New materials for perovskite solar cells

Organic and inorganic hybrid perovskite solar cells (PSCs) make use of organometallic halide semiconductors as light-absorbing materials and have been one of the most promising candidates for third-generation photovoltaics. In recent years, research activities have strongly focused on boosting the power conversion efficiency (PCE) of PSCs due to their excellent optoelectronic properties, such as high absorption coefficient, high carrier mobility, tunable bandgap, and long charge carrier diffusion lengths. The PCE has improved from 3.9% to 25.2%, reflecting enormous development potential. However, for commercialization, PSCs still face challenge and show improvement potential for intrinsic stabilities, efficiency, and large-scale fabrication.

The chemical formula of perovskite is ABX_3 with an octahedron and cubic crystal structure. As shown in Figure 1, the A-site is a cation: methylammonium (MA^+), formamidine (FA^+), Cesium (Cs^+), Rubidium (Rb^+), or a large size organic spacer cation such as butylammonium (BA^+) or 2-phenyl-ethyl ammonium (PEA^+). The B-site is a transition metal cation: Pb^{2+} or Sn^{2+} and the X-site is a halogen anion: Cl^-, Br^-, or I^-. Herein, we will briefly introduce several common battery types: first, the widely used $MAPbI_3$-based PSCs have the advantage of low-cost and large-scale fabrication as well as simple solution-processing synthesis, whilst the power conversion efficiency (PCE) can reach more than 18%. However, MA is unstable, and easy to degrade and volatilize, resulting in low efficiency. Furthermore, $MAPbI_3$-based PSCs also face tetragonal-pseudo-cubic phase transition issue occurring approximately at 56 °C, which hinder further development, because of higher operating temperatures reaching 85 °C in practical applications. Second, $FAPbI_3$-based PSCs have a lower bandgap (Eg=1.48 eV), higher absorption coefficients, and longer carrier diffusion lengths, thus can obtain higher current-density compared with $MAPbI_3$ (Eg=1.57 eV). However, $FAPbI_3$ also encounters stability issues in ambient conditions and tends to form the non-perovskite hexagonal phase rather than the cubic phase at room temperature. Third, to avoid the toxicity of Pb, low-toxicity Sn can be used, which have narrower bandgaps (about 1.3 eV), and relatively high intrinsic or thermodynamic[1]. However, the easy oxidation of divalent Sn^{2+} into tetravalent Sn^{4+}, causes chemical instability of the perovskite, defect density and as a result low efficiencies.

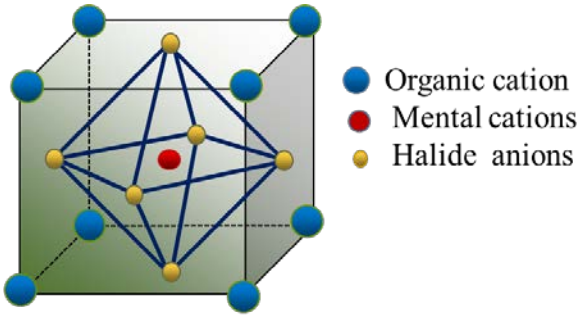

Figure 1. The crystal structure of perovskite ABX_3

To improve the moisture stability of the above materials, the quasi-2D perovskite with superior photo-stability and chemical stability is applied and could achieve remarkable improvements. Owing to the poor crystal orientation and charge transport, it will lead to quasi-2D perovskite like an insulator, resulting in low efficiency. Thus a new strategy has been developed to fabricate high stability and long longevity mixed-dimensional 2D-3D perovskites or to form a 2D perovskite layer on top of 3D perovskite, as shown in Figure

