



Research Highlight

Oxygen makes better inorganic perovskite solar cells

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Halide perovskites have attracted enormous attention and made great progress recently, especially in photovoltaic field. Compared with the widely used hybrid organic-inorganic halide perovskites (HHPs), all-inorganic halide perovskites (IHPs) have the following unique advantages: (i) high thermal stability due to the replacement of volatile organic cations with inorganic cations such as Cs⁺; (ii) high chemical stability with no concerns about the deprotonation of the organic components under the effect of oxygen and light illumination [1,2].

The above excellent stabilities enable the fabrication of IHPs-based devices in dry air atmosphere [3]. Zhao's group [4] reported that CsPbI₃ perovskite solar cells (PSCs) fabricated in a dry box with a <10% relative humidity (RH) delivered a certified efficiency over 18% in early 2019. Very recently, they achieved the record efficiency over 19% via ambient processing [5]. Liu's group [6] reported an efficiency of 12.5% for large-area CsPbI₂Br PSCs fabricated in ambient condition. Although all these high-efficiency devices are fabricated in air atmosphere, how the air atmosphere affects the performance of PSCs is seldom investigated in depth. A few literatures reported that the adsorbed oxygen molecules can passivate the surface defects in HHPs [7]. However, the mechanism of oxygen passivation for perovskites, especially for IHPs, is still unraveled [4].

In a recent paper, Profs. Ding-Jiang Xue and Jin-Song Hu at the Institute of Chemistry, Chinese Academy of Sciences (ICCAS) systematically investigated the passivation effect of oxygen on IHPs [8]. The authors chose CsPbI₂Br as an ideal candidate to investigate the passivation effect of oxygen due to its higher moisture tolerance than CsPbI₃ and more suitable bandgap than CsPbBr₃. Theoretical simulation and experiments found that oxygen molecule adsorbed on halide vacancies of CsPbI₂Br and could dissociate into O atoms with a low reaction barrier (0.392 eV) during annealing process. Together with the results of X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (ToF-SIMS), it was concluded that two forms of oxygen existed in CsPbI₂Br thin films prepared under ambient condition (RH < 15%): adsorbed oxygen molecules on surface and dissociated oxygen atoms in form of Pb–O throughout the film after annealing (Fig. 1a).

The steady-state photoluminescence (PL) measurement was carried out on two sides of the films (Fig. 1b). For the reference film prepared in N₂ atmosphere (N₂-CsPbI₂Br), the PL emission collected at the film side displayed a slight blue-shift compared with that collected at the glass side, which should be ascribed to the passivation of adsorbed oxygen molecules on the top. In contrast, for the film fabricated in air (air-CsPbI₂Br), the significantly blue-shifted PL peaks with much stronger intensity indicated that the passivation of dissociated oxygen atom was much more effective than that of adsorbed oxygen molecules. The PL peak position and intensity were independent of the excitation light directions for air-CsPbI₂Br, suggesting that the entire film was passivated by the dissociated oxygen atoms. Such passivation mechanism was further rationalized by theoretical calculation: the oxygen atom interacted with perovskite more effectively than oxygen molecule at halide vacancy, leading to a better passivation effect. As a result, the power conversion efficiency (PCE) and stability were significantly enhanced for air-CsPbI₂Br based solar cells compared with N₂-CsPbI₂Br devices (Fig. 1c).

In contrast, high-efficiency HHPs based solar cells are seldom fabricated in ambient conditions although the adsorbed oxygen molecules are reported to be able to passivate the surface defects in HHPs [7]. The fast degradation can be seen when HHPs are exposed to oxygen and light. It is believed that the highly reactive superoxide species generated by the reaction of oxygen molecule and photoexcited electron and their fast diffusion in HHPs mediated by halide vacancies should be responsible for the degradation of organic moieties [1,2]. The key point of ambient fabrication of HHP film and devices might be the exclusion of light illumination before the dissociation of oxygen molecules into oxygen atoms. While the halide vacancies are passivated by oxygen atoms and the formation of superoxide species are prevented, the degradation pathway will be significantly inhibited. Therefore, the knowledge from this work and the related references gives the clues for the ambient processing of not only IHP but also possibly HHP optoelectronics with improved stability.

