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学位論文

An investigation of single-particle photoluminescence blinking in halide perovskite nanocrystals and quantum dots

(ハライドペロブスカイトナノ結晶と量子ドット における単一粒子発光の点滅についての研究)

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Abstract

Lead halide perovskites are promising materials for next-generation optoelectronic devices and photovoltaics. This class of materials has high absorption cross-sections, long photoluminescence lifetimes, high charge carrier mobilities, and high photoluminescence quantum yields. However, there are certain limitations to be lifted for practical applications of these semiconductors. For example, these perovskites are susceptible to moisture, water, oxygen, or light. This thesis collects factors responsible for the degradation of lead halide perovskite nanocrystals and quantum dots and analyzes how to suppress these factors. The main focus is single-particle photoluminescence stability, blinking, and charge carrier dynamics of perovskite nanocrystals and quantum dots. I assign the factors responsible for the deterioration of perovskites to the nonradiative recombinations assisted by halide and cation vacancies. This thesis contains five chapters. In Chapter 1, I introduce the general properties of lead halide perovskites. I explain their chemical structure and various synthesis methods for nanocrystals, quantum dots, thin films, and microcrystals. I describe the band-edge states and the effect of spin-orbit coupling in these perovskites. Next, I introduce their charge carrier dynamics followed by absorption and photoluminescence properties. I review extrinsic and intrinsic factors responsible for degrading the photoluminescence and structure of perovskites. Furthermore, halide perovskites show blinking, which is the stochastic fluctuation of photoluminescence intensity between bright (ON) and dark (OFF) states. I summarize the photoluminescence blinking mechanisms in perovskite nanocrystals and quantum dots. Next, I briefly explain the emerging applications of halide perovskites to lasers, solar cells, and LEDs, followed by my motivation for the research conducted in this thesis. In Chapter 2, I give detailed information about the materials used and the synthesis of lead halide perovskites. I used ligand-mediated transport, ligand-assisted reprecipitation, and hot-injection methods to synthesize these nanocrystals and quantum dots. Also, I describe the working principles of the instruments used in analyzing the structure and optical properties of perovskites, such as absorption spectroscopy, fluorescence spectroscopy, transmission electron microscopy, and X-ray diffraction. Also, I explain the time-resolved fluorescence spectroscopy for analyzing the photoluminescence decay profiles and charge carrier recombination rates of perovskites. Next, I explain the single-particle microspectroscopy system for examining the photoluminescence intensity trajectories of nanocrystals and quantum dots. In Chapter 3, I

sketch the role of oxygen on the stability of methylammonium lead iodide perovskite nanocrystals at the ensemble and the single-particle levels. I show the photoluminescence behavior of the nanocrystals in air, argon, and polymer atmospheres. The photoluminescence intensity in the air continuously decreases, whereas argon or a polymer matrix stabilizes the emission. This photoluminescence behavior is similar at the ensemble and single-particle levels. In halide perovskites, the electron transfer from the perovskite to oxygen generates superoxide at the halide vacancies. Superoxide disintegrates the perovskite structure into lead iodide, methylamine, and water. In an argon or a polymer environment, the photoluminescence intensity is stable, suggesting the suppression of superoxide generation and oxidation of perovskites. Also, the photoluminescence intensity recovery after a long-OFF event shows the stability of the perovskites in the ionized state. Such a long-OFF event associated with a low electron transfer rate suggests that the perovskites do not produce or react with superoxide in the ionized state. In the last section, I explain the degradation mechanism by considering the role of the halide vacancies on superoxide generation. In Chapter 4, I focus on the suppression of the halide vacancies or charge carrier traps in methylammonium lead iodide or bromide perovskite quantum dots at the ensemble and single-particle levels. Halide vacancies are intrinsic defects that create deep traps in the bandgaps of perovskites. These vacancies are the prominent reason for nonradiative recombination or trapping of photogenerated charge carriers. These vacancies are filled by halide salts to reduce their effect on the degradation of the perovskites. At the single-particle level, the photoluminescence intensity trajectories of the vacancy-filled sample show blinking suppression. I assign the relationship between the vacancies and blinking by analyzing over 200 single perovskite quantum dots and construct the ON- and OFF-time probability distributions before and after the vacancy filling. The probability distributions suggest that the blinking behavior changes from type-A to type-B after the filling. That means the charging-discharging processes in the perovskite switch to the trapping-detrapping mechanism. Therefore, the halide salts fill the halide vacancies. Further, the photoluminescence quantum yields and lifetimes of the perovskite quantum dots increase after the halide salt treatment at the ensemble level. Apart from the vacancy filling, the halide-vacancy-assisted nonradiative recombination rate is estimated at 1×10^8 s⁻ ¹ for lead bromide perovskite and 1.9×10^9 s⁻¹ for lead iodide quantum dots. In Chapter 5, I show the role of A-and B-site cation vacancies on the photoluminescence of caesium lead bromide perovskite quantum dots at the ensemble and single-particle levels. The cation vacancies form shallow trap states in the energy levels of the lead halide perovskite.

Caesium oleate or lead oleate are applied to fill the Cs⁺ or Pb²⁺ vacancies. At the ensemble level, the pristine perovskite quantum dot's photoluminescence intensity continuously decreases with time. Although caesium oleate slightly lowers the photodegradation rate of the quantum dots, lead oleate does not affect the photoluminescence. Also, no difference in the average photoluminescence lifetime is observed for the quantum dots before and after the addition of caesium or lead oleate. Similarly, the photoluminescence blinking of single quantum dots does not change before and after adding the caesium or lead oleate. Furthermore, I show the ON- and OFF-time probability distributions by analyzing >200 blinking perovskite quantum dots before and after the addition of caesium oleate. Although the perovskite quantum dots show type-A blinking regardless of the caesium oleate treatment, the overall ON-time increases after the treatment. Therefore, I assume that the caesium oleate treatment reduces the surface Cs⁺ vacancies, whereas lead oleate has a negligible effect on the charge carrier dynamics. In summary, this thesis unveils the factors responsible for the degradation and blinking of lead halide perovskite nanocrystals. Further, it demonstrates photoluminescence blinking suppression and intensity enhancement of these nanocrystals by halide vacancy filling.

Abbreviations and Symbols

Å	Angstrom
Α	Absorbance
A ₀	Constant
A_i	Amplitude of i^{th} time
<i>a</i> , <i>b</i> , or <i>c</i>	Lattice constant
ASE	Amplified spontaneous emission
AVC	Antisolvent vapor-assisted crystallization
°C	Degree Celsius
С	Concentration
са	Centered around
cm	Centimeter
cw	Continuous-wave
CB	Conduction band
CBM	Conduction band minimum
CsAc	Caesium acetate
CsOL	Caesium oleate
d_{hkl}	Interplanar spacing
$D_{n,p}$	Diffusion coefficient
DCM	Dichloromethane
DMF	N, N-dimethylformamide
DMSO	Dimethyl sulfoxide
Ε	Integrated area of the emission
e	Electronic charge
e	Electron
eV	Electronvolt
EMCCD	Electron multiplying charge-coupled device
ETM	Electron transport material
FA	Formamidinium
FABr	Formamidinium bromide
FAI	Formamidinium iodide
FLID	Fluorescence lifetime intensity distribution

fs	Femtosecond
FTO	Fluorine-doped tin oxide
g	Gram
GBL	γ-Butyrolactone
h	Hour
h^+	Hole
HDA	Hexadecyl amine
<i>h</i> , <i>k</i> , or <i>l</i>	Miller indices
HTM	Hole transport material
Hz	Hertz
ITC	Inverse temperature crystallization
ITO	Indium tin oxide
<i>k</i> 1	The rate constant of monomolecular recombination
<i>k</i> ₂	The rate constant of bimolecular recombination
<i>k</i> ₃	The rate constant of Auger recombination
h.	The rate constant of additional nonradiative
ĸA	relaxation
<i>k</i> _B	Boltzmann constant
<i>k</i> _{et}	The rate constant of electron transfer
<i>k</i> _{nr}	The rate constant of nonradiative relaxation
kr	The rate constant of radiative relaxation
LD	Diffusion length
LARP	Ligand-assisted reprecipitation
LED	Light-emitting diode
LHP	Lead halide perovskite
LPF	Long-pass filter
<i>M_{eff}</i>	Effective masses
Μ	Molar
MA	Methylammonium
MABr	Methylammonium hydrobromide
MAI	Methylammonium hydroiodide
mg	Milligram
MHz	Megahertz

min	Minute
mL	Milliliter
mm	Millimeter
mmol	Millimole
ms	Millisecond
mW	Milliwatt
<n></n>	The average number of photons
N_i	Occurrence of i^{th} time
NA	Numerical aperture
NIR	Near-infrared
NREL	National renewable energy laboratory
nm	Nanometer
ns	Nanosecond
OA	Oleic acid
$P(\tau)$	Probability distribution
PbAc	Lead acetate
Pb(OL) ₂	Lead oleate
PCE	Power conversion efficiency
PDOS	Projected density of states
PeLED	Perovskite light-emitting diode
PL	Photoluminescence
PMMA	Poly(methyl methacrylate)
PNC	Perovskite nanocrystal
PSC	Perovskite solar cell
PTFE	Polytetrafluoroethylene
PQD	Perovskite quantum dot
QD	Quantum dot
QY	Quantum yield
r_a	The radius of A-site cation
<i>r</i> _b	The radius of B-site cation
r_X	The radius of X-site cation
rpm	Rotation per minute
RT	Room temperature

S	Second	
SEM-EDX	Scanning electron microscopy with energy dispersive	
	X-ray spectroscopy	
SOC	Spin-orbit coupling	
STEM	Scanning transmission electron microscopy	
Т	Temperature	
TiO ₂	Titanium dioxide	
XRD	X-ray diffraction	
UV	Ultraviolet	
VB	Valence band	
VBM	Valence band maximum	
W	Watt	
WGM	Whispering Gallery Mode	
μJ	Microjoule	
μm	Micrometer	
$\mu_{n,p}$	Charge carrier mobility	
δ_o	Orthorhombic phase	
δ_H	Hexagonal phase	
σ^*	Sigma antibonding orbitals	
π^*	Pi antibonding orbitals	
T 01 T	Photoluminescence lifetime or average	
τ or τ_{avg}	photoluminescence lifetime	
$ au_c$	Truncation time	
3	Molar extinction coefficient	
λ	Wavelength	
η	Refractive index	

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Chapter 1

Introduction

Abstract

Lead halide perovskites are emerging into potentially low-cost and efficient optoelectronic devices. The interest in this class of materials is increasing due to their unique optical and electronic properties. In this chapter, I introduce the general properties of lead halide perovskite, such as the chemical composition and structure. Subsequently, I explain the various synthesis methods for preparing thin films and microcrystals of lead halide perovskites. Then, I introduce the energy states of the perovskites by discussing the factors affecting the bandgaps, such as the Rashba effect and spin-orbit coupling, which is followed by the charge carrier dynamics by considering monomolecular, bimolecular, and Auger recombination pathways. In the next section, I describe the most intriguing properties of lead halide perovskites, such as the tunable absorption and the photoluminescence from UV-visible to near-infrared region. Further, I summarize the intrinsic and extrinsic factors affecting the photoluminescence and the stability of lead halide perovskites. In the second section, I introduce lead halide perovskite nanocrystal and quantum dot synthesis methods through ligand-assisted reprecipitation or hot-injection, which are known for yielding narrow size distribution of particles. These nanocrystals and quantum dots show intense photoluminescence in the blue-green-red region. However, the photoluminescence intensity stochastically fluctuates among different energy levels, which is called blinking. This blinking is a significant limitation to furthering the application of the perovskites. For example, the blinking decreases the photoluminescence quantum yields and degrades the device efficiencies of lead halide perovskites due to random switching between the radiative and nonradiative recombinations. In the third section, I review the leading and emerging applications of lead halide perovskites. In the last section, I describe my motivation for the research presented in the subsequent chapters to view future uses of the lead halide perovskites.

1.1 General Introduction

Perovskites were first discovered in the early 1800s as calcium titanate oxide (CaTiO₃) by Gustav Rose in Russia and later named after the mineralogist Lev Perovski, which has the general formula ABX₃. After a while, Møller et al. showed the first crystallographic details of caesium lead halide (CsPbX₃, X= Cl, Br, I) perovskites in 1958.¹ However, the interest in this class of materials surged in the early 21st century. Lead halide perovskites (LHPs) gained popularity due to their cost-effective, straightforward synthesis and unique optical and electronic properties. They show high photoluminescence (PL) quantum yield (QY), and PL is tunable in the visible-to-near infrared region (NIR).²⁻⁴ The LHPs also show long charge carrier diffusion lengths, long PL lifetimes, high charge carrier mobilities, and large absorption coefficients, making them suitable to engineer efficient real-world devices, such as solar cells, color-tunable light-emitting diodes (LEDs), and lasers, photodetectors, and single-photon devices.^{5–12} The first report on perovskite solar cell (PSC) fabricated using methylammonium lead halide (MAPbI₃) perovskite film was published in 2009, which showed the power conversion efficiency (PCE) 3.8%.¹³ Over a decade, the maximum PCE had increased up to 26% [National Renewable Energy Laboratory (NREL) efficiency chart] by modifying the charge-injection layers and improving the film quality.¹⁴ LEDs with layered perovskite compounds were demonstrated even before the PSC, but the electroluminescence was observed only at very low temperatures.^{15–17} Friend and coworkers fabricated brightly luminescent green and red perovskite LEDs (PeLED) at room temperature with the external quantum efficiencies of 0.1% and 0.76%, respectively.¹⁸ Currently, the highest achieved external quantum efficiencies of blue, green, and red LEDs are 11%, 20.7%, and 21.6%, respectively.^{19–21} Soon after the first fabrication of a PSC, the research broadened in defining the electronic states, exciton binding energies, phonons, and spin-orbit coupling in the lead and the lead-free halide perovskites.^{22–24}

Halide perovskites have the general formula ABX_3 (X= Cl, Br, I). The insertion of bigger halide ions than oxygen stabilizes the octahedral geometry of perovskites by balancing the size with the B-site metal ions. The A-site cation is in the +1 oxidation state and surrounded by $[BX_6]^{4-}$ octahedrons. The B-site cation is in the +2 or +3 oxidation states and coordinated by six halide ions as shown in Figure 1.1.²⁵ The most common A-site cations are methylammonium (MA, CH₃NH₃⁺), formamidinium (FA, [CH(NH₂)₂]⁺), and caesium (Cs⁺).²⁻⁴ The most common B-site cations consist of 3d, 4d, or 5d post-transition

metals, such as lead (Pb²⁺), tin (Sn²⁺), germanium (Ge²⁺), etc. Recently, interest in double perovskites (A₂BB'X₆) is increased for replacing the potentially toxic Pb²⁺ by silver (Ag⁺), indium (In³⁺), bismuth (Bi³⁺), and antimony (Sb³⁺), which form, Cs₂AgBiX₆, Cs₂AgInX₆, and Cs₂AgBiInX₆.^{26–33}



Figure 1.1. A schematic representation of the perovskite structure.

1.1.1 Synthesis of Halide Perovskites

The chemical composition of organic-inorganic halide perovskites can be varied by using different A-, B- and X-site ions. The Goldschmidt tolerance factor (t) is appropriate to predict the stability of the structure; t is given by

$$t = \frac{r_a + r_x}{\sqrt{2} (r_b + r_x)}$$
(1.1)

Here, r_a , r_b , and r_x , are the radii of A-site cation, B-site cation, and X-site anion, respectively.²⁵ The tolerance factor ranges from 0.81 to 1.00, and beyond this range, the perovskite structure is unstable. Another parameter in calculating the stability of the octahedral cavity of perovskite is the octahedral factor, $\mu = r_b/r_x$, which ranges from 0.44 to 0.9.²⁵ Figure 1.2 shows the common area covered by the tolerance and octahedral factors in determining the stabilities of lead and tin halide perovskites with Cs, MA, or FA cations. The non-spherical geometry of an A-site organic cation and its lattice's constant rotation makes it difficult to determine the exact ionic radius. Therefore, Kieslich *et al.* modified r_a



Figure 1.2. Estimation of the stability of LHPs from the radii of A-site cation and the radii of halide. The solid and dash lines represent the tolerance and octahedral factors, respectively. Reproduced from Manser *et al.*²⁵

to r_{Aeff} , which is equivalent to the radius of the atom and the distance between the center of masses.³⁴ For calculating the r_x , the anisotropy was considered in the estimation of the tolerance factor. Another example is that Li *et al.* tuned the tolerance factor by forming a cubic phase of α -FA_xCs_{1-x}PbI₃ by alloying two perovskites in the solid-state.³⁵ One is the orthorhombic phase δ_o -CsPbI₃, and the second is the hexagonal phase δ_H -FAPbI₃ having <0.8 and >1 tolerance factor, respectively. Based on the tolerance and octahedral factors, the halide perovskites are most stable when the A-site cation is Cs, MA, or FA.

LHP films and microcrystals are synthesized by various processes, as shown in Figure 1.3. LHP films are mostly used as light-harvesting layers in PSCs and are fabricated by a single or sequential (two) step process.^{13,27,36–38} In such a fabrication, the precursor salts (CsX or FAX or MAX and PbX₂) are dissolved completely in a polar organic solvent, such as *N*, *N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), or γ -butyrolactone (GBL) for crystallization. These solvents have low vapor pressures and high boiling temperatures, making the evaporation, nucleation, and crystal growth slow. Generally, in a one-step process, the precursor salts are mixed in a solvent and spin-coated on a substrate, as shown in Figure 1.3a. The deposition techniques also vary for uniform coating of the LHP films, such as antisolvent-assisted deposition, vacuum- or gas-pumping, and hot-casting.³⁹ For example, Xiao *et al.* used dichloromethane (DCM) as an antisolvent to



Figure 1.3. Schematic representations of the synthesis of thin films and microcrystals of LHPs. (a) One-step deposition of a precursor solution, (b) sequential deposition of precursors (IPA; isopropanol), (c) inverse temperature crystallization (ITC), and (d) antisolvent vapor-assisted crystallization (AVC).

fabricate uniform MAPbI₃ LHP films.³⁷ Here, MAPbI₃ precursors were dissolved in DMF and spin-coated on the TiO₂ substrate. This film was exposed to DCM to induce fast crystallization of the perovskite and form a grain-free film. In sequential deposition (Figure 1.3b), typically, each precursor salt is separately dissolved in a solvent and deposited on a substrate. For example, Im *et al.* dissolved PbI₂ and MAI in DMF separately.³⁸ Firstly, PbI₂ was spin-coated on a mesoporous TiO₂ substrate, and sequentially, MAI was spin-coated on the PbI₂ layer. A uniform film was obtained after annealing it at 100 °C for 20 s. Apart from spin-coating, other methods such as spray-coating, blade-coating, brush-painting, soft-cover deposition, screen-printing, inkjet-printing, and slot-die coating are used for fabricating uniform LHP films.³⁹

For synthesizing LHP microcrystals, some simple methods have been used, such as ITC (Figure 1.3c), AVC (Figure 1.3d), and vapor-melt approaches. For example, Saidaminov *et al.* used ITC for synthesizing single crystals of MAPbX₃ and FAPbX₃.^{40,41} The retrograde solubility of precursor salts is the main parameter to control in the ITC technique. The temperature of the precursor salt solution (FAI and PbI₂) in GBL was

maintained from 80 °C to 120 °C to synthesize FAPbI₃ single crystals. In AVC, an antisolvent such as DCM, ethyl acetate, or chlorobenzene slowly diffuses into the precursor solution for the formation of microcrystals.⁴² Another technique to synthesize high-quality single microcrystals is the vapor-phase melt approach. This technique uses a quartz tube in a furnace kept at a very high temperature (500 °C to 600 °C). For example, to grow the CsPbX₃ crystals, CsX and PbX₂ powders were inserted in a quartz tube, where the temperature of the furnace was slowly increased to 600 °C.^{43,44}

1.1.2 Band-Edge Structure

LHPs are direct bandgap semiconductors with strong band-edge optical absorption and tunable PL in visible to NIR region. The intriguing optical properties of perovskites emerge from their unique distribution of energy states at the band edge. Density functional theory calculations have shown that the electronic structures of halide perovskites are governed by the bonding and antibonding atomic orbitals of $[BX_6]^{4-}$ octahedra.²⁵ The electronic structure of an LHP is shown in Figure 1.4a. In LHPs, the valence band maximum (VBM) is mainly contributed by the halogen *p*- atomic orbital and by the Pb 6*s*-X (3*p*, 4*p*, 5*p*) s*, Pb 6*p*-X (3*s*, 4*s*, 5*s*) s^{*b*} (bonding), Pb 6*p*-X (3*p*, 4*p*, 5*p*) p^{*b*} (bonding), and Pb 6*s*-X (3*p*, 4*p*,



Figure 1.4. (a) Band-edge states of LHPs without considering spin-orbit coupling (SOC). (b) Comparison of electronic band structures of MAPbI₃ LHPs (right panel) with and without the SOC and (left panel) the projected density of states. (b) is Reproduced from Im *et al.*⁴⁵

5p) s^b orbitals. And, the conduction band minimum (CBM) is constituted by the sigma (σ^*) and pie (π^*) antibonding orbitals. These orbitals in the CBM are formed by the hybridization of the Pb 6*p* and halogen *s*- and *p*- atomic orbitals. The comparison of electronic band structures with and without the SOC and the projected density of states is shown in Figure 1.4b. When the SOC is absent, the VBM is nondegenerate while the CBM is three-fold degenerate. In the presence of SOC, the degeneracy of CBM at the highly symmetric R-point and M-point (of Brillouin zone) splits into the doublet spin-orbit split-off states and the quadruplet states. This splitting increases the dispersion of the conduction band, lowers the bandgap, and affects the optical properties of perovskites by shifting PL spectra to the red. This situation is the opposite in most conventional semiconductors, where the splitting of bands is encountered in the valence band. Therefore, such band structures in perovskites are called the inverted band structure. Also, such splitting in the CBM induces the Rashba effect due to the breaking of the inversion symmetry. Here, the singlet state (highest lying) is optically inactive, whereas the nondegenerate triplet states are optically active.^{45,46}

1.1.3 Charge Carrier Dynamics

In LHPs, the charge carrier dynamics play a significant role in their devices, such as solar cells, LEDs, lasers, etc. This class of materials shows a long carrier lifetime, carrier diffusion lengths, and high charge carrier mobility. According to the exciton binding energy, the photogenerated charge carriers in LHPs can freely diffuse or excitonically bind. The mobility for the free charge carriers can be calculated by Einstein's equation

$$\mu_{n,p} = \frac{eD_{n,p}}{k_B T} \tag{1.2}$$

Here, $\mu_{n,p}$ is the charge carrier mobility, *e* is the electronic charge, $D_{n,p}$ is the diffusion coefficient, k_B is the Boltzmann constant, and *T* is the temperature. The parameters *e*, k_B , and *T* depend on the effective masses (m_{eff}) of the charge carriers. In LHPs, the m_{eff} of electrons and holes are comparable, resulting in balanced diffusion lengths of electrons and holes. This diffusion length (L_D) is related to the charge carrier mobility and the PL lifetime (τ), and it can be calculated as

$$L_D = \sqrt{\frac{k_B T \mu_{n,p} \tau}{e}} = \sqrt{D_{n,p} \tau}$$
(1.3)

MAPbI₃ single crystals have reported long electron-hole diffusion length (>175 µm) and high charge carrier mobility >100 cm² V⁻¹ s^{-1.5} Another point to consider when the thermal energy overcomes the exciton binding energy is the dissociation of free charge carriers. The high charge carrier mobility and long diffusion length also result in a long PL lifetime. The PL lifetime of LHPs varies from sub-nanoseconds- to a few tens of nanoseconds in nanocrystals and up to a few hundred microseconds in films and bulk single crystals. For example, a MAPbI_{3-x}Cl₃ LHP film shows carrier lifetime as long as 734 ns,⁴³ whereas CsPbX₃ (X=Cl, Br, I) perovskite nanocrystals (PNC) shows carrier lifetime in the 1-29 ns range.⁴ Unlike bulk single crystals and films, the very short carrier lifetime in perovskite nanocrystals is the consequence of an increase in the overlapping of electron and hole wave functions with a decrease in the crystal size. Further, as the LHP crystals' size decreases to the nanoscale regime, the surface trap states are likely to increase due to an increase in the surface-to-volume ratio, which induces additional nonradiative relaxation of charge carriers. Even transient absorption spectroscopic studies at low and high energy excitonic states have confirmed the presence of hot exciton relaxation in CsPbI₃ PNCs, including the Auger recombination and intrinsic decay paths.⁴⁷ The PL lifetime of LHPs is divided into short-lived and long-lived components determined through their exciton recombination rates.

