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Influence of halide mixing on thermal and photochemical stability of hybrid perovskites: XPS studies

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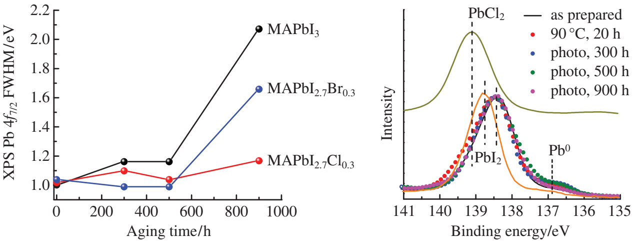
The effect of I^-/Cl^- and I^-/Br^- mixing on the thermal and photochemical degradation of organometallic perovskite $MeNH_3PbI_3$ ($MAPbI_3$) was studied by X-ray photoelectron spectroscopy, which revealed the opportunity to essentially increase the photo and thermal stabilities of the material depending on the level and position of halide-mixing. The largest positive effect was observed for the small concentration of chloride substituent ($MAPbI_{2.7}Cl_{0.3}$), while the full halide substitution ($MAPbBr_3$) had a negative effect on the stability of hybrid perovskite.



The organometal perovskite solar cells $MAPbX_3$ (where MA is $MeNH_3^+$ and X is either Cl^-, Br^-, or I^-) have gained incredible research interest in recent years. The power conversion efficiency of these materials has been increased from 3.8%[1] to over 22.1%[2] within six years, showing that they have a promising potential as a renewable energy resource to compete with the conventional silicon solar cells. However, the long-term stability of such solar cells is still far from the practical requirements. The crucial challenge is to overcome their limited lifetime under operating conditions (light, temperature, humidity, and O_2).[3] In this connection, the understanding of physicochemical processes that induce degradation is of great interest to further development of the perovskite solar cells with enhanced stability. The structural, electronic and optical properties of $MAPbI_3$ can be changed by chemical engineering, *e.g.*, through mixing halogen atoms.[4–7] Therefore, Cl and Br are expected to be the most efficient candidates for tuning the properties of this material. The halogen-mixing has already been shown[6] as providing an improved stability for both $MAPbI_{3-x}Cl_x$ and $MAPbI_{3-x}Br_x$ as compared to $MAPbI_3$. Here, we report on the effect of iodide/chloride and iodide/bromide mixing on the thermal and photochemical degradation of organometallic perovskite $MAPbI_3$, which was studied by X-ray photoelectron spectroscopy (XPS), an effective tool to probe the chemical bonding and electronic structure of such materials.[8–10]

According to the reported[11] X-ray diffraction (XRD) data, the structural changes during the degradation of $MAPbI_3$ involve the disappearance of its characteristic peaks in XRD spectra and appearance of PbI_2 peaks. This suggests the following reaction:

$$MeNH_3PbI_3 = PbI_2 + MeNH_3I,$$

which means that the decomposition yields the two products: PbI_2 and $MeNH_3I$.

According to XPS measurements of Pb $4f_{7/2}$ spectra in this work,† $MAPbI_3$ and PbI_2 have binding energies of 138.4 and 138.8 eV. Therefore, the decomposition of $MAPbI_3$ with formation of PbI_2-phase can be detected by XPS Pb 4*f*-measurements. Figure 1(*a*) shows XPS survey spectra of $MAPbI_3$ measured before and after photo and thermal treatment. One can see that no uncontrolled impurities were detected by XPS survey spectra and a low oxygen signal of pristine sample confirmed a high quality of samples under investigation. The presence of In and Sn on the surface of some samples can be related to a contribution from indium tin oxide substrate due to a lower thickness of lead halide perovskite layer in comparison with other samples. Figure 1(*b*) shows the high-energy resolved XPS Pb $4f_{7/2}$ spectra of initial, photo-treated, and annealed $MAPbI_3$.

