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Sources of Pb(0) artefacts during XPS analysis of lead halide perovskites.

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Abstract

X-Ray Photoelectron spectroscopy (XPS) spectra of methyl ammonium lead halide perovskite films typically show the presence of lead as Pb(II), but Pb(0) is also often observed, potentially influencing the interpretation of the device physics. In this article the reproducible evolution of Pb(0) peaks which are likely artefacts generated under typical XPS analytical conditions are demonstrated from methyl ammonium lead halide films that contain no Pb(0) initially. The evolution of Pb(0) occurs via (1) X-ray photolysis under typical analytical conditions and (2) alongside other chemical changes as a result of film aging in air. In both cases we note the presence of PbI_2 as a common factor contributing to *in situ* reactions to generate Pb(0) artefacts. Hence the observation of Pb(0) should be treated with extreme caution and here we recommend simple precautions to ensure materials analysis of these films gives reliable information when analyzed under UHV conditions.

Keywords

XPS
Perovskite Solar Cell
Stability
Pb(0)

1. Introduction

Photovoltaic cells based on methyl ammonium lead trihalide (MAPX_3) perovskite materials offer high efficiencies, with the certified cells over 23%[1]. The combination of efficiency with chemical tunability and low cost manufacture has excited considerable interest since the first perovskite cells were demonstrated[2,3].

XPS has been used to understand the presence of PbI_2 and the migration of iodide at interfaces within the perovskite film [4–6] and to monitor the stability of perovskite films [7–11]. One

inconsistent aspect of this data is the appearance of Pb(0) peaks, with the implications that follow, such as the possibility of metallic conduction, extension of electron density up to the Fermi level, and the mechanism of Pb(II) to Pb(0) evolution[11–13]. Many publications show no Pb(0) [5,8,14–16], or show variability in Pb(0) [17]. Conings *et al* speculate that Pb(0) observed in their early experiments[18] is the result of degradation[19]. Finally, an EPR study by Shkrob and Marin has been cited to *confirm* the presence of Pb(0) in perovskite films, but notes the formation of Pb(0) clusters as *effects* of radiolysis by intense X-rays [20].

In this work we show the evolution of Pb(0) artefacts under typical experimental conditions and discuss factors contributing to their appearance. Two problems are identified: (1) the potential for X-ray induced photolysis under visible light illumination and (2) instability due to film degradation. In both cases we note stoichiometric changes suggestive of PbI₂ formation as the root cause. As the variability in the literature highlights, it is possible to produce high quality XPS spectra without any presence of Pb(0) artefacts and hence we suggest that, with mechanistic understanding, precautions can be taken to improve the reproducibility of data and eliminate such artefacts.

2. Experimental Methods

The preparation of “Carbon” (Triple Mesoporous Carbon) perovskites [21] or “MAPI” planar methyl ammonium lead iodide films via sequential deposition [22] are detailed elsewhere.

XPS was recorded on an Axis Supra (Kratos Analytical) using a 15 mA (225 W) monochromated Al K_α source. Unless otherwise stated, X-ray exposure was limited to << 30 min and all vacuum procedures were performed in the dark, with the charge neutralizer on. For stability testing, four cases were tested for one hour each. 1) “Dark” – all lights & charge neutralizer are disabled. 2) “Ambient” – internal lighting is switched on. 3) “Neutralizer” – the charge

neutralizer is enabled. 4) “Bright” – A BRIDGELUX 9000 lumen LED array is shone onto the samples through the leaded-glass viewing ports. Quantification used CasaXPS(2.3.17dev6.4k), the Kratos RSF library and transmission function. Shirley backgrounds were used with GL(70) fitted components to quantify peak areas. Both Pb 4f_{7/2} & 4f_{5/2} peaks were fitted, with Pb(0) at 136.5 eV and Pb(II) at 138.1 eV & FWHM identical for all components. Charge is corrected to adventitious carbon at 284.8 eV. A Pb(II):I:N At% ratio of 1:3:1 indicates perovskite, with 1:2:0 indicating PbI₂. %Pb converted to perovskite is based on %N for 11 films, with the remaining Pb:I giving a 1:2 ratio consistent with PbI₂. Peak positions are from NIST Database[23] and Phi XPS Handbook[24].

