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Electronic Properties of Metal Halide Perovskites and their Interfaces with Charge Extraction Layers in Lateral Heterojunction Configuration

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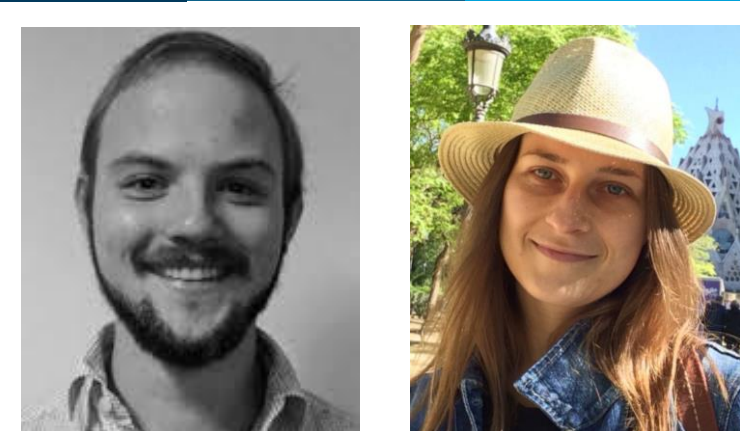
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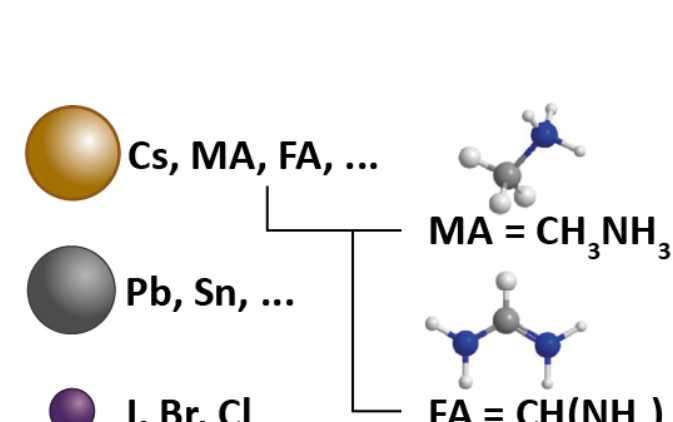
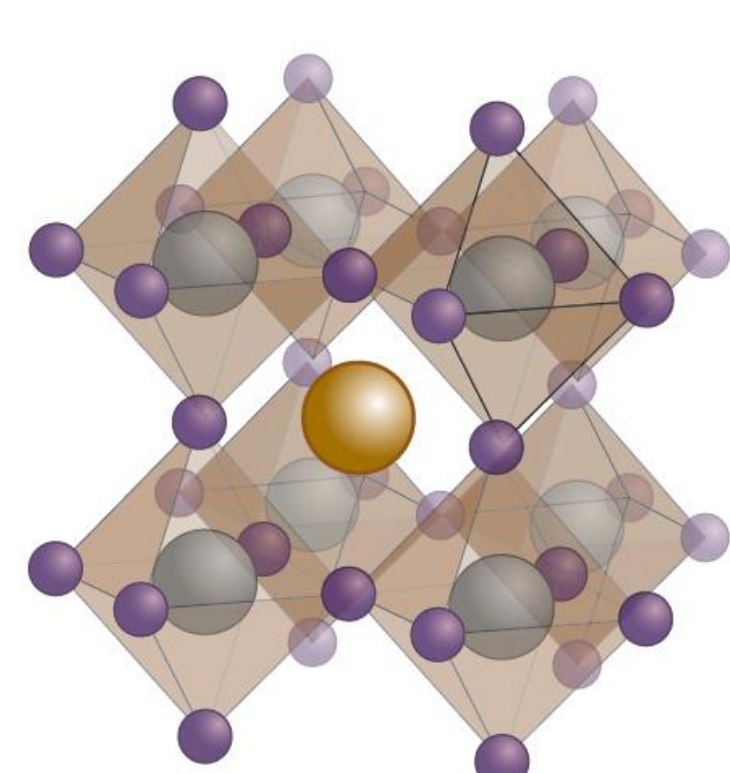
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Electronic Properties of Metal Halide Perovskites and their Interfaces with Charge Extraction Layers in Lateral Heterojunction Configuration

