

Cite this: *Mater. Chem. Front.*,
2023, 7, 3797Received 17th May 2023,
Accepted 8th July 2023

DOI: 10.1039/d3qm00574g

rsc.li/frontiers-materials

Lessons learned: how to report XPS data incorrectly about lead-halide perovskites

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X-Ray photoelectron spectroscopy is a powerful tool for identifying the interactions of additives or surface treatments with components in lead halide perovskites. However, with the increasing number of studies using XPS, inaccurate or faulty data analysis has been encountered during a literature survey. Herein, we describe the fundamental principle of chemical shifts of Pb atoms in XPS and critically review the commonly seen mistakes in the literature: (i) misinterpretation of the XPS mechanism; (ii) misinterpretations due to disturbed chemical environments; (iii) lack of awareness of the properties of the passivator; iv. misquoted references. We hope that this perspective can help the community avoid the pitfalls in applying the XPS technique and in explaining their experimental results.

Perovskite solar cells (PSCs)^{1–12} have become a game changer in the field of solar cells, and specifically an up-and-coming candidate in replacing the otherwise predominant silicon solar cells due to their relatively low preparation costs and more straightforward fabrication process.^{13,14} PSCs, however, do show poor long-term stability—and to circumvent this issue, additives or surface treatments (namely passivation) that target the origins of various defects are commonly adopted.^{7,15–18} In this context, the interactions between these various additives and the components in the perovskites could readily be unveiled qualitatively and quantitatively using X-ray photoelectron spectroscopy (XPS). By analyzing the XPS data of a target material, it is possible to determine its elemental composition and empirical formula as well as the electronic and chemical states of its elements. Therefore, XPS, which involves recording the kinetic energy of electrons that are emitted from the top 1–10 nm of the material being irradiated with a beam of X-rays, is gaining popularity in characterizing the role of these passivation strategies¹⁹ (Fig. 1). The basis of a correct XPS data analysis is the accurate calibration of the binding energy (E_B),²⁰ including calibration of the energy scale of the spectrometer and the deviation caused by the charging effect (usually with C 1s data of adventitious carbon²¹ or decorated noble metal²²).

The electron binding energy (E_B) could be calculated using the equation $E_B = h\nu - E_K - WF$,²³ in which $h\nu$ is the photon energy, E_K is the measured kinetic energy, and WF is the

spectrometer work function. E_B is characteristically distinct for atoms with different electronic shells, and it is also, to some extent, dependent on the chemical environment of the atom. Namely, a change in the chemical state (chemical environment) could be reflected in shifted energies of expelled photoelectrons.²⁴ The higher the electron density around an atom, the higher the E_K of photoelectrons originating from its core levels, and hence the lower the chemical shift of the corresponding E_B peaks in the spectrum (Fig. 2).²⁵ In studies of PSCs, the chemical shift of the Pb 4f signal is the most commonly chosen one to verify the interaction of perovskite with functional groups of additives. Theoretically, depending on the nature (electron-accepting or electron-donating) of the functional group, a shift of the Pb 4f signal toward a higher

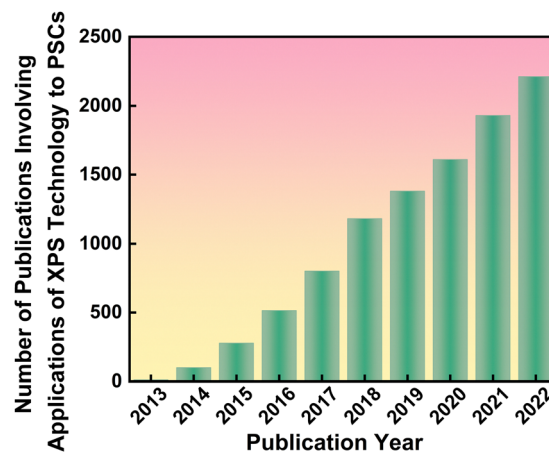


Fig. 1 Plot of the number of publications per year involving perovskite solar cells and XPS according to a Google Scholar search performed in January 2023 for the term “perovskite solar cell AND (XPS OR X-ray photoelectron spectroscopy)”.

