学 位 論 文 内 容 の 要 約/Dissertation Summary

博士（環境科学）　　氏　名/Applicant　GHOSH DASTIDAR Rahul

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Investigation of optical modulation of organic-inorganic hybrid copper halide microcrystals
（有機-無機ハイブリッド銅ハライド
微結晶における光学的制御の研究）

Metal halide semiconductors show a wide diversity in both composition and structural dimensionality. In chapter 1, I first presented a classification of metal halide semiconductors based on compositional variation, which indicates three types: binary inorganic metal halides, ternary metal halides, and organic-inorganic hybrid metal halides. Subsequently, the organic-inorganic hybrid metal halides are classified into two types based on molecular structural confinement: perovskite-like and non-perovskite low-dimensional hybrid metal halide structures. Besides morphological confinement in hybrid perovskites, the addition of a larger organic cation as a structural component modifies the molecular structure by controlling the connectivity among the metal halide clusters. Using bulky organic cations, 2D layered structures, 1D chain-like structures, and even 0D isolated metal halide clusters, it is possible to obtain these structures. So far, several metals, including Sn, Bi, In, Cu, Ag, and Mn, have been used to fabricate 0D hybrid metal halides. Among these, copper halides are attracting significant research interest due to their low toxicity and the high abundance of copper in nature. This chapter explains the general structural and optical properties of 0D OIHCHs. So far, using a wealth of different organic cations, diverse copper halide components have been formed, including individual polyhedra and clusters composed of two or more edge-, face-, or corner-shared polyhedra. This structural diversity helps to probe the structure-optical properties correlation. I discuss various synthesis and crystallization methods for growing highly luminescent 0D OIHCH crystals. The electronic band edge structure of 0D OIHCHs is determined by the isolated copper halide clusters, resulting in flat band edges and strong exciton confinement. I also elaborate on the general optical properties observed in 0D OIHCHs. The optical properties, such as strong UV absorption, broad PL bands, and delayed PL, provide evidence of the formation of self-trapped excitons in the lattice. I discuss the formation mechanism of self-trapped excitons in a soft lattice, where lattice vibrations, so-called phonons, play a vital role in exciton self-trapping. I mention vari

ous strategies to tune the STE-based PL emission, which can be leveraged in different applications. The potential applications of 0D OIHCHs are also included in Chapter 1.

Recently, several 0D OIHCHs have been developed in the form of powders, microcrystals, and bulk crystals, exhibiting superior optical properties and excellent PLQYs. These features make them suitable for applications such as white light-emitting diodes, sensors, UV photodetectors, and anticounterfeiting. The 0D OIHCHs are gaining popularity due to their facile synthesis methods and the ease with which they can be tailored to achieve desired optical properties for different applications. For example, in 2022, Xu et al. reported single crystals of a 0D hybrid copper bromide, namely, 1-butyl 1-methylpiperidinium copper bromide [$(Bmpip)_2Cu_2Br_4$]. The crystals exhibit broad PL spectra with a peak at 620 nm under 320 nm UV light excitation. However, the PL lifetime is reported to be very fast (10 ns). Although they reported that the fast lifetime is attributed to defect-bound STEs, there is a knowledge gap regarding the relationship between the fast lifetime and delayed STE emission in 0D OIHCHs. Additionally, the STE formation mechanism, the origin of broad PL with large Stokes shift, external stimuli-induced STE emission tuning, and detailed STE recombination dynamics in 0D OIHCHs remain major issues that need to be addressed.

