Simulating Materials for Energy Conversion and Storage from First Principles

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Advances, Challenges, and Long-Term Opportunities of Electrochemistry
Chemical Sciences Roundtable · November 18, 2019

PennState
College of Earth
and Mineral Sciences

Department of Materials
Science and Engineering
CHANGE THE WORLD

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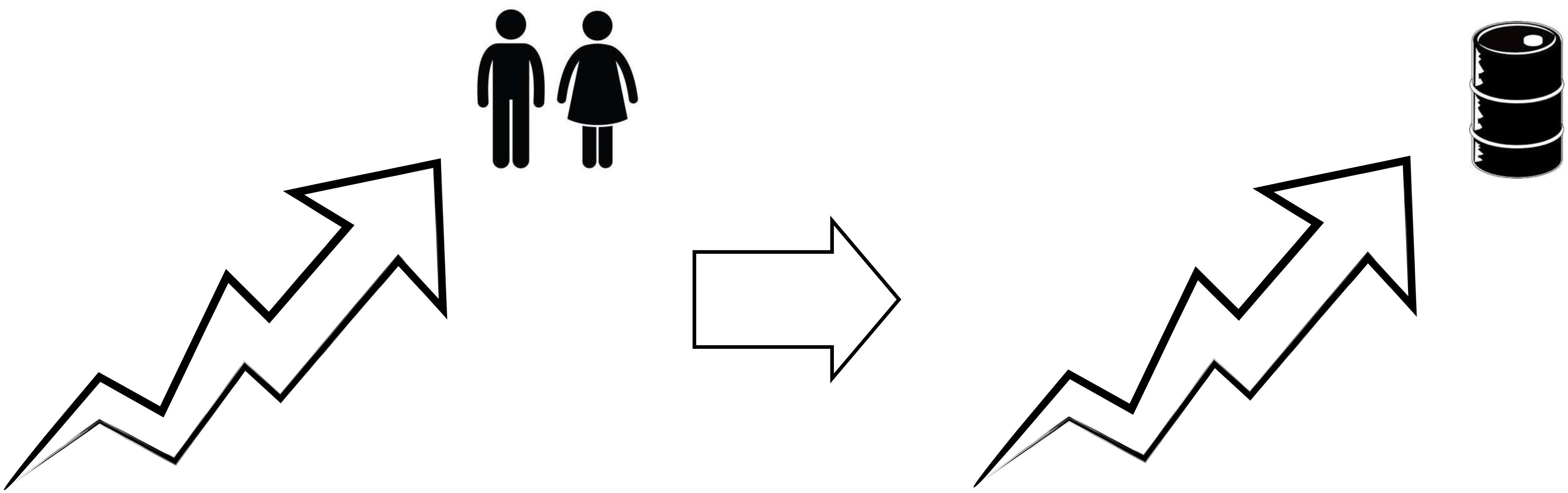
Cathy Badding	Characterization of photocatalysts, Cornell
Steven Baksa	Modeling of interfaces, Penn State
Quinn Campbell	Screening of photocatalysts, Penn State
Chitiphon Chuaicham	Synthesis and characterization of photocatalysts, Kyushu
Julian Fanghanel	Synthesis and screening of photocatalysts, Penn State
James Goff	Modeling of fuel cell catalysts, Penn State
Nicole Hall-Kirchner	Modeling of interfaces, Penn State
Jared Mondschein	Synthesis of photocatalysts, Penn State
Paul Orbe	Modeling of interfaces (RET), Penn State
Xavier Quintana	Screening of photocatalysts (REU), Penn State
Tiffany Rivera	Synthesis of photocatalysts (REU), Penn State
Kriti Seth	Synthesis of photocatalysts, Penn State
Nathan Smith (REU)	Modeling of interfaces (REU), Penn State
Hugo Haiyu Wang	Characterization of photocatalysts, Penn State
Andrés Villarino	Characterization of photocatalysts, Cornell
Vincent Yihuang Xiong	Modeling of interfaces, Penn State

How to achieve global energy sustainability?

To get a sense of the magnitude of the challenge…

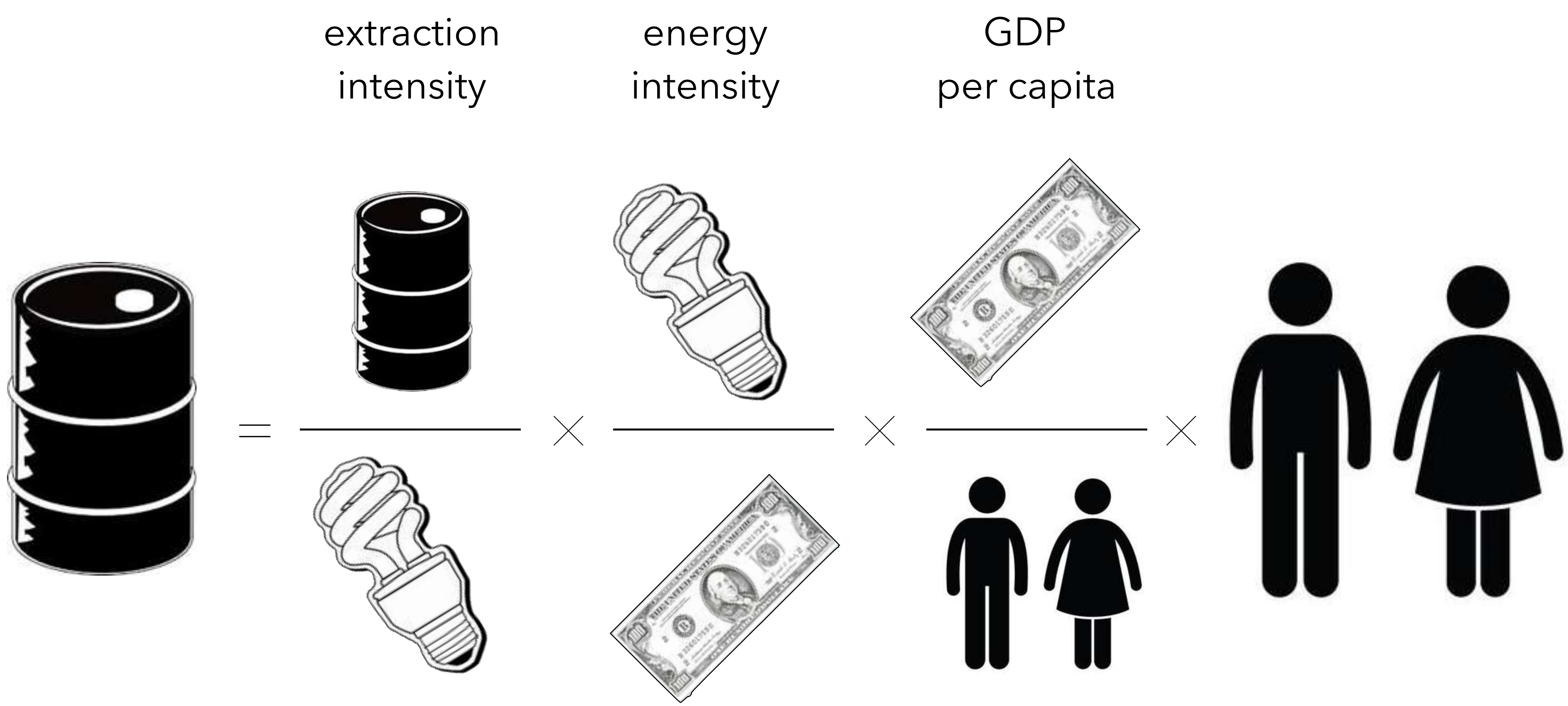


growth
of world population

depletion
of fossil resources

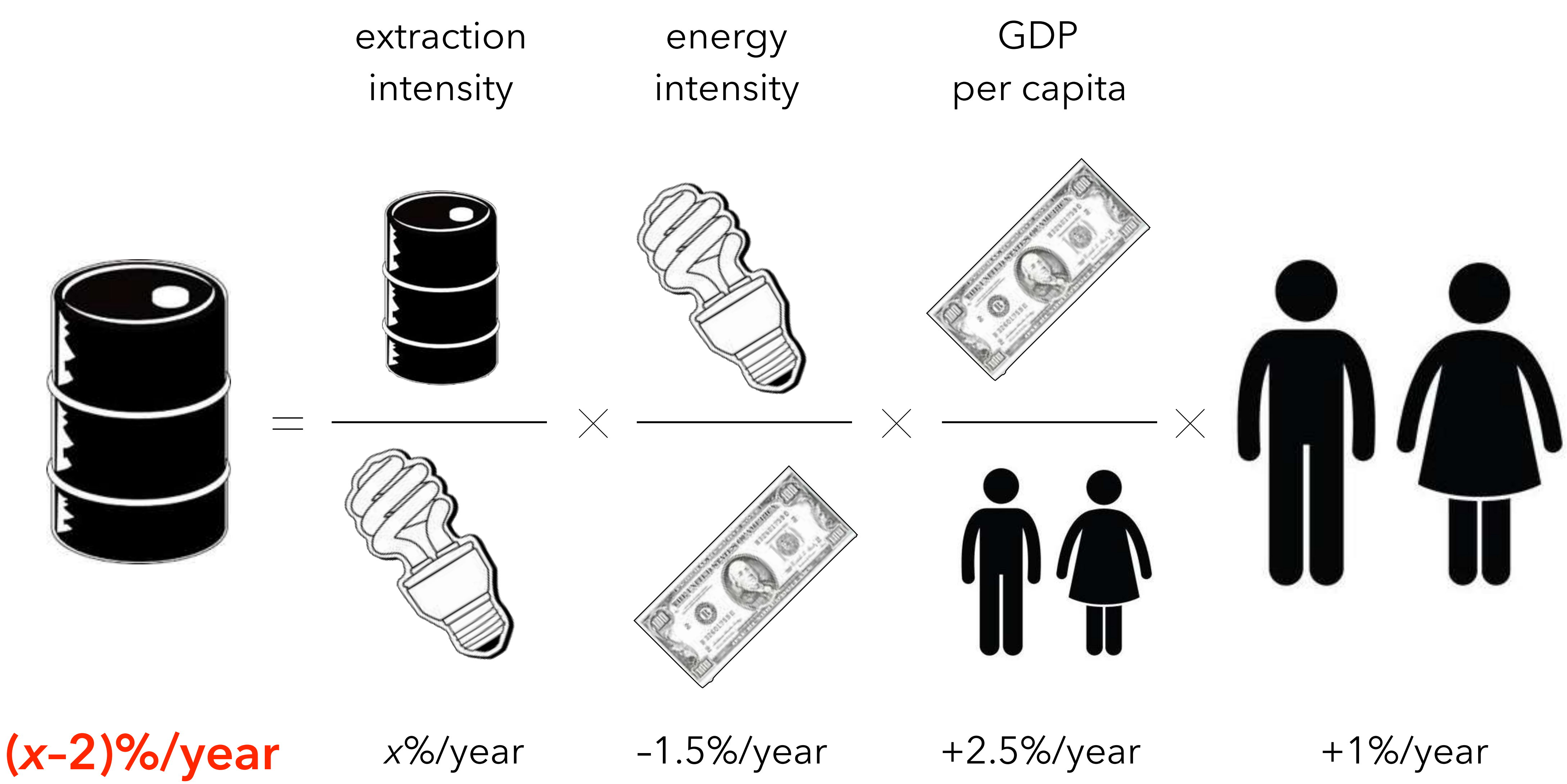
How to achieve global energy sustainability?

The relation involves **3 factors**



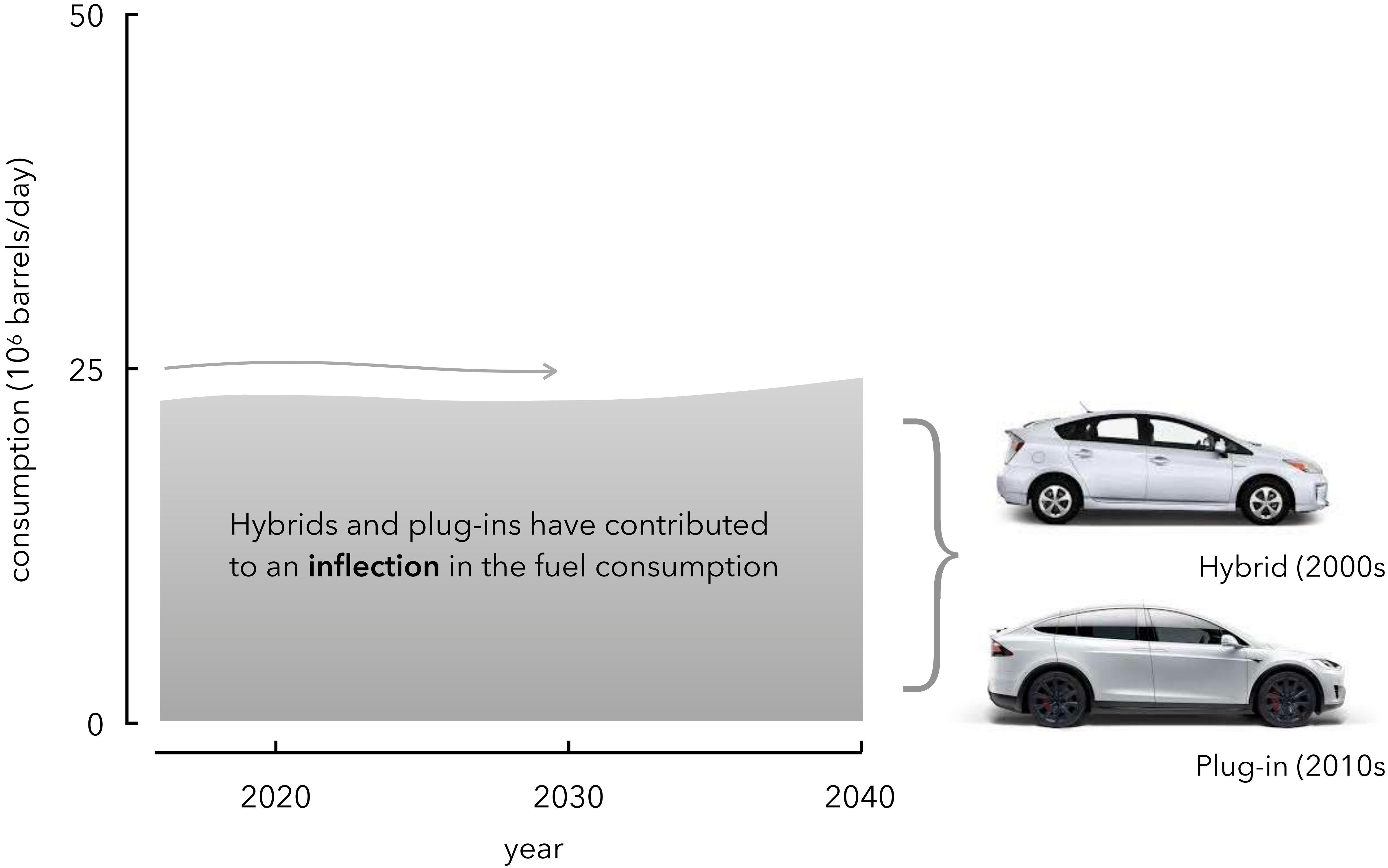
How to achieve global energy sustainability?

The **pace** of the transition to renewables must be **>2%/year**



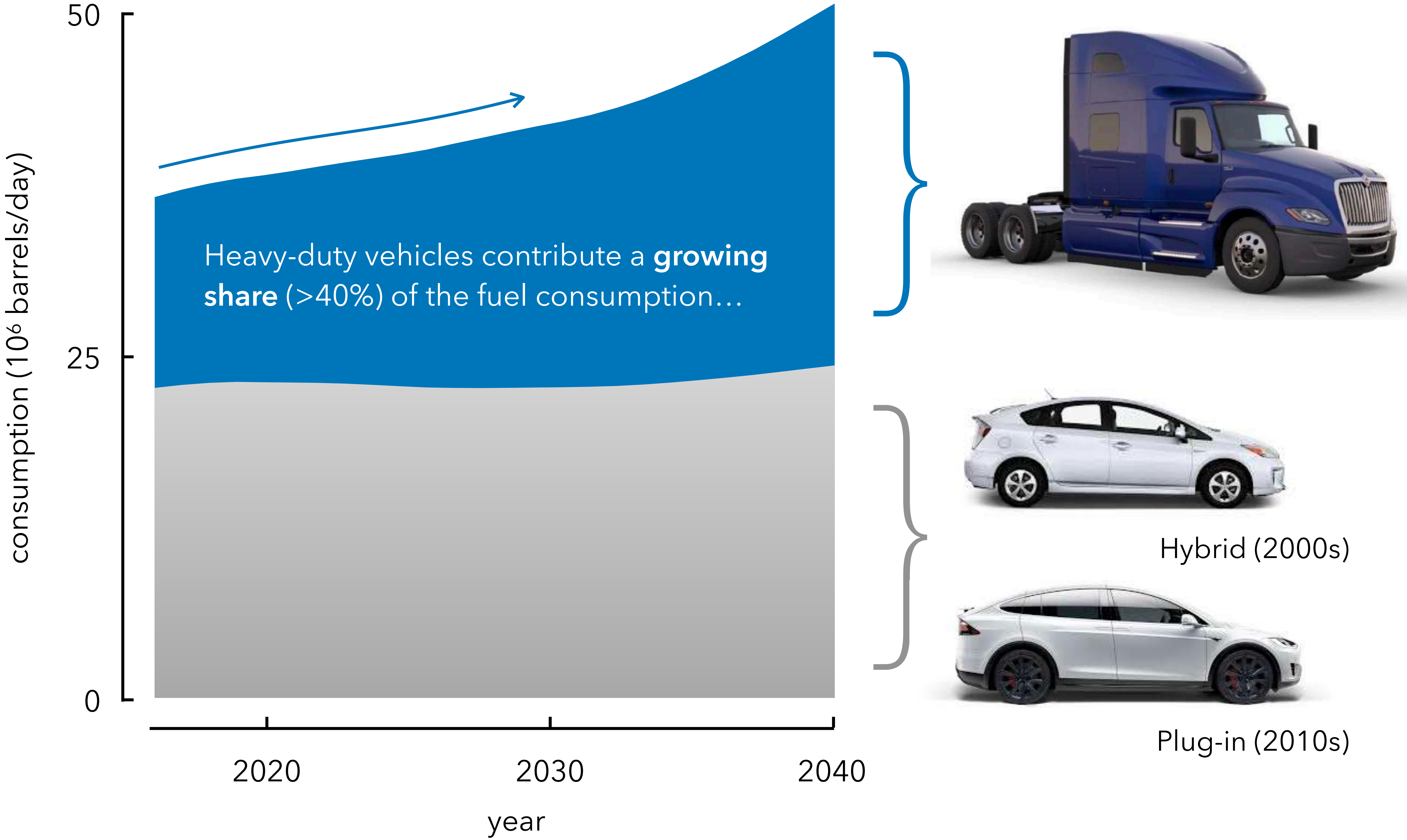
World Bank, *World Development Indicators* (2018)
Enerdata, *Global Energy Statistical Yearbook* (2019)

