THE UNIVERSITY OF CHICAGO

Argonne NATIONAL LABORATORY

Materials for sustainable energy generation and use from quantum simulations

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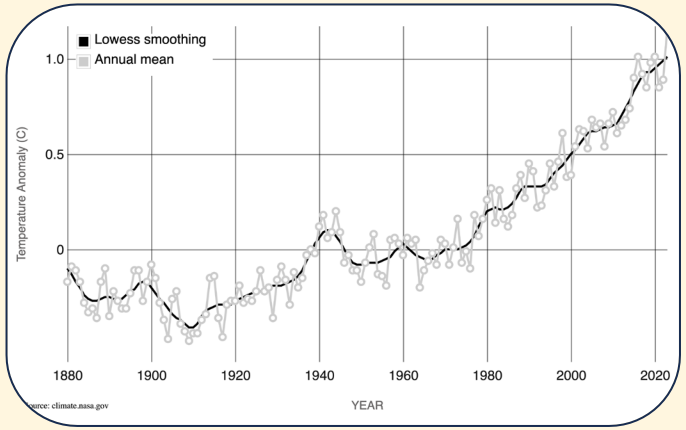
The physics and chemistry of materials for sustainability

Sustainability

- Sustainable energy sources that do not destroy the ability of the human race to live on the planet
- Broadly available clean water for energy & food

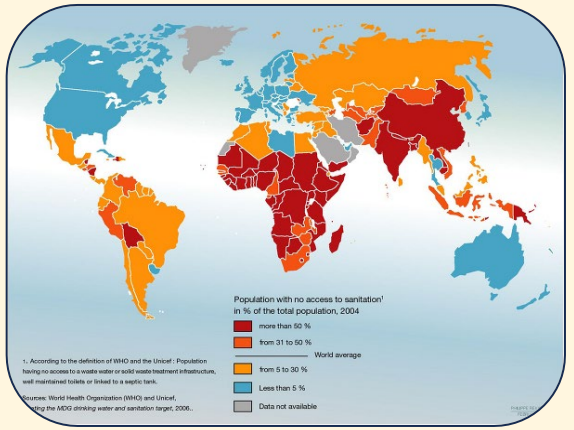
Change in global surface temperature relative to long-term average from 1951 to 1980



https://climate.nasa.gov/vital-signs/global-temperature/?intent=121

The 10 most recent years are the warmest years on record

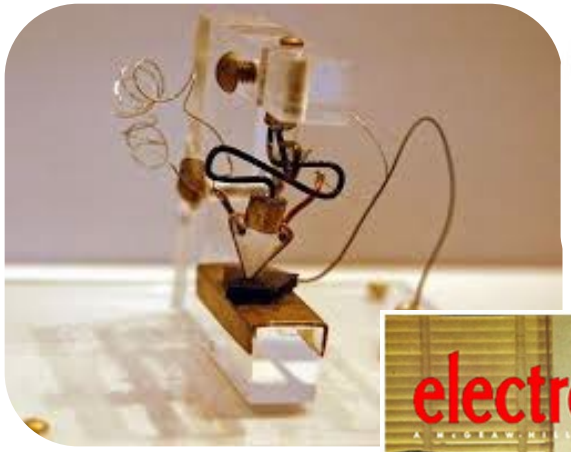
Water stress

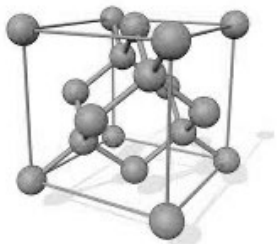


https://www.un.org/waterforlifedecade/scarcity.shtml

Materials that changed science and society

Silicon





Brattain, Bardeen, Shockley Nobel Prize in Physics 1956

Fastest classical computers in the world

Materials that changed science and society

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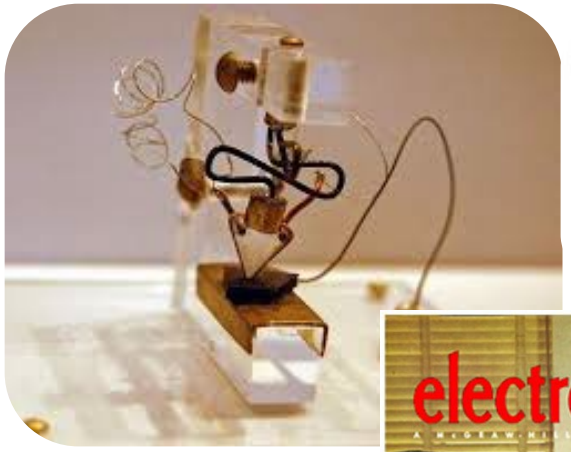

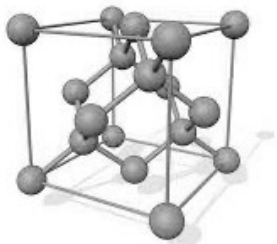

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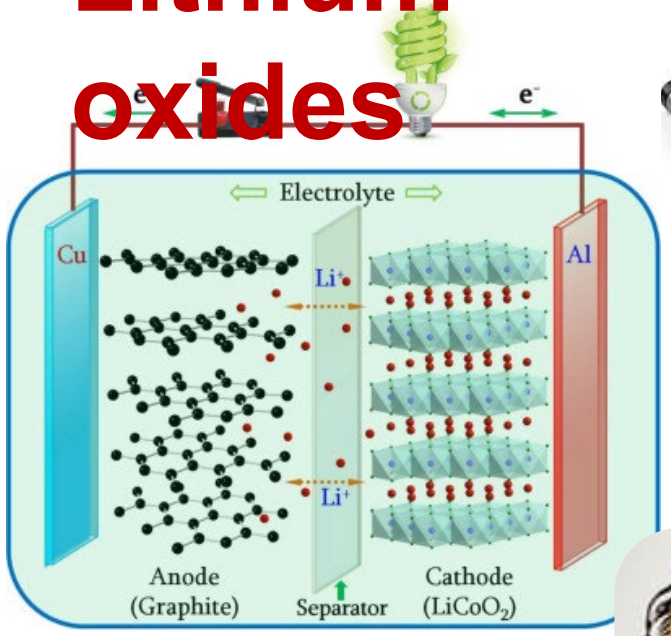
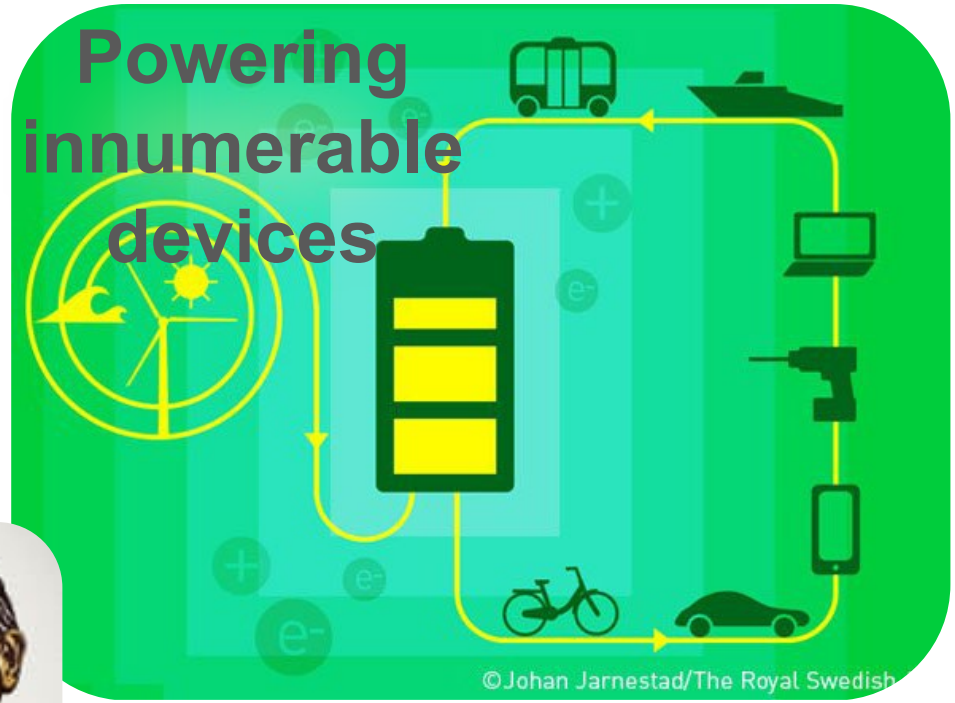
Materials that changed science and society

Lithium oxides

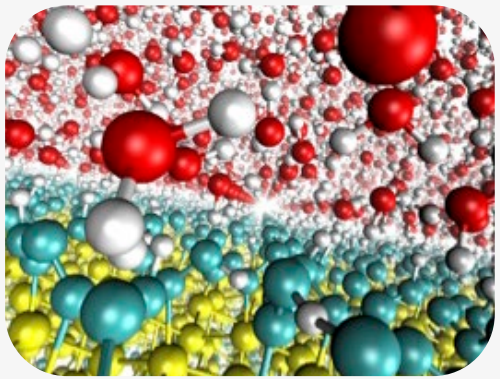




Goodenough,
Whittingham,
Yoshino
Nobel Prize in
Chemistry 2019

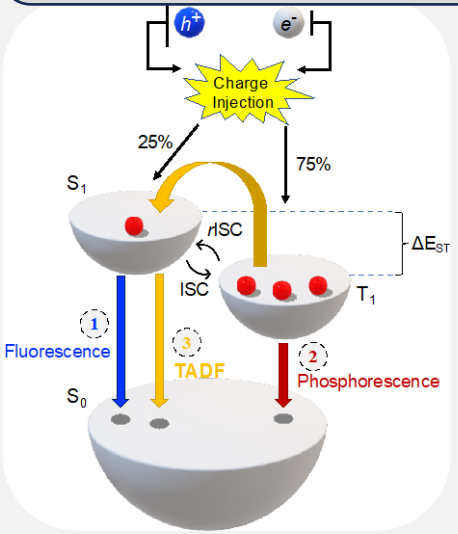
Complex materials for energy generation and use

What are the best materials to trigger desired photo-reactions to **generate clean fuel** from water?

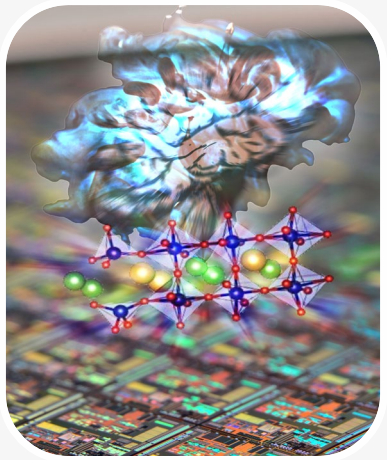


Can we engineer membranes to **remove** organic **pollutants from water ?**

How do we tackle these problems using theory and computation?



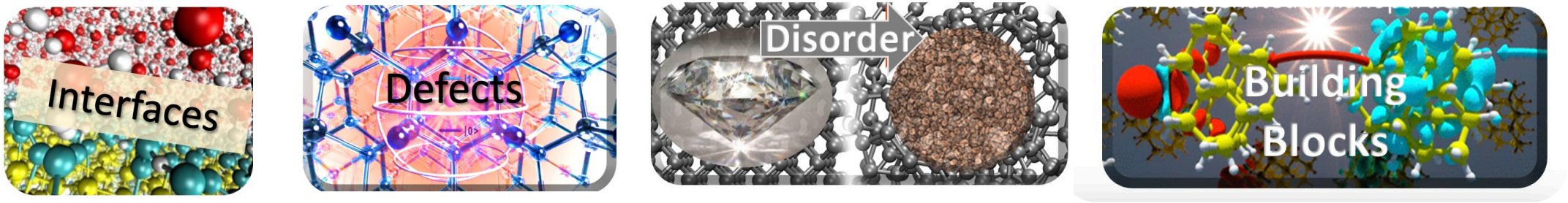
How do we design efficient **all organic** light emitting diodes (**OLEDs**)?



Which systems are suitable for energy-efficient **neuromorphic platforms** and **low power electronics** ?

