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(Article begins on next page)

Crystal nano-engineering: a new era for perovskite photovoltaics

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Photovoltaics appears today as a mission accomplished: crystalline Si junctions-based and metal halide perovskite-based devices reached comparable power-conversion efficiency, so that they can be exploited in cooperative tandem solar cells ready to enter the market of renewable energies with great expectations. Therefore, research directions are now addressed at reducing fabrication costs, by simplifying cell architecture through, for example, the drastic removal of ancillary layers, and by boosting the shelf-life for better device durability. In a recent work appeared in Nature, He and coworkers demonstrated for the first time the possibility of p-doping the perovskite with anchored molecules, obtaining a remarkable certified stabilized PCE of 25% for up to 1000 h. In this work, a compact hole-transporting material-free inverted perovskite solar cell is presented, thus paving the way for a new era of sustainable optimization of materials and layers in the fabrication of solar devices.

The power conversion efficiency (PCE) of crystalline Si heterostructures-based devices reached 26.8% in 2023, whereas perovskite solar cells gained the 26.1% value in 2024 (see <https://www.nrel.gov/pv/cell-efficiency.html>): it is obvious that perovskite technological development has now reached the high quality of established silicon architectures and that the two can work together in tandem to target the exploitation of the complete solar spectrum^[1]. The efforts of the scientific community are now moving towards the cost optimization,^[2] in light of the need to reduce economic and social impacts of modern technologies,^[3] for allowing perovskite-based device to become fully accepted items in the worldwide energy market. Three are the main issues that keep the technology far from industrial application: stability, thin-film and top electrode processing. The stability of perovskite solar cells (PSCs) has been reported only for 10,000 h, a relatively low value if compared to crystalline Si technology^[4]; furthermore, the roll2roll processing of the different layers needs substantial refinement in terms of cost and fabrication^[5] as well as the top metal processing – usually a noble metal like Ag or Au in n-i-p architectures – is thermally evaporated and more scalable techniques like spray coating^[6] or screen printing^[7] should be promoted.

Therefore, the currently pursued routes by researchers are mainly two: i) the simplification of the architectures by replacing/substituting selective layers like Spiro-OMeTAD, the benchmark material for hole-transporting layers (HTMs), that has been already demonstrated as not suitable for long term activity^[8]; and ii) the doping of the perovskite layer with other materials to boost the chemical stability of devices. The inverted architecture (p-i-n) addresses the first point by the implementation of stable p-type organic films (made of C₆₀-based molecules) that guarantee low hysteresis, and discrete efficiency. In the last decade a rush for closing the efficiency gap with respect to direct solar

cells has begun passing from about 4% PCE to overcome the psychological limit of 25% and well-reviewed in literature^[9].

He and coworkers^[10] have recently published an outstanding contribution to the topic, by establishing a milestone in the doping chemistry of perovskite light absorbers. In detail, they demonstrated the covalent modification of perovskite grains with a small molecule [namely 4-(2,7-dibromo-9,9-dimethylacridin-10(9H)-yl)butyl)phosphonic acid (DMAcPA), whose structure is shown in Figure 1A)] exploiting an unprecedented methodology called by the authors “molecule-extrusion process”. With this strategy, molecules are extruded from the precursor solution to the grain boundaries and the bottom of the film surface in a chlorobenzene-quenched crystallization process, as evidenced by AFM-IR analysis (Figure 1B).

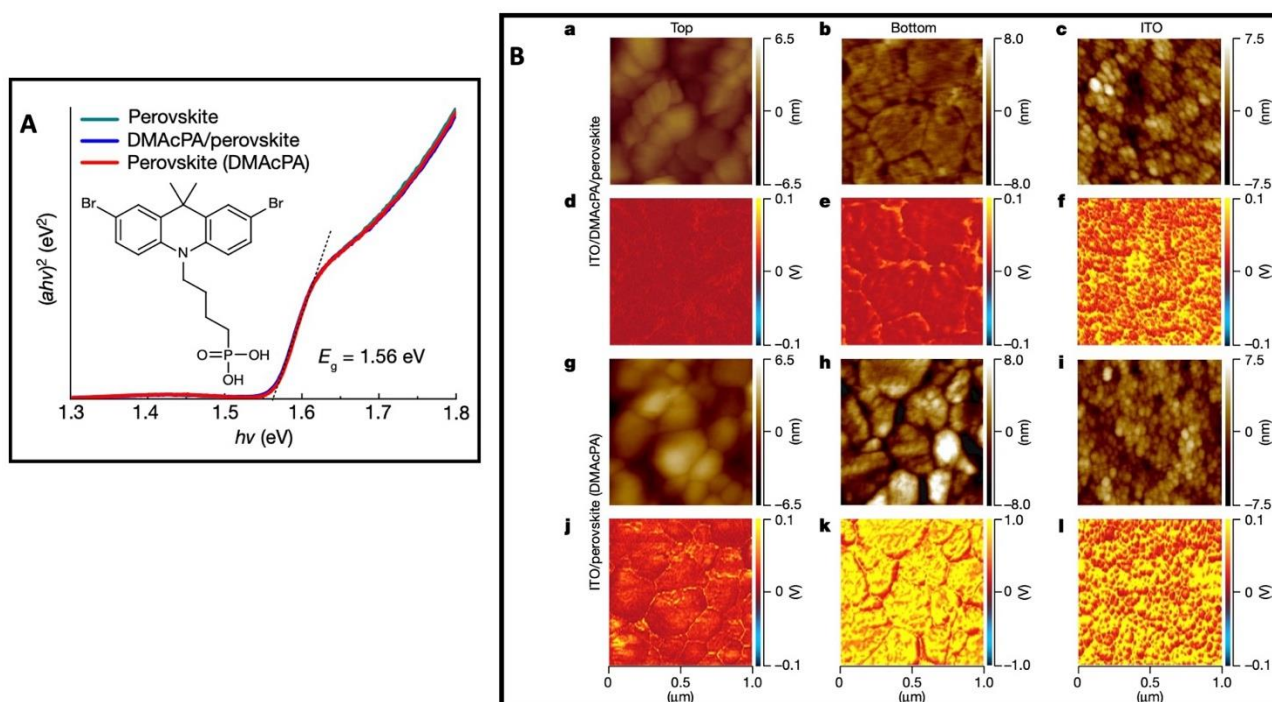


Figure 1. Tauc plot analysis of the DMAcPA/perovskite interface (A); AFM-IR study of the different samples (B). Adapted from ^[10] with permission from Springer Nature.