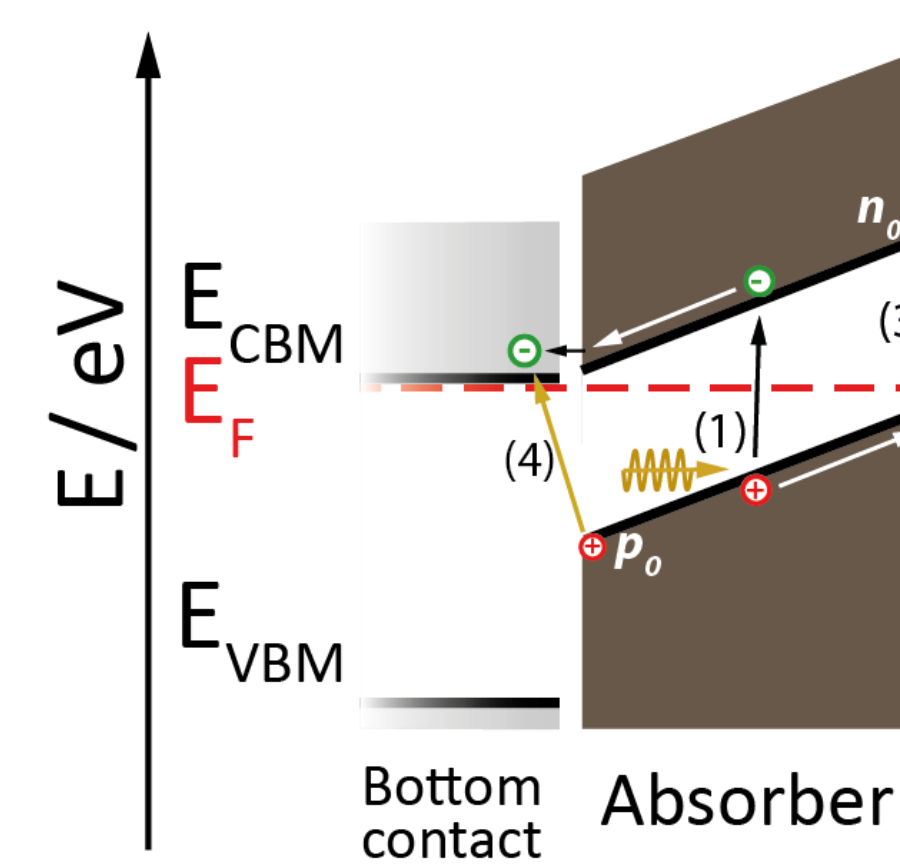
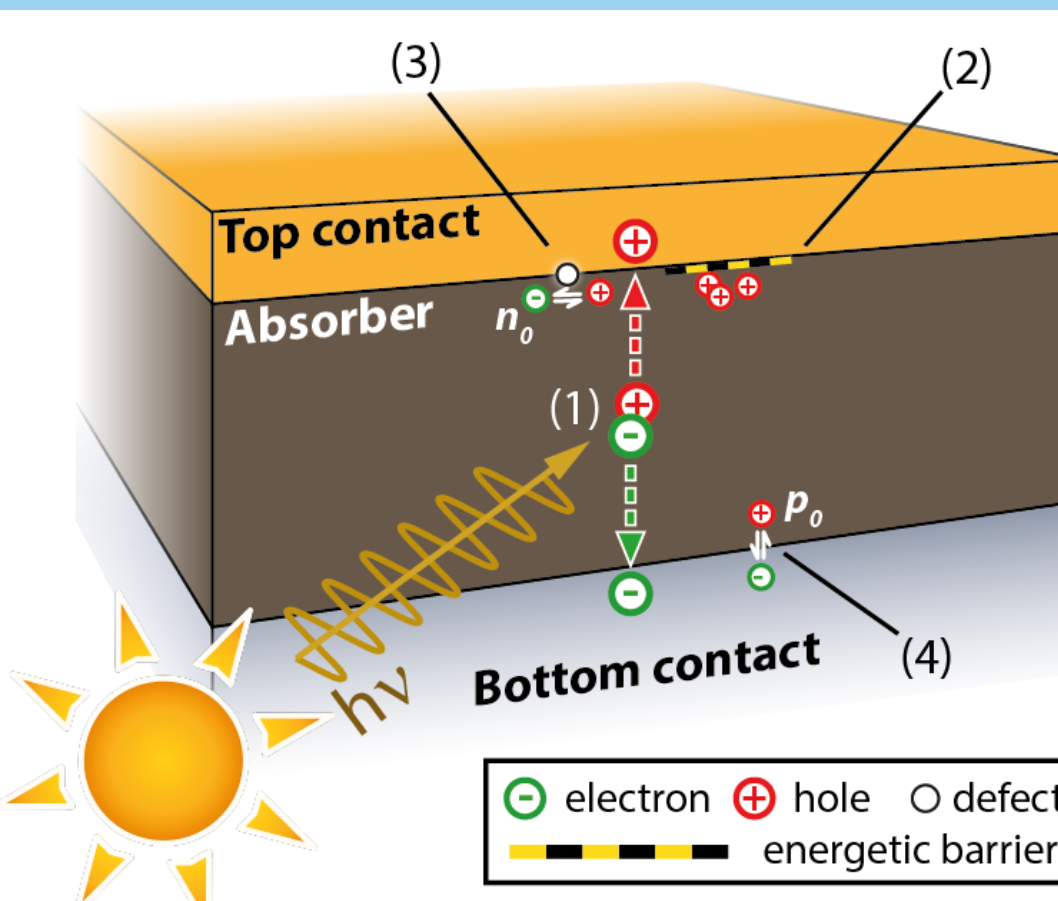
Metal Halide Perovskites: Applications and Interfaces



Hybrid organic-inorganic metal halide perovskite (MHP) with complex chemical structure ABX_3

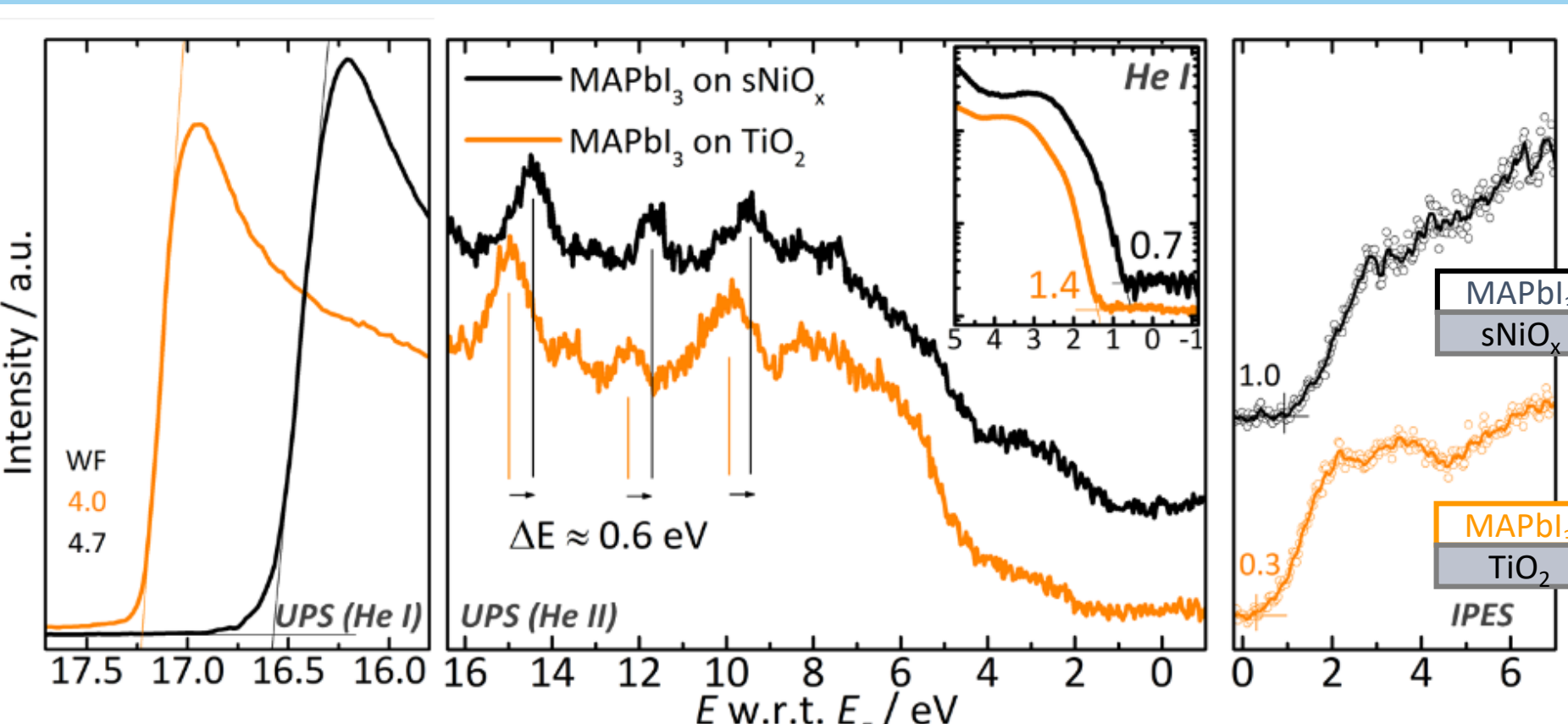
Semiconductor with unique combination of optoelectronic and mechanical properties¹

