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Electronic Structural Origin of Efficiency Enhancement from Underlayer in Hematite Photoanode

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MICHELIN

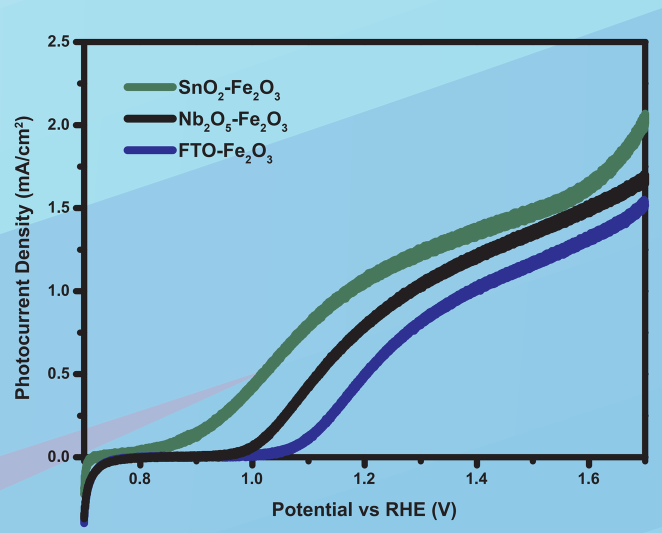
Yelin Hu[1,2], Florent Boudoire[1,3], Matthew Mayer[2], Michael Graetzel[2], Artur Braun[1]

[1] Laboratory for High Performance Ceramics, EMPA-Swiss Federal Laboratories for Materials Science & Technology, Switzerland
[2] Laboratory for Photonic and Interfaces, Ecole Polytechnique Federal de Lausanne, Switzerland
[3] Department of Chemistry, University of Basel, Switzerland

Introduction

Hematite (α-Fe_2O_3) is an important photoanode material capable of high quantum conversion efficiency in the oxygen evolution reaction upon water splitting. However, one primary limitation for the application of ultrathin hematite layer is the slow transportation of photoexcited electrons to an external circuit, increasing efficency losses during operation. It has been shown that these losses can be limited by implementation of metal oxide interfacial layers, such as Nb_2O_5, SnO_2, SiO_x and SnO_2, between conducting substrate and ultrathin hematite layer. However, the detailed mechanism for electrode activation is still unknown. In the present study, synchrotron-based X-ray spectroscopy is used to study the electronic structure origins of interfacail enhancement in metal oxide/hematite photoanodes.

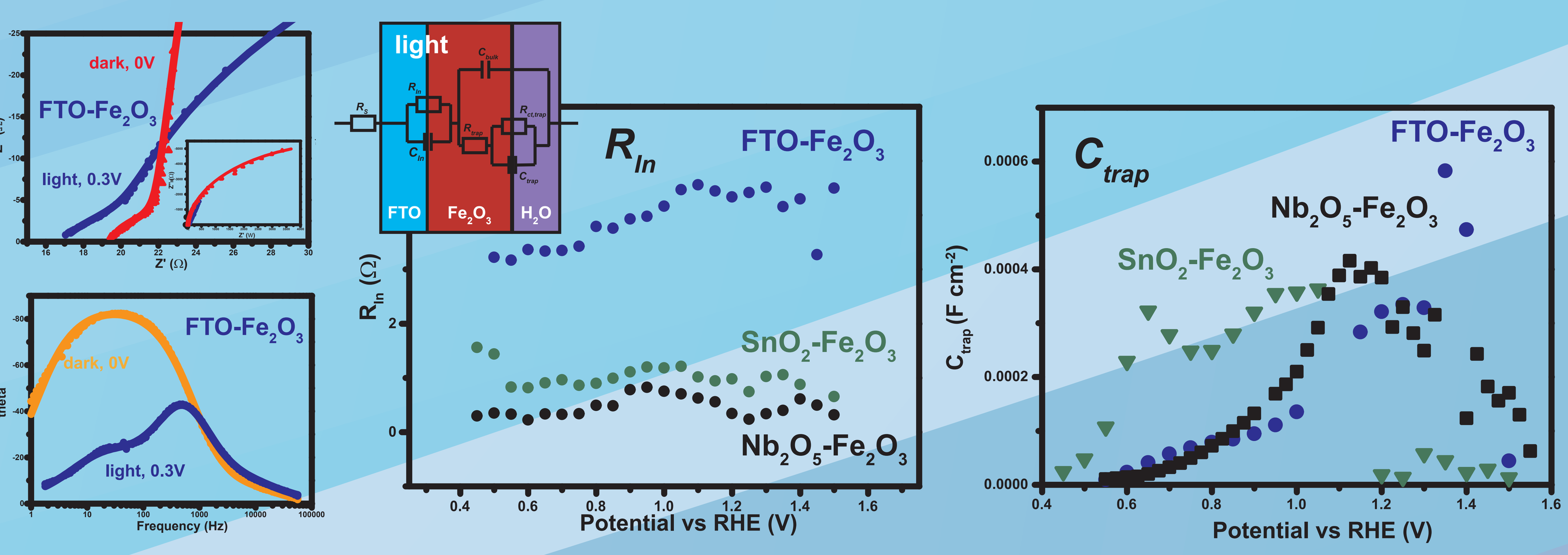
Preparation & Photoelectrochemical Analysis



