

Improving the films quality of Sn-based perovskites through additive treatment for high-performance light-emitting diodes

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Hybrid lead halide perovskites have received great attention in the field of light-emitting diodes (LEDs) owing to their excellent optoelectronic properties, low cost, and high color purity. To date, the external quantum efficiency (EQE) of lead halide perovskites LEDs has been reported to exceed 20%^[1]. Even so, the toxicity of conventional lead has cast a gloomy shadow over their further application. Fortunately, tin (Sn)-based perovskite are promising for realizing high performance non-toxicity perovskite LEDs due to their environment-friendly and similar optoelectronic properties to lead-based perovskites^[2, 3]. However, there are many challenges in preparing quality thin films for superior Sn-based devices. First, due to the lower thermodynamic stability, Sn²⁺ tends to form the Sn⁴⁺ oxidation state. Then, the rapid crystallization of the Sn-based perovskite results in low surface coverage^[4–6]. To address the above problems, tremendous efforts have been devoted, including solvent engineering^[7, 8], low/mixed dimensional perovskite designs, surface coordination based on the perspective of Lewis acid–base coordination, reducing or antioxidants agent assistance^[9], composition regulation. Even so, how to effectively avoid the formation of defects is still unclear. In addition, achieving efficient Sn-based perovskite LEDs remains a major challenge, with a recorded EQE of just over 5%^[10].

Following this line of thought, Wang *et al.* reported an efficient near-infrared Sn-based perovskite LEDs with an EQE of 8.3% by additive treatment, and they revealed that major defects in the films were formed instantaneously during the rapid aggregation of clusters at the initial growth process by using *in-situ* spectroscopy (*Nat. Photonics*, <https://doi.org/10.1038/s41566-023-01231-y>)^[11]. According to the test results of photoluminescence (PL) measurements, the crystallization process of perovskite can be divided into three stages (Fig. 1(a)). During spin-coating, with the removal of solvent molecules, many nucleation sites can be formed (Phase I), followed by a rapid aggregation of perovskite clusters (Phase II). This process involves the fall off of plenty solvent ligands, and many defects can be formed along with the imperfect stacking of perovskite clusters, which leads to severe PL quenching. During the sequential growth process (Phase III), some internal lattice defects can be eliminated by rearrangement or recrystallization of nanoparticles, but most bulk defects will be maintained.

After revealing the mechanism of defect formation, the authors introduced the additives PEAI-Vitamin B1 (VmB1) into

the precursor solutions to form a strong interaction with SnI₂, which effectively prevent the fast aggregation of clusters and avoid the formation of luminescence quenchers (Fig. 1(b)). Specifically, after introducing the PEAI, the weak interaction between PEAI and [SnI₃]_n[−] can partially block this aggregation process. In addition, the strong interaction between the VmB1 additive and SnI₂ can delay the nucleation process. And the VmB1 ligands can significantly inhibit the aggregation of perovskite nanocrystals due to the steric hindrance effect. Thus, through the combined action of PEAI and VmB1, the homogeneous nucleation and initial aggregation can be greatly suppressed. In addition, both PEAI and VmB1 additives can significantly suppress the oxidation of Sn²⁺. On this basis, the prepared LED demonstrates excellent performance. The device shows a maximum radiance of ~12 W/(sr·m²), and reaches a peak EQE of 8.3% with an emission peak at ~894 nm, representing a record EQE of Sn-based perovskite LEDs.

The research highlights of this work are mainly reflected in three aspects, revealing the formation mechanism of Sn-based perovskites defects, introducing additives to inhibit defect formation and breakthrough in device performance. In particular, the research results of defect formation mechanism break through the bottleneck of Sn-based perovskite development for a long time, and it provides theoretical support for the subsequent improvement of film coverage and crystallization quality. The research results obtained in this paper fill the gap in the synthesis mechanism of Sn-based perovskite, which is conducive to the preparation of quality Sn-based materials, and lay a foundation for the improvement of device performance.

