HOKKAIDO UNIVERSITY

Title	Exploring exciton recombination, migration, and transfer in halide perovskite systems [an abstract of entire text]
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Degree Grantor	北海道大学
Degree Name	博士(環境科学)
Dissertation Number	甲第16235号
Issue Date	2025-03-25
Doc URL	https://hdl.handle.net/2115/95355
Type	doctoral thesis
File Information	KHATUN_Farida_summary.pdf

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Doctoral Thesis

Exploring exciton recombination, migration, and transfer in halide perovskite systems

（ハロゲン化物ペロブスカイト系における励起子の再結合、移動、および転移の探求）

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March 2025

Abstract

Lead halide perovskites (LHPs) exhibit facile synthesis, strong optical absorption, tunable bandgaps, and high charge carrier mobility, making them suitable for applications in solar cells and other photovoltaic devices. LHP nanocrystals (hereafter PNCs) have gained significant attention due to their exceptional optoelectronic properties. However, PNCs suffer from instability, decreased carrier diffusion, and reduced carrier extraction at the interface. The basic aim of this thesis is to address these issues. The thesis is structured into five chapters. Chapter 1 introduces perovskites, focusing on their structures, photoluminescence (PL) behavior, and carrier diffusion dynamics across different LHP sample types. Chapter 2 details the materials, methodologies, and scientific instruments used in my thesis. Chapter 3 focuses on the defect passivation of $CsPbBr_3$ PNCs, where halide vacancies cause nonradiative recombination. Elemental analysis confirms the bromide vacancies, which cause the low PL quantum yield (QY) and short PL lifetime. Among the halide sources used for the post-treatment of PNCs, NaBr was proven to be the most effective, increasing PLQY from 58% to 98% and PL lifetime from 11.6 ns to 13.8 ns. The suppressed PL blinking of PNCs after NaBr treatment also supports vacancy filling. Chapter 4 explores the polymer-induced assembly formation of $FAPbBr_3$ perovskite quantum dots (PQDs) to achieve a longer carrier diffusion length. The solvent evaporation and polymer shrinkage during drying enable assembly formation, leading to a redshifted PL spectrum and an increased PL lifetime due to wave function overlap and miniband formation. In contrast, increasing temperature leads to a blue-shifted PL spectrum and a decreased PL lifetime, indicating thermal dissociation of the assembly. Cooling the assembly partially restored the optoelectronic properties. In Chapter 5, I focus on the rapid carrier extraction from $CsPbBr_3$ PNCs using multiwall carbon nanotubes (MWCNTs) as the electron acceptor. MWCNTs were functionalized with terminal phenylamine groups to ensure binding with the PNCs. PNC-MWCNT conjugates were prepared using both post-mixing of PNC with MWCNT and in-situ hot-injection PNC synthesis methods. These conjugates exhibit hot-electron transfer at the interface and a reduction in biexciton-mediated Auger recombination (AR). This thesis presents strategies for enhancing PNC quality through halide vacancy filling and improving carrier diffusion and extraction. These advancements contribute to developing more efficient and durable optoelectronic devices.

Thesis Summary

In Chapter 1, I discussed the historical evolution and structural features of LHPs. Perovskite was first identified in 1839 by German mineralogist Gustav Rose in the Ural Mountains of Russia as $CaTiO_3$, a naturally occurring mineral. The perovskite structure can accommodate various cations and anions, which allows calcium and titanium to be replaced with different elements. LHPs have gained immense popularity in optoelectronic and energy applications. HP solar cells have achieved efficiencies comparable to silicon photovoltaic devices within a decade. These materials possess attractive, tunable optical and electronic properties. The ABX_3 crystal structure of HPs enables the inclusion of a wide range of chemical species, imparting significant structural and compositional versatility. This Chapter explains the structural parameters that govern their stability, including the Goldschmidt tolerance and octahedral factors. The electronic band structure of HPs is shaped by the $[BX_6]^{4-}$ octahedral units and spin-orbit coupling effects, which are responsible for the defect tolerance of LHPs. I discuss the challenges, such as structural instability and toxicity, that hinder their commercialization. I also elaborate on how defects introduce shallow and deep traps within the band structure, leading to the nonradiative recombination of carriers. PL and exciton dynamics of various LHP samples, including polycrystalline films, single crystals, and PNCs, are also discussed. I mention the various carrier extraction strategies to improve device performance. The potential applications of LHP are also included in Chapter 1.

