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Highlight

Omnidirectional annealing process for scalable perovskite films

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Abstract: Halide perovskites are promising photovoltaic materials due to the outstanding photoelectric properties and low-cost solution process; however, the low scalability and reproducibility of perovskite films hinder the commercialization. Liquid medium annealing (LMA) method has provided a robust liquid environment and an omnidirectional heating field to modulate the growth of perovskite films for high quality with low defect density, desirable stoichiometry, high homogeneity, and less environmental influence. The fabricated perovskite solar cells exhibited excellent reproducibility and power conversion efficiencies exceeding 24.04% with 0.08 cm^2 area and 23.15% with 1 cm^2 area.

Keywords: halide perovskite; scalable and reproducible fabrication; liquid medium annealing

Perovskite solar cells (PSCs) have attracted great attention due to high power conversion efficiency (PCE), low-cost, and simple fabrication process. The PCE has boosted 25.7%, compared to the commercial silicon solar cells [1–2]. The scalable fabrication of PSCs is the prerequisite for their commercialization. Grätzel's group developed a fully printable PSC with $(HOOC(CH_2)_4NH_3)_2PbI_4/CH_3NH_3PbI_3$ hybrid perovskite and achieved 11.2% efficiency for 100 cm^2 modules [3]. Solaronix in Switzerland produced all-printed 500 cm^2-area PSC modules with 12% efficiency [4]. Huang's group employed the surfactant-assisted blade coating method for the perovskite solar module and achieved an active area of >33 cm^2 and an efficiency of 15.3% [5]. However, the inferior PCE of large-scale PSCs hinders the commercialization.

Large-scale polycrystalline perovskite films are endowed with ohmic loss and defects as charge recombination centers [6]. Thus, their manufacturing process must be improved to produce scalable and reproducible devices without obviously sacrificing the PCE. The fabrication of scalable perovskite films is usually composed of sequential processes of scalable deposition and heat treatment. In the scalable deposition process, the commonly used solution deposition methods, such as blade coating and slot-die coating, are economical and beneficial for the commercialization of PSCs [7]. Vapor-phase deposition using solid precursors is a solvent-free, environment-friendly technique with precisely controlled components [8]. In conventional heat treatment, numerous defects are inevitably formed by unfavorable loss in volatile components, resulting in substantial inhomogeneity in the large area film.

A method of liquid medium annealing (LMA) that can modulate crystal growth in heat treatment was developed to produce scalable and reproducible halide perovskite films [9]. The liquid medium of anisole with high thermal conductivity of 0.137 W/(m·K) and low viscosity of 0.99 mPa·s at 20°C provides a uniform temperature field that allows for omnidirectional and fast heating, especially "top-down" heat transfer (Fig. 1(a)). According to the finite element analysis, the perovskite film by LMA took only ~4 s to reach 141°C while the film with the conditional bottom-up annealing required ~13 s to reach 140°C. The high heating rate in the initial stage can largely accelerate the diffusion of reactants and promote the grain growth rate. The residual solvent, such as dimethyl sulfoxide (DMSO), is easily to be extracted from the dry perovskite film, which could provide sufficient reactants to participate in crystal growth (Fig. 1(b)), resulting in high-quality perovskite films with the grain size of (2.25 ± 0.66) mm.

Meanwhile, the liquid medium creates a robust microenvironment in which to inhibit volatile component evaporation, such as MA^+/FA^+ and I^-, and form desired stoichiometry during annealing process, ensuring superior uniformity and decreasing the defect density of the films (Fig. 1(b)). Therefore, the PSCs achieve the champion PCE of 24.04% with the area of 0.08 cm^2 and PCE of 23.15% with the area of 1 cm^2 (Fig. 1(c)). This is the smallest efficiency gap between small and large-area devices ever reported, demonstrating the potential of scalable device with this method.

