.; Zhu, K.; van de Lagemaat, J.; Luther, J. M.; Beard, M. C. Observation of a Hot-Phonon Bottleneck in Lead-Iodide Perovskites. *Nat. Photonics* 2016, 10, 53–59.
- Jia, X.; Jiang, J.; Zhang, Y.; Qiu, J.; Wang, S.; Chen, Z.; Yuan, N.; Ding, J.
 Observation of Enhanced Hot Phonon Bottleneck Effect in 2D Perovskites. *Appl. Phys. Lett.* 2018, *112*, 143903.
- (44) Misra, P. K. Physics of Condensed Matter; Elsevier, 2012.
- (45) Srivastava, G. P. *The Physics of Phonons*; Routledge, 2019.
- (46) Bretschneider, S. A. Photophysics of Lead-Halide Perovskites. Johannes Gutenberg-Universität Mainz 2018.
- (47) Klemens, P. G. Anharmonic Decay of Optical Phonon in Diamond. *Phys. Rev. B* 1975, 11, 3206–3207.
- (48) Ridley, B. K. Electron Scattering by Confined LO Polar Phonons in a Quantum Well. *Phys. Rev. B* 1989, *39*, 5282–5286.
- (49) Review, P.; Lo, T.; Raman, S. Coherent Time-Resolved Investigation of LO-Phonon Dynamics in GaAs. *Phys. Rev. B* 1991, 43, 12049
- (50) Barman, S.; Srivastava, G. P. Long-Wavelength Nonequilibrium Optical Phonon Dynamics in Cubic and Hexagonal Semiconductors. *Phys. Rev. B-Condens. Matter Mater. Phys.* 2004, 69, 235208.
- (51) Yang, J.; Wen, X.; Xia, H.; Sheng, R.; Ma, Q.; Kim, J.; Tapping, P.; Harada, T.; 23

Kee, T. W.; Huang, F.; et al. Acoustic-Optical Phonon up-Conversion and Hot-Phonon Bottleneck in Lead-Halide Perovskites. *Nat. Commun.* **2017**, *8*, 14120.

- (52) Chen, J.; Messing, M. E.; Zheng, K.; Pullerits, T. Cation-Dependent Hot Carrier Cooling in Halide Perovskite Nanocrystals. J. Am. Chem. Soc. 2019, 141, 3532– 3540.
- (53) Price, M. B.; Butkus, J.; Jellicoe, T. C.; Sadhanala, A.; Briane, A.; Halpert, J. E.; Broch, K.; Hodgkiss, J. M.; Friend, R. H.; Deschler, F. Hot-Carrier Cooling and Photoinduced Refractive Index Changes in Organic–Inorganic Lead Halide Perovskites. *Nat. Commun.* 2015, *6*, 8420.
- (54) Prabhu, S. S.; Vengurlekar, A. S. Hot-Carrier Energy-Loss Rates in Alloy Semiconductors. *Phys. Rev. B* 1996, 53, 7815–7818.
- (55) Li, M.; Bhaumik, S.; Goh, T. W.; Kumar, M. S.; Yantara, N.; Grätzel, M.; Mhaisalkar, S.; Mathews, N.; Sum, T. C. Slow Cooling and Highly Efficient Extraction of Hot Carriers in Colloidal Perovskite Nanocrystals. *Nat. Commun.* 2017, 8, 14350.
- (56) Dai, L.; Deng, Z.; Auras, F.; Goodwin, H.; Zhang, Z.; Walmsley, J. C.; Bristowe, P. D.; Deschler, F.; Greenham, N. C. Slow Carrier Relaxation in Tin-Based Perovskite Nanocrystals. *Nat. Photonics* 2021, 1-7.
- (57) Boehme, S. C.; Brinck, S. ten; Maes, J.; Yazdani, N.; Zapata, F.; Chen, K.; Wood, V.; Hodgkiss, J. M.; Hens, Z.; Geiregat, P.; et al. Phonon-Mediated and Weakly Size-Dependent Electron and Hole Cooling in CsPbBr₃ Nanocrystals Revealed by Atomistic Simulations and Ultrafast Spectroscopy. *Nano Lett.* **2020**, *20*, 1819– 1829.
- (58) Narayanasamy, S. A.; Vellalapalayam, D. N. Revolution of Perovskite; Springer, 2020.
- (59) Kobayashi, Y.; Tsujimoto, Y.; Kageyama, H. Property Engineering in Perovskites via Modification of Anion Chemistry. *Annu. Rev. Mater. Res.* 2018, 48, 303–326.
- (60) Stranks, S. D.; Snaith, H. J. Metal-Halide Perovskites for Photovoltaic and Light-Emitting Devices. Nat. Nanotechnol. 2015, 10, 391–402.
- (61) Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. J. Am. Chem. Soc. 2009, 131,

24

6050-6051.

- (62) National Renewable Energy Laboratory, Best Research-Cell Effciencies Chart, Https://Www.Nrel.Govpvcell-Effciency.Html. 2021.
- (63) Zhu, Z.; Sun, Q.; Zhang, Z.; Dai, J.; Xing, G.; Li, S.; Huang, X.; Huang, W. Metal Halide Perovskites: Stability and Sensing-Ability. J. Mater. Chem. C 2018, 6, 10121–10137.
- (64) Parrey, K. A.; Ansari, S. G.; Aziz, A.; Niazi, A. Enhancement in Structural and Optical Properties of Cd Doped Hybrid Organic-Inorganic Halide Perovskite CH₃NH₃Pb_{1-x}Cd_xI₃ Photo-Absorber. *Mater. Chem. Phys.* **2020**, *241*, 122387.
- (65) Zhou, C.; Tarasov, A. B.; Goodilin, E. A.; Chen, P.; Wang, H.; Chen, Q. Recent Strategies to Improve Moisture Stability in Metal Halide Perovskites Materials and Devices. J. Energy Chem. 2022, 65, 219–235.
- (66) Bartel, C. J.; Sutton, C.; Goldsmith, B. R.; Ouyang, R.; Musgrave, C. B.; Ghiringhelli, L. M.; Scheffler, M. New Tolerance Factor to Predict the Stability of Perovskite Oxides and Halides. *Sci. Adv.* **2019**, *5*, 1–10.
- (67) Lou, S.; Xuan, T.; Wang, J. Stability: A Desiderated Problem for the Lead Halide Perovskites. Opt. Mater. X 2019, 1, 100023.
- (68) Haug, H.; Koch, S. W. Quantum Theory of the Optical and Electronic Properties of Semiconductors, Fifth Edition; World Scientific Publishing Company, 2009.
- (69) Zaini, M. S.; Ying, J.; Liew, C.; Ainliah, S.; Ahmad, A.; Mohmad, A. R.; Kamarudin, M. A. Quantum Confinement Effect and Photoenhancement of Photoluminescence of PbS and PbS/MnS Quantum Dots. *Appl. Sci.* 2020, 10, 1– 10.
- (70) García de Arquer, F. P.; Talapin, D. V.; Klimov, V. I.; Arakawa, Y.; Bayer, M.; Sargent, E. H. Semiconductor Quantum Dots: Technological Progress and Future Challenges. *Science.* 2021, 373, 8541.
- (71) Yuan, M.; Liu, M.; Sargent, E. H. Colloidal Quantum Dot Solids for Solution-Processed Solar Cells. Nat. Energy 2016, 1, 16016.
- (72) Zhou, Y.; Chen, J.; Bakr, O. M.; Sun, H.-T. Metal-Doped Lead Halide Perovskites: Synthesis, Properties, and Optoelectronic Applications. *Chem. Mater.* 2018, 30, 6589–6613.

- (73) Pradhan, N. Mn-Doped Semiconductor Nanocrystals: 25 Years and Beyond. J. Phys. Chem. Lett. 2019, 10, 2574–2577.
- (74) Bhargava, R. N.; Gallagher, D.; Hong, X.; Nurmikko, A. Optical Properties of Manganese-Doped Nanocrystals of ZnS. *Phys. Rev. Lett.* **1994**, *72*, 416–419.
- (75) Das Adhikari, S.; Guria, A. K.; Pradhan, N. Insights of Doping and the Photoluminescence Properties of Mn-Doped Perovskite Nanocrystals. J. Phys. Chem. Lett. 2019, 10, 2250-2257.
- (76) Luo, B.; Li, F.; Xu, K.; Guo, Y.; Liu, Y.; Xia, Z.; Zhang, J. Z. B-Site Doped Lead Halide Perovskites: Synthesis, Band Engineering, Photophysics, and Light Emission Applications. J. Mater. Chem. C 2019, 7, 2781–2808.
- (77) Chen, D.; Fang, G.; Chen, X. Silica-Coated Mn-Doped CsPb(Cl/Br)₃ Inorganic Perovskite Quantum Dots: Exciton-to-Mn Energy Transfer and Blue-Excitable Solid-State Lighting. ACS Appl. Mater. Interfaces 2017, 9, 40477–40487.
- (78) Parobek, D.; Roman, B. J.; Dong, Y.; Jin, H.; Lee, E.; Sheldon, M.; Son, D. H. Exciton-to-Dopant Energy Transfer in Mn-Doped Cesium Lead Halide Perovskite Nanocrystals. *Nano Lett.* **2016**, *16*, 7376–7380.
- (79) Tanaka, M.; Qi, J.; Masumoto, Y. Comparison of Energy Levels of Mn²⁺ in Nanosized-and Bulk-ZnS Crystals. J. Lumin. 2000, 87, 472–474.
- (80) Chen, W.; Tang, X.; Zang, Z.; Shi, Y.; Yang, Z.; Du, J. Tunable Dual Emission in Mn²⁺-Doped CsPbX₃ (X = Cl, Br) Quantum Dots for High Efficiency White Light-Emitting Diodes. *Nanotechnology* **2019**, *30*, 075704.
- (81) Das Adhikari, S.; Dutta, S. K.; Dutta, A.; Guria, A. K.; Pradhan, N. Chemically Tailoring the Dopant Emission in Manganese-Doped CsPbCl₃ Perovskite Nanocrystals. Angew. Chemie - Int. Ed. 2017, 56, 8746–8750.
- (82) Ball, J. M.; Petrozza, A. Defects in Perovskite-Halides and Their Effects in Solar Cells. Nat. Energy 2016, 1, 1-13.
- (83) Euvrard, J.; Yan, Y.; Mitzi, D. B. Electrical Doping in Halide Perovskites. Nat. Rev. Mater. 2021, 6, 531–549.
- (84) Kröger, F. A.; Vink, H. J. Relations between the Concentrations of Imperfections in Crystalline Solids. Solid state Phys. 1956, 3, 307–435.
- (85) Rau, U.; Schock, H. W. Cu(In,Ga)Se₂ Thin-Film Solar Cells; Elsevier Ltd, 2018.

26

- (86) Freysoldt, C.; Grabowski, B.; Hickel, T.; Neugebauer, J.; Kresse, G.; Janotti, A.;
 Van De Walle, C. G. First-Principles Calculations for Point Defects in Solids. *Rev.* Mod. Phys. 2014, 86, 253–305.
- (87) Kang, J.; Wang, L. W. High Defect Tolerance in Lead Halide Perovskite CsPbBr₃.
 J. Phys. Chem. Lett. 2017, 8, 489–493.
- (88) Yong, Z. J.; Guo, S. Q.; Ma, J. P.; Zhang, J. Y.; Li, Z. Y.; Chen, Y. M.; Zhang, B. B.; Zhou, Y.; Shu, J.; Gu, J. L. Doping-Enhanced Short-Range Order of Perovskite Nanocrystals for near-Unity Violet Luminescence Quantum Yield. J. Am. Chem. Soc. 2018, 140, 9942–9951.
- (89) Chen, J. K.; Ma, J. P.; Guo, S. Q.; Chen, Y. M.; Zhao, Q.; Zhang, B. B.; Li, Z. Y.; Zhou, Y.; Hou, J.; Kuroiwa, Y.; et al. High-Efficiency Violet-Emitting All-Inorganic Perovskite Nanocrystals Enabled by Alkaline-Earth Metal Passivation. *Chem. Mater.* 2019, 31, 3974–3983.
- (90) Ye, J.; Byranvand, M. M.; Martínez, C. O.; Hoye, R. L. Z.; Saliba, M.; Polavarapu,
 L. Defect Passivation in Lead- Halide Perovskite Nanocrystals and Thin Films:
 Toward Efficient LEDs and Solar Cells. *Angew. Chemie Int. Ed.* 2021, 202102360.

Chapter 2

Methodology

In this chapter, a brief introduction to the methodology used in this thesis project has been provided. Firstly, we will introduce the spectroscopy methods for the photopoysical characterization and their working mechanism, including steady-state and ultrafast spectroscopy. Afterward, other structural characterizations will be discussed, including X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR), inductively coupled plasma mass spectrometry (ICP-MS), transmission electron microscopy (TEM) equipped with structural and composition detectors and X-ray absorption spectroscopy (XAS). Finally, the synthesis methods of lead halide perovskite (LHP) QDs and Mn-doped LHP QDs are introducted. The methodology in this chapter will be beneficial for the analysis and understanding of the excited state dynamics studied in the following chapters.

2.1 Steady-state and ultrafast spectroscopies

2.1.1 Steady-state UV-vis absorption spectroscopy

Semiconductors containing energy levels (CB/VB) and energy band gap could absorb the photons in the range of ultraviolet (UV) and infrared light to excite the electrons to high energy levels. For a semiconductor, the lower energy gap between VBM to CBM, means it could absorb the light with longer wavelength. Absorption spectroscopy refers to the techniques that measure the absorption ability of photon as a function of wavelength by the material. The measured range of the absorption spectroscopy, or called Ultraviolet–visible (UV-vis) spectroscopy is in part of the ultraviolet, the visible regions and even part of infrared light from the optical spectrum.¹ The Beer-Lambert law is commonly applied to understand attenuation in physical optics. This law can be used to express the relationship between the attenuation of light through the materials and corresponding optical properties as shown in the following equation.

$$A = \varepsilon cl = \log \left(I_0 / I \right) \tag{2.1}$$

where A is the measured absorbance, I_{θ} is the intensity of the incident light, I is the transmitted intensity of light, ε is the molar absorptivity or extinction coefficient. l is the path length through the sample, and c the concentration of the absorbing species. From the Beer-Lambert law (equation 2.1), it can be seen that the absorbance is proportional to samples' concentration, molar absorbance coefficient and the distance the light travels through the sample.²



Figure 2.1 Schematic diagram of UV- visible spectrophotometer.

Based on the Beer-Lambert, the instrument used in ultraviolet-visible spectroscopy to measure the absorption spectroscopy is called UV-vis spectrophotometer. The main components of the UV-vis spectrophotometer are light source, samples holder, and detector (Figure 2.1). Depending on the wavelength, the light source normally selects tungsten filament (300-2500 nm), deuterium arc lamp (190-400 nm), Xenon arc lamp (160-2000 nm), and single beam or double beam is used in different spectrophotometer. The double beam can be seen as follows with reference to be compared. Total transmission (or zero Absorbance) will be taken for the reference beam, and the measurement is to calculate the ratio of the beam intensities between reference and measurement. With a single beam, the reference, I₀ usually is measured by blank sample or the cuvette only containing the solvent. Typically, the detector selects a photodiode, a photodiode array, a photomultiplier tube, or a charge-coupled device (CCD). The purpose of monochromator

is to select a narrow range of specific wavelengths of light from a broader range of wavelength to collect the intensity as a function of wavelength.¹

2.1.2 Steady-state photoluminescence spectroscopy

When a photon possessing the energy above the band gap energy, it will excite the electrons to occupy the allowed excited energy levels. Because this state is non-equilibrium, the excited electrons will return to the ground state by dissipating their excess energy through radiative and non-radiative processes. The photoluminescence occurs typically at the wavelength around the band gap energy, which could be allowed to determine the band gap energy, impurities level, and even composition. Meanwhile, photoluminescence can also be classified by fluorescence $(10^{-8}-10^{-4})$ and phosphorescence $(10^{-4}-10^{-2})$ according to the lifetime.³



Figure 2.2 Schematic diagram of the measurement of emission spectra in a spectrofluorometer.

The fluorescence of the QDs is recorded by an analytical instrument known as spectrofluoremeter. The excitation spectra, emission spectra and photoluminescence quantum yield (PLQY) can be carried out in this equipment. The main components of spectrofluorometer contain a laser source, monochromator of excitation light, sample holder, monochromator of emission light, detector, signal amplifier and recorder system (Figure 2.2). The laser source typical uses Xenon arc lamp to supply continuous light with a range of 160-2000 nm. The purpose of monochromators, excitation or emission, are used to mechanically select a narrow range of optical wavelengths from a broader range of wavelengths available at the laser. The two slits control the bandpass of the incident light or fluorescence intensity signal. Similar to the UV-vis spectrometer, there are two types

of detectors, one is a signal detector, and the other is a reference detector. The signal detector is to count the emission photons. The purpose of the reference detector is to monitor the Xenon laser for the correction of wavelength and output of the laser.⁴

2.1.3 Transient absorption spectroscopy (TA)

Transient absorption spectroscopy, also known as pump-probe spectroscopic technique, can be utilized to measure the photo-induced excited state dynamics of materials. This technique can be traced back to 1950 published by George Porter and Ronald G. W. Norrish, who discovered the high-intensity flash. In 1967, they were awarded by Nobel Prize in Chemistry "for their studies of extremely fast chemical reactions, effected by disturbing the equilibrium by means of very short pulses of energy".⁵ According to the timescale of photophysical process, two types of TA are needed: femtosecond TA (fs-TA) for fast processes, such as charge injection, defect trapping, singlet excited states and nanosecond TA (ns-TA) for slow processes, like energy transfer, electron transfer, triplet states or triplet-triplet annihilation. In transient absorption spectroscopy, the pumpprobe technique is set so that a laser pulse for exciting the sample is called pump, and a second pulse with certain delay time for measuring the changes in absorption as a function of time and wavelength, is called probe. The fraction of pump pulse typically is in safe range so that the excited state structure of the sample is not distubured during the probing. The transient absorption spectra ΔA (λ , τ) is achieved in the experiment through changing the delay time τ and recording the spectrum at each delay. This technique could be an important method to measure the dynamics of the excited charge carriers, including the electron and energy transfer, carrier trapping dynamics, hot carriers cooling and so on. The advantage of TA spectroscopy is that it could investigate the non-emissive or dark states in comparison to time-resolved fluorescence which we will discuss later.

Some characteristics signals can be observed in TA data (Figure 2.3). The first one is ground state bleach. After being excited by the pump pulse, part of species, i.e. molecules or semiconductors, will be excited into an excited state, and the population of species at the ground states will decrease. Consequently, the ground state absorption of excited samples will be less than non-excited samples, resulting in the negative signal. Meanwhile, due to the excited electrons populated at the excited state after pump, the absorption of probe pulse could contribute to the optically allowed transition from the lower excited state to higher excited states. This excited-state absorption will consequently contribute to a positive signal in the TA spectra. In a two-level system, stimulated emission will also occur when the probe pulse passes through the excited samples. The photons generated by the stimulated emission show the same direction and energy as the probe photons. The result is the increased intensity of photons which leads to a negative TA signal.⁶



Figure 2.3 (a) The schematic diagram of the TA with the pump pulse and the delayed probe pulse. (b) The schematic diagram for the TA with the ground-state bleach (GSB), stimulated emission (SE) and excited-state absorption (PIA).

Figure 2.4 shows a schematic diagram of an ultrafast TA setup, which describes the basic components used in this thesis. Some parameters need to be modified according to the requirement of experiments, but it does not affect the understanding of the TA equipment. The pulse is generated from a broadband oscillator with the duration of about 30 fs and wavelength of 800 nm. The amplification is needed because this pulse is too weak to perform any meaningful spectroscopy and it is achieved by the chirped-pulse amplification. The seed pulse from the oscillator is first stretched by temporally delaying the blue wavelength concerning the red wavelength. Afterward, the seed pulse will pass through the Pockels cell. After traveling back and forth in the cavity, it will pass through Ti:sapphire crystal until the saturation is reached after several passage, amplified and then compressed by temporally synchronization. Consequently, the laser system with specific fs pulse, energy, center wavelength, bandwidth, and a repetition rate is obtained. However, the wavelength at around 800 nm cannot be used to perform most of the TA experiments. In order to shift the wavelength to regions for our experiments, like visible light and near-IR, non-linear optical parametric amplifier (NOPA) is typically used. In

the NOPA system, the signal and idler are amplified by nonlinear polarization of the crystal. Due to the polarization,



Figure 2.4 Schematic diagram of the measurement of femtosecond transient absorption spectroscopy

the group velocity of the signal, idler, and pump beam are different, the idler beam can be adjusted by changing the angle between symmetry axis and laser beam. Therefore, the pump beam is allowed to be converted to idler and signal beam over a large propagation length. Besides wavelength, another important parameter delay time between the pump pulse and probe pulse can be regulated by a high-precision motorized computer-controlled translation state. In our setup system, it is possible to achieve the delay time 100 fs to 1 ns through this delay stage. Afterward, in order to evaluate the pump-induced absorption changes, the white-light continuum range from UV to infrared can be used as probe pulse. The wavelength range of probe beam varies depending on the non-linear optical crystals we used including sapphire or calcium fluoride. To adjust the fluence of pump beam, a neutral-density filter, or ND filter, is needed, especially for some fluence-dependent spectroscopic experiments.

