

Blueprint for Photocatalytic Water Splitting: Mapping Multidimensional Compositional Space to Simultaneously Optimize Thermodynamics and Kinetics

Sara Abdel Razek,¹ Melissa Popeil,¹ Nuwanthi
Suwandarathne,² Justin L. Andrews,³ David Watson,²
Sarbajit Banerjee,³ Louis F. J. Piper^{1*}

NSF DMREF: ¹ Binghamton University; ² University at
Buffalo; ³ Texas A&M

Jinghua Guo,^{4‡} David Prendergast⁵

DOE HydroGEN: ⁴Advanced Light Source; ⁵ Molecular
Foundry

‡jguo@lbl.gov

*lpiper@binghamton.edu



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Summary

Achieving hydrogen evolution reactions or high efficiency of water splitting requires the development of visible light responsive metal oxide heterostructure photocatalysts. Chalcogenide quantum dots (QD) are visibly active materials, however, photocorrosion limits application to a heterostructure system.¹ Metal oxides can be used to facilitate hole transfer away from the QD which decrease photocorrosive effects and enable hydrogen generation.^{2,3} For most d^0 or d^{10} transition metal photocatalysts, the valence band (VB) is derived of deep O2p states which lie ~ 2 eV below the oxygen redox level. We have demonstrated the ability to intentionally control the VB offset between the QD and metal oxides through the intercalation of stereo active lone pairs into the ζ - V_2O_5 framework. A zero energy VB offset was achieved with 1st generation β - $Pb_{0.33}V_2O_5/CdS$ and latter with higher performance 2nd generation β - $Sn_{0.33}V_2O_5/CdSe$ heterostructures.⁴ To further enhance hydrogen generation, MoS_2 flakes with high edge density will be attached to CdX QDs. The MoS_2 flakes should act as sites of high hydrogen production activity. The aim of DMREF-ENM collaboration is to ultimately perform *in-situ* absorption studies to accelerate the rational design of the new ternary photocatalysts.

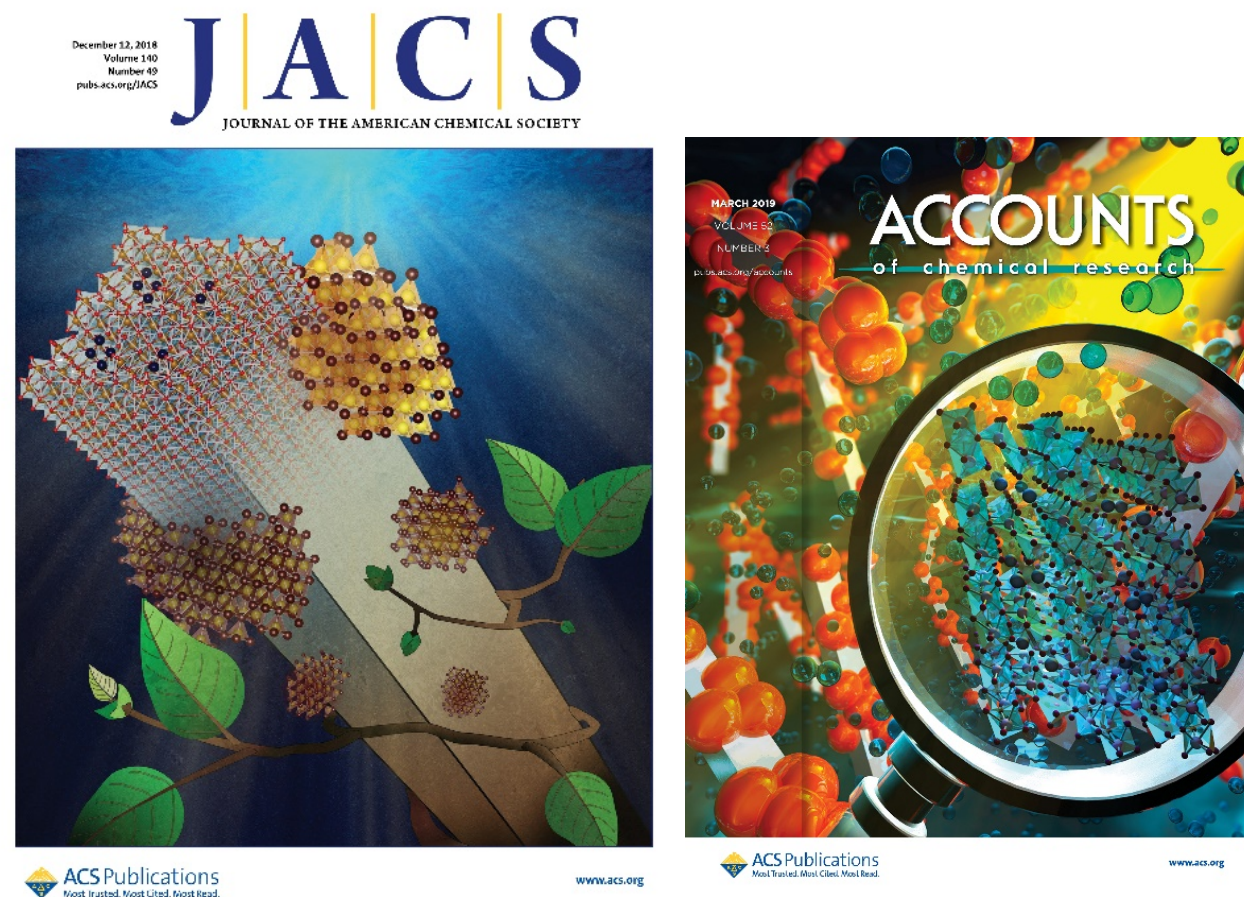


Figure 1. Recent research highlights: Left: Schematic illustration of $CdSe/\beta$ - $Sn_xV_2O_5$ heterostructures that enable photocatalytic water splitting; Right: illustration of design of $M_xV_2O_5$ compounds with p-block cations that yield mid-gap states.³

