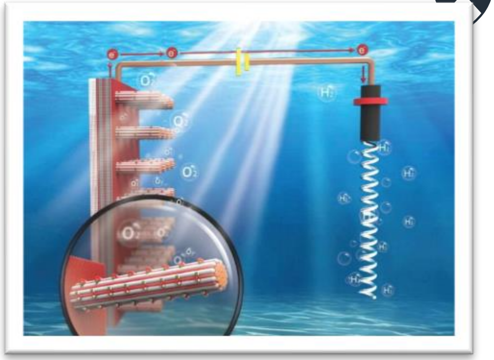
Does Polaronic Self-Trapping Occur at Anatase TiO_2 Surfaces?

John Carey
Keith McKenna

N8 presentation: Friday (04-01-2019)

TiO_2 applications

Solar cells



Water splitting

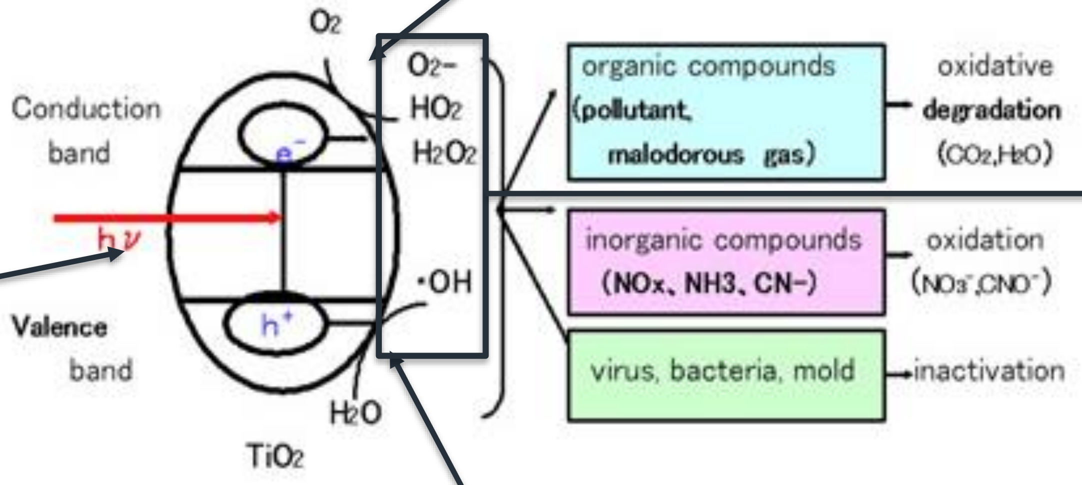
TiO_2
Photocatalyst

Pollution

Paint

TiO_2 as a photocatalyst

Reduction: $O_2 + e^- \rightarrow O_2^-$



Light

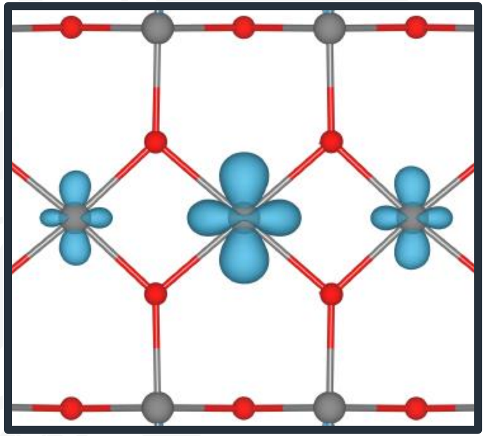
Active species

Oxidation: $H_2O + h^+ \rightarrow OH^- + H^+$

Polarons in TiO_2

Reduction

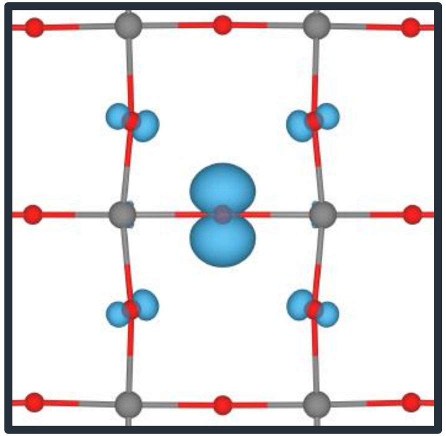
$Ti^{4+} + e^{-} \rightarrow Ti^{3+}$



Electron polaron on Ti site

Oxidation

$O^{2-} \rightarrow O^{-} + h^{+}$



Hole polaron on O site

Previous work

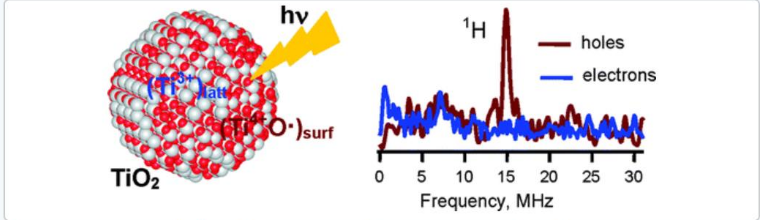
Effect of Size and Shape of Nanocrystalline TiO_2 on Photogenerated Charges. An EPR Study

Nada M. Dimitrijevic*†‡, Zoran V. Saponjic†, Bryan M. Rabatic‡, Oleg G. Poluektov†, and Tijana Rajh‡
Chemistry Division and Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois 60439

J. Phys. Chem. C, **2007**, *111* (40), pp 14597–14601
DOI: 10.1021/jp0756395
Publication Date (Web): September 18, 2007

Cite this: *J. Phys. Chem. C* 2007, 111, 40, 14597-14601

Abstract



Trapped Holes on TiO_2 Colloids Studied by Electron Paramagnetic Resonance†

Olga I. Micic,‡ Yuenian Zhang, Keith R. Cromack, Alexander D. Trifunac, and Marion C. Thurnauer*
Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439
Received: December 11, 1992; In Final Form: March 30, 1993

Langmuir **2001**, *17*, 5368–5374

EPR Study of the Surface Characteristics of Nanostructured TiO_2 under UV Irradiation

Juan M. Coronado,*,† A. Javier Maira,† José Carlos Conesa,† King Lun Yeung,‡ Vincenzo Augugliaro,†,§ and Javier Soria†
Instituto de Catálisis y Petroleoquímica, CSIC, Campus UAM, Cantoblanco, Madrid 28047, Spain, and Department of Chemical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong
Received January 29, 2001. In Final Form: April 24, 2001

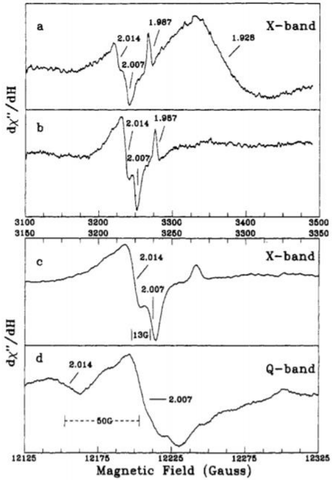


Figure 1. EPR spectra of degassed aqueous colloidal TiO_2 prepared under various conditions and irradiated at 77 K: (a) colloids (0.1 M monomeric concentration, 100-Å average diameter), pH 3, irradiated with 308-nm excimer laser recorded at 30 K, X-band (300-G scan); (b) same as in 1a after aging 3 months; (c) colloidal gel (0.07 M), pH 4, irradiated at 77 K (308-nm excimer laser), recorded at 13 K, X-band (9.1 GHz); (d) same conditions as in 1c, Q-band (34 GHz).

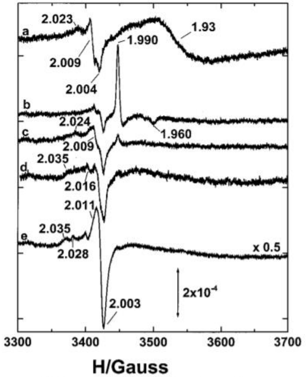


Figure 2. EPR spectra of the TiO_2 gel sample outgassed 1 h at RT and (a) irradiated for 15 min at 77 K; H6 sample treated in a vacuum for 1 h at RT and (b) subsequently irradiated during 15 min at 77 K; and (c) contacted with O_2 at 77 K; T16 material outgassed at RT for 1 h and (d) irradiated for 15 min and (e) subsequently exposed to O_2 at 77 K.

Experimental evidence for polarons

EPR studies

Previous work

Small polarons in Nb- and Ta-doped rutile and anatase TiO_2

Benjamin J. Morgan *, David O. Scanlon and Graeme W. Watson *
School of Chemistry, Trinity College Dublin, Dublin 2, Ireland. E-mail: morganb@tcd.ie; watsong@tcd.ie

Received 11th March 2009 , Accepted 6th May 2009
First published on 10th June 2009

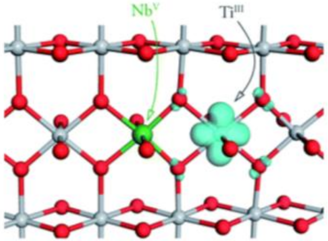


Fig. 4 A slice through a (001) plane of the Nb-doped anatase TiO_2 system, showing the charge density associated with the gap state in Fig. 3(b). The Nb dopant is shown in green. Ti atoms are grey and oxygen atoms are red. The charge isosurface is shown at a density of 0.05 e Å^{-3}.