SEM was performed on a Jeol JSM-7800F FEG-SEM with 5 kV beam at 6-10 mm working distance. XRD was performed on a Bruker D8 Discover with a Cu K_α beam at 40 kV, 40 mA emission and 0.01° 2θ step size.

3. Results and Discussion

3.1 Perovskite Stability and Pb(0) Evolution Under X-rays

It is impossible to know how all papers deal with perovskite stability under X-rays, due to the variability of instrument pump down times, charge neutralization, x-ray flux, and the possibility of perovskite film degradation prior to analysis. However, a typical experiment would monitor iodine, lead and nitrogen over time. In this case we began in the “Dark” for 1 hour with all light and electron sources disabled. “Ambient” (internal instrument LED’s on), “Neutraliser” (with the integral electron source enabled), and “Bright” (with 9000 lumen source) conditions were also studied. The Carbon perovskite architecture is used as it is not prone to differential charging artefacts in the dark. By contrast for planar MAPI films, differential charging exceeded

23 eV over 1 hour in the dark. Neither planar MAPI nor Carbon perovskites display differential charging when illuminated.

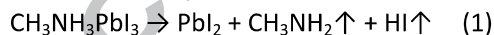
Figure 1 shows overall chemistry (Figure 1a) and Pb chemistry (Figure 1b) during a typical study. During the initial 30 mins, typical of an XPS experiment, there is a reduction in the amount of nitrogen (Figure 1a). When the ratio of Pb:I:N is considered over time, this nitrogen loss causes stoichiometry of the initial MAPI-like surface to gradually shift towards a more PbI_2 -like surface (Figure 1b). Lead and iodine peaks show almost no change up to 180 minutes, even when Ambient light is present or electrons are introduced via the Neutralizer.

As noted above, MAPI films display very different charging behavior in light and dark. Coupled with previously observed changes under a blue laser over several hours[25] suggesting that the influence of light on perovskite films is profound. Hence illumination by a 9000 lumen white LED was studied, and this light causes evolution of a $\text{Pb}(0)$ peak to 10% of total lead present (Figure 1b, 180-240 mins), with the $\text{Pb}(4f)$ envelope clearly showing evolution of $\text{Pb}(0)$ at 136.5 eV alongside the main $\text{Pb}(II)$ peak at 138.1 eV (Figure 1c) – similar results are observed for the more widely studied planar MAPI films (Figure 1d). This evolution of metallic lead coincides with a slight loss of iodine from 64.5 At% to 62.0 At% over 180-240 min. During the same time period, nitrogen is stable, suggesting that changes are not linked to accelerated methylamine evolution.

This change appears to be consistent with a loss of iodine from lead iodide. The X-ray photolysis of halides is well-known for PbX_2 materials[26] – and is reproducible for a lead iodide film after 10 minutes (Figure 1e). The mobility of ions within MAPX_3 materials, and the reversible conversion of MAPX_3 materials to PbI_2 under bias is already reported[6,27–29]. Finally, PbI_2 may be present as unreacted precursor material[5].

The Carbon perovskite, with microns thick triple mesoporous layers, differs from the more widely used MAPI thin films, so MAPI films deposited via sequential deposition were also examined. The XPS surveys (Figure 2a) showed unexpected peaks. The presence of 19 ± 7 At% O(1s) and the 7 ± 3 At% Ti(2p) signal at 458.8 eV are consistent with TiO₂ from the underlying n-type layer. Considering only the MAPI film, comparing the atomic ratios of Pb:I:N suggests that 83 ± 8 % of the Pb present on the surface is present as perovskite, with the remainder of the Pb(II) as PbI₂. XRD confirms the presence of PbI₂ in the bulk (Figure 2b) and SEM shows particles present on the surface alongside pinhole defects in the coating that expose the underlying TiO₂ (Figure 2c).

