Summary of thesis : Luminescence fine structures and exciton–phonon interactions in halide perovskite nanocrystals
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Halide perovskites ABX$_3$ (A = Cs, MA (CH$_3$NH$_3$), FA (HC(NH$_2$)$_2$), B= Pb, X = Cl, Br, I) are new direct-gap semiconductors with superior optical properties for optoelectronic devices. Since the first report of the synthesis of halide perovskite nanocrystals (NCs) in 2015, they have been gathering much attention as next-generation light-emitting device materials because of their extremely high photoluminescence (PL) quantum yields and the bandgap tunability over the whole visible region.

In conventional semiconductor NCs, the recombination of trions and biexcitons and the exciton–phonon couplings influence their PL properties. For example, the binding energies of trions and biexcitons determine the optical gain of lasers and the purity of single-photon sources. In addition, the exciton–phonon couplings affect the PL linewidth, which is an important physical property for quantum light source applications. However, the size dependence of the trion and biexciton binding energies in perovskite NCs is still unclear. Furthermore, halide perovskites have complex phonon structures, which make it difficult to clarify the phonon modes: which play a dominant role in the exciton–phonon couplings and their coupling strengths in perovskite NCs. At low temperatures, the PL of trions and biexcitons and the phonon-sideband of exciton emerges in PL spectra of single NCs. Therefore, the single dot spectroscopy at low temperatures is a powerful method to reveal the trion and biexciton binding energies and to conduct the phonon-mode-resolved analysis of exciton-phonon coupling in perovskite NCs. To solve these questions, we investigated PL spectra in single perovskite NCs by using single dot spectroscopy.

Here, we first studied the size dependences of trion and biexciton binding energies in perovskite NCs of different compositions (CsPbBr$_3$, CsPbI$_3$, and FAPbBr$_3$). In CsPbBr$_3$ and CsPbI$_3$ NCs, the exciton peaks have fine structure splittings originating from bright triplet excitons. The trion and biexciton peaks appear in the low energy side of strong exciton peak. The trion peaks have single peak structures while the biexciton peaks have antisymmetric shapes to the exciton peaks because of the biexciton-exciton cascade emission via the exciton fine structure levels. The trion (biexciton) binding energy was extracted from the energy difference between the exciton and trion (biexciton) PL peaks. We found that the trion and biexciton binding energies in the three types of perovskite NCs increase with decreasing the NC size. Furthermore, to gain deeper insight into the size dependence, we normalized the binding energies and NC sizes by the bulk exciton binding energy

and exciton Bohr radius, respectively. From the normalized size dependence of the binding energies, we revealed that the size dependences of trion and biexciton binding energies in perovskite NCs of the different compositions are determined by quantum confinement effect, not A-site cations and halogens. Discussing the difference between experimental data and theoretical calculations with the effective mass approximation, we found the importance of the frequency dependence of the dielectric constant, i.e., the effect of dynamic dielectric screening.

Next, we examined the exciton–phonon couplings in perovskite NCs at 5.5 K. In single $CsPbBr_3$ NCs, four LO phonon replicas were observed, which have symmetric shapes to the exciton peaks. The theoretical calculations using density functional theory revealed that these four LO phonon replicas originate from different LO phonon modes, which are attributed to the $PbBr_6$ octahedra. We evaluated the ratio of PL intensity of LO phonon replicas of exciton to that of exciton peak and also performed the same evaluation with respect to trions. From the PL ratios, we obtained the exciton–phonon and trion–phonon coupling strengths, i.e., the Huang-Rhys factors of excitons and trions, and found that both of them increase with decreasing the NC size. The Huang-Rhys factors of trions are larger than those of excitons for NCs with sizes larger than exciton Bohr diameter. However, in the smaller NCs, the Huang-Rhys factors of trions become smaller than those of excitons. The origin of these size dependences can be explained by the spatial overlap of electron and hole wavefunctions modulated by the internal electric field inside the NCs.

Finally, we studied the effect of the crystal phase transition on the exciton–phonon couplings and the size dependence of the phase transition temperature. In this study, we used $FAPbBr_3$ NCs, which shows the orthorhombic-to-tetragonal crystal phase transition under room temperature. From the analysis of the temperature dependence of PL linewidth, we found that the exciton–phonon coupling strengths and effective LO phonon energy do not change at around the phase transition temperature. In other words, the exciton–phonon couplings are not affected by the crystal structure. In addition, in the NCs smaller than 10 nm, the phase transition temperature becomes lower than that of the bulk counterpart. This is the first observation of the size dependence of the phase transition temperature in perovskite NCs.

In this thesis, we discuss the trion and biexciton binding energies, exciton-phonon couplings, and crystal phase transitions in perovskite NCs by using single dot spectroscopy. The results of this dissertation will advance our understanding of the PL properties of perovskite NCs and provide important insights into their application to new light-emitting devices.