

MOSAIC
Materials Optimization and Simulation
by Ab Initio Computation



Computational modeling of (photo)electrocatalytic materials and interfaces

Ismaila Dabo

Department of Materials Science and Engineering &
Department of Physics · Pennsylvania State University

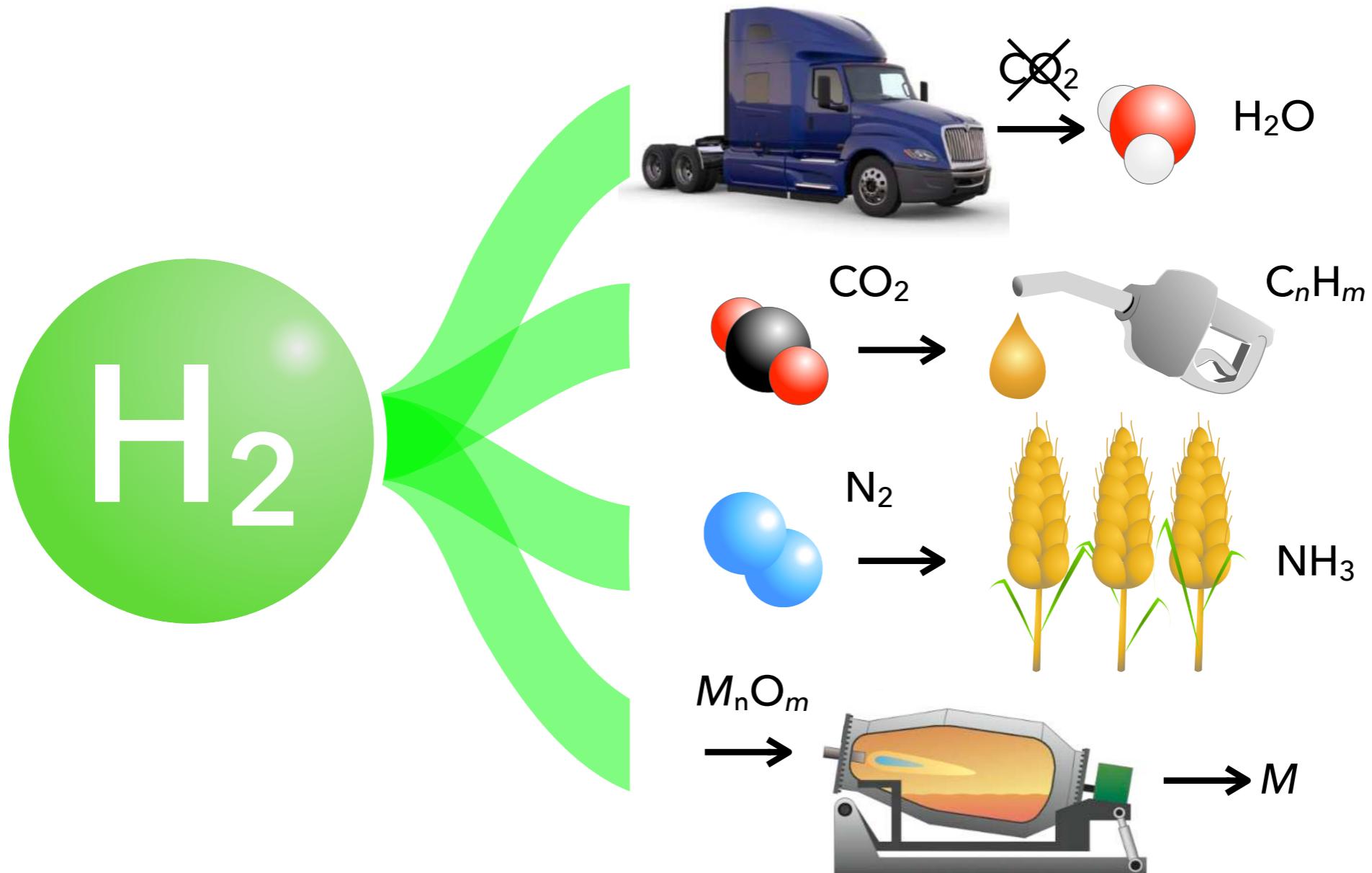
Chemistry in Solution and at Interfaces (CSI) Workshop: Deep Modeling for Molecular Simulation
Princeton University · June 26, 2024



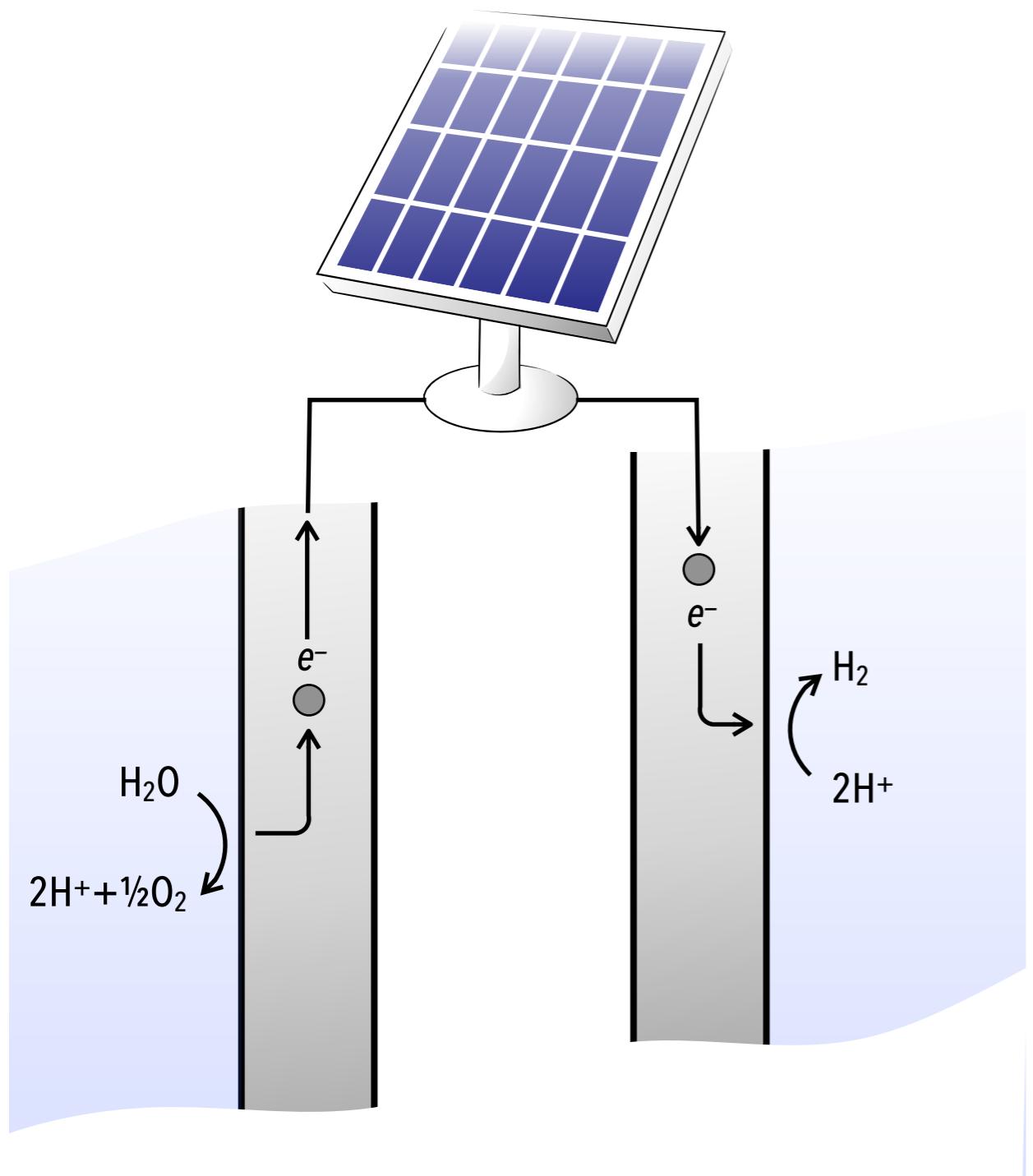
HydroGEN
Advanced Water Splitting Materials



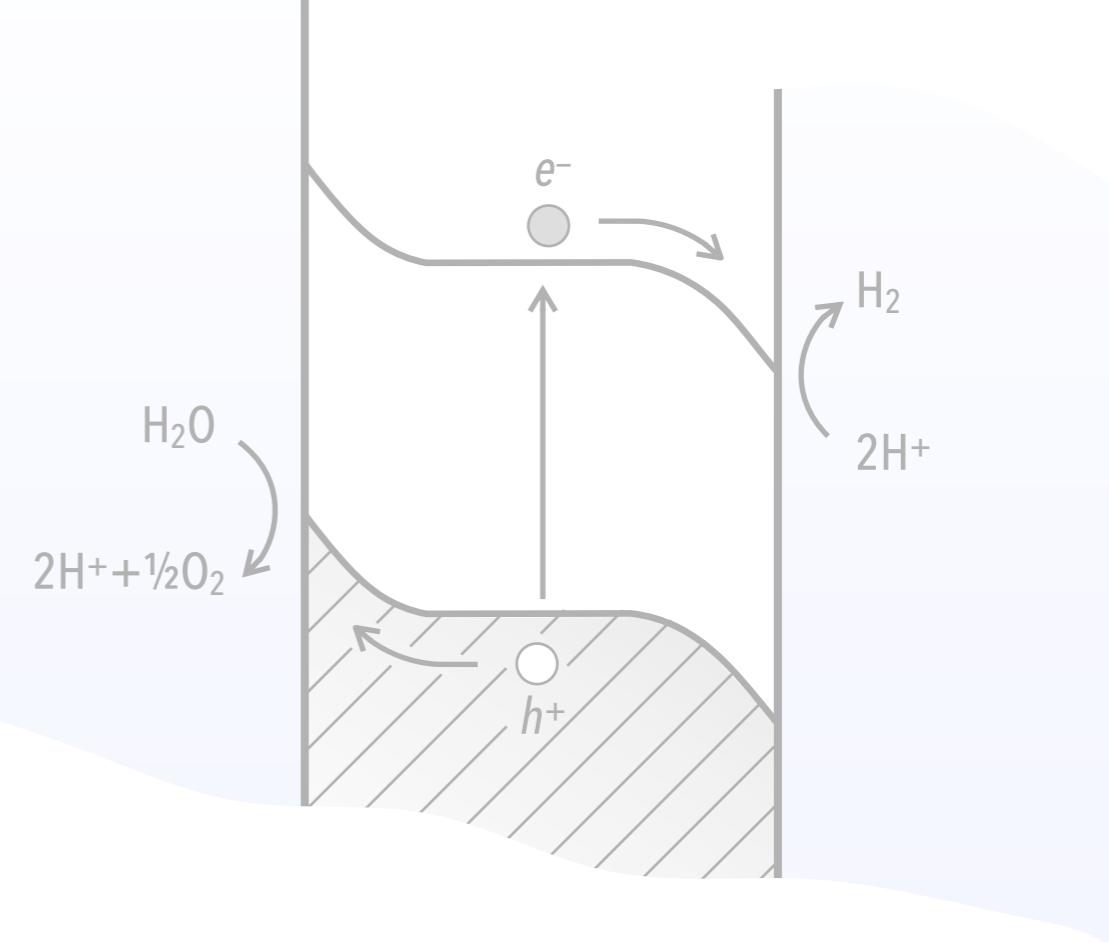
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Why H_2 ? How?

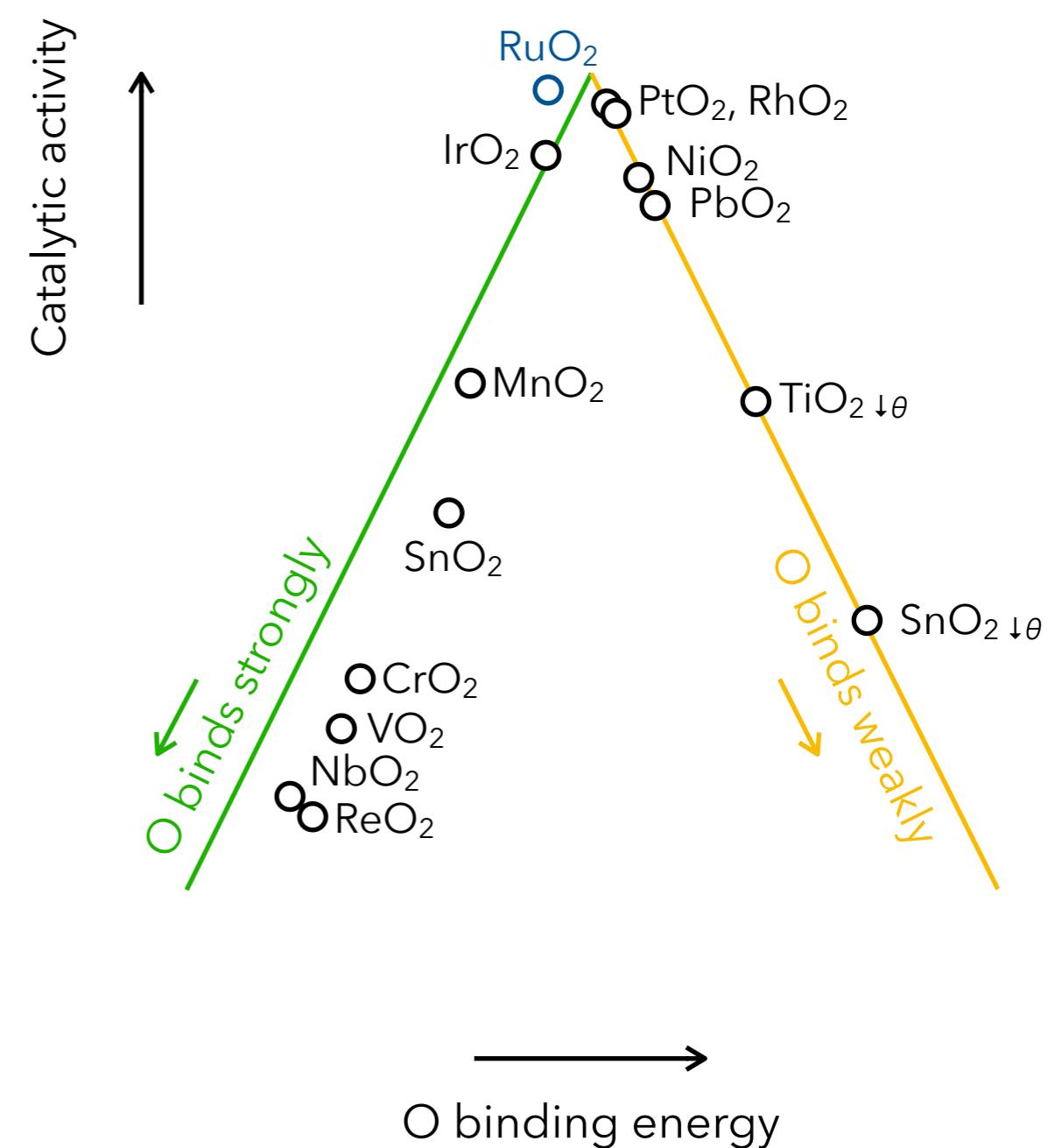
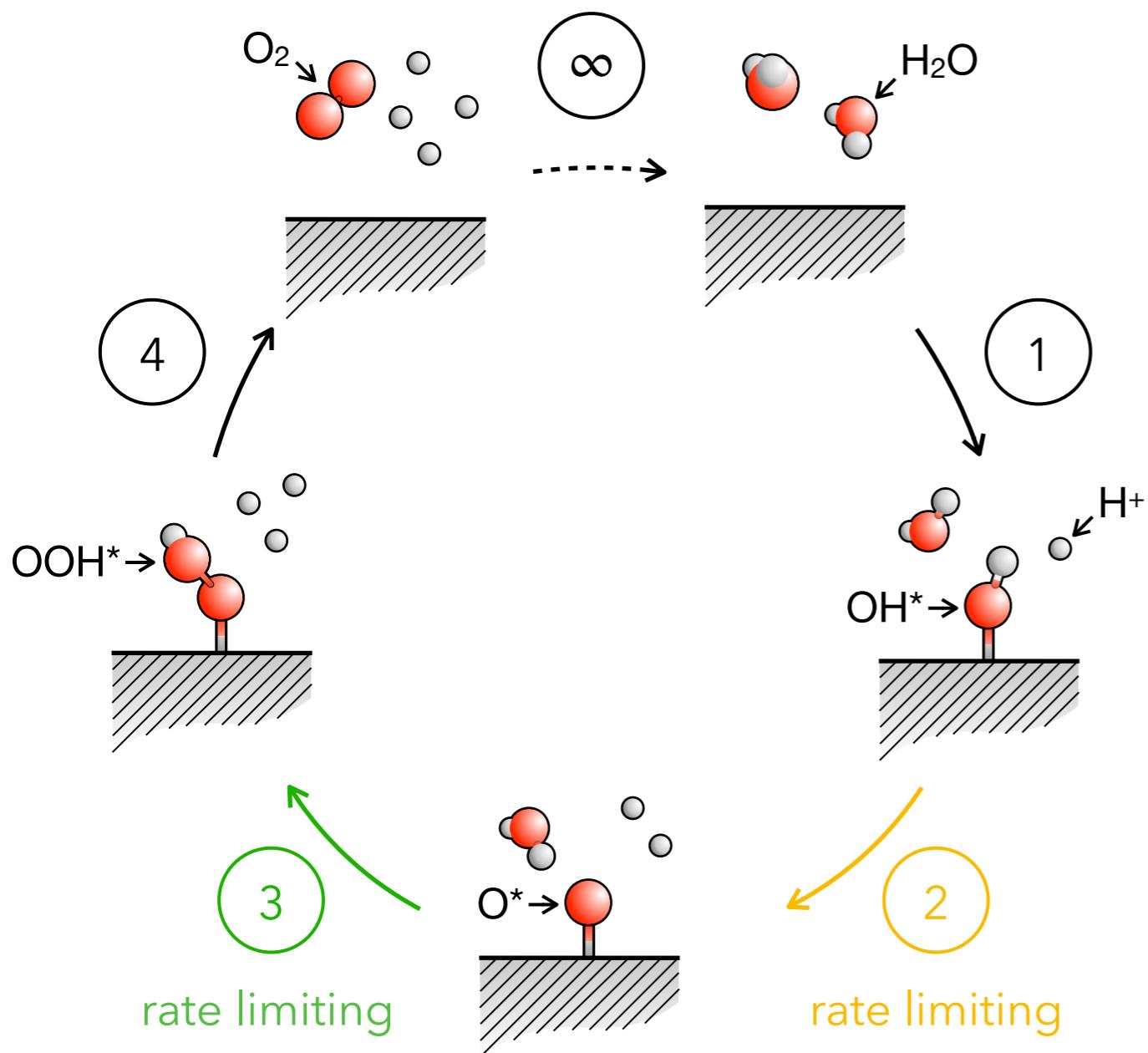


Solar-powered electrolysis

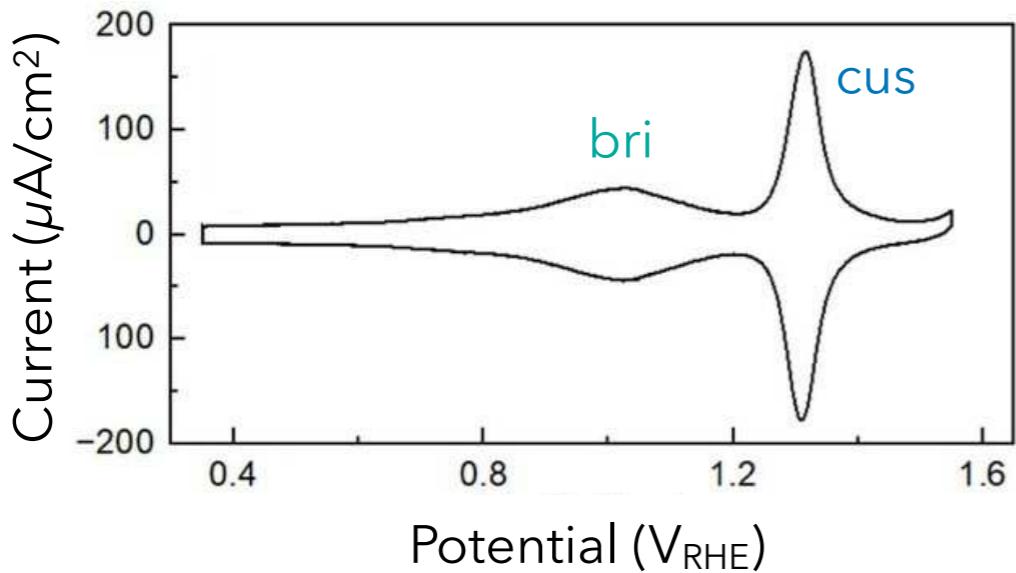


Photoelectrolysis

Catalysts for the oxygen evolution reaction



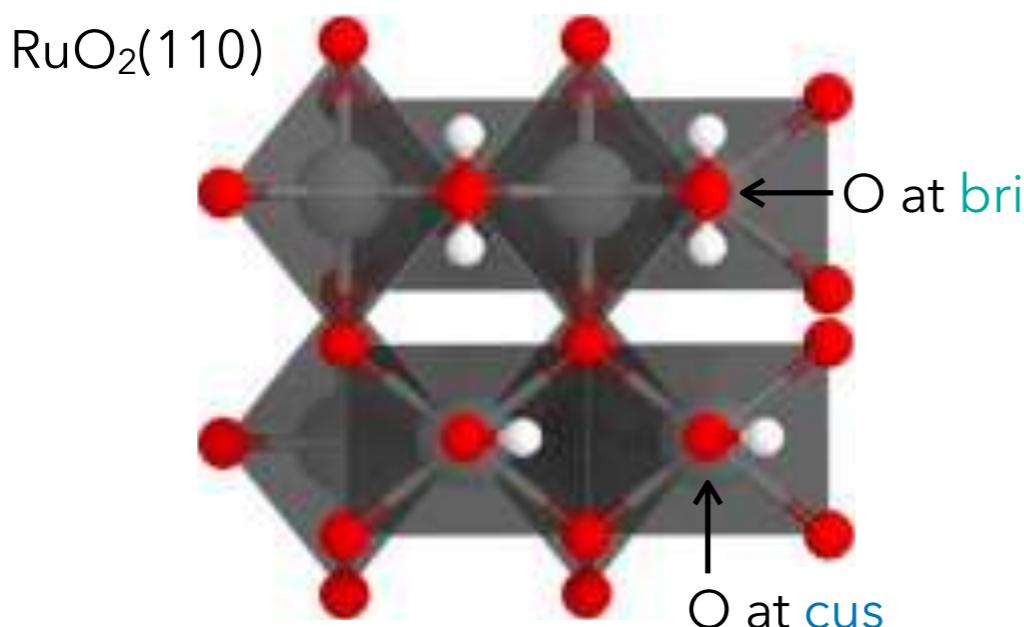
Cyclic voltammetry of deposited RuO₂ catalysts



