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A Computational Investigation of TiO_2-Terminated Barium Titanate Surface Interactions

March 9, 2023

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APS March Meeting 2023

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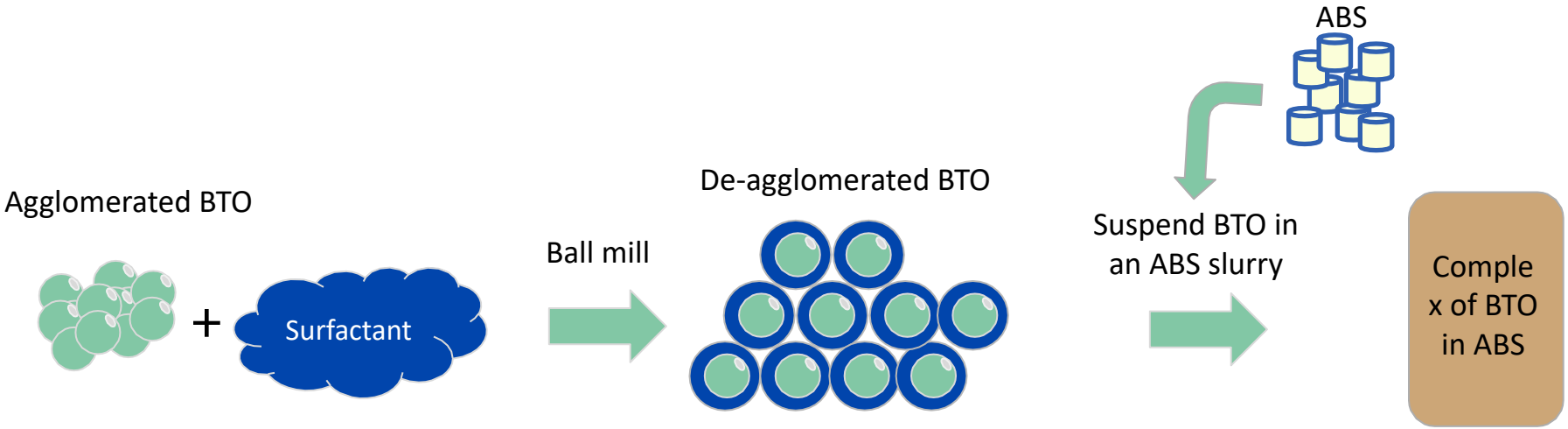
BTO Fabrication Alters Surface Chemistry



Surfactants help to reduce particle de-agglomeration but interact with BTO nanoparticle surface

Cooper et al., *MRS Adv*, 2022, 7, 31, 799-804.

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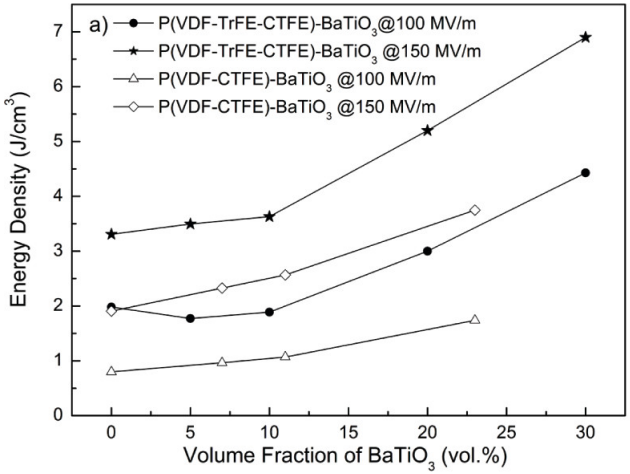
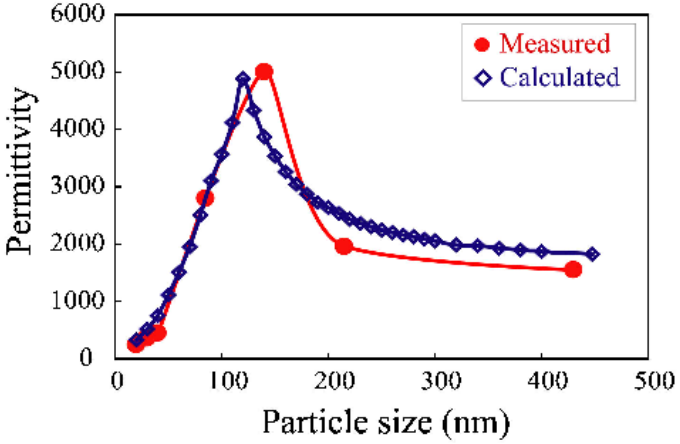
Electrical Properties Depend on Manufacturing Parameters