Localized Electronic States from Surface Hydroxyls and Polarons in TiO_2(110)

N. Aaron Deskins*, Roger Rousseau and Michel Dupuis
Chemical and Material Sciences Division, Pacific Northwest National Laboratory, Richland, Washington 99352

J. Phys. Chem. C, **2009**, *113* (33), pp 14583–14586
DOI: 10.1021/jp9037655
Publication Date (Web): July 27, 2009

* Corresponding author. E-mail: nathaniel.deskins@pnl.gov.

Cite this: *J. Phys. Chem. C* 2009, 113, 33, 14583-14586

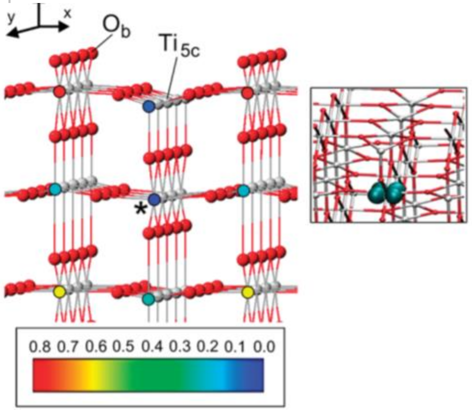


Figure 1. Relative energies (eV) for polaronic structures with an excess electron near a (110) surface for $U = 4.1$ eV. Red spheres represent O atoms, and gray spheres represent Ti atoms. Colored circles indicate sites where excess electrons were localized to form Ti^{3+} centers, and the colors indicate their stability relative to the most stable Ti site (marked by an asterisk). Ti_{5c} and O_b atoms are also indicated. The inset shows the spin density at the most stable site with a filled d_{xy} orbital.

DFT+U work shows electron localisation but positive energy distribution

Previous work

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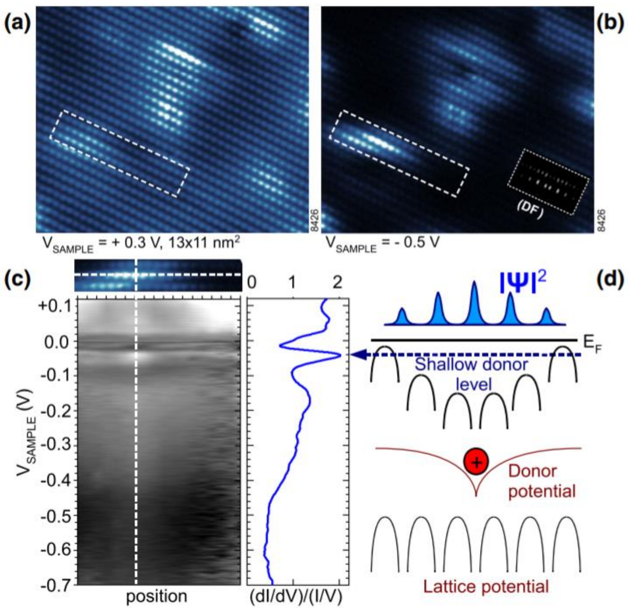
Direct View at Excess Electrons in TiO_2 Rutile and Anatase

Martin Setvin, Cesare Franchini, Xianfeng Hao, Michael Schmid, Anderson Janotti, Merzuk Kaltak, Chris G. Van de Walle, Georg Kresse, and Ulrike Diebold

Phys. Rev. Lett. **113**, 086402 – Published 18 August 2014



Shallow donor states

Carrier-free description

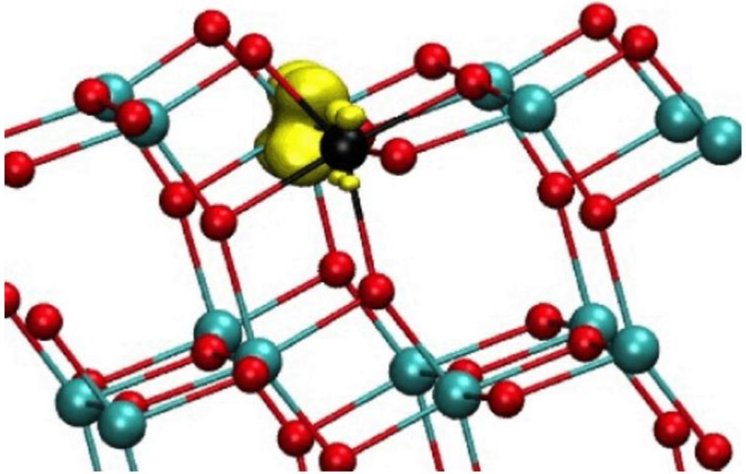
rapid research letters

Rapid Research Letter | Full Access

Polarons and oxygen vacancies at the surface of anatase TiO_2

Peter Deák, Jolla Kullgren, Thomas Frauenheim

First published: 05 May 2014 | https://doi.org/10.1002/pssr.201409139 | Cited by: 22



HSE06 predicts electron trapping

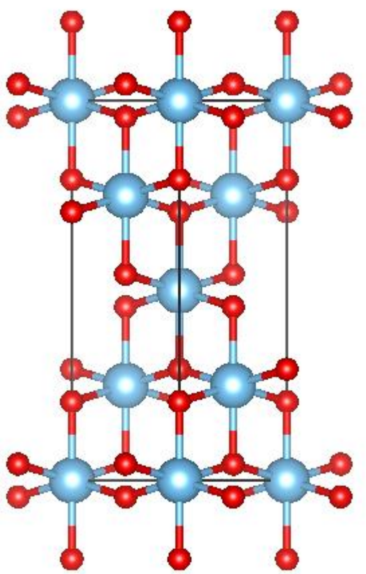
Methodology

- Density functional theory in CP2K
- Hybrid functional PBE-tr
- HF exchange is determined by Koopmans Theorem
  - 10.5% exact exchange obeys linearity by < 0.05

- Large TiO_2 bulk and surfaces, ranging from 400-700 atoms
- K-point sampling is at the Gamma point (1x1x1)
- Auxiliary density matrix method (ADMM)
  - Basis set cut off is 60Ry (810 eV)
  - Fine grid level density cut off is 600 Ry (8000 eV)

