Microspectroscopic investigations and correlations of photoluminescence in microcrystals, nanocrystals and assemblies of lead halide perovskites

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Microspectroscopic investigations and correlations of photoluminescence in microcrystals, nanocrystals and assemblies of lead halide perovskites

Halide perovskites have become highly cherished material among researchers because of their interesting optoelectronic properties such as long-range carrier diffusion, large absorption coefficient, high defect tolerance, wide and tunable photoluminescence (PL) color, and high PL quantum yield (QY). Further, potential applications of perovskites in photovoltaic and lighting emitting devices are highly promising and competing with the existing semiconductor industry. Motivated by such intriguing properties and potential applications of perovskites, this thesis aims to design and develop close-packed lead halide perovskite (nano or micro) structures that allow for the long-range diffusion of charge carriers. Further, the thesis also demonstrates the applications of such charge carrier properties of lead halide perovskites in electron harvesting and amplified spontaneous emission (ASE). The study is very helpful to understand, on the one hand, the fundamentals of carrier dynamics in lead halide perovskites when the individual crystallites are closely arranged in an assembly and, on the other hand, the applications of these materials in solar cells and lasers.

Lead halide perovskites have the general formula A\(\text{PbX}_3\), where the A-site cation such as \(\text{Cs}^+\), methylammonium (\(\text{CH}_3\text{NH}_3^+, \text{MA}^+\)) or formamidinium (\(\text{CH(NH}_2\text{)}_2^+, \text{FA}^+\)) occupies the octahedral cavities formed by the corner-sharing lead halide octahedra (\(\text{PbX}_6, \text{X=Cl, Br, I}\)). The structure of lead halide perovskites is shown in Figure 1.
Concerning the toxicity of lead, alternatively, different isomorphs of lead halide perovskites are prepared by replacing Pb$^{2+}$ with Sn$^{2+}$, Ge$^{2+}$, Bi$^{3+}$, In$^{3+}$, or Sb$^{3+}$ cations. However, the optoelectronic properties and device performance of lead-based perovskites are superior to all these isomorphs. Being direct band-gap semiconductors, the optoelectronic properties of lead halide perovskites are influenced by the unique band-edge electronic structure, which is mainly contributed by the atomic orbitals of [PbX$_6$]$^{4-}$ octahedra. Therefore, the bandgap and PL color of these materials can be tuned in the entire UV-vis-NIR region through the modulation of valence band minimum (VBM), irrespective of the size and shape, which is simply by changing the halogen composition from Cl to Br and Br to I. On the other hand, the charge carrier properties of lead halide perovskites are influenced by the interplay of bound excitonic and free charge carrier states in bulk and nanostructures. Lead halide perovskite single crystals and films show free charge carrier properties, which dominate over the bound excitons at room temperature as the consequence of low exciton binding energy. The free charge carrier property of halide perovskites is associated with long carrier diffusion length (>145 µm) and delayed PL (several hundreds of ns to µs). Further, the shallow defects and low defect densities in perovskites also help for such a long-range migration and delayed recombination of photogenerated charge carriers with high PLQY.

The isolated nanocrystals and quantum dots (QDs) of these materials, on the other hand, show weak to strong quantum confinement regime in which the carrier recombination is mainly governed by the bound excitonic recombination. Even in such nanocrystals, carrier migration is possible through the hopping of excitons when these tiny crystals are closely-packed into films. In this thesis, I present the study of charge carrier dynamics in lead halide perovskite nanocrystals, microcrystals and their close-packed assemblies. The above brief introduction on
perovskites, literature review, motivation, and objectives of this research are presented in chapter 1.

In chapter 2, I discuss different experimental methods and instrumentation techniques used in this thesis. I prepare the pellets, nanocrystals, microcrystals, and thin films of MA-, FA-, and Cs-based lead halide perovskites by using various novel and established methods. Pellets of MAPbX₃ (X=Cl, Br, I) and bromide-iodide heterojunction perovskites are synthesized by using piezoechemical method, which is a novel method for the synthesis of perovskites. Here, thoroughly mixed precursor salts (MAX and PbX₂) in their solid state are subjected to a hydraulic pressure of 2.4 GPa for 30 min to obtain disk-shaped perovskite pellets. I use antisolvent vapor-assisted crystallization (AVC) method to synthesize MAPbBr₃ microcrystals. Here, the precursor salts (MABr and PbBr₂) are dissolved in N,N-dimethyl formamide (DMF), and dichloromethane (DCM) is used as antisolvent. On the other hand, nanocrystals of MA- and FAPbBr₃ perovskites are synthesized by using ligand-assisted reprecipitation (LARP) method, and CsPbBr₃ perovskites are synthesized by using hot-injection method. I use oleic acid, hexadecyl amine, and n-octylammonium bromide as ligands to cap the nanocrystal surface. Further, I prepare thin films of these perovskite nanocrystals (PNCs) by a drop-cast technique under the ambient condition.