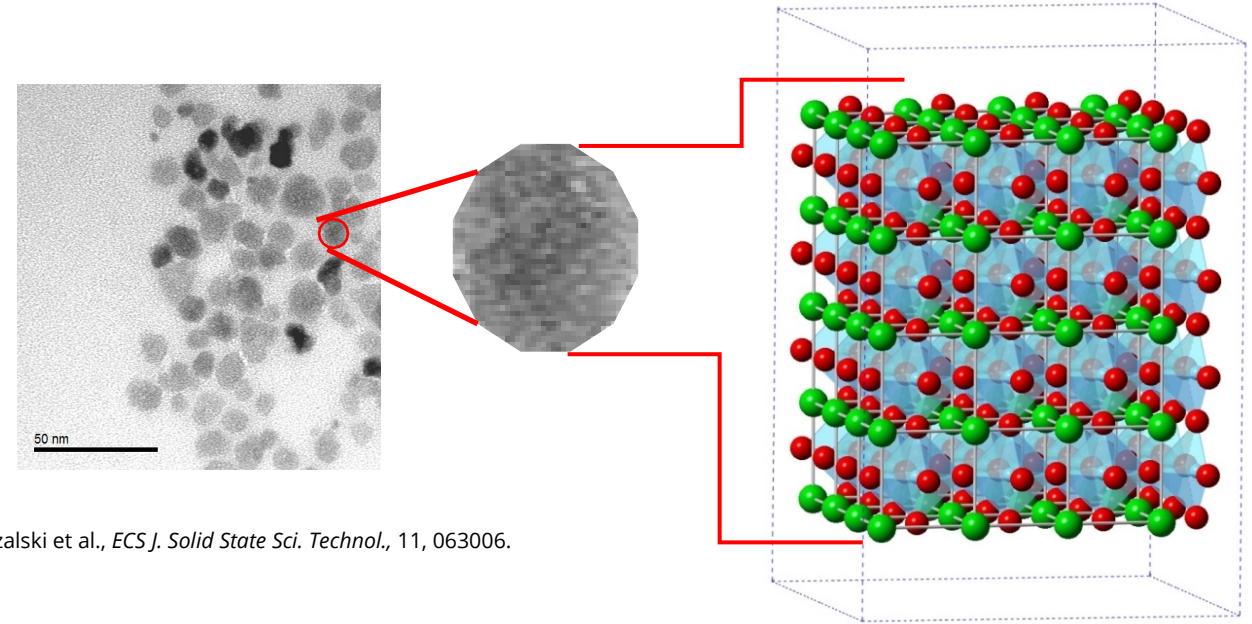
Li et al., *Chem. Matter*, 2008, 20, 20, 6304-6306.



Hoshina et al., *JCS-Japan*, 2013, 121, 156-161.

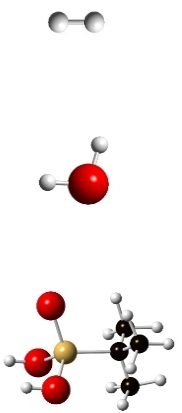
Electric properties depend on **surface interactions, particle size** and **volume fraction**

Represent BTO Nanoparticle as Periodic Slab



Domrzalski et al., *ECS J. Solid State Sci. Technol.,* 11, 063006.