Breakthrough application in photovoltaics: Perovskite solar cells (PSC)



- Relevant loss-channels:
- (1) Photoexcitation and transport to interface
 - (2) Band misalignment of as barrier for charge extraction
 - (3) Recombination at interface defect states
 - (4) Back-recombination
- Predominantly losses at interface^{2,3}

Substrate-dependent Fermi Level Alignment and Lateral Heterojunction (LHJ)

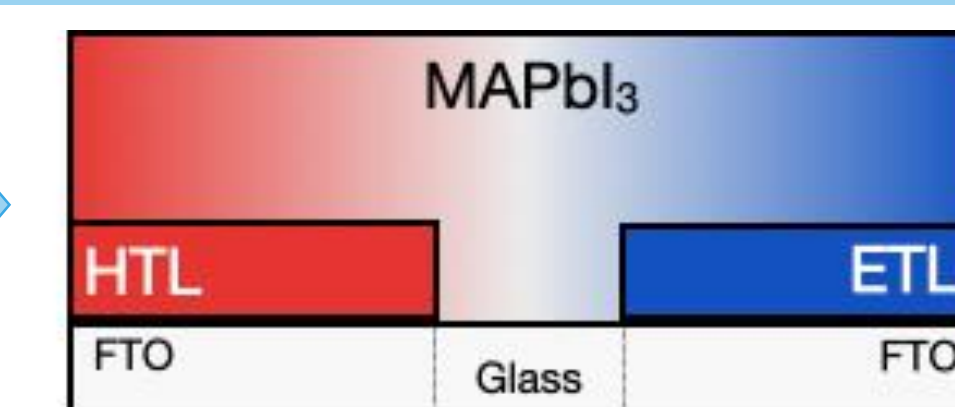
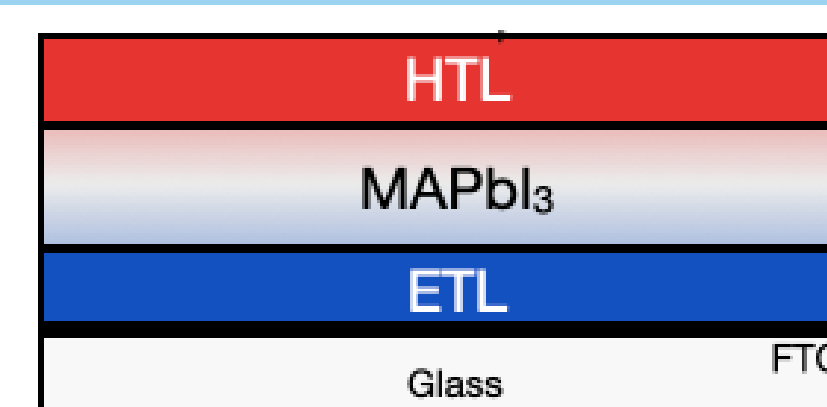


Combined ultraviolet and inverse photoemission spectroscopy (UPS/IPES)⁴:

Optoelectronic properties of MHP can be altered by the substrate (or selective contact) underneath

Position of Fermi level (E_F) at the surface of the perovskite film (MAPbI_3 , 400 nm) changes on different substrate, with E_F close to the perovskite conduction band on TiO_2 and in a mid-gap position on NiO