1. Engineering Photogenerated Hole Transfer to Avoid Photcorrosion of CdX QDs

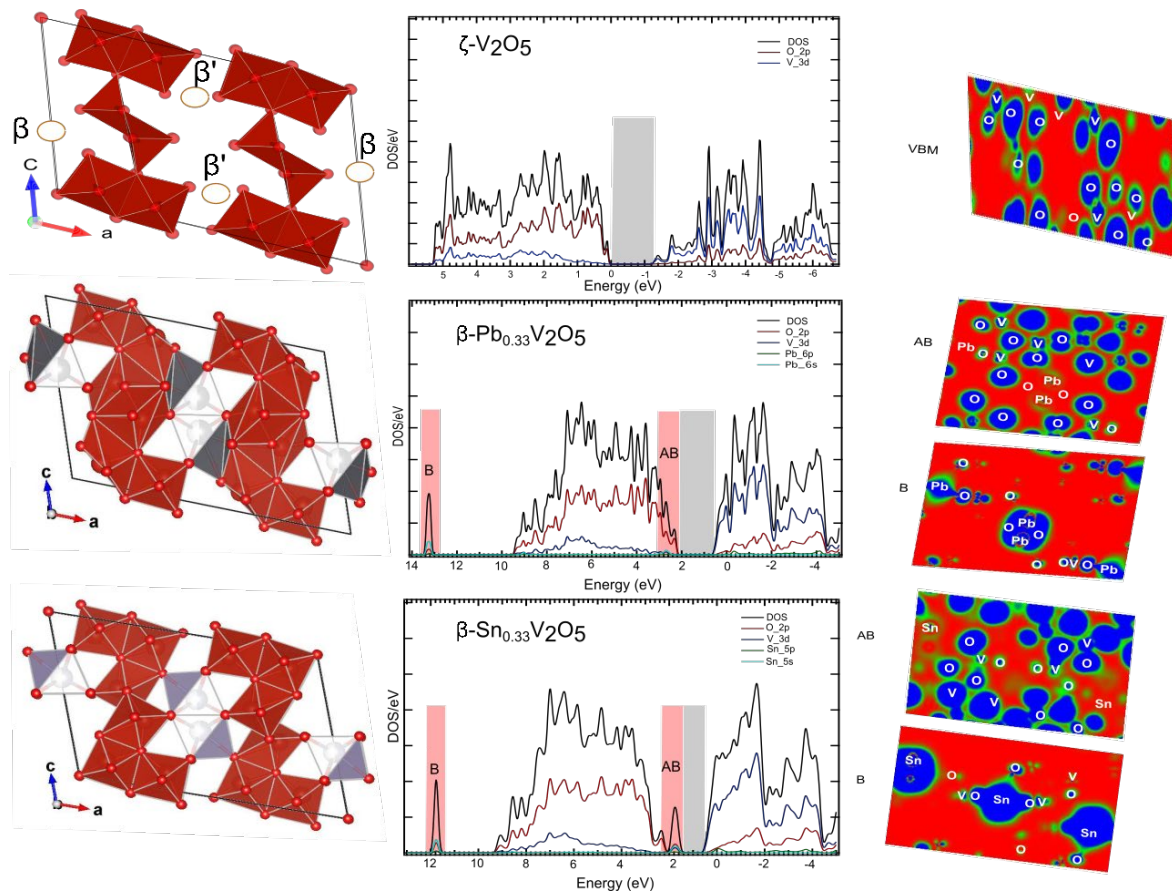


Figure 2. Electronic structure calculations of lone-pair doping V_2O_5 : Structure, DOS and charge density of $\zeta - V_2O_5$, $\beta - Pb_{0.33}V_2O_5$ and $\beta - Sn_{0.33}V_2O_5$. The reduction in $\beta - Sn_{0.33}V_2O_5$ is more than $\beta - Pb_{0.33}V_2O_5$ due to the strong hybridization of Sn 5s-O 2p.

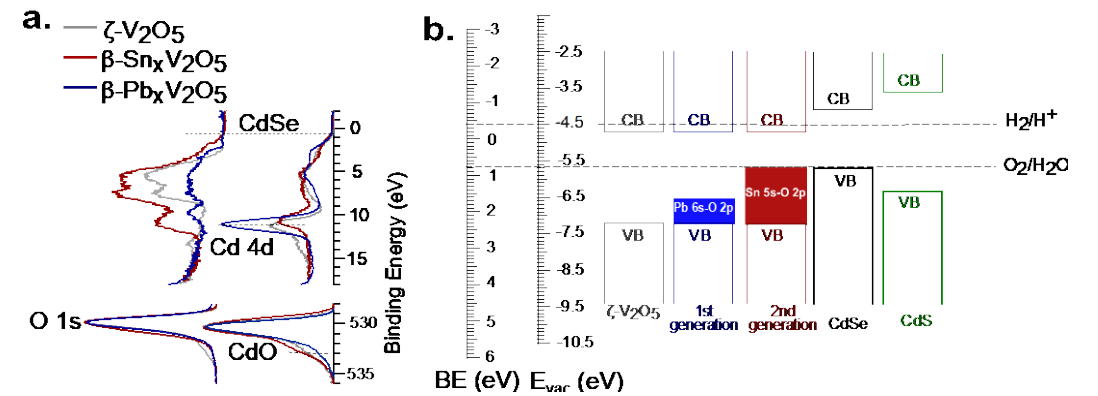


Figure 3. Measured band offsets: (a) HAXPES valence band and O 1s spectra of $\zeta - V_2O_5$, $\beta - Pb_{0.33}V_2O_5$, and $\beta - Sn_{0.33}V_2O_5$ with and without CdSe QDs, (b) the band offsets showing favorable hole transfer from valence band of CdSe QDs to the valence band of $\beta - Sn_{0.33}V_2O_5$.