TiO_2 bulk and surfaces

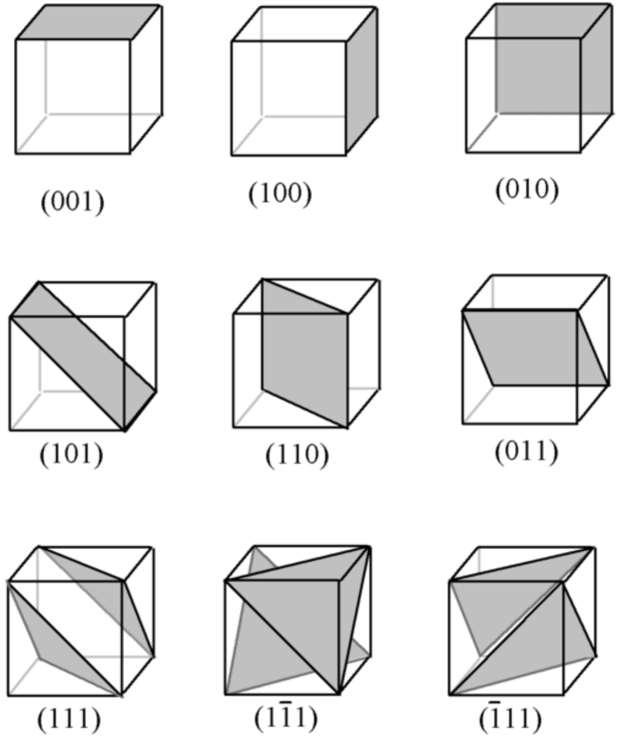
TiO_2 Anatase Unit cell



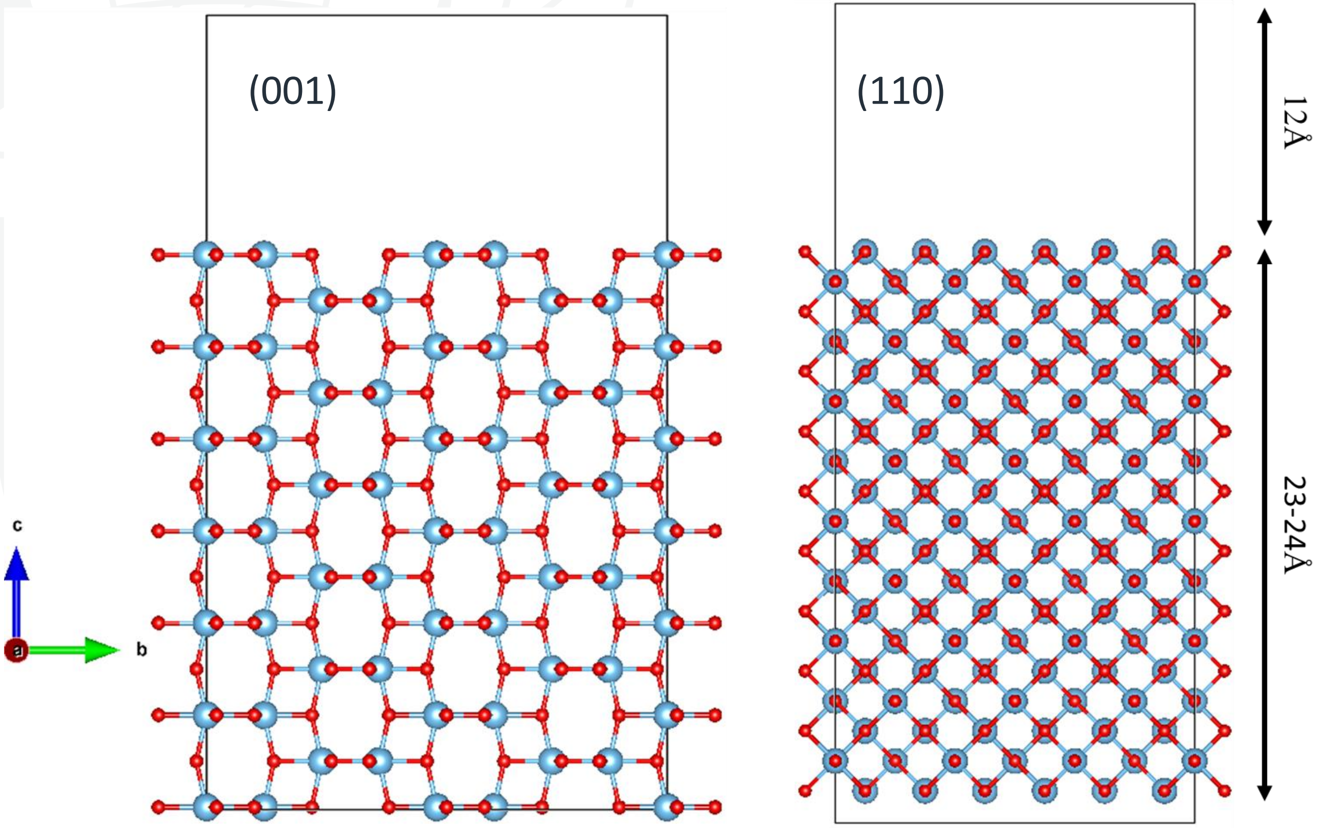
Ti cations

O anions

Generate low and high index surfaces of anatase



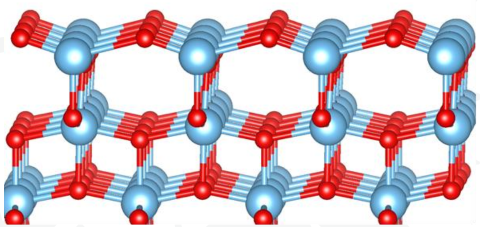
Anatase Surfaces



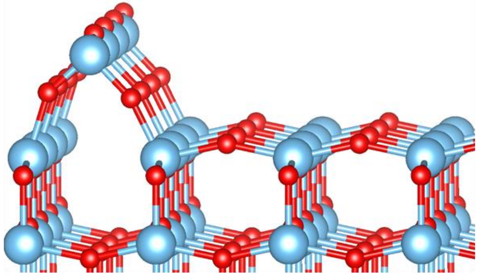
All surfaces contain around 500-700 atoms

Anatase surfaces

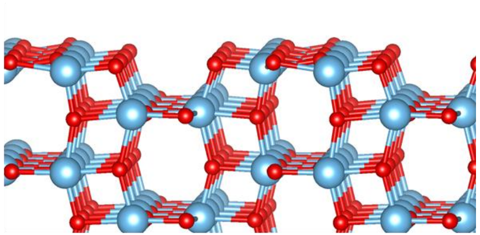
(001)



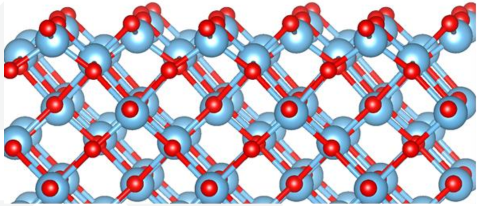
(001) - reconstructed



(100)



(110)



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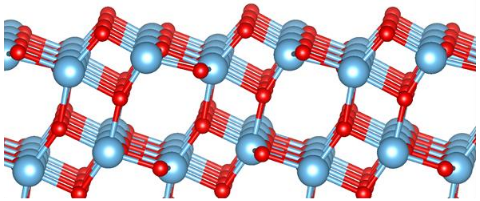

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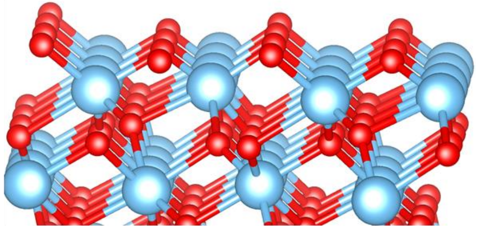

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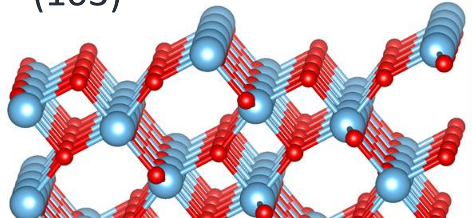

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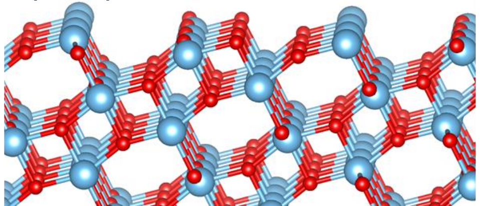

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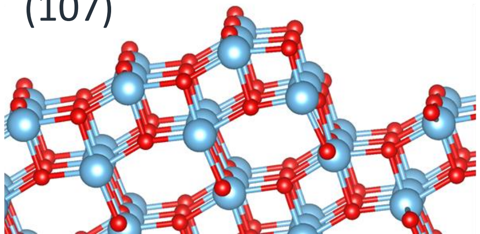
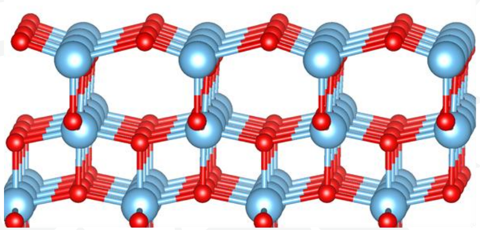
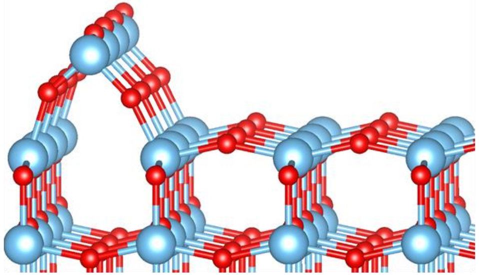


Anatase surfaces

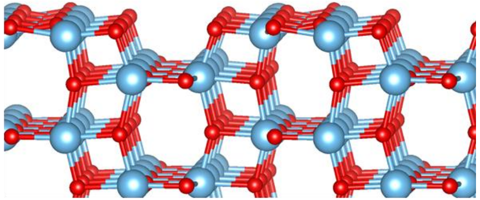
(001)



(001) - reconstructed



(100)



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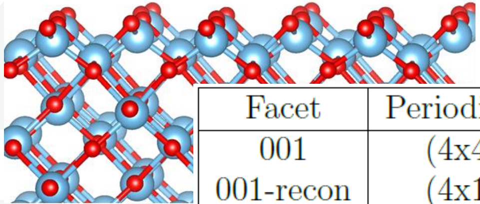

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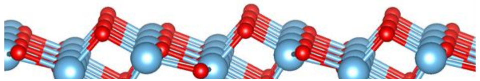

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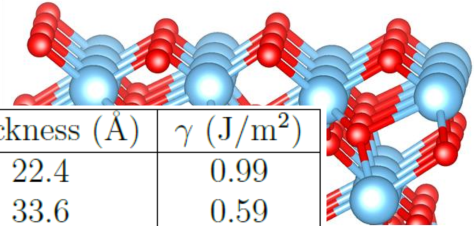
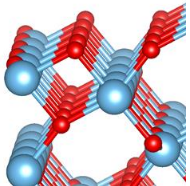
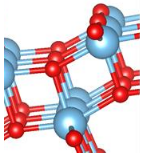


(103)