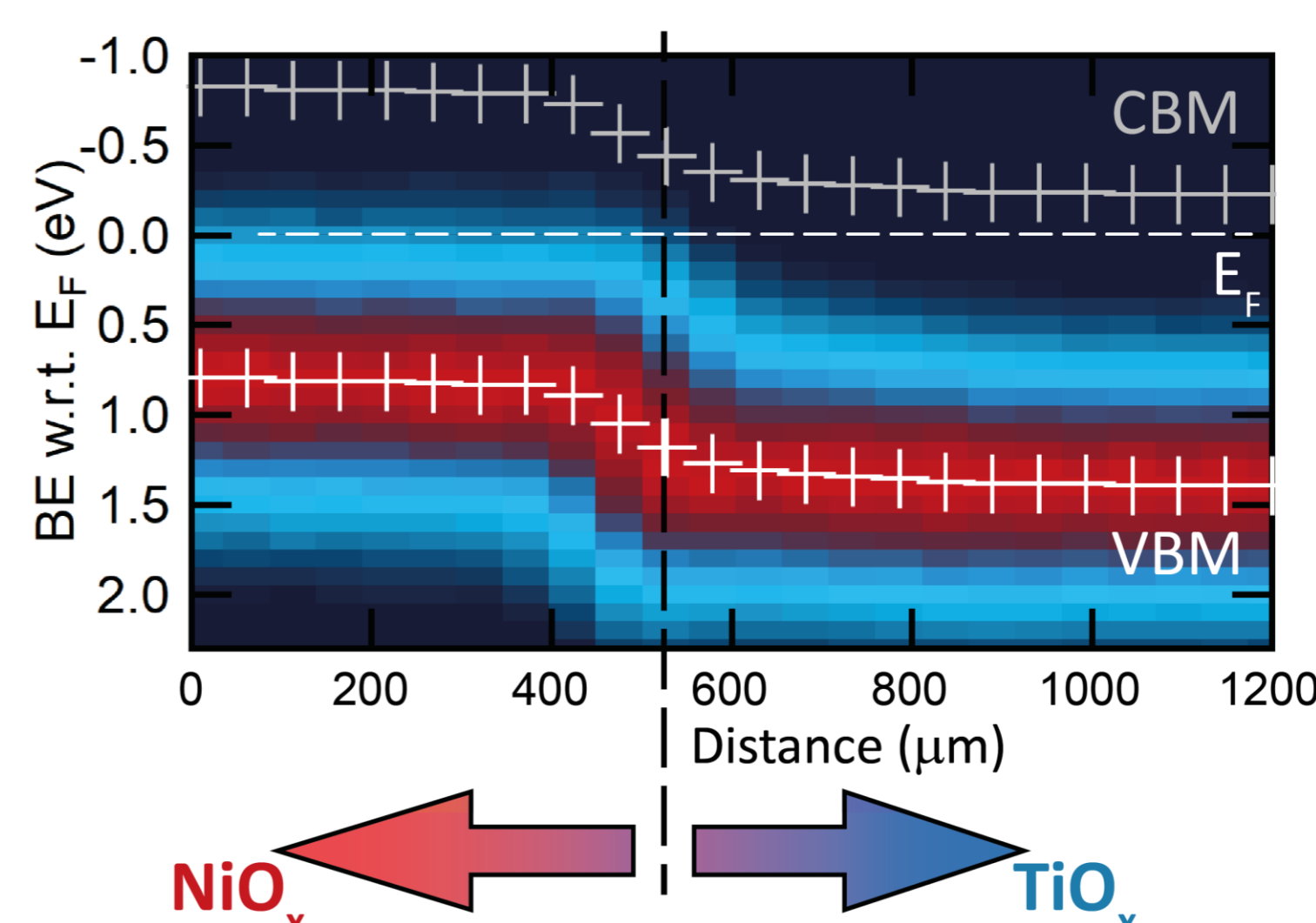
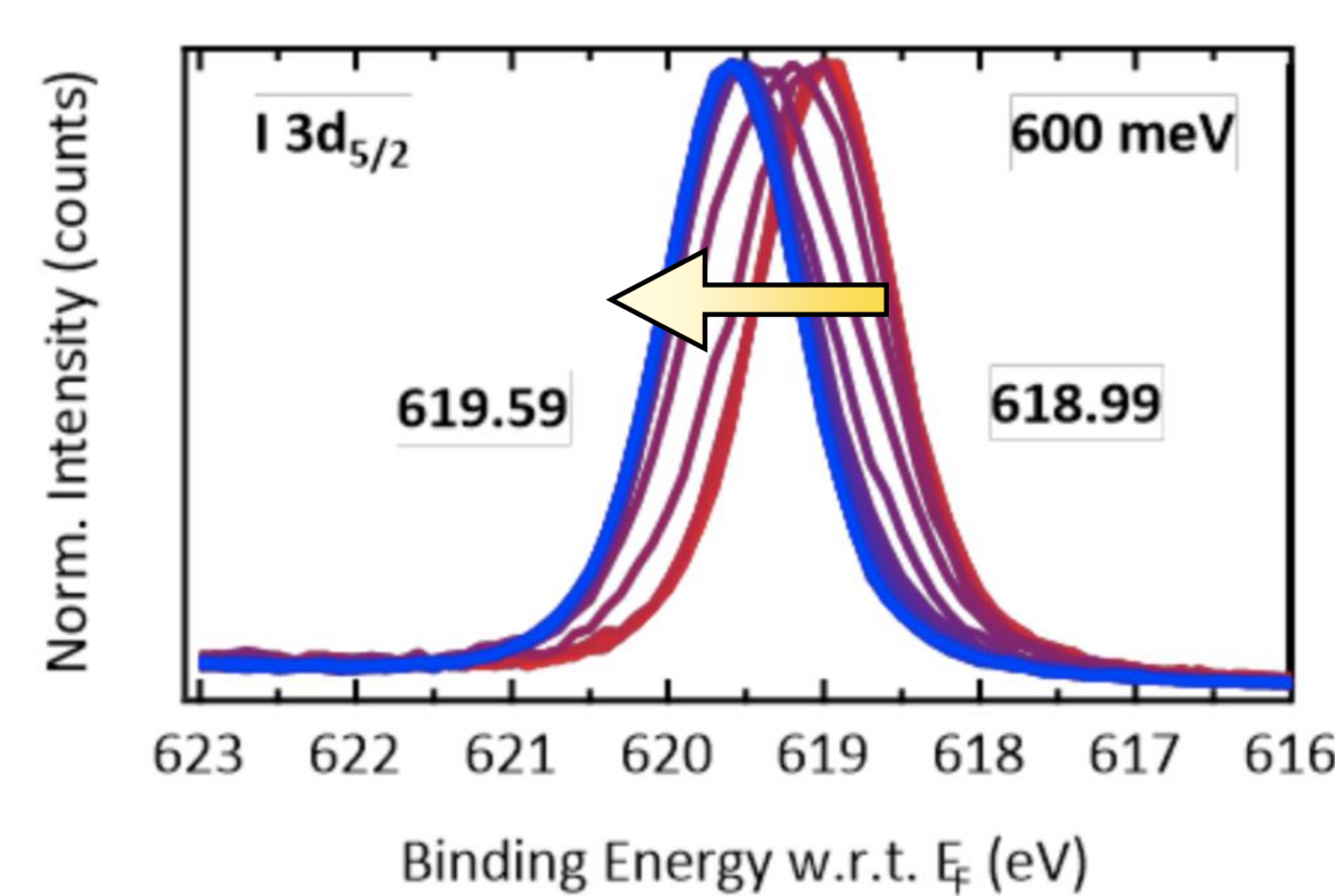
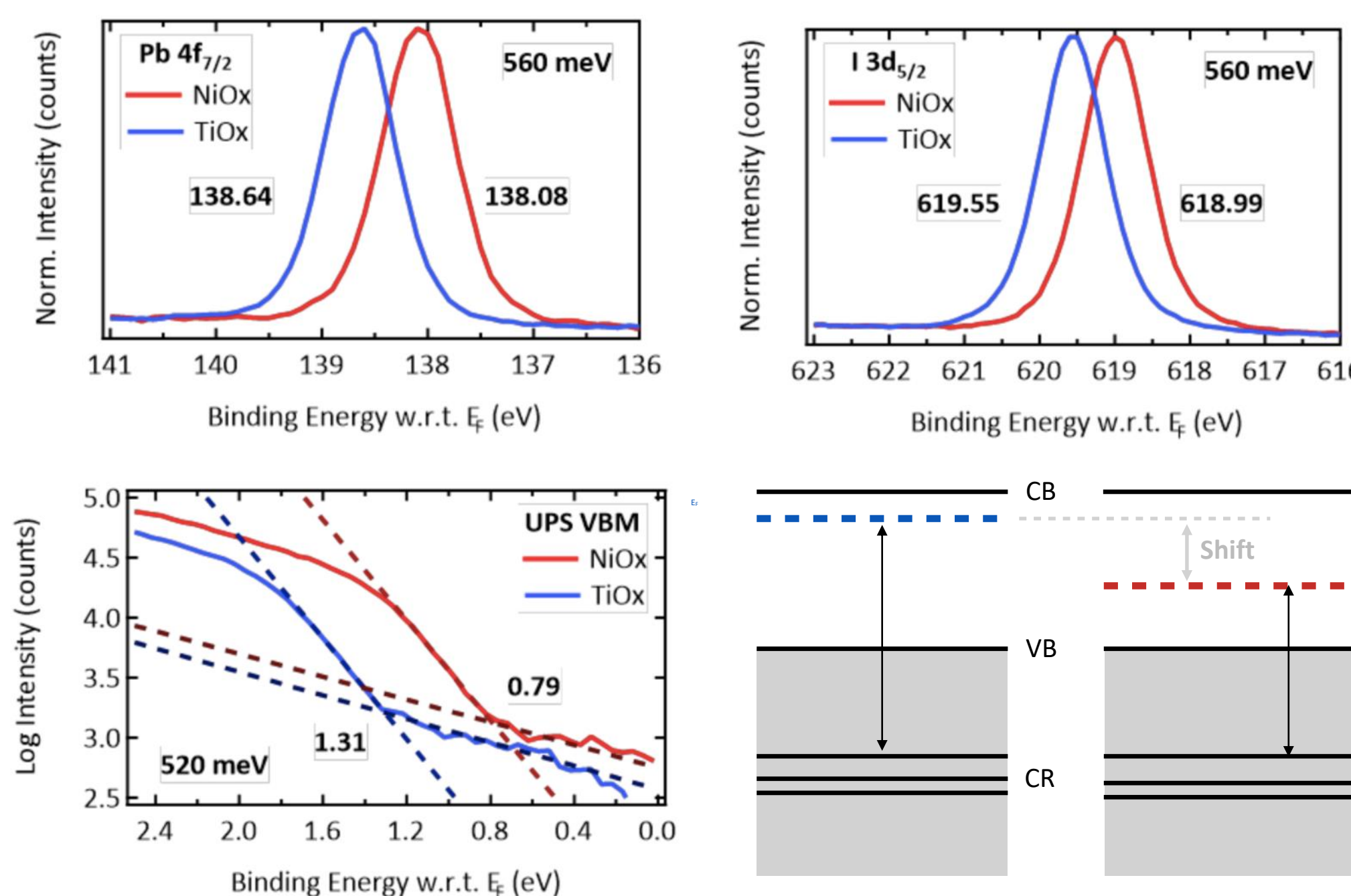