Some reasons to be optimistic…



U.S. Energy Information Administration, *Annual Energy Outlook* (2018)
International Energy Agency, *Global Electric Vehicle Outlook: 'Two Million and Counting'* (2017)

Some reasons to worry…



U.S. Energy Information Administration, *Annual Energy Outlook* (2018)
International Energy Agency, *Global Electric Vehicle Outlook: 'Two Million and Counting'* (2017)

Artificial photosynthesis as a sustainable option

Artificial photosynthesis uses sunlight to convert carbon dioxide and water into chemical fuels

$$CO_2 \xrightarrow[2H_2O]{h\nu} CH_4 + 2O_2$$

$$n\,CO_2 \xrightarrow[n\,H_2O \;\to\; {}^{(3n-1)}/_{2}\,O_2]{h\nu} C_nH_{2n+1}OH$$

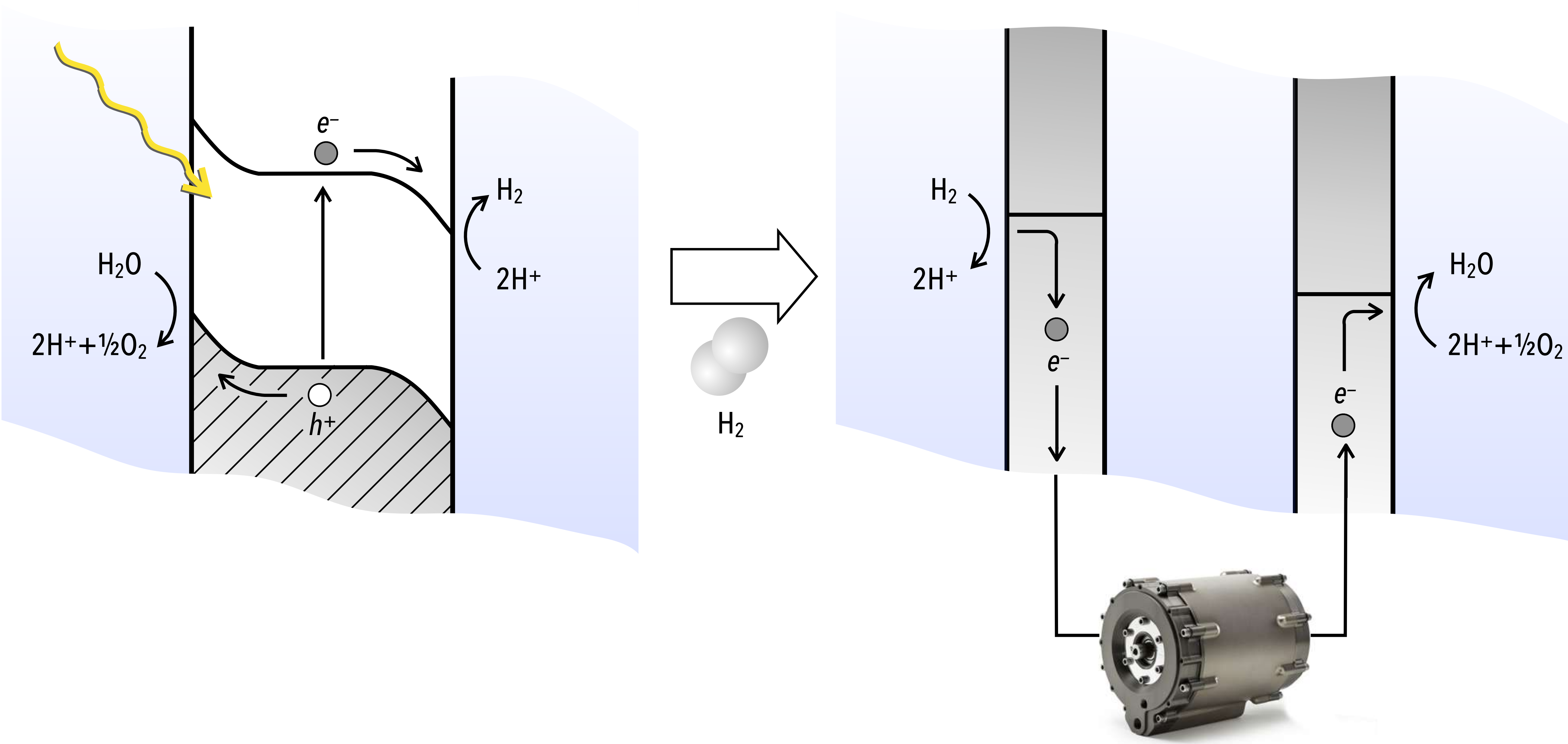
$$H_2O \xrightarrow{h\nu} H_2 + {}^{1}/_{2}O_2$$

Powering the Planet, Lewis and Nocera (2006)

Hydrogen as energy carrier

Water splitting can be promoted
on a photocatalytic semiconductor

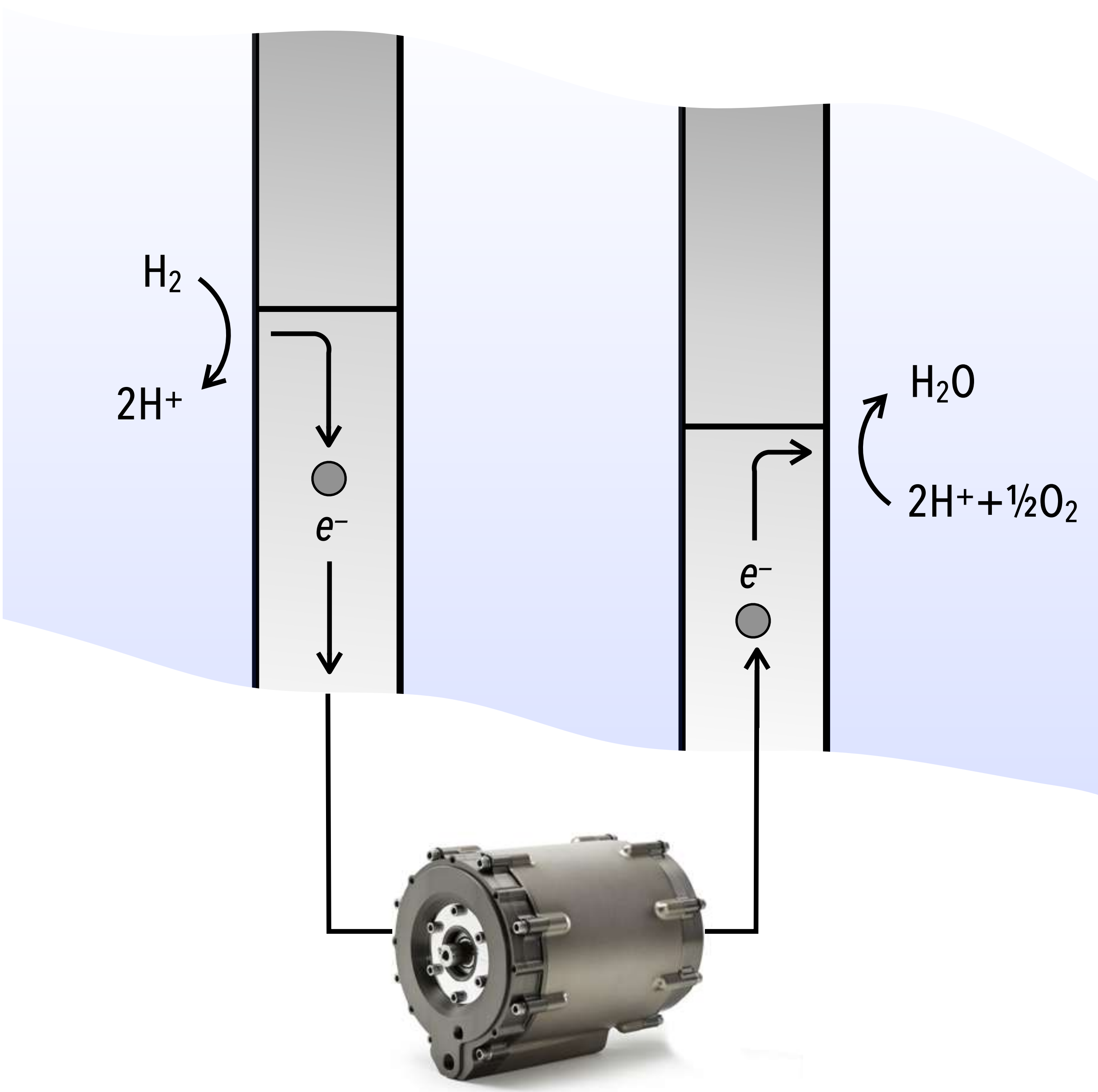
The process can be reversed
in a fuel cell to produce electrical work

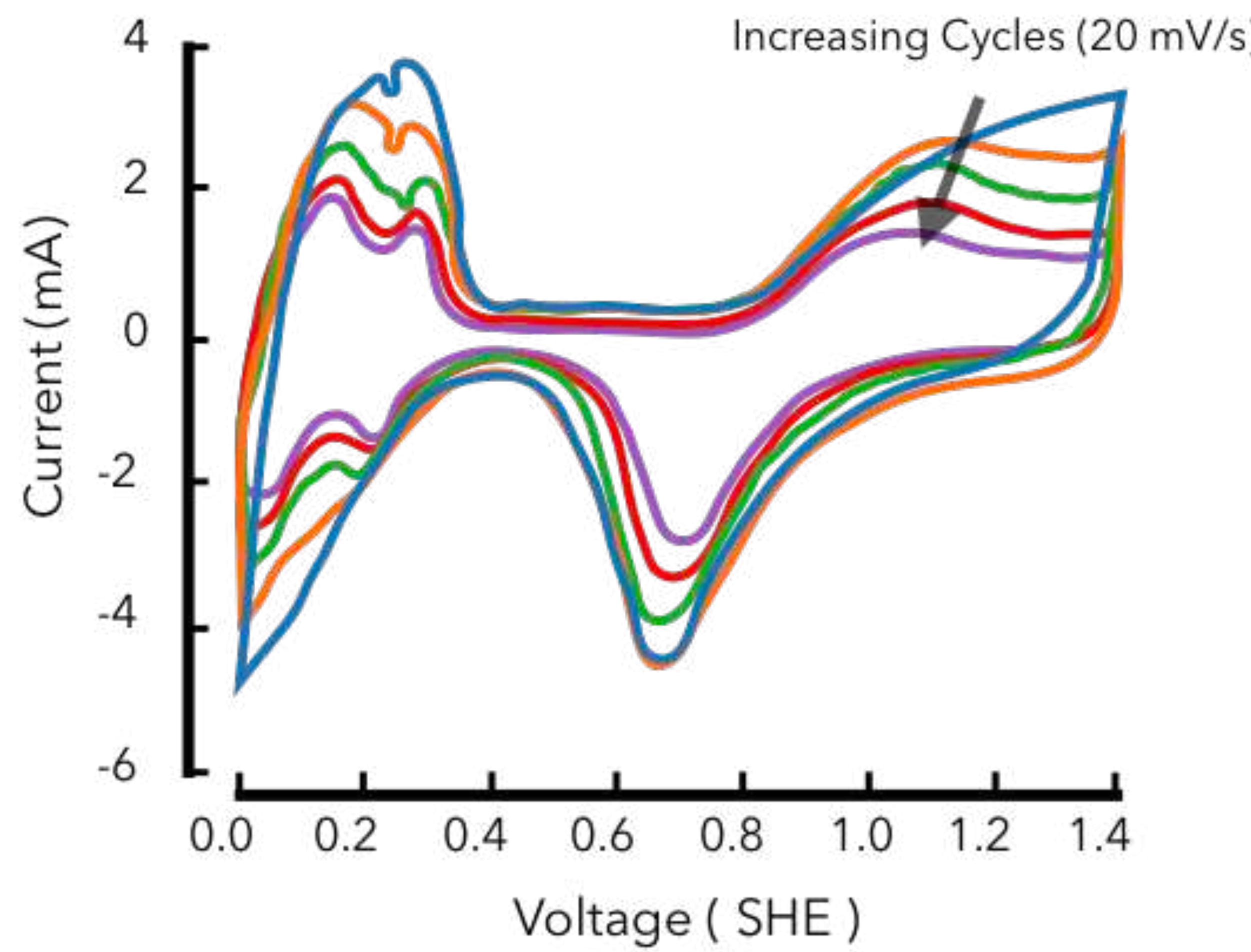


The cycle can be repeated, making hydrogen an attractive **energy carrier**

Challenge: Durability of fuel-cell electrodes

The voltage window of fuel cells is limited due to
the dissolution of catalytic nanoparticles

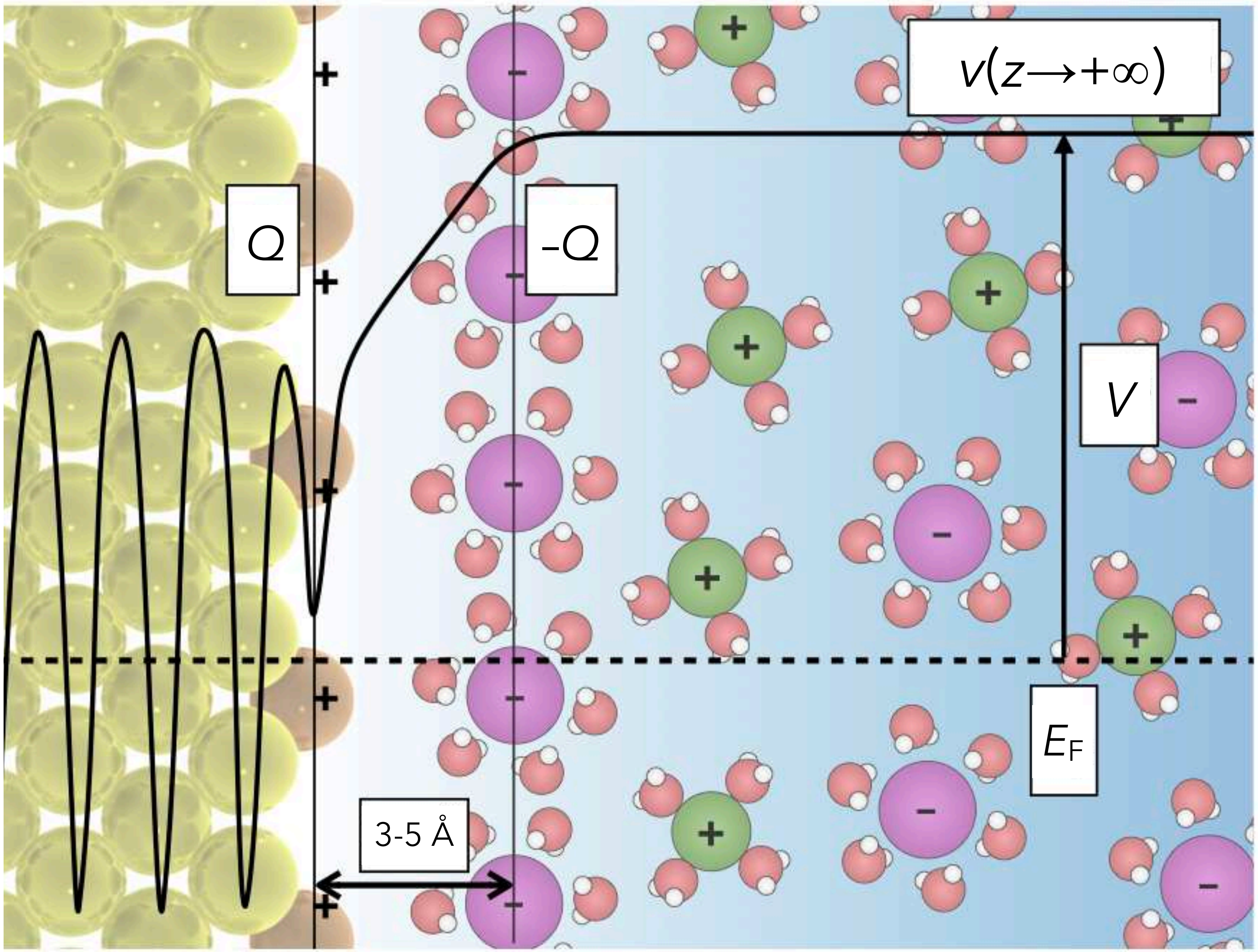




Sugawara *et al.*, *Journal of Electroanalytical Chemistry* 662, 379 (2011)