Requirements to study complex systems using theory and computation

- Realistic materials are **heterogeneous systems**
  - Understanding and controlling the role of disorder, interfaces, defects and building blocks is key and it requires atomic characterization and hence atomistic & molecular control



- Prediction and design of materials and emergent behaviors require the ability to compute **multiple properties** and describe phenomena that are **out of equilibrium** and in **excited states**

Outline

- Theoretical and computational strategies

Materials for Sustainability

- Light activated phenomena in photoelectrochemical cells
- Low power oxides

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Materials for Sustainability

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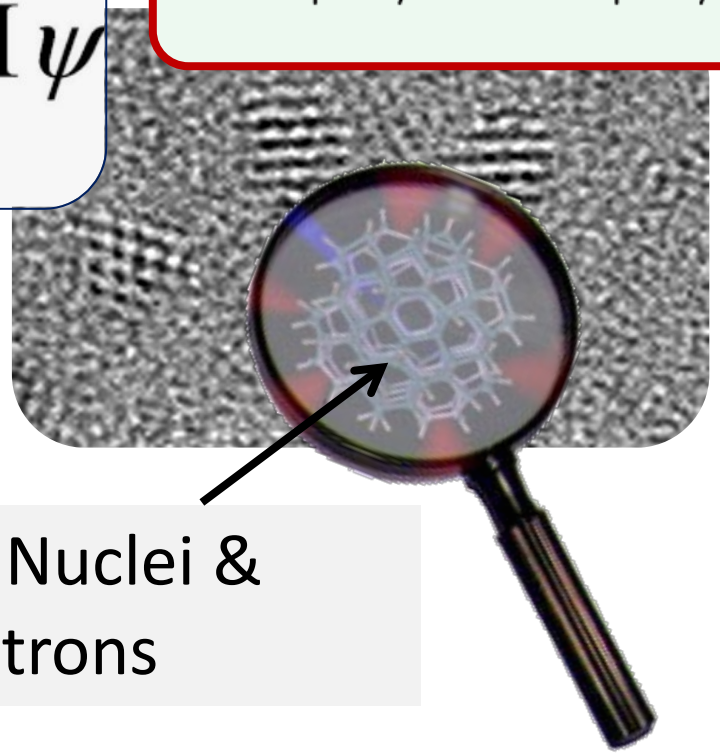
Insights and understanding at the microscopic scale using quantum mechanics

$$i\hbar \frac{\partial \psi}{\partial t} = \mathrm{H}\psi$$

$$\hat{\mathrm{H}}|\Psi\rangle = E|\Psi\rangle$$



Atomic Nuclei & Electrons

Approximations to solve fundamental equations:

- Density functionals theory &
  Quantum chemistry methods

Efficient numerical methods to obtain accurate solutions and to generate data to train 'models' (improve efficiency with AI/ML)

Exploration of phase space

Description of matter-light interaction

Approximate quantum mechanical theories

- **Density functionals theory**: 'born' within condensed matter physics (CMP), ~ 1964, and then applied also to molecules, with a variety of approximate functionals
- **Quantum chemistry methods**: 'born' within the chemistry community with Hartree-Fock, ~ early 1900s, and used for molecules & some solids; key to the development of hybrid functionals & **embedding theories**
- **Many Body Perturbation Theory**: 'born' within CMP, ~ 1965, to study light-matter interaction; key to the development of computational spectroscopy of condensed systems

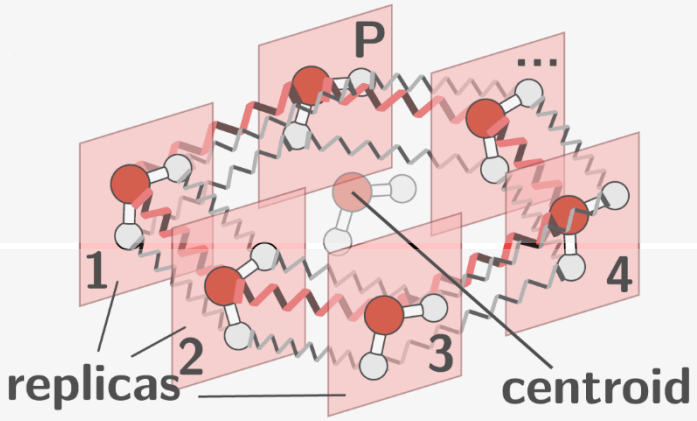
Approximate, general frameworks and a *'universal language'* to tackle disparate problems from first principles

Including temperature & exploring phase space

$$M\ddot{\mathbf{R}}_I = -\frac{\partial E}{\partial \mathbf{R}_I} = F_I[\{\mathbf{R}_J\}]$$

Molecular dynamics (MD): classical nuclei

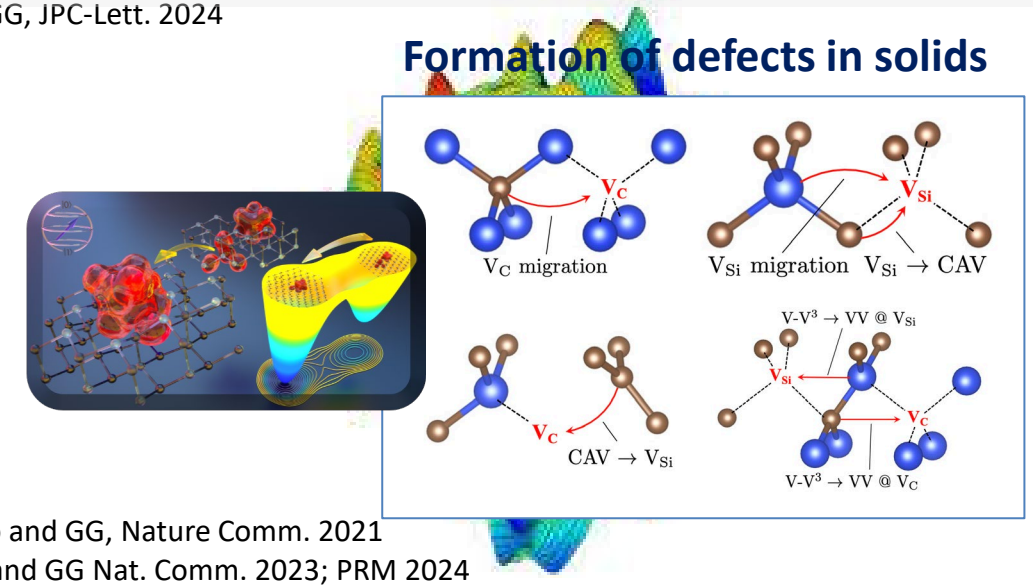
E from Density Functional Theory (DFT)



Path Integral MD: quantum nuclei

A. Kundu H. Yang, M.Govoni, F.Gygi, M.Ceriotti and GG, PRM-Lett 2021; A. Kundu, Y.Song and GG PNAS 2022, A.Kundu &GG, JPC-Lett. 2024

Formation of defects in solids



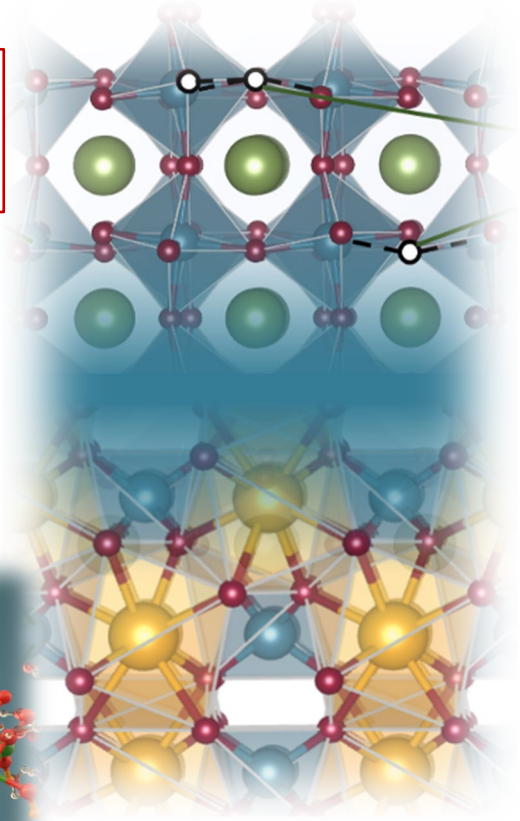
Advanced sampling to compute free energies and 'overcome' barriers

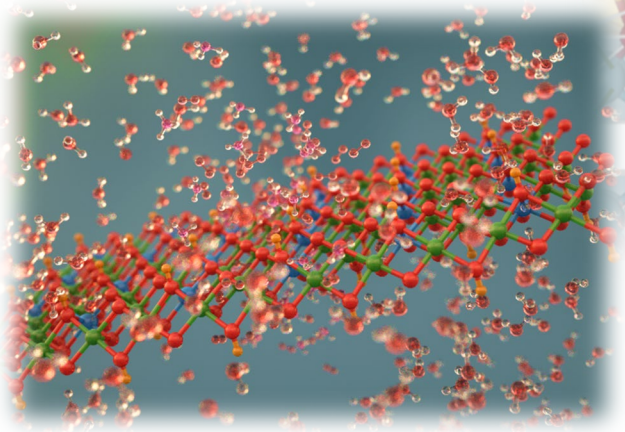
E.Lee, J. de Pablo and GG, Nature Comm. 2021
C. Zhang, F.Gygi and GG Nat. Comm. 2023; PRM 2024

Structural models derived with the aid of DFT and first principles molecular dynamics (FPMD)

$$M\ddot{\mathbf{R}}_I = -\frac{\partial E}{\partial \mathbf{R}_I} = F_I[\{\mathbf{R}_J\}]$$

E from Density Functional Theory (DFT)





