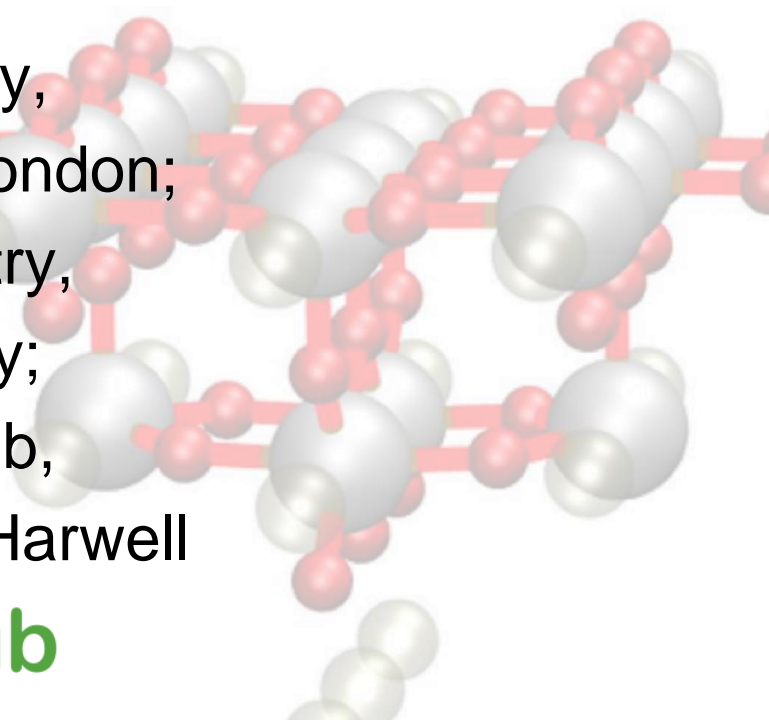


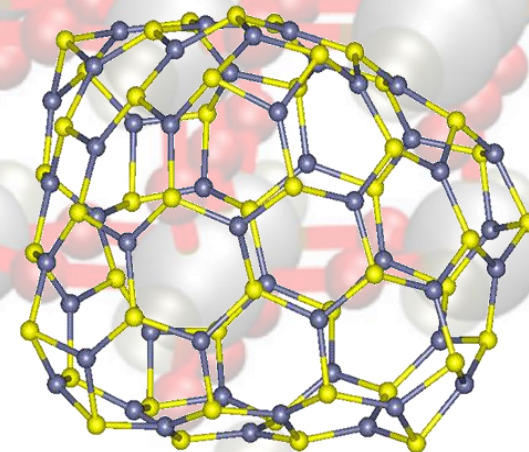
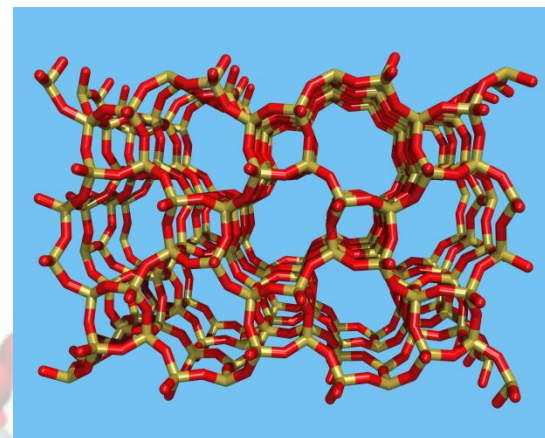
INTERATOMIC POTENTIALS: Do we still need them and how can we improve them

Richard Catlow
Dept of Chemistry,
University College London;
School of Chemistry,
Cardiff University;
UK Catalysis Hub,
Research Complex at Harwell



Modelling of Materials at the Atomic and Molecular Level

- Structures (crystal and amorphous)
- Surfaces and Interfaces
- Defects and Atomic Transport
- Sorption and Diffusion
- Synthesis, Nucleation and growth
- Nanochemistry
- Reactivity and Catalysis



IP methods have important roles in all.

Nature Materials, 7, 937, (2008)

REVIEW ARTICLE

Crystal structure prediction from first principles

The prediction of structure at the atomic level is one of the most fundamental challenges in condensed matter science. Here we survey the current status of the field and consider recent developments in methodology, paying particular attention to approaches for surveying energy landscapes. We illustrate the current state of the art in this field with topical applications to inorganic, especially microporous solids, and to molecular crystals; we also look at applications to nanoparticulate structures. Finally, we consider future directions and challenges in the field.

SCOTT M. WOODLEY* AND RICHARD CATLOW
are in the Department of Chemistry, University College London, Kathleen
Lonsdale Building, Gower Street, London WC1E 6BT, UK.

model for the structure of a new zeolite (zeolite nu-87), which after minimization gave a structure with a different symmetry that more satisfactorily refined the crystallographic data. Such calculations are



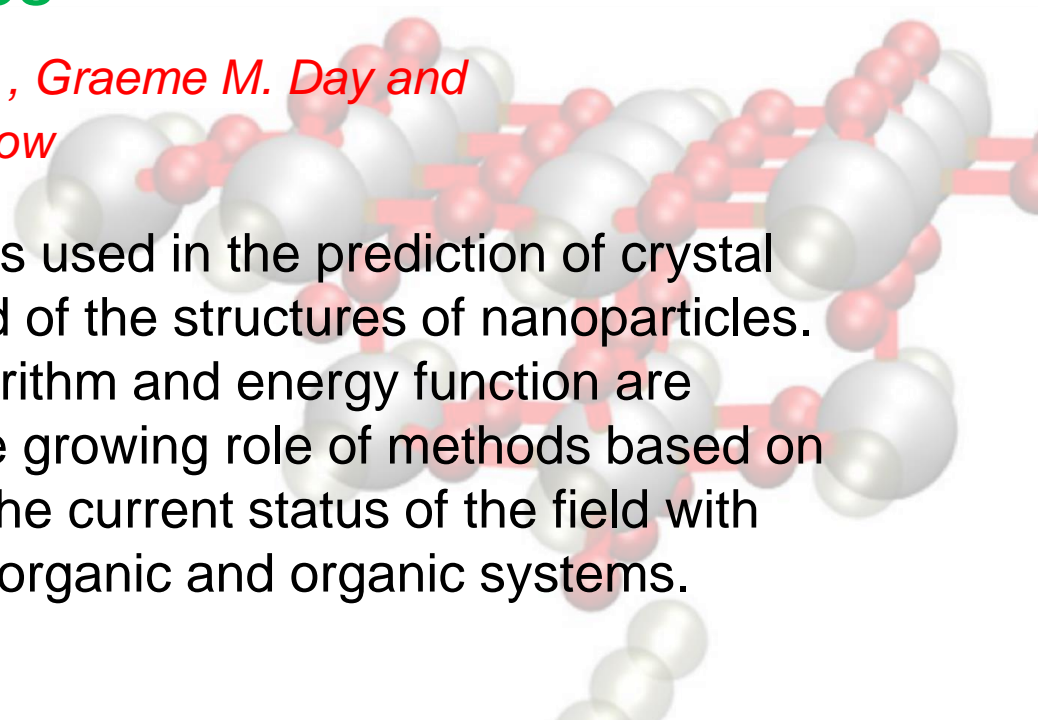
royalsocietypublishing.org/journal/rsta Review Cite this article: Woodley SM, Day GM, Catlow CRA. 2020 Structure prediction of crystals, surfaces and nanoparticles. *Phil. Trans. R. Soc. A* 378: 20190600.

<http://dx.doi.org/10.1098/rsta.2019.0600> Accepted: 19 June 2020

Structure prediction of crystals, surfaces and nanoparticles

*Scott M. Woodley , Graeme M. Day and
C. Richard A. Catlow*

- We review the current techniques used in the prediction of crystal structures and their surfaces and of the structures of nanoparticles. The main classes of search algorithm and energy function are summarized, and we discuss the growing role of methods based on machine learning. We illustrate the current status of the field with examples taken from metallic, inorganic and organic systems.

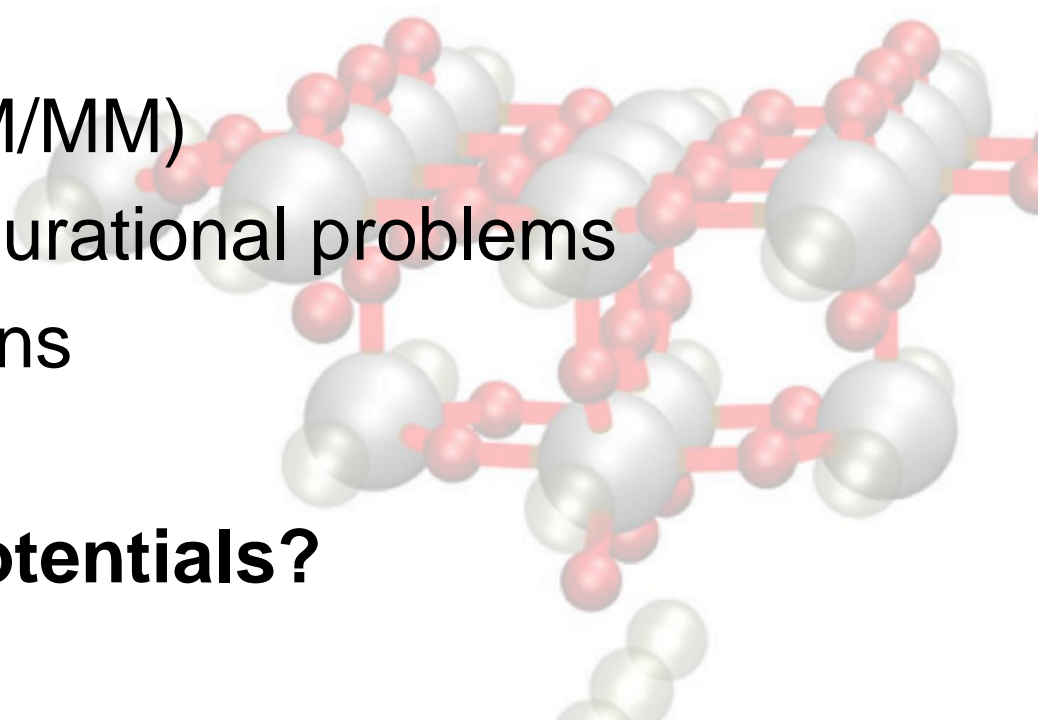


THEMES:

Why do we still need potentials?

- Sometimes they are as good (and perhaps better) than DFT
- Hybrid methods (QM/MM)
- Complex multiconfigurational problems
- Dynamical simulations

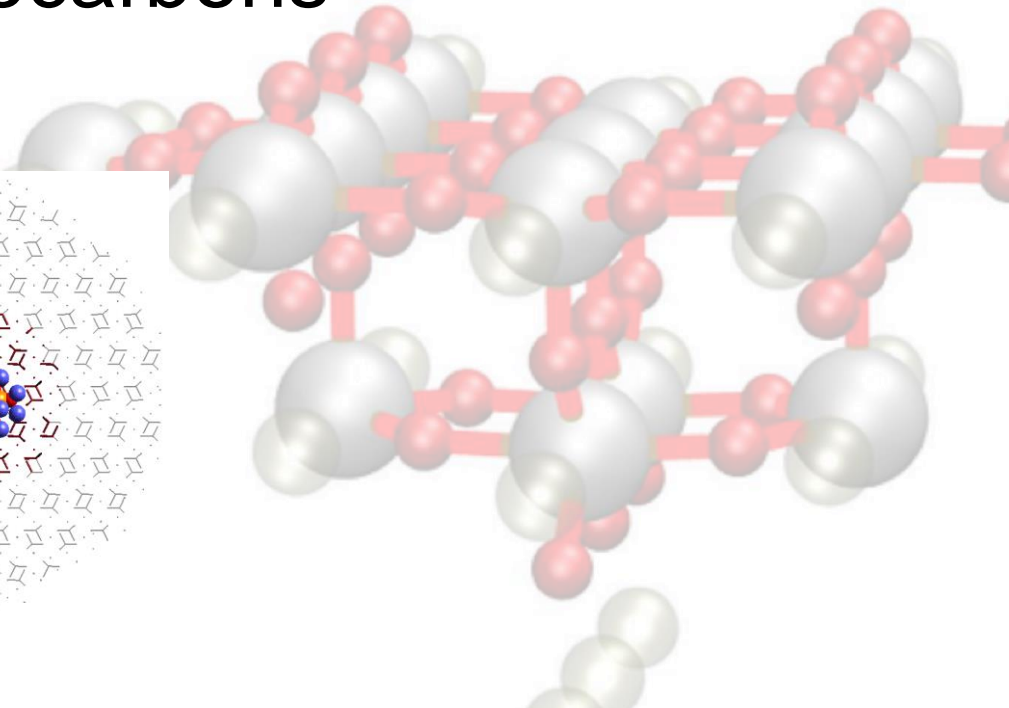
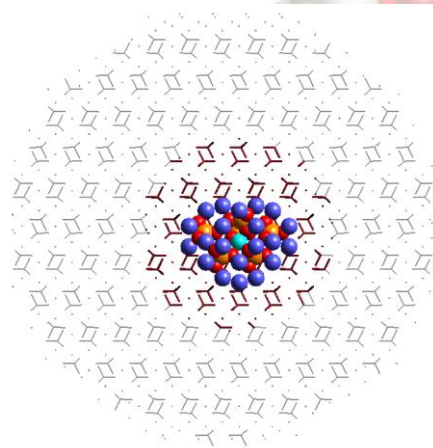
How do we improve potentials?



THEME ONE:

When are potentials as good as DFT?

- Defects in Ionic Solids
- Physisorbed hydrocarbons



DEFECTS in MgO

(or how to keep on working without getting any further!)

Mott Littleton (Catlow Norgett *et al.*, *J.Phys C*, 1976)

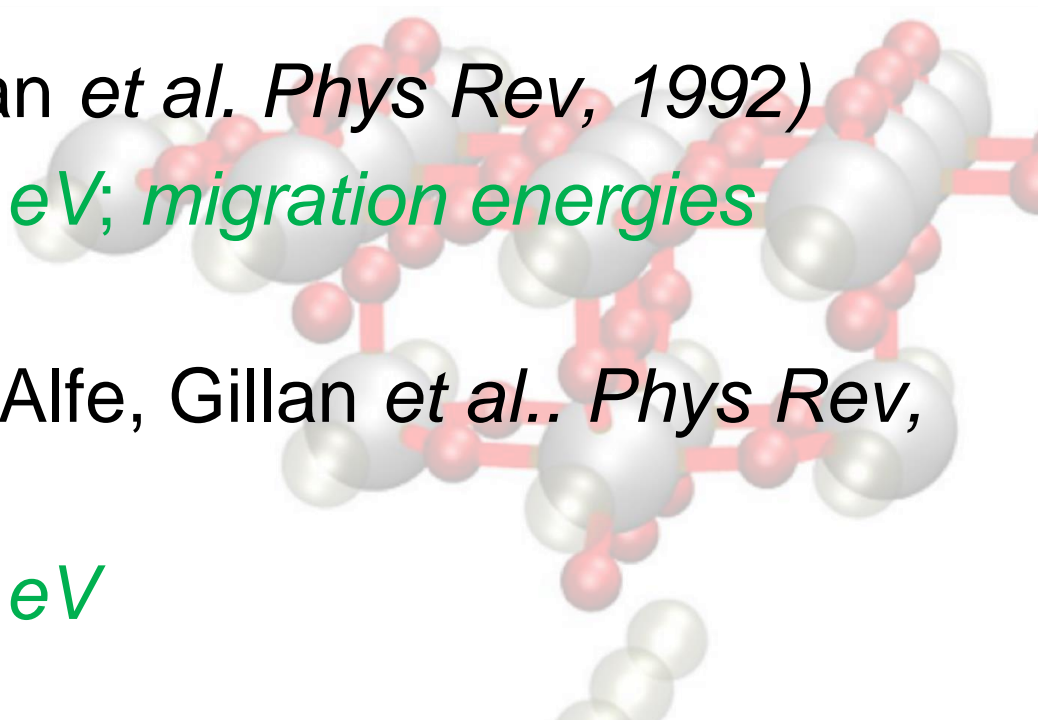
Schottky Energy: 7.4 – 7.9 eV; vacancy migration energies 2.1 – 2.2 eV

DFT PBC (De Vita, Gillan *et al.* *Phys Rev*, 1992)

Schottky Energy: 6.9 eV; migration energies 2.4eV

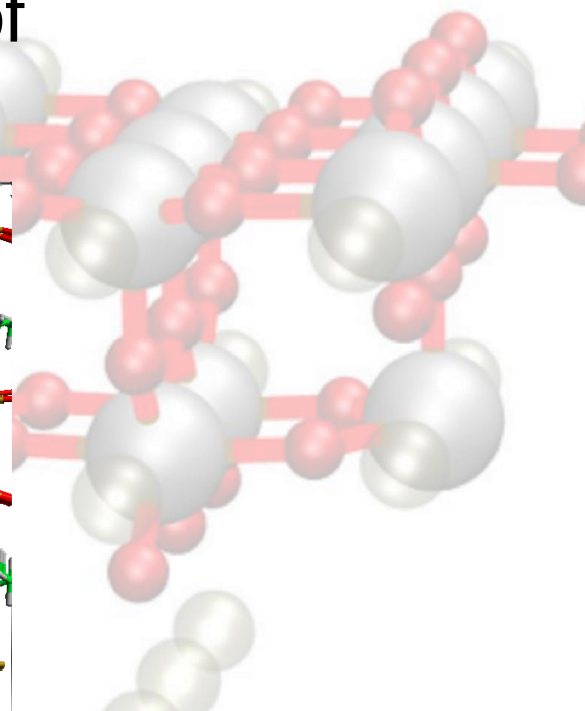
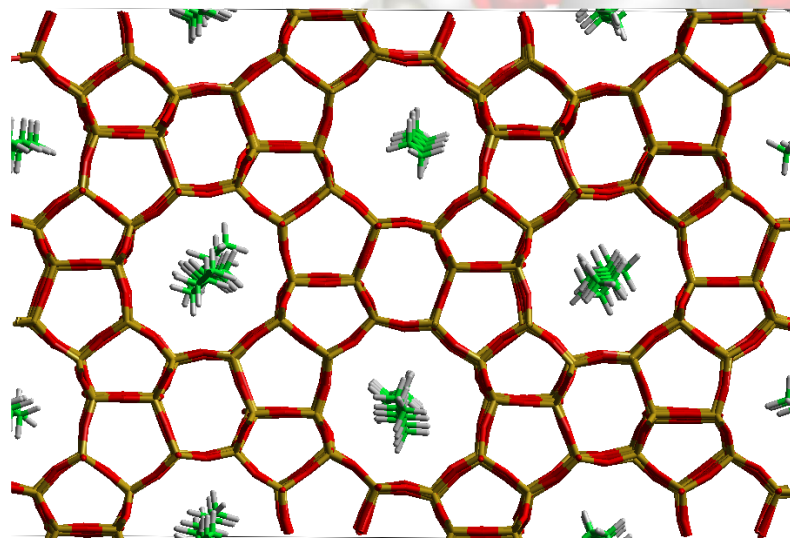
Quantum Monte-Carlo (Alfe, Gillan *et al.* *Phys Rev*, 2005)

Schottky Energy: 7.5 eV



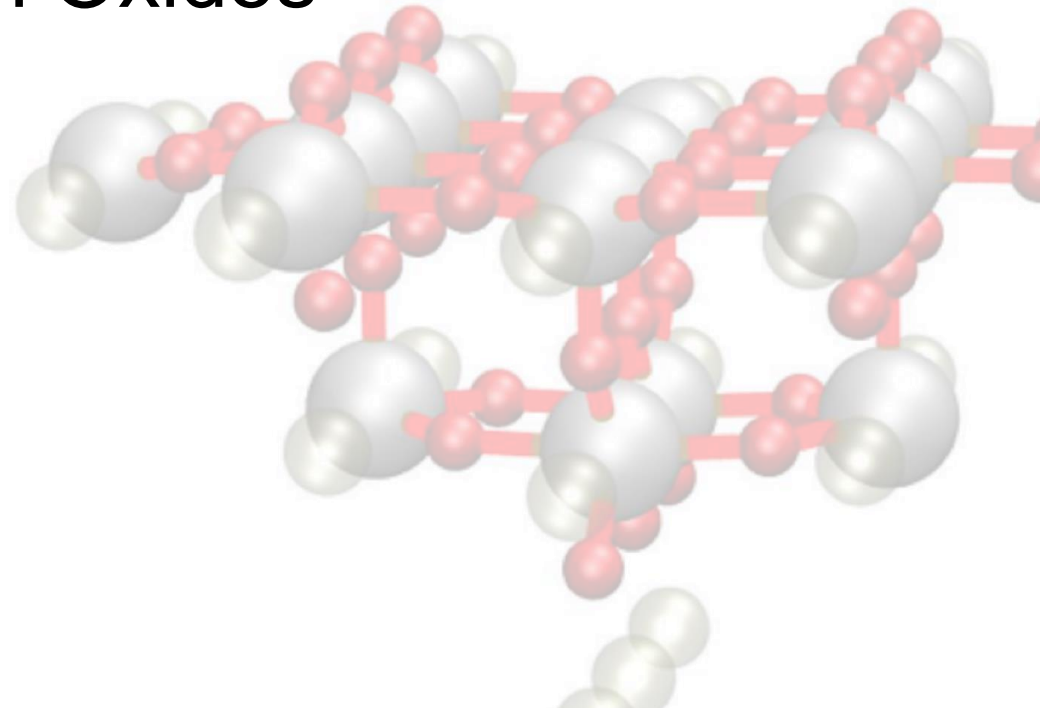
PHYSISORBED HYDROCARBONS

- Predominant interaction is van der Waals
- Well parameterised IP as good if not better than DFT
- Weakly bound and large numbers of configurations



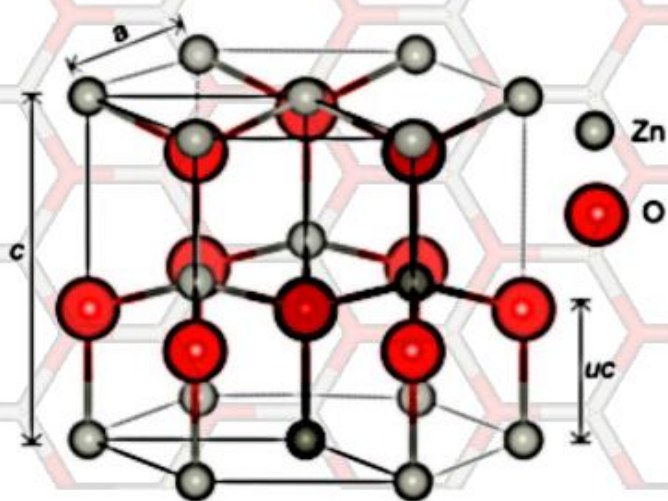
THEME TWO: Complex Multiconfigurational Systems

- ZnO Surfaces
- Mono-clusters on Oxides



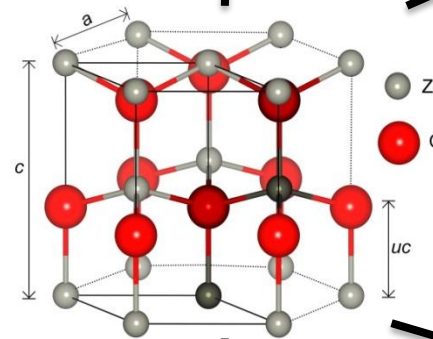
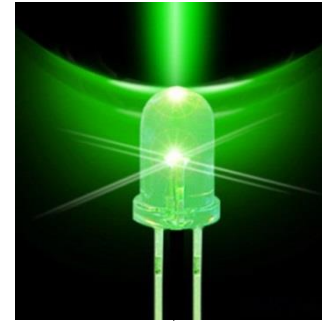
Stability and Structure of ZnO surfaces

David Mora-Fonz, Richard Catlow
(*J.Phys Chem C*, 2015; *Chem Mater*, 2017)



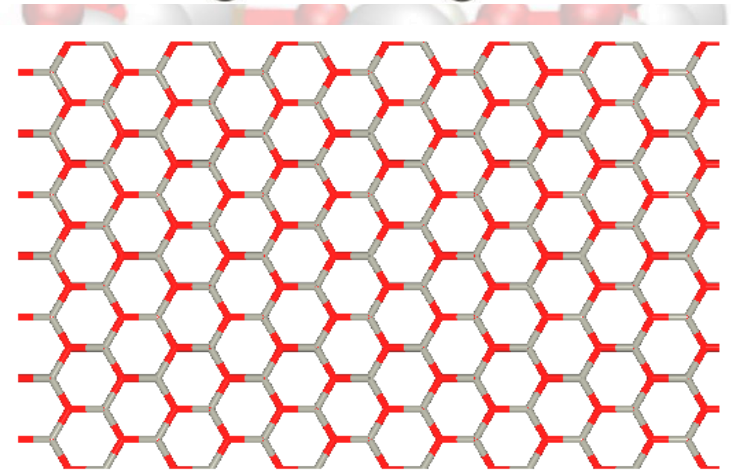
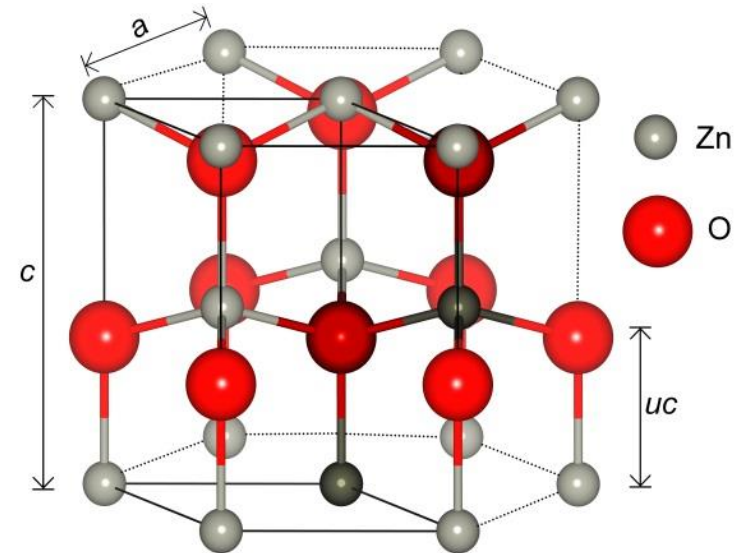
Zinc Oxide: Properties and Uses