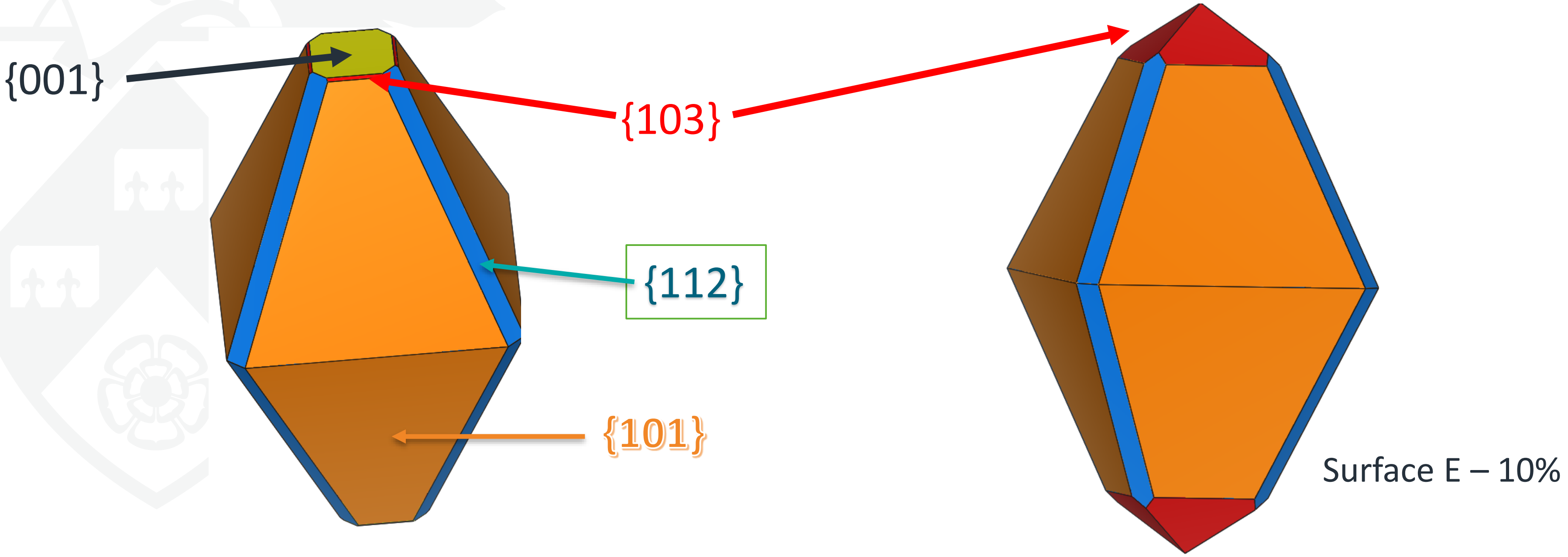




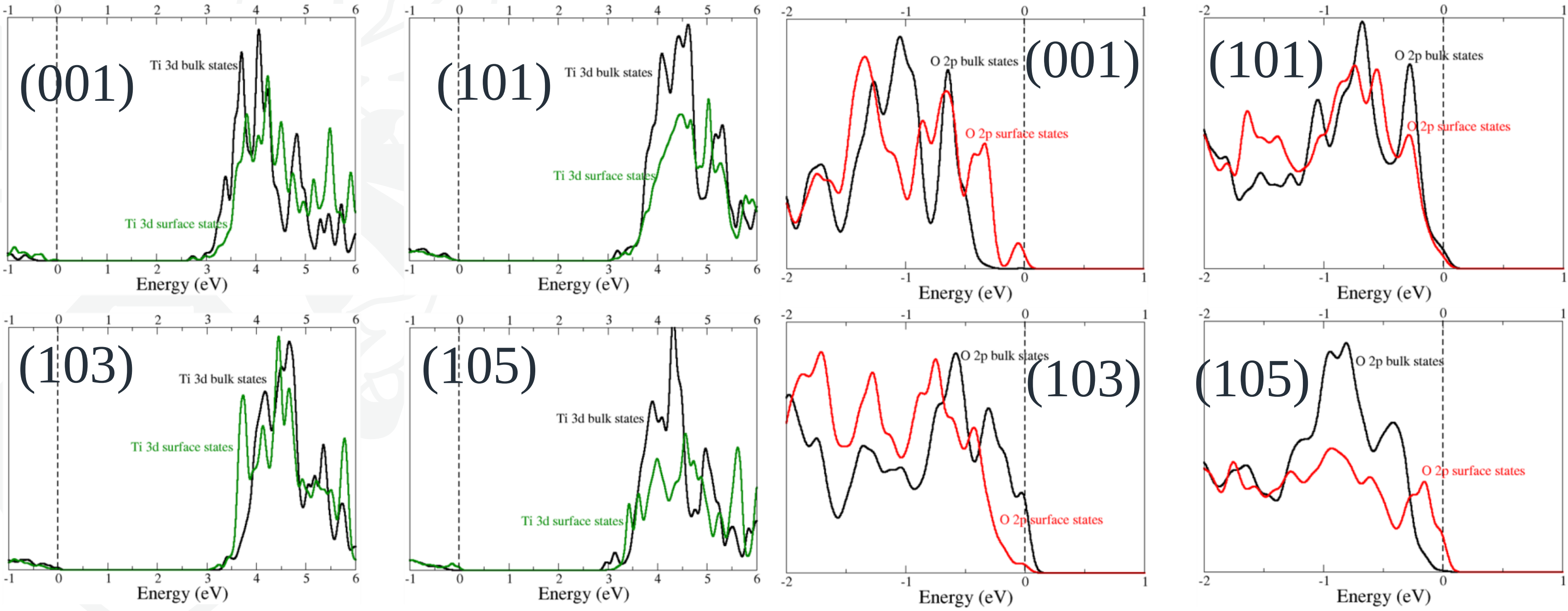
Facet	Periodicity	Stoichiometry	Area (Å^2)	Thickness (Å)	γ (J/m^2)
001	(4x4)	$Ti_{160}O_{320}$	237.3	22.4	0.99
001-recon	(4x1)	$Ti_{200}O_{400}$	237.3	33.6	0.59
100	(4x2)	$Ti_{208}O_{416}$	296.3	23.1	0.56
110	(2x3)	$Ti_{228}O_{456}$	314.3	24.2	0.97
101	(4x2)	$Ti_{224}O_{448}$	319.1	23.9	0.46
112	(4x1)	$Ti_{176}O_{352}$	268.5	25.6	0.58
103	(5x1)	$Ti_{160}O_{320}$	289.2	20.1	0.97
105	(4x1)	$Ti_{192}O_{384}$	331.1	19.6	1.07
107	(1x3)	$Ti_{168}O_{336}$	330.2	20.5	1.01

Anatase Nanoparticle

- A Wulff construction using the calculated surface energies



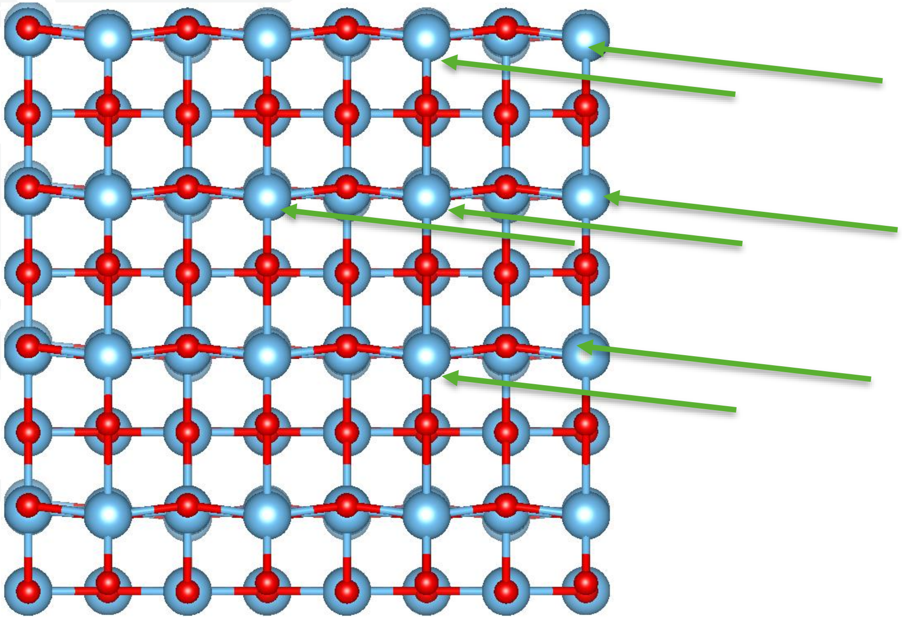
Anatase Surfaces



Examined the surface and bulk partial decomposed electron density of states

Electron Trapping: Anatase

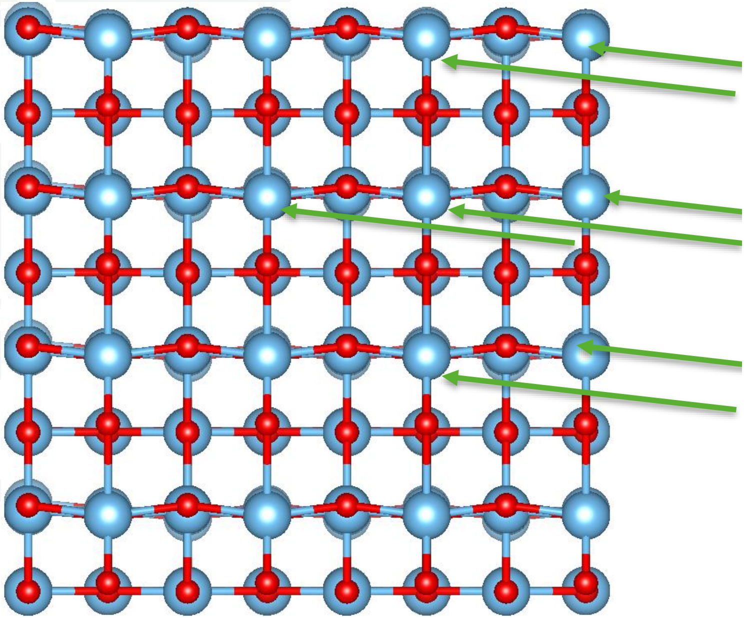
- Similar to bulk anatase TiO_2, there is no trapping of electrons at the surface facets
  - A delocalised solution is preferred on all low index surfaces

