Is the working principle of perovskite solar cells n-i-p or n-n-p? The controversy on perovskite doping

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In literature it is standard to assume that solar cells with organic inorganic metal halide perovskite absorbers function according to the working principle n-i-p, with the intrinsic perovskite sandwiched between the n-type electron and the p-type hole extraction layer. This assumption is based on low charge densities derived e.g. from electrical conductivity, Hall-conductivity, intensity-dependent photo-luminescence quantum yield, CELIV (all in) [1], EBIC [2], and KPFM [3].
In contrast with photoelectron spectroscopy PES we find a large energy distance between the valence band maximum VBM and the Fermi level, independent of the substrate being the n-electron or the p-hole extraction layer. Strong measures have to be taken though, to measure near thermodynamic equilibrium as photovoltages induced by unconsidered light sources and even by the PES source itself can lead to misinterpretation of the VBM position. PES on device stacks in classical and inverted architecture [4] (figures 1,2) as well as on the tapered cross section [5] of working devices also clearly evidence, that the photovoltaically active contact is the p-type hole extraction layer, be it on top or below the perovskite. From these findings we propose the working principle of well working perovskite solar cells to be n-n-p.

1. Francisco Peña-Camargo, J.T., Hannes Hempel, Artem Musiienko, Vincent M. Le Corre, Jonas Diekmann, Jonathan Warby, Thomas Unold, Felix Lang, Dieter Neher, Martin Stolterfoht, Revealing the doping density in perovskite solar cells and its impact on device performance. *submitted*, 2022.
2. Edri, E., Kirmayer, S., Henning, A., Mukhopadhyay, S., Gartsman, K., Rosenwaks, Y., Hodes, G., and Cahen, D., Why Lead Methylammonium Tri-Iodide Perovskite-Based Solar Cells Require a Mesoporous Electron Transporting Scaffold (but Not Necessarily a Hole Conductor). *Nano Letters*, 2014. 14(2): p. 1000-1004.
3. Bergmann, V.W., Weber, S.A.L., Ramos, F.J., Nazeeruddin, M.K., Gratzel, M., Li, D., Domanski, A.L., Lieberwirth, I., Ahmad, S., and Berger, R., Real-space observation of unbalanced charge distribution inside a perovskite-sensitized solar cell. *Nature Communications*, 2014. 5.
4. Hellmann, T., Das, C., Abzieher, T., Schwenzer, J.A., Wussler, M., Dachauer, R., Paetzold, U.W., Jaegermann, W., and Mayer, T., The Electronic Structure of MAPI-Based Perovskite Solar Cells: Detailed Band Diagram Determination by Photoemission Spectroscopy Comparing Classical and Inverted Device Stacks. *Advanced Energy Materials*, 2020. 10(42).
5. Wussler, M., Mayer, T., Das, C., Mankel, E., Hellmann, T., Prawobo, C., Zimmermann, I., Nazeeruddin, M.K., and Jaegermann, W., Tapered Cross-Section Photoelectron Spectroscopy of State-of-the-Art Mixed Ion Perovskite Solar Cells: Band Bending Profile in the Dark, Photopotential Profile Under Open Circuit Illumination, and Band Diagram. *Advanced Functional Materials*, 2020. Article Number 1910679.

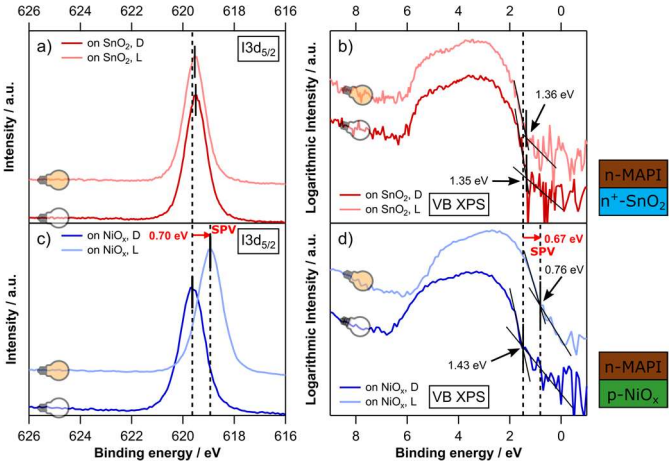

Figure 1. XPS I3$d_{5/2}$ core level measurements (a,c) and XPS valence band measurements (b,d) of a MAPI film on top of a n-type SnO_2 substrate (a and b) and on top of a p-type NiO_x substrate (c and d). In the dark both perovskites appear n-type with VBM values of around 1.40 eV, while the band gap is around 1.6 eV. Under illumination a PV is observed for the perovskite absorber deposited onto NiO_x, indicated by a shift of all emission lines to lower binding energies.[4]

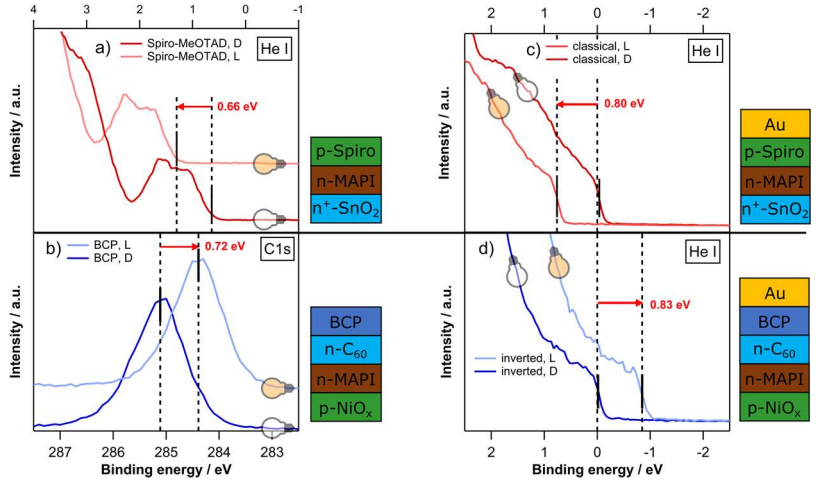

Figure 2. He I measurements of the classical architecture device with the HEL (p-type Spiro) on top of the perovskite (a) and XPS C1s core level measurements of the inverted architecture device with the EEL on top of the perovskite (n-type BCP). In subfigures (c) and (d) He I measurements of the Au back electrode of the completed devices are shown. [4]