Finally, we will talk about the collection of TA spectra and how the TA experiment is proceeded as the following description. At a specific delay, the time between pump and probe beam is fixed. The pump beam will first pass through a mechanical chopper which is synchronized to the amplifier before reaching the sample to excite and not excite the sample alternatively. Correspondingly, the detector alternatively measures intensity of the probe beam or called white light of a pumped $(I(\lambda)_{pumped})$ and unpumped $(I(\lambda)_{unpumped})$ sample, and, respectively, the difference in absorbance spectrum ΔA can be calculated by the following equation.

 $\Delta A (\lambda) = -\log (I(\lambda)_{pumped} / I(\lambda)_{unpumped})$ (2.2)

Then the delay line moves to the next delay time between the pump beam and probe beam. Sufficient shots are needed to improve signal-to-noise ratio for data analysis.⁷

2.1.4 Time-correlated single photon counting (TCSPC)

Time-correlated single photon counting (TCSPC) is a useful and statistical technique to characterize the fluorescence lifetime. In TCSPC, there are two beams involved in the measurement, one is the emission signal from samples, and the other is a reference signal generated from the light source. The monitoring of a single photon is achieved by the measurement of the arrival time of the signal from the sample in respect to a reference signal. This process can be repeated many times under a repetitive excitation laser pulse. Consequently, the phonon distribution over the decay time will be built up (Figure 2.5).



Figure 2.5 TCSPC technique for fluorescence lifetime analysis. (a) The schematic diagram of TCSPC technique. The reference pulse starts the clock and the clock will stop when the sample signal arrive. (b) The time measured for one such start-stop measurement is then stored by increasing count in a histogram.

The main components for the TCSPC contains light source, sample holder, detector, constant fraction discriminators (CFD), electrical delays (DEL), the time-to-amplitude converter (TAC), amplifier (between the TAC and ADC), analog to digital converter (ADC)

and digital memory (Mem) (Figure 2.6). The incoming pulse is evaluated by pulse height and only events with the pulse height higher than a given threshold are selected for next signal processing. The wavelength of the beam source replies on the requirement of the experiment and the electronic band gap of the sample. The detector will determine the fraction, threshold zero-crossing level and constant fraction delay. The function of CFD is applied to collect accurate timing information from the detector and then the signal from the CFD will be fed to a Time to TAC. This circuit is very important in determining when is started and stopped by signal. The voltage obtained from the TAC to ADC will provide the digital timing value to address the histogram.⁸



Figure 2.6 The schematic diagram of the components for TCSPC.

2.2 Structural characterizations

2.2.1 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a powerful characterized technique for revealing material surface information about the elemental compositions, electronic state, and chemical states. The XPS spectra are obtained through collecting electrons as a function of their kinetic energies from the surface of materials irradiated by X-ray beam at around 1-10 nm. Because each atom has characteristic orbitals and corresponding peaks, the energy and intensity of these peaks can be identified to elements with the exception of hydrogen and helium. The absorption of the incident X-ray beam will lead to the ejection of the photoelectrons of samples to escape the atom in a given material. The energy of the ejected electrons is measured by the detector for further analysis. A typical XPS spectrum plots the number of electrons with specific energy and characteristic XPS peaks for each element. The energy of incident X-ray with a particular wavelength is E_{photon} , and the measure emitted electrons' kinetics energy is $E_{kinetics}$. Therefore, the binding energy $E_{binding}$ (BE) can be calculated by following equation.

$E_{binding} = E_{binding} - (E_{binding} + \Phi)$ (2.3)

 Φ is the work function for the specific surface of the material. In measurement, the correction for the work function is needed due to the existence of contact potential. For a typical XPS system, the main components are X-ray source, vacuum system, sample holder, electron energy analyzer and data process system. The irradiated X-rays are usually generated by an anode (typically Mg or Al Ka radiation with 1253.6 eV or 1486.6 eV) hit by a high-energy (~10 keV) electron beam. Depending on the anode materials used, X-rays with different energy will be emitted. A cooling system with cycled water is needed to decrease the heat converted from incident electron energy. After illumination with sufficient energy from X-ray, photoelectrons will escape from the sample's surface into the vacuum chamber to be further analyzed by the energy dispersive analyzer and data acquisition.⁹

2.2.2 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) has been widely used in measuring morphology, microstructures and elemental information, including the QDs in this thesis. The above information is mainly obtained from electron matter interaction, such as transmitted electrons, elastic/inelastic scattering, characteristic X-ray and so on. When electron beam hits on the samples, signals are generated. The composition, valence, and structure information is contained in these signals. The transmitted electrons are used to characterize the morphology of samples. The resulting images are based on the massthickness contrast, phase contrast and diffraction contrast.

In contrast, scanning transmission electron microscopy (STEM) normally uses an annular detector, like high-angle angular dark field (HAADF), to collect the scattered electrons. Therefore, the HAADF-STEM is highly sensitive to the atomic number, also called Z-contrast. The elemental composition can be measured by the characteristic X-rays using

energy-dispersive X-ray (EDX) detector. Meanwhile, because crystal can be regarded as a periodic array, a collective scattering phenomenon with electrons being (nearly elastically) scattered could generate electron diffraction. Hence, from electron diffraction, we could analyze the structural information.

The main components of TEM mainly include electron gun, vacuum system, electromagnetic lenses, specimen stage, and imaging system. The electron gun could be made of tungsten filament or lanthanum hexaboride source. There are two types to emit electrons, thermionic and field electron emission. The whole system should be maintained in a high vacuum to avoid scattering between air and electrons and this scattering will reduce the resolution. Meanwhile, high vacuum system is beneficial to protect the filament. A number of airlocks and pumps are needed to evacuate the whole column. The electromagnetic lens is designed to focus the parallel electrons. The lens typically consists of coils. The electromagnetic field is created when an electric current passed through these coils. The strength of electromagnetic is dependent on the current. Normally, there are three stages of lens in the TEM, condenser lens for primary beam formation, objection lens for focusing the beam and project lenses for expanding the beam onto the phosphor screen. The specimen stage allows the holder to be rotated within angles. Finally, for the imaging devices, fluorescent screen for real-time imaging and adjustments and chargecoupled device (CCD) for images are the two basic imaging devices in modern TEM instruments.¹⁰

2.2.3 Electron paramagnetic resonance (EPR)

Electron paramagnetic resonance (EPR) is a non-destructive, noninvasive, highly sensitive, and accurate analytical technique method to characterize the materials with unpaired electrons, especially useful for studying the metal complexes, organic metals and transition metals.

Each electron has spin quantum number $s = \frac{1}{2}$ and a magnetic moment with $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$. When applying the external magnetic field B_0 , the magnetic moment will align either parallel ($m_s = +\frac{1}{2}$) or antiparallel ($m_s = -\frac{1}{2}$) to the field. Due to the Zeeman effect desribed in the following equation, each alignment has a specific energy. $E = m_s g_{e UB} B_0$ (2.4)

37

In this equation, g_e is called g-factor and u_B is the Bohr magneton. Because g_e and u_B are constant, the splitting of the energy is proportional to the strength of magnetic according to the following description. The electron spin can be changed by absorbing or emitting a phonon when the energy of the phonon obeyed the resonance condition $hv = \Delta E$.

 $\Delta E = E_{\frac{1}{2}} - E_{-\frac{1}{2}} = g_{e}u_{B}B_{0} \qquad (2.5)$ Experimentally, the collection of paramagnetic centers is exposed to microwaves at a fixed frequency. The gap of energy states between the ms = $+\frac{1}{2}$ and ms = $-\frac{1}{2}$ will be widen when increasing an external magnetic field until microwave energy matches the splitting energy.¹²

2.2.4 Inductively coupled plasma mass spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry (ICP-MS), as a type of mass spectrometry, is widely used to detect metals or several non-metals in a liquid solution even at very low concentration. The components of ICP-MS mainly include an ion source, a sample interface, ion lens, a mass spectrophotometer, and a detector. The ion source can ionize over 90% of many elements. The ionized elements will then pass through the sampling interface for the further mass analysis. There are there parts in the sampling interface unit, the sampling cone, the skimmer cone, and a rotary gear pump ventilates between two cones. The main purpose of sampling cone and skimmer cone is to converge ions into the mass spectrophotometer through the ion lens. Finally, the ions will be sorted by mass spectrophotometer detected by the ion detector.¹³

2.2.5 X-ray absorption spectroscopy (XAS)

X-ray absorption spectroscopy (XAS) is an advanced technique for determining the local geometric and electronic structures with tunable X-ray beam. The information measured from XAS is the X-ray absorption coefficient of a material as a function of energy. Since each element has its own characteristic absorption edges, XAS is a powerful method in studying: (i) spatial locations under local environments, (ii) their oxidation state, (iii) disordered structure, (iv) bond distance, and so on.¹⁴

XAS contains two parts: one is extended X-ray absorption fine structure (EXAFS) and the other is X-ray absorption near edge structure (XANES). Generally, in the low kinetic energy in the range of 5-150 eV, the multiple scattering is dominant in XANES spectra

because the photoelectron backscattering amplitude by neighbor is very large. While in the high kinetic energy above 150 eV, the excited photoelectron is related to the single backscattering because amplitude photoelectron scattering is very low. Therefore, EXAFS is a powerful tool in determining the fine structure, like interatomic distances.¹⁵

2.3 Synthesis of Mn-doped QDs

Typically, the Mn-doped CsPbX₃ LHPs (X is halogen, like Cl, Br and I) QDs are prepared by hot injection methods. The first step is to synthesize Cs-OA. An amount of Cs₂CO₃, oleic acid (OA), and 1-octadecene (ODE) are added into a three-neck round-bottom, evacuated to vacuum and refilled with argon or N₂, dried at about 120 °C for a certain time, then heated to around 150 °C and waiting for several minutes until all Cs₂CO₃ reacted with OA before using. Then, the next step is to prepare Mn-doped LHPs QDs. Typically, an amount of PbX₂, MnX₂, oleylamine (OAm), OA, ODE were added to a three-neck round bottom flask, evacuated and refilled with Ar or N₂ similar to the description as above to remove the air. Then the solution was heated to 120 °C for 30 minutes. Then an amount of dried OAm and dried OA were subsequently injected to the solution. The Cs-oleate precusor will be swiftly injected under the injection temperature. Followed by injection, the solution will be cooled by ice/water bath. After reaction, the aggregated QDs will be centrifuged, purified and redispersed in toluene for further measurement. The details for each part can be seen in experiment part (Chapter 3-4).¹⁶

References

- Hanlan, J.; Skoog, D. A.; West, D. M. Principles of Instrumental Analysis; Cengage learning, 1973; Vol. 18.
- (2) Swinehart, D. F. The Beer-Lambert Law. J. Chem. Educ. 1962, 39, 333.
- (3) Harris, D. C.; Bertolucci, M. D. Symmetry and Spectroscopy: An Introduction to Vibrational and Electronic Spectroscopy; Courier Corporation, 1989.
- Bostian, K. A. Instrumentation for Differential Fluorescence Spectroscopy. Anal. Biochem. 1977, 82, 353–361.
- (5) The Nobel Prize in Chemistry 1967. NobelPrize.Org. Nobel Media AB 2020. Fri.
 27 Mar 2020. Https://Www.Nobelprize.Org/Prizes/Chemistry/1967/Summary/.
- Berera, R.; van Grondelle, R.; Kennis, J. T. M. Ultrafast Transient Absorption Spectroscopy: Principles and Application to Photosynthetic Systems. *Photosynth. Res.* 2009, 101, 105–118.
- (7) Monti, S.; Chiorboli, C. Transient Absorption Spectroscopy. In *The Exploration of Supramolecular Systems and Nanostructures by Photochemical Techniques*; Springer, 2012; 185–207.
- (8) O'Connor, D. Time-Correlated Single Photon Counting. In *The IUPAC Compendium of Chemical Terminology*; International Union of Pure and Applied Chemistry (IUPAC): Research Triangle Park, NC, 2014.
- (9) Watts, J. F.; Wolstenholme, J. An Introduction to Surface Analysis by XPS and AES; Wiley, 2019.
- (10) Subramanian, S.; Rai, R. Transmission Electron Microscopy. In Microelectronics Failure Analysis; ASM International, 2019; 461–484.
- (11) Tang, C. Y.; Yang, Z. Transmission Electron Microscopy (TEM). In *Membrane Characterization*; Elsevier, 2017; 145–159.
- (12) Weil, J. A.; Bolton, J. R. Electron Paramagnetic Resonance: Elementary Theory and Practical Applications, Second Edition; John Wiley & Sons, 2006.
- (13) Nageswaran, G.; Choudhary, Y. S.; Jagannathan, S. Inductively Coupled Plasma Mass Spectrometry. In Spectroscopic Methods for Nanomaterials Characterization; Elsevier, 2017; Vol. 2, 163–194.

- (14) Cruz, I. F.; Freire, C.; Araújo, J. P.; Pereira, C.; Pereira, A. M. Multifunctional Ferrite Nanoparticles: From Current Trends Toward the Future. In *Magnetic Nanostructured Materials*; Elsevier, 2018; 59–116.
- (15) Yano, J.; Yachandra, V. K. X-Ray Absorption Spectroscopy. *Photosynth. Res.* 2009, 102, 241–254.
- Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* 2015, *15*, 3692–3696.

Chapter 3 Charge–carrier dynamics in Mn-doped CsPbCl₃ QDs

Doping transition metal ions in semiconductor quantum dots (QDs) especially perovskite QDs recently has been proved as an effective approach to tune the photo-physical features of the QDs. On one hand, some transition metal ions in the QDs (e.g. Mn²⁺, or Cu²⁺) can provide d-d emissive state with a long lifetime. Their broad yellow-orange emission have exhibited potential application in white light-emitting diodes (LEDs). On the other hand, the doping is also expected to distort the local lattice structures and consequently induce many defects and traps in QDs restricting the final photoluminescence quantum yield. Although some efforts have been made to minimize the effect of defects and improve the PLQY in such doped QDs, the detailed influence of transition metal ion doping on the defect states and consequently on the emission properties of QDs has not yet been clearly rationalized. The simultaneous contribution from intrinsic emission of QDs, QD-todopant energy transfer as well as defect trapping on the photo-physics increase the complexity to interpret the charge carrier dynamics. We noticed some recent researches proposed a two-step shallow trap mediated energy transfer model where the shallow trap states between the Mn^{2+} states and intrinsic exciton states of the QDs serve as an intermediate channel for the migration of charge carriers. However the origins of such trap states have not been justified. Furthermore, such model cannot fully rationalize the dependence of doping level on the final PLQY, which is the crucial parameter for the device application.

In this work, we studied the correlation between structure and photo-induced charge carrier dynamics in Mn^{2+} doping in CsPbCl₃ perovskite QDs (one of the benchmark samples nowadays for efficient dopant emission) with different doping level. We first discovered the defect structure that would be induced by Mn^{2+} doping via DFT calculation, which reveals that Mn^{2+} doping qualitatively changes the type of the defects from shallow

antisites Pb_{Cs} (undoped) for electron trapping to deep interstitials Cl_i (doped) for hole trapping. The complementary spectroscopic studies by transient absorption and timeresolved photoluminescence unambiguously assign the pathway and rate of QD to dopant energy transfer, which has been confused with charge carrier trapping in the previous literature. The detailed analysis of spectroscopic results shows parallel competition instead of mediation between exciton-dopant energy transfer and defect trapping at early timescale (<100 ps), which determines the final PLQY of the CsPbCl₃ QDs. Such competition also rationalizes the non-monotonic evolution of PLQY with the Mn²⁺ doping level.

This chapter is a published article: J. Phys. Chem. Lett. 2020, 11, 9, 3705–3711, https://doi.org/10.1021/acs.jpclett.0c01050.

This published article is given below and with reproduced here with the permission of Journal of Physical Chemistry Letters, which is ACS journal.



pubs.acs.org/JPCL

Modulating Charge-Carrier Dynamics in Mn-Doped All-Inorganic Halide Perovskite Quantum Dots through the Doping-Induced Deep Trap States

Jie Meng, ◆ Zhenyun Lan, ◆ Mohamed Abdellah, Bin Yang, Susanne Mossin, Mingli Liang, Maria Naumova, Qi Shi, Sol Laura Gutierrez Alvarez, Yang Liu, Weihua Lin, Ivano E. Castelli, Sophie E. Canton, Tönu Pullerits, and Kaibo Zheng*

Cite This: J. Phys	s. Chem. Lett. 2020, 11, 3705–3.	711	Read Online		
ACCESSI	III Metrics & More		E Article Recommendations	I	Supporting Information

ABSTRACT: Transition-metal ion doping has been demonstrated to be effective for tuning the photoluminescence properties of perovskite quantum dots (QDs). However, it would inevitably introduce defects in the lattice. As the Mn concentration increases, the Mn dopant photoluminescence quantum yield (PLQY) first increases and then decreases. Herein the influence of the dopant and the defect states on the photophysics in Mn-doped CsPbCl₃ QDs was studied by time-resolved spectroscopies, whereas the energy levels of the possible defect states were analyzed by density functional theory calculations. We reveal the formation of deep interstitials defects (Cl₁) by Mn^{2+} doping. The depopulation of initial QD exciton states is a competition between exciton-dopant energy transfer and defect trapping on an early time scale (<100 ps), which determines the final PLQY of the QDs. The present work establishes a robust material optimization guideline for all of the emerging applications where a high PLQY is essential.



Letter

oping Mn²⁺ ions into the lattice of quantum dots (QDs) has attracted extensive attention because it creates stable sub-band-gap Mn^{2+} d-d emission (${}^{4}T_{1}-{}^{6}A_{1}$) with an extremely long lifetime.¹⁻⁴ This property broadens the scope of the optoelectronic application of these QDs.^{5,6} Because the Mn²⁺ d-d emission is triggered by the energy transfer (ET) from the QDs after photoexcitation, selecting host QDs with a suitable optical band gap and a high photoluminescence quantum vield (PLQY) is essential. Doping Mn²⁺ in conventional II-VI semiconductors QDs is feasible, but the PL of the QDs themselves is restricted by the sub-band-gap defect states.⁶⁻¹¹ On the contrary, the highly ionic lattice of all inorganic cesium lead halide (CsPbX₃) perovskite QDs renders these nanomaterials highly tolerant to defects with a much higher PLQY compared with the II-VI QDs.^{12,13} In addition, Mn²⁺ and Pb²⁺ have similar ionic radii and comparable bond dissociation energies toward halide ions.¹⁴ Therefore, doping Mn^{2+} ions in perovskite QDs has recently been widely investigated.^{15–21} However, the reported PLQY of the Mn^{2+} d-d emission in doped QDs is below expectations.^{21,22} This raises important questions regarding the dynamics of the excitons and charge carriers after the excitation of host QDs and their correlations with the dopants.²¹ Previous research focused on the exciton-dopant ET process without considering any influence from the defect trapping 15,23,24 Recent studies put forward a trap-mediated exciton-dopant ET model where initially excited charge carries would first be localized in

a shallow trap before they could migrate to the Mn^{2+} states.^{5,25,26} However, the origin and energy alignment of such a trap state versus a dopant state remain unjustified. In addition, doping metal ions could generate deep defects in the lattice to quench the PL emission,^{27–29} which may more greatly affect the final PLQY of the doped QDs.

In this contribution, we first confirm the major internal trap states in Mn-doped CsPbCl₃ QDs to be the doping-induced interstitials Cl_i via density functional theory (DFT) calculations. Such defect states locate deep within the Mn²⁺ orbitals. The charge-carrier trapping as well as the exciton—Mn ET dynamics with various doping concentrations are then analyzed using transient absorption (TA) and time-resolved photoluminescence (TRPL) spectroscopies. We conclude that exciton—Mn ET occurs within tens of picoseconds, with the transfer rate first increasing and then decreasing with the increase in Mn dopants. Concurrently, hole trapping at the doping-induced Cl_i states happens at ~83 ps. Instead of mediating exciton—dopant ET, such deep trap states mainly quench the intrinsic emission from the QDs, which competes

 Received:
 April 3, 2020

 Accepted:
 April 24, 2020

 Published:
 April 24, 2020



The Journal of Physical Chemistry Letters

with the ET process. Such competition determines the overall PLQY of the dual emission in QDs. This work provides a novel foundation for understanding the photophysics of transitionmetal-doped perovskites ODs.

