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## 学 位 論 文 審 査 の 要 旨

博士（環境科学）

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## 学 位 論 文 題 名

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)

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. This thesis assigns 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, the candidate introduces the general properties of lead halide perovskites. Here, an explanation is given about their chemical structure and various synthesis methods for nanocrystals, quantum dots, thin films, and microcrystals. Then, the candidate describes the band-edge states and the effect of spin-orbit coupling in these perovskites. Next is an introduction to the charge carrier dynamics followed by absorption and photoluminescence properties of perovskites. Here a review is given about the 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. This chapter is summarized with the photoluminescence blinking mechanisms in perovskite nanocrystals and quantum dots. Finally, the emerging applications of halide perovskites to lasers, solar cells, and LEDs, followed by research motivation, are given.

Chapter 2 gives detailed information about the materials used and the synthesis of lead halide perovskites. Here, ligand-mediated transport, ligand-assisted reprecipitation, and hot-injection methods are used to synthesize these nanocrystals and quantum dots. Also, this chapter describes 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, the candidate explains the time-resolved fluorescence spectroscopy for analyzing the photoluminescence decay profiles and charge carrier recombination rates of perovskites. Next, the single-particle microspectroscopy system for examining the photoluminescence intensity trajectories of nanocrystals and quantum dots is introduced.

Chapter 3 sketches the role of oxygen on the stability of methylammonium lead iodide perovskite nanocrystals at the ensemble and the single-particle levels. The candidate shows 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 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, the candidate explains the degradation mechanism by considering the role of the halide vacancies on superoxide generation.

Chapter 4 focuses 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. The relationship between the vacancies and blinking is discussed 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  $1 \times 10^8 \text{ s}^{-1}$  for lead bromide perovskite and  $1.9 \times 10^9 \text{ s}^{-1}$  for lead iodide quantum dots.

Chapter 5 is about 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  $\text{Cs}^+$  or  $\text{Pb}^{2+}$  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 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, the ON- and OFF-time probability distributions are studied 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, it was found that the caesium oleate treatment reduces the surface  $\text{Cs}^+$  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.

審査員一同は、これらの成果を高く評価し、また研究者として誠実かつ熱心であり、大学院博士課程における研鑽や修得単位などもあわせ、申請者が博士（環境科学）の学位を受けるのに十分な資格を有するものと判定した。