Bulk LHPs exhibit superior carrier diffusion properties. These properties make them suitable for application in optoelectronic devices. However, thin film preparation is complex using bulk perovskite. PNCs are gaining popularity due to the ease of synthesizing films with the desired thickness. Increased carrier diffusion and extraction are necessary for improving device performance. When PNCs are organized to form self-assembly, the carrier lifetime and carrier diffusion increase. Defect-free NCs further enhance carrier migration and extraction. Also, quick carrier extraction from PNC using acceptors could be beneficial. Therefore, defect passivation, systematic arrangement of PNC, and interfacial engineering are essential. Although researchers are trying to solve these issues, a significant scope of improvement in this field remains.

Chapter 2 outlines the various materials and experimental methods utilized in the thesis. I provide detailed synthesis procedures for LHPs, including PNCs and PQDs. I also describe the characterization techniques with an explanation of their fundamental principles. This

Chapter also includes the functionalization procedure of MWCNTs and the instrumentation used to investigate the conjugates. I synthesized LHP PQDs and PNCs following the hot injection method. UV-visible absorption spectroscopy was used to measure the absorption characteristics, while steady-state fluorescence spectroscopy was used to assess the emission properties of the synthesized LHPs. X-ray diffraction (XRD) determined the crystal structure of the LHPs. Small-angle X-ray scattering (SAXS) provided insights into interparticle distances during assembly formation. Meanwhile, functionalized MWCNT was investigated using X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR), and Raman spectroscopy. The PNC-MWCNT conjugates are prepared following both post-mixing and in-situ hot injection methods. The size and shape of PQDs, PNCs, MWCNTs, and PNC-MWCNT conjugates were analyzed using scanning transmission electron microscopy (STEM). Additionally, STEM, coupled with energy-dispersive X-ray spectroscopy (EDX), determined the composition of PNCs. I investigated the PL blinking of individual PNCs and PQDs through single-particle microscopy. To assess carrier lifetime, I measured the PL decays using time-correlated single-photon counting (TCSPC) techniques, employing ultrafast pulse laser systems that operate in the picosecond (ps) and femtosecond (fs) ranges. Furthermore, I utilized Quantaurus-Tau for PL lifetime measurements of colloidal PNCs, where LEDs serve as excitation sources to evaluate the carrier lifetime. These techniques enabled me to understand charge carrier recombination in the samples. To explore excited-state carrier dynamics and carrier transfer in conjugates, I employed transient absorption (TA) spectroscopy with a 400 nm fs pulse laser as the pump and a white light continuum as the probe.

In Chapter 3, I discussed the halide vacancy filling in $CsPbBr_3$ PNCs. These vacancies are accountable for lattice degradation, halide ion migration, and PL blinking, which consequently decrease the performance of devices. These vacancies create localized defects in the crystal lattice. These defects generate energy levels within the material's band structure, acting as a trap. These traps function as centers for nonradiative recombination. Vacancy-induced exciton/carrier trapping is one of the prominent factors in reducing carrier lifetime. Therefore, addressing these vacancies is vital for enhancing the performance of LHP in optoelectronic applications. Initially, $CsPbBr_3$ PNCs were prepared following the hot injection technique. Oleic acid and hexadecylamine were used as the ligands, while cesium acetate and $PbBr_2$ were employed as precursors. The as-synthesized $CsPbBr_3$ PNC shows excitonic absorption and emission peaks in toluene at 501 nm and 510 nm, respectively. The size, shape, and morphology of the PNCs were analyzed using STEM. Well-dispersed cubic shape PNCs