Chapter 2 outlines the various materials and experimental methods employed in the thesis. I provide detailed synthesis procedures for undoped and Sb^{3+}-doped $(Bmpip)_2Cu_2Br_4$ microcrystals (MCs) in air and inert atmospheres. Additionally, I synthesized undoped $(Bmpip)_2Cu_2Br_4$ MCs with varied Br/Cu ratios by systematically varying the precursor ratio. To investigate the substrate-dependent optical properties, the $(Bmpip)_2Cu_2Br_4$ MCs are grown on borosilicate glass, Silicon, Fe, ITO, and Au substrates. I also describe the characterization techniques, explaining their fundamental principles. I synthesized the microcrystals using a simple wet chemistry method. Single-crystal X-ray analysis determines the crystal structure of the $(Bmpip)_2Cu_2Br_4$ MCs. I performed powder X-ray diffraction to check the purity of the crystalline phase of the synthesized MCs. The size and shape of the MCs grown on borosilicate and ITO glass are analyzed using scanning electron microscopy (SEM). Additionally, SEM, coupled with energy-dispersive spectroscopy (EDX), determined the composition and surface elemental distribution of the MCs. Further, I performed EDX elemental mapping to check the presence of Sb in doped MCs. Meanwhile, both the Sb^{3+} doped and undoped MCs are analyzed using X-ray photoelectron spectroscopy to check the oxidation states of copper and antimony. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was employed to investigate the Sb^{3+} doping efficiency and detect the actual Sb concentration. I obtained optical microscope images, PL images, and PL spectra of both isolated Sb^{3+}-doped and undoped MCs grown on different substrates using a fluorescence microscope under 404 nm CW laser and 365 nm UV LED excitation. Steady-state fluorescence spectroscopy was used to measure the PL excitation (PLE) spectra of the MCs grown on borosilicate and ITO glass substrates to identify the excitation wav

elength responsible for the PL emission. Temperature-dependent PL and PLE measurements were performed to understand the role of phonons in the formation of different STE states and to provide insights into the activation energy barrier between these states, as well as the strength of exciton-phonon coupling. We investigated the detailed STE recombination dynamics using time-resolved PL spectroscopy. To assess the carrier lifetime, I measured PL decays using a Streak-camera and time-correlated single-photon counting (TCSPC) techniques, employing ultrafast pulse laser systems with pulse widths in the picosecond (ps) and femtosecond (fs) ranges. These techniques help me understand the tunability of PL emission and the corresponding changes in exciton recombination dynamics. Furthermore, using structural and spectroscopic characterization techniques, I intend to understand STE emission modulation in 0D OIHCHs.

In chapter 3, I showcase optical properties modulation in $(Bmpip)_2Cu_2Br_4$ MCs through interactions with insulating and conductive substrates and investigate the corresponding evolution of exciton recombination dynamics. In 0D hybrid copper halides, PL emission is mainly governed by STE formation due to strong exciton-phonon coupling in such soft lattices. The STEs are very sensitive to external stimuli, e.g., temperature, pressure, and light, owing to changes in the lattice vibrational modes. Investigating the role of conductivity of the substrate on the evolution of STE recombination dynamics in 0D $(Bmpip)_2Cu_2Br_4$ MCs unravels a new pathway to control the STE emission and paves the way for a more systematic understanding of structure-optical properties correlation. To understand these aspects, I initially grow microcrystals on borosilicate glass and ITO glass substrates. SCXRD analysis reveals that the MCs belong to the P_{bca} phase group with lattice parameters a = 13.82 Å, b = 12.04 Å and c = 17.08 Å, $\alpha = \beta = \gamma = 90°$ and confirms the 0D structure of the MCs where individual $[Cu_2Br_4]^{2-}$ clusters are isolated from each other in the bulky $Bmpip^+$ cationic framework. The PXRD patterns completely match the SCXRD-simulated pattern, indicating the absence of polycrystalline phase formation. I analyzed the chemical composition of both MCs_{glass} and MCs_{ITO} using SEM-EDX. MCs grown on both borosilicate and ITO glass show a homogeneous distribution of copper, bromine, and carbon throughout the surface, while no oxygen signal was detected, which excludes the possibility of surface oxidation. Additionally, the Cu/Br ratio obtained from the EDX analysis was 1:2, matching the stoichiometric ratio of the material, indicating the crystallization purity of the MCs. To check the optical properties, I kept the microcrystals under a fluorescence microscope. The MCs are optically transparent under visible light, indicating that the MCs have negligible absorption in the visible spectrum. The MCs grown on borosilicate glass (MCs_{glass}) exhibit weak green and red dual color photoluminescence (PL) under a 404 nm CW laser. After deconvolution, I found two well-defined peaks at ca. 541 nm and ca. 619 nm. Although the green emission intensity was very weak for the MCsglass, the MCs grown on ITO glass (MCsITO) show intense green emission with a peak at ca. 541 nm under identical excitation conditions. To understand these distinct PL emission properties, I checked t