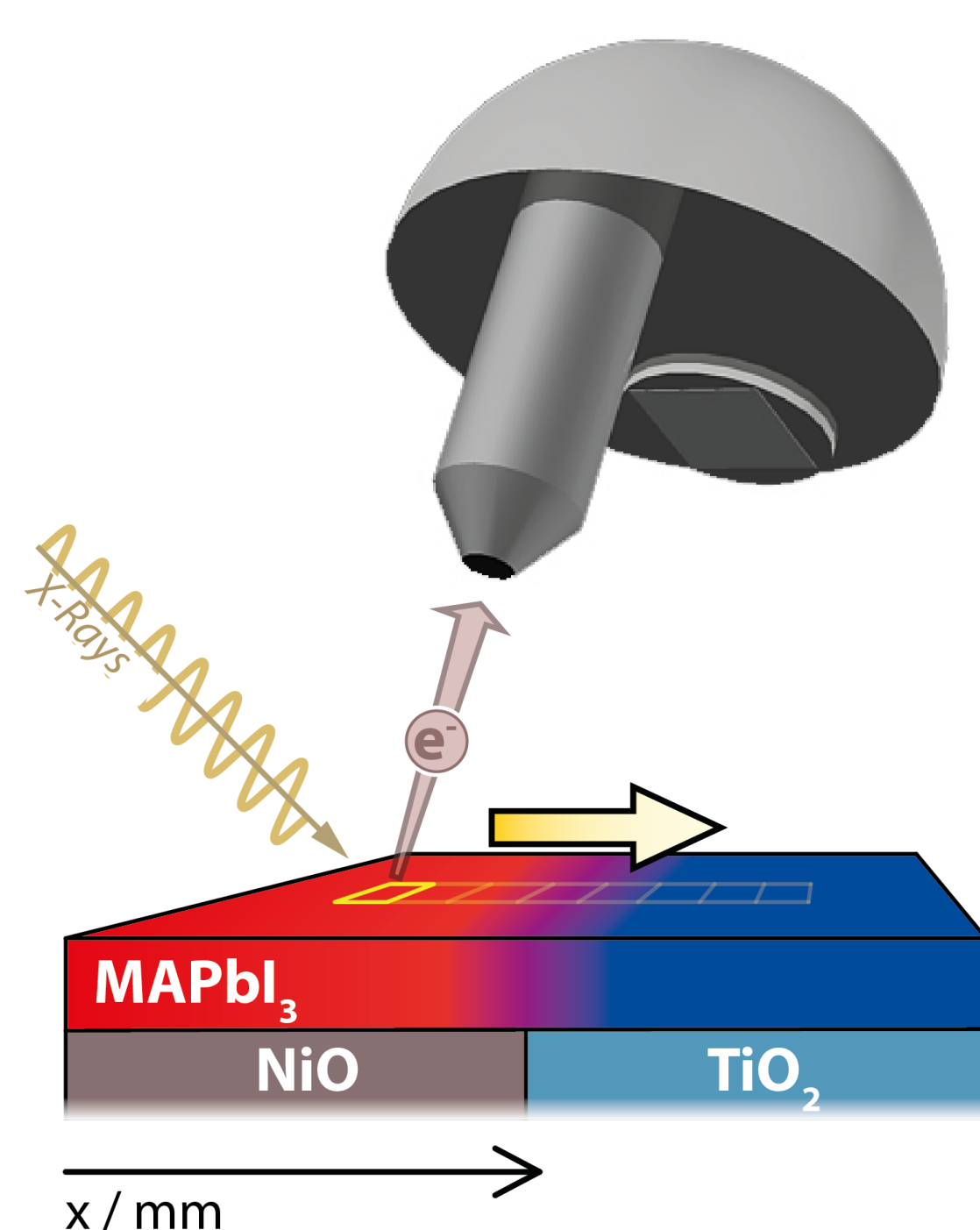
Need to track interface formation and energy level alignment