The perovskite displays a p-type character that allows the formation of an ITO/p-perovskite Schottky junction, making possible the realization of an HTM-free perovskite solar cell. Chemical analysis of the system shows the key role of the phosphonic acid termination: the released protons are captured by dimethyl formamide (DMF) molecules present in the precursor solution leading to the formation of solvated $H^+[DMF]_x$ moieties. DFT calculations help to demonstrate that the absorption of DMAcPA occurs on PbI_2 -terminated perovskite crystal structure through bonding between $-P-O^-$ and Pb (Figure 2A). Furthermore, the strong chemical modification affects the work function of underlying ITO substrate with the formation of a charge transfer complex constituted by the phosphonic acid and $Pb(I)_x$ polyhedra. Still, the perovskite band shows an upward bending along with a much lower energy offset of 0.21 eV, improving its hole-extraction rate at the interface (Figure 2B).

The performance of the ITO/perovskite-DMAcPA/PCBM/BCP/Ag solar cell is remarkable: the champion device shows notable figures of merit for an inverted architecture (25.86% PCE, 1.187 V open-circuit voltage, 25.69 mA cm^{-2} short-circuit current and 84.73% fill factor), as shown in Figure 2C. However, what it is really noteworthy is the excellent long-term stability of the solar cell (Figure 2D), as it maintains the 96.6% of its initial PCE after 1000h of light soaking, whereas in the control

sample PCE lowers below the 80% of the starting value after 500h. The authors attribute this result to the all-round passivation of grain boundaries by DMAcPA, which affects the deep-level defect states distribution of the perovskite film, suppressing them at the grain boundaries and surfaces. The one-pot extrusion process can naturally realize all-round passivation, demonstrating a new-era for fabrication processes of polycrystalline semiconductors-based thin-film technologies.

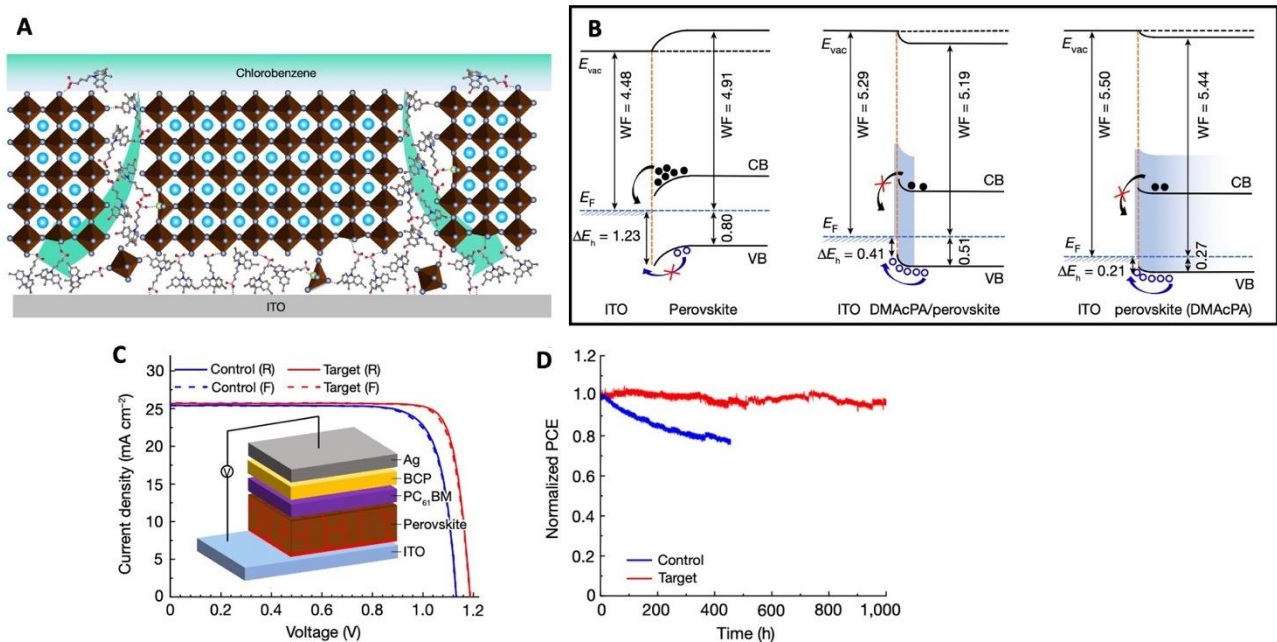


Figure 2. Molecule-extrusion process happening during perovskite crystallization proposed in the work of He and coworkers (A); Energy-level diagram of the ITO/perovskite junctions (B); Current density-voltage characteristics of the best device, with sketch of the inverted architecture also displayed (C); Maximum power-point tracking of the PCE under AM 1.5 illumination in ambient air (D). Adapted from ^[10] with permission from Springer Nature.

Competing interests. The authors declare no conflict of interests.

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