

# ***In Situ* Investigation of Degradation at Organometal Halide Perovskite Surfaces Using Near-Ambient Pressure X-ray Photoelectron Spectroscopy**

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Perovskite solar cells have emerged as one of the most promising photovoltaic technology due to their competitive power conversion efficiency at a relatively low cost. However, the light absorbers utilised, metal halide perovskites, have serious instability issues against moisture, which hinder the advances in commercialisation. Therefore, to develop moisture-tolerant perovskite materials is of paramount importance in the current research stage.

Three key factors for improving the stability of perovskites have been identified: materials, processing, and understanding of degradation mechanisms. In this study, we focus on the latter two elements to investigate the widely used perovskite material, methylammonium lead iodide (MAPI). MAPI is facile to fabricate and gives devices sufficient electrical output; nevertheless, this material is particularly moisture-intolerant, which easily undergoes decomposition. In accordance with our previous work, upon exposure to water vapour, MAPI decomposes into hydrocarbon chains and lead iodide, through release of ammonia and hydrogen iodide gases.[1] Hence, improving the stability of MAPI against moisture is an urgent research topic.

In this work, we utilised aerosol-assisted chemical vapour deposition (AACVD) to prepare stable MAPI films by a novel lead precursor, lead thiocyanate. Using this type of precursor, films can be processed under ambient conditions and show superior resistivity to humid air.[2] We found that AACVD-grown films are much more stable compared to those spin-coated films after aging in air. Moreover, in order to understand degradation mechanisms, we conducted X-ray photoelectron spectroscopy (XPS) measurements to study the surface properties of MAPI thin films in detail. After 1-week aging in ambient air, lead iodide clearly formed in the spin-coated MAPI whilst AACVD-grown film was still dominated by MAPI, showing better stability. Nonetheless, following aging for a month, the peaks of oxidised species can be observed in XPS spectra for both films.

More importantly, we employed cutting edge near-ambient pressure XPS (NAP-XPS) to observe the effect of moisture solely on the AACVD-grown MAPI thin film. The stoichiometry of the film does not significantly change following water vapour exposure under a pressure of 9 mbar. This is an obvious contrast to the film deposited from lead chloride precursor:[1] under the same environment, the nitrogen moiety of the MAPI film from lead thiocyanate remained at the surfaces whereas the film deposited from lead chloride completely lost its nitrogen part. Most interestingly, we observed an additional peak in N 1s spectra, which can be assigned to amine-species at the surfaces. This surface chemical bonding may play a key role in the enhancement of stability by lead thiocyanate precursor and its passivation effect will be discussed in the talk.

## References:

[1] Jack Chun-Ren Ke, Alex S. Walton, David J. Lewis, Aleksander Tedstone, Paul O'Brien, Andrew G. Thomas, Wendy R. Flavell, *Chem. Commun.* **53**, 5231 (2017)

[2] Qidong Tai, Peng You, Hongqian Sang, Zhike Liu, Chenglong Hu, Helen L.W. Chan, Feng Yan, *Nature Communications* **7**, 11105 (2016)