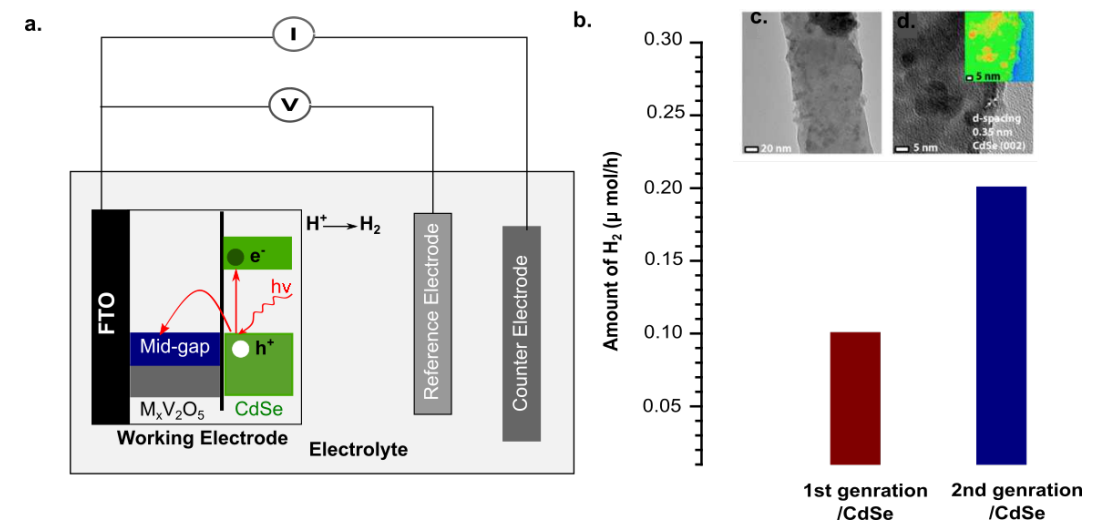


Figure 4. Hydrogen evolution of our binary photocatalysts: (a) photoelectrochemical cell for $M_xV_2O_5/CdSe$, (b) amount of H_2 produced by using 1st generation ($\beta - Pb_{0.33}V_2O_5$)/CdSe and 2nd generation $\beta - Sn_{0.33}V_2O_5$ /CdSe, (c) low magnification HRTEM, and (d) HRTEM of $\beta - Sn_{0.33}V_2O_5/CdSe$.

2. Proposed Ternary Structure of $M_xV_2O_5/CdX/MoS_2$

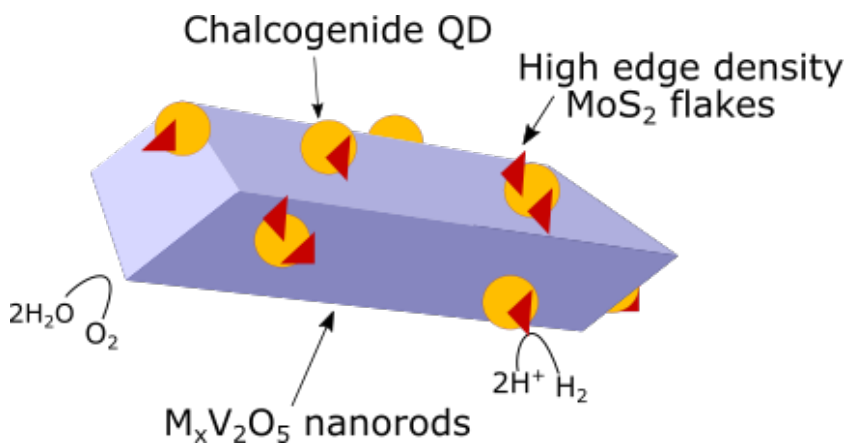


Figure 5. Schematic of proposed ternary photocatalytic system. The grey nanorod acts as host transport material, the yellow circles represent light absorbing quantum dots, and the red triangles represent the MoS_2 as hydrogen evolving sites