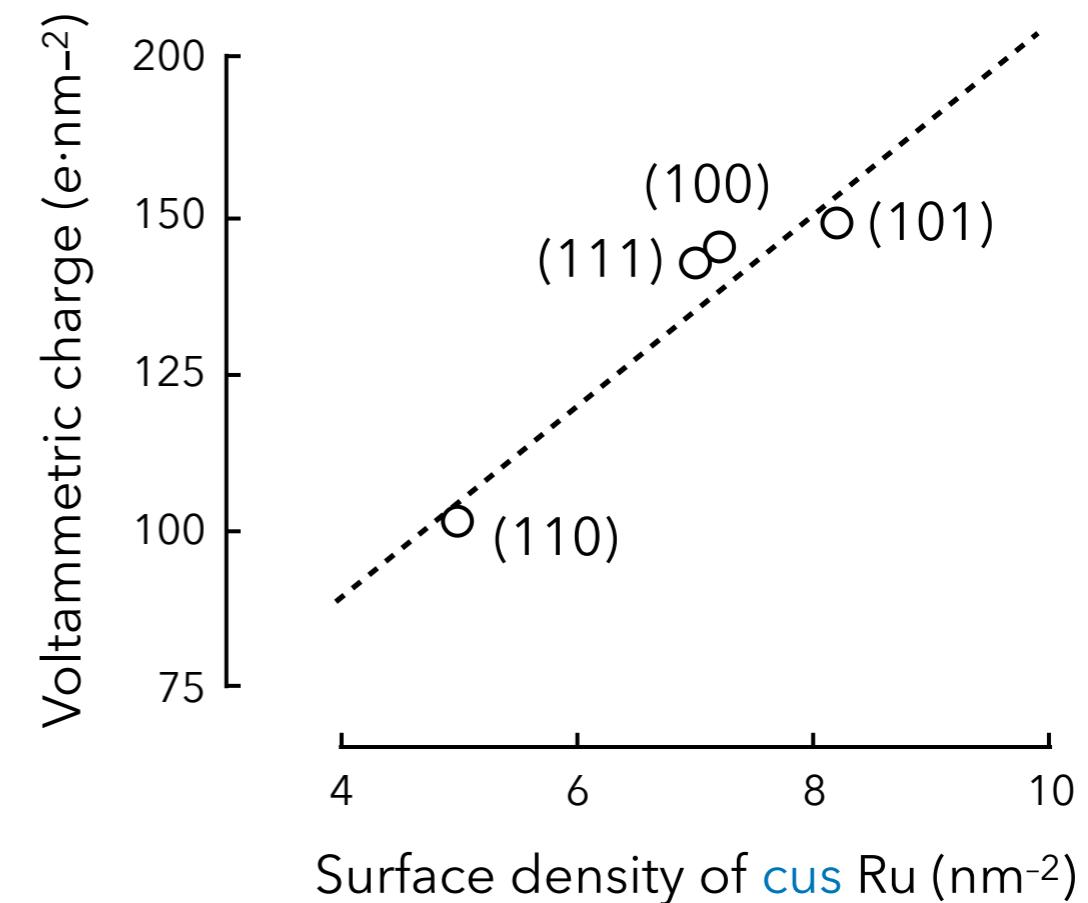
Jin Suntivitch



Darrell Schlom



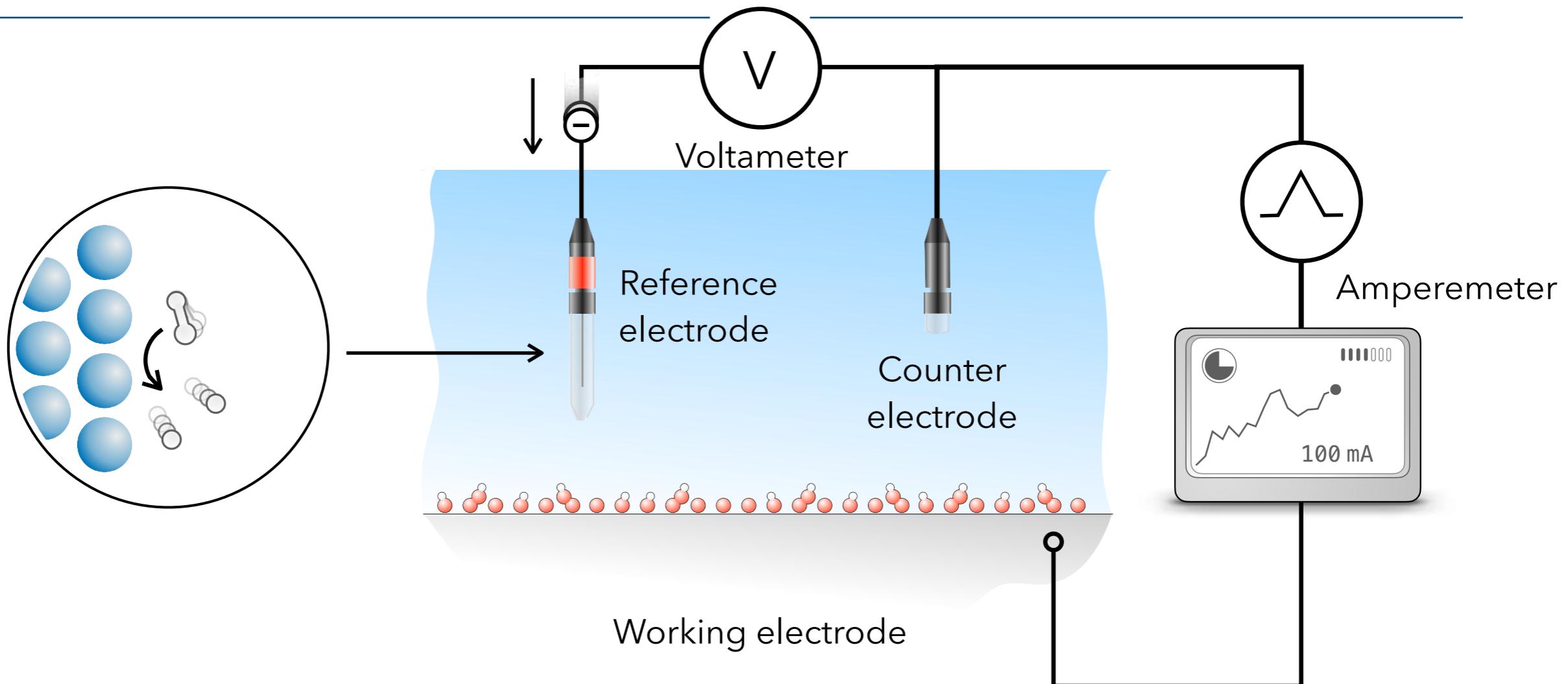
bri: bridge
cus: coordinatively unsaturated



Stoerzinger, Shao-Horn *et al.*, ACS energy Letters 2, 876-881 (2017)

Which processes occur at the **cus** sites?

Basis of the model: the computational hydrogen electrode

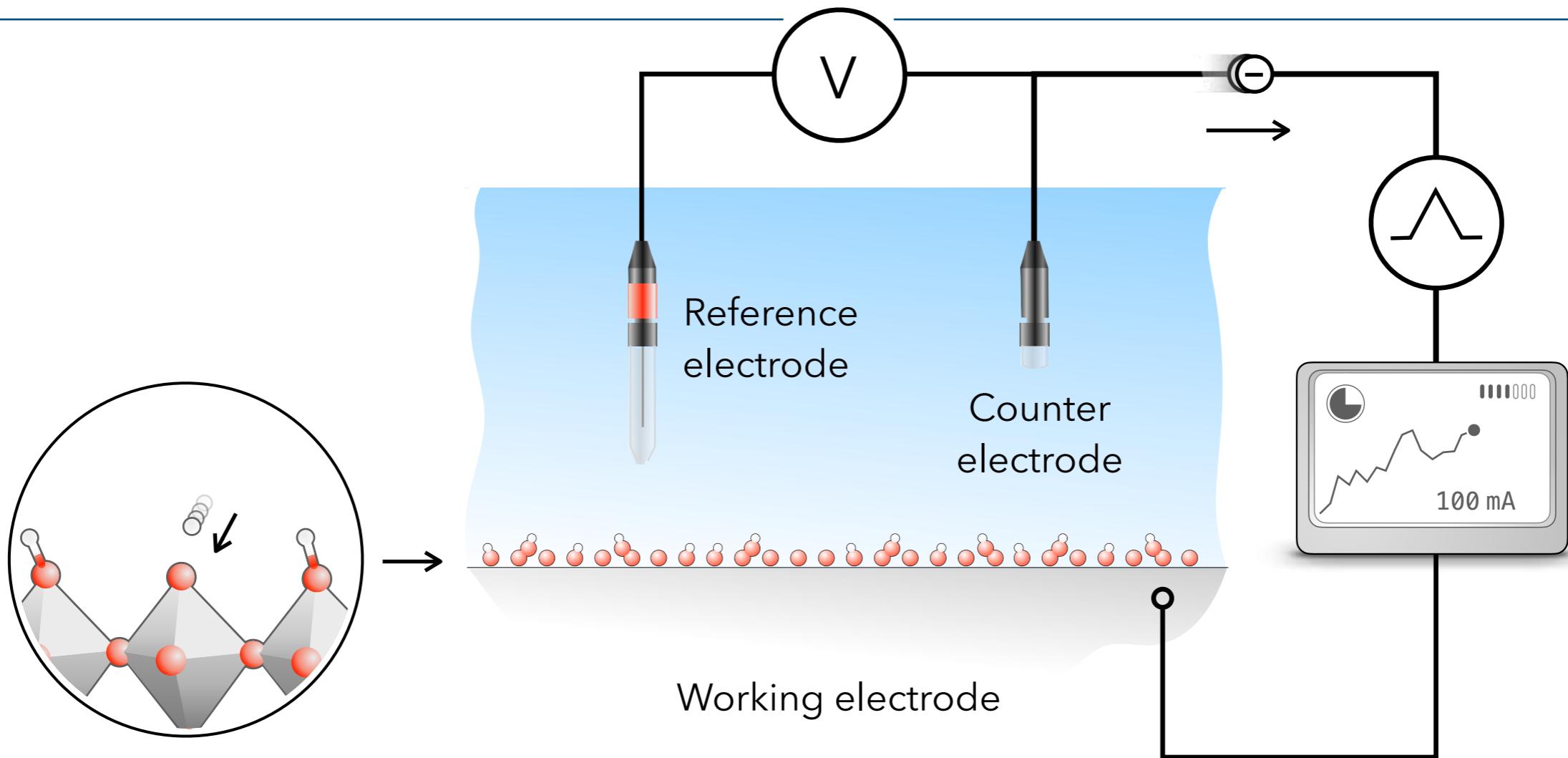


Reversible hydrogen electrode: $0 = \mu(\text{H}^+) - \frac{1}{2}\mu(\text{H}_2) - e(\Phi_{\text{RE}} - \Phi_{\text{CE}})$

↑ computationally demanding

$W_{\text{CE} \rightarrow \text{RE}}$

Basis of the model: the computational hydrogen electrode



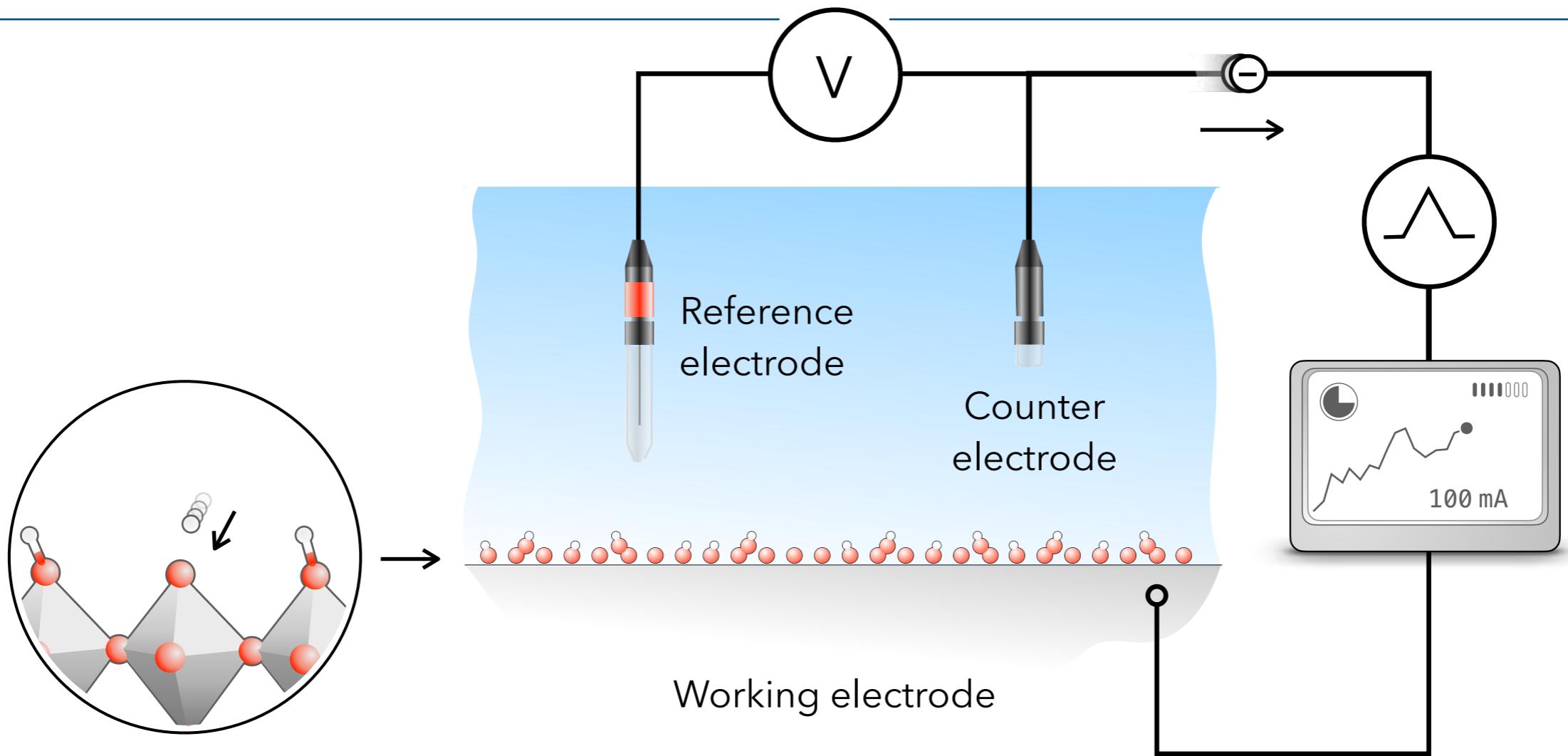
Reversible hydrogen electrode: $0 = \mu(\text{H}^+) - \frac{1}{2}\mu(\text{H}_2) - e(\Phi_{\text{RE}} - \Phi_{\text{CE}})$

Hydrogen adsorption reaction: $\Delta\mu = \mu(\text{H}^*) - \mu(\text{*}) - \mu(\text{H}^+) - e(\Phi_{\text{WE}} - \Phi_{\text{CE}})$

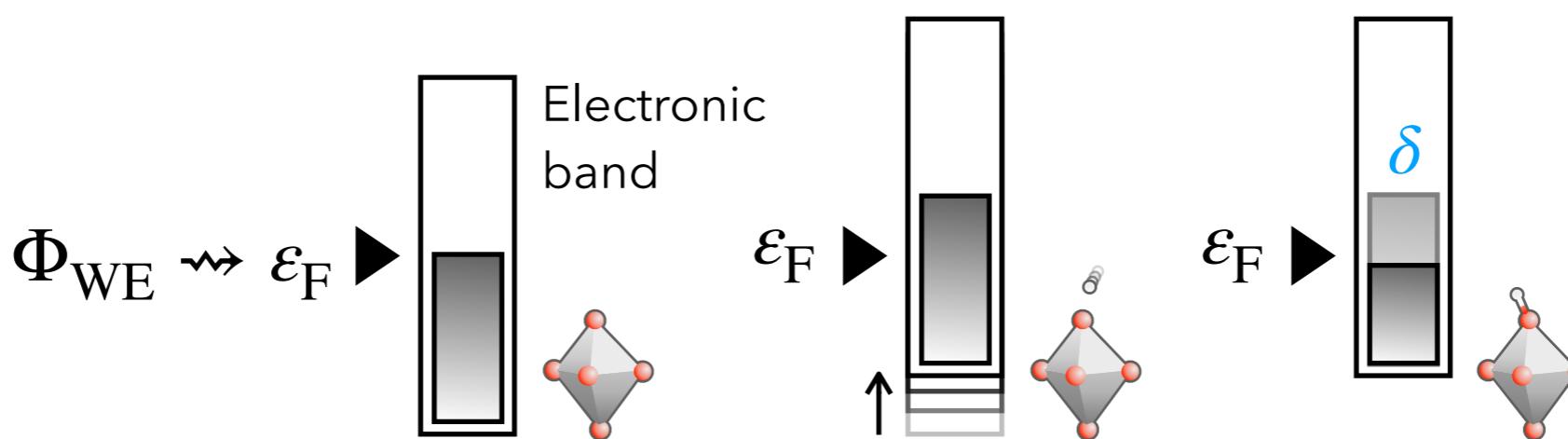
$$\Delta\mu = \mu(\text{H}^*) - \mu(\text{*}) - \frac{1}{2}\mu(\text{H}_2) - e(\Phi_{\text{WE}} - \Phi_{\text{RE}})$$

The working electrode remains neutral ↗

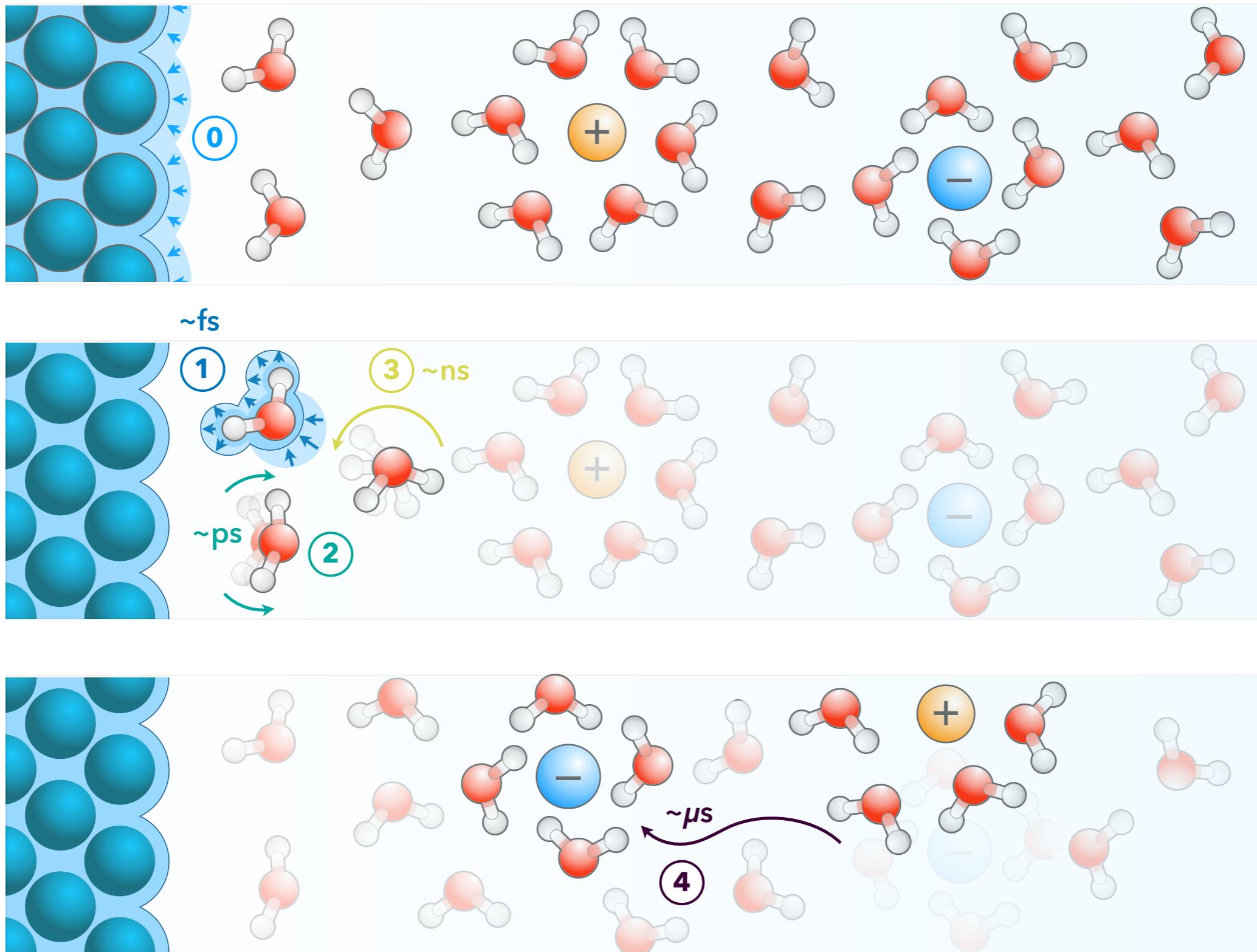
Beyond the computational hydrogen electrode



Under **fixed potential**, the working electrode acquires a charge δ



Characteristic times of dielectric screening at electrochemical interfaces

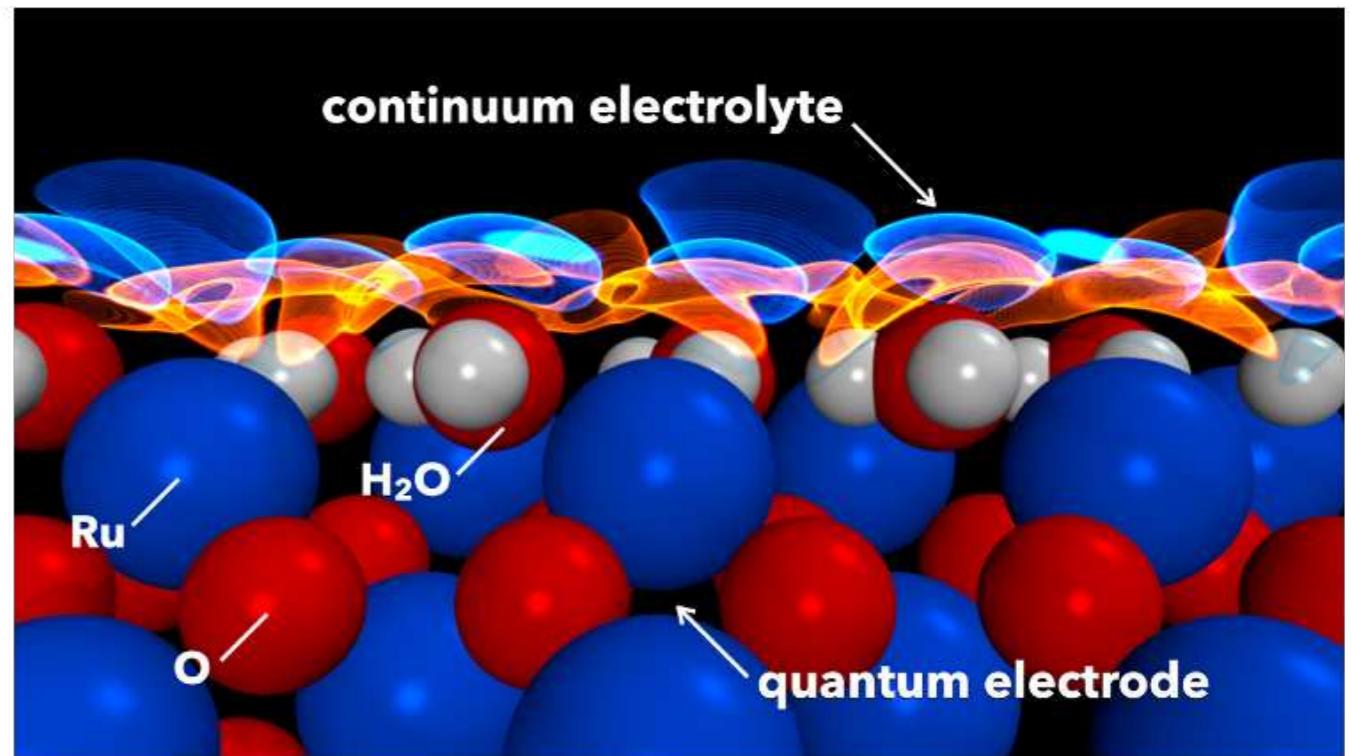


Self-consistent continuum solvation for electrochemical interfaces

$$\mathbf{P}(\mathbf{r}) = \epsilon_0(\epsilon_\rho(\mathbf{r}) - 1)\mathbf{E}(\mathbf{r})$$