he PLE spectra for both MCsglass and MCsITO at 540 nm and 600 nm. The PLE spectral features of MCs_{glass} are the same, with a peak at 331 nm for both the green and red emissions, highlighting that the same excited state is responsible for both green and red emissions. The MCs_{ITO} also exhibit identical PLE spectral features. To investigate the origin of intense green emission, I checked the effect of humidity on the MCs. For this information, I added 10 μL of deionized water onto a clean borosilicate glass coverslip, followed by the deposition of 2 mL of the $(Bmpip)_2Cu_2Br_4$ precursor solution. However, the resulting MCs exhibit a green-red dual emission similar to that of MCsglass, ruling out humidity as the origin of the green emission. Furthermore, the absence of oxygen on the surface of the MCs grown on both borosilicate and ITO glass indicates that copper oxidation is not responsible for the green emission. Eventually, I assume there are different possible origins of the intense green emission in the MCs_{ITO}. Firstly, I checked the semiconductor-conductor interfacial interaction-induced PL emission modulation. To verify this effect, I cracked and then powdered an MCglass sample using a stainless-steel spatula, which is a conductor. The purpose of cracking and powdering is to increase the surface-to-volume ratio of the MCs, which promotes better surface contact. Interestingly, the powdered MCs exhibit a substantial increase in the PL intensity ratio of green/red emission (ca. 7.5), accompanied by a drastic change in the PL spectral shape. Subsequently, I confirmed the effect of powder-induced defects on emission modulation by cracking and powdering MCglass with a plastic spatula (ABS resin), which is an insulator. The MC powder by plastic shows no change in the PL spectral shape or in the intensity of the green emission, which excludes the possibility of strain- or defect-induced modification of the emissive state. To check the possibility of any phase change, I performed PXRD measurements for the MCsglass, MCsITO, and MCs powders prepared with a stainless-steel spatula and compared them with the SCXRD-simulated pattern of the $(Bmpip)_2Cu_2Br_4$ MCs. The powdered MCs and MCsITO show a PXRD pattern similar to that of the MCsglass, and the SCXRD simulated pattern, which excludes the possibility of ITO glass or mechanical force-induced phase transition. To understand the semiconductor-conductor interfacial interaction-induced emission modulation of an MCglass, I investigated the exciton recombination dynamics of an intact MCglass and of one after cracking by plastic followed by powdering using a stainless-steel spatula. It is observed that the as-prepared sample exhibits delayed emission, and the corresponding 2D photocount map obtained from a streak camera shows a broad PL spectrum ranging from 500 to 700 nm, with emission persisting over several microseconds (~μs), indicating long-lived excited states. The microsecond ordered lifetime is persistent with STE emission. After powdering using plastic, I observed an increase in the fast-decay component, and photocounts at ca. 540 nm also increased to some extent. Surprisingly, there is an enormous decrease in average lifetime after powdering with a stainless-steel spatula, and the corresponding photocounts map also shows an intense green emission with rapid decay. Stainless-steel- or ITO-induced changes in the PL lifetime and emission color indicate the role of static charge transfer from the M