The rate of recombination of charge carriers in the LHPs can be expressed as

$$-\frac{dn}{dt} = k_1 n + k_2 n^2 + k_3 n^3 \tag{1.4}$$

Here, *n* is the total carrier concentration, and k_1 , k_2 , and k_3 are monomolecular (trap-state assisted), bimolecular (free carrier), and Auger recombination rate constants. The trapassisted recombination (Figure 1.5a) of excitons is a geminate type that depends on the density and distribution of traps. Traps in LHPs are formed from elemental vacancy, interstitials, and antisites. Trap states in LHPs are shallow and low in concentrations. Therefore, a lower rate of monomolecular recombination, which usually dominates in a low charge carrier density, is the characteristic of LHPs. For instance, Wehrenfennig *et al.* reported a low monomolecular recombination rate of $4.9 \times 10^6 \text{ s}^{-1}$ in MAPbI₃ films.⁴⁸ Similarly, many other reports show the trap-assisted recombination rate in the order of 10^6 s^{-1} for lead trihalide and mixed halide perovskites.⁴⁹



Figure 1.5. A scheme of the charge carrier recombination pathways in LHPs. (a) Monomolecular or trap-assisted recombination, (b) bimolecular recombination, and (c) Auger recombination.

The bimolecular recombination (Figure 1.5b) is non-geminate type recombination, which depends on the composition and band structure of LHPs. In some reports, the bimolecular recombination rate has been explained from the Langevin recombination model's viewpoint when the free charge carriers have low mobility.^{48,50} The Langevin recombination takes place when the electrons and holes are inside their joint Coulombic radius. In non-Langevin recombination, the overlapping of the Coulombic radius is less, leading to low charge carrier mobility and a low bimolecular recombination rate. Therefore, the Langevin recombination limit is defined between 1 to 10 cm² V⁻¹ s⁻¹ for charge carrier mobilities, similarly to LHP photovoltaics. In LHPs, the bimolecular recombination varies significantly due to their band structure and chemical composition.

While the monomolecular and bimolecular recombinations dominate at low-charge carrier density, the Auger recombination dominates at higher charge carrier density. Auger recombination occurs when the energy and momentum transfer to third carriers or phonons (Figure 1.5c). The Auger recombination rate constant (k_3) varies from 10⁻²⁷ to ~10⁻²⁸ cm⁶ s⁻¹ in pure and mixed halide perovskite films.⁴⁹ It shows strong phase specificity, where it decreases in the low-temperature orthorhombic phase, increases in the room temperature tetragonal phase, and decreases in the high-temperature cubic phase. This phase-specific variation of the Auger recombination rate in LHPs is associated with the change in the

electronic band structure due to varying SOC degrees and hydrogen bonding in different crystalline structures.

1.1.4 Absorption and Photoluminescence Properties

The absorption and PL of LHPs are tunable from the visible to the NIR region by varying the halide composition. The PL of the chloride LHPs lies in the blue region, bromide in the green region, and iodide in the red and NIR regions.^{3,4,51,52} The absorption and PL spectra of FAPbX₃ PNCs in the 415-740 nm range are shown in Figure 1.6.⁵¹ The corresponding images of the colloidal solution of PNCs are shown in Figure 1.6b. With the increase in the concentration of Cl⁻ content in FAPbCl_{3-x}Br_x, the PL blue shifts, and with the increase in the Γ content in FAPbBr_{3-x}I_x PNCs, the PL is redshifted. The linear relationship between the halide composition and the PL peak positions is shown in Figure 1.6c. Since the contribution by the halide *p*-orbitals to the VBM of LHPs is high, the SOC increases and the bandgap decreases from Cl⁻ to Br⁻ and from Br⁻ to Γ . For instance, in the case of MAPbX₃ single crystal, the bandgap varies in the order 2.88 eV (cubic MAPbCl₃)⁵⁴ > 1.51 eV (tetragonal MAPbI₃).⁵⁴



Figure 1.6. Characteristics of FAPbX₃ colloidal PNC solutions. (a) Absorption and PL spectra. (b) The corresponding images of the colloidal solutions under photoexcitation. (c) The shift in PL peak with the bromine composition in FAPbCl_{3-x}Br_x, and FAPbBr_{3-x}I_x PNCs. Reproduced [(a), (b), and (c)] from Levchuk *et al.*⁵¹

Furthermore, the bandgap of LHPs is modified by the octahedral tilt, crystal phase, pressure, temperature, and crystal size. The octahedral tilt is noticeable when the Pb-X-Pb dihedral angle increases, which is with an increase in the A-site cation size. For example, the Pb-I-Pb angle increases from 153.2 to 179.9° when Cs⁺ is replaced by FA⁺.⁵⁵ The octahedral tilt is also responsible for the weakening of the SOC because of the less orbital overlapping, thereby increasing the bandgap. Another reason for the octahedral tilt is the change of the crystal structure from tetragonal to orthorhombic and cubic (or other phases). The stable phase for LHPs is the cubic in most cases, where the octahedral tilt is minimized because of the strong SOC.

The temperature during the synthesis and processing also affects the steady-state properties of LHPs. The temperature difference induces different structural phases and affects the exciton-phonon interactions. For instance, the phase of methylammonium lead iodide perovskites at higher temperatures is cubic. At room temperature, it is tetragonal, and at low temperatures, it is orthorhombic.⁴⁹ Another temperature effect is exciton-phonon interactions, which are appreciable at a high temperature, broadening the absorption band of LHPs. Similar to temperature, pressure affects the absorption and PL properties of LHPs. Pressure modifies the Pb-X-Pb angle, compresses the Pb-X bond, changes the structural phase, or enhances the octahedral tilt. For instance, by applying certain hydrostatic pressure to FAPbBr₃, the structure varies from the cubic to the orthorhombic.⁵⁶

Another factor that controls the absorption and PL properties of LHPs is the crystal size. The absorption and emission maxima blue-shift with decreasing size and vice-versa.^{51,57–60} As the size decreases below the exciton Bohr radius, the quantum confinement increases in LHPs, which results in sharp excitonic absorption bands and narrow PL bands. The sizes of an A-site cation and a halogen ion play an important role in determining the Bohr radius. For example, the Bohr radii are *ca* 2, 2.2, 2.5, 3.5, and 6 nm for MAPbBr₃, MAPbI₃,⁶¹ CsPbCl₃, CsPbBr₃, and CsPbI₃,⁴ respectively. Malgras *et al.* deduced the bandgap of MAPbI₃ PNC with the crystal size.⁵⁹ According to their experimental and theoretical analyses, the bandgap increased from 1.6 to 2.0 eV by decreasing the crystal size from 7 to 3 nm.

1.1.5 Stability

Despite the numerous advantages of LHPs in the optoelectronic field, the stability of this class of materials significantly affects their properties. LHPs are susceptible to light, humidity, oxygen, and temperature.^{62–66} However, exposure of LHPs to moisture and light enhances the performance of LHP devices,^{67,68} but long-term exposure has detrimental effects.^{63,64,69–72} For example, Solanki *et al.* showed a decrease in the rates of monomolecular and bimolecular recombination after treating a MAPbI₃ perovskite film with 1% H₂O. In contrast, Aristidou *et al.* showed a decrease in the absorption intensity of MAPbI₃ perovskite films when photoirradiated in dry air, which disintegrated the perovskite lattice (Figure 1.7 a-d). As shown in Figure 1.7a-d, the perovskite reacts with oxygen and generates superoxide when photoirradiated. This superoxide deprotonates the methylammonium cation and gradually disintegrates the perovskite into MA, PbI₂, and H₂O. Such a reaction with oxygen and light can impact device performance and photostability of LHPs.⁶⁴ Furthermore, Zhang *et al.* described that the reaction with superoxide results in Pb-O formation at the surface of an LHP.⁶²



Figure 1.7. (a-d) Deterioration of MAPbI₃ perovskite induced by reaction with oxygen and light (a) the diffusion of oxygen into the lattice, (b) photoexcitation of the lattice and the formation of electrons and holes, (c) the generation of superoxide at iodide vacancy, and (d) disintegration of the perovskite. Reproduced (a-d) from Aristidou *et al.*⁶⁴ (e) Theoretical charge-state transition levels of intrinsic defects in MAPbI₃ perovskite. The blue states represent the transition 0/-, the orange states represent the transition 0/+, and the thick lines represent the deep defects. Reproduced from Agiorgousis *et al.*⁷³

Another factor that determines the stability of LHPs is the density and the diffusion of intrinsic defects. The density of defects varies by different synthetic approaches and the local atmosphere. Although LHPs are termed defect-tolerant,^{74,75} they have several intrinsic defects, such as cationic and anionic vacancies (V_{MA} , V_{Pb} , V_X), interstitial sites (MA_i , Pb_i ,

 X_i), and antisites (MA_{Pb} , Pb_{MA} , Pb_X , X_{Pb} , X_{MA} , MA_X).^{66,73,76} Among these defects, halide vacancy and interstitials form deep level defects, as shown in Figure 1.7e. Agiorgousis *et al.* showed that in MAPbI₃ perovskite, Pb-dimers and I-trimers are formed because of the strong covalency between two Pb²⁺ and 3 I⁻ ions.⁷³ Furthermore, they calculated the deep defect transition levels $\varepsilon(0/-)$ and $\varepsilon(0/+)$ for each intrinsic defect; the energies of the defect levels are shown in Figure 1.7e. According to their evaluation, iodine vacancy, Pb_i interstitial, and antisites of Pb_{MA} and I_{MA} form deep defects. Among these defects, the halide vacancies and antisites contribute to nonradiative recombination and trigger fluctuations in the PL intensity. Therefore, the PLQY and device performance of LHPs can be improved by suppressing the transition of deep defects and controlling the relative humidity.

1.1.6 X-ray Diffraction (XRD)

XRD patterns help to identify different phases and dimensionality of perovskites by analyzing the unit cells, space groups, and Miller indices. LHPs have various crystal structures and phases, such as the cubic, orthorhombic, trigonal, monoclinic, pseudocubic, hexagonal, and tetragonal. The phases change with temperature, pressure, chemical composition, and crystal size. As shown in Figure 1.8, the microcrystal of MAPbBr₃ shows the diffraction pattern of the cubic phase, whereas the microcrystal of MAPbI₃ shows the diffraction pattern of the tetragonal phase.⁴⁰ Each diffraction pattern has specific Miller



Figure 1.8. The XRD patterns of LHP microcrystals. (a) MAPbBr₃, and (b) MAPbI₃. Reproduced from Saidaminov *et al.*⁴⁰

indices. The main Miller indices for the cubic phase are (100), (110), (200), and (210), which lie around 15, 22, 30, and 34 (20) degrees. The diffraction peaks are similar to the cubic in the orthorhombic phase, but it splits into two around 30°. The major Miller indices for the tetragonal phase are (110), (220), (114), and (224).^{40,42} In LHPs, the space group for the cubic phase is Pm3m,^{4,42} for the tetragonal phase it is I4/mcm or I4/m,^{42,77} for the pseudocubic phase it is P4mm,⁷⁷ and for the orthorhombic phase it is Pnma.⁴

LHPs are synthesized in various structures, such as single crystal, thin-film, nanocrystal, nanocubes, nanoplatelets, nanowire, quantum dots, quantum cubes, platelets, or sheets. A significant difference between the bulk and nanoparticle structures is that the XRD peaks shift toward smaller angles for nanoparticles. The XRD peaks shift from large angles to small angles when going from chlorine to bromine and from bromine to iodine due to an increased lattice contraction and an increase in the halide ion radius.^{4,51}

1.2 Perovskite Nanocrystals and Quantum Dots

1.2.1 Synthesis

PNCs can be synthesized by the hot injection (Figure 1.9a) or ligand-assisted reprecipitation (LARP, Figure 1.9b) method. These methods use long-chain organic ligands composed of carboxylic acids and amines for controlling the growth of PNCs by surface capping (Figure 1.9c). In general, PNCs are prepared from the mixture of precursor solutions of AX and PbX₂, and ligands such as oleic acid, hexadecyl amine, octadecene, and octylamine. PNCs are precipitated out at the end of the reaction and separated by the addition of a poor solvent such as acetone, toluene, or hexane. The first synthesis of MAPbBr₃ PNCs was carried out by a simple hot-injection method. In this method, a solution of PbBr₂ was injected into the mixture of octyl ammonium bromide or octadecyl ammonium bromide. Furthermore, MABr solutions with different concentrations were added to the above solution, which was along with oleic acid and octadecene, and the reaction mixture was heated at 80 °C. The resulting solution was washed with acetone, and MAPbBr₃ PNCs were dispersed in toluene. The size of the PNCs was 6 nm, the shape was cubic with the *Pm-3m* space group, and the emission maxima was ca 527 nm.⁷⁸ By varying the amount of alkylammonium salt, lead salt, and the temperature, the size, and shape of the PNCs were varied. Similarly, Vybornyi et al. synthesized MAPbI₃ PNCs by the hotinjection method. Octadecene and PbI₂ were loaded in a round bottom flask and heated at



Figure 1.9. A schematic representation of the synthesis of LHP nanocrystals by the (a) hotinjection and (b) LARP methods. (c) Attachment of ligands to the PNCs and different PNCs morphologies synthesized through the above methods.

120 °C. Oleylamine and oleic acid were added to the above reaction mixture under the nitrogen atmosphere and the temperature was decreased to 50-60 °C. In parallel, a methylamine solution was prepared by dissolving methylamine in tetrahydrofuran and oleic acid. The methylamine solution was quickly injected into the reaction mixture and the solution was centrifuged. The residue was dispersed in toluene or hexane. Here, by varying the amount of the ligands, differently shaped MAPbI₃ PNCs were formed, such as nanowires, nanocubes, nanoplatelets, and quantum dots. The edge size of MAPbI₃ PNCs was ~10 nm, the shape was tetragonal, and the emission maxima was *ca* 750 nm.⁷⁹ Also, CsPbX₃ PNCs can be prepared by the hot-injection method.^{4,80,81} For synthesizing CsPbX₃ (X= Br, I) perovskite quantum dots (PQDs), first caesium oleate was prepared by dissolving caesium carbonate and oleic acid in octadecene at 200 °C. After completely dissolving, the solution was kept under vacuum at 130 °C. Parallelly, PbI₂ (or PbBr₂) was dissolved in the mixture of oleic acid and oleyl amine in octadecene and at 120 °C. Next, the temperature was raised to 180 °C and caesium oleate was injected into the PbX₂ mixture. The reaction

was arrested quickly after the injection and the reaction mixture was cooled down in an ice bath. The PQDs were collected by centrifugation. The sizes of CsPbBr₃, CsPbBr_{1.5}I_{1.5}, and CsPbI₃ PQDs were 9.3, 10.7, and 11.2 nm, respectively. The emission maxima of CsPbBr₃, CsPbBr_{1.5}I_{1.5}, and CsPbI₃ PQDs were *ca* 510, 585, and 683 nm, respectively.⁸¹

The LARP method is routinely used to synthesize PNCs at room temperature. For example, MAPbBr₃ PNCs were prepared by completely dissolving MABr and PbBr₂ in DMF supplemented with a mixture of *n*-octylamine and oleic acid. This precursor solution was added dropwise into toluene under vigorous stirring. The color of the solution changes into yellow-green, indicating the precipitation of PNCs. The precipitate was washed with toluene and centrifuged. The residue was discarded and the PNCs were collected in the supernatant. The size of MAPbBr₃ PNCs was 3.3 nm, and the emission maximum was ca 515 nm.³ Similarly, Hassan et al. synthesized MAPbI₃ PNCs by the LARP method. The precursor mixture was prepared by dissolving the equimolar ratio of MAI and PbI₂ in acetonitrile. This mixture formed a black precipitate, into which methylamine gas was bubbled. It led to the formation of a translucent pale yellow colored solution of the perovskite-MAI complex. In parallel, oleic acid and oleylamine were mixed in anhydrous toluene at room temperature to 60 °C. The precursor solution was rapidly injected into the ligand mixture under vigorous stirring for 30-120 s. The solution was centrifuged and the residue was discarded. The supernatant was filtered through a PTFE filter (200 nm-size). The size of the MAPbI₃ PNCs synthesized at 60 °C for 30 s was ~10 nm with the tetragonal shape (space group of *I4/mcm*), for which the emission maxima was *ca* 698 nm. Whereas the size of the MAPbI₃ PNCs synthesized over a long time varied from 17-20 nm. It showed a redshifted PL (between 698 and 715 nm).⁸² Also, Sun et al. synthesized CsPbX₃ PQDs by the LARP method. PbBr₂ was dissolved in a mixture of DMF, hexanoic acid, and octylamine at room temperature in a flask. After this, Cs-oleate dissolved in octadecene was added to the above mixture. 0.05 mL of this precursor-ligand mixture was added to 2 mL toluene to obtain CsPbBr₃ PQDs. The average size of the PQD was 4.3 nm and the shape was orthorhombic with a space group of *Pbnm*. The emission maxima of the PQD was *ca* 505 nm.⁸³

1.2.2 Photoluminescence Blinking

PL properties and charge carrier dynamics of LHPs have been studied using steady-state and time-resolved spectroscopic techniques. Such studies reveal the ensemble-averaged properties of LHPs. Thus, single-molecule microspectroscopy has been widely applied to obtaining insight into the properties at the single-particle level. The signature of singlemolecule microspectroscopy is evident in the field of cadmium- and lead- chalcogenidebased single quantum dots (QDs),^{84–88} where it helped revealing the PL intermittency or blinking. PL blinking is the stochastic fluctuation of emission intensity observed at the single-particle level, characterized by a sequence of bright 'ON' and dark 'OFF' events. An example of such a PL blinking of a CsPbI₃ PQD is shown in Figure 1.10a. As shown in Figure 1.10, an ON-state is dominated by radiative recombination of photogenerated charge carriers, whereas an OFF-state is dominated by nonradiative recombination. The characterization of such single QDs can be carried out by examining their photon antibunching behavior and the second-order correlation function { $g^2(0)$ } at zero-time. For example, as shown in Figure 1.11a, a QD with single-photon emission shows near-zero { $g^2(0)$ } value at zero-time.



Figure 1.10. (a) Single CsPbI₃ PQD. (i) PL blinking and (ii) the corresponding occurrences. Reproduced from Park *et al.*⁸¹ (b) A model of two-state blinking induced by photogenerated charge carriers.

In a PQD, the band-edge states are nondegenerate, which is explained in section 1.1.2. The nondegeneracy is due to the splitting of states and the Rashba effect. To conserve the total exciton momentum, the momentum of electrons and holes combine during the exchange interactions of excitons. In a PQD, this process leads to the breaking of the inversion symmetry of the crystals, making the highest lying singlet state optically inactive. In contrast, the nondegenerate triplet states are optically active and show multiphoton emissions, enhancing the $\{g^2(0)\}$. The threefold band-edge triplet state $(\Psi_x, \Psi_y, \text{ and } \Psi_z)$



Figure 1.11. (a) Photon antibunching from the second-order correlation function of CsPbI₃ PQD. Reproduced from Park *et al.*⁸¹ (b) Schematic representation of electronic states of LHP with SOC and Rashba effect. Reproduced from Becker *et al.*⁴⁶

increases the { $g^2(0)$ }. The entangled photons from these states should be separated to maintain a very low { $g^2(0)$ } or coherent single-photon emission. This separation is achieved by temporally filtering the entangled photons and spectrally selecting the exciton zero-phonon line using the interferometric method.⁸⁹ Temperature also plays a role in determining the degeneracy of the band-edge states. With an increase in temperature, the degeneracy of states increases. For example, at low temperatures (~3 K), the photons of single PQDs show strong antibunching, suggesting emission from single-state.^{46,89} Similarly, an increase in the excitation light intensity increases the { $g^2(0)$ } value due to the formation of bright biexcitons or multiexcitons.