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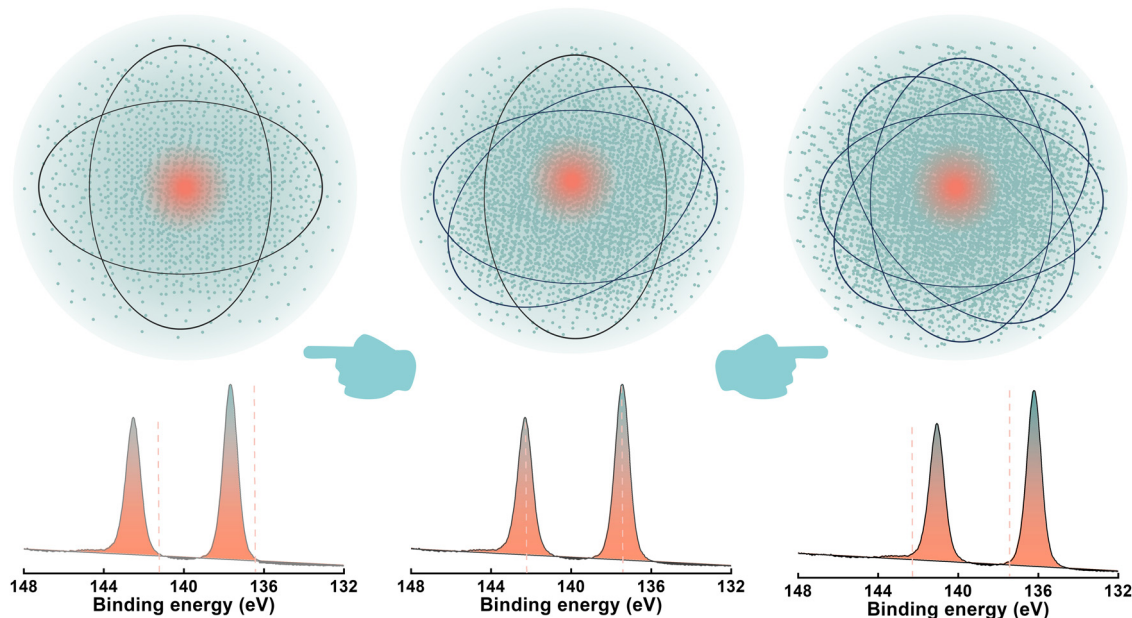


Fig. 2 Schematic relationship between the electron density on the Pb atom and the chemical shift.

E_B is due to a decrease in the electron density on the Pb atom. In fact, the standard conduction of XPS on perovskites has already been introduced by Schulz *et al.*, including the normative measurement conditions and correct analysis of binding energy spectra.^{26,27} However, as said by Aristotle, “one may go wrong in many different ways, but right only in one, which is why it is easy to fail and difficult to succeed”, and so it is necessary to point out directly the mistakes made subconsciously in XPS measurements.

Unfortunately, some reports have provided inaccurate or inappropriate analysis of the XPS data (*e.g.*, Pb 4f spectra) due to (i) misinterpretation of the XPS mechanism, (ii) misinterpretation due to a disturbed chemical environment, (iii) lack of awareness about the properties of the passivator, and (iv) misquoted references. Herein, a perspective on the correct understanding of XPS data is given based on examples containing erroneous/inadequate analysis of the chemical shifts in XPS. We hope that this critical perspective, which complements the work done by Schulz *et al.* on properly analyzing XPS data,²⁷ will help the community avoid the pitfalls of applying the XPS technique when explaining their experimental results.