Cs to the conductive substrates. To confirm the role of charge transfer, I grew the MC on A u, Fe, and Si substrates. The MCs grown on Au (MCs_{Au}) and Fe (MCs_{Fe}) show intense gree n emission under 404 nm excitation. Conversely, the intensity of the green emission is quenc hed in the MCs grown on the Si substrate (MCs_{Si}) and shows prominent red emission. I co mpared the Fermi energy level alignments of the respective metals with the green and red e missive states of the MCs. Based on DFT calculations and partial density of states (PDOS) f or (Bmpip)2Cu2Br4, I considered the Cu2Br4 cluster-centered electronic structure of this 0D s ystem. According to UPS and XPS spectroscopy results, well documented in the literature, the VBM is located at -5.73 eV relative to the vacuum level. Correspondingly, the green emissi ve state (541 nm = 2.29 eV) and the red emissive state (619 nm = 2.00 eV) are at -3.44 an d -3.73 eV. Additionally, the Fermi energy levels of Au, Fe, ITO, and Si are located at -5.2 7, -5.12, -4.90, and -4.60 eV, respectively. This energy-level alignment shows the presence of downhill energy between the emissive states of the MCs and the Fermi energy levels of the respective substrates, allowing an efficient transfer of accumulated static charge from the MC s to the conductive substrates. However, such a charge-transfer process isn't efficient on boros ilicate or Si substrates. The accumulated static charge causes exciton annihilation via static cha rge-exciton coupling, thereby suppressing STE formation. I correlate the green and red emissio ns with the formation of two different STE states in the lattice. The green and red emissions are attributed to exciton coupling with surface and lattice phonons, respectively. To confirm t he role of two different phonons, I performed temperature-dependent PL spectral measurement s for both the MCs_{glass} and MCs_{ITO} in the temperature range of (18-35 ºC). The MCs_{glass} show intense green emission at 18 ºC, which converts to a green-red dual emission with increasin g temperature. The PL intensity ratio remains constant with increasing temperature above roo m temperature. Although I observed a similar trend in the PL emission color change with inc reasing temperature for MCsITO, the threshold temperatures for changes in the green/red PL i ntensity ratio differ between MCs_{glass} and $MCs_{ITO.}$

In Chapter 4, I demonstrated modulation of optical properties in $(Bmpip)_2Cu_2Br_4$ MCs und er intense laser irradiation without any significant structural changes. 0D OIHCHs are a comm on example in which STE formation is very facile owing to their host-guest-like structure. Th ere are several reports of STE emission modulation induced by reversible or irreversible struct ural phase transitions in response to external stimuli, such as pressure and heat. Although the role of non-phase transitional subtle structural changes in STE emission modulation has been i nvestigated in many reports, the detailed analysis of modulation of STE recombination dynami cs accompanied by subtle lattice distortion remains less explored. Here, I discussed a PL inten sity enhancement in these 0D $(Bmpip)_2Cu_2Br_4$ MCs under continuous CW laser irradiation (40 5 nm, >66 kW cm^{-2}). For this study, I synthesized the $(Bmpip)_2Cu_2Br_4$ MCs with the sizes r anging from 50 to 100 μm using the same method, discussed in Chapter 3. Under low-intens ity 405 nm excitation, the as-synthesized MCs exhibit dual green and red emission, as discuss