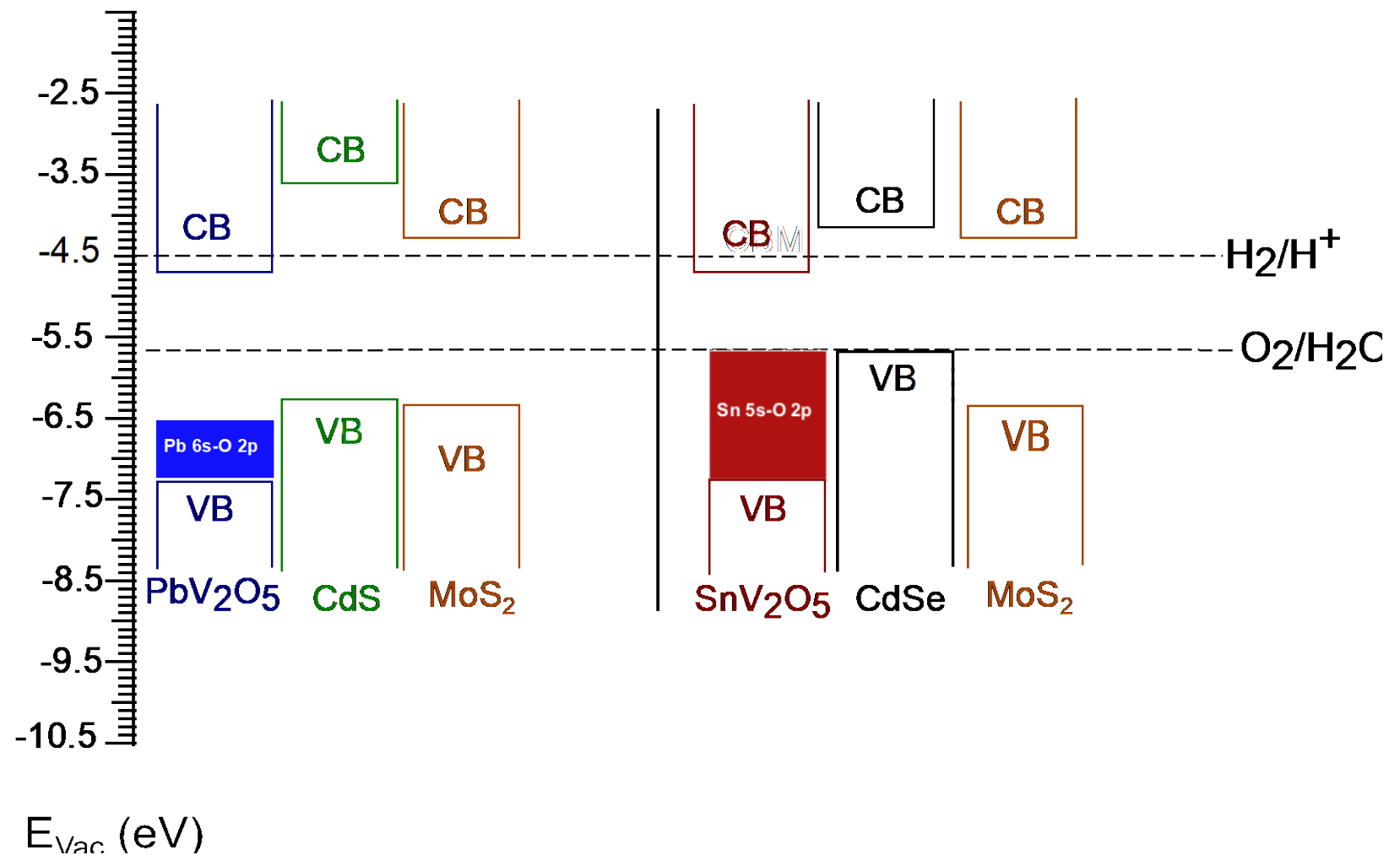


Figure 6. Band alignment of two possible Ternary systems for water splitting. In the ternary system, MoS_2 will be added so the photogenerated electron can transfer from the conduction band of QDS to the conduction band of MoS_2 .