Different molecules interact with the surface



Our nanoparticles are represented by slabs **periodic in x and y** directions, but **finite in the z** direction

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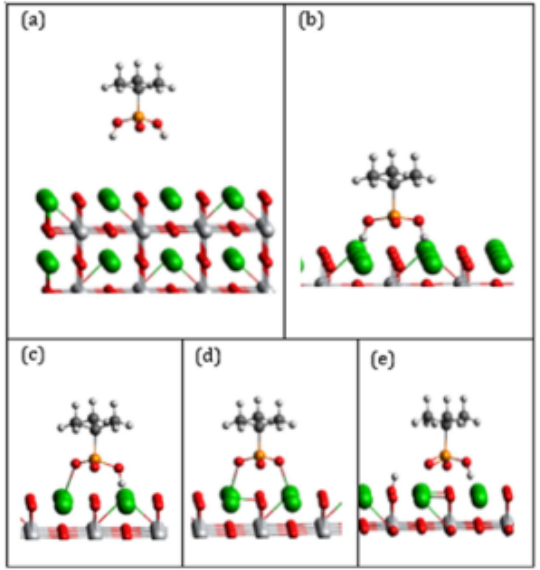
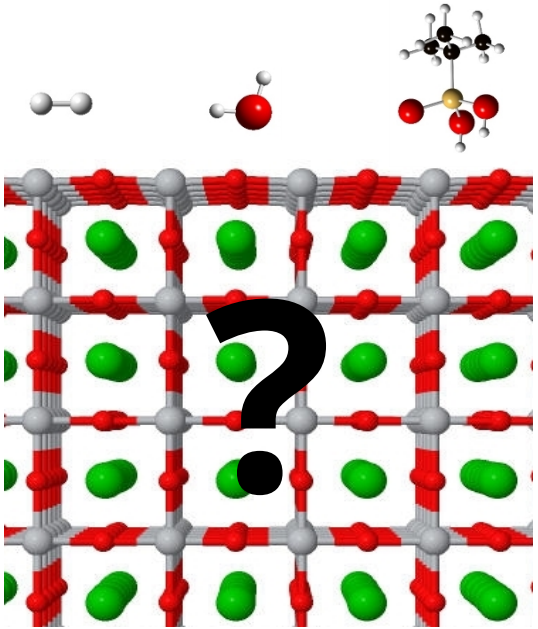
TiO_2 Surface Analysis to Fully Understand BTO Surface Chemistry



Domrzalski et al., *ECS J. Solid State Sci. Technol.,* 11, 063006.



Past research has focused primarily on the BaO terminated surface.
How does the TiO_2 terminated surface respond to interacting ligands?

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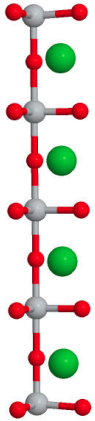
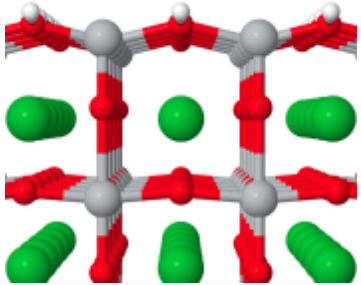
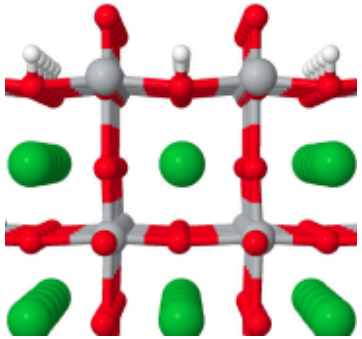
DFT Simulation Method using SEQQUEST Code

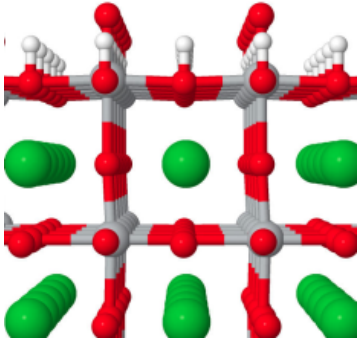




Hydrogen
Base case



Hydroxyl groups
Polar



Water
Multiple Binding Modes

Convergence criteria of 0.05eV/Å for 23 atom BTO system

PBE version of GGA functional accepted for weak surface interactions

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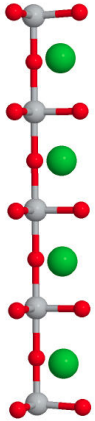
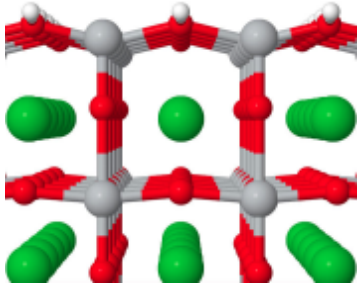
DFT Simulation Method using SEQQUEST Code





