

EDITORIAL

Advancements and challenges of HAXPES for materials sciences and technologies

The advancement of key materials technologies, such as surface functionalization, microelectronics, energy conversion, joining, catalysis, and medical implants, critically relies on the understanding of the chemistry and electronic structure of **buried solid–solid**, **solid–gas**, and **solid–liquid** interfaces. Recent developments in instrumentation, microelectronics, and detector technologies have enabled routine investigations of such interfaces by hard X-ray photoemission (HAXPES) techniques at synchrotrons worldwide, as well as in the laboratory (J. F. Watts, 0223.R1). The increase in kinetic energy of emitted photoelectrons with increasing photon energy is accompanied by an increase in photoelectron probing depth. Typical probing depths in the range of 20–30 nm are obtained for shallow core-level photoelectrons emitted by hard Cr- $\kappa\alpha$ X-rays from inorganic solids and detected at a near-normal angles with respect to the sample surface. Clearly, for such large probing depths, the combined effects of surface contamination and film surface reconstructions on the chemical state analysis of thin films and nanomaterials are greatly suppressed. This probing depth range also exceeds typical nanolayer thicknesses used in semiconductor devices, which enables investigations of the chemistry and electronic structure at buried functional interfaces in such nanomultilayered devices (T. Spelta et al., 0084.R2). Furthermore, “useful” chemical information from air-sensitive materials, such as battery materials and/or heterogeneous catalysts, may still be extracted after short-time exposes to ambient conditions. Also, the unperturbed chemistry below contaminated surface regions, such as in the interior of air-exposed catalytic nanoparticles (F. Longo et al., 0169.R2) or below a passive oxide film on steel (C. Olsson et al., 0168.R1), can be easily assessed by HAXPES. Hence, the relatively strict requirements on surface “cleanness” for conventional XPS measurements of air-sensitive materials are much less critical for HAXPES, which is especially interesting for tackling applied and thus industrial-relevant technologic challenges in the fields of, for example, batteries, catalysis, and surface functionalization of alloys.

The recent availability of HAXPES systems has also advanced analytical capabilities to extract structural and morphological information from the shape of the background of the inelastically scattered electrons over the extended binding energy range of up to several thousands of electronvolts. Inelastic background analysis over such larger energy loss ranges can reveal structural and morphological details over probing depths exceeding 100 nm. The large probing depths and the inelastic backgrounds in HAXPES analysis truly enable chemical analysis of *bulk* instead of *surface* properties of thin films and nanomultilayers, thereby redefining the core analytical

capabilities of lab-based photoemission spectroscopy (Tougaard et al., 0203.R1).

On the downside, the photoionization cross-section drastically decreases with increasing photon energy, especially for the shallow core-level electrons. From our daily experience, as a rule of thumb, detailed chemical analysis of a single functional surface or thin-film system by a dual-beam XPS/HAXPES instrument in a lab-based environment typically requires a total measurement time of 10–20 h per sample point to obtain a satisfactory signal-to-noise ratio for the two surveys and all relevant photoelectron lines and sharp Auger transitions, as recorded with both the soft and hard X-ray sources. This implies that dual-beam lab-based HAXPES/XPS analysis is not (yet) suited for performing high-throughput chemical state analysis of material libraries for, for example, heterogeneous catalysis and batteries. Hence, a clear research strategy is needed to smartly combine high-throughput combinatorial materials analysis with targeted HAXPES studies of selected material compositions and structures within a given materials system library. Notably, lab-based dual-beam XPS/HAXPES systems interconnected to a glove-box and/or a UHV processing chamber are still very sparsely installed world-wide but enable to design and conduct unique in-situ experiments on a daily basis, which are complementary or in some cases even comparable to synchrotron ones. Such advancements in lab-based HAXPES instrumentation and experimentation further push the developments at the synchrotron towards cutting-edge operando photoelectron spectroscopic studies under realistic service conditions (C. Colbea et al., 0117.R1).

Finally, the use of hard X-rays also gives access to deep core-level photoelectron lines, which cannot be measured by conventional XPS. The correspondingly large core-level binding energies result in much lower kinetic energies of the emitted photoelectrons, which gives a similar surface sensitivity as for conventional XPS. Furthermore, photoemission of deep core-level electrons (e.g., from the 1s shell) can trigger sharp and intense core–core–core Auger transitions, particularly KLL transitions, which can be exploited for local chemical state analysis on the basis of the Auger parameter, originally proposed by Wagner. Such local chemical state studies using the Auger parameter were very popular during the beginning of the XPS era, since the Bremsstrahlung from traditional non-monochromatic X-ray sources could be exploited to excite deep core-level 1s photoelectrons for triggering the KLL transitions. With the invention and broad commercialization of monochromatic, focused, and scanning X-ray sources for lab-based XPS, such measurements of the sharp KLL Auger lines were

no longer possible. The recent development and commercialization of lab-based hard X-ray sources for dual-beam XPS/HAXPES has clearly led to a revival of such local chemical state analysis (C. Cancellieri et al., 0233.R1; F. Longo et al., 0169.R2). As follows from a quick assessment of the reported 1s core-level binding energy with increasing elemental mass, the commercially available hard X-ray lab sources principally allow measurements of the 1s photoelectron line and its associated KLL transitions up to an elemental mass of $U = 23$ for Cr-K α radiation ($h\nu = 5414.7$ eV; including elements such as Mg, Al, Si, S, and Ti) and up to $U = 29$ for Ga-K α radiation ($h\nu = 9252.13$ eV; thus also including elements like Cr, Mn, Fe, Co, Ni, and Cu). Notably, all Auger transitions shift to higher “apparent” binding energies with increasing photon energy, thereby minimizing possible overlaps with the shallow bulk-sensitive photoelectron lines (S. Leadley, 0143.R1). This advantage turns out to be very useful in the daily analysis of photoelectron spectra of complex catalysts, high-entropy phases, as well as for steel, since partially overlapping Ni and Co LMM Auger transitions are shifted to higher binding energies.


This special issue collects key examples and latest developments of state-of-the-art applications of HAXPES and related instrumentations for cutting-edge research in the field of materials sciences and technologies. We thank all the co-authors who have contributed to this special issue and hope you will enjoy its reading.

FUNDING INFORMATION

Swiss National Science Foundation, R'Equip program, Grant/Award Number: 206021_182987

DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this editorial.

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