3. Importance of High Edge Density in MoS₂

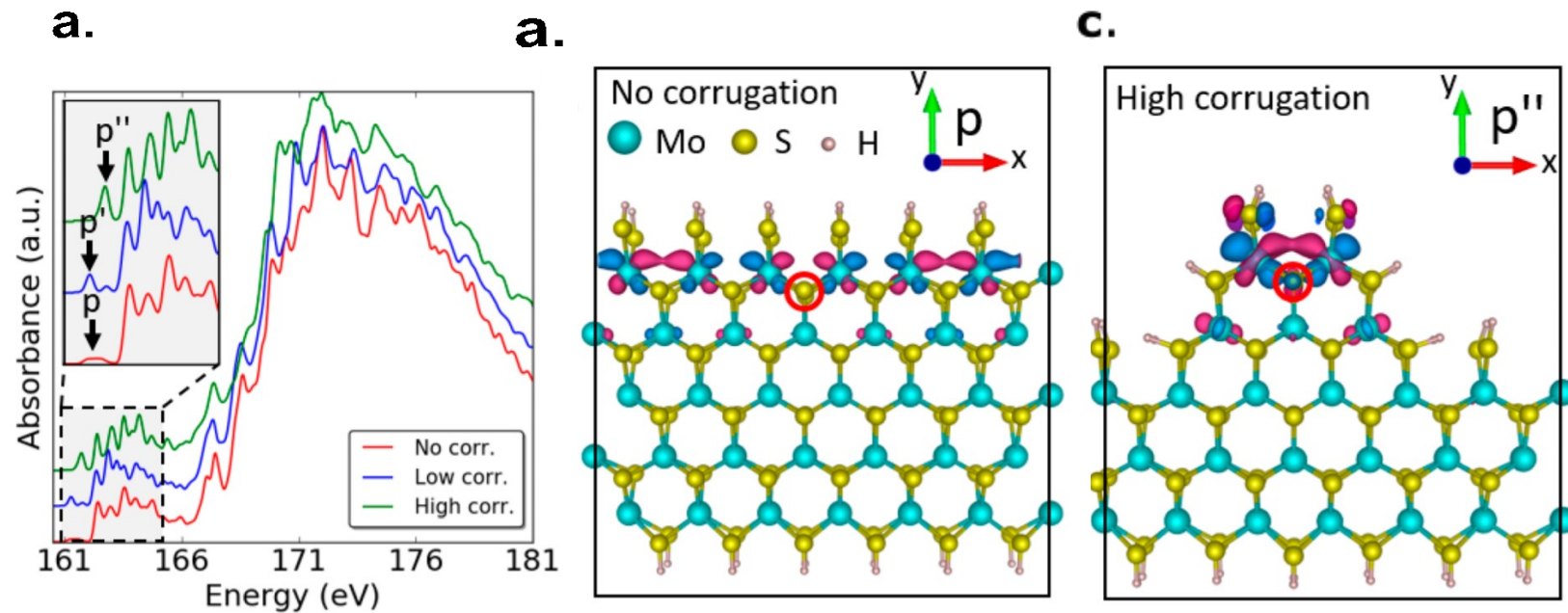


Figure 7. Calculated electronic structure of MoS₂ edge states: a) Simulated the S L_{2,3} edge at different levels of corrugation to show the importance of corrugation to the spectral features observed (b) no and (c) high corrugation to the 2H-MoS₂ structure. The increase in the p feature is related to excited Mo 4d which becomes localized and hybridizes with the S 3p edge. At 161.7 eV there is the greatest hybridization with 4 S edges due to higher corrugation.⁵

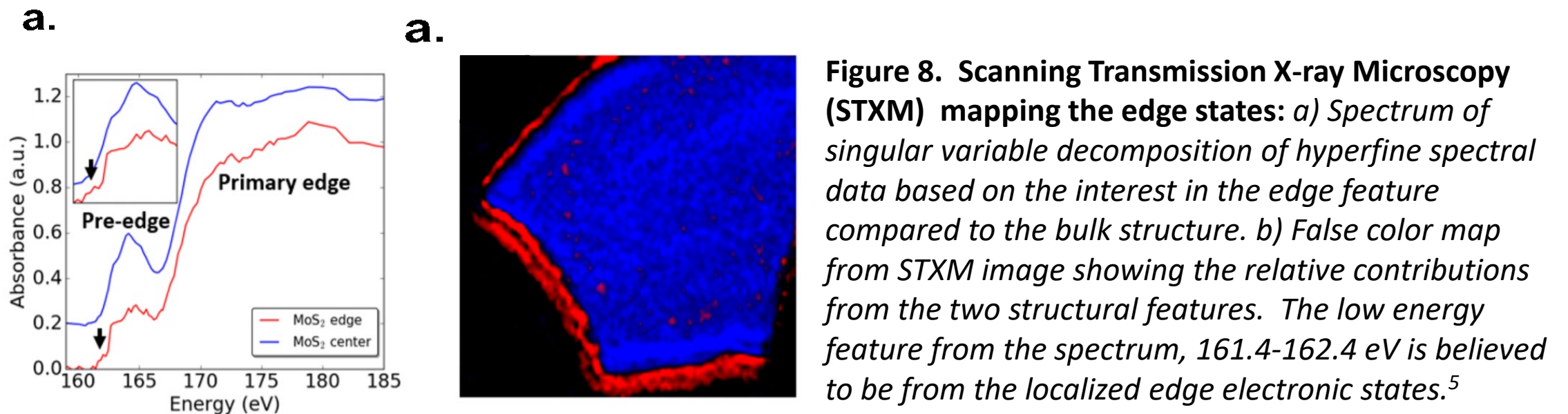


Figure 8. Scanning Transmission X-ray Microscopy (STXM) mapping the edge states: a) Spectrum of singular variable decomposition of hyperfine spectral data based on the interest in the edge feature compared to the bulk structure. b) False color map from STXM image showing the relative contributions from the two structural features. The low energy feature from the spectrum, 161.4-162.4 eV is believed to be from the localized edge electronic states.⁵

4. Towards *In-situ* XAS: Part 1

Our current activities have focused on understanding the effects of attaching MoS₂ to our nanos-engineered photocatalysts. We have performed benchmark studies and are currently determining the band offsets and charge transfer rates. X-ray absorption simulations and PEC experiments were performed ahead of our in-situ XAS measurements (by Fall 2019).

- **Jinghua Guo's experimental set-up at Advanced Light Source to perform *in-situ* XAS measurements**

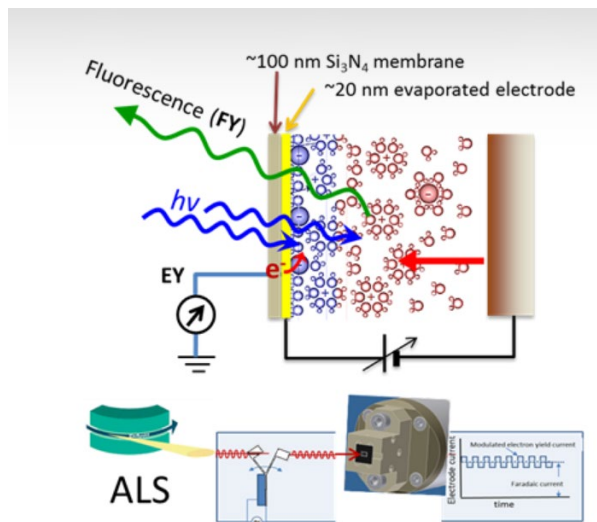


Figure 9. Schematic of *in-situ* XAS cell for measurements. The electrodes are inside the cell, which is a small volume of a few mm³.