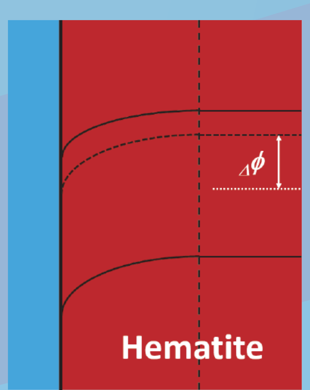
Ultrathin Hematite: ~ 20 nm by spray pyrolysis

SnO_2: ~ 3 nm, Nb_2O_5: ~ 5 nm by ALD

	SnO_2-Fe_2O_3	Nb_2O_5-Fe_2O_3	FTO-Fe_2O_3
Onset (V_{RHE})	0.88	0.97	1.06



- Onset potential shift to cathodic direction with SnO_2 and Nb_2O_5 underlayer.
- The EIS feature at high frequency relates to charge transfter on substrate-hematite interface. One more Randle Circuit added for EIS analysis.
- Interfacial-charge-transfer resistance decreases after implementation of SnO_2 and Nb_2O_5 underlayer.
- Kelvin probe suggests increased interface band bending by underlayer, improving charge transfer on substrate-hematite interface.

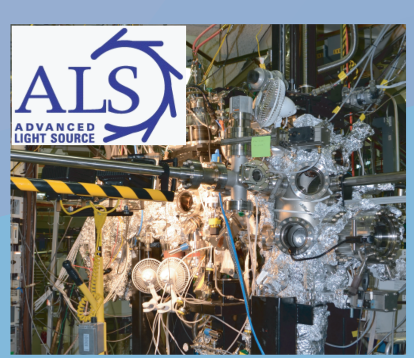


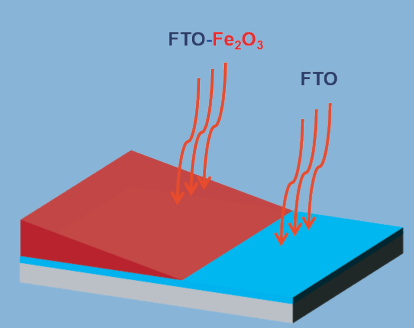
$\Delta\phi$ by Kelvin probe spectroscopy