The Mechanism of PL Blinking in Nanocrystals

The nature of PL blinking in LHPs differs with respect to the chemical composition, shape, size, excitation intensity, density, and type of defects.^{71,81,90–92} For example, multi-state blinking with large amplitudes has been observed in the first report of PL blinking in MAPbI₃ PNCs and microcrystals.⁹⁰ In chalcogenide QDs, the blinking enhances with an increase in the excitation intensity, whereas, unlike QDs, the blinking in LHPs enhances at lower excitation intensities. To identify such a PL behavior, a super-resolution microscopy technique was used. It revealed that multi-state blinking occurs due to the difference in



Figure 1.12. Types of PL blinking of (a) MAPbI₃ PNC and (b) a MAPbI₃ film. Reproduced from Tian *et al.*⁹⁰

emission localization positions in the crystal, or quenching sites (Figure 1.12). The quenching sites are analogous to charge traps, or crystal defects. In PNCs, the blinking is explained with two models: the quenching-site and the emitting-site models, which are shown in Figure 1.13. In the quenching-site model, under the ON-state, the whole PNC is emissive, and the emission localization position lies at the center of the crystal. The



Figure 1.13. A mechanism of the PL blinking in PNCs. (i) The quenching-site model, and (ii) the emitting-site model. Reproduced from Tian *et al.*⁹⁰
emission localization position shifts when the photogenerated quencher is present, resulting in a decrease of PL intensity or switching from the ON- to the OFF-state. These quenchers are charge traps that form at either end of the crystal. On the other hand, in the emittingsite model, several emitting sites form in the crystal at various positions. During the ONstate, the photogenerated charge carriers at various emitting sites diffuse efficiently and recombine radiatively. Here, traps and defects quench one or more emitting sites and decrease the PL intensity, resulting in either an intermediate-state or the OFF-states. In PNCs, the amplitude of blinking decreases with an increase in the PL intensity, which can be attributed to the filling of traps and defects. Under a high excitation intensity, the concentration of charge carriers increases, and the PL intensity averages over the emitting sites.

The characteristics of PL blinking in PNCs were also examined by temperaturedependent studies. Gerhard *et al.* showed that the PL blinking could be suppressed, and the overall PL intensity could be increased by cooling.⁹² This behavior is similar in different MAPbI₃ PNCs during the cooling-heating cycles. When the emitting-site quenchers overcome the thermal barrier, the emitting-site switches between an active and a passive states. This thermal barrier of the activation of quenchers matches with the energy barrier for halide ion migration in LHPs. So, the PL blinking also results from the diffusion of ions in a PNC, which is responsible for switching nonradiative centers between passive and active states.

The Mechanism of PL Blinking in Quantum Dots

The mechanism of PL blinking in PQDs is assigned to type-A and type-B. Type-A blinking occurs due to the random charging and discharging of charge carriers and the generation of trions. Type-B blinking occurs due to the trapping and de-trapping of photogenerated charge carriers. These mechanisms are rooted in the random switching among the nonradiative Auger recombination, neutralization of charges, and radiative recombination. These models are precisely considered in several blinking studies of single QDs. These mechanisms can be confirmed by correlating the PL lifetime with the PL intensity of a PQD through the fluorescence lifetime intensity distribution (FLID) technique and the ON-and OFF-times probability distribution. In type-A blinking, the PL intensity exponentially decreases with the decrease in PL lifetime [Figure 1.14a(i)], and the ON- and OFF-time



Figure 1.14. (a) Schemes of PL blinking mechanisms in PQDs along with their FLID characteristics and charge carrier recombination pathways: (i) type-A, (b) type-B, and (c) type-C. Reproduced from Kim *et al.*⁹⁴ (b) Power-law fittings for CsPbI₃ PQDs through (i) the truncated power-law, and (ii) the linear power-law. Reproduced from Park *et al.*⁸¹

probability distributions follow the truncated power-law behavior (eq. 1.5). In type-B blinking, there is no correlation between the PL intensity and the PL lifetime [Figure 1.14a(ii)], and the ON- and OFF-time probability distributions follow the linear power-law behavior (eq. 1.6).

$$P(\tau) = A_0 \tau^{-\alpha} e^{-\frac{\tau}{\tau_c}}$$
(1.5)

$$P(\tau) = A_0 \tau^{-\alpha} \tag{1.6}$$

Here, A_0 is a constant, α is the power-law coefficient, τ_c is the truncation time, and the probability distribution $[P(\tau)]$ is calculated using eq. 1.7.

$$P(\tau) = \frac{2N_i}{(\tau_{i+1} + \tau_i) - (\tau_i + \tau_{i-1})}$$
(1.7)

Here, N_i is the occurrence of i^{th} time, and τ refers to the time. PQDs tend to show both the mechanisms tandemly.^{71,93} For example, the power-law fitting for CsPbI₃ PQD shown in

Figure 1.14b, follows the truncated power-law behavior for the ON-time probability distribution, whereas the OFF-time probability distribution follows the linear power-law behavior, suggesting both the mechanisms.⁸¹ Also, Trinh *et al.* verified that during the ON-and OFF-time, FAPbBr₃ PQDs show both the type-A and type-B behavior by analyzing the PL intensity trajectories. Here, initially, for 50 ms, the PQDs showed a truncated power-law behavior, and after 50 ms, the PQDs showed the linear power-law behavior. The type-B mechanism has recently been subcategorized into type-B-BC and type-B-HC, which correspond to the trapping-detrapping of the band-edge charge carriers, and hot charge carriers, respectively (Figure 1.14a).^{94,95}

In PQDs, the generation of the trion, biexciton, or multiexciton states is expected when photoexcited with a high-intensity light source, which induces PL blinking and modifies the PL quantum yield. Generally, two mechanisms can create biexcitons in a QD. The first is when two photons are simultaneously absorbed with equal or higher energy than the bandgap energy. The second is when the photon energy becomes equal to or greater than the bandgap energy. Therefore, the relaxation of biexcitons occurs through two steps, it emits from a higher excitonic state to the singlet excitonic state and then from the singlet excitonic state to the ground state. On the contrary, under a low excitation intensity, only single excitons emit, which show low $\{g^2(0)\}$ or strong photon antibunching.

The activation and deactivation of multiple recombination centers (MRC) are also responsible for nonradiative recombination in a PQD. When the number of activated MRCs increases, the rate of nonradiative recombination increases, decreasing the PL intensity and lifetime of a PQD. The MRCs cause blinking at multiple intensity levels. Li *et al.* showed the PL behavior of a PQD at different excitation intensities for $\langle N \rangle = 0.02$, 0.2, and 2.⁹⁶ They correlated the PL blinking behavior with the PL lifetime values. At high intensities, $\langle N \rangle = 0.2$, frequent blinking with more OFF-states were observed as compared to a low intensity, $\langle N \rangle = 2$. The PQD showed multiple state blinking or flickering at $\langle N \rangle = 2$. At high intensities, the PL blinking of a PQD was caused by both type-A and type-B mechanisms and the activation and deactivation of MRCs.

The crystal size is another crucial factor that affects the nonradiative Auger recombination and PL blinking. Kim *et al.* showed the changes in PL blinking with respect to the PQD size.⁹⁴ With the increase in the MAPbBr₃ PQD size from ~2 nm to ~10 nm, the fraction of ON-events was increased with a decreased trapping rate and an increased de-

trapping rate. These rates depended on three factors- photoionization of a PQD, the electron and hole trapping-time, and charge tunneling from a PQD to a trap state. During photoionization of a PQD, trions are generated and annihilated by fast Auger nonradiative recombination. The trapping-detrapping time can be analyzed from the ON- and OFF- time probability distributions to explain a difference in the rates of nonradiative recombination. For example, if a hole is trapped in a short-lived state, it increases the rate of nonradiative recombination, which affects the PLQY of the PQD.

PL Blinking Suppression

As stated above, the PL blinking of LHPs varies with the chemical composition, such as the difference in the A, B, or X-site ions, and defect density. For example, Yoshimura *et al.* showed an increase in the ON-time after halide exchange of CsPbBr₃ to CsPbI₃ PQD.⁹⁷ Apart from the halide exchange, filling the halide vacancies can also increase the ON-time. Similarly, blinking suppression in PQDs is achieved by the passivation of surface defects.^{98–102} Tang *et al.* encapsulated CsPbBr₃ PQDs with CdS shells, and the PL blinking was suppressed by the passivation of deep electron and hole traps (Figure 1.15).⁹⁹ Ahmed *et al.* showed that treatment of PNCs with NaBF₄⁻ reduces the trap states near band-edge states, and hot-carrier states, contributing to the nonradiative recombination.¹⁰⁰ This increased both the ON-time and the brightness of CsPbBr₃ PNCs.



Figure 1.15. PL blinking suppression in CsPbBr₃ PQDs (a) before and (b) after encapsulation in a CdS shell. Reproduced from Tang *et al.*⁹⁹

The PL blinking studies of PQDs with various chemical compositions have been carried out by systematic single-particle microspectroscopic experiments. Although surface passivation and halide exchange are consistent with the theories of PL blinking mechanisms, the roles of A-site and B-site cations on blinking are yet to be understood. Nonetheless, the A-site doesn't contribute to the band-edge states, but the size and the dipole moment of an A-site cation affect the bandgaps. The most common A-site inorganic cation, Cs⁺, is unipolar, whereas the A-site organic cations, MA^{+,} and FA⁺ are dipolar. Among them, MA⁺ has a higher dipole moment and is more susceptible to external charges and local current fluctuations. Within a lattice, the rapid motion of MA⁺ causes a polaronic screening of charge carriers, which results in the suppression of exciton-exciton interactions in MA-based LHPs. Despite the above clarification of the PL blinking mechanism and efforts to suppress blinking, nonblinking perovskite is an open challenge. It is necessary to suppress blinking and develop nonblinking PQDs and PNCs.

1.3 Applications

Owing to the intriguing properties such as high PLQY, large absorption cross-section, long PL lifetime, and long-range diffusion of carriers, LHPs find their way into potential applications such as lasers, solar cells, and LEDs. After the first demonstration of ultralow threshold (12 μJ cm⁻²) amplified spontaneous emission (ASE) from solution-processed polycrystalline MAPbX₃ thin films,¹⁰³ studies have been carried out in different perovskite films,¹⁰⁴ and micro-/nanostructures¹⁰⁵ to explore their potentials for optical gain media. In LHPs, when the excitation intensity increases, the broad spontaneous emission redshifts with the appearance of higher energy ASE. Furthermore, LHPs show single and multimode lasing having ultra-narrow emission band and high-quality factor tunable in the entire visible to the NIR region (Figure 1.16a). ASE or lasing in all-inorganic, organic-inorganic, and mixed-halide LHPs has been demonstrated by arranging different types of cavities such as the vertical microcavity, spherical Whispering Gallery Mode (WGM) cavity, planer WGM cavity, random lasing cavity, or Fabry-Pérot cavity.

Apart from ASE and lasing, perovskites are promising for PCE. LHPs have low defect density and ambipolar carrier migration, which enable efficient injection and transport of charges across interfaces. Miyasaka and coworkers verified the PCE of a



Figure 1.16. (a) Single-mode lasing in CsPbX₃ microspheres and the corresponding photographs of the laser spots. Reproduced from Tang *et al.*¹² (b) The energy levels of several electron transport material (ETM) and hole transport material (HTM) layers for fabricating PSC and PeLEDs.

MAPbI₃ PSC at 3.8%.¹³ In 2018, Seo and coworkers reported the 23.3 % PCE by the fabrication of a solar cell with an HTM.³⁶ According to the recent NREL chart of solar cell efficiency, PSCs show >26% PCE.¹⁴ For making efficient PSCs, high-quality perovskite layers are essential. Various techniques of device fabrication to form uniform and grain boundary-free perovskite layers have been established. The fabrication of thin layers of perovskites in a PSC the single- and two-step deposition techniques is explained in section 1.1.1. Furthermore, by optimizing ETMs and HTMs, PSCs are at the forefront of next-generation solar cells. Yet another emerging and promising application of perovskites is PeLEDs. By tuning the bandgap by halide exchange and using PNCs with different halides, multicolor PeLEDs were developed. The external quantum efficiencies of PeLEDs have become as high as 20.3% (green PeLED),²⁰ and 20.1 % (red PeLED).²¹

Typical PSC and PeLED architectures include perovskite as the intrinsic semiconductor sandwiched between an ETM and an HTM. Figure 1.16b shows the energy levels of the conduction and valence bands of several ETMs and HTMs with respect to LHPs. In a PSC, the perovskite layer absorbs the light and generates electrons and holes. The electrons in the perovskite conduction band are transported to the ETM and then to the fluorine-doped tin oxide (FTO) or indium tin oxide (ITO) electrode. On the other hand, holes in the valence band move to the HTM and then to the counter electrode.¹⁰⁶ In a PeLED under an external bias, the electrons and holes from the ETM and HTM layer confine into the perovskite layer. For achieving a high external quantum yield of a green

electroluminescent PeLED, a device was fabricated by using a polymer matrix as an insulator between the perovskite and ETM layers.

Despite the above promising advantages and applications of perovskites, nonradiative carrier/exciton recombination continues to be a significant challenge for the advancement of perovskite technology. For example, PL blinking involving traps and ionization of particles diminishes the PLQY. Thus, single-particle blinking studies are expected to provide a deep understanding of the carrier/exciton relaxation processes and distinguish between different emissive and non-emissive states.

1.4 Motivation

Lead halide perovskites have shown excellent optical and electronic properties and are promising materials for next-generation optical and photovoltaic technologies. Despite their unique properties, LHPs face degradation under photoirradiation and in humid environments due to superoxide generation, which reacts with perovskites and deteriorates their structure and properties. Also, this reduces the PLQY and the PCE. The main view of this thesis is to understand the degradation mechanism of lead halide PNCs and PQDs by analyzing the PL properties at the ensemble and single-particle levels. This thesis will guide the understanding of the PL blinking mechanism and the exciton/carrier recombination pathways in LHPs, which will help in the efficient engineering of perovskite devices.

I used nanocrystals and quantum dots of bromide and iodide perovskites. In **chapter 2**, I give detailed information about the synthesis of MAPbBr₃, MAPbI₃, and CsPbBr₃ PNCs or PQDs. I characterized these LHPs by using absorption and UV-vis fluorescence spectroscopy, transmission electron microscopy, and X-ray diffraction. I examined the PL blinking by using single-particle microspectroscopy and PL decays by using time-resolved PL spectroscopy. The working principles of all the instruments are briefly explained in this chapter.

In **chapter 3**, I examined the PL behavior of MAPbI₃ PNCs at different environmental conditions such as in air, argon, or a polymer, which was for determining the LHP degradation mechanism under light and oxygen. MAPbI₃ PNCs were found to react with oxygen and generate superoxide. The latter occupies the iodide vacancies in a PNC, deprotonates MA⁺, and deteriorates the PNC. I correlated the ensemble-level and single-particle level PL properties under the above atmospheres of these PNCs. I observed the PL blinking of MAPbI₃ PNCs and analyzed the ON and OFF-time probabilities. By examining PL lifetimes, I calculated the rate of electron transfer to oxygen and the rate of nonradiative recombination. PL blinking, PL lifetimes, and the rate of electron transfer helped me understand and suppress the undesired oxidation and degradation of PNCs.

In **chapter 4**, I examined the role of halide vacancies in the blinking and degradation of MAPbBr₃ and MAPbI₃ PQDs. Halide vacancies play a significant role in degrading LHPs, as they form deep traps in the energy levels of LHPs. I filled the halide vacancies in MAPbBr₃ and MAPbI₃ PQDs post-synthetically by treating them with MABr and MAI solutions, respectively. Also, I examined the real-time differences in the PL blinking before and after the treatment. I observed PL blinking suppression and PL intensity enhancement by halide vacancy filling. I analyzed the probability distributions of the ON- and OFFtimes before and after the vacancy filling and identified that the PL blinking mechanism changes from type-A to type-B after halide vacancies were filled. Then, by evaluating PL decay profiles, I found that the blinking suppression is correlated with the halide vacancyassisted nonradiative recombination rate.

In chapter 5, I examined the role of A- and B-site cations on the stability and blinking of PL in CsPbBr₃ PQDs. While the B-site cation (Pb²⁺) also forms trap-levels in LHPs, which affects the long-term stability of these materials, an A-site cation changes the energy by affecting the octahedral tilt in the perovskite lattice. Thus, the A- and B-site vacancies can also affect the stability and properties of LHPs. I filled the A-site cation vacancies by treating CsPbBr₃ PQDs with caesium oleate (CsOL). I observed an increase in the PL intensity after the filling but without changing the blinking behavior. As there isn't any direct contribution of the A-site cation to the VBM or CBM, I assumed that the effect of an A-site cation vacancy on the PL of LHPs is negligibly small. On the other hand, I added lead oleate to CsPbBr₃ PQDs, which resulted in a decrease in the PL intensity. This decrease is attributed to an increase in the effective halide ion vacancy by coordinating the excess Pb to the surface halide ions.

Finally, I summarize the results and present my perspectives about the significance of single-particle studies and nonblinking perovskites for applications to quantum optical switches and single-photon light sources.

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Chapter 2

Experiments

Abstract

This chapter introduces the experimental and characterization techniques in the study. Here, I listed the materials and samples used throughout my work. Next, I explained the methods to synthesize lead halide perovskite nanocrystals and quantum dots by the ligand-mediated transport, ligand-assisted reprecipitation, and hot-injection methods. These methods yielded a narrow and uniform size distribution of the perovskite nanocrystals and quantum dots. The X-ray diffraction data helped me understand the structural phases of lead halide perovskites. Also, the sizes of perovskite nanocrystals were calculated from the images collected by transient electron microscopy. I estimated the elemental composition of the halide vacancies in perovskite quantum dots by using the scanning electron microscopy with the energy dispersive X-ray spectroscopy. The band-edge absorption and the emission maxima of these perovskite nanocrystals and quantum dots were determined using UV-vis absorption spectrophotometry and steady-state fluorescence spectroscopy. For analyzing the photoluminescence intensity trajectories of isolated single particles, I used singleparticle microspectroscopy equipped with an electron multiplying charge-coupled device. Single-photon coincidence measurement was carried out to confirm the emission from isolated single particles. The time-resolved fluorescence spectroscopy was used to detect the photoluminescence decay profiles. The photoluminescence intensity trajectories and average lifetimes helped understand the recombination pathways of photogenerated charge carriers in perovskite nanocrystals and quantum dots.

2.1. Materials

Chemicals used in synthesizing and preparing the samples for experimental studies: methylammonium hydroiodide [CH₃NH₃I (MAI), >98%, Tokyo Chemicals Industry (TCI)], methylammonium hydrobromide [CH₃NH₃Br (MABr), >98%, TCI], caesium acetate [C₂H₃CsO₂ (CsAc), 99.9%, Sigma-Aldrich], lead iodide (PbI₂, >99%, Aldrich), lead bromide (PbBr₂, >98%, Aldrich), lead acetate trihydrate [Pb(CH₃CO₂)₂.3(H₂O) (PbAc), \geq 99%, Sigma-Aldrich], hexadecyl amine [C₁₆H₃₅N , >95%, TCI], oleic acid [C₁₈H₃₄O₂ (OA), >85 %, TCI], 1-hexadecene (C₁₆H₃₂, Fujifilm Wako), 1-octadecene (C₁₈H₃₆, >90%, TCI), dehydrated *N*,*N*-dimethylformamide [C₃H₇NO (DMF), Fujifilm Wako], γ butyrolactone [C₄H₆O₂ (GBL), >99.0%, TCI], dehydrated toluene (C₆H₅CH₃, Fujifilm Wako), dehydrated hexane (C₆H₁₄, Fujifilm Wako), *n*-butanol (C₄H₁₀O, >99%, Fujifilm Wako), dichloromethane [CH₂Cl₂ (DCM), Fujifilm Wako], poly(methyl methacrylate) [(C₅O₂H₈)_n (PMMA), Aldrich], indium tin oxide glass (ITO) substrates-pixelated anode [6 pixel, thickness 1.1 mm, Ossila], coverglass (24×50 mm², and 25×50 mm², thickness 0.13-0.17 mm, Matsunami Neo Cover Glass), and micro coverglass (76×26 mm², thickness 0.8-1.0 mm, Matsunami Neo Pre-cleaned).

2.2. Methods

2.2.1 Synthesis of Perovskite Nanocrystals and Quantum Dots

Ligand-Mediated Transport Method

Synthesis of MAPbI₃ Perovskite Nanocrystals (PNC)

I used the modified ligand-mediated transport method (Figure 2.1) from the literature to synthesize MAPbI₃ PNC.¹ In the literature, PbI₂ and MAI were mixed in a mixture of hexane, octylamine, and OA and vigorously stirred for 1 h. This solution was centrifuged at 6000 rpm for 5 min, and the MAPbI₃ PNCs were collected in the supernatant.¹ In this study, I modified the reported procedure by using HDA instead of octylamine and changing the purification method. In a glass vial, MAI (0.12 mmol, 19 mg) and PbI₂ (0.15 mmol, 69 mg) were weighed together and dried under vacuum for 15 min. Parallelly, I completely dissolved HDA (0.12 mmol, 29 mg) and OA (0.13 mmol, 40 μ L) in hexane (1 mL). The ligand solution was added to the precursor mixture containing MAI and PbI₂. The reaction was carried out under vigorous stirring at room temperature. On the top of the glass vial,

an orangish-red layer was formed, which was decanted, and discarded. At the bottom of the glass vial, a brown precipitate was formed. I added 1.5 mL toluene to this precipitate and the mixture was sonicated for 5 min. The sample was centrifuged for 10 min at 10000 rpm and the residue was discarded. The supernatant was centrifuged again for 45 min at 14000 rpm. The MAPbI₃ PNCs were collected in the residue and the supernatant was discarded. The residue in toluene, formed a clear brownish-red solution. Photoluminescence (PL) properties of the MAPbI₃ PNCs are discussed in Chapter 3.



Figure 2.1. A schematic of the synthesis of MAPbI₃ PNCs.

Ligand-Assisted Reprecipitation Method

Synthesis of MAPbI₃ Perovskite Quantum Dots (PQDs)

The synthesis of MAPbI₃ PQD was carried out by the ligand-assisted reprecipitation (LARP) method.^{2–4} In the reported method, Dong and co-workers² dissolved MAI and PbI₂ in DMF, octylamine, and OA. This precursor solution was added to toluene under vigorous stirring at room temperature. The solution was centrifuged at 7000 rpm for 10 min, and the residue was discarded. The MAPbI₃ PQDs were collected in the supernatant. In my studies, I slightly modified the LARP method by using GBL instead of DMF, set the temperature at 80 °C, and changed the purification method. The scheme of MAPbI₃ PQD synthesis is shown in Figure 2.2. PbI₂ (0.72 mmol, 346 mg) and MAI (0.72 mmol, 114 mg) were dissolved in 1 mL GBL. In a round bottom flask, I dissolved OA (3.6 mmol, 1.14 mL) and HDA (0.72 mmol, 174 mg) in 25 mL dehydrated toluene under an argon atmosphere with vigorous stirring. When the temperature of the ligand mixture reached 80 °C, the precursor solution was quickly injected. The color of the reaction mixture was changed from yellow to brown, and a precipitate was formed. After 15 min, the reaction mixture was cooled down to room temperature. The residue was suspended in toluene and separated by centrifugation at 7000 rpm for 5 min. The residue was discarded, and the supernatant was

centrifuged again at 12000 rpm for 10 min. The PQDs were collected in the residue, and the supernatant was discarded. The PL properties of this MAPbI₃ PQD sample are reported in Chapter 4.