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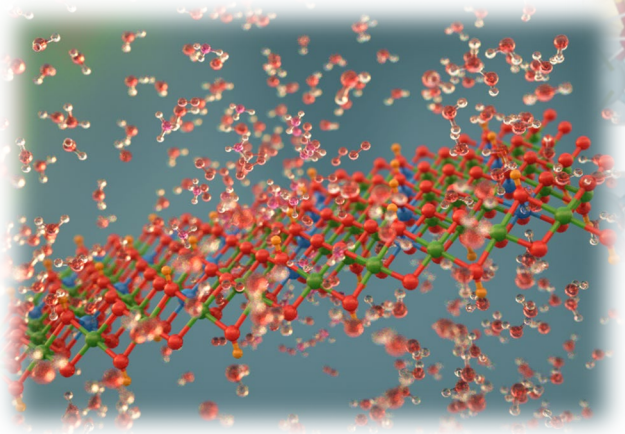
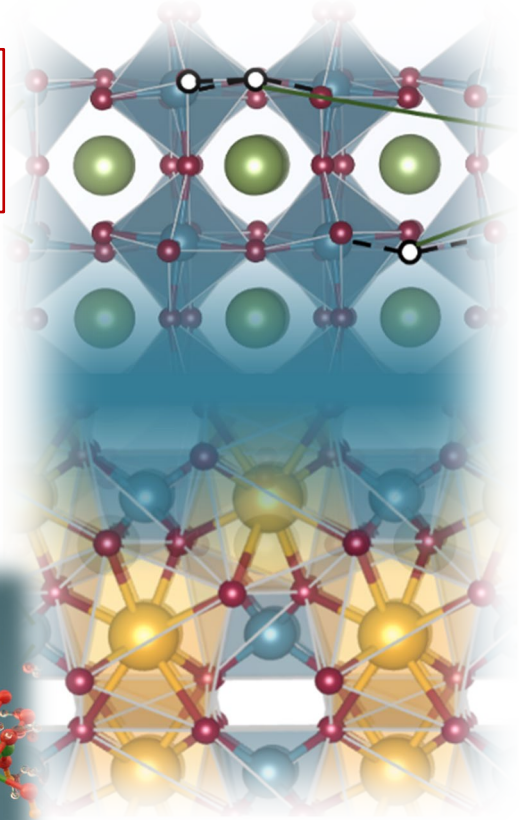
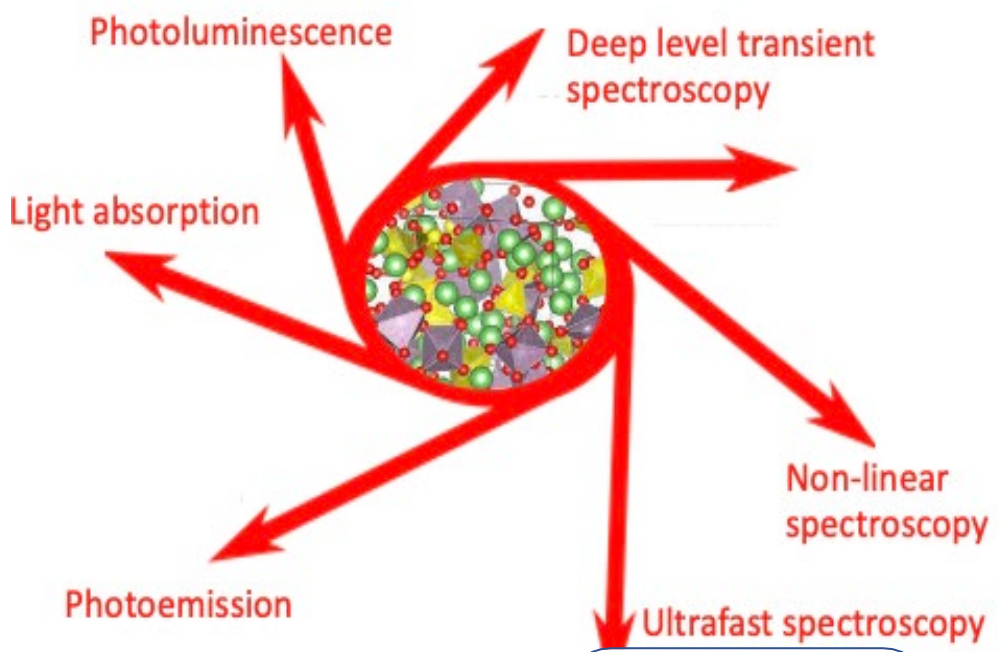
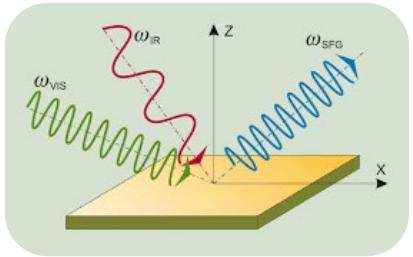


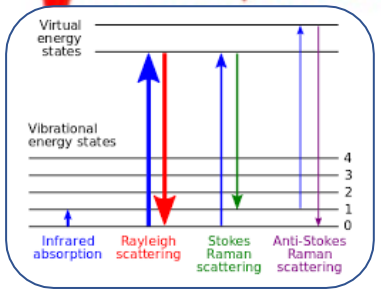


Probe

Spectroscopic signatures







Spectroscopy on *samples* obtained from DFT or FPMD

Use of multiple probes and iterative 'refinement' procedures are necessary in the majority of cases

Spectroscopic Characterization

Many Body Perturbation Theory & **Embedding theories**

- *Photoemission*
- *Absorption*
- *X-ray photoemission*
- *Photoluminescence*
- Deep level transient spectroscopy
- Ultrafast spectroscopy
- Non-radiative recombination

Key role of computational spectroscopy

- **To validate atomistic structural models by comparing with experiments**
- **To understand & predict light-matter & external field interaction processes**

H. Wilson, F. Gygi, and GG, PRB 2008; M.Govoni & GG, JCTC, 2015 & 2018; Nguyen et al. PRL 2019; Ma He et al, JCTC 2019 and JCTC 2020; S.Dong, M.Govoni & GG, Chem.Sci. 2021; H.Yang, M.Govoni and GG, JCTC 2022; Y. Jin, M.Govoni & GG, JCTC 2023

H. Ma, M. Govoni, GG, npj Comp.Mat. 2020; N.Sheng, C.Vorwerk, M.Govoni & GG, JCTC 2022; C.Worwerk, N.Sheng, M.Govoni & GG, Nature Comp. Sci. 2022

Quantum simulations to characterize & *design* materials & processes: what does it take?

- Develop/use **approximations** to solve the fundamental equations of quantum mech
  - Density fun ds
- Develop effici urate solutions of the fundame train 'models' (improve effi
- Explore phas **stabilities**
- Describe **interaction between matter & external field**, including light

Quantum simulations to characterize & *design* materials & processes: what does it take?

Software for high-performance architectures

Outline

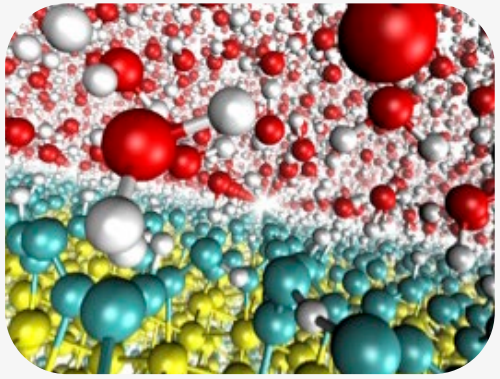
- Theoretical and computational strategies

Materials for Sustainability

- **Light activated phenomena in photoelectrochemical cells**
- **Low power oxides**

Multi-faceted processes and complex materials

What are the best materials to trigger desired photo-reactions to **generate clean fuel** from water?



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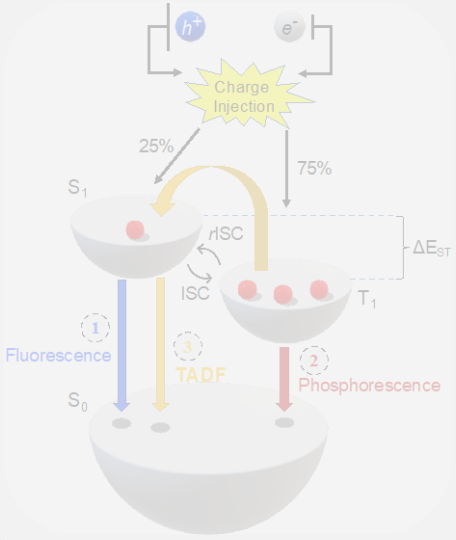

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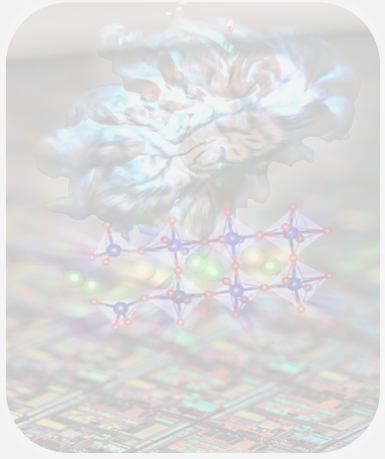
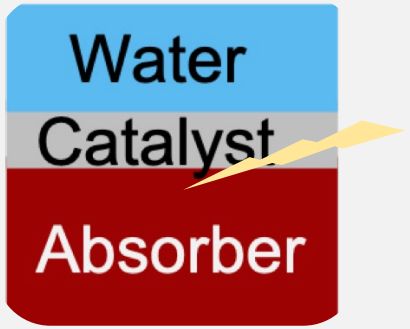


Which systems are suitable for energy-efficient **neuromorphic platforms** and **low power electronics** ?

Navigating the puzzle of heterogeneous photo-catalysis

Absorb light $\xrightarrow{h\nu}$ $2\,H_2O \rightarrow 2H_2 + O_2$

- Transport (e^-, h^+) pairs from the solid absorber to water
- Harvest charges for chemical reactions



Navigating the puzzle of heterogeneous photo-catalysis

Condensed matter physics meets electrochemistry

to investigate solid-liquid and solid-solid interfaces and light-matter interaction

Interdisciplinary science

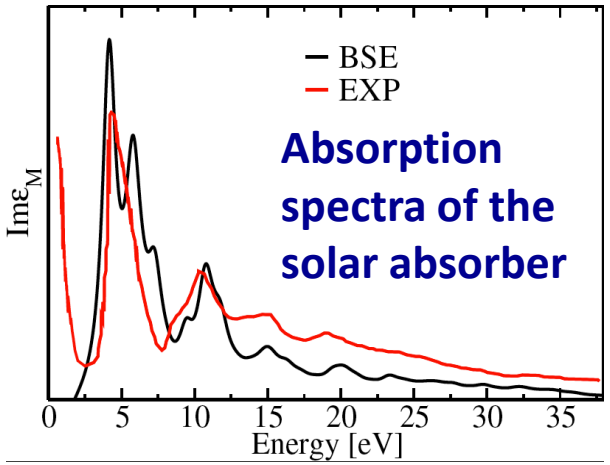
A difficult problem with many components

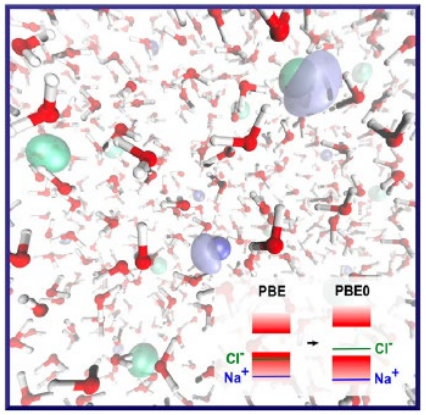
Simulations and predictions of numerous properties

Reasonable model of photo-absorber (MPBT) and of (salty) **water** (FPMD)

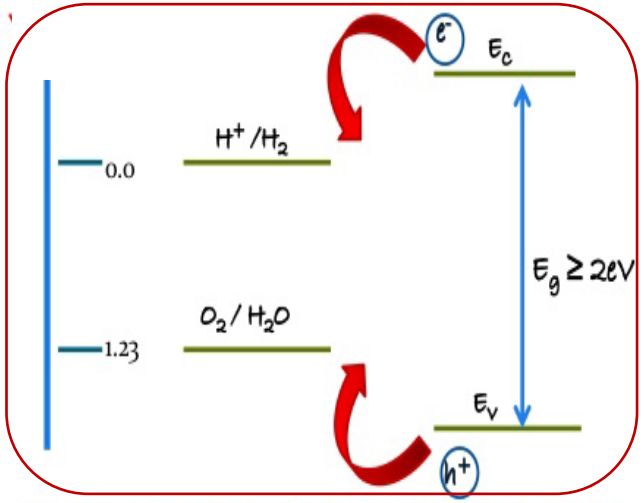
Atomistic model of solid/liquid interfaces (FPMD) & their electronic properties (**band offsets** and **Schottky barriers**)

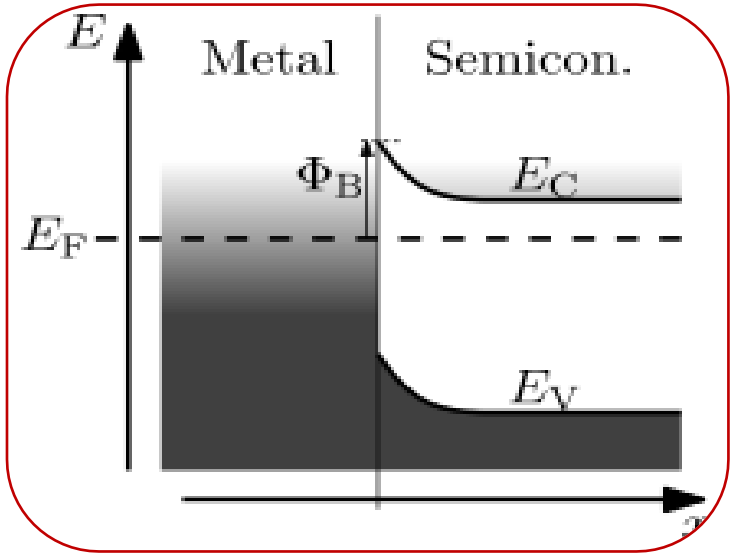
Charge transport @ interfaces





A.Gaiduk, T.A.Pham, F.Paesani and GG. Nature Comm 2018
A.Gaiduk, et al 2016; T.P.Anh, Sci. Adv. 2017