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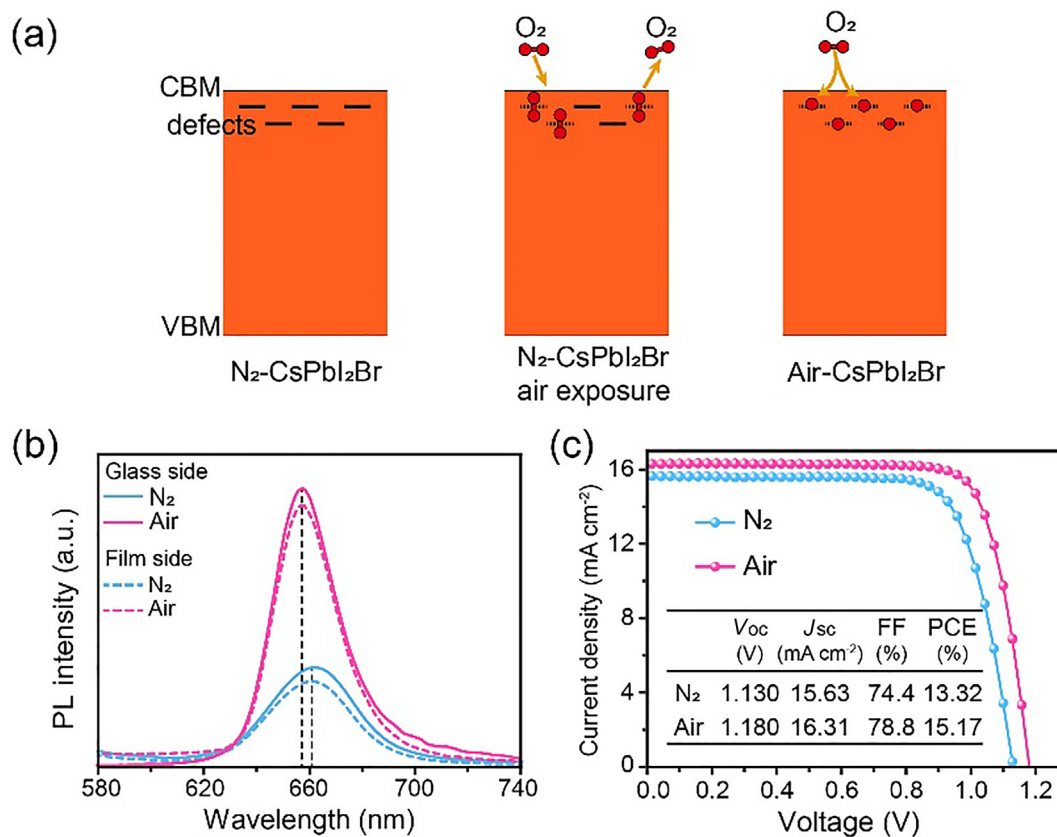


Fig. 1. (a) Schematic of adsorbed oxygen molecules passivation and oxygen atoms passivation. (b) Steady-state PL spectra from glass side and film side. (c) The current density-voltage (*J-V*) curves and photovoltaic performance of the two devices. (b) and (c) are adapted with permission from Ref. [8], Copyright 2019 ACS.

Conflict of interest

The author declares that he has no conflict of interest.

References

- [1] Aristidou N, Eames C, Sanchez-Molina I, et al. Fast oxygen diffusion and iodide defects mediate oxygen-induced degradation of perovskite solar cells. *Nat Commun* 2017;8:15218.
- [2] Aristidou N, Sanchez-Molina I, Chotchuangchutchaval T, et al. The role of oxygen in the degradation of methylammonium lead trihalide perovskite photoactive layers. *Angew Chem Int Ed* 2015;54:8208–12.
- [3] Zhou Y, Zhao Y. Chemical stability and instability of inorganic halide perovskites. *Energy Environ Sci* 2019;12:1495–511.
- [4] Wang Y, Dar MI, Ono LK, et al. Thermodynamically stabilized β -CsPbI₃-based perovskite solar cells with efficiencies >18%. *Science* 2019;365:591–5.
- [5] Wang Y, Liu X, Zhang T, et al. The role of dimethylammonium iodide in CsPbI₃ perovskite fabrication: additive or dopant? *Angew Chem Int Ed* 2019;58:16691–6.
- [6] Fan Y, Fang J, Chang X, et al. Scalable ambient fabrication of high-performance CsPbI₂Br solar cells. *Joule* 2019;3:2485–502.

- [7] Fang H-H, Adjokatse S, Wei H, et al. Ultrahigh sensitivity of methylammonium lead tribromide perovskite single crystals to environmental gases. *Sci Adv* 2016;2:e1600534.
- [8] Liu S-C, Li Z, Yang Y, et al. Investigation of oxygen passivation for high-performance all-inorganic perovskite solar cells. *J Am Chem Soc* 2019;141:18075–82.



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