Figure 2.2. A scheme of the synthesis of MAPbI₃ PQDs.

Synthesis of MAPbBr₃ PQDs

I synthesized MAPbBr₃ PQD by following the LARP method.^{2,5,6} In the literature method, MABr and PbBr₂ were dissolved in a mixture of DMF, octylamine, and OA. This precursor solution was added to toluene under vigorous stirring at room temperature. The solution was centrifuged at 7000 rpm for 10 min, and the residue was discarded. The supernatant was bright yellow, which contained the MAPbBr₃ PQDs. In my studies, I slightly modified the LARP method by changing octylamine to HDA and changing the purification method. The scheme of MAPbBr₃ PQDs synthesis is shown in Figure 2.3. The precursors PbBr₂ (0.27 mmol, 100 mg) and MABr (0.25 mmol, 28 mg), and the ligands OA (0.25 mmol, 80 µL) and HDA (0.19 mmol, 46 mg) were dissolved in DMF (1 mL). This mixture was warmed in a water bath at 60 °C to obtain a clear solution. This precursor-ligand mixed solution was injected into a round bottom flask containing dehydrated toluene (50 mL) and kept on vigorously stirring at room temperature. After 15 min, the stirring was stopped and the reaction mixture was centrifuged at 10000 rpm for 5 min. The supernatant was discarded, and the residue was suspended in toluene and centrifuged at 5000 rpm for 5 min. The MAPbBr₃ PQDs were collected in the centrifugate. The PL properties of this MAPbBr₃ POD sample are reported in Chapter 4.



Figure 2.3. Schematic representation of the synthesis of MAPbBr₃ PQDs.

Hot-Injection

Synthesis of CsPbBr₃ PQDs

I synthesized CsPbBr₃ PQDs by following a reported hot-injection method,^{5,7,8} and the synthesis scheme is shown in Figure 2.4. In a 500 mL round bottom flask, PbBr₂ (1.88 mmol, 690 mg), OA (12.6 mmol, 4 mL), HDA (15.2 mmol, 3.67 g), and 1-hexadecene



Figure 2.4. A scheme of the synthesis of CsPbBr₃ PQDs.

(90 mL) were mixed by stirring for 1 h under vacuum at 120 °C. Parallelly, in another round bottom flask, CsAc (0.5 mmol, 9 mg) was solubilized in OA (3.15 mmol, 1 mL) and 1-hexadecene (10 mL) and kept stirring under vacuum at 120 °C. After every 20 min, argon and vacuum were switched alternatively in the reaction mixture. When PbBr₂ was completely dissolved, the temperature was increased to 170 °C and kept under an inert atmosphere. The hot CsAc-ligand solution was injected into the PbBr₂-ligand solution. The color of the reaction mixture was changed to green. The reaction was arrested within 1 min by placing the reaction mixture in an ice-water bath. The mixture was centrifuged at 6000 rpm for 25 min, and the supernatant was discarded. The residue was suspended in a hexane-*n*-butanol mixture and further centrifuged. The remaining residue was dispersed in toluene for further studies. The PL properties of this CsPbBr₃ PQD are reported in Chapter 5.

Synthesis of Caesium Oleate (CsOL)

The synthesis was carried out similarly to a literature report.⁹ In a round bottom flask, CsAc (1 mmol, 0.192 g) and OA(1 mmol, 0.32 mL) were dissolved in 1-octadecene (4.68 mL) by stirring at 110 °C under an argon atmosphere. After 30 min, the vacuum was applied at 110 °C for 3 h until all the bubbles subsided. The vacuum was applied very slowly to avoid vigorous bubble formation and the removal of acetic acid. After 3 h, argon was flushed again in the reaction mixture, and while cooling down to room temperature, the solution became like white-jelly. This synthesis yielded 0.2 M of CsOL in 1-octadecene. The studies related to CsOL are reported in Chapter 5.

Synthesis of Lead Oleate [Pb(OL)2]

The synthesis was carried out similarly to a literature report.¹⁰ In a round bottom flask, PbAc (12 mmol, 4.6 g) and OA (24 mmol, 7.6 mL) were dissolved in 1-octadecene (16.4 mL) at room temperature and under vacuum. After the gas evolution, the temperature was slowly increased to 120 °C (only after the bubbles subsides at each increase). The heating and stirring of the reaction mixture were stopped after 1 h, and the solution was stored in a glass vial. This reaction yielded 0.5 M of Pb(OL)₂ in octadecene. The Pb(OL)₂ was stored under argon and melted before use. The studies related to Pb(OL)₂ are reported in Chapter 5.

2.2.2 Sample Preparation for Single-Particle Imaging and Photoluminescence Lifetime Studies

For single-particle studies, a dilute suspension of PNCs (or PQDs) in toluene was dropped onto a glass coverslip and dragged using Whatman lens-cleaning paper. The amounts of PNCs or PQDs were selected to isolate 10-15 particles in a $50 \times 50 \,\mu\text{m}^2$ single-particle image frame. The samples were photoirradiated with 460 or 532 nm laser and observed on a fluorescence microscope. A PNC (or PQD) solution was drop-casted on a glass coverslip and photoirradiated with a 400 or 465 nm laser for lifetime studies.

In Chapter 3, a silicon chamber was prepared for studying the effect of argon environment on PNCs, as shown in Figure 2.5. First, a PNC suspension was dropped and dried inside the chamber. Then, another glass coverslip was attached with silicone glue on top of the chamber, and argon was flushed into the chamber from an argon-filled balloon.



Figure 2.5. A silicon chamber for argon atmosphere-related studies.

In Chapter 4, for understanding the role of MAX on the PL properties of PQDs, first, the PL intensity trajectories and decay profiles of PQDs were recorded. Later, the MAX solution was carefully spread on the PQDs without disturbing the glass coverslip, as shown in Figure 2.6. Then, the PL intensity trajectories and decay profiles of MAX-treated PQDs were re-recorded. Through this approach, I observed the PL behavior of the same PQDs before and after the argon treatment. In chapter 5, I followed a similar procedure to understand the role of CsOL or Pb(OL)₂ on CsPbBr₃ PQDs. I recorded the PL intensity trajectories of the same CsPbBr₃ PQD before and after the treatment with CsOL [or Pb(OL)₂].



Figure 2.6. A scheme of sample preparation for analyzing the role of A-, B-, or X-site ions on PQDs.

2.2.3 UV-vis Absorption Spectroscopy

I used absorption spectroscopy to examine the optical excitation properties of the PNCs or PQDs. The PNC (or PQDs) were suspended in toluene, and the absorption spectra of the suspension were recorded by using a UV-*vis* spectrophotometer (Evolution 220, Thermo Fischer Scientific). The scheme for detecting the optical absorption of samples is shown in Figure 2.8. The absorption spectrophotometer works on the Beer-Lambert-Bouguer law. According to this law, the absorbance (*A*) of the solution is proportional to the concentration (*c*) and the path length (*l*), $A = \varepsilon c l$, where ε is the molar extinction coefficient (M⁻¹ cm⁻¹). Typically, for absorbance, an excitation source with a wavelength in the 190-900 nm region is used. The excitation from the source passes through a monochromator and the sample solution. The solution absorbs a definite number of photons of a particular energy and the



Figure 2.8. Schematic representation of the monochromator and the absorption detection.

nanocrystals/quantum dots get excited from the ground to the excited states. The detector records the transmitted light from the solution. In this thesis, I recorded the absorption spectra of the PNCs or PQDs from 400 to 900 nm wavelength range.

2.2.4 Steady-State Fluorescence Spectroscopy

I used a fluorescence spectrometer to examine the emission properties of the PNCs or PQDs. The spectrometer was used to understand the relaxation of excitons from the excited to the ground states. The fluorescence of PNC or PQD solutions, and PQD films were examined using the Fluorescence Spectrometer (F-4500, Hitachi) equipped with a Xe-lamp as the excitation source. The method of collecting the emitted light from the samples is shown in Figure 2.7. The Xe-lamp emits bright white light, which covers the UV to visible region. The desired excitation wavelength focused on the sample was selected by the excitation monochromator. The monochromator uses an assembly of diffraction gratings and slits, by which it selectively passes the desired wavelength. The sample was excited and emited photons were passed the emission monochromator. The emission starts at a longer wavelength than the excitation, so the emission monochromator efficiently filters the excitation light. The 90° angle between the excitation and emission paths limits the excitation light reaching the emission monochromator. Finally, the emission was detected by the photomultiplier tube. In this study, the PNC or PQDs solutions were prepared by suspending the samples in toluene, and the PQD films were prepared by drop-casting a suspension of PQDs on a micro slide glass (cut into 3.8 ×1.3 mm). A PQD film was kept



Figure 2.7. A scheme of a steady-state fluorescence spectroscopy system.

inside an empty cuvette at a 45° angle to maintain the maximum emission from the sample. The emission intensities from the samples were scanned as a function of the detection wavelength. The excitation wavelength was set at 500 nm for MAPbI₃ PNCs or PQDs, and 450 nm for MAPbBr₃ PQDs, and CsPbBr₃ PQDs.

2.2.5 Time-Resolved Fluorescence Spectroscopy

I used time-resolved fluorescence spectroscopy to analyze the average PL lifetime (τ_{avg}) of PNCs or PQDs. The τ_{avg} refers to the average time a photon excited sample spends in the excited state before relaxing to the ground state. The PL lifetime is inversely proportional to the sum of radiative and nonradiative recombination rates. Therefore, it can help in calculating the rates of trap-assisted nonradiative recombination of PNCs and PQDs. So, calculating PL lifetime assists in understanding the excitonic properties of PNCs or PQDs. The optical setup of time-resolved spectroscopy is shown in Figure 2.9.



Figure 2.9. A scheme of the optical setup for collecting fluorescence decays.

The diode pump lasers were used as the excitation source for oscillator (Mira900, Coherent) with the repetition rate of 76 MHz. The mode-locked pulses from Mira900 were amplified to microjoules by the regenerative amplifier (RegA9000, Coherent). The 800 nm output from RegA frequency doubled in an OPA (optical parametric amplifier). The 405 nm

output from the OPA was used as the excitation light source in PL lifetime studies. The PL decay profiles of PNCs (or PQDs) were recorded using an assembly of a polychromator (model 250IS, Chromex) and a photon-counting Streak-camera (C4334, Hamamatsu Photonics).

I placed the PNC- (or PQD-) coated glass coverslip on an XY stage attached to an inverted optical microscope (IX70, Olympus). The emission signals from the samples passed through an objective lens (40x, 0.60 NA, Olympus) and filtered using a long-pass filter (LPF). The objective lens with a high numerical aperture was used for a higher spatial resolution, which can diminish the backscattering and collect the maximum emission. Further, the emission was focused at the polychromator entrance slit and detected with the Streak-camera. I used 580 nm LPF for MAPbI₃ PNCs (or PQDs), and 500 nm LPF for MAPbBr₃ PQDs. I also used neutral density filters for controlling the excitation power intensity.

The PL decays were fitted with the following third-exponential fitting equation,

$$y = y_0 + A_1 e^{-\frac{t-t_0}{\tau_1}} + A_2 e^{-\frac{t-t_0}{\tau_2}} + A_3 e^{-\frac{t-t_0}{\tau_3}}$$
(2.1)

and or the fourth-exponential fitting equation,

$$y = y_0 + A_1 e^{-\frac{t-t_0}{\tau_1}} + A_2 e^{-\frac{t-t_0}{\tau_2}} + A_3 e^{-\frac{t-t_0}{\tau_3}} + A_4 e^{-\frac{t-t_0}{\tau_4}}$$
(2.2)

Here, *t* is time, A_1 , A_2 , A_3 , and A_4 are amplitudes, and τ_1 , τ_2 , τ_3 , and τ_4 are the corresponding lifetime components. The intensity-averaged lifetime (τ_{avg}) was calculated by using the,

$$\tau_{avg} = \sum \frac{A_i \tau_i}{A_i} \tag{2.3}$$

Time-Correlated Single-Photon Counting System (TCSPC)

I used a TCSPC system attached with a 465 nm picosecond laser (Advanced Laser Diode Systems, 1 MHz) for detecting the PL decays of PQDs. Figure 2.10 shows the optical setup used for recording PL decay profiles on a confocal fluorescence microscope (IX71, Olympus). This setup uses an avalanche photodiode (SPCM-AQR, PerkinElmer) and a single-photon counting module (SPC-830, Becker & Hickl GmBH). The suspension of PQDs in toluene was drop-cast on a glass coverslip, and the sample was placed on the

microscopr-XY movable stage. The laser reflected on a dichroic mirror (transmission >90% in 460-700 nm, and >15% at 750-950 nm) before irradiating the PQDs. The emission from the PQDs was collected by an objective lens (40x, 0.75 NA, UPLanFL N), passed the dichroic mirror, and filtered through a 500 nm LPF. Further, the emission was detected through the TCSPC system. The PL decays were fitted with eq. 2.2, and the τ_{avg} of the PQDs was estimated with eq. 2.3.



Figure 2.10. A schematic of the optical setup for recording time-resolved fluorescence decays.

I also used a Qunataurus-tau (Hamamatsu, C11367-21) system for recording PL decay profiles of CsPbBr₃ PQDs. The Qunataurus-tau system consists of several LEDs at different wavelengths as excitation sources. I recorded the PL decays of PQDs for 3 min by exciting with the 470 nm LED. The τ_{avg} of the PQDs was estimated with eq. 2.3.

2.2.6 Single-Particle Microspectroscopy

I used single-particle microspectroscopy with a wide-field illumination optical setup to examine the PL from single PNCs (or PQDs). Wide-field fluorescence spectroscopy yields a more prominent focal spot than confocal fluorescence spectroscopy, which helps obtain collective fluorescence from all the PNCs (or PQDs) in the field of view. I placed the PNC-or PQD- coated glass coverslip on an XY stage attached to an inverted optical microscope (IX70, Olympus), and photoexcited the samples with a cw laser (450 nm, Figure 2.11a). The microscope was equipped with an electron-multiplying charge-coupled device (EMCCD, iXON, Andor Technology), and an objective lens (40x, 0.60 NA, Olympus). The

focal spot in this optical setup was greater than the Abbe diffraction limit. The binning time of the EMCCD was set at 32 ms for collecting the PL signals from the samples. In other words, the PL signals were averaged every 32 ms. An EMCCD camera amplifies the emission signal before it reaches the detector and limits the noise signals. The inside structure of the EMCCD is shown in Figure 2.11b.



Figure 2.11. (a) The optical setup for single-particle imaging. (b) The inside structure of an EMCCD sensor.

An EMCCD collects and multiplies the signals at high speed. I used the operation of frame transfer for acquiring data from the EMCCD. The frame transfer feature is divided into two portions, (i) sensor and (ii) storage area. In the sensor area, the image is captured when exposed to light during the measurements. This image is transferred to the storage area. The storage area is shielded with an opaque mask, which acts as an electronic shutter. In the storage area, the image is already saved before reading the signals. While reading the signals, another image will be captured by the sensor and transferred to the storage, as the sample is continuously exposed to light. After reading out the signals from frame transfer areas, they will shift towards the multiplication chip to amplify before reaching the output. I set the EM gain at 100, where the signal-to-noise ratio is at the optimum for my studies. This way, from a single frame, complete PL blinking statistics of many isolated PNCs or PQDs were collected rapidly with high precision. The PL intensities were recorded as a function of time to distinguish between the high (ON) and low (OFF) intensity durations.

The excitation sources for MAPbI₃ PNCs (or PQDs) was a 532 nm cw laser (Millenia IIs, Spectra Physics), MAPbBr₃ PQDs were a 404 nm LED laser (ThorLabs) or a 460 nm cw laser (ACAN, A12), and CsPbBr₃ PQDs was the 460 nm cw laser. The LPF used in the

experiment for MAPbI₃ PNCs (or PQDs) was 580 nm, and for MAPbBr₃ and CsPbBr₃ PQDs was 500 nm. The ON- and OFF-time probability distributions of single-particle PL intensity trajectories were fitted by the truncated and linear power-laws described in Chapter 1 (Section 1.2.2, eq. 1.5-1.7).

Single-Photon Correlation Measurements

I used the photon correlation function for estimating the single-emitting particles. Photon antibunching is the process of determining the correlation between equally spaced photons. The emission was collected by using a confocal fluorescence microscope. Here, the laser diverges from a beam splitter and passes through an objective lens to the sample. A sample placed on the microscope stage is excited and emits photons. The emitted photons were collected by an objective lens and passed a LPF and a lens. In the end, the photons were detected by two APDs. In this study, the PQDs were photoexcited with a 450 nm pulsed laser (125 fs pulse width, 8 MHz repetition rate). Two APDs detected the coincidence counts of the photons, and the correlation of photons was scanned as a function of time. The photon coincidence counts of MAPbI₃ PQDs are shown in chapter 4.

2.2.7 Scanning Transmission Electron Microscopy (STEM)

I used the STEM Hitachi HD-2000 Ultra-thin Film instrument, operating at 200 kV for analyzing the shape and size of the PNCs or PQDs. In the STEM, an image of the sample is obtained after an electron beam is transmitted through the particles in the observation area. I used carbon-coated STEM Cu100P grids as the sample holder. I prepared suspensions of PNCs or PQDs in toluene and dropped the suspension on the Cu-grid. The Cu-grids were dried under vacuum overnight before the examination. The collected images were analyzed by ImageJ software for calculating the mean size of the PNCs or PQDs.

2.2.8 Powder X-ray Diffraction

I used XRD for analyzing the phase and shape of the PNCs. I used an X-ray diffractometer (RINT 2200, Rigaku), which uses $Cu K\alpha_1$ excitation at λ =1.5406 Å. The XRD spectroscopy consists mainly of three components, (i) a cathode ray tube, (ii) a sample holder, and (iii) a detector. The cathode ray tube generates an X-ray beam when electrons from the inner shell

 $(K\alpha_I)$ are knocked out using an electron beam. The X-ray beam is directed towards the sample, which is rotating continuously with the detector. The reflected X-ray is collected by the detector. Here, the sample rotates at an angle θ , whereas the detector rotates at an angle 2 θ . The rotation of the sample provides the XRD from all the possible lattices scanned by the detector. The XRD peaks can be designated by miller indices, and the miller indices (*hkl*) are calculated by using Bragg's Law,

$$d_{hkl} = \frac{\lambda}{2\sin\theta} \tag{2.4}$$

where λ is the X-ray wavelength, and d_{hkl} is the interplanar spacing. For a tetragonal unit cell, d_{hkl} is calculated as,

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$
(2.5)

Here, *a* and *c* are the lattice constants.

For collecting the XRD pattern of MAPbI₃ PNCs, I dried the PNCs under vacuum and crushed the powder with a hand mortar. This way, I prepared a fine powder of the PNCs. From that, *ca* 30 mg of the MAPbI₃ PNC powder was examined under an XRD. The obtained XRD pattern was compared with the reference data for confirming the phase of the PNCs. I calculated the miller indices for MAPbI₃ PNCs by using the lattice constants for MAPbI₃ (*a*=8.83 Å, *c*=12.69 Å) from the literature.¹¹

2.2.9 Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX)

I used SEM (Hitachi SU8230) attached with an EDX (Bruker QUANTEX EDS) system, which operates at 15 kV, for analyzing the elemental composition in PQDs. In SEM, an image of the sample is obtained after an electron beam hits the sample and the energy transports to the atom. This energy excites an electron from a shell, which leaves a hole behind. A characteristic X-ray is released when the electron from a higher shell recombines with the hole in the lower shell. The energies of the X-rays are analyzed through EDX. I prepared a suspension of PQDs in toluene and drop-cast on an ITO glass. The sample was dried under vacuum for 2 h before the experiment. The PQDs coated on the ITO glass were analyzed using the SEM-EDX.
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Chapter 3

Photostability of Perovskite Nanocrystals

Abstract

In this chapter, I studied the role of oxygen on the methylammonium lead halide perovskite nanocrystals at the ensemble and the single-particle level. The perovskite nanocrystals are prone to degradation under moisture, oxygen, and light. Therefore, to overcome this issue, I analyzed the mechanism of electron transfer and charge carrier recombination to understood the degradation process of perovskite nanocrystals. Under the photoexcited state of perovskite nanocrystals, the electron transfers from perovskite to molecular oxygen and forms superoxide, which occupies the halide vacancy in the perovskite nanocrystal and deteriorate the PNCs. Therefore, the photoluminescence intensity of the methylammonium lead halide perovskite nanocrystals continuously decreases in air. For suppressing oxygen reactivity, I introduced argon to PNCs or coated the PNCs with polymer-matrix to enhance the photoluminescence of perovskite nanocrystals. I also found single-particle photoluminescence intensity trajectories with a long-living OFF-state in air, which showed complete photoluminescence recovery to the original level. Such photoluminescence behavior and the lower rate of electron transfer than that of the rate of nonradiative relaxation during an OFF-state suggest that the perovskite nanocrystals don't undergo degradation and generate superoxide during the ionized state. The neutral excited state of perovskite is vulnerable to oxygen reactivity, which degrades the perovskite nanocrystals, whereas the ionized state prevents the oxidation of perovskite. I distinguished between charge carrier recombination and electron transfer mechanisms in methylammonium lead iodide perovskite nanocrystals by considering the photoluminescence behavior in ON- and **OFF-states**.

