AN ABSTRACT OF THE THESIS OF

Devon Paige Frazier for the degree of Honors Baccalaureate of Science in Chemical Engineering presented on 31 May 2013. Title: Interface Analysis of Titanium Dioxide and Graphene.

Abstract approved:

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Titanium dioxide, in the anatase form, is a photocatalyst and has applications in water pollution reduction. Efficiency can be improved with a graphene substrate, which delays electron-hole recombination and may reduce the band gap. In this work, we determine if graphene can also act as a morphactant, changing the shape of anatase particles to expose a larger area of catalytic surface.

Varying slabs of anatase planes – (001), (100), (101), and (110) – were uploaded into SIESTA, a program which undergoes an iterative process to determine the relaxed surface energy. Atom positions within the slab were adjusted slightly and the new surface energy was calculated using Density Functional Theory. A unit cell of graphene was constrained to fit each plane of anatase to reduce end effects. The overall slab energies of anatase (001), (100), (101), and (110) were -959.328, -959.472, -959.065, and -959.472 eV/atom, respectively. The resulting graphene strains produced energies of 0.451, 0.011, 0.044, and 0.022 eV/atom, respectively.

Graphene was then added to the anatase slabs to find relaxed energies of the combination, which are still in progress as they have not converged by the submission of this thesis.

Wulff constructions were created in Mathematica and revealed that lowering the (100) surface energy would yield the lowest overall energy and be the most favorable configuration. However, for the photocatalytic surface of (001) to be maximized, the surface energy of the (101) plane would need to be reduced. Future work should focus on making the addition of graphene, or another substrate, to the (101) anatase surface more favorable than addition to the (100) surface. The difference in overall energy between the two planes is only 0.1 J/m2, so the reduction in surface area of (101) by graphene does not need to be much larger than (100) to favor the best configuration for (001).

Keywords: photocatalysis, titanium dioxide, anatase, graphene
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# Interface Analysis of Titanium Dioxide and Graphene

By

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I understand that my project will become part of the permanent collection of Oregon State University, University Honors College. My signature below authorizes release of my project to any reader upon request. I also affirm that the work represented in this thesis is my own work.

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Devon Paige Frazier, Author

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# Interface Analysis of Titanium Dioxide and Graphene

## Introduction

Titanium dioxide, in the anatase form, is a photocatalyst and has applications in water pollution reduction [3]. Through the Honda-Fujishima effect, the surface of the molecule can separate water to form radicals, which break down organic compounds [3]. Ultraviolet light is needed for titanium dioxide to become photocatalytic. The efficiency can be improved with a graphene substrate, which delays electron-hole recombination and may reduce the band gap. In this work, we determine if graphene can also act as a morphactant, changing the shape of anatase particles to expose a larger area of catalytic surface.

Density Functional Theory (DFT) can be used to model the electronic structure of the anatase-graphene system. As the surface energies of anatase change with different exposures to graphene, the modified energies are computed with DFT and the new equilibrium shapes of anatase are represented through a Wulff construction.

# Background

## Surface Energy

Surface energy is the excess energy in a system compared to the same volume of bulk per unit surface area. It is created from dangling bonds at the boundaries of a bulk material. For small quantities, such as crystals, the equilibrium shape is greatly influenced by these forces to favor more stable configurations with minimized overall surface energy.

## Photocatalytic Titanium Dioxide

Photocatalysts are an important area of study to improve water pollution reduction. Titanium dioxide has been heavily researched and is a common material for photocatalytic applications [1]. A photocatalyst facilitates electron transfer by absorbing light. If the photon of light exceeds or matches the band gap energy, an electron will be excited from the valence band to the conductance band. A positive hole will remain in the valence band [2].

When applied to polluted aquatic systems, titanium dioxide splits water in what is called the Honda-Fujishima effect [1]. Water molecules are split into oxide and hydroxyl radicals, which are unstable. The hydroxyl radical will oxidize organic pollutants if recombination does not occur [1]. This is shown in **Figure 1**.

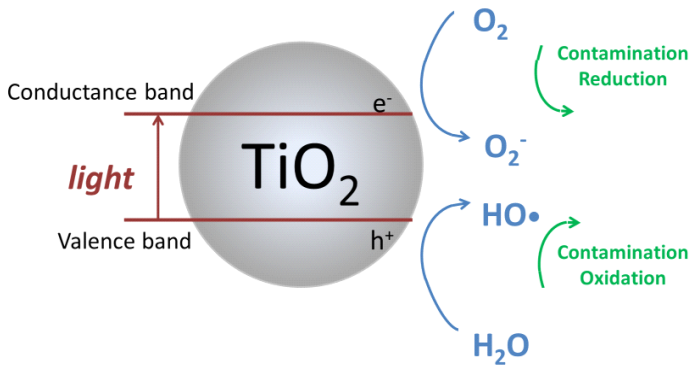


*Figure 1: Titanium dioxide is a photocatalyst under UV irradiation. If a photon exceeds the band gap, an electron is excited from the valence to the conductance band. This enables water to be split into a hydroxyl and oxide radicals, which oxide organic pollutants.*

Titanium dioxide is naturally found in a variety of forms, with anatase being a particularly efficient photocatalyst [3]. The natural crystal structure and unit cell of anatase is shown in **Figure 2**.