Transition from common, vertically stacked sample geometry to lateral heterojunction architecture⁵

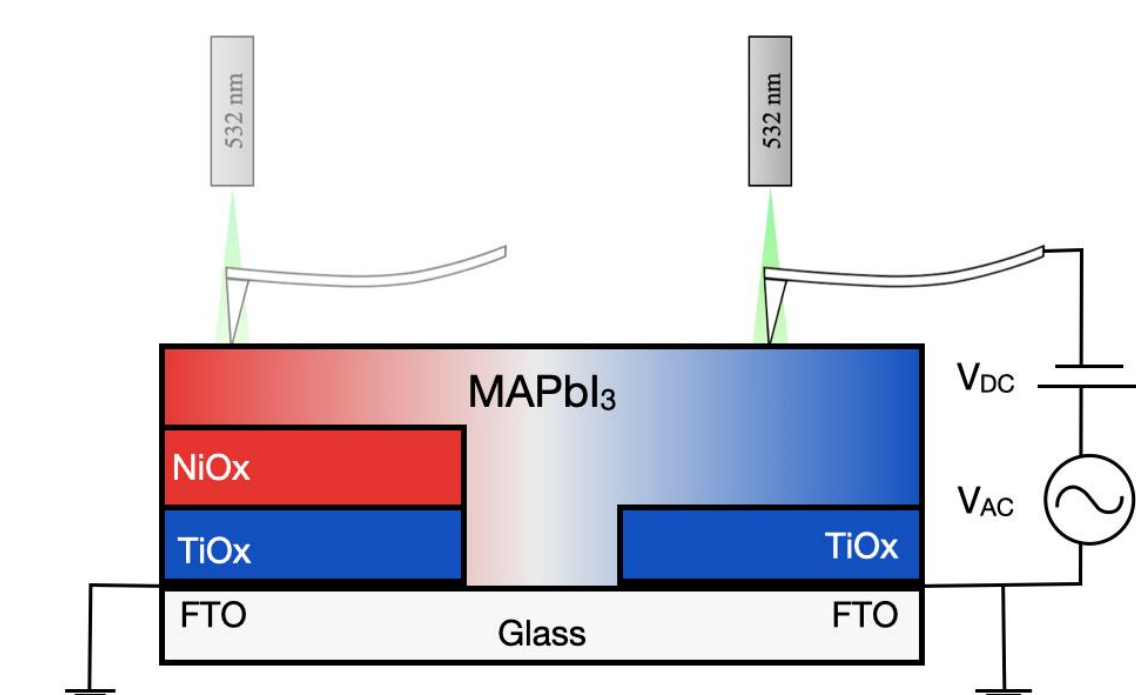
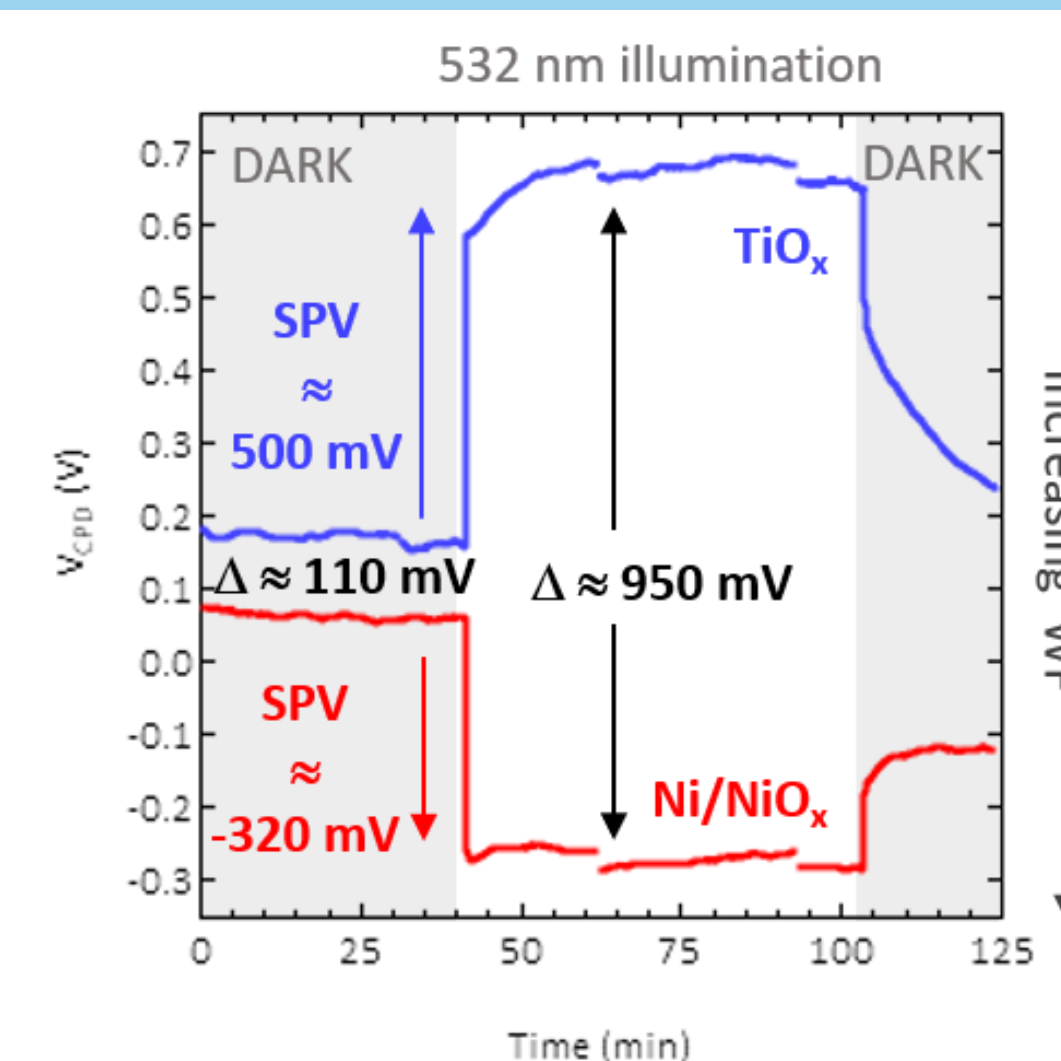
Access to surface electronic and chemical properties across channel