- Ionic
- *n*-type semiconductor
- Wide-bandgap (3.44 eV @ 0K)
- Stable polar surfaces
- No inversion symmetry – Piezoelectric and pyroelectric properties
- Good transparency
- High electron mobility
- Strong room temperature luminescence

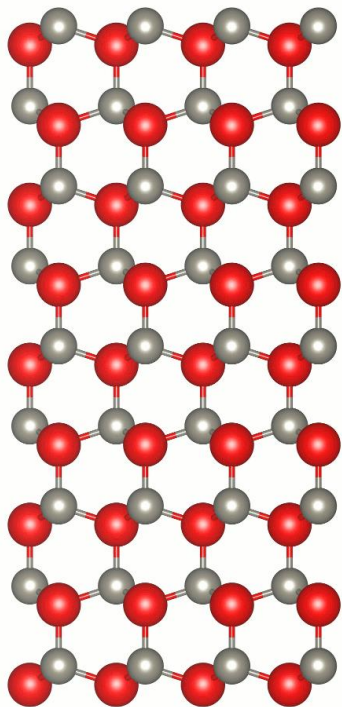


Zinc Oxide: Structure

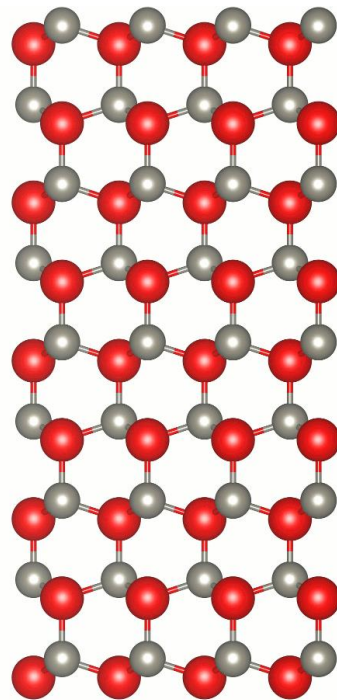
- Tetrahedral coordination
- AA' stack of one atom thick, forming hexagonal patterns
- The wurtzite structure has 4 principal low-index surfaces, two side faces nonpolar: $(10\bar{1}0)$ and $(11\bar{2}0)$ and two opposite polar faces: (0001) -Zn and $(000\bar{1})$ -O



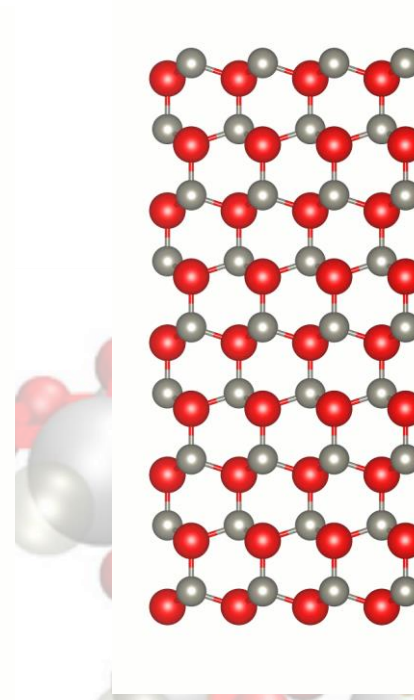
Stabilization methods for the ZnO polar surfaces



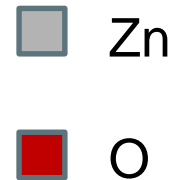
Metallization



Zn vacancies

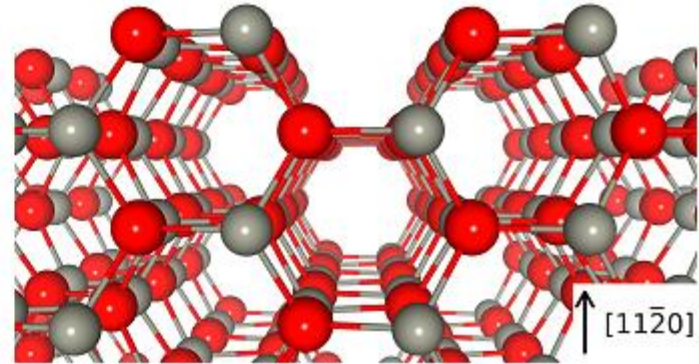
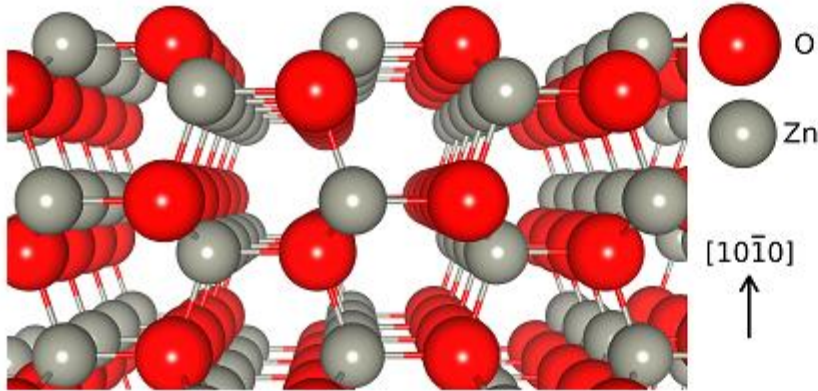


Adatoms

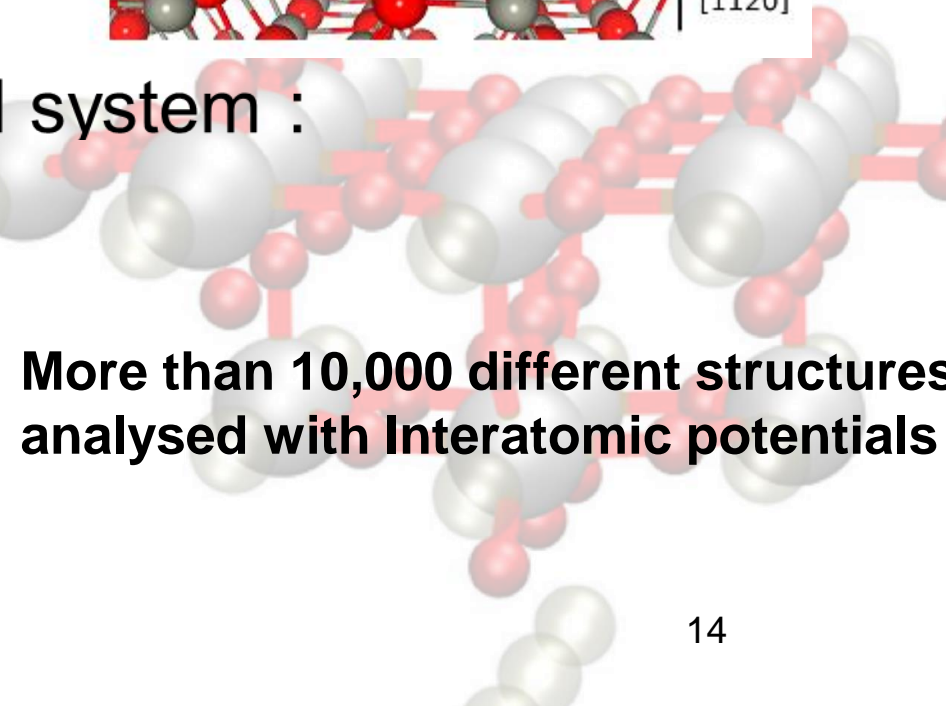
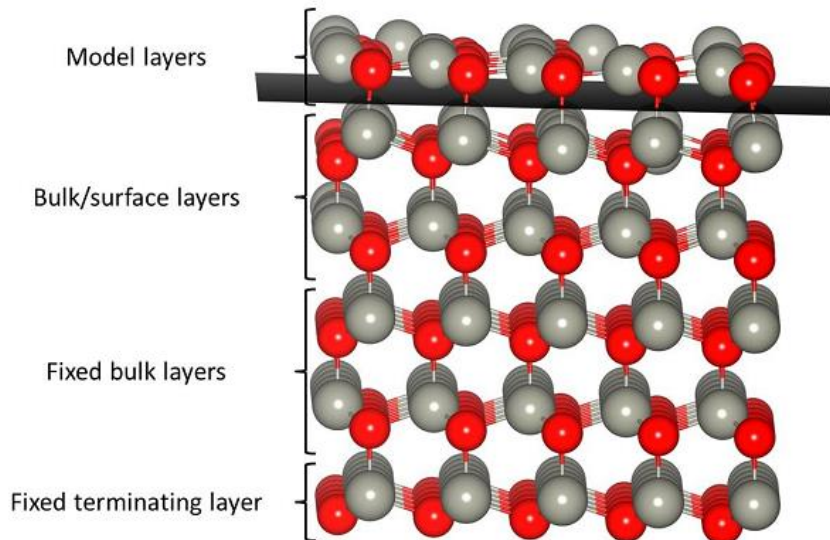


Surface models

- $(10\bar{1}0)$ and $(11\bar{2}0)$:



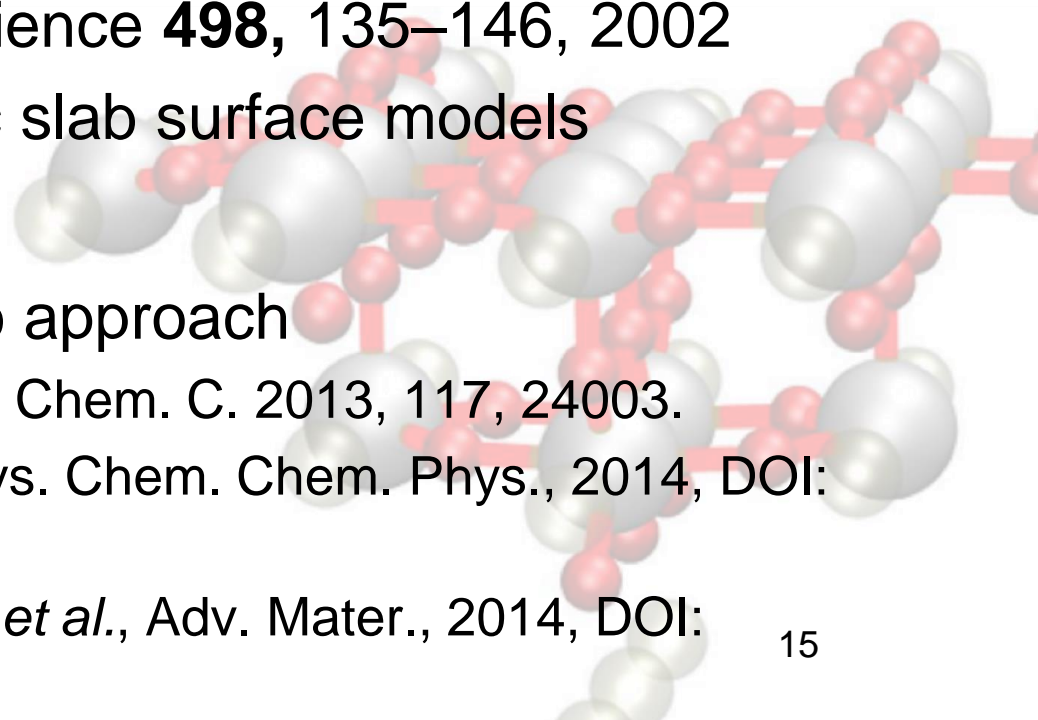
- (0001) -Zn / KLMC model system :



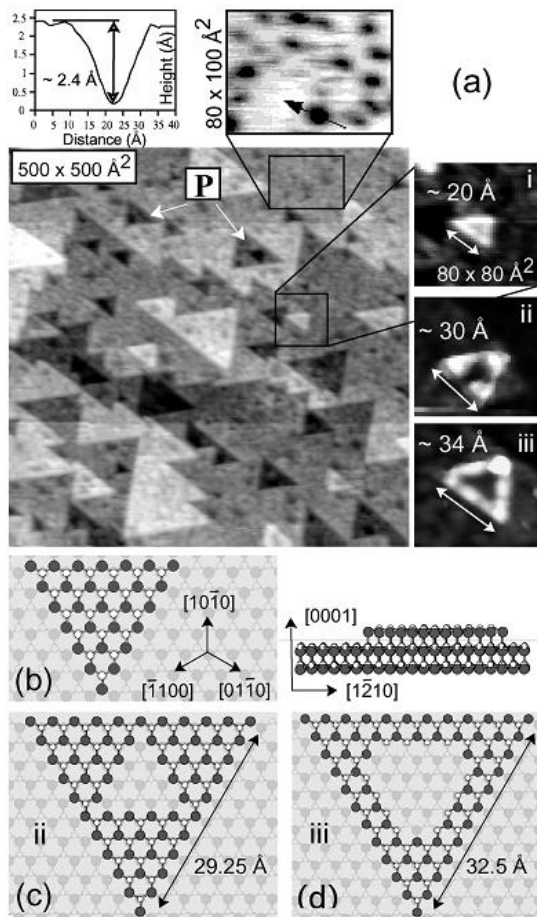
More than 10,000 different structures analysed with Interatomic potentials

Computational details

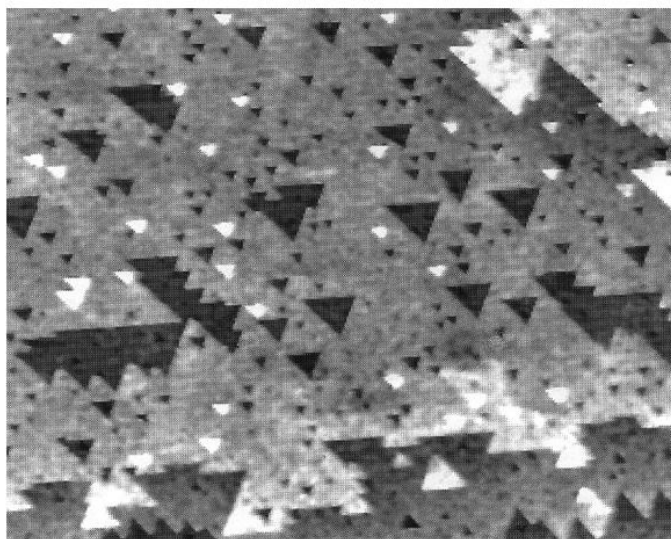
- VASP
 - GGA functionals: PBE and PBEsol.
 - Hybrid functionals: PBE0 and PBEsol0 (25% of the exact exchange from HF).
- GULP
 - Potentials: Surface Science **498**, 135–146, 2002
 - One-sided 3D-periodic slab surface models
- KLMC
 - Statistical Monte-Carlo approach
 - [1] S. M. Woodley, J. Phys. Chem. C. 2013, 117, 24003.
 - [2] M. R. Farrow, *et al.*, Phys. Chem. Chem. Phys., 2014, DOI: 10.1039/C4CP01825G
 - [3] D. E. E. Deacon-Smith, *et al.*, Adv. Mater., 2014, DOI: 10.1002/adma.201401858



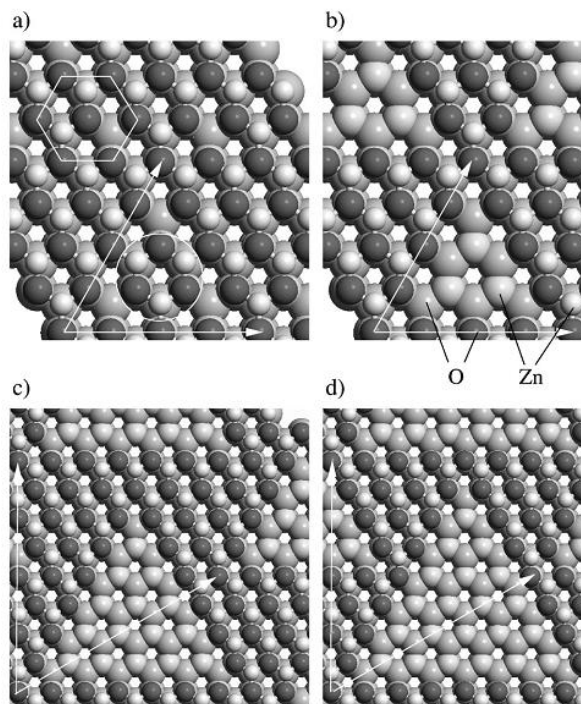
(0001)-Zn surface



Dulub *et al.* Phys. Rev. Lett. **90**, 0161021-0161024, 2003



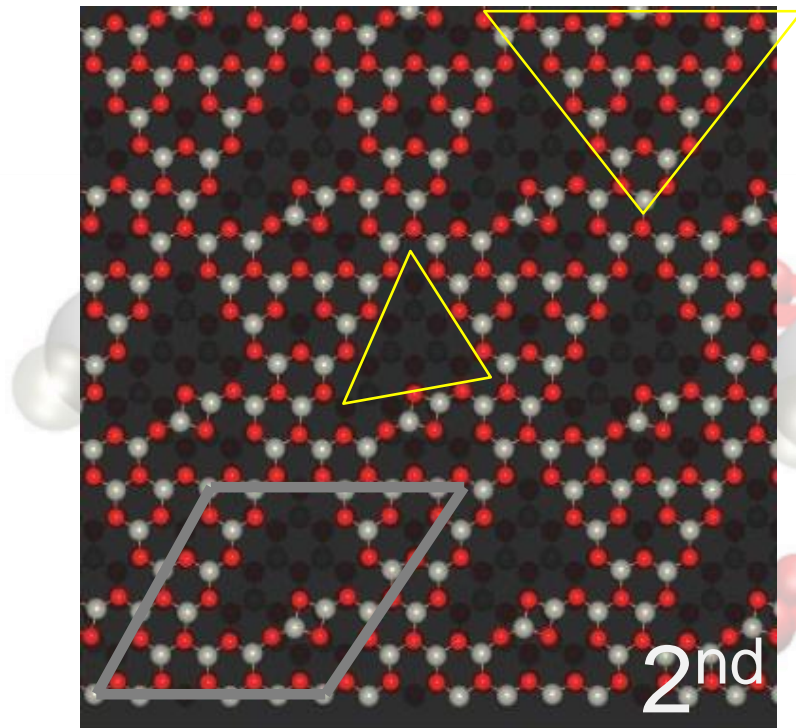
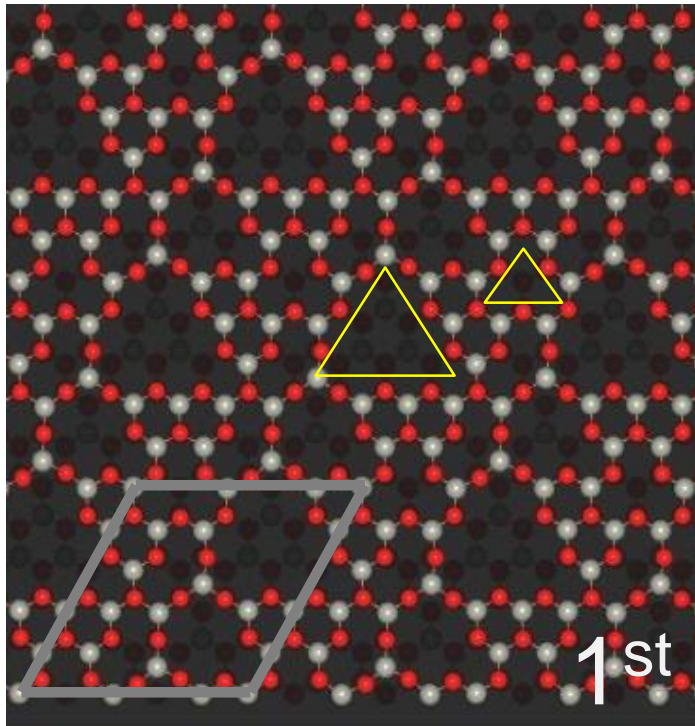
Parker *et al.* Surface Science **415**, L1046–L1050, 1998



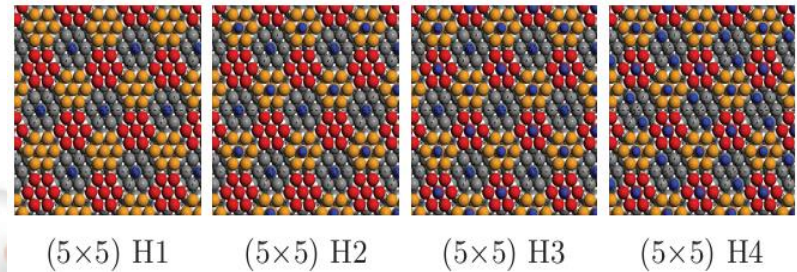
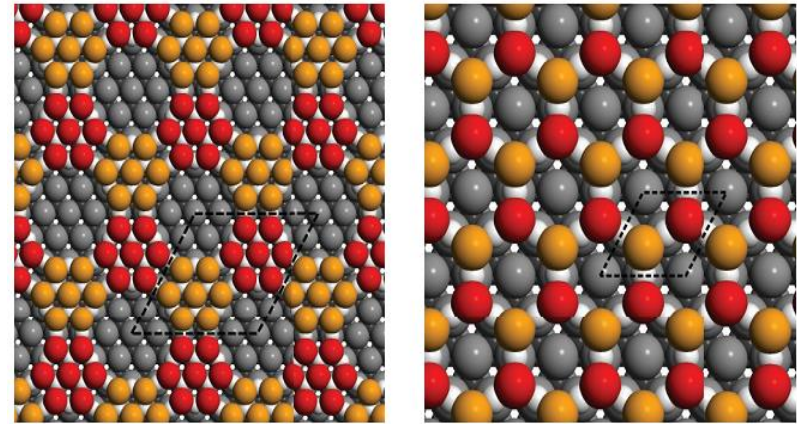
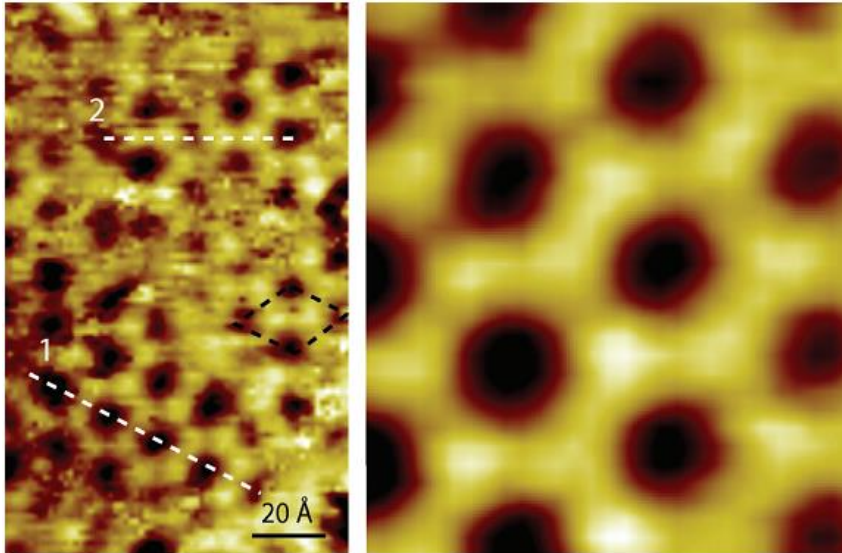
Kresse *et al.* Physical Review **B68**, 245409, 2003

Polar (0001)-Zn surface

- Global optimization reveals triangular patterns



Polar $(000\bar{1})$ -O surface



High-resolution STM image of the hexagonal (5×5) reconstruction present on the terrace places.

Schematic ball model of the most stable structure for the experimentally found hexagonal (5×5) supercell.

