Stability lies at interfaces

Perovskite solar cells are developing fast but their lifetime must be extended. Now, large-area printed perovskite solar modules have been shown to be stable for more than 10,000 hours under continuous illumination.

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Organic-inorganic halide perovskite solar cells benefit from high power conversion efficiency (now beyond 22 %), ease of fabrication and low cost. Despite these advantages, their operational stability and materials toxicity remain of foremost concern. Stability issues appear in the halide perovskite itself but also in other constituent materials, as well as at interfaces between the various layers of the device. Correspondingly, several options have been proposed to reduce device degradation: inverting the solar cell structure to reduce reactivity, replacing organic semiconductors with oxides at interfaces to improve moisture and oxygen stability, or tuning the composition of the halide perovskite to stabilize its crystal structure and improve thermal strength[1], for example. Among the different organic-inorganic halide perovskite structures, three dimensional (3D) hybrid compounds currently lead to the most impressive power conversion efficiency. These compounds are characterized by their excellent photophysical properties, such as high absorbance and long excitation and charge diffusion lengths. However, 3D halide perovskites, which contain small organic cations, are moisture-sensitive and this leads to rapid performance degradation. In contrast, layered 2D halide perovskite structures accommodate bulkier and more hydrophobic organic cations, which results in superior moisture stability, making them more attractive for large-scale industrial implementation. Nevertheless, 2D halide perovskites show lower power conversion efficiencies, currently around 12 %[2]. Now, writing in *Nature Communications*, Mohammad Khaja Nazeeruddin and colleagues, from Switzerland and Italy, combine 3D and 2D halide perovskite structures using functional organic molecules, and report 1 year of operational stability for printed 10 cm x 10 cm photovoltaic modules fabricated in air[3].

The key feature of the solar cells fabricated by Nazeeruddin and colleagues is found at the interfaces (Figure 1). They show that a 2D halide perovskite and the pure 3D halide perovskites can be bonded together at a 2D/3D interface by aminovaleric acid iodide. The protonated form of this small organic acid can coordinate on one hand with semiconductor oxides, like the TiO_2 used as the electron transport electrode, thanks to its carboxyl functional group (Figure 1c,e), and on the other hand with various halide perovskite compounds, thanks to both its amine and carboxyl functional groups (Figure 1d,e). The final 2D/3D material contains the best of both structures: the ease of fabrication and moisture stability of the 2D perovskite, and the panchromatic absorption and good photovoltaic properties of the 3D perovskite.

Spin-coated solar cells using these 2D/3D perovskites (Figure 1a) exhibit a champion 14.6 % photoconversion efficiency and an enhanced stability when compared to similar devices made only

with the 3D compound. After 300 h of continuous illumination under one sun (at 45 ℃, in an argon atmosphere, for encapsulated devices), the spin-coated 2D/3D perovskite-based solar cell shows a 30 % decrease in its original efficiency value, while the solar cell made with only the 3D perovskite shows a 50 % efficiency decrease, demonstrating the beneficial and synergetic effect attained by interface engineering.

In a second step towards scalability and improved stability, the researchers avoid the use of unstable hole transport layers, like Spiro-OMeTAD. Instead, they employ a nanoparticulated TiO_2 thin film, followed by a coating of an inert layer of ZrO_2 nanoparticules used as a scaffold, and is finally completed with a carbon-based coating which acts as back current collector and a water-retaining layer. The halide perovskite is introduced into the oxides thin films via infiltration. All the layers are fabricated by a combination of spray and screen printing, and the fabrication process is carried out completely in ambient atmosphere (Figure 1b). This promising fabrication method, developed back in 2014[6], has already produced solar cells with one of the highest lifetime stabilities for perovskite solar cells under illumination[6]. In the work reported by Nazeeruddin and colleagues, they demonstrate the possibility to use this printing method with their new 2D/3D perovskite to fabricate 10 cm x 10 cm modules (47.6 cm^2 active area, ~10 % efficiency). Device stability was tested under realistic conditions (employing ISOS standards) on encapsulated devices under continuous illumination and protected from UV light, achieving an impressive module stability of more than 10,000 h (more than 1 year).