Furthermore, because of the sensitivity of perovskite to moisture and oxygen, the perovskite film with the conven-

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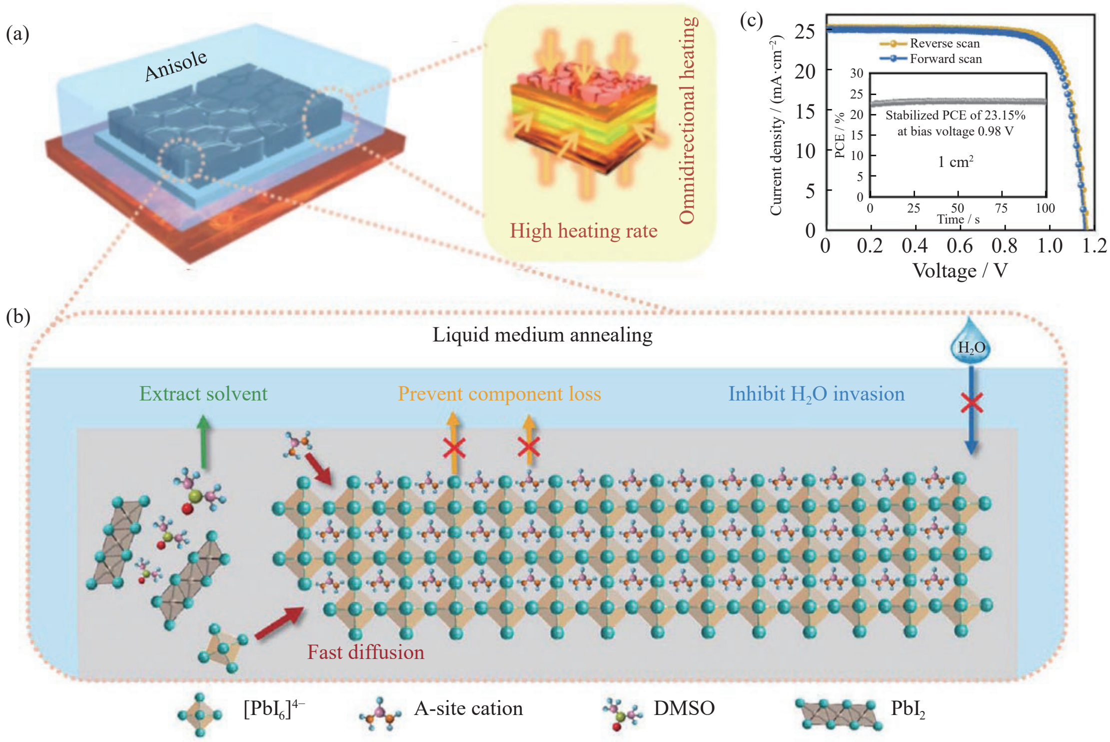

Fig. 1. (a) Illustration of the LMA method with anisole as liquid medium; (b) growth process of the stoichiometric perovskite crystal without the influence of atmospheric environment; (c) current density-Voltage curve of the LMA-based PSC with the area of 1 cm^2. Inset: Stabilized PCE at the maximum power point tracking under 0.98 V bias. From N.X. Li, X.X. Niu, L. Li, *et al.*, *Science*, 373, 561-567 (2021) [9], Reprinted with permission from AAAS.

tional annealing in the atmosphere shows bad reproducibility. Instead of the expensive control of the annealing atmosphere, the perovskite film prepared with the economical LMA method is immersed in the liquid anisole, showing less influence of the fabrication climate (Fig. 1(b)). Thus, the LMA-based PSCs have the average PCE of >23% and show good reproducibility of perovskite photovoltaics.

In summary, the commercial application of PSCs largely depends on the scale and reproducible fabrication of high-quality perovskite films. The LMA method provides a uniform temperature field to omnidirectional heat perovskite film, avoids the evaporation of volatile component in perovskite, and effectively inhibits the influence of water, oxygen in the atmosphere on perovskite film, resulting in the high-quality perovskite film with good scalability and reproducibility. This work elucidates a promising route to fabricate the commercial perovskite film and photovoltaic devices. To realize the full potential of commercialization of perovskite photovoltaic, more efforts should also be paid, such as the composition and crystal structure design of perovskite materials, interfacial engineering, and packaging technology.

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Conflict of Interest

The authors declare no conflict of interest.

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