

Supporting Information

Spatially-resolved insight into the chemical and electronic structure of solution processed perovskites – why to (not) worry about pin-holes

Claudia Hartmann, Golnaz Sadoughi, Roberto Félix, Evelyn Handick, Hagen W. Klemm, Gina Peschel, Ewa Madej, Alexander B. Fuhrich, Xiaxia Liao, Simone Raoux, Daniel Abou-Ras, Dan Wargulski, Thomas Schmidt, Regan G. Wilks, Henry Snaith, and Marcus Bär**

Cl K and N K EDX maps

No conclusions can be (easily) drawn from the EDX maps based on the Cl K and N K fluorescence measured on the same sample spot as show in Figure 1a in the manuscript. The N K signal is partly overlapped with the Ti L fluorescence line, which makes a deconvolution and thus separation from the Ti L signal difficult. The low signal-to-noise ratio of the Cl K map can be explained by the presence of very little, if any, Cl in the sample.

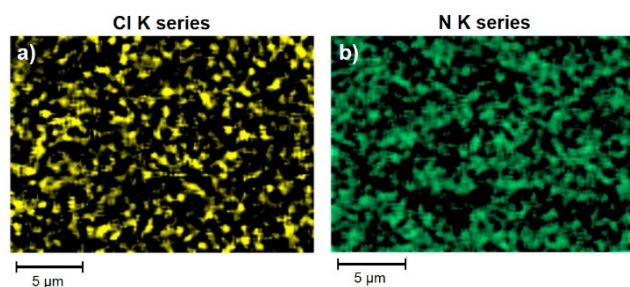


Figure S1. EDX maps of the chlorine K (a) and nitrogen K (b) fluorescence of the same sample spot as show in Figure 1a in the manuscript.

I 4d XPS

For more information about the chemical environment of the perovskite layer and its spatially inhomogeneous interface with compact TiO₂, PEEM-XPS measurements were performed. Figure 3 shows the I 4d XPS spectra of the three areas of interest (as defined in Figure 1b). The I 4d photoemission line is spin-orbit split with a 4d_{3/2} and 4d_{5/2} contribution separated by 1.76 eV.^[1] Since a clear (but less intense – note the different magnification factors indicated for each spectrum on the right side of Figure 3) I 4d XPS signal is also obtained in the “exposed TiO₂” area (blue box, Figure 1b), either an I-containing species is present at the substrate surface or iodine is incorporated into the TiO₂. Close inspection of the spectra and a thorough curve fit analysis reveals that for the I 4d spectra of the “perovskite” and “intermediate” areas reasonable fits can be obtained by using one spin-orbit split doublet. Only for the “exposed TiO₂” area, two spin-orbit split doublets are needed, suggesting the presence of different iodine chemical species (indicated as components I and II in Figure 3). The main (I) contribution to the I 4d_{5/2} peak as measured in the areas indicated by the blue (“exposed TiO₂”), green (“intermediate”), and red (“perovskite”) box in Figure 1b can be found at BEs of 49.78, 49.71, and 49.45 (\pm 0.20) eV, respectively. The secondary (II) peak for the “exposed TiO₂” is at BE = (50.85 \pm 0.20) eV. The comparison with BE values of I-containing reference compounds found in literature^[2] reveals that the main I 4d (I) contribution (at low BE) can be ascribed to iodine in an iodide/perovskite environment (i.e., CH₃NH₃PbI₃). The identification of the smaller I 4d (II) contribution (at high BE) is not that straight forward; most of the literature reference data is reported for the more prominent I 3d

[1] L. Karlsson, S. Svensson, P. Baltzer, M. Carlsson-Göthe, M. P. Keane, A. Naves de Brito, N. Correia, B. Wannberg, *J. Phys. B: At., Mol. Opt. Phys.* **1989**, 22, 3001.

[2] National Institute of Standards and Technology, “NIST X-ray Photoelectron Spectroscopy (XPS) Database.” [Online]. Available: <http://srdata.nist.gov/xps/Default.aspx>

core level, and so the process through which we infer I 4d BEs from published I 3d data is discussed below.