3.1 Introduction

The emerging semiconductor class of halide perovskites are promising for low-cost optical, electronic, and photovoltaic devices such as solar cells, LEDs, lasers, batteries, and photodetectors.^{1–14} In the last decade, the power conversion efficiency of perovskite solar cells has increased from 3.8% to >26%, and the external quantum efficiency of perovskite LEDs also boosted from 0.76 to >20%.^{1,15–17} However, the stability of these devices is a challenge for commercialization. The responsible factors for long-term stability are the intrinsic defects present in the crystal lattice. In an ideal case, all the atoms occupy specific positions in the lattice, such as MA^+ locates inside the $[PbX_6]_4^-$ octahedrons. Any variation in the localization of the atoms can be term as defects. Such as structural defects, which consist of atom vacancies, antisites, and interstitial sites. The structural defects can restrict the movement of free charge carriers and trap them at the defect sites. The energy levels of these defects are at a different level (deep or shallow) as that of the valence and conduction bands, where photogenerated charge carriers get trap. The shallow defects, close to the valence and conduction bands, are less harmful than those of the deep defects. These shallow defects mainly contribute to the loses of internal energy of the perovskite. A small amount of additional energy (thermal or activation) can help trap charge carriers to escape from the shallow defects.^{18,19} On the other hand, deep defects form within the material bandgap contribute to trapping the charge carriers and fast nonradiative recombination.²⁰

In lead halide perovskites, the local atmosphere plays a significant role in forming shallow and deep traps in the energy levels of perovskite, such as moisture, water, oxygen, temperature, pressure, and light.^{21–24} Furthermore, the oxygen-induced degradation of lead halide perovskite is one of the main unresolved issues.^{23,25–34} The role of oxygen in decreasing photoluminescence (PL) efficiency has been reported by Haque and coworkers.^{23,25} They demonstrated superoxide generation by the electron transfer from the methylammonium lead iodide (MAPbI₃) perovskite to molecular oxygen. The generated superoxide occupies the halide vacancy and deprotonates methylammonium (CH₃NH₂), I₂, lead iodide (PbI₂), and H₂O.²⁵ To control the electron transfer to oxygen, they employed a layer of TiO₂ on the perovskite and minimized perovskite's oxidation by blocking the generation of superoxide.²³ Furthermore, ab initio studies by Zhang and Sit on the generation of superoxide from MAPbI₃ perovskite suggested that the surface Pb²⁺ ions react with superoxide. The superoxide will break the Pb-X bond and form a covalent bond with

lead, Pb-O, which is responsible for the disintegration of the octahedral structure PbX₆.²⁸ The disintegration of perovskite by the oxygen species enhanced under photoexcitation leading to the formation of charge carrier traps because of the uncoordinate bond between the superoxide and the crystal. These traps cause two times faster nonradiative recombination compared to that of the pristine sample. Therefore, charge carrier dynamics of the perovskite are greatly affected by the superoxide, which promotes atomic fluctuations by the breaking of crystal geometry.^{35,36} Péan et al. showed that superoxide generation depends on various factors such as the intensity of oxygen diffusion, the density of defects and grains, and the perovskite morphology.³⁷ Conversely, various contradicting theories about the role of oxygen in the structural deterioration of halide perovskite are present. For example, the passivation of superoxide at halide vacancies and other defects with oxides increases the PL quantum efficiency.^{31,38-40} Scheblykin and coworkers observed enhanced PL quantum efficiencies through the photochemical reaction of oxygen to trap states in MAPbI₃.³⁹ Also, Brenes *et al.* explained through density functional theory calculations that in the perovskite film, oxygen molecule and surface iodide vacancies bind strongly. This correlation leads to the formation of a thin passivating layer of moisture, which reduces the subband gap traps and reorganizes the band structure to that of a pristine case.³¹ The two contradicting theories related to the roles of oxygen on the defect passivation, degradation, and quenching and enhancement of PL quantum efficiency of perovskites attracted me to investigate the relation between oxidation and reactive state on PL of perovskite nanocrystals (PNCs).

This chapter correlates the ensemble and single-particle PL behavior of MAPbI₃ PNCs in aerobic and anaerobic conditions. Here, I analyzed the effect of superoxide on PNCs during the ON- and OFF-state and observed that the ON-states are susceptible to react with superoxide, whereas OFF-state hinders the oxidation of perovskite. Through ensemble and single-particle studies, I examined that the PL intensity of PNCs continuously decreases in air. In contrast, PL stabilizes in argon and polymer environments under a similar photoexcitation intensity. Additionally, in air, after a long-OFF state, the PNC recovers its PL to the original level, suggesting that the ionized form of PNCs doesn't involve in the oxidation of PNC, the generation and reaction of superoxide with PNC. From analyzing the PL decay profiles of MAPbI₃ PNCs, I observed that argon atmosphere increases the charge carrier lifetime compared to the air atmosphere irrespective of the excitation intensity. I also estimated that under OFF-state, the rate of nonradiative

recombination is higher than that of the electron transfer rate to oxygen, which guided the photodegradation and PL blinking mechanism of PNCs.

3.2 Results and Discussion

3.2.1 Characterization of MAPbI₃ Perovskite Nanocrystals

I synthesized MAPbI₃ PNCs by a modified ligand-mediated transport method.⁴¹ In this synthesis, I dissolved lead iodide and methylamine hydroiodide in hexane along with the ligands, oleic acid and hexadecylamine. The synthesis is described in section 2.2.1. The PNCs were characterized by absorption and fluorescence spectroscopy, XRD, and TEM. The absorption and fluorescence spectra of these PNCs are shown in Figure 3.1a. The PNCs showed broad absorption in the UV-visible region and narrow emission in the near-infrared region *ca* 720 nm, with full-width at half maximum of ~55 nm. For single-particle studies, the PNCs were suspended in toluene and drop-cast on a glass coverslip. The uniform distribution of single PNCs was observed under an EMCCD (Figure 3.1b). Further, for



Figure 3.1. (a) Absorption and emission spectra of MAPbI₃ PNCs suspended in toluene. [Inset: Images of MAPbI₃ PNC suspension in cuvette under room light (left) and UV light (right)]. (b) Single-particle PL image of MAPbI₃ PNCs photoexcited with 532 nm cw laser (excitation intensity was 825 W cm⁻², scale bar: 10 μ m)

calculating the size of the PNCs, TEM images were analyzed. One such TEM image is shown in Figure 3.2a. I used ImageJ software to estimate >100 PNCs and constructed the size distribution histogram (Figure 3.2b). The average size of MAPbI₃ PNCs is estimated

at 11.5±2.1 nm. I also analyzed the crystal phase and space group from the XRD pattern. Figure 3.2c shows the XRD pattern with the corresponding miller indices for MAPbI₃ PNCs. I compared the XRD pattern of the tetragonal phase of MAPbI₃ single crystal from Saidaminov *et al.* In the tetragonal phase, two among three lattice constants (*a*, *b*, *c*) are the same, a=b=8.83Å and c=12.68Å.¹⁴ In this report, the main miller indices of tetragonal phase with space group *I4/m* for MAPbI₃ crystal were (110), (112), (211), (202), (220), (114), (312), (224), and (314), which lies around 14°, 20°, 23°, 24°, 28°, 32°, 35°, 41°, 43°, 46°, and 47° Bragg's diffraction peaks, respectively. As shown in Figure 3.2c, the XRD pattern of MAPbI₃ PNCs in this study matches to that in the literature. Thus, I confirm that the PNCs are in the tetragonal phase with space group *I4/m*.



Figure 3.2. Characterization of size and shape of MAPbI₃ PNCs. (a) TEM image (Scale bar: 50 nm) and (b) its corresponding PNC size histogram. (c) XRD peaks with corresponding miller indices.

3.2.2 Photodegradation and Photostability

To confirm the photostability of MAPbI₃ PNCs, I carried out a time-controlled PL experiment. I suspended MAPbI₃ PNCs in toluene and photoexcited with 532 nm laser at excitation power intensity of 50 mW cm⁻². The PL intensities of MAPbI₃ PNCs were recorded every 2 min of photoexcitation in air and argon environment. As shown in Figures 3.3a and b(i), the PL intensity drastically decreased by 68% in 30 min, when the PNC suspension was saturated by air. This decrease in the PL intensities under air saturation corresponds to the generation of superoxide and its reaction with the MAPbI₃ PNCs. Haque and coworkers demonstrated that the electron transfers from the excited perovskite to the oxygen and generates the superoxide, deprotonates the MA-cation, occupies the halide



Figure 3.3. Photostability of MAPbI₃ PNCs. (a) PL spectra of PNCs saturated with air under photoexcitation by 532 nm cw laser (50 mW cm⁻²), and (b) the relative PL intensities recorded every 2 min of photoirradiation under (i) air and (ii) argon atmosphere.

vacancies, and deteriorates the MAPbI₃ PNCs.^{23,25} Another report by Hong *et al.* reported that the decrease in PL attributes to the activation and deactivation of photoinduced quenching traps.⁴² By acquiring halide vacancies, the superoxide contributes to the formation of electron and hole traps and quenches the PL. Therefore, to suppress the oxygen reactivity, I checked the PL behavior under argon environment. I continuously purged argon into the suspension of PNCs during the experiment and recorded the PL intensities every 2 min of photoexcitation. As shown in Figure 3.3b(ii), when argon was introduced, the PL intensities of the MAPbI₃ PNCs were stable for a long time under similar

photoexcitation. This suggests that the electron transfer from oxygen to the PNCs was reduced under argon atmosphere, and the superoxide generation was suppressed.

3.2.3 Photoluminescence Blinking of MAPbI₃ Nanocrystals

To understand the mechanism of the generation of superoxide and the oxidation of PNCs, single-particle experiments were carried out. I recorded the PL intensity trajectories of single MAPbI₃ PNCs under air/glass, argon/glass, polymer/glass, and dry-air/glass interfaces. Detailed information about the experimental setup of single-particle microspectroscopy is given in Chapter 2, section 2.2.6. For recording PL intensity trajectories of single PNCs under air/glass interface, I drop-cast the PNCs on a glass coverslip and excited with 532 nm cw laser (825 W cm⁻²). The PL intensity trajectories of single PNCs at the air/glass interface show distinct ON- and OFF-events, as shown in Figure 3.4. When the particle was in ON-state, there was a gradual decrease in the PL



Figure 3.4. Typical single-particle PL intensity trajectories of MAPbI₃ PNCs in air. The PNCs were excited with a 532 nm cw laser.

intensity, which varied from particle to particle. Some PNCs degraded slowly [Figure 3.4(i)], and some degraded within 1 min of photoirradiation [Figure 3.4(ii)]. The decrease in PL intensity attributes to the disintegration of the PNCs by the passivation of superoxide on the surface iodine vacancies. As explained in the literature, the more the concentration

of halide defects, the more likely the superoxide will generate.²⁵ Therefore, the ability of oxygen to diffuse in the PNC will determine the rate of degradation.



Figure 3.5. Typical single-particle (i) PL intensity trajectories and (ii) the corresponding occurrences of MAPbI₃ PNCs (a,b) at argon/glass interface and (c,d) after surface polymerization with poly(methyl methacrylate) [PMMA] and photoexcited by a 532 nm cw laser. The dashed line denotes the threshold for determining ON and OFF-events.

Like the ensemble experiment, for suppressing the oxygen reactivity and the degradation of PNCs, I saturated the PNCs with argon. For argon/glass interface, a silicon

chamber was prepared, as explained in section 2.2.2. Also, I analyzed the PNCs by coating them with a polymer-matrix to avoid the moisture effect. For polymer/glass interface, 5 mg of PMMA was dissolved in 1 mL toluene, and 10 µL of this PMMA solution was added to the suspension of MAPbI₃ PNCs. This solution was drop-cast on a glass coverslip and observed under the microscope. The PL intensity trajectories of single MAPbI₃ PNCs were recorded similarly by photoexciting the sample with 532 nm cw laser. The typical PL intensity trajectories of single PNCs at argon/glass and polymer/glass interface are shown in Figure 3.5a-d(i), respectively. From the occurrences of the PL intensity [Figure 3.5 ad(ii)], the blinking behavior with distinct ON- and OFF-event is apparent. The occurrence of ON-events was more than that of the OFF-events because the excitation intensity was high (875 W cm⁻²). Tian *et al.* reported that with the increase in excitation intensity, the OFF-events decrease because the efficiency of active quenchers in trapping a large number of charges decreases. In other words, the emission of the PNC increases at high-intensity excitation.^{43,44} Nevertheless, at high-excitation intensity, the PNC degrades fast under air atmosphere. In contrast, the PL stabilizes under argon and polymer atmosphere. The stability in argon and polymer environment supports the ensemble PL results, suggesting that the perovskite oxidation and the superoxide generation and perovskite oxidation can be suppressed by avoiding oxygen and moisture.

To understand whether oxygen or moisture is responsible for the degradation of PNCs, I analyzed the single-particle PL intensity trajectories after saturating a single-particle sample chamber with dry air. I dried the air by sequentially passing through the columns filled with sodium hydroxide, molecular sieves (5 Å), and granular silica gel. The PNCs were drop-cast on a glass coverslip covered with a silicon chamber, and the dry air was passed inside the chamber. The PNCs in dry air were observed under an EMCCD, and the PL intensity trajectories were recorded (Figure 3.6). Even after eliminating the moisture, PNCs in dry air showed photobleaching and PL blinking. Thus, I assume oxygen itself generates superoxide and oxidizes the PNCs, which leads to the degradation of PNCs. Nonetheless, the role of moisture alone is not examined by considering several reports about degradation of halide perovskites in humid atmospheres.



Figure 3.6. Typical single-particle PL intensity trajectories of MAPbI₃ PNCs in dry air. The PNCs were excited with a 532 nm cw laser.

However, the blinking was independent of the atmosphere. To determine the changes in ON-and OFF-event occurrences according to the local atmosphere, I analyzed the distribution of ON- and OFF-times in >100 single MAPbI₃ PNCs each at air/glass, argon/glass, and polymer/glass interface shown in Figures 3.7a-c, respectively. For this



Figure 3.7. (i) ON and (ii) OFF time histogram of >300 single MAPbI₃ PNCs at (a) air/glass interface, (b) argon/glass interface, and (c) polymerized PNCs.

analysis, I estimated the PL intensity threshold, where it turns ON from the OFF-event in each PL intensity trajectory. For example, in Figure 3.5, the blue dashed line represents the threshold point in the corresponding PL intensity trajectories under argon and polymer atmosphere. In the case of air atmosphere, PL intensity was continuously decreasing. So, for estimating the threshold, baseline correction was carried out for each PL intensity trajectory. I also analyzed the variation in the average OFF-intensities in air/glass, argon/glass, and polymer matrix, as shown in Figure 3.8. From Figures 3.7 and 3.8, I observed that the number of ON-events was more than that of the OFF-events in all the cases, suggesting the number of emitting sites and quenchers are almost equal at air/glass, argon/glass, and polymer matrix. In a PNC, the quenchers can form from halide or cationassisted traps. As the quenchers act as the nonradiative recombination centers, I assume that those trap centers will become inactive under argon and the polymer environment. Therefore, argon and polymer atmosphere aids in reducing the traps.



Figure 3.8. Variation of average PL intensity with its OFF-time in >300 single MAPbI₃ PNCs at (a) air/glass interface, (b) argon/glass interface, and (c) in polymerized PNCs.

3.2.4 The Mechanism of Photodegradation

Although MAPbI₃ PNCs at air/glass interface showed a gradual decrease in PL intensity during an ON-event, some PL intensity trajectories of MAPbI₃ PNCs at air/glass interface also showed a long-OFF-event. Figure 3.9 shows the typical examples of such PL intensity trajectories with long-OFF events. In these PL intensity trajectories, when the particle was in the OFF-state, the PL intensity before and after turning OFF was at the same level, as shown by the dashed line in Figure 3.9. Such PL intensity trajectories lead to the understanding of the role of oxygen reactivity towards PNCs. It shows that under an OFF-

event, when the PNC is in the ionized excited state, the photodegradation does not occur, and the PNC does not react with the superoxide. In general, PL blinking in PNCs occurs from the surface trap states, charging-discharging of the trap states, photoinduced defects, and fast nonradiative Auger relaxation.^{43–50} On the other hand, oxidation of PNC leads to the superoxide generation by electron transfer from PNC to molecular oxygen during photoexcitation.^{23,25,27–29,51,52} Furthermore, electron transfer from one state to another is the main reason for both the blinking and the oxidation. Therefore, based on the above statements, I am considering four different states involved in the blinking, oxidation, and



Figure 3.9. Typical PL intensity trajectories of MAPbI₃ PNCs saturated by air photoexcited by a 532 nm cw laser having long OFF-events.

degradation of PNC. These states are (i) ground, (ii) excited, (iii) neutral, and (iv) ionized states. The ON-state includes ground, neutral, and excited states, whereas OFF-state includes ground and excited ionized states. The oxidation of PNC by photoinduced electron transfer to molecular oxygen is a dark reaction. Thus, the above states can be affected by the superoxide generation and the oxidation of PNC. But in Figure 3.9, the complete recovery of the PL intensity after a long-OFF event in the PNC suggests that the ionized PNC does not generate superoxide during an OFF-state when the charge carriers nonradiatively recombine. So, under the OFF-event nonradiative recombination dominates the electron transfer to oxygen. Therefore, the oxidation of PNCs stops, and the superoxide doesn't generate and react with the PNC.

Generally, in blinking, the nonradiative recombination represents the OFF-state. In the case of halide perovskite, oxidation of PNC and the generation of superoxide is a dark state. Therefore, superoxide generation is high when the electron transfer rate is more than that of the nonradiative recombination rate. However, recovery of PL intensity during OFFevent suggests that the ionization of PNCs prevents it from oxidation and its reaction towards superoxide. In other words, the rate of nonradiative recombination is higher than that of the electron transfer to oxygen. To prove this, I recorded the PL decay profiles of MAPbI₃ PNCs at low- and high-excitation intensities under air and argon environment (Figure 3.10). I fitted the PL decays using the third exponential equation (Chapter 2, eq. 2.1) and estimated the average PL lifetime through the intensity averaged equation (Chapter



Figure 3.10. PL decay profiles of MAPbI₃ PNC films at (i) air/glass, and (ii) argon/glass interfaces under (a) low-excitation intensity (0.007 W cm⁻²), and (b) high-excitation intensity (1.4 W cm⁻²) of a 400 nm fs laser.

2, eq. 2.3). The average PL lifetime of MAPbI₃ PNC under a low-intensity excitation in air was 1.9 ± 0.16 ns, which was lower than that of argon atmosphere, 3.55 ± 0.22 ns. Similarly, under a high-excitation intensity, the average PL lifetime of MAPbI₃ PNCs in air atmosphere (0.99 ± 0.11 ns) was lower than in argon atmosphere (1.37 ± 0.05 ns). Irrespective of laser excitation intensity, the low PL lifetime values in air atmosphere suggest that electron transfer to oxygen plays a significant role in quenching the emissive states. From the average PL lifetimes in the four cases, I calculated the approximate rate of electron transfer and the nonradiative recombination. At low-excitation intensity, the PL lifetime of MAPbI₃ PNC is

$$\tau_1 = \frac{1}{k_r + k_{nr} + k_{et}}$$
(3.1)

Here, τ_I is 1.9±0.16 ns, k_r is the rate of radiative relaxation, k_{nr} is the rate of nonradiative relaxation, and k_{et} is the rate of electron transfer to oxygen. When argon was introduced in the MAPbI₃ PNC atmosphere, the reactivity of oxygen towards PNC stopped. So, I ruled out the electron transfer to oxygen when PNCs were in argon atmosphere, and the PL lifetime of MAPbI₃ PNC at low excitation in argon atmosphere became

$$\tau_2 = \frac{1}{k_r + k_{nr}} \tag{3.2}$$

Here, τ_2 is 3.55±0.22 ns. By solving equations 3.1 and 3.2, I estimated the rate of electron transfer from MAPbI₃ PNC to oxygen at 2.45×10⁸ s⁻¹.

For calculating the fast nonradiative recombination, the PL lifetime of MAPbI₃ PNC at high-excitation intensity is considered as

$$\tau_3 = \frac{1}{k_r + k_{nr} + k_A + k_{et}}$$
(3.3)

Here, τ_3 is 0.99±0.11 ns, and k_A is the additional rate of nonradiative relaxation.

By solving equation 3.3 from equations 3.1 and 3.2, I estimated the additional rate of nonradiative relaxation in MAPbI₃ PNC at 4.84×10^8 s⁻¹. Similar to PL lifetime at low excitation intensity, I ruled out the electron transfer at a high-excitation intensity under argon atmosphere, and the PL lifetime at this condition is

$$\tau_4 = \frac{1}{k_r + k_{nr} + k_A}$$
(3.4)

Here, τ_4 is 1.37±0.05 ns. By solving equations 3.1 to 3.4, I confirmed the rate of additional nonradiative relaxation ($k_A = 4.54 \times 10^8 \text{ s}^{-1}$). Thus, I proved that the $k_{et} < k_A$ at high-excitation intensity.

The mechanism of PL blinking and photodegradation of MAPbI₃ PNCs are shown in Figure 3.11. This mechanism takes into account the four electronic states for the electron transfer, radiative, and nonradiative relaxation pathways. The first is the ground state of the perovskite, which corresponds to its valence band maximum. The second is the excited state corresponding to the conduction band of the perovskite, which lies at higher energy. The third corresponds to neutral states. The neutral ground, and excited states are included



Figure 3.11. (a) Scheme of the electron transfer mechanism, the generation of superoxide by oxidizing MAPbI₃ PNCs, and all four electronic states. (b) The disintegration of MAPbI₃ PNCs by superoxide.

for determining the ON-state. The fourth is the ionized state corresponding to the electron and hole trap states. The ground, excited, and ionized states are included for determining the OFF-state. Under the ON-state, the electron will radiatively recombine, represented by the red arrow in Figure 3.11. Conversely, the electron will nonradiatively recombine from the excited state if it transfers to the molecular oxygen or the ionized state, represented by the curvy black arrow in Figure 3.11. According to Tian *et al.*, the inhomogenous blinking in the PNC occurs by the photoactivation and deactivation of the quenching and emitting sites, which corresponds to the chemical and structural defects of the PNC.⁴³ Further, Aristidou *et al.* reported the structural defects such as the halide vacancies are responsible for the photogenerated superoxide, which diffuses into the MAPbI₃ PNCs, deprotonates the methylammonium cation, and subsequently deteriorates the perovskite geometry into CH₃NH₂, PbI₂, and H₂O as shown in Figure 3.11b. By referring to the literature, I hypothesize that when the perovskite is in its excited state, the electron transfers from PNC to oxygen and oxidizes the PNC. The electron transfer competes with the other recombination pathways when the PNC is in a neutral state. After the electron transfer to oxygen, the superoxide generates at the halide vacancies in the PNCs.

