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学位論文内容の要旨

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学位論文題名

Spatially controlled bandgap engineering and charge carrier recombination in lead halide perovskites by optical trapping

（光トラッピングによるハロゲン化鉛ペロブスカイトにおけるバンドギャップ工学と電荷キャリア再結合の空間的制御）

Organic-inorganic lead halide perovskites have attracted extensive attention to the next generation energy-harvesting and light-emitting devices, which is owing to their strong absorption of visible to near-infrared light, brilliant photo- and electro- luminescence, long-range diffusion of electrons and holes, low-temperature solution processability, and. High degree of defect tolerance. In addition, being a direct bandgap material, the optical and electronic properties of this class of materials can be easily modified in the entire UV-visible to near infrared region by tuning their bandgaps. On the other hand, the laser based optical trapping is being used in a wide variety of fields to manipulate microscopic objects by confining, assembling, or modifying them from the beginning of the inception by Arthur Ashkin. The optical tweezer is often used in biological system to manipulate viruses, living cells and organelles as well as in chemistry to grow or confine several molecules such as proteins, amino acids, polymers, nanoparticles, and quantum dots in the focal volume, where the assemblies are formed through trapping. In this thesis, I utilize the potential of optical trapping system for the site-specific bandgap tuning and halide vacancy filling of lead halide perovskite materials and study the charge carrier dynamics in the fabricated bandgap-graded heterojunctions. This thesis consists of five chapters.

In **chapter 1**, I reviewed the general introduction of lead halide perovskites in terms of their chemical composition, structure, properties, and applications. I discuss the most widely synthesis techniques of perovskite microcrystals, nanocrystals, and thin films. I have highlighted the characterization methods of perovskite materials using different microscopic and spectroscopic tools. Subsequently, I explain the charge carrier properties and their recombination pathways, followed by the absorption and emission properties. Furthermore, I describe the halide exchange reactions of perovskites in different dimensions such as nanocrystals, microcrystals, and nanowires, which proceeds homogeneously or site-specifically in the parent crystals. Despite being highly defect tolerant, the abundant defects limit the overall performance of perovskite materials. Hence, I reviewed the origin and types of the defects present in perovskite materials. I further discuss the working principle of an optical trapping system utilized to modify the bandgap and passivate defects in perovskite crystals. In the application section, I reviewed the perovskite solar cells, LEDs, and lasers and finally, I describe the motivation and objectives of my research work.

Chapter 2 discusses the experimental methods and materials used in this dissertation. The chapter includes detail information of the chemicals and materials used and the synthesis process of perovskite microcrystals, nanocrystals, and thin films. In the instrumentation section, I discuss the basic working principle and instrumental setup for the laser trapping system using the 1064 nm near-infrared laser and spectroscopic analysis using 1064 nm and 405 nm continuous wave lasers. The charge carrier dynamics in perovskites are studied using a time-correlated single-photon counting system. I characterize the perovskite samples using steady-state fluorescence and UV-vis absorption spectroscopy techniques. The sample surface analysis and elemental mapping are also performed using a scanning electron microscope and the energy-dispersive X-ray spectroscopy.

In **chapter 3**, I demonstrate a new laser trapping based methodology for the site-specific halide exchange reaction in the halide perovskite crystals. In general, the halide exchange reaction proceeds homogeneously in the whole crystal and the bandgap is varied in the entire region when they are exposed to the reactant halide solutions. Here, I introduce the use of a focused near-infrared laser beam to induce halide exchange reaction in the entire region of the selected small microplates and also at the desired center part of the large microplate- and microrod-shaped perovskite crystals in a temporally and spatially controlled manner. I confirmed the site-specific halide exchange reaction via spatio-temporal changes in the photoluminescence emission and spectra under near-infrared laser irradiation and wide-field ultraviolet laser irradiation. I discuss the possible mechanism of the exchange reaction from the viewpoint of local concentration increase of the halide ions at the focal volume under laser trapping.

In **chapter 4**, I discuss the suppression of halide exchange reaction by optically controlled site-specific halide vacancy filling of the perovskite microcrystals. The spontaneous halide exchange reaction of the as-prepared crystals occurs homogeneously in the entire region, which can be suppressed by treating the crystals with a constituent reaction solution. The precursor treatment reduces the halide vacancies of the initial crystals and inhibit the halide exchange reaction in the entire region. I demonstrated such halide exchange suppression at specific sites of the microrod crystals through vacancy filling using a NIR laser beam. The NIR laser irradiation fills the halide vacancies exclusively at the irradiated part, while the characteristic features of the nonirradiated parts remain unchanged. The corresponding photoluminescence spectra, scanning electron microscope images, and energy dispersive x-ray mapping confirm the halide vacancy filling of the crystals. Furthermore, an increase in the PL lifetime at the irradiated part suggests the suppression of nonradiative recombination through vacancy filling.

In **chapter 5**, I prepare perovskite heterojunction at desired locations as well as control the transport and accumulation of charge carriers across the heterojunction in perovskite microcrystals or nanocrystal films. Through the site-specific halide exchange reaction, I fabricate microscopic heterojunctions with two distinct bandgap-gradient regions composed of iodide-rich and bromide-rich regions. I observed the efficient accumulation of charge carriers in the narrow-bandgap iodide-rich region in the built-in halide gradient structures. The corresponding time-resolved spectroscopic analysis revealed the transportation of photogenerated excitons/charge carriers from the surrounding wide-bandgap bromide-rich regions to the narrow-bandgap iodide-rich region.

In **summary**, this thesis develops the construction of perovskite heterostructures with distinct emission color and bandgap and enable controlling the intrinsic properties of halide perovskite. Such laser trapping based findings offer a new area of interest toward the fabrication of high-quality perovskite heterojunction based optoelectronic devices.