Due to the same lone-pair s orbitals, the Sn analogues have similar band and electronic structures, and remarkable optoelectronic properties to the lead-based perovskites^[12]. In addition to LEDs field, it has also been widely studied in the field of solar cells^[13] and photodetectors^[14]. Similarly, the lower stability and low surface coverage of Sn-based films lead to poor stability of the devices, and it is difficult to improve the performance. In addition, the measurements of most of the reported work were performed in a nitrogen filled glovebox, which is not conducive to practical application^[14, 15]. Therefore, the results obtained in this paper are significant. The above research results provide guidelines for preparing high-quality Sn-based perovskite optoelectronic devices, including solar cells, photodetectors, and LEDs. From a long-term perspective, the improvement of device performance and long-term stability will also be the research focus. For example, the high efficiency devices reported in the literature are mostly instantaneous result, and the efficiency of the devices will decrease after multiple tests. Additionally, the

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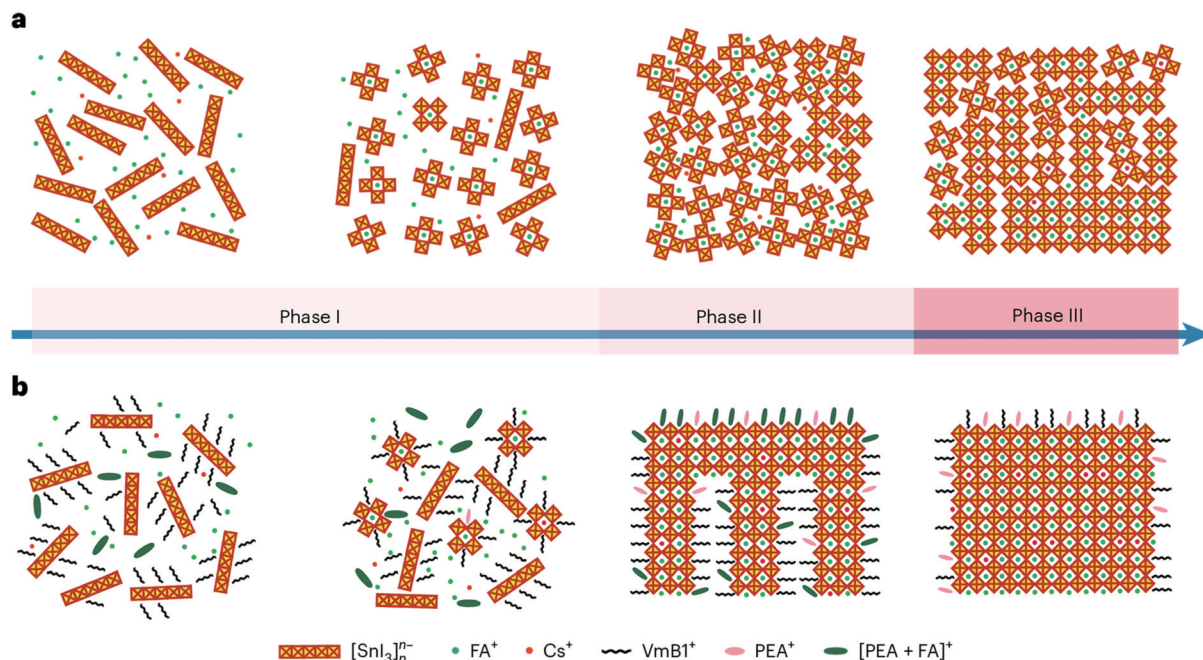


Fig. 1. (Color online) Schematic illustration of the growth pathways of $\text{FA}_{0.9}\text{Cs}_{0.1}\text{SnI}_3$ perovskites without additive or with PEAI-VmB1. (a) Without additive. This shows notable aggregation during the initial growth, resulting in many defects. (b) With PEAI and VmB1. This shows that the VmB1 ligands can effectively suppress aggregation, facilitating oriented growth with the assistance of PEAI in sequential growth^[11].

ambient atmosphere of the glove box has a great influence on the device, resulting in poor repeatability of the high-efficiency device. Reasonable modification or passivation of perovskite interface, mixed halogen doping for functional design, and development of new additives for defect passivation may be the effective ways.

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