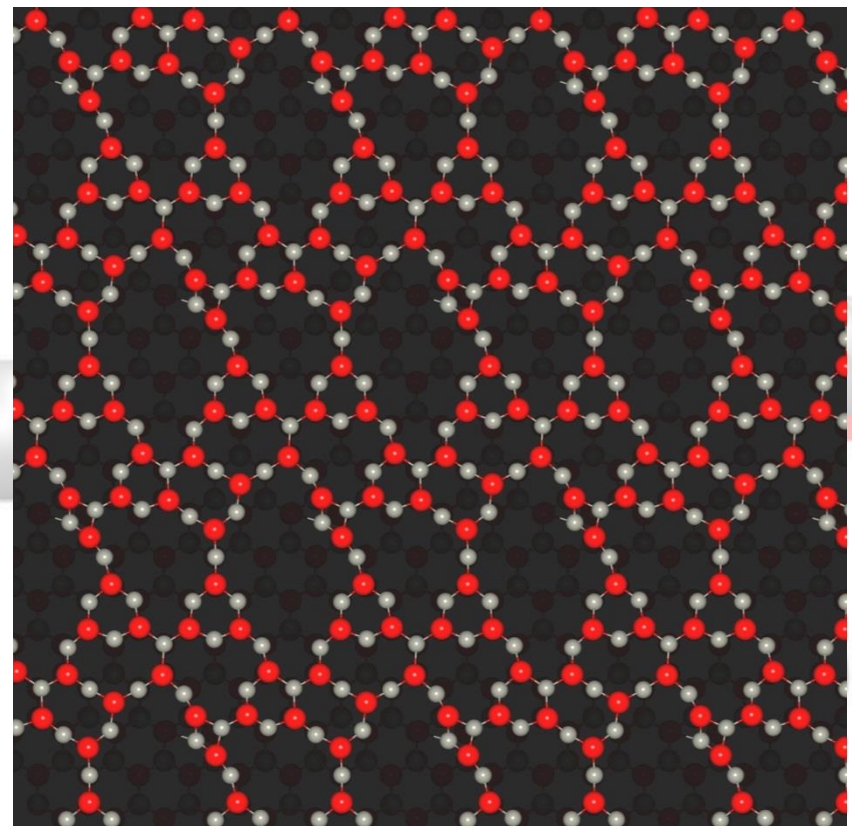
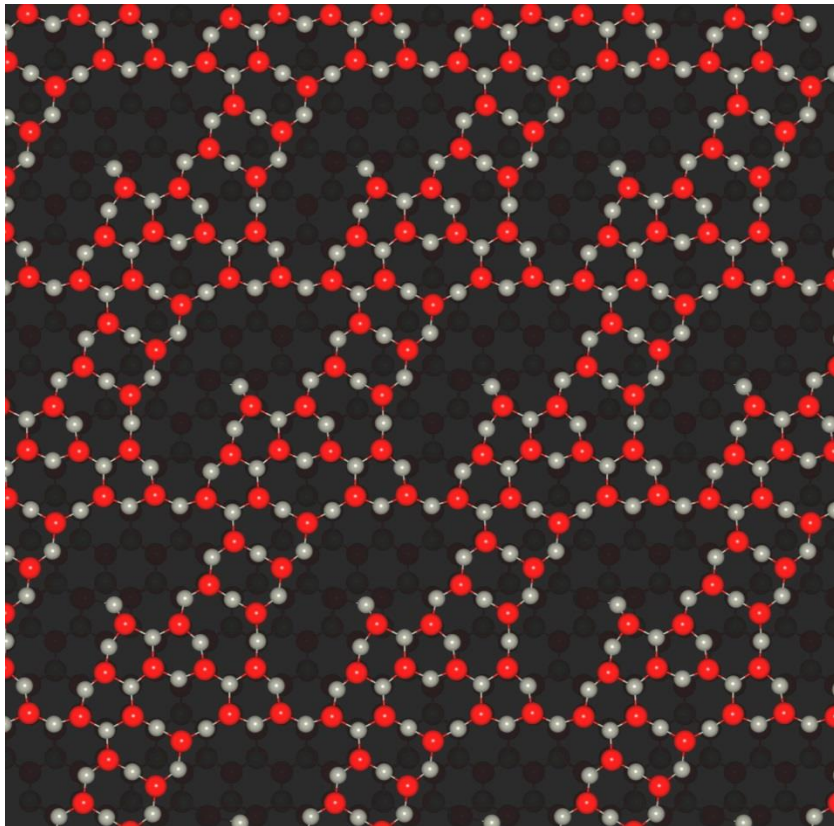
Calculations in progress

Wahl *et al.* Physical Review **B87**, 085313, 2013

Lauritsen *et al.* ACS NANO **5**, No. 7, 5987-5994, 2011

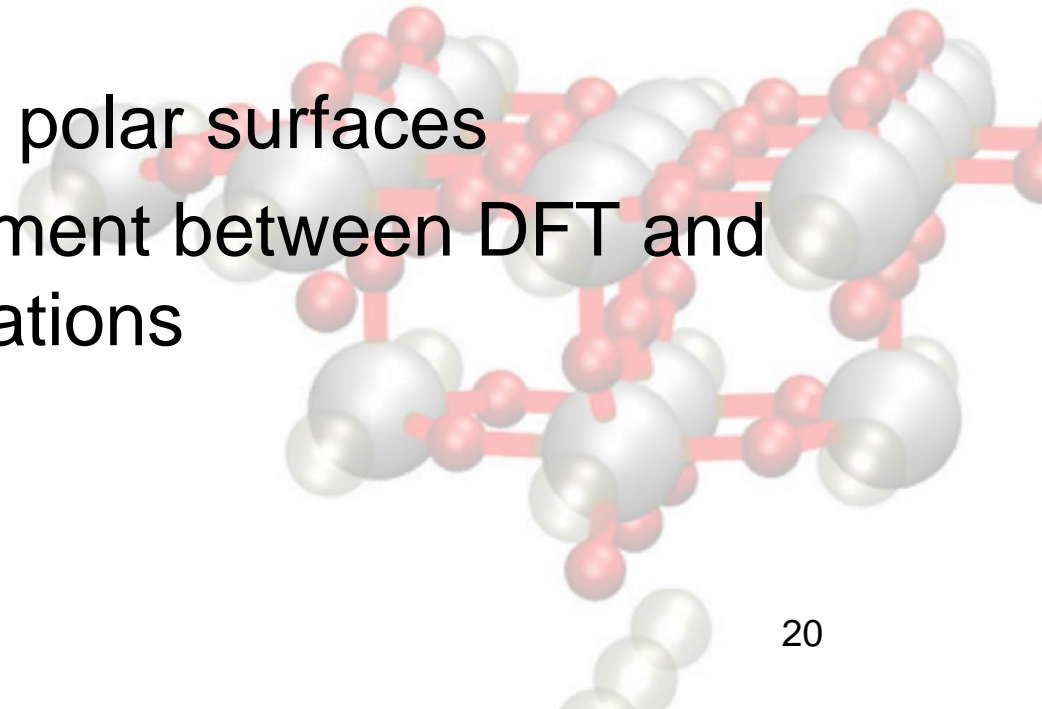
Polar (000-1)-O surface

- Global optimization



Conclusions: Zinc Oxide

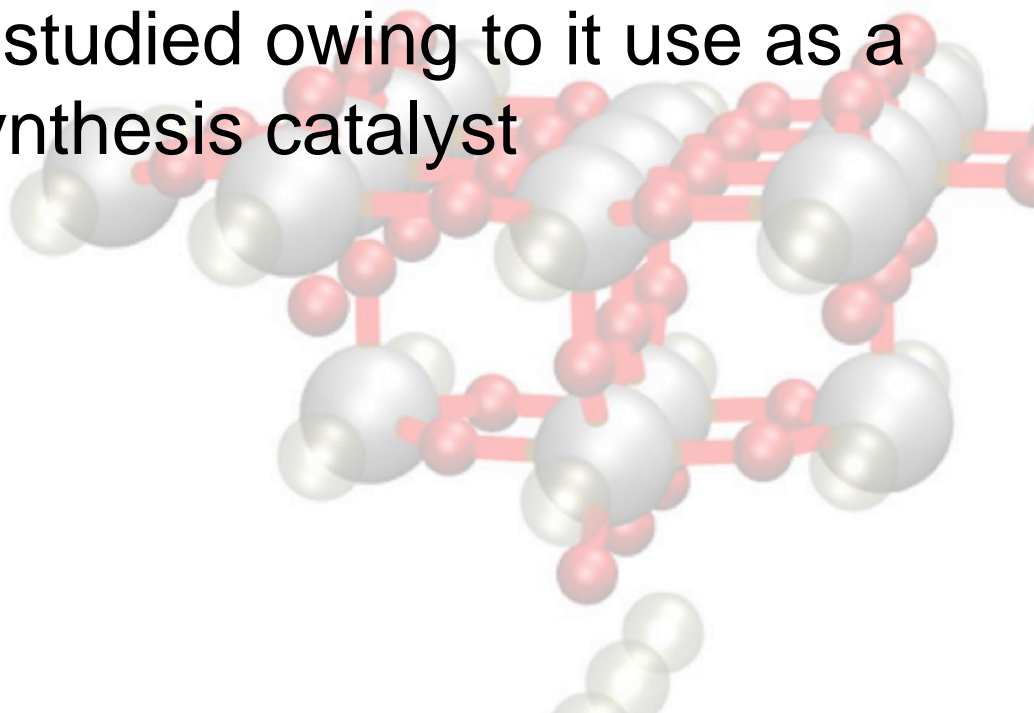
- Complex Surface structures for apparently simple oxide
- Low energy for vacancy and step formation on non-polar surfaces
- Triangular patterns on polar surfaces
- Generally good agreement between DFT and potential based calculations



Cu Nano-Particle Structures on ZnO

David Mora Fonz, Alexei Sokol, Richard Catlow

- Cu/ZnO intensively studied owing to its use as a commercial methanol synthesis catalyst

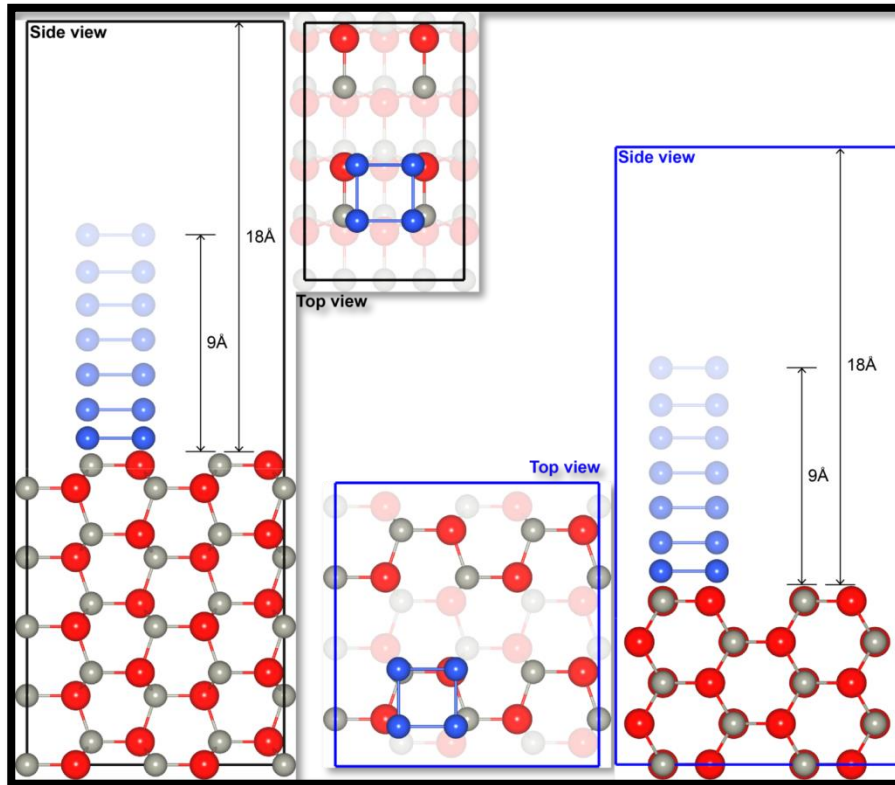


Modelling the Cu/ZnO System – Non Polar Surfaces

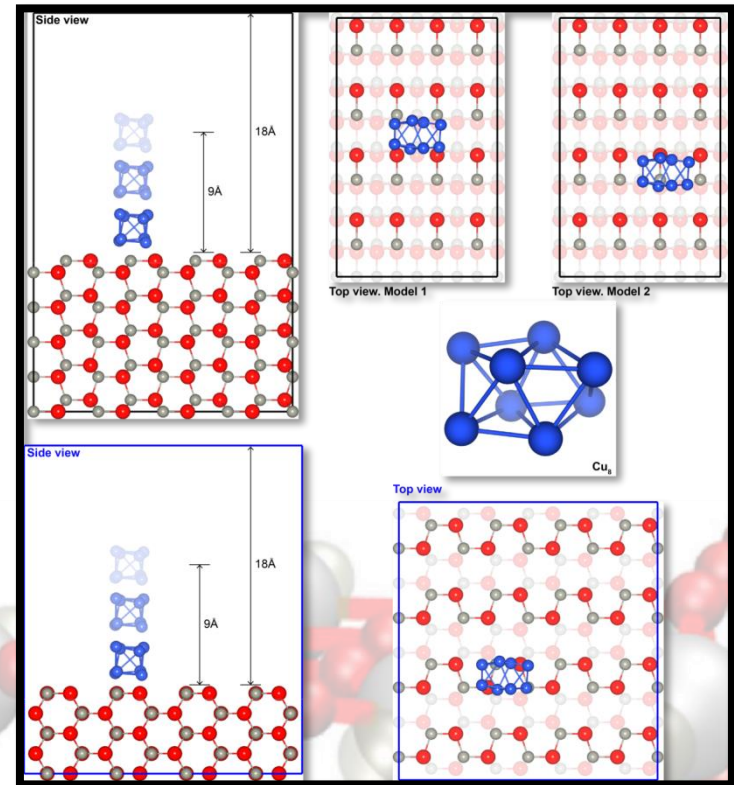
(Mora – Fonz et al. J.Phys Chem, 2017)

- Cu/ZnO interatomic potentials were fitted to DFT calculations.
- Our interatomic potentials were developed with the aim of performing global optimisation calculations in the search for the thermodynamically most stable Cu/ZnO structure and to study large systems, which are required for modelling Cu growth on ZnO surfaces

Methodology: Fitting of Potentials



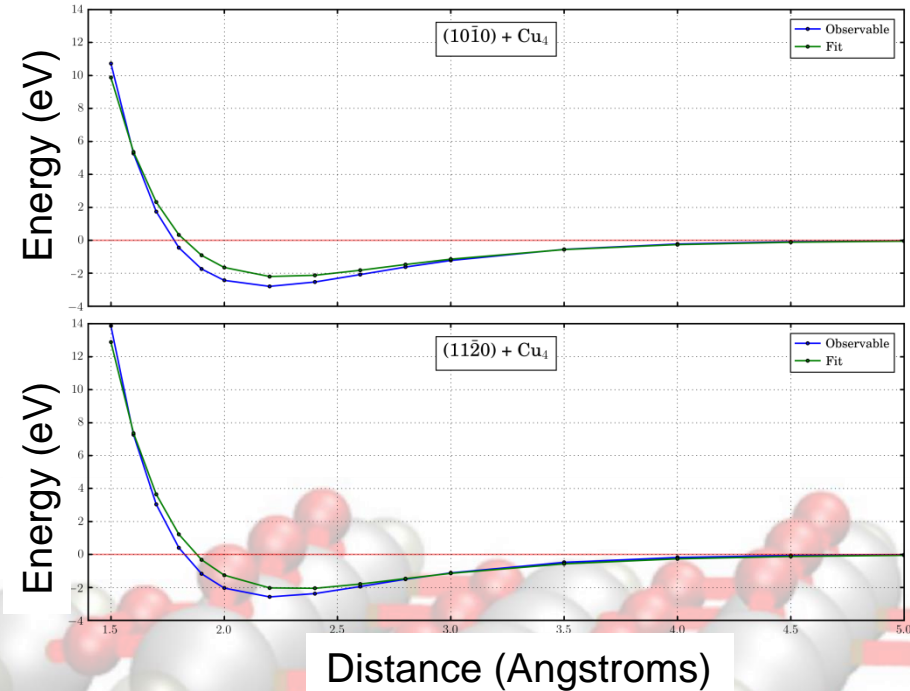
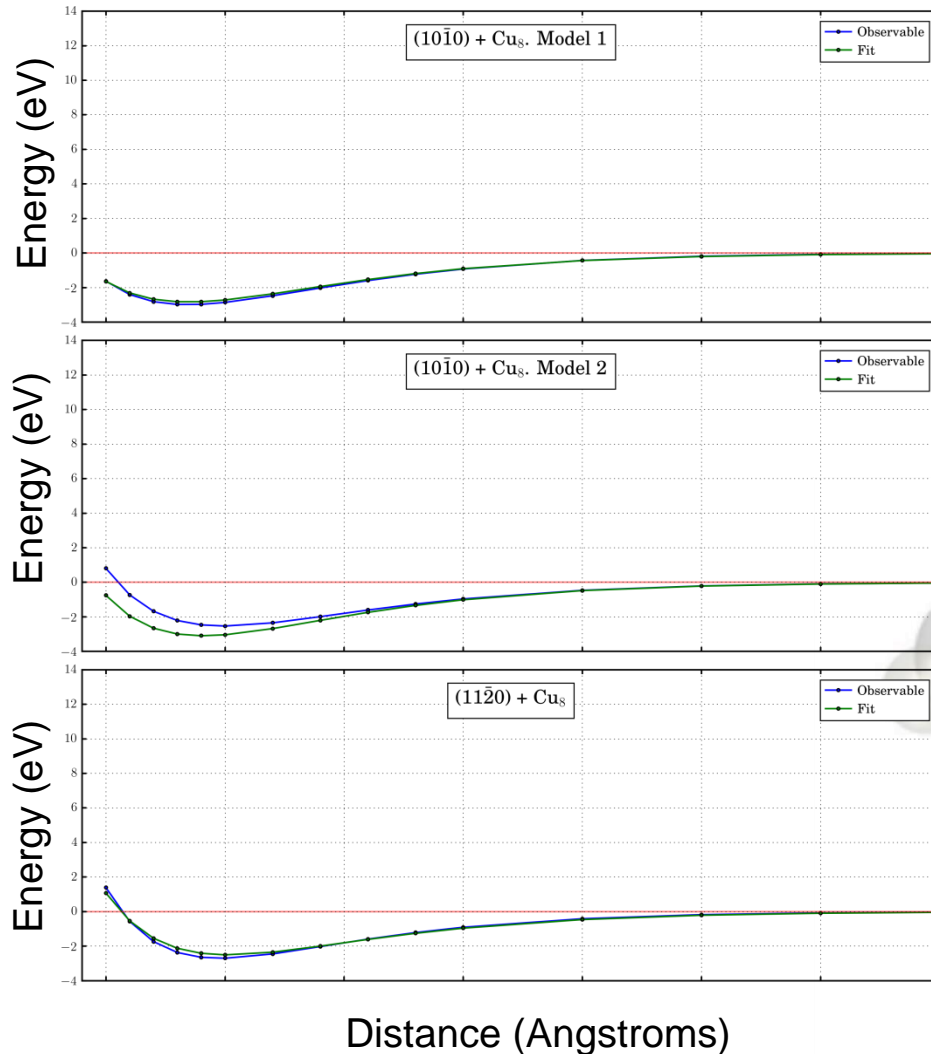
Cu₄ over the (10-10) and (11-20) ZnO surfaces



Cu₈ over the (10-10) and (11-20) ZnO surfaces

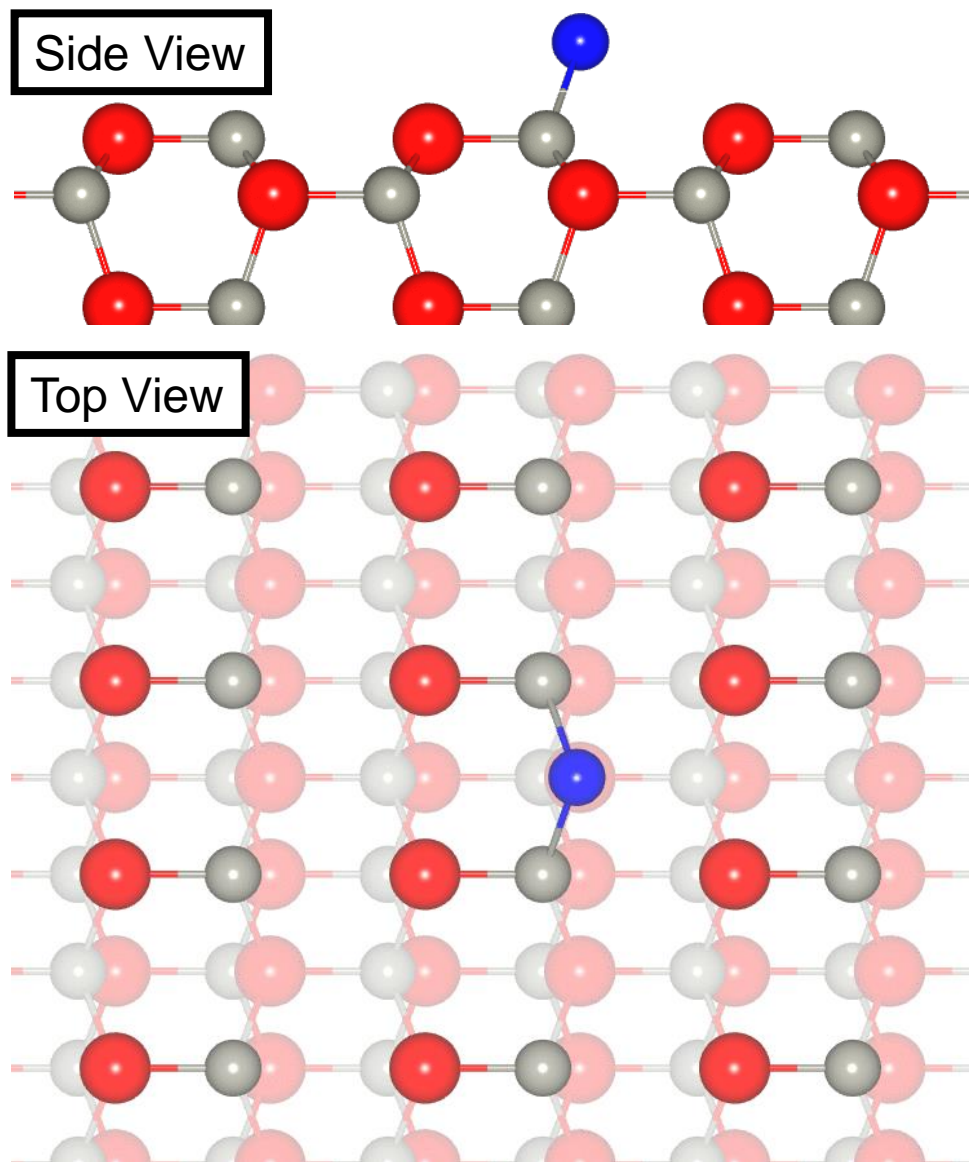
- **Cu/ZnO IP fitted to 90 SP DFT calculations**
- **Surface and cluster morphology independent**
- **Born-Mayer (Cu-O) and Morse (Cu-Zn) potentials**

Methodology: IP and DFT Adsorption Energies



Strong agreement between IP and DFT:
A good representation of the energy depth and the equilibrium interatomic distance.

Cu Growth on ZnO Surfaces Using IP



- Preference for planar structures and strong attraction between Cu and Zn species.
- Cu triangular based structures are predominant.
- Higher stability for bigger Cu clusters.
- ZnO substrate shows a strong influence on the Cu growth, as the 3D shape of the most stable gas phase Cu clusters disappear when in contact with the ZnO surface - *not predicted by simpler methodologies*

Stability of Cu Nanoclusters on the Stepped (10-10) ZnO Surface

Adsorption site

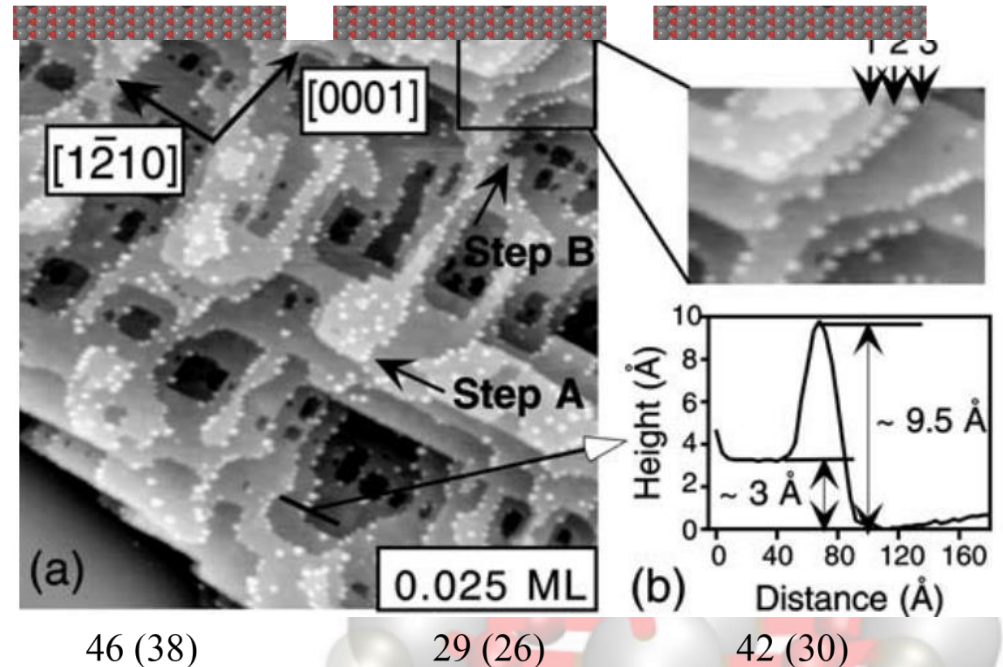
A

B (O)

Terrace

B (Zn)

Patterson, M. C. et al. *The Journal of Physical Chemistry C*, 117(36), 18386–18397. (2013).