Phillipe et al suggested that Equation (1) takes place when annealing at 100°C[30], and it is probable that this evolution takes place slowly in UHV, with the low pressures favoring gas evolution. The subsequent photolysis of PbI₂ in Equation (2) is expected and the evolution of Pb(0) is probably an artefact driven by presence of PbI₂ or the equivalent dihalides. This is important for in situ studies by application of electrical bias[6] or light[25] where ion migration is expected to generate PbI₂ centers and hence increase the risk of observing Pb(0) where no Pb(0) artefacts are present initially.



We propose caution when performing UHV experiments of perovskites, as pristine materials can evolve Pb(0) features that can only be interpreted as experimental artefacts. As a minimum we recommend: quick experiments to minimize MAI loss; storing samples in the dark; and running the experiments in darkness to limit ion migration.

3.2 Pb(0) Evolution on Aging Samples

Analyses were carried out on a planar MAPI sample after storage in a desiccator cabinet in the dark for 4 months. 7 equidistant points are examined across the 28 mm sample, with points 1-4 notably yellowed prior to the XPS experiment and points 5-7 apparently still brown.

The as-produced film (Figure 3a, noted Initial) shows no Ti(2p), but after aging for 4 months a drop from 100% film coverage to 97.7 ± 0.4 %, as estimated by the area of the observed Ti(2p) signal in the yellowed areas (Figure 3a 1-4), as the perovskite film densifies and exposes the underlying TiO₂. Once the film densification is accounted for, ratios of Pb, N & I show that ~25% of the lead in the brown areas is perovskite. The remaining lead and iodine signals show a 1:2 Pb(II):I ratio, again consistent with PbI₂ and an accompanying Pb(0) signal is observed. The yellowed region (locations 1-4) is nitrogen and iodine deficient, and the iodine:lead ratio drops considerably below 2:1. Pb is still retained mainly as Pb(II) oxidation state, with increased O(1s) content from oxidized lead compounds[15], however there is little Pb(0) observed in this region. For this degrading film, Pb(0) peaks occur where MAPI has begun to degrade via PbI₂, but not where the degradation has proceeded further to Pb oxides, suggesting again that PbI₂ is the cause of Pb(0) evolution. Degrading perovskites that are more prone to evolution of Pb(0) have been reported[19] in the literature.

Overall it is clear that X-rays can induce photolysis of Pb(II) to Pb(0) under XPS experimental conditions, via both light induced generation of PbI₂ and via aging of the perovskite films – but it is also clear that such artefacts can potentially be reduced or eliminated completely, at least, for freshly produced materials.

4. Conclusions

Controlled evolution of Pb(0) in XPS spectra from materials containing no Pb(0) component initially was demonstrated based on instrument experimental conditions. Similarly materials

were shown to be prone to evolution of Pb(0) as a consequence of degradation in air. Understanding that this Pb(0) signal is often an artefact of damage, or degradation of, the sample during the measurement process should allow Pb(0) to be eliminated in most cases. In particular, care must be taken to rigorously control sample storage and analysis conditions to ensure both accurate nitrogen quantification and to prevent the evolution of erroneous Pb(0) artefacts. For freshly made perovskite films, elimination of the artefact is a reasonable target, but researchers and reviewers should note that the instability of degraded films may make complete elimination of Pb(0) impossible.