ed in Chapter 3. I used a band-pass (535-550 nm) and a long-pass (>600 nm) optical filters to isolate the green emission from the surface region and red emission from the inner region of the MC. After deconvolution of the corresponding PL spectrum, two well-defined PL band s with peaks at 540 and 630 nm, respectively, were obtained. Interestingly, under a tightly fo cused laser beam (I = 264 kW cm-2), I observe a large PL intensity enhancement (~10-fold) in the MC, and the green-red color collapses into yellow by 30 minutes of continuous laser irradiation. PL spectral analysis also reveals a change in the PL spectral shape, with a peak at ~600 nm and several weak shoulder peaks. To investigate the STE-based recombination pr ocess, I monitored the time-resolved PL (TRPL) decays before and after laser-induced PL inte nsity enhancement. The TRPL decay analysis reveals delayed emissions with an average lifeti me of 12 ns from the MCs before PL intensity enhancement. Conversely, after PL intensity e nhancement, a fast PL decay with an average lifetime of 2 ns is observed. I obtained PL dec ay curves separately for green and red emission using band-pass and long-pass filters, respecti vely. For the green emission band, the PL lifetime is decreased, and the delayed component disappears after PL intensity enhancement. Although the lifetime of the red emission band is also decreased, the delayed component remains. In these 0D copper halide crystals, the delaye d component is attributed to the STE trapping-detrapping process, which is removed after PL intensity enhancement, leading to an increase in the rate constant of radiative recombination. I investigated the effect of laser excitation intensity on the rate of PL intensity enhancement to determine the threshold for triggering PL intensity enhancement. To get such information, I i rradiated the MCs with a tightly focused laser beam (spot size ~ 3 μm) at different excitation intensities, including 66 kW. cm^{-2}, 132 kW. cm^{-2}, 264 kW. cm^{-2}, 396 kW. cm^{-2}, 594 kW. c m^{-2}. The rate of PL intensity enhancement increases with increasing laser intensity. To evaluat e the reversibility and stability of the PL-enhanced states of the MCs, I irradiated an MC wit h an intense laser beam intermittently (ON: 150 seconds; OFF: 300 seconds) in air. The PL spectra were recorded at 30-second intervals during the ON period, and the PL intensity at 5 90 nm was monitored. The PL intensity was found to be constant during the OFF duration, i ndicating that the MC was in an enhanced PL state even when the laser irradiation was inter rupted. Additionally, I performed the same measurement under an argon atmosphere to assess the effects of moisture and atmospheric oxygen. To examine such influences, the MCs were placed in a closed chamber filled with argon gas. The MCs show similar trends in PL inten sity enhancement under argon as observed in air, ruling out moisture- or oxygen-induced STE emission modulation. I examined the photostability of the PL-enhanced state by measuring th e PL spectra and decays of the MC at 0, 24, 48, and 72 hours after the PL intensity enhanc ement. Although the enhanced PL spectral shape and the decay components of the MC were maintained for 72 hours, the PL intensity gradually decreased over time. The unaltered PL s pectral shape of the MC during this decrease suggests that PL intensity declines due to MC degradation, not due to the reversal to the dual emission state. To understand the mechanism

of PL intensity enhancement, I monitored the time evolution of the PL spectra of the MCs during 55 minutes of laser irradiation. The laser intensity was kept at 66 kW. cm^{-2}. I recorded PL spectra of the MC at 30 s intervals. Initially, the red emission component gradually increased during the first 10 minutes of laser irradiation. Between 10 and 15 minutes, the red emission peak was blue-shifted, accompanied by a continuous increase in PL intensity. Beyond 15 minutes, the PL intensity continued to increase while the spectral shape remained unchanged. To analyze the PL spectral shape evolution in more detail, I deconvoluted the PL spectra obtained at different times using multiple Gaussian functions, indicating that from 1 to 10 minutes, the spectra can be fitted with two peaks at 538.7 nm (green) and 646.9 nm (red). However, after 10 minutes, the PL spectrum cannot be fitted with two components. An additional band at 585 nm was added while retaining the original green and red peaks. Furthermore, the evolution of the full width at half maximum (FWHM) and the PL peak intensity for the three peaks was analyzed at different laser irradiation times. The unchanged FWHM of the three peaks during the PL intensity enhancement suggests stable emissive states without any spectral broadening. The PL peak-intensity analysis shows that the green emission intensity remains constant throughout the enhancement. Conversely, the peak intensities of both the red and yellow emission band increased progressively with increasing laser irradiation time. Initially, the red emission peak intensity increases rapidly, then becomes almost constant between 1 and 20 minutes. Conversely, the yellow emission peak emerged and gradually increased from 10 to 55 minutes. Interestingly, a subtle inversion of the FWHM of the red and yellow peaks was observed over a 10-30 minute period, indicating dynamic changes in the emissive environments. To check the photothermal effect, I examined temperature-dependent PL spectral modulation in the 18-35 ºC range for the as-prepared MCs. At low temperature (<23 ºC), the MCs exhibit intense green emissions, whereas with increasing temperature, the yellow emission peak intensity increases, accompanied by a decrease in green emission intensity. Although the PL decays show progressively faster dynamics with increasing temperature, the temperature-dependent PL modulation is a reversible process below 35 ºC. The MCs melted after increasing the temperature beyond 35 ºC, which excludes the role of the photothermal effect in the PL intensity enhancement process. To investigate the origin of the change in PL color and the PL intensity enhancement, I examined the crystal structure and phase of the MC before and after the PL intensity enhancement. SCXRD analysis indicates that the crystalline phase remains the same before and after PL intensity enhancement, and the experimental XRD pattern shows good agreement in peak positions and relative intensities. To understand the origin of the yellow emission, I irradiated the as-prepared MCs with a 365 nm UV LED light. Under 365 nm excitation, the Pl spectrum shows a broad orange emission band, which can be deconvoluted into two components centered at 585 nm (yellow) and 654 nm (red). Indicating the yellow-emitting state is an intrinsic energy state in the $(Bmpip)_2Cu_2Br_4$ MCs. These findings provide detailed insight into how intense laser irradiation modulates the activation energy barriers amon