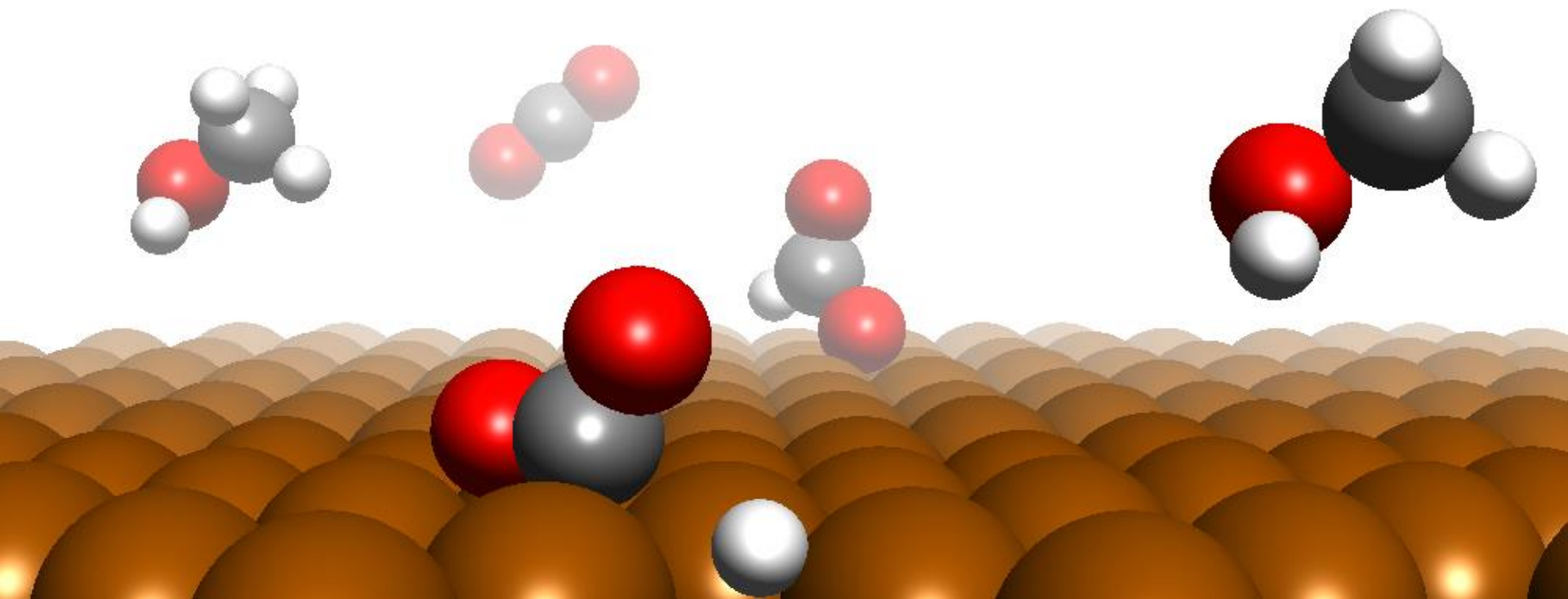


Dulub, O., Boatner, L. A., & Diebold, U. *Surface Science*, 504, 271–281. (2002)

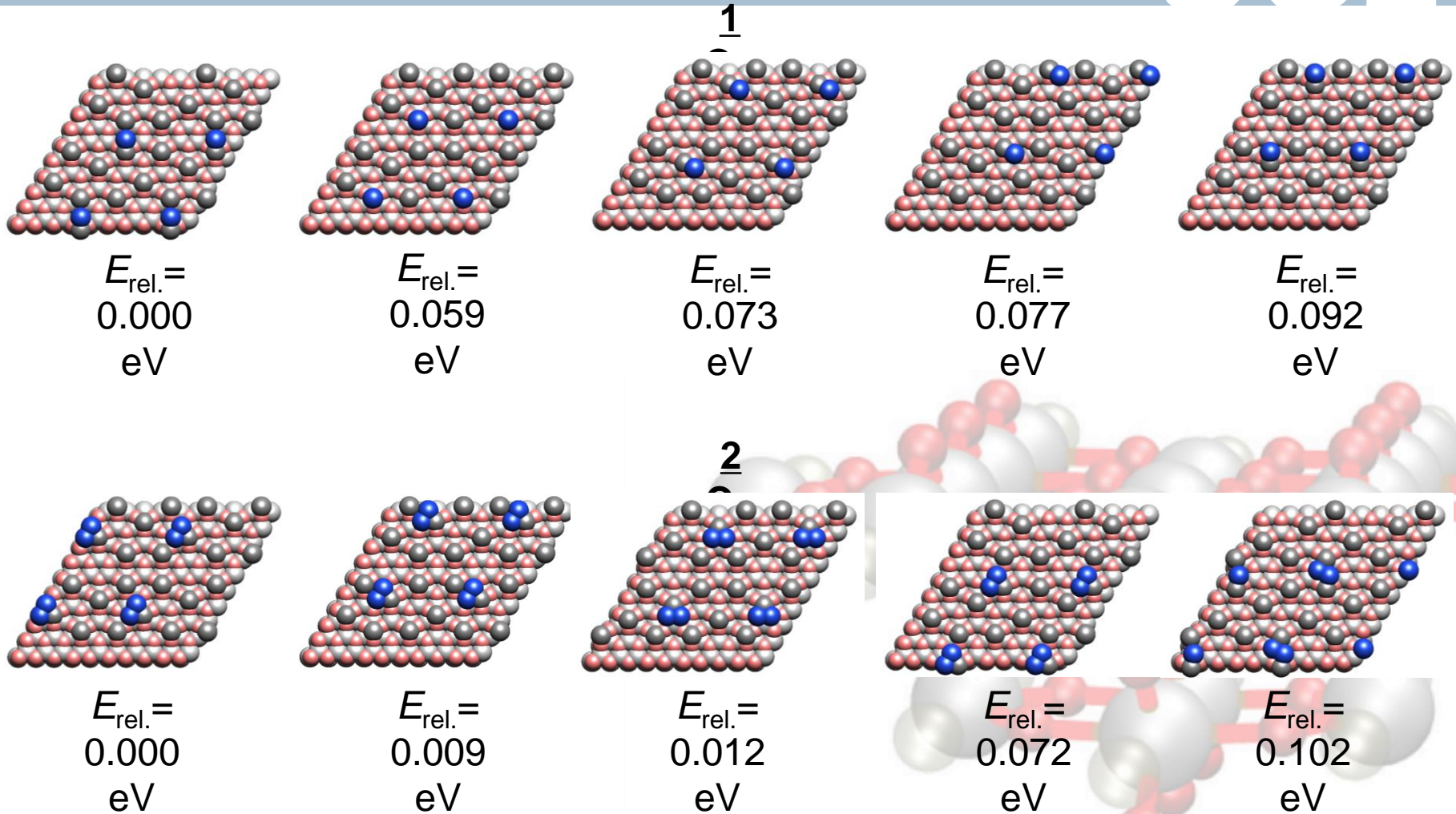
Growth of Cu Clusters over Reconstructed Polar ZnO Surfaces and Cu/ZnO CO₂ Activation

Michael Higham, David Jurado, Matthew
Quesne, David Mora-Fonz, Alexey Sokol,
Richard Catlow

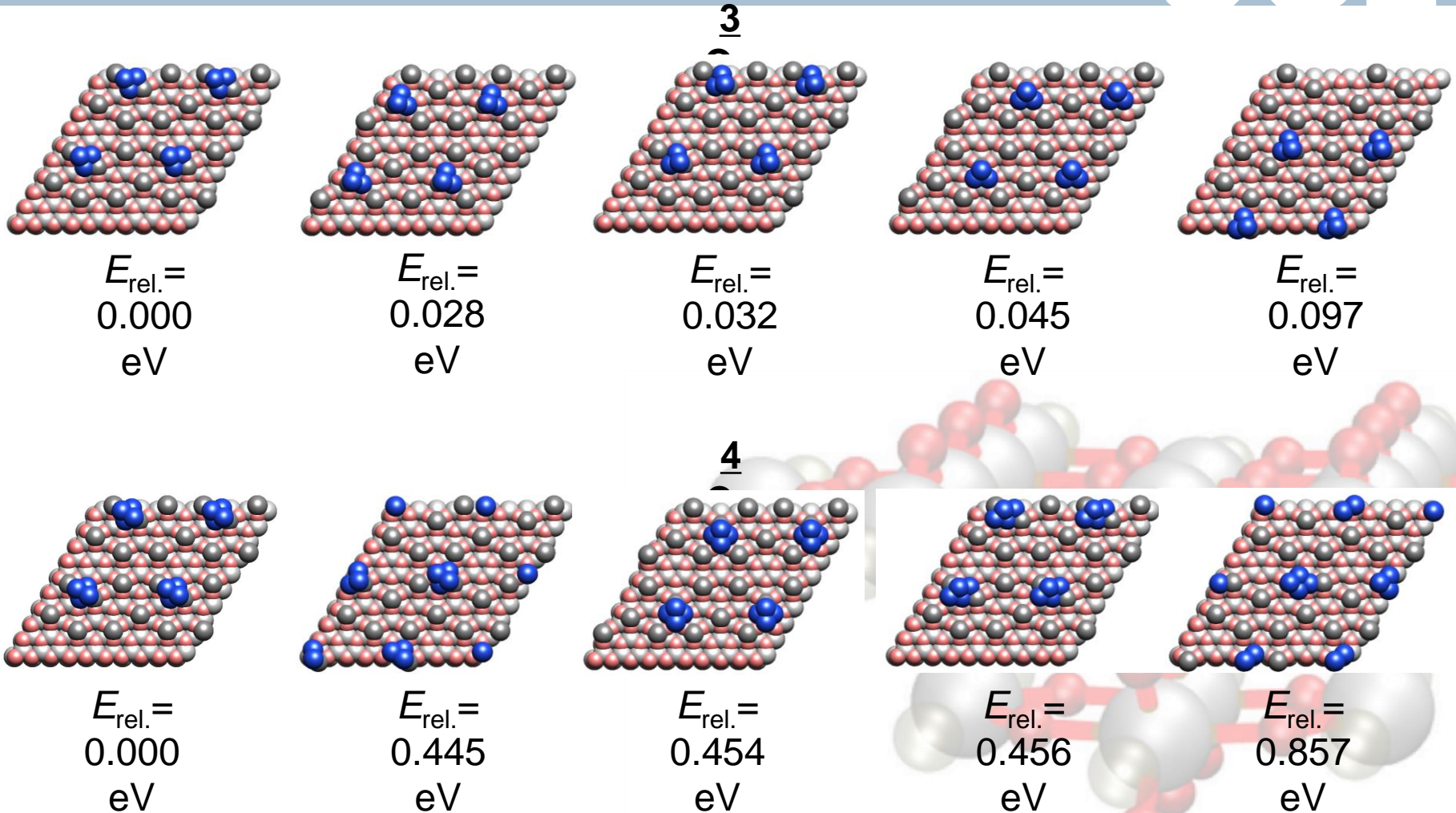
J. Materials Chem A - accepted



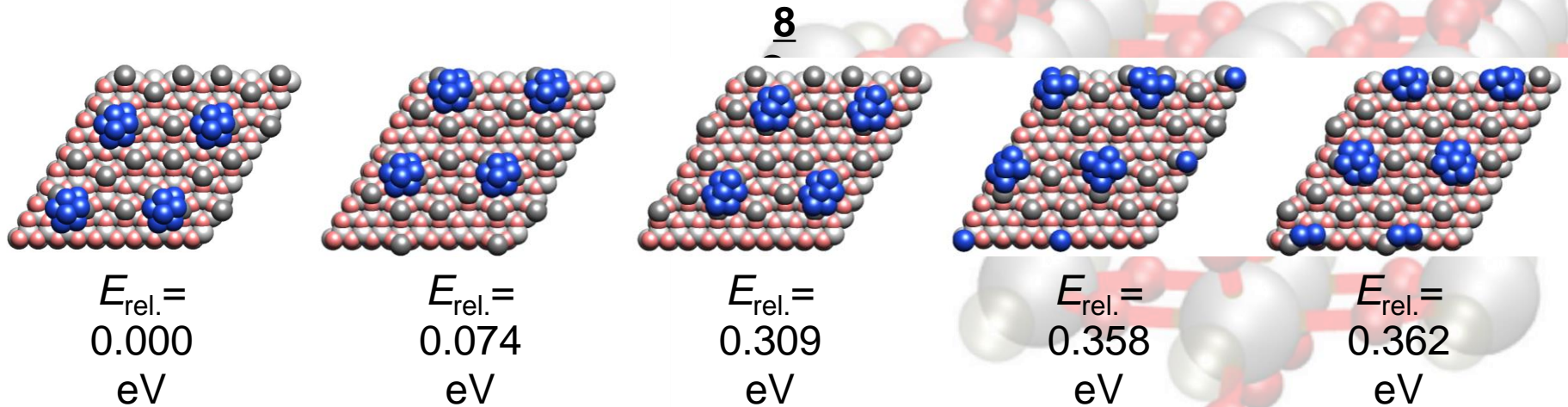
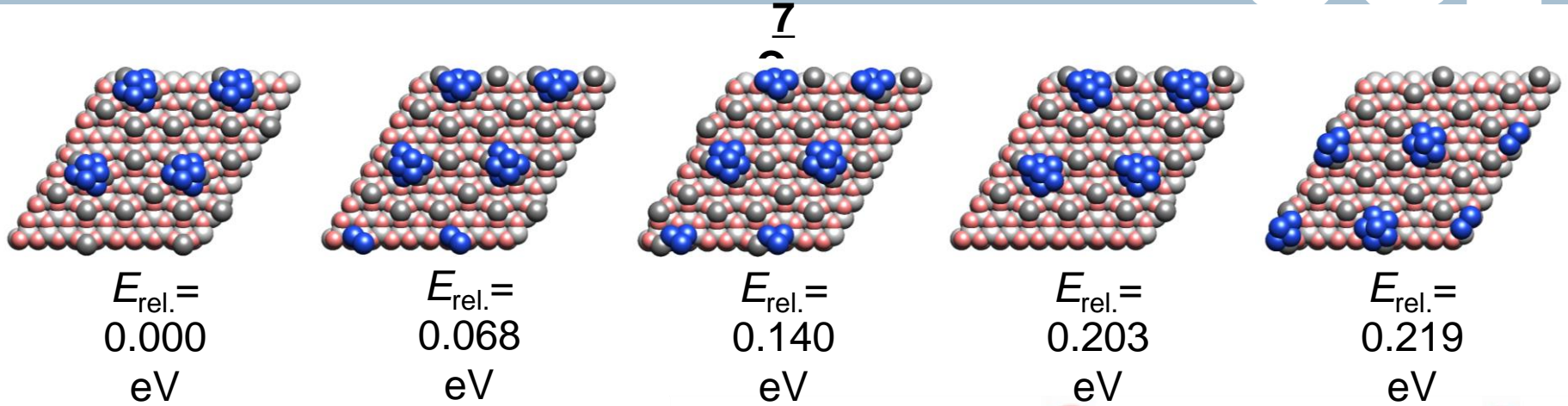
Results - Relative Stability of Low-Energy Structures



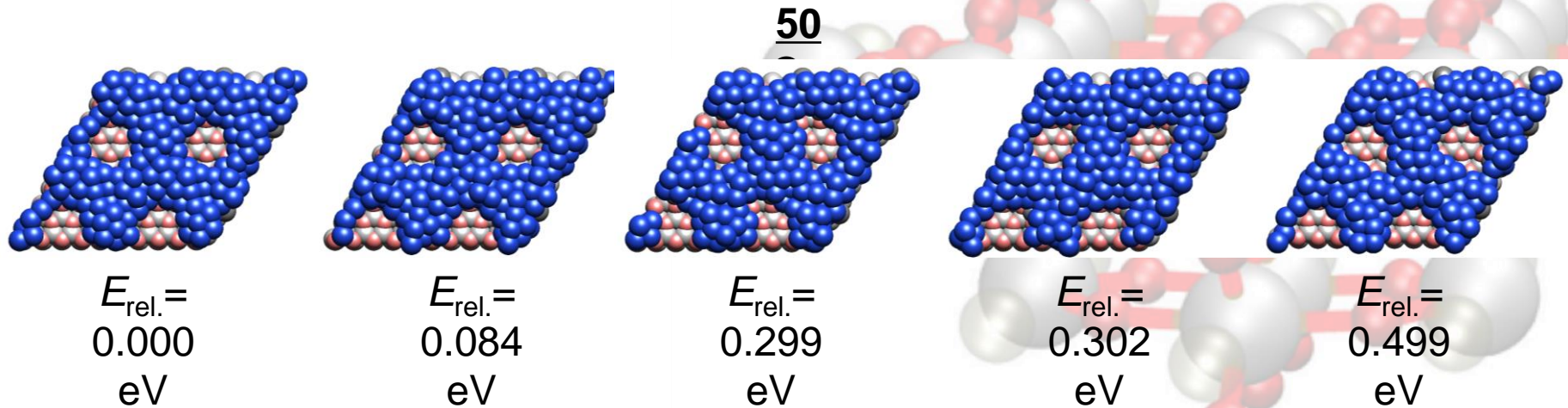
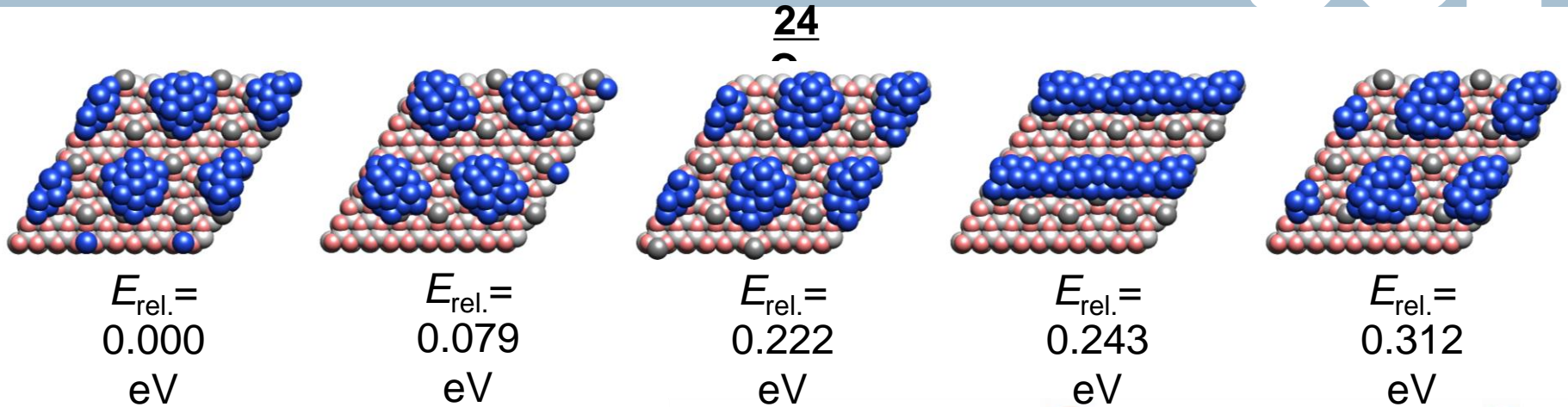
Results - Relative Stability of Low-Energy Structures



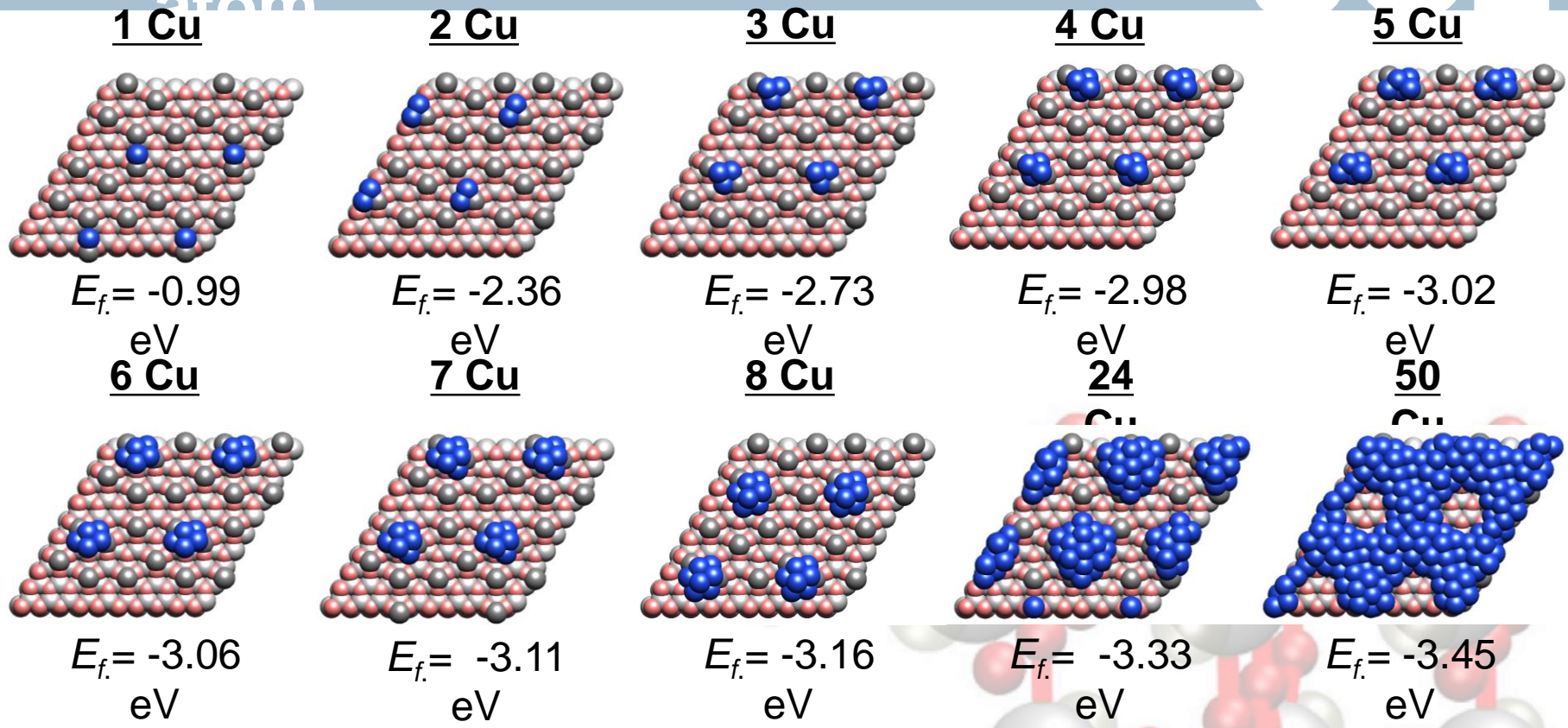
Results - Relative Stability of Low-Energy Structures



Results - Relative Stability of Low-Energy Structures



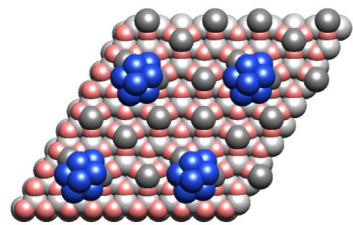
Cu Cluster Formation Energy of Most Stable Structures – w.r.t. Atomic Cu



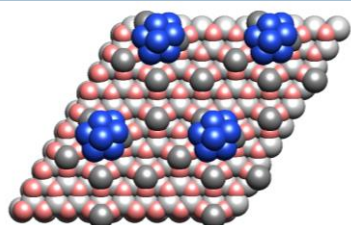
$$E_f = (E_{\text{Cu}(n)\text{-ZnO}} - E_{\text{ZnO-slab}}) / n$$

Where $E_{\text{ZnO-slab}}$ refers to the energy of the Zn-T reconstructed polar ZnO slab, n refers to the number of Cu atoms per 5x5 reconstructed polar ZnO slab, and $E_{\text{Cu}(n)\text{-ZnO}}$ refers to the energy of a Cu_n cluster adsorbed on said reconstructed ZnO slab.