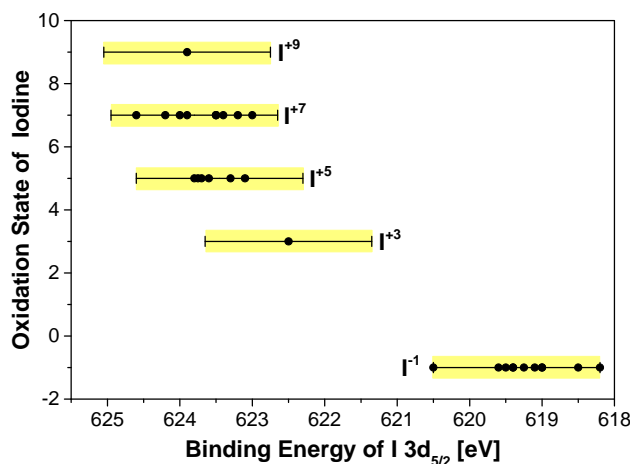


Figure S2. Oxidation state of iodine plotted over BE of I 3d_{5/2} for different iodine compounds from literature.^[3,4,5,6,7] The dots represent published BE values and the bars/yellow boxes indicates the (assumed) BE spread.

For identification of the second iodine species in the I 4d photoemission spectra, which is denoted I 4d (II) in the main text, reference energies for the more prominent I 3d photoemission line were examined. Iodine can have oxidation states of -1, +1, +3, +5 or +7. Figure S2 shows a general shift to higher binding energies as the formal oxidation state

[3] Z. Bastl, H. Gehlmann, *Collect. Czech. Chem. Commun.* **1988**, 53, 425.

[4] M. J. Van Stipdonk, V. Santiago, E. A. Schweikert, C. C. Chusuei, D. W. Goodman, *Int. J. Mass Spectrom.* **2000**, 197, 149.

[5] X.-L. Zhou, F. Solymosi, P. M. Blass, K. C. Cannon, J. M. White, *Surf. Sci.* **1989**, 219, 294.

[6] P. M. A. Sherwood, *J. Chem. Soc., Faraday Trans. 2* **1976**, 72, 1805.

[7] A. N. Mansour, C. A. Melendres, *Surf. Sci. Spectra* **1994**, 3, 287.

increases. Yellow boxes indicate the expected BE spread for each I oxidation state. Their BE interval was defined by the BE range in which data for I^{-1} – the oxidation state for which most data points can be found – is reported in literature. Under the assumption of a constant energy separation between I 3d and I 4d, the BE intervals defined in Figure S2 were transferred to the I 4d spectra shown in Figure S3. Note that no BE value for I^{+1} can be found in literature and thus is missing in Figure S2 and S3. Following the oxidation state – BE trend indicated in Figure S2, it can, however be expected that the I^{+1} BE interval is located in-between and partially overlaps with that of I^{+3} and I^{-1} . The transferred BE intervals for the I oxidation states in Figure S3, suggest the I $4d_{5/2}$ (II) peak to be ascribed to an iodite I^{+3} ($\rightarrow IO_2^-$) species. We caution that this assignment is hypothetical, because this compound is not stable; it does however exist as intermediate in iodide \leftrightarrow iodate reactions.^[8] Furthermore, considering the uncertainty of BE interval transfer from I 3d to 4d and the large (partially overlapping) BE intervals also the formation of a hypoiodite I^{+1} ($\rightarrow IO^-$) and/or an iodate I^{+3} ($\rightarrow IO_3^-$) species cannot be excluded – based on our measurements and the limited availability of I 4d BE values for different iodine compounds in literature there is no unambiguous identification possible. In conclusion, we will refer to this compound as “oxidized” iodine species. Its presence in the “exposed TiO_2 ” area can be interpreted as the formation of a perovskite/iodite “seed layer” (see main text). Its “effective” thickness can be estimated by assuming a complete coverage of the “exposed” TiO_2 for the “perovskite” area and correlating the ratio of the Pb 4f photoemission scaling factors (see Figure 4) for the “perovskite” and “exposed TiO_2 ” area to an exponential intensity decrease of Pb with decreasing coverage of TiO_2 . By using the inelastic free mean path value of PbI_2 as an approximation,^[9,10] the “effective” thickness of this “seed layer” can be estimated to be approximately 0.14 nm.

[8] Y. K. Gupta, D. N. Sharma, *J. Phys. Chem.* **1971**, 75, 2516.