The Mn-doped CsPbCl₃ QDs were prepared by the reported hot-injection methods.²³ (For details, see the Experimental Section in the SI.) Figure 1a,b shows the morphology and the



Figure 1. (a) Atomic model demonstrating the replacement of Mn in the substitution position of Pb in the CsPbCl₃ lattice. (b) HADDF-STEM image of Mn-doped CsPbCl₃ QDs, with the inset showing the atomically resolved image of an individual QD. The red dots represent the Cs atom columns, and the yellow dots represent the (Pb+Cl) atom positions. (c) Absorption (solid line) and emission spectra (dotted line) of Mn-doped CsPbCl3 with different Mn concentrations. (d) Photograph of QDs in toluene solutions with the increase in Mn concentration under UV lamp excitation and the corresponding absolute PLQY of Mn-doped CsPbCl3 with different Mn concentrations. (e) Room-temperature X-band EPR spectra of Mn-doped CsPbCl₃ QDs with different Mn concentrations in the toluene solution. The spectrum of the most concentrated sample is also plotted after zooming out 20 times. (f) EPR spectra of Mn-doped CsPbCl₂ QDs with 0.6% Mn concentration in hexane solution at room temperature, in the solid-state, and in a frozen hexane solution at 77 K. The asterisk denotes a small g = 2 impurity.

structure of the doped QDs. The TEM images in Figure S1 indicate that Mn doping could slightly shrink the crystal size of QDs from 8.6 to 7.3 nm, probably due to the higher formation energy of doped QDs confirmed in the following calculations, which reduces the critical particle size during the Ostwald ripening. The Mn concentrations in the lattice determined from coupled plasma mass spectroscopy (ICP-MS) are about 0, 0.1, 0.2, 0.6, 1.8, and 38% with the increasing MnCl₂ precursor concentration. (See Table S1 for the feeding ratio.) Figure 1c illustrates the absorption and emission spectra of undoped and doped QDs. The absorption band edge of all QDs is ~405 nm, corresponding to an optical band gap (E_g) of 3.06 eV regardless of the doping level. No obvious dopantrelated absorption band can be observed due to the spinforbidden d-d transition of the Mn^{2+} dopant states (${}^{4}T_{1} - {}^{6}A_{1}$). The doped QDs exhibit an extra broad Mn²⁺ d-d emission band at ~600 nm, in addition to the narrow exciton emission

pubs.acs.org/JPCL

Letter

at ~405 nm. Figure 1d and Table S2 illustrate the evolution of the PLQY for these two types of emission with the increasing doping level. The band-edge exciton PLQY decreases monotonously, whereas the Mn²⁺ emission QY first increases and then decreases with the maximal QY at a Mn concentration of 0.6%. Consequently, the overall PLQYs of the QDs follow the same trend as those of the Mn²⁺ emission. The PLQY change should directly correlate with the rates between the radiative and nonradiative recombinations of photogenerated charge carriers. For conventional QDs, it is generally interpreted by the diminishing/introduction of the defect states. However, in our case, the QD-Mn ET also contributes to depopulating the initial photoexcited charge carriers in the host QDs,¹⁶ which complicates the scenario. Here we first analyze the possible condition of doping-induced defects via structure characterization. TEM studies confirm the absence of long-range-order lattice changes after doping (cf. Figures S2 and S3). The electron paramagnetic resonance (EPR) measurement of the as-obtained QDs (Figure 1e) and QDs under various conditions (Figure 1f) demonstrates that Mn²⁺ ions occupy Pb²⁺ sites with an octahedral ligand field and uniform distribution in the lattice. (For a detailed discussion, see the SI.) The Cs 3d, Pb 4f, and Cl 2p X-ray photoelectron spectroscopy (XPS) core levels also remain constant for all samples (Figure S4). These results all indicate the unchanged local structure with different doping concentrations.

To further establish the appearance of the doping-induced defect states in the QDs, DFT calculations (Figure 2 and Figures S6-S9) have been conducted. (For details of the calculation, see the Experimental Section in the SI.) The calculated E_g from the valence band maximum (VBM) to the conduction band minimum (CBM) of undoped CsPbCl₃ is ~ 2.5 eV (Figure 2), which is naturally smaller than the experimental values when using the PBE exchange-correlation functional. The CBM and VBM are dominantly contributed by Pb and Cl orbitals, respectively (Figure S6). The calculated Mn d orbital resides within the $E_{g'}$ with the d-d transition energy around 2.0 eV, which is consistent with the Mn²⁺ emission energy observed in the PL spectra. In the next step, all of the possible point defects in the Mn-doped lattice, namely, vacancies $(Mn-V_{Cs}, Mn-V_{Pb}, and Mn-V_{Cl})$, interstitials $(Mn-Cs_{\nu}, Mn-Pb_{i\nu})$ and $Mn-Cl_i)$, and antisites (Mn-Cs_{Pb}, Mn-Cs_{Cb}, Mn-Pb_{Cs}, Mn-Pb_{Cb}, Mn-Cl_{Cs}, and Mn-Clpb) were simulated. The intrinsic point defects in undoped QDs were also evaluated as a reference. (For a detailed methodology, see the SI.) The energy configurations of the calculated VBM/CBM and the Mn2+ states in the presence of all types of defect states for undoped and doped QDs are summarized in Figure 2a,b, with the corresponding formation energy of each defect listed in Tables S3 and S4, respectively. Here three conditions proved by experiment should be simultaneously fulfilled to determine which defects can be valid: (1) Mn^{2+} states should locate within the E_{qr} (2) the E_g of the host QDs and the energy gap of the $Mn^{2+\circ}d-d$ states should stay unchanged when defects are induced, as evidenced by the absorption and PL results, and (3) the formation energy of such a defect should be low. Three points (A, B, and C in Figure 2c) representing various Cl compositions were chosen to evaluate the defect formation energies due to the narrow available equilibrium chemical potential region for CsPbCl₃ (Figure 2d). Here the dominating defect states, Pb_{Cs}, in neat CsPbCl₃ are much easier to generate with lower formation energy as well as shallower energy

45



Figure 2. (a) Energy diagram of undoped CsPbCl₃ and (b) Mn-doped CsPbCl₃ with the existence of defects from DFT calculation. The green and blue columns represent the CB and the VB, respectively. The orange bars are the Mn d orbitals, the black bars represent the defect levels, and the pink dotted lines are the positions of the Fermi level. (The core-level Pb s orbitals are set as the reference.) (c) Stability regions of different compounds against Cl and Pb chemical potentials in CsPbCl₃. The shaded region indicates the available equilibrium chemical potential region for CsPbCl₃. Three representative points A ($\mu_{Cl} = -0.300$, $\mu_{Pb} = -2.700$, $\mu_{Cs} = -4.000$), B ($\mu_{Cl} = -0.983$, $\mu_{Pb} = -1.350$, $\mu_{Cs} = -3.303$), and C ($\mu_{Cl} = -1.665$, $\mu_{Pb} = 0$, $\mu_{Cs} = -2.605$) are chosen for the calculations of the formation energies. (d) Schematic picture of vacancies, interstitials, and antisites defects. Their positions are marked by red dashed circles.

compared with the previously reported V_{Cl} in the same system. 27 On the contrary, Mn^{2+} doping induces new possible defects, Cl interstitials (Cl_i). According to the energy level alignment, the Pb_{Cs} in neat QDs tend to trap electrons, and Cl_i in doped QDs are more likely to trap the holes. These defects are all generated by the displacement of the Pb ions from the $[PbCl_6]^{4-}$ octahedra toward the A cation sites after the partial substitution of Pb^{2+} ions with Mn^{2+} ions, as illustrated in Figure 2d.

The above structural analysis suggests diminished intrinsic shallow traps together with the formation of deep hole traps in the CsPbCl₃ lattice owing to the Mn²⁺ doping. TA was then used to explore the impact of doping on the charge-carrier dynamics (Figure 3 and Figures S10 and S11). The TA spectra of all samples show characteristic band-edge ground-state bleach (GSB) at ~400 nm due to the band-edge-state filling. The singular value decomposition (SVD) fitting of the spectra resolves four main components in undoped QDs with lifetimes of 3.2 ps, 38 ps, 540 ps, and 15 ns (Figure 3a). The spectral features for all components reflect the depopulation of the band-edge excited states. Any high-order Auger processes can first be excluded due to the low excitation intensity with excitation density per QD, $\langle N \rangle \ll 1$. (See the SI for details.) The lifetime of the longest component is similar to the slow decay component in the TRPL kinetics of undoped QDs (7.3 ns, Figure S12) and therefore should be assigned to the radiative recombination. The other three components should then be related to the nonradiative recombination of the excited charge carriers. In doped QDs, four main spectral

components can still be fitted but with shorter lifetimes, as shown in Figure 3b (i.e., 3.2 ps, 20 ps, 540 ps, and 6.5 ns). The GSB recovery kinetics in Figure 3c further demonstrates the faster excited-state depopulation in doped QDs with extra charge-carrier recombination pathways. Previous reports have directly compared the GSB kinetics in doped and undoped QDs and extracted the dopant-Mn ET time to be 380 ps.^{15,16,24} However, additional trapping processes are introduced via Mn doping, as previously discussed. Here we can probe the rising edge of the ps-TRPL kinetics for the Mn²⁺ emission in doped QDs to unambiguously assign the dopant-Mn ET dynamics (Figure 4a). The time constants for the rising first decreases and then increases with the increasing Mn concentration, as illustrated in Figure 4a. Such a trend also resembles the early time dynamics of TA GSB decays in Figure 3c. As summarized in Table S5, the lifetimes of two TA spectral components, $\tau_1 = 3.2$ ps and $\tau_3 = 540$ ps, are similar for the undoped and the doped samples regardless of the doping level. We propose that these concurrent components represent the same surface trapping pathways where the excited electrons get trapped within 3.2 ps and then relax to ground state in 540 ps. Such trapping only occurs within a part of the QDs overwhelming other recombination processes in those dots. Otherwise, the trapping would quench the emission from all QDs. This surface-trapping process should also be insensitive to the internal defects induced by the doping. Such fast surface trapping within picoseconds is also observed in conventional CdSe QDs.³⁰ The spectral features of the second components are identical for undoped and all doped QDs

The Journal of Physical Chemistry Letters



Figure 3. TA spectra (bottom) of (a) undoped CsPbCl₃ QDs and (b) Mn-doped CsPbCl₃ QDs (0.6%) and the corresponding SVD fitting (upper) ($\lambda_{exc} = 370 \text{ nm}$). (c) TA kinetics at the main GSB, illustrating the depopulation of the excited state for CsPbCl₃. (d) Schematic illustration of the kinetic parameters for a three-level Mn-doped QD system. S_0 , S_1 , and S_2 represent the ground states, dopant excited states, and QD excited state, respectively. k_{ET} refers to the QD to Mn^{2+} ET rate, and k_{mr}^{QD} is the hole-trapping rate together with other nonradiative recombination pathways. k_{Mn} is the Mn²⁺ decay rate constant.

(blue line in Figure 3b and Figure S11), implying the similar excited species. The lack of positive excited-state absorption after the band-edge bleach (410 nm) indicates the absence of an excitonic Stark shift and therefore should be assigned to the transfer of dissociated free charge carriers. Their rate constants (k_1) change with the doping level, following the same trend as the ET rates, $k_{\rm ET}$, extracted from TRPL but with higher values, as depicted in Figure 4c. We noticed that such "delayed" building up of the Mn2+ emission has been observed and explained by other groups using the shallow trap-state intermediated ET model 5,25 However, on the basis of our theoretical calculation, the Cl_i trap states reside well above the Mn ⁶A₁ orbital by 0.45 eV (Figure 2b), which is much larger than the thermal energy. This means that the detrapping of the localized holes at the trap states to Mn²⁺ states is unlikely. Instead, the trapped hole tends to relax to the ground state, serving as an additional nonradiative recombination pathway. Therefore, the overall excited-state depopulation dynamics in the pool of QDs with QD-Mn²⁺ ET can be expressed by the three-level system (Figure 3d), whereas the TA decay rate k_1 should be a sum of the nonradiative recombination rate, k_{nr}^{QD} , and the $k_{\rm FT}$.³¹ (For a detailed explanation, see the SI.) This is consistent with the observation in Figure 4c. We can extract a nonradiative recombination rate related to hole trapping, $k_{\rm nr}^{\rm QD}$ $\approx k_1 - k_{\rm ET}$, to be ~0.012 ps⁻¹ (83 ps), which remains constant regardless of the doping level. The competition between ET and carrier trapping can then be quantified by ET efficiency, η_i as plotted in Figure 4d,

$$\eta = \frac{I_{\rm Mn}}{I_{\rm tr} + I_{\rm Mn}} = \frac{k_{\rm ET}}{k_{\rm nr}^{\rm QD} + k_{\rm ET}} = \frac{k_{\rm ET}}{k_{\rm 1}}$$
(1)

The dependence of the η complies with the PLQY depicted in Figure 1c. On the contrary, the Mn²⁺ emission efficiency after ET is independent of the doping levels, as evidenced by the constant emission lifetime, as shown in Figure 4b. Moreover, the lifetime of the slowest TA GSB components (i.e., τ_4 in Figure 4d) decreases with the increasing Mn doping level. This component should be attributed to the other pool of QDs without dopant-Mn ET and the fast surface trapping. The shortened lifetime demonstrates the enhanced nonradiative recombination of excited charge carriers in this pool of QDs. Therefore, we can conclude that the evolution of the PLQY with the Mn doping should be dominated by (1) the competition between the dopant-Mn ET efficiency and the doping-induced trapping at Cl_i defect states and (2) the extra nonradiative recombination in the remaining QDs induced by the Mn doping.

Figure 5 summarizes the photoinduced charge-carrier dynamics in both undoped and doped QDs. There exist three different pools of undoped QDs (Figure 5a), where the photoexcited charge carriers in each pool will: (1) undergo fast surface trapping (3 ps) and then relax to the ground state nonradiatively (540 ps) (Pool A), (2) get trapped by Pb_{Cs} states within 38 ps (Pool B), and (3) undergo intrinsic radiative recombination (15 ns) (Pool C). In doped QDs (Figure 5b), the situation in QD pool A remains insensitive to the doping level, whereas some extra fast nonradiative

47





Figure 4. (a) Rising edge of Mn emission kinetics from time-correlated single-photon counting (TCSPC) illustrating the ET. (The response function (RF) is set as a standard Gaussian pulse.) (b) TRPL kinetics of Mn-doped CsPbCl₃ with different concentrations measured in ms-TRPL with a milliseconds time window. (c) Rate constant of the components changes with the doping level following the same trend but displays higher values than the ET rates extracted from TRPL. (d) Calculated ET efficiency η versus Mn concentration. τ_4 is the time from TA fitting, which can be seen in Table S5.



Figure 5. Schematic diagram of the photophysical processes in (a) neat CsPbCl₃ QDs and (b) Mn-doped CsPbCl₃ QDs with appropriate Mn doping concentration.

recombination will occur in QD pool C to shorten the chargecarrier lifetime. In pool B of QDs, the dopant–Mn ET (28–79 ps) competes with the hole trapping (83 ps) at Cl_i states induced by Mn doping, which accounts for the change of the PLQY (Pool B). When the doping level is high (e.g., 38%), both the intrinsic emission in the host QDs and the Mn d–d emission would be quenched, as proved by the faster emission decay in Figure 4b, resulting in the further declined PLQY, which is not discussed in Figure 5.

In conclusion, we have systematically studied the effect of Mn^{2+} doping on the photophysics of CsPbCl₃ QDs. Through DFT calculations, we demonstrated a change of main defect state from shallow Pb_{Cs} electron traps to deep Cl interstitials (Cl_i) hole traps after Mn^{2+} doping. The investigation of the charge-carrier dynamics via time-resolved spectroscopies reveals the competition instead of mediation between the exciton–dopant ET and the hole trapping. Such competition rationalizes the nonmonotonic evolution of the PLQY with the doping level. Furthermore, because the ET to the Mn dopant mainly competes with the hole trapping, it is vital to passivate the hole traps to maximize the Mn^{2+} emission, for instance, by dual-doping.²⁶ Meanwhile, the surface traps exist in QDs among the different Mn doping concentrations, which means the surface treatment should be important during doped QD

The Journal of Physical Chemistry Letters

preparation. Hence, this work provides a general model to optimize the structure of such nanomaterials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.0c01050.

Detailed methods for sample preparation, the characterization, DFT calculations, TEM images and size distribution, SEAD patterns, HADDF-STEM images of undoped and Mn-doped QDs, XPS spectra, DFT model and results, EPR analysis, rate constant equation model, TA spectra and fitting components, PLQY data, formation energy of the defect from DFT calculations, and TRPL kinetics (PDF)

AUTHOR INFORMATION

Corresponding Author

Authors

- Jie Meng Department of Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark; Ocid.org/ 0000-0002-3813-5221
- Zhenyun Lan Department of Energy Conversion and Storage, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark; @ orcid.org/0000-0001-7943-5936
- Mohamed Abdellah Chemical Physics and NanoLund, Lund University, 22100 Lund, Sweden; Department of Chemistry, Qena Faculty of Science, South Valley University, 83523 Qena, Egypt; © orcid.org/0000-0002-6875-5886
- Bin Yang State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Science, Dalian 116023, China; Occid.org/ 0000-0001-9583-921X
- Susanne Mossin Department of Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark; orcid.org/0000-0001-7763-9660
- Mingli Liang Department of Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark; orcid.org/0000-0002-1854-7026
- Maria Naumova Deutsches Elektronen Synchrotron (DESY), D-22607 Hamburg, Germany
- Qi Shi Chemical Physics and NanoLund, Lund University, 22100 Lund, Sweden
- Sol Laura Gutierrez Alvarez Department of Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark
- Yang Liu The Center of New Energy Materials and Technology, School of Materials Science and Engineering, Southwest Petroleum University, Chengdu 610500, China; Chemical Physics and NanoLund, Lund University, 22100 Lund, Sweden
- Weihua Lin Chemical Physics and NanoLund, Lund University, 22100 Lund, Sweden
- Ivano E. Castelli Department of Energy Conversion and Storage, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark; ◎ orcid.org/0000-0001-5880-5045

- Sophie E. Canton Deutsches Elektronen Synchrotron (DESY), D-22607 Hamburg, Germany; ELI-ALPS, ELI-HU Non-Profit Ltd., Szeged 6720, Hungary; ⊙ orcid.org/0000-0003-4337-8129
- Tönu Pullerits Chemical Physics and NanoLund, Lund University, 22100 Lund, Sweden; • orcid.org/0000-0003-1428-5564

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpclett.0c01050

Author Contributions

◆J.M. and Z.L. contributed equally to this work

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was funded by the Danish Council for Independent Research no. 7026-0037B and the Swedish Research Council no. 2017-05337 (K.Z.). J.M., Z.L., M.L., Q.S., Y.L., and W.L. acknowledge financial support from the China Scholarship Council. The ELI-ALPS project (GINOP-2.3.6-15-2015-00001) is supported by the European Union and cofinanced by the European Regional Development Fund.

REFERENCES

(1) Zhou, Y.; Chen, J.; Bakr, O. M.; Sun, H.-T. Metal-Doped Lead Halide Perovskites: Synthesis, Properties, and Optoelectronic Applications. *Chem. Mater.* **2018**, *30*, 6589–6613.

(2) Zhou, Y.; Zhou, Z.; Chen, M.; Zong, Y.; Huang, J.; Pang, S.; Padture, N. P. Doping and Alloying for Improved Perovskite Solar Cells. J. Mater. Chem. A 2016, 4, 17623–17635.

(3) Bryan, J. D.; Gamelin, D. R. Doped Semiconductor Nanocrystals: Synthesis, Characterization, Physical Properties, and Applications. *Prog. Inorg. Chem.* **2005**, *54*, 47–126.

(4) Han, P.; Zhang, X.; Luo, C.; Zhou, W.; Yang, S.; Zhao, J.; Deng, W.; Han, K. Manganese-Doped, Lead-Free Double Perovskite Nanocrystals for Bright Orange-Red Emission. ACS Cent. Sci. 2020, 6, 566–572.

(5) Wei, Q.; Li, M.; Zhang, Z.; Guo, J.; Xing, G.; Sum, T. C.; Huang, W. Efficient Recycling of Trapped Energies for Dual-Emission in Mn-Doped Perovskite Nanocrystals. *Nano Energy* **2018**, *51*, 704–710.

(6) Erwin, S. C.; Zu, L.; Haftel, M. I.; Efros, A. L.; Kennedy, T. A.; Norris, D. J. Doping Semiconductor Nanocrystals. *Nature* 2005, 436, 91–94.

(7) Pradhan, N.; Peng, X. Efficient and Color-Tunable Mn-Doped ZnSe Nanocrystal Emitters: Control of Optical Performance via Greener Synthetic Chemistry. J. Am. Chem. Soc. 2007, 129, 3339– 3347.

