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New Light on an Old Story: Perovskites Go Solar

*Bettina V. Lotsch**

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There are only few inorganic materials that have been shaping the progress in the solid-state sciences as much as perovskites. Although they are deceivingly simple in structure, the archetypal ABO_3-type perovskites have a built-in potential for complexity and surprising discoveries. The history of perovskites is both winding and dazzling, but they have always been a major player in solid-state chemistry and physics because of their many intriguing properties. Perovskites, which were named after the Russian mineralogist Lew A. Perowski, span a large class of ternary oxides, but nitrides, halides, and other compositions are also known. Apart from notable exceptions, such as $SrTiO_3$, perovskites commonly unfold their full potential when they gain complexity, for example, by undergoing structural distortions, by adopting complex intergrowth structures as in Aurivillius phases, or by doping in general. Subtle distortions of the octahedral sublattice give rise to magnetism and orbital ordering phenomena, non-stoichiometries paired with electron correlations boost the critical temperature in high-T_c superconductors, such as $YBa_2Cu_3O_{7-x}$, and oxygen vacancies may increase the ionic conductivity by orders of magnitude. Owing to these and other properties, such as ferro- and piezoelectricity or giant magnetoresistance, numerous perovskites have gained an indisputable rank among high-performance materials for capacitors, electrooptical switches, electrode materials, or memory devices.

Ironically, a technology that has never been associated with these materials has recently sparked a renaissance of the perovskites, namely photovoltaics. Even more ironically, a small and somewhat exotic class of perovskites, which is quite different from the common rock-solid perovskite oxides, has now turned over a new leaf in solar cell research. Recently, methylammonium tin and lead halides with the general formula $(CH_3NH_3)MX_{3-x}Y_x$ (M = Pb or Sn; X, Y = I, Br, Cl) attracted particular attention; they are members of a family of artificial hybrid perovskites with differing dimensionality that were first discovered by Weber and later significantly advanced by Mitzi and co-workers.[1,2] This class of perovskites has now pushed the limits of dye-sensitized solar cell (DSSC) technologies to photoconversion efficiencies (PCEs) beyond 15 %, a benchmark value nobody would have dreamed of hardly more than a year ago.

Hybrid perovskites made a re-entry into the literature in the early nineties, as they show a tunable metal-to-semiconductor transition as a function of the thickness of the perovskite blocks.[3] Starting from the 3D perovskite ABX_3 with $n = \infty$, where small A site alkylammonium ions are encased by corner-sharing MX_6 octahedra, the perovskite blocks can be gradually electronically decoupled and "quantum-confined" by interspersing the perovskite matrix with organic modulation layers that are composed of bulky organoammonium cations (Figure 1). Like their closely related alkali halide counterparts (A = alkali), organometal halide perovskites may be processed in solution, which allows the low-temperature deposition of the perovskite structure by self-assembly from completely soluble precursors. Organoperovskites do not only possess modular structures and an inherently high tendency for crystallization, but also feature high molar absorption coefficients and panchromaticity, that is, excellent light-harvesting performance that spans the entire visible range, high charge-carrier mobilities, unusually large exciton diffusion lengths, and, importantly, band-level characteristics that favorably match those of common hole- and electron-transport materials in DSSCs.[4,5] This is a rather ideal combination of properties, which should give the long-standing concept of all-solid-state solar cells a sizable boost.

The pace at which DSSC-type solar-cell technologies have been developing since their discovery by O'Regan and Grätzel in 1991[6] has been intimately linked to the weaknesses of such intricately optimized systems on the one hand, and benchmark discoveries that overcame these limitations on the other hand. Compared to other systems, namely thin-film silicon, CdTe, and CIGS (CIGS = copper indium gallium selenide) solar cells, which currently reach efficiencies of up to 20 %, the performance of DSSCs has been competitive, but nevertheless lower and less robust. The subtle interplay between the TiO_2 photoanode, the dye, and the electrolyte requires a balance in the choice of materials that is notoriously hard to achieve. At the same time, however, DSSCs are based on inexpensive materials and feature exceptional flexibility, both with respect to materials selection and the manufacturing processes. DSSCs can be engineered into a plethora of shapes, flexible sheets, and colorful designs at low cost, which would bode well for a bright future, if it was not for their inherent weaknesses, including photobleaching

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[*] Prof. B. V. Lotsch
Max Planck Institute for Solid State Research
Heisenbergstr. 1, 70569 Stuttgart (Germany)
and
Chemistry Department
Ludwig-Maximilians-Universität München
Butenandtstr. 5–13, 81377 München (Germany)
E-mail: b.lotsch@fkf.mpg.de

