Investigating the buried Band Structure of Co-coated photoactive Oxynitrides using Soft-X-Ray ARPES

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Photoactive semiconductors responsive to visible light can drive catalytic surface reactions with the help of sunlight, enabling emission-free production of molecular fuels. Transition metal oxides, deposited on top of these semiconductors, can promote solar-driven electrochemistry, such as the oxygen evolution reaction (OER) during water splitting [1]. Notably, the interface between semiconductor and the top cocatalyst governs the transport of photogenerated charge carriers to the surface. Nevertheless, for most systems, the bonding environment and potential landscape at the interface remains unexplored, with insufficient understanding of the cocatalyst's role.

With a bandgap in the visible light regime, we have focused our study on thin film samples of perovskite-type oxynitride photoanodes for the OER [2]. Using angle-resolved photoelectron spectroscopy (ARPES), we have tracked the oxynitride band structure of $LaTiO_xN_y$ during top cobalt deposition and oxidation. This work reveals the surface doping effect of the cobalt cocatalyst on the underlying semiconductor bands, whose locations are closely related to the electrochemical potentials for water splitting.

We discuss the changes in the band structure of the semiconductor in conjunction with the oxidation states and the bonding environment of the cobalt oxide monolayer obtained from XPS and resonant ARPES, respectively. We also introduce our latest progress in relating the subatomic properties seen with ARPES to the system under working conditions with the help of complementary techniques such as transport measurements.

The extracted semiconductor properties serve as a basis for establishing a comprehensive band diagram model for oxynitride photoanodes during operation. Ultimately, such a model enables the optimization of semiconductor-(co)catalyst systems towards the fabrication of highly efficient photoanodes.

References

[1] F.A.L. Laskowski et al., Nat. Mater. **19**, 69–76 (2020).
[2] C. Lawley et al., Nat. Commun. **11**, 1728 (2020).