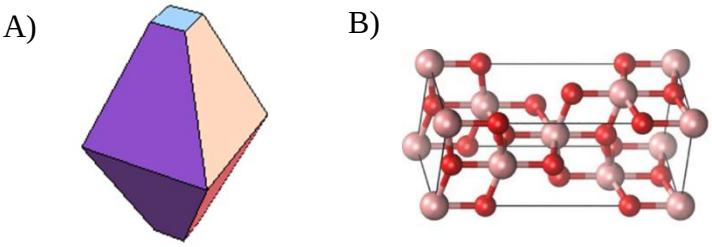


*Figure 2: Representations of anatase as a crystal. A) The Wulff construction of an anatase crystal using the natural surface energies [3]. B) The base tetragonal unit cell of anatase.*

**Graphene**

The existence of single-layer graphene was first demonstrated in 2004 and has been researched heavily since then. It has a two-dimensional structure consisting of pure $sp^2$-bonded carbon and is inexpensive to produce on the large-scale as graphene-oxide, making it feasible for many applications [2]. **Figure 3** shows a representation of graphene [4] and **Figure 4** is the unit cell used in this research.

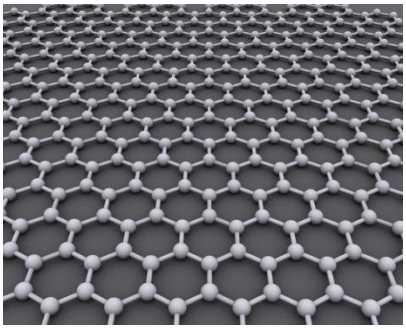

*Figure 3: A sheet of graphene, made of pure carbon with $sp^2$ bonding.*

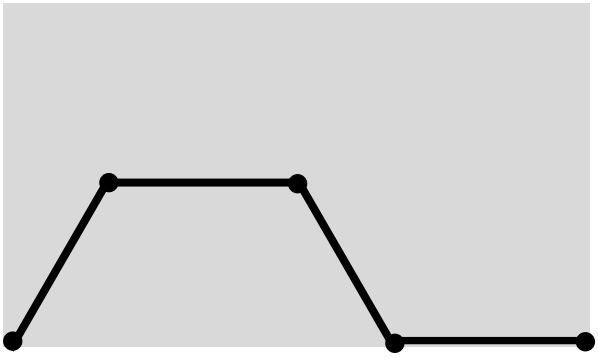

*Figure 4: The unit cell of graphene, with dimensions of 2.46 Å by 4.26 Å.*

Graphene has been found to have high conductivity, excellent electron mobility, and a relatively large specific area [2]. These properties make graphene a focus of research to improve the photocatalytic properties of anatase.

Electron-hole pairs created in photocatalysts are very unstable. Recombination is fast and energy is dissipated as heat [2]. Graphene has been shown to transfer electrons away from titanium dioxide and reduce the rate of recombination before pollution degradation [2]. **Equations 1** through **5** demonstrate the process steps [2] and are shown in **Figure 5**.

$$TiO_2 + hv \rightarrow TiO_2(e^- + h^+) \quad (1)$$

$$TiO_2(e^-) + Graphene \rightarrow TiO_2 + Graphene(e^-) \quad (2)$$

$$Graphene(e^-) + O_2 \rightarrow Graphene + O_2^- \quad (3)$$

$$TiO_2(h^+) + OH^- \rightarrow TiO_2 + \bullet OH \quad (4)$$

$$\bullet OH + Pollutants \rightarrow Degradation\ products \quad (5)$$

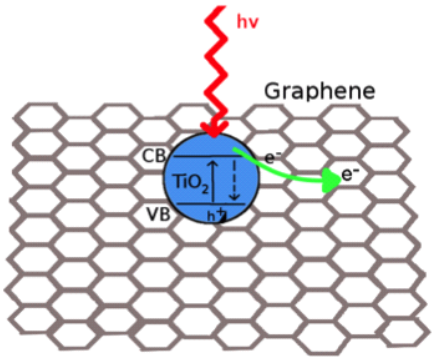


*Figure 5: Excited titanium dioxide electrons transfer to the graphene sheet, allowing anionic charge to be taken up by oxygen atoms instead of recombining with the positive hole left in the valence band. This improves the overall efficiency.*

The addition of graphene is hypothesized to lower the band gap for titanium dioxide photocatalysis, expanding the process from UV light to the visible spectrum [2]. Increased photocatalytic activity has been shown with both titanium dioxide-graphene and titanium dioxide-graphene oxide [2].

**Surface Energies**

Anatase has multiple planes with potentially varying photocatalytic properties. Graphene increases the efficiency of titanium dioxide in photocatalysis, but may change the surface structure and energy. The most catalytic plane [3] of anatase is (001) and the area to volume ratio should be maximized with the addition of graphene.

**Density Functional Theory**

Density Functional Theory (DFT) uses the theory that the ground state of a many-body electron system and all its properties are a functional of the total electron density. It computes the ground state energy of bulk and surface atoms in many-electron systems [5] and can be used to analyze changes to anatase as graphene is added. DFT methods recast the many body Schrödinger Equation of a system of single particle states and minimizes the total energy with respect to variations in the charge density.