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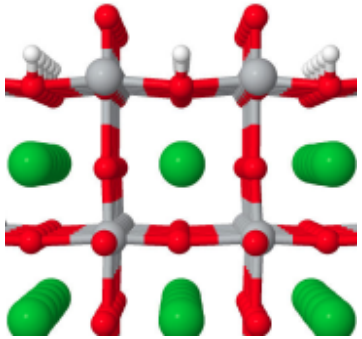
Base case



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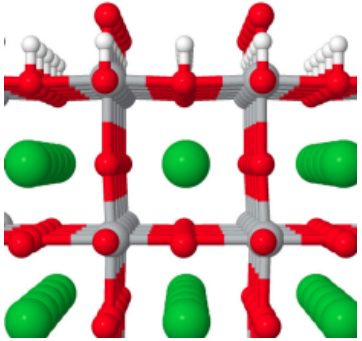

Water
Multiple Binding Modes

SEQQUEST DFT code computes ligand-slab binding energy and displacement of Ti atom which inform the surface response

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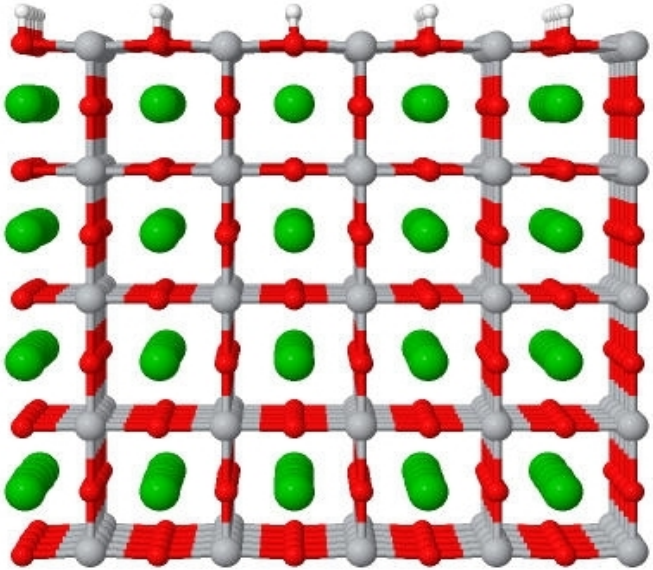
Constrained Relaxation of Surface Hydrogen

Relax successive layers



Focus on surface chemistry: Nanoparticles have high surface area to volume ratios

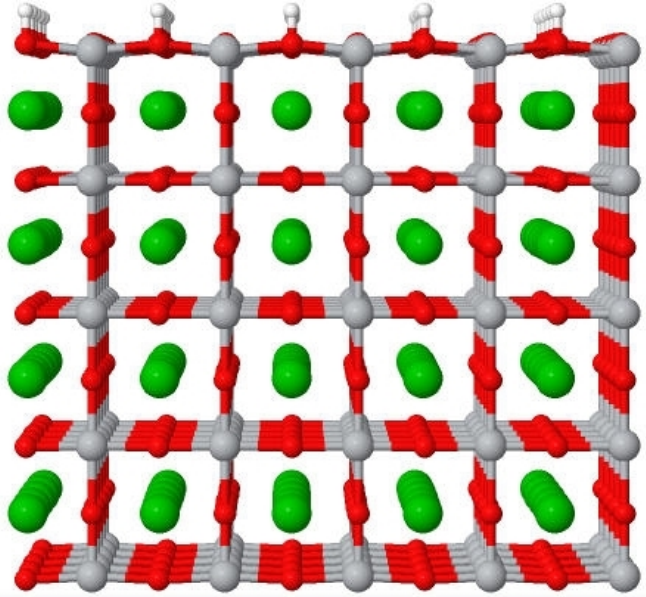
Start with a simple case: Measure response of H through the slab