(8) Mikulec, F. V.; Kuno, M.; Bennati, M.; Hall, D. A.; Griffin, R. G.; Bawendi, M. G. Organometallic Synthesis and Spectroscopic Characterization of Manganese Doped CdSe Nanocrystals. *MRS Proc.* **1999**, 582.

(9) Norris, D. J.; Efros, A. L.; Erwin, S. C. Doped Nanocrystals. *Science* **2008**, 319, 1776–1779.

(10) Vlaskin, V. A.; Janssen, N.; van Rijssel, J.; Beaulac, R.; Gamelin, D. R. Tunable Dual Emission in Doped Semiconductor Nanocrystals. *Nano Lett.* **2010**, *10*, 3670–3674.

(11) Huang, H.; Bodnarchuk, M. I.; Kershaw, S. V.; Kovalenko, M. V.; Rogach, A. L. Lead Halide Perovskite Nanocrystals in the Research Spotlight: Stability and Defect Tolerance. ACS Energy Lett. 2017, 2, 2071–2083.

(12) Akkerman, Q. A.; Rainò, G.; Kovalenko, M. V.; Manna, L. Genesis, Challenges and Opportunities for Colloidal Lead Halide Perovskite Nanocrystals. *Nat. Mater.* **2018**, *17*, 394–405.

The Journal of Physical Chemistry Letters

Letter

(13) Kovalenko, M. V.; Protesescu, L.; Bodnarchuk, M. I. Properties and Potential Optoelectronic Applications of Lead Halide Perovskite Nanocrystals. *Science* **2017**, 358, 745–750.

(14) Wu, Z.; Zhang, H.; Gao, H.; Liu, H.; Yao, D.; Shao, J.; Liu, Y.; Yang, B.; Yu, W. CsPb X Mn 1– X Cl 3 Perovskite Quantum Dots with High Mn Substitution Ratio. ACS Nano 2017, 11, 2239–2247.

(15) De, A.; Mondal, N.; Samanta, A. Luminescence Tuning and Exciton Dynamics of Mn-Doped CsPbCl3 Nanocrystals. *Nanoscale* 2017, 9, 16722-16727.

(16) Parobek, D.; Roman, B. J.; Dong, Y.; Jin, H.; Lee, E.; Sheldon, M.; Son, D. H. Exciton-to-Dopant Energy Transfer in Mn-Doped Cesium Lead Halide Perovskite Nanocrystals. *Nano Lett.* 2016, 16, 7376–7380.

(17) Das Adhikari, S.; Dutta, S. K.; Dutta, A.; Guria, A. K.; Pradhan, N. Chemically Tailoring the Dopant Emission in Manganese-Doped CsPbCl3 Perovskite Nanocrystals. *Angew. Chem., Int. Ed.* 2017, 56, 8746–8750.

(18) Xu, K.; Lin, C. C.; Xie, X.; Meijerink, A. Efficient and Stable Luminescence from Mn 2+ in Core and Core–Isocrystalline Shell CsPbCl 3 Perovskite Nanocrystals. *Chem. Mater.* **2017**, *29*, 4265– 4272.

(19) Xu, W.; Li, F.; Lin, F.; Chen, Y.; Cai, Z.; Wang, Y.; Chen, X. Synthesis of CsPbCl 3 -Mn Nanocrystals via Cation Exchange. *Adv. Opt. Mater.* **2017**, *5*, 1700520.

(20) Pradhan, N. Mn-Doped Semiconductor Nanocrystals: 25 Years and Beyond. J. Phys. Chem. Lett. 2019, 10, 2574-2577.

(21) Das Adhikari, S.; Guria, A. K.; Pradhan, N. Insights of Doping and the Photoluminescence Properties of Mn-Doped Perovskite Nanocrystals. J. Phys. Chem. Lett. 2019, 10, 2250–2257.

(22) Guria, A. K.; Dutta, S. K.; Adhikari, S. D.; Pradhan, N. Doping Mn 2+ in Lead Halide Perovskite Nanocrystals: Successes and Challenges. *ACS Energy Lett.* **201**7, *2*, 1014–1021.

(23) Parobek, D.; Roman, B. J.; Dong, Y.; Jin, H.; Lee, E.; Sheldon, M.; Son, D. H. Exciton-to-Dopant Energy Transfer in Mn-Doped Cesium Lead Halide Perovskite Nanocrystals. *Nano Lett.* **2016**, *16*, 7376-7380.

(24) Rossi, D.; Parobek, D.; Dong, Y.; Son, D. H. Dynamics of Exciton-Mn Energy Transfer in Mn-Doped CsPbCl 3 Perovskite Nanocrystals. J. Phys. Chem. C 2017, 121, 17143-17149.

(25) Pinchetti, V.; Anand, A.; Akkerman, Q. A.; Sciacca, D.; Lorenzon, M.; Meinardi, F.; Fanciulli, M.; Manna, L.; Brovelli, S. Trap-Mediated Two-Step Sensitization of Manganese Dopants in Perovskite Nanocrystals. ACS Energy Lett. 2019, 4, 85–93.

(26) Xing, K.; Yuan, X.; Wang, Y.; Li, J.; Wang, Y.; Fan, Y.; Yuan, L.; Li, K.; Wu, Z.; Li, H.; et al. Improved Doping and Emission Efficiencies of Mn-Doped CsPbCI 3 Perovskite Nanocrystals via Nickel Chloride. J. Phys. Chem. Lett. 2019, 10, 4177–4184.

(27) Yong, Z.-J.; Guo, S.-Q.; Ma, J.-P.; Zhang, J.-Y.; Li, Z.-Y.; Chen, Y.-M.; Zhang, B.-B.; Zhou, Y.; Shu, J.; Gu, J.-L.; et al. Doping-Enhanced Short-Range Order of Perovskite Nanocrystals for near-Unity Violet Luminescence Quantum Yield. J. Am. Chem. Soc. 2018, 140, 9942–9951.

(28) Kang, J.; Wang, L.-W. High Defect Tolerance in Lead Halide Perovskite CsPbBr3. J. Phys. Chem. Lett. 2017, 8, 489-493.

(29) An, R.; Zhang, F.; Zou, X.; Tang, Y.; Liang, M.; Oshchapovskyy, I.; Liu, Y.; Honarfar, A.; Zhong, Y.; Li, C.; et al. Photostability and Photodegradation Processes in Colloidal CsPb13 Perovskite Quantum Dots. ACS Appl. Mater. Interfaces 2018, 10, 39222–39227.

(30) Zheng, K.; Židek, K.; Abdellah, M.; Zhang, W.; Chábera, P.; Lenngren, N.; Yartsev, A.; Pullerits, T. Ultrafast Charge Transfer from CdSe Quantum Dots to P-Type NiO: Hole Injection vs Hole Trapping, J. Phys. Chem. C 2014, 118, 18462–18471.

(31) Beaulac, R.; Archer, P. I.; Ochsenbein, S. T.; Gamelin, D. R. Mn 2+ -Doped CdSe Quantum Dots: New Inorganic Materials for Spin-Electronics and Spin-Photonics. *Adv. Funct. Mater.* 2008, *18*, 3873– 3891.

Supporting Information

Modulating Charge Carrier Dynamics in Mn-Doped All-inorganic Halide Perovskite Quantum Dots through the Doping-Induced Deep Trap States

Jie Meng^{†,1}, Zhenyun Lan^{‡,1}, Mohamed Abdellah^{#,^}, Bin Yang[¶], Susane Mossin[†], Mingli Liang[†], Maria Naumova[¬], Qi Shi[#], Sol Laura Gutierrez Alvarez[†], Yang Liu^{§,#}, Weihua Lin[#], Ivano E. Castelli[‡], Sophie E. Canton^{¬,+}, Tönu Pullerits[#] and Kaibo Zheng^{*,†, #}

[†]Department of Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark;
[‡]Department of Energy Conversion and Storage, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark
[‡]Chemical Physics and NanoLund, Lund University, Box 124, 22100 Lund, Sweden;
[^]Department of Chemistry, Qena Faculty of Science, South Valley University, 83523 Qena, Egypt;
[¶]State Key Laboratory of Molecular Reaction Dynamics Dalian Institute of Chemical Physics Chinese Academy of Science, Dalian 116023, China;
[¶]Deutsches Elektronen Synchrotron (DESY), Notkestrasse 85, D-22607 Hamburg, Germany;
[§]The Center of New Energy Materials and Technology, School of Materials Science and Engineering, Southwest Petroleum University, Chengdu 610500, China;
⁺ELI-ALPS, ELI-HU Non-Profit Ltd., Dugonics ter 13, Szeged 6720, Hungary

*Corresponding Author

Kaibo Zheng: kzheng@kemi.dtu.dk, kaibo.zheng@chemphys.lu.se

¹*The authors contributed equally to this work*

Experimental Section

Materials and Chemicals. Cesium carbonate (Cs₂CO₃, ReagentPlus 99%, Sigma-Aldrich), Lead (II) chloride (PbCl₂, Powder 98% metals basis, Sigma-Aldrich), Manganese chloride (MnCl₂·(H₂O)₄, \geq 95%, The British Drug House LTD), Oleylamine (OAm, technical grade 70%, Sigma-Aldrich), Oleic acid (OA, technical grade 90%, Sigma-Aldrich), 1-Octadecene (ODE, technical grade 90%, Sigma-Aldrich), Toluene (anhydrous 99.8%, Sigma-Aldrich).

Preparation of Cs-OA. Cs₂CO₃ (0.415 g), OA (1.76 mL), and ODE (18 mL) were added to a 50-mL 3-neck round bottomed flask and evacuated and refilled with argon, then heated to 150 °C for 10 minutes before using.

Synthesis of Mn-doped CsPbCl₃ NCs. The Pure CsPbCl₃ and Mn doped CsPbCl₃ nanocrystals (NCs) were prepared following a procedure which is similar to the one previously reported.¹ Typically, PbCl₂ (0.0661 g), MnCl₂•(H₂O)₄ (0.0615g), OAm (0.8 mL), OA (0.8 mL), and ODE (5 mL) were added to a 25-mL 3 neck round bottom flask and were evacuated and refilled with Ar followed by heating the solution to 120 °C for 30 minutes. The temperature was then increased to 165 °C and then 200 °C. At 200 °C, dried OAm (0.8 mL) and dried OA (0.8 mL) were subsequently injected to solubilize the solution. The Cs-oleate (0.4 mL) was then swiftly injected and after 10 minute the solution was cooled with an ice/water bath. The NCs were centrifuged followed by dissolution in toluene. The feed ratios of Mn precursor can be seen as follow.

Pb-Mn	PbCl ₂ /g	MnCl ₂ ·(H ₂ O) ₄ /g
1:0		0
4:1		0.0154
2:1	0.0615	0.0308
1:1		0.0615
1:2		0.123
1:4		0.246

Characterization. The absorption spectra were measured in a UV-Vis absorption spectrophotometer from Agilent Technologies (Santa Clara, USA). Steady-state photoluminescence was measured using a FluoroMax@-4 spectrofluorometer (HORIBA JOBIN YVON, Inc., Edison, NJ) with the excitation at 370 nm. Transmission electron microscopy (TEM) imaging was conducted on Tecnai G² T20 TEM and FEI Titan Analytical 80-300ST TEM from FEI Company. The obtained TEM images were processed with the Gatan Microscopy Suite software X-ray photoelectron spectroscopy (XPS) (ThermoScientific) was performed to analyze the valence and compositions of samples, with Al Ka (1486 eV) as the excitation X-ray source. The peak of C 1s at about 284.8eV was used to calibrat the energy scale. The pressure of the analysis chamber was maintained at 2×10⁻¹⁰ mbar during measurement. The EPR spectra were collected on a CW X-band Bruker EMX EPR spectrometer with an ER 4102ST cavity and a gunn diode microwave source at room temperature in toluene solution (The spectra were simulated in the Easyspin program with spin Hamiltonian parameters for the sextet of $g_{iso} = 2.00$, $A_{iso} = 242$ MHz = 86.5 Gauss = 8.65 mT).

The transient absorption (TA) experiments were performed on a femtosecond pump-probe setup. Laser pulses (800 nm, 80 fs pulse length, 0.5 kHz repetition rate) were generated by a femtosecond oscillator (Mai Tai SP, both Spectra Physics). The pump pulses at 370 nm were generated by an optical parametric amplifier (Topas, Light Conversion). The excitation photon fluxes were $5 \times$

 10^{12} photons/cm²/pulse. For the probe, we used the super-continuum generation from a thin CaF₂ plate. The mutual polarization between pump and probe beams was set to the magic angle (54.7°) by placing a Berek compensator in the pump beam. The probe pulse and the reference pulse were dispersed in a spectrograph and detected by a diode array (Pascher Instruments). Global SVD analysis was performed with the Glotaran software package (http://glotaran.org).

Time-correlated single photon counting (TCSPC) was performed triggered externally at 2.5 MHz to excite the sample at 375 nm. The emitted photons were detected by a fast avalanche photodiode (SPAD, Micro Photon Device) with response time less than 50 ps after passing through a 470 nm long band pass filter. To compare the energy transfer rate among Mn doped CsPbCl₃ ODs samples, we used the time-correlated single photon counting (TCSPC) to confirm by a 470 nm long band pass filter. Under the 470 nm cut-off filter, the signal from excitons excited by UV light at 375 nm were filtered. The time of energy transfer from exciton to dopant can be well evaluated by the rising edge of Mn emission kinetics from TCSPC. In our experiment, the frequency of TCSPC was set to 2.5 MHz, indicating the interval time between two pulses is 4×10^{-10} 7 s. If the beam goes through the same area of samples, it could excite the sample repeatedly every 4×10^{-7} s, which would affect some of the photophysical processes with long time scale. Hence, we use the rotate holder with spinning cell to avoid this interference through the measurement. The rotation speed is kept at 3000 rpm which leads to the velocity of the sample movement at the laser beam position to be $3 \times 10^7 \,\mu$ m/s, which means the maximum number of pulses excited at one spot should be 8 considering the beam-size of the excitation laser pulse is 100 µm. As the excitation density per QD <N> << 0.1 with the laser fluence used in TRPL measurement, we can conclude the re-excitation on individual OD should be negligible in this case.

The PL quantum yield (PLQY) was measured by using Rhodamine 6G in distilled water for emission at about 450 nm, Quinine sulfate in 0.5 M H_2SO_4 for emission at around 565 nm as reference, respectively.^{2,3} Fluorescence quantum yields (relative values) of the samples were calculated according to the following expression:

$$\Phi_{\rm S} = \frac{F_{\rm S}}{F_{\rm R}} \times \frac{(1 - 10^{-A_{\rm R}})}{(1 - 10^{-A_{\rm S}})} \times \frac{\eta_{\rm S}^2}{\eta_{\rm R}^2} \times \Phi_{\rm S}$$
(S1)

where the subscripts S and R respectively refer to the sample and the reference, F is the fluorescence quantum yield using integrated fluorescence intensity under fluorescence emission spectrum, A is the absorbance at the excitation wavelength and η is the refractive index of the solvent.

DFT calculation

The structural and electronic properties were obtained by Vienna ab initio package (VASP) within the framework of the DFT.⁴ The electronic wave functions were calculated by using projected augmented wave (PAW).⁵ A plane-wave cutoff of 500 eV was chosed. The exchange-correlation interaction was described by the functional generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) parametrization.⁶ Due to the heavy Pb atom in CsPbCl₃, spin-orbit coupling was included for the electric properties calculation. A 2 x 1 x 2 supercell containing of 80 atoms was choosed for the defects calculation. Substitution of a single Pb atom by a Mn atom in the 2 x 1 x 2 supercell corresponds to Mn concentration of 6.25%. The Brillouin zone samplings were carried out with a Γ -center 4 x 3 x 4 k-point mesh. The atomic forces were relaxed to be less than 0.01 eV Å⁻¹. The lattice parameter for CsPbCl₃ structure was calculated to be 8.13 Å for a, 11.40 Å for b and 7.91 Å for c (Figure S5). There exists a certain region where CsPbCl₃ exists and the chemical potentials should satisfy the following condition⁷:

$$\mu_{Cs} + \mu_{Pb} + 3\mu_{Cl} = \Delta H \ (CsPbCl_3) = -7.60 \ eV$$
 (S2)

$$\mu_{Cs} + \mu_{Cl} < \Delta H (CsCl) = -3.99 \text{ eV}$$
 (S3)

$$\mu_{Pb}+2\mu_{Cl} < \Delta H (PbCl_2)=-3.33 \text{ eV}$$
 (S4)

Where ΔH (CsPbCl₃), ΔH (CsCl) and ΔH (PbCl₂) are the formation energy of CsPbCl₃, CsCl and PbCl₂, respectively. The chemical potential μ_i is referenced to Cs metal, Pb metal, or Br₂ molecule. An ideal gas model was applied for Cl, which can be define as⁸

$$\mu_{Cl} = [H_0 + c_p(T - T_0) - TS_0 + Tc_p \ln(T/T_0) + k_B T \ln(P/P_0)]/2$$
(S5)

Where k_B is the Boltzmann constant and $c_p = 3.5k_B$ is the constant pressure heat capacity for ideal gas of diatomic molecules. T₀=298.15K and P₀=1 atm respond to H₀=9175.51J/mol and S₀=222.96 J/mol/K at a reference state.⁹ Under T=300 K and P = 1 atm ambient conditions, μ_{Cl} is -0.30 eV, which is a more reasonable upper boundary comparing to μ_{Cl} =0 eV.



Figure S1. The TEM images of Mn doped CsPbCl₃ NCs and corresponding size distribution with different Mn concentration. (a) 0%, (b) 0.1%, (c) 0.2%, (d) 0.6%, (e) 1.8% and (f) 38%. The scale bar is 50 nm


Figure S2. The Selected area electron diffraction (SAED) of Mn doped CsPbCl₃ NCs with different Mn concentration. (a) 0%, (b) 0.1%, (c) 0.2%, (d) 0.6%, (e) 1.8% and (f) 38%. The scale bar is 2 1/nm. The red, yellow and blue lines are ascribed to (121), (202) and (242) three main crystal planes, respectively.



Figure S3. The atomically resolved high-resolution HAADF-STEM images of undoped and Mn doped CsPBCl₃ QDs.



Figure S4. XPS spectra of Mn doped $CsPbCl_3 NCs$ with different Mn concentration. (a) Cs 3d,

(b) Pb 4f and (c) Cl 2p.



Figure S5. The CsPbCl₃ model for DFT calculation.



Figure S6. The DFT calculations of density of state (DOS) for undoped CsPbCl₃ and Mn doped CsPbCl₃ without any defects.



Figure S7. The DFT calculations of density of state (DOS) for Mn doped $CsPbCl_3$ with

vacancies defects.



Figure S8. The DFT calculations of density of state (DOS) for Mn doped $CsPbCl_3$ with

interstitials defects.



Figure S9. The DFT calculations of density of state (DOS) for Mn doped CsPbCl3 with antisites

defects.



Figure S10. TA spectra of Mn doped CsPbCl₃ QDs with different Mn concentration. (a) 0%, (b)





Figure S11. The fitting components from TA spectra of Mn doped CsPbCl₃ QDs with different Mn concentration. (a) 0%, (b) 0.1%, (c) 0.2%, (d) 0.6%, (e) 1.8% and (f) 38%.



Figure S12. TRPL kinetics of undoped CsPbCl₃ QDs excited at 375 nm with excitation 5×10^{12} photons/cm²/pulse .

References

- Parobek, D.; Roman, B. J.; Dong, Y.; Jin, H.; Lee, E.; Sheldon, M.; Son, D. H. Exciton-to-Dopant Energy Transfer in Mn-Doped Cesium Lead Halide Perovskite Nanocrystals. *Nano Lett.* 2016, *16*, 7376–7380.
- (2) Zhu, L.; Yin, Y.; Wang, C. F.; Chen, S. Plant Leaf-Derived Fluorescent Carbon Dots for Sensing, Patterning and Coding. *J. Mater. Chem. C* 2013, *1*, 4925– 4932.
- (3) Kubin, R. F.; Fletcher, A. N. Fluorescence Quantum Yields of Some Rhodamine Dyes. J. Lumin. 1982, 27, 455–462.
- (4) Kresse, G.; Hafner, J. *Ab Initio* Molecular Dynamics for Liquid Metals. *Phys. Rev. B* 1993, 47, 558.
- (5) Blöchl, P. E. Projector Augmented-Wave Method. Phys. Rev. B 1994, 50, 17953.