**Wulff Construction**

Substances tend to form shapes based on lowest overall surface energy, and predicting these configurations can be helpful when trying to maximize a particular plane of anatase. For isotropic materials, a sphere produces the lowest overall surface energy. Anatase is anisotropic, meaning the surface energy is dependent on direction and does not favor a spherical shape. A Wulff plot is a three-dimensional representation used to predict the crystal facets producing the lowest energy configuration. This representation is only a prediction, based on relative minimums [6], and is the most likely shape a substance will

form. While not guaranteeing the exact shape, a Wulff plot enables the favored relative area exposures for each plane to be seen. **Figure 6** shows the process of constructing a Wulff plot [5]. **Figure 2A** is a Wulff construction, generated in Mathematica, of anatase using the original surface energies, unmodified by graphene [3].

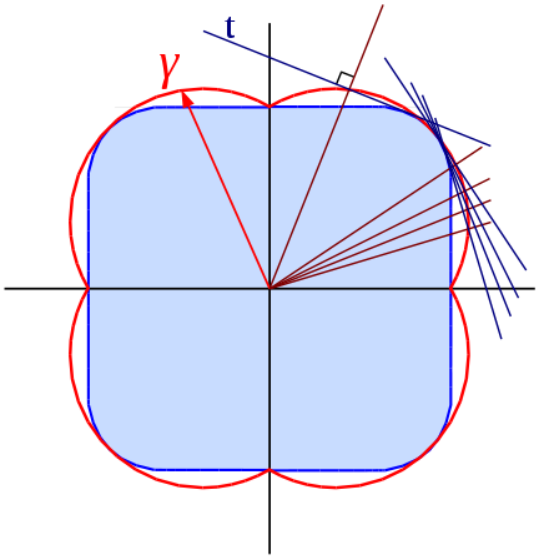


*Figure 6: The Wulff construction predicts crystal shape by carving out facets of lowest energy from the initial body. This method is helpful for anisotropic materials.*

A Wulff plot is commonly applied to convex bodies and can yield curved equilibria shapes as well as polyhedral [7]. **Equation 6** describes the surface energy $\gamma_i$ as a function of perpendicular distance $h_i$ from an interior point to the *i*th face [8] :

$$h_i = \lambda \gamma_i \qquad (6)$$

A constant λ is present, and is the same for all the surfaces in a given crystal [7].

It is proposed that graphene acts as a morphactant for anatase, changing the shape to expose a larger area of catalytic surface.

## Methods

The research is composed of two separate parts. First, the anatase Wulff plot with modified surface energies to maximize the fractional area of the most catalytic plane. Second, the calculation of surface energy changes with graphene added to anatase.

The Wulff plots were generated in Mathematica:

1. All the possible bounding planes, and the corresponding normal distance from the particle center, were defined
2. The common vertex was then found by going through each triplet of planes
3. The subset of vertices that lie on the inner boundary of the volume enclosed by the possible faces was found
4. Boundary vertices that lie on the plane were found for each plane. These boundaries mark the edge of each face
5. Boundary points for each face are ordered clockwise about the central outward normal vector
6. The area of each facet was computed using the sum of cross products of face center boundary point position vectors.
7. The subtended particle volume was calculated using the pyramid volume equation: $V = \frac{A_i \cdot h_i}{3}$, where $A_i$ is area of each face and $h_i$ is the distance from the center of the particle to the face surface.

**Computational Modeling**

A computational modeling program, Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA), was used to compute the electronic structure of the molecules. Atomic coordinates of various anatase planes and graphene were uploaded to the program and energies were calculated. Calculations were performed using the Generalized Gradient Approximation with the exchange correction functional of Wu-Chon [9]. SIESTA represents the wave functions of the system using a linear sum of the local atomic orbital like functions. This is numerically efficient. The inner core electrons of the titanium and oxygen atoms were replaced with core correction relativistic pseudo potentials that were created using the utility atom.

Atoms were adjusted by SIESTA in order to find the lowest energy position, or relaxed state. Anatase and graphene were calculated separately to determine baseline energies before combination. Certain atoms at the bottom of the anatase planes were held in place to simulate the bulk state, which prevented structures and energies that an individual molecule of anatase would approach without the addition of graphene.

**Surface Energy Equations**

Using available tools, such as SIESTA, surface energies can be calculated. The general balanced surface energy is presented in **Equation 7**:

$$\gamma_R + \gamma_N = \frac{E_{slab} - nE_{bulk}}{A_{slab}} \quad (7)$$

The surface energies of the relaxed state $\gamma_R$ and the non-relaxed state $\gamma_N$ can be calculated from the energy difference of the slab of material $E_{slab}$ and bulk $E_{bulk}$, multiplied by the number of unit cells used *n*. The energy difference must be normalized by the area of slab exposed, $A_{slab}$.

