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学 位 論 文 内 容 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 a high absorption cross-sections, long photoluminescence lifetimes, high charge-carrier mobilities, and high photoluminescence quantum yields. However, some limitations of lead halide perovskites are yet to overcome for practical applications. For example, these perovskites are susceptible to moisture, water, oxygen, or light. They tend to degrade and lose their efficiency after exposing to 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 on examining the single-particle photoluminescence 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 of 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 their absorption and photoluminescence properties. I review extrinsic and intrinsic factors responsible for degrading the photoluminescence and the structure of perovskites. Furthermore, halide perovskites show blinking, which is the stochastic fluctuations 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 process of synthesizing lead halide perovskites. I used ligand-mediated transport, ligand-assisted reprecipitation, and hot-injection methods to synthesize these perovskite nanocrystals and quantum dots. Also, I describe the working principle 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 photoluminescence spectroscopy method used for analyzing the photoluminescence decay profiles and charge-carrier recombination rates of perovskites. Next, I explain the single-particle microspectroscopy system used for examining the photoluminescence intensity trajectories of perovskite single-nanocrystals or -quantum dots. In Chapter 3, I sketch the role of oxygen on methylammonium lead iodide perovskite nanocrystals at the ensemble and the single-particle levels. I show the photoluminescence behavior of the nanocrystals in the air, argon, or polymer atmospheres. The photoluminescence intensity in the air shows a continuous decrease, whereas the

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. The superoxide disintegrates the perovskite structure into lead iodide, methylamine, and water. In an argon or a polymer environment, the photoluminescence intensity is stabilized, suggesting that the superoxide generation and perovskite oxidation are suppressed. Also, the photoluminescence intensity recovery after long-OFF event in some trajectories shows the stability of the perovskites in the ionized state. Such a long-OFF event is associated with a low rate of electron transfer suggests that the perovskites do not oxidize or react with superoxide in an ionized state. In the last section, I explain the perovskite degradation mechanism by considering that the halide vacancies are responsible for superoxide generation. In Chapter 4, I focus on the suppression of the halide vacancy-assisted 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 the 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 blinking and construct the ON- and OFF-time probability distributions before and after the halide salt treatment. The probability distributions suggest that the perovskite quantum dots' blinking behavior changed from type-A to type-B after the treatment. That is, the charging-discharging processes in the perovskite have switched to the trapping-detrapping mechanism. Therefore, the halide salts fill the halide vacancies. Further, at the ensemble level, the photoluminescence quantum yields and lifetimes of the perovskite quantum dots show increases after the halide salt treatment. Apart from the controlled experiments, the rates of halide-vacancy-assisted nonradiative recombinations are at $1 \times 10^8 \text{ s}^{-1}$ for lead bromide perovskite and $1.9 \times 10^9 \text{ s}^{-1}$ for lead iodide perovskite quantum dots. In Chapter 5, I show the role of A- and B-site cation vacancies on the photoluminescence of cesium 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. Cesium oleate or lead oleate are applied to fill the Cs^+ or Pb^{2+} vacancies. At the ensemble level, the pristine perovskite quantum dot's photoluminescence intensity has continuously decreased with time. Although cesium oleate slightly reduced the rate of photodegradation of the perovskite quantum dots, lead oleate does not affect photoluminescence. Also, no difference in the average photoluminescence lifetime is observed in the perovskite quantum dots before and after the addition of cesium or lead oleate. Similarly, at the single-particle measurements, the photoluminescence blinking behavior of perovskite quantum dots does not change before and after adding the cesium 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 cesium oleate. Although the perovskite quantum dots show type-A blinking regardless of the treatment with cesium oleate, there is a slight increase in the truncation ON-time after the treatment. Therefore, I assume that the cesium oleate treatment can reduce the surface Cs^+ vacancies in the lead halide perovskite, whereas lead oleate has a negligible effect on the charge-carrier dynamics. In summary, this thesis unveils the possible factors responsible for the degradation of lead halide perovskite. Also, it demonstrates the process through which the photoluminescence of perovskite increases.