A high-energy shift of 0.2 eV is observed in XPS $4f_{7/2}$-spectra of $MAPbI_3$ photo-treated for 300 and 500 h. In the case of samples exposed to light for 900 h and annealed at 90 °C, the maximal energy shifts of 0.4 eV were detected in a full coincidence with the

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† Glass/ITO substrates (5 Ω, Luminescence Technology Corp.) were sequentially cleaned with toluene and acetone, and sonicated in deionized water, acetone, and isopropanol. The $MAPbX_3$ precursor solutions in DMF (~45 wt%) were spin-coated at 5000 rpm inside a nitrogen glove box. The toluene (200 μl) was dropped on the film 4–5 s after the initiation of spin-coating, inducing the film crystallization. The spinning was continued for 45 s and then the deposited films were annealed at 100 °C for 15 min on a hotplate installed inside the glove box.

XPS was used to measure core excitation and valence band spectra on a PHI XPS 5000 VersaProbe spectrometer (ULVAC-Physical Electronics) with a spherical quartz monochromator and an energy analyzer working in the range of binding energies from 0 to 1500 eV. The energy resolution was $\Delta E \leqslant 0.5$ eV. The samples were kept in the vacuum chamber for 24 h prior to the experiments and were measured at a pressure of 10^{-7} Pa.

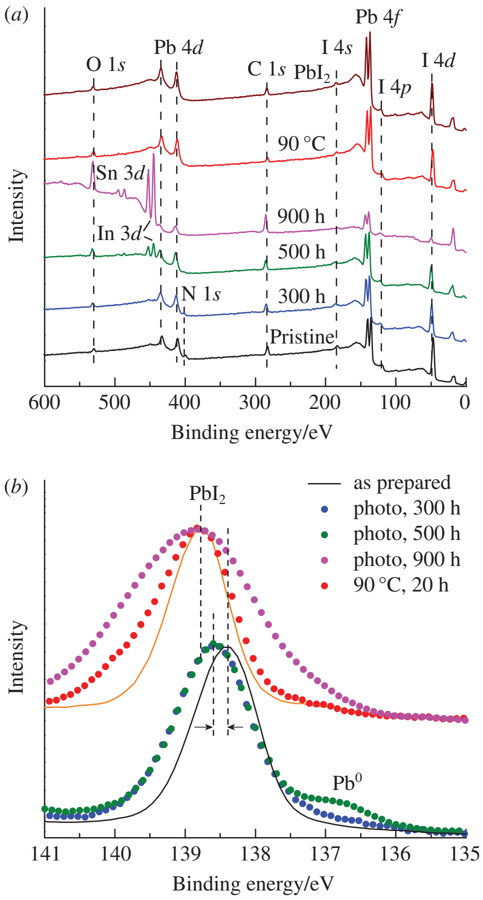

Figure 1 (*a*) XPS survey and (*b*) Pb $4f_{7/2}$ spectra of $MAPbI_3$ as prepared and after thermal and photochemical treatment.

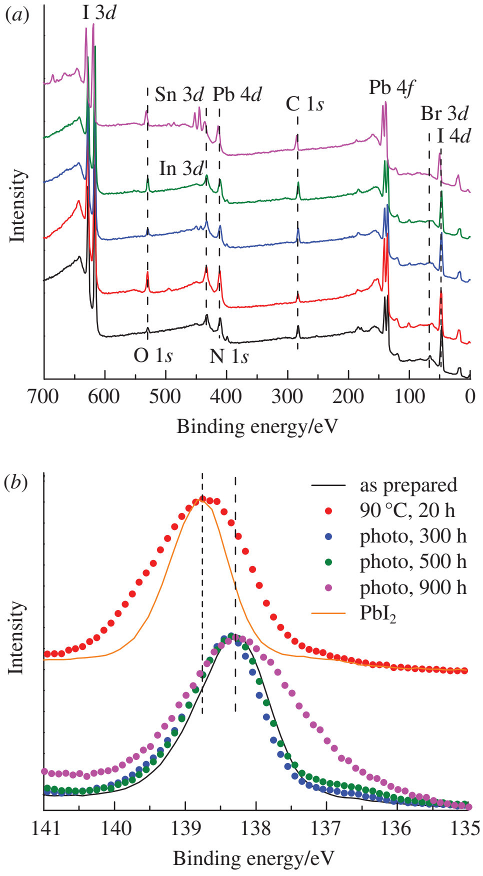

Figure 2 (*a*) XPS survey and (*b*) Pb $4f_{7/2}$ spectra of $MAPbI_{2.7}Br_{0.3}$ as prepared and after thermal and photochemical treatment.

spectrum of reference PbI_2 samples. In addition, the consecutive increase of full width at the half of maximum in XPS Pb $4f_{7/2}$ spectrum at the time of exposure was observed as the broadening of high energy part of spectrum. This indicates the decomposition of initial compound *via* a consecutive increase of the PbI_2 contribution in the spectrum. The discussed maximal high-energy shift was due to the full decomposition of $MAPbI_3$.