- (6) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77, 3865.
- (7) Kang, J.; Wang, L. W. High Defect Tolerance in Lead Halide Perovskite CsPbBr₃. J. Phys. Chem. Lett. 2017, 8, 489–493.
- Paudel, T. R.; Jaswal, S. S.; Tsymbal, E. Y. Intrinsic Defects in Multiferroic BiFeO₃ and Their Effect on Magnetism. *Phys. Rev. B Condens. Matter Mater. Phys.* 2012, *16*, 7376-7380.
- (9) Wagman, D. D.; Evans, William, H.; Parker, Vivian, B.; Schumm, Richard, H.; Halow, I.; Bailey, Sylvia, M.; Churney, Kenneth, L.; Nuttall, Ralph, L. The NBS Tables of Chemical Thermodynamic Properties-Selected Values for Inorganic and C₁ and C₂ Organic Substances in SI Units. *J. Phiysical Chem. Ref. Data* 1982, *18*, 1807-1812.

Chapter 4 Hot carrier cooling in Mn-doped CsPbI₃ NCs

Rapid photo-generated hot-carrier (HCs) cooling is the primary channel for energy loss in single-junction solar cells. According to theoretical calculation, an ideal single-junction HCs solar cell can reach power conversion efficiency as high as 66% if the excess energy of the HCs is fully utilized to overcome Shockley–Queisser (SQ) limit. However, it is extremely challenging to extract the HCs. Previous studies only focused on the competition between HCs extraction and HCs cooling rates. However, the excess energy of the HCs in this case will still be lost in the energy selected electrodes if the HCs cooling is completely suppressed. Therefore, the optimal dynamics for the HCSC should be initiated by the efficient establishment of a thermal quasi-equilibrium where the excess energy of the HCs is converted to reheat the cold carriers. Subsequently, such quasi-equilibrium states should be long-lived to facilitate the HCs extraction.

This means the HCs cooling dynamics need to be finely tailored to be employed in the HCSC. However, most state-of-art research still focuses on the characterization of such a process where the methodology to modulate it is seldomly developed. In semiconductors, the HCs cooling is a competition consequence involving carrier excitation, carrier-LO-phonon scattering, and LO-phonon decay (LO is longitudinal optical mode). Those dynamic processes are determined by the electronic and phononic structures of the material. Transition-metal doping could be a promising strategy to modify both the electronic and phononic structures of the semiconductors and thus modulate the cooling process.

Here in this paper, we investigate the effect of transition metal (Mn^{2+}) doping of lead halide perovskites on their HCs cooling dynamics through both ultrafast laser spectroscopy and DFT calculation. We found the HCs cooling rate is modified by the Mn doping, but the trend is excitation energy-dependent. Acceleration in HCs cooling at high excitation energy but deceleration in HCs cooling at band edge excitation energy have been observed. From DFT calculations, temperature-dependent PL measurement as well as X-ray absorption spectroscopy characterization, we conclude the excitation energydependent HCs cooling process is the consequence of the trade-off among the following features induced by the doping 1) enhanced electron-phonon coupling, 2) reduced effective mass, 3) available Mn^{2+} states in HC cooling pathways, and 4) enlargement in opticalacoustic phonon band gaps. Our results open up a new possibility to modulate the HCs cooling in semiconductors via element doping with fine control on the host materials' electronic and phononic structure. But more importantly, the enhanced electron-phonon coupling and efficient thermalization of HCs at high energy together with delayed heat dissipation after thermalization with HCs at low energy are optimal for the HCSC application according to our argumentation above. This indicates the transition metal doped perovskites can be promising building blocks for future hot carrier solar cell application. This chapter is submitted: Tailoring the Hot Carrier Cooling by Transition Metal Doping in All-inorganic Lead Halide Perovskite Nanocrystals with authors of Jie Meng, Zhenyun Lan, Weihua Lin, Maria Naumova, Mingli Liang, Xianshao Zou, Qian Zhao, Huifang Geng, Ivano E. Castelli, Sophie E. Canton, Tönu Pullerits, and Kaibo Zheng.

This article is given below.

Tailoring the Hot Carriers Cooling by Transition Metal Doping in All-inorganic Lead Halide Perovskite Nanocrystals

Jie Meng^{†,1}, Zhenyun Lan^{‡,1}, Weihua Lin[#], Maria Naumova[⊽], Mingli Liang[†], Xianshao Zou[#], Qian Zhao[†], Huifang Geng[¶], Ivano E. Castelli[‡], Sophie E. Canton[§], Tönu Pullerits[#], and Kaibo Zheng^{*,†,} #

[†]Department of Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark;

[‡]Department of Energy Conversion and Storage, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark;

[#]Chemical Physics and NanoLund, Lund University, Box 124, 22100 Lund, Sweden;

[¶]Ultrafast Electron Microscopy Laboratory, The MOE Key Laboratory of Weak-Light Nonlinear Photonics, School of Physics, Nankai University, Tianjin 300071, China;

⁷ Deutsches Elektronen Synchrotron (DESY), Notkestrasse 85, D-22607 Hamburg, Germany;

[§] European XFEL, Holzkoppel 4, 22869 Schenefeld, Germany.

*Corresponding Author

Kaibo Zheng: <u>kzheng@kemi.dtu.dk</u>, <u>kaibo.zheng@chemphys.lu.se</u>.

¹The authors contribute equally in this work

ABSTRACT

Hot carriers (HCs) cooling accounts for the major energy loss in lead halide perovskites (LHPs) solar cells. Here, we study HCs relaxation dynamics in Mn-doped LHP CsPbI3 nanocrystals (NCs) combining transient absorption spectroscopy and density functional theory (DFT) calculations. We demonstrate that Mn^{2+} doping 1) enlarges the longitudinal optical (LO)-acoustic phonon bandgap, 2) enhances the electron-LO phonon coupling strength, and 3) adds HCs relaxation pathways via Mn orbitals within the bands. The spectroscopic study shows that the HCs cooling process is decelerated after doping under band-edge excitation due to the dominant phonon bandgap enlargement. When the excitation photon energy is larger than the optical bandgap and the Mn²⁺ transition gap, the doping accelerates the cooling rate owing to the dominant effect of enhanced carrier-phonon coupling and relaxation pathways. We demonstrate such a phenomenon is optimal for the application of hot carrier solar cells. The enhanced electron-LO phonon coupling and accelerated cooling of high-temperature hot carriers efficiently establish a high-temperature thermal quasi-equilibrium where the excessive energy of the hot carriers is transferred to heat the cold carriers. On the other hand, the enlarged phononics band-gap prevents further cooling of such quasi-equilibrium, which facilitates the energy conversion process. Our results manifest a straightforward methodology to optimize the HCs dynamics for hot carrier solar cells by element doping.

INTRODUCTION

In a single-junction solar cell, the rapid cooling of the hot carriers (HCs) excited by photons with energy well above the bandgap is a major energy loss channel responsible for the Shockley– Queisser (SQ) limit.¹ The hot carrier solar cell (HCSC) is set to tackle this issue by keeping the HCs in a sufficiently high energy quasi-equilibrium (i.e. with a mean carrier temperature > 500 K) with a subset of the thermal environment directly coupled to the electrons. In this way, the carriers can be extracted at significantly higher energy than the bandgap of the semiconductor thereby making efficient use of the excess energy of the HCs.² An ideal single-junction HCs solar cell can reach power conversion efficiency as high as 66%.¹ However, achieving an efficient HCs extraction with all the excess energy to be harvested is extremely challenging. As illustrated in Schematic 1, previous studies attributed the bottleneck to the suppression of HCs extraction by faster HC cooling to the band edge (Schematics 1a), and seek materials with slow HCs cooling rate to ensure the HCs injection to the electrodes at hot states (Schematics 1b) ^{3,4}. However, the excess energy of the HC in this case will still be lost in the energy selected electrodes. Therefore, the optimal dynamics for the HCSC should initiate the efficient establishment of the abovementioned thermal quasi-equilibrium where the excess energy of the HC is converted to heat the cold carriers. Subsequently, such a quasi-equilibrium state should be long-lived to facilitate the HC extraction (Schematics 1c).



Schematic 1. Schematics of HCs cooling versus HCs extraction to energy selective electrodes (ESC) in HCSCs: a) HC cooling is so efficient that HCs cool from initial temperature (T_0) to a thermal quasi-equilibrium (T_E) combined with emitted LO phonons (process 1) and finally all reach to the cold carriers (CC) state after LO phonons decay (process 2) at a temperature of T_L b) HCs cooling is extremely slow so that all the HCs are directly injected into ESC (process 3) without thermalization, where the excess energy is dissipated during the injection. c) HCs undergoes efficient process 1 to establish the thermal equilibrium, and such equilibrium is long-lived to ensure the subsequent HCs extraction to the ESCs.

In general, HCs cooling in conventional semiconductors mainly involves carrier excitation, carrier–LO–phonon scattering, and LO-phonon decay.^{5,6} The competition between the phonon

emission and decay in those processes determines the final HCs cooling dynamics.⁷ Among them, the first two steps contribute to the establishment of the thermal quasi-equilibrium, while the last step promotes the heat dissipation to dissociate such equilibrium. Therefore, the objectives for the HCSC material engineering need to be revised by enhancing carrier–LO–phonon scattering and diminishing LO-phonon decay simultaneously so as to construct a stable thermal quasi-equilibrium.

Emerging lead halide perovskites (LHP) with promising potential in the solar cell application can be perfect target materials to practice the above strategy. The thermal quasi-equilibrium state is easy to form in LHP with long lifetime due to large polaron screening effect,⁸ hot-phonon effect,⁹ and pronounced acoustical–optical phonon upconversion.⁷ Increasing attention has been focused on the HCs dynamics in these materials since the first report of HCs cooling in methylammonium lead iodine (MAPbI₃) polycrystalline thin films.^{10,11} Highly efficient HCs extraction (up to ≈83%) could be achieved by an energy-selective electron acceptor layer from surface-treated MAPbBr₃ LHP nanocrystals (NCs) film.¹² In formamidinium Sn-based perovskite FASnI₃, a long HCs cooling lifetime of up to a few ns was reported.¹³ In particular, the transport of persistent HCs over long distances (up to ≈600 nm)³ makes LHPs greatly promising for HCs solar cells.

In parallel, transition metal doping has been widely explored to impart novel optical, magnetic, and electronic properties to LHPs.¹⁴ A representative study in this regard is the Mn-doping of LHPs materials (e.g., CsPbCl₃). Such doping can generate long-lived sensitized dopant luminescence and create a magnetically-coupled exciton state.¹⁵ The unique Mn²⁺ triplet emission in doped LHPs is derived from the Mn²⁺ d-d transition (⁴T₁ \rightarrow ⁶A₁) after energy transfer or charge transfer from the excited state of the host LHPs.¹⁶ In addition, we have previously demonstrated that partial replacement of Pb²⁺ by Mn²⁺ also causes a local structural distortion and defects formation due to the difference in cation radius between Mn²⁺ and Pb^{2+,17} It should noted that the HCs dynamic processes are determined by both electronic and phononic structures of the material. For instance, an enlarged phononic bandgap between optical phonon and acoustic phonon branches can efficiently suppress the channel for LO phonon decay, while a small LO phonon energy requires more phonons to be emitted for a given energy loss of HCs.¹⁸ Since both electronic states and local structures are modified by the Mn²⁺ doping in LHPs, we thereby expect it can be a robust tool also to modulate the HCs cooling dynamics towards enhanced carrier–LO–phonon scattering and diminished LO-phonon decay as mentioned above. In this work, we investigated the HCs cooling dynamics in Mn-doped CsPbI₃ nanocrystals (NCs) using transient absorption (TA) spectroscopy combined with theoretical and experimental characterization of the material structures. Compared to CsPbCl₃ and CsPbBr₃, CsPbI₃ has a lower optical bandgap so that the Mn d orbitals are located within the conduction band (CB) and valence band (VB), and thereby contribute to the cooling pathways. We found that the HCs cooling rate is modified by the Mn doping but the trend is excitation energy-dependent. Acceleration in HCs cooling at high excitation energy, but a deceleration in HCs cooling at band edge excitation energy have been observed. The temperature-dependent photoluminescence (PL) measurement and density functional theory (DFT) calculation confirmed the addition of in-band states and enhancement in the carrier-LO phonon coupling by Mn doping. On the other hand, the phonon bandgap between the optical modes and the acoustic modes is enlarged by the Mn-doping. We believe that the trade-off among all those factors is the main reason for the excitation energydependent HCs cooling dynamics in Mn-doped LHP NCs. The enhanced carrier-LO phonon coupling and enlarged phonon bandgap comply well with the optimal feature of HCSC materials described in Fig. 1c. This work demonstrates that the HCs cooling dynamics can be optimized by the element doping that tailors the electronic as well as lattice structure of the materials for the application of HCSCs.

RESULTS AND DISCUSSION

Sample Characterization:

Both pristine CsPbI₃ and Mn-doped CsPbI₃ NCs were synthesized by a reported hot-injection method (details are given in the Experimental section).¹⁹ Figure 1a schematically shows how Mn metal ions can be incorporated into perovskite lattices with homovalent B-site substitution (ionic radii: Pb²⁺: 133 pm, Mn²⁺: 97 pm).¹⁵ The transmission electron microscopy (TEM) images show that doped NCs retain the cubic morphology of undoped NCs with an average particle size around 17 nm (Figure 1c-1d and Figure S1). Subsequently, the absorption and emission spectra were measured (Figure 1b). The absorption band-edge of all NCs is ~680 nm, corresponding to an optical bandgap (E_g) of ~1.8 eV. The introduction of Mn does not influence the absorption edge of the CsPbI₃ NCs. In addition, no dopant-related absorption/emission bands can be observed since the Mn d orbitals are not located within the bandgap of CsPbI₃.²⁰

We probed the HCs cooling dynamics of the Mn-doped NCs mainly via transient absorption spectroscopy (TA) under various excitation energies and intensities. Figure 2a shows a pseudo-color TA plot of Mn-doped CsPbI₃ NCs excited at 500 nm and high excitation intensity with the average number of excitons per NCs $\langle N \rangle \approx 7.7$ corresponding to the initial average carrier density $n \approx 4.2 \times 10^{18}$ cm⁻³ (for details of pump fluence and absorption coefficient calculation, see Figure



Figure 1. (a) Schematic structure of Mn-doped CsPbI₃ NCs. The doping concentration is 5%. (b) The absorption (solid line) and PL spectra (dashed line) of undoped (bottom, black line) and Mn-doped (top, red line) CsPbI₃ NCs. TEM image of (c) undoped and (d) Mn-doped CsPbI₃ NCs.

S2-S3 and Table S1). All the other pseudo-color TA plots with different excitation energies and intensities for undoped and doped NCs are summarized in Figure S4-S9. In general, the TA plot shows three distinct spectral features (see Figure 2b): 1) the ground state bleach (GB) band centered at around 1.9 eV that arises from the band edge state filling (B1); 2) the excited state absorption (ESA) above bandgap (larger than 1.9 eV) that later evolved into a GB signature (A2);

3) Toward the lower energy, the asymmetric derivative is the probe-induced Stark effect (A1).⁵ In addition, we can observe a red shifting of the GB peak position with the delay time (Figure 2a), which becomes more pronounced at high excitation fluence (Figure S4-S9). Such a GB position shift can be attributed to two effects: the Moss–Burstein effect and the bandgap renormalization at short timescales (before 2 ps).²¹ The Moss–Burstein effect refers to the increase of effective bandgap of a semiconductor when the lower energy states in the CB or VB have been populated or blocked.²² On the other hand, bandgap renormalization is induced by the screening of Coulomb repulsion leading to a decrease in the electronic bandgap of semiconductors.²³ Those two effects should compensate each other near the band-edge of the LHPs, resulting in a slight shift in the observed optical band-edge.



Figure 2. (a) Pseudocolor representation TA spectra of Mn-doped CsPbI₃ NCs for 500 nm (2.48 eV) excitation at high excitation intensity with $\langle N \rangle \approx 7.7$ (corresponding to $n \approx 4.2 \times 10^{18} \text{ cm}^{-3}$). (b) Normalized TA spectra of Mn-doped CsPbI₃ NCs for 500 nm excitation at high excitation intensity with $\langle N \rangle \approx 7.7$ (corresponding to $n \approx 4.2 \times 10^{18} \text{ cm}^{-3}$) with the time delay from 0.3 ps to

30 ps. The higher energy tails (between 2.02 and 2.2 eV marked by a dashed rectangle) are globally fitted to a Boltzmann distribution from which the carrier temperature is extracted. Carrier temperature decay kinetics with 500 nm excitation at four different excitation intensities for (c) undoped and (d) Mn-doped CsPbI₃ NCs. The solid lines are the multi-exponential fits, and fitting parameters can be seen in supporting information.

Figure 2b shows the normalized TA spectra $-\Delta A$ of Mn-doped CsPbI₃ NCs with delay time between 0.3 and 3 ps extracted from the TA plot in Figure 2a. In Mn-doped CsPbI₃ NCs, after high-energy photon excitation, the excited carriers first undergo carrier–carrier scattering within 100 fs, a process which is called carrier thermalization.²⁴ The HCs then reach a Fermi-Dirac distribution with a carrier temperature T_c larger than the lattice temperature T_L . Following carrier thermalization, the HCs equilibrates with the lattice mainly through an inelastic carrier–phonon interactions, known as the "cooling" process. To ensure that the HCs have redistributed their energies and reached a quasi-temperature as Boltzmann distribution, we analyzed the HCs cooling dynamics after a delay of 0.3 ps, when the initial thermalization process should be finished. In order to extract the HCs temperature, we fitted the high energy tail of the TA spectra (i.e., between 2.02 eV and 2.20 eV) using the Maxwell–Boltzmann distribution function: ²¹

$$\frac{\Delta A}{A} \propto \exp\left(-\frac{E-E_f}{k_B T_c}\right) \tag{1}$$

Here, ΔA is TA signal in the region of interest, E_f is the quasi-Fermi energy, k_B is the Boltzmann constant, and T_c is the carrier temperature. Since electron/hole show similar effective masses based on the calculation shown in Table S1 (pure CsPbI₃: $m_e = 0.10m_0$, $m_h = 0.15m_0$; Mn doped CsPbI₃: $m_e = 0.13m_0$, $m_h = 0.19m_0$), we expect comparable contributions from hot electrons and hot holes to the extracted HCs temperatures. Figure 2c shows the fitted HCs cooling dynamics with increasing carrier densities (or pump fluence). The HCs cooling rates become lower with increasing carrier densities in both doped and undoped samples. The HCs cooling decay can be well-fitted by bi-exponential functions with a fast component and a slow component. The fast component should be attributed to the emission of the LO phonons through carrier-phonon interaction, and the slow component is due to the reduction of energy loss rate by reduced decay of LO phonon.^{25,26} We then used the average time to compare the cooling rates of undoped and

doped NCs. Under low excitation density below 10¹⁸ cm⁻³, the average decay times are 1.8 ps and 0.6 ps for undoped and doped NCs, respectively. When excitation density is higher than 10¹⁸ cm⁻³, the average decay times for undoped and doped NCs reach 20.2 and 17.9 ps, respectively (Table S4-S5). Notably, the same trend occurs in all the samples with various excitation photon energies (Figure S10-S15, Figure S16-S17, Table S2-S7). Such general carrier density dependence of the HCs cooling dynamics can be interpreted by the enhanced hot-phonon bottleneck, which is widely observed in semiconductors and LHPs.^{5,9,24,27,28} It is mainly induced by the presence of a non-equilibrium LO-phonon population in the phonon pool that reduces the net LO-phonon emission as well as enhances the cold carrier reheating, which consequently slow down the cooling process.^{5,24,29}

Excitation energy-dependent role of Mn doping in HCs dynamics:

In order to elucidate the influence of Mn-doping on the HCs cooling, we first compared the cooling dynamics between undoped and Mn-doped CsPbI₃ NCs excited at different excitation energies at very low excitation intensity (<N> \leq 1) (Figure 3). At such low excitation intensity, the many-body effects that influence the HCs cooling, such as Auger reheating, are negligible.¹²

We can also fit all the HCs cooling decay by multiple exponential components as summarized in Table 1. When the samples are excited at 570 nm with the phonon energy close to the bandgap energy, the cooling decay of the undoped NCs can be fitted with a fast component (0.1 ps) and a slow component (0.7 ps), delivering an average lifetime of 0.3 ps. Upon Mn-doping, the kinetics can be fitted by an exponential component with a lifetime of 0.4 ps together with an ultra-long live equilibrium temperature higher than the RT. This manifests that the HCs cooling in doped NCs becomes slower with the excitation energy near the band-edge position (Figure 3c).

When the sample is excited at 400 nm, the kinetics for the undoped NCs can be fitted by a fast component (0.2 ps) and a slow component (0.9 ps), giving an average lifetime of 0.5 ps. Upon Mn doping, the average lifetime becomes much faster (0.2 ps) (Figure 3a). The same trend can also be seen in the excitation energy of 500 nm (Figure 3b) (For detailed fitting parameters, see Table S9). The above excitation energy-dependent comparison can be further confirmed by the rising time of TA kinetic at the maxima GB position, which monitors the population of the band-edge states (Figure 3d-f).