- **David Prendergast's X-ray Simulations at the Molecular Foundry for characterizing XAS spectra**

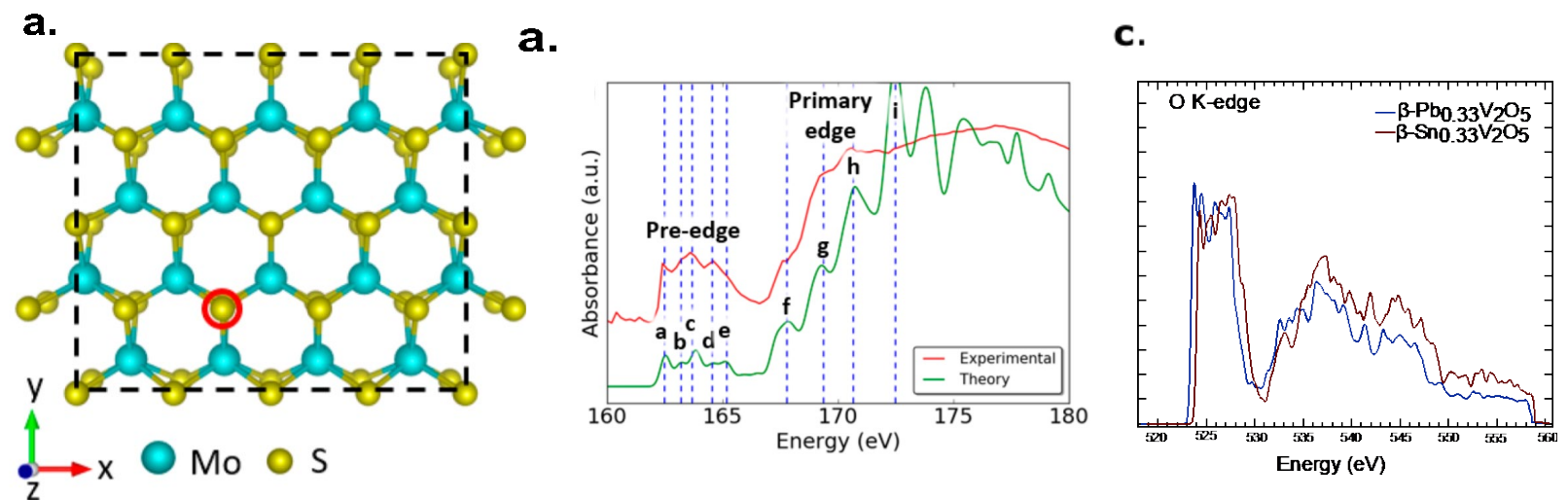


Figure 10. Simulated XAS spectra: a) Supercell of monolayer b) Comparison of the computational and experimental S L_{2,3} edge XANES spectra of the supercell. Both a pre-edge and main edge feature are shown. The pre-edge occurs due to a break in symmetry, however, the intensity is suppressed due to orbital angular momentum selection rules c) O K-edge of M_xV₂O₅.⁵ These simulations will allow for better understanding and interpretations of experimental measurements.

4. Towards *In-situ* XAS: Part 2

Measurement of Hydrogen production of binary system

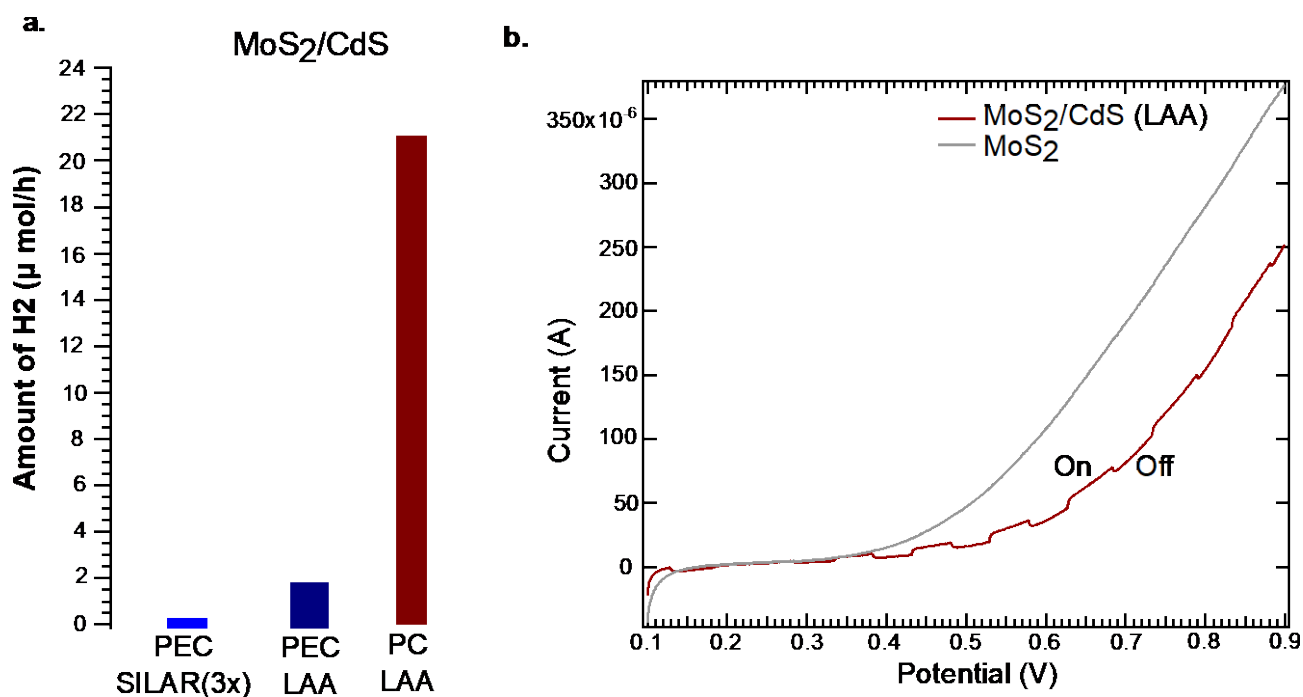


Figure 11. Photoelectrochemical measurements: a) The amount of H₂ of MoS₂/CdS sensitized by different two methods and measured by two different techniques b) catalytic hydrogen evolution from MoS₂/CdS heterostructure