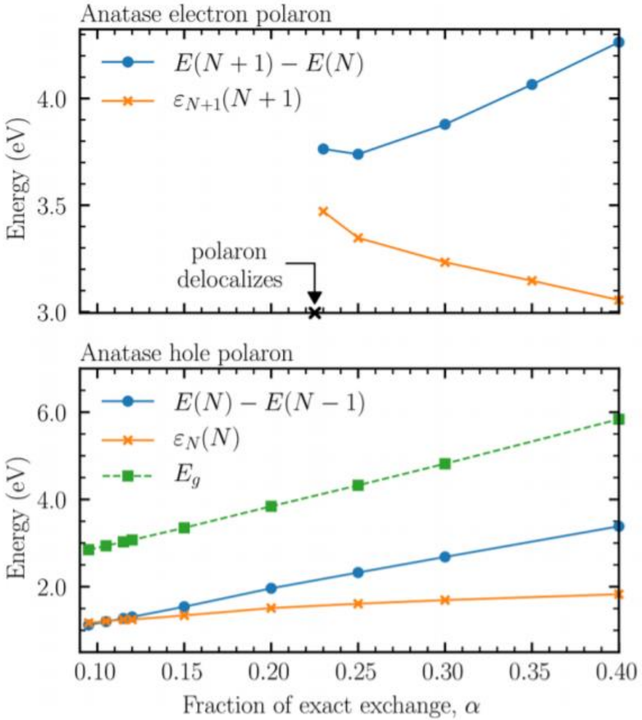


Formation of Ti(4-γ)+

Electron Trapping: Anatase

- Similar to bulk anatase TiO_2, there is no trapping of electrons at the surface facets
  - A delocalised solution is preferred on al

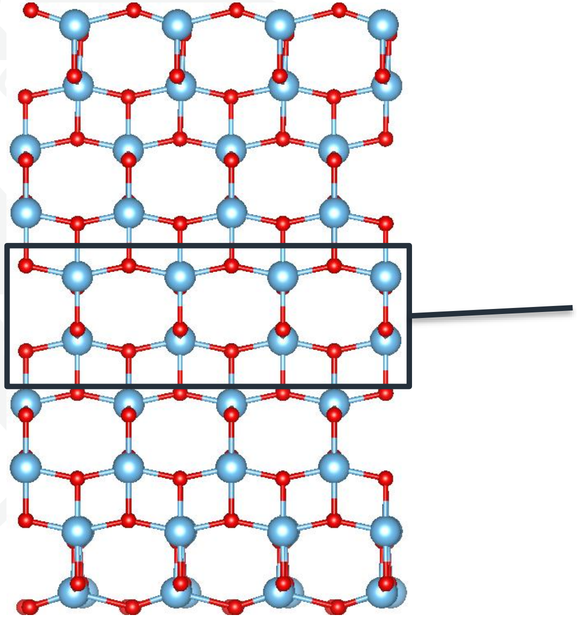


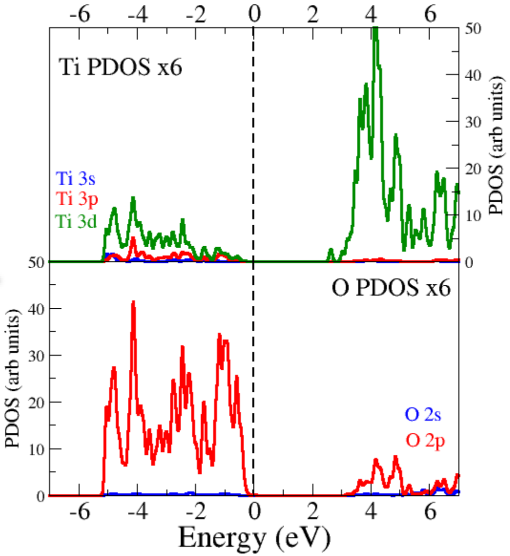


·γ)+

Electron Trapping: Anatase

- Similar to bulk anatase TiO_2, there is no trapping of electrons at the surface facets





Electron Trapping: Anatase

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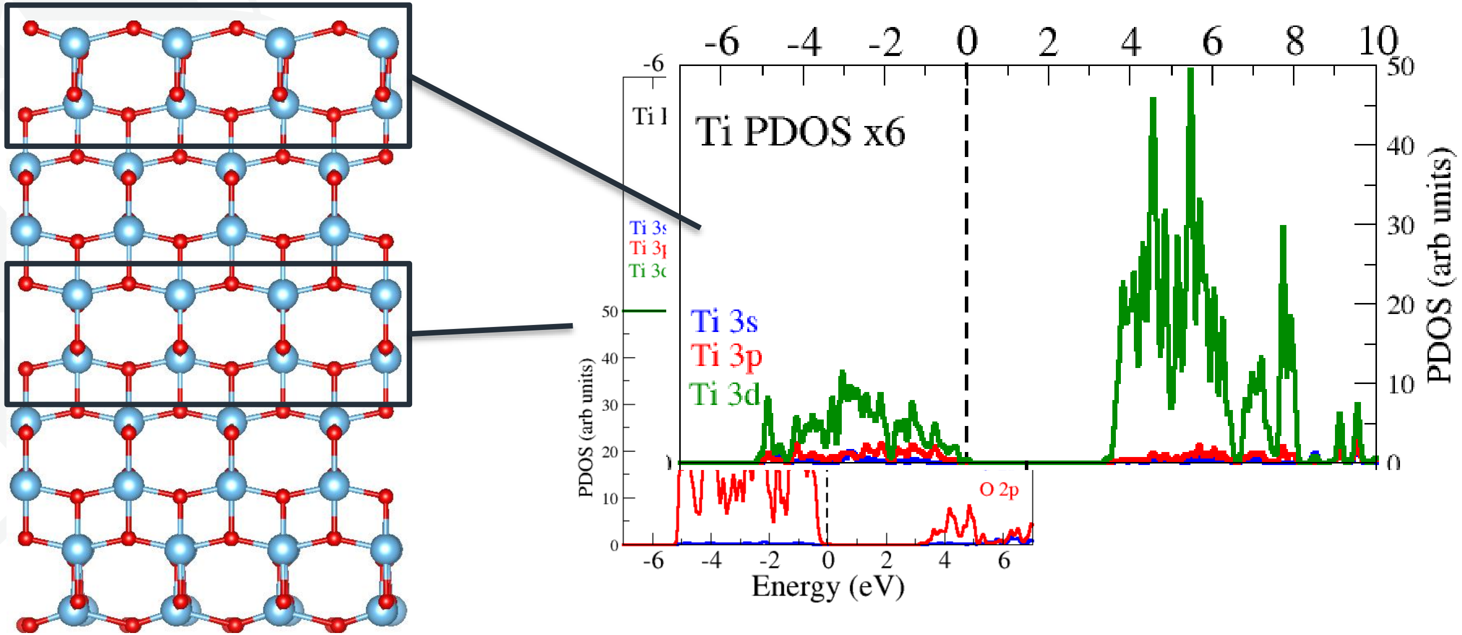
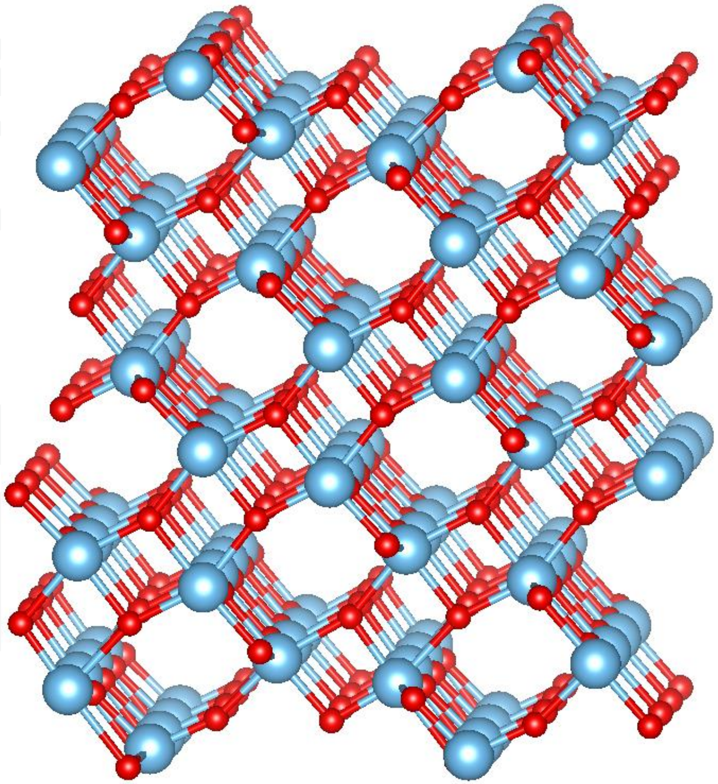
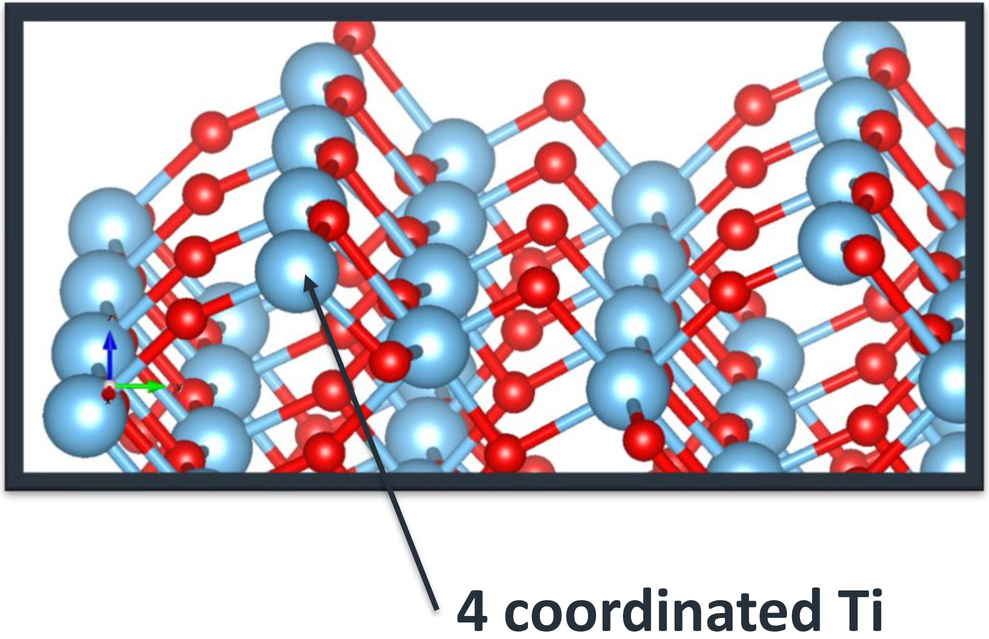
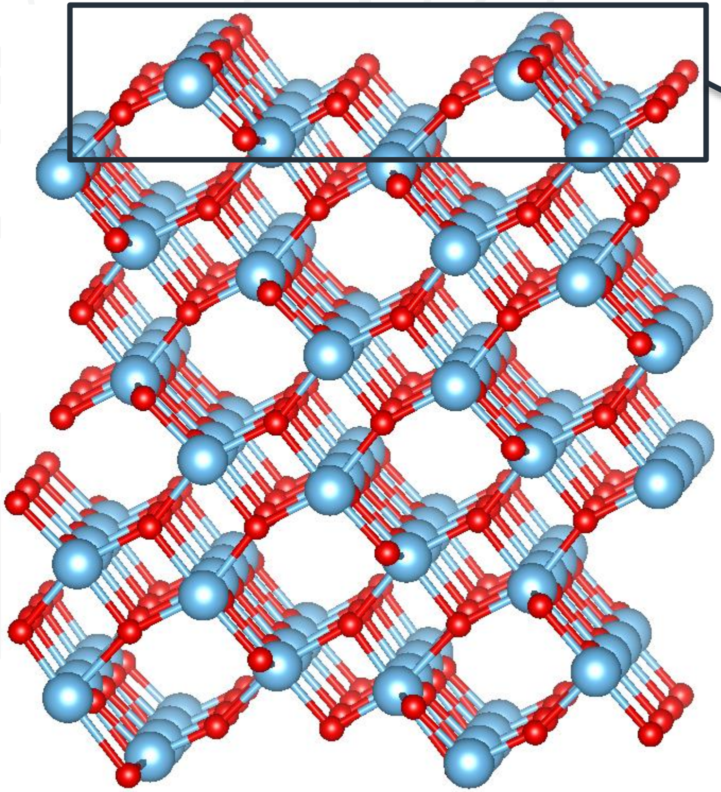