In general, the hot carrier cooling dynamics in semiconductors are related to the coupling between various thermal pools. Here the above analysis monitors the temperature of the electronic pool, which is coupled to the pool of LO phonons. Owing to the anharmonicity of the vibrations, the LO phonon pool gives up energy efficiently to the acoustic phonon pool. This is eventually followed by the energy dissipation to the solvent environment.³⁰ In order to identify the dominant steps of HCs relaxation at various time delays, we have extracted the electronic energy power loss as a function of carrier temperature by using the conventional model of hot electron relaxation via optical-phonon emissions in Figure 3g-3i.¹²

Table 1. Fit parameters for carrier temperature decay kinetics of Mn-doped CsPbI₃ NCs with 400 nm, 500 nm, and 570 nm excitation. The unit of time t is ps.

Exc. Wavelength		A_1	t 1	A_2	t 2	tave
400 nm	Undoped	0.85	0.2	0.15	0.9	0.5
	Doped	0.97	0.1	0.03	0.5	0.2
500 nm	Undoped	0.94	0.1	0.06	4.1	1.8
	Doped	1	0.6	-	-	0.6
570 nm	Undoped	0.95	0.1	0.05	0.7	0.3
	Doped	1	0.4	-	-	0.4

Here the energy loss rate (P) of the carriers can be derived from the equation $P = \frac{d(\frac{3}{2}k_BT_c)}{dt}$ where T_c refers to the carrier temperature. The power loss plots in Figure 3g and 3i first further confirm that HCs cooling in doped NCs is faster under 400 nm and 500 nm excitation and slower under 570 nm excitation compared with doped NCs. In addition, two distinctive slopes can be observed in the plot corresponding to two power loss regimes. As shown in Figure 3g, for the undoped NCs excited at 400 nm, the power loss rate slowly decreases from 1 to 0.2 eV ps⁻¹, until T_c reaches \approx 700 K. Subsequently, as the hot carrier temperature approaches the lattice temperature, P drops rapidly. We defined the temperature at the transition point between these two regions as transition temperature (T_r). The Mn doping leads to lower T_r under 400 nm and 500 nm excitation and higher T_r under 570 nm excitation (Figure 3g-i). The distinctive two regions of HCs power loss are mainly dependent on the electronic and phononic structure of the materials. Notably, at low carrier density

 $(\sim 10^{-17} \text{ cm}^{-3})$, the power loss of the HC during the cooling process is dominated by the scattering between carriers and LO phonons. The initial rapid HCs cooling (i.e., the higher power loss rate) with T_c above T_r is due to the efficient LO phonon emission through the dominant Fröhlich interaction that dissipates the excess energy of the HCs. These LO phonons decay into acoustic phonons until T_c cools to the lattice temperature. The subsequent slower cooling of the HCs closer to the band edges (i.e., around 300–600 K in Figure 3g) is determined by the thermal equilibration between LO phonons and acoustic phonons.¹² In this scenario, the T_r between the two power loss regions qualitatively reflects the impact of the hot-phonon bottleneck, which is determined by the population dynamics of non-equilibrium LO phonons in the phonon pools. At high excitation energy, the Tr values of undoped and doped NCs are generally increased compared to low excitation energy as shown in Figure 3 g-i. This can be explained as more LO phonons are emitted due to the higher excess energy of the excited HCs. On the other hand, the change of T_r after Mn doping in NCs indicates a modified phonon generation and decay dynamics. When the samples are excited at 570 nm, the T_r for the undoped and doped NCs are about 410 K and 450 K, respectively (Figure 3i). At 400 nm excitation, the T_r for the undoped and doped NCs are about 780 K and 580 K, respectively.

In the following, we interpret the excitation energy-dependent role of Mn-doping in the HCs cooling dynamics observed in Figure 3 from the perspective of the intrinsic electronic/phononic structure of the doped NCs. We first revealed the electronic band structure of the samples via DFT calculation, as shown in Figure 4a-4b. The effective electron mass and hole mass of Mn-doped CsPbI₃ ($m_e = 0.13m_0$, $m_h = 0.19m_0$) are larger than those of pure CsPbI₃ ($m_e = 0.10m_0$ and $m_h = 0.15m_0$). This is because of the perturbation in the periodicity of the Pb 6p orbitals after Mn doping which leads to the reduction of both VBM and CBM dispersion. It indicates a more localized electron and hole state in the doped NCs.³¹ In the absence of hot-phonon effect at low carrier concentrations, the energy loss rate of HCs via carrier-LO phonon interaction is predominantly affected by the effective mass as illustrated in equation 2.⁵

$$P = \frac{m^{1/2}e^2}{\pi\varepsilon_0\hbar^2} \left(\frac{\hbar\omega_{L0}}{2}\right)^{3/2} \left[\frac{1}{\varepsilon_{Opt}} - \frac{1}{\varepsilon_{Stat}}\right]$$
(2)

Here ε_{Opt} and ε_{Stat} are the optical and static dielectric constants. Therefore, the heavier carrier effective mass in doped NCs should induce an intrinsically faster HCs relaxation than in undoped NCs.



Figure 3. Time-dependent carrier temperature for undoped and Mn-doped CsPbI₃ NCs at low excitation density ($\langle N \rangle \langle 1 \rangle$) with (a) 400 nm, (b) 500 nm and (c) 570 nm excitation energy. Normalized GB dynamics probed at the band-edge for undoped and Mn-doped CsPbI₃ NCs at low excitation intensity with (d) 400 nm, (e) 500 nm, and (f) 570 nm excitation energy. Power loss as a function of the inverse carrier temperature for the exponential fitting data from Figure 3a-3c of undoped and Mn-doped CsPbI₃ NCs at low excitation intensity with (g) 400 nm, (h) 500 nm, and (i) 570 nm excitation energy.

Secondly, we calculated the density of states (DOS) of pure CsPbI₃ NCs and Mn-doped levels shown in Figure 4a-4c. For the undoped NCs, the pathways of HCs cooling are mediated by states building from Pb and I orbitals. The doping adds Mn orbitals into the electronic structures of the NCs are shown in Figure 4c. According to the previous theoretical calculation, the first excitation on every symmetry point shows high optical strength.^{32,33} From Figure 4b, when the doped samples are excited at high energy, (e.g., 400 nm, 3.1 eV) more channels are available for electronic relaxation of the HCs. When the doped samples are excited at near band-edge energies, the excited electron /holes possess energy lower than the majority of the Mn orbitals. Therefore, we believe the participation of the Mn orbital in HCs cooling should be negligible.

Following the discussion of the effect of electronic structure, we now examine the role of carrierphonon coupling. For most inorganic semiconductors, coupling or scattering between charge carriers and phonons are functional dependencies of the PL linewidth $\Gamma(T)$ on temperature.³⁴ To evaluate such coupling, temperature-dependent PL spectra were acquired. They are shown in Figure S18-S19. We calculated the electron-phonon coupling strength from the FWHMs of temperature-dependent PL spectra using the following model:³⁵

$$\Gamma(\mathbf{T}) = \Gamma_0 + \Gamma_{\mathrm{ac}} + \Gamma_{\mathrm{LO}} + \Gamma_{\mathrm{imp}}$$
$$= \Gamma_0 + \gamma_{ac}T + \gamma_{LO}N_{\mathrm{LO}}(T) + \gamma_{imp}e^{-E_b/k_BT}$$
(3)

Here, Γ_0 is a temperature-independent inhomogeneous broadening that arises from scattering due to disorder and imperfections. Γ_{ac} is the contribution from acoustic-phonon scattering and γ_{ac} is the corresponding phonon-coupling strength. Γ_{LO} corresponds to the homogeneous broadening that results from LO-phonon scattering with a coupling strength γ_{LO} . In N_{LO} (T) = $1/(e^{E_{LO}/k_BT}-1)$, E_{LO} is an energy representative of the frequency for the weakly dispersive LO phonon branch, and k_B is Boltzmann constant. Γ_{imp} is the inhomogeneous broadening due to the ionized impurities. Γ_{ac} and Γ_{imp} do not contribute much to the temperature dependence at higher temperatures (> 100 K) so that they can be treated as constant and merged into Γ_0 . Hence, we model the linewidth broadening of these three SCs using equation 4 (Figure S19), and the linewidth parameters are shown in Table 2.

$$\Gamma(\mathbf{T}) = \Gamma_0 + \gamma_{LO} N_{\rm LO}(T) \tag{4}$$

Specifically, the LO phonon term in equation (4) accounts for the Fröhlich interaction between LO phonons and carriers. The difference between fitted and calculated E_{LO} is within the experimental error range. The fitted γ_{LO} for undoped NCs (74.8 meV) is 1.7 times smaller than that of doped NCs (126.5 meV). This clearly demonstrates the strengthened electron-LO phonon coupling by Mn-doping.

Samples	Γ_0/meV	γ_{LO}/meV	$\mathrm{E_{LO}}/\mathrm{meV}$	$\mathrm{E}_{\mathrm{LO-min}}/\mathrm{meV}$	E_{LO-max}/meV
			(Fitting)	(Calculated)	(Calculated)
Undoped	51.25	74.8	23.79	4.3	14.0
Doped	52.87	126.5	30.45	4.1	9.9

Table 2. Linewidth parameters and calculated ELO extracted from Figure S4 and Figure S5.

The last critical factor for determining the HCs cooling dynamics is the phonon band structures that dominate the pathways of LO-phonon decay and energy transfer to the acoustic phonons. We performed first-principles calculations of phonon dispersion spectra to uncover the possible phonon decay dynamics (for detailed calculation, see S.I.). The projected DOS on each atom is also given in Figure 4d-4e to show the detailed contributions from each atom. As well accepted, the most efficient pathway for LO phonon decay to acoustic phonon is the Klemens channel, where one optical phonon decays into two acoustic phonons with symmetric momentum.³⁶ However, the Klemens decay requires that the phononic bandgap between LO and acoustic phonons ($\hbar\omega_{LO-min}$ – $\hbar\omega_{LA-max}$) is lower than the maximum $\hbar\omega_{LA}$ ($\hbar\omega_{LA-max}$) energy (i.e., $\hbar\omega_{LO-min} - \hbar\omega_{LA-max} < \hbar\omega_{LA-max}$ max).³⁷ Otherwise, the large phononic bandgap hinders the LO phonon decay and hence leads to the formation of a non-equilibrium phonon population where a LO hot-phonon bottleneck arises. In the undoped CsPbI₃ NCs, the majority of the LO vibrational modes are the Pb–I stretch vibrations with frequencies at around 4.4 meV ($\hbar\omega_{LO_2-min}$) and 13.5 meV ($\hbar\omega_{LO_1-min}$), while the maximum acoustic LA phonon frequency lies around 2.9 meV ($\hbar\omega_{LA-max}$) (Figure. 4d). The gap between LO and LA ($\hbar\omega_{\rm LO-min} - \hbar\omega_{\rm LA-max}$) is calculated to be about 1.5 meV. The lower LO phonon energy compared with twice the LA phonon energy guarantees an efficient Klemens decay in the undoped NCs. In contrast, the Pb-I stretch vibration (LO) frequencies in doped NCs are around 4.1 meV $(\hbar\omega_{LO2-min})$ and 9.9 meV ($\hbar\omega_{LO1-min}$), while the maximum acoustic phonon frequency LA lies around

1.3 meV. The gap between LO and LA ($\hbar\omega_{LO-min} - \hbar\omega_{LA-max}$) is about 2.8 meV. Such enlargement of the phonon bandgap between LO and acoustic phonon should be induced from the strain due to the Mn doping in the local structures.³⁸ The separation between the LO and LA phonon branches ($\hbar\omega_{LO-min} > 2\hbar\omega_{LA-max}$) after Mn-doping should significantly hinder the Klemens channel, so that the LO phonons can only decay via alternative less efficient channels, such as the Ridley channel.³⁶ This suggests that more LO phonons will be emitted to cool down the HCs with the same excess energy, which inevitably leads to a large non-equilibrium LO phonon population.



Figure 4. Electronic band structure of (a) CsPbI₃ and (b) Mn-doped CsPbI₃ including Mn orbitals shown as pink color. (c) The contribution of Mn d orbitals in the electronic band structure of Mn-doped CsPbI₃. Phonon energy as a function of phonon momentum and density of states (DOS) of (d) undoped CsPbI₃ and (e) Mn-doped CsPbI₃. The size of these circles is proportional to the contribution of the corresponding orbitals. The two blue lines are the LO phonon mode. The red lines are the acoustic phonon mode.

We believe that the above three factors, i.e. integration of the doping levels, electron-LO phonon coupling, and phononic band structure, all influence the HCs cooling dynamics. Therefore, the excitation wavelength dependence of HCs cooling dynamics as shown in Figure 3 should be induced by the competition among all of these factors as summarized in Figure 5a-c. Under bandedge excitation (e.g. excited at 570 nm), the influence of additional Mn orbitals within the CB and VB can be neglected as their energies are well above excited states, as shown in Figure. 4c. The increased phononic bandgap induced by Mn doping is the dominant factor for the HCs cooling dynamics here. As discussed, it hinders the decay of excited LO phonons and promotes the non-equilibrium phonon population, while enhancing the hot-phonon bottleneck. This accounts for the slow HCs cooling and high T_r in power loss for doped NCs as shown in Figure 3c.

Under high energy excitation (e.g. excited at 400 and 500 nm), the participation of the Mn orbital in the cooling pathways, together with other factors induced by Mn doping should all play a role in the HCs cooling dynamics as discussed above. The faster cooling rates for doped NCs in this scenario indicate the influence of the Mn orbital participation, and the enhanced e-ph coupling competes with the enlargement of the phonon bandgap to accelerate the cooling process.

Summarizing the role of Mn doping on the HCs with various energy, we noticed that such a situation does fit the optimal scenario for the materials applied in HCSCs. HCs at very high energy will undergo strong electron-phonon coupling to be efficiently thermalized to the quasi-equilibrium state integrating the carriers with LO phonons to keep the thermal pool 'warm' enough. In this case, the carrier temperature reaches 400 to 600 K reflected by the T_r values. The phonon bandgap enlargement prevents further heat dissipation when the quasi-equilibrium is established and the HCs possesses lower energy.

Role of the dopant concentration in HCs cooling dynamics:

The samples with different doping levels are now considered. From the average HCs cooling time t_{ave} shown in Figure 5d-f, we find that the cooling rates become slower with the increasing doping concentration under low excitation energies (570 nm). Since the HCs cooling process at low excitation energy is exempt from the Mn orbital participation as discussed above, such relationship indicates the combined influence from the change of phonon structure and e-ph coupling evolves monotonously with the doping concentration. The influence of phonon bandgap enlargement is always dominant and becomes more pronounced with high doping concentration. On the other

hand, at high excitation energy at 400 nm, the average cooling time first decreases and then increases with the doping concentration. At 500 nm, the average cooling time decreases with the doping concentration. This indicates that the effect of Mn orbitals pathways and enhanced e-ph coupling (i.e. factors that accelerate HCs cooling) will be significantly suppressed by the phonon bandgap enlargement (i.e. factor that decelerate HCs cooling) at a high doping concentration.



Figure 5. Schematic mechanism diagram of hot carriers cooling for Mn-doped CsPbI₃ with (a) undoped CsPbI₃ NCs, (b) Mn-doped CsPbI₃ with high energy excitation, (c) Mn doped CsPbI₃ with low energy excitation NCs and (d) average lifetime of hot carrier cooling for Mn-doped CsPbI₃ with different doping concentration under 400 nm, 500 nm and 570 nm excitation energies, respectively. The added orange lines in Figure 5b-c represent Mn dopant orbitals.

In order to rationalize such a phenomenon, we need to get insight into the role of doping concentration in the local structure of doped NCs. Transition metal ion doping into pristine lattice inevitably introduces local structure distortion. The energy of the phonon modes and the strength of carrier-phonon coupling are significantly affected by such local distortion in the crystal structures, as evidenced by the DFT calculation and the XANES around Mn, also reported by previous works.^{39,40} Meanwhile, transition metals orbitals in the CB also add pathways for HCs



Figure 6. a) XANES spectra and b) magnified near edge XANES spectra at Mn-K edge of Mndoped NCs with various doping concentrations, c) Proposed structural motif representing the octahedron in undoped and Mn-doped NCs.

cooling process. As observed above, those factors are excitation energy-dependent as well as doping concentration-dependent. X-ray absorption spectroscopy (XAS) measurements were then conducted at the Mn K-edge to characterize the local bonding environment around the Mn^{2+} ions (for experimental details, see S.I.). Figure 6a shows the XAS profile of the samples containing 5% (orange), 7% (red) and 10% Mn (brown). Figure 6b zooms on the near-edge (XANES) region. The inset shows the first derivative of the XANES profiles as a function of ΔE defined as the difference between the incident photon energy and the threshold values of Mn^0 for the 3 samples (orange, red and brown lines) and a reference Mn foil (grey line). The energy position of the first inflection point correlates with the effective oxidation state of the absorbing atom. For the 3 samples, it falls between the values observed in Mn-oxides of +2 and +3..^{41,42} The XANES profile consists of the weak pre-edge feature P centered around 6541 eV and a strong white line at 6560 eV. Forbidden in ideal octahedral symmetry, the pre-edge feature arises from the transition of a Mn 1s electron to the unoccupied Mn 3d levels hybridized with the ligand 4p levels as a consequence of symmetry

lowering and distortions.⁴³ The while line is attributed to the transition of a Mn 1s electron to the molecular levels built from unoccupied 4p levels. In Mn-containing materials, the fine structure of the white line is affected by the balance between order and disorder⁴⁴ through their influence on the 3d population,⁴⁵ the Mn 3d-4p exchange interaction,⁴⁶ the hybridization of Mn 4p by the ligand orbitals (Hu)⁴⁷ and the Madelung constant.⁴⁵

At low doping concentration (i.e., 5%), P is weak but rather sharp and the white line presents a distinct shoulder A which can be ascribed to the hybridization of the Mn 4p, along with a clear double peak structure (B and C). As the doping concentration increases (7%, 10%), the oscillator strength of P gets more diffused, A disappears and the double structure B-C broadens. All these spectral features signal an elongation of the average Mn-I bond and a more pronounced disordering around the Mn atoms. Such local distortion should first modify the metal-halide vibrational modes, and thus enhance e-ph coupling in perovskites materials.⁴⁸ In addition, it will also weaken the mixing between Mn and I orbitals and therefore affect the available states in the pathway for the cooling of the HCs.

CONCLUSIONS

In summary, the HCs cooling dynamics in Mn-doped CsPbI₃ NCs have been studied by using transient absorption spectroscopy in combination with theoretical calculation and local structure characterization. Under the high energies excitation of 400 nm and 500 nm, Mn-doping promotes fast HCs cooling rates. However, Mn doping contributes to slowing the HCs cooling rate after excitation with 570 nm. From DFT calculations, Mn-doped CsPbI₃ show higher effective electrons/holes masses in comparison with undoped NCs. Meanwhile, temperature-dependent PL characterization further confirmed that Mn-doping also helps to strengthen the electron-phonon coupling. However, a large energy separation between the optical mode and acoustic modes is observed, implying that Mn-doping suppresses the efficient Klemens channel for LO phonon decay. The HCs cooling process is therefore the consequence of the competition between all the above factors, which leads to the excitation energy and doping concentration dependence. The enhanced electron-phonon coupling and efficient thermalization of HCs at high energy together with delayed heat dissipation after thermalization with HCs at low energy is optimal for the HCSC application. Our results open up a new possibility to optimize the HCs cooling dynamics in HCSC

materials via element doping with fine control on both electronic and phononic structures of the host materials.

ASSOCIATED CONTENT

Supporting Information

Experimental section for synthesis and characterization, DFT calculation, TEM images and size distribution, pump fluence dependent TA kinetics, cross section calculation, TA spectra with different wavelength and fluence, time-dependent carrier temperature with different excitation energies, temperature dependent PL emission, carrier temperature for doping concentration, Table for the cross section and exponential fitting of cooling process.

Corresponding Author

* kzheng@kemi.dtu.dk, kaibo.zheng@chemphys.lu.se

ORCID

Jie Meng: 0000-0002-3813-5221

Kaibo Zheng: 0000-0002-7236-1070

Sophie E. Canton: 0000-0003-4337-8129

Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENT

This work was funded Danish Council for Independent Research No. 7026-0037B, Swedish Research Council No. 2017-05337, Crafood foundation (no.20200522), Swedish Energy Agency research grant, and Research Fund for International Young Scientists from NSFC, China (no. 21950410515) (K. Z.). J. M., Z. L., Q. Z., acknowledge financial support from China Scholarship Council. We acknowledge DESY (Hamburg, Germany), a member of the Helmholtz Association HGF, for the provision of experimental facilities. Parts of this research were carried out at Petra III and we would like to thank Morgane Desmau, Edmund Welter and Vadim Murzin for assistance in working at P65 beamline.