A difficult problem with many components

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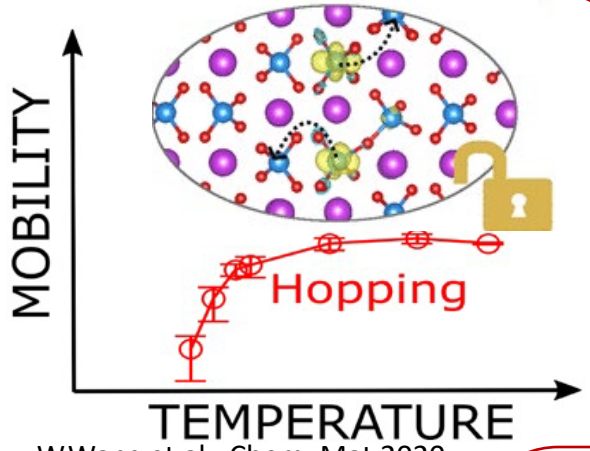
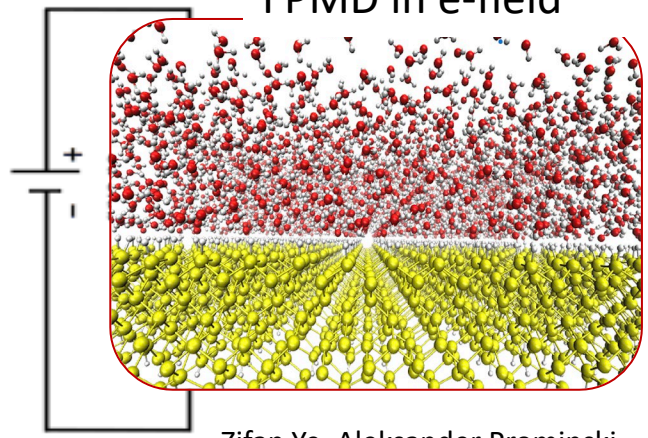


W.Wang et al., Chem. Mat 2020

FPMD in e-field



Zifan Ye, Aleksander Prominski, Bozhi Tian, and GG, PNAS 2021 & Z. Ye, F. Gygi & GG, JPC-Lett 2024

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Photocathode : functionalized Si surf.

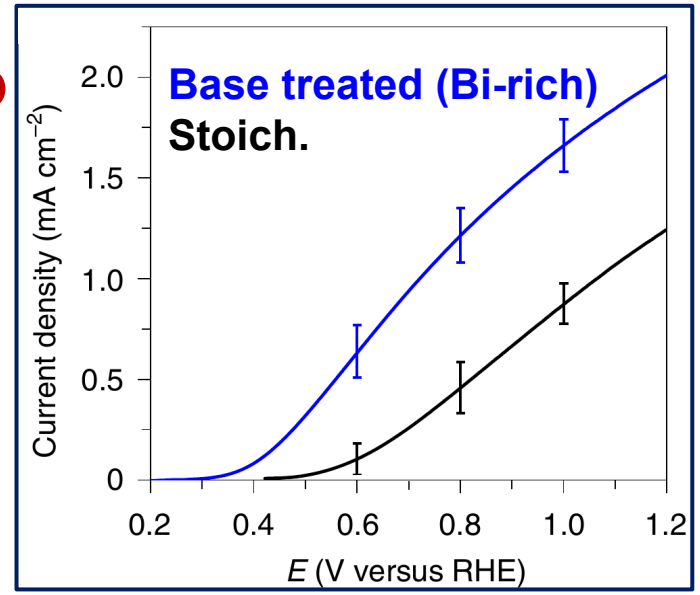
T.A.Pham, D,Lee, E.Schwegler and GG, JACS 2014; T.Pham, Y.Ping & GG, Nature Mat. 2017

Phonoanodes: WO_3 & $BiVO_4$

M.Gerosa, M.Govoni, F.Gygi and GG, Nature Mat. 2018; W. Wang et al. Nature Energy 2021 & JACS 2022 & JACS 2023

An *excellent* photoanode: $BiVO_4$

How do we model (prepare) the *sample*?



- **Oxide substrates are defective**
  - Understand the role of oxygen vacancies & inpurities in the bulk and at the surface

T. Kim et al., Nat. Comm. 2015; H.Seo et al. Chem. Mat. 2018 ; W.Wang et al. Chem. Mat. 2020

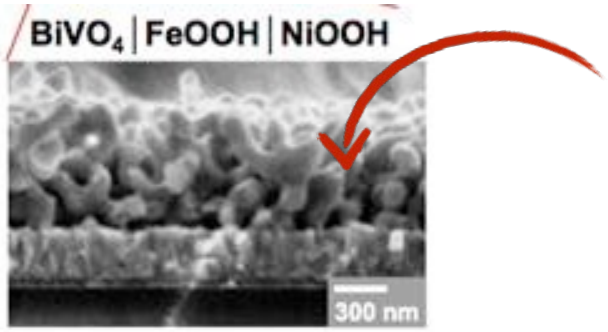
- **Oxide photoanodes are n-doped**
  - Understand the role of excess electrons at surfac W.Wang et al. JACS 2022

- **Morphology and surface composition of the photoanode surface matter:**
  - What is the most suitable surface to improve the efficiency of the OER in water?
    - STM images, XPS, vibrational spectroscopy, work-functions

D. Lee et al, Nature Energy 2021

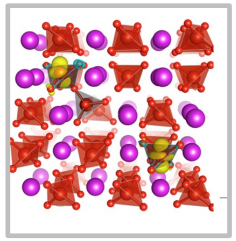
We identified promising, realistic surface exposed to water: hydroxilated Bi-terminated surface with oxygen vacancies

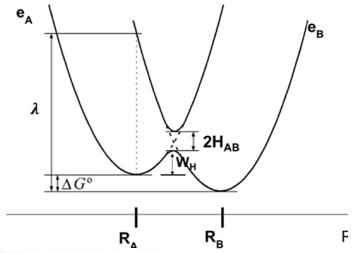
Charge transport @ interfaces

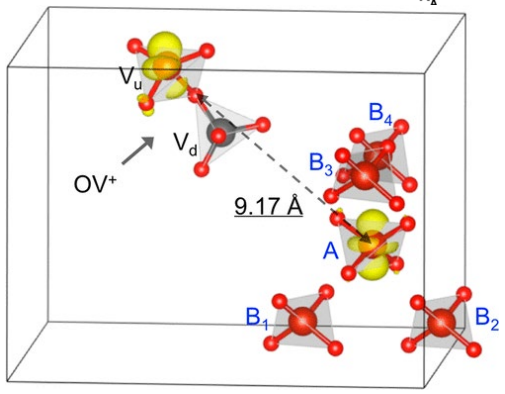


$BiVO_4$: Charge transport occurs via polarons. Control of defects is key: increasing concentration of O vacancies increases mobilities because (i) # of charge carriers increase and (ii) polaron hopping activation energy decreases **T.W.Kim, Y. Ping,** GG & KS Choi, Nat. Comm. 2015

Constrained DFT w/hybrid functionals



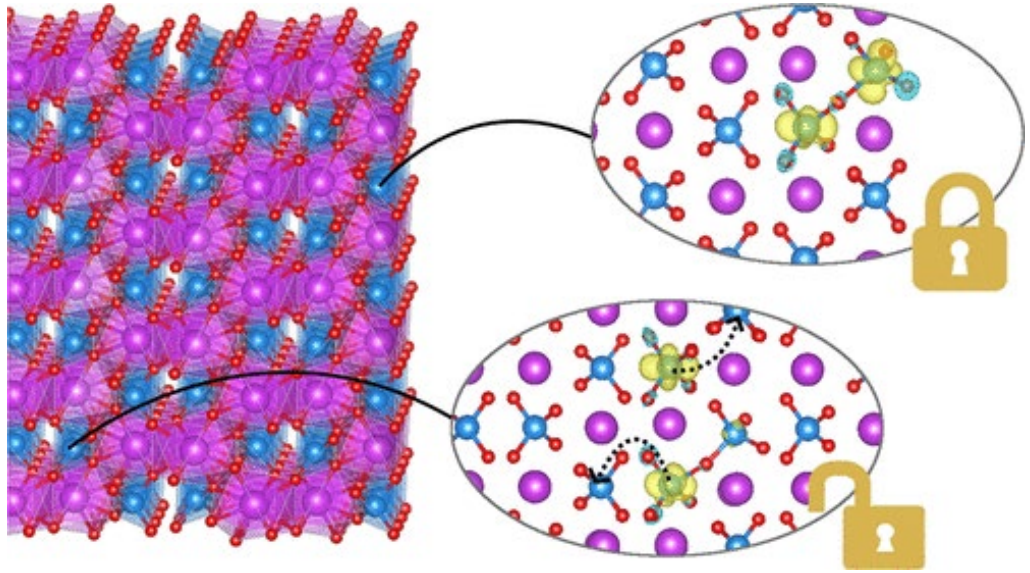




H.Seo, Y.Ping &GG, Chem. Mat. 2018

W.Wang et al. & GG Chem. Mat. 2020

Important differences in charge hopping in the bulk and @ the surface



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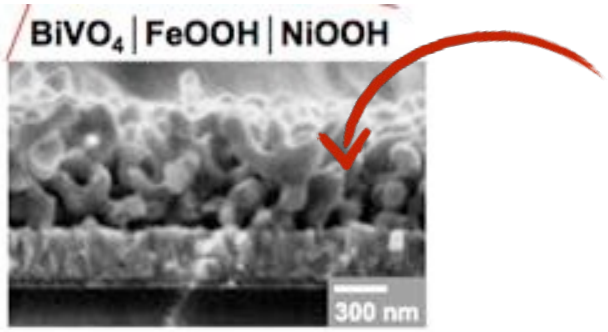

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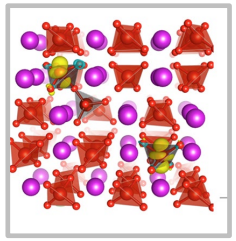
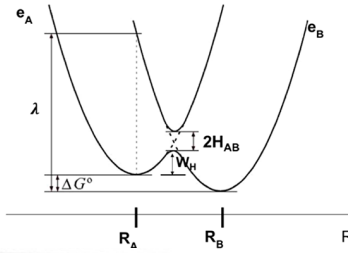
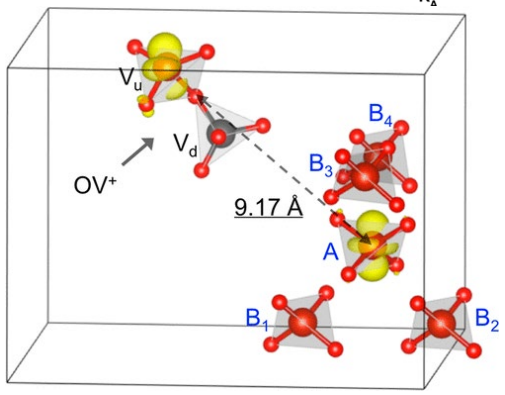




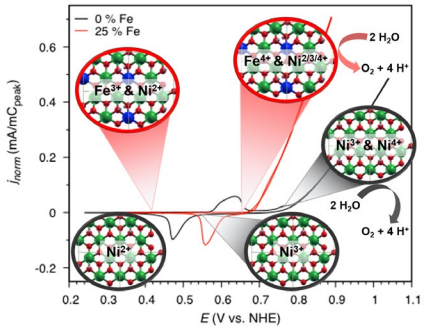


H.Seo, Y.Ping &GG, Chem. Mat. 2018

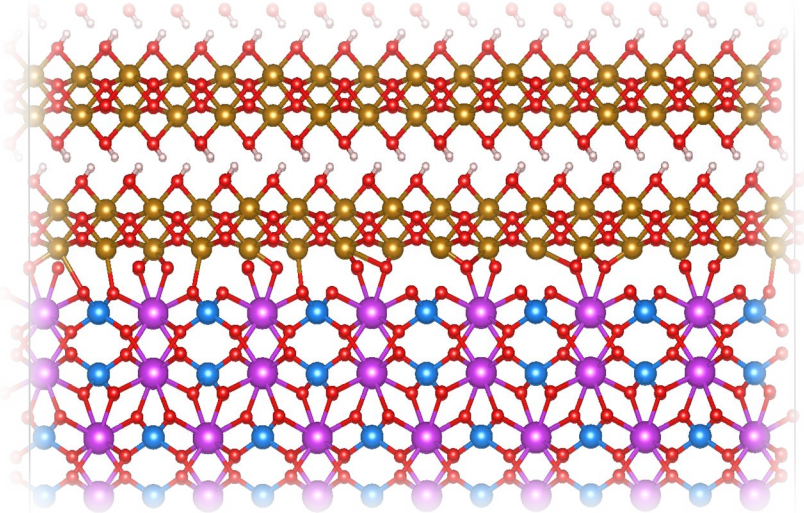
W.Wang et al. & GG Chem. Mat. 2020

What about the absorber/catalyst interface ?