Different instrumentation techniques that are used in this study are UV-vis absorption, steady-state and time-resolved PL, and transient absorption spectroscopies, single-particle microspectroscopy, fluorescence microscopy, powder X-ray diffraction (XRD), and transmission electron microscopy (TEM). I use UV-vis absorption and steady-state fluorescence spectroscopies for the optical characterization of lead halide perovskites. Transmission electron microscopy (TEM) and powder X-ray diffraction (XRD) are used for the morphological and structural characterization of these materials. I use time-resolved PL and transient absorption spectroscopies to study the PL and charge carrier properties of perovskites. During the time-resolved PL measurements, a 400 nm wavelength femtosecond laser with a pulse width of 140 fs and repetition rate of 200 kHz is used to excite the samples in a setup equipped with an inverted microscope, a polychromator, and a streak-camera. The transient absorption studies are carried out by using a 400 nm femtosecond pump (250 Hz, 100 fs)-white light supercontinuum probe setup. Single-particle PL measurements are recorded in an inverted optical microscope, which is equipped with an objective lens (40×, NA 0.60,
Olympus), a 440 nm long-pass filter, and an electron-multiplying charge-coupled device (EMCCD) camera.

In chapter 3, photon recycling by nonradiative energy transfer is demonstrated in lead halide perovskite pellets by piezochemically synthesizing and close packing perovskite crystallites with distinct donor-acceptor states (Figure 2a). This study is the first report on the piezochemical synthesis of lead halide perovskites, where the applied pressure converts the chains of edge-sharing orthorhombic PbX₂ into corner-sharing PbX₆ octahedra. I hypothesize that, under the applied pressure, such transformation is assisted by the deformation of MAX, squeezing out the halide ion to become a part of the octahedra. In parallel, MA⁺ is pushed into the cavity between the octahedra to form a stable perovskite structure. Piezochemical method

Figure 2 (a) PL image of the bromide-iodide (heterojunction) perovskite. The image size is 100 µm×100 µm. (b) PL decay profiles of (i) a pristine MAPbBr₃ and (ii) bromide-rich (green emitting) domain in the heterojunction perovskite pellet. The two decays are collected in the 500-575 nm region. (c) A scheme of photon recycling and energy transfer in the heterojunction perovskite.

not only renders the formation of perovskites from its precursors, but also close pack their crystallites. In such close-packed perovskite structures, photoexcitation may result in the long-range energy transfer either by the photon recycling or the charge carrier migration. Photon
recycling occurs in thick samples of perovskites by repeated self-absorption and re-emission of photons. In this work, efficient nonradiative transfer of excitation energy is realized in a mixed bromide-iodide (heterojunction) perovskite with distinct higher (bromide) and lower (iodide) bandgap domains (Figure 2). Across the bromide-iodide heterojunction, the PL from the donor becomes less and less intense which is accompanied by the more and more intense PL from the acceptor, suggesting energy transfer from bromide-rich to iodide-rich domains. The phenomenon of nonradiative energy transfer is verified by temporally- and spectrally-resolved PL (Figure 2b), where the extremely fast relaxation of photoexcited bromide-rich domain (ca. 1.77 ns) when compared to that of pristine MAPbBr₃ (ca. 15 ns) perovskite is associated with the depopulation of excited state in donor by the efficient nonradiative energy transfer to acceptor across the heterojunction. Therefore, in such heterojunction perovskites, photon recycling by self-absorption of emitted photon alone does not contribute to a fast PL relaxation of the donor. A scheme showing photon recycling by nonradiative energy transfer in piezochemically synthesized bromide-iodide (heterojunction) perovskites is shown in Figure 2c. These results suggest that nonradiative energy transfer plays important roles on photon recycling in close-packed perovskites. Although the migration of charge carriers under photoactivation in these perovskite samples cannot be excluded, based on the fast PL decays of these samples when compared to the films and single crystals of perovskites, one can say that there is no long-range diffusion of charge carriers. One possible reason for this is the dominance of trap states or defects in these samples.