While the molecular functionalization of interfaces in halide perovskite solar cells is not new, the study of their effect on device lifetime is rather rare. Examples from the literature suggest that, although at different extent of improvement, the stability of the solar cell is always enhanced after interface engineering, independently of the type of solar cell configuration, the type and duration of the stability test performed, or the organic functional molecule used (Figure 2). What's more, improvement in stability is observed regardless of the interface being modified: the oxide/perovskite[8], the perovskite/perovskite[2,3,5,6], the perovskite/transport layer[7-9] and even the interface with the back metal electrode. Here, the work reported by Nazeeruddin and colleagues furthermore demonstrates that a single molecule with double-anchoring groups is able to modify multiple interfaces. It permits the functionalization of the halide perovskite, allowing the formation of a new and improved hybrid organic-inorganic 2D/3D perovskite interface where the functional groups interact through metal-to-amino, hydrogen-to-halogen bonding[4-5] or by the interaction of the amine and the A sites in the perovskite structure[4]. It also permits the anchoring, through its carboxylic acid terminal groups, to the TiO_2 oxide layer, resulting in the presence of fewer defects, preventing charge recombination[3,6]. But probably the most attractive feature from a technological point of view is the possibility to also modify the inert ZrO_2 scaffold via carboxylate bonding. Without the ZrO_2 scaffold the stability of the device is rather poor (Figure 2, molecule 2)[3,6]. Indeed, it is specifically the combination of the dual functionalization, the 2D/3D perovskite structure and the bonding to the perovskites and the TiO_2 and ZrO_2 oxides that leads to the remarkable stability, with no loss in performance for more than 10,000 h (Figure 2, molecule 9).

Given the rich chemistry of hybrid halide perovskites, the ample variety of organic modifiers with diverse anchoring groups, and the vast amount of oxides (semiconductors or scaffolds), the work from Nazeeruddin and colleagues suggests that developing matching sets of chemically binded materials will be of tremendous importance to combine their respective advantages. This work heralds the imminent and inexorable development of large-scale perovskite solar cells with competitive lifetimes, which may soon reach commercialization.

References

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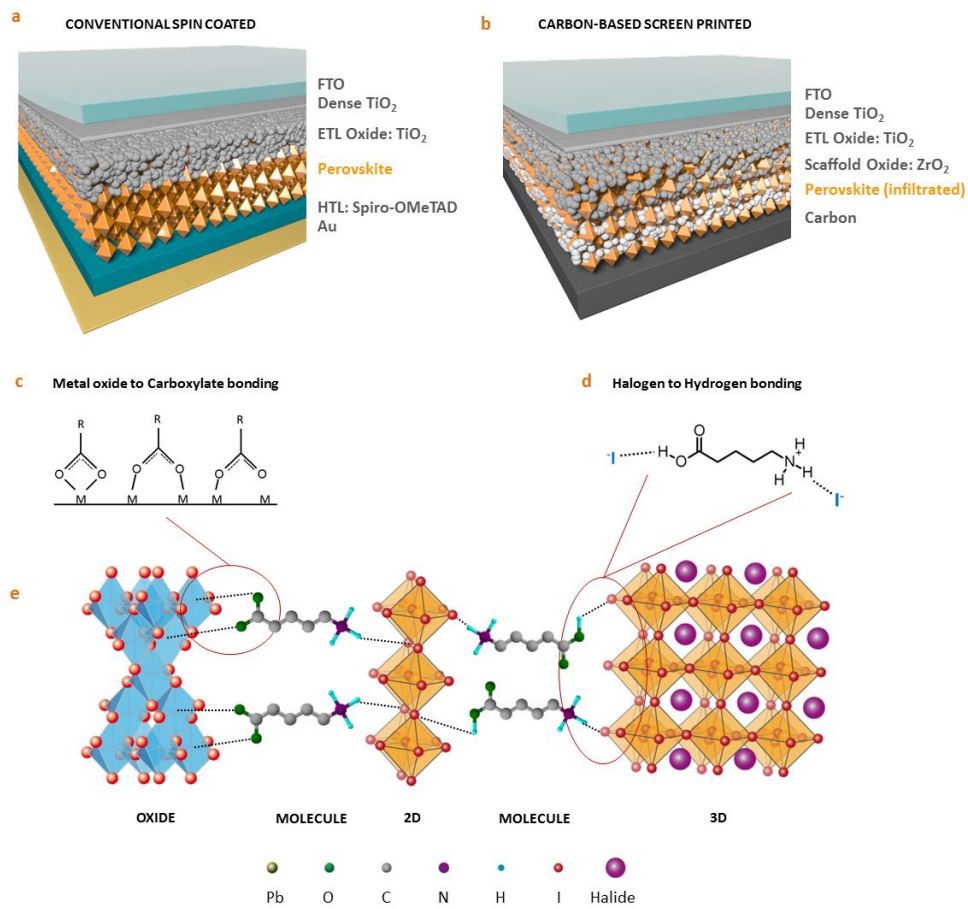10. K. Yao, X. Wang, Y.-x. Xu, F. Li, L. Zhou. *Chem. Mater.* **28**, 3131-3138 (2016).