Active sites @ NiFeOOH



Z. K. Goldsmith, A. K. Harshan, J. B. Gerken, M. Vörös, G. Galli, S. S. Stahl, S. Hammes-Schiffer, *PNAS 2017*



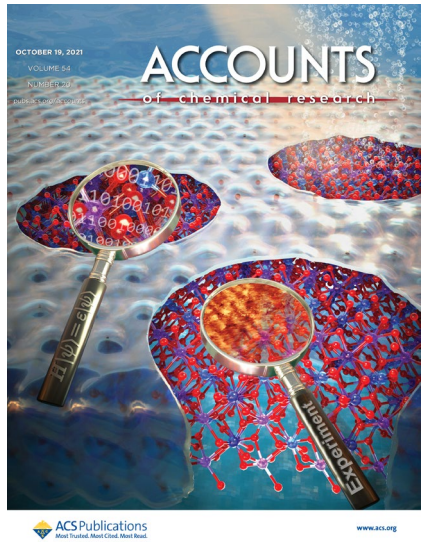
FeOOH

$BiVO_4$

Adam M. Hilbrands, Shenli Zhang, Chenyu Zhou, Giacomo Melani, Dae Han Wi, Dongho Lee, Zhaoyi Xi, Ashley R. Head, Mingzhao Liu, Giulia Galli, and Kyoung-Shin Choi, J. Am. Chem. Soc. 2023.

What did we learn about photo-absorbers and catalysts for oxygen evolution reaction ?

- Intrinsic properties of materials are insufficient to predict materials for water photo-catalysis
  - Defects cannot be ignored; in fact, they may be *useful*
  - Surface & interface morphology is critical



Wennie Wang, Andjela Radmilovic, Kyoung-Shin Choi & GG, Acc. Chem. Res. 2021

- Electronic properties @ finite T and dynamical fluctuations are key to understand not only charge transport mechanisms but also structural properties and spectroscopic signatures.
  → **Dynamical, defective interfaces**

M.Gerosa, F.Gygi, M.Govoni and GG, Nature Materials 2018; [#]Y.Ping, W.Goddard & GG, JACS 2015; [+]T.W.Kim, Y. Ping, GG & KS Choi, Nat. Comm. 2015; H.Seo, Y.Ping &GG, Chem. Mat. 2018; T.A.Pham, D. Lee, E.Schwegler and GG JACS 2014; T.A.Pham, Y.Ping and GG Nature Materials 2017, W.Wang , KS Choi, GG, Chem Mat 2020 & Nature Energy 2021, W.Wang et al., JACS 2022 ; A. Hilbrads et al. JACS 2023; G. Melani et al. 2024 (in preparation)

What did we learn about photo-absorbers and catalysts for oxygen evolution reaction ?

The interface is *still* the device and defects take center stage

Simulation time scale and sample size are still open problems

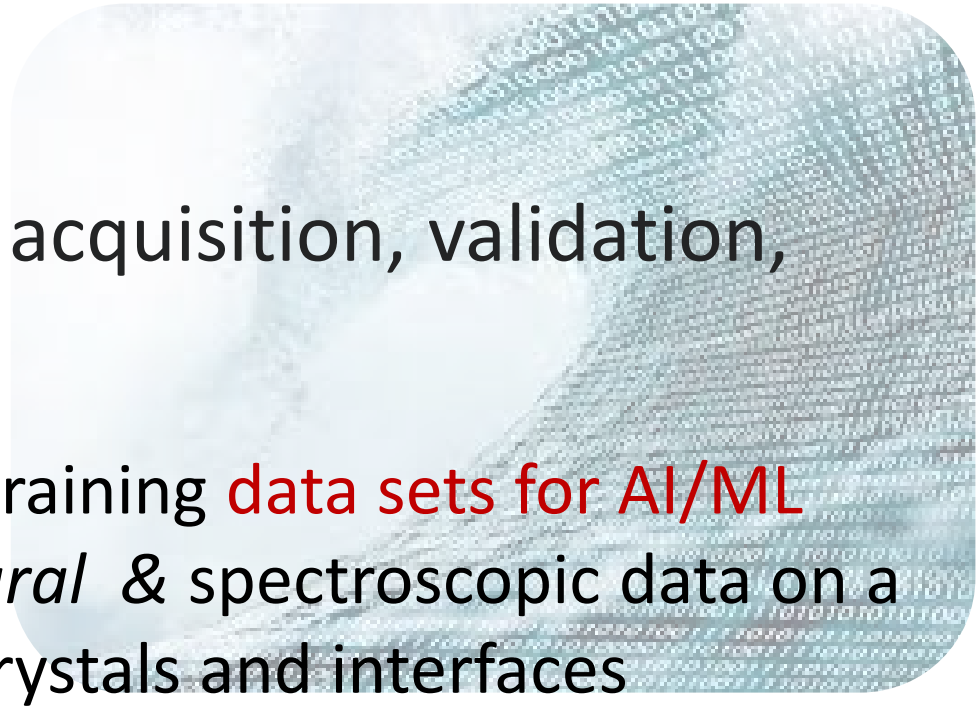
We did not predict a *magic* new material but we understood the **material characteristics** (descriptors) that **matter** for the catalytic reaction & several **predictions** were **validated experimentally**

Machine Learning, AI???

Do we have everything we need? Just a matter of generating more data and let AI/ML do the job?

- **Not yet… we need more data!**

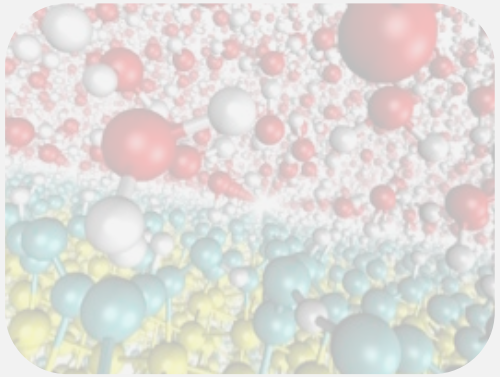
Do we have everything we need? Just a matter of generating more data and let AI/ML do the job?



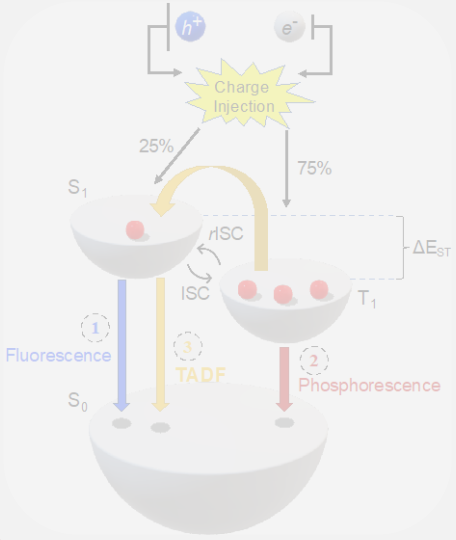
- **Not yet… we need more data!**
  - **Improved data strategies are in need**: acquisition, validation, curation, preservation
    - Validation, benchmarking and building training data sets for AI/ML require availability of ‘mundane’ *structural* & spectroscopic data on a ‘massive’ scale, including well defined crystals and interfaces (computing **& measuring** samples at speed)
    - Availability of reproducible data and building of workflows will be critical to the success of AI/ML in physics, chemistry and materials science

Multi-faceted processes and complex systems

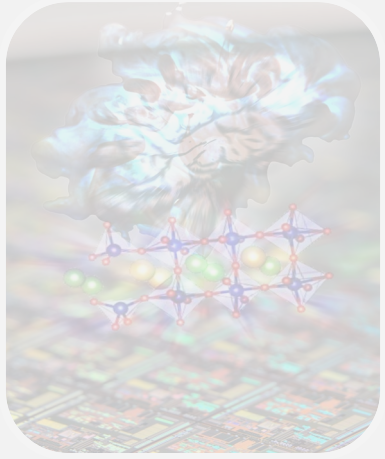
What are the best materials to trigger desired photo-reactions to **generate clean fuel** from water?



Can we engineer membranes to **remove** organic **pollutants from water ?**



How do we design efficient **all organic** light emitting diodes (**OLEDs**)?



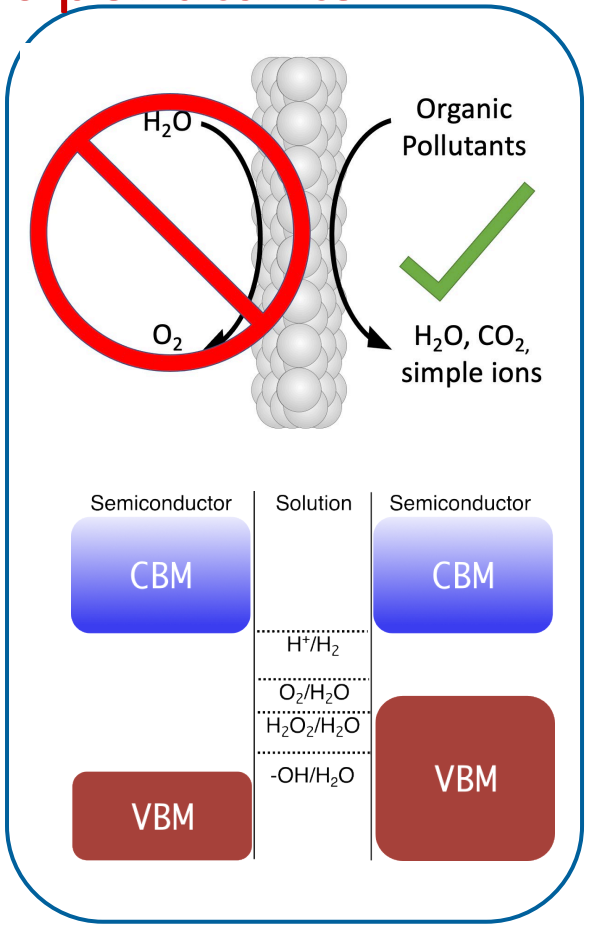
Which systems are suitable for energy-efficient **neuromorphic platforms** and **low power electronics** ?