The partial replacement of iodine with bromine ($MAPbI_{2.7}Br_{0.3}$) significantly enhanced the photostability of hybrid perovskite at an exposure time of 300–500 h. This was confirmed by the absence of the XPS Pb $4f_{7/2}$ line shift and only its slight broadening [Figure 2(*b*)].

However, a further prolongation of the exposure time up to 900 h led to a significant broadening of the spectrum, as well as annealing at 90 °C for 20 h, which also resulted in a high-energy shift of 0.5 eV to full coincidence with the energy position of the spectrum for the PbI_2 compound. One can see from the XPS survey spectrum [Figure 2(*a*)] that no contaminations were detected. Therefore, the partial replacement of iodine by bromine provided only an incomplete improvement in the photostability, without solving the whole problem including achieved stability at high aging times and annealing at 90 °C.

This problem was solved by a partial replacement of iodine with chlorine giving $MAPbI_{2.7}Cl_{0.3}$ (Figure 3).[‡] The XPS Pb $4f_{7/2}$ spectra [Figure 3(*b*)] exhibited their complete identity with the spectrum of initial sample both with respect to the binding energy and the spectral width (FWHM). To further illustrate the effect of Cl introduction, Figure 4 shows the changes in the full width on half maximum in the XPS Pb $4f_{7/2}$ spectra of the $MAPbI_3$, $MAPbI_{2.7}Br_{0.3}$ and $MAPbI_{2.7}Cl_{0.3}$ compounds starting from the

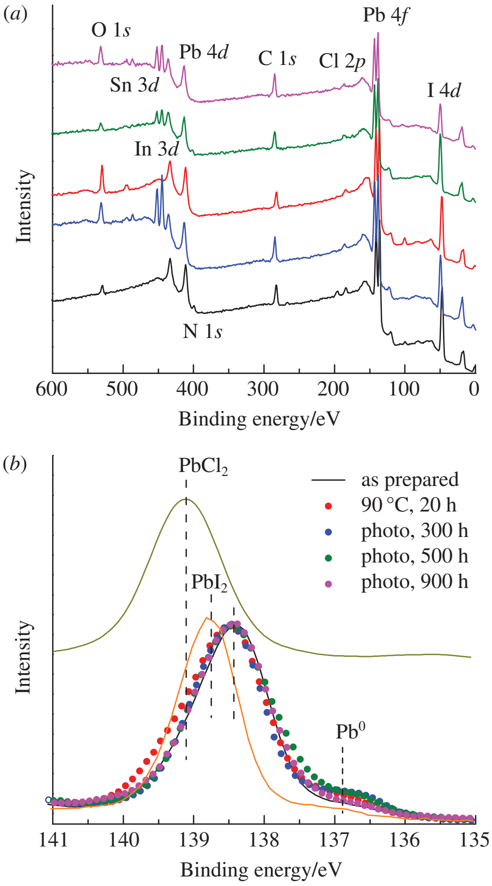

Figure 3 (*a*) XPS survey and (*b*) Pb $4f_{7/2}$ spectra of $MAPbI_{2.7}Cl_{0.3}$ as prepared and after thermal and photochemical treatment.

[‡] The survey spectra of $MAPbI_{2.7}Cl_{0.3}$ [Figure 3(*a*)] did not show the presence of uncontrolled impurities.