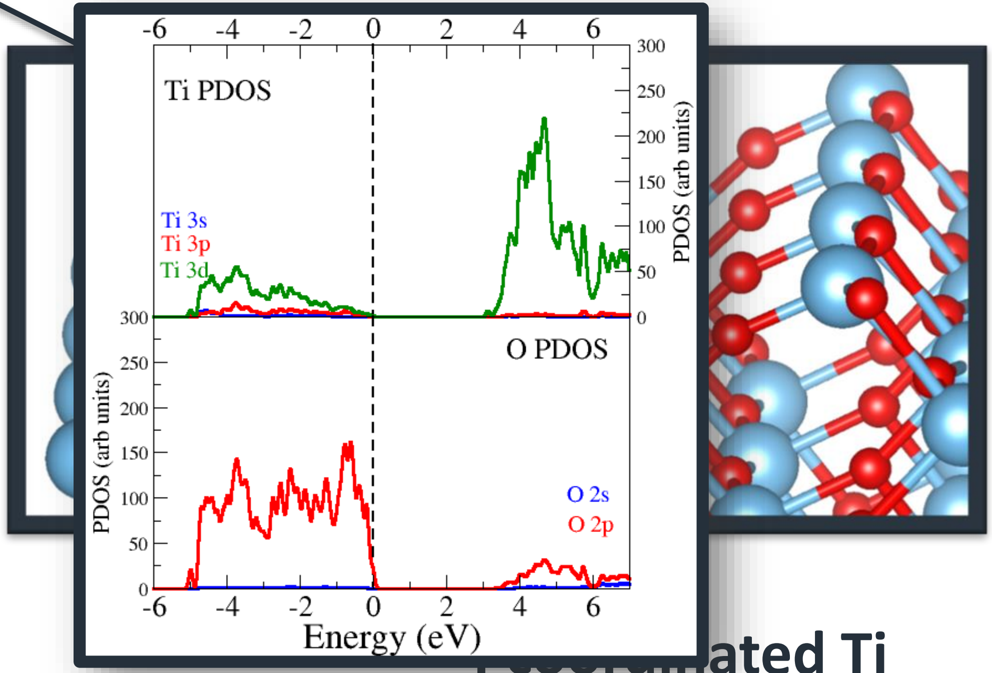
Stepped surface: 103 facet





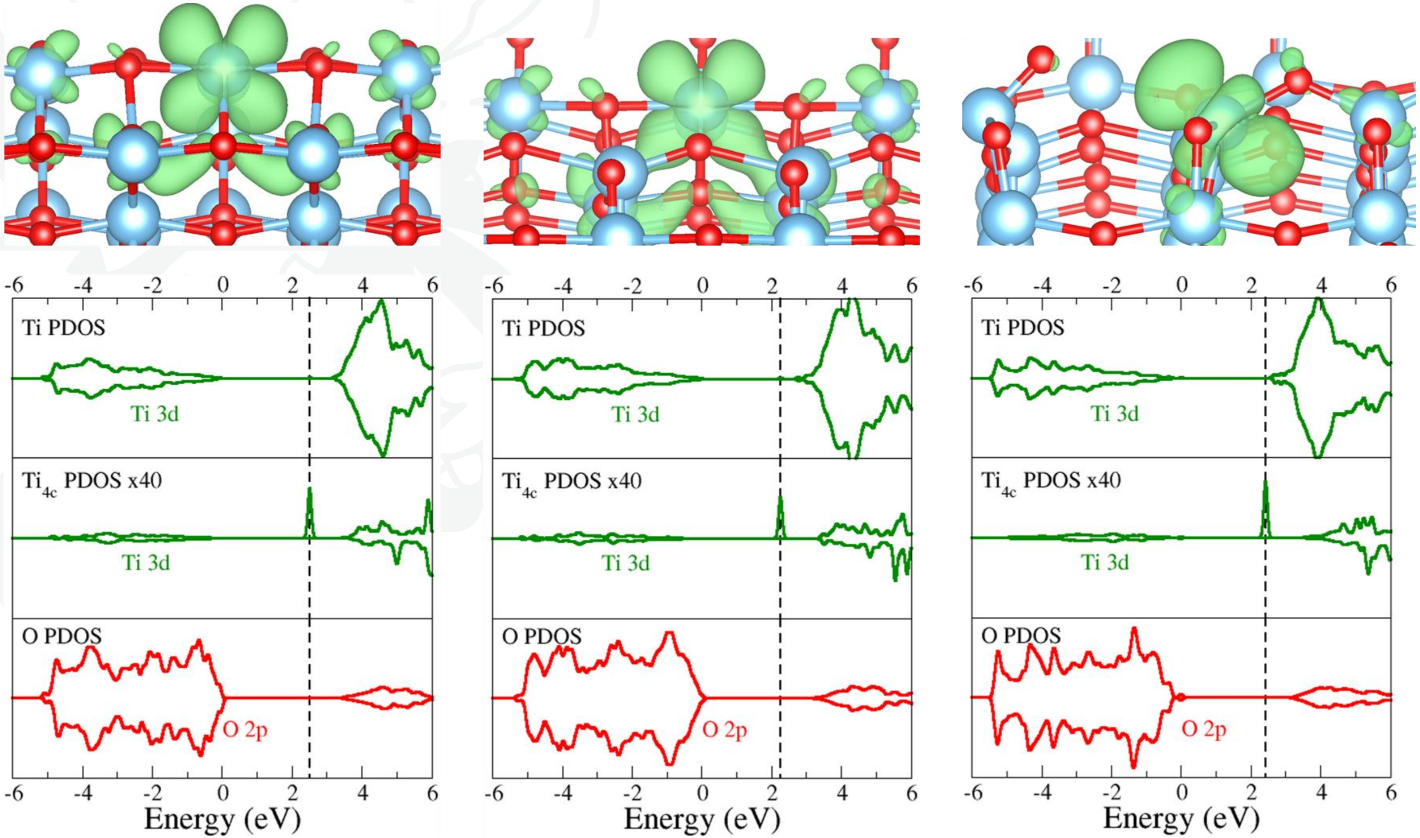
Stepped surface: 103 facet



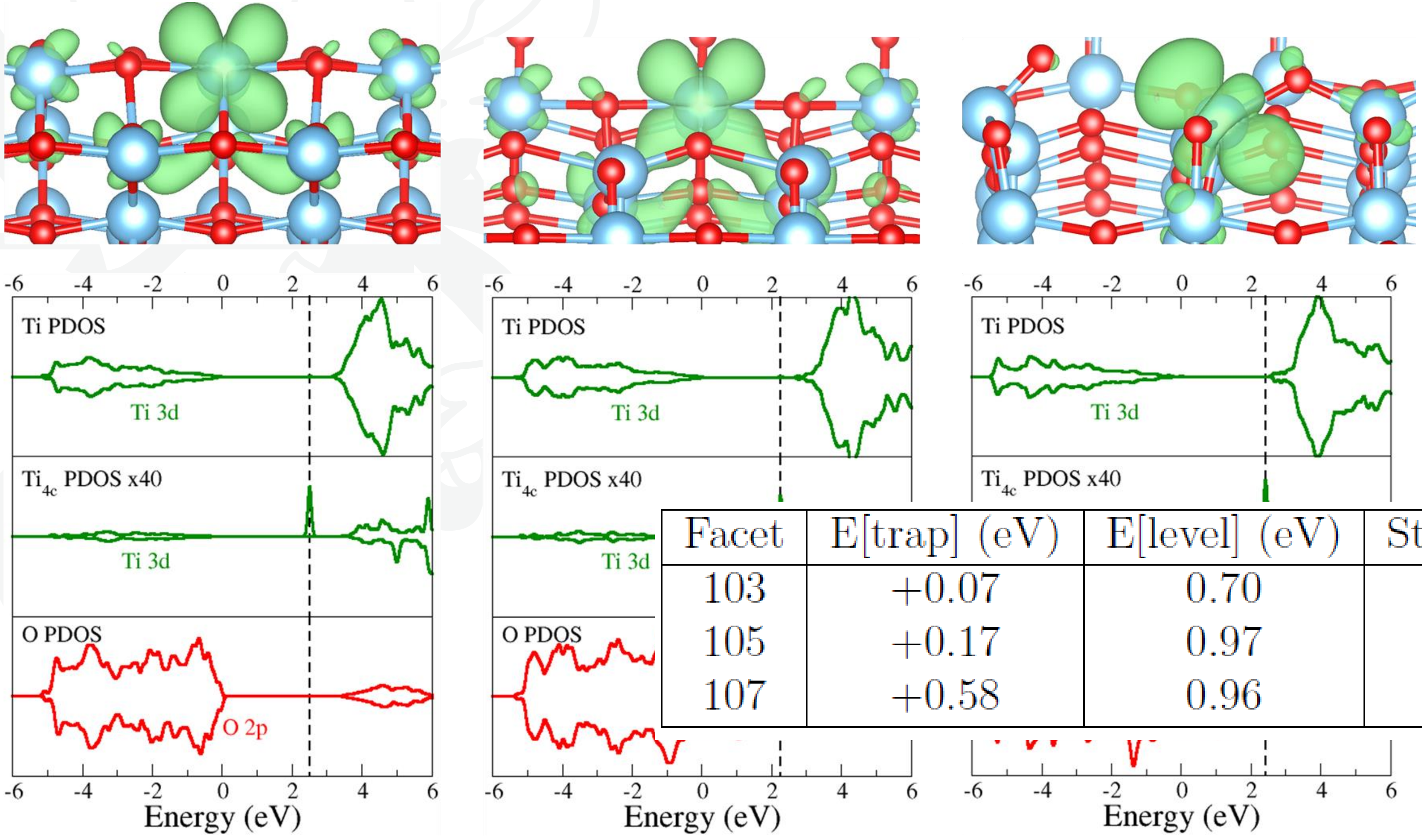


ated Ti

Stepped surface: 103 facet

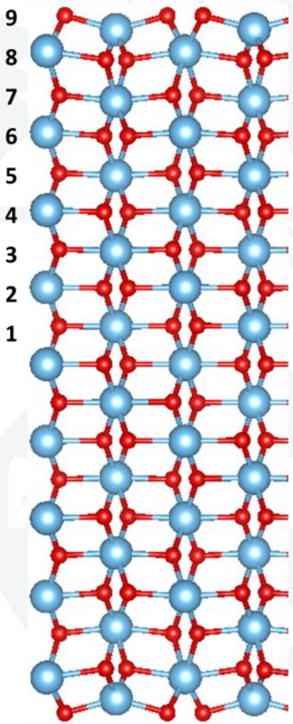


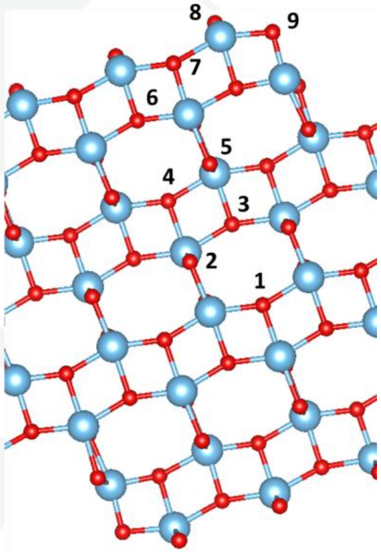
Stepped surface: 103 facet



Facet	E[trap] (eV)	E[level] (eV)	Strain (eV)	Spin (μ_B)
103	+0.07	0.70	1.05	0.73
105	+0.17	0.97	0.97	0.61
107	+0.58	0.96	1.25	0.89

Hole Trapping