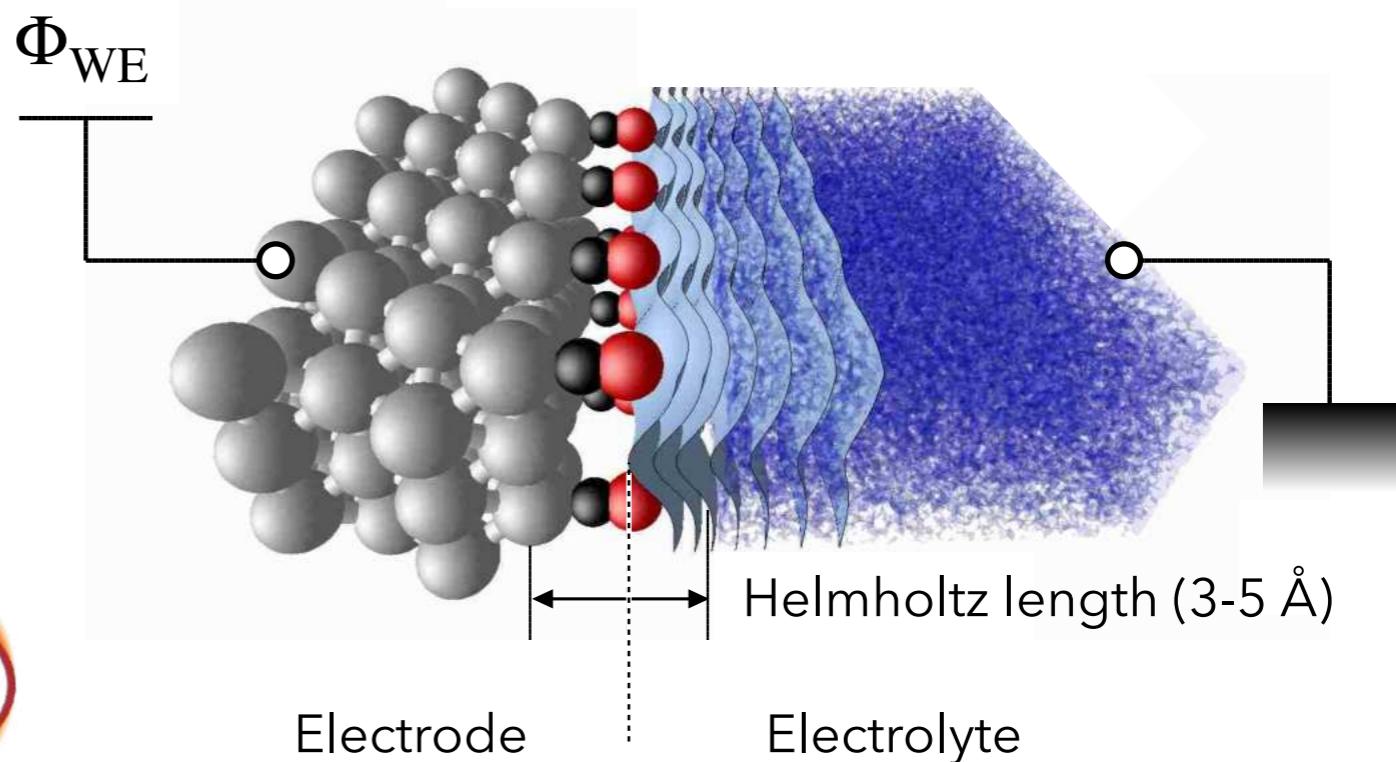
Permittivity from electron density

$$\rho^{\text{pol}}(\mathbf{r}) = -\nabla \cdot \mathbf{P}(\mathbf{r})$$

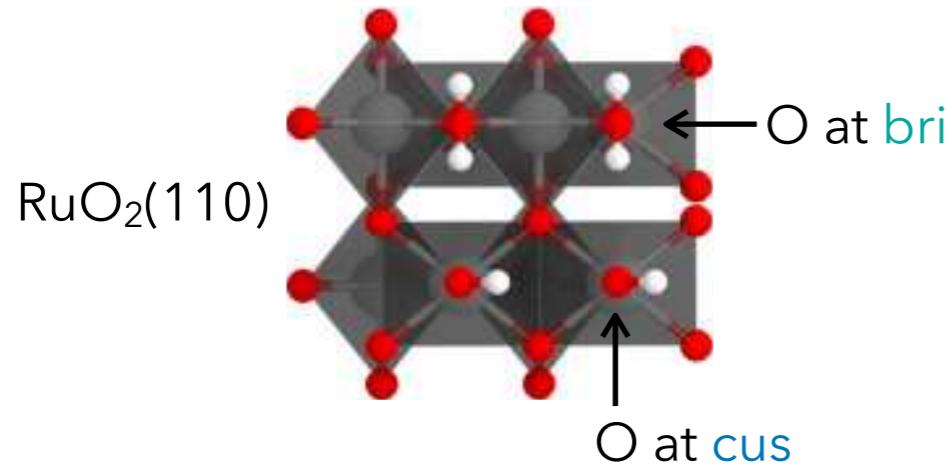


$$\rho^{\text{ion}}(\mathbf{r}) = \varrho_\rho(\mathbf{r}) \exp\left(\mp \frac{ze\varphi(\mathbf{r})}{k_B T}\right)$$

Saturated ion concentration from electron density



Database of energies and potentials for 500+ RuO₂ configurations

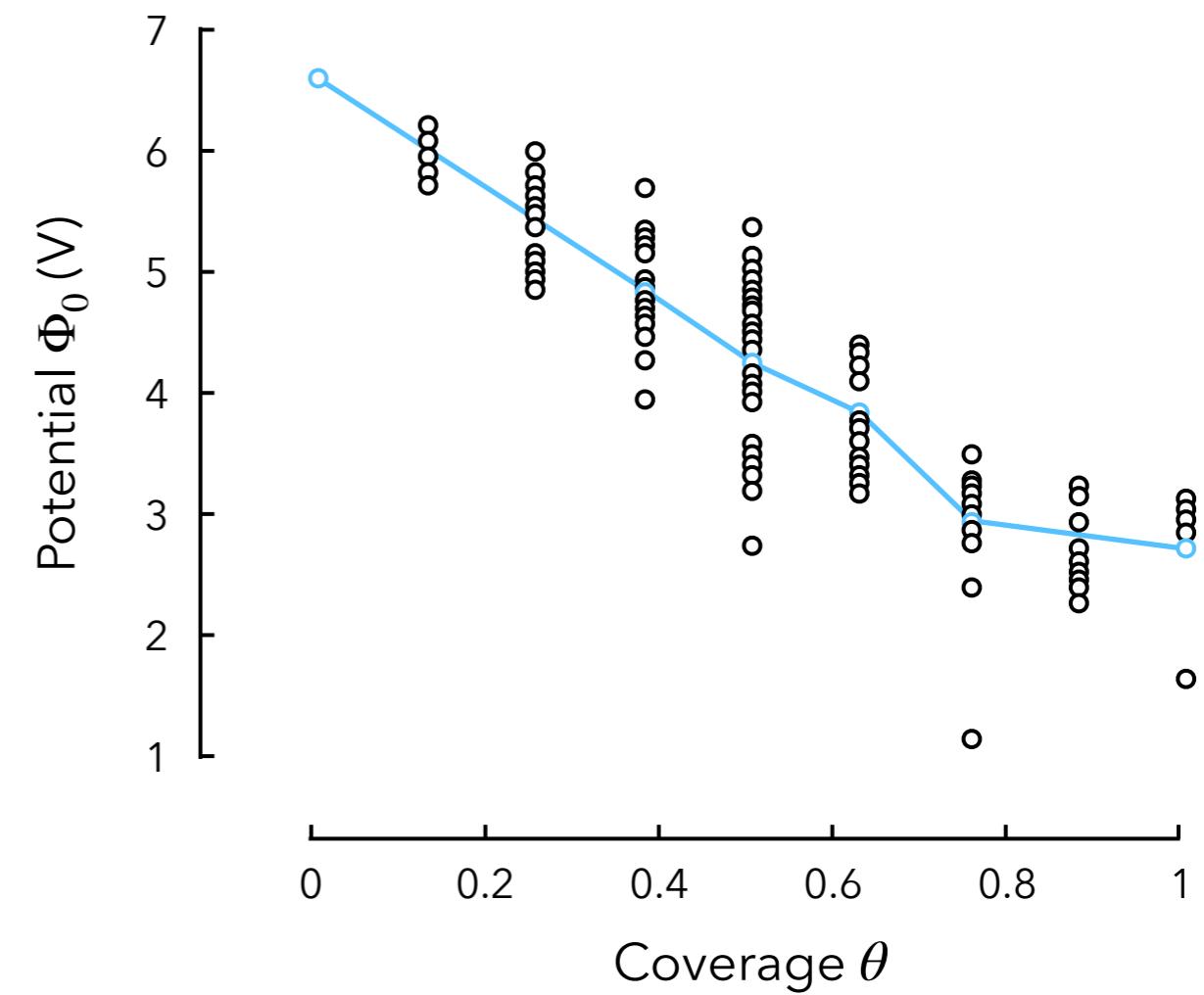
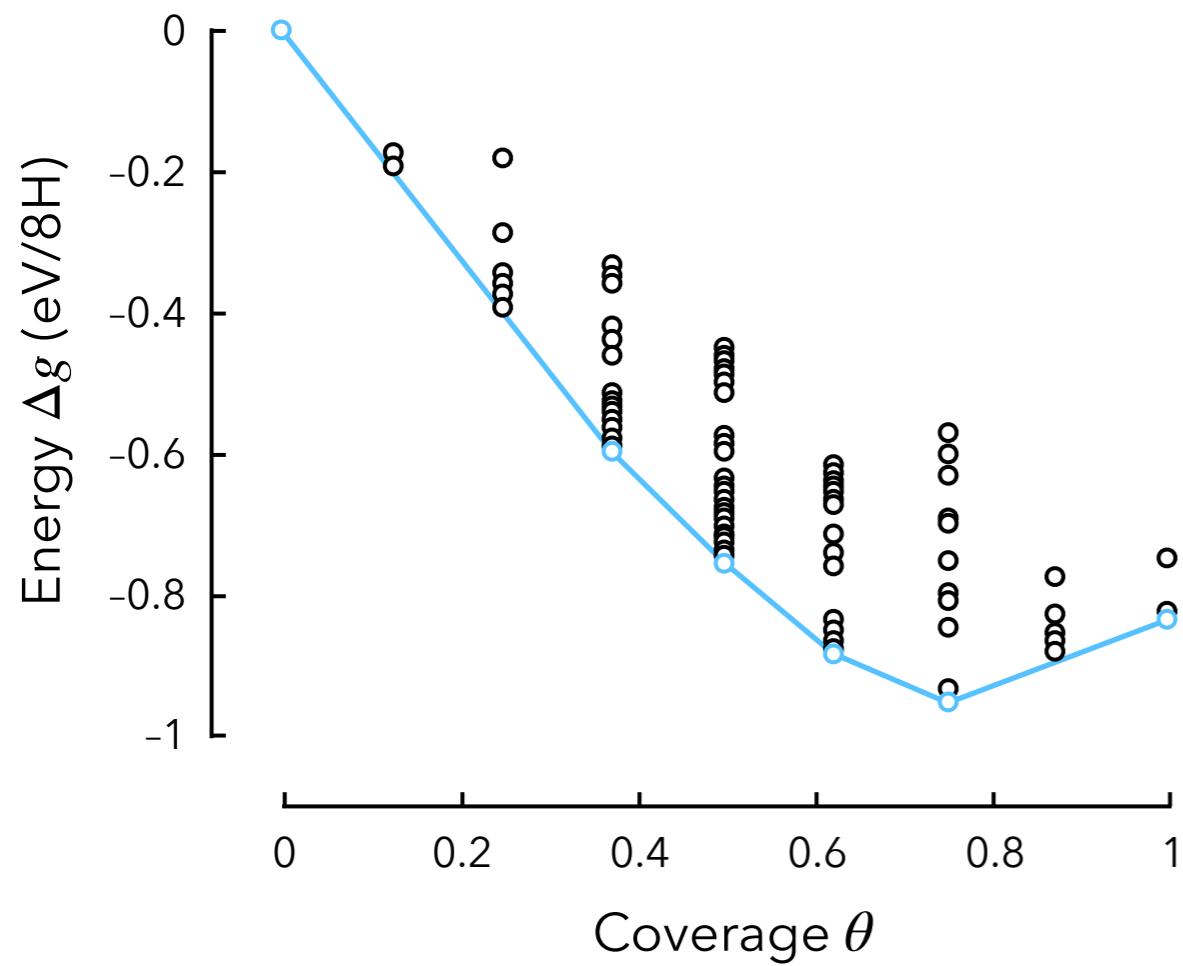


Free energy of zero charge

$$\Delta g = g(\theta) - g(0) - \frac{\theta}{2} \mu(\text{H}_2)$$

$$\delta = \mathcal{C}_0(\Phi_{\text{WE}} - \Phi_0)$$

Potential of zero charge



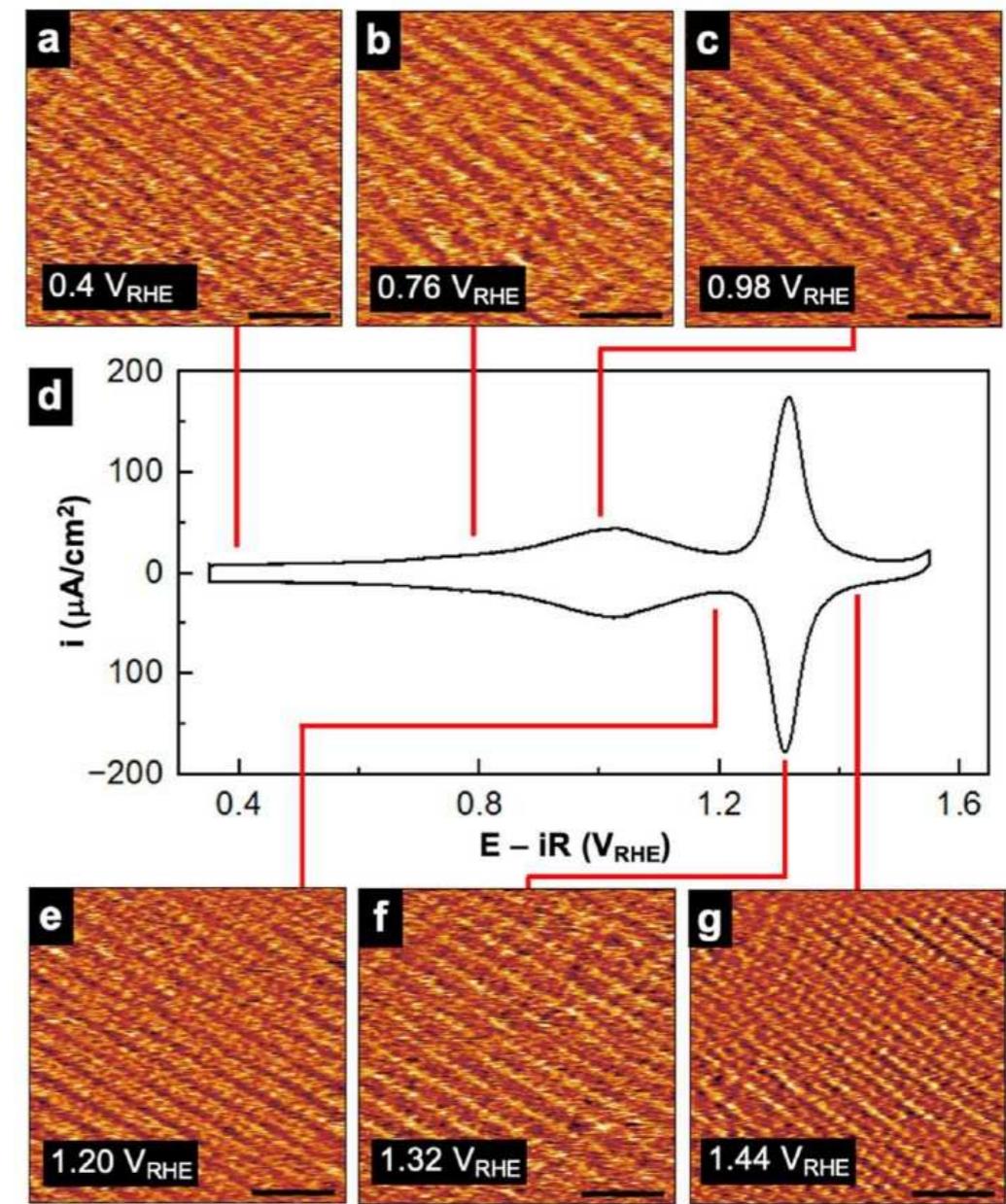
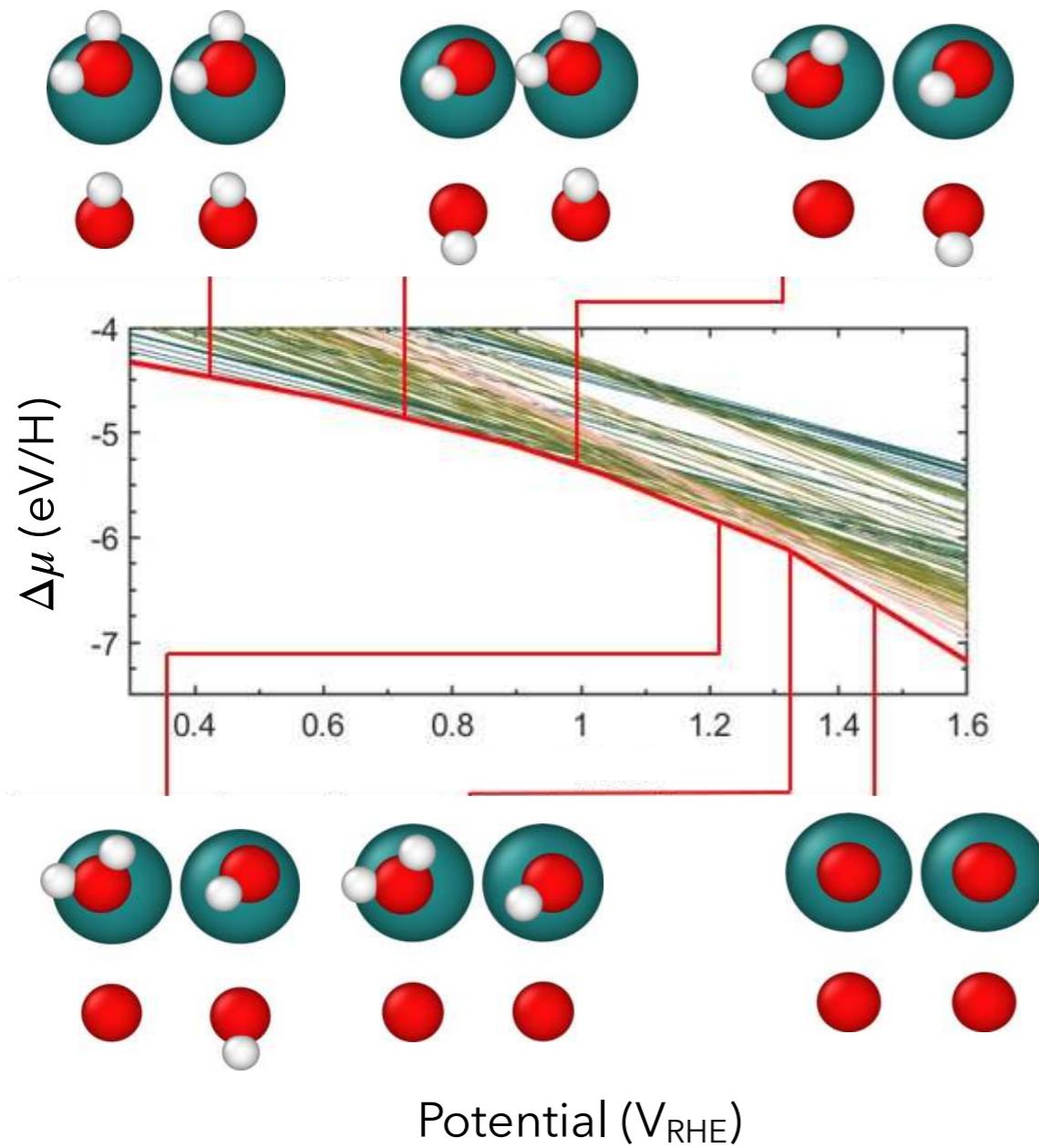
Surface motifs on epitaxially grown RuO₂(110) under applied potential



Maria Maalouf, Simon Gelin

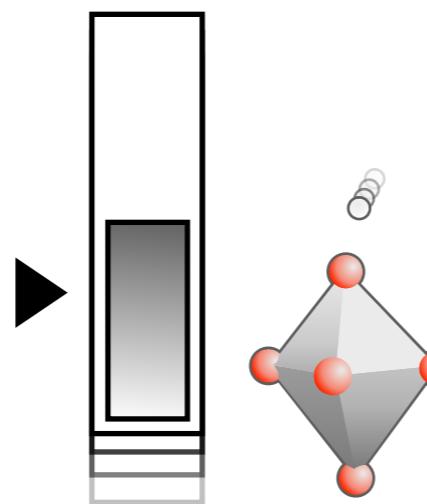


Austin Reese

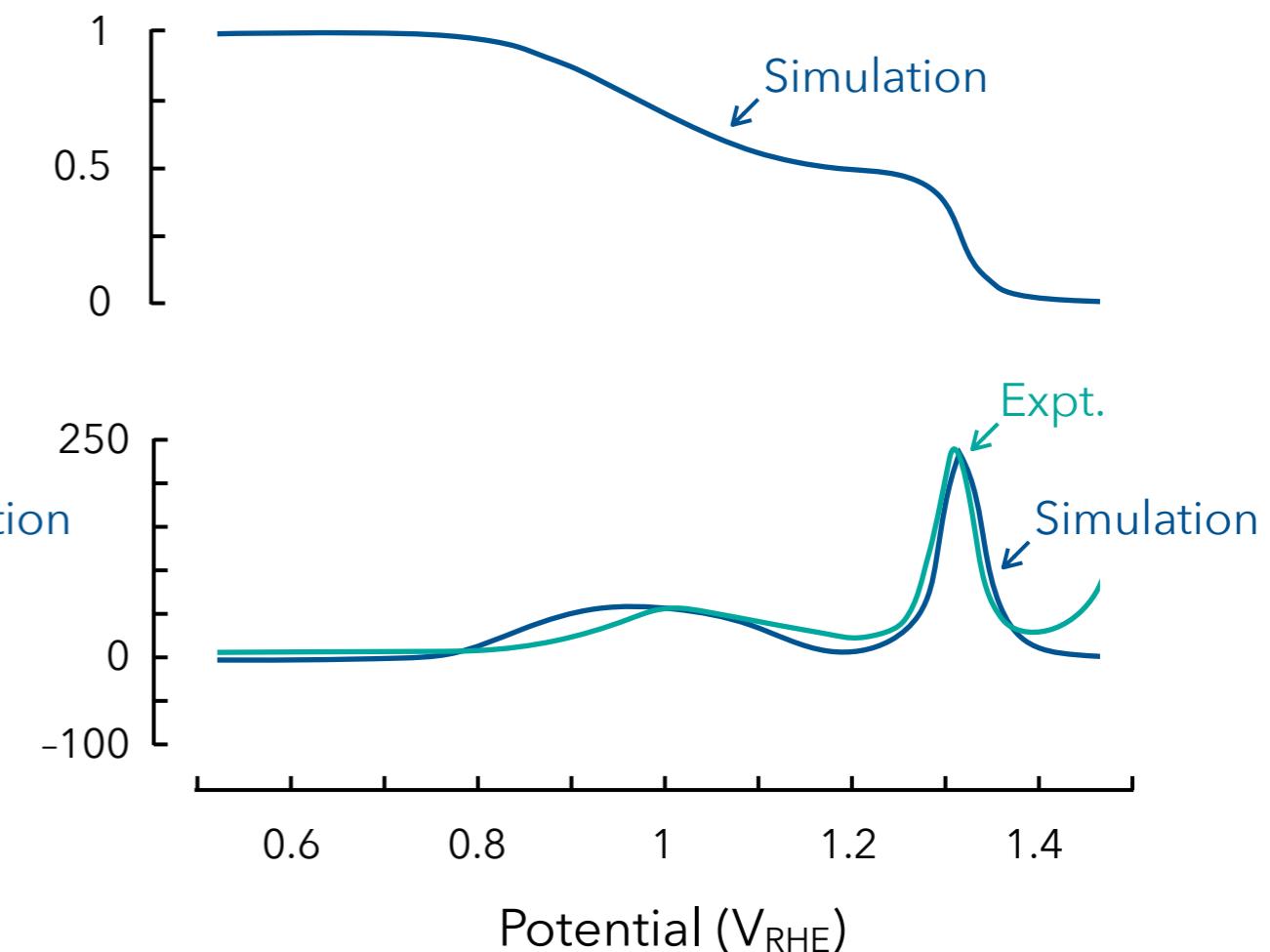
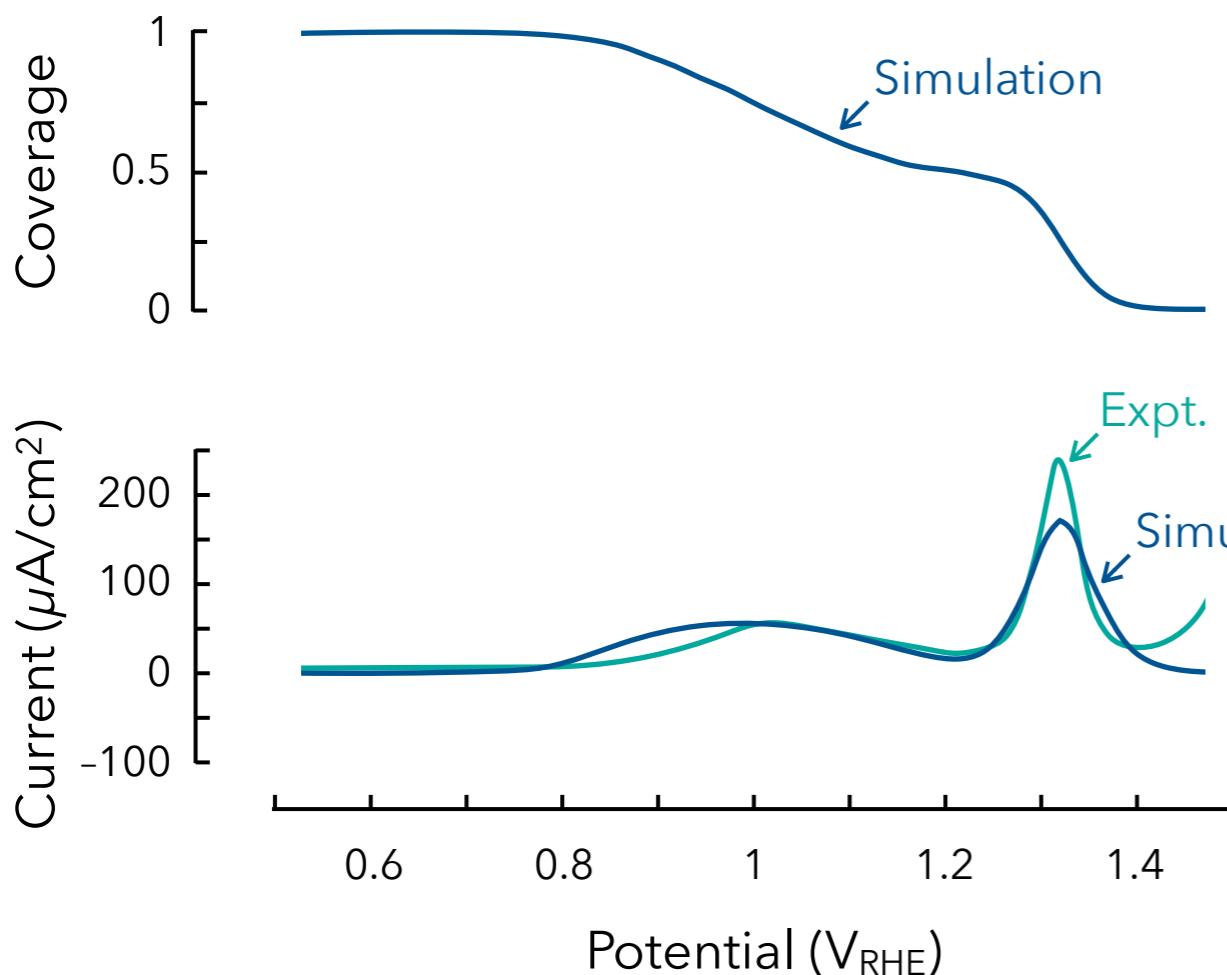
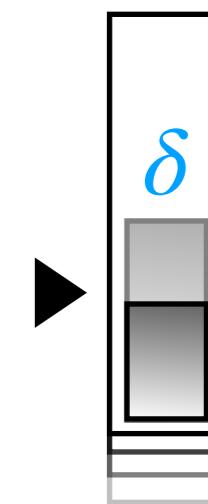


