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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士（理学）　氏名　ジャイカイ　チェン

学 位 論 文 題 名

Synthesis and Surface Modification of Formamidinium Tin Iodide Perovskite Crystals
（ホルムアミジニウムヨウ化錫ペロブスカイト結晶の合成と表面修飾）

Lead halide perovskites have aroused intense scientific attention in recent years owing to their low cost and outstanding optoelectronic properties, which lead them to applications in high-efficiency solar cells, light-emitting diodes, single-photon sources, lasers, and so on. A major application limit for lead halide perovskites is the presence of the highly toxic lead element, raising critical concerns of environmental pollution and health problems. To address this issue, developing lead-free halide perovskites have been in the forefront of the current research. Tin halide perovskites thus have come under the spotlight by virtue of their low toxicity and eco-friendly merit and tantalizing photophysical properties.

Organic-inorganic hybrid tin halide perovskites, especially formamidine tin iodide (FASnI3), have emerged as a promising semiconductor material for a range of optoelectronic applications. For example, the power conversion efficiency of solar cells based on FASnI3 as light-absorber has reached over 14%, gradually narrowing the gap with their lead counterpart. However, the structure-photophysical property relationship remains ambiguous owing to the ready occurrence of structural defects in the fragile lattice of FASnI3, and the synthesis of highly luminescent colloidal nanocrystals (NCs) is still a long-standing challenge due to the lack of a fundamental understanding of how to rationally suppress the formation of intrinsic as well as surface structural defects.

To address the above issues, this thesis aims at getting insight into the defect behaviors in the photophysical properties of FASnI3 crystals, and developing effective synthesis routes, including judiciously adopting Sn-rich reaction condition as well as regulating surface conditions by appropriative ligands, for obtaining high-quality FASnI3 crystals with great optical properties.

Chapter 1 provides a general background about metal halide perovskites. Particularly, I critically summarize and assess the latest advances in the synthesis approaches of tin halide perovskite NCs. The state-of-the-art preliminary studies in modulating their photophysical properties and in enhancing the stability with a variety of strategies are also concluded. In addition, the remaining challenges that need to be overcome to attain high-quality tin halide perovskite NCs are also highlighted. Finally, the purposes regarding my research and the framework of whole research topic are clarified.

Chapter 2 shows the defect behaviors in the photophysical properties of FASnI3. Using FASnI3 microcrystals synthesized with tailored reaction conditions as the model systems, I unveil that structural defects can induce bandgap widening and abnormal photoluminescence. Based on combined analysis of X-ray photoelectron spectroscopy, solid nuclear magnetic resonance, and optical spectroscopy, I propose that bandgap widening could stem from defect-mediated lattice distortion. Temperature-dependent photoluminescence measurements lead me to the discovery of a new near-infrared photoluminescence band between 185 and 10 K and negative thermal quenching in a broad range of 110∼200 K, both of which are associated with structural defects.

Chapter 3 develops an innovative surface capping ligand, zwitterionic phosphatidylcholine, replacing traditional amine ligands for the synthesis of colloidal FASnI3 NCs. By introducing a small amount of phosphatidylcholine in the reaction, the particle size of FASnI3 crystals could be reduced from several hundred nanometers to around 30 nanometers. Three phosphatidylcholines with different chain lengths were studied, and all of them could produce small-size, uniform-morphology FASnI3 NCs. A maximum PLQY of 1.2% was achieved by reasonably tuning the reaction parameters. Importantly, stability tests reveal that phosphatidylcholine-capping FASnI3 NCs have excellent long-time colloidal stability and structural stability in glovebox, indicating that as-prepared NCs could serve as an ideal platform for the future exploration of their potential optoelectronic applications.

Chapter 4 proposes a general one-pot surface modification strategy for highly luminescent organic-inorganic hybrid tin iodide perovskite NCs. Guided by density functional theory (DFT) calculations, I predict that, highly luminescent FASnI3 NCs could be obtained through meeting three important factors: Sn-rich reaction condition; quasi-AI-terminated surface; suppression of surface iodine vacancies. After creating a Sn-rich reaction condition through simply tuning the reactant ratio, large-sized organic ammonium and alkali metals are used for constructing a quasi-AI-terminated surface. By this means, high-efficiency near-infrared emitting FASnI3 NCs with a maximum PLQY of $36.9 \pm 0.7\%$, which is over 50 times larger than those previously reported, can be obtained. A wide range of optical and structural characterizations, coupled with DFT calculations, clarify that NC surface is modified by organic ammonium and alkali metal ions. Finally, I showcase the generalizability of our concept by further demonstrating the synthesis of highly luminescent FA0.9Cs0.1SnI3 and FA0.8Cs0.2SnI3 NCs which have better tolerance factors, benefiting the future application explorations.

Chapter 5 summarizes the above research findings, and provides an outlook on the unresolved challenges for tin halide perovskites, as well as offers my perspective on how to achieve stabler, higher-quality, device-applicable FASnI3 crystals.

In conclusion, this thesis focuses on the synthesis chemistry, surface modification, and structural characterization of FASnI3 crystals, uncovering the relationship between defect and photophysical properties, offering feasible synthetic roadmap to prepare high-quality FASnI3 crystals. The knowledge gained here may help others better understand the structural properties of tin halide perovskites, and inspire their explorations on related high-performance optoelectronic devices.