Interface Formation in Perovskite Solar Cells: Insights from Photoemission Spectroscopies Across Buried Interfaces

The formation and electronic structure of interfaces between the perovskite absorber and adjacent transport layers are key factors governing charge extraction, recombination, and long-term stability. While favorable alignment is often inferred from nominal energy levels of individual materials, real device interfaces are shaped by chemical reactions, defect formation, interfacial dipoles, and band bending. These effects are particularly critical at buried interfaces, where direct experimental access is limited. In this contribution, I present our recent advances in photoemission-based studies of interface chemistry and energetics in perovskite solar cells, with a focus on the role of hole transport layer, organic buffer layer and low dimensional perovskites in controlling energy level alignment.

We first address the integration of atomic layer deposited nickel oxide (ALD-NiO) as a hole transport layer in n-i-p device architectures. Using synchrotron based hard X ray photoelectron spectroscopy (HAXPES), we show that ALD-NiO films grown directly on metal halide perovskites contain a high concentration of hydroxide and oxyhydroxide species. In parallel, nitrogen and lead related defect states form in the perovskite near the buried interface. These chemically induced changes lead to unfavorable interface energetics and degraded device performance. Introducing a thin organic poly[bis(4 phenyl)(2,4,6 trimethylphenyl)amine] (PTAA) interlayer between the perovskite and ALD-NiO suppresses interfacial reactions, stabilizes the energy level alignment, and results in improved efficiency and operational stability.[1]

We then investigate inverted perovskite solar cells employing nickel oxide hole transport layers, focusing on the impact of ultraviolet ozone treatment and organic molecular passivation. Photoemission measurements reveal that ultraviolet ozone treatment increases the surface reactivity of NiO and promotes the formation of defect states at the NiO/perovskite interface, while leaving the bulk electronic structure largely unchanged. In contrast, the incorporation of [2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid (MeO-2PACz) as an organic interlayer effectively mitigates the formation of interfacial defects and stabilizes the interface energetics.[2]

Finally, we examine energy level alignment in 2D/3D halide perovskite heterostructures and their interfaces with organic hole transport layers. By systematically increasing the thickness of a 2D perovskite layer based on 4-fluorophenethylammonium iodide on a triple cation 3D perovskite, and subsequently depositing 2,2',7,7'-tetra(N,N-di-*p*-tolyl)amino-9,9-spirobifluorene (spiro TTB), we track the evolution of band offsets using UPS XPS and IPES. Supported by density functional theory calculations, we find that ultrathin 2D layers can provide favorable alignment and surface passivation, whereas thicker layers induce band edge shifts and band bending that can hinder hole extraction.

Overall, our results demonstrate that energy level alignment in perovskite solar cells is an emergent interfacial property rather than a fixed materials parameter. Organic interlayers and low dimensional perovskites offer powerful levers to control interface chemistry and electronic structure. Advanced photoemission techniques, particularly HAXPES and operando XPS measurements, are essential for resolving these effects at buried interfaces and for guiding the rational design of stable and high efficiency perovskite solar cells.

References: (1) N. Mallik et al. Energy Environ. Sci. Solar 2025, 10.1039/d5el00044k.
(2) J. Hajhemati et al. ACS Appl. Mater. Interfaces 2025, 17, 66683–66695