First-principles voltammograms of RuO₂(110) at finite temperature

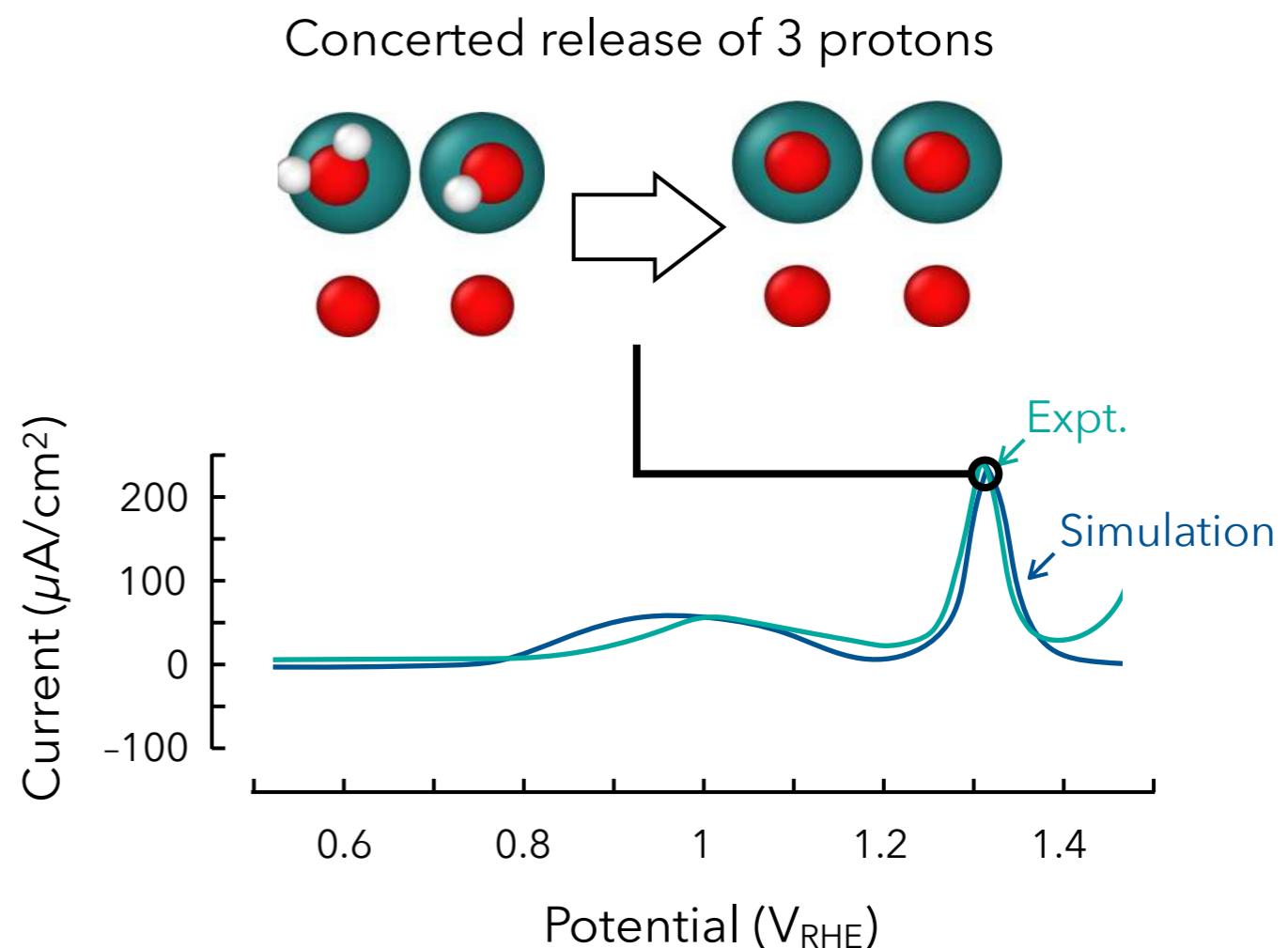
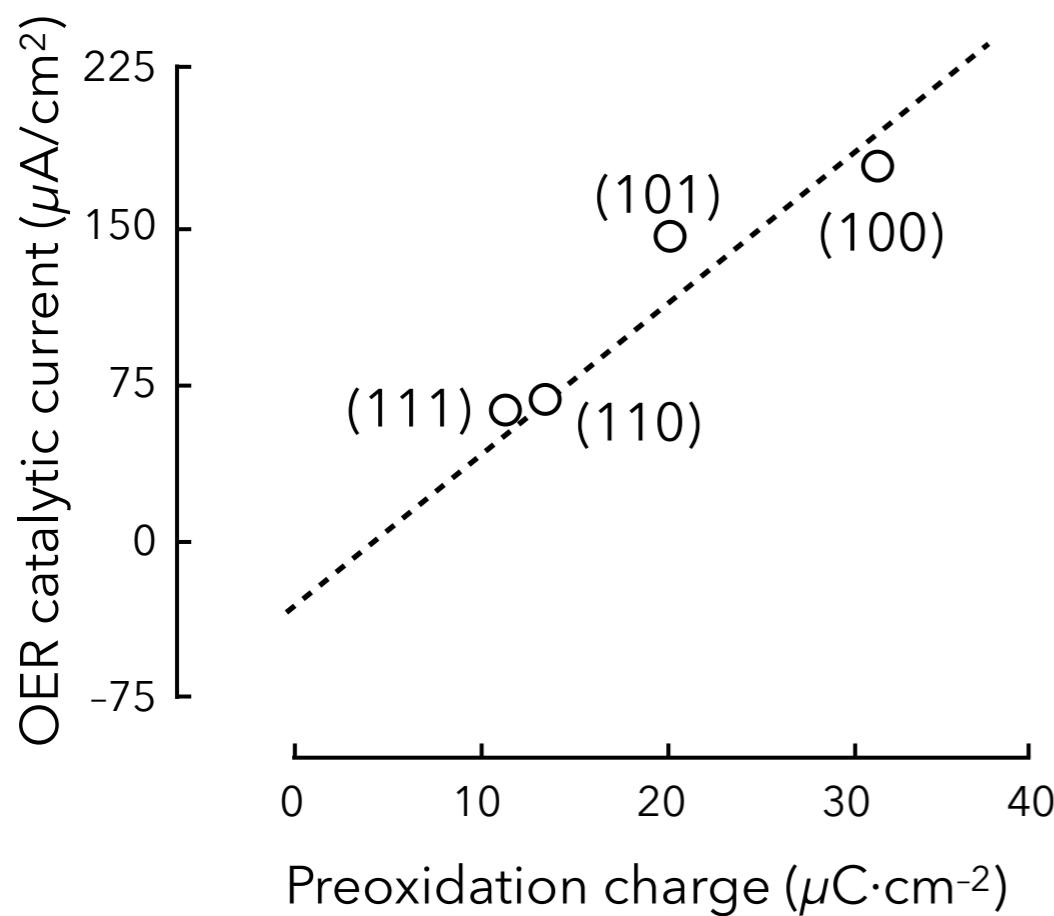
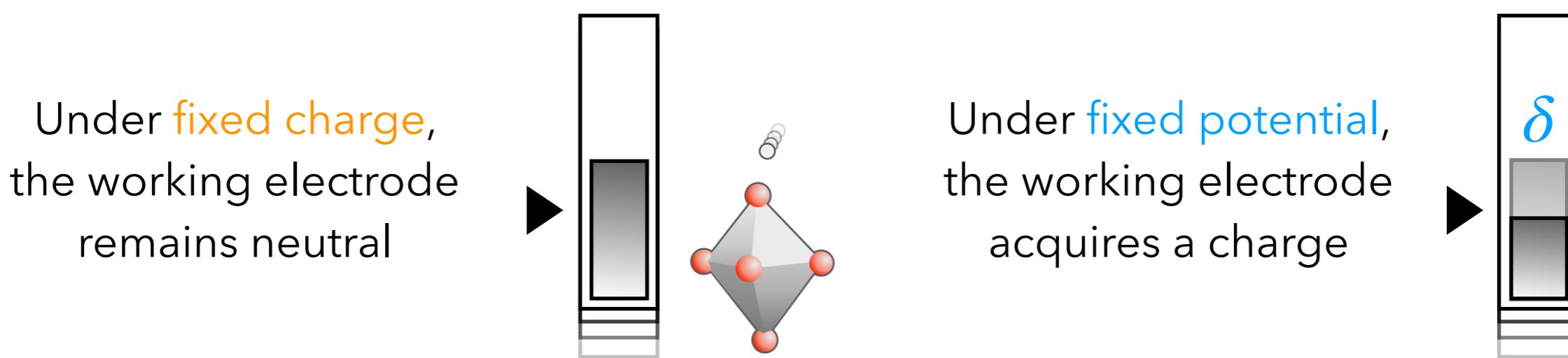
Under **fixed charge**,
the working electrode
remains neutral

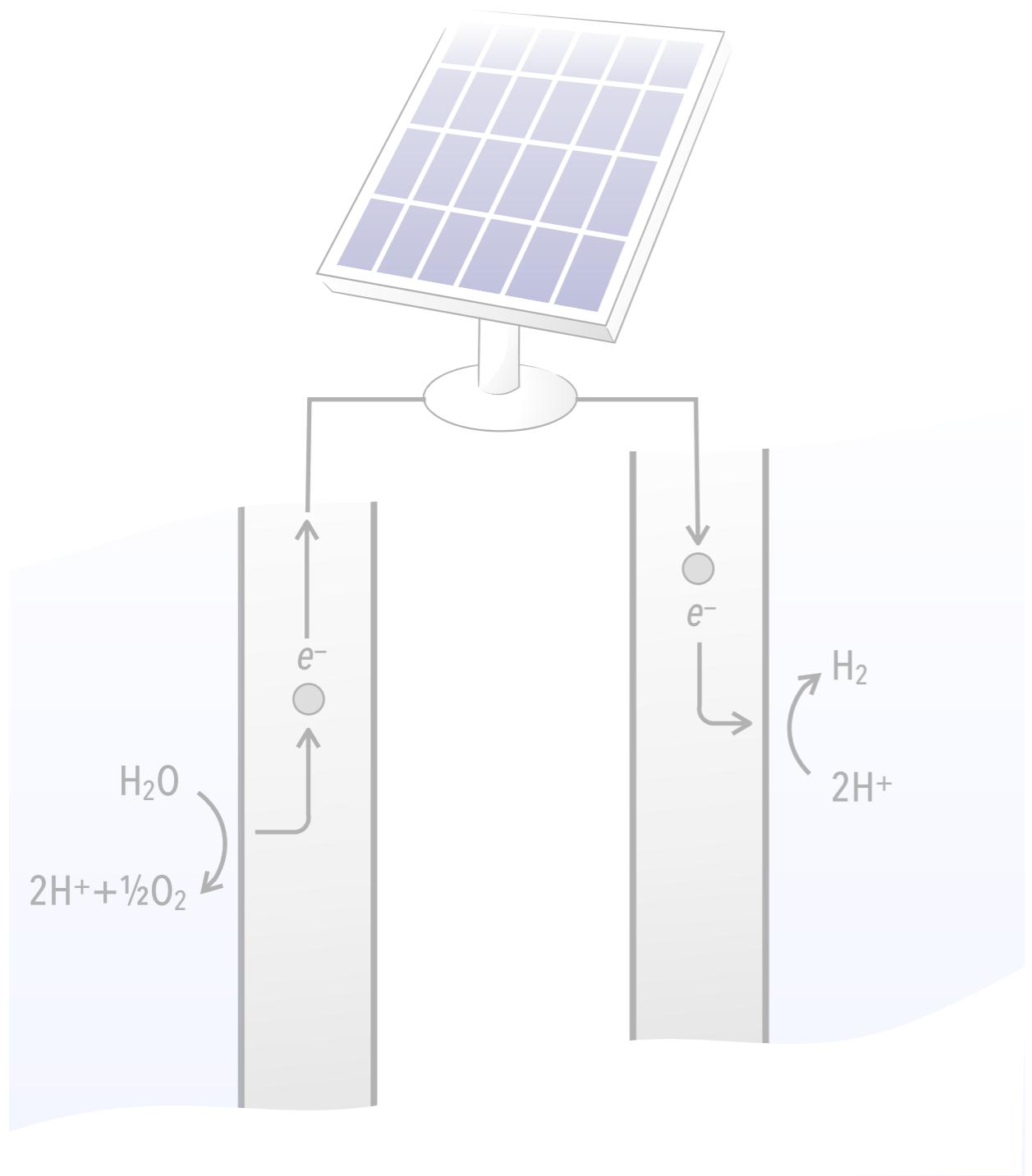


Under **fixed potential**,
the working electrode
acquires a charge

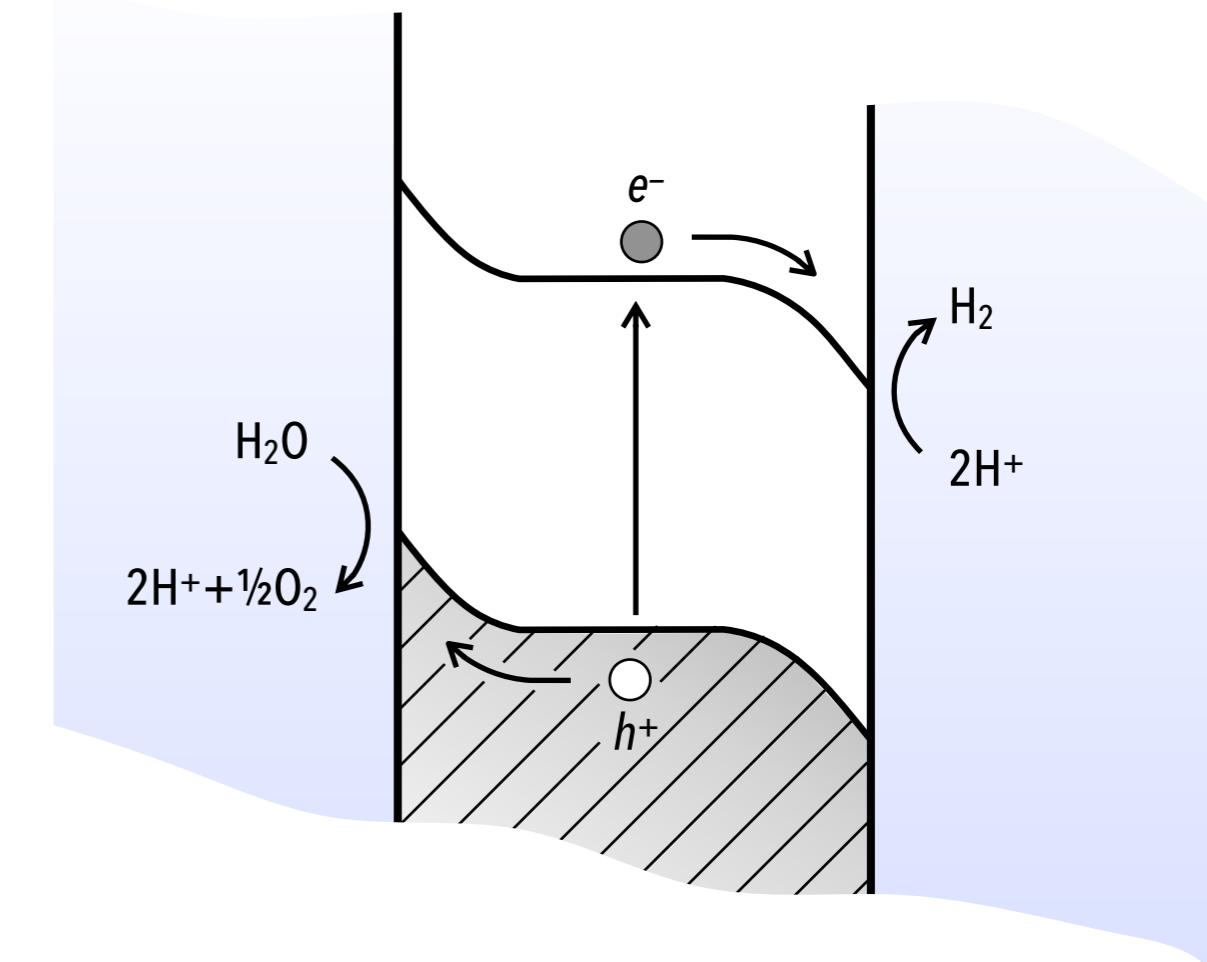


First-principles voltammograms of RuO₂(110) at finite temperature



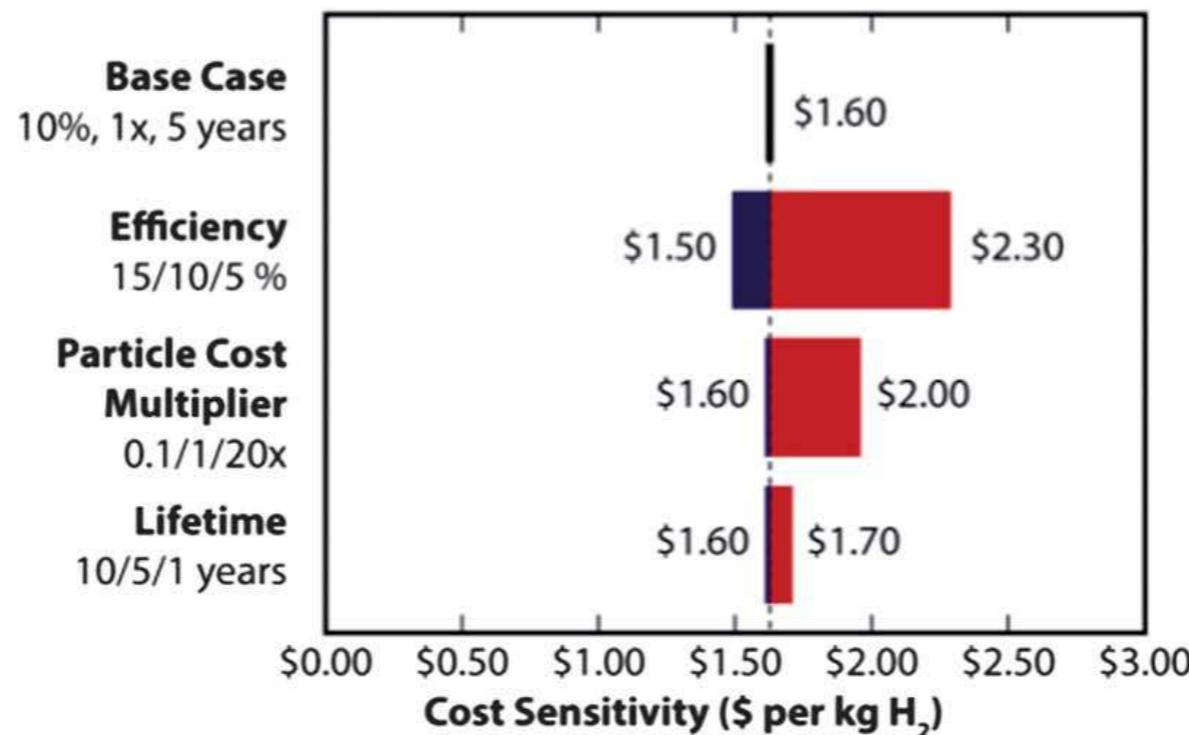
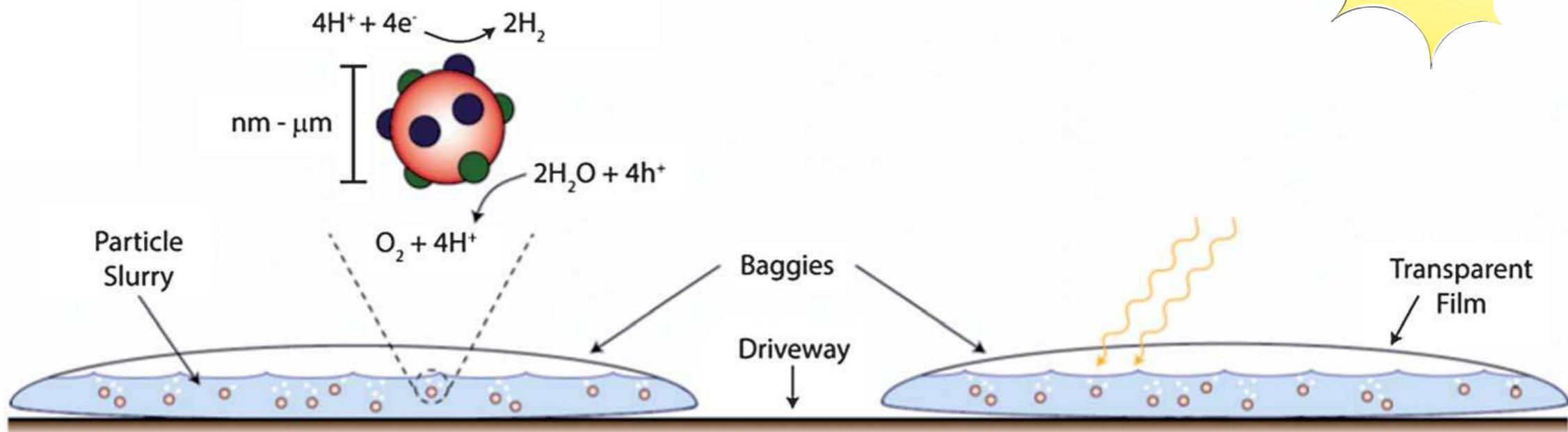