**Equation 7** can be rearranged to solve for the instance of anatase surface energy in a vacuum $\gamma_{AV}$, shown in **Equation 8**.

$$\gamma_{AV} = \frac{E_{slab} - nE_{bulk}}{A_{slab}} - \gamma_N \quad (8)$$

The difference between surface energies of the non-relaxed state and graphene combined with anatase is calculated in **Equation 9** using the same principles. The energy of anatase in the bulk $E_{Abulk}$and of graphene $E_G$can be subtracted from the entire energy of graphene combined with the slab of anatase $E_{G+slab}$. **Equation 10** shows that the overall energy of graphene $E_G$ represents the combined energy from the relaxed state and the strained state and can be separated in **Equation 11**.

$$(\gamma_N - \gamma_{GA}) = \frac{E_{G+slab} - nE_{ABulk} - nE_G}{A_{slab}} \quad (9)$$

$$E_G = E_{GR} + E_{Gstrain} \quad (10)$$

$$\gamma_{GA} = \frac{E_{G+slab} - nE_{Abulk} - nE_{GR} - nE_{GS}}{A_{slab}} - \gamma_N \quad (11)$$

A change in energy between the combined graphene-anatase and the anatase in a vacuum can be calculated with **Equation 12**.

$$\Delta\gamma_S = \gamma_{GA} - \gamma_{AV} = \frac{1}{A_{slab}}(E_{G+slab} - E_{slab} - nE_{GR} - E_{GS}) \quad (12)$$

The change in surface energy of the relaxed state is the combined graphene and slab energy, with the independent energies of the slab and relaxed graphene subtracted from it.

This is shown in **Equation 13**. In order to find the change of relaxed surface energy, these three values must be found.

$$\Delta\gamma_R = \frac{1}{A_{slab}}(E_{G+slab} - E_{slab} - nE_{GR}) \quad (13)$$

**Planes of Anatase**

Four planes of anatase were considered: (001), (100), (101), and (110). A unit cell of each plane was uploaded into SIESTA and certain atoms were held in position during relaxation. A program called Visual Molecular Dynamics (VMD) was used to visualize the planes of anatase and help determine which atom positions should be fixed. The unit cell equivalent of each anatase plane was oriented with the z-axis running vertical to the screen. Atoms with positions closest to the z=0 plane were fixed.

**Table 1** shows the position of stationary atoms for each plane. **Figure 7** shows the planes of anatase on a unit cell box and the corresponding VMD image.

| Anatase Plane | Fixed Atoms |
|---|---|
| (001) | 1, 4 |
| (100) | 31, 32, 33, 34, 35, 36 |
| (101) | 1, 3, 6, 8, 9 |
| (110) | 1, 2, 3, 4, 9, 14 |

*Table 1: The four anatase planes and the fixed atom positions.*

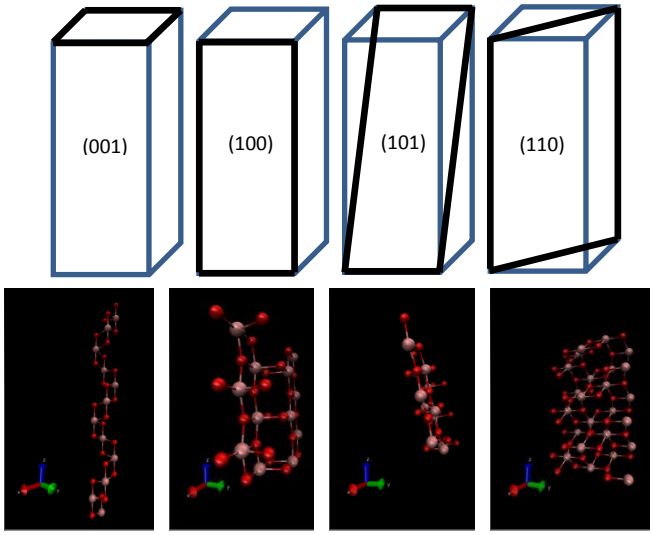


*Figure 7: The four anatase planes being considered, drawn in the unit cell box, and the corresponding three-dimensional images in VMD.*

**Anatase with Graphene**

Graphene was added to the surface of each anatase slab and strained accordingly to align the two slabs. This alignment reduced end effects in the modeling. The unit cell of graphene was strained, instead of the anatase cell, because it has a relatively simple structure and the constrained energy could be more easily removed after analysis.