On the other hand, when the PNC gets ionized, it prevents electron transfer to oxygen. As shown in Fig. 3.9, the similar level of PL intensity before and after a long-living OFF-state represents no degradation of the PNC, which means the PNC doesn't react to oxygen in an ionized state. Furthermore, the rate of nonradiative recombination in the ionized state overcomes the rate of electron transfer, which also supports the calculated rates obtained from the average PL lifetimes. Thus, the suppression of superoxide generation provides stability in the PNCs. These results in aerobic and anaerobic conditions and the rates of electron transfer and nonradiative recombination suggest that under a neutral state, the MAPbI₃ PNCs will continuously degrade due to the generation of superoxide.

3.3 Conclusion

This chapter has demonstrated the relation between photoluminescence blinking and oxidation of MAPbI₃ perovskite nanocrystals. I examined the photoluminescence behavior at the ensemble and single-particle levels in different environmental conditions- air, argon, polymer, and dry air. I confirmed the continuous decrease of photoluminescence in MAPbI₃ perovskite nanocrystals by the oxidation of perovskite and superoxide generation when interacted with oxygen and light. The photoluminescence intensity trajectories of singleparticle showed that the photodegradation was suppressed in argon and polymer atmosphere. The photoluminescence intensity trajectories with long-OFF events and the recovery of photoluminescence intensity suggested that ionized excited state prevents the electron transfer from perovskite nanocrystal to oxygen, the oxidation of perovskite nanocrystals, and the superoxide generation. Thus, during an ON-state, the MAPbI₃ perovskite nanocrystals continuously generate superoxide, and the photoluminescence decreases gradually over time. Furthermore, by calculating the average photoluminescence lifetimes of perovskite nanocrystals under high and low excitation intensity in air and argon atmosphere, I estimated that the rate of electron transfer to oxygen $(2.45 \times 10^8 \text{ s}^{-1})$ is lower than that of the nonradiative relaxation $(4.84 \times 10^8 \text{ s}^{-1})$ during an OFF-state. Therefore, suppressing the electron transfer to oxygen and the superoxide generation will increase the photoluminescence of perovskite nanocrystals.

3.4 References

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Chapter 4

Photoluminescence Blinking Suppression by Halide Vacancy Filling

Abstract

Halide perovskites are promising semiconductor materials for next-generation optical and electronic devices. However, the long-term durability and stability against the environment, such as moisture, oxygen, and light, cause adverse effects. The ionic and electronic defects generated by intrinsic or extrinsic factors disintegrate the perovskite structure and deteriorate the photoluminescence properties. One such defects are the halide vacancies, which form deep traps in the energy levels, and the leading cause for the nonradiative recombination or trapping of photo- or electro-generated charge carriers, causing undesired stochastic fluctuations of luminescence in perovskite nanocrystals and quantum dots, called blinking. This chapter demonstrates the suppressions of photoluminescence blinking and fast nonradiative recombination of the excitons by the real-time filling of halide vacancies in MAPbBr₃ and MAPbI₃ perovskite quantum dot with MABr and MAI, respectively. Furthermore, the post-synthetic treatment of perovskite quantum dots with halide salts helped in increasing the charge carriers' photoluminescence intensities and lifetimes. Also, I estimated the rate of halide-vacancy-assisted nonradiative recombinations at 1×10^8 s⁻¹ for MAPbBr₃ and 1.9×10⁹ s⁻¹ for MAPbI₃ perovskite quantum dots. Apart from the controlled real-time experiments, I constructed the ON- and OFF- times probability distributions, which suggested the change in blinking behavior from type-A to type-B after the treatment. In other words, the charging-discharging of excitons changed to the trapping-detrapping of the trap states, confirming the filling of halide vacancies.

4.1 Introduction

Halide perovskites are the class of semiconductors having potential for real-world applications^{1–5} due to their unique optical and electronic properties, such as tunable photoluminescence (PL) with high quantum yield (QY),^{6–8} long lifetime,^{9–11} and long diffusion length of photogenerated charge carriers.^{12–14} These properties vary by size, composition, temperature, pressure, synthetic methods, and environmental factors. As discussed in chapter-3, these perovskites are susceptible to moisture, humidity, oxygen, and light.^{15–18} These factors promote intrinsic defects in perovskites, such as cationic and anionic (halide) vacancies (*V_{MA}*, *V_{Pb}*, *V_X*), interstitial sites (*MA_i*, *Pb_i*, *X_i*), and antisites (*MA_{Pb}*, *Pb_{MA}*, *Pb_X*, *X_{Pb}*, *X_{MA}*, *MA_X*), which are responsible for the degradation of the structural and optical properties.^{10,19,20} Most of these defects form shallow traps near the band-edge of perovskites. In contrast, halide-related defects form deep traps in the energy levels and are the centers of fast nonradiative recombinations affecting the PLQY and causing PL blinking.^{16–28} Therefore, halide vacancy passivation and PL blinking suppression may overcome the obstacles in achieving stable PL and improved efficiencies of the perovskite-based applications.

The PL blinking was first identified in cadmium selenide quantum dots (QD) in 1996 by Nirmal et al., where the photoionization and charge neutralization results in distinct ONand OFF- times.³⁴ After that report, the mechanism of PL blinking is widely investigated in QDs and nanocrystals.^{35–38} Galland *et al.* demonstrated that the PL blinking behaves in two different mechanisms in QDs, expressed as (i) type-A and (ii) type-B, where the pathways of nonradiative recombination are different.³⁵ Similar mechanisms are applicable in lead halide perovskites microcrystals, nanocrystals (PNCs), and PQDs.^{26-29,39} In the conventional type-A blinking, the charging and discharging leads to the random switching between ON- and OFF- periods. Here, in the neutral state, perovskite undergoes radiative recombination (ON-event), and when charged as trions, Auger nonradiative recombination dominates (OFF-event), which leads to the decrease in PL intensity. On the other hand, in type-B blinking, activation and deactivation of the trap centers lead to random blinking. Conversely, the dynamics of trapping and detrapping of charge carriers are a dominant factor in type-B blinking. Fluorescence lifetime intensity distribution (FLID) and the probability distribution of ON- and OFF- times help to differentiate between these two mechanisms. Type-A and type-B simultaneously occur in the case of PQDs.^{26–29} For instance, Trinh et al. described the blinking in formamidinium lead bromide (FAPbBr₃) PQD is due to the diffusion-controlled electron transfer and Auger ionization which is causing simultaneous type-A and type-B blinking and photodegradation.²⁷ In another report, they verified the concurrent blinking mechanisms with FLID and ON-OFF-probability distribution under different photon collection bin time.²⁸ According to their result, OFF-time's probability distribution showed truncation power-law in the starting few minutes and linear power-law in the rest of the time.

Apart from FLID and probability distribution, other methods like super-resolution localization microscopy and electron microscopy help correlate structural or chemical defects and PL blinking by analyzing the nonradiative relaxation pathways.^{24,30–32} The structural or chemical defects, such as ionic vacancies, can act as quenchers of emitting sites or trap the charge carrier and lead to nonradiative recombination. The rate of the quenching and trapping dramatically depends on the excitation intensity for the PL. For example, the OFF-events decrease at the high-excitation power in MAPbI₃ nanocrystals.³⁰ As explained by Agiorgousis et al., in the case of MAPbI₃, iodine vacancies form a deep defect transition level (I^0/I^-) .¹⁰ Once the iodine vacancies are negatively charged, they act as donors, leading to the formation of the strong covalent Pb-Pb dimer and the decomposition of the structural morphology. Similarly, in MAPbBr3 PNCs, bromine vacancies and interstitials form deep defect levels and are responsible for PL blinking by acting as the nonradiative recombination centers.³³ These trap centers are continuously activated and deactivated when introduced with oxygen and water from the environment and the light, which affects the rate of nonradiative recombination. Therefore, in lead halide perovskites, the surrounding atmosphere is the main criterion for determining the stability and its PL.

The relationship among the PL, surface states, and the atmosphere has been examined from the passivation of the lead halide perovskites by ligands,⁴⁰ polymers,⁴¹ A-site cations,⁴² and halide ions.^{43,44} Among these, passivating halide ion defects post-synthetically has improved the PL stability in PNCs. For example, surface passivation with halide salts,⁴³ tetrafluoroborate salt (NaBF₄)²³ or Ag(I) complex⁴⁴ in PNCs, and perovskite coating with CdS QDs⁴⁵ or anhydrous silica spheres⁴⁶ showed increased PL intensity and suppressed PL blinking. Haque and coworkers used organic and inorganic halide salts and passivated the halide vacancies in MAPbI₃ perovskite film, and observed the suppression of superoxide generation and PL stability.⁴³ Another report by Samanta and coworkers showed the passivation of bromine in CsPbBr₃ PNCs by NaBF₄⁻, which resulted in PL

blinking suppression and partial decrease in Auger recombination centers, hot-carrier, and band-edge carrier traps.²³ However, the correlation of halide vacancies with PL blinking and charge carrier dynamics in PQDs is yet to understand at the single-particle level.

This chapter has demonstrated the suppressions in PL blinking and fast nonradiative recombination with the increases in PL lifetime and PL intensity of MAPbX₃ (X=Br, I) PQDs at real-time filling of halide vacancies with MAX (X=Br, I) treatment. I performed controlled experiments for examining the PL intensity trajectories of the same PQD before and after the MAX treatment at the single-particle level. I observed the suppression of PL blinking in single MAPbX₃ PQDs after the treatment. I also recorded the PL quantum yields (QY) and lifetimes before and after the treatment and evaluated the nonradiative recombination rate assisted by halide vacancies in the perovskites. Along with assessing PL behavior, I analyzed ON-and OFF-probability distributions of PQDs before and after the treatment and confirmed the change in blinking behavior from type-A to type-B models.

4.2 **Results and Discussion**

4.2.1 Characterization of Perovskite Quantum Dots

I synthesized MAPbBr3 and MAPbI3 PQDs by modification of ligand-assisted reprecipitation (LARP) methods.⁷ The modification of the synthesis and its purification are described in section 2.2.1. LARP method is used to obtain uniform and isolated small-sized PQDs by using long-chain organic ligands (oleic acid and hexadecene) for crystal growth. I characterized these MAPbX₃ PQDs by absorption spectroscopy, UV-vis spectroscopy and TEM. For absorbance and PL spectra, the MAPbX₃ PQDs were dispersed in toluene, and for TEM imaging, the MAPbX₃ PQDs suspended in toluene was dropped on a copper grid and dried under vacuum overnight. The MAPbBr₃ PQDs in this study shows broad absorption and narrow emission ca 530 nm with the full width at half maximum (FWHM) of ~22 nm (Figure 4.1a). The size of MAPbBr₃ PQDs is estimated from the TEM image (Figure 4.1b) around 10.6±1.6 nm. The size distribution of >100 MAPbBr₃ PQDs is shown in Figure 4.1c. Similarly, MAPbI₃ PQDs shows broad absorption and emission ca 750 nm with FWHM of ~46 nm, as shown in Figure 4.2a. The red-shift absorbance and PL of MAPbI₃ PQDs in comparison to MAPbBr₃ is due to the size of the halide ion.^{39,47,48} In perovskites' valence band maxima, the contribution of halide *p*-character is more when the *p*-orbital of halogen and *s*-orbital of metal mixes. The increase in halide *p*-character (from



Figure 4.1. Characteristics of MAPbBr₃ PQDs. (a) Absorption and emission spectra of a MAPbBr₃ PQDs suspended in toluene. (b) TEM image (scale: 50 nm) and (c) the corresponding histogram of MAPbBr₃ PQD size.

Br⁻ to I⁻) decreases the perovskite bandgap due to the rise in spin-orbit coupling. Hence, the decrease in the bandgap shifts the spectra towards the low energy region. Figure 4.2b shows the TEM image of MAPbI₃ PQDs, with a size of around 8.6 ± 1.5 nm. The size distribution of >100 MAPbI₃ PQDs is shown in Figure 4.2c. To investigate the role of halide vacancies on PL blinking of the MAPbX₃ PQDs, single-particle microspectroscopy is used. The



Figure 4.2. Characteristics of MAPbI₃ PQDs. (a) Absorption and emission spectra of a MAPbI₃ PQDs suspended in toluene. (b) TEM image (scale: 50 nm) and (c) the corresponding histogram of MAPbI₃ PQD size.

sample for this measurement was prepared by drop-casting the MAPbX₃ PQDs suspended in toluene on a glass coverslip and dragged with the lens cleaning paper for the uniform distribution of single PQDs. Through this process, I was able to control particles' density in the field of view (~10 to 15 single PQDs per $50 \times 50 \,\mu\text{m}^2$ frame). For example, the images recorded from the EMCCD camera of photoluminescent isolated single MAPbBr₃ and MAPbI₃ PQDs are shown in Figure 4.3a and b, respectively, when irradiated with cw lasers.



Figure 4.3. Single-particle images of isolate (a) MAPbBr₃ PQDs photoexcited with 460 nm cw laser (6.2 W cm⁻², scale: 10 μ m) and (b) MAPbI₃ PQDs photoexcited with a 532 nm cw laser (2 W cm⁻², scale: 10 μ m).

The single-photon emitting particles were characterized by correlating the coincidence photon counts by the photoexcitation of the PQDs. Park *et al.* and Yuan *et al.* showed strong antibunching of photons in CsPbI₃ PQDs by measuring the lowest second-order correlation function (~0.1) at zero delay time, which is the signature of quantum emitters with efficient Auger recombination.^{26,49} For obtaining single-photon coincidence counts of MAPbI₃ PQDs, PQDs suspended in toluene was spin-coated on a glass coverslip and photoexcited with 450 nm pulsed laser. The excited photons were detected by two avalanche photodiodes at each 125 s delay time. As shown in Figure 4.4a, MAPbI₃ PQD shows low coincidence counts at zero delay time, suggesting that photons were excited one by one from a single-emitting particle. On the other hand, a high coincidence counts at zero delay time confirms the presence of a multiphoton-emitting particle or the aggregation of small particles, as shown in Figure 4.4b. The multiphoton emission generally occurs when the excitation intensity is high or when multiple photons absorb tandemly, so we can rule out multiphoton emissions by keeping the low excitation intensity.

This chapter aims to suppress the PL blinking by filling halide vacancies in PQDs. For recording PL intensity trajectories of MAPbX₃ (X=Br, I), MAPbX₃ PQDs suspended in toluene was drop-cast on a glass coverslip and dragged by using lens cleaning paper. The isolated single MAPbBr₃ and MAPbI₃ PQDs were obtained through this method, which was photoexcited by 460 and 532 nm cw laser, respectively, and observed under EMCCD. Figure 4.4c-f show some representative PL intensity trajectories observed in MAPbBr₃ (Figure 4.4c,d) and MAPbI₃ (Figure 4.4e,f) PQDs. These are the two extreme PL blinking behavior observed in the same field of view of PQDs- (i) with frequent ON- and OFF-event and (ii) with long ON-events. Such PL behavior concludes that the PL blinking differs from particle to particle irrespective of the preparation and the excitation intensity. So, for checking the role of halide vacancy filling, I analyzed the PL blinking in the same PQDs before and after the treatment. I also evaluated the probability distribution of ON- and OFF-times in more than 200 single PQDs.



Figure 4.4. Single-particle PL behavior of MAPbX₃ PQDs. (a,b) Single-photon coincidence counts of MAPbI₃ PQDs irradiated with a 450 nm pulsed laser (30 nW). (a) Single-emitting MAPbI₃ PQD and (b) multiphoton emission or aggregates of MAPbI₃ PQDs. (c,d) PL intensity trajectories of MAPbBr₃ PQDs with (c) high- and (d) low-frequency blinking behavior when photoexcited with a 460 nm cw laser (6.2 W cm⁻²). (e,f) PL intensity trajectories of MAPbI₃ PQDs with (c) high- and (d) low-frequency blinking behavior when photoexcited with a 460 nm cw laser (6.2 W cm⁻²). (e,f) PL intensity trajectories of MAPbI₃ PQDs with (c) high- and (d) low-frequency blinking behavior when photoexcited with a 532 nm cw laser (2 W cm⁻²).

4.2.2 Halide Vacancy Filling in Single Perovskite Quantum Dots

In lead halide perovskites, ion migration is an obstacle for achieving high PL efficiency and long-term stability. For MAPbX₃ perovskite, all the ions MA⁺, Pb²⁺, and X⁻, migrate in the crystal under photoexcitation. Huang *et al.* said that the distance between two halide

ions is less than two MA⁺ and Pb²⁺ cations in perovskites.⁵⁰ Therefore, the migration of halide ions is faster than MA⁺ and Pb²⁺ cations. Halide defects in perovskites constitute vacancies, antisites, and interstitials sites. These defects form deep electron and hole traps in the bandgaps of perovskite and responsible for the fast Auger nonradiative recombination.^{10,33,50–52} According to the migrating ability, halide defects are first to be filled in the perovskites compared to MA⁺ cation. Therefore, to understand the role of halide vacancies of MAPbX₃ PQD, I examined the PL blinking before and after the treatment of PQDs with MAX (Br, I), shown in Figures 4.5 and 4.6. 10 mM MAX solutions were prepared by dissolving 0.05 mmol of MAX (MABr= 5.6 mg, MAI= 8 mg) in 5 mL dichloromethane (DCM). Firstly, the PL intensity trajectory of a single MAPbI₃-coated glass coverslip and observed PL behavior of the same PQD [Figure 4.5a (ii)]. Initially, after the



Figure 4.5. PL intensity trajectories of MAPbI₃ PQDs. (a, b) The real-time treatment of PQDs before (i) and after (ii) the 10 mM MAI.

MAI addition, the PL fluctuated because of the change in the refractive index, and after a while, the blinking was suppressed. In other words, the time of ON-events increased, resulting in the enhancement of PL. Another example of the real-time addition of MAI on MAPbI₃ PQD is shown in Figure 4.5b. Here, the untreated MAPbI₃ PQDs showed high-frequency blinking with short ON-and OFF-events. This blinking behavior changed to low-frequency blinking with long ON-events after the treatment.

Similarly, I treated the MAPbBr₃ PQDs with MABr and successfully suppressed the PL blinking, as shown in Figure 4.6. Here as well, the PL blinking of the untreated MAPbBr₃ PQDs [Figure 4.6a, b(i)] showed high-frequency PL blinking with more OFFevents, which was changed to low-frequency PL blinking with more ON-events after the MABr treatment [Figure 4.6a, b(ii)]. By observing the PL blinking suppression of MAPbX₃ PQDs after the treatment with MAX, I conclude that the addition of excess MAX successfully fills the halide vacancies. As the halide-vacancy-related defects constitute deep traps in the bandgaps, filling such defects will reduce the fast Auger nonradiative recombination. According to Chapter-3, the halide vacancy generates superoxide, which ultimately degrades the lead halide perovskites. Therefore, in addition to blinking suppression, the halide vacancy filling also suppresses the generation of superoxide and perovskite oxidation.



Figure 4.6. PL intensity trajectories of MAPbBr₃ PQDs. (a, b) The real-time treatment of PQDs before (i) and after (ii) the 10 mM MABr.

I analyzed the PL blinking of untreated PQDs and the PL blinking suppression by filling halide vacancy after the treatment. Generally, the blinking in PQDs is based on the charging and discharging of excitons (type-A blinking) and the trapping and detrapping of charge carriers (type-B blinking). In type-A blinking, the charging and discharging of excitons results in the generation of trions and the fast Auger nonradiative recombination. Here, the trion generates in a deep trap resulting in the exciton quenching and subsequently decreases the PL intensity and the lifetime. The probability distribution of ON- and OFF
times follow a truncated power law, which is the type-A blinking signature, as explained in Chapter 1 (Section 1.2.2, equation 1.5), $P(\tau) = A_0 \tau^{-\alpha} e^{-\frac{\tau}{\tau_c}}$. Here, A_0 is a constant, α is the power-law coefficient, τ_c is the truncation time, and the probability distribution $[P(\tau)]$ is calculated using equation 1.7 (Chapter 1, Section 1.2.2), $P(\tau) = \frac{2N_i}{(\tau_{i+1}+\tau_i)-(\tau_i+\tau_{i-1})}$, here, N_i is the occurrence of i^{th} ON- or OFF- time, and τ is the time. The N_i of ON-and OFF-times for pristine MAPbI₃ PQDs are shown in Figure 4.7a,b, whereas the MAI-treated PQDs are shown in Figure 4.7c,d. In type-B blinking, charge carriers trap at the band edge or shallow



Figure 4.7. The occurrences (N_i) of (a,c) ON- and (b,d) OFF- times of MAPbI₃ PQDs before (a,b) and after (c,d) the MAI treatment.

trap states. Trapping and detrapping of short-lived electrons and holes trap states govern nonradiative recombination rate and control the PL intensity and lifetime of the charge carriers, as suggested by Xiao *et al.*²² The probability distribution of ON- and OFF times follow a linear power law, which is the type-B blinking signature (Chapter 1, Section 1.2.2, equation 1.6), $P(\tau) = A_0 \tau^{-\alpha}$. For correlating the role of halide vacancies with the blinking mechanism (type-A and -B), I analyzed more than 200 single MAPbI₃ PQDs before and after the treatment. I fitted the ON- and OFF-time probability distribution by truncated and linear power laws.

The pristine MAPbI₃ PQDs showed the truncated power-law behavior of ON-and OFF-times probability distribution (Figure 4.8a,b). Whereas, the MAI-treated PQDs followed linear power-law behavior (Figure 4.8c,d). Pristine PQDs simultaneously show



Figure 4.8. The probability distribution of (a,c) ON- and (b,d) OFF- times of MAPbI₃ PQDs before (a,b) and after (c,d) the MAI treatment.

both type-A and -B blinking, as explained in the literature.^{26–29} Also, type-B blinking in PQDs is subcategorized into two divisions: (i) hot electron and hot hole trapping, which doesn't modulate the PL lifetime, (ii) short-lived band-edge charge carrier trapping or shallow trapping, which linearly decreases the PL lifetime with time.^{28,29} Kim *et al*.observed that the deep traps associate with type-A blinking, whereas shallow traps associate with type-B blinking.²⁹ Therefore, from these findings, I deduce that pristine MAPbX₃ PQDs fitted with truncated power-law show both type-A and -B blinking, where type-A dominates for the charge carrier recombination. And the MAX treated MAPbX₃ PQDs, fitted with linear power-law, show the dominance of type-B blinking. The change

of blinking from type-A to type-B attributes to the reduction of deep traps associated with halide-vacancy and the suppression of fast nonradiative recombination in MAPbX₃ PQDs.