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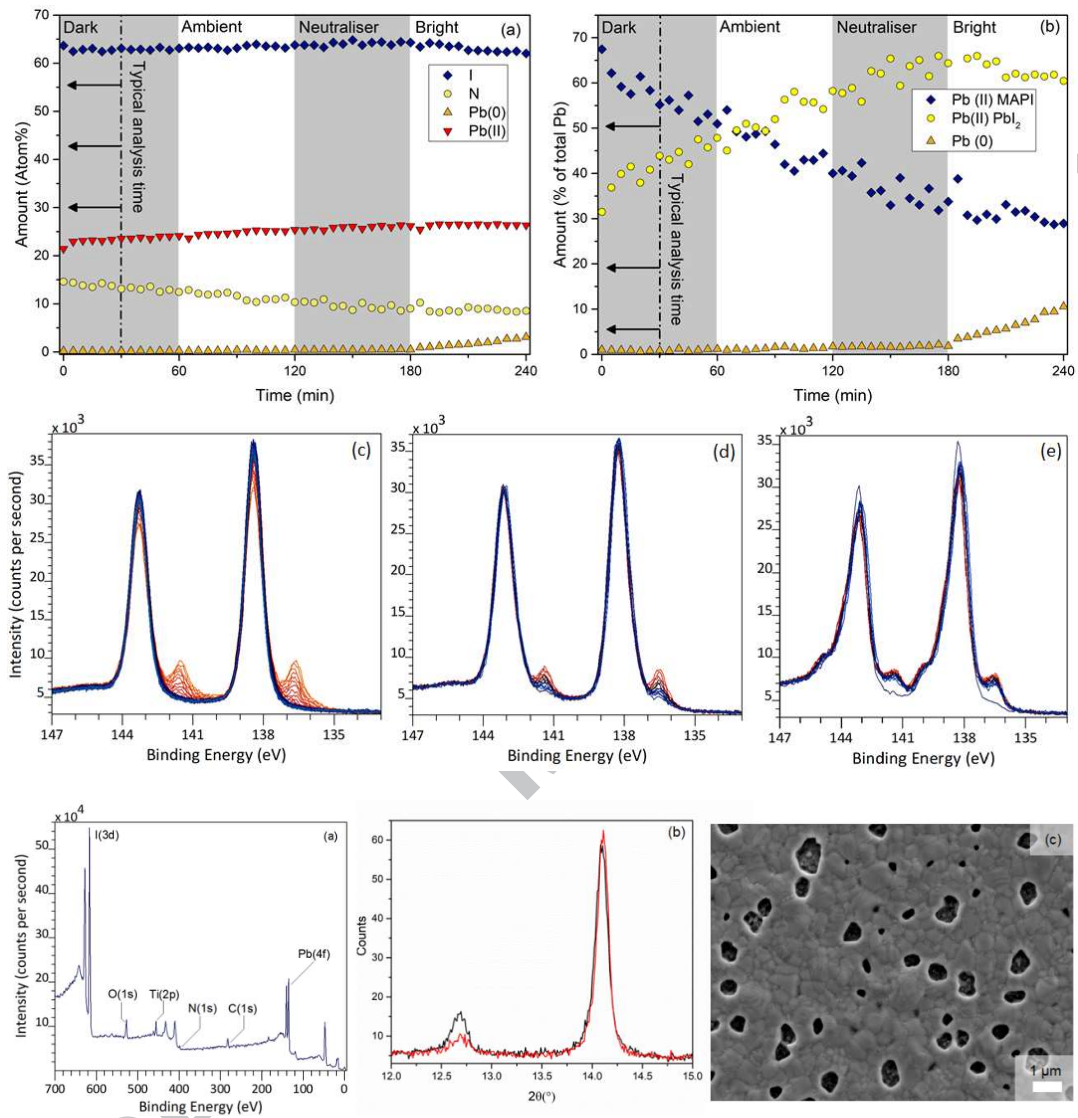
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