**Figure 8** shows the Mathematica images of graphene added to each anatase slab.

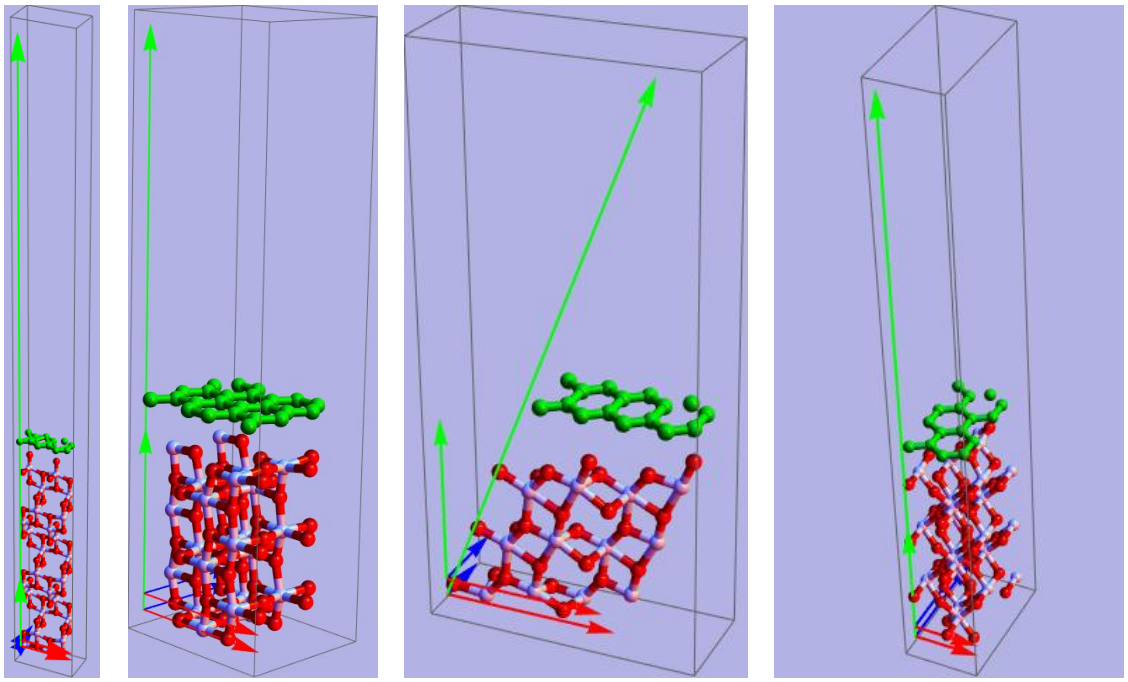


*Figure 8: The four slabs of anatase with the corresponding constrained graphene, before relaxation. The double arrows confirmed that the graphene size matched the lattice vectors of the computational cell.*

# Results

### Prediction Wulff Plots

**Figure 9** shows the unmodified state of anatase, with the two main surfaces – (001) and (101) – labeled. **Figure 10** demonstrates the effects of changing surface energy on each plane that may occur when graphene is added. The (110) plane was not shown because it produced a concave crystal shape.

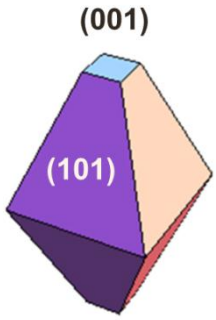


*Figure 9: The unmodified surface energy of anatase with the main surfaces labeled.*

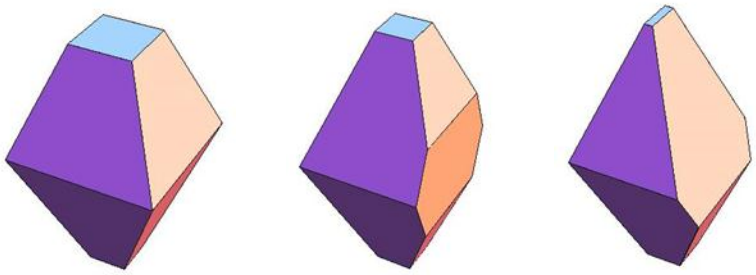


*Figure 10: Representations of surface energy changes by anatase plane.*

**Figure 10** shows that a substrate addition to the (101) plane produces the lowest overall surface energy. However, in order to maximize the area to volume ratio of the most catalytic plane (001), the substrate should be added to the (100) plane.

Some major conclusions can be drawn from the predictive Wulff plots:

1. There are four choices for an anatase nanoparticle to come into contact with grapehene. Two faces – (001) and (101) – are existing, while two others – (100) and (110) – are excluded. Contact with graphene will lower the system area for all choices, but the lowest overall energy (per fixed volume) will be selected
2. The available surface area of (001) will be reduced by applying graphene to the (001) or (101) surfaces. The actual surface area of (001) is increased by adding graphene to the surface, but it is not available due to the fact that it is now covered by the substrate. Selecting these two planes will reduce the catalytic potency of the (001) plane.
3. Favoring contact with the (100) or (110) surface will reduce the overall volume of the anatase crystal without reducing the surface area of the (001) plane. This will increase the catalytic activity because the surface area to volume ratio is higher.
4. In order for the (100) surface to be favored, $\gamma_{100} < \frac{\gamma_{101}}{\sin(21.7 \text{ deg})}$.
5. The energy of (100) and (101), not in contact with graphene, is only 0.1 J/m$^2$. Graphene would not need to change $\gamma_{100}$by much more than $\gamma_{101}$to provide the maximized area of (001).

6. Several visual observations show how the condition $\gamma_{100} < \frac{\gamma_{101}}{\sin(21.7\ \mathrm{deg})}$ could be favored:
    a. The (100) surface is closer to being commensurate with graphene than (101). Cutting into the (100) facet would shorten than distance from the center of the crystal, $h_i$, sooner than reducing the (101) plane distance.
    b. The (101) surface has a natural corrugation that requires graphene to deform when in contact. As shown in **Figure 7**, the (101) plane is actually an angled cut within the unit cell and produces a toothcomb structure on the surface in contact with graphene. Full contact with anatase would require graphene to ripple, which is not likely to produce a favorable overall system energy when compared to (100) surface application.

**Independent Energies of Graphene and Anatase**

The anatase slabs, with fixed bulk atom positions, and the corresponding strained graphene unit cells, were submitted to SIESTA. The relaxed anatase slab energies provide a baseline for evaluating overall system energy changes. These values are shown in **Table 2**. In addition, an unstrained graphene unit cell was submitted to provide a baseline for the graphene strained energies.

| | eV/atom | | |
|---|---|---|---|
| | $E_{slab}$ | $E_{GR}$ | $E_{GS}$ |
| 001 | -959.328 | -649.31 | 0.451 |
| 100 | -959.472 | | 0.011 |
| 101 | -959.065 | | 0.044 |
| 110 | -959.472 | | 0.022 |

*Table 2: The relaxed energies for the four anatase slabs and the corresponding graphene unit cell strains. The unstrained graphene unit cell energy was also calculated.*

**Anatase and Graphene**

The combined anatase and graphene systems shown in **Figure 8** have been submitted to SIESTA but had not converged before submission of this thesis.