g the green, yellow, and red STE states, enabling the reconfiguration of the STE energy land scape.

In chapter 5, I investigated the role of Sb^{3+} doping in the modulation of photophysical pr operties of 0D $(Bmpip)_2Cu_2Br_4$. Heterometal ion doping is an effective strategy in tuning the opto-electronic properties of 0D OIHMHs. Using Sb^{3+} as a dopant is advantageous owing to i ts moderate ionic radius and ability to act as a light-absorption center. Additionally, the ns^2 el ectronic configuration of Sb^{3+} introduces multiple excited states, including the singlet 1P1 state and the triplet manifold (3P0, 3P1, 3P2), enabling efficient energy transfer from the host mat erial to the dopant, thereby improving the overall radiative recombination efficiency of the hos t material. While the previous chapters discuss the roles of substrate interfaces, heat, and laser irradiation in modulating STE emission, the influence of external metal-ion doping on lattice distortion and changes in STE recombination dynamics remains unclear. To address this aspec t, I used SbBr3 as the dopant precursor to investigate modulation of the emission properties a nd systematically varied the amount of SbBr3 to develop Sb-doped crystals with different Sb doping concentrations. I synthesized Sb3+-doped MCs with nominal doping percentages of 2, 2.8, 6, and 8 mol%, using the same synthesis method as for undoped MCs. To investigate o ptical property modulation, I obtained optical microscope and PL images of the undoped and 2.8 mol% doped crystals under ambient light and under a 405 nm CW laser, respectively. Bo th doped and undoped crystals are optically transparent to visible light and exhibit rhombic m orphologies. Under 405 nm laser excitation, while the undoped MCs exhibit green-red dual e mission with two emission peaks at approximately 543 nm and 630 nm, the sb^{3+} doped MCs exhibit dominant orange-red emission with an emission peak at 636 nm. The spectral shape evolution with emission peak shift reveals modulation in the STE recombination pathway. Pho toluminescence excitation spectral measurement reveals a noticeable blue shift in the excitation peak from 331 nm in undoped MCs to 320 nm in the doped crystals, indicating an optical bandgap expansion or PL emission facilitated through a new higher excited state associated w ith Sb^{3+} doping. Conversely, I observed a gradual red shift and spectral broadening with incre asing Sb^{3+} doping concentration. The redshift and spectral broadening are likely associated wit h enhanced exciton-phonon coupling and lattice relaxation, respectively. The coexistence of ex citation blue shift and PL emission redshift corresponds to deeper STE state formation and str onger lattice distortion in the lattice after Sb^{3+} doping. To confirm whether the doping is succ essful or not, I performed multiple characterizations of Sb-doped crystals. I performed scannin g electron microscopy coupled to energy-dispersive spectroscopy, which showed a homogeneo us distribution of Cu, Br, and Sb on the surface of the MCs, confirming the presence of the Sb element on the surface of the crystals. In addition, EDX spectra also exhibit a strong pe ak at 3.6 kV, corresponding to Sb-L_α peak, excluding the possibility of Sb segregation as a s econdary phase. For quantitative detection of actual Sb^{3+} content in the Sb^{3+} doped MCs, I pe rformed coupled plasma optical emission spectroscopy for Sb^{3+}-doped MCs with each doping

concentration. The measurement results reveal that the actual doping concentration is lower tha n the nominal doping percentages, indicating less efficient doping of Sb3+ in the host lattice, attributed to the charge mismatch between Cu^{+} and Sb^{3+}.