Misinterpretation of the XPS mechanism

Misinterpretations of the chemical shifts in XPS spectra are easily found in the literature. For instance, Cheng *et al.* concluded that the electron density around the Pb atom increased based on an actually higher-energy-shifted E_B .²⁸ In another case, Zheng *et al.* claimed that the higher E_B at the Pb 4f level resulted from additional negative charges surrounding Pb.²⁹ These studies conceptually misinterpreted the rule of chemical shifts in XPS, since there is no direct effect on the binding energy of core-level electrons for the different valence-charge

densities because electrons do not have different energies but simultaneously share the total energy of the whole system.^{19,30} A photoelectron from Pb in a Pb–Cl unit would reach the detector with a lower kinetic energy than would that from a Pb–I unit due to the higher electronegativity of Cl and poor screening of the core holes.³⁰

Misinterpretation due to disturbed chemical environments

In fact, the evolution of the chemical environment of the observed atomic species can be determined by tracking chemical shifts in the photoelectron binding energy (E_B) for the multicomponent halide perovskite.²⁷ But the operation of the XPS equipment and collection of data may not be normative. This issue is reflected in two works on the same compound, with opposite reported effects on the chemical shift of a Pb 4f signal.^{31–36} For example, the Pb 4f E_B was reported by Wang *et al.* to shift to lower energy in perovskite films with a PEG/PVA overlayer³¹ (Fig. 3a), but the same polymers were reported to show the opposite shifts by Chen *et al.*³² (Fig. 3b). The former attributed the down-shifting of Pb 4f binding energy to increased electron cloud density of the Pb atom due to a strong interaction with PVA/PEG,³¹ while the latter believed that the observed up-shifting of the Pb core level was due to decreased electron density by the same polymer *via* a weaker coordination between the functional groups with Pb than with I^- .³² Likewise, contradictory conclusions have been reported in works about ammonium-salt-modified perovskites: Kang *et al.* reported down-shifting Pb 4f and I 3d E_B values in the presence of 2D TBA₂PbI₄ in an FAPbI₃ film and speculated that the TBA cation reduced the oxidation state of Pb and I or weakened the Pb–I bond (Fig. 3c);³³ in contrast, Liu *et al.* reported no change in the oxidation state of Pb and I in CsPbI₃ after TBAI treatment and formation of 1D



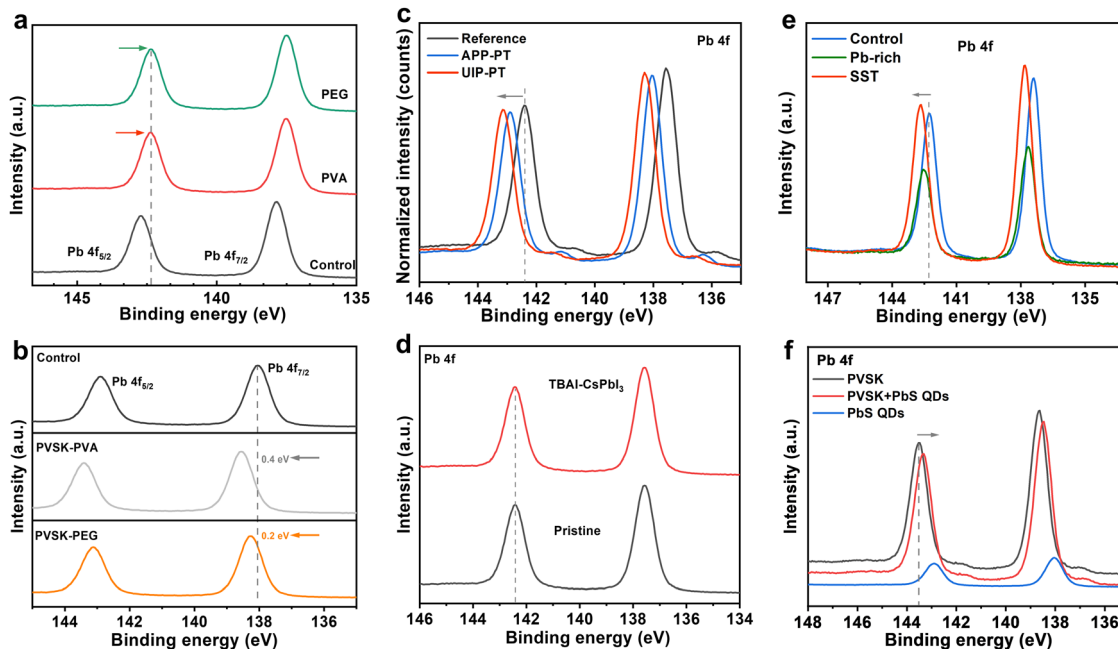


Fig. 3 XPS spectra of Pb 4f peaks in perovskite films (a) without and (b) with PEG/PVA; (c) before (reference) and after post-treatment by UIPPT or APP-PT; (d) CsPbI₃ films before and after TBAI treatment; (e) perovskite films (control), Pb-rich perovskite films (Pb-rich) before and after surface sulfidation treatment (SST-based); (f) pristine PbS QDs, perovskite films without (PVSK) and with PbS QDs (PVSK + PbS QDs).