Solar-powered
electrolysis

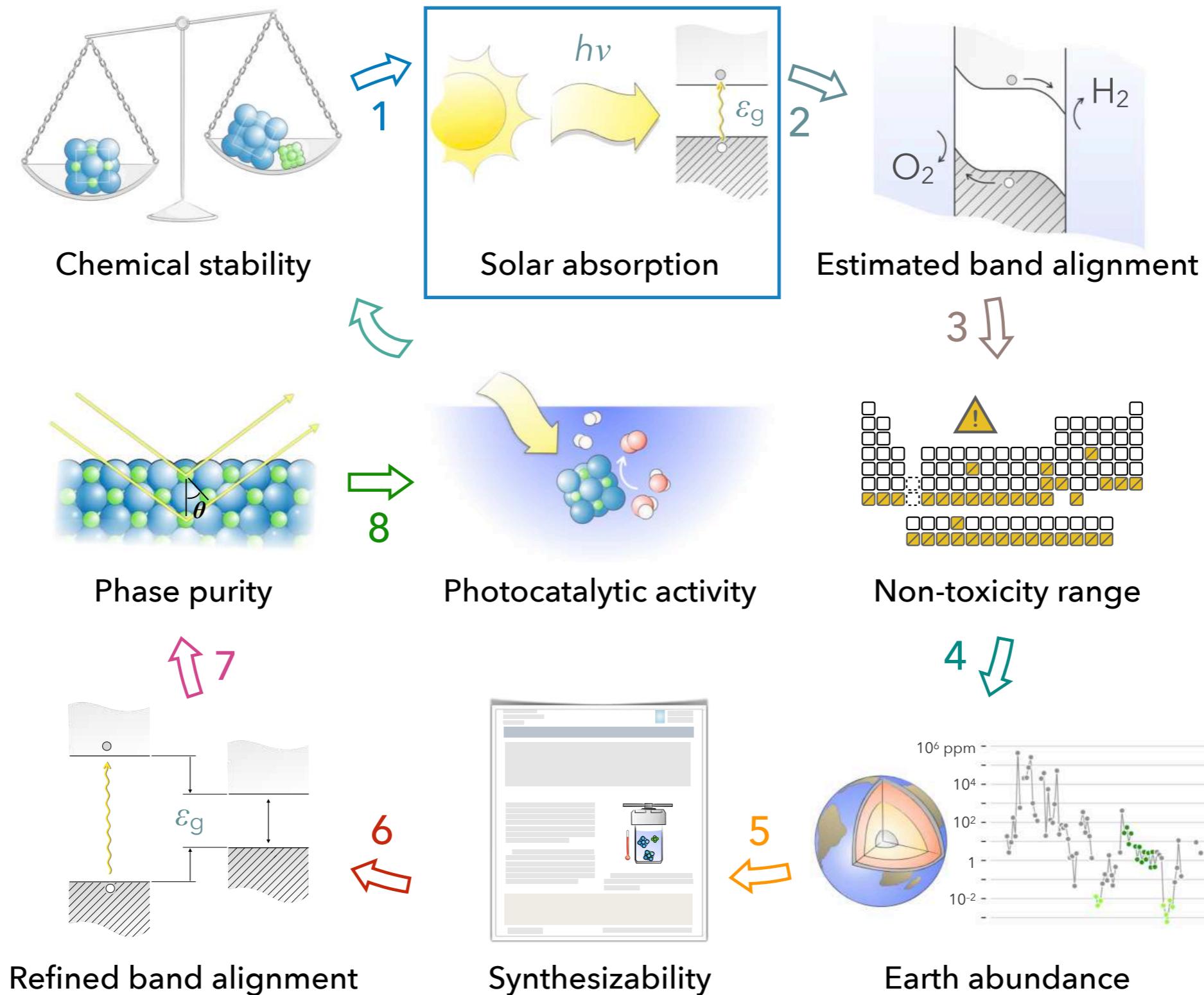


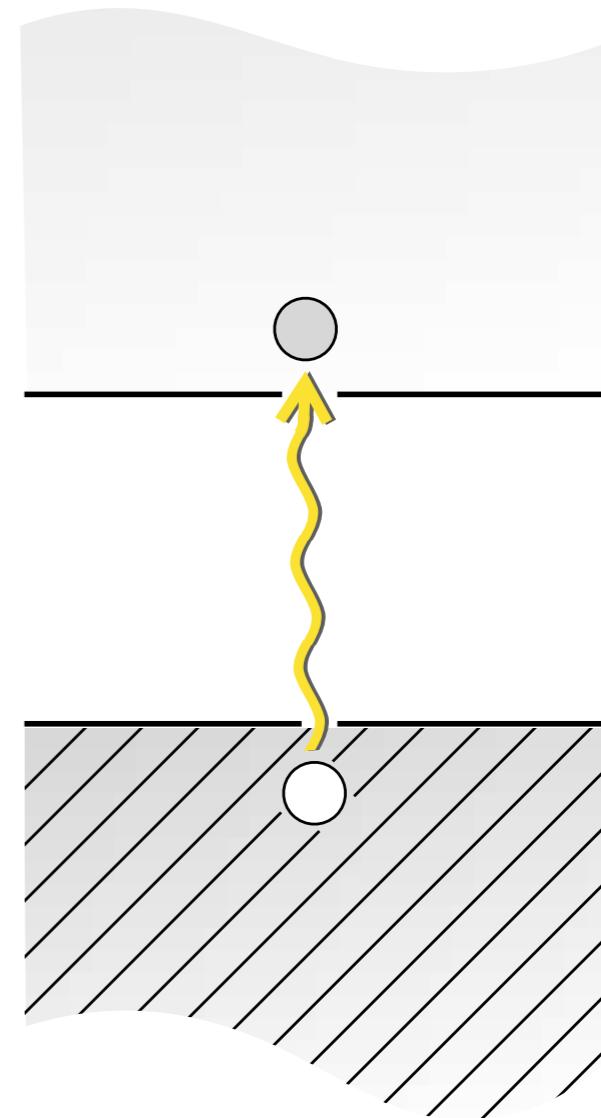
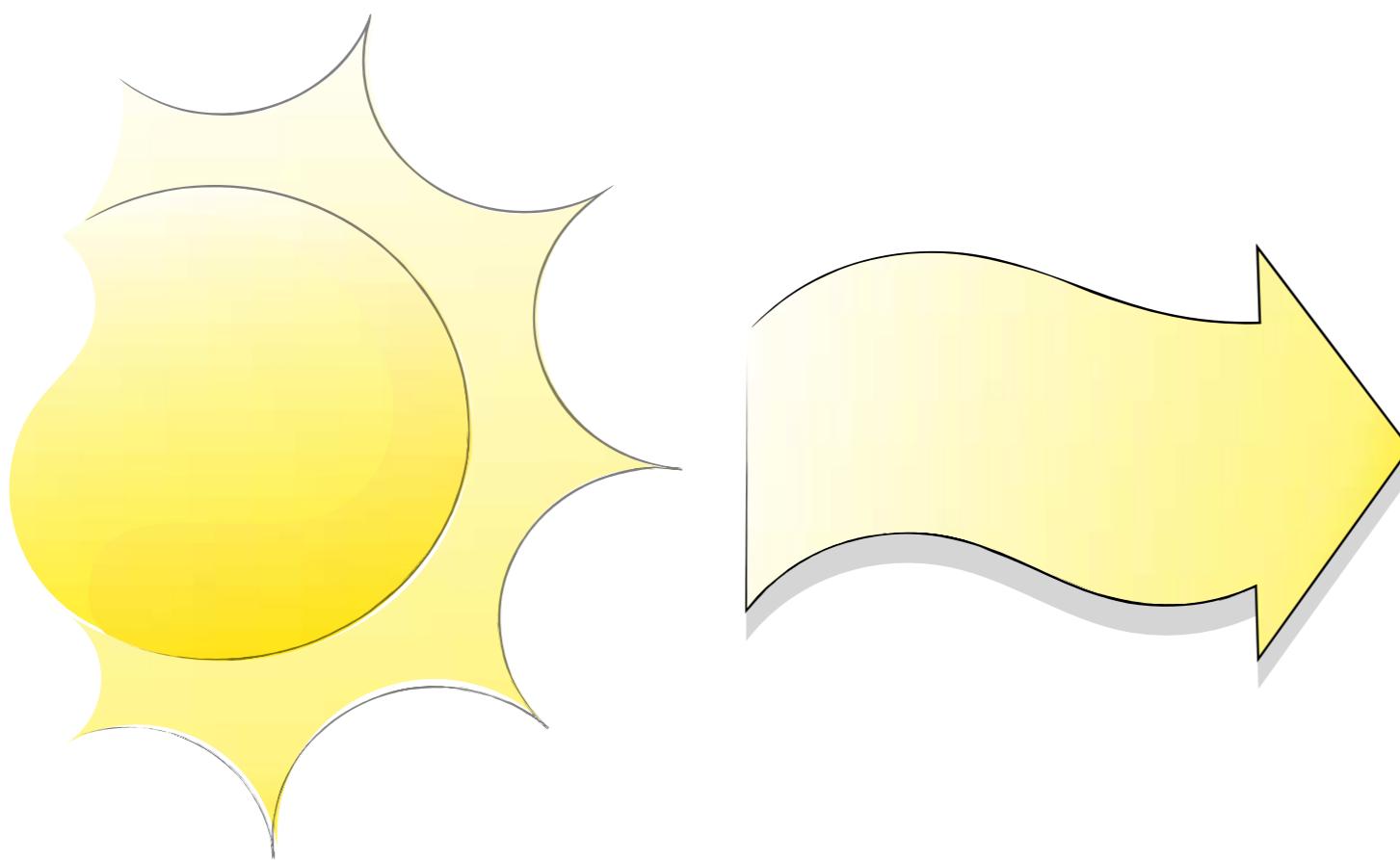
Photoelectrolysis

Photoelectrolysis could bring cost down to \$1.5-3 per kg H₂



Data-informed materials discovery with cross-validated theory and experiment



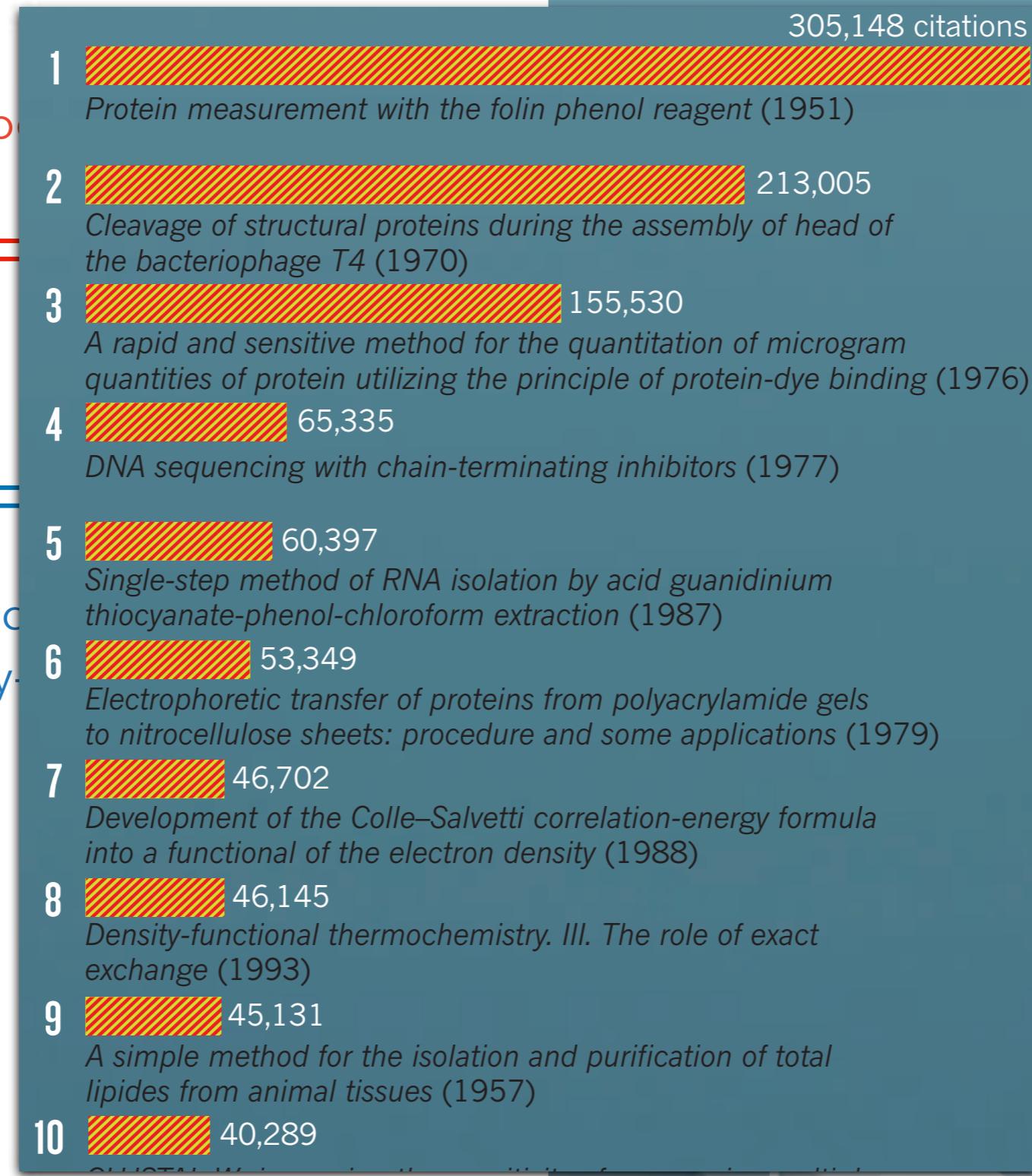


Solar absorption

Density-functional theory

$H\Psi =$
many-body

$h\rho\varphi =$
one-body
(density)



THE PAPER MOUNTAIN

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6	Electrophoretic transfer of proteins from polyacrylamide gels to nitrocellulose sheets: procedure and some applications (1979)	53,349
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30 OCTOBER 2014 | VOL 514 | NATURE | 551

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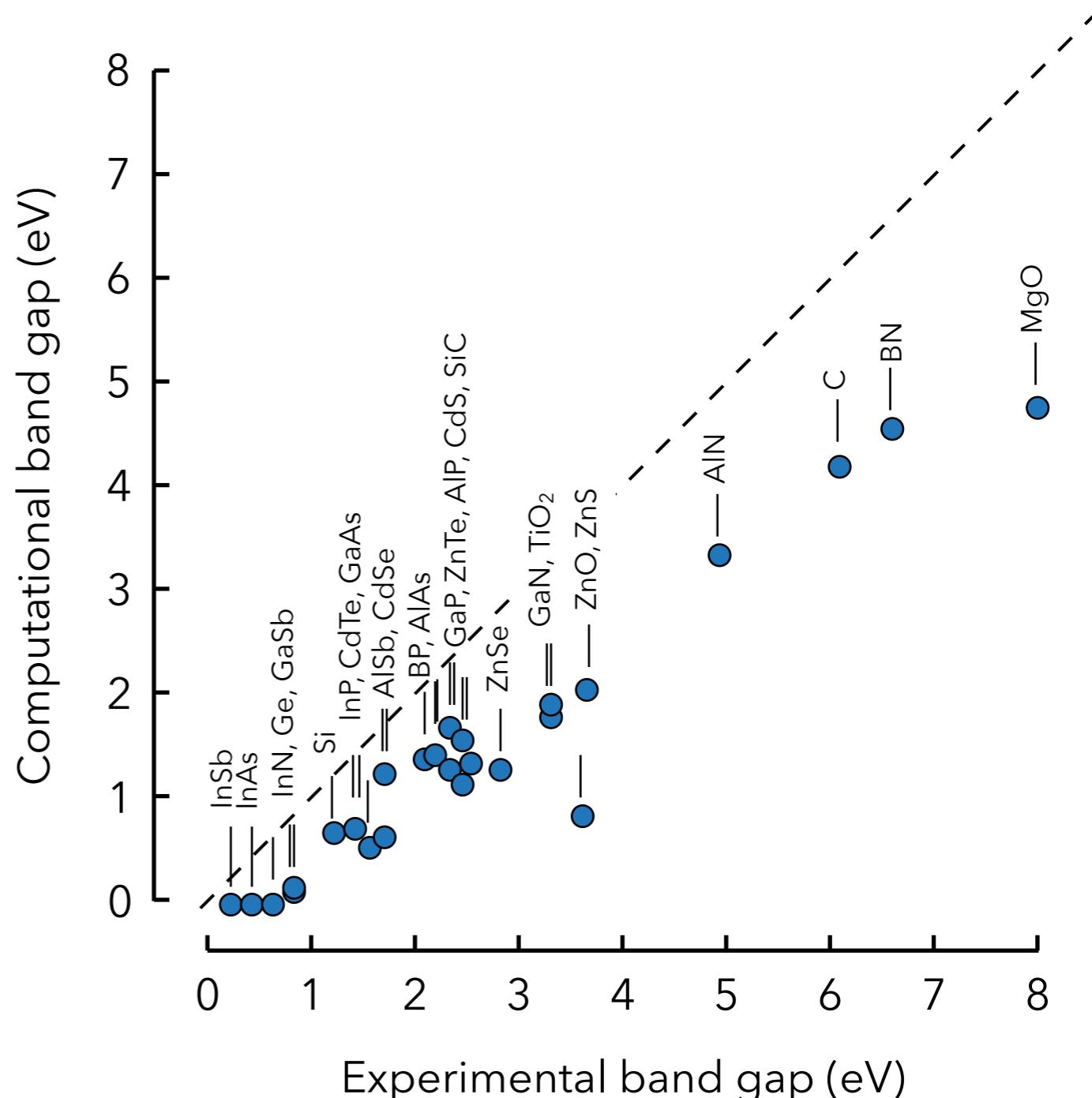
Density-functional theory

$$H\Psi = E\Psi$$

many-body

$$h_p \varphi = \varepsilon \varphi$$

one-body, effective-field
(density-dependent)



ID et al., *Physical Review B* **82**, 115121 (2010)
Borghi et al., *Physical Review B* **90**, 075135 (2015)

Nguyen et al., *Physical Review Letters* **114**, 166405 (2015)
Nguyen et al., *Physical Review X* **8**, 021051 (2018)

Electron correlation in narrow energy bands

II. The degenerate band case

By J. HUBBARD

Theoretical Physics Division, A.E.R.E Harwell

(Communicated by B. H. Flowers, F.R.S.—Received 11 June 1963)

It was noted in §3 that the energy splitting between atomic levels E_p with different number of electrons was in general much greater than the splittings between levels with the same number of electrons. This circumstance suggests that it might be a useful approximation to consider a model in which all the levels with a given number of electrons have the same energy. Such a model might be called a 'zero configuration with' model since the splittings between energy levels arising from the same d^n configuration are assumed to vanish. For such a model the Hamiltonian (4) will assume the simple form

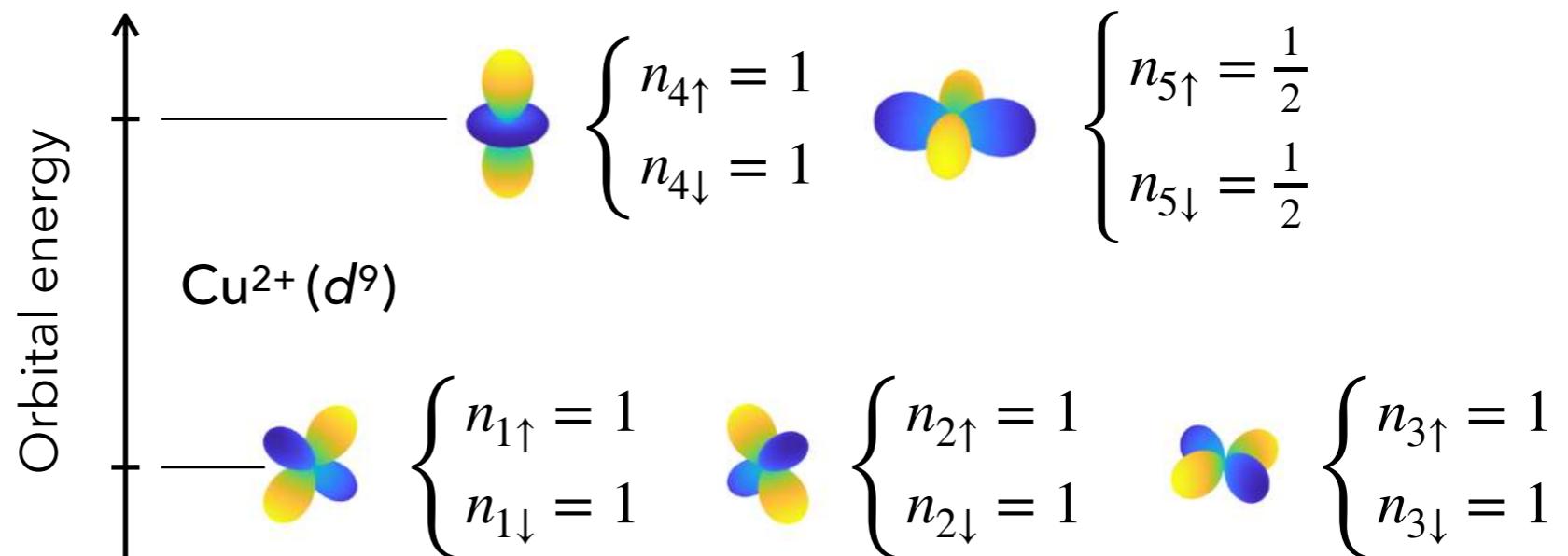
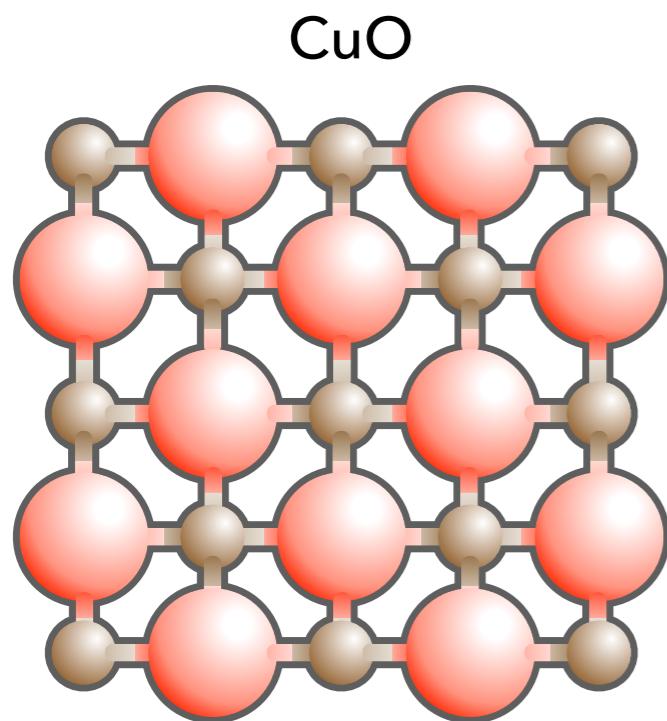
$$H = \sum_{i,j} \sum_{\mu, \nu} T_{ij}^{\mu\nu} c_{i\mu}^+ c_{j\nu} + \frac{1}{2} I \sum_i N_i(N_i - 1), \quad (73)$$

where $N_i = \sum_{\mu} c_{i\mu}^+ c_{i\mu}$ is the total number operator for atom i and I is the parameter which appears in (20).