Although piezochemical synthesis is a novel method for synthesizing close-packed perovskite structures which are ideal for studying the energy transfer and the photon recycling processes, the poor migration of charge carriers is not promising for their applications to energy-harvesting and lighting devices. Therefore, in Chapter 4, I assemble PNCs into close-packed films and clusters in which long-range migration of charge carriers and delayed PL occur (Figure 3). Here, I study the clusters and films formed by the ligand-assisted self-assembly of MA-, FA-, and CsPbBr₃ PNCs. While the PNCs in colloidal solution or at the single particle level are stabilized by the capping ligands, the hydrophobic interaction between their long alkyl-chains facilitate the formation of close-packed assemblies on a substrate. The isolated PNCs show short PL lifetime in a colloidal solution (<15 ns) and at the single particle level (ca. 7 ns), whereas in their clusters and films, I detect unusually delayed (>1 μs) recombination of charge carriers at low-intensity excitation, which becomes extremely fast (<<100 μs) at high-
Figure 3 (a) PL decay profiles of a MAPbBr$_3$ PNC film under increasing intensity of excitation laser (0.0024 to 24.00 mJ cm$^{-2}$). (b) Plots of average PL lifetime values and the total number of photons emitted by a MAPbBr$_3$ PNC film as the function of excitation intensity. (c) Scheme of charge carrier diffusion and spatial confinement of charge carriers in a PNC self-assembly.

intensity excitation (Figure 3a). Similarly, with the increasing intensity of excitation, an increase in the number of emitted photons is also observed, which suggests a strong correlation among excitation intensity, the density and diffusion of charge carriers, and the rate of radiative recombination in ligand-assisted self-assemblies of PNCs. Here, as shown in Figure 3b, the number of emitted photons is increased, and the average PL lifetime value is decreased, both nonlinearly with increase in excitation intensity.

The dynamics of charge carriers generated in a PNC film at low- and high-intensity excitations are shown schematically in Figure 3c. Exposure of PNC films to high-intensity laser results in the generation of multitude of charge carriers among different PNCs in the irradiated area. At low-intensity excitation, the density of photogenerated charge carriers is low, minimizing carrier-carrier interactions and allowing for long-range carrier diffusion in the film through interparticle states formed among close-packed PNCs. Because of such a long-range carrier
diffusion, PNC films excited with low-intensity laser show unexpectedly long PL lifetime values. On the other hand, by increasing the intensity of excitation laser, the diffusion of photogenerated charge carriers is spatially confined, which is due to an increase in the carrier concentration. Consequently, the rate of radiative recombination within the irradiated area dominates over diffusion, providing amplified emission. I precisely detect the photoluminescence from an irradiated area or outside and reveal the migration as well as confinement of photogenerated charge carriers in such PNC self-assemblies. Here, the larger average PL lifetime value (>800 ns) and the red-shifted spectrum outside the irradiated area support the diffusion of photogenerated charge carriers from the irradiated to the non-irradiated area. Further, the extent of charge carrier migration across PNCs depends upon how closely the interparticle states formed among nanocrystals are spaced, which is confirmed from the red-shifted PL spectrum and the associated long PL lifetime of a closely-packed PNC film when compared to the loosely-packed films. While such a stabilization of charge carriers at low-intensity excitation is promising for their efficient harvesting in solar cells, the generation and radiative recombination of multiple charge carriers at high-intensity excitation suggest the potential application of PNC assemblies in lighting devices.

While chapters 3 and 4 highlight the implications of photon recycling and charge carrier migration in perovskites; chapter 5 demonstrates the applications of these materials in electron harvesting and ASE. Lead halide perovskites are promising light absorbing materials for solar cells and low-threshold optical gain media for lasing. Here, I show an efficient extraction of the freely diffusing charge carriers generated in a close-packed assembly of PNCs by using Buckminster fullerene (C60) as electron acceptor. I study the electron transfer process from a PNC film to C60 by using time-resolved PL and transient absorption studies. I also discuss ASE in PNC films and isolated microcrystals. The ensemble averaging of PL in PNC films does not offer any spectral narrowing even at very high-intensity excitation. On the other hand, the microcrystals of MAPbBr3 perovskites show temporal and spectral narrowing of PL beyond a certain excitation threshold.