2. Compared with 3D PSCs, 2D-3D hybrid PSCs tend to have better stability without sacrificing efficiency [2].

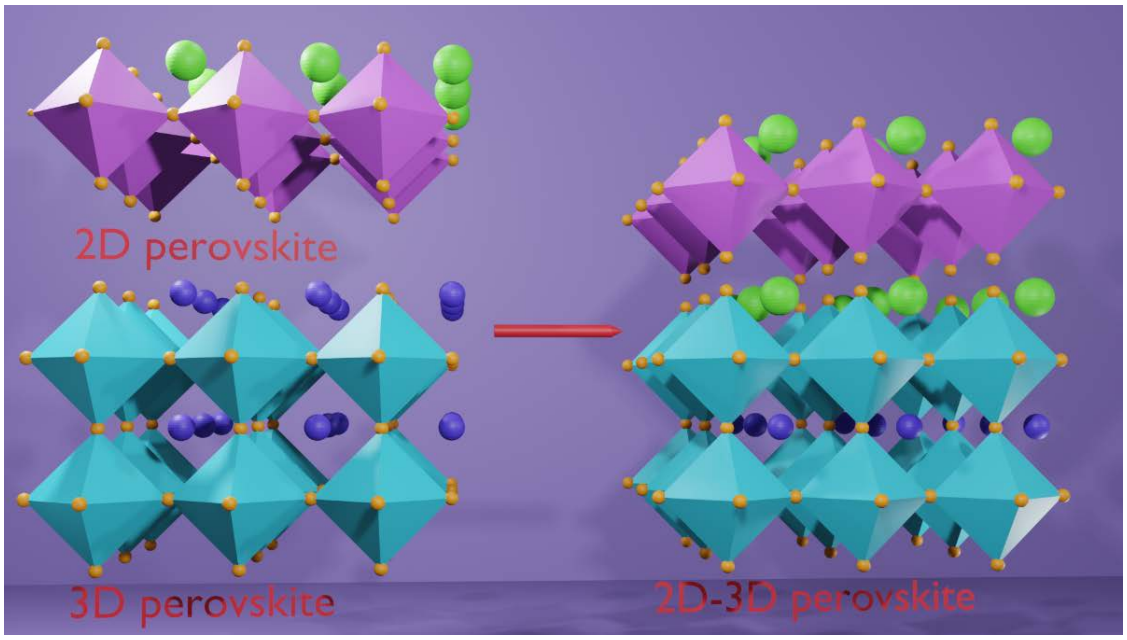

Figure 2. Schematic illustration of the crystal structures of 2D perovskite, 3D perovskite and 2D-3D perovskite

The organic cation with a long-chain alkyl can functionalize the perovskite surface and form two-dimensional layered structures along certain crystallographic planes. The 2D perovskite shows strong resistance to water and plays a dominant role in stabilizing the metastable perovskite phase. For example, forming a 2D layer $(FEA)_2PbI_4$ on the surface of a $FAPbI_3$ film can functionalize the grain boundaries as well as facilitate the formation of phase-pure $FAPbI_3$, to protect the $FAPbI_3$ phase from moisture and assist in charge separation/collection[3]. To study the crystal phase and crystal orientation of the 3D/2D perovskite thin films as well as its effect on solar cell performance, Grazing-incidence wide-angle X-ray scattering (GIWAXS) can be applied[4, 5]. That helps to gain deeper insights into the working mechanisms of 2D perovskites in PSCs.

[1] Zhang, T., Dar M. I., Li G., et al. Bication lead iodide 2D perovskite component to stabilize inorganic α-$CsPbI_3$ perovskite phase for high-efficiency solar cells. *Science advances,* 2017, 3(9): e1700841.

[2] Hu, Y., Schlipf, J., Wussler, M., et al. Hybrid perovskite/perovskite heterojunction solar cells. *ACS nano*, 2016, 10(6): 5999-6007.

[3] Lee, J. W., Dai, Z., Han, T. H., et al.: 2D perovskite stabilized phase-pure ormamidinium perovskite solar cells. *Nature communications,* 2018, 9 (1): 1-10.

[4] Schlipf, J., Hu, Y., Pratap, S., et al.: Shedding light on the moisture stability of 3D/2D hybrid perovskite heterojunction thin films. *ACS Applied Energy Materials,* 2019, 2(2): 1011-1018.

[5] Schlipf, J., Müller-Buschbaum, P.: Structure of Organometal Halide Perovskite Films as Determined with Grazing-Incidence X-Ray Scattering Methods. *Advanced Energy Materials*, 2017, 7(16): 1700131.