

Defect engineering on all-inorganic perovskite solar cells for high efficiency

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Perovskite solar cells based on organic–inorganic hybrid perovskite materials have become a research hotspot in photovoltaics field due to their outstanding power conversion efficiency (PCE)^[1]. Nonetheless, the organic cations are volatile and have rotation freedom, which is not good for photo- and thermal-stability of the devices. Fortunately, these issues can be solved by all-inorganic perovskites, which consist of Cs, Pb and I (or Br)^[2, 3]. Moreover, the all-inorganic perovskites, such as CsPbI₃, are excellent candidates as top-cell absorbers in tandem solar cells because of their suitable bandgaps and high stability. All-inorganic perovskites were first used as light absorbers in solar cells in 2015^[4, 5]. All-inorganic perovskite solar cells experienced rapid development in last few years, and the PCE reaches 20.4% at the end of 2020^[6]. Most recently, Meng *et al.* pushed the PCE to >21.0% (unpublished). Despite these advances, we should recognize that there still remains a big gap between the PCEs for all-inorganic perovskite solar cells and hybrid perovskite solar cells (Fig. 1(a))^[7, 8]. The PCE for hybrid cells has reached 80% of the theoretical limit, while the PCE for all-inorganic cells is still below 70% of the theoretical limit^[9]. A detailed analysis on performance parameters of these cells suggests that the PCE for all-inorganic cells is mainly limited by the open-circuit voltage (V_{oc}) and fill factor (FF) (Fig. 1(b)). In solar cells, these two parameters correlate to non-radiative charge loss caused by defects^[10]. Therefore, defect engineering is the most critical approach for achieving higher PCE for all-inorganic perovskite solar cells.

Though CsPbI₃ has similar bulk defects to that of hybrid perovskites (Fig. 1(c))^[11], it presents more charge recombination and much shorter carrier lifetime. All-inorganic perovskites might have a higher degree of atom (or lattice) disorder and defect distribution because the crystals experience complicated phase transformation processes under relatively high temperature. Thus, improving the crystallization of all-inorganic perovskites is an effective approach to reduce the defects^[6, 12, 13]. Recently, Seok *et al.* controlled the intermediate stages during the crystallization process by adding

methyl ammonium chloride^[6]. CsPbI₃ films showed high crystallinity and good surface morphology. Thermally stimulated current test indicated that the defect density decreased from 3.947×10^{16} to $2.803 \times 10^{16} \text{ cm}^{-3}$. With surface passivation, CsPbI₃ solar cells gave a PCE of 20.37%. At the same time, Meng *et al.* added NH₄I into perovskite precursor solution to adjust the nucleation and crystallization, thus reducing the defects (Fig. 1(d))^[13]. Thermal admittance spectroscopy showed that the charge capture in crossing the perovskite was reduced by about one order of magnitude. Recently, Meng *et al.* controlled perovskite crystallization by using coordination-active additives or synergistic additives, and the solar cells delivered a PCE of over 21.0%.

Another defect suppression strategy is element doping at the Pb site in perovskite. The 6s and 6p orbitals of Pb²⁺ significantly contribute to the energy band of CsPbX₃ (X = Cl, Br and I) perovskites, and using divalent metal ions (i.e. Cu²⁺, Mn²⁺ and Sn²⁺) doping or alloying Pb sites will affect the defect tolerance^[14]. Recently, Liu *et al.* found that Mn²⁺ incorporation could passivate the defects at the grain boundary and surface, thus reducing carrier recombination (Fig. 1(e))^[15].

Surface passivation is widely used for enhancing the performance of all-inorganic perovskite solar cells^[16]. Bulky organic ammonium halides, such as quaternary ammonium salt, were used to passivate the defects in hybrid perovskites. This method can also be used to passivate the surface defects of all-inorganic perovskites. In 2018, Zhao *et al.* treated CsPbI₃ film with choline iodide to reduce surface defects^[17]. Phenyltrimethylammonium halides and 3,3-diphenylpropylamine were used for surface passivation, accelerating the development of all-inorganic perovskite solar cells^[18, 19]. The recently reported high PCE of 20.37% benefited from the surface passivation by octylammonium iodide^[6]. Organic materials having Coulombic interaction with the terminal atoms of perovskites can be applied for surface or interface passivation. Ye *et al.* theoretically and experimentally proved that an amino-functionalized polymer and a dopant-free hole-transporting polymer can help passivating both the top and the bottom surface of CsPbI₂Br films (Fig. 1(f))^[20]. The numerous organic ligands synthesized for enhancing the luminescence of all-inorganic perovskite nanocrystals may be suitable for passivating perovskite surface and grain boundaries^[21, 22].