X-ray Simulations of Hard X-ray Photoelectron

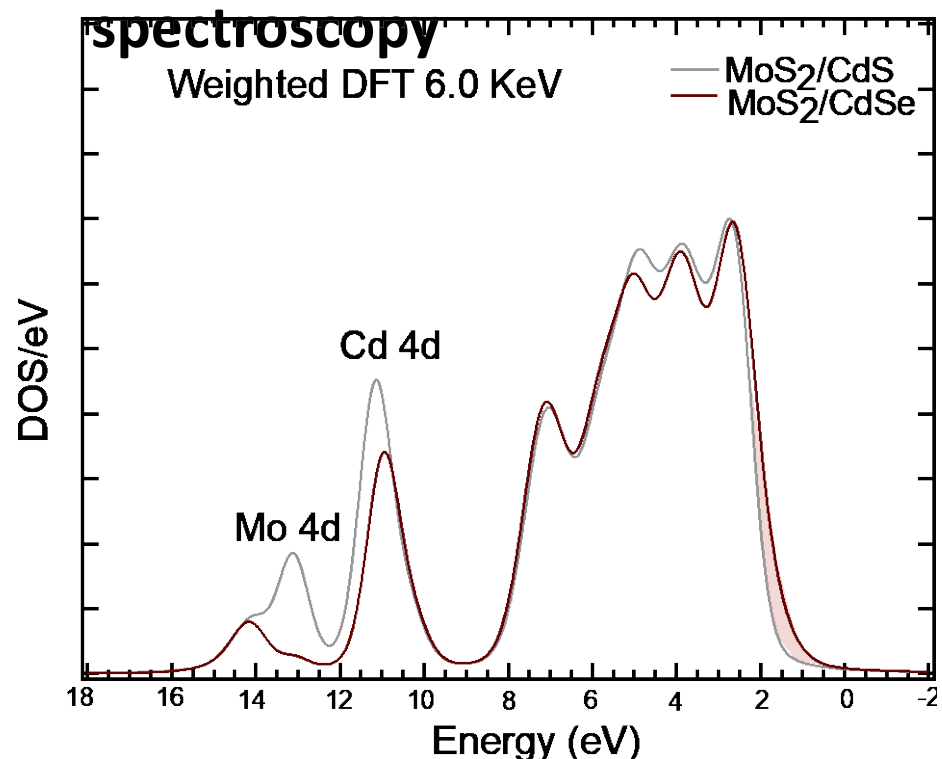


Figure 12. Predicted photoemission spectra.: Simulated DFT of MoS₂/CdX for comparison to future HAXPES measurements

The band edge offsets will be determined for the ternary system, and then used to constrain our computational modeling help interpret our *in-situ* XAS studies.

Acknowledgments

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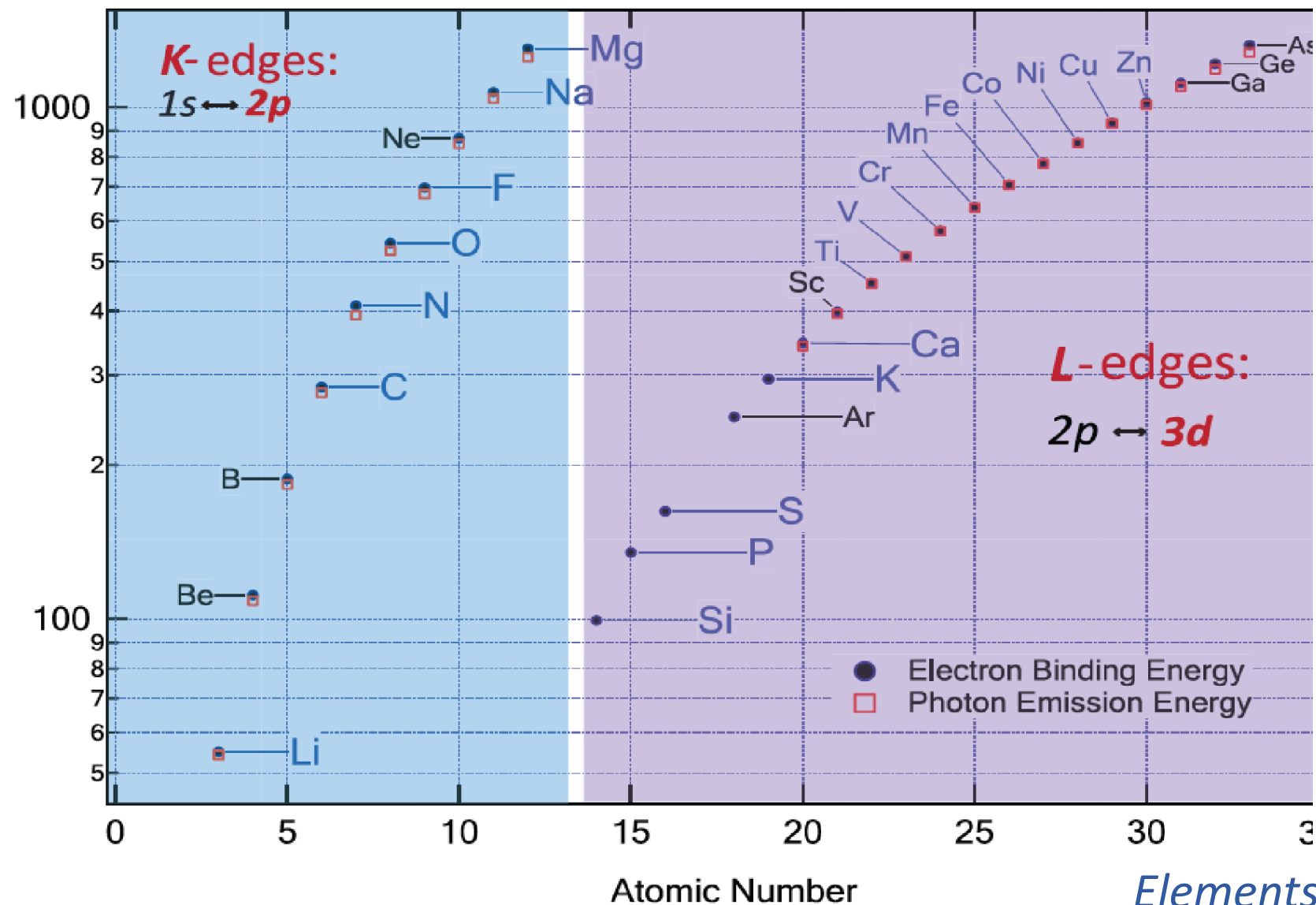