In the zero band-width limit, $T_{ij}^{\mu\nu} \rightarrow T_0 \delta_{ij} \delta_{\mu\nu}$, the Hamiltonian (73) becomes $H = \sum_i H_i$, where

$$H_i = T_0 N_i + \frac{1}{2} I N_i(N_i - 1). \quad (74)$$

Hubbard model: the zero-configuration-width approximation



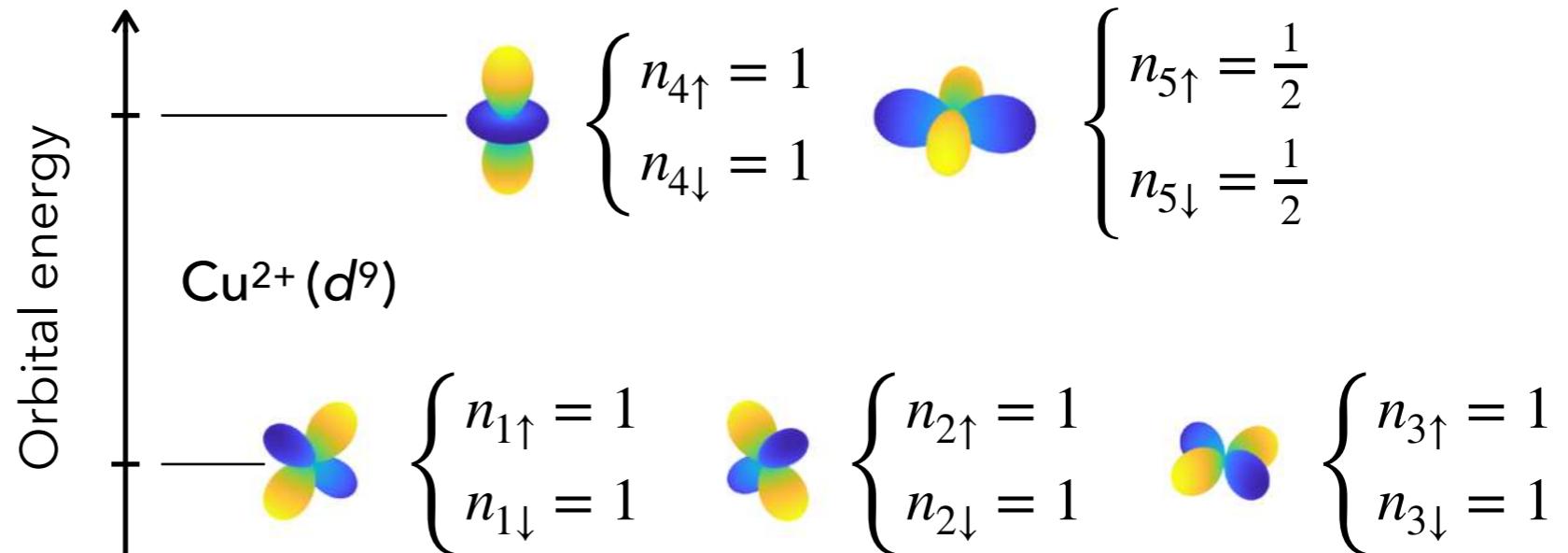
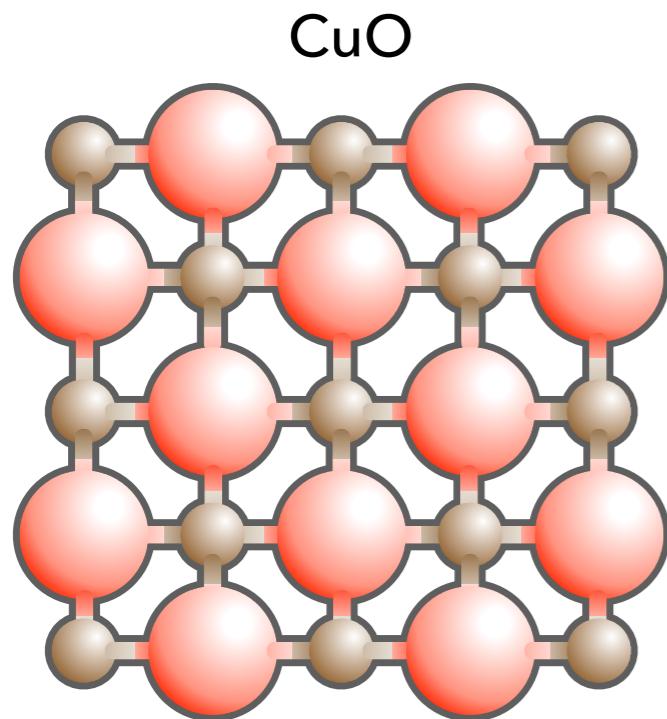
$$\tilde{E} = 9\epsilon + \frac{9 \cdot 8}{2}u = 9\epsilon + 36u \quad (\text{effective counting})$$

$$E = 9\epsilon + \left(\frac{8 \cdot 7}{2} \cdot (1 \cdot 1 \cdot u) + 8 \cdot 2 \cdot (1 \cdot 0.5 \cdot u) + \frac{2 \cdot 1}{2} \cdot (0.5 \cdot 0.5 \cdot u) \right)$$

$$= 9\epsilon + 36.25u \quad (\text{pairwise counting})$$

$$\Delta E = 0.25u \quad (\text{correction})$$

Hubbard model: the zero-configuration-width approximation

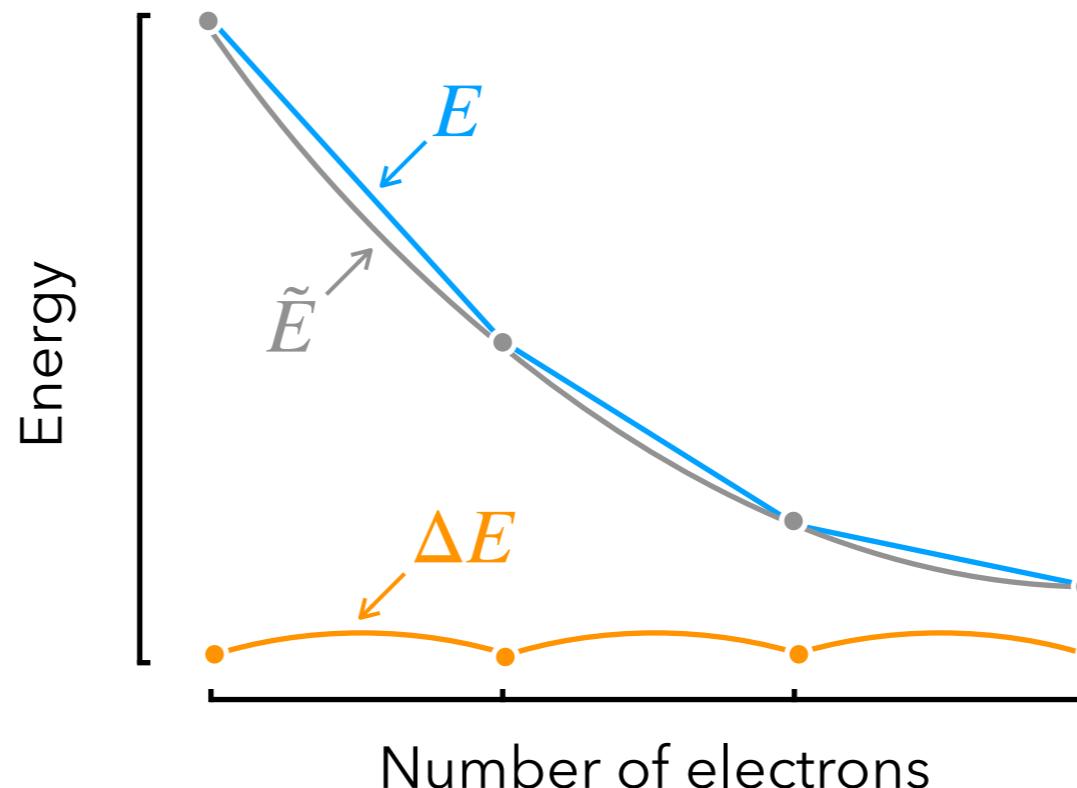


$$\tilde{E} = \varepsilon \left(\sum_{m\sigma} n_{m\sigma} \right) + \frac{u}{2} \left(\sum_{m\sigma} n_{m\sigma} \right) \left(\sum_{m\sigma} n_{m\sigma} - 1 \right) \quad (\text{effective counting})$$

$$E = \varepsilon \left(\sum_{m\sigma} n_{m\sigma} \right) + \frac{u}{2} \left(\sum_{m\sigma} n_{m\sigma} \left(\sum_{m'\sigma'} n_{m'\sigma'} - n_{m\sigma} \right) \right) \quad (\text{pairwise counting})$$

$$\Delta E = \frac{u}{2} \sum_{m\sigma} n_{m\sigma} (1 - n_{m\sigma}) \quad (\text{correction})$$

Hubbard model: the zero-configuration-width approximation



$$\tilde{E} = \varepsilon \left(\sum_{m\sigma} n_{m\sigma} \right) + \frac{u}{2} \left(\sum_{m\sigma} n_{m\sigma} \right) \left(\sum_{m\sigma} n_{m\sigma} - 1 \right) \quad (\text{effective counting})$$

$$E = \varepsilon \left(\sum_{m\sigma} n_{m\sigma} \right) + \frac{u}{2} \left(\sum_{m\sigma} n_{m\sigma} \left(\sum_{m'\sigma'} n_{m'\sigma'} - n_{m\sigma} \right) \right) \quad (\text{pairwise counting})$$

$$\Delta E = \frac{u}{2} \sum_{m\sigma} n_{m\sigma} \left(1 - n_{m\sigma} \right) \quad (\text{correction})$$

Assessment of Hubbard correction for band gaps



$$H\Psi = E\Psi$$

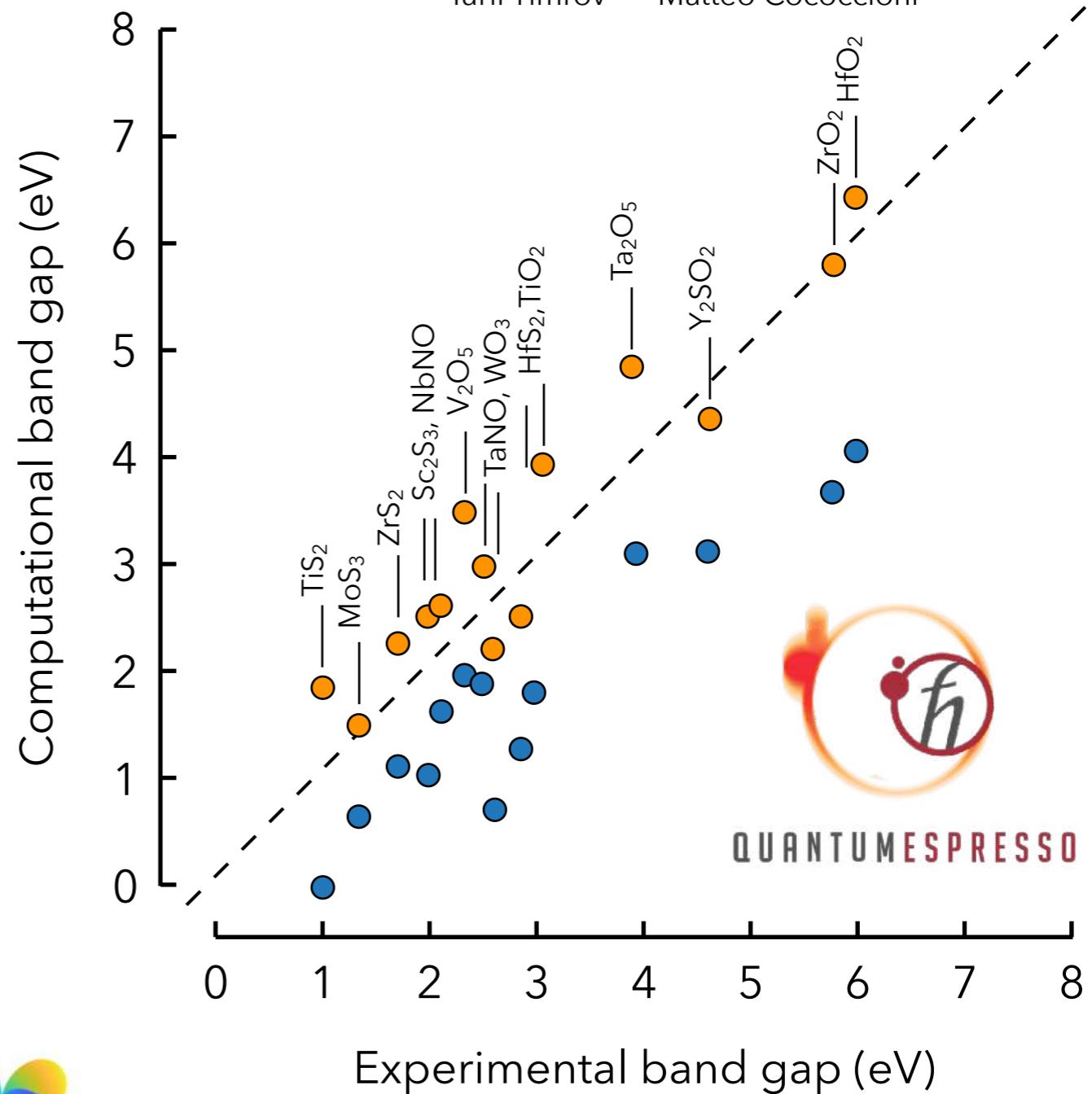
many-body

$$h_{\rho} \varphi = \varepsilon \varphi$$

one-body, effective-field
(density-dependent)

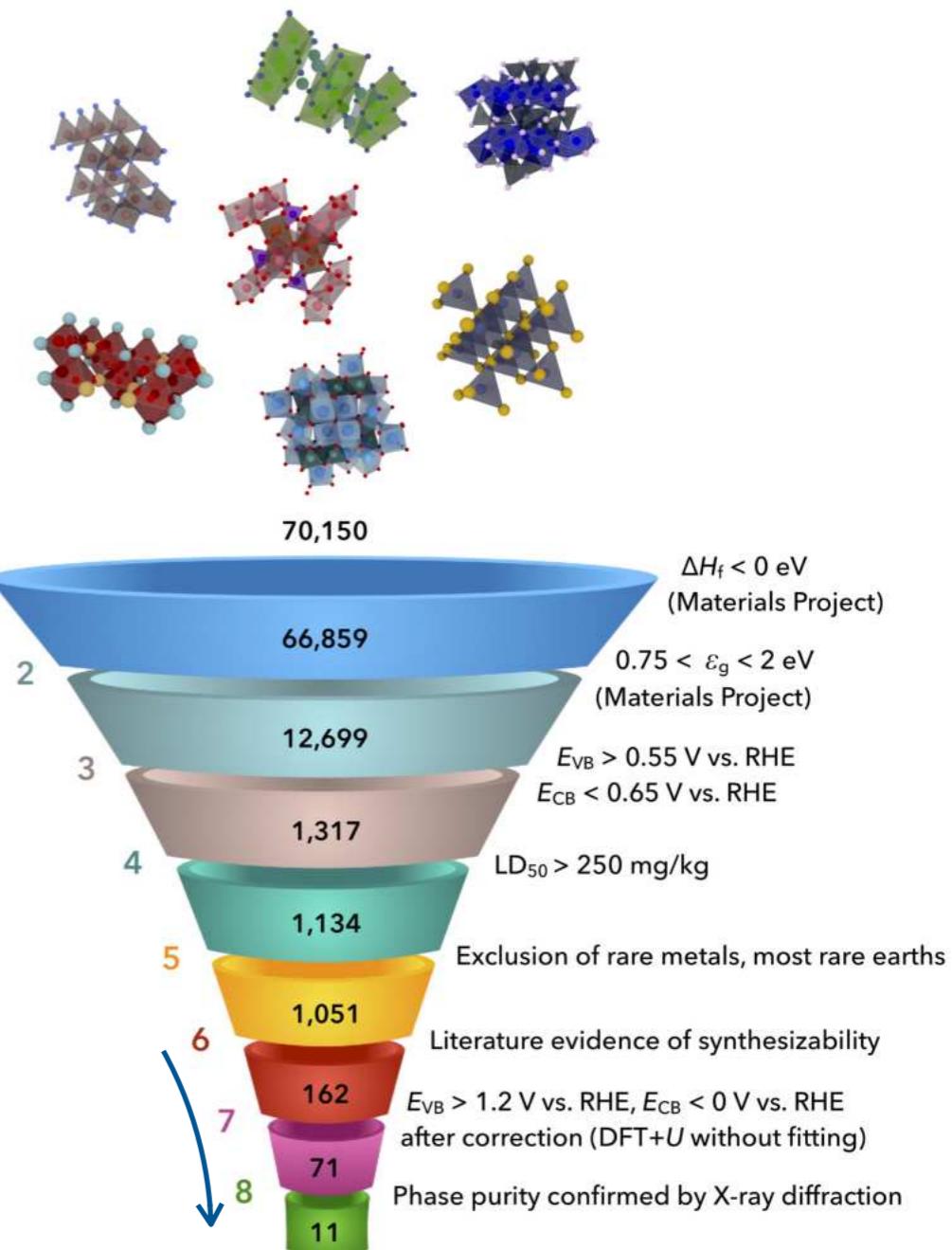
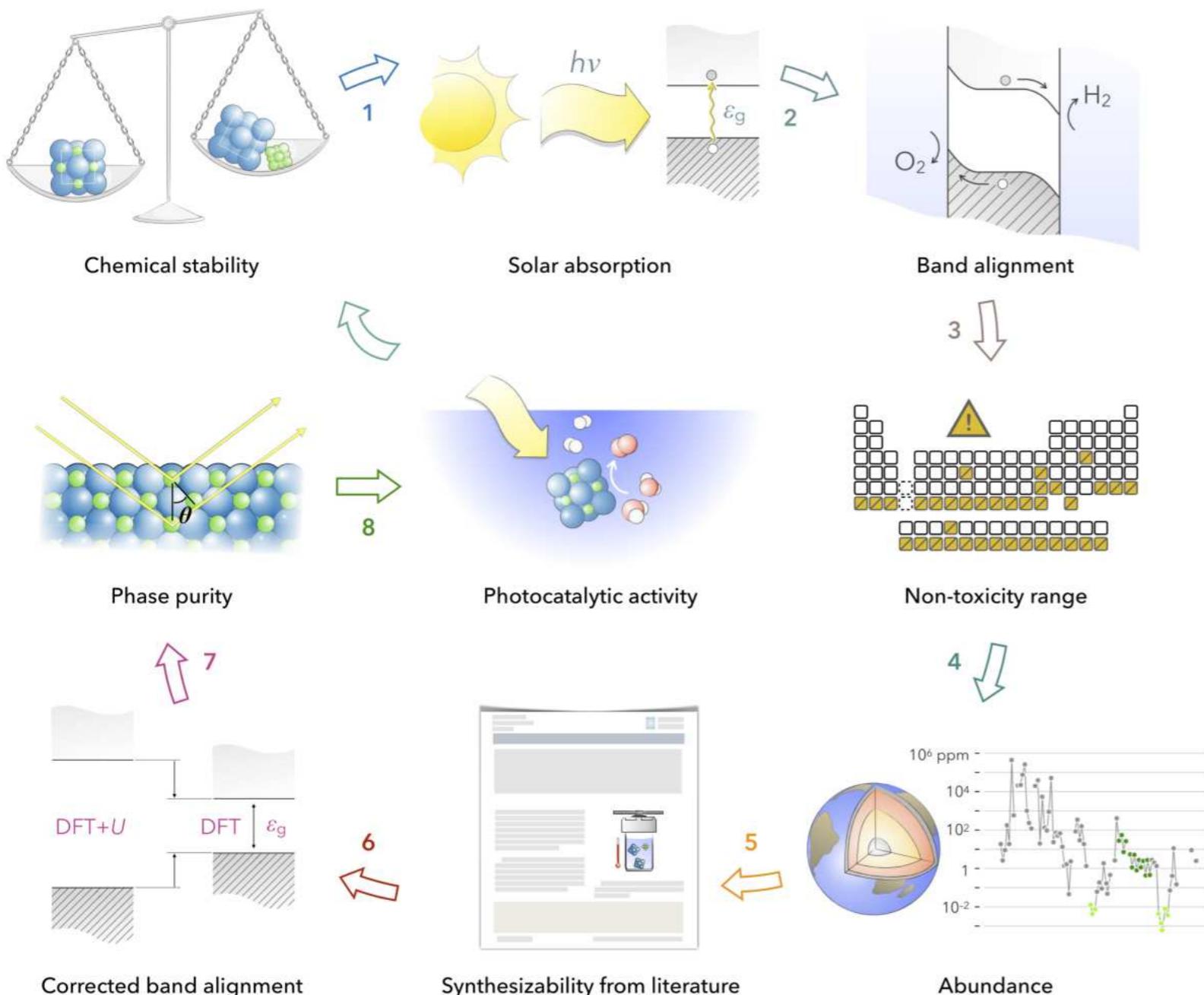
$$h_{\rho, (n_{m\sigma})_{m\sigma}} \varphi = \varepsilon \varphi$$

one-body, effective-field
(occupancy-dependent)

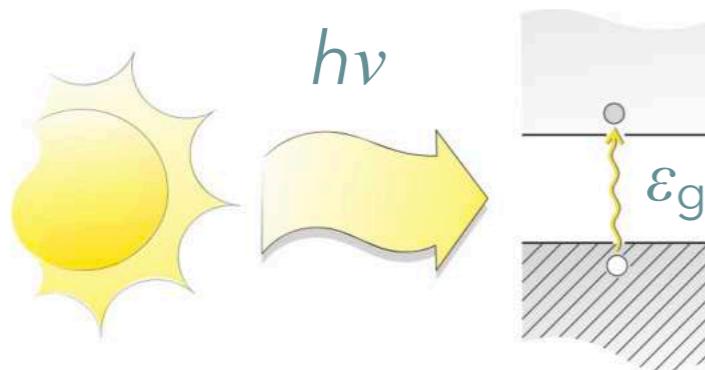


Kirchner-Hall et al., Applied Sciences 11, 2395 (2021)
Timrov et al., Physical Review B 103, 045141 (2021)

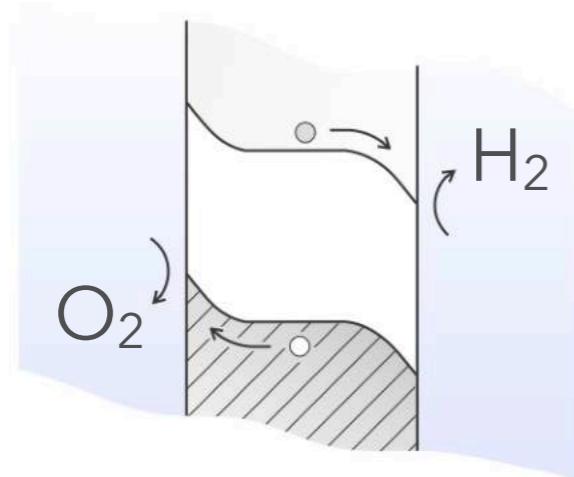
Screening of 71 candidate photocatalysts starting from 70,150 materials



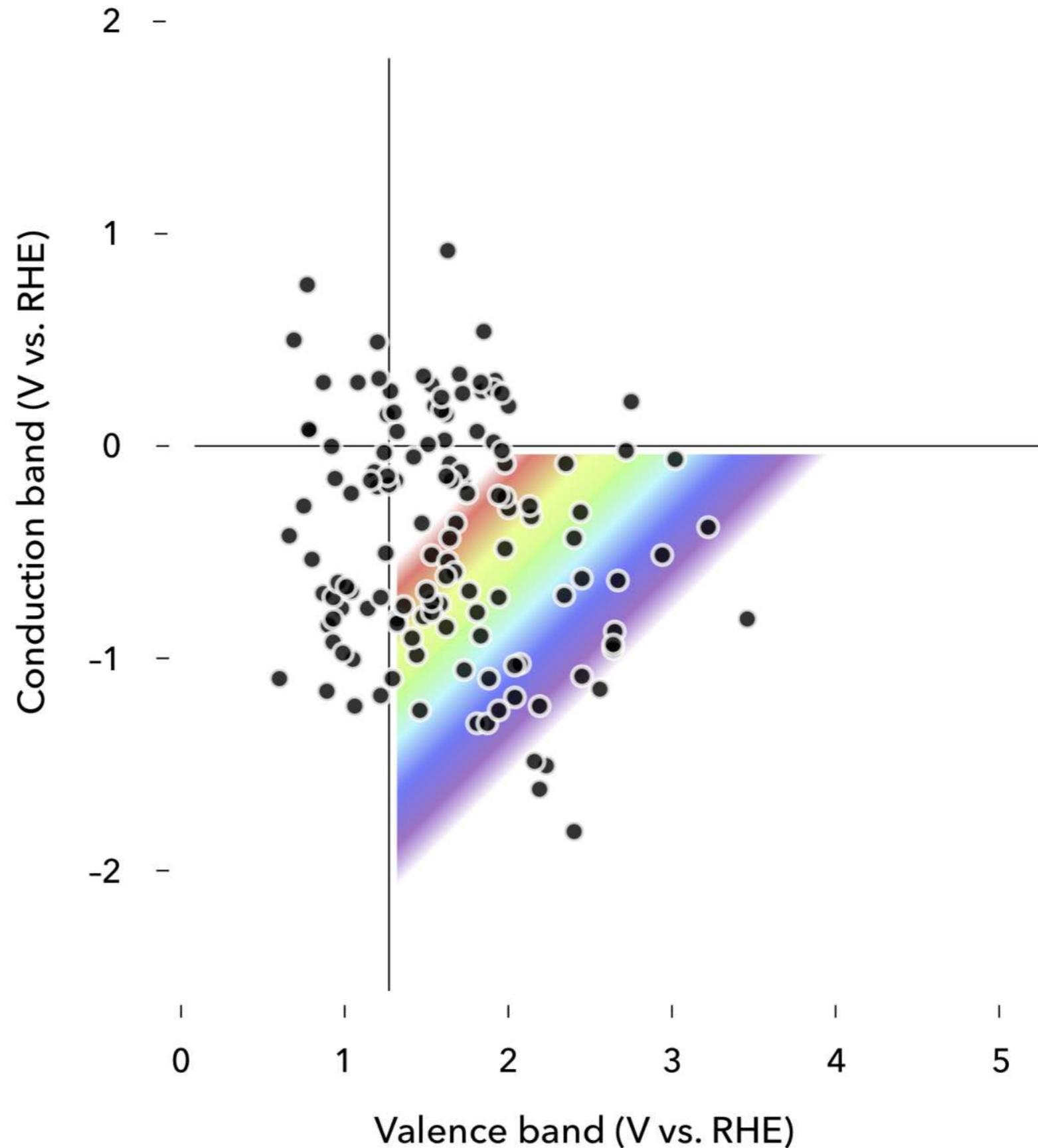
Screening of 71 candidate photocatalysts starting from 70,150 materials