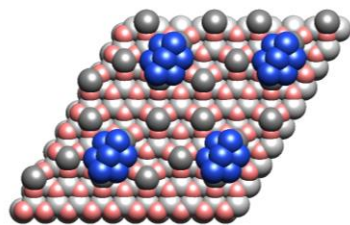
DFT Refinement – Cu₈



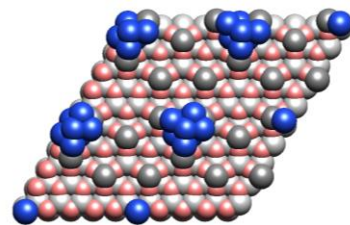
$E_{\text{rel.}} =$
0.000
eV



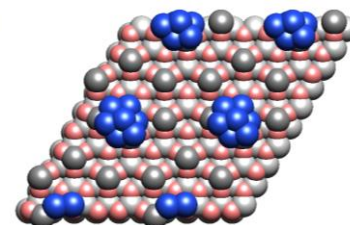
$E_{\text{rel.}} =$
0.074
eV



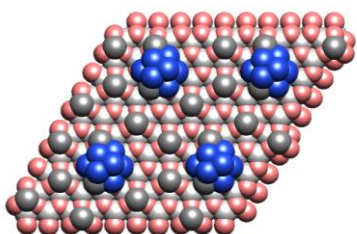
$E_{\text{rel.}} =$
0.309
eV



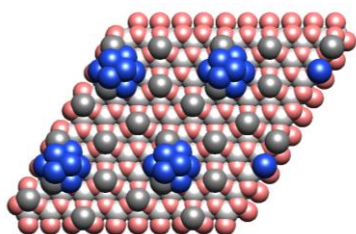
$E_{\text{rel.}} =$
0.358
eV



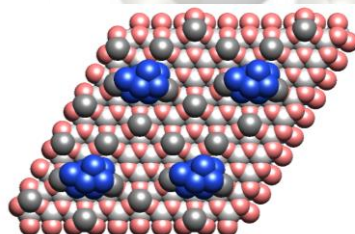
$E_{\text{rel.}} =$
0.362
eV



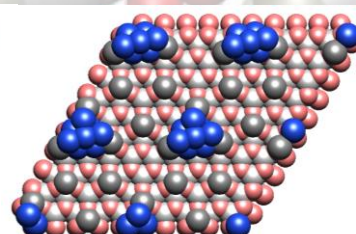
$E_{\text{rel.}} =$
0.000
eV



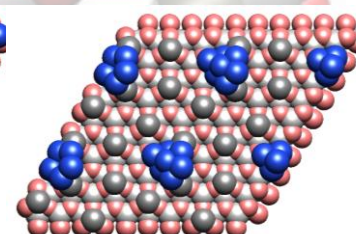
$E_{\text{rel.}} =$
0.045
eV



$E_{\text{rel.}} =$
0.897
eV



$E_{\text{rel.}} =$
1.059
eV

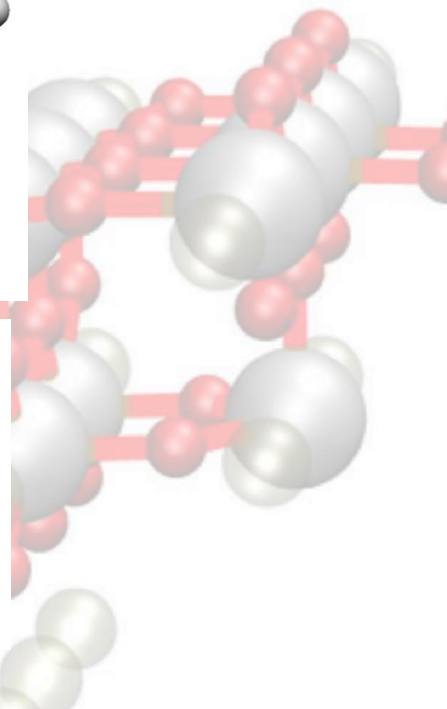
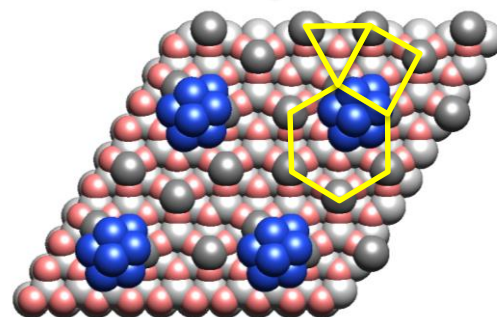
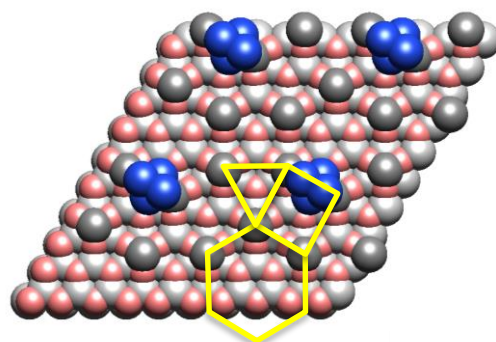
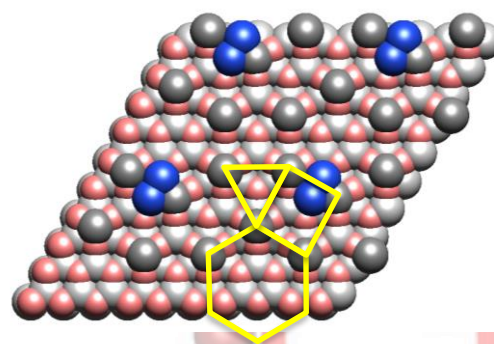
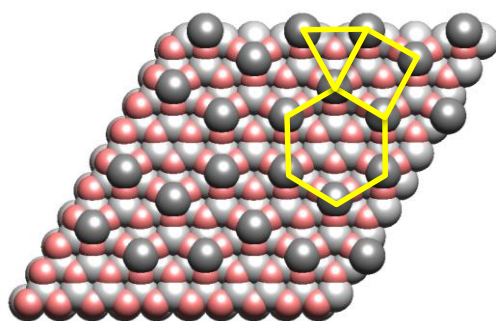


$E_{\text{rel.}} =$
0.696
eV

Cu Cluster Formation: observations



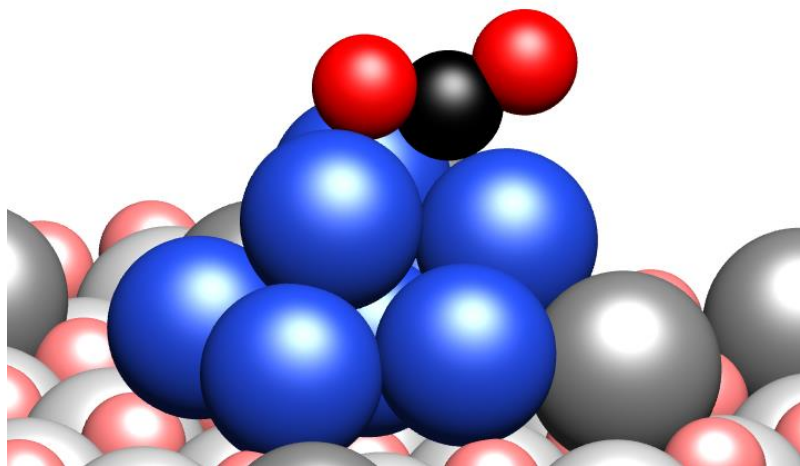
- 3 distinct surface regions defined by surface Zn atoms – triangular, rectangular, hexagonal.
- All Cu concentrations up to 8 Cu atoms per ZnO surface cell show preferential growth on hexagonal-rectangular region boundary – optimal Cu – Zn coordination due to ideal Zn-Zn distance along this boundary to accommodate Cu cluster. Tetrahedral Cu_4 cluster at this site is especially stable - ~ 0.45 eV more stable than the next lowest energy structure.



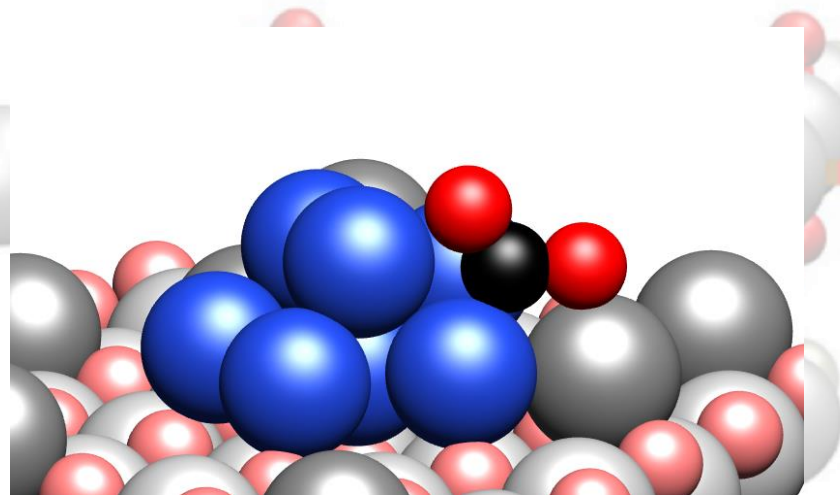
CO₂ Activation over Cu₈-ZnO



- Calculations identify stable bent CO₂ adsorption on top of Cu cluster and at interfacial site, but not on isolated Zn surface sites.
- Bader charge analysis – charge transfer to CO₂ from substrate comparable to unsupported Cu, but greater for interfacial CO₂ compared to CO₂ on top of Cu cluster. Reflected in smaller \angle (O-C-O) for interfacial site.
- Al substitutional doping in bulk layers for Zn to simulate role of Al in industrial Cu-ZnO-Al₂O₃ – calculations underway.
- Future work will explore full CO₂ hydrogenation reaction mechanism over model Cu/ZnO surfaces.



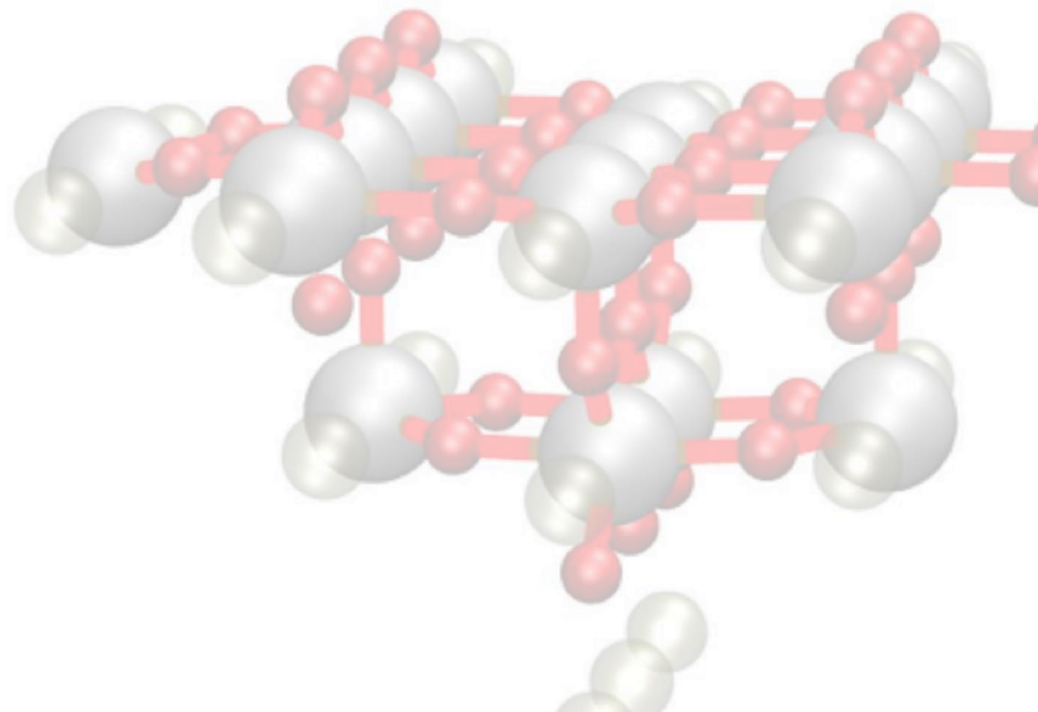
CO₂ on top of Cu cluster
 $\Delta\beta = 0.65$
 \angle (O-C-O) = 133.35°



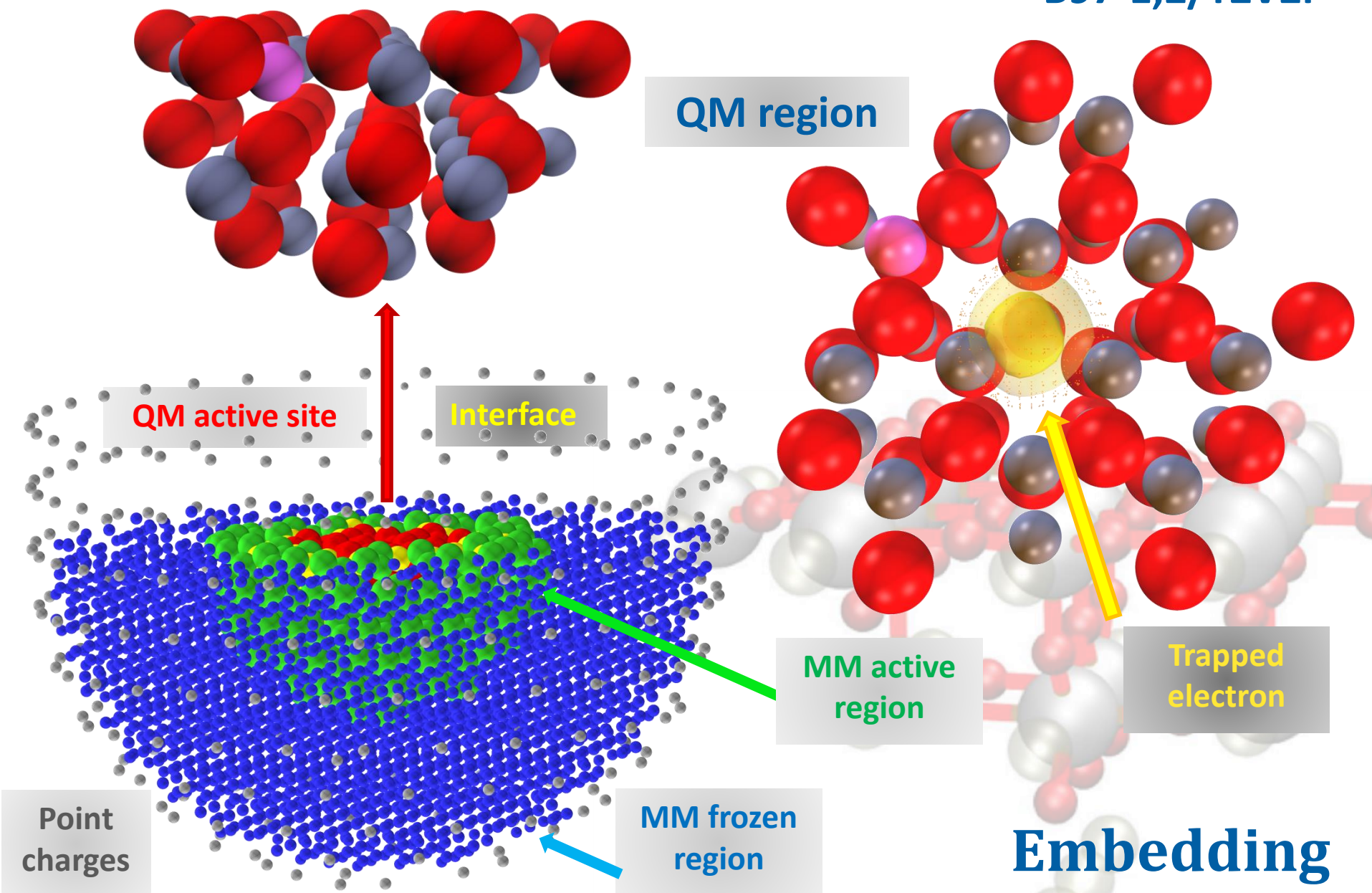
CO₂ at Cu-Zn interfacial site
 $\Delta\beta = 0.77$
 \angle (O-C-O) = 123.95°

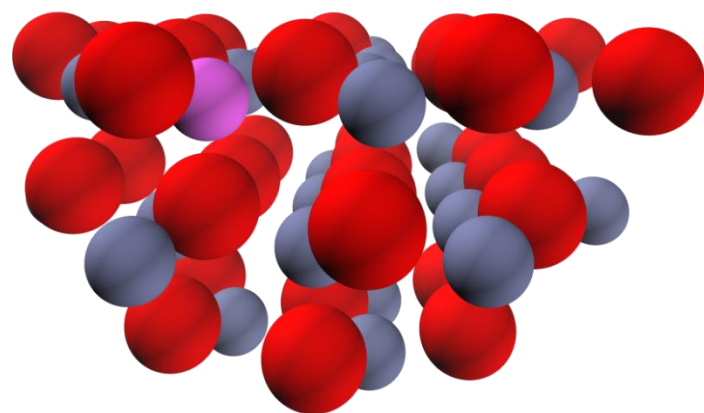
THEME THREE: QM/MM Techniques

- Titania Polymorphs as Photo-Catalysts



B97-1,2/TZV2P

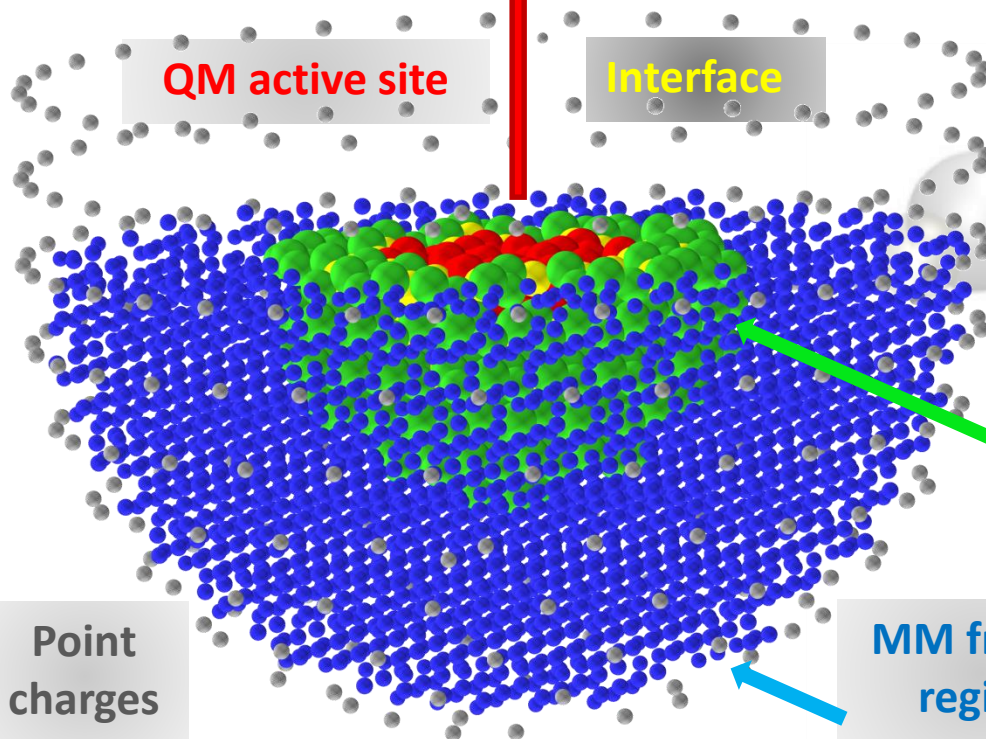




QM region

No spurious interactions between periodically repeated charged defects as in plane wave supercell methods

Unambiguous energy reference
→ ionization energies



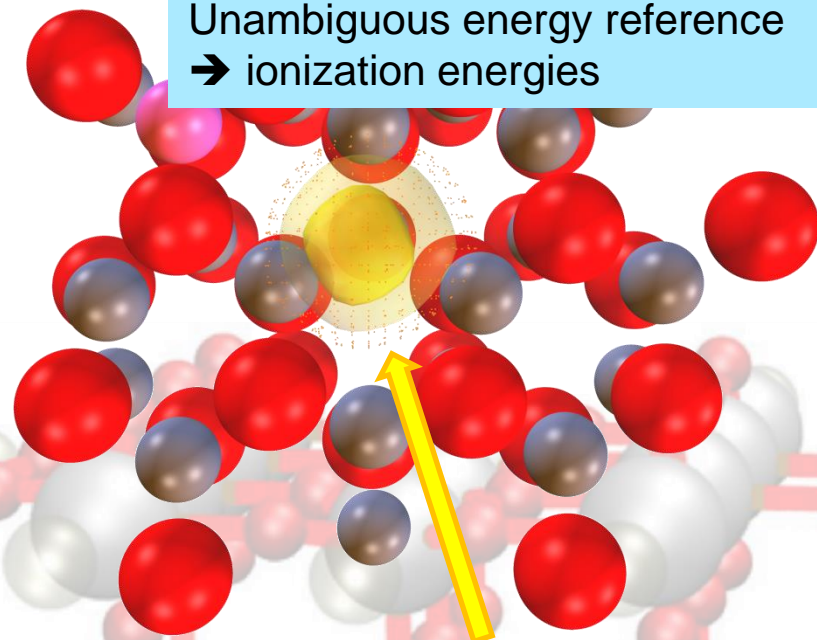
QM active site

Interface

MM active region

MM frozen region

Point charges



Trapped electron

Embedding

Electronic structure of TiO₂: polymorph engineering for photocatalysis

John Buckeridge, D. O. Scanlon^{1,2}, Andrew J. Logsdail¹, Scott M. Woodley¹, Alexey A. Sokol¹, Keith T. Butler³, Aron Walsh³, and C. Richard A. Catlow¹

(Scanlon et al., *Nature Materials*, 12, 798, 2013;

Buckeridge et al., *Chem Mater*, 27, 3844, 2015)

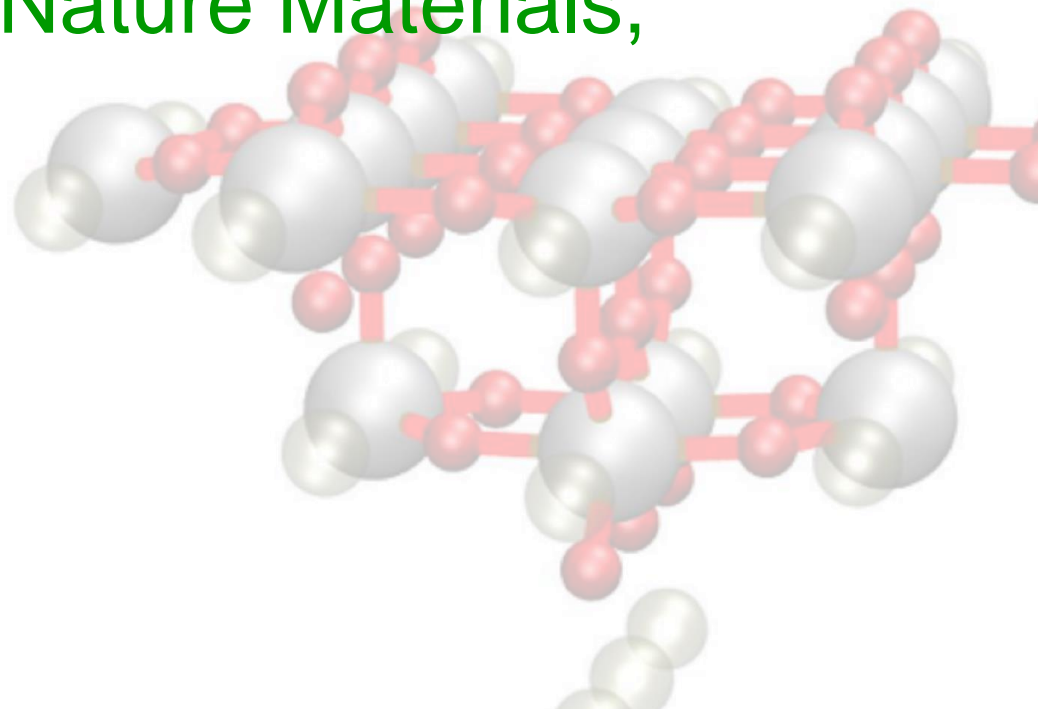
¹Kathleen Lonsdale Materials Chemistry, University College London

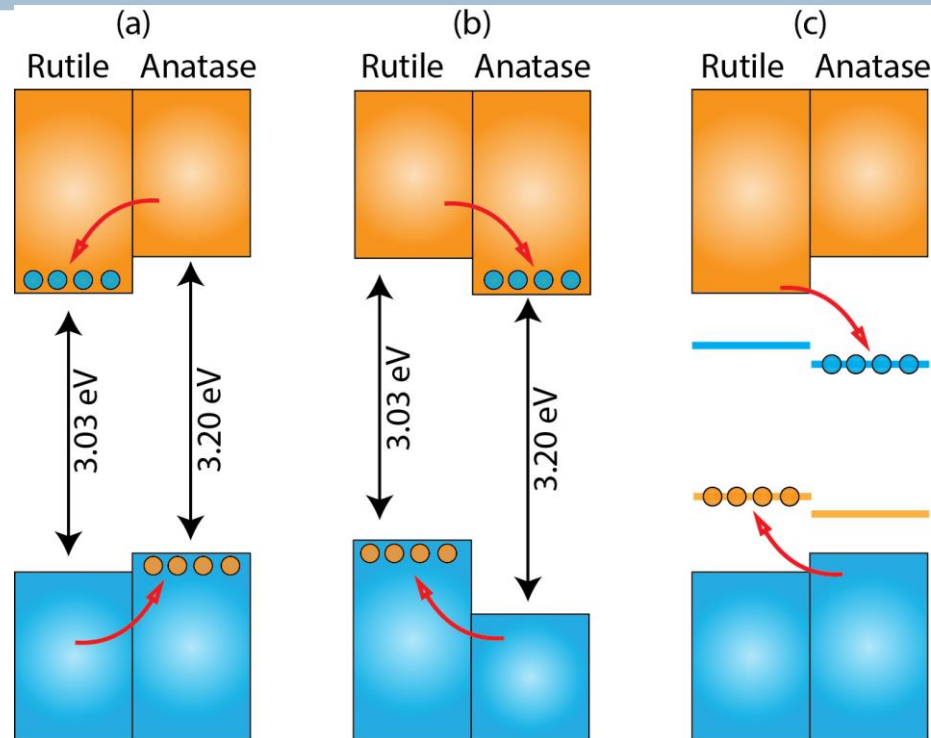
²Diamond Light Source Ltd., Harwell Science and Innovation Campus, Didcot

³Centre for Sustainable Chemical Technologies and Department of Chemistry, University of Bath

BAND ALIGNMENT IN RUTILE/ANATASE

David Scanlon, Ivan Parkin, Richard Catlow,
Andy Logsdail et al., Nature Materials,
12,798,2013



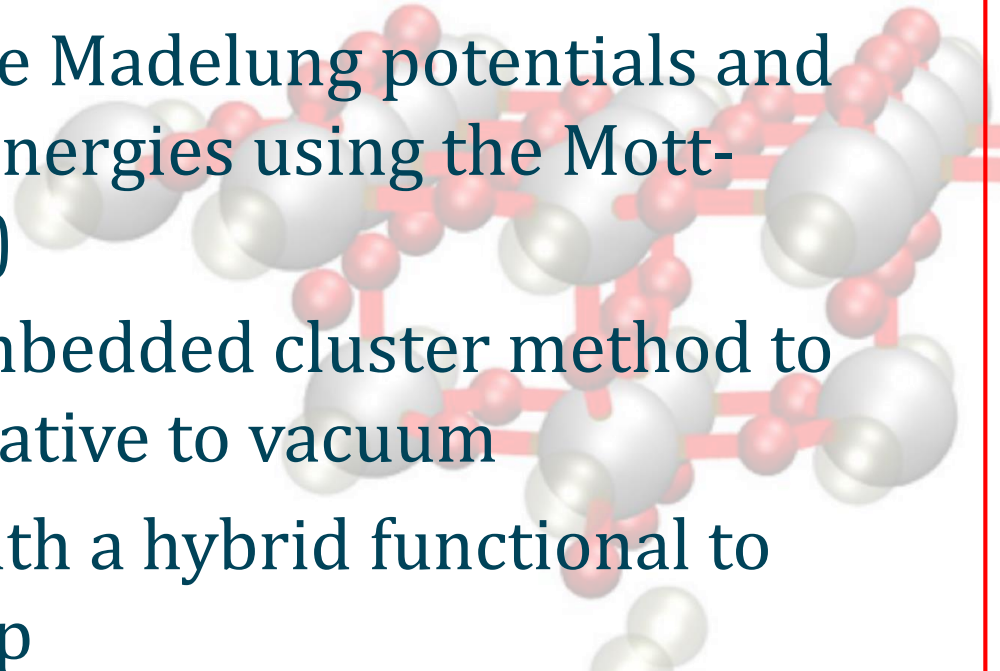


(a) 1996 measurement – normal model.