Photoelectron Spectroscopy across LHJ channel

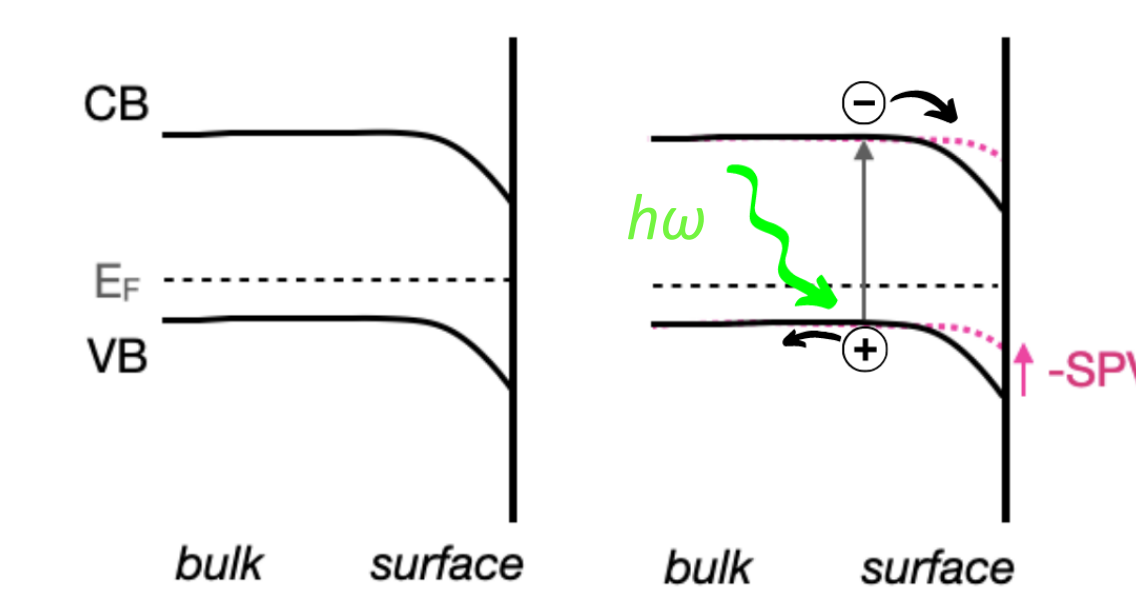


- Lateral contact design as in interdigitated back contacts
- Perovskite deposition on top
- XPS/UPS data acquisition at end points
- Scanning PES (XPS, $\text{I } 3d_{5/2}$) across lateral heterojunction (LHJ)
- Drift-diffusion modelling to determine origin of surface potential^{5,6}
- Observed profile of surface potential requires low doping concentration in MHP ($<10^{13} \text{ cm}^{-3}$)

Complementary Kelvin Probe Force Microscopy



- Assess surface potential / work function
- Measurement in dark and under illumination to capture surface photovoltage (SPV)
- Significant difference in SPV between MHP on TiO_x vs MHP on NiO_x indicates change of carrier extraction at interface⁵



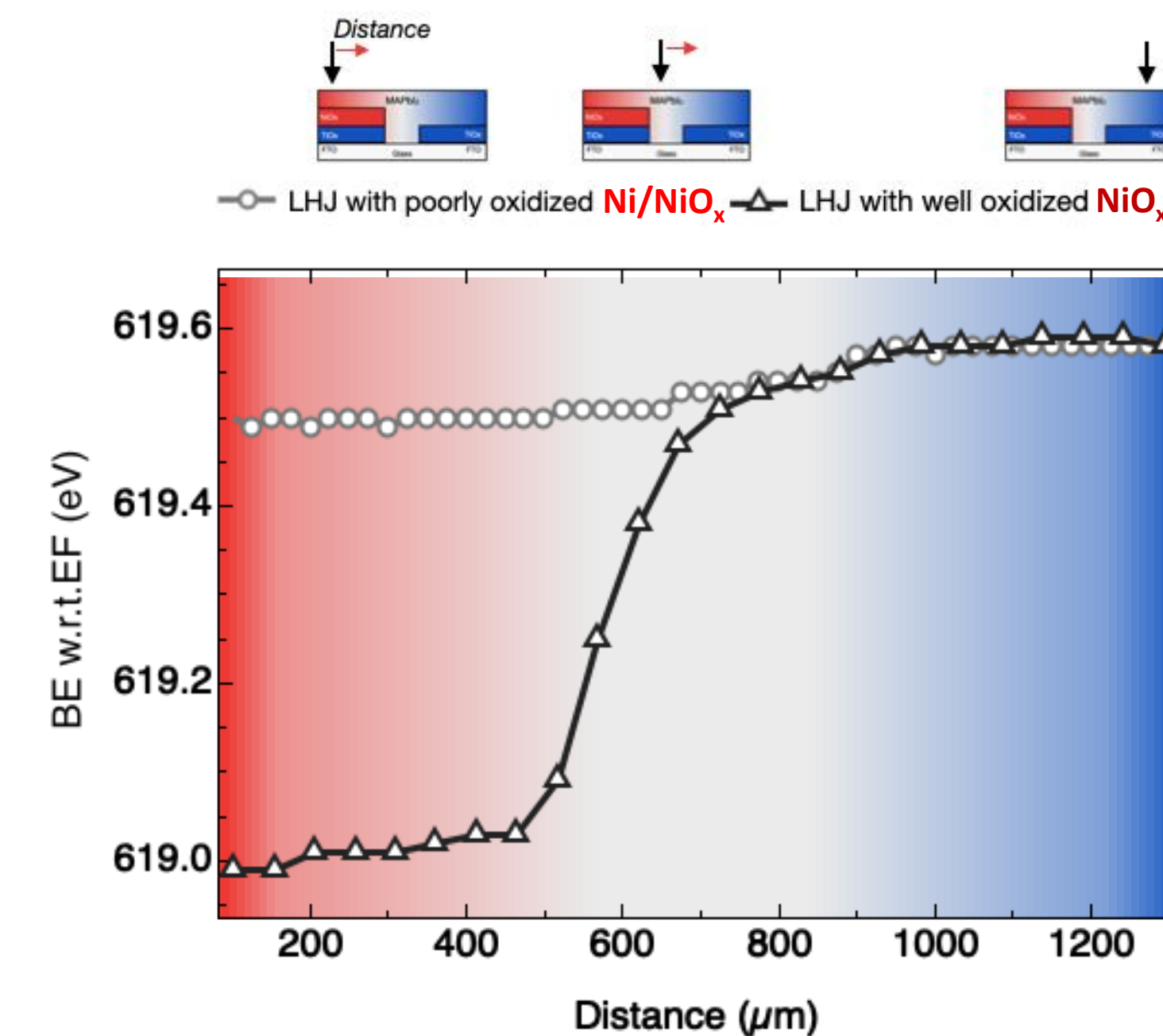
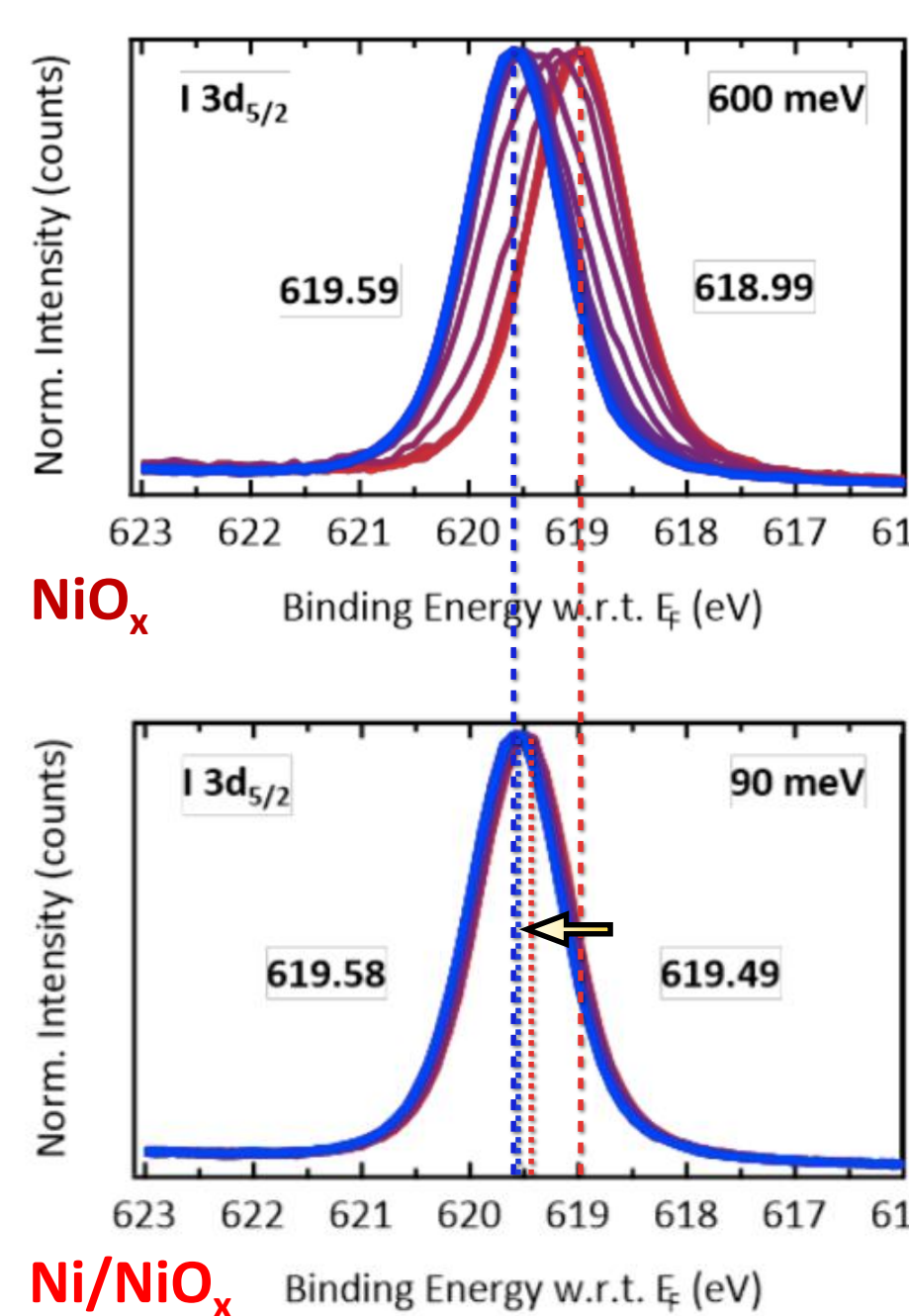
Modified Charge Selectivity at NiO_x Contact