REFERENCES

- Ross, R. T.; Nozik, A. J. Efficiency of Hot-Carrier Solar Energy Converters. J. Appl. Phys. 1982, 53, 3813–3818.
- (2) Lim, S. S.; Giovanni, D.; Zhang, Q.; Solanki, A.; Jamaludin, N. F.; Lim, J. W. M.; Mathews, N.; Mhaisalkar, S.; Pshenichnikov, M. S.; Sum, T. C. Hot Carrier Extraction in CH₃NH₃PbI₃ Unveiled by Pump-Push-Probe Spectroscopy. *Sci. Adv.* **2019**, *5*, 3620.
- (3) Guo, Z.; Wan, Y.; Yang, M.; Snaider, J.; Zhu, K.; Huang, L. Long-Range Hot-Carrier Transport in Hybrid Perovskites Visualized by Ultrafast Microscopy. *Science*. 2017, 356, 59–62.
- (4) Hopper, T. R.; Gorodetsky, A.; Frost, J. M.; Müller, C.; Lovrincic, R.; Bakulin, A. A. Ultrafast Intraband Spectroscopy of Hot-Carrier Cooling in Lead-Halide Perovskites. ACS Energy Lett. 2018, 3, 2199–2205.
- (5) Fu, J.; Xu, Q.; Han, G.; Wu, B.; Huan, C. H. A.; Leek, M. L.; Sum, T. C. Hot Carrier Cooling Mechanisms in Halide Perovskites. *Nat. Commun.* 2017, 8, 1300.
- (6) Lee, S. H.; Sim, H. S.; Lee, J.; Kim, J. M.; Shin, Y. E. Three Temperature Model for Nonequilibrium Energy Transfer in Semiconductor Films Irradiated with Short Pulse Lasers. *Mater. Trans.* 2006, 47, 2835–2841.
- Yang, J.; Wen, X.; Xia, H.; Sheng, R.; Ma, Q.; Kim, J.; Tapping, P.; Harada, T.; Kee, T. W.; Huang, F.; et al. Acoustic-Optical Phonon up-Conversion and Hot-Phonon Bottleneck in Lead-Halide Perovskites. *Nat. Commun.* 2017, *8*, 14120.
- (8) Zhu, H.; Miyata, K.; Fu, Y.; Wang, J.; Joshi, P. P.; Niesner, D.; Williams, K. W.; Jin, S.; Zhu, X. Y. Screening in Crystalline Liquids Protects Energetic Carriers in Hybrid Perovskites. *Science.* **2016**, *353*, 1409–1413.
- (9) Yang, Y.; Ostrowski, D. P.; France, R. M.; Zhu, K.; van de Lagemaat, J.; Luther, J. M.; Beard, M. C. Observation of a Hot-Phonon Bottleneck in Lead-Iodide Perovskites. *Nat. Photonics* **2016**, *10*, 53–59.
- (10) Xing, G.; Mathews, N.; Sun, S.; Lim, S. S.; Lam, Y. M.; Gratzel, M.; Mhaisalkar, S.; Sum,

T. C. Long-Range Balanced Electron- and Hole-Transport Lengths in Organic-Inorganic CH₃NH₃PbI₃. *Science*. **2013**, *342*, 344–347.

- (11) Sum, T. C.; Mathews, N.; Xing, G.; Lim, S. S.; Chong, W. K.; Giovanni, D.; Dewi, H. A. Spectral Features and Charge Dynamics of Lead Halide Perovskites: Origins and Interpretations. *Acc. Chem. Res.* **2016**, *49*, 294–302.
- (12) Li, M.; Bhaumik, S.; Goh, T. W.; Kumar, M. S.; Yantara, N.; Grätzel, M.; Mhaisalkar, S.; Mathews, N.; Sum, T. C. Slow Cooling and Highly Efficient Extraction of Hot Carriers in Colloidal Perovskite Nanocrystals. *Nat. Commun.* **2017**, *8*, 14350.
- (13) Fang, H.-H.; Adjokatse, S.; Shao, S.; Even, J.; Loi, M. A. Long-Lived Hot-Carrier Light Emission and Large Blue Shift in Formamidinium Tin Triiodide Perovskites. *Nat. Commun.* 2018, 9, 243.
- (14) Zhou, Y.; Chen, J.; Bakr, O. M.; Sun, H.-T. Metal-Doped Lead Halide Perovskites: Synthesis, Properties, and Optoelectronic Applications. *Chem. Mater.* **2018**, *30*, 6589–6613.
- (15) Guria, A. K.; Dutta, S. K.; Adhikari, S. Das; Pradhan, N. Doping Mn²⁺ in Lead Halide Perovskite Nanocrystals: Successes and Challenges. ACS Energy Lett. 2017, 2, 1014–1021.
- (16) Ji, S.; Yuan, X.; Cao, S.; Ji, W.; Zhang, H.; Wang, Y.; Li, H.; Zhao, J.; Zou, B. Near-Unity Red Mn²⁺ Photoluminescence Quantum Yield of Doped CsPbCl₃ Nanocrystals with Cd Incorporation. *J. Phys. Chem. Lett.* **2020**, *11*, 2142–2149.
- (17) Meng, J.; Lan, Z.; Abdellah, M.; Yang, B.; Mossin, S.; Liang, M.; Naumova, M.; Shi, Q.; Gutierrez Alvarez, S. L.; Liu, Y.; et al. Modulating Charge-Carrier Dynamics in Mn-Doped All-Inorganic Halide Perovskite Quantum Dots through the Doping-Induced Deep Trap States. J. Phys. Chem. Lett. 2020, 11, 3705–3711.
- König, D.; Casalenuovo, K.; Takeda, Y.; Conibeer, G.; Guillemoles, J. F.; Patterson, R.; Huang, L. M.; Green, M. A. Hot Carrier Solar Cells: Principles, Materials and Design. *Phys. E Low-dimensional Syst. Nanostructures* 2010, *42*, 2862–2866.
- (19) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with

Wide Color Gamut. Nano Lett. 2015, 15, 3692-3696.

- (20) Luo, B.; Li, F.; Xu, K.; Guo, Y.; Liu, Y.; Xia, Z.; Zhang, J. Z. B-Site Doped Lead Halide Perovskites: Synthesis, Band Engineering, Photophysics, and Light Emission Applications. *J. Mater. Chem. C* 2019, *7*, 2781–2808.
- (21) Price, M. B.; Butkus, J.; Jellicoe, T. C.; Sadhanala, A.; Briane, A.; Halpert, J. E.; Broch, K.; Hodgkiss, J. M.; Friend, R. H.; Deschler, F. Hot-Carrier Cooling and Photoinduced Refractive Index Changes in Organic–Inorganic Lead Halide Perovskites. *Nat. Commun.* 2015, 6, 8420.
- (22) Yogamalar, N. R.; Chandra Bose, A. Burstein–Moss Shift and Room Temperature near-Band-Edge Luminescence in Lithium-Doped Zinc Oxide. *Appl. Phys. A* 2011, *103*, 33–42.
- (23) Cunningham, P. D.; Hanbicki, A. T.; McCreary, K. M.; Jonker, B. T. Photoinduced Bandgap Renormalization and Exciton Binding Energy Reduction in WS₂. ACS Nano 2017, 11, 12601–12608.
- (24) Li, M.; Fu, J.; Xu, Q.; Sum, T. C. Slow Hot-Carrier Cooling in Halide Perovskites: Prospects for Hot-Carrier Solar Cells. *Adv. Mater.* **2019**, *31*, 1802486.
- (25) Cao, W.; Yuan, L.; Patterson, R.; Wen, X.; Tapping, P. C.; Kee, T.; Veetil, B. P.; Zhang, P.; Zhang, Z.; Zhang, Q.; et al. Difference in Hot Carrier Cooling Rate between Langmuir-Blodgett and Drop Cast PbS QD Films Due to Strong Electron-Phonon Coupling. *Nanoscale* 2017, *9*, 17133–17142.
- (26) Klimov, V.; Haring Bolivar, P.; Kurz, H. Hot-Phonon Effects in Femtosecond Luminescence Spectra of Electron-Hole Plasmas in CdS. *Phys. Rev. B* 1995, *52*, 4728–4731.
- (27) Wang, L.; Chen, Z.; Liang, G.; Li, Y.; Lai, R.; Ding, T.; Wu, K. Observation of a Phonon Bottleneck in Copper-Doped Colloidal Quantum Dots. *Nat. Commun.* **2019**, *10*, 4532.
- (28) Sekiguchi, F.; Hirori, H.; Shimazaki, A.; Nakamura, T.; Wakamiya, A.; Kanemitsu, Y. Enhancing the Hot-Phonon Bottleneck Effect in a Metal Halide Perovskite by Terahertz Phonon Excitation. *Phys. Rev. Lett.* **2021**,*126*, 077401.
- (29) Jia, X.; Jiang, J.; Zhang, Y.; Qiu, J.; Wang, S.; Chen, Z.; Yuan, N.; Ding, J. Observation of

Enhanced Hot Phonon Bottleneck Effect in 2D Perovskites. *Appl. Phys. Lett.* **2018**, *112*, 143903.

- (30) Chen, J.; Messing, M. E.; Zheng, K.; Pullerits, T. Cation-Dependent Hot Carrier Cooling in Halide Perovskite Nanocrystals. J. Am. Chem. Soc. 2019, 141, 3532–3540.
- (31) Feldmann, S.; Gangishetty, M. K.; Bravić, I.; Neumann, T.; Peng, B.; Winkler, T.; Friend, R. H.; Monserrat, B.; Congreve, D. N.; Deschler, F. Charge Carrier Localization in Doped Perovskite Nanocrystals Enhances Radiative Recombination. *J. Am. Chem. Soc.* 2021, jacs.1c01567.
- (32) Kawai, H.; Giorgi, G.; Marini, A.; Yamashita, K. The Mechanism of Slow Hot-Hole Cooling in Lead-Iodide Perovskite: First-Principles Calculation on Carrier Lifetime from Electron–Phonon Interaction. *Nano Lett.* 2015, *15*, 3103–3108.
- (33) Even, J.; Pedesseau, L.; Katan, C. Analysis of Multivalley and Multibandgap Absorption and Enhancement of Free Carriers Related to Exciton Screening in Hybrid Perovskites. J. Phys. Chem. C 2014, 118, 11566–11572.
- (34) S. Rudin, T. L. Reinecke, and B. S. Temperature-Dependent Exciton Linewidths in Semiconductors. *Phys. Rev. B* 1990, 42, 218–231.
- (35) Wright, A. D.; Verdi, C.; Milot, R. L.; Eperon, G. E.; Pérez-Osorio, M. A.; Snaith, H. J.; Giustino, F.; Johnston, M. B.; Herz, L. M. Electron–Phonon Coupling in Hybrid Lead Halide Perovskites. *Nat. Commun.* **2016**, *7*, 11755.
- (36) Kahmann, S.; Loi, M. A. Hot Carrier Solar Cells and the Potential of Perovskites for Breaking the Shockley–Queisser Limit. J. Mater. Chem. C 2019, 7, 2471–2486.
- (37) Conibeer, G. J.; König, D.; Green, M. A.; Guillemoles, J. F. Slowing of Carrier Cooling in Hot Carrier Solar Cells. *Thin Solid Films* **2008**, *516*, 6948–6953.
- (38) Shafique, A.; Shin, Y. H. Strain Engineering of Phonon Thermal Transport Properties in Monolayer 2H-MoTe₂. *Phys. Chem. Chem. Phys.* **2017**, *19*, 32072–32078.
- (39) Iaru, C. M.; Geuchies, J. J.; Koenraad, P. M.; Vanmaekelbergh, D.; Silov, A. Y. Strong Carrier–Phonon Coupling in Lead Halide Perovskite Nanocrystals. ACS Nano 2017, 11,

90

11024-11030.

- (40) Ma, J.; Yang, R.; Chen, H. A Large Modulation of Electron-Phonon Coupling and an Emergent Superconducting Dome in Doped Strong Ferroelectrics. *Nat. Commun.* 2021, *12*, 1–9.
- (41) Thibault-starzyk, F.; Ristic, A.; Rajic, N. Manganese-Containing Silica-Based Microporous Molecular Sieve MnS-1: Synthesis and Characterization. *Scanning* **2003**, 11, 4745–4750.
- (42) Resasco, J.; Dasgupta, N. P.; Rosell, J. R.; Guo, J.; Yang, P. Uniform Doping of Metal Oxide Nanowires Using Solid State Diffusion. J. Am. Chem. Soc. 2014, 136, 10521–10526.
- (43) Farges, F. Ab Initio and Experimental Pre-Edge Investigations of the Mn K -Edge XANES in Oxide-Type Materials. *Phys. Rev. B Condens. Matter Mater. Phys.* **2005**, *71*, 1–14.
- (44) Chaboy, J.; Prieto, C.; Hernando, M.; Parras, M.; González-Calbet, J. Ab Initio X-Ray Absorption Study of the Manganese K -Edge XANES Spectra in Mn- and Zn-Related Hexagonal Perovskites. *Phys. Rev. B - Condens. Matter Mater. Phys.* 2006, 74, 1–11.
- (45) De Vries, A. H.; Hozoi, L.; Broer, R. Origin of the Chemical Shift in X-Ray Absorption near-Edge Spectroscopy at the Mn K-Edge in Manganese Oxide Compounds. *Int. J. Quantum Chem.* 2002, *91*, 57–61.
- (46) Hozoi, L.; de Vries, A. H.; Broer, R. X-Ray Spectroscopy at the Mn K Edge in (Formula Presented) An Ab Initio Study. *Phys. Rev. B-Condens. Matter Mater. Phys.* 2001, 64, 4–7.
- (47) Hu, Y.; Borca, C. N.; Kleymenov, E.; Nachtegaal, M.; Delley, B.; Janousch, M.; Dönni, A.; Tachibana, M.; Kitazawa, H.; Takayama-Muromachi, E.; et al. Experimental and Ab Initio Investigations of the X-Ray Absorption near Edge Structure of Orthorhombic LuMnO₃. *Appl. Phys. Lett.* **2012**, *100*.
- (48) Straus, D. B.; Hurtado Parra, S.; Iotov, N.; Gebhardt, J.; Rappe, A. M.; Subotnik, J. E.; Kikkawa, J. M.; Kagan, C. R. Direct Observation of Electron-Phonon Coupling and Slow Vibrational Relaxation in Organic-Inorganic Hybrid Perovskites. *J. Am. Chem. Soc.* 2016, *138*, 13798–13801.

Supporting Information

Tailoring the Hot Carrier Cooling by Transition Metal Doping in All-inorganic Lead Halide Perovskite Nanocrystals

Jie Meng^{†,1}, Zhenyun Lan^{‡,1}, Weihua Lin[#], Maria Naumova[⊽], Mingli Liang[†], Xianshao Zou[#], Qian Zhao[†], Huifang Geng[¶], Ivano E. Castelli[‡], Sophie E. Canton[§], Tönu Pullerits[#], and Kaibo Zheng^{*,†,} #

[†]Department of Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark;

[‡]Department of Energy Conversion and Storage, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark;

[#]Chemical Physics and NanoLund, Lund University, Box 124, 22100 Lund, Sweden;

[¶]Ultrafast Electron Microscopy Laboratory, The MOE Key Laboratory of Weak-Light Nonlinear Photonics, School of Physics, Nankai University, Tianjin 300071, China;

⁷ Deutsches Elektronen Synchrotron (DESY), Notkestrasse 85, D-22607 Hamburg, Germany;

[§] European XFEL, Holzkoppel 4, 22869 Schenefeld, Germany.

*Corresponding Author

Kaibo Zheng: <u>kzheng@kemi.dtu.dk</u>, <u>kaibo.zheng@chemphys.lu.se</u>.

¹ The authors contribute equally in this work

Experimental Section

Materials and Chemicals. Cesium carbonate (Cs₂CO₃, ReagentPlus 99%, Sigma-Aldrich), Lead iodide (PbI₂, 99%, Sigma-Aldrich), Manganese iodide (MnI₂ anhydrous, 99.99% trace metals basis, Sigma-Aldrich), Oleylamine (OAm, technical grade 70%, Sigma-Aldrich), Oleic acid (OA, technical grade 90%, Sigma-Aldrich), 1-Octadecene (ODE, technical grade 90%, Sigma-Aldrich), Toluene (anhydrous 99.8%, Sigma-Aldrich).

Preparation of Cs-OA. Cs_2CO_3 (0.407 g), OA (1.5 mL), and ODE (20 mL) were added to a 50-mL 3-neck round-bottomed flask, evacuated and refilled with argon, dried at 120 °C for 30 min, then heated to 150 °C for at least 10 minutes until all Cs_2CO_3 reacted with OA before using.

Synthesis of Mn-doped CsPbI₃ NCs. Typically, PbI₂ (0.087 g, 0.188 mmol), MnI₂ (0-0.01), OAm (0.5 mL), OA (0.5 mL), ODE (5 mL) were added to a 25-mL 3 neck round bottom flask and were evacuated and refilled with Ar followed by heating the solution to 120 °C for 30 minutes. Then dried OAm (0.5 mL) and dried OA (0.5 mL) were subsequently injected to solubilize the solution. The solution was then increased to 160 °C. At 160 °C, the Cs-oleate (0.4 mL) was swiftly injected and after 1 minute the solution was cooled with an ice/water bath. After reaction, the aggregated NCs were centrifuged at 6000 rpm for 5 min. After centrifugation, the supernatant was discarded and the precipitate was redispersed in dried toluene. And then, the solution will be centrifuged at 6000 rpm for 5 min and the supernatant will be redispersed in toluene for further measurement.

Characterization. The absorption spectra were measured in a UV-Vis absorption spectrophotometer from Agilent Technologies (Santa Clara, USA). Steady-state photoluminescence was measured using a FluoroMax@-4 spectrofluorometer (HORIBA JOBIN YVON, Inc., Edison, NJ) with the excitation at 500 nm. Transmission electron microscopy (TEM) imaging was conducted on Tecnai G^2 T20 TEM. The Mn doping concentration was determined by coupled mass spectrometry (*ICP*-MS)

TA measurement. The transient absorption (TA) experiments were performed on a femtosecond pump-probe setup. Laser pulses (800 nm, 80 fs pulse length, 0.5 kHz repetition rate) were generated by a femtosecond oscillator (Mai Tai SP, both Spectra Physics). The pump pulses at 400 nm, 500 nm and 570 nm were generated by an optical parametric amplifier (Topas, Light Conversion). For the probe, we used the super-continuum generation from a thin CaF_2 plate. The
mutual polarization between pump and probe beams was set to the magic angle (54.7°) by placing a Berek compensator in the pump beam. The probe pulse and the reference pulse were dispersed in a spectrograph and detected by a diode array (Pascher Instruments). Excitation power and spot size measurements were used to determine the excitation fluence.

Absorption cross-section determination. NCs can be excited to multiple exciton states by high excitation fluence. With a usual assumption, the initially generated multiple exciton population follows the Poissonian distribution

$$P_N = \frac{e^{-\langle N \rangle \cdot \langle N \rangle^N}}{N!}$$
(S1)

where $\langle N \rangle$ is the average number of excitons per NCs, *N* is the number of excitons, and *P_N* is the fraction of NCs with *N* excitons. We can use $\langle N \rangle = \sigma \cdot I$ to present the average number of excitons per NCs, where σ is the absorption cross-section at the excitation wavelength and *I* is the excitation intensity in units of the number of photons per pulse per excitation area. From equation S1, we can calculate the fraction of excited NCs, *P_{exc}*, as:

$$P_{exc} = \sum_{N=1}^{\infty} P_N = 1 - P_0 = 1 - e^{-\langle N \rangle} = 1 = 1 - e^{-\sigma \cdot I}$$
(S2)

If we know P_{exc} , σ can be calculated from (S2). We obtain P_{exc} by measuring the excitation intensity dependence of the late-time region signal (t > 1 ns), which corresponds to the last remaining exciton after the Auger process. Due to multiple excitations generated at high pump intensity excitation in NCs is rapidly lost via Auger process leaving only one excitation at latetime region (t > 1 ns). The signal ΔA_0 (I, t > 1 ns) intensity can be rescaled to the corresponding signal at t=0, which we call $\Delta A_0(I)$. We use the lowest excitation intensity as reference excitation intensity and corresponding average number of excitons per NCs, $\langle N \rangle_0$ as reference number of excitons per NCs.

$$\Delta A_0(I) = \frac{\Delta A(I,I>1ns)}{e^{-t/\tau}} = \Delta A_{0,max} \cdot (1 - e^{-(I/I_0) \cdot \langle N \rangle_0})$$
(S3)

 ΔA_0 , denotes the largest possible single-exciton signal rescaled to *t*=0.