In summary, all-inorganic perovskites have a complic-

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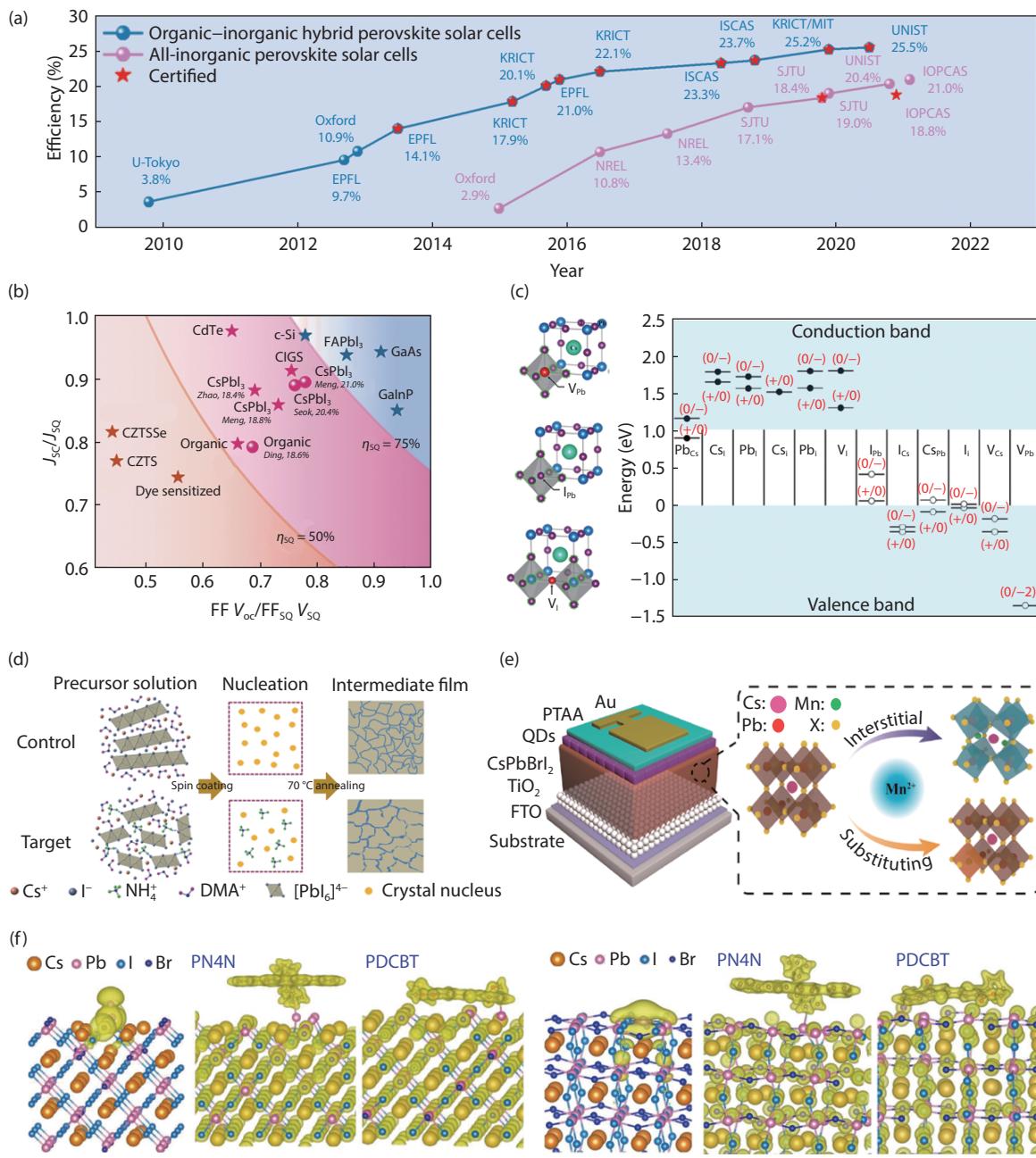


Fig. 1. (Color online) (a) Efficiency evolution of organic–inorganic hybrid perovskite solar cells and all-inorganic perovskite solar cells. (b) Performance parameters of the current record-efficiency cells in comparison with Shockley-Queisser detailed-balance limit. (c) The defect transition levels of CsPbI₃. Reproduced with permission^[11], Copyright 2017, AIP publishing. (d) Effect of NH₄⁺ on the crystallization of CsPbI₃. Reproduced with permission^[13], Copyright 2021, WILEY-VCH. (e) Illustration of Mn²⁺ doping in CsPbBr₂. Reproduced with permission^[15], Copyright 2018, American Chemical Society. (f) Illustration of the passivation effect of PN4N and PDCBT. Reproduced with permission^[20], Copyright 2019, WILEY-VCH.

ated formation process and large lattice distortion caused by phase competition. Besides the top surface, more attention should be paid to passivating the defects at bottom surface and inside the bulk. Interface materials which can withstand high temperature should be developed to buffer the energy level mismatch, lattice mismatch, and interface stress between inorganic charge-transport layers and all-inorganic perovskites.

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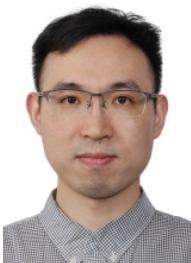
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