were observed. The average size of PNCs was 7.12±0.96 nm, which was analyzed using the image-j program. The crystallographic structure of the as-synthesized PNCs was investigated through XRD analysis, which shows the characteristic peak at 15.05°, 21.48°, 30.63°, 33.96°, 37.92°, 44.10°, and 48.55°, corresponding to 100, 110, 200, 210, 211, 220, and 310. These peaks represent the cubic phase (*Pm3m* crystal structure) of $CsPbBr_3$ PNCs. To assess the quality of synthesized PNCs and to understand defect states, I measured the PLQY (Φ) of the as-prepared $CsPbBr_3$ PNCs. The calculated Φ for the PNCs is 57%, which is much lower. PLQY represents the ratio of emitted photons to absorbed photons. A low PLQY indicates that a substantial fraction of the absorbed energy in a material is not re-emitted as light but is lost through nonradiative processes. To further elucidate the nature of these defects, I conducted STEM-EDX. The elemental ratios were Cs:Pb:Br = 1.0:1.1:2.64. This lower amount of bromine compared to the expected stoichiometric ratio (Cs:Pb:Br = 1:1:3) indicates the presence of bromine vacancies. These Br^-vacancies are the reason for the low Φ value. Post-synthetic passivation is a common strategy for filling vacancies in PNCs. Typically, a range of organic and inorganic compounds serve as halide sources. I investigated the passivation of halide vacancies using CsBr, NaBr, and KBr. First, a saturated solution of the salts was prepared by dissolving them in water. The PNC dispersion in toluene was added to the mixture, followed by vigorous shaking to ensure thorough mixing. The phases were then allowed to settle. This process was conducted multiple times. Since the solution was saturated, the likelihood of water dissolving the PNCs was minimized. Finally, the toluene part was collected and measured. Among these salts, NaBr exhibits the most effective passivation results. Moreover, CsBr shows double perovskite formation, and KBr is reported to produce impurities. Therefore, I selected NaBr for further experiments. After post-treating the PNC in toluene with saturated aqueous NaBr solution, STEM-EDX analysis was performed to reassess the atomic composition. The post-treatment composition was found to be Cs:Pb:Br = 1.0:1.17:2.98, closely approximating the standard stoichiometric ratio. These findings indicate the effective filling of anion vacancies within the lattice. Additionally, the PLQY of the treated PNCs was measured, showing a significant increase to 98 ± 2% within 15 minutes, further supporting the efficacy of the NaBr post-treatment in enhancing material quality and luminescence efficiency. PL intensity increases, and PL lifetime changes from 11.6 ns to 13.8 ns after NaBr treatment. The calculated radiative recombination rate (k_r) of as-synthesized PNCs is $4.9 \times 10^7\ s^{-1}$, whereas the nonradiative recombination rate (k_{nr}) is $3.7\times 10^7\ s^{-1}$. Following the NaBr treatment, k_{nr} is decreased to $1.4 \times 10^6\ s^{-1}$. The reduction in nonradiative pathways further substantiates the passivation of vacancy-related defects. I measured the single particle PL blinking of PNCs

before and after NaBr treatment to confirm the successful defect passivation because the trap is one of the reasons for blinking. I observed the single PNC dots using the EMCCD camera and noticed different blinking behaviors in the as-synthesized PNC sample. Some poorly luminescent PNCs showed gradual photo-brightening, and other PNCs showed suppressed blinking after NaBr treatment. The blinking that remained in a PNC after NaBr treatment can be assigned type A blinking because of the nonradiative Auger process. This defect passivation strategy enhances the optoelectronic properties and holds promise for developing stable, water-soluble HPs, which opened new possibilities for high-performance perovskite devices.

In Chapter 4, I focused on the exciton diffusion control in $FAPbBr_3$ PQD assemblies within polymer microenvironments using external stimuli. Reversible changes in optoelectrical properties by the controlled assembling and disassembling of PQDs are essential for advancing stimuli-responsive device functionality. First, $FAPbBr_3$ PQDs were synthesized using the hot injection method. Oleic acid and n-octylammonium bromide in 1-octadecene were used as the ligand solution, while FABr and $PbBr_2$ in dry DMF served as the precursor solution. The precursor solution was injected into the ligand solution at 80℃. This process yielded PQDs with a light-yellow color that emits blue light under 365 nm UV excitation. The prepared sample exhibited a pronounced excitonic absorption peak at 437 nm and a PL peak at 441 nm. These spectral features indicated strong quantum confinement effects and high exciton binding energy, typically observed in low-dimensional LHPs. STEM images showed spherical shape PQDs with an average diameter of 5 nm. The excitonic lifetime was determined through the TCSPC technique. A 405 nm 150 fs laser pulse was used to excite the PQDs dispersed in toluene. The obtained decay was fitted mono-exponentially. A very short PL lifetime, 1.3 ns, was obtained from the as-prepared PQD colloidal solution. SAXS and XRD analyses were also conducted to confirm the structure of the $FAPbBr_3$ PQDs. SAXS helped to understand the interparticle distance and dispersity of the PQDs. A sharper peak at 2.4 nm^{-1} indicated a more regular ordering of PQDs in a film. The calculated interparticle distance is 2.6 nm. The XRD analysis of the PQD films revealed the diffraction peaks corresponding to the (100) and (200) crystal planes. A polymer matrix enabled controlled assembly/disassembly of photo-responsive nanomaterials. Here, I modulated excitonic recombination by thermally tuning $FAPbBr_3$ PQD assemblies in a polybutadiene (PBD) matrix. PBD is chosen because of its elasticity, transparency, and low glass transition temperature (T_g < 210 K). PQD-PBD film was prepared by mixing 10 mg/mL $FAPbBr_3$ PQDs and 25 mg/mL PBD in toluene. The final concentration of PBD was 12.5 mg/mL. 5 μL sample from this mixture was deposited onto a glass coverslip

