Physics of degradation processes in hybrid perovskites

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Organic inorganic (hybrid) perovskites such as methylammonium lead halides (MAPbX$_3$, where MA=$CH_3NH_3^+$, and X=I, Br or Cl) have attracted tremendous attention in the last years as an absorber material for next-generation solar cells due to the fact that such cells have shown exceptionally fast rise of power conversion efficiencies reaching recently 22.7%. Moreover, a possibility of application of low temperature ink-jet printing techniques for solar cell preparation gives hope for low price of their fabrication on commercial scale. However, despite all these advantages, serious questions concerning stability of perovskites remain to be addressed. In particular, it is well known that exposition of perovskite films to moisture and oxygen causes their fast degradation. It has been demonstrated that exposure of iodide perovskite, MAPbI$_3$ to light and oxygen leads to the formation of very reactive superoxide (O_2^-) species which are able to deprotonate the MA cation of photo-excited perovskite, leading to its decomposition into PbI2, water, methylamine and iodine. Theoretical calculation of formation energies have indicated that vacant iodine sites are the preferred location for oxygen. Chlorine (Cl)-containing perovskite ($MAPbI_{3-x}Cl_x$, called mixed perovskite) seems to be a potential cure for the degradation problem since according to Density Functional Theory (DFT) calculations Cl atoms preferentially substitute iodine atoms reducing the concentration of iodine vacancy sites, and therefore diminishing the diffusion of oxygen into the perovskite layers.

Our aim was to study degradation processes in iodide and mixed perovskites and find influence of different factors on its stability. In order to perform ageing analysis, samples were exposed to air of 65% humidity at room temperature. Using X-ray Photoelectron Spectroscopy (XPS) technique we traced native elements of perovskites and also oxygen content versus time of aging experiment. Moreover, by means of X-ray Diffraction (XRD) presence of different phases was followed. It occurred that decomposition of both iodine and mixed perovskites can be described by first order kinetics with practically the same time constant of about 80 hours. It is surprising, since according to XPS data the oxygen content grew much faster in pure iodine perovskite than in mixed with chlorine one, in agreement with the DFT predictions. In case of iodide perovskite creation of PbI$_2$ evidently followed the decomposition of the fresh material, with the same time constant as for perovskite disintegration process. On the other hand, in case of mixed perovskite, its decomposition was not correlated with noticeable increase of PbI$_2$. For the latter perovskite we found evidence of metallic Pb increase versus time of aging experiment which was not the case for pure iodide perovskite. We hope that these data will allow to reconstruct the course of chemical reaction responsible for mixed perovskite decomposition. We also checked a very promising method of perovskite stabilization - covering it with different oxides deposited by ALD (Atomic Layer Deposition) technique. Such coating layer provides a robust isolation from the influence of atmosphere. The aging experiment was performed on uncoated and coated perovskites and it showed full stabilization of the materials coated with Al2O3 layer during 50 days of the aging experiment. The studies of other coating layers are in progress.