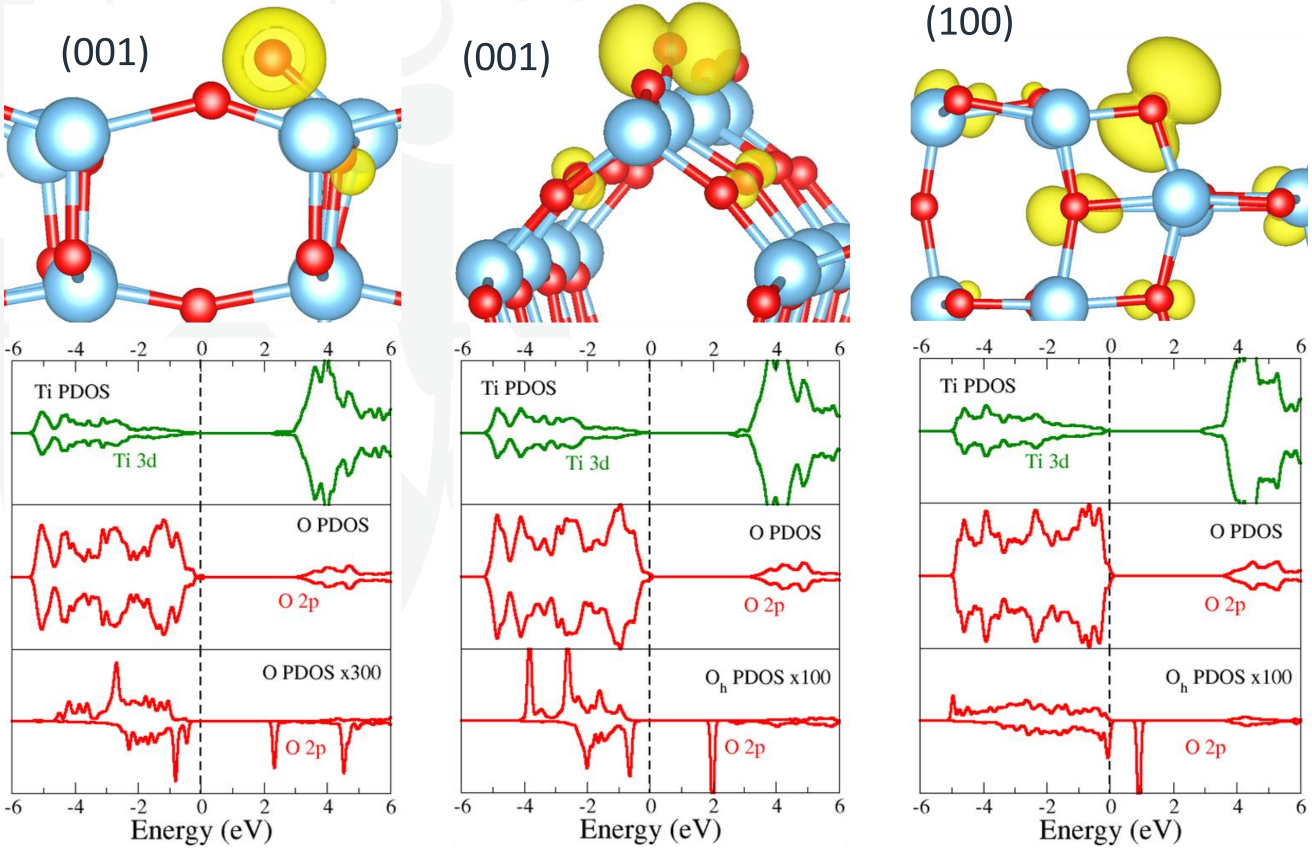




Facet	1	2	3	4	5	6	7	8	9
001	0.00	0.00	0.00	0.01	0.06	-	-	-	-1.13
001-recon	0.00	0.00	0.00	0.01	0.09	-	-	-0.16	-1.17
100	0.00	0.00	0.05	0.03	0.19	-0.05	0.02	-0.12	0.07
101	0.00	-0.09	0.05	-0.06	0.17	-0.15	-0.06	-0.06	0.30
110	0.00	-0.08	-0.08	-0.08	0.07	-0.11	0.20	-0.18	-0.02
112	0.00	0.00	0.00	0.00	0.04	-0.06	0.06	0.06	0.13
103	0.00	0.00	0.00	0.08	0.07	-0.04	0.26	0.10	0.21
105	0.00	0.00	0.03	-0.09	-0.11	-	-	-	-1.37
107	0.00	0.00	0.00	0.03	-0.09	0.13	-0.75	-0.83	-0.75