Based on the rescaled signal $\Delta A_0(I)$, we perform exponential fit to equation S3. From the fitting, we get the value of $\langle N \rangle_0$, and absorption cross-section σ of Mn doped CsPbI₃ NCs at 400 nm (3.1

eV) were calculated. The absorption cross-section σ at 500 nm and 570 nm were calculated based on the values of σ at 400 nm and absorption spectra.

Power loss of the hot carriers. The power loss of hot carriers is obtained from the time-dependent hot carriers temperature Tc using follow equation. k_B is Boltzmann constant.

$$P = \frac{d(\frac{3}{2}k_BT_c)}{dt}$$
(S4)

Average lifetime calculation

A multi-exponential model was used to fit the cooling process curves. The model is described as follows:

$$f(x) = \mathbf{A} + \Sigma \mathbf{B}_{i} \exp(-x/t_{i})$$
(S5)

where t_i represents the time constants and B_i represents the amplitudes of the fast and slow components, respectively. The average lifetime was calculated as follows:

$$t_{ave} = (\Sigma B_i t_i^2) / (\Sigma B_i t_i)$$
(S6)

DFT calculation

The density functional theory (DFT) calculations were performed using Perdew-Burke-Ernzerhof (PBE) exchange correlation functional,¹ as implemented in the Vienna ab initio package (VASP).² The electronic wave functions were calculated by using projected augmented wave (PAW)³ with a plane-wave cutoff of 520 eV. Due to the heavy Pb atom in CsPbCl₃, spin-orbit coupling (SOC) was included for the electronic properties calculation. The unit cell CsPbCl₃ structure is cubic containing 5 atoms with lattice parameter of 6.401 Å. A single Pb atom was replaced by a Mn atom in the 2 x 2 x 2 supercell corresponding to Mn concentration of 6.25%. Phonon spectrum was calculated using the DFPT method by the Phonon code. The Brillouin zone samplings were carried out with a Γ -center 4 x 4 x 4 k-point mesh. The atomic forces were relaxed to be less than 0.01 Å⁻¹. While for the HSE06 band structure calculation, the plane wave cutoff was set as 300 eV and the Brillouin zone was sampled by 2 x 2 x 2 Γ -centered k-point grid. It should also be noted that the imaginary phonon modes with a negative frequency result from the metastable lattice of

the perovskite where the permanent displacement of the atoms is possible through distortions of the crystal lattice.

X-ray absorption measurements

X-ray absorption spectra were acquired at P65 beamline of Petra III, Deutsches Elektronen -Synchrotron (DESY), Hamburg.⁴ Si (111) monochromator crystal was used. Higher harmonics rejection was done with two Si-coated mirrors. Solutions of Mn-doped nanoparticles in toluene were filled into 2 mm quartz capillaries (wall thickness 0.02 mm) which were positioned horizontally at 45 degrees to the incoming beam. Beam size on the sample was 2 mm (hor.) * 0.5 mm (ver.). Data were acquired in fluorescence mode using a 4 pixel Silicon drift detector. Spectra were taken in continuous scanning mode. First, damage tests were done by performing 30 s scans in -50 to 100 eV energy range around Mn K-edge. Then, based on the data quality, extended XANES range was chosen for the study: -100 to 300 eV measured for 120 s; many repetitions were done to improve the data quality. Mn foil was installed downstream of the sample for energy calibration. The maximum of first derivative of the foil was calibrated to 6539 eV.



Figure S1. The TEM images and size distribution of samples. The TEM images of (a) undoped CsPbI₃ and (b) Mn doped CsPbI₃. The corresponding size distribution of (c) undoped CsPbI₃ and (d) Mn doped CsPbI₃.



Figure S2. Pump fluence dependent TA kinetics for Mn doped CsPbI₃ NCs pumped at 400 nm (3.1 eV) probed at band-edge, $I_0=1.603 \times 10^{13}$ photons/cm²/pulse. (a) 0%, (b) 5%, (c) 7% and (d) 10%.



Figure S3. TA signal ΔA_0 rescaled from $\Delta t \ge 1$ ns as a function of pump fluence for Mn doped CsPbI₃ NCs pumped at 400 nm (3.1 eV) and probed at band-edge. (a) 0%, (b) 5%, (c) 7% and (d) 10%.



Figure S4. Pseudocolor representation TA spectra of undoped $CsPbI_3$ NCs for 400 nm excitation with different excitation intensities. (a) I_1 , (b) I_2 , (c) I_3 and (d) I_4 .



Figure S5. Pseudocolor representation TA spectra of Mn doped CsPbI₃ NCs for 400 nm excitation with different excitation intensities. (a) I_1 , (b) I_2 , (c) I_3 and (d) I_4 .



Figure S6. Pseudocolor representation TA spectra of undoped $CsPbI_3$ NCs for 500 nm excitation with different excitation intensities. (a) I_1 , (b) I_2 , (c) I_3 and (d) I_4 .



Figure S7. Pseudocolor representation TA spectra of Mn doped CsPbI₃ NCs for 500 nm excitation with different excitation intensities. (a) I_1 , (b) I_2 , (c) I_3 and (d) I_4 .



Figure S8. Pseudocolor representation TA spectra of undoped $CsPbI_3$ NCs for 570 nm excitation with different excitation intensities. (a) I_1 , (b) I_2 , (c) I_3 and (d) I_4 .



Figure S9. Pseudocolor representation TA spectra of Mn doped CsPbI₃ NCs for 570 nm excitation with different excitation intensities. (a) I_1 , (b) I_2 , (c) I_3 and (d) I_4 .



Figure S10. Normalized TA spectra of undoped CsPbI₃ NCs under 400 nm excitation with different excitation energies. (a) I_1 , (b) I_2 , (c) I_3 and (d) I_4 . The shortest time delay (red) is 0.3 ps and the longest (yellow) is 30 ps.



Figure S11. Normalized TA spectra of Mn doped CsPbI₃ NCs under 400 nm excitation with different excitation energies. (a) I_1 , (b) I_2 , (c) I_3 and (d) I_4 . The shortest time delay (red) is 0.3 ps and the longest (yellow) is 30 ps.



Figure S12. Normalized TA spectra of undoped CsPbI₃ NCs under 500 nm excitation with different excitation energies. (a) I_1 , (b) I_2 , (c) I_3 and (d) I_4 . The shortest time delay (red) is 0.3 ps and the longest (yellow) is 30 ps.



Figure S13. Normalized TA spectra of Mn doped CsPbI₃ NCs under 500 nm excitation with different excitation energies. (a) I_1 , (b) I_2 , (c) I_3 and (d) I_4 . The shortest time delay (red) is 0.3 ps and the longest (yellow) is 30 ps.



Figure S14. Normalized TA spectra of undoped CsPbI₃ NCs under 570 nm excitation with different excitation energies. (a) I_1 , (b) I_2 , (c) I_3 and (d) I_4 . The shortest time delay (red) is 0.3 ps and the longest (yellow) is 30 ps.



Figure S15. Normalized TA spectra of Mn doped CsPbI₃ NCs under 570 nm excitation with different excitation energies. (a) I_1 , (b) I_2 , (c) I_3 and (d) I_4 . The shortest time delay (red) is 0.3 ps and the longest (yellow) is 30 ps.



Figure S16. Time-dependent carrier temperature with 400 nm excitation at four different excitation intensities for (a) undoped and (b) Mn doped CsPbI₃ NCs.



Figure S17. Time-dependent carrier temperature with 570 nm excitation at four different excitation intensities for (a) undoped and (b) Mn doped CsPbI₃ NCs.



Figure S18. Temperature dependent PL emission spectra of Mn doped $CsPbI_3$ NCs as function of temperature (80 K to 180 K) for different doping concentration. (a) 0% and (b) 5%.



Figure S19. FWHM of the steady-state PL spectra as a function of temperature for of Mn doped CsPbI₃ NCs (80 K to 180 K) for different doping concentration. (a) 0% and (b) 5%.



Figure S20. Time-dependent carrier temperature for different doping concentration at low excitation intensity with (a) 400 nm, (b) 500 nm and (c) 570 nm excitation energy.

Table S1. The Absorption cross-sections of Mn doped $CsPbI_3$ at 400 nm, 500 nm and 570 nm. The values for 500 nm and 570 nm are calculated combining the absorption cross-section at 400 nm and absorption spectra in Figure 1c.

	0%	5%	7%	10%
400 nm (3.10 eV)	$4.2 \times 10^{-14} \text{ cm}^2$	$6.0 \times 10^{-14} \text{ cm}^2$	$8.0 \times 10^{-14} \text{ cm}^2$	$1.4 \times 10^{-14} \text{ cm}^2$
500 nm (2.48 eV)	$1.5 \times 10^{-14} \text{ cm}^2$	$2.0 \times 10^{-14} \text{ cm}^2$	$2.8 \times 10^{-14} \text{ cm}^2$	$0.5 \times 10^{-14} \text{ cm}^2$
570 nm (2.18 eV)	$0.7 \times 10^{-14} \text{ cm}^2$	$0.9 \times 10^{-14} \text{ cm}^2$	$1.2 \times 10^{-14} \text{ cm}^2$	$0.2 \times 10^{-14} \text{ cm}^2$

Table S2. Fit parameters for time-dependent carrier temperature of undoped CsPbI₃ NCs with 400 nm excitation at different intensities $n \approx 3.5 \times 10^{17}$ (I₁), 1.7×10^{18} (I₂), 3.5×10^{18} (I₃) and 6.9×10^{18} (I₄) photon/cm²/pulse, corresponding to $\langle N \rangle \approx 0.7$, 3.7, 6.7 and 13.5, respectively. The unit of time t is *ps*.

	A ₁	t_1	A ₂	t ₂	A ₃	t ₃	tave
I ₁	0.77	0.2	0.22	0.7	0.02	19.2	9.9
I_2	0.74	0.7	0.21	0.7	0.05	24.0	16.4
I_3	0.60	0.6	0.35	0.6	0.06	20.8	14.1
I_4	0.56	0.9	0.32	0.9	0.13	5.4	3.0

Table S3. Fit parameters for time-dependent carrier temperature of Mn doped CsPbI₃ NCs with 400 nm excitation at different intensities $n \approx 5.3 \times 10^{17}$ (I₁), 2.7×10^{18} (I₂), 5.3×10^{18} (I₃) and 1.1×10^{19} (I₄) photon/cm²/pulse, corresponding to $\langle N \rangle \approx 1.0$, 4.8, 9.6 and 19.2, respectively. The unit of time t is *ps*.

	A ₁	t_1	A ₂	t ₂	A ₃	t ₃	t _{ave}
I ₁	0.97	0.1	0.03	0.4	0.0005	29.4	3.8
I_2	0.97	0.7	0.03	14.0	-	-	8.3
I_3	0.93	0.6	0.07	17.7	-	-	12.2
I_4	0.89	0.8	0.11	12.4	-	-	8.2

Table S4. Fit parameters for time-dependent carrier temperature of undoped CsPbI₃ NCs with 500 nm excitation at different intensities $n \approx 3.0 \times 10^{17}$ (I₁), 1.5×10^{18} (I₂), 3.0×10^{18} (I₃) and 4.4×10^{19} (I₄) photon/cm²/pulse, corresponding to $\langle N \rangle \approx 0.6$, 2.9, 5.8 and 8.7, respectively. The unit of time *t* is *ps*.

	A ₁	t_1	A ₂	t ₂	A ₃	t ₃	t _{ave}
I ₁	0.94	0.4	0.06	4.1	-	-	1.8
I_2	0.89	0.5	0.11	27.4	-	-	23.7
I_3	0.84	0.6	0.16	23.2	-	-	20.2
I_4	0.87	0.7	0.13	12.7	-	-	9.7

Table S5. Fit parameters for time-dependent carrier temperature of Mn doped CsPbI₃ NCs with 500 nm excitation at different intensities $n \approx 4.2 \times 10^{17}$ (I₁), 2.1×10^{18} (I₂), 4.2×10^{18} (I₃) and 6.4×10^{18} (I₄) photon/cm²/pulse, corresponding to $\langle N \rangle \approx 0.8$, 3.9, 7.7 and 11.5, respectively. The unit of time *t* is *ps*.

	A ₁	t_1	A ₂	t ₂	A ₃	t ₃	tave
I ₁	1	0.6	-	-	-	-	0.6
I_2	0.93	0.6	0.07	18.8	-	-	13.1
I_3	0.86	0.7	0.14	21.4	-	-	17.9
I_4	0.86	0.6	0.14	11.7	-	-	9.0

Table S6. Fit parameters for time-dependent carrier temperature of undoped CsPbI₃ NCs with 570 nm excitation at different intensities $n \approx 2.6 \times 10^{17}$ (I₁), 7.9×10^{17} (I₂), 1.8×10^{18} (I₃) and 2.9×10^{18} (I₄) photon/cm²/pulse, corresponding to $\langle N \rangle \approx 0.5$, 1.5, 3.6 and 5.6, respectively. The unit of time *t* is *ps*.

	A_1	t_1	A ₂	t ₂	A ₃	t ₃	t _{ave}
I ₁	0.95	0.1	0.05	0.7	-	-	0.3
I_2	1	0.5	-	-	-	-	0.5
I_3	1	0.9	-	-	-	-	0.9
I_4	0.87	0.5	0.13	16.8	-	-	14.1

Table S7. Fit parameters for time-dependent carrier temperature of Mn doped CsPbI₃ NCs with 570 nm excitation at different intensities $n \approx 3.6 \times 10^{17}$ (I₁), 1.1×10^{18} (I₂), 2.5×10^{18} (I₃) and 4.0 $\times 10^{18}$ (I₄) photon/cm²/pulse, corresponding to $\langle N \rangle \approx 0.7$, 2.0, 4.6 and 7.2, respectively. The unit of time *t* is *ps*.

	A ₁	t_1	A ₂	t ₂	A ₃	t ₃	t _{ave}
I ₁	1	0.4	-	-	-	-	0.4
I_2	1	0.6	-	-	-	-	0.6
I_3	0.92	0.1	0.05	0.9	0.03	49.4	45.6
I_4	0.81	0.7	0.19	12.1	-	-	9.8

Table S8. Fit parameters for time-dependent carrier temperature of Mn doped CsPbI₃ NCs with 400 nm excitation at different doping concentration. $n \approx 3.5 \times 10^{17}$ (0%), 5.3×10^{17} (5%), 8.0×10^{17} (7%) and 2.9×10^{17} (10%) photon/cm²/pulse, corresponding to $\langle N \rangle \approx 0.7$, 1.0, 1.2 and 0.2, respectively. The unit of time *t* is *ps*.

	A ₁	t_1	A ₂	t ₂	A ₃	t ₃	t _{ave}
0%	0.85	0.2	0.15	0.9	-	-	0.5
5%	0.97	0.1	0.03	0.5	-	-	0.2
7%	0.91	0.1	0.09	0.4	-	-	0.2
10%	0.97	0.3	0.03	1.4	-	-	0.5

Table S9. Fit parameters for time-dependent carrier temperature of Mn doped CsPbI₃ NCs with 500 nm excitation at different doping concentration. $n \approx 3.0 \times 10^{17} (0\%)$, $4.2 \times 10^{17} (5\%)$, $6.7 \times 10^{17} (7\%)$ and $2.5 \times 10^{17} (10\%)$ photon/cm²/pulse, corresponding to $\langle N \rangle \approx 0.6$, 0.8, 1.1 and 0.2, respectively. The unit of time *t* is *ps*.

	A ₁	t_1	A ₂	t_2	A ₃	t ₃	tave
0%	0.94	0.1	0.06	4.1	-	-	1.8
5%	1	0.6	-	-	-	-	0.6
7%	1	0.4	-	-	-	-	0.4
10%	0.95	0.1	0.03	0.2	0.02	0.5	0.1

Table S10. Fit parameters for time-dependent carrier temperature of Mn doped CsPbI₃ NCs with 570 nm excitation at different doping concentration. $n \approx 2.6 \times 10^{17}$ (0%), 3.6×10^{17} (5%), 5.5×10^{17} (7%) and 1.9×10^{17} (10%) photon/cm²/pulse, corresponding to $\langle N \rangle \approx 0.5$, 0.7, 0.9 and 0.1, respectively. The unit of time *t* is *ps*.

	A ₁	t_1	A ₂	t_2	A ₃	t ₃	tave
0%	0.95	0.1	0.05	0.7	-	-	0.3
5%	1	0.4	-	-	-	-	0.4
7%	1	0.6	-	-	-	-	0.6
10%	0.55	0.3	0.42	0.4	0.03	2.0	0.6

References

- (1) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B* 1993, 47, 558–561.
- (3) Blöchl, P. E. Projector Augmented-Wave Method. Phys. Rev. B 1994, 50, 17953–17979.
- Welter, E.; Chernikov, R.; Herrmann, M.; Nemausat, R. A Beamline for Bulk Sample X-Ray Absorption Spectroscopy at the High Brilliance Storage Ring PETRA III. *AIP Conf. Proc.* 2019, 2054, 1–6.

Chapter 5 Conclusion and perspective

In this thesis, we studied the photophysical properties of Mn-doped lead halide perovskite with a special focus on the exciton to dopant energy transfer and hot carrier cooling dynamics. These photophysical properties have a significant relationship with the doping. Our results show that both electronic structures and the crystal structures are modified by Mn doping in the perovskite structure, which both act as critical factors in determining the charge carrier dynamics.

Firstly, the photoluminescence properties of perovskite QDs can be well-tuned by elemental doping due to the introduction of defect states. The first work (**Chapter 3**) systematically revealed the formation of defect state by dopant and their influence on the photo-induced charge carrier dynamics in Mn-doped CsPbCl₃ perovskite QDs. As the Mn concentration increases, the exciton photoluminescence quantum yield (PLQY) decreases and the Mn dopant emission QY first increases and then decreases. The experiments and calculations reveal that Mn²⁺ doping qualitatively changes the type of the defects from shallow antisites Pbc₈ (undoped) to deep interstitials Cl_i (doped), which locate deep at the energy between the Mn²⁺ doping orbital. The depopulation of initial exciton states of the CsPbCl₃ QDs after excitation is a competition between exciton-dopant energy transfer and defect trapping at early timescale (< 100 ps), which determines the final PLQY of the CsPbCl₃ QDs. The present work establishes a reference and guidelines for optimizing such materials for all the emerging applications where high PLQY is essential.

In the second work (**Chapter 4**), we focused on investigating the influence of Mn doping on the HCs cooling dynamics which is the main energy loss process in LHPs solar cells. We demonstrate that transition metal doping may be a promising strategy to change the electronic and phononic structure of LHPs, thereby regulating the cooling process. Here, we combined femtosecond transient absorption spectroscopy and DFT calculations to study the HCs relaxation kinetics in Mn-doped CsPbI₃ NCs, with particular attention to the effect of Mn doping on the electronic and phononic structure. We proved that Mn²⁺ doping, 1) enlarges the LO acoustic phonon band gap, 2) enhances the electron-LO phonon coupling strength, and 3) increases the HCs relaxation pathway. The first two factors are related to the local deformation after Mn^{2+} replaces Pb^{2+} in the lattice, and the last effect is attributed to the positions of the Mn orbitals in the LHPs band. Spectral studies have shown that, due to the dominant role of LO phonon band gap expansion, the HCs cooling process slows down after doping under band edge excitation. When the excitation photon energy is much larger than the optical band gap and the Mn^{2+} transition gap, doping accelerates the cooling rate due to the enhanced carrier-phonon coupling and the dominant role of the relaxation path. Our results establish a direct method to control the dynamics of the excited charge carriers, from the cooling processes when they are 'hot' residing above the band edge and recombination processes when they are 'cold', locating from the band edge of the materials, all through element doping, thus hoping to optimize the optoelectronic properties. On one hand, the Mn orbitals within the electronic structure that dominate the cooling process of HCs. On the other hand, the existence of Mn orbitals will induce defects acting as trapped states located within the band gap. The depopulation of initial exciton states of the host materials after excitation is a competition between exciton-dopant energy transfer and defect trapping at early timescale. We expect the above-mentioned findings in this thesis will supply the theoretical and experimental foundation in improving the efficiency of optoelectronic devices.

Here, based our understanding, some perspectives are proposed in the future study as follow.

1) Photophysics with materials doped with other elements. This includes other transition metal element, or even non-metal and their corresponding photophysical dynamics could be considered. Furthermore, due to differences in the ion radius and valences, the carrier dynamics behind doping, defects, and corresponding dopant states, trapping state is still worth exploring.

2) The systematic correlation between doping concentration/local structure and the photophysics of the materials. The doping concentration and local structure states act a critical factors in determining the carrier dynamics. Meanwhile, the surface defects or inner defects should also be well addressed.

3) Besides optical effects, the response of the doped materials to other external triggers such as the magnetic or electric fields, could also be used to regulate the carrier dynamics. For example, the magnetic properties of transition metals, like Mn, Fe, Co and Ni, could be efficient strategies in modulating the carrier dynamics or HCs cooling.