Solar absorption



Band alignment



Experimental verification of phase purity, yielding 11 final candidates



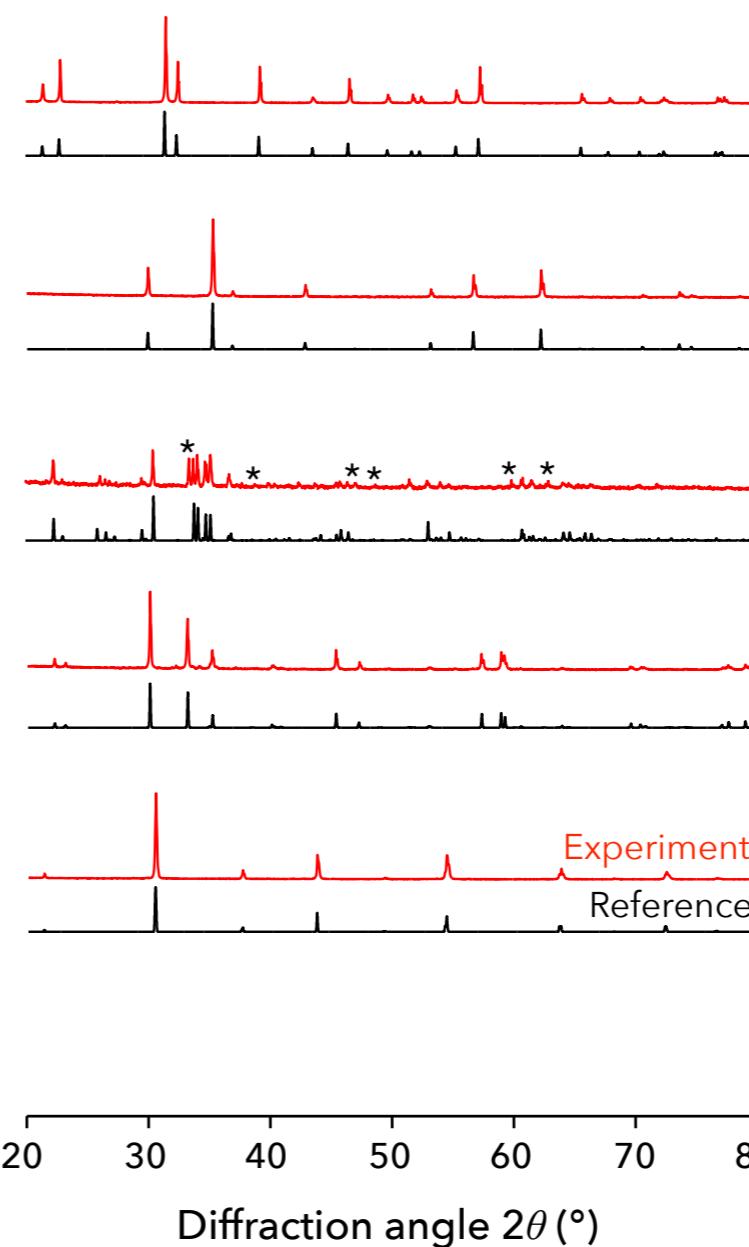
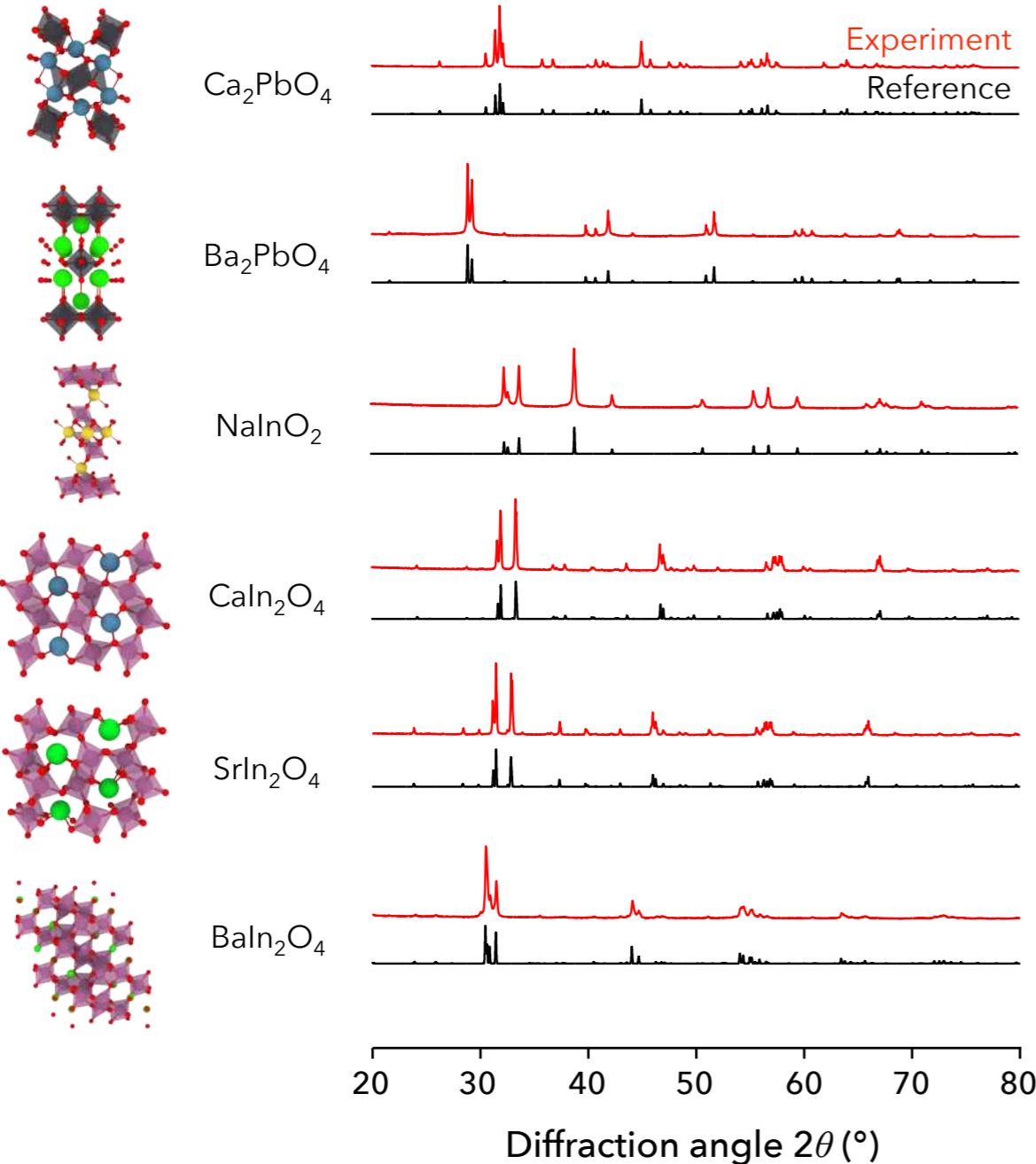
Julian Fanganel



Rowan Katzbaer



Raymond Schaak



Experimental measurement of band gaps, unveiling possible mid-gap states



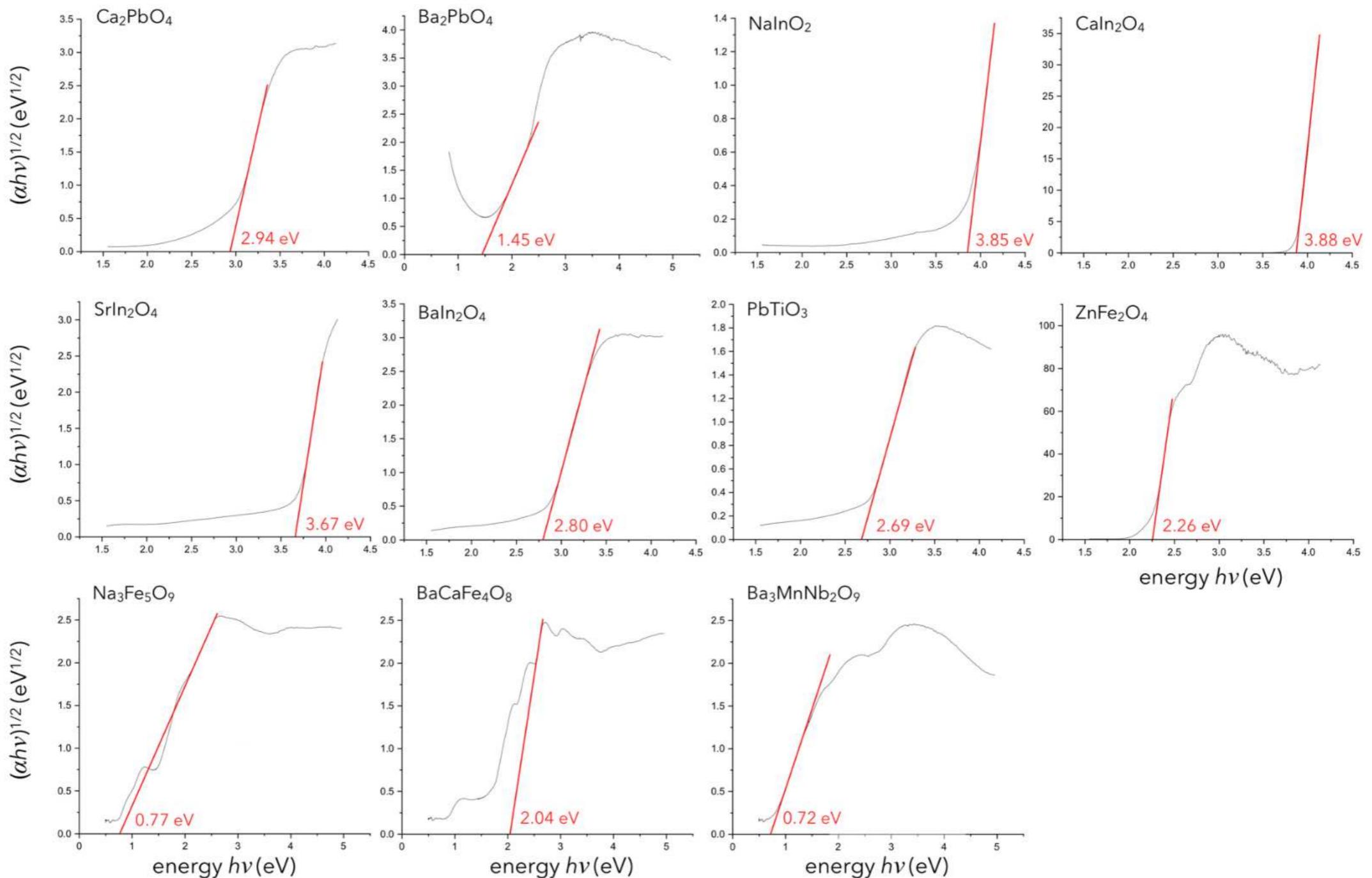
Julian Fanganel



Rowan Katzbaer



Raymond Schaak



Experimental verification of band gaps



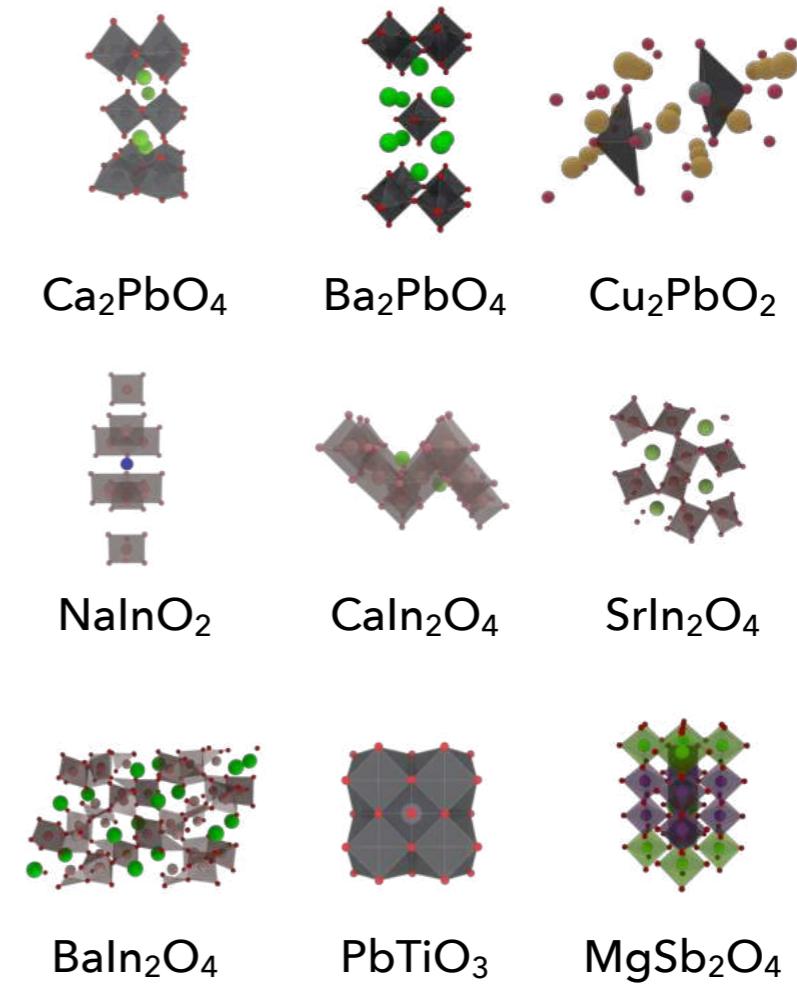
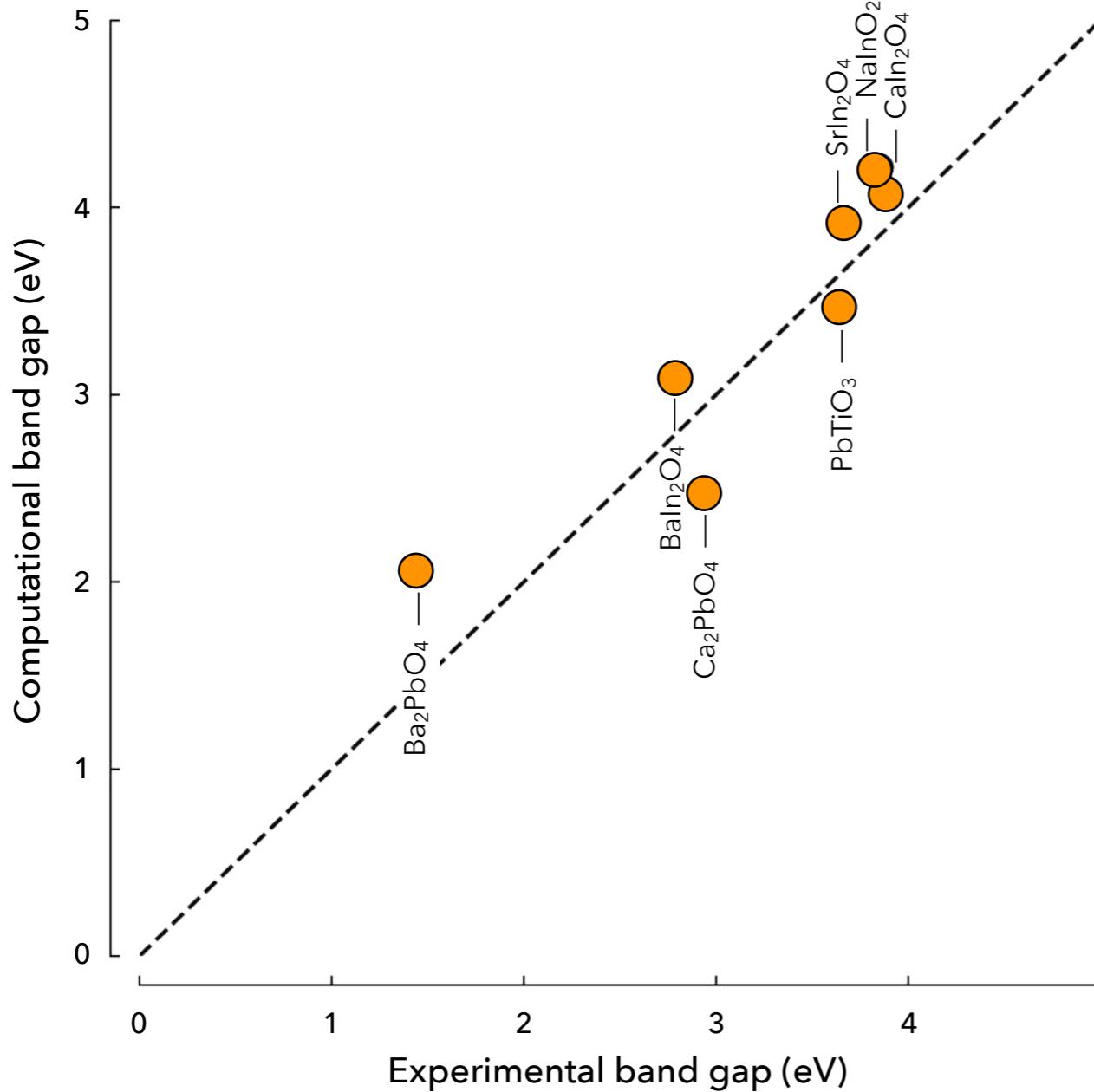
Julian Fanganel



Rowan Katzbaer



Raymond Schaak



Experimental verification of band gaps



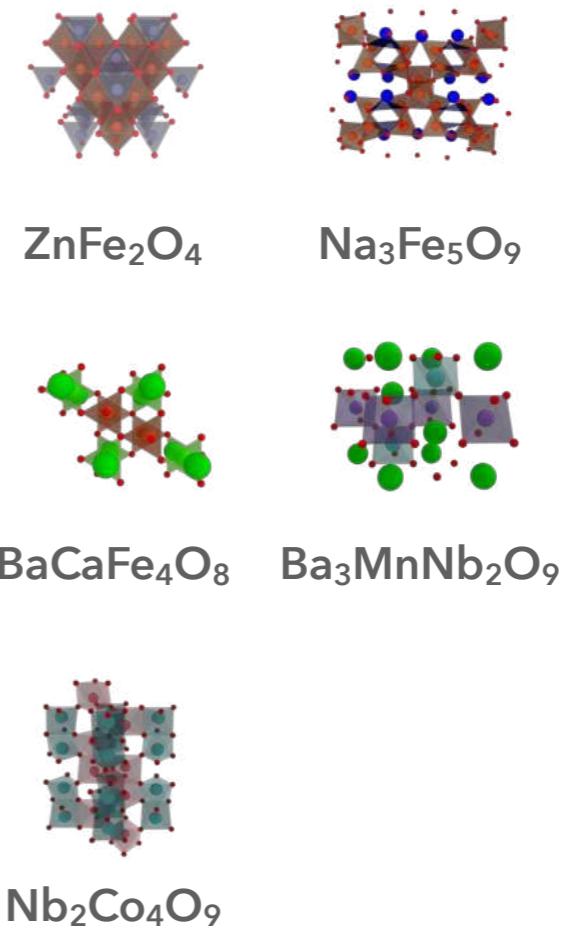
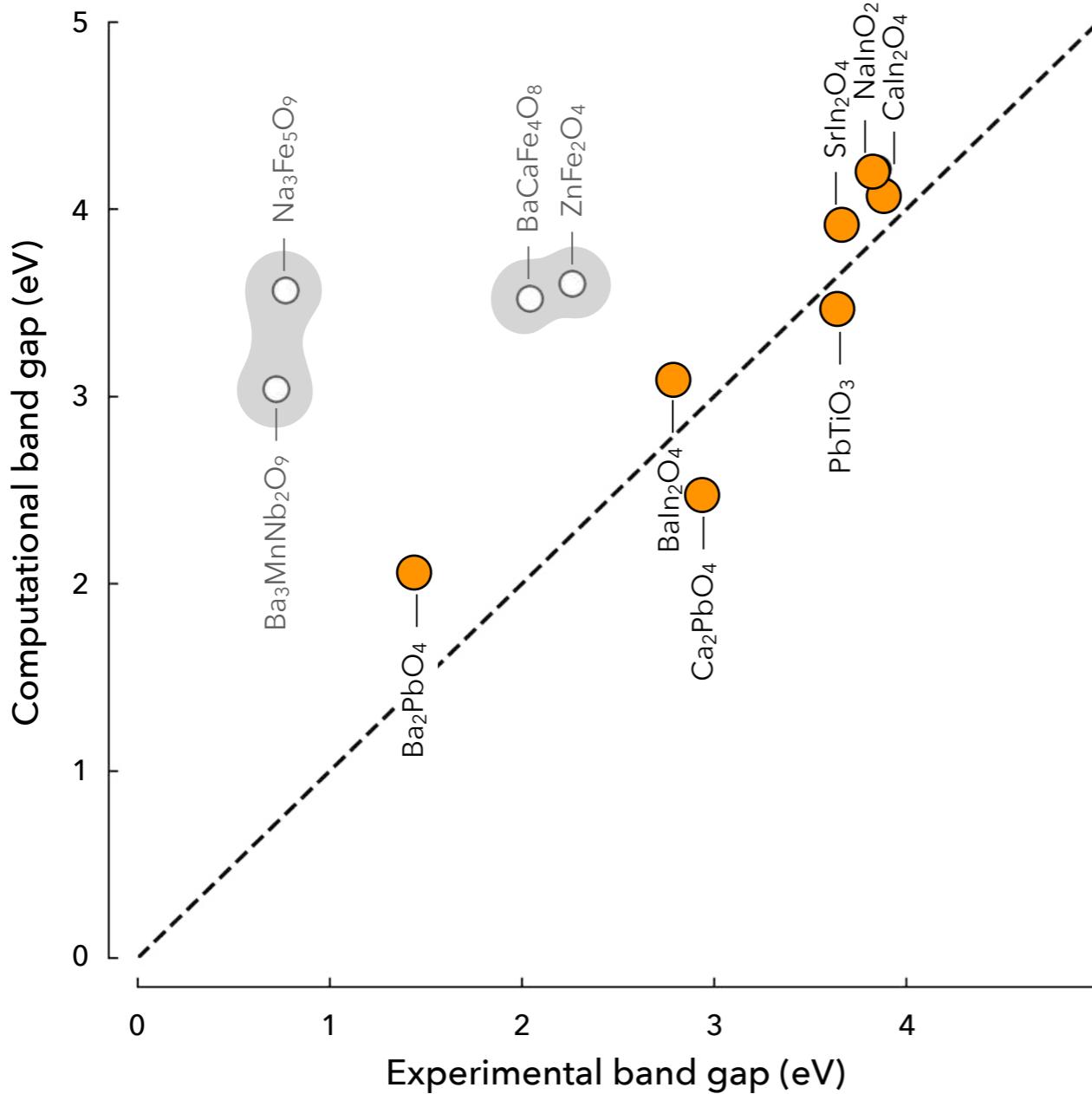
Julian Fanganel