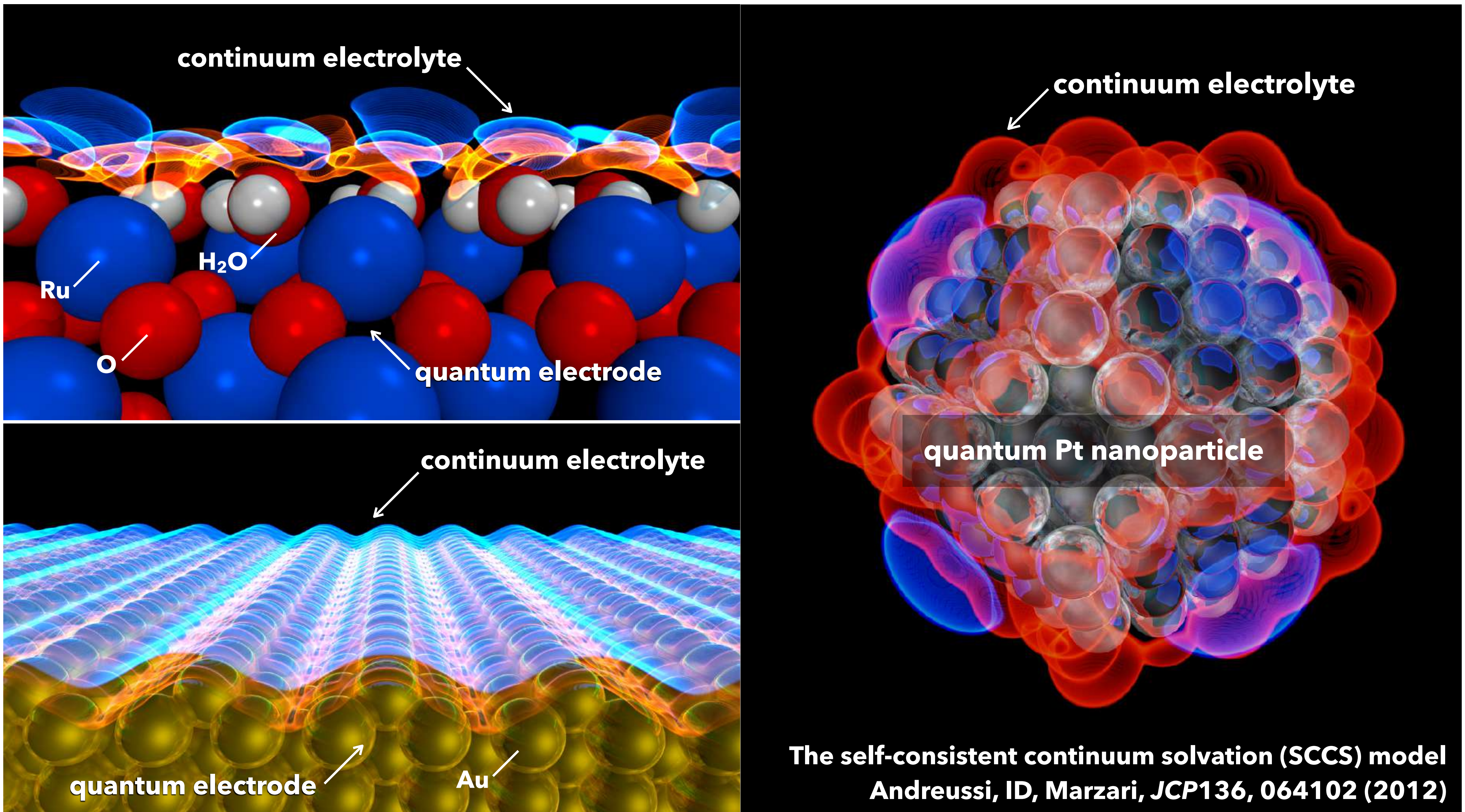
Simulating electrochemical interfaces

Increasing the voltage causes charge accumulation and interface polarization



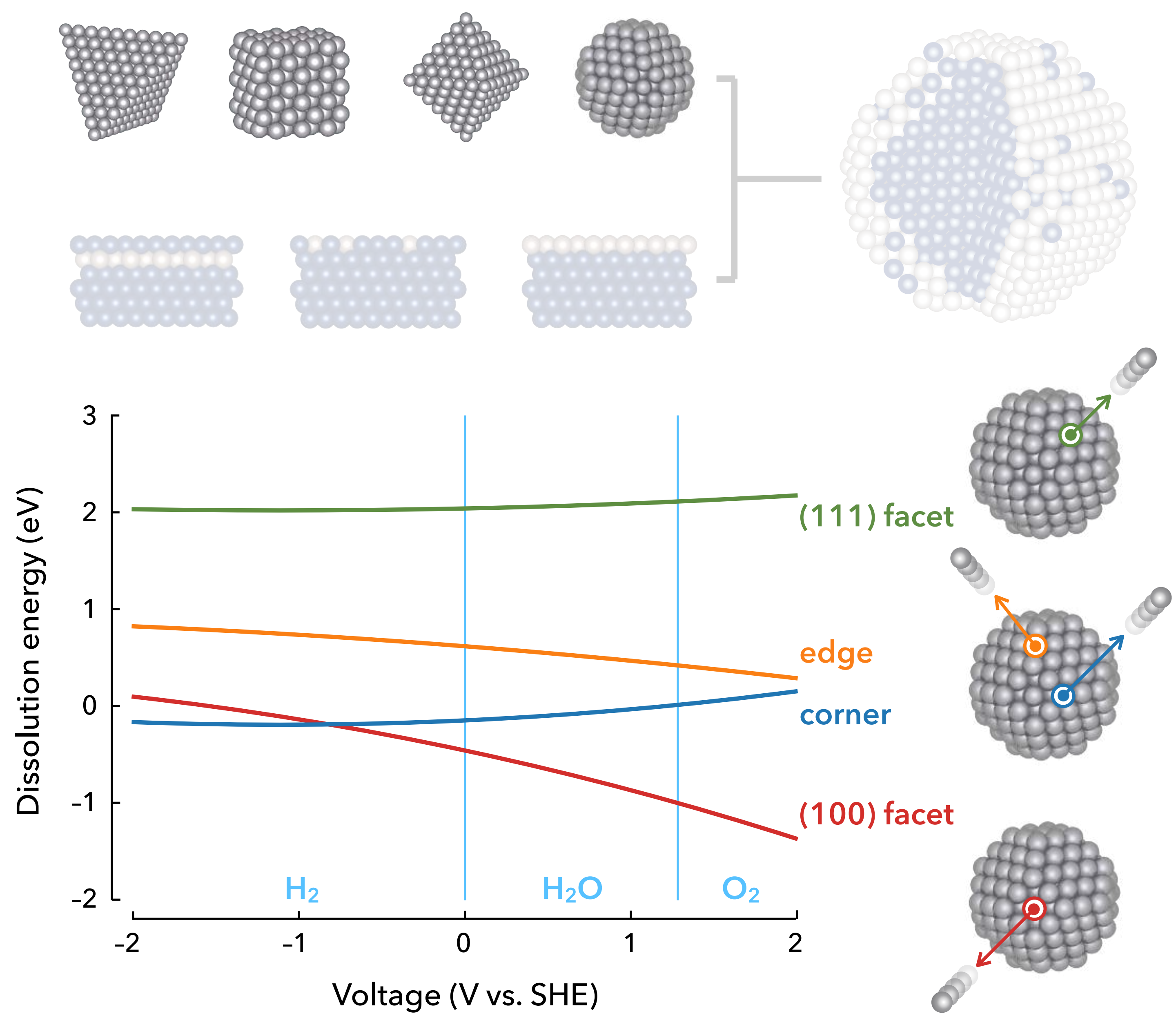
How to account for long-range interface polarization in quantum simulations?

Quantum-continuum embedding is an effective approach
to model quantum systems in electrochemical environments



Predicting electrochemical dissolution and restructuring

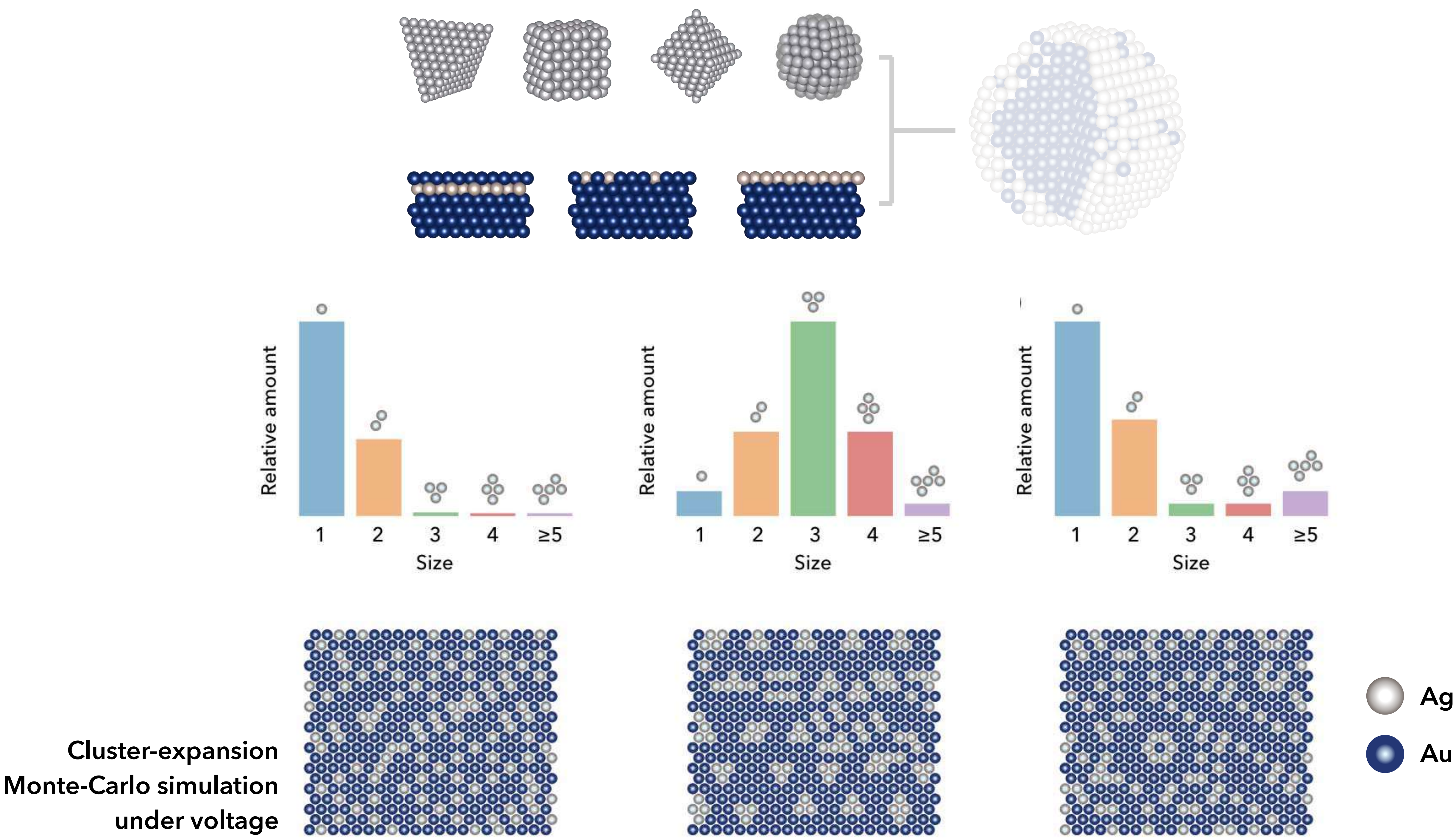
The ability to model electrochemical systems is of interest to understand which surface sites are the most susceptible to electrodissolution…



Goff, Sinnott, ID, *Journal of Chemical Physics* (submitted, 2019)
Weitzner and ID, *Journal of Chemical Physics* 150, 041715 (2019)

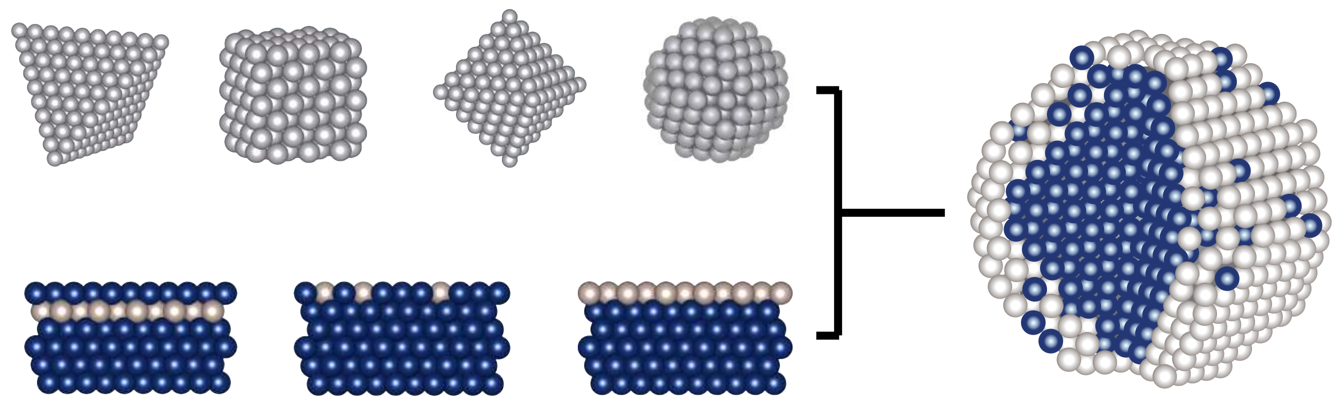
Predicting electrochemical dissolution and restructuring

The model can predict the influence of the voltage
on clustering trends at bimetallic electrodes

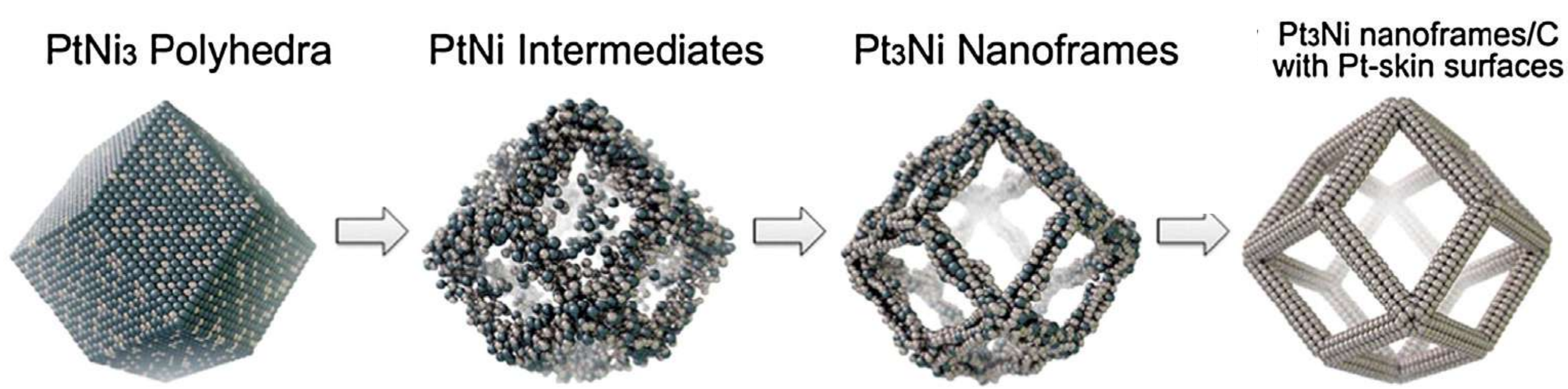


Predicting electrochemical dissolution and restructuring

The model is being developed to tackle
the stability of bimetallic and shape-controlled nanoparticles…