[9] S. Tougaard, *QUASES-IMFP-TPP2M*. 2002

[10] S. Tanuma, C. J. Powell, D.R. Penn, *Surf. Interface Anal.* **1994**, 21, 165.

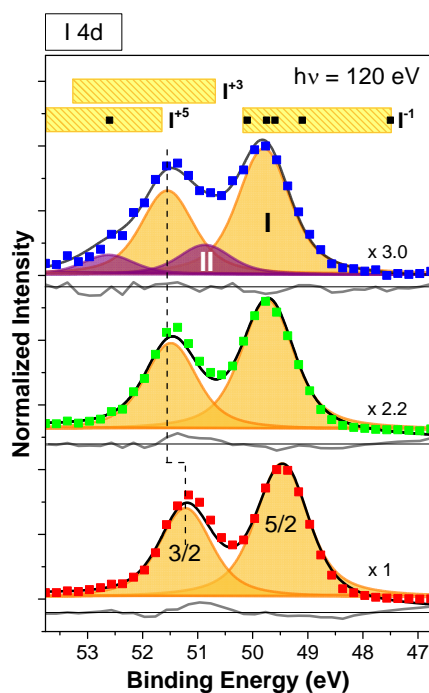


Figure S3. PEEM-XPS I 4d detail spectra recorded in different areas of interest. At the top I 4d_{5/2} BE ranges (transferred from the oxidation state – I 3d BE plot in Figure S2) for different iodine oxidation states are depicted. The black squares represent : ■ exposed TiO₂ data from literature.^[3,4,5,6,7]

■ intermediate
■ perovskite

Shallow core levels & valence band

The region of the shallow core levels (i.e., the 0 – 50 eV BE range) is examined. In addition to the valence band maximum (VBM), this energy range includes the Ti 3p, O 2s and Pb 5d lines. Figure 5 shows the spectra of the three areas of interest. Despite a significantly lower signal-to-noise ratio than achieved for the narrower I 4d and Pb 4f detail spectra, the spectrum of the “exposed TiO₂” area (blue spectrum in Figure 5) clearly shows three spectral features that can be assigned to the O 2p derived VBM, O 2s (BE ≈ 23 eV), and Ti 3p (BE ≈ 38 eV). The detected O 2s and Ti 3p signals derive from the TiO₂ substrate. Note that the Pb 5d signal (BE ≈ 21 eV) partially overlaps with the O 2s line. Together with the low signal-to-noise ratio, this overlap prevents the Pb 5d line from being clearly resolved. However, the presence of Pb (most likely in the form of CH₃NH₃PbI_(3-x)Cl_x) in the “exposed TiO₂” sample area, is

unambiguously shown by the clear Pb 4f signal (see Figure 4). The spectrum of the “perovskite” area (red spectrum in Figure 5) displays a clear Pb 5d doublet peak and the VBM that is formed by hybridized Pb 6s and I 5p states.^[11] In this particular area of the sample, the perovskite layer is sufficiently thick to completely attenuate the Ti 3p photoelectrons. The spectrum of the “intermediate” area (green spectrum in Figure 5) shows signals from the VBM and all shallow core levels (i.e., Pb 5d, O 2s, and Ti 3p), confirming an intermediate layer topography / thickness state.

Energy level alignment

In order to derive a complete energy level alignment picture, we employed the electronic band gaps of $\text{CH}_3\text{NH}_3\text{PbI}_{(3-x)}\text{Cl}_x$ (1.7 eV) and TiO_2 (3.3 eV) as derived by Schulz et al.^[12] using a combination of ultraviolet and inverse photoemission spectroscopy to estimate the relative position of the conduction band minimum (CBM = VBM + band gap) for the “exposed TiO_2 ” and “perovskite” areas. The resulting relative VBM and CBM positions are schematically depicted in Figure 6.

[11] R. Lindblad, D. Bi, B.-w. Park, J. Oscarsson, M. Gorgoi, H. Siegbahn, M. Odellius, E. M. J. Johansson, H. Rensmo, *J. Phys. Chem. Lett.* **2014**, *5*, 648.

[12] P. Schulz, E. Edri, S. Kirmayer, G. Hodes, D. Cahen, A. Kahn, *Energy Environ. Sci.* **2014**, *7*, 1377.