Figure 1. Interface engineering of Perovskite solar cells. Schematic representation of halide perovskite solar cells made by (**a**) the conventional spin coating method and (**b**) the carbon-based screen printing method. (**c-e**) The interface modification of interlayers is made through the aminovaleric acid iodide molecule, with carboxyl and amine anchoring groups. (**c**) Some examples of carboxyl functional groups bonding with semiconducting (TiO_2) or inert scaffold (ZrO_2) metal oxides[6] and (**d**) Schematic representation of one possible perovskite/perovskite interaction, the halogen to hydrogen bonding to 2D/3D perovskites [2,4] . M stands for metal, FTO for fluorine doped tin oxide, ETL for electrode transport layer and HTL for hole transport layer.
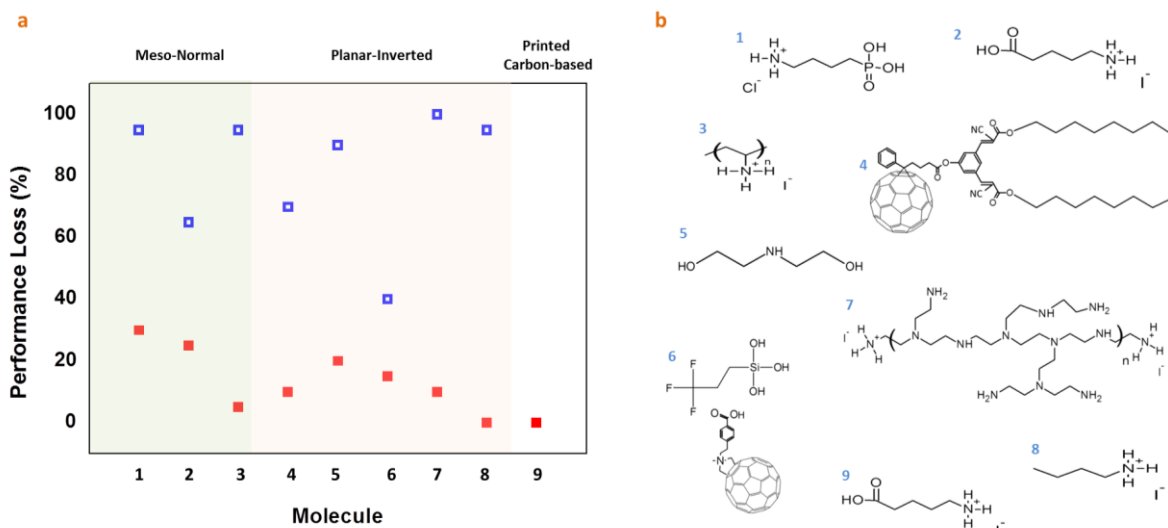
Figure 2. Stability of Perovskite Solar Cells. a) Performance loss (%) observed after stability analysis for interface engineered Perovskite Solar Cells (red squares) and the comparison to its reference device without modification (blue hollow squares). Results published in the literature show that, although at different level of stability improvement, all solar cells applying anchoring molecules are more stable (show less performance loss) than the corresponding reference device without interface modification, independently of the solar cell configuration, the type and duration of the stability test performed, or the thin film layer of the device where the interface modification is made. **b)** The molecules used as interface modifiers and the stability test conditions of the corresponding perovskite solar cell are: **1)** Butylphosphonic acid 4-ammonium Chloride (4-ABPA·Cl), 1000 h, encapsulated, stored in the dark, ambient atmosphere, ~55% RH[5]. **2)** Aminovaleric Acid Iodide (AVA·I), 300h, 1 sun AM 1.5G illumination, argon atmosphere, 45 ºC, encapsulated[3]. **3)** Polyvinyl-amine hydroiodide (PVAm·HI), 1200 h, unencapsulated, stored in the dark, RH 30%, ambient atmosphere[4]. **4)** [6,6]-phenyl-C61-butyric acid-dioctyl-3,3'-(5-hydroxy-1,3-phenylene)-bis(2-cyanoacrylate) ester (PCBB-2CN-2C8), 500h, unencapsulated, stored in the dark, ambient atmosphere, RH 45–50%[7]. **5)** Diethanol amine (DEA), 200 h, stored in the dark, ambient atmosphere, unencapsulated[8]. **6)** C60-trichloro(3,3,3-trifluoropropyl) silan, 240h (reference device) and 750 h (interfacial engineered device), unencapsulated, stored in the dark, ambient atmosphere[9]. **7)** Polyethylenimine hydriodide (PEI·HI), 500 h, stored in the dark, unencapsulated[10]. **8)** Butylammonium hydroiodide (BA·HI), 2500 h, 1 sun AM1.5G illumination, encapsulated[2]. **9)** Aminovaleric Acid Iodide (AVA·I), 10 000 h, 1 sun AM 1.5G illumination, 55 ºC, UV filter, encapsulated[3].