学 位 論 文 審 査 の 要 旨

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Studies of photoinduced electron transfer and exciton dynamics in halide perovskite films and single particles
(ハロゲン化物ペロブスカイト膜と単一粒子における光誘起電子移動と励起子ダイナミクスの研究)

Lead halide perovskites have become the most promising semiconductor materials for light-harvesting and light-emitting applications. These materials in the nanocrystalline forms, obtained by reliable colloidal synthesis approaches, show high photoluminescence quantum yield, high charge carrier mobilities, long photoluminescence lifetimes, and high photostability. However, their exciton, charge carrier properties, and interfacial electron transfer dynamics need optimization for next-generation perovskite devices. The above unique excitonic and charge carrier properties attracted the candidate to prepare various halide perovskite quantum dots, nanocrystals, and thin films and analyze the exciton, charge carrier, and electron transfer dynamics.

In chapter 1, the candidate discussed the general properties and significance of lead halide perovskites by thoroughly reviewing the literature. First, the candidate introduced the structure, chemical compositions, and stability factors of perovskites, followed by explaining various perovskite nanocrystal synthesis methods. The preparation methods for self-assembled perovskite nanocrystal thin films and different characterization techniques are discussed in the second section of this chapter. Next, the bandgap and fundamental optical properties of perovskite nanomaterials are discussed as functions of their halogen compositions, size, and shape, followed by describing the charge carrier and quantum confinement properties in single particles and films. In the final section of this chapter, the candidate explained various optical and photovoltaic applications of these materials.

Chapter 2 provides complete details about the materials, nanoparticle synthesis, sample preparation and characterization, and theoretical and practical aspects of instrumentation techniques. Perovskite nanocrystals were synthesized by hot injection, ligand-assisted reprecipitation, and a modified spray technique. Next, the candidate provided microscopic and spectroscopic techniques for characterizing perovskite single particles, and films. These techniques included UV-vis absorption spectroscopy, scanning electron microscopy, transmission electron microscopy, steady-state and time-resolved fluorescence spectroscopy, single-particle microspectroscopy, and transient absorption spectroscopy.

In chapter 3, the candidate summarized the extent of carrier diffusion, the degree of radiative loss, and

the rate of diffusion-controlled interfacial electron transfer in heterojunction films of cesium or formamidinium lead bromide nanocrystals and C_{60} or TiO_2. Electron transfer and charge separation were confirmed by measuring the photoluminescence decays, photoluminescence intensities, and transient absorption kinetics. By measuring the distance-dependent photoluminescence lifetimes and photocounts in samples containing halide perovskite-C_{60} or halide perovskite-TiO_2 donor-acceptor junctions, the candidate found long-range (>100 μm) carrier diffusion and distance-dependent (>800 μm) interfacial electron transfer.

In chapter 4, the candidate demonstrated the electron transfer dynamics at the single-particle level by analyzing the photoluminescence blinking of single perovskite nanocrystals with or without electron donor molecules like tetracyanoquinodimethane (TCNQ) or tetracyanobenzene (TCNB). The Gibbs free energy changes of electron transfer were estimated to be negative for perovskite-TCNQ and perovskite-TCNB donor-acceptor systems. Also, the photoinduced electron transfer rates were determined for these systems from time-resolved photoluminescence measurements. Further, the statistical analyses of the ON-time and OFF-time probability distributions for several single perovskite nanocrystals helped the candidate understand photoluminescence blinking to the electron transfer relationships.

In chapter 5, the candidate demonstrated the effect of gold nanoparticle's surface plasmon resonance on enhancing the photoluminescence intensities of bromide perovskite quantum dots by exploring the gold-bromine chemical coupling and plasmon-coupled energy transfer from gold nanoparticles to perovskites. The candidate found a huge photoluminescence intensity enhancement for perovskite single quantum dots directly synthesized in gold nanoparticle nanogaps. The gold-perovskite chemical coupling and plasmon coupling were accomplished by creating the nanogaps by the controlled gold sputter-coating on glass substrates, followed by the spray-synthesis of perovskite quantum dots on the gold-sputtered substrates. The samples were characterized using optical spectroscopy, transmission electron microscopy, scanning electron microscopy, and fluorescence microscopy methods. Time-resolved photoluminescence and single particle photoluminescence measurements helped the candidate rationalize the chemically and plasmon coupled photoluminescence intensity enhancement.

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充分な資格を有するものと判定した。