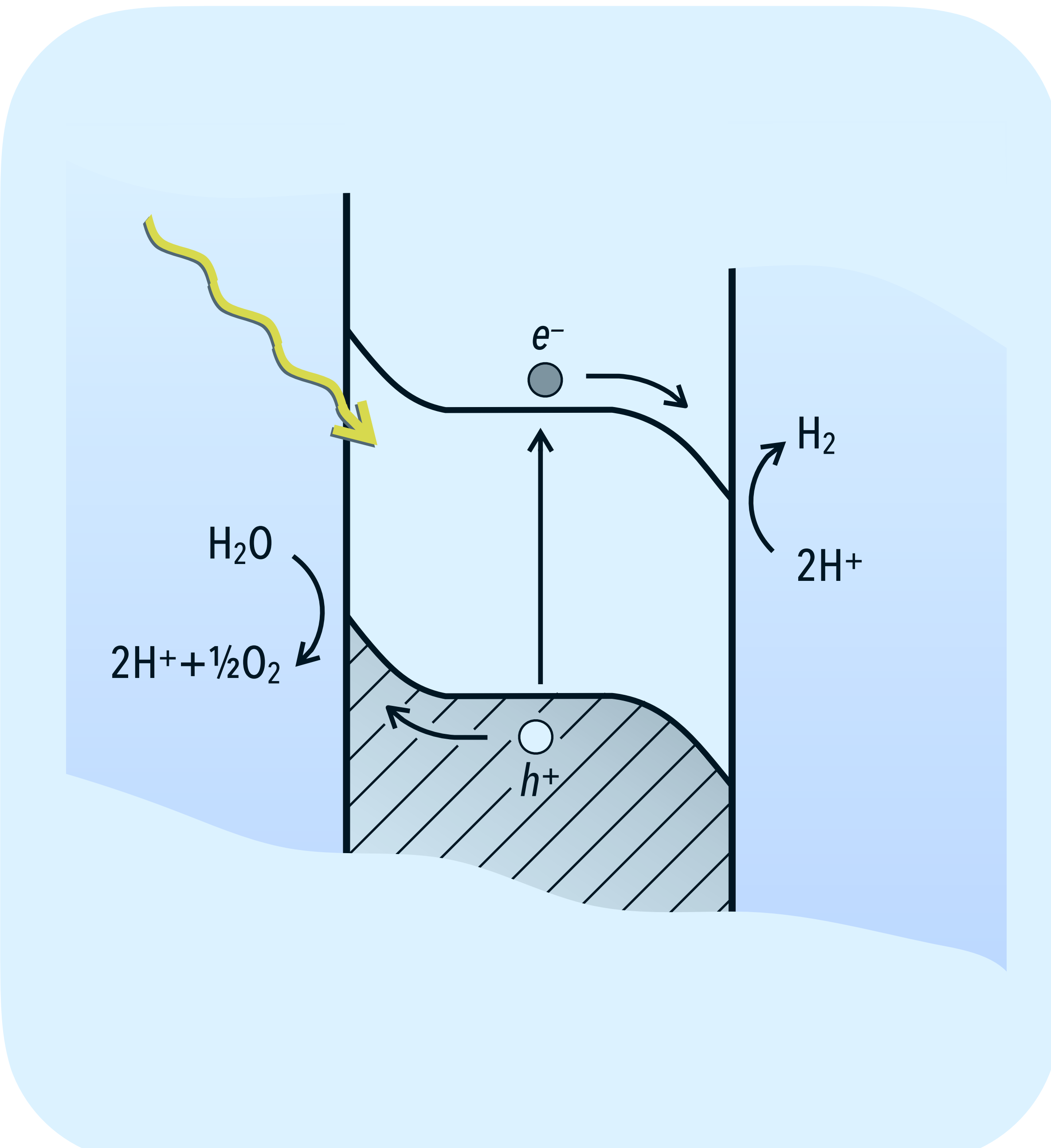


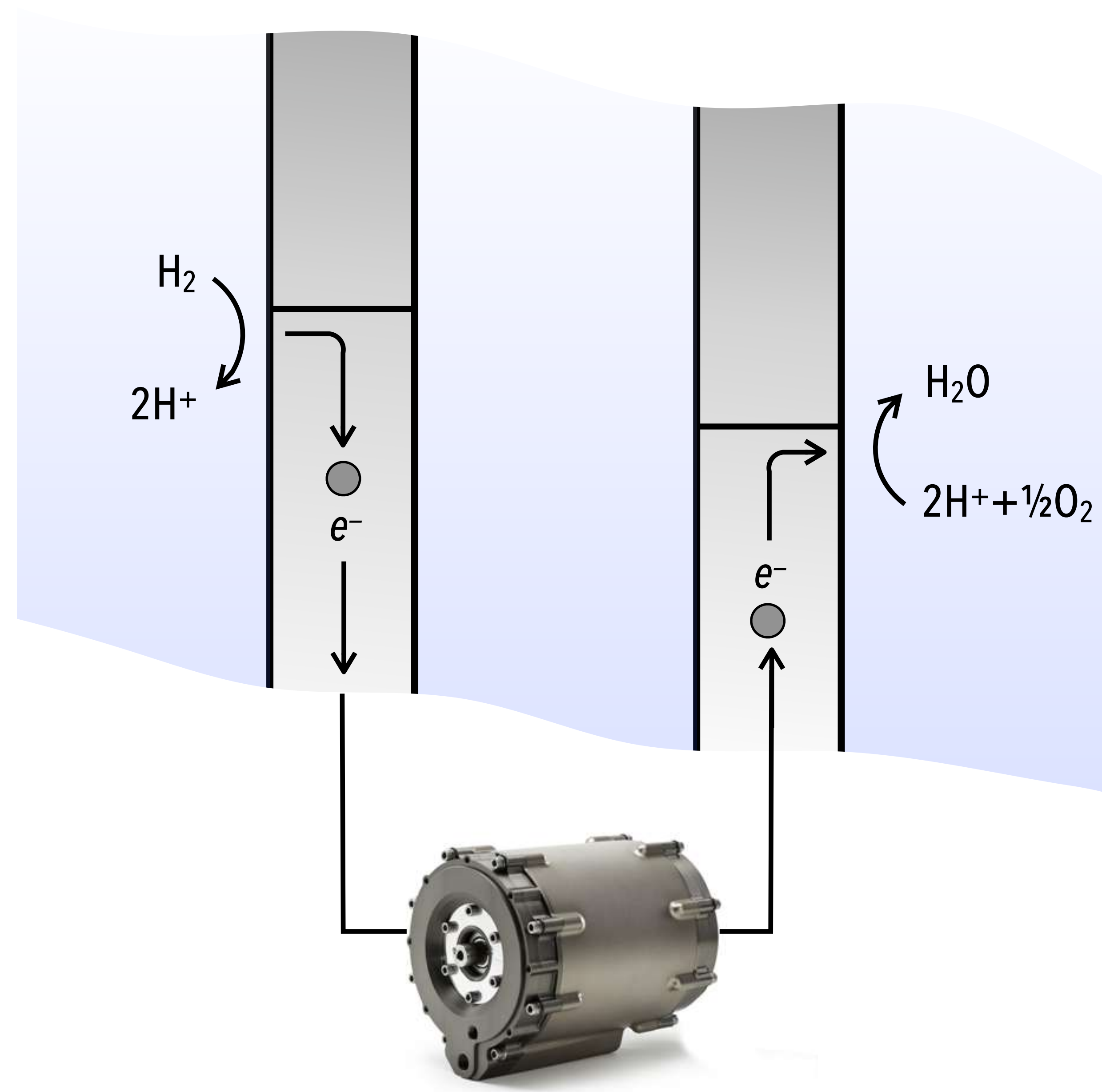
DOE, Office of Science, Basic Energy Sciences, CPIMS Program,
Award No. DE-SC0018646 (2018)



Kang, Yang, Markovic, Stamenkovic, *Nano Today* 11, 587 (2016)

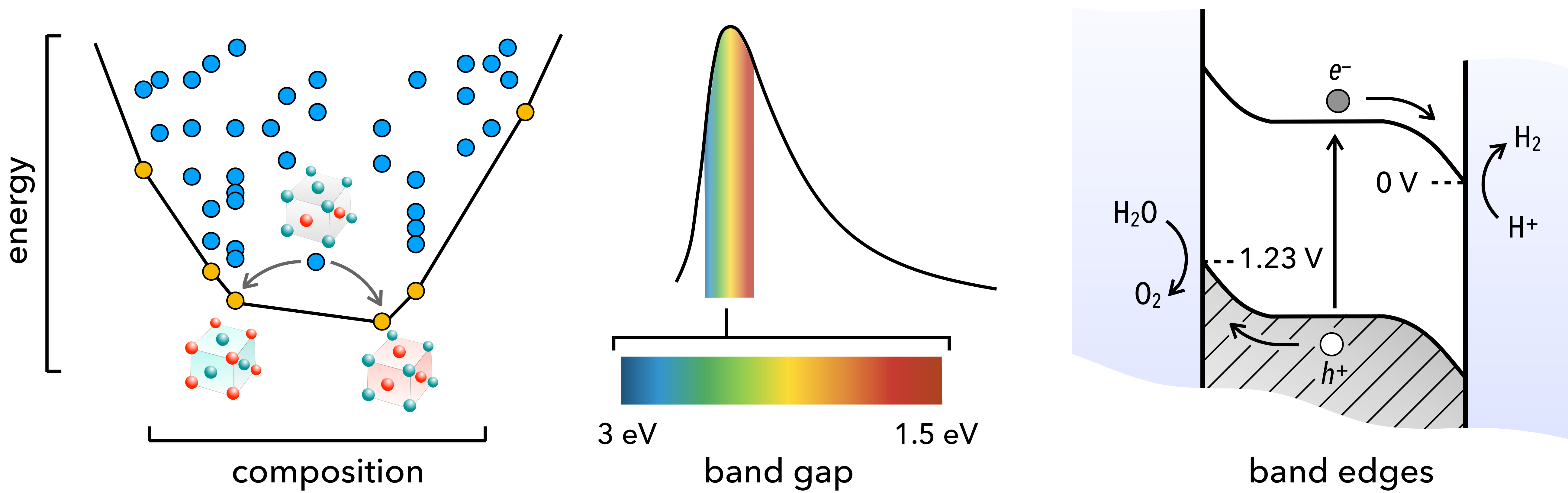
Challenge: Discovering water-splitting semiconductors





First-principles computational screening

Fundamental **properties** of relevance to water splitting can be calculated from first principles



The **success** of this screening is critically dependent on the reliability of the first-principles approximation

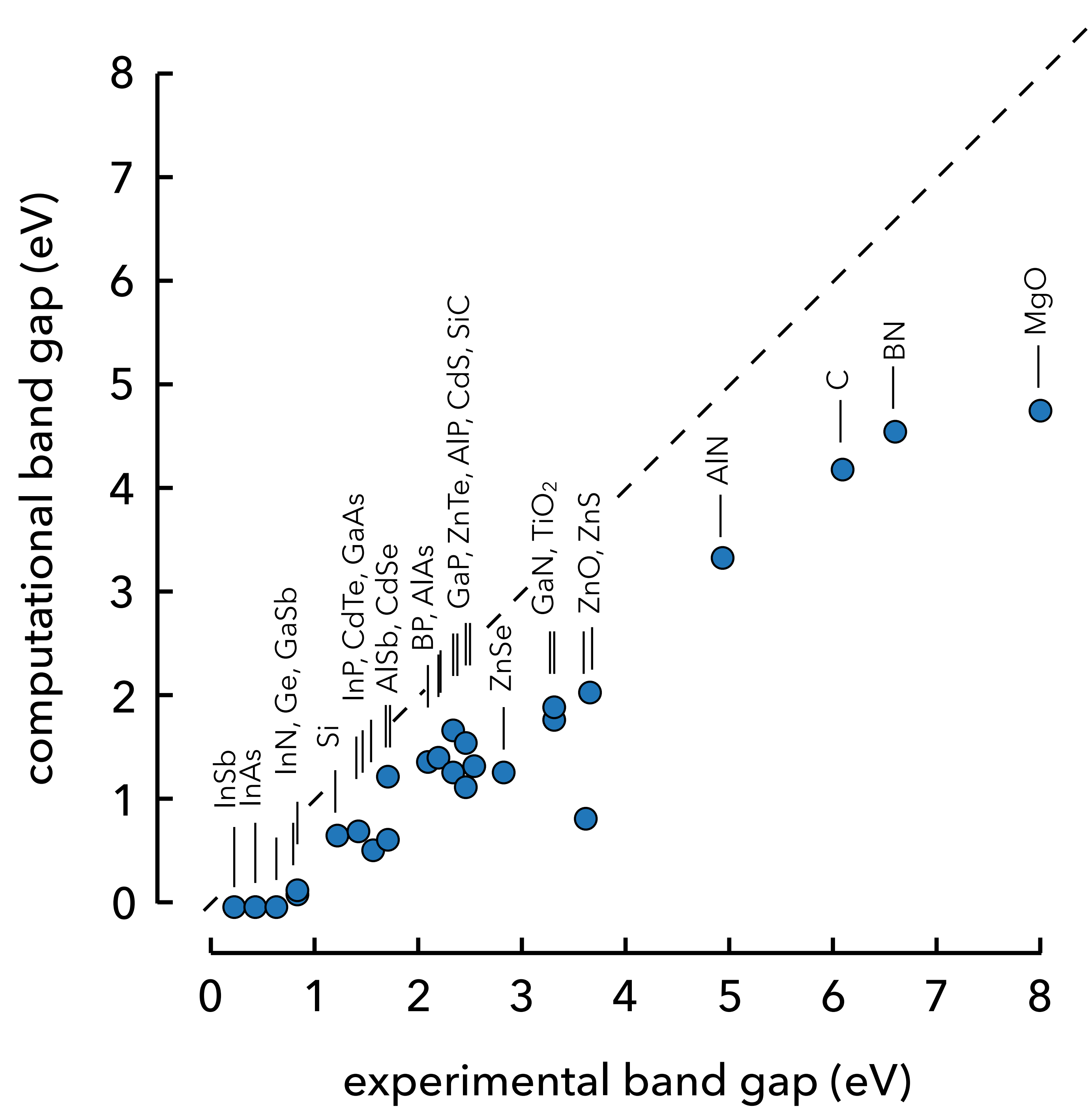
What makes a reliable prediction?

many-body

$$H\Psi = E\Psi$$

$$h_\rho \varphi = \varepsilon \varphi$$

one-body



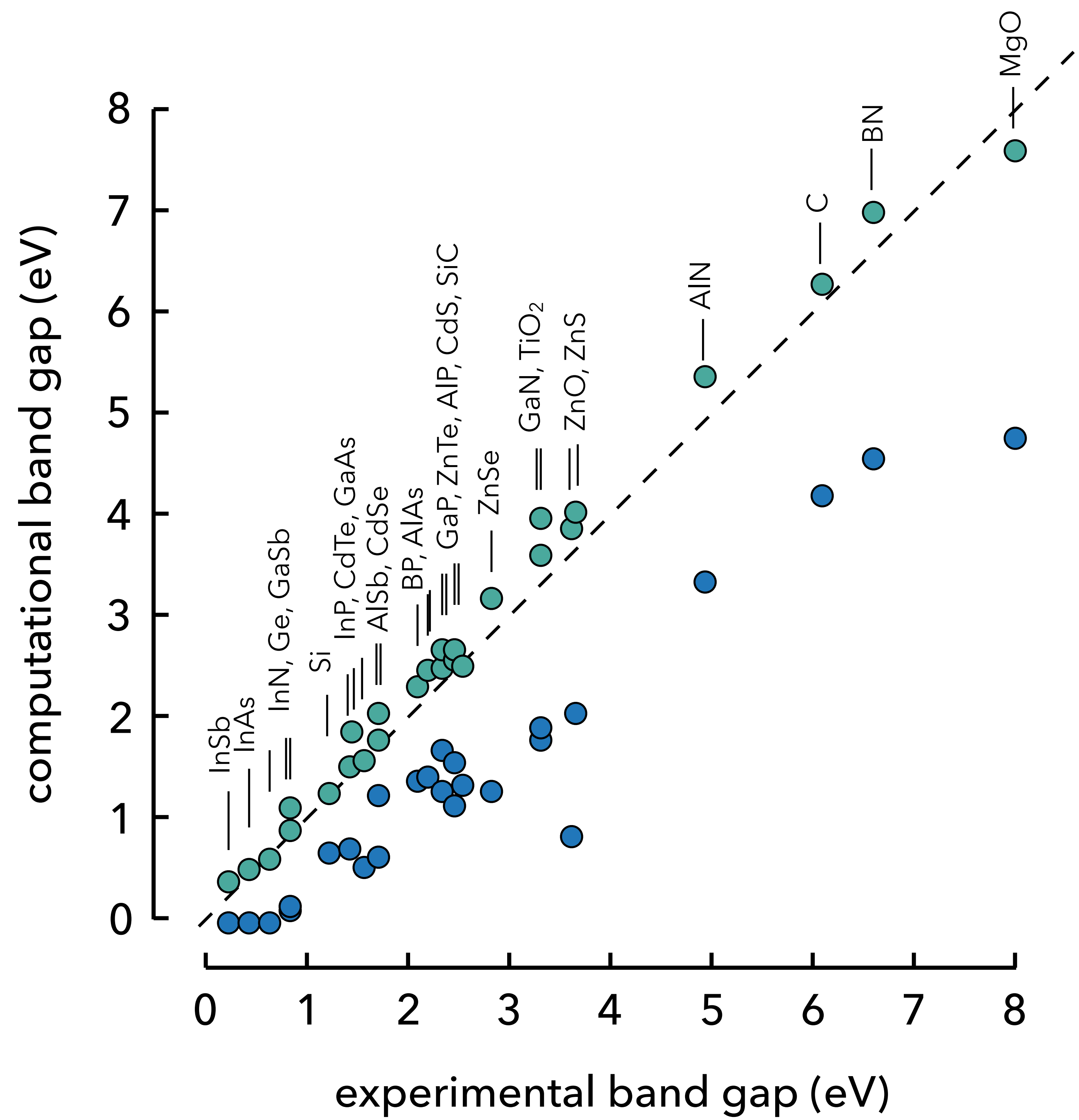
Borghi *et al.*, *PRB* 90, 075135 (2015)
ID *et al.*, *PRB* 82, 115121 (2010)
Nguyen *et al.*, *PRL* 114, 166405 (2015)
Nguyen *et al.*, *PRX* 8, 021051 (2018)

What makes a reliable prediction?

$$H\Psi = E\Psi$$

$$h_\rho \varphi = \varepsilon \varphi$$

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



Borghi *et al.*, *PRB* 90, 075135 (2015) Nguyen *et al.*, *PRL* 114, 166405 (2015)

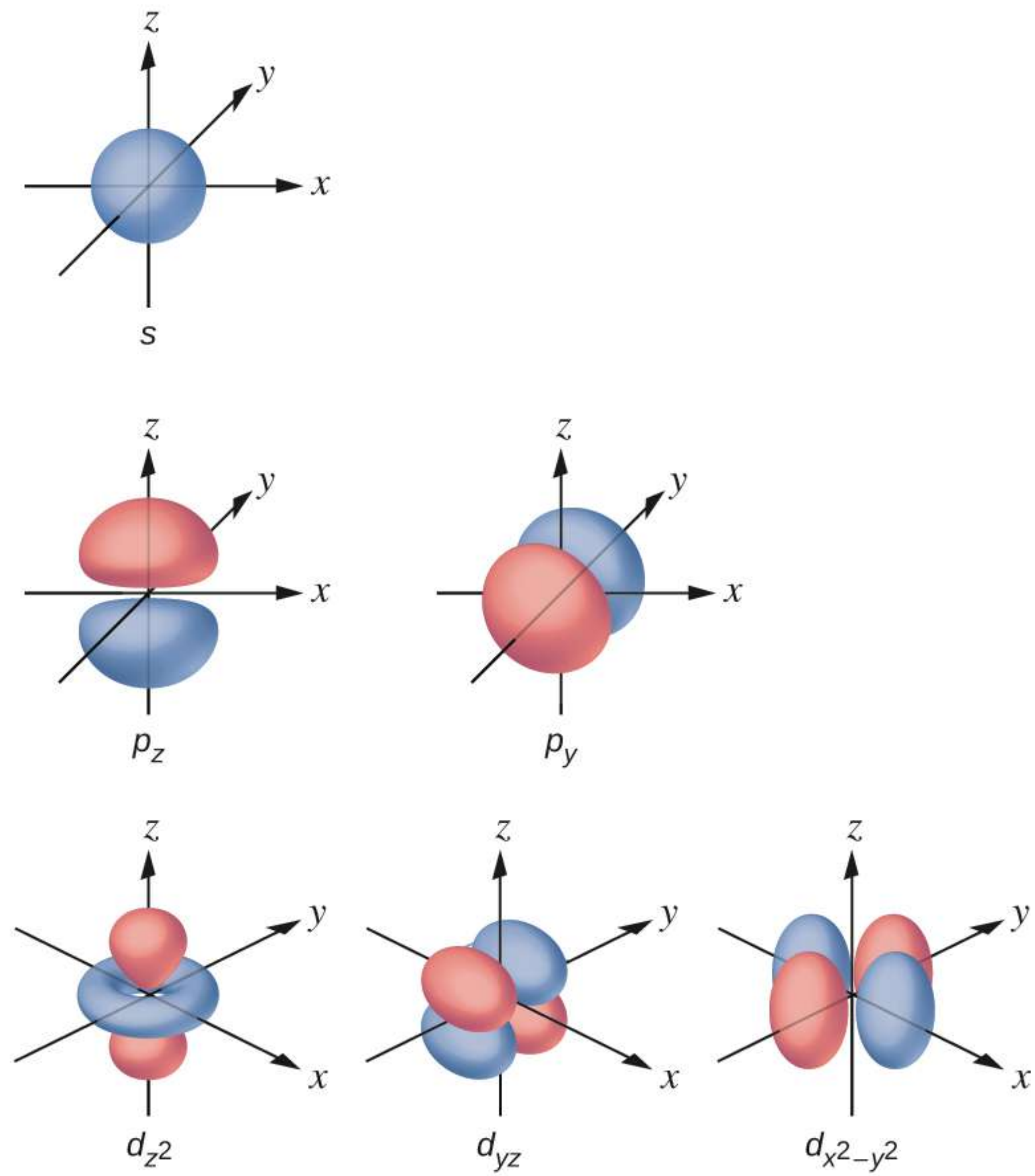
ID *et al.*, *PRB* 82, 115121 (2010) Nguyen *et al.*, *PRX* 8, 021051 (2018)

What makes a reliable prediction?