In_2O_3 as a catalyst for advanced oxidation processes

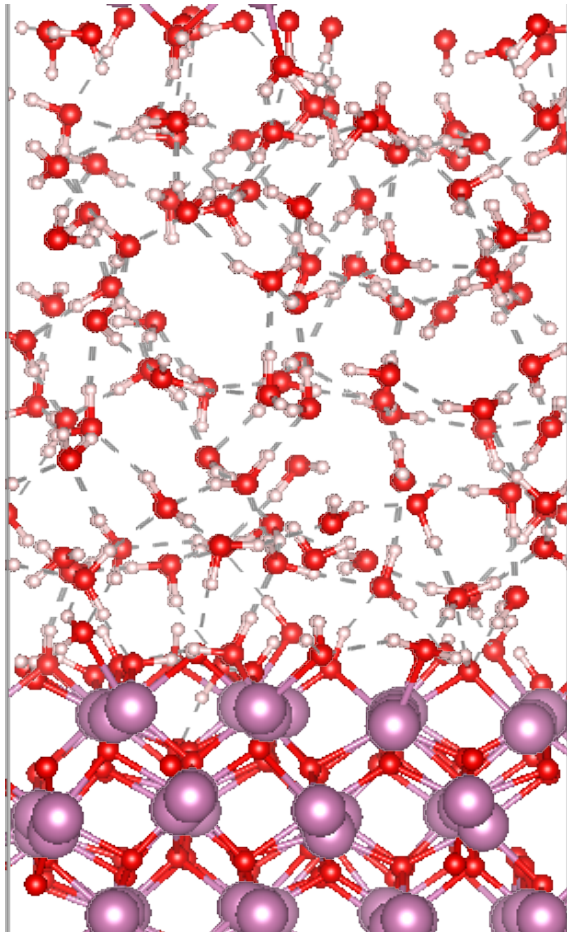
Generate hydroxyl radicals (•OH) to remove water organic pollutants

- We find that the (001) surface is hydrophilic, in contrast with the local hydrophobicity of the (111) surface
  - Water binding site to Indium identified→ a possible, initial step towards the formation of ˙OH radicals

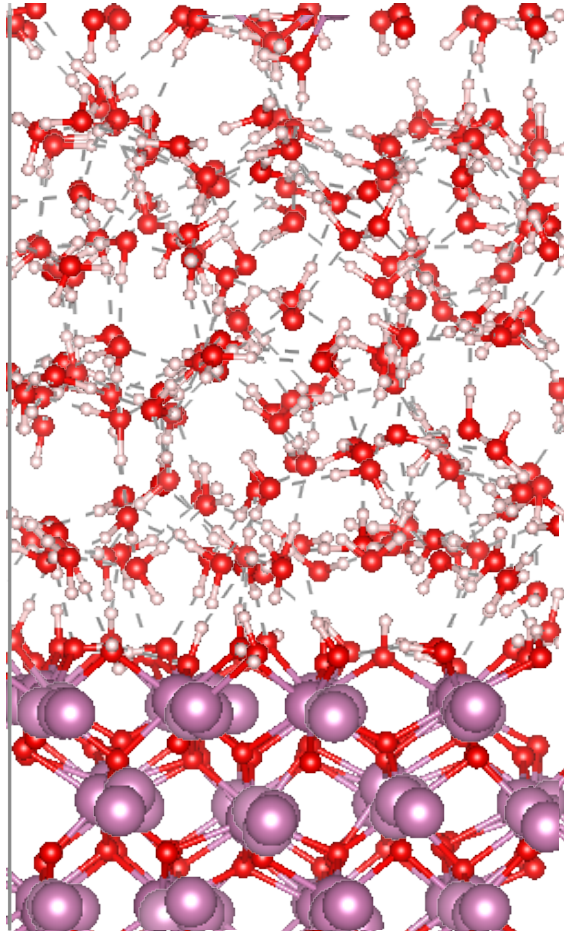
- Calculation of band offsets as a function of coverage to investigate the competition between different oxidation reactions: the Oxygen Evolution Reaction may hinder the generation of hydroxyl radicals and should be **avoided.**



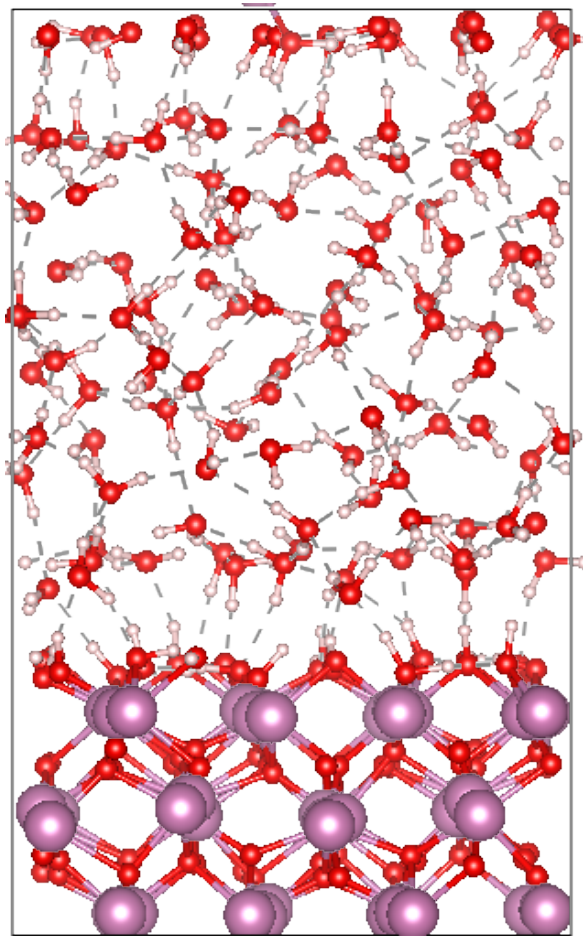
Water binds to open indium sites when surface hydroxyl coverage is reduced



66% OH Coverage

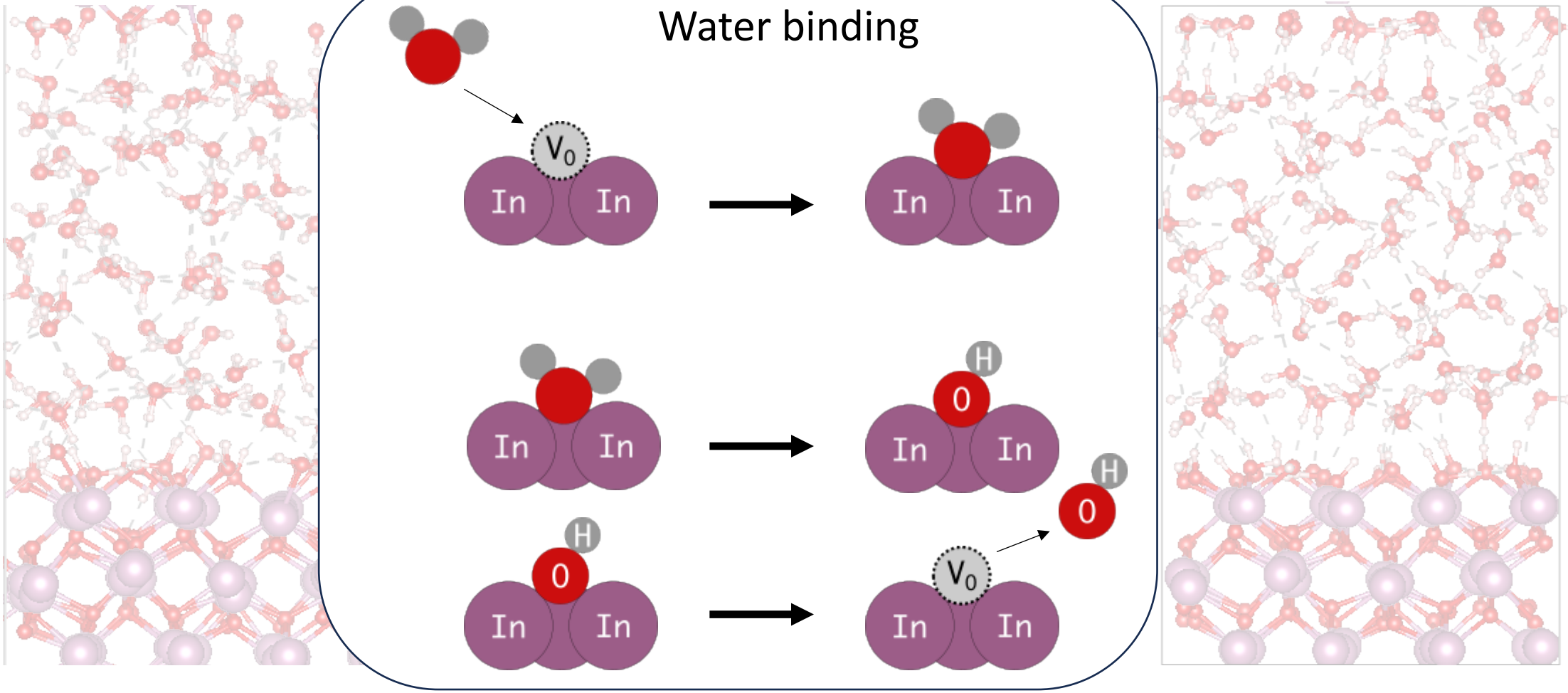


83% OH Coverage



96% OH Coverage

Water binds to open indium sites when surface hydroxyl coverage is reduced



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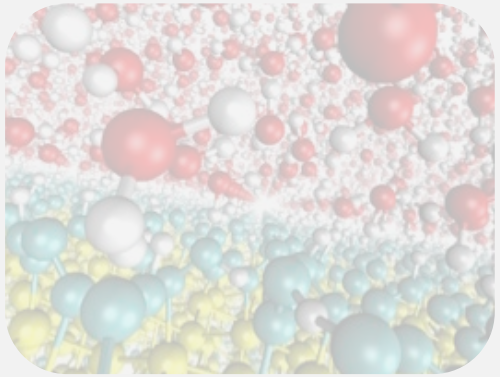

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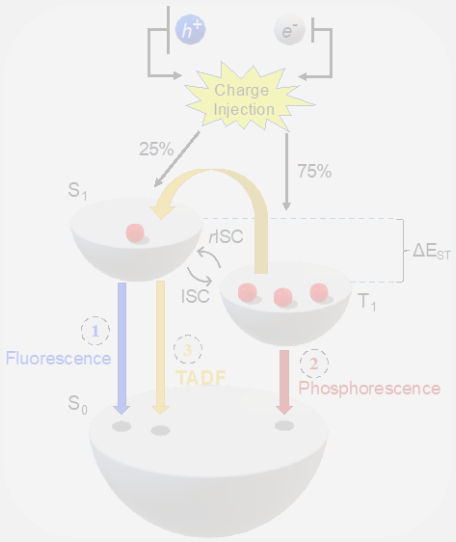