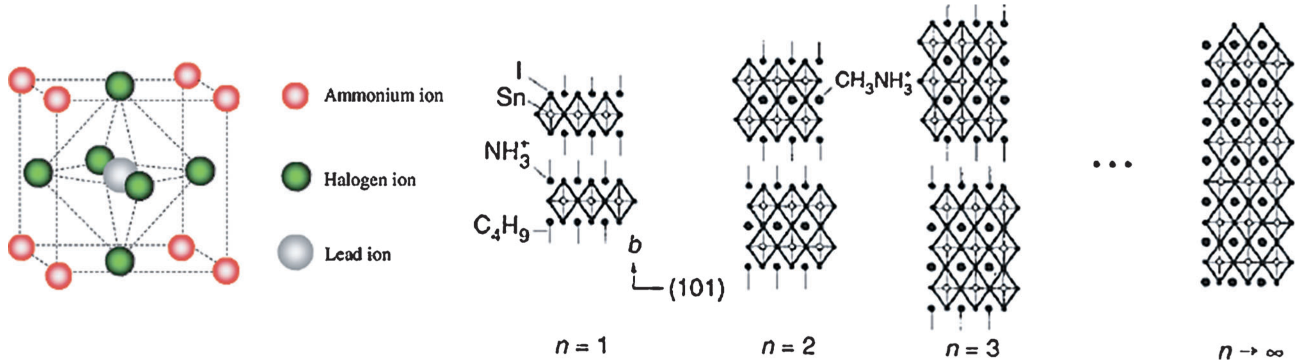

Figure 1. Unit cell of lead hybrid perovskites (left) and schematic representation of a series of layered tin perovskites with block sizes that range from $n=1$ to infinity for the composition ABX_3 (right).[3,7]

of the dyes, sealing issues, and fundamental interfacial energy losses.

In light of these challenges, the recent discovery of perovskite-based solar cells is a huge leap forward. First promising results were obtained by Miyasaka et al. in 2009, who developed photocells based on mesoporous TiO_2 photoanodes that were sensitized with $CH_3NH_3PbX_3$ (X = I, Br). However, PCEs were only moderate ($\eta = 3.81\,\%$ for the triiodide), and the cell stabilities were poor.[7] However, unusually large open-circuit voltages (V_{oc}) of almost 1 V were observed for a lead bromide cell;[7,8] this set the stage for a turnaround in solar-cell design and sparked enormous interest in the exploration of perovskite solar cells (PSCs). In 2012, Kanatzidis and co-workers presented a cell in which the inorganic perovskite $CsSnI_3$ served as a p-type semiconductor. Although the traditional dye-sensitized architecture was retained, the use of a perovskite as the hole conductor revived the concept of all-solid-state inorganic solar cells, with efficiencies reaching approximately 10 %.[9] At the same time, Grätzel and co-workers used $(CH_3NH_3)PbI_3$ as a light harvester in combination with the solid hole conductor 2,2′,7,7,′-tetrakis(*N*,*N*-dimethoxyphenylamine)-9,9′-spirobifluorene (spiro-MeOTAD), which led to a PCE of 9.7 % (Figure 2).[10]

This already pointed to the versatility of perovskites, as they serve equally efficiently either as a dye replacement or as the hole transporter. Consequently, the next aim was to develop a "two-in-one structure" within a perovskite/TiO_2 heterojunction cell, where the perovskite simultaneously acts as both the absorber and the hole conductor.[11]

But the perovskites had even more to offer: Snaith and co-workers recently discovered that in "meso-superstructured" solar cells the n-type oxide can be replaced by an inert scaffold, such as Al_2O_3, onto which $CH_3NH_3PbI_2Cl$ is coated. This architecture reveals that both light absorption and electron transport occur in the perovskite, thus minimizing energy losses at the absorber/electron acceptor interface.[12]

In their following seminal reports, Snaith and co-workers aimed at further reducing complexity, ultimately returning to the very essentials of planar thin-film solar cells. With a low-temperature processing route for the Al_2O_3 substrate in hand,[13] the next task was to get rid of the mesoporous scaffold altogether without sacrificing efficiency. Dual-source vapor deposition was used to create uniform flat films of