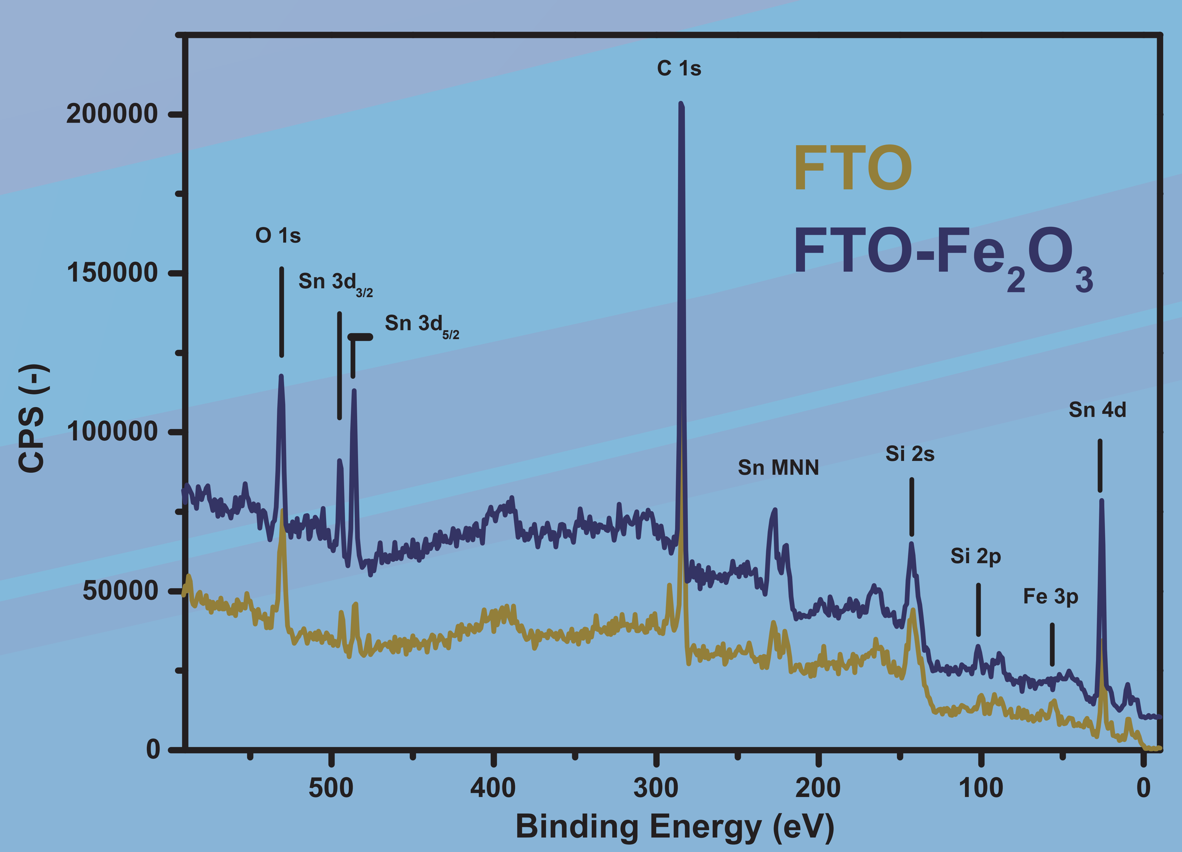
	SnO_2-Fe_2O_3	Nb_2O_5-Fe_2O_3	FTO-Fe_2O_3
$\Delta\phi$ (eV)	0.92	0.83	0.79