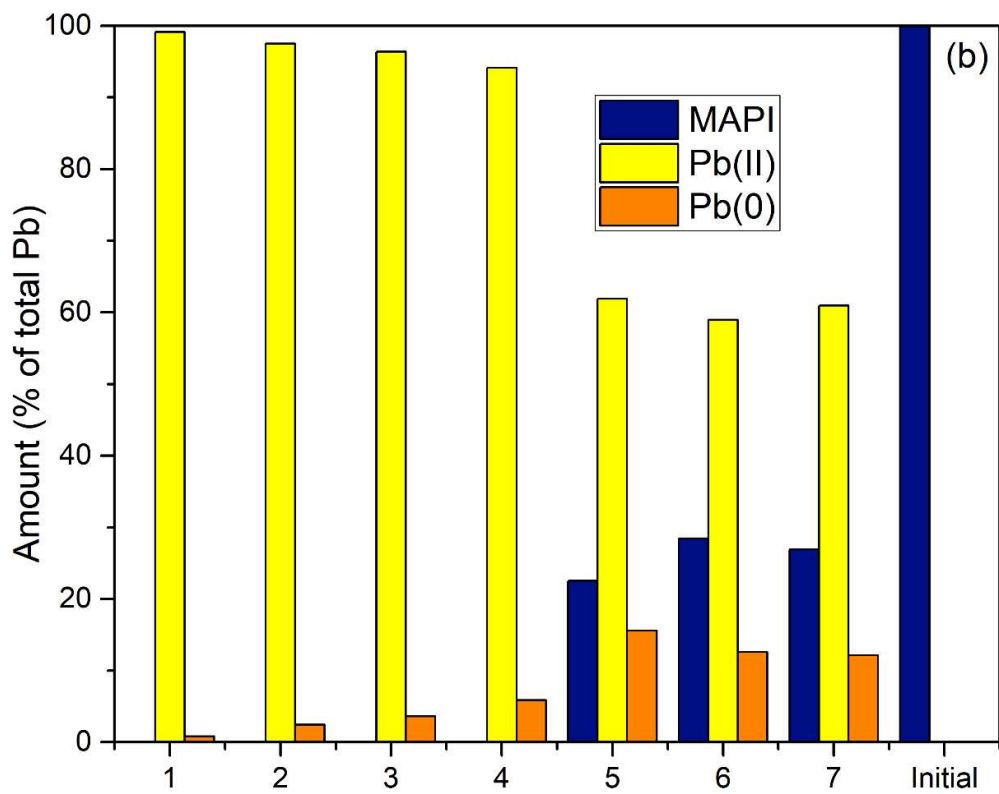
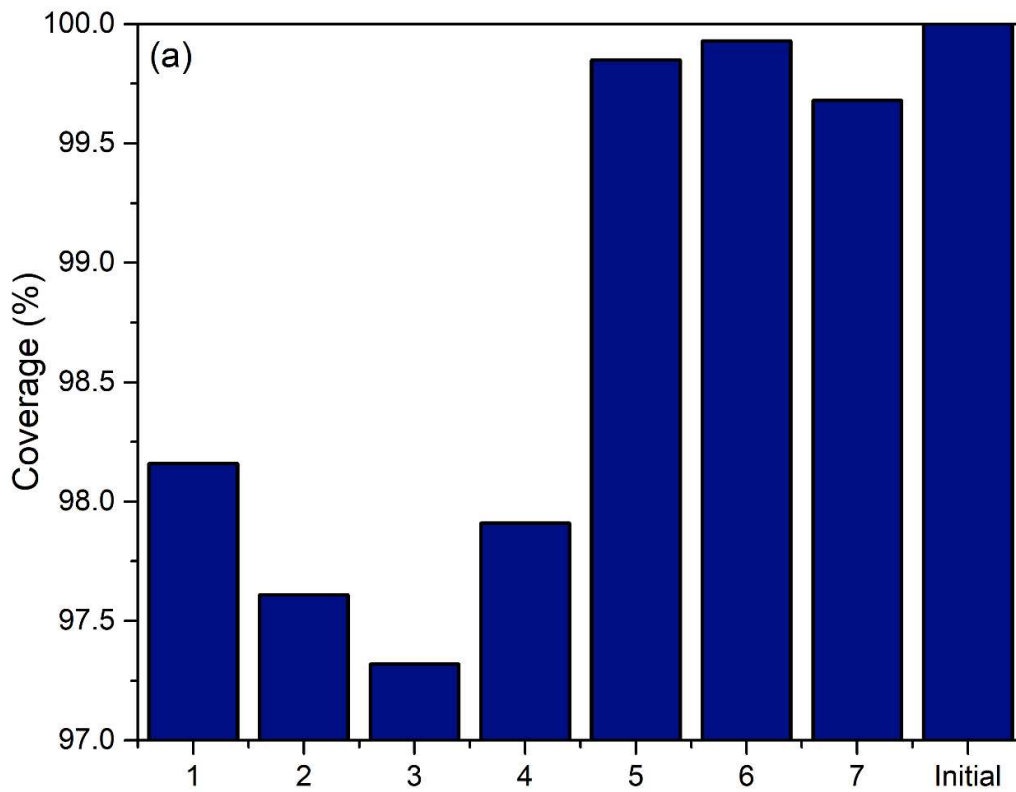
Figure Captions