4.2.3 Halide Vacancy Filling in Ensemble of Perovskite Quantum Dots

The single-particle experiment revealed the suppression of PL blinking by the halide vacancy filling. The halide vacancy role on the charge carrier recombination rates and efficiencies is also verified at the ensemble level by recording the PL intensities and decay profiles before and after the MAX treatment on MAPbX₃ PQDs. For recording PL intensities, the MAPbBr₃ and MAPbI₃ PQDs suspensions in toluene were drop-cast on glass coverslips. The PL intensities of the samples are recorded at 2 min interval. For the MAX treatment, I dropped 10 mM MABr and MAI solution (in DCM) on the MAPbBr₃- or MAPbI₃- coated glass coverslips, respectively. The change in relative PL intensities before and after the treatment is shown in Figure 4.9. The PL intensity of MAPbBr₃ PQDs increased by 185%, and after the MABr treatment, the PL intensity increased by 280% (Figure 4.9a). In the case of pristine MAPbI₃ PQDs, the PL intensity is increased by 150%,



Figure 4.9. Relative PL intensities of (a) MAPbBr₃ PQDs and (b) MAPbI₃ PQDs before (i) and after (ii) the treatment with MABr and MAI, respectively.

and after the MAI treatment, the PL intensity increased by 210% (Figure 4.9b). The more percentage increase of PL intensities after the treatment results in the filling of halide vacancies. The enormous rise in PL intensities in both cases relates to the photo-brightening effect and reduction in halide-vacancy-related defects, suppressing the nonradiative

recombination of photogenerated charge carriers. The photo-brightening effect in perovskites is possible when the excitation intensity is very low and the sample is kept under dark, which reduces the chance of the oxidation of perovskite and the generation of superoxide.

Also, by SEM-EDX measurement, I estimated the density of halide vacancies in the MAPbX₃ PQDs by analyzing the elemental composition of lead and iodide in MAPbI₃ PQDs before and after the MAI treatment. Here, the PQD samples were prepared by dropcasting MAPbI₃ PQDs suspended in toluene on an ITO glass. The sample was dried under vacuum for 2 h, and the PQDs were examined under the SEM-EDX, and the SEM images and elemental compositions of the PQDs were obtained. Figure 4.10a shows typical SEM-EDX spectrum of MAPbI₃ PQDs. Then, I treated the same PQDs with a 10 mM MAI solution in DCM. The SEM-EDX spectrum of the same area after the treatment was examined (Figure 4.10b). From the EDX spectra, I estimated that the elemental ratio of I to Pb was increased by *ca* 4 % after the MAI treatment. Nevertheless, the sample to sample variations of this elemental ratio and the E-beam induced sample damage did not allow me to precisely quantify the defect density.



Figure 4.10. SEM-EDX spectra of MAPbI₃ PQDs (a) before and (b) after MAI treatment.

Further, to confirm the role of halides on PL, I analyzed the relative PLQY of the MAPbBr₃ PQD suspension with reference to fluorescein. As shown in Figure 4.11a, the emission maxima of fluorescein is *ca* 516 nm, and that of MAPbBr₃ is *ca* 532 nm. For reference, fluorescein was used because MAPbBr₃ emission maximum lies within the

fluorescein emission. According to the literature, the QY of the fluorescein is 0.79 in ethanol. The relative QY of MAPbBr₃ is calculated by

$$QY = QY_{ref.} \times \frac{A_{ref}}{A_{PNC}} \times \frac{E_{PNC}}{E_{ref}} \times \frac{\eta_{PNC}^2}{\eta_{ref}^2}$$
(4.1)



Figure 4.11. PLQY estimation. (a) Emission spectra of fluorescein and MAPbBr₃ PQDs. (b,c) Linear fit for absorbance to integrated emission area in (b) fluorescein and (b) MAPbBr₃ PQDs.

$$QY = QY_{ref.} \times \frac{b_{PNC}}{b_{ref}} \times \frac{\eta_{PNC}^2}{\eta_{ref}^2}$$
(4.2)

Here, *A* is the absorbance, *E* is the integrated area of the emission, η is the refractive index of the solvent, *b* is the slope of the fitting equation (y=a+bx), and *ref.* denotes the reference. I recorded absorbance and PL of fluorescein and MAPbBr₃ PQDs at various dilutions and plotted *A* vs. *E*, as shown in Figure 4.11b, c, respectively. The PLQY of the MAPbBr₃ PQD calculated from the above equations (4.1 and 4.2) is 0.35, and that of MABr treated MAPbBr₃ PQD is 0.98.

Similarly, I calculated the PLQY of fresh MAPbI₃ PQD with reference to AlexaFluor700 Figure 4.12. The PL maxima of the AlexaFluor700 is *ca* 714 nm and the PLQY is 0.25 in phosphate-buffer saline solution. As the sample lies in the near-infrared region, the relative PLQY was calculated after applying the correction to the quantum efficiency of the detector in the 650 to 800 nm region. The relative PLQY of MAPbI₃ PQD is estimated at 0.23, and that of MAI treated MAPbI₃ PQD is 0.48. Thus, the filling of halides in the PQDs leads to the enhancement of the PL.



Figure 4.12. PLQY estimation. (a) Emission spectra of AlexaFluor 700 and MAPbI₃ PNCs. (b,c) Linear fit for absorbance to integrated emission area in (b) AlexaFluor 700 and (b) MAPbI₃ PQDs.

To verify it further, the relationship among halide vacancy filling, PL blinking, and the charge carrier dynamics before and after the treatment of MAPbX₃ PQDs, the PL decay profiles are recorded. The samples were prepared by drop-casting the MAPbX₃ PQD suspended in toluene on glass-coverslips. First, the PL decay profiles were recorded for the pristine PQD sample, then the 10 mM MAX solution (in DCM) was dropped on the MAPbX₃-coated glass coverslips (Figure 4.13). Again, the PL decay profiles of the treated area were recorded. The excitation intensity for recording the PL lifetime of MAPbBr₃ PQD samples was 3.5 mW cm⁻², and for MAPbI₃ PQD samples was 9 mW cm⁻². Similar to chalcogenide QDs, the perovskite also shows multiphase decay dynamics.^{35,37} Therefore, I fitted the PL decay profile with a fourth order exponential decay equation and calculated



Figure 4.13. PL decay profiles of ensembled-averaged (a) MAPbBr₃ PQDs and (b) MAPbI₃ PQDs before (i) and after (ii) the treatment with MABr and MAI, respectively.

the average PL lifetime (Chapter 2, section 2.2.5, equation 2.2 and 2.3). The average PL lifetime of ensemble-averaged MAPbBr₃ PQDs increased from 11.5 to 23 ns after treating with MABr solution (Figure 4.13a). And the average PL lifetime of ensemble-averaged MAPbI₃ PQD increased from 27 to 65 ns after treating with MAI solution (Figure 4.13b). The dynamics of emissive and nonemissive states can be convoluted by the fitting of the decay profiles. Here, the PQDs showed fast decay in the starting few ns, which associates with nonemissive states. This fast decay was suppressed after the treatment with MAX. However, the long decay, which associates with an emissive state, remains similar before and after the treatment.

For estimating the rates of nonradiative recombination through halide-vacancies, the relative PL intensities and the average PL lifetimes before and after the treatment of MAPbX₃ PQDs were considered. In the case of MAPbI₃ PQDs, an increase by 2.1 fold in relative PL intensities and 2.4 fold increase in average PL lifetime were observed. The PL lifetime (τ_0) for the pristine MAPbI₃ PQDs can be written as,

$$\tau_0 = \frac{1}{(k_r + k_{nr_1} + k_{nr_2}) + k_{nr_{l_v}}}$$
(4.3)

here, k_r is the rate of radiative recombination, k_{nr_1} and k_{nr_2} are the rates of nonradiative recombination through the states other than iodide vacancies, and k_{nrl_v} is the rate of nonradiative recombination through the iodide vacancies. The PL lifetime (τ) of MAPbI₃ treated with MAI can be written as

$$\tau = \frac{1}{(k_r + k_{nr_1} + k_{nr_2})} \tag{4.4}$$

Thus, by combining equations 4.3 and 4.4,

$$\frac{\tau}{\tau_0} = \frac{(k_r + k_{nr_1} + k_{nr_2}) + k_{nrl_v}}{(k_r + k_{nr_1} + k_{nr_2})}$$
(4.5)

By putting τ as 27 ns and τ_0 as 65 ns, I calculated the k_{nrl_n} at 1.54×10⁷ s⁻¹.

Similarly, I calculated the rate of nonradiative recombination through bromide vacancies (k_{nrBr_v}) in the case of MAPbBr₃ PQDs. I observed a 2.8 fold increase in relative PL intensities and a 2.0 fold increase in average PL lifetime. Therefore, by putting τ as 11.5 ns and τ_0 as 23 ns, I calculated the k_{nrBr_v} at 4.35×10^7 s⁻¹. The >10⁷ s⁻¹ rate is minimal as

per the standard nonradiative recombination, which is $>10^9$ s⁻¹. Thus, it was necessary to consider the fast component of isolated single PQDs.

For analyzing the PL lifetime of isolated MAPbX₃ PQDs, the PQDs were diluted in toluene and drop-casted on a glass coverslip. In this experiment, I consider only 5-10 isolated single-particles under the field of view. The MAPbX₃ PQDs were irradiated with 460 nm cw laser, and the PL decays were recorded before and after MAX treatment using a time-correlated single-photon counting system. The instrumentation of the time-correlated single-photon counting system is detailed in Chapter-2, section 2.2.5. The PL decays were fitted similarly, using the fourth order exponential equation. The PL decay profiles of isolated MAPbBr₃ and MAPbI₃ PQDs before and after MABr and MAI treatment are shown in Figure 4.14. Here, the initial rapid decay of PQDs was suppressed



Figure 4.14. PL decay profiles of (a) MAPbBr₃ PQDs and (b) MAPbI₃ PQDs before (i) and after (ii) the treatment with MABr and MAI, respectively.

after the treatment, which results in the decrease of deep traps and the fast nonradiative relaxation associated with halide vacancies. In the case of MAPbBr₃ PQDs, the fast component increased from 2.5 to 3.2 ns after MABr treatment (Figure 4.14a), and in the case of MAPbI₃ PQDs, it increased from 0.26 to 0.51 ns after the MAI treatment (Figure 4.14b). While considering the lifetime of fast component, I estimated the rate of nonradiative recombination through halide vacancies from equations 4.3 to 4.5 at 1×10^8 s⁻¹ for MAPbBr₃ and 1.9×10^9 s⁻¹ for MAPbI₃ PQDs. These high rates indicate the fast nonradiative recombination of excitons is mainly by the halide vacancies. Hence, the halide vacancies act as quenchers for PL intensity and lifetime in MAPbX₃ PQDs, and they are responsible for the PL blinking in PQDs.

4.2.4 The Mechanism of Photoluminescence Blinking

In Figure 4.15, I schematically represented the effect of halide-vacancy filling with the PL blinking suppression, increases in PL intensity, and PL lifetimes of MAPbX₃ PQDs. Figure 4.15a shows the filling of halide vacancies in pristine PQD. Figure 4.15b shows the mechanism of type-A and type-B blinking in pristine PQD and treated PQDs, respectively. If deep electron and hole traps are present in the energy levels of PQD, the positive or negative trions can generate [Figure 4.15b(i)]. In type-A blinking, charging-discharging of these photogenerated trions is responsible for the fast Auger nonradiative recombination. The deep traps correspond to the halide vacancies in the as-synthesized PQDs electronic levels.^{10,33,50–52} And the fast Auger nonradiative recombination decreases the PL intensity and the PL lifetime of the PQDs. When the MAPbX₃ PQDs were treated with MAX, it helped in filling the deep-traps related to halide vacancies [Figure 4.15b(ii)]. Hence, it changed the power-law behavior from truncated (type-A) to linear (type-B), analyzed from



Figure 4.15. (a) Schematic representation of the filling of halide vacancies in PQD and (b) the corresponding change in the models of PL blinking mechanism in (i) type-A and (ii) type-B.

the probability distribution of ON-and OFF- times. In type-B blinking, trapping and detrapping of shallow or band-edge trap states are responsible for the nonradiative recombination of photogenerated excitons.

4.3 Conclusion

In summary, I studied the role of halide vacancies in the photoluminescence properties and the charge carrier dynamics of the MAPbX₃ perovskite quantum dots at the single-particle and the ensemble level. When the lead halide perovskite interacts with light and air, it oxidizes and reacts with environmental oxygen to generate superoxide. This superoxide occupies the halide vacancies present in the lead halide perovskite and degrades the nanocrystals. Therefore, in this chapter, I aimed to fill the halide vacancies and prevent superoxide generation under air atmosphere. For this, I chose MAX salts for increasing the halide ions concentration in the perovskite quantum dots. I demonstrated the role of halide vacancies before and after the addition of MABr (and MAI) on MAPbBr₃ (and MAPbI₃) perovskite quantum dots. I synthesized MAPbBr₃ and MAPbI₃ with a size of ~10.6 and ~8.5 nm, respectively, using the ligand-assisted reprecipitation method. MAPbBr₃ and MAPbI₃ both showed narrow and single emission maximum ca 530 and 750 nm. These perovskite quantum dots showed photoluminescence blinking when photoexcited with distinct ON(radiative)- and OFF(nonradiative)-times. The blinking varies from particle to particle independent of excitation intensity. Some perovskite quantum dots showed strong photon-antibunching verifying the emission from a single-emitting particle, whereas some showed multiphoton emission. Therefore, I checked the post-synthesis filling of halide ions on the same perovskite quantum dot before and after the halide salt treatment. I suppressed the photoluminescence blinking at real-time addition of halide ions in MAPbX₃ perovskite quantum dots. After the treatment with MAX, the duration of ON-events increased compared to before the treatment. This promotes the increase in photoluminescence and the reduction of halide-vacancy-assisted nonradiative recombination. After analyzing more than 200 single-particles of MAPbI₃, I constructed the probability distribution of ON-and OFF-times, which showed the change in blinking mechanisms from type-A to type-B after the treatment, suggesting decreased deep-traps. In other words, the dominance of chargingdischarging of photogenerated excitons in MAPbI₃ perovskite quantum dots changed by the trapping-detrapping of excitons after the treatment. I also verified the

photoluminescence behavior of MAPbX₃ before and after the filling of halide vacancies at ensemble-level experiments. MAPbBr3 and MAPbI3 perovskite quantum dots showed an increase of 2.8- and 2.1-fold in the photoluminescence intensities after the treatment. From the SEM-EDX data, I estimated that the halide vacancy concentration in the perovskite quantum dots is ca 4%. I examined the photoluminescence decay profiles of the ensemble of single MAPbBr₃ and MAPbI₃ perovskite quantum dots before and after the treatment and observed the increase in photoluminescence lifetime with the filling of halide vacancies suggesting the decrease in the suppression of nonradiative relaxation pathways. With the help of the average lifetimes of MAPbX₃ perovskite quantum dots, I calculated the halidevacancy-assisted nonradiative recombination rates at 1×10⁸ s⁻¹ for MAPbBr₃ and 1.9×10⁹ s⁻¹ for MAPbI₃ perovskite quantum dots. Thus, I demonstrated the real-time suppression of PL blinking with the suppression of halide-vacancy-assisted nonradiative recombination and increases in photoluminescence lifetime and intensity in MAPbX₃ perovskite quantum dots by filling the halide vacancies. In lead halide perovskites, the blinking changes from type-A to type-B by filling up deep-traps related to halide vacancies, but cation vacancies are yet to consider for better photoluminescence efficiencies and more extended stability.

4.4 References

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Chapter 5

The Roles of A-Site and B-Site Cations on Photoluminescence Properties

Abstract

Halide perovskites offer efficient light-harvesting and light-emitting applications due to their unique optical and electronic properties. However, these perovskites are susceptible to moisture, water, oxygen, and light. The halide perovskite consists of many intrinsic defects, such as interstitials, antisites, and ionic vacancies. These defects form shallow or deep traps in the bandgap, causing nonradiative carrier/exciton recombination and inducing photoluminescence blinking. In this chapter, I explicitly analyze the role of cation vacancies-assisted defects in caesium lead bromide (CsPbBr₃) perovskite quantum dots. For filling the Cs⁺ or Pb²⁺ vacancies, I supplemented the quantum dots with caesium oleate or lead oleate. The quantum dot photoluminescence intensity decreases upon treating it with a vacancy filling agent, with or without photoirradiation. Although caesium oleate slightly suppresses quantum dot photodegradation, lead oleate does not affect photoluminescence. Further, I examined the photoluminescence decay profiles of CsPbBr₃ perovskite quantum dots. I observed that caesium oleate or lead oleate does not change the photogenerated charge carrier's average lifetime. Also, I recorded the single-particle photoluminescence intensity trajectories of CsPbBr3 with and without caesium oleate and lead oleate. By analyzing >200 single-particle photoluminescence intensity trajectories, I find that type-A blinking dominates in CsPbBr3 quantum dots regardless of the cation vacancies filling. Therefore, the Cs^+ or Pb^{2+} traps have a negligible effect on the photoluminescence blinking and charge carrier properties of the CsPbBr₃ quantum dots.

5.1 Introduction

Lead halide perovskites emerge into next-generation semiconductor materials for realworld application to photovoltaic and electrooptic devices such as solar cells, LEDs, and lasers.^{1–10} This class of materials shows a long charge carrier diffusion length, high carrier mobility, high absorption cross-section, a wide range of emission wavelength on par with chalcogenide quantum dots.^{11–15} Additionally, lead halide perovskites are defect tolerant.^{16–} ¹⁸ Through thermodynamic modeling, Kang *et al.* demonstrated high photoluminescence (PL) quantum yield (QY) for CsPbBr₃ perovskites without any electronic passivation. Most of their intrinsic defects have shallow transition levels, which require low formation energies.^{16,17} However, some intrinsic or point defects, such as interstitials and antisites of anions and cations, have high defect formation energies.^{16,17,19,20} Thus, suppressions of such defects are necessary for achieving long-term stability goals.

In lead halide perovskites, the most crucial passivation is to reduce the deep traps formed by the halide vacancies. In Chapter-4, I investigated the nonradiative relaxation and PL blinking of perovskites quantum dots (PQDs) before and after filling the halide vacancies with halide salts.²¹ In PQDs and perovskite nanocrystals (PNCs), the removal of surface ligands during purification can create undercoordinated halide ions or cations, which act as surface traps. Furthermore, the vacancies of A- and B-site cations, their interstitials, and antisites inside the crystal lead to trap formation. These trap states are responsible for nonradiative relaxation, lowering the device efficiencies. A-site cations lie in the center of the four $[BX_6]^-$ octahedra.^{22,23} Although an A-site cation doesn't contribute to the valence band maximum (VBM) or conduction band minimum (CBM), it stabilizes the octahedral geometry of the perovskite structure. The size of the cation maintains the Pb-X-Pb dihedral angle as well as the octahedral tilt. For instance, Cs⁺ cation, which is smaller than formamidinium cation (FA⁺), leads to a sizeable octahedral tilt by lowering the Pb-X-Pb angle to ~153° from the ideal 180°.^{23,24} Further, the octahedral tilt induces spin-orbit coupling and affects halide perovskites' charge carrier dynamics. Hence, the spin-orbit coupling increases with a decrease in the A-site cation size, reducing the perovskite bandgap. To improve the charge carrier mobility and stabilize the halide perovskites, filling the ionic vacancies is necessary. For instance, Ling et al. demonstrated the surface passivation of CsPbI₃ PQDs films with caesium acetate to enhance the electronic coupling and reduce the trap-assisted nonradiative recombination. The surface passivation stabilized the PQDs from moisture and improved the stability in the ambient atmosphere.²⁵ Another study by Guo *et al.* on the surface passivation of a mixed-cation mixed-halide perovskite through caesium oleate (CsOL), the device performance of the perovskite was improved.²⁶ Thus, the PL efficiency of halide perovskites enhances by reducing the A-site cation vacancy. Although several groups investigated the PL blinking of CsPbX₃ (X=Br, I) PNCs and QDs, ^{27–33} a relation between PL blinking and A-site cation is yet to be identified.

Besides A-site cations, B-site cation vacancies also form defects in the energy levels of the halide perovskites. In the lead halide perovskite structure, the B-site cation is octahedrally coordinated with halide ions. The *6s* and *6p*- orbitals of lead contribute to the VBM and CBM of perovskites by hybridizing with the halide *p*-orbitals.^{22,23,34} Vogel *et al.* explained that a Pb²⁺ vacancy creates an unoccupied state near the VBM. This defect causes fast nonradiative relaxation, decreasing the PL quantum yield of perovskite.²⁰ Filling of lead vacancies deep in a crystal is challenging. Thus, many researchers focused on the surface vacancy passivation by chemically bonding lead with the uncoordinated bonds or dangling bonds. Huang and coworkers passivated the uncoordinated lead centers using lead oxysalts such as PbSO₄ and Pb₃(PO)₄.³⁵ This passivation decreased the defect density and enhanced the radiative recombination rate. The lead oxysalts formed a layer on the perovskite surface by chemically bonding with the uncoordinated halide ions. This layer helped in reducing the detrimental factors of moisture and water. Although most of the studies are on surface defect passivation at the ensemble level, the role of B-site cation vacancy-assisted degradation is still unknown at the single-particle level.

This chapter demonstrates the roles of A-site and B-site cations on the PL of CsPbBr₃ PQDs. I examined the PL properties of PQDs at the single-particle and the ensemble levels with or without CsOL or lead oleate [Pb(OL)₂]. These compounds helped me understand the role of A- or B-site trap-assisted recombination of photogenerated charge carriers in the PQDs. Firstly, I examined the PL intensities and lifetimes of CsPbBr₃ PQDs before/after adding CsOL or Pb(OL)₂. I observed additional Pb-cations quickly degrade the PQDs, whereas additional Cs-cations slightly enhance the PL intensity. Further, I recorded the single-particle PL intensity trajectories of the PQDs before and after the addition of CsOL or Pb(OL)₂. Also, I analyzed >200 PL intensity trajectories for obtaining the ON- and OFF-time probability distributions.

5.2 **Results and Discussion**

5.2.1 Characterization of CsPbBr₃ Perovskite Quantum Dots

I synthesized CsPbBr₃ PQDs by the hot-injection method.^{9,36} In this synthesis, a hot solution of caesium acetate in hexadecane was injected into a solution of PbBr₂ in a mixture of oleic acid and hexadecyl amine at 120 °C. The details of the CsPbBr₃ PQDs, CsOL, and Pb(OL)₂ syntheses and purification are given in Chapter 2. I synthesized CsOL and Pb(OL)₂ according to literature methods for passivating the cation vacancies.^{37,38} As shown in Figure 5.1a, a suspension of CsPbBr₃ PQDs in toluene showed the characteristic band-edge absorption and narrow emission bands. For single-particle studies, samples were prepared by drop-casting a dilute solution of CsPbBr₃ PQDs on a glass coverslip and dragged with a lens cleaning paper. Through this process, I was able to control the density of PQDs in the field of view from ~10 to 15 single PQDs in a 50×50 μ m² frame, as shown in Figure 5.1b.