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References

1. Lee, Wonjoo, et al. "Suppression of photocorrosion in CdS/CdSe quantum dot-sensitized solar cells: Formation of a thin polymer layer on the photoelectrode surface." *Synthetic Metals* 165 (2013): 60-63.
2. Pelcher, Kate E., et al. "Integrating β -Pb_{0.33}V₂O₅ nanowires with CdSe quantum dots: toward nanoscale heterostructures with tunable interfacial energetic offsets for charge transfer." *Chemistry of Materials* 27 (2015): 2468-2479.
3. Junsang Cho et al. "The Middle Road Less Taken: Electronic-Structure-Inspired Design of Hybrid Photocatalytic Platforms for Solar Fuel Generation" *Acc. Chem. Res.*, 52 (2019), pp 645–655
4. Andrews, Justin L., et al. "Hole Extraction by Design in Photocatalytic Architectures Interfacing CdSe Quantum Dots with Topochemically Stabilized Tin Vanadium Oxide." *Journal of the American Chemical Society* 140 (2018): 17163-17174.
5. Parija, Abhishek, et al. "Mapping Catalytically Relevant Edge Electronic States of MoS₂." *ACS central science* 4 (2018): 493-503.

Soft X-Ray Spectroscopy, Imaging and Scattering

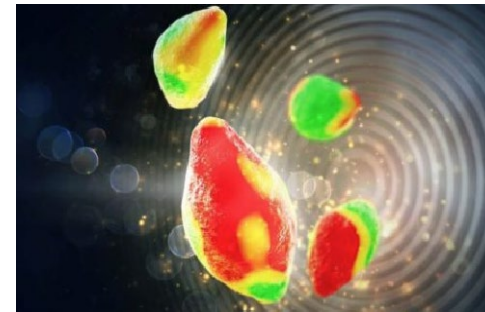
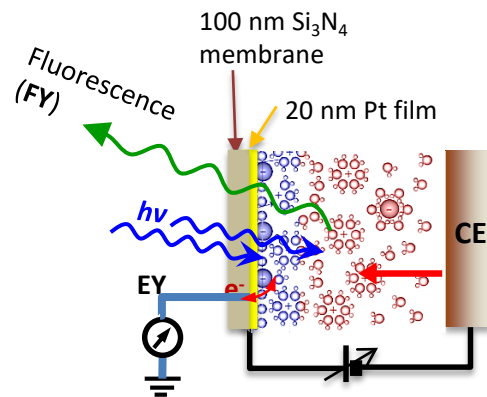


Elements are Critical to Energy Materials Research

- *Soft x-ray spectroscopy, imaging and scattering at absorption resonances is an element specific technique and able to detect species that are solids of amorphous or crystalline, liquids, and solid/liquid interfaces*
- *It detects the $1s - 2p(3p)$ transitions of low-Z elementals (B, C, N, O, F, Na, Mg, Al, P, S), and the $2p - 3d$ transitions of 3d transition metals (Ca, Ti, V, Mn, Fe, Co, Ni, Cu, Zn)*

Operando Soft X-Ray Characterization Techniques

Probing charge/discharge processes



Operando XAS/RIXS

Knowledge of the structure and composition of nanometer-thin solid-liquid interface regions is key for understanding wetting, membranes, and electrochemical phenomena.

1. *Electrochem. Commun.* **12**, 820 (2010)
2. *J. Phys. Chem. C* **116**, 16870 (2012)
3. *Science* **346**, 831 (2014)
4. *Nano Energy* **38**, 82 (2017)
5. *J. Am. Chem. Soc.* **140**, 16237 (2018)

Operando STXM

A new microscopy platform for imaging nanoscale changes inside lithium-ion battery particles, which provides new insights about performance and charging that could improve batteries.

1. *Science* **353**, 566 (2016)
2. *Nature Mater.* **17**, 915 (2018)

A Multimodal Characterization of Electrochemical Processes