## Conclusion and Future Work

The (101) plane of anatase was shown in predictive Wulff plots to be most favorable for a substrate addition, as it produced the lowest overall surface area. The (100) plane, however, maximizes the area to volume ratio of the (001) catalytic surface.

From visual observation, using graphene as the substrate may favor the (100) plane over (101). The (101) plane has a jagged surface and full contact would require graphene to ripple. In addition, cutting into the crystal to form the (100) plane reduces the distance $h_i$ from the inside of the crystal face to the surface.

Immediate continuation of work will focus on converging the combined graphene and anatase files within SIESTA. The effectiveness of graphene to favor the (100) plane over the (101) plane will be assessed and further research may focus on alternative substrates to produce this outcome.

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# APPENDICES

# Appendix A

SIESTA Input File

```
# Read the structure from file

%include Anatase-Slab-x010-y001-z100-36at_structure.fdf                # 100 surface: fix atoms
31 32 33 34 35 36
#%include Anatase-Slab-x010-y001-z101-36at_structure.fdf                # 101 surface: fix atoms
1 3 6 8 9
#%include Anatase-Slab-x100-y010-z001-36at_structure.fdf                # 001 surface: fix atoms
1 4
#%include Anatase-Slab-x11b0-y001-z110-72at_structure.fdf     # 110 surface: fix atoms  1 2 3 4
9 14

SpinPolarized           T
#FixSpin                F
#TotalSpin              0.0
#NetCharge              0

SlabDipoleCorrection    T

#-------Convergance-----------------------------

# K points
%block kgrid_Monkhorst_Pack
5  0  0 0
0  3  0 0
0  0  1 0
%endblock kgrid_Monkhorst_Pack

MeshCutoff              200 Ry
XC.functional           GGA
XC.authors              WC

SolutionMethod                  diagon

#-------Restart Options-------------------------

MD.UseSaveXV        T
MD.UseSaveDM        T
WriteMDXmol         T

#-------Self consistency------------------------

MaxSCFIterations                1200
SCFMustConverge                         F
```

```
DM.Tolerance                    0.0001
DM.NumberPulay                  2
DM.NumberBroyden                8
DM.Broyden.Cycle.On.Maxit       T
DM.Broyden.Variable.Weight      T
DM.MixingWeight                 0.005
DM.MixSCF1                      T
DM.NumberKick                   600
DM.NumberKickMixingWeight       0.25
DM.Pulay.Avoid.First.After.Kick T

#-------Basis set--------------------------------

#PAO.BasisSize        DZP
#PAO.BasisSize        DZP

%Block PAO.Basis
Ti   5     1.91
 n=3   0   1   E    93.95     5.20
   5.69946662616249
   1.00000000000000
 n=3   1   1   E    95.47     5.20
   5.69941339465994
   1.00000000000000
 n=4   0   2   E    96.47     5.60
   6.09996398975307       5.09944363262274
   1.00000000000000       1.00000000000000
 n=3   2   2   E    46.05     4.95
   5.94327035784617       4.70009988294302
   1.00000000000000       1.00000000000000
 n=4   1   1   E     0.50     1.77
   3.05365979938936
   1.00000000000000
O    3    -0.28
 n=2   0   2   E    40.58     3.95
   4.95272270428712       3.60331408800389
   1.00000000000000       1.00000000000000
 n=2   1   2   E    36.78     4.35
   4.99990228025066       3.89745395068600
   1.00000000000000       1.00000000000000
 n=3   2   1   E    21.69     0.93
   2.73276990670788
   1.00000000000000
#C   3     .35201
##n=2  0  2  E   50.37145    5.22551
##    5.43077    3.08484
##    1.00000    1.00000
##n=2  1  2  E   13.53326    6.81234
```

```
##    6.83094    3.01366
##    1.00000    1.00000
##n=2   2   1   E   110.78225     .01065
##    5.04748
##    1.00000
#H    2     0.22
# n=1    0    2   E     2.07      0.00
#   4.971   1.771
#   1.000   1.000
# n=2    1    1   E     0.89      0.01
#   4.988
#   1.000
%EndBlock PAO.Basis

#PAO.EnergyShift                    100 meV

#------------------------------------
#Relaxed molecules
MD.TypeOfRun             FIRE
MD.MaxForceTol        0.01 eV/Ang
MD.NumCGsteps         100
MD.MaxCGDispl                  0.025 Ang

SaveRho              T #use denchar to convert .Rho (spatial charge density map)
WriteDenchar         T
WriteMullikenPop      1 #measure of charge ef each atoms *Verioni cell
```