Freeze deeper layers on slab: Approximate restoring forces from particle interior

Relax top three layers of nine layer slab to simulate a physically realistic system

Constrained Relaxation of Surface Hydrogen

1



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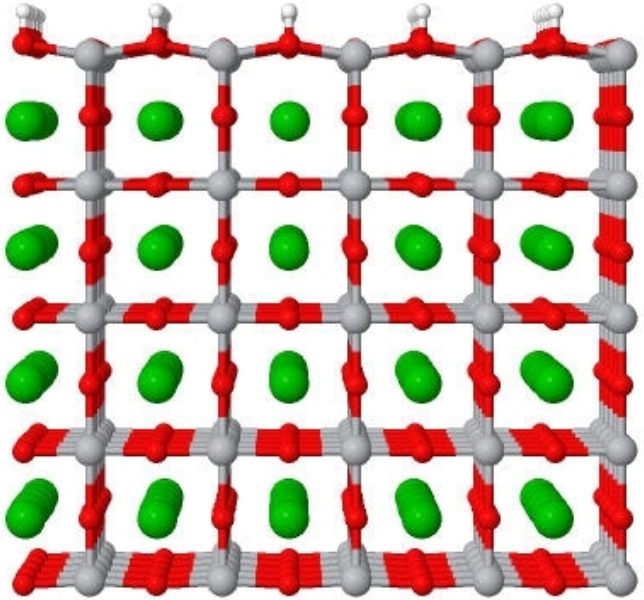
Constrained Relaxation of Surface Hydrogen

1

2



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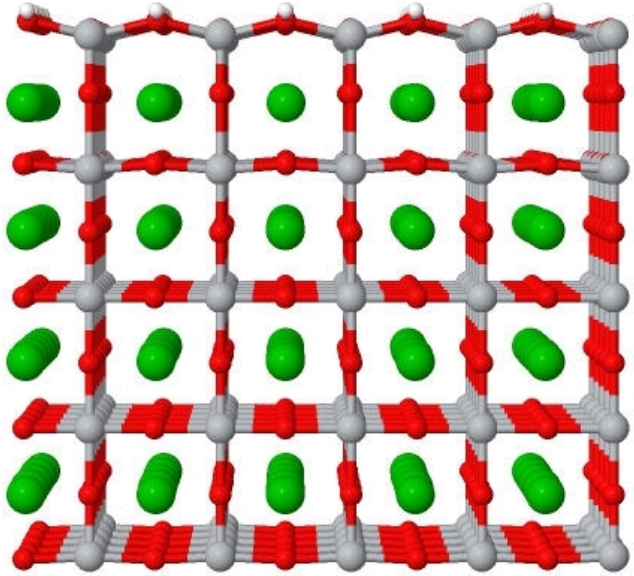
Constrained Relaxation of Surface Hydrogen

1
2
3

Relax successive layers



Focus on surface chemistry: Nanoparticles have high surface area to volume ratios

Start with a simple case: Measure response of H through the slab

Freeze deeper layers on slab: Approximate restoring forces from particle interior

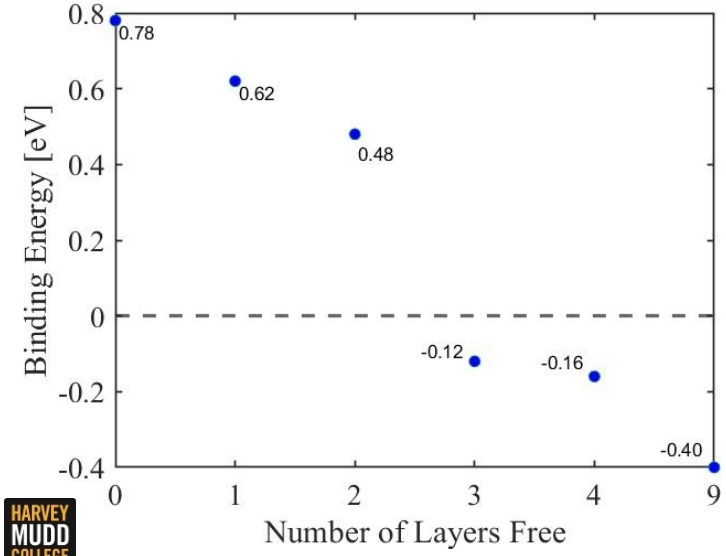
Relax top three layers of nine layer slab to simulate a physically realistic system