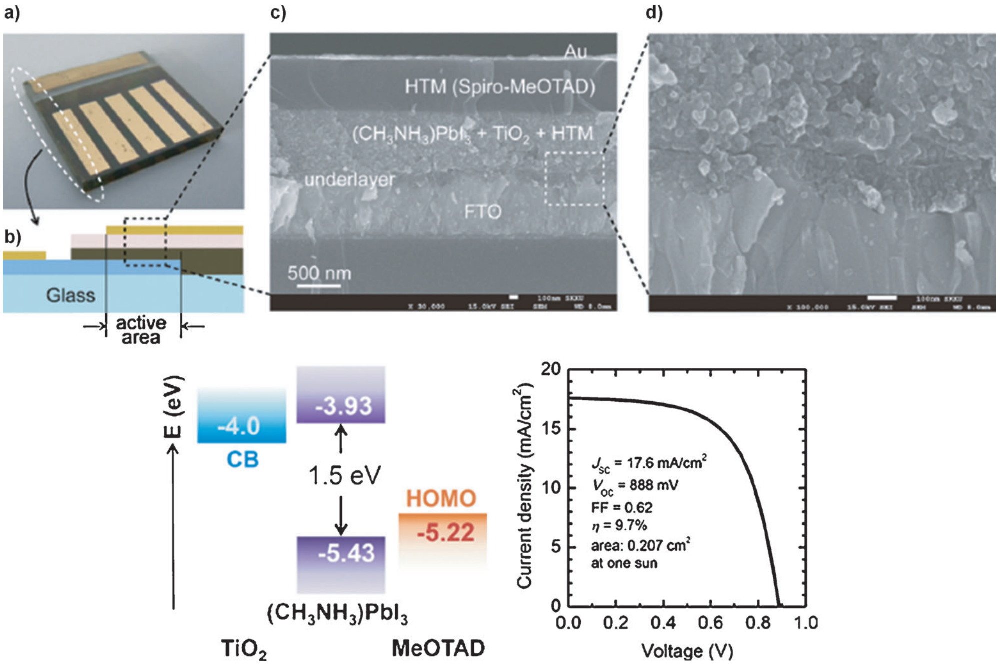

Figure 2. a, b) Solid-state mesoscopic solar cell. c, d) Cross-sectional SEM images. Bottom: Energy level diagram of the perovskite sensitized solar cell (left) and photocurrent density as a function of forward bias (right).[10] FTO = fluorine-doped tin oxide, HTM = hole transport material.

$CH_3NH_3PbI_{3-x}Cl_x$ as part of a conventional thin-film architecture. Here, the perovskite, which is sandwiched between two charge-selective contacts, effectively operates as a thin-film absorber and an ambipolar charge-transport material, just like in a planar p-i-n heterojunction solar cell. Remarkably, the vapor-deposited film is much more homogenous than a solution-processed film, which gives rise to record efficiencies of over 15 % (Figure 3).[14]

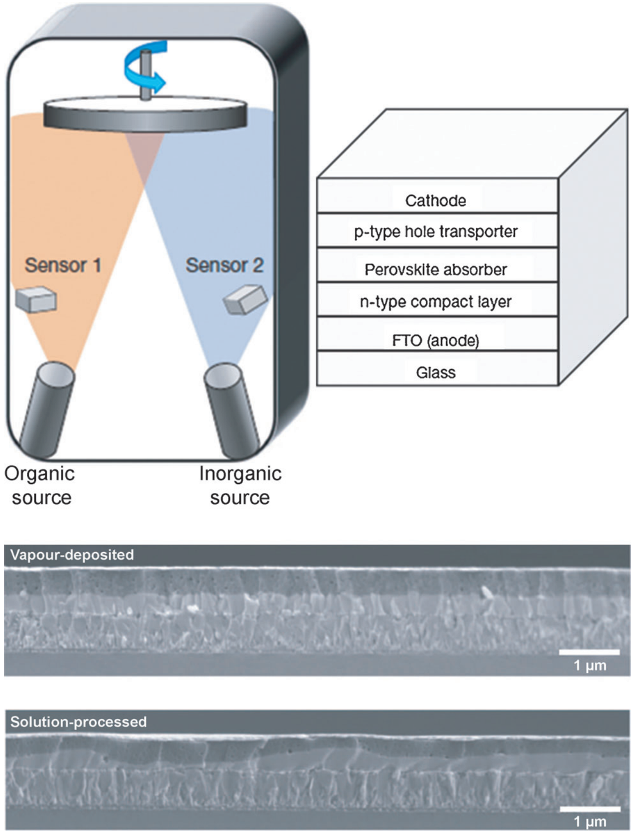

Figure 3. Top: Dual-source thermal evaporation system that operates with organic methylammonium iodide and $PbCl_2$ as the sources for depositing the perovskite absorber (left) and layout of the planar heterojunction perovskite solar cell (right). Bottom: Cross-sectional SEM images of a vapor-deposited perovskite film and a solution-processed film.[14]

Although the inherent potential of perovskites was rapidly appreciated by the photovoltaics community, there is still ample space for improvement. What is next? There is certainly a need for replacing lead for less toxic, but equally abundant elements. The European Union and other countries have severely restricted the use of lead and other hazardous substances in electronic devices, thus calling for the development of lead-free perovskites.[15] Likewise, fine-tuning the perovskite/hole-conductor interface,[16] exploring new and also layered perovskites with even better light-harvesting properties, improving long-term stabilities, and understanding the photophysics of charge generation and transport in PSCs will be key to gauge the perspectives of optimization. Finally, the demonstrated flexibility in processing[14,17] makes PSCs promising candidates as highly efficient top cells in tandem configurations to further improve the PCEs of early-generation thin-film solar cells.[18] The future for perovskites is bright once again.

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