$$H\Psi = E\Psi$$

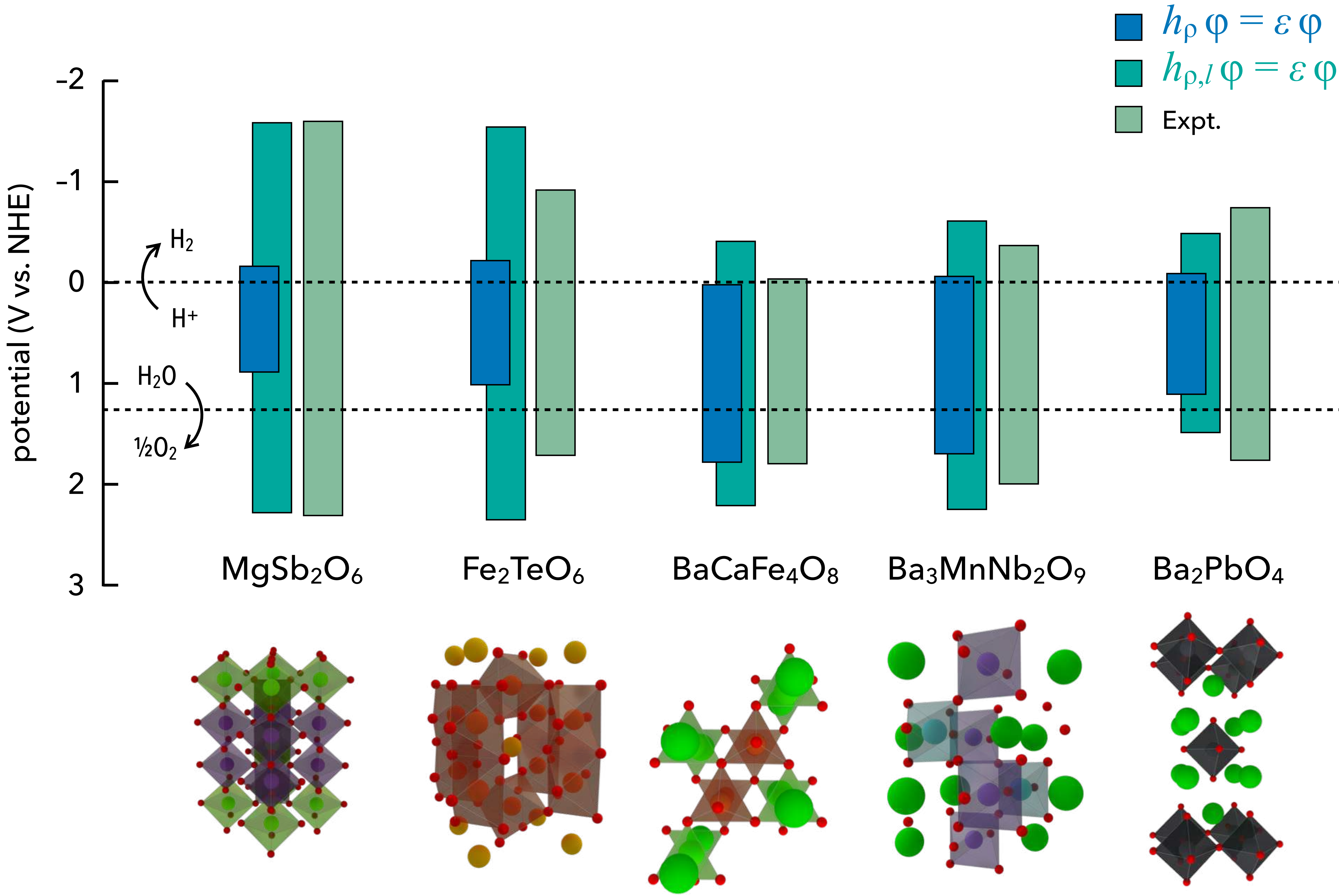
$$h_\rho\,\varphi = \varepsilon\,\varphi$$

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

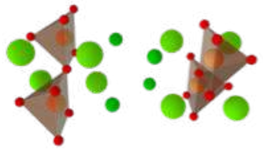
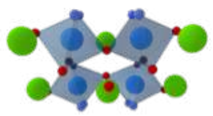
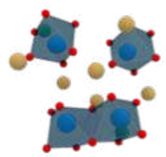
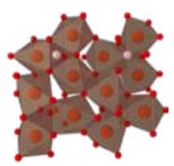
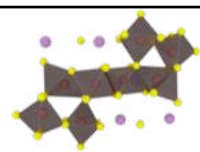
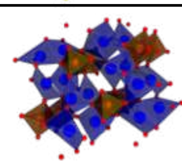
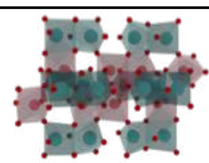
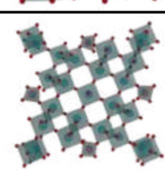
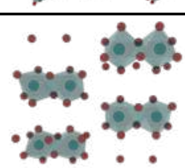
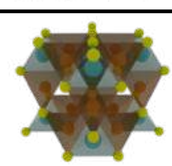


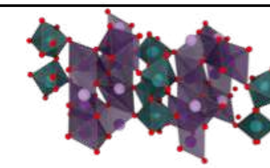
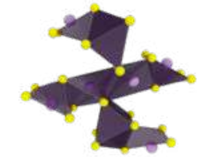
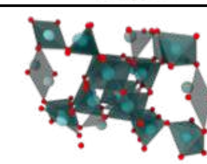
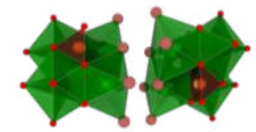
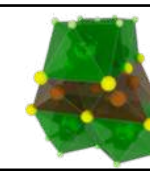
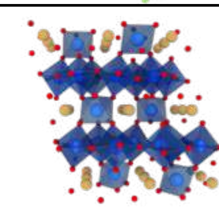
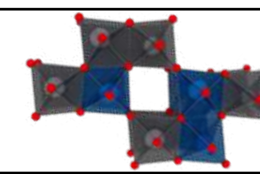
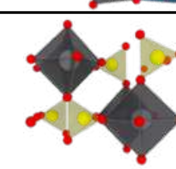
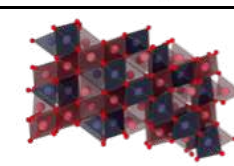
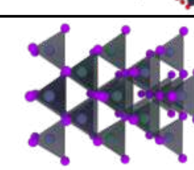
Timrov *et al.*, *PRB* 98, 085127 (2018)
Campbell *et al.*, *in preparation* (2018)

Comparative assessment

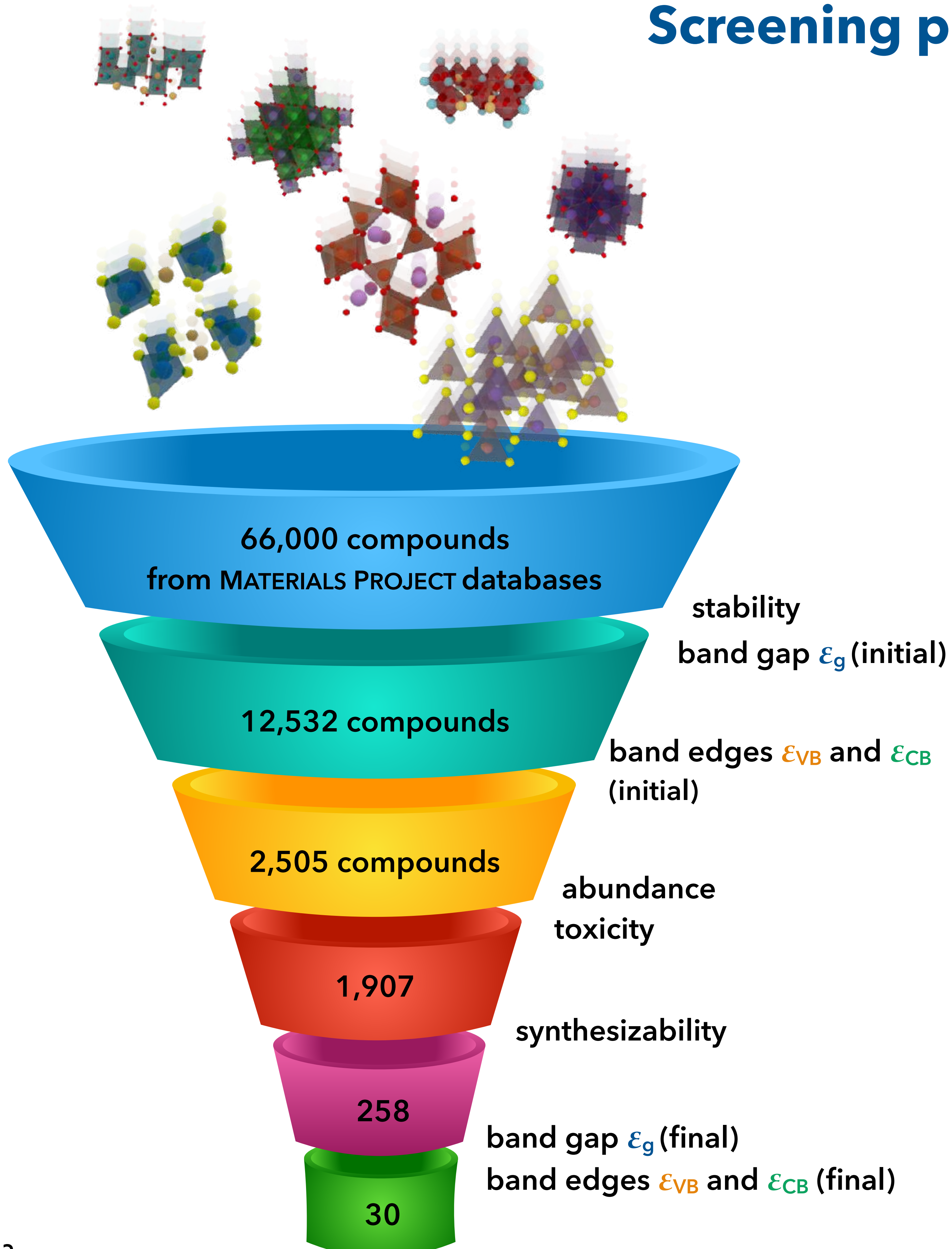


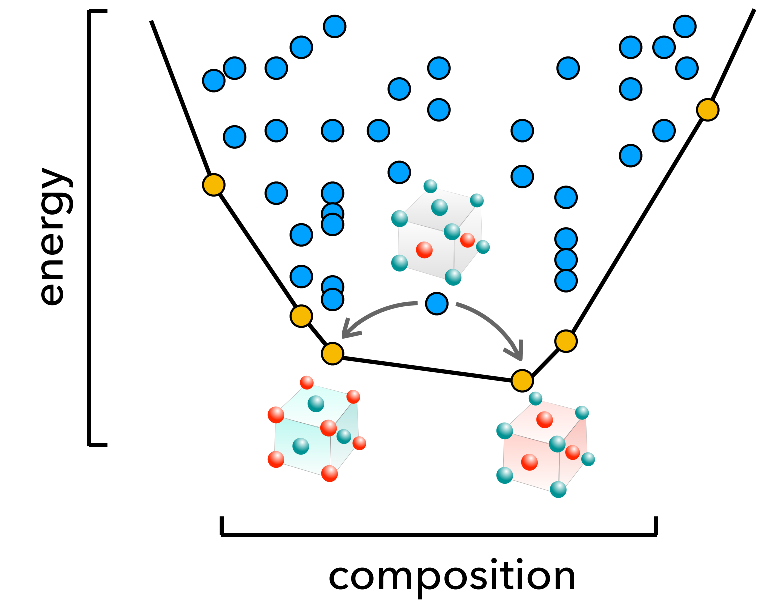
Which candidates can be made?

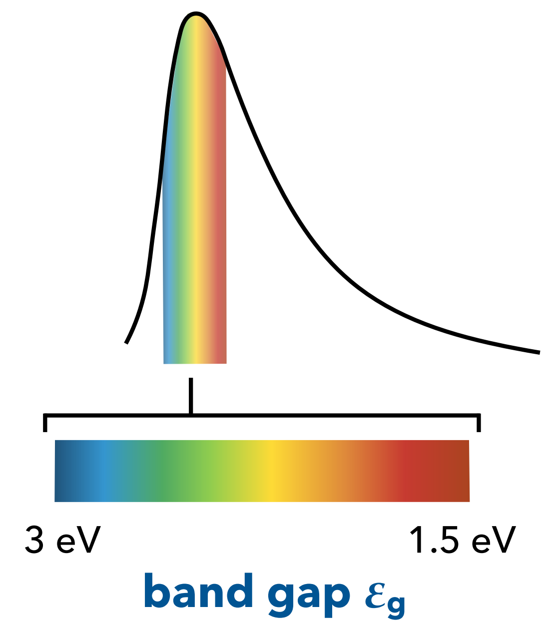
Ca_2FeClO_3		$CaCl_2$ + Fe_2O_3 in $CaCl_2$ flux at 850 °C for 5 h in Pt crucible	Ref. 63
$CaTaNO_2$		$CaCO_3$ + Ta_2O_5 at 900 °C in ammonia	Ref. 260
Cu_2WO_4		$CuWO_4$ (CuO and WO_3 at 800 °C for 20 h) + Cu	Ref. 52
Fe_3BO_6		Na_3BO_3 + Fe_2O_3 at 200 °C, then 1200 °C in air for 18 h then heated in boiling water then treated with HCl	Ref. 335
$In_4Bi_2S_9$		Bi + In + S + I via chemical vapor transport with thermal gradient of 680-600 °C	Ref. 268
Na_2TeO_4		NaOH + $Te(OH)_6$ in hydro-thermal furnace at 580 °C	Ref. 343
$Nb_2Co_4O_9$		Nb_2O_5 + CoO heated at 1300 °C for 10 h	Ref. 337
Nb_9VO_{25}		Nb_2O_5 + V_2O_5 + Na_2CO_3 at 350 °C for 24 h and 925 °C for *x* hours	Ref. 450
$NbBr_5$		$NbBr_5$ can be purchased	–
$NbCu_3S_4$		Cu + Nb + S + I via chemical vapor transport across 850-780 °C for 120 h	Ref. 277

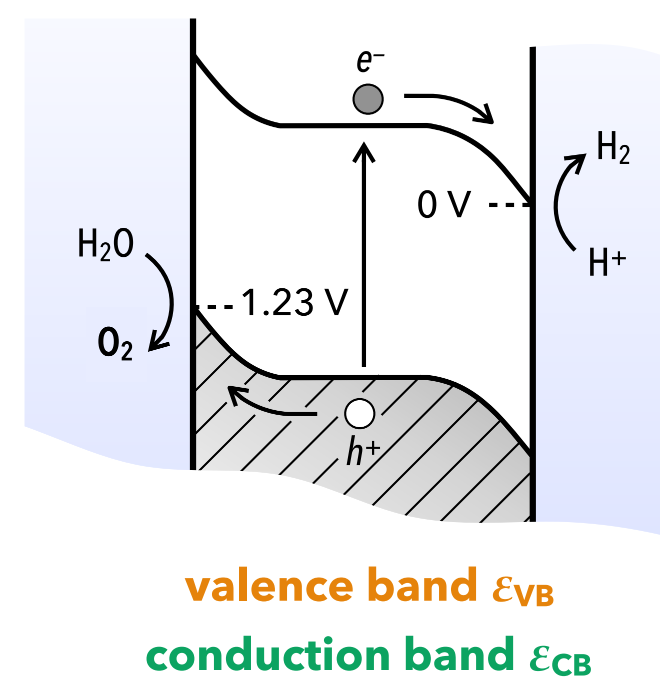
Sb_2MoO_6		Sb2O3 + MoO_3 in sealed ampoule at 490 °C for 24 h	Ref. 187
Sb_2S_3		Sb_2S_3 can be purchased	–
$SnMo_5O_8$		SnO_2 + 2MoO_3 +3Mo in sealed Mo crucible at 1757 °C for 1 h	Ref. 60
Sr_2FeBrO_3		Fe_2O_3 + $SrCO_3$ + $SrBr_2$ at 850 °C in air for 4 days	Ref. 171
SrCuSF		SrF_2 + SrS ($SrSO_4$ under H_2 at 1100 °C for 15 h) + Cu_2S in sealed ampoule at 500 °C for 6 h	Ref. 229
$Ta_4Cu_2O_{11}$		CuCl + Ta_2O_5 in CuCl flux heated to 665 °C for 1 h	Ref. 140
$V_5W_3O_{20}$		WO_3, V_2O_5 + V_2O_3 in sealed ampoule at 1100 °C	Ref. 107
VSO_5		$VSO_5 \cdot 5H_2O$ heated to 330 °C for 1 h	Ref. 225
$Zn(CoO_2)_2$		ZnO + Co_2O_3	Ref. 35
$ZnGeP_2$		Zn + Ge + P in Bi flux in sealed ampoule	Ref. 109