Fully oxidized NiO_x at 300°C / 120 min anneal

Oxygen-deficient Ni/NiO_x at 275°C / 30 min anneal

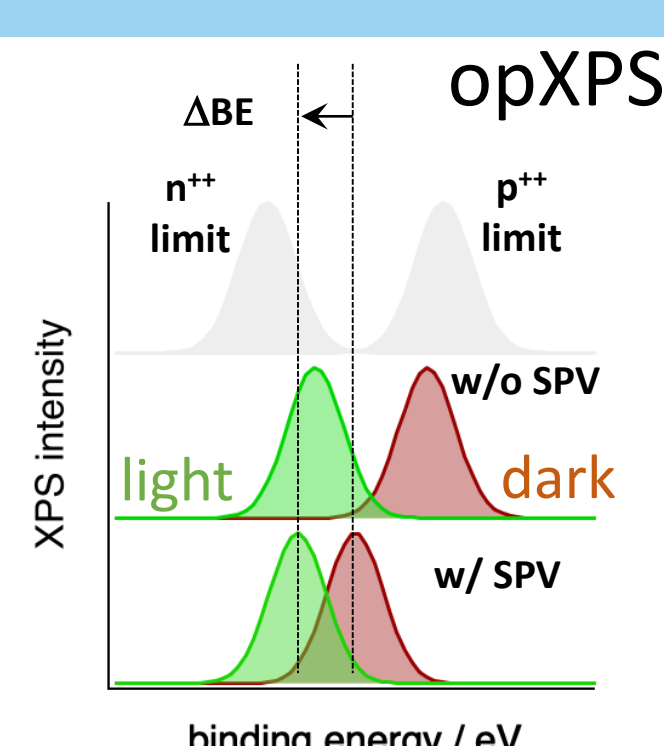
Adaptation of contact selectivity by variation of NiO_x oxidation level through controlled annealing

Reduced shift of E_F in gap for poorly oxidized Ni/NiO_x in line with results of higher recombination seen in photoluminescence measurements⁵



Conclusion and Next Steps

- Charge selective contacts shift the Fermi level in metal halide perovskites (MHPs)
- Effect is readily observable because of low defect and doping concentrations in the MHP
- Contact selectivity determines carrier extraction across MHP/contact interfaces
- Tailoring charge selective contacts to design MHP-based lateral heterojunction devices
- Operando measurements⁷ (opXPS & KPFM) to track dynamic effects and potential ion migration
- Access to buried interfaces via HAXPES measurements



References

- D. Egger et al. *Adv. Mater.* **2018**, *30*, 1800691
- P. Schulz *ACS Energy Lett.* **2018**, *3*, 1287–1293
- P. Schulz, D. Cahen, A. Kahn. *Chem. Rev.* **2019**, *119*, 3349–3417
- P. Schulz, et al., *Adv. Mater. Interfaces* **2015**, *2*, 1400532
- S. Dunfield, A. Bojar, et al., *Cell Rep. Phys. Sci.* **2021**, *2*, 100520
- D. Regaldo, A. Bojar, et al., *Prog. Photovolt.: Res. Appl.* **2021** <https://doi.org/10.1002/pip.3529>
- G. Teeter, P. Schulz, *Photoelectron Spectroscopy Methods in Solar Cell Research*, **2020** https://doi.org/10.1049/PBPO166E_ch12