Fullerenes are efficient electron acceptors because of their broad-band absorption in visible to NIR region, high photostability, and ability to accommodate multiple charges. The photoexcitation of C60-doped perovskites results in the separation of charges at the perovskite-C60 interface and the transfer of electrons to the lowest unoccupied molecular orbital (LUMO) of C60, which lies energetically below that of the perovskites, resulting in the quenching of PL.
This quenching of PL is attributed to the additional nonradiative decay channel offered by the C₆₀ which acts as the electron trap. In this work, I confirm electron harvesting from self-assembled PNCs by using C₆₀ by estimating and comparing the PL lifetime values of pristine and C₆₀-doped films of PNCs (Figure 4a). At low-intensity excitation, I estimate the average PL lifetime value at 4.2 µs and 1.06 µs for undoped FAPbBr₃ and MAPbBr₃ PNC films, respectively. When these PNCs are doped with C₆₀, the PL lifetime decreases to 0.28 µs for FAPbBr₃ and 0.5 µs for MAPbBr₃ films. Further, this decrease in PL lifetime is accompanied by the enormous quenching of PL (>90%) which confirms efficient electron transfer from perovskites to C₆₀. Transient absorption studies of these samples, on the other hand, could not detect the C₆₀ radical anion (ca. 1070 nm), which indicates that the electron transfer from PNCs in the film to C₆₀ is occurring outside the time window of the measurement. The efficient harvesting of photogenerated charge carriers from perovskites using C₆₀ can be promising for the development of perovskite-based high efficiency solar cells.

Beside the harvesting of freely diffusing charge carriers from a PNC self-assembly, the multitude of charge carriers generated at high-intensity excitation in these materials can be utilized in lasers for optical gain. PNC films show an amplification of PL under the increasing intensity of excitation, which is the consequence of an increase in the rate of radiative recombination. However, in this study, I could not observe any spectral narrowing from such samples, indicating the ensemble averaging of PL from close-packed PNCs in the film. To

**Figure 4** (a) PL decay profiles of FAPbBr₃ PNC films with and without C₆₀ at low-intensity excitation. (b) PL spectra of a MAPbBr₃ microrod under increasing pump fluence showing ASE. Insets are the PL microscopic images of a MAPbBr₃ microrod (i) before and (ii) after the ASE threshold (68 µJ cm⁻²). Scale bars correspond to 20 µm.
validate the phenomena of ASE and lasing in perovskites, I study MAPbBr$_3$ microcrystals under the increasing intensity of excitation. Beyond a threshold of 68 $\mu$J cm$^{-2}$, ASE is observed from the microcrystals during which PL spectra is characterized by the appearance of a sharp and red-shifted band whose intensity increases nonlinearly and the full width at half maximum (FWHM) decreases with the further increase in the intensity of excitation (Figure 4b). The ASE or lasing from perovskite microcrystals and nanocrystals depend upon the quality of the crystals, which are often challenged by the crystallinity, phase purity, defect density, and thermal and environmental stability. Therefore, high-quality perovskite crystals with excellent PLQY, higher optical gain, and photostability are desirable for observing low-threshold ASE and lasing.

In summary, this thesis describes the study of PL and charge carrier properties of perovskite nanocrystals, microcrystals and their assemblies. While photon recycling by nonradiative energy transfer is revealed in piezoechemically synthesized and close-packed perovskite pellets, charge carrier migration is discussed in self-assembled PNC clusters and films. For the study of nonradiative energy transfer, I prepare a mixed bromide-iodide (heterojunction) perovskite with bromide-rich domain as donor and iodide-rich domain as acceptor. In these samples, photon recycling by nonradiative energy transfer is confirmed by the extremely fast relaxation of photoexcited donor by the efficient energy transfer to the acceptor across the heterojunction. Although photon recycling by nonradiative energy transfer occurs in such perovskite samples with closely-spaced donor-acceptor type states, carrier migration across the crystallites cannot be ruled out. Therefore, I study diffusion and spatial confinement of charge carriers in self-assembled PNC films and clusters as the function of excitation intensity. Unusually long PL lifetime at low-intensity excitation in PNC films and clusters is attributed to the long-range diffusion of low-density charge carriers. On the other hand, spatial confinement of high-density charges is confirmed at high-intensity excitation, where the PL lifetime is extremely short. Moreover, the carrier recombination in these samples is radiative at either low or high-intensity excitation, which is confirmed by the enhancement of PL and an increase in the photon counts under the increasing intensity of excitation. Further, I validate the potential utilization of these close-packed self-assemblies of perovskites in light-harvesting applications by efficiently extracting the photogenerated electrons, which are diffusing among nanocrystals in the film, by employing C$_{60}$ as electron acceptor. I also demonstrate the potential applications of perovskites in lasers by detecting ASE from the microcrystals of lead halide perovskites.