and dried to form a uniform thin film. In a PQD-PBD film, the polymer chains rearranged and packed more closely during drying, causing film shrinkage. This property helped PQDs come closer and assemble in a film. The film's emission color shifted from blue to green, with a redshift from approximately 460 nm to 532 nm. This redshift is attributed to decreased inter-PQD distances, which enhances the exciton dielectric screening and increases electronic wave function overlap between neighboring QDs. Such an overlap facilitated the formation of minibands. These minibands allowed for extended excitonic states and lowered bandgap, manifesting as the observed PL redshift. The exciton lifetime increased from 1.3 ns (isolated PQDs) to 83.8 ns (PQD-PBD film) within 4.5 hours. The increased PL lifetime during assembly formation was due to lower surface traps in the PQDs and more extended carrier diffusion. The temperature of an assembly was increased up to 323 K to understand the influence of temperature on exciton recombination. A shoulder band at 495 nm was generated at high temperatures, and the prominent PL peak at 544 nm underwent a 14 nm blue shift. Moreover, at higher temperatures, the carrier lifetime was decreased from 345 ns to 74 ns. When the PQD–PBD film was heated, the polymer matrix expanded, disrupting the PQD assemblies and increasing the inter-dot distance. This disruption weakened the inter-PQD interactions, diminishing wavefunction overlap and reversing the miniband formation. As a result, the PL emission shifted to higher energies (blue-shifted PL), consistent with the emission from isolated PQDs. In our study, the small blue shift in the main PL peak (544 to 530 nm) explains the temperature-dependent exciton-phonon interactions. I cooled the PQD-PBD film to verify whether PQD assembly formation and dissociation are reversible. Cooling the film back to 296 K from 323 K caused the main PL peak to shift from 530 nm to 544 nm, accompanied by a decrease in the intensity of the shoulder band. By cooling, the PL lifetime was increased from 74 to 128 ns. These results indicated the reassembly formation of the PQDs. However, the incomplete recovery of the spectral features and PL lifetime upon cooling suggests that a fraction of the PQDs remain spatially separated, likely due to the presence of polymer chains between them. These findings highlight the potential of perovskite-polymer composites for designing advanced, switchable devices.

In Chapter 5, I investigated the hot carrier (HC) extraction from $CsPbBr_3$ PNCs using MWCNTs, which have exceptional charge transport properties. In HP solar cells, sunlight generates electron-hole pairs within the HP layer. These charge carriers must be extracted rapidly to minimize recombination losses and ensure efficient power generation. Band-edge electron extraction is a fundamental process in solar cells, leading to intra-band relaxation or

internal conversion-assisted energy loss in the form of heat. Therefore, extracting HCs is crucial for improving solar cell power conversion efficiency (PCE). HC extraction can be achieved by modulating the carrier relaxation dynamics using an acceptor. The carrier relaxation kinetics in these donor-acceptor hybrid systems remain an active area of investigation and debate, with no ideal solution for hot electron extraction at the interface. In this Chapter, to create an intimate interface between $CsPbBr_3$ PNCs donor and MWCNTs acceptor, I first functionalized the MWCNTs with phenylamine (MWCNT-NH_2). Initially, MWCNTs were treated with 4-nitrobenzene diazonium tetrafluoroborate (~150°C), generating nitrobenzene radicals that covalently bonded to the MWCNT surface. The attached nitro groups were then reduced to amines using $NaBH_4$. FTIR, XPS, and Raman spectroscopy helped confirm the successful functionalization. Next, PNC-MWCNT conjugates were prepared by either post-mixing PNCs with functionalized MWCNTs or following the in-situ hot injection method. STEM images showed that MWCNTs are anchored with a sub-monolayer of PNCs in the post-PNC mixing sample, while the in-situ method resulted in MWCNTs coated with dense layers of PNCs. The excitonic absorption peaks are observed at 502 nm and 505 nm, while the PL peaks are at 511 nm and 513.5 nm for the post-mixing and in-situ synthesized samples, respectively. No significant shift in the absorption and PL peak positions for the post-mixing sample was observed compared to the PNC-only sample, indicating no change in the band structure. However, the redshift in both absorption and PL peaks in the in-situ prepared conjugate, compared to the PNC-only sample, is attributed to a multilayer of PNC around the MWCNT. The change in the PL lifetime observed in both conjugates compared to single PNCs suggested that charge or energy transfer occurred at the interface within the conjugates. To further elucidate the excited state carrier dynamics, TA spectroscopy was performed. The characteristics TA peaks are i) a negative ground-state bleach (GSB) peak at 510 nm, which appeared because of the depletion of the ground-state electrons and a state-filling effect, ii) a lower energy short-lived photoinduced absorption peak at around 530 nm appeared due to the bandgap renormalization, and iii) a higher energy long-lived photoinduced absorption peak appeared due to re-excitation of the bandedge carriers to high energy states. A slight redshift in the GSB of the PNC-only sample at longer time delays suggested a biexciton-mediated Stark effect, which is absent in conjugate samples. This phenomenon occurred due to the interaction between excitons within the PNCs. The GSB peak broadening of the PNC-only sample at a lower time delay compared with PNC-MWCNT also supports the biexciton formation in the PNC-only sample. The bleach kinetics at 510 nm were fitted tri-exponentially. For the PNC-only sample, the calculated time constants are τ_1 = 250 fs (40%), τ_2 = 150 ps (34%), and τ_3 =