Figure 1. Evolution of Pb(0) peaks under illumination for various systems. (a) Stoichiometry as a function of time for Carbon cells. (b) Estimating the various lead chemistries for Carbon cells based on high resolution peak fitting. Pb(4f) spectra for (c) Carbon cells, (d) planar MAPI, and (e) PbI_2 all show evolution of Pb(0).

Figure 2. (a) Typical wide scan XPS surface chemistry for planar MAPI cells. (b) XRD at different points on the film shows PbI_2 at 12.7° in the film in addition to the MAPI 110 at 14.2° and (c) SEM confirms the presence of coating defects.

Figure 3. XPS planar MAPI films at seven points across a 28 mm wide MAPI film after 4 months aging in a dessicator in the dark (1-7) and the freshly produced film (Initial). (a) Perovskite surface volume coverage. (b) Estimating the various lead chemistries.



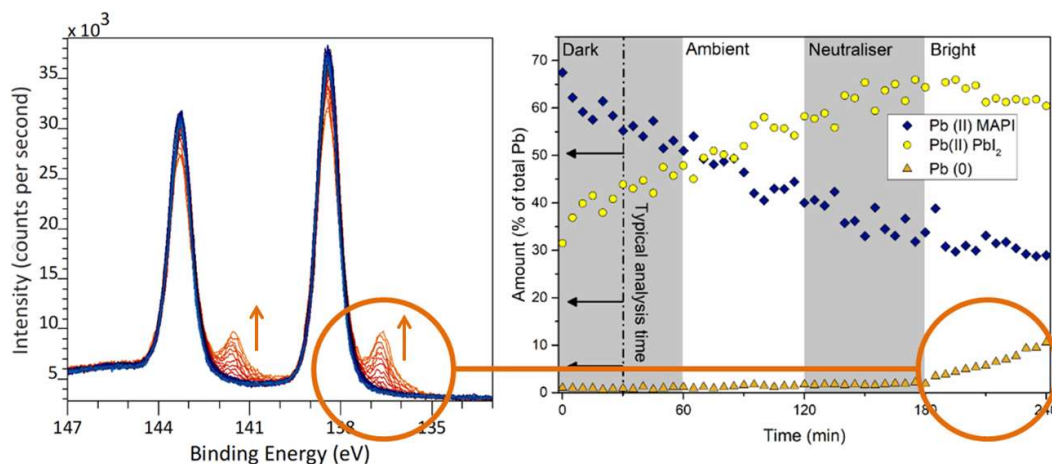


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We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

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Sources of Pb(0) artefacts during XPS analysis of lead halide perovskites.

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- Evolution of Pb(0) from methyl ammonium lead halide is demonstrated under illumination and via perovskite film aging.
- The presence of Pb(0) and its relation to PbI₂ is demonstrated.
- It is suggested that the observation of Pb(0) is a common artefact of PbI₂ photolysis.

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