Figure 5.1. Characteristics of CsPbBr₃ PQDs. (a) Absorption and emission spectra (b) Single-particle image of isolate CsPbBr₃ PQDs photoexcited with a 460 nm cw laser (1.5 W cm⁻², scale: 10μ m). Inset: photographs of a CsPbBr₃ PQD sample under the visible and UV lights.

5.2.2 Vacancy Filling Using CsOL and Pb(OL)₂

Halide perovskites are susceptible to moisture, oxygen, and light. Mulvaney and coworkers reported that PQDs undergo irreversible decomposition in a moist environment due to

oxygen and water reaction.³⁰ This decomposition of PQDs further accelerates when photoirradiated. Therefore, to understand the stability of CsPbBr₃ PQDs, I recorded the PL intensities of a toluene saturated PQD solution with or without photo-irradiation (Figure 5.2). The PL intensity of a CsPbBr₃ PQD solution showed a decrease of 29% PL intensity during 30 min (Figure 5.2a). A PQD solution was photo-irradiated, and the PL intensity was re-recorded after every 1 min irradiation. The solution's PL intensity was decreased by 88% (Figure 5.2b), which suggests the degradation of the photoexcited PQDs due to reaction with moisture and oxygen.



Figure 5.2. Relative PL intensities of solutions of (i) CsPbBr₃ PQDs, (ii) CsPbBr₃ PQDs with CsOL and (iii) CsPbBr₃ PQDs with Pb(OL)₂ (a) without and (b) with photoirradiation by a 430 nm cw laser (100 mW cm⁻²).

To understand the roles of A- and B-site cations on the degradation of PQDs, I treated a PQD sample with CsOL or Pb(OL)₂. Here, a 0.1 mM CsOL or 10 nM Pb(OL)₂ solution was added to a PQD sample, and the PL intensity was recorded with or without photoirradiation. The PL intensities of the PQD solution supplemented with CsOL were decreased by 28% without and 69% with photo-irradiation. Similarly, the PL intensities of the PQD solution supplemented with Pb(OL)₂ were decreased by 37% without and 81% with photo-irradiation. By comparing these two results, I assume that CsOL decelerates the degradation of photoexcited CsPbBr₃ PQD. This deceleration is attributed to photoinduced passivation of the surface Cs⁺ vacancies and stabilization of the peripheral [PbBr₆]⁻ octahedra in the PQD. In contrast, the continuous PL intensity decrease with Pb(OL)₂, which is like untreated PQDs, suggests that Pb²⁺ ions cannot passivate any Pb²⁺ vacancy within the octahedra.

The degradation of the PQD solution was likely enhanced by the moisture and oxygen content of the solvent itself.³⁹⁻⁴¹ Hence, to examine the effect of moisture and oxygen, I recorded the PL intensities of CsPbBr₃ PQD films with or without CsOL or Pb(OL)₂ (Figure 5.3a). For this measurement, CsPbBr₃ PQD films were prepared by drop-casting of PQD solutions on glass coverslips and dried. The PL intensities of PQD films with or without CsOL or Pb(OL)₂ were recorded every 2 min. Relative PL intensities of the film samples are shown in Figure 5.3. Unlike the sample solutions discussed above, a film with or without the passivating agents showed stable PL intensity. Although the PL intensity was decreased by 8% for the pristine PQD film or a film treated with the 10 nM Pb(OL)₂ solution and dried, interestingly, the PL intensity of a PQD film treated with the 0.1 mM CsOL solution and dried was increased to 122% over 30 min photo-irradiation. This increase could be due to the surface Cs⁺ vacancy passivation of PQDs by Cs⁺. This result also suggests that the decrease in the PL intensity of a PQD solution (Figure 5.2) is due to the effect of moisture and oxygen. Mathews and coworkers reported that the passivation of halide perovskite through Cs⁺ prevents the formation of low-dimension perovskite structures (from 3D or 2D to 1D or 0D) when the Cs⁺ diffuses inside the cuboctahedral vacancies.²⁶



Figure 5.3. Relative PL intensities of the film samples of (i) CsPbBr₃ PQDs, (ii) CsPbBr₃ PQDs with CsOL, and (iii) CsPbBr₃ PQDs with Pb(OL)₂ (a) without and (b) with photoirradiation by a 430 nm cw laser (100 mW cm⁻²).

Also, I investigated the effect of photo-irradiation on the PL stability of CsPbBr₃ PQD films with or without CsOL or Pb(OL)₂. The film samples of PQDs were prepared as explained above. A PQD film was irradiated with a 430 nm cw laser, and the PL intensity was recorded every 2 min. The PL intensity of a pristine CsPbBr₃ PQD film was decreased by 22% over 60 min (Figure 5.3b), which was 36% for a film treated with a Pb(OL)₂ solution. The reductions in the PL intensities suggest partial degradation of the PQDs by heterogeneous moisture and oxygen actions. Conversely, the CsOL treated PQD film showed a 5% increase in the PL intensity over 60 min. As explained by Hao *et al.*, oxygen molecules can form a strong bond with the surface lead atoms and form lead oxide. This lead oxide further makes the perovskite more vulnerable to humidity.⁴² Therefore, Pb(OL)₂ addition has a diverse effect on the PQDs.

To further understand the charge carrier dynamics of CsPbBr₃ with and without the addition of CsOL and Pb(OL)₂, I recorded the PL decay profiles, as shown in Figure 5.4. For this, a thin film of CsPbBr₃ PQD was prepared on a glass coverslip ($18 \times 18 \text{ mm}^2$) by dropping a PQD solution in toluene and drying under the ambient atmosphere. First, the PL decay of a pristine CsPbBr₃ PQD film was recorded. Then, 0.1 mM CsOL was dropped on the glass coverslip, and the solvent was dried. The PL decay of this sample was recorded and compared with the pristine sample. Similarly, the PL decays of another PQD film on a glass coverslip before and after the treatment with a 100 nM Pb(OL)₂ solution was examined. The intensity averaged PL lifetimes calculated by the equation ($\Sigma \tau_i A_i / \Sigma A_i$) show 8.2±0.3 ns for pristine CsPbBr₃ PQDs, 9.7±0.6 ns for CsOL treated PQDs, and 8.8±0.04 ns for Pb(OL)₂ treated PQDs. These lifetime values suggest that CsOL or Pb(OL)₂ does not significantly impact the carrier recombination rates in the PQDs.



Figure 5.4. PL decay profiles of CsPbBr₃ PQDs with or without CsOL or Pb(OL)₂. The samples were excited by a 470 nm LED.

5.2.3 The Roles of CsOL and Pb(OL)₂ on Photoluminescence Blinking

To understand the cation-vacancies assisted degradation of PQDs at the single-particle level, I investigated PL blinking of single CsPbBr₃ PQDs with or without supplementing the complementary cation salts. For recording PL intensity trajectories of CsPbBr₃ PQDs, a dilute PQD solution was drop-casted on a glass coverslip and dragged using lens cleaning paper. A PL image of CsPbBr₃ PQDs isolated in a single particle sample, photoexcited with a 460 nm cw laser, and recorded using an EMCCD camera resembles Figure 5.1b. Figure 5.5 a(i) and b(i) show representative PL intensity trajectories of single CsPbBr₃ PQDs. Similar to MAPbX₃ PQDs in Chapter 4, the CsPbBr₃ PQDs show two extreme PL blinking behaviors in the same field of view: those with intense blinking showing short ON-OFF events [Figure 5.5 a(i)], and those with long ON-events [Figure 5.5 b(i)]. The corresponding PL intensity histograms are shown in Figure 5.5 a(ii) and Figure 5.5 b(ii). Here, the occurrence of ON events is more than the OFF events. Such PL intensity distributions show that the PL blinking differs from particle to particle.



Figure 5.5. Single-particle PL intensity trajectories of CsPbBr₃ PQDs with [a(i)] a highand [b(i)] low-frequency blinking behavior under photo-excitation with a 460 nm cw laser (1.5 W cm⁻²). [a(ii) and b(ii)] The corresponding occurrences of PL intensities.

For A-site cation vacancy filling, first, I used the 0.1 mM CsOL solution in toluene. The solution of CsOL was drop-casted on a glass coverslip to distribute it on single CsPbBr₃ PQDs uniformly, and the single-particle PL images and trajectories were recorded. The PL



Figure 5.6. Single-particle PL intensity trajectories of CsPbBr₃ PQDs after adding 0.1 mM CsOL with [a(i)] high- and [b(i)] low- frequency blinking behavior when photoexcited with 460 nm cw laser (1.5 W cm⁻²). [a(ii) and b(ii)] The corresponding occurrences of PL intensity.

intensity trajectories of the PQDs treated with CsOL are shown in Figure 5.6 a(i), and b(i). Similar to pristine CsPbBr₃ PQDs, the CsOL-treated PQDs showed two extreme blinking behaviors. Therefore, to understand the role of Cs⁺ cation in CsPbBr₃ PQDs at the singleparticle level, I examined the ON- and OFF-time probability distributions. Here, I analyzed the blinking trajectories of over 200 CsPbBr₃ single PQDs with or without the CsOL treatment, and the threshold intensity for the ON- and OFF-time probability was determined (Figure 5.5 and 5.6). ON- and OFF-events occurrences are shown in Figure 5.7 before and after the treatment with CsOL in CsPbBr₃ PQDs. These occurrences were further converted to the probability distribution of ON and OFF-times by using the power-law equation. For CsPbBr₃ PQDs, the ON and OFF-time probability distributions (Figure 5.8) follow a truncated power-law behavior before and after CsOL addition; (Chapter 1, Section 1.2.2, equation 1.5), $P(\tau) = A_0 \tau^{-\alpha} e^{-\frac{\tau}{\tau_c}}$. The truncated power-law is the signature of the type-A blinking due to the charging and discharging of the POD. After the treatment with CsOL, the truncation time (τ_c) increased from 2 to 3 s. As the ON-truncation time increased, the OFF- truncation time decreased from 0.6 to 0.4 s. The truncation time denotes the average time the particles took for switching from the ON-to-OFF or the OFF-to-ON states. In other words, it determines the time of charging and discharging of the particles. Therefore, on

average, a minimal effect of the Cs⁺ cation passivation in CsPbBr₃ PQDs is observed in the single-particle experiments.



Figure 5.7. The occurrence histogram of (a,c) ON- and (b,d) OFF- times of CsPbBr₃ PQDs before (a,b) and after (c,d) the CsOL treatment.

Conversely, to understand the role of B-site cation vacancies on the PL blinking, I used 1 nM Pb(OL)₂ for filling the vacancies in CsPbBr₃ PQDs. The sample for Pb²⁺ cation filling is prepared by following the method for CsOL. A solution of Pb(OL)₂ was dropped on the glass coverslip coated with CsPbBr₃ PQDs, and the single-particle PL behavior was recorded. The PL intensity trajectories of PQDs treated with Pb(OL)₂ are shown in Figure 5.9 a(ii), b(ii). Photodegradation of several PQDs was enhanced after Pb(OL)₂ addition, and the PL intensity was decreased due to two reasons: (i) the formation of PbO on the surface of PQDs, and (ii) the inability of the large Pb²⁺ ions to passivate the perovskite lattice.



Figure 5.8. The probability distributions of (a,c) ON- and (b,d) OFF- time of CsPbBr₃ PQDs before (a,b) and after (c,d) the CsOL treatment.



Figure 5.9. Single-particle PL intensity trajectories of CsPbBr₃ PQDs after adding 1 nM Pb(OL)₂. Trajectories with [a(i)] high- and [b(i)] low-frequency blinking when photoexcited with a 460 nm cw laser (1.5 W cm⁻²). [a(ii) and b(ii)] The corresponding occurrences of PL intensity.

To reduce the adverse effect of Pb-ions on lead halide perovskite, I synthesized leadfree Cs₃Bi₂I₉ PNCs through the hot-injection method.⁴³ I used CsOL and BiI₃ as the precursors and oleic acid and oleylamine as the ligands in this synthesis. However, the photoluminescence intensity of Cs₃Bi₂I₉ PNCs was extremely low. Therefore, the photostability of Cs₃Bi₂I₉ PNCs was challenging to analyze at the single PQD level. The poor PL intensity is attributed to many defects and an increased rate of nonradiative carrier/exciton recombination. Thus, to date, compared to lead halide perovskites, the leadfree perovskites are not promising for light-harvesting and light-emitting applications.⁴⁴

5.2.4 The Mechanism of Vacancy Filling

In Figure 5.10, I schematically represented the effect of excess Cs⁺ ion on CsPbBr₃ PQDs. In lead halide perovskites, A-site cations don't contribute to the VBM or CBM. However, their vacancies form shallow defects near the VBM in the energy states of the perovskites. Guo *et al.* explained that CsOL passivates the interfacial defects and vacancies in a CsPbBr₃ perovskite film. And the oleate group reacts with the uncoordinated lead ions to make the perovskite hydrophobic.²⁶ Therefore, for filling the A-site vacancies, CsOL was added to CsPbBr₃ PQDs. At the ensemble and single-particle experiments, I observed a slight increase in the PL intensity and the truncation of the ON-time probability distribution. Hence, I assume that Cs⁺ ions from CsOL occupy the surface A-site vacancies of the perovskites.



Figure 5.10. A scheme of the surface Cs⁺ ion vacancy filling in a CsPbBr₃ PQD.

5.3 Conclusion

I studied the role of A-site and B-site cations in CsPbBr₃ perovskite quantum dot at the ensemble and single-particle levels. This quantum dot contains defects such as cation and anion vacancies, interstitials, and antisites, which cause nonradiative relaxations, photoluminescence blinking, and degradation of the perovskite. I used caesium oleate and lead oleate to prevent perovskite degradation by filling the Cs⁺ and Pb²⁺ vacancies. I synthesized the quantum dot by the hot-injection method. This quantum dot showed an excitonic band ca 500 nm and a narrow emission band ca 520 nm. Two types of photoluminescence blinking with bright (ON) and dark (OFF) states were observed when the quantum dots were excited with a high-intensity laser. I observed frequently switching ON and OFF events in one type of blinking, whereas the second type was dominated by long ON events. Next, I examined the time-dependent photoluminescence with or without photoirradiation to understand the quantum dot's stability. I observed a rapid decrease in the photoluminescence intensity when the quantum dot was photo-irradiated. Then, I studied the photoluminescence behavior with the addition of caesium oleate or lead oleate. Although the photoluminescence intensity of a quantum dot sample supplemented with caesium oleate increased, lead oleate showed the opposite effect.

To further correlate the cation vacancies with the rates of exciton/carrier relaxation, I calculated the average photoluminescence lifetime of the quantum dot samples with or without the addition of Cs^+ or Pb^{2+} . Also, I recorded the photoluminescence intensity trajectories of single quantum dots with or without the addition of Cs^+ or Pb^{2+} . Similar to pristine quantum dots, the caesium oleate or lead oleate treated ones showed photoluminescence blinking. I analyzed more than 200 single quantum dots with or without caesium oleate and fitted the ON- and OFF-time probability distribution to the truncated power-law. Both the pristine and the treated quantum dots showed type-A blinking due to charging and discharging. Nevertheless, the caesium oleate-treated quantum dots showed a slight increase in the truncation ON-time, whereas the truncation OFF-time was decreased. Therefore, I assume that the caesium oleate passivated the surface Cs^+ vacancies.

5.4 References

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Summary and Perspectives

In summary, I have studied the photoluminescence and charge carrier dynamics of lead halide perovskite nanocrystals and quantum dots at the single-particle and ensemble levels. This thesis was mainly focused on the single-particle photoluminescence blinking of the lead halide perovskites. I examined the charge carrier recombination pathways in perovskite nanocrystals and quantum dots by analyzing the photoluminescence decay profiles and single-particle photoluminescence intensity trajectories. The experiments were carried out in various atmospheric conditions to stabilize the perovskite nanocrystals and quantum dots. Further, I passivated their defect states to enhance the photoluminescence quantum yields and suppress the photoluminescence blinking.

I synthesized the APbX₃ (A=MA, Cs; X=Br, I) perovskite nanocrystals and quantum dots using the ligand-assisted reprecipitation and hot-injection methods. I estimated the perovskite crystal's size and shape by using TEM and powder-XRD. Also, I examined the excitation and emission properties of the perovskite nanocrystals and quantum dots through the absorption and fluorescence spectroscopic techniques. For studying the charge carrier dynamics, I used time-resolved fluorescence spectroscopy and time-correlated single-photon counting setups. For analyzing the blinking of the nanocrystals and quantum dots, I used a single-particle microspectroscopy system equipped with an EMCCD camera.

The foremost aim of this study was to stabilize and enhance the photoluminescence intensity of the lead halide perovskite nanocrystals and quantum dots. Lead halide perovskites have several intrinsic defects, and one of such defects is the halide vacancies. Superoxide is generated at the halide vacancies by an electron transfer from the perovskite to oxygen. Superoxide disintegrates the perovskite structure and lowers the photoluminescence quantum efficiency. To understand the role of oxygen, I examined the PL of the perovskite nanocrystals in air, argon, or a polymer environment. In air, the photoluminescence intensity of the perovskite nanocrystals and quantum dots continuously decreased, whereas, in the argon or a polymer atmosphere, it was stable for a long duration. Some photoluminescence intensity trajectories in air showed long OFF-events. In the ONstate, the photoluminescence intensity continuously decreased, while in the OFF-state, it was steady. The photoluminescence intensity was recovered after turning ON from the dark state. This suggested that under an OFF-event, the superoxide is not reacting with
perovskite. Further, from the photoluminescence decay profiles, I estimated that the rate of nonradiative relaxation is higher than the rate of electron transfer to oxygen. Hence, I concluded that the perovskite nanocrystals and quantum dots were not oxidized or reacted with superoxide under the ionized state because superoxide was not produced as the nonradiative recombination dominates over the electron transfer to oxygen.

To enhance the photoluminescence intensity and suppress the blinking, it is inevitable to fill the halide vacancies. For this purpose, I used halide salts to fill the vacancies in the perovskite quantum dots. I examined the suppression of photoluminescence blinking in the real-time treatment with halide salts. Further, the treatment helped to increase the photoluminescence quantum yield and to decrease the halide-vacancy-assisted nonradiative recombination. The blinking mechanism was changed from the type-A to the type-B blinking, which means the change from charging-discharging to trapping-detrapping of charge carriers. Hence, the halide salts successfully filled the halide vacancies in the perovskite quantum dots. Similar to the halide vacancy filling, I supplemented the perovskite quantum dots with excess cations to fill any A- and B-site cation vacancies. I found that the cation vacancies have minimal effect on the charge carrier dynamics of the perovskite quantum dots. Nevertheless, the lead halide perovskites are becoming cost-effective and efficient materials for optical and electronic devices. The passivations of halide vacancies and surface defects improve the optoelectronic properties and the stability of halide perovskite for durable technologies.

Publications and Patent

Peer-Reviewed Articles

- State of the Art and Prospects of Halide Perovskite Nanocrystals Polavarapu, L.; Rogach, A.; Hofkens, J.; Biju, V.; <u>Chouhan, L.</u>; *et al.* ACS Nano 2021 (Submitted).
- 2. Real-Time Blinking Suppression of Perovskite Quantum Dots by Halide Vacancy Filling

<u>Chouhan, L.;</u> Ito, S.; Thomas, E. M.; Ghimire, S.; Miyasaka, H.; Biju, V. *ACS Nano* **2021**, *15*, 2831–2838.

- 3. Synthesis, Optoelectronic Properties and Applications of Halide Perovskites <u>Chouhan, L.</u>; Ghimire, S.; Subrahmanyam, C.; Miyasaka, T.; Biju, V. *Chem. Soc. Rev.* 2020, *49*, 2869–2885. (Featured on the cover page).
- 4. Blinking Beats Bleaching: The Control of Superoxide Generation by Photo-Ionized Perovskite Nanocrystals

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Angew. Chem. Int. Ed. 2019, 58, 4875–4879 (Hot paper and featured on the cover page).

5. Amplified and Multicolor Emission from Films and Interfacial Layers of Lead Halide Perovskite Nanocrystals

Ghimire, S.; <u>Chouhan, L.</u>; Takano, Y.; Takahashi, K.; Nakamura, T.; Yuyama, K.; Biju, V.

ACS Energy Lett. 2019, 4, 133-141.

Book Chapter

 Photosynergetic Responses in Molecules and Molecular Aggregates. *Chapter Title*. The Confinement and Migration of Charge-Carriers in Lead Halide Perovskites. Ghimire, S.[†]; <u>Chouhan, L.</u>[†]; Biju, V. *Springer Nature Singapore*. 2020, 197–210 ([†]Equal contribution).

Patent

1. Perovskite Nanocrystal Thin Film: Method for Manufacturing Perovskite Nanocrystal Thin Film, Light Emitting Device, Photoelectric Conversion Device, Display Device, and Electronic Device.

ペロブスカイトナノ結晶薄膜、ペロブスカイトナノ結晶薄膜の製造方法、発

光素子、光電変換素子、表示装置および電子機器。

Biju, V.; Ghimire, S.; Chouhan, L.

Application No. PCT/JP2019/040788, Japanese Patent No. 629742

Papers Presented in Conferences

1. Passivation of Halide Vacancies in Lead Halide Perovskite Quantum Dots for Photoluminescence Blinking Suppression

<u>Chouhan, L</u>.; Biju, V. *The 101st Annual Meeting of the Chemical Society of Japan*, Japan, 19–22 March **2021**. [e-Poster]

- Photoluminescence Blinking in Lead Perovskites Assisted by Halide Vacancy <u>Chouhan, L</u>.; Biju, V. Japanese Chemical Society Hokkaido Branch 2021 Winter Research Presentation, Sapporo, Japan, 26–27 January 2021. [Oral]
- 3. Real-Time Suppression of Photoluminescence Blinking in Lead Halide Perovskite Quantum Dots

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4. Photoluminescence Blinking Suppression in Lead Halide Perovskite Quantum Dots Revealed by Single-Molecule Spectroscopy

<u>Chouhan, L.;</u> Takano, Y.; Ito, S.; H. Miyasaka, Biju, V. *Annual Meeting of the Japanese Photochemistry Association 2020*, Japan, 9–11 September **2020**. [e-Poster]

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