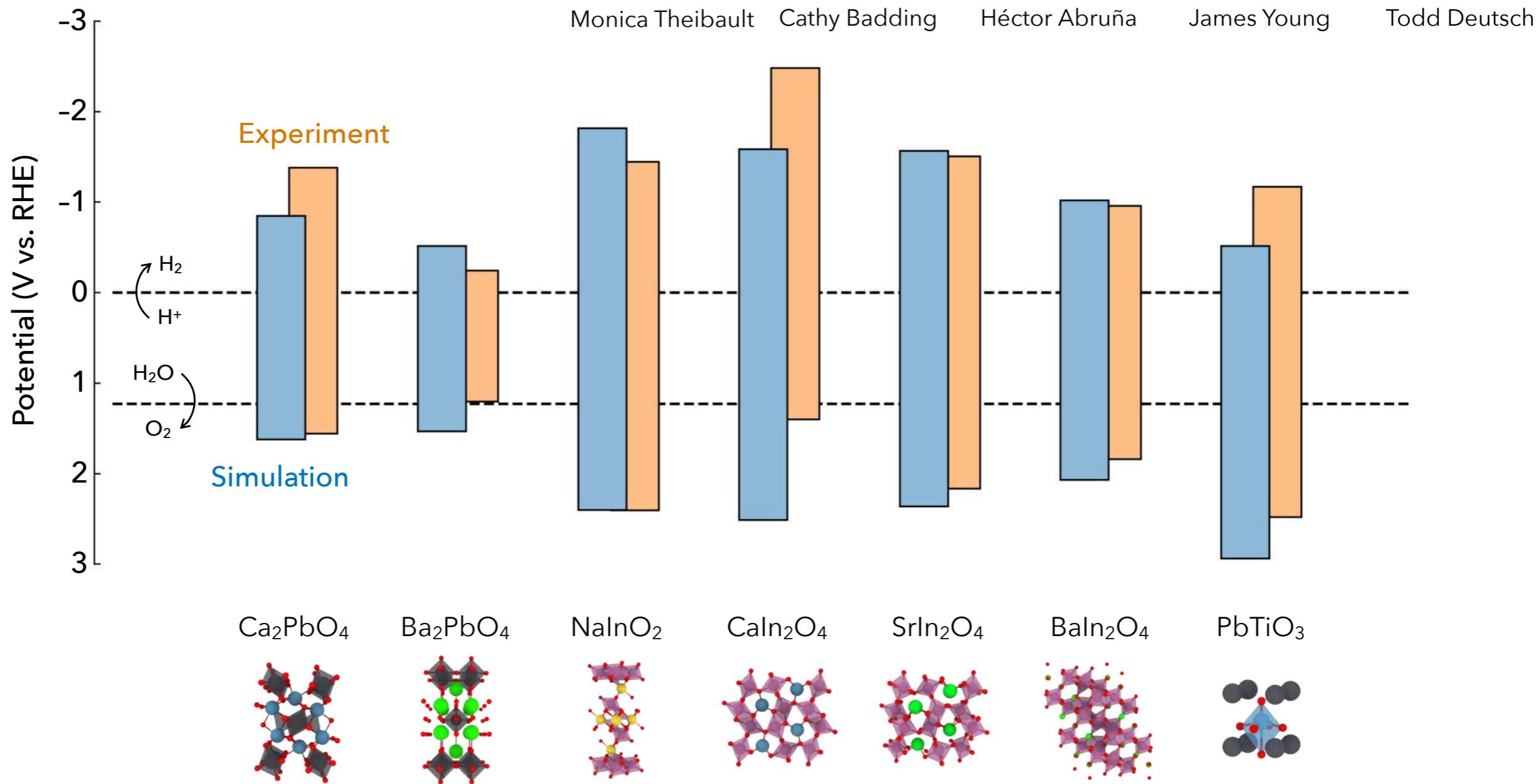
Rowan Katzbaer



Raymond Schaak



Experimental verification of band edges



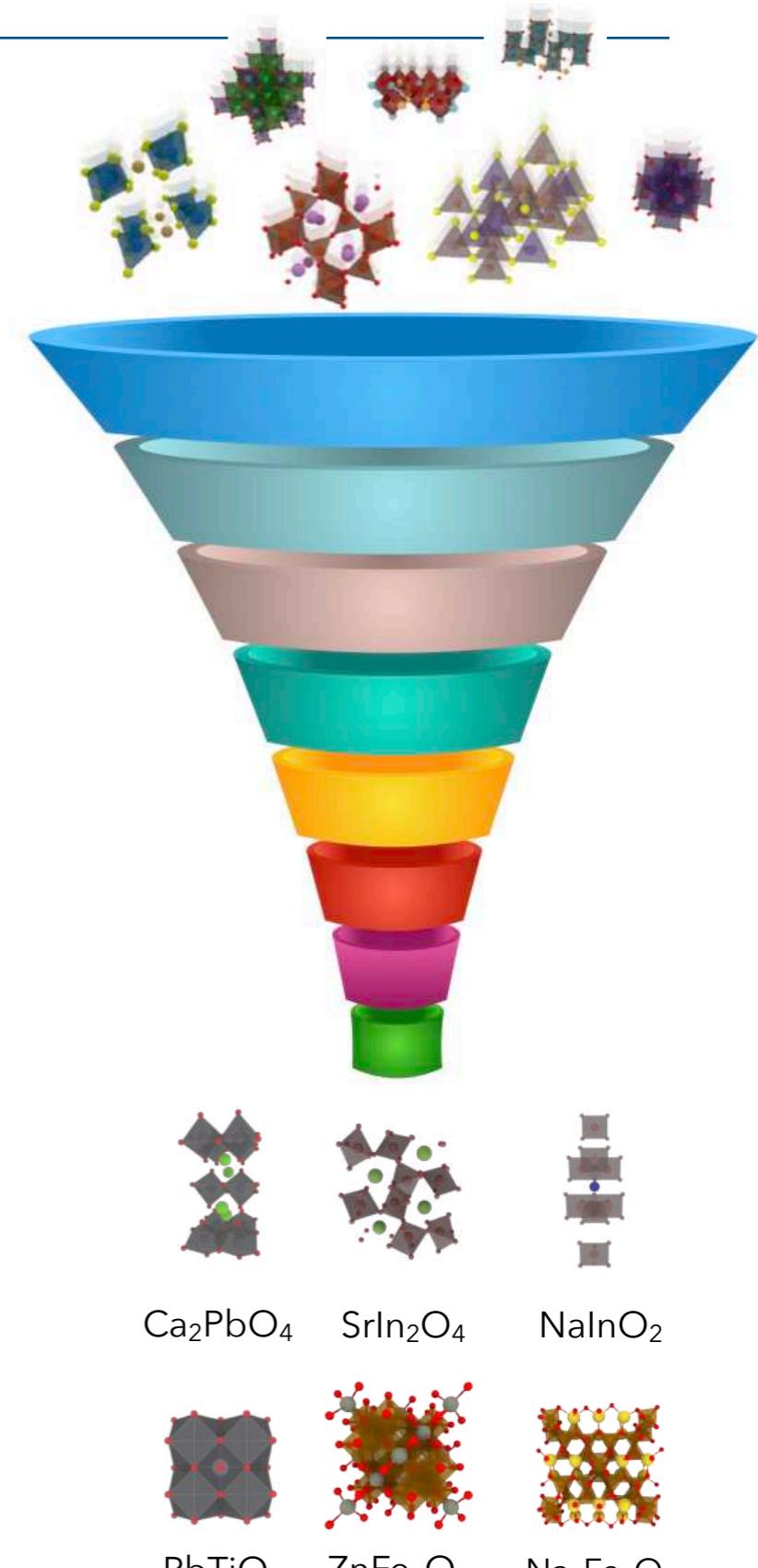
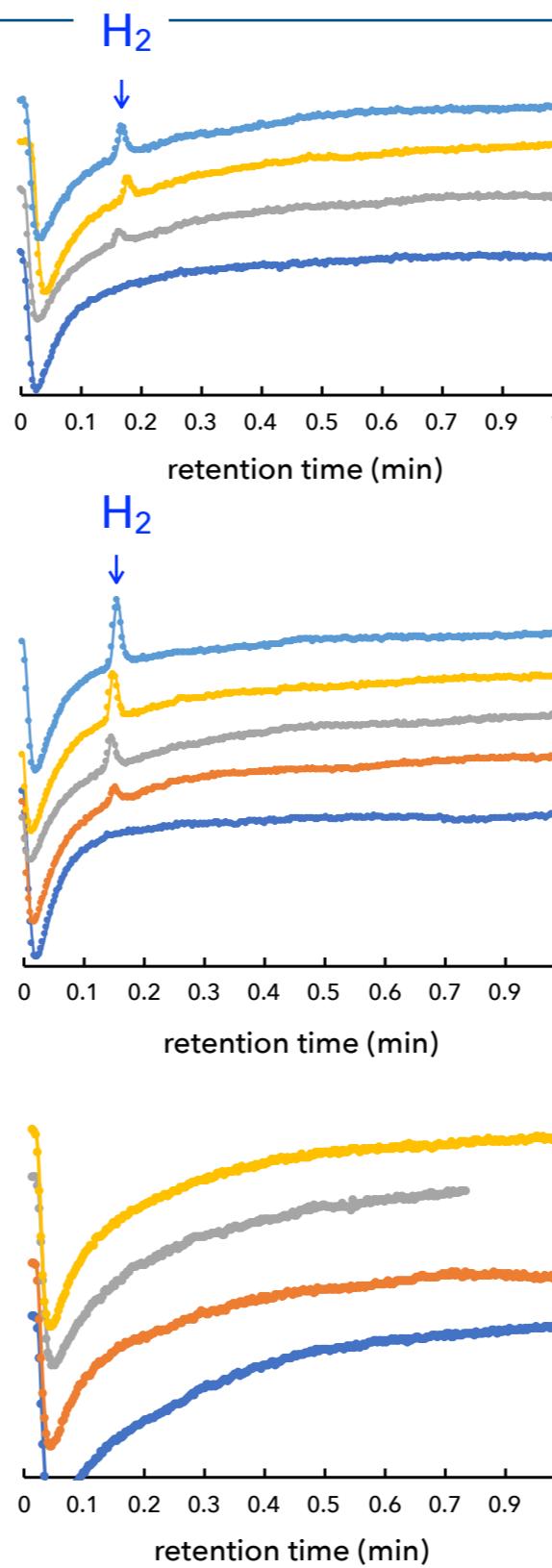
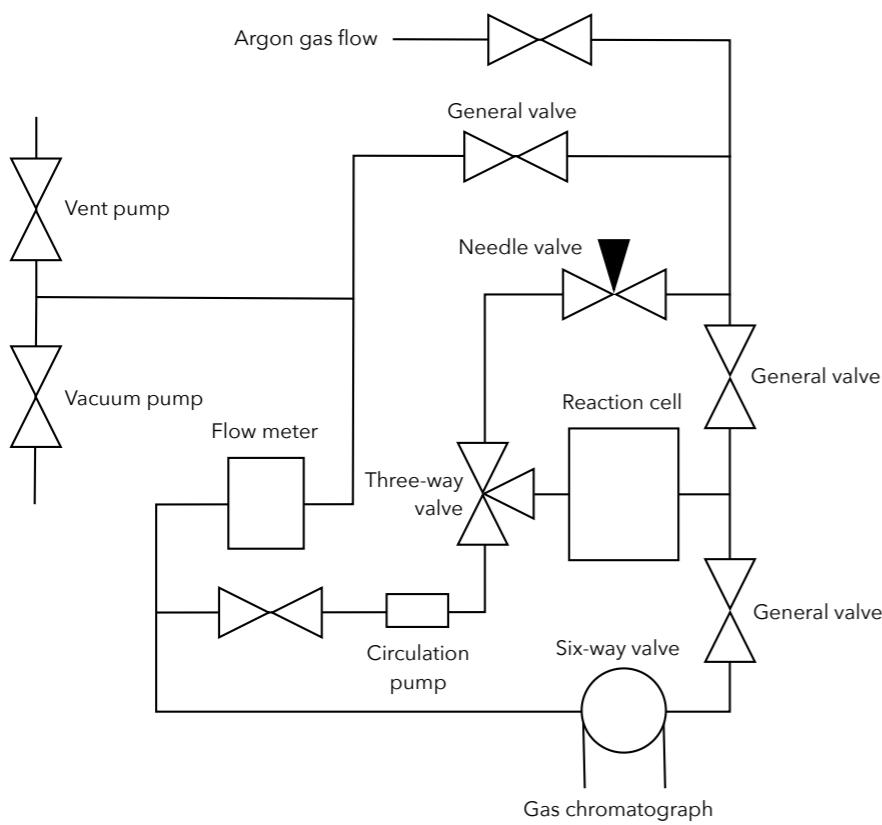
Experimental verification of photoelectrolysis



Hugo Wang



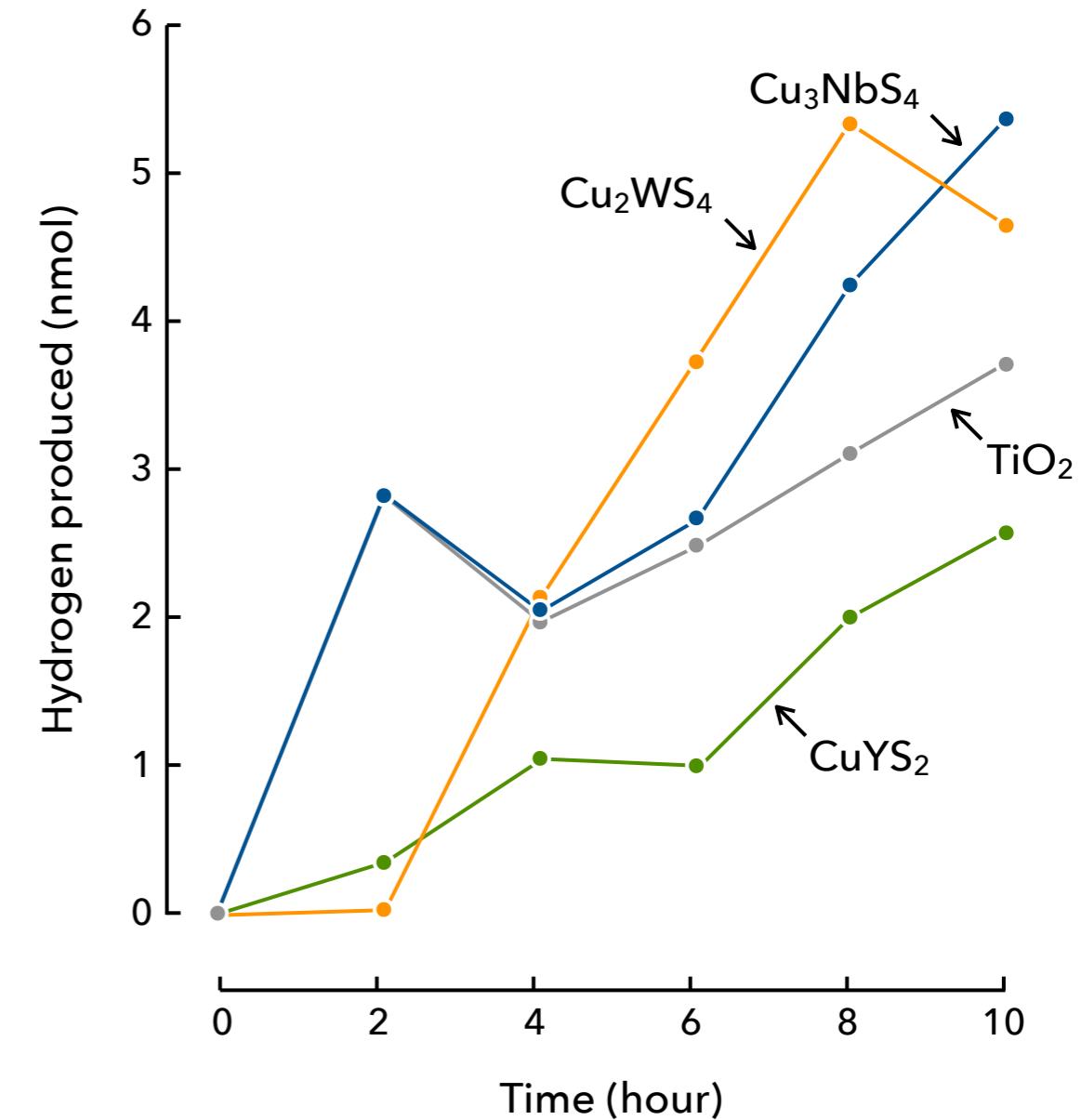
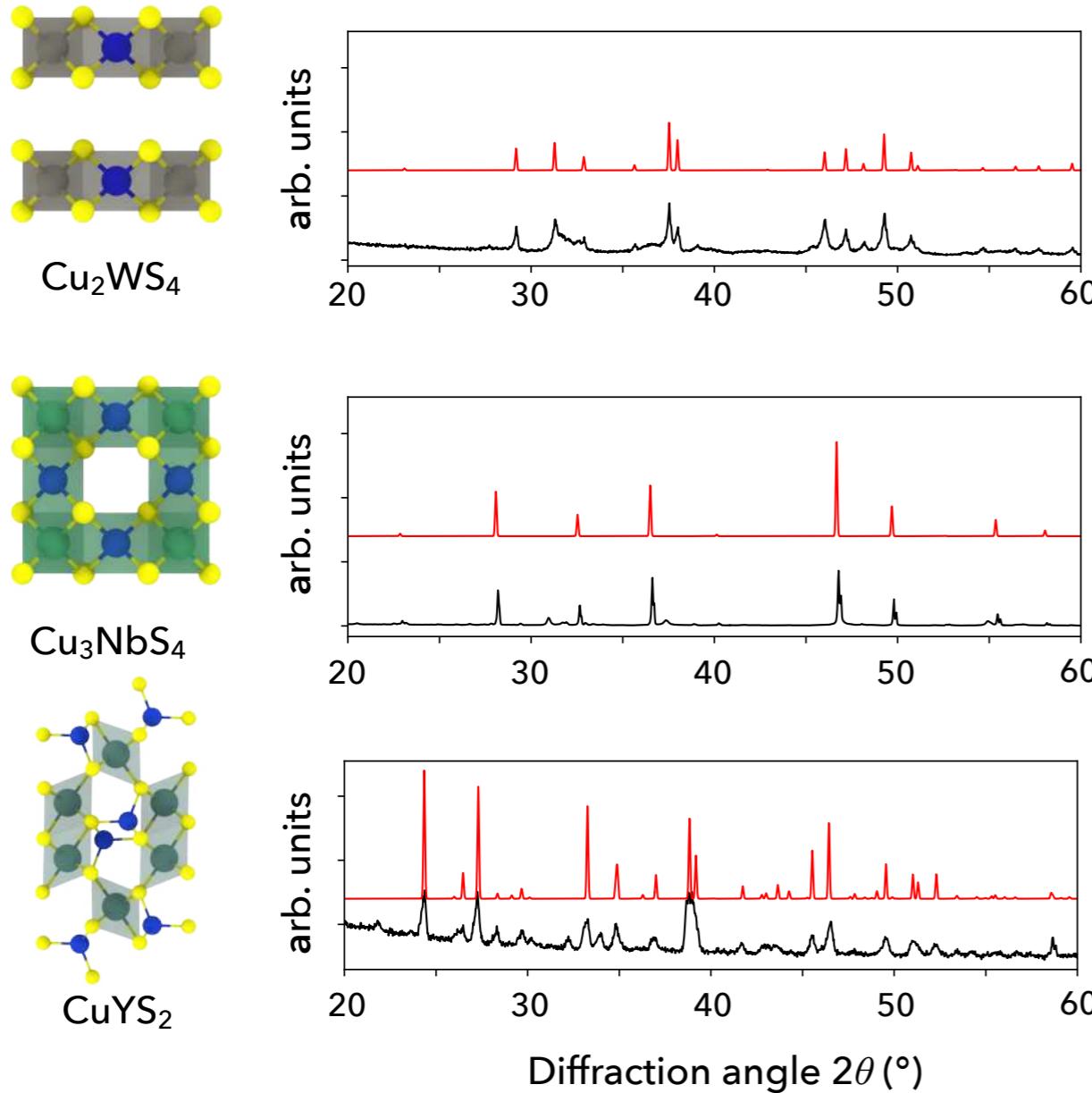
Venkat Gopalan



National Science Foundation,
Award No. DMREF/INFEWS-1729338

2nd and 3rd iteration: discovery of copper-based sulfides and oxysulfides

Second iteration of the discovery protocol, focusing on sulfides



Several of which are cuprous sulfides with efficiency comparable to TiO_2

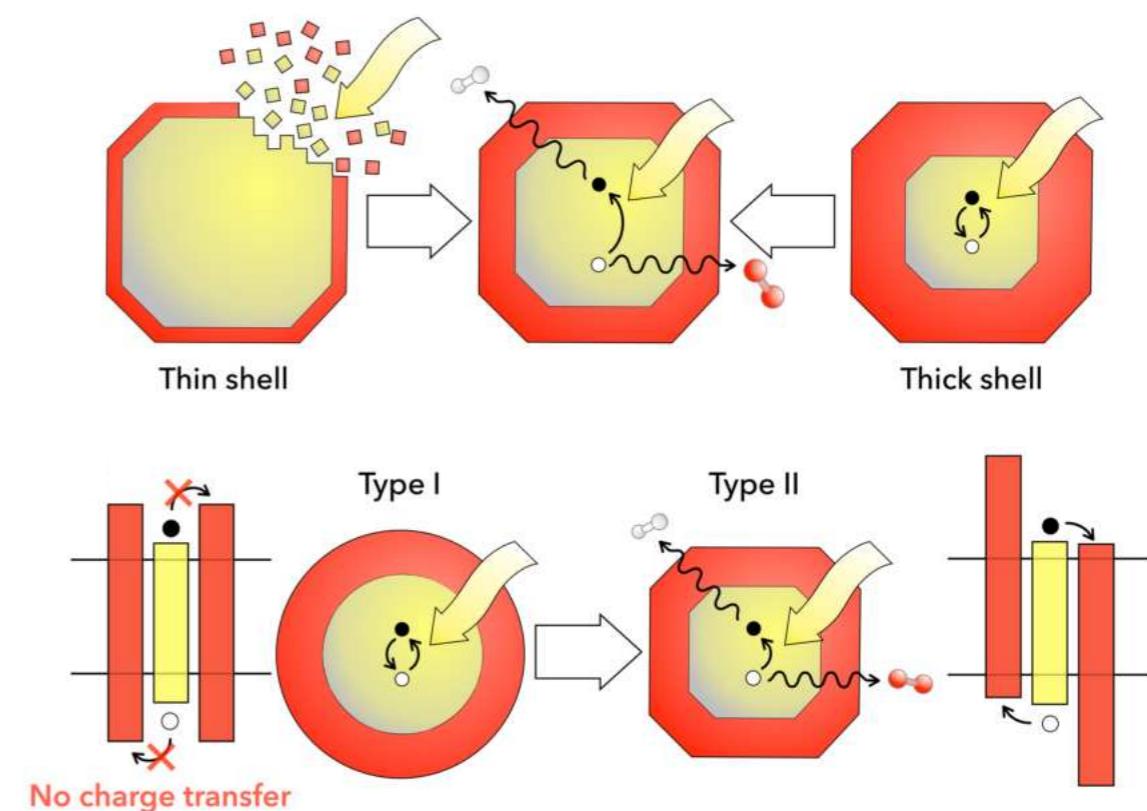
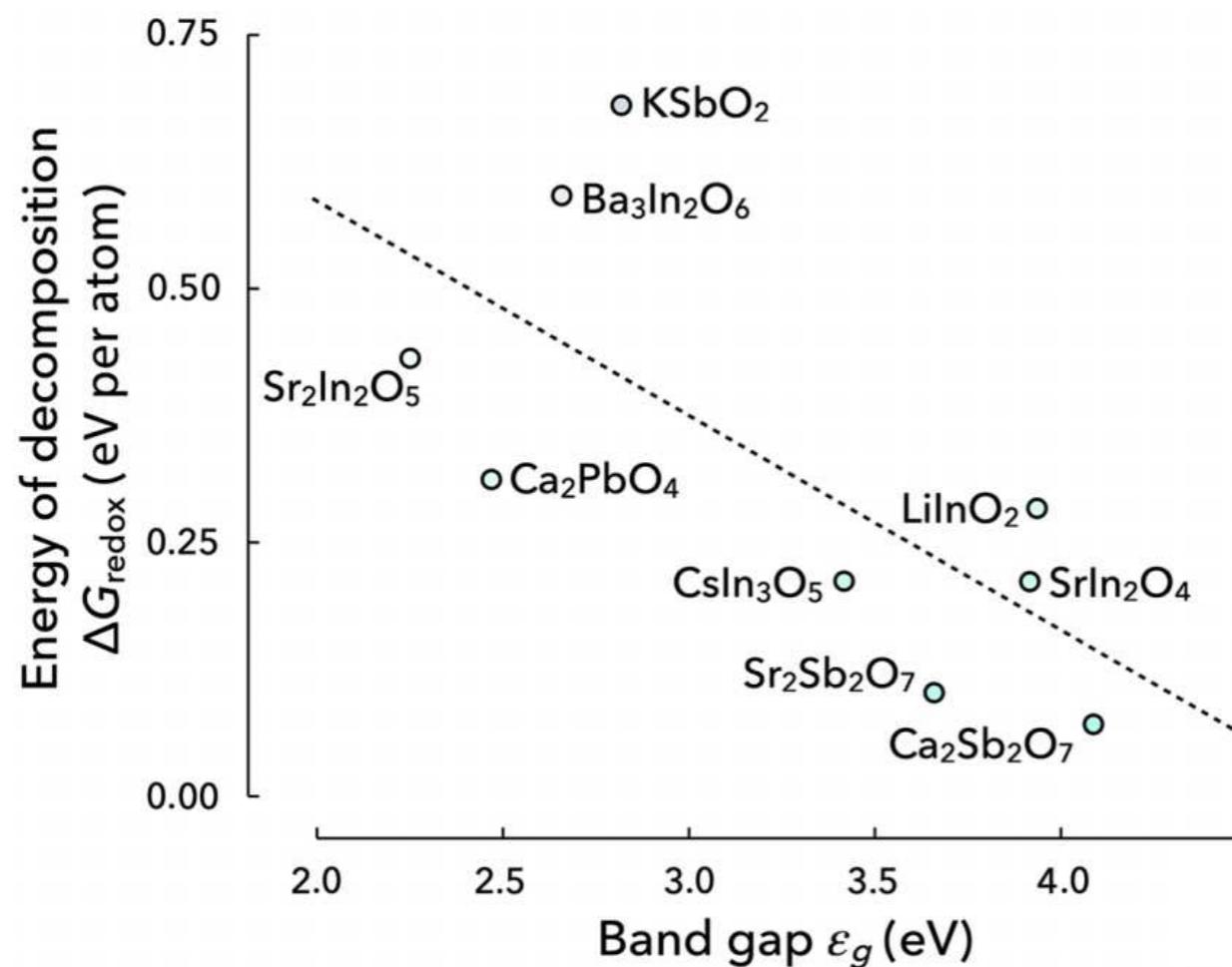
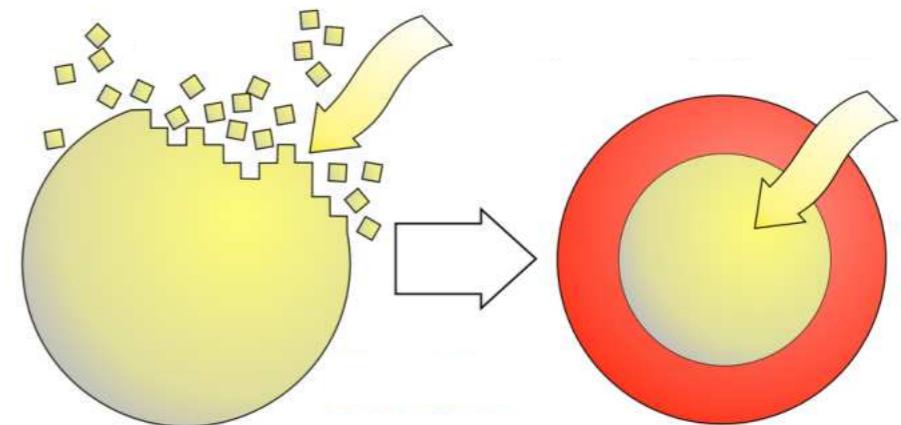
4th iteration: discovery of ternary oxides of s- and p-block metals

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Featured in Physics

Ternary Oxides of s- and p-Block Metals for Photocatalytic Solar-to-Hydrogen Conversion

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Model development for interfacial electrochemistry



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Materials discovery for photoelectrolysis



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