TBAPbI₃ (Fig. 3d).³⁴ Similarly, the Pb 4f E_B was reported to shift differently in two separate works using PbS as the surface sulfidation treatment (SST) material for perovskites: to higher energy in one report, attributed to the strong bonding between S and Pb (Fig. 3e),³⁵ but with a reversed chemical shift on the same core level after the same treatment according to the other work (Fig. 3f).³⁶ We believe that these contradictory experimental data could be due to unregulated operation by inexperienced researchers, which may result in artifacts in the measured chemical shifts under the same chemical environment.

Lack of awareness of the properties of the passivator

As described by Schulz *et al.*, the case of Pb is interesting because the corresponding E_B is influenced by the halide to which it is bound.²⁷ It is generally believed that the electron-donating nature of a Lewis base can lead to a downward shift in the E_B of the Pb 4f peak.^{14,31,37–42} Assuming that the experimental conditions in the same publication are consistent, the changes in Pb binding energy should be attributed to the added passivator. Unfortunately, the logical relationship between the XPS chemical shift and the role of additives in some reports is not self-consistent. For instance, the dipolar PCBB-3N-3I was deposited, in a work published in 2019, to passivate under-coordinated Pb²⁺ *via* the negatively charged terminal groups.⁴³ However, this work reported an upward-shifted Pb 4f core level energy, indicating decreased electron density. So how could a more electron-poor under-coordinated Pb²⁺ be called passivated? Similarly, Liu *et al.* reported the use of (5-mercapto-1,3,4-thiadiazol-2-ylthio) acetic

acid (MTDAA) as a multi-active-site Lewis-base that shifted the Pb 4f E_B towards higher energy.⁴⁴ The contradictory conclusions suggest that the authors did not establish a clear connection between the concept of increased electron density in a passivated under-coordinated Pb²⁺ and the specific passivator they employed.^{45–49}

Misquoted references

Sometimes, a report may blindly cite the conclusion from another published report with different experimental results, leading to a biased interpretation. By illustration, Hu *et al.*, when using XPS to prove the incorporation of Ln³⁺ into CsPbBr₃, first claimed the increased electron density around the Pb atom (down-shifting Pb 4f E_B) to be due to a stronger interaction between Ln³⁺ and Br⁻.⁵⁰ Later, another work by Duan *et al.* misquoted the conclusion from ref. 45 to explain the observed up-shifting of Pb and Br core levels after Ln³⁺ doping.⁵¹ Also, pyridine is commonly regarded as a Lewis base to bind with a Lewis acid and, therefore, as a passivator for perovskite.⁵² However, such a conclusion has been arbitrarily used, including even when the nitrogen of the pyridine was quaternized, in which the positive nitrogen cation cannot function as an electron donor and, therefore, cannot be indicated to be responsible for the upward shifting Pb 4f core level.⁵³ To avoid these situations, it is essential to “seek truth from facts” and fully understand the previous studies before using them to support the new data.

In brief, to use XPS as a powerful tool for understanding the material science of perovskites, more comprehensive knowledge combining the fundamental mechanism of XPS and the electronic structure of the target compounds is needed.



Furthermore, a consistent logical data analysis should be used for drawing conclusions based on XPS and chemical theories. Last but not least, rigorous handling, correct calibration, and careful referencing are also crucial for reporting XPS data.

Data availability statement

The data that support the findings of this study are available from the corresponding author on request and will be supplied on a reasonable time period.

Author contributions

C. L. and N. Z. performed the leading research, prepared the manuscript, and contributed equally to this work. P. G. provided financial support and guided the project.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

P. G. acknowledges the National Natural Science Foundation of China (Grant No. 22175180, 21975260).

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