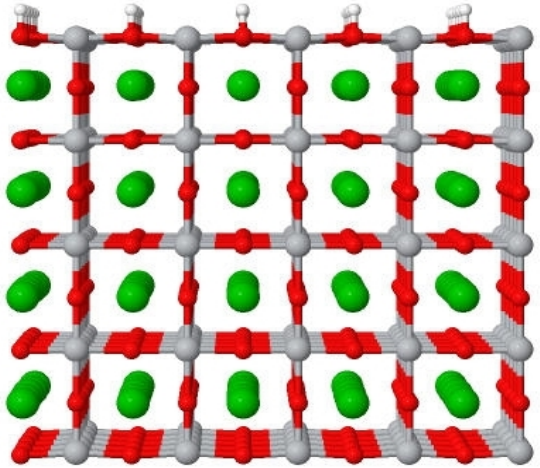
Layer Relax Simulations with Hydrogen

$E_{bind} = E_{(relaxed\ slab\ +ligand)} - E_{slab} - E_{molecule}$

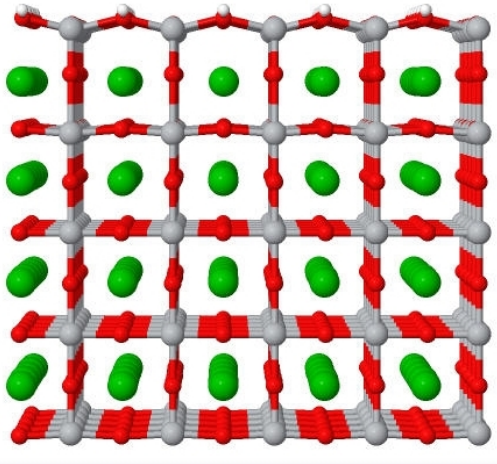
Impact of hydrogen interaction on surface propagates through the slab

9 layer 1x1 slab





9 layer slab with H
All BTO slab fixed



9 layer slab with H
Top 3 BTO layers free

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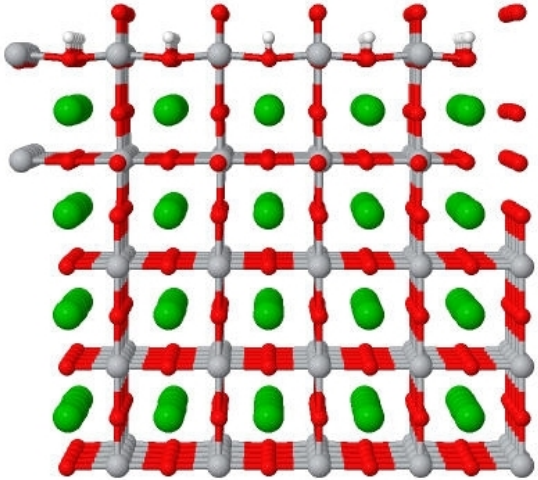
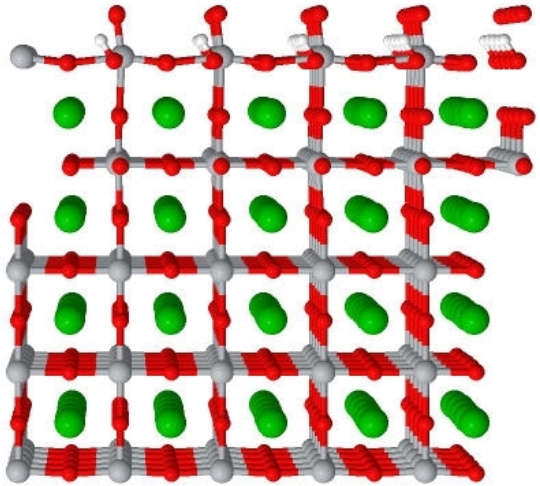
TiO_2 Surface Coverage: Hydroxyl