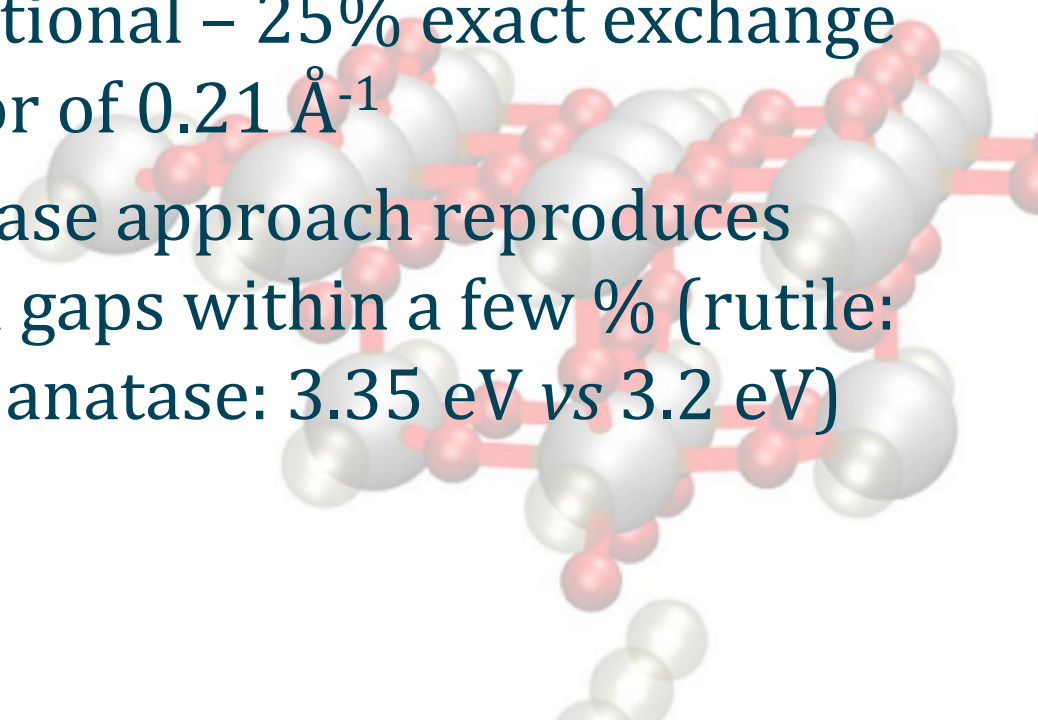
(b) 2007 UPS workfunction (W) study: Anatase 5.1 eV, Rutile 4.9 eV

– Challenges normal model?

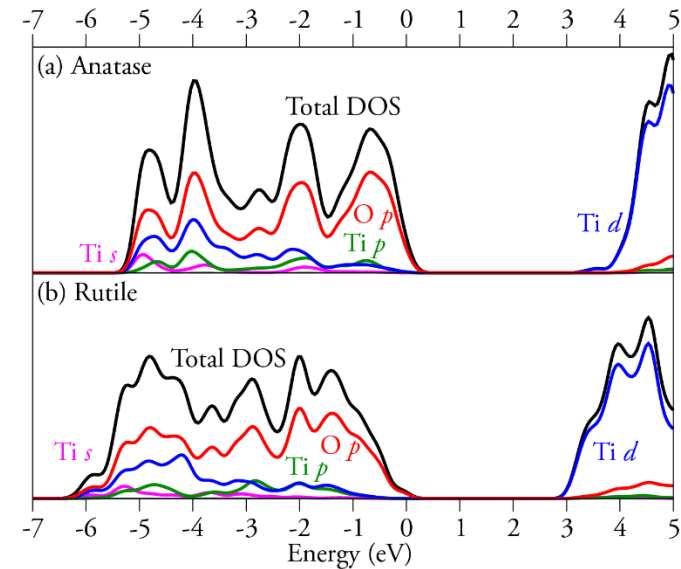
(c) EPR experiments indicate that electrons flow into anatase, but use “deep trap levels” to explain, still based on 1996 model

- To determine the bulk band alignments we need for each polymorph:
 - Valence band maximum (VBM) relative to vacuum
 - Accurate band gap
 - Use three computational approaches:
 - Initial 'rough' estimate via classical forcefields (by determining the Madelung potentials and electron and hole energies using the Mott-Littleton approach)
 - Hybrid QM/MM embedded cluster method to determine VBM relative to vacuum
 - Plane-wave DFT with a hybrid functional to determine band gap
- 
- A 3D ball-and-stick model of a molecular structure, likely a polymer or crystal lattice. It features a chain of large grey spheres (possibly carbon) connected by red spheres (possibly oxygen or nitrogen), with smaller white and red spheres branching off. The structure is semi-transparent, allowing the text behind it to be visible.

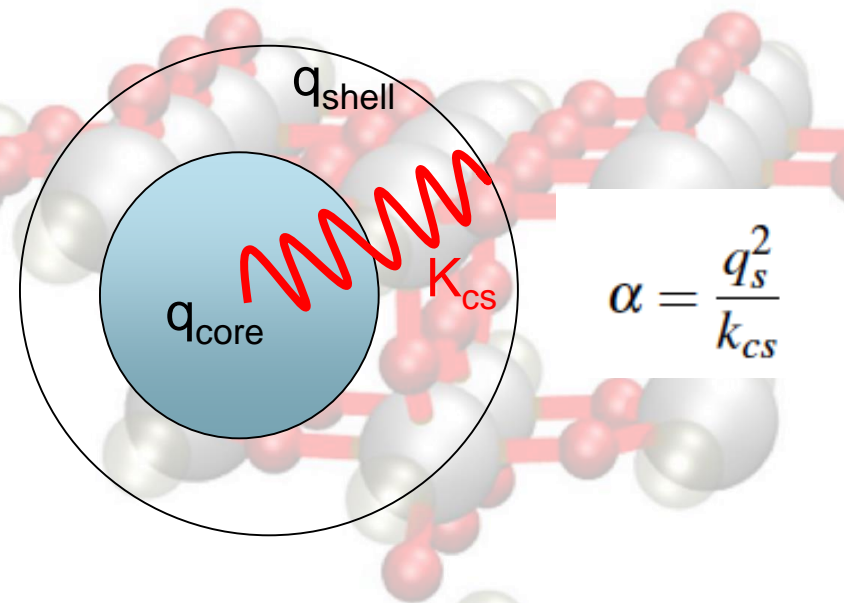
- Plane-wave DFT with hybrid functional:
 - VASP code used
 - Plane-wave cut-off 500 eV
 - PAW approach for core (Ti:[Ar], O:[He]) and valence electron interaction
 - HSE06 hybrid functional – 25% exact exchange screened by a factor of 0.21 \AA^{-1}
 - For rutile and anatase approach reproduces experimental band gaps within a few % (rutile: 3.09 eV vs 3.03 eV; anatase: 3.35 eV vs 3.2 eV)



- Similar upper VB width => no significant chemical broadening
- Band edge positions determined by:
 - onsite electrostatic potential (Madelung)
 - optical dielectric response
- VB edge: O $2p$, CB edge: Ti $3d$ =>
 - energetics of hole on O and electron on Ti will approximately correspond to VB and CB relative positions



- Polarisable shell forcefield used to account for local dipoles in TiO_2
- Ions represented by core and shell connected by spring
- Spring constant and core-shell charge split fitted to reproduce optical dielectric response
- Use model to determine Madelung potentials and Mott-Littleton electron and hole energies



- Madelung Potential:

$$V_i = \sum_{j \neq i} \frac{z_j}{r_{ij}}$$

	V_O	V_{Ti}
Anatase	26.232 V	-45.025 V
Rutile	25.767 V	-45.199 V
Difference	0.465 V	0.174 V

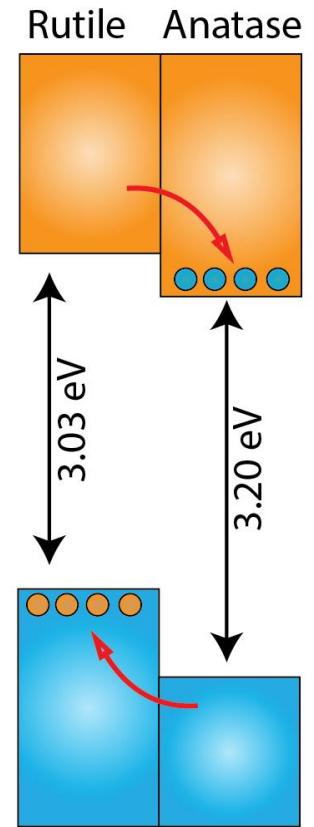
From on site potentials =>

VBM of rutile **0.47 eV above** anatase
 CBM of rutile **0.17 eV above** anatase

- Energy of charge carriers propagating via the Mott-Littleton approach agrees with the Madelung potentials =>

VBM of rutile **0.39 eV above** anatase
 CBM of rutile **0.24 eV above** anatase

Band alignment favours charge separation! ←

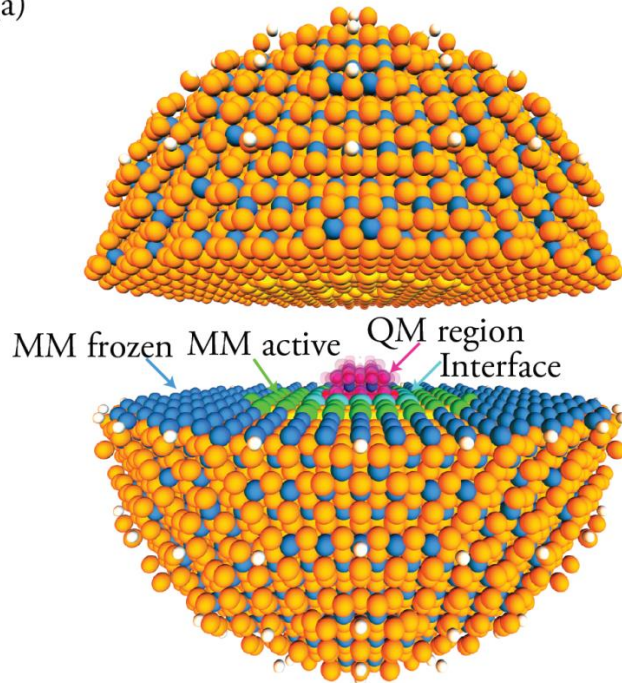


Scanlon, Dunnill, Buckeridge *et al.*,
Nature Mater. **12** 798 (2013)

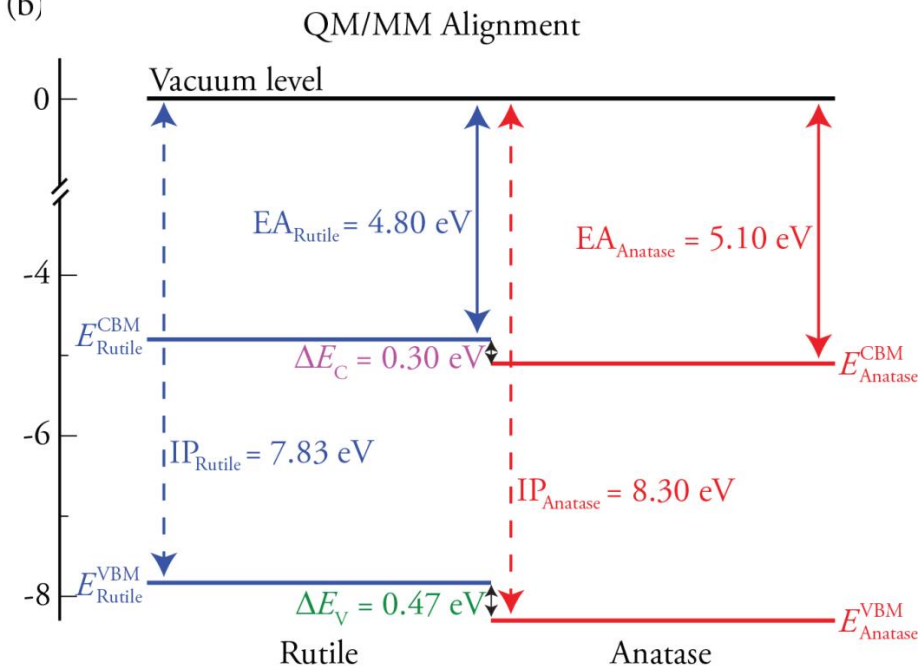
QM/MM results

QM/MM calculations of IP for rutile and anatase for a range of cluster sizes (~50 to ~80 atoms)

(a)



(b)



IP_{Rutile}	=	7.83 eV
IP_{Anatase}	=	8.30 eV
Difference	=	0.47 eV

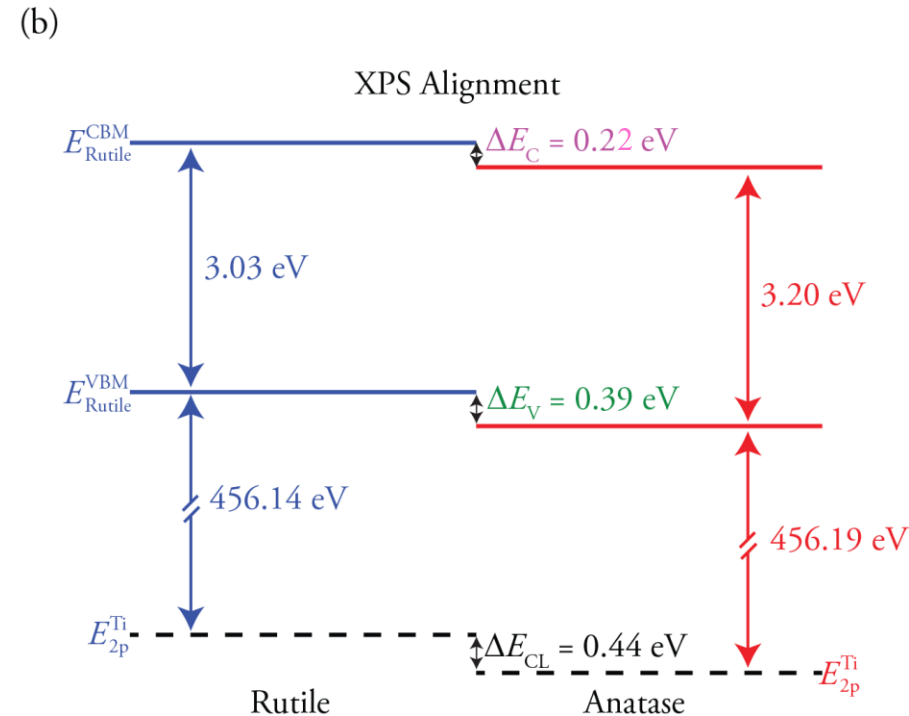
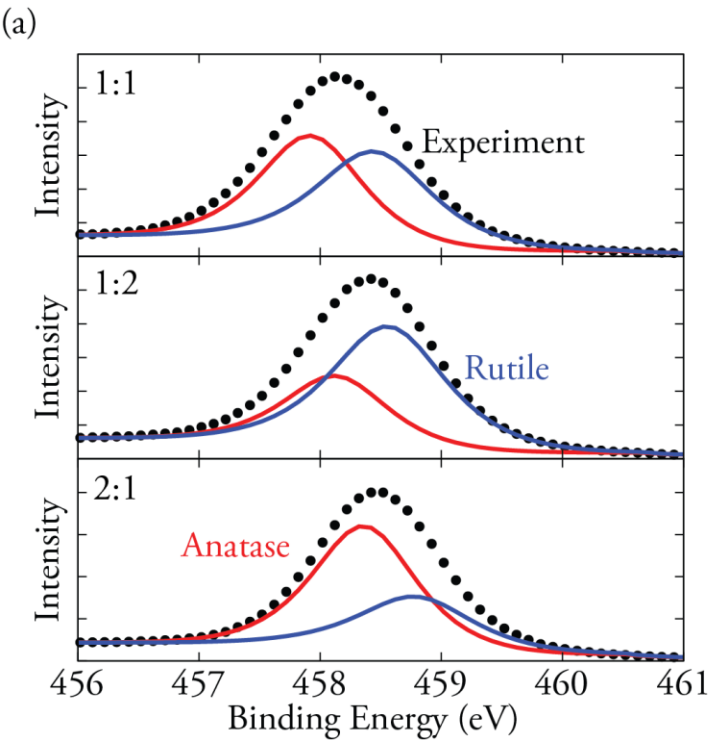
Calculated IP of ZnO is 7.71 eV [1]

- 0.12 eV less than rutile
- 0.14 eV is experimental offset [2]
- Thus further excellent agreement

[1] Sokol *et al.*, Faraday Discuss. **134** 267 (2007)

[2] Swank, Phys. Rev. **153** 844 (1967)

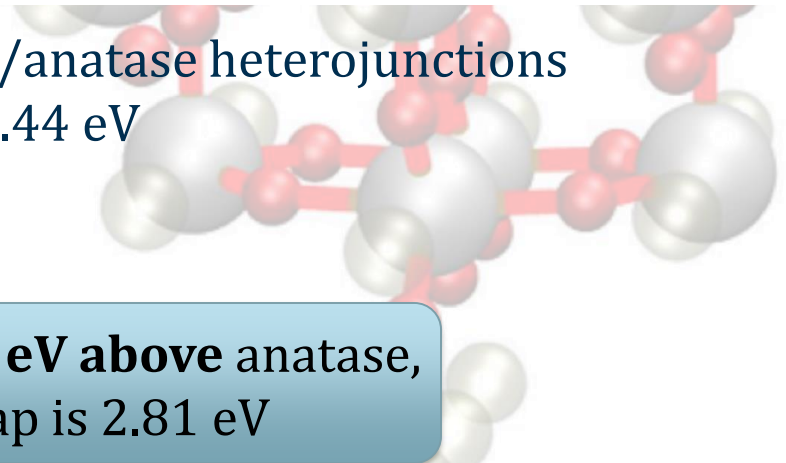
Experiment: XPS Measurements



Independent XPS measurements on rutile/anatase heterojunctions find a shift in the core level alignment of 0.44 eV

Core level to VBM separations indicates:

VBM of rutile is **0.39 ± 0.02 eV above** anatase,
and effective band gap is 2.81 eV

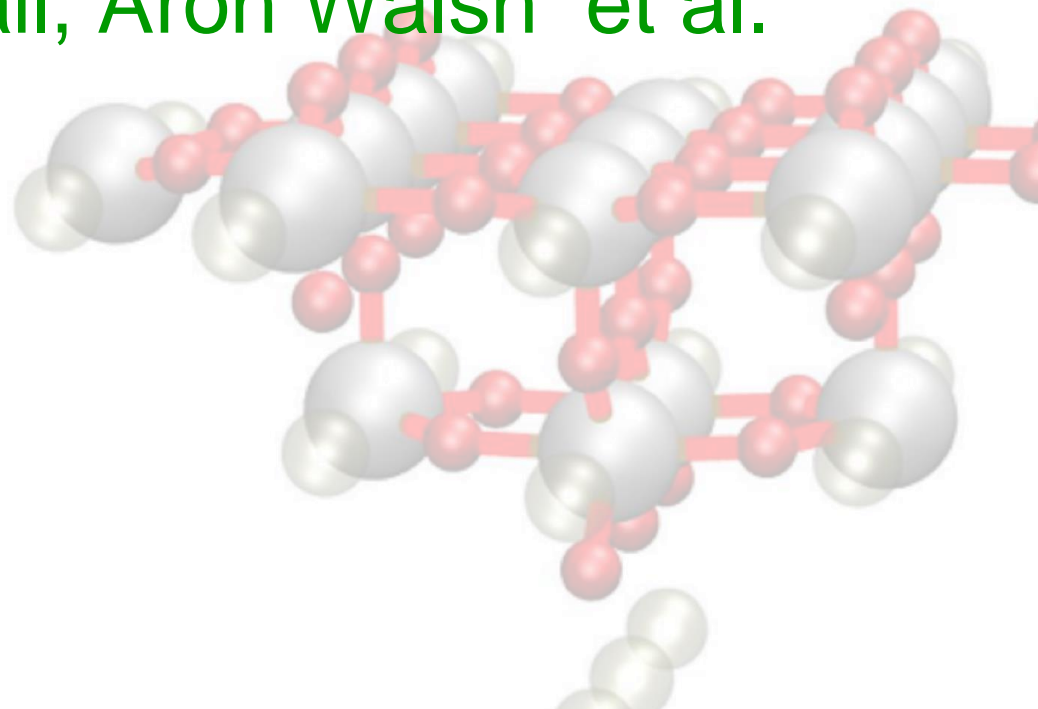


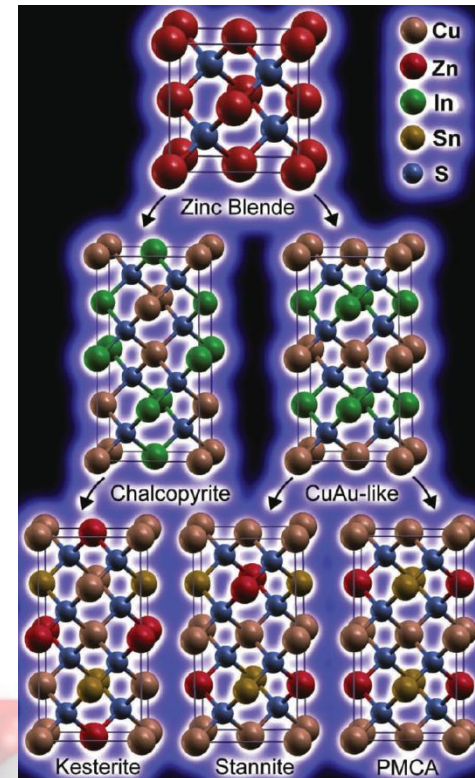
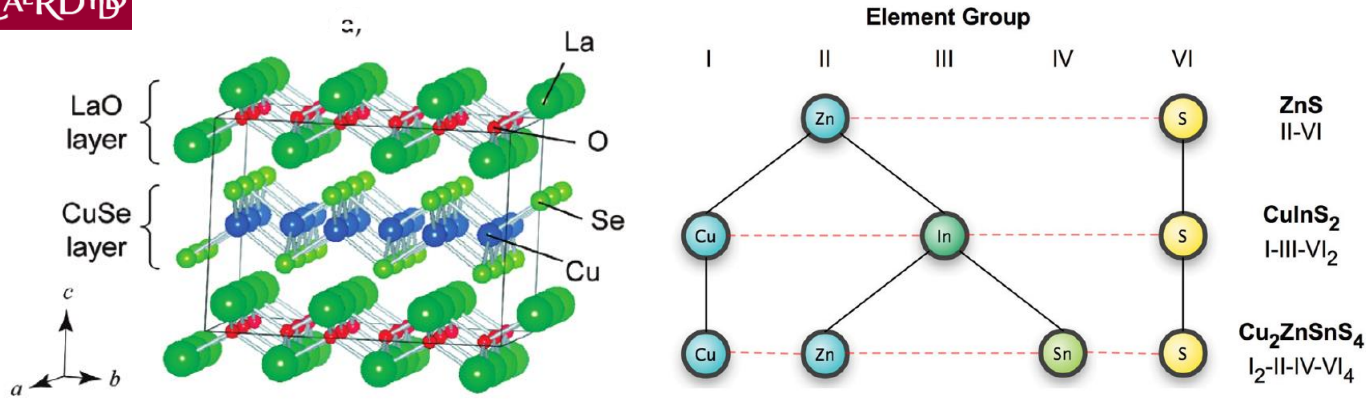
- Analysis of bonding in anatase and rutile TiO₂ reveals that alignment of VBM and CBM should be determined by madelung potentials.
- Madelung potentials indicate that the VBM of rutile should be 0.47 eV above that of anatase – opposite to the “accepted” model.
 - Mott-Littleton approach supports this, with an offset of 0.39 eV.
- QM/MM alignment place the VBM of Rutile 0.47 eV above Anatase.
 - This approach allows access to the vacuum level – not surface dependent like periodic approaches.
- XPS alignment of rutile/anatase interfaces place the VBM of rutile 0.39 +/- 0.02 eV above anatase.
 - Experiments carried out independently of calculations.