# Appendix B

SIESTA STRUCTURE FILES

----------(100) Bare slab----------

```
#-------Description of the system----------------

SystemName          Anatase-slab-100
SystemLabel         Anatase-slab-100

#-------Define structure-------------------------

NumberOfAtoms 36
NumberOfSpecies 2

%block ChemicalSpeciesLabel
1           8           O
2           22          Ti
%endblock ChemicalSpeciesLabel

%block GeometryConstraints
   position 31 32 33 34 35 36
%endblock GeometryConstraints

LatticeConstant 1.  Ang
%block  LatticeVectors
0.          0.          -34.06049999999999
0.          3.784499999999999           0.
9.514299999999999           0.          0.
%endblock

AtomicCoordinatesFormat Ang
%block AtomicCoordinatesAndAtomicSpecies
-4.361083333334072  2.838249999999878   9.487900000000227   2   Ti
-2.3810833333340766 2.838249999999878   9.487900000000227   1   O
2.7749166666659253  0.9462499999998785  9.487900000000227   2   Ti
4.754916666665926   0.9462499999998785  9.487900000000227   1   O
0.7949166666659252  0.9462499999998785  9.487900000000227   1   O
3.173916666665923   2.838249999999878   9.487900000000227   1   O
0.39591666666592457 0.9462499999998785  7.595400000000229   2   Ti
-0.00208333333407514 2.838249999999878  7.595400000000229   1   O
-3.962083333334076  2.838249999999878   7.595400000000229   1   O
-4.361083333334072  2.838249999999878   5.70340000000023    2   Ti
-2.381083333334076  2.838249999999878   5.703400000000229   1   O
-1.5830833333340744 0.9462499999998785  7.595400000000229   1   O
-1.9820833333340755 2.838249999999878   7.595400000000229   2   Ti
2.774916666665925   0.9462499999998785  5.70340000000023    2   Ti
4.754916666665926   0.9462499999998785  5.703400000000229   1   O
0.7949166666659253  0.9462499999998785  5.70340000000023    1   O
2.3769166666659256  0.9462499999998785  7.595400000000229   1   O
3.173916666665923   2.838249999999878   5.703400000000229   1   O
0.39591666666592457 0.9462499999998785  3.8109000000002284  2   Ti
-0.0020833333340750846      2.838249999999878   3.8109000000002284  1   O
```

```
-3.9620833333340757  2.838249999999878   3.810900000000228   1   O
-4.361083333334072   2.838249999999878   1.9189000000002299  2   Ti
-2.381083333334076   2.838249999999878   1.9189000000002294  1   O
-1.5830833333340744  0.9462499999998785  3.8109000000002284  1   O
-1.9820833333340753  2.838249999999878   3.8109000000002284  2   Ti
2.7749166666659253   0.9462499999998785  1.9189000000002294  2   Ti
4.754916666665926    0.9462499999998785  1.9189000000002299  1   O
0.7949166666659252   0.9462499999998785  1.918900000000229   1   O
2.3769166666659256   0.9462499999998785  3.810900000000228   1   O
3.173916666665923    2.838249999999878   1.918900000000229   1   O
0.39591666666592457  0.9462499999998785  0.02640000000023157 2   Ti
-0.00208333333407514 2.838249999999878   0.02640000000023157 1   O
-3.962083333334075   2.838249999999878   0.02640000000023246 1   O
-1.5830833333340746  0.9462499999998785  0.02640000000023157 1   O
-1.9820833333340757  2.838249999999878   0.026400000000230683    2   Ti
2.376916666665926    0.9462499999998785  0.02640000000023157 1   O
%endblock AtomicCoordinatesAndAtomicSpecies


----------(101) Bare Slab----------

#-------Description of the system----------

SystemName          Anatase-slab-101
SystemLabel         Anatase-slab-101

#-------Define structure----------

NumberOfAtoms 36
NumberOfSpecies 2

%block ChemicalSpeciesLabel
1          8          O
2          22         Ti
%endblock ChemicalSpeciesLabel

%block GeometryConstraints
   position 1 3 6 8 9
%endblock GeometryConstraints

LatticeConstant 1.  Ang
%block  LatticeVectors
12.588877968809483   0          31.648662084461378
0          3.7845000000000004   0
-10.239352750052124  0          0
%endblock

AtomicCoordinatesFormat Ang
```

```
%block AtomicCoordinatesAndAtomicSpecies
-7.316179897667304  0.9462499999998782  0.21483241554517285  2  Ti
-9.15597528902191   0.9462499999998782  0.9466472267852541   1  O
-7.6869265447130015 2.838249999999878   0.3623041881132494   1  O
-4.406163349028687  0.9462499999998782  1.0940371338272117   2  Ti
-4.036345891574579  2.838249999999878   0.9469349646991554   1  O
0.7132812466986307  2.838249999999878   1.0938602769453185   2  Ti
-1.1265141446559723 2.838249999999878   1.825675088185399    1  O
-2.567297147265675  0.9462499999998782  0.36259192602715196  1  O
-2.196550500219974  2.838249999999878   0.21512015345907454  2  Ti
-5.917415678910694  0.9462499999998782  3.7313504249297718   2  Ti
-7.757211070265298  0.9462499999998782  4.4631652361698535   1  O
-4.077620287556089  0.9462499999998782  2.999535613689691    1  O
-6.246887929974887  0.9462499999998782  1.8262215485073132   1  O
-6.288162325956392  2.838249999999878   3.8788221974978474   1  O