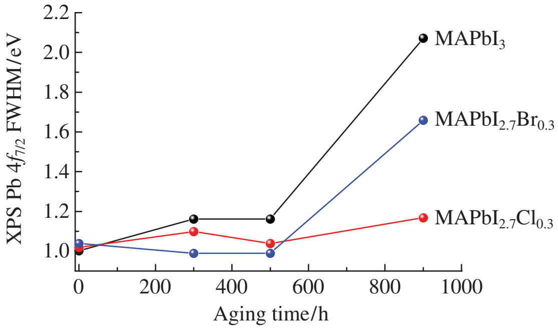

Figure 4 Full width on the half of maximum (FWHM) in XPS Pb $4f_{7/2}$ of $MAPbI_3$, $MAPbI_{2.7}Cl_{0.3}$, and $MAPbI_{2.7}Br_{0.3}$ during aging time under photochemical treatment.

time of photo-irradiation, which clearly demonstrates the absence of significant changes in the half-width of the XPS Pb $4f_{7/2}$ line for $MAPbI_{2.7}Cl_{0.3}$.

The last step in this work was to evaluate the effect of complete replacement of iodine with bromine in $MAPbBr_3$ on its photo and thermal stabilities. Figure 5 shows the acquired data for this compound. Again, the absence of uncontrolled impurities was confirmed by the analysis of XPS survey spectra [Figure 5(*a*)].

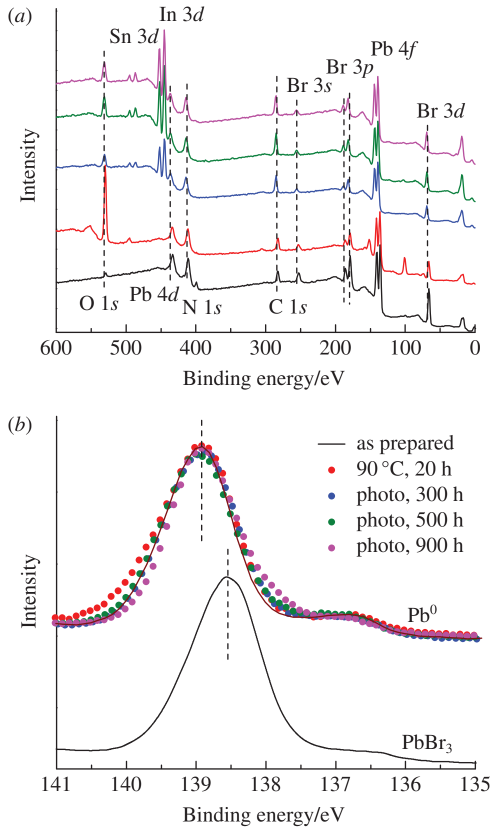

Figure 5 (*a*) XPS survey and (*b*) Pb $4f_{7/2}$ spectra of $MAPbBr_3$ as prepared and after thermal and photochemical treatment.

The high-energy resolved XPS Pb $4f_{7/2}$ spectra [Figure 5(*b*)] indicated the complete degradation of the $MAPbBr_3$ compound caused by both irradiation and annealing, confirmed by the complete coincidence of the binding energies and half-widths in its spectra with those in the spectrum of the $PbBr_2$ compound.

Therefore, the performed investigation of $MAPbI_3$, $MaPbI_{2.7}Br_{0.3}$, $MAPbI_{2.7}Cl_{0.3}$, and $MAPbBr_3$ compounds by the XPS method in their initial state and after their exposure to the photo irradiation (from 300 to 900 h) and annealing at 90 °C for 20 h. The high-energy resolved XPS Pb $4f_{7/2}$ spectra revealed that partial replacement of iodine with bromine ($MaPbI_{2.7}Br_{0.3}$) resulted in a remarkable improvement in photostability upon the irradiation for 500 h. The further increase in irradiation time to 900 h as well as annealing at 90 °C led to the sample degradation. On the other hand, the partial replacement of iodine by chlorine led to a fruitful result: both photo irradiation and annealing at 90 °C did not cause the degradation of the $MAPbI_{2.7}Cl_{0.3}$ compound, which remained stable upon irradiation for 900 h and annealing at 90 °C for 20 h. Meamtime, $MAPbBr_3$, the product of complete replacement of iodine with bromine, was completely decomposed upon irradiation for 300 h or annealing at 90 °C.

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