Screening protocol



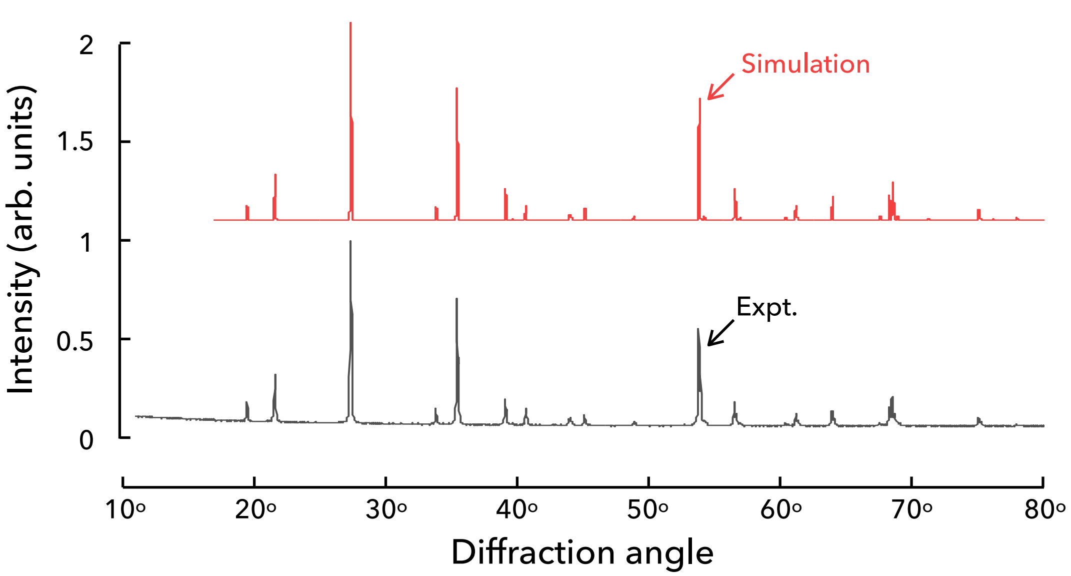


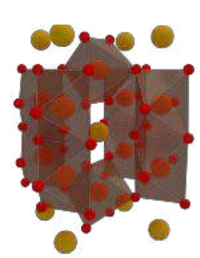




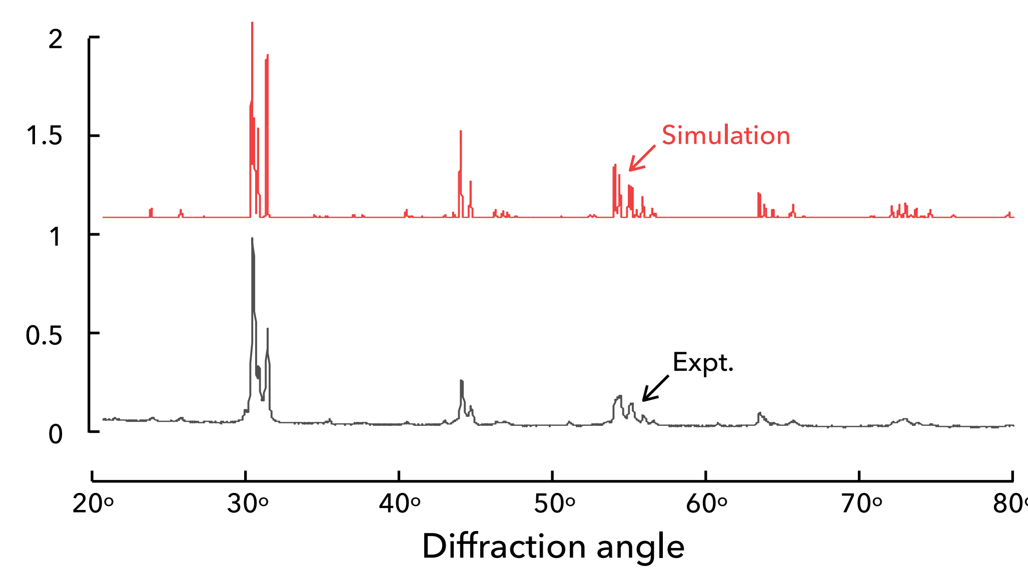
Materials synthesis and testing

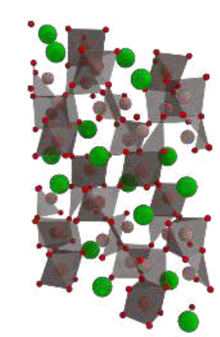
12 of the 30 compounds have been successfully synthesized with high purity and tested photoelectrochemically…





Fe_2TeO_6

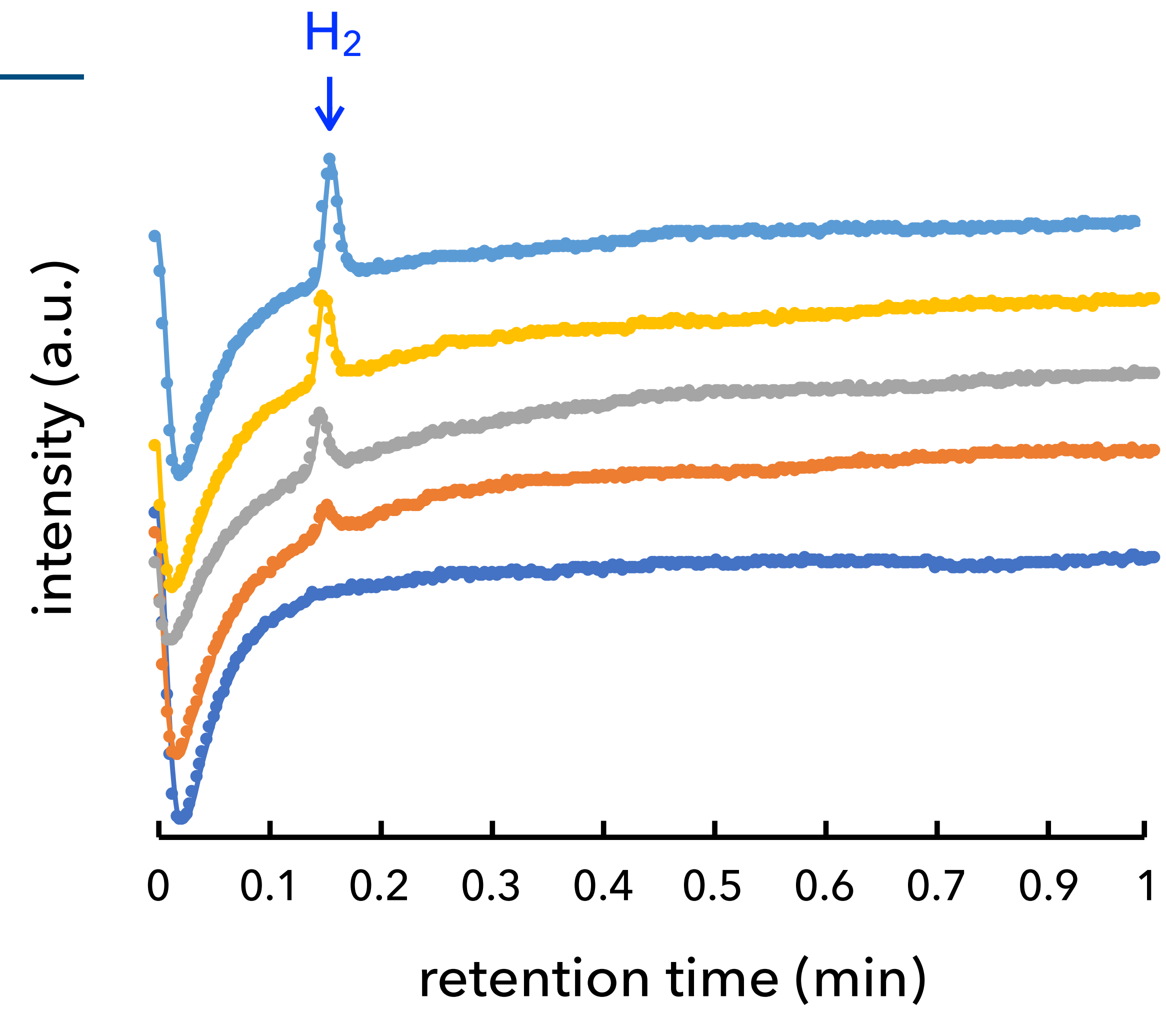


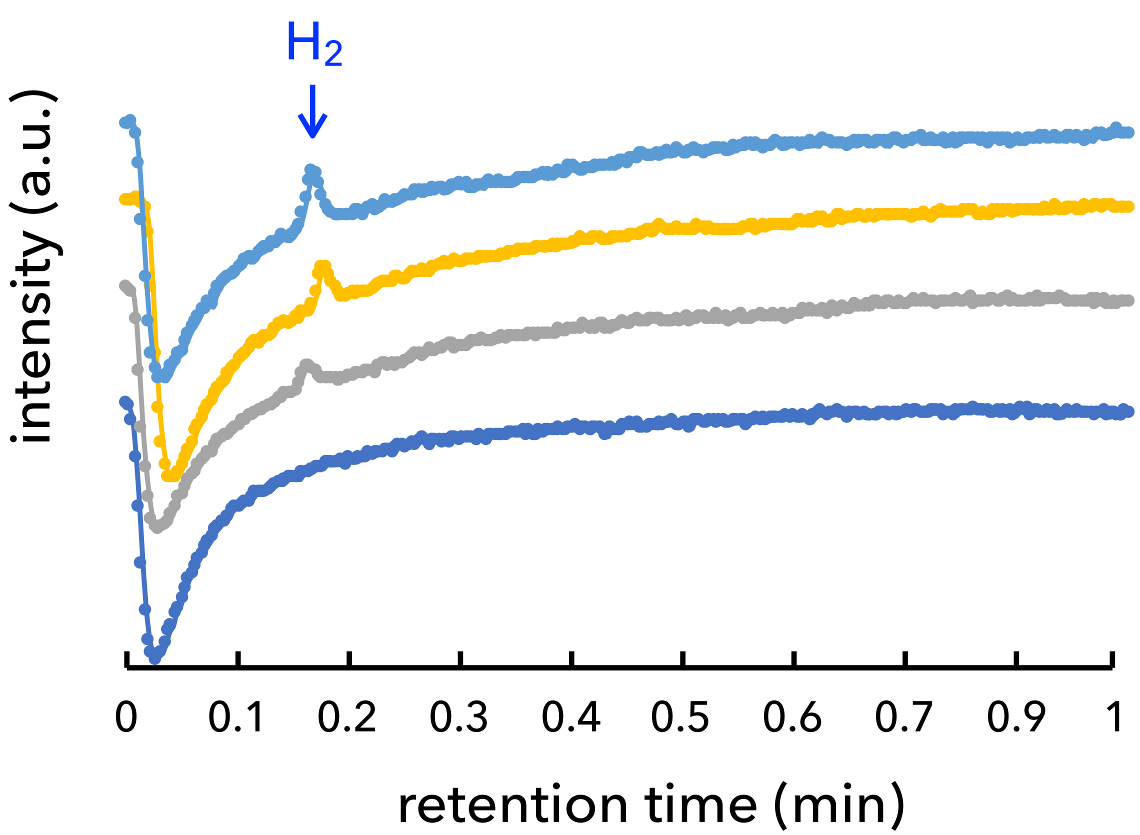


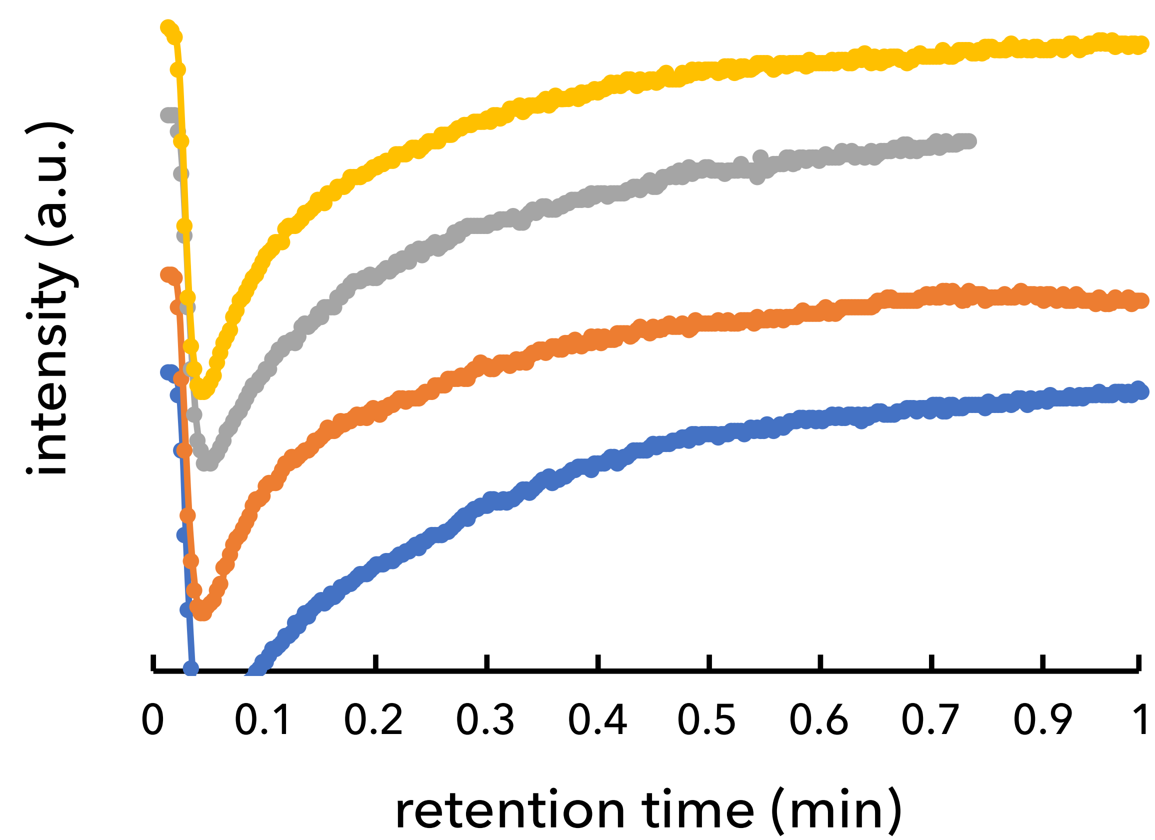
$BaIn_2O_4$

Materials synthesis and testing

Ultimately, **7 of the 12 compounds** show hydrogen generation through gas chromatography

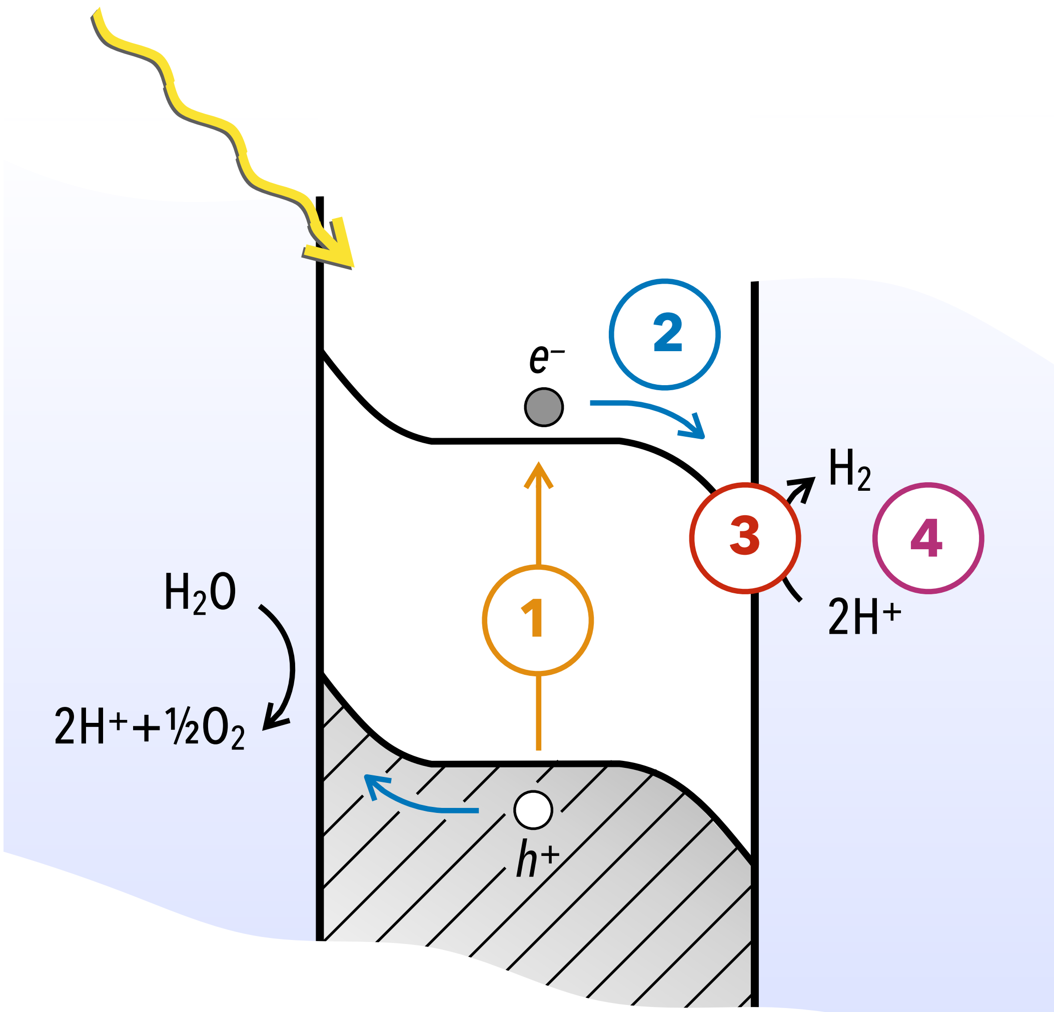






Other limiting factors

Beyond solar compatibility and charge transfer, we need to examine other limiting mechanisms



1 SOLAR COMPATIBILITY

2 CHARGE SEPARATION ?

3 CHARGE TRANSFER

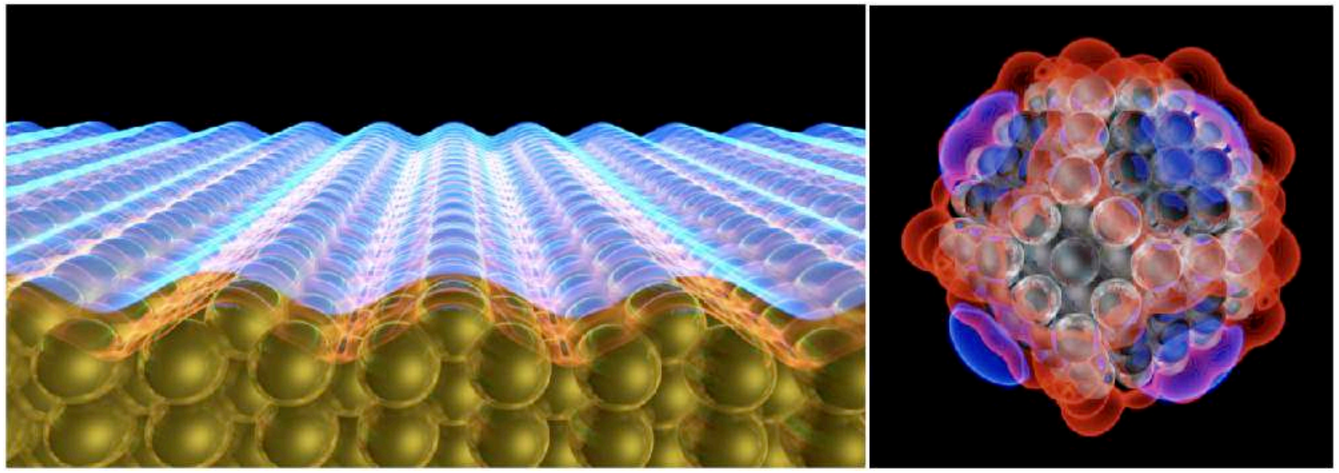
4 SURFACE ACTIVITY ?