9.8 ns (26%). In contrast, for the PNC-MWCNT heterostructures, the time constants are τ_1 = 320 fs (38.5%), τ_2 = 1.0 ps (17.3%), and τ_3 = 3.7 ns (44.2%). τ_1 is assigned for HCs relaxation to the band edge. The τ_2 corresponds to nonradiative recombination processes. In the PNC-only sample, biexciton-mediated nonradiative recombination mainly contributed to the τ_2. It is well known that the time needed for the AR in the case of $CsPbBr_3$ PNC is several tens to hundreds of picoseconds. This is comparable with the value of 150 ps, guiding me to assign τ_2 as a biexciton-mediated AR process for the PNC-only sample. The 150 ps component is absent in the PNC-MWCNT sample, indicating that the AR was suppressed in the conjugates due to HC transfer. In contrast, the τ_2 value for the conjugates was significantly lower (1 ps) compared to the PNC-only sample, and its contribution was halved. This rapid recovery indicated that a small fraction of the depleted electrons quickly returned to the ground state of the PNC. This quick recovery may be due to a hot hole transfer from PNC to the MWCNT. The longest lifetime (τ_3) can be attributed to radiative bandage recombination for the PNC-only sample and nonradiative back electron transfer for the conjugates. These findings emphasize the potential of PNC-MWCNT conjugates to develop high-performance HC LHP solar cells.

General Conclusions

In conclusion, this thesis has explored the processes of exciton migration, recombination, and transfer in LHPs. These materials exhibited exceptional optoelectronic properties, making them promising candidates for optical and photovoltaic applications. However, particular challenges, including radiative and nonradiative recombination, limit device efficiencies. In solar cells, recombination processes at interfaces hinder carrier extraction, while in LEDs and lasers, nonradiative losses diminish luminescence efficiency. Addressing these issues requires strategies to minimize defects, enhance carrier diffusion length, and facilitate efficient carrier extraction. This thesis focused on three key strategies to improve LHP performance. Chapter 3 explored defect passivation in $CsPbBr_3$ PNCs to reduce nonradiative recombination. Using NaBr as a bromide source, I significantly increased the PLQY of PNCs, as confirmed by STEM-EDX and extended PL lifetime measurements. This approach highlights an effective defect management strategy to enhance material stability and optoelectronic performance. Chapter 4 focused on the assembly of $FAPbBr_3$ PQDs within a polybutadiene matrix to increase carrier diffusion length. The self-assembly facilitated electronic wave function overlap, forming a miniband, redshifting the PL spectrum, and extending the PL lifetimes. Temperature modulation studies revealed that polymer expansion at high temperatures disrupted the assemblies, leading to blue-shifted PL spectra and reduced exciton lifetimes, with partial

recovery upon cooling. Chapter 5 examined the HC extraction from $CsPbBr_3$ PNCs to MWCNTs. Functionalization of MWCNTs with phenylamine ensured the attachment of PNCs to MWCNTs. These PNC-MWCNT conjugates showed hot electron transfer, reduced nonradiative AR, and suppressed radiative recombination at the interfaces, as confirmed by TA spectroscopy. Overall, optimizing PNC quality, regulating carrier diffusion, and improving HC extraction are promising to enhance LHP-based device performance.