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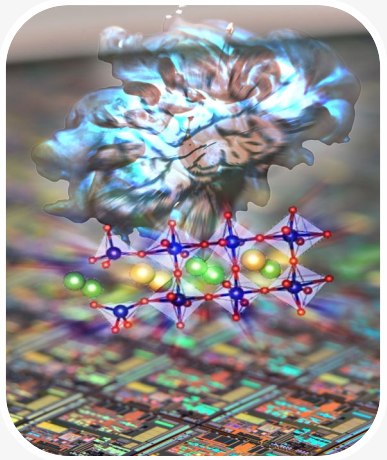
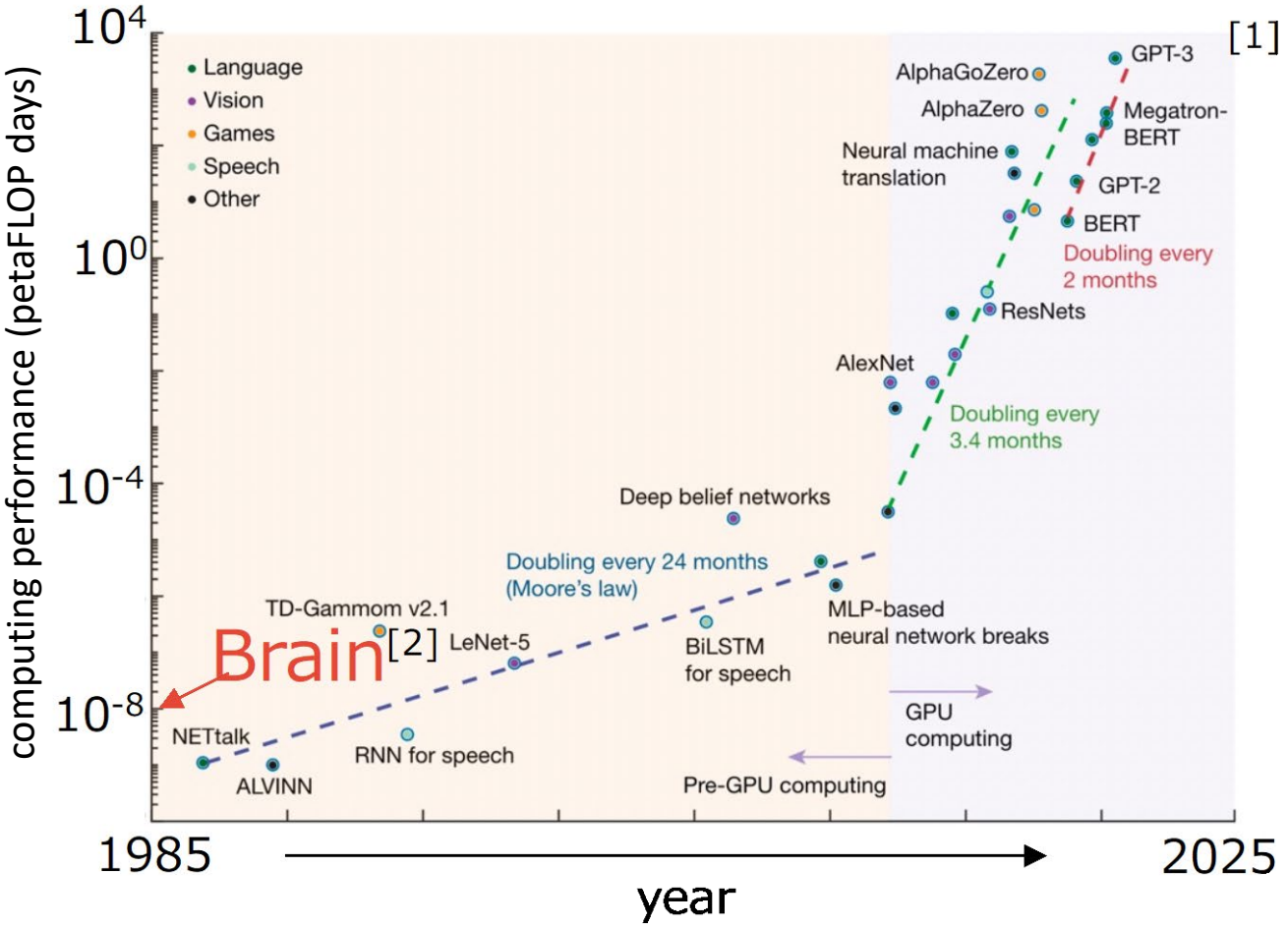


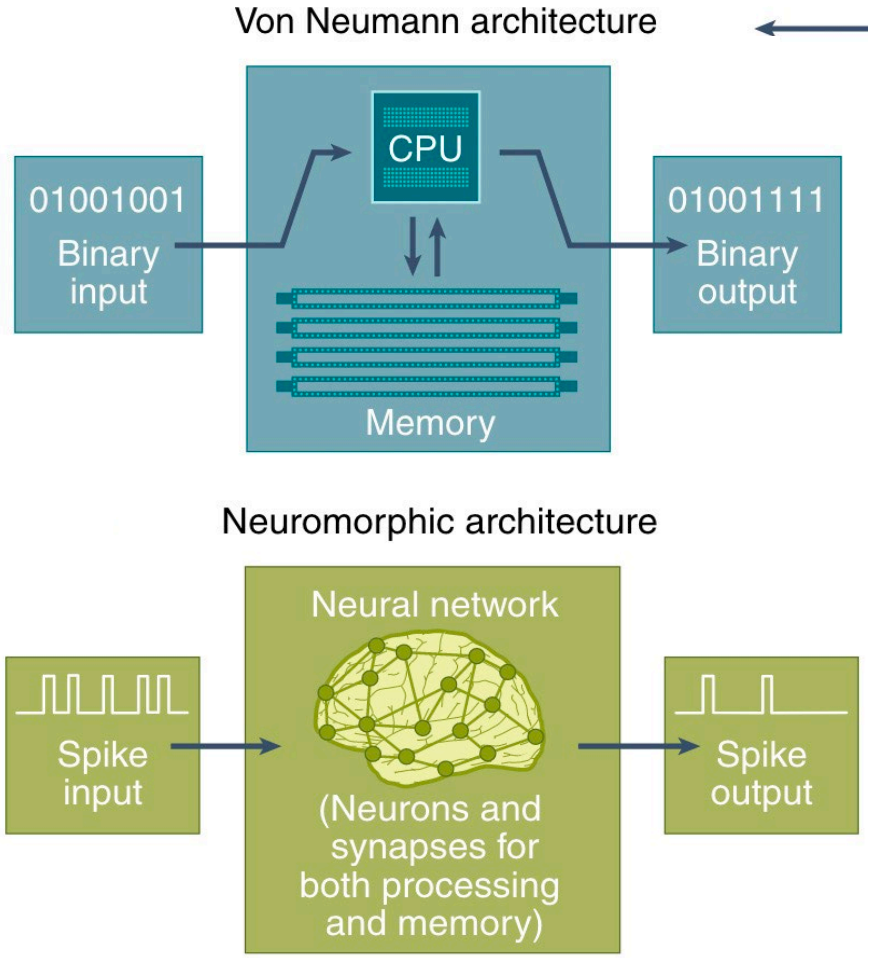
Which systems are suitable for energy-efficient **neuromorphic platforms** and **low power electronics** ?

Energy consumption in the digital era

The challenge: energy cost



Saving energy at the hardware level

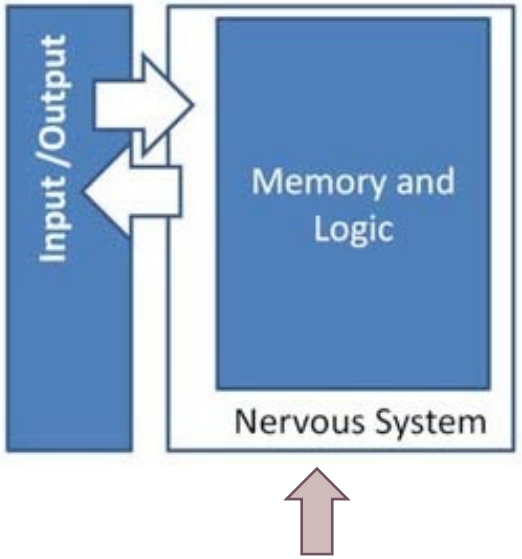


[1] A. Mehonic & A. J. Kenyon, *Nature*, 604, 255-260 (2022)
[2] P. A. Merolla et al., *Science*, 345, 668-673 (2014)

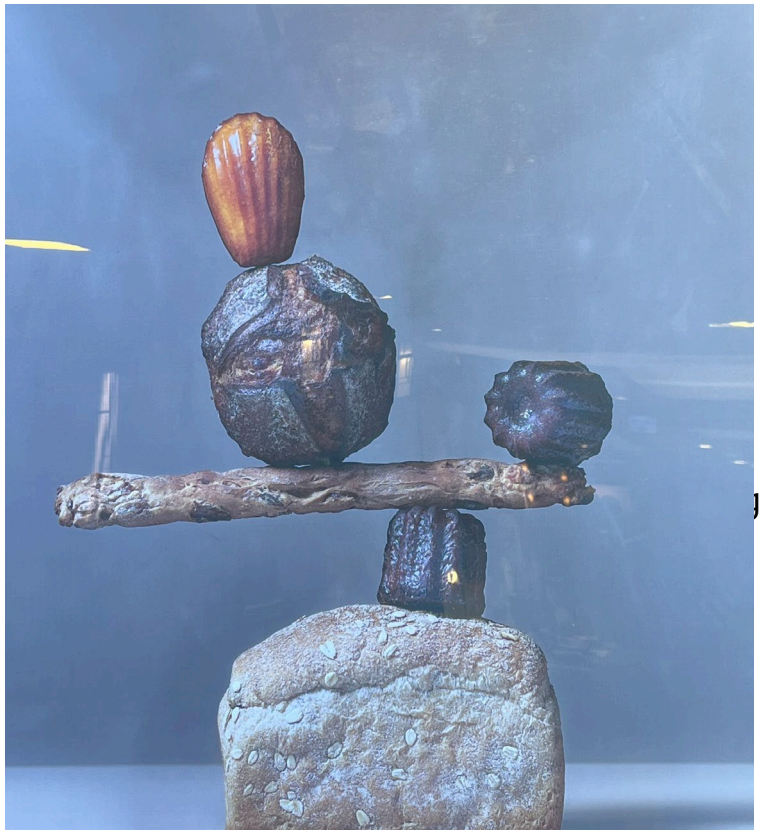
C. D. Schuman et al., *Nat. Comput. Sci.* 2, 10-19, 2022

Search for candidate materials for energy-efficient neuromorphic devices

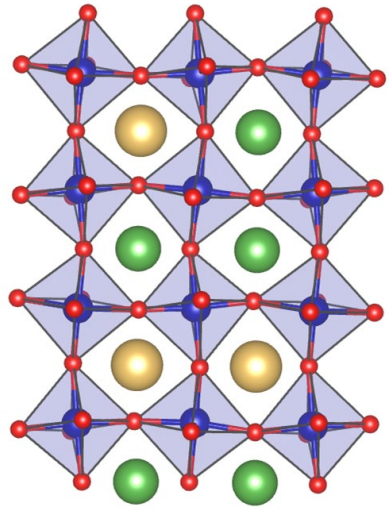
Brain-inspired



Materials with energy-efficient resistive switching behavior



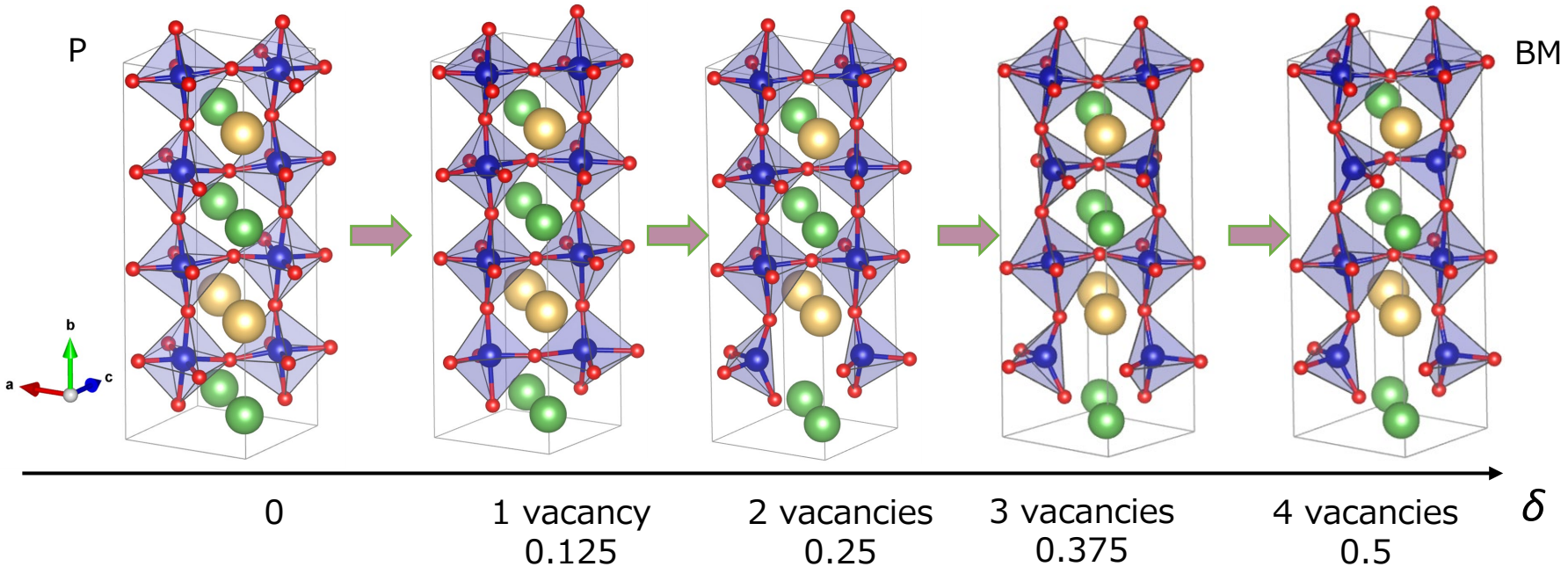
Our focus:
$La_{1-x}Sr_xCoO_3$ (LSCO)



10^4 change in resistivity with T, P, Sr doping and strain

Metal-insulator transition (MIT) to realize resistive switching

Understanding the metal-to-insulator transition as a function of defect content using DFT calculations



- Sampled defect positions and different magnetic states

We identified the structural transition path from two different crystal structures—a metal and an insulator— and the associated structural deformations

S. Zhang and G. Galli, npj Comput. Mater. **6**, 170 (2020)

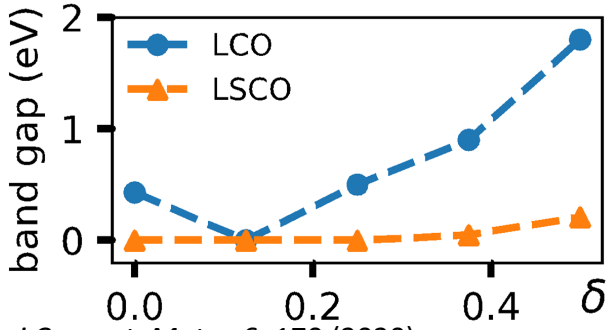
A detailed physical characterization of the system, including predictions

- **Characterized the transformation** as a function of defect concentration, and the distinctive magnetic and electronic properties of each phase.