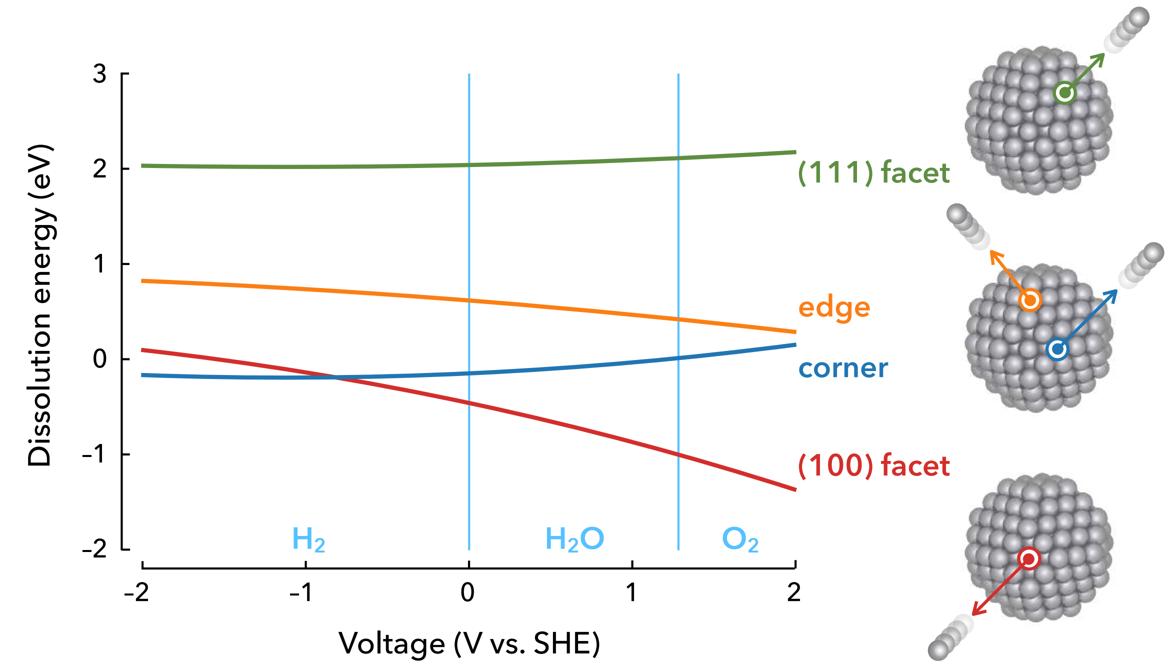
DMREF/INFEWS-1729338

HydroGEN Advanced Water Splitting Materials

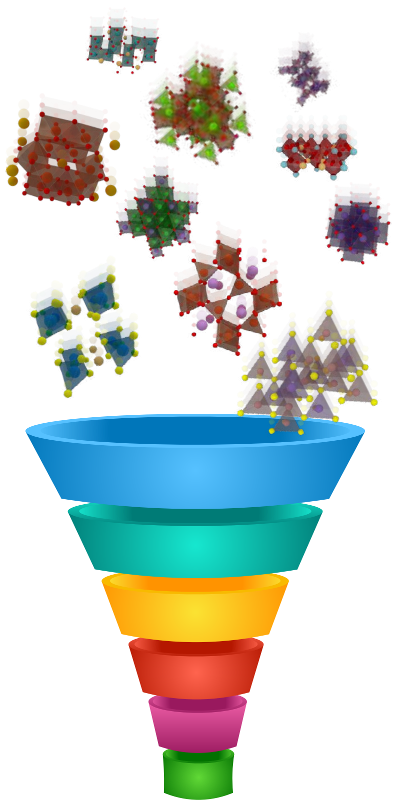
NREL NATIONAL RENEWABLE ENERGY LABORATORY

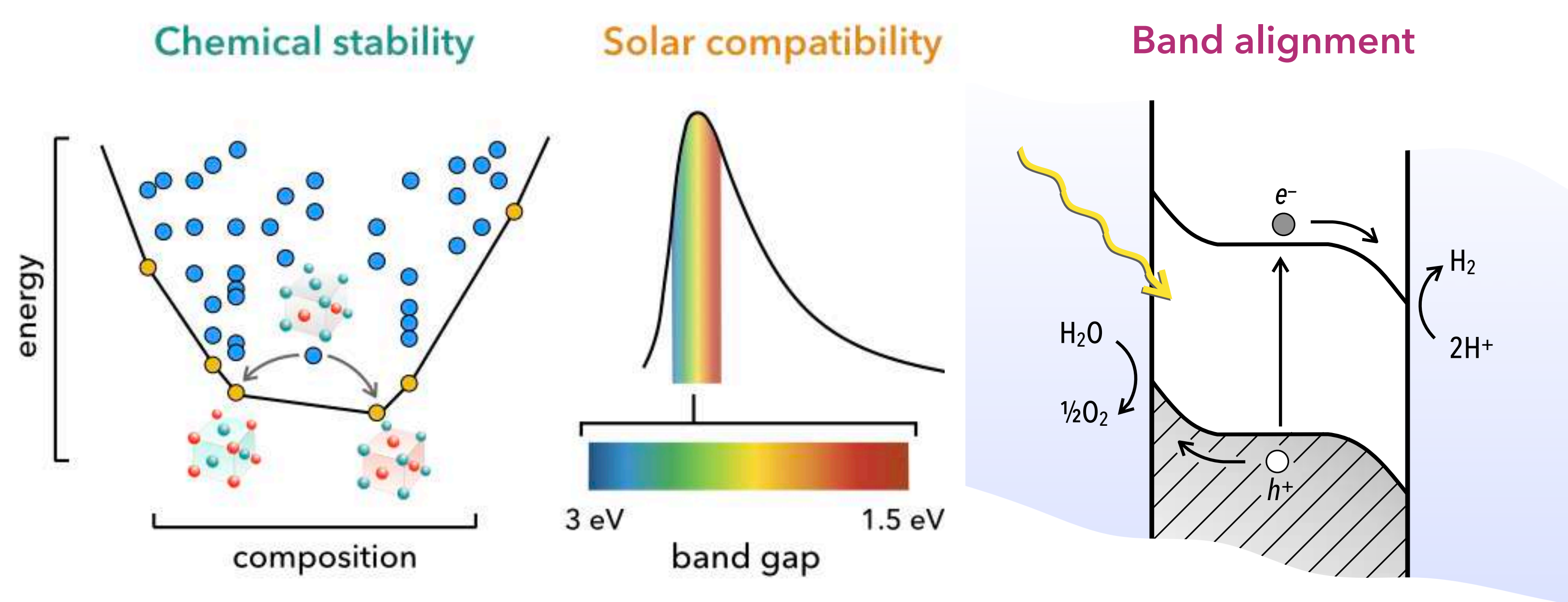
Summary





DOE, Office of Science, Basic Energy Sciences,
CPIMS Program, Award No. DE-SC0018646





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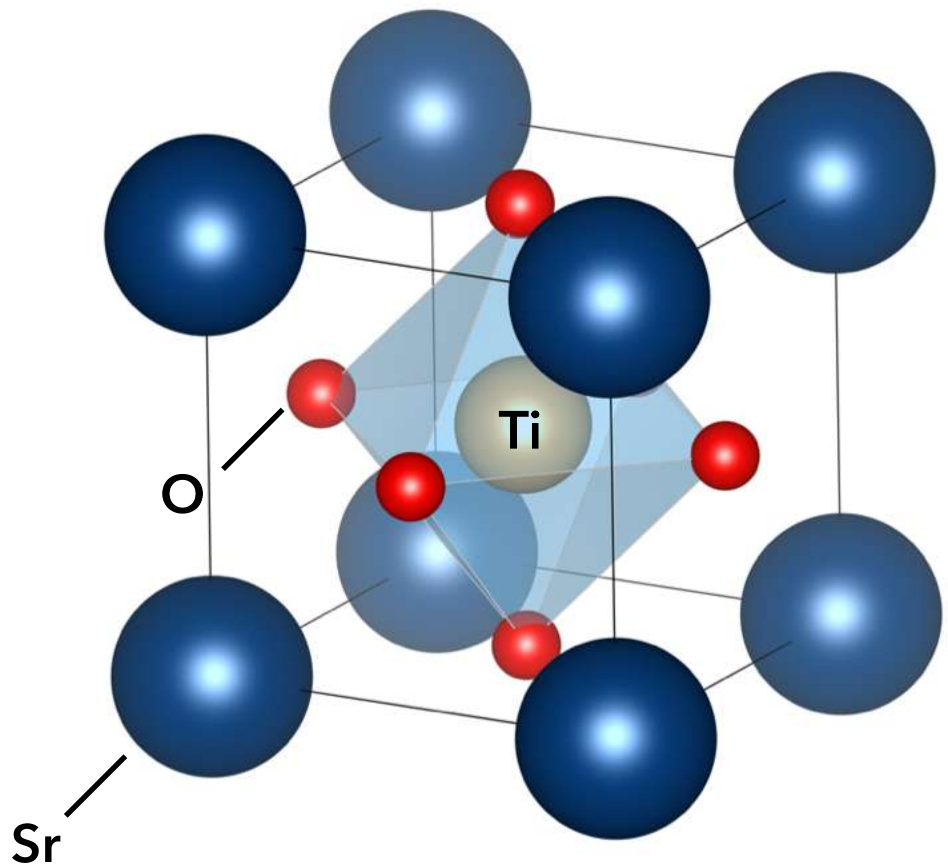
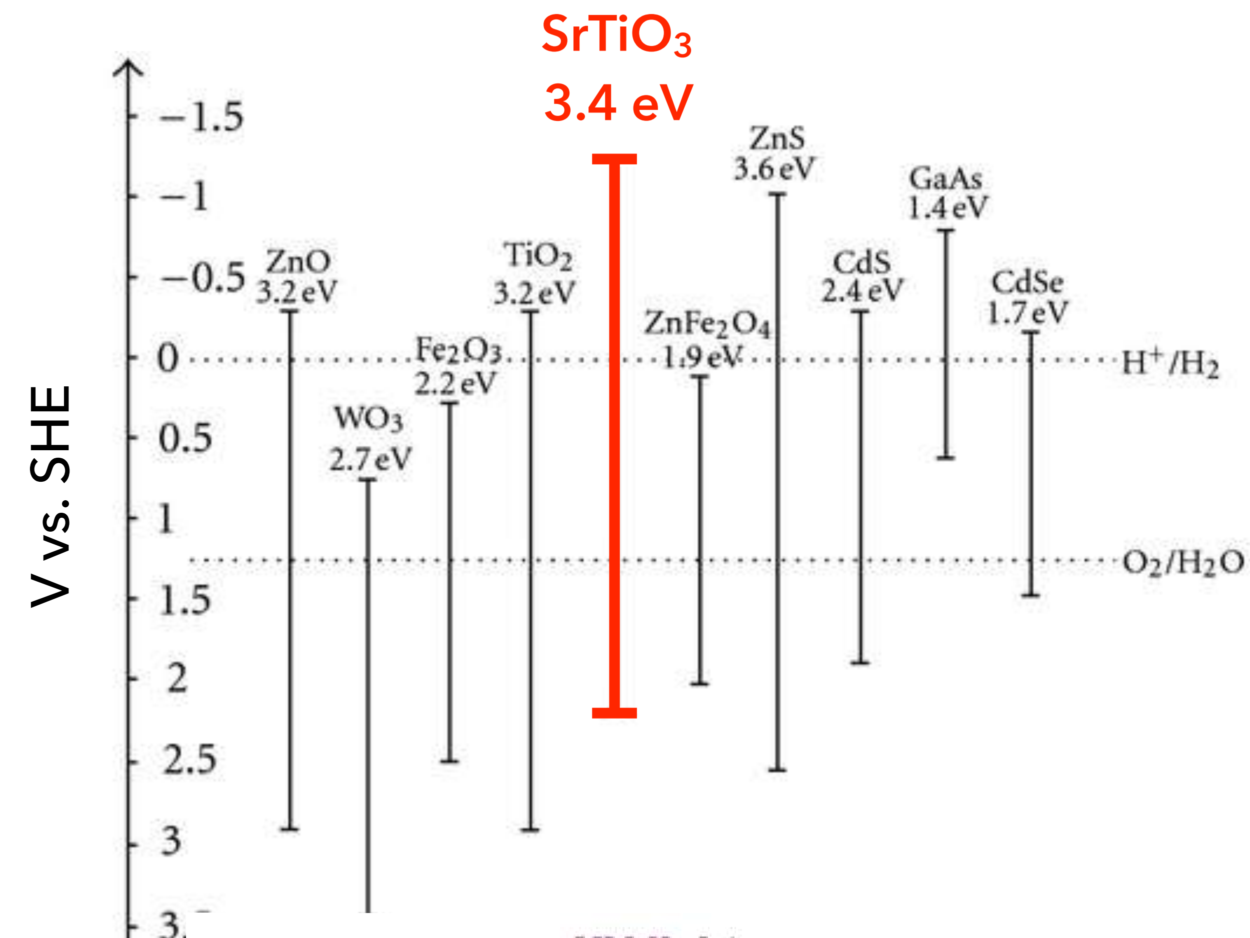
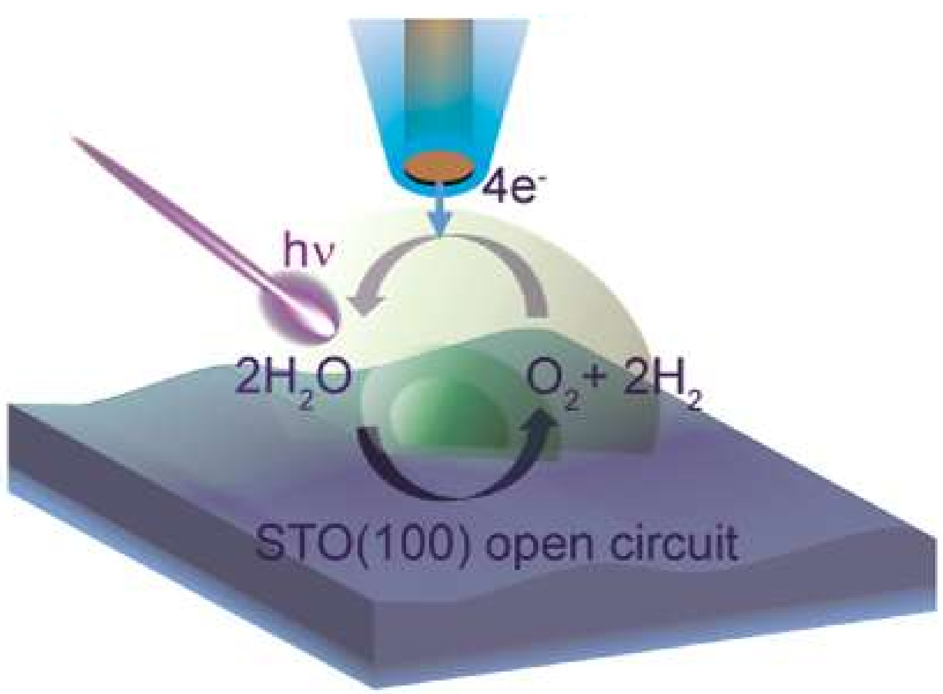
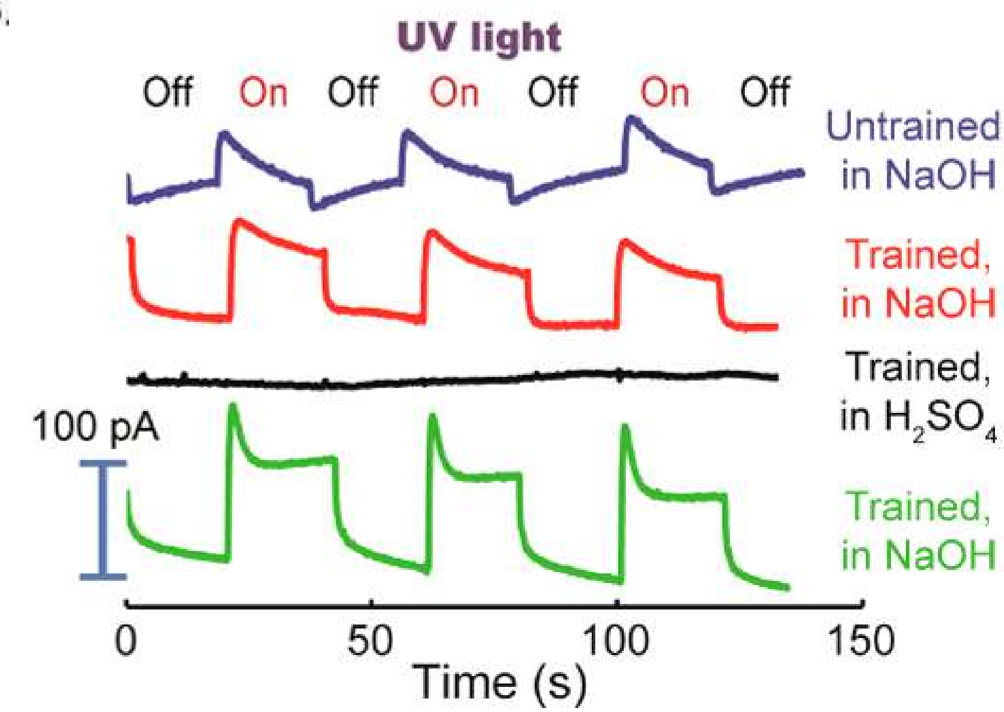
Towards predicting surface photocatalytic activity