Furthermore, X-ray photoelectron spectroscopy confirms the oxidation states of each eleme nt present in the Sb^{3+}-doped MCs. High-resolution XPS analysis confirms the +1 and +3 oxid ation states of copper and antimony. The absence of Cu^{2+} satellite peaks in the Cu-2p region excludes the possibility of Cu^{2+} oxidation. To obtain a deeper insight into the exciton recom bination dynamics, a time-resolved PL decay measurement was performed. The undoped MCs exhibit an average lifetime of 15 ns, with a significant contribution from the fast-decay com ponent, associated with non-radiative recombination. In contrast, the 2.8 mol% Sb^{3+}-doped MC s exhibit an average lifetime of 40 ns, and the contribution from the fast component was dec reased, indicating suppression of non-radiative recombination. To confirm the trend, I collected the average lifetimes of 50 Sb3+-doped and 50 undoped MCs and summarized them in hist ograms. The histogram analysis reveals a pronounced shift towards longer PL lifetimes compa red to the undoped MCs. Furthermore, wavelength-dependent PL decay analysis indicates that the PL lifetimes of both the green and red emission components increase with Sb^{3+}-doping. T hese results suggest that Sb^{3+} doping effectively suppresses the non-radiative recombination acr oss the entire emission spectrum.

Conclusions

In conclusion, the thesis demonstrates the photophysics of optical property modulation in zero-dimensional organic-inorganic hybrid copper halide (OIHCH) microcrystals (MCs) through diff erent strategies, including interactions with various substrates during nucleation and growth, an d by employing heat, laser light, and heterometal ion doping. It is well known that 0D OIH CHs emerge as an ideal candidate for optoelectronic device-based applications due to their ex ceptional optical properties, owing to the formation of self-trapped excitons (STEs) in the latti ce. However, the mechanism of external-stimulus-induced modulation of STE recombination d ynamics and the corresponding changes in the intrinsic lattice dynamics still need further inve stigation, which would enable greater viability for diverse applications. Chapter 3 explores the optical modulation mechanism in green-red dual-emissive 0D (Bmpip)2Cu2Br4 MCs through interactions with borosilicate, Si, Fe, Au, and ITO substrates, and by applying heat. Steady-sta te and time-resolved microspectroscopy analyses reveal that the static charges accumulated on the surface of the MCs modulate the STE emission. Temperature-dependent PL spectroscopy r eveals excitonic coupling with surface and lattice phonons, responsible for the green and red emissions, respectively. Growing crystals on insulating and conductive substrates effectively mo dulates the contribution from surface phonon-exciton coupling, enabling advances in interface-c ontrolled optical functionality. In chapter 4, I demonstrated STE emission modulation mechanis m through interaction with CW laser light. Importantly, laser irradiation activates a new STE energy state by altering the activation energy barriers between multiple STE states, providing i

nsights into the modulation of OIHCH photophysical properties through intense photoexcitation.

In chapter 5, I investigated the mechanism of Sb3+ doping-induced modulation of STE emis sion, suggesting more efficient STE emission through a deeper, lattice-phonon-coupled emissiv e state, as confirmed by the PL peak redshift and increased average lifetime for the Sb^{3+}-dop ed MCs. Overall, this study highlights a crucial role of Sb^{3+} in modulating STE-based emissio n, enhancing emission efficiency and enabling spectral tuning. These findings provide valuable insights into previously unexplored aspects of the photophysics of 0D OIHCHs, offering prac tical strategies for designing and applying next-generation optoelectronic materials.