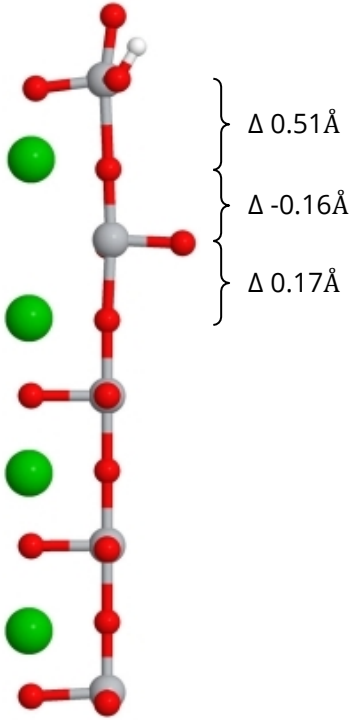
Ligand Binding Energy: -18.9 eV
Titanium atom shifts up 0.52 Å



Front



Right



9 layer BTO with OH

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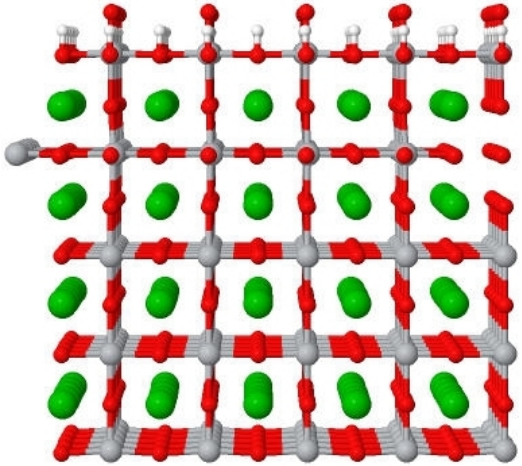
TiO_2 Surface Coverage: Water

Ligand Binding Energy: +0.60 eV
Titanium atom shifts up 0.35 Å



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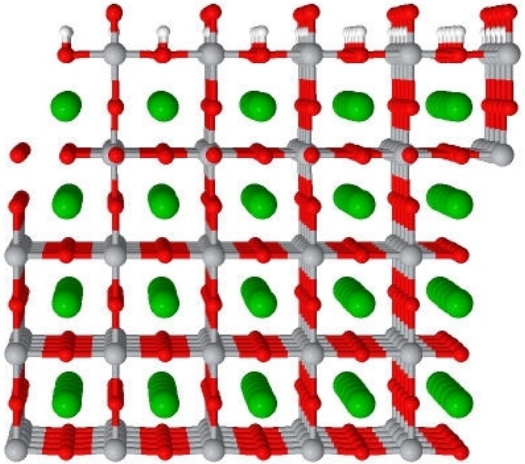

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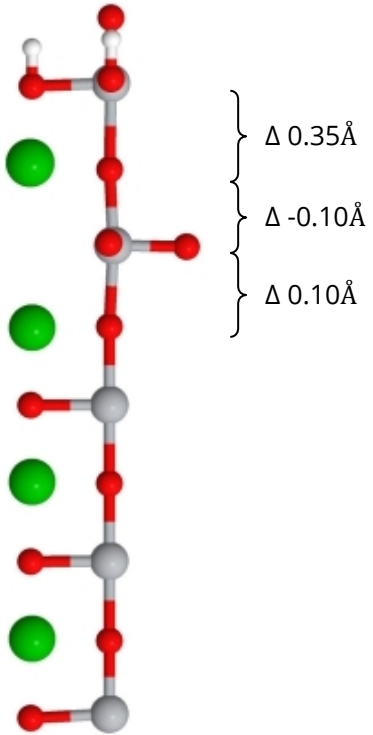

9 layer BTO with H_2O

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Summary & Acknowledgments

1. Relaxing **three of the nine** layers is sufficient and also preserves rigidity
2. **Hydrogen and OH** can bind to the TiO_2 surface of BTO with high surface density, while **water cannot**
3. Future work:
    a. Analyze **tert-butylphosphonic acid** interactions
    b. Vary **initial position** and **density** of ligands

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