Hematite Samples for Interface Analysis

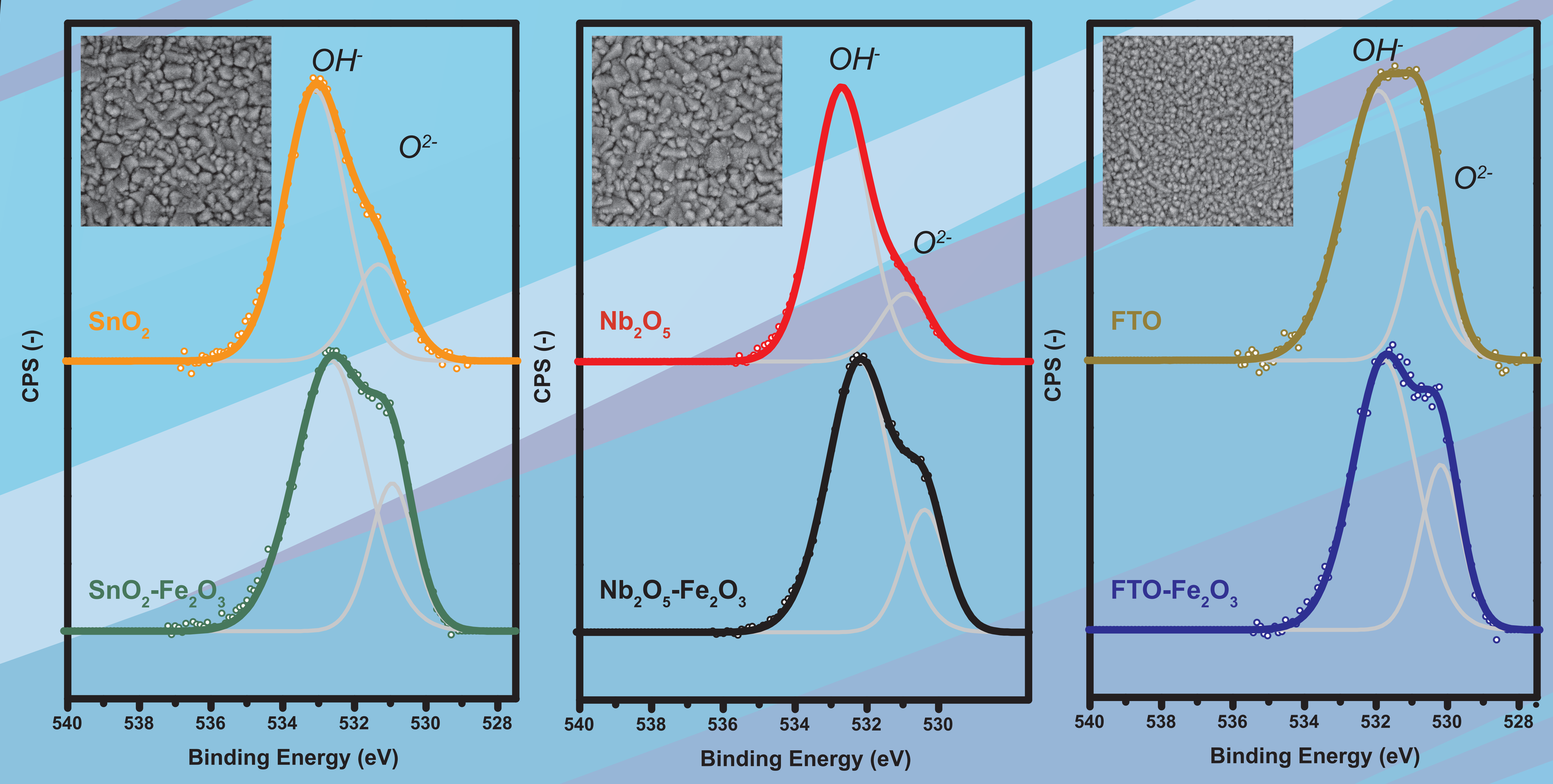
- XPS & NEXAFS studied in ALS BL 9.3.2
- Hematite with gradient thickness prepared to identify substrate-Fe_2O_3 interface