- Hole trapping energies calculated by the bulk like atom in the slab center
- Energies around slab center are similar
- (001), (001)-recon, (100), (105) and (107) prefer surface sites
- (101), (110) prefer sub-surface sites
- Hole trapping on (112) and (103) surfaces unlikely occur

Hole Trapping

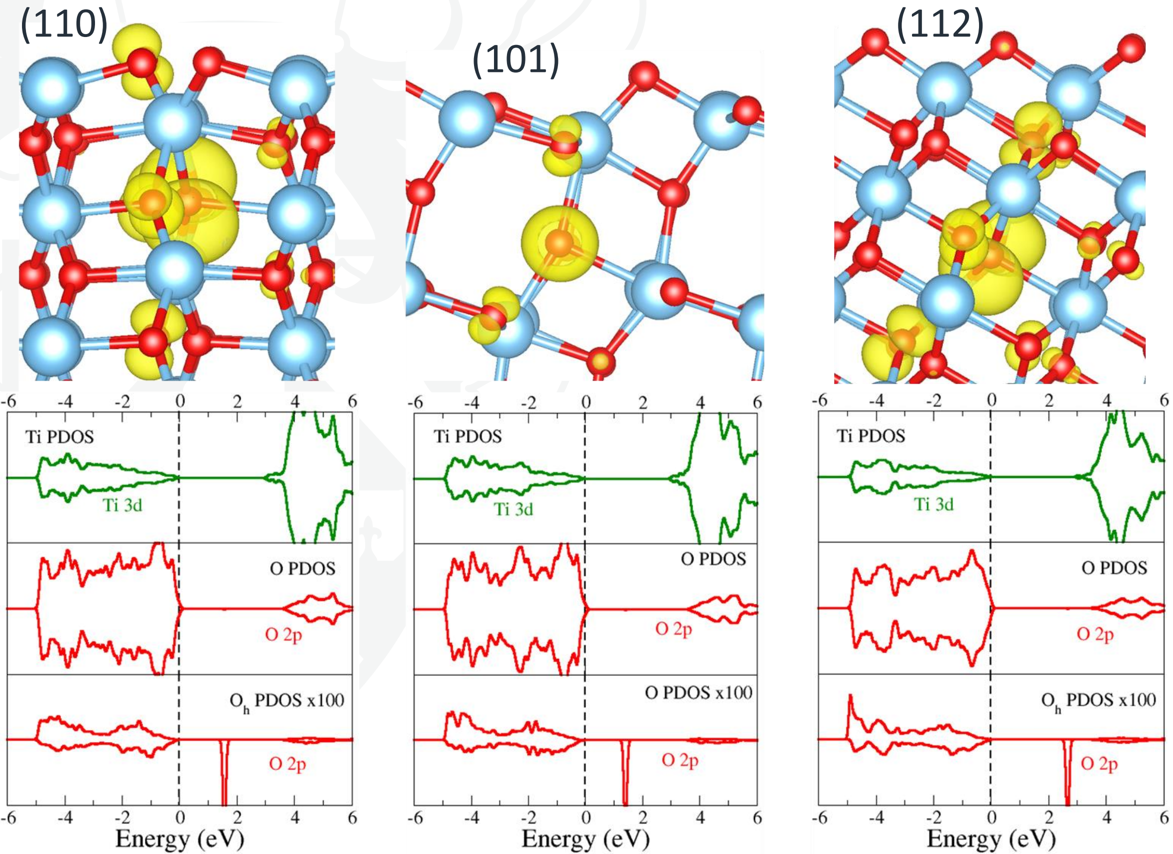


Surface hole traps

(001) Surfaces have deep hole traps around 2 eV

(100) Has shallower trap

Hole Trapping



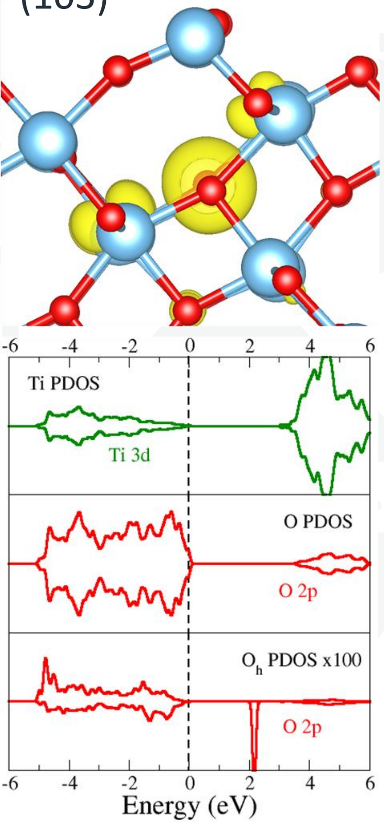
Sub Surface hole traps

(112) Surface has a deep hole trap around 2.8 eV

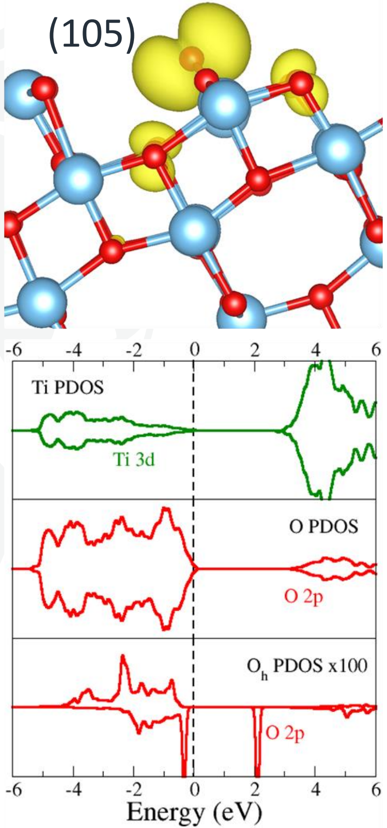
(110) And (101) Have shallower traps

Hole Trapping

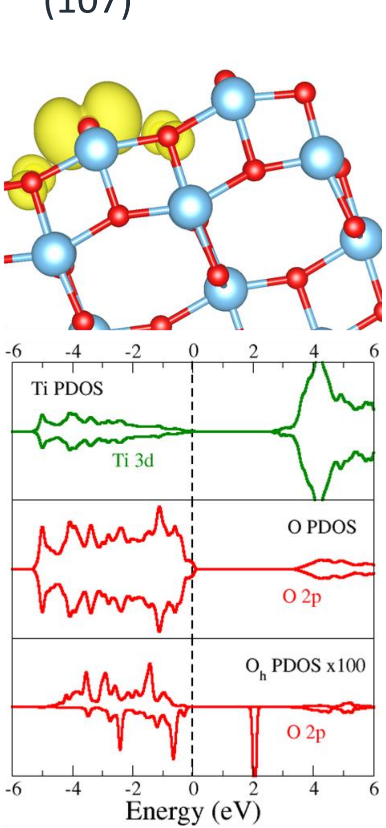
(103)



(105)



(107)



Sub Surface hole traps

All around 2eV

Conclusions

- There is no electron trapping in low index surfaces
  - Point and structural defects trapping electrons??
- Structural defects play a role in electron self trapping
  - Low lying Ti 3d states are accessible by low coordinated Ti cations
- Holes trap in all surfaces of anatase TiO_2
  - Different facets have various hole trapping locations

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First-Principles Modeling of Polaron Formation in TiO_2 Polymorphs

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J. Chem. Theory Comput., **2018**, *14* (7), pp 3740–3751
DOI: 10.1021/acs.jctc.8b00199
Publication Date (Web): June 6, 2018

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Cite this: *J. Chem. Theory Comput.* 2018, 14, 7, 3740-3751

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J. Phys. Chem. C, **2018**, *122* (48), pp 27540–27553
DOI: 10.1021/acs.jpcc.8b09437
Publication Date (Web): November 5, 2018

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Cite this: *J. Phys. Chem. C* 2018, 122, 48, 27540-27553

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