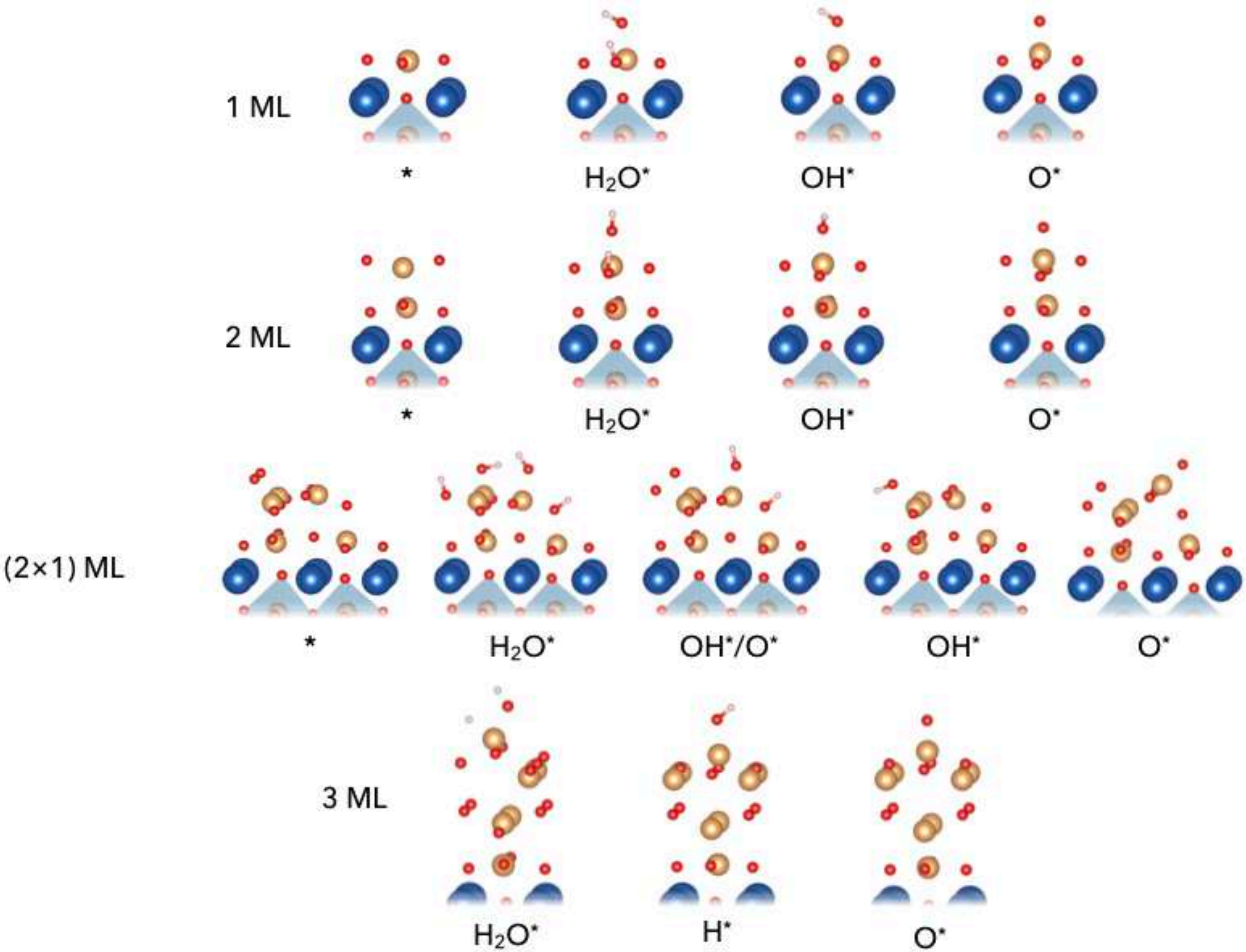
Scanning electrochemical microscopy





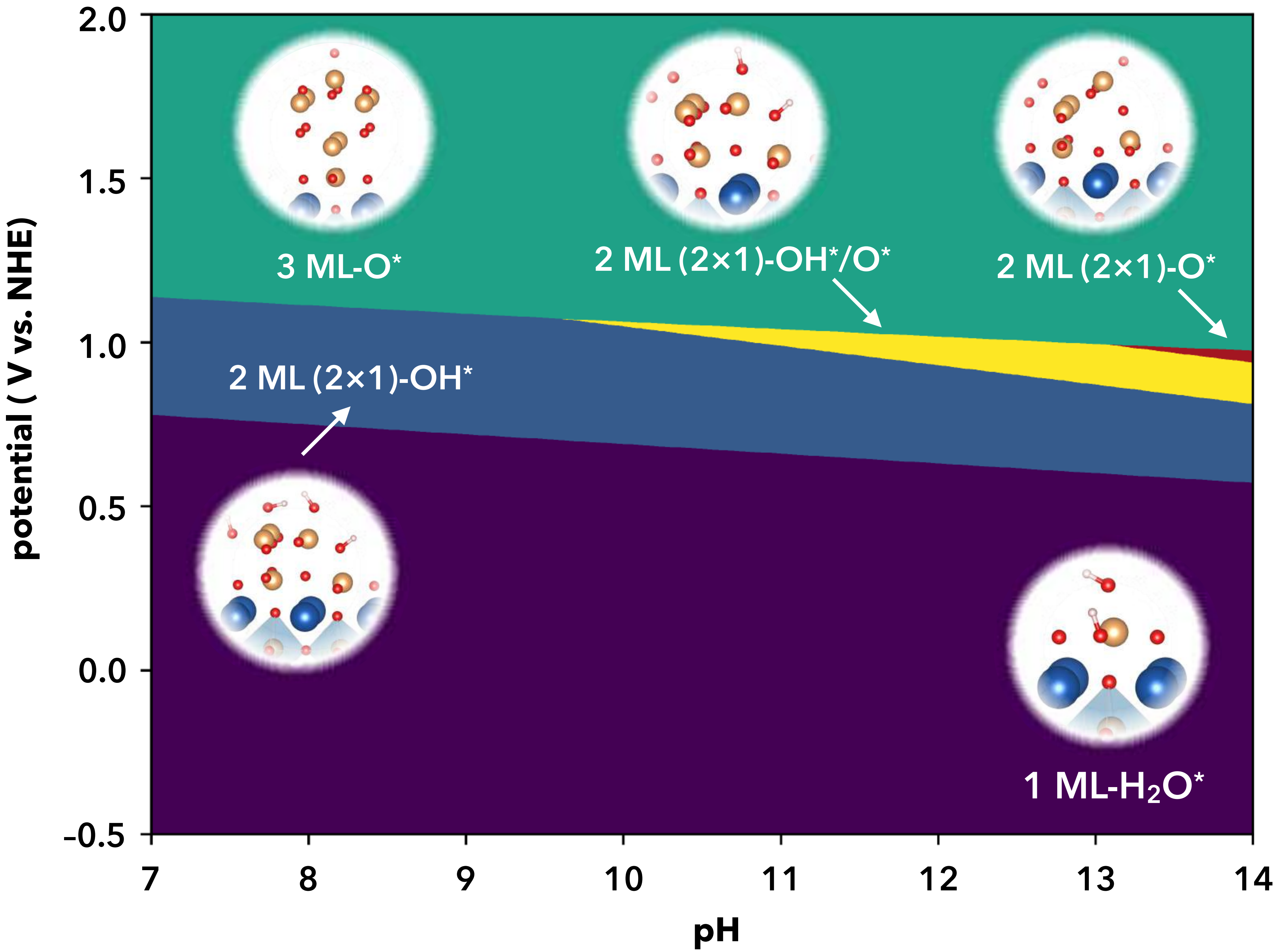
Plaza *et al.*, *J. Am. Chem. Soc.* 138, 7816 (2016)

Towards predicting surface photocatalytic activity



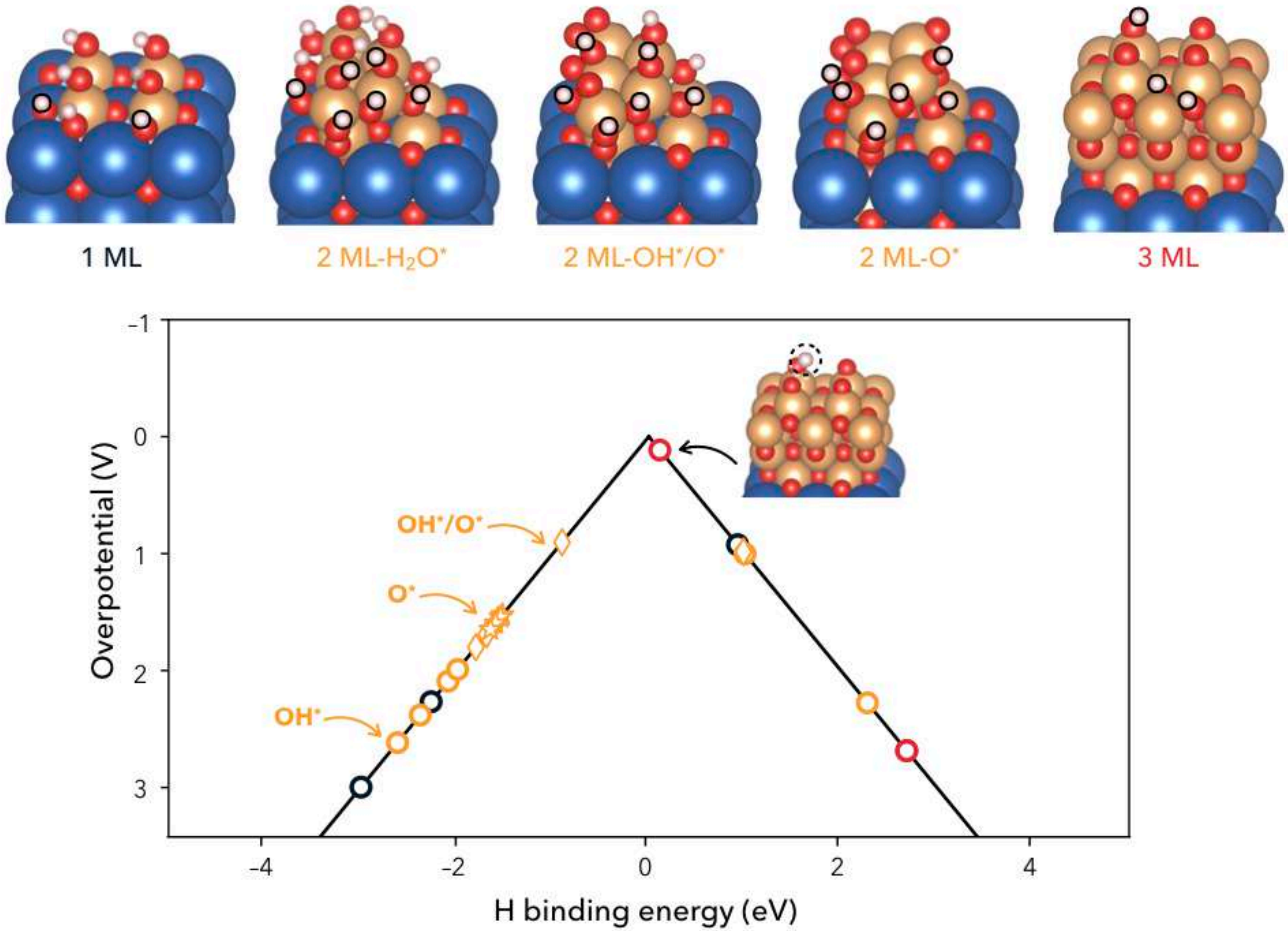
Xiong and ID, *Phys. Rev. M* 3, 065801 (2019)

Towards predicting surface photocatalytic activity



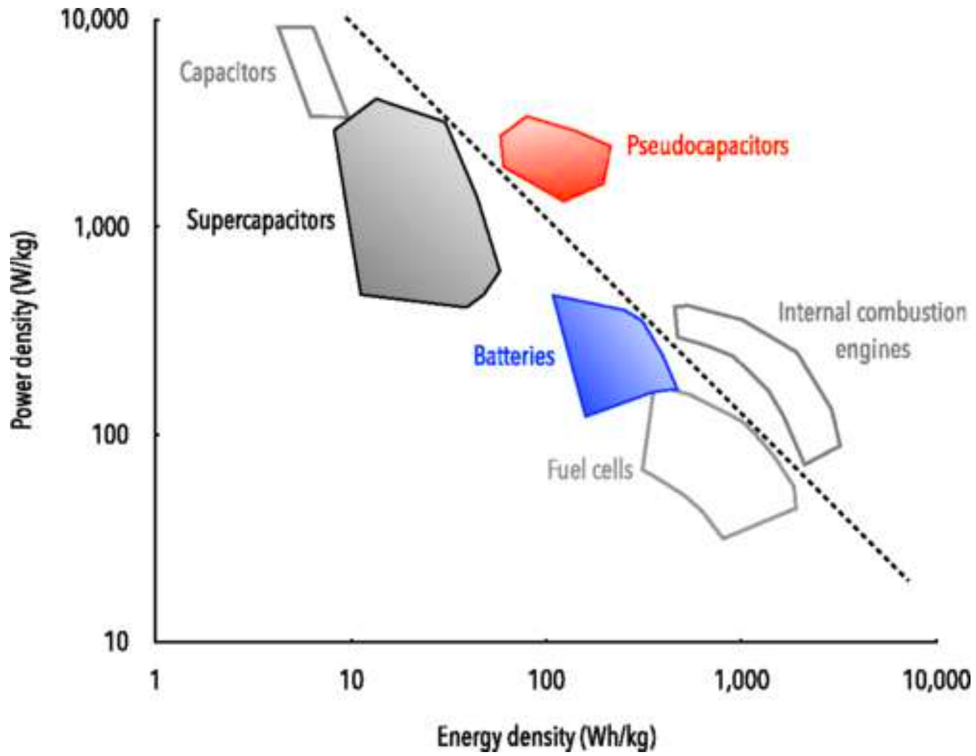
Xiong and ID, *Phys. Rev. M* 3, 065801 (2019)

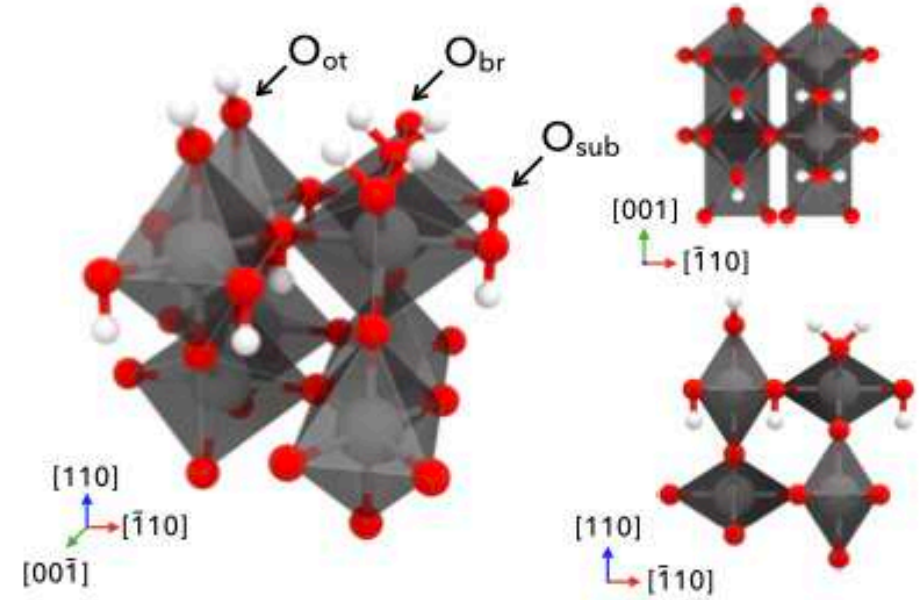
Towards predicting surface photocatalytic activity

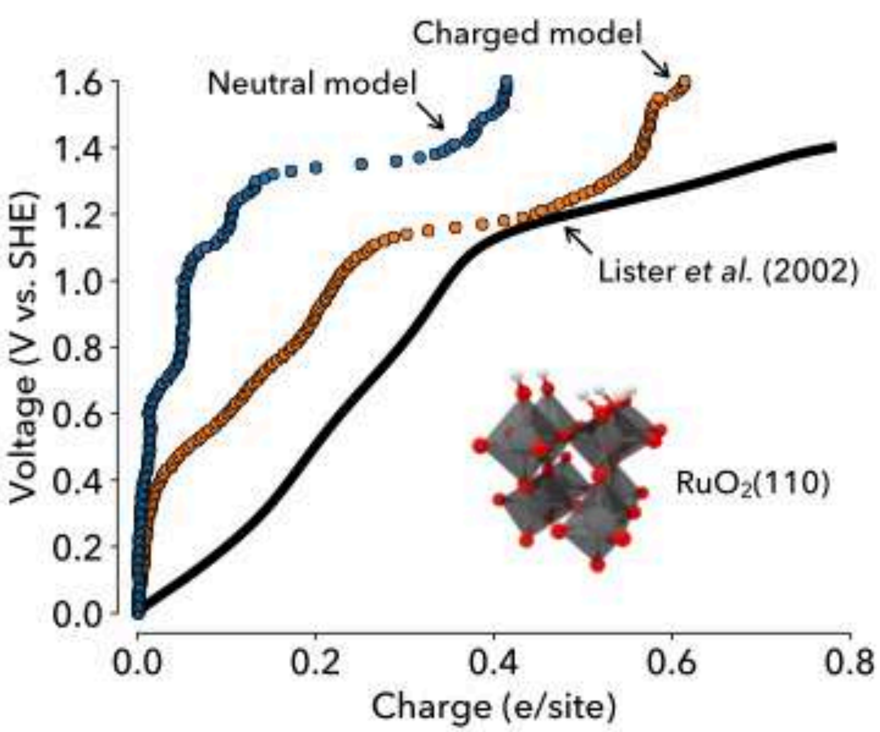


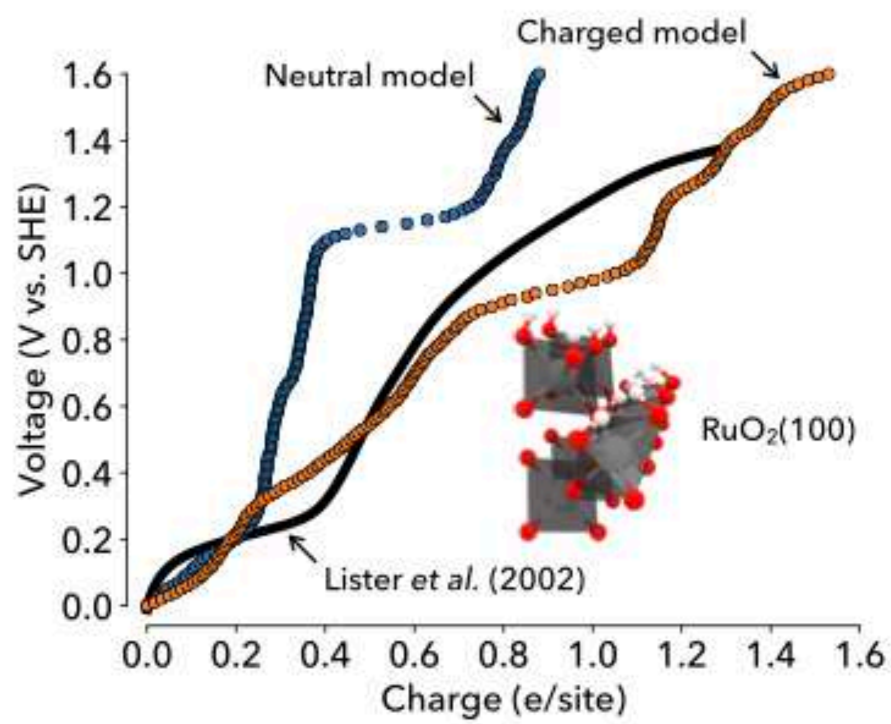
Xiong and ID, *Phys. Rev. M* 3, 065801 (2019)

Towards predicting pseudocapacitive charge storage









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