(Scanlon et al., Nature Materials, 12,798,2013)

OPTIMISING PHOTO-ACTIVITY of TITANIA POLYMORPH COMPOSITES

John Buckeridge, David Scanlon, Richard
Catlow, Andy Logsdail, Aron Walsh et al.
Chem Mater, (2015)

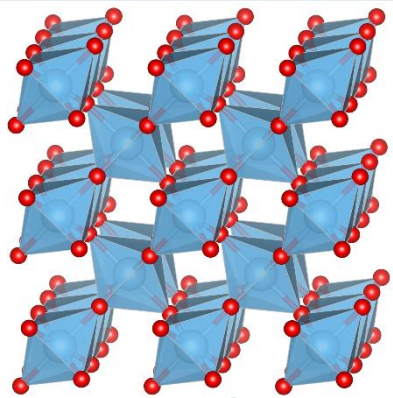




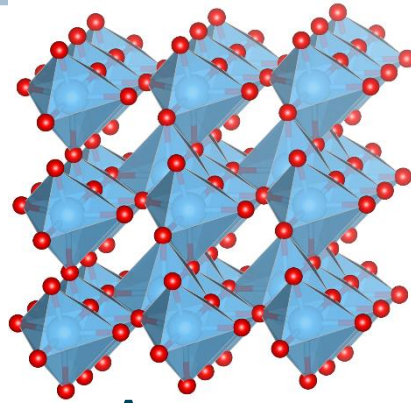
- Optical and electronic engineering has led to increasingly complex multi-component systems
- Inherent chemical and structural disorder presents challenge for applications

- Alternative =>
 - Fewer chemical components
 - Alter structure rather than composition
 - Focus on TiO₂ as a test case

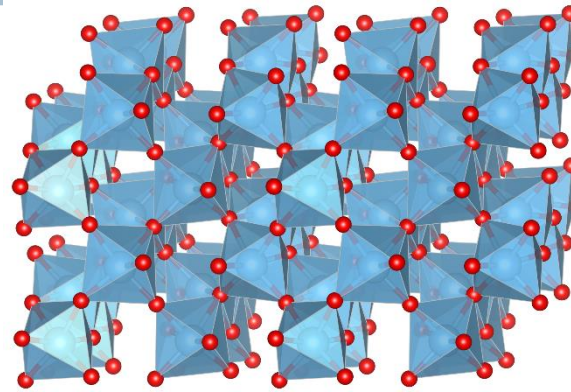
Further TiO₂ polymorphs



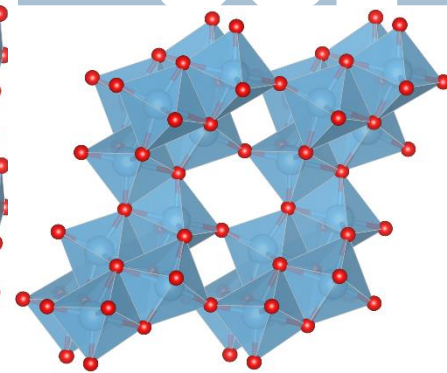
Rutile



Anatase



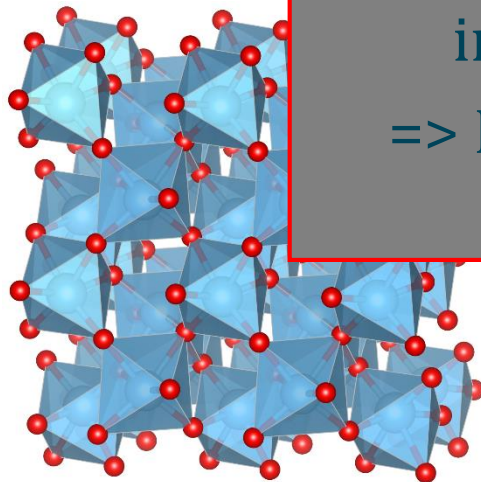
Brookite



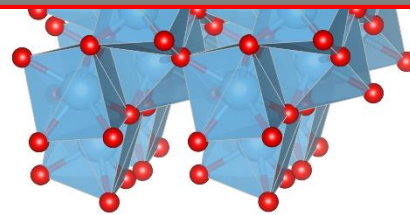
TiO₂-B

- Phases occurring in nature

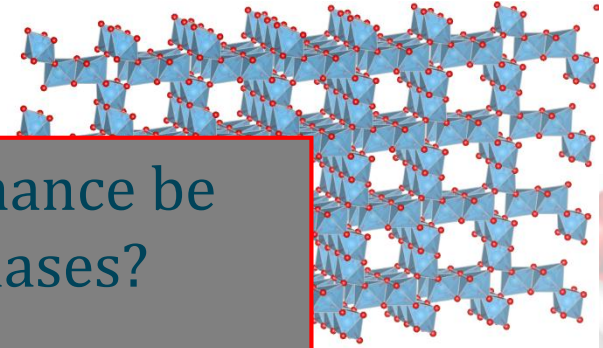
Can photocatalytic performance be improved using these phases?
=> Need to know how their energy bands align



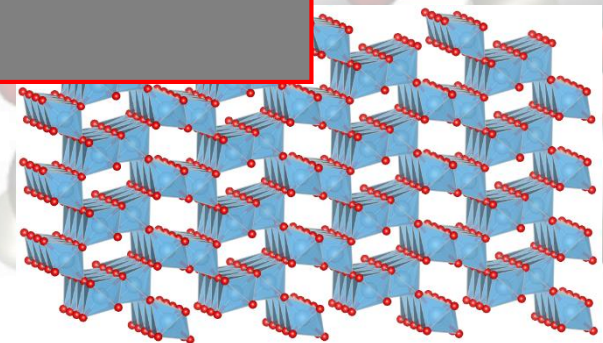
α -PbO₂



Baddeleyite



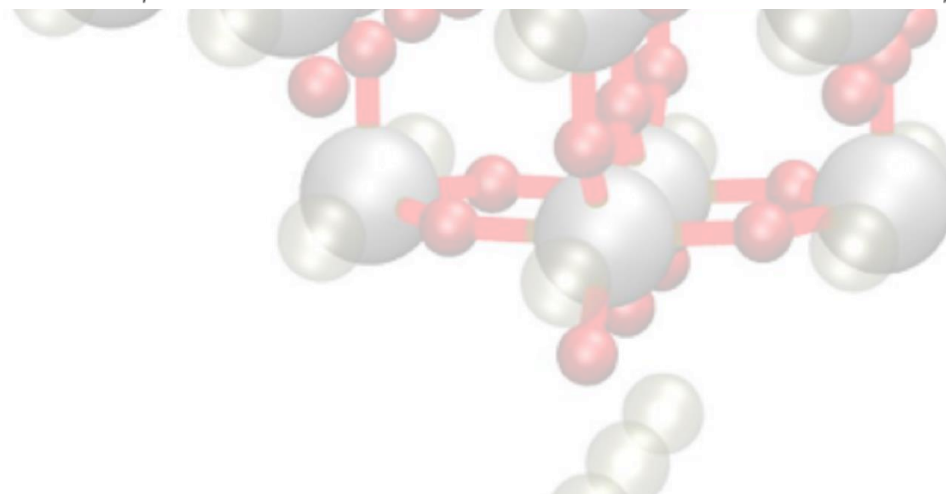
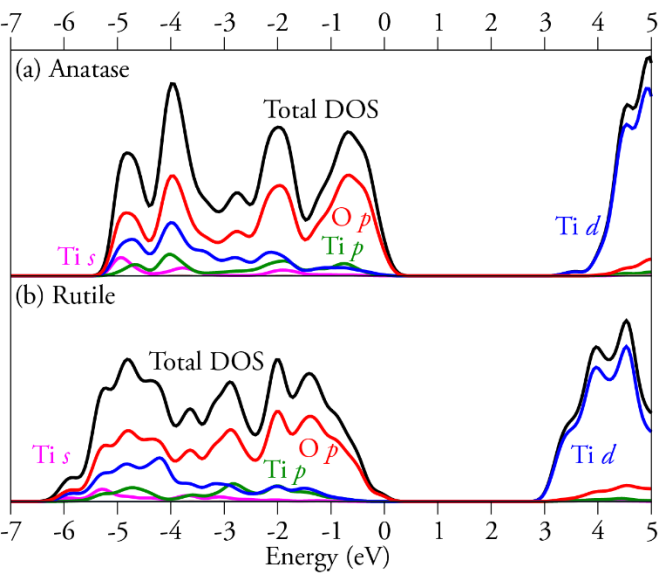
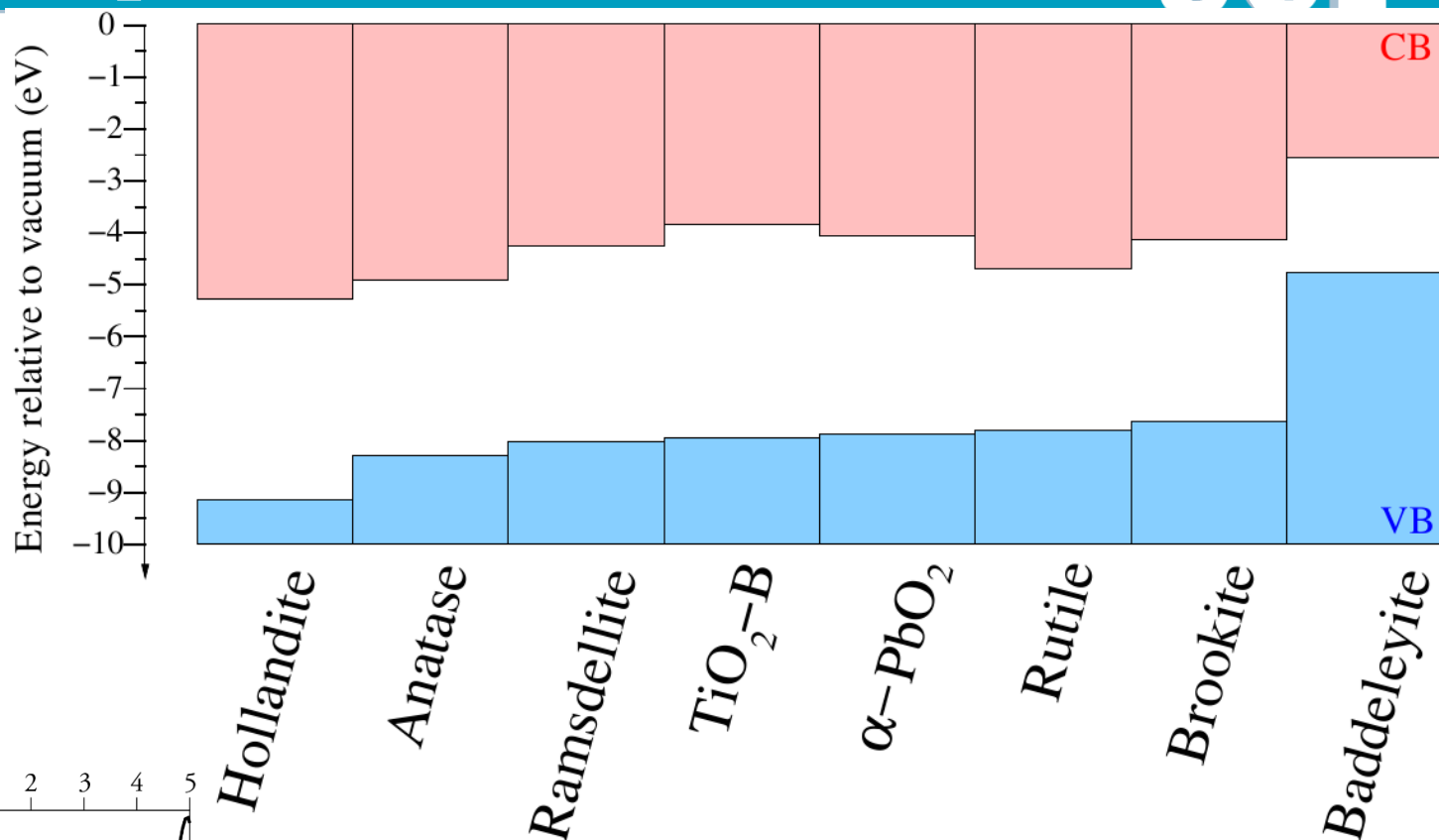
Ramsdellite



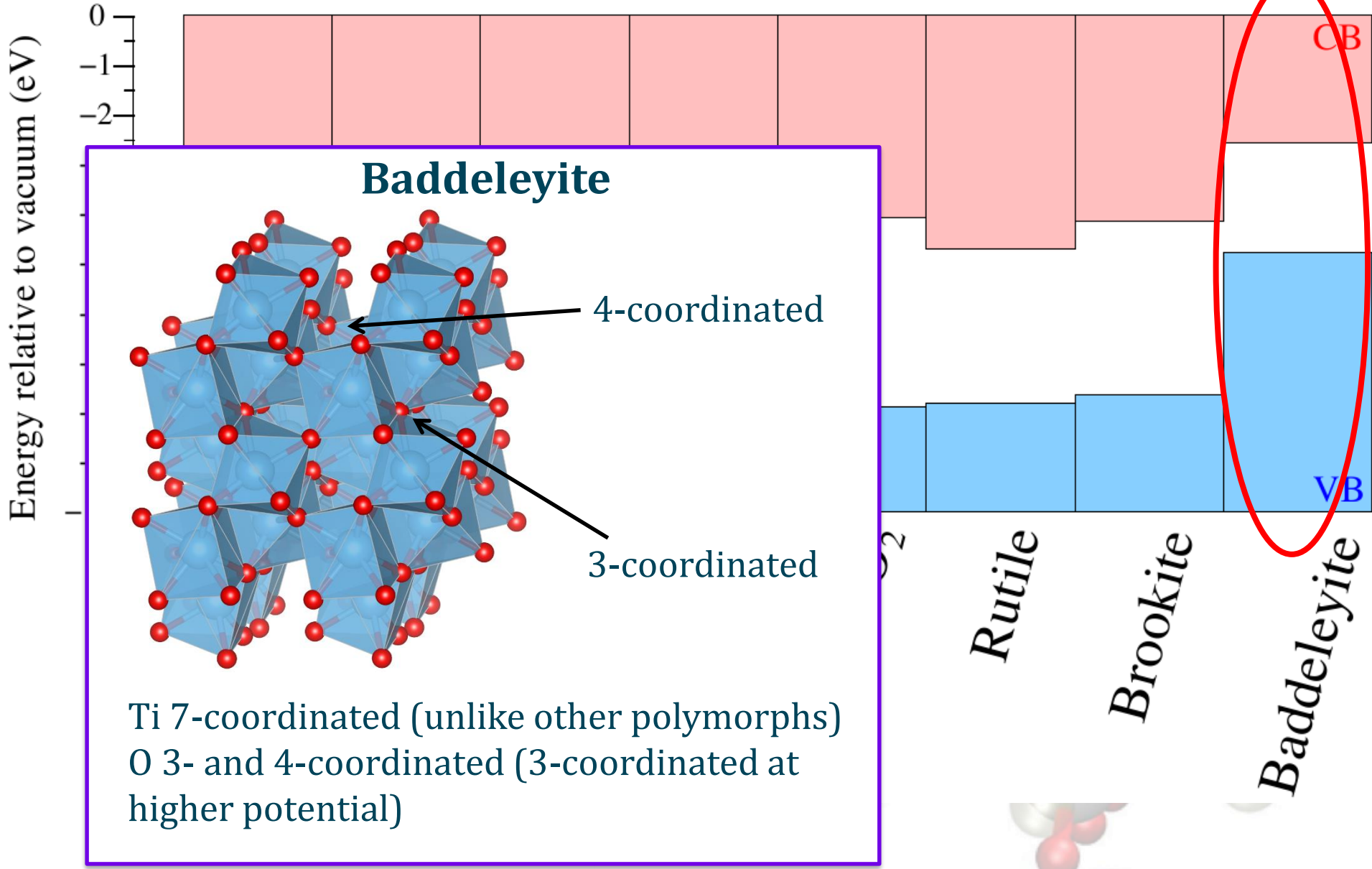
Ramsdellite

- High pressure phases

- Porous phases

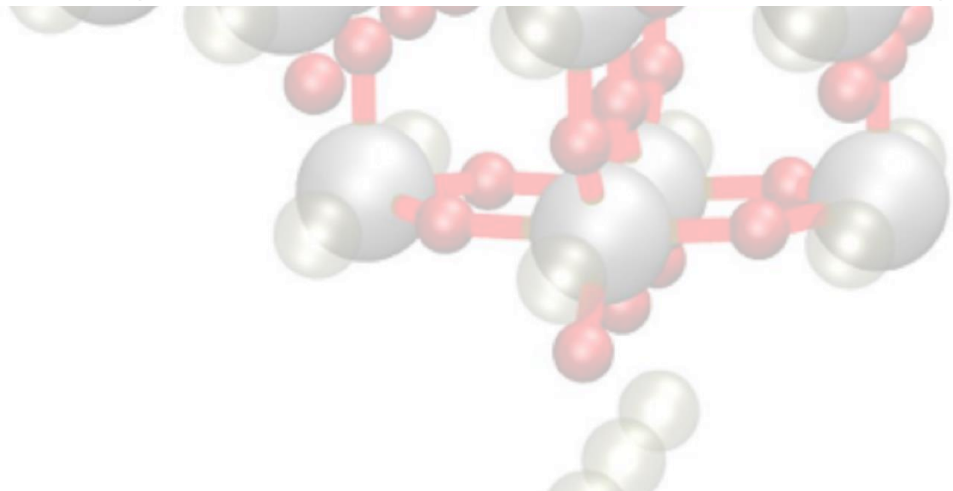
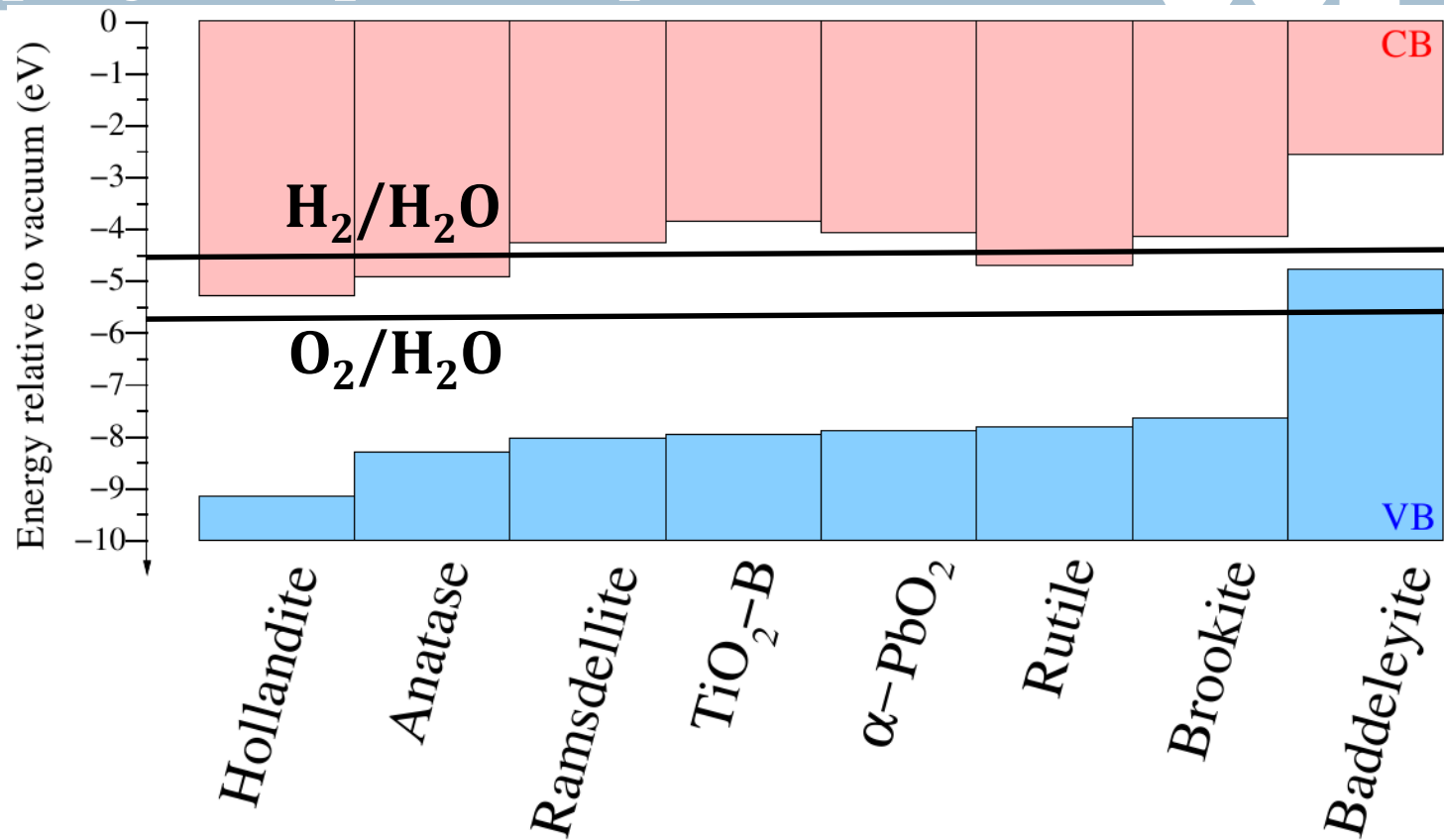


