All-inorganic perovskite solar cells with efficiency >20%

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The power conversion efficiency (PCE) of organic-inorganic hybrid metal halide perovskite solar cells (PSCs) has rocketed from around 3% to more than 25% in a decade, showing a miracle in the development history of photovoltaics [1]. However, the hybrid perovskites still suffer from the issue of thermodynamic instability due to the volatile organic cations in perovskites. All-inorganic metal halide perovskites, in which the organic cations of the hybrid perovskite are substituted with cesium ions such as CsPbX_3 ($X = \text{Cl, Br or I}$), would address the issues above. Thereinto, CsPbI_3 with the perovskite structure has been considered as one of the ideal photovoltaic absorbers for high-efficiency solar cells due to the suitable bandgap (~ 1.7 eV). Nevertheless, the perovskite structure (namely black phase) of CsPbI_3 is only maintained at high temperatures (175–360°C) because of the small radius of Cs^+ ions. At room temperature, the black phase is easily converted to the non-perovskite yellow phase ($\delta\text{-CsPbI}_3$) [2].

To stabilize the perovskite structure of CsPbI_3 , the bromine ions was early introduced to form mixed halide perovskites such as CsPbI_2Br and CsPbIBr_2 . But this strategy widened the bandgap of the inorganic perovskites, thus sacrificing the light harvesting range and photogeneration current density. To date, the efficiency of the champion $\text{CsPbI}_{3-x}\text{Br}_x$ (x varies from 0.3 to 0.5) solar cell is around 18% [3]. In addition to composition engineering, dimensional engineering is also used to improve the black phase stability due to that the small sized crystals could stabilize the black phase by large surface energy. Swarnkar *et al.* [4] developed CsPbI_3 quantum dot solar cells with an efficiency more than 10%. But the charge mobility of quantum dot films is suppressed by the organic ligands on the surface of quantum dots. Although the surface ligand exchange [5] and metal-ion doping [6] have been introduced to improve the

mobility and collection of carriers, the efficiency of the state-of-the-art CsPbI_3 quantum dot solar cell is much lower than 20%. In short, the fabrication of stable CsPbI_3 bulk film is still considered as the most promising approach for achieving high-efficiency devices with PCE of over 20%. As early as 2015, Snaith and coworkers [7] stabilized the black phase of CsPbI_3 films *via* a solution process by adding HI into the precursor solution, which shrinks the grain size of the perovskites. The subsequent studies demonstrated that HI induced decomposition of *N,N*-dimethylformamide (DMF) to form cationic dimethylammonium (DMA) in the precursor solution, which is beneficial for stabilizing the black phase structure of CsPbI_3 [8]. Zhao and co-workers [9,10] adopted the additive of dimethylammonium iodide (DMAI) to achieve high-efficiency CsPbI_3 solar cells with PCE more than 19%. They also demonstrated DMAI is an effective volatile additive rather than dopant [10].

In a recent work published in *Joule* by Sang II Seok and co-workers [11], the efficiency of the CsPbI_3 solar cell reached more than 20%. In this work, DMAI was introduced into the precursor solution, and meanwhile, the sequential dripping of a methylammonium chloride (MACl) solution was used to control the intermediate stage of the crystallization process. In this process, MACl promoted the sublimation of DMAI during annealing by interrupting the coordination of intermediate states, leading to the rapid crystallization of perovskite layers (Fig. 1a). The thermogravimetric analysis (TGA) demonstrated that the addition of MACl promoted the sublimation of DMAI (Fig. 1b). As a result, the PCE of the champion solar cell was up to 20.37% (Fig. 1c).

Recently, Meng and co-workers [12] reported CsPbI_3 solar cells with high efficiency (>20%) and long-term stability. They developed a strategy of urea-ammonium thiocyanate (UAT) molten salt modification to obtain

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Figure 1 (a) Diagram of the fabrication process of CsPbI₃ film, (b) TGA curves and (c) *J*-*V* curves of the control and target CsPbI₃ solar cells. Reprinted with permission from Ref. [11]. Copyright 2020, Elsevier Inc. (d) PCE tracking of the CsPbI₃ solar cell over 1000 h under a steady-state bias voltage of 0.9 V and a continuous white LED light illumination. (e) PCE tracking over 1000 h for the unencapsulated CsPbI₃ solar cell stored in ambient and dark conditions. Reprinted with permission from Ref. [12]. Copyright 2020, Wiley-VCH GmbH.

high-quality CsPbI₃ films on the basis of the additive of DMAI. The UAT was formed through the hydrogen bond interaction between urea and NH₄⁺ from NH₄SCN. Thus, the SCN⁻ coordinated with the Pb-I octahedrons, which decreases defects of the perovskite film. As shown in Fig. 1d, the device was subjected to PCE tracking for over 1000 h at a steady-state bias voltage of 0.9 V under a

continuous white light-emitting diode (LED) illumination, indicating excellent work stability. In addition, after 1000 h of storage in ambient and dark conditions (temperature: 25°C, relative humidity: 20%–30%), the unencapsulated cell retained 89% of its initial PCE (Fig. 1e).

The recent studies make us believe that more and more stable inorganic perovskite solar cells with efficiency over

20% will be reported. The study of high-performance all-inorganic perovskite devices will enter a prosperous period.

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