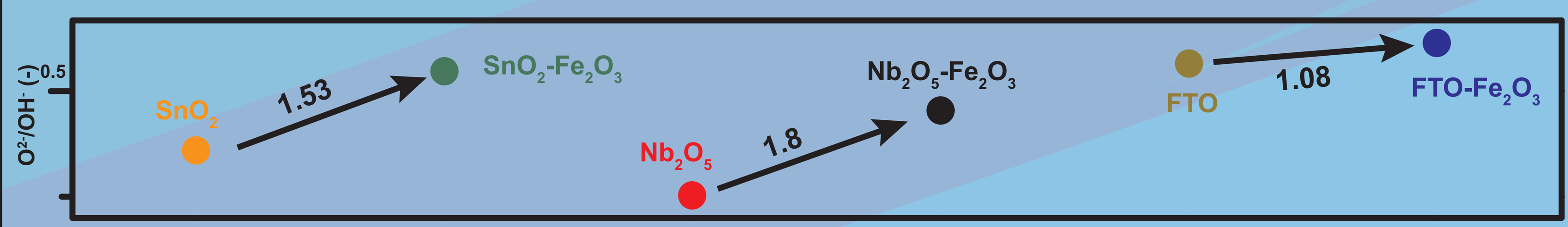






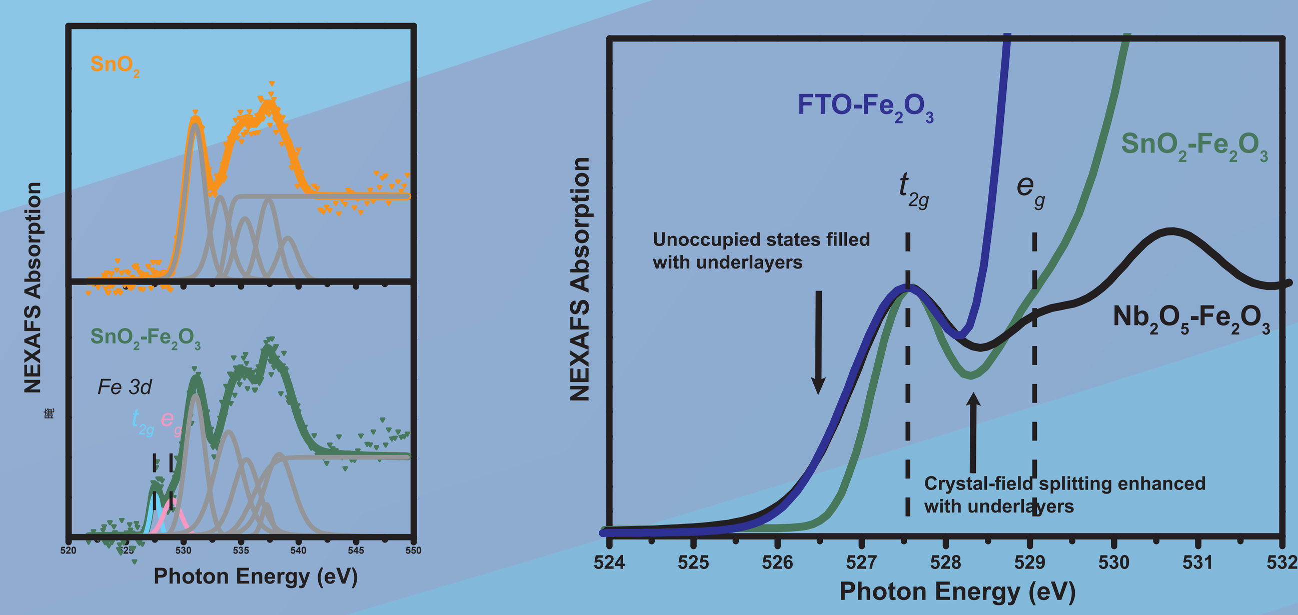
O 1s XPS & NEXAFS





O 1s core level XPS

- Crystal lattice O increases when hematite deposited on the substrates, especially for the ones with metal oxide underlayers, suggesting that SnO_2 and Nb_2O_5 improve crystallinity of ultrathin hematite.
- It matches SEM results.



	SnO_2-Fe_2O_3	Nb_2O_5-Fe_2O_3	FTO-Fe_2O_3
FWHM of fitted t_{2g} peak	0.9258	1.56	1.6

O k edge NEXAFS

- Unoccupied O *p* states below the lowest unoccupied Fe *d* orbitals (features around 526.5 eV) are presented by FWHM of t_{2g} peak, and it shows that they are eliminated with metal oxide underlayer, suggesting reduced displacement of Fe^{3+} ions in the corundum structure and improved crystallinity.
- Features around 528.3 eV represent crystal-field splitting of hematite. The broadening of Fe 3d-O 2p hybridized states reduced with metal oxide underlayer, leading to improved *p-d* orbital hybridization.

Conclusion

- Interface of metal oxide/ultrathin hematite was studied. Two metal oxides chosen: SnO_2 & Nb_2O_5
- Impedance spectroscopy suggests improved interfacial charge transfer on substrate/hematite interface. It may be attributed to stronger band bending on interface.
- O 1s XPS shows improved crystallinity and reduced oxygen vacancy with implantation of underlayer
- Metal oxide underlayers have been shown to improve the degree of *p-d* orbital hybridization.