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Title	Microspectroscopic investigations and correlations of photoluminescence in microcrystals, nanocrystals and assemblies of lead halide perovskites [an abstract of dissertation and a summary of dissertation review]
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Degree Grantor	北海道大学
Degree Name	博士(環境科学)
Dissertation Number	甲第13896号
Issue Date	2020-03-25
Doc URL	https://hdl.handle.net/2115/78588
Rights(URL)	https://creativecommons.org/licenses/by/4.0/
Type	doctoral thesis
File Information	Ghimire_Sushant_abstract.pdf, 論文内容の要旨



学 位 論 文 内 容 の 要 旨

博士 (環境科学)

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学 位 論 文 題 名

Microspectroscopic investigations and correlations of photoluminescence in
microcrystals, nanocrystals and assemblies of lead halide perovskites
(ハロゲン化鉛ペロブスカイトのマイクロ結晶、ナノ結晶および集合体の発光挙動に関する
顕微分光学的相関研究)

Lead halide perovskites are greatly attracted to energy-harvesting and light-emitting applications, which is owing to their long-range carrier diffusion, large absorption coefficient, high defect tolerance, wide and tunable photoluminescence color, and high photoluminescence quantum yield. In this thesis, I present the study of the charge carrier dynamics in lead halide perovskite nanocrystals, microcrystals and their close-packed assemblies. While I assign energy transfer and carrier migration to be two important factors which influence charge carrier dynamics in perovskites, I focus my research on electron harvesting and amplified emission in nanocrystals, microcrystals and films of perovskites excited with low- and high- intensity pulsed laser beams. The thesis consists of five chapters. In Chapter 1, general introduction to lead halide perovskites with special reference to their preparation, optical and charge carrier properties, and applications are reviewed. This chapter begins with brief introduction to the crystal structure and characterization of lead halide perovskites. Different wet-chemical and mechanochemical routes, such as ligand-assisted reprecipitation, hot-injection, antisolvent vapor crystallization, one-step or sequential deposition, hand grinding and ball-milling techniques for the synthesis of perovskite nanocrystals, microcrystals and thin films are discussed. Next, the optical properties of perovskites are discussed by referring to the influences of composition, temperature and pressure on the electronic band structure of perovskites. The charge carrier dynamics in perovskites are reviewed in terms of monomolecular, bimolecular and trap-assisted recombination, which is followed by an overview of the solar cell and lasing applications of these materials. Finally, the motivation and the main objectives of my research are stated. Chapter 2 is the experimental section which includes various materials and methods used in this thesis. In the study, I synthesize the close-packed pellets, microcrystals, nanocrystals, clusters and thin films of perovskites by solid-state and wet-chemical methods. I introduce piezochemical method as the new solid-state method for the synthesis of pure methylammonium lead or mixed bromide-iodide perovskites. I prepare nanocrystals of methylammonium, formamidinium, or cesium lead bromide perovskites by ligand-assisted reprecipitation and hot-injection methods. Successively, these nanocrystals are self-assembled into clusters and thin films. On the other hand, the microcrystals of methylammonium lead bromide perovskites are obtained by antisolvent vapor-assisted crystallization. I characterize these perovskite samples by X-ray diffraction, UV-visible and steady-state photoluminescence spectroscopic techniques, single-particle microspectroscopy, transmission electron

microscopy, and fluorescence microscopy. The charge carrier dynamics are studied by time-resolved photoluminescence and transient absorption spectroscopic techniques. In Chapter 3, I study photon recycling and energy transfer in piezochemically-synthesized closely-packed perovskite crystallites. In such closely-packed perovskite structures, a nonradiative energy transfer among different crystalline domains through the distributed energy states is obvious. I construct a distinct band gap heterojunction of a mixed bromide-iodide perovskite to confirm the nonradiative energy transfer from bromide- to iodide- rich domains and its role on photon recycling. The fast relaxation of photoexcited donor (bromide-rich domain), which is associated with the depopulation of its excited state by the acceptor (iodide-rich domain) confirms nonradiative energy transfer across the heterojunction. However, I do not rule out the carrier migration among closely-packed crystallites through the distributed band gaps in these samples. To study the carrier migration in close-packed perovskite structures, in Chapter 4, I arrange the perovskite nanocrystals in self-assembled clusters and films. The low-intensity excitation of closely-packed perovskite nanocrystals renders delayed photoluminescence (>1 microsecond) which is attributed to the long-range diffusion of photogenerated charge carriers. On the other hand, a multitude of charge carriers are photogenerated in the closely-packed perovskite nanocrystals at high-intensity excitation. The high-density charges are spatially confined, resulting in the high rate of radiative recombination and amplified photoluminescence. Besides carrier migration, photon recycling by reabsorption-emission in such closely-packed perovskite self-assembly may complicate the carrier dynamics. To confirm the diffusion of photogenerated charge carriers in such self-assembled structures of perovskite nanocrystals, in Chapter 5, I efficiently extracted photogenerated electrons from photoactivated perovskite nanocrystal films by doping with Buckminster fullerene. Here, the electron transfer from perovskite nanocrystals to fullerene is obvious from the enormous decrease of photoluminescence intensity and increase in the rate of carrier relaxation in fullerene-doped nanocrystal film when compared to the pristine film. These results also demonstrate the harvesting of charge carriers from a photoexcited perovskite self-assembly, which will have important implications to the development of high-efficiency solar cells. While the delayed recombination of charge carriers is promising for their efficient harvesting in solar cells, the generation and radiative recombination of multiple charges at high-intensity excitation suggest the potential application of perovskite nanocrystal assemblies in amplified spontaneous emission and lasing. However, in this study, the ensemble averaging of photoluminescence from the self-assembled perovskite nanocrystals does not show any spectral narrowing or the signature of amplified spontaneous emission. Therefore, in Chapter 5, I also discuss the importance of well-defined optical cavity for amplified spontaneous emission and lasing by demonstrating amplified spontaneous emission from the isolated microcrystals of methylammonium lead bromide perovskites. I estimate the threshold of amplified spontaneous emission at $68 \mu\text{Jcm}^{-2}$. In short, the thesis develops close-packed lead halide perovskite structures that allow for the nonradiative energy transfer, and multiplication and long-range migration of charge carriers. While nonradiative energy transfer among closely-packed heterojunctions plays an important role on photon recycling, the long-range carrier diffusion at the low-intensity and the multiplication of charge carriers at high-intensity excitation are important for carrier harvesting in solar cells and amplified emission in lasers.