- Developed a **model**, based on first principles, to predict the **electrical bias** required to drive the MIT.

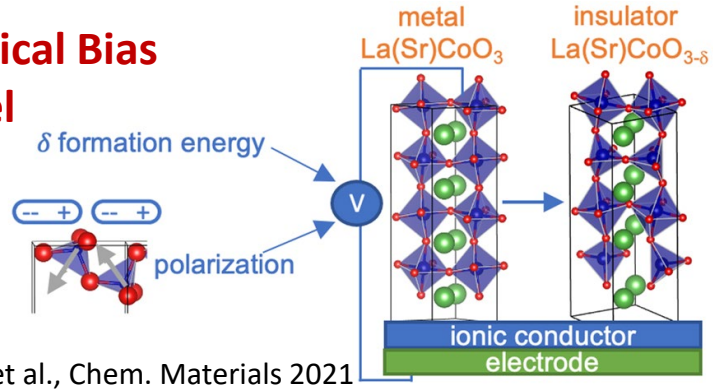
- Provided a robust **protocol to determine the defect concentration**.

Electronic and magnetic properties



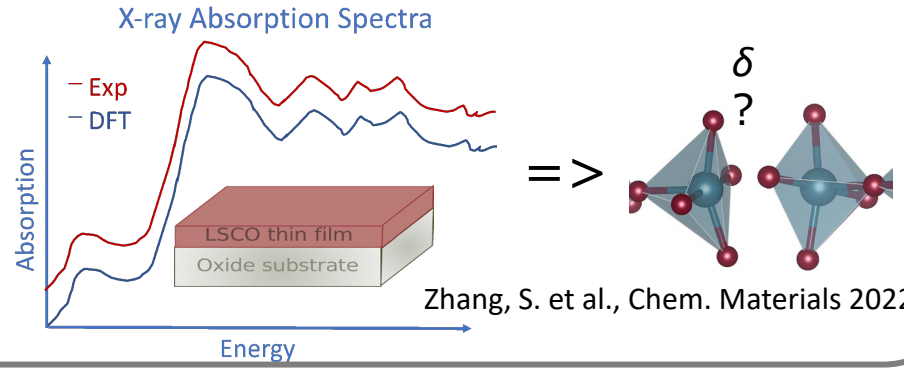
Zhang, S. & Galli, G. *npj Comput. Mater.* 6, 170 (2020).

Electrical Bias Model



Zhang, S. et al., Chem. Materials 2021

Protocol to determine oxygen stoichiometry



Zhang, S. et al., Chem. Materials 2022

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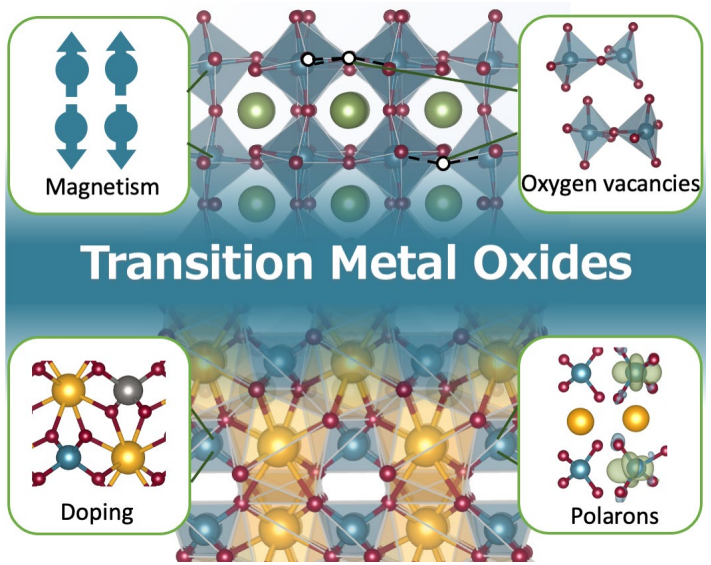
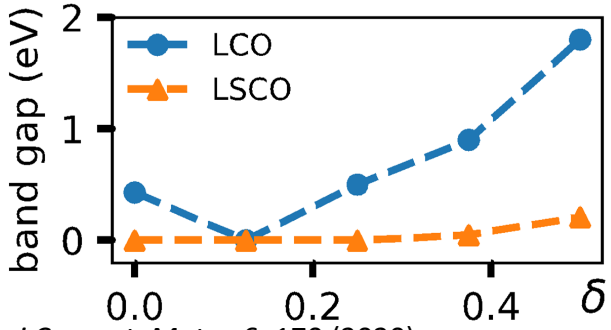


Key insight into the properties of materials with energy-efficient resistive switching for neuromorphic architectures. Several predictions verified experimentally.

Electronic and magnetic properties



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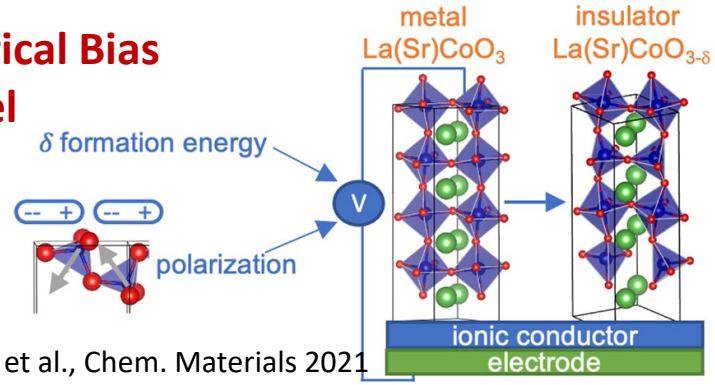

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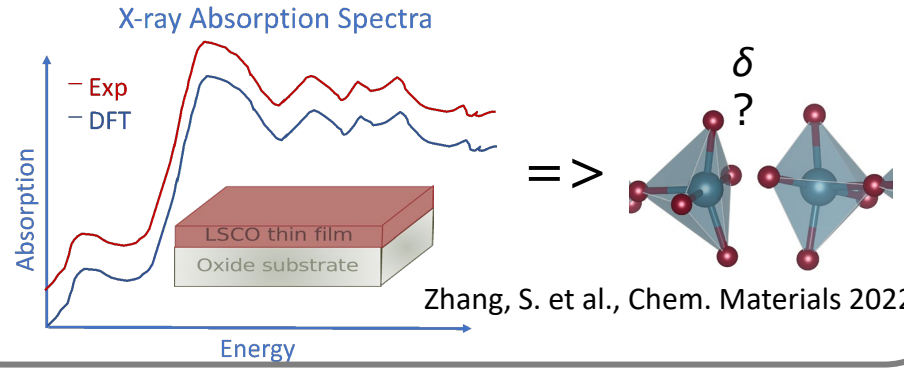


Zhang, S. et al., Chem. Materials 2022

Quantum simulations are expensive

- Algorithmic and code development are challenging
  - Software development and sustainability are ‘expensive’ and of paramount importance
  - Training is not at the level of many other disciplines
  - Acceptance as first-class scientific endeavors & as *key instrumentation* still in the making

- Hardware is a moving target
  - Availability
  - Cost
  - Rate of change
  - Hybrid architectures

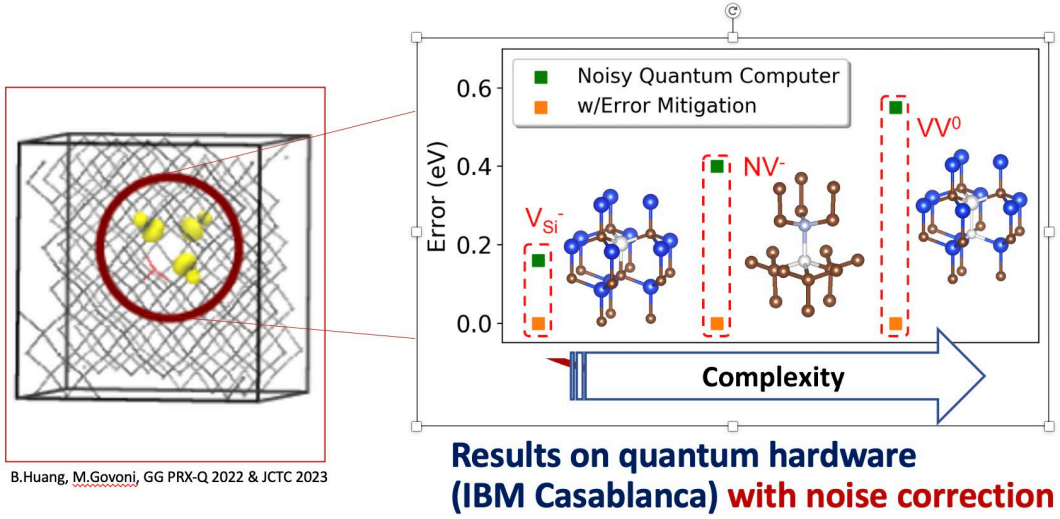
Computers are boring, they only give answers, Pablo Picasso
We've tended to forget that no computer will ever ask a new question, Grace Hopper

Scalability and quantum computing

- Interesting promises, e.g. for quantum chemistry problems (beating the exponential ‘wall’ might be possible but it is not the only exciting goal)

- The community is still working with NISQ architectures (noisy intermediate-scale quantum computers) which requires noise resilient algorithms

- There are not yet physics or chemistry problems solved entirely on a quantum computer



B.Huang, M.Govoni, GG PRX-Q 2022 & JCTC 2023

Results on quantum hardware (IBM Casablanca) with noise correction

Concluding remarks

- Computational chemistry/physics and materials science are on an exciting upward trajectory and will play an increasingly critical role in solving material energy problems

- Integration and coupling with experiments is not a given; it is happening, but it requires new strategies for maximum impact

- Software and hardware integrated planning is of paramount important

- The excitement in AI and new computing platforms (e.g. quantum computing) is justified, but, as usual, not giving in to the hype is a good thing; academic AI/ML projects require careful consideration on *connection* between academia & industry

The most dangerous phrase in the language is, 'We've always done it this way, Grace Hopper

Innovation and inventing the future

Acknowledgements

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Senior Collaborators: Marco Govoni (Modena, Italy); @UoC & ANL: David Awschalom, Supratik Guha, Alex High, Hannes Bernien, Peter Mauer, Laura Gagliardi, Aash Clerk & Danna Friedman (MIT), Joel Davidsson (Linkoping U., Sweden), Shun Kanai and Hideo Ohno (Tohoku Univ.)

Thank you for your attention!

It is a real honor for me to be here