Other TiO₂ polymorphs

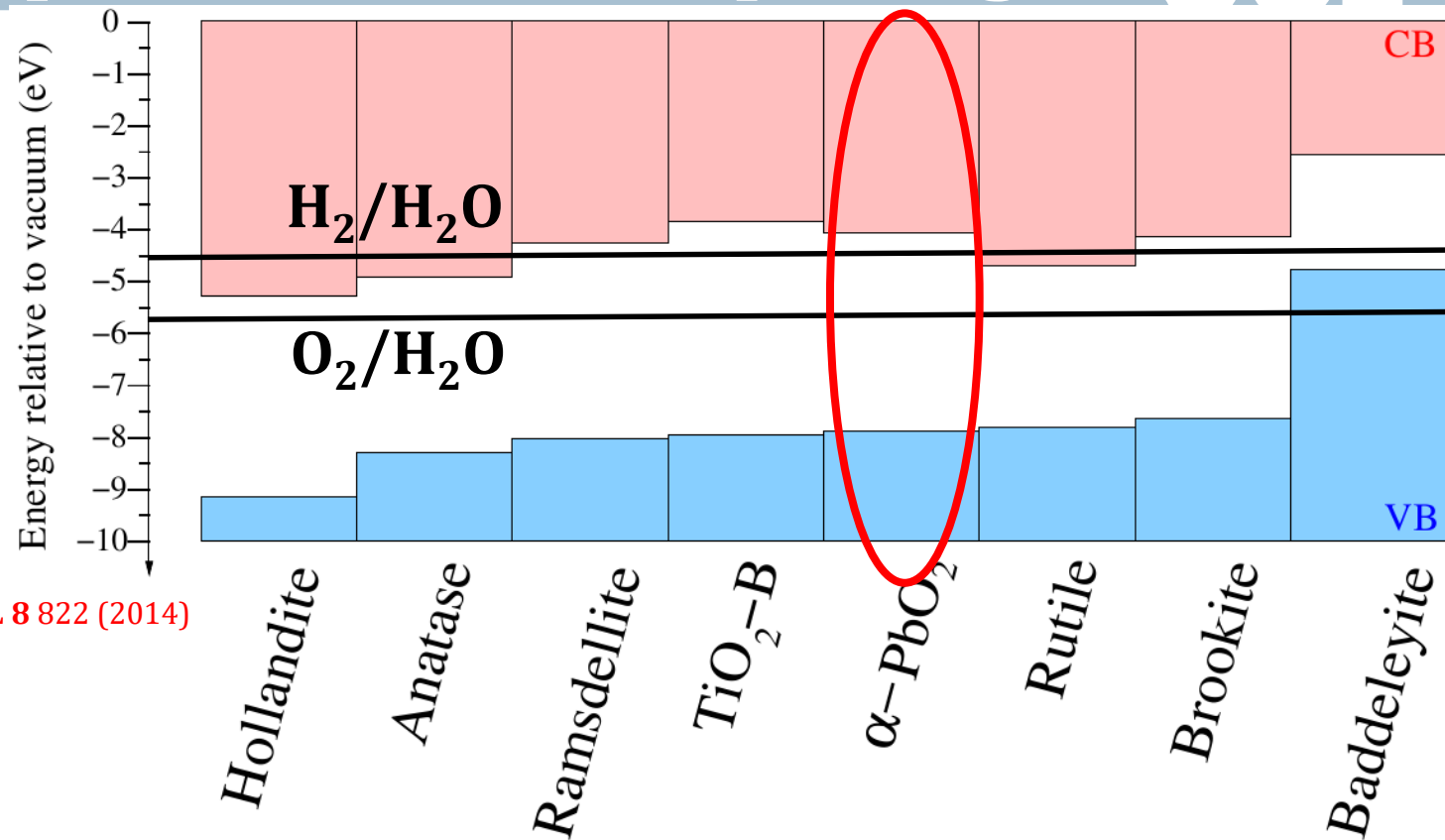


Using QM/MM and hybrid DFT

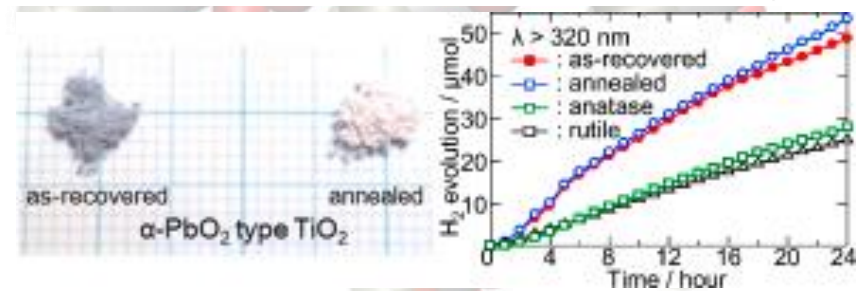
Other TiO₂ polymorphs: implications



- Improved efficiency with $\alpha\text{-PbO}_2$

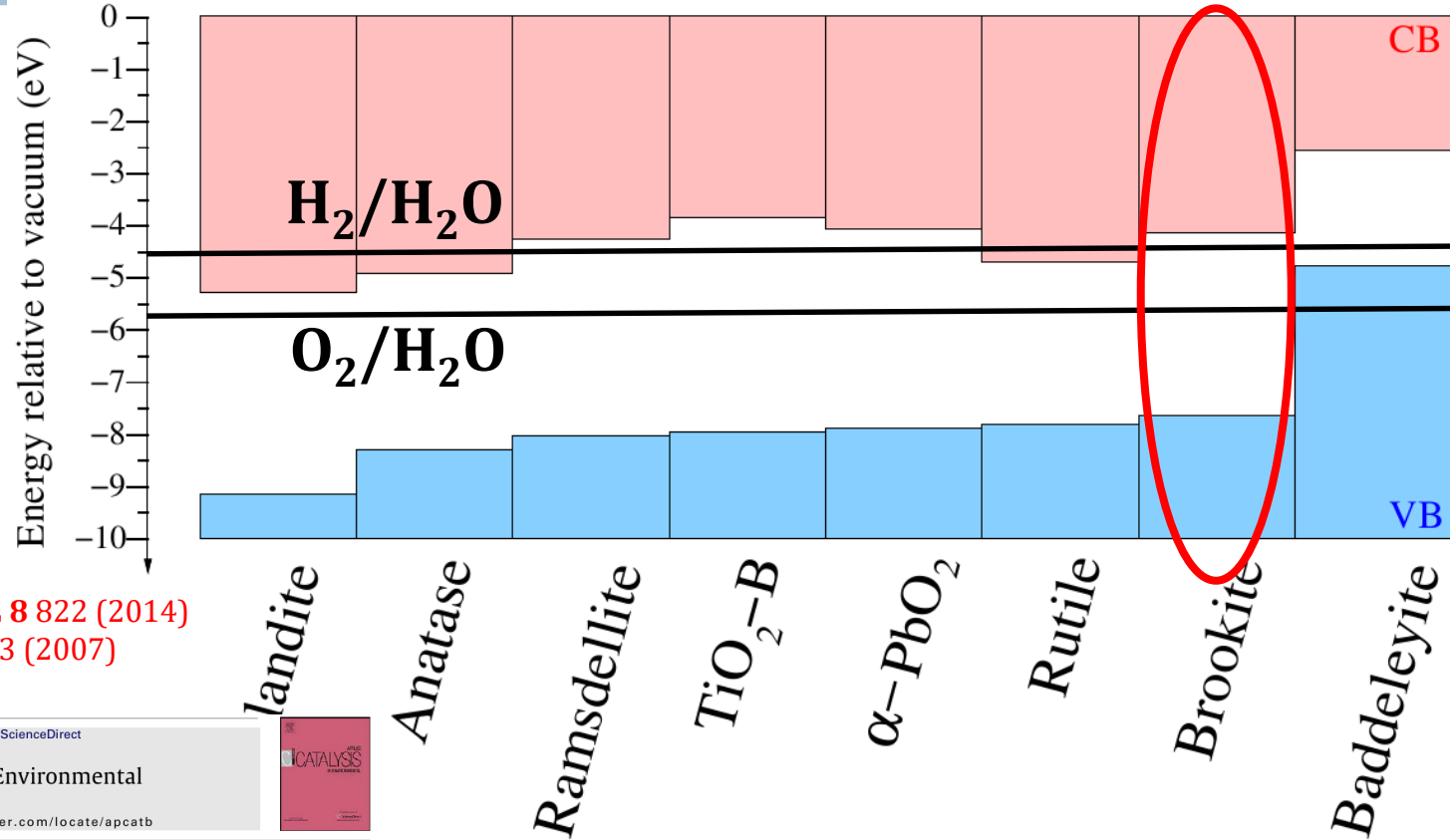


Murata *et al.*, Phys. Stat. Sol. RRL 8 822 (2014)



Applications: water splitting

- Improved efficiency with $\alpha\text{-PbO}_2$
- Also with brookite



Murata *et al.*, *Phys. Stat. Sol. RRL* **8** 822 (2014)
 Li and Gray, *Chem. Phys.* **339** 173 (2007)

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journal homepage: www.elsevier.com/locate/apcatb

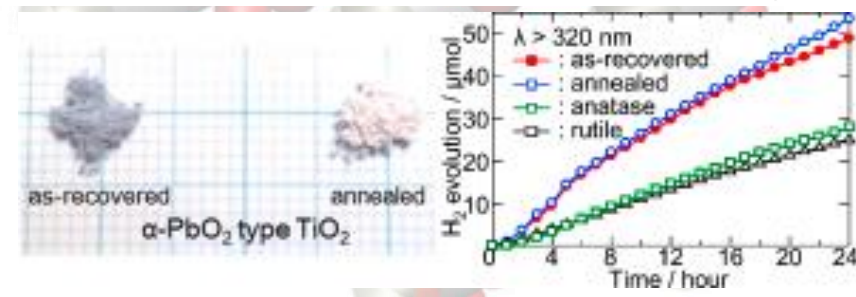
Fabrication and characterization of brookite-rich, visible light-active TiO_2 films for water splitting

Hui Pan^a, Xiaofeng Qiu^b, Iliia N. Ivanov^c, Harry M. Meyer^d, Wei Wang^a, Wenguang Zhu^e, M. Parans Paranthaman^b, Zhenyu Zhang^{d,e}, Gyula Eres^d, Baohua Gu^{a,*}

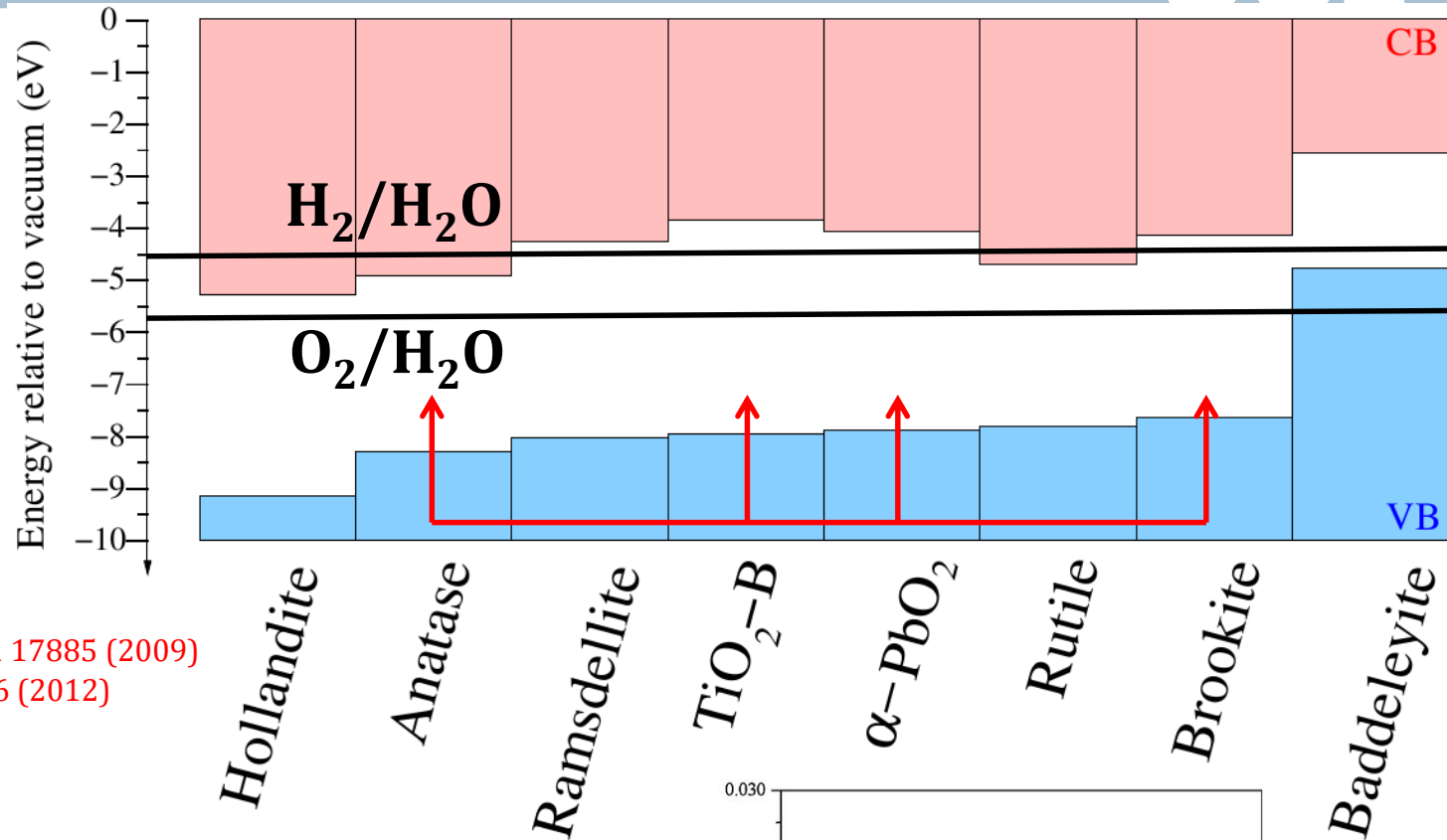
^a Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States
^b Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States
^c Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States
^d Materials Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States
^e Department of Physics and Astronomy, University of Tennessee, Knoxville, TN 37996, United States

ARTICLE INFO ABSTRACT

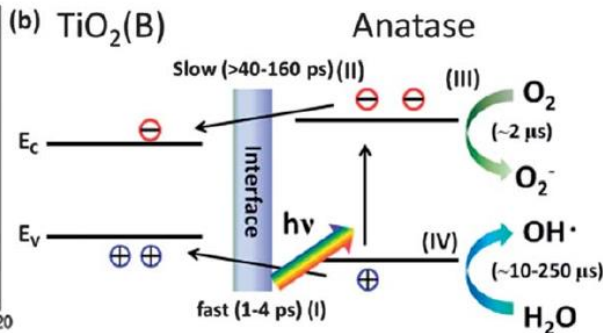
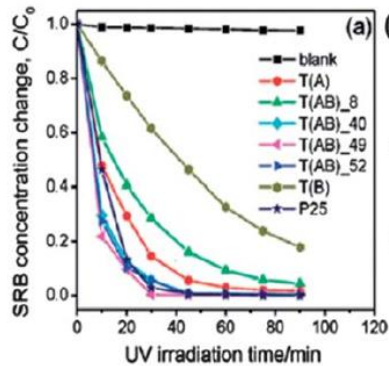
Article history: We report that mild oxidation of Ti foils in air results in brookite-rich titanium oxide (TiO_2) films with show that enhanced visible light absorption correlates with the presence of Ti interstitials. Photocurrent density measurements of water splitting reveal that the brookite-rich TiO_2 exhibits the highest photocatalytic performance among the different forms of TiO_2 produced by oxidation of Ti foils. With increasing oxidation temperature transformation to the rutile phase accompanied by declining visible range photoactivity is observed.



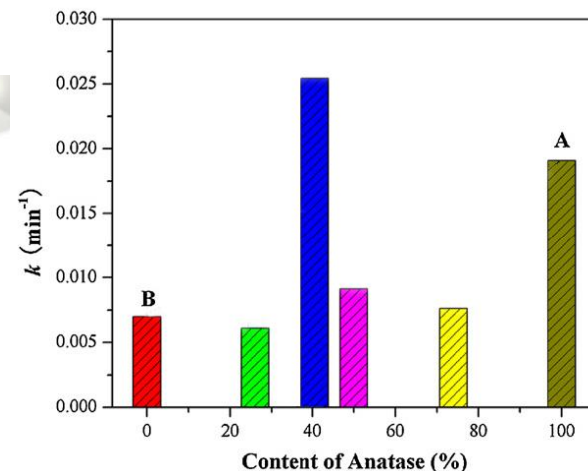
- How to improve photocatalytic activity?
- Mixing anatase with brookite, $\text{TiO}_2\text{-B}$, or $\alpha\text{-PbO}_2$ should give improvement



Yang *et al.*, *J. Am. Chem. Soc.* **131** 17885 (2009)
Jiao *et al.*, *Colloids Surf. A* **402** 66 (2012)



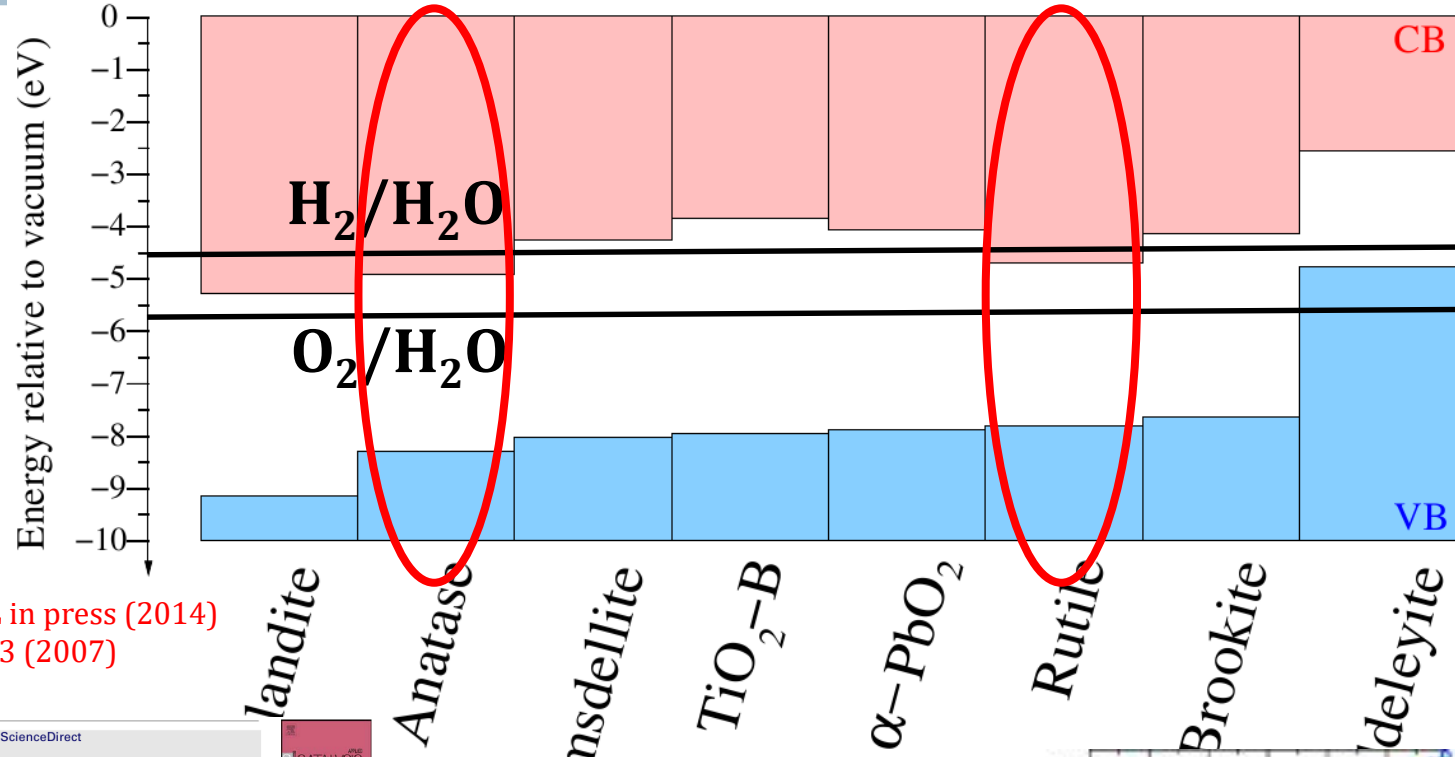
Sulfurhodamine B degradation by $\text{TiO}_2\text{-B}$ /anatase



Methylene blue degradation by brookite/anatase

Other TiO₂ polymorphs: implications

- Improved photocatalysis with $\alpha\text{-PbO}_2$
- Also with brookite
- Why do anatase and rutile work?
- (Need to include effects of surfaces and interfaces)



Murata *et al.*, *Phys. Stat. Sol. RRL* in press (2014)
 Li and Gray, *Chem. Phys.* **339** 173 (2007)

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journal homepage: www.elsevier.com/locate/apcatb

Fabrication and characterization of brookite-rich, visible light-active TiO₂ films for water splitting

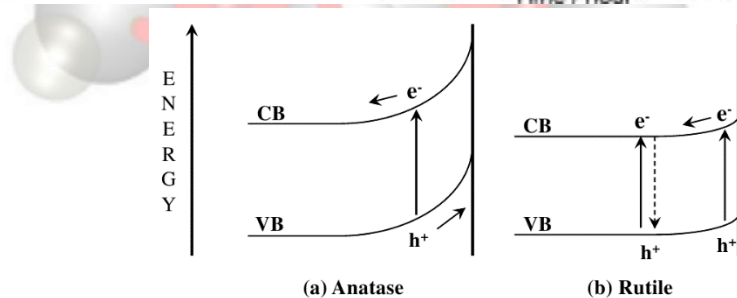
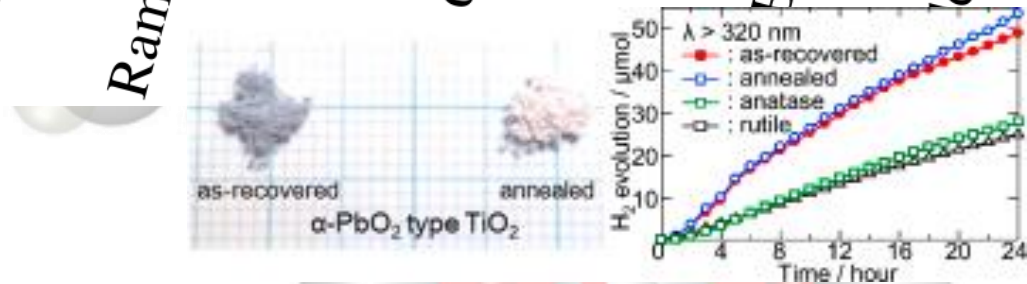
Hui Pan^a, Xiaofeng Qiu^b, Iliia N. Ivanov^c, Harry M. Meyer^d, Wei Wang^a, Guang Zhu^e, M. Parans Paranthaman^b, Zhenyu Zhang^{d,e}, Gyula Eres^d, Baohua Gu^{a,*}

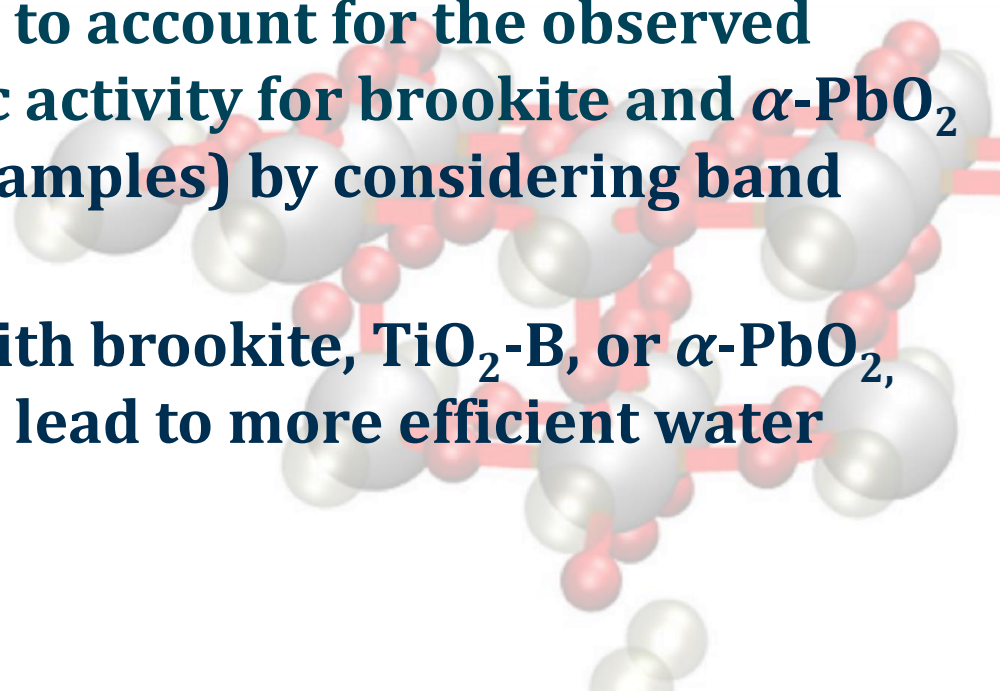
^a Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States
^b Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States
^c Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States
^d Materials Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States
^e Department of Physics and Astronomy, University of Tennessee, Knoxville, TN 37996, United States

ARTICLE INFO

ABSTRACT

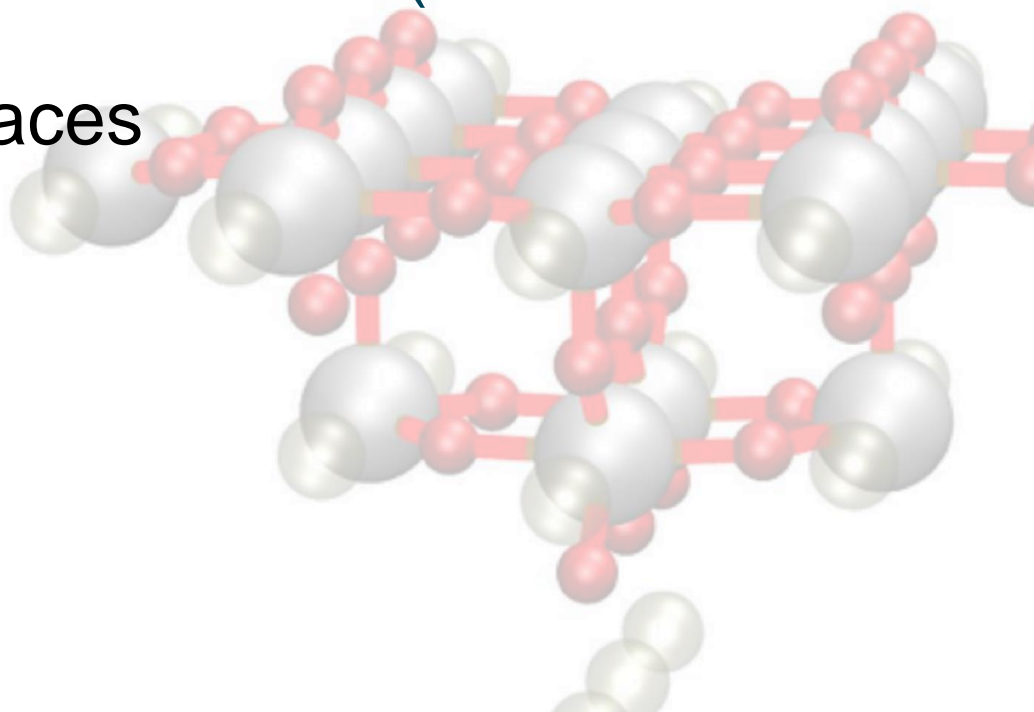
Article history: We report that mild oxidation of Ti foils in air results in brookite-rich titanium oxide (TiO₂) films with show that enhanced visible light absorption correlates with the presence of Ti interstitials. Photocurrent density measurements of water splitting reveal that the brookite-rich TiO₂ exhibits the highest photocatalytic performance among the different forms of TiO₂ produced by oxidation of Ti foils. With increasing oxidation temperature transformation to the rutile phase accompanied by declining visible range photoactivity is observed.



- **Understanding how the energy bands align with reference to vacuum is essential to understanding the basic driving force of photocatalytic processes**
 - **Our multiscale approach gives accurate bulk ionisation potentials and band gaps for TiO_2 polymorphs**
 - **Surface and interface effects are not included in our model**
 - **Nevertheless, we are able to account for the observed increase in photocatalytic activity for brookite and $\alpha\text{-PbO}_2$ (as well as mixed-phase samples) by considering band alignment**
 - **Predict mixing anatase with brookite, $\text{TiO}_2\text{-B}$, or $\alpha\text{-PbO}_2$, rather than rutile, should lead to more efficient water splitting**
- 
- A 3D ball-and-stick model of a metal oxide crystal structure. The structure consists of a network of atoms represented by spheres: larger grey spheres for metal ions and smaller red spheres for oxygen ions. The atoms are connected by bonds, forming a complex, interconnected lattice structure.

How do we improve potentials?

- Empirical Fitting – more data? (lattice dynamics)
- Ab initio energy surfaces
- Machine learning?



ACKNOWLEDGEMENTS

John Buckeridge, Aron Walsh, David Scanlon, David Mora Fonz, Michael Higham, Scott Woodley, Alexei Sokol

EPSRC - *funding*