-3.0073991302720775 0.9462499999998782  4.610555143211809    2  Ti
-2.63758167281797   2.838249999999878   4.4634529740837525   1  O
1.0420091098912412  2.838249999999878   2.999823351603591    1  O
2.112045465455238   2.838249999999878   4.610378286329914    2  Ti
0.2722500741006364  2.838249999999878   5.342193097569995    1  O
-1.1685329285090664 0.9462499999998782  3.8791099354117486   1  O
-0.7977862814633647 2.838249999999878   3.7316381628436717   2  Ti
-4.518651460154086  0.9462499999998782  7.247868434314367    2  Ti
-6.358446851508691  0.9462499999998782  7.979683245554449    1  O
-2.67885606879948   0.9462499999998782  6.516053623074287    1  O
-4.848123711218278  0.9462499999998782  5.34273955789191     1  O
-4.889398107199784  2.838249999999878   7.395340206882443    1  O
-1.6086349115154672 0.9462499999998782  8.127073152596408    2  Ti
-1.2388174540613603 2.838249999999878   7.979970983468352    1  O
2.4407733286478512  2.838249999999878   6.516341360988189    1  O
3.510809684211848   2.838249999999878   8.126896295714513    2  Ti
1.6710142928572456  2.838249999999878   8.858711106954594    1  O
0.23023129024754363 0.9462499999998782  7.395627944796347    1  O
0.6009779372932451  2.838249999999878   7.248156172228271    2  Ti
-1.2800918500428704 0.9462499999998782  10.032571632458886   1  O
-3.4493594924616677 0.9462499999998782  8.85925756727651     1  O
3.8395375474044595  2.838249999999878   10.032859370372785   1  O
%endblock AtomicCoordinatesAndAtomicSpecies


--------------------------------(001) Bare Slab----------------------------------------------------

#-------Description of the system-----------------

SystemName          Anatase-slab-001
SystemLabel         Anatase-slab-001

#-------Define structure--------------------------
```

```
NumberOfAtoms 36
NumberOfSpecies 2

%block ChemicalSpeciesLabel
1       8       O
2       22      Ti
%endblock ChemicalSpeciesLabel

%block GeometryConstraints
   position 1 4
%endblock GeometryConstraints

LatticeConstant 1.  Ang
%block  LatticeVectors
3.7845  0       0
0       3.7845  0
0       0       85.62870000000001
%endblock

AtomicCoordinatesFormat Ang
%block AtomicCoordinatesAndAtomicSpecies
0.9462499999992602   0.9462499999998784   -13.875533333333108   2   Ti
2.8382499999992596   0.9462499999998784   -11.496533333333108   2   Ti
2.8382499999992596   0.9462499999998784   -9.516533333333108    1   O
2.8382499999992596   0.9462499999998784   -13.476533333333109   1   O
0.9462499999992602   0.9462499999998784   -11.894533333333108   1   O
2.8382499999992596   2.838249999999878    -11.097533333333107   1   O
0.9462499999992602   0.9462499999998784   -4.361233333333107    2   Ti
0.9462499999992602   2.838249999999878    -4.759233333333107    1   O
0.9462499999992602   2.838249999999878    -8.719233333333108    1   O
2.8382499999992596   2.838249999999878    -9.118233333333107    2   Ti
2.8382499999992596   2.838249999999878    -7.138233333333108    1   O
0.9462499999992602   0.9462499999998784   -6.3402333333331065   1   O
0.9462499999992602   2.838249999999878    -6.739233333333107    2   Ti
2.8382499999992596   0.9462499999998784   -1.982233333333106    2   Ti
2.8382499999992596   0.9462499999998784   -0.0022333333331090444   1   O
2.8382499999992596   0.9462499999998784   -3.9622333333331063   1   O
0.9462499999992602   0.9462499999998784   -2.3802333333331056   1   O
2.8382499999992596   2.838249999999878    -1.5832333333331086   1   O
0.9462499999992602   0.9462499999998784   5.153066666666895     2   Ti
0.9462499999992602   2.838249999999878    4.755066666666895     1   O
0.9462499999992602   2.838249999999878    0.7950666666668944    1   O
2.8382499999992596   2.838249999999878    0.39606666666689705   2   Ti
2.8382499999992596   2.838249999999878    2.376066666666894     1   O
0.9462499999992602   0.9462499999998784   3.1740666666668957    1   O
0.9462499999992602   2.838249999999878    2.775066666666895     2   Ti
2.8382499999992596   0.9462499999998784   7.532066666666896     2   Ti
```

```
2.8382499999992596    0.9462499999998784    9.512066666666897    1    O
2.8382499999992596    0.9462499999998784    5.552066666666896    1    O
0.9462499999992602    0.9462499999998784    7.134066666666897    1    O
2.8382499999992596    2.838249999999878     7.931066666666894    1    O
0.9462499999992602    2.838249999999878     14.26936666666689    1    O
0.9462499999992602    2.838249999999878     10.309366666666897   1    O
2.8382499999992596    2.838249999999878     9.910366666666896    2    Ti
2.8382499999992596    2.838249999999878     11.890366666666893   1    O
0.9462499999992602    0.9462499999998784    12.688366666666894   1    O
0.9462499999992602    2.838249999999878     12.289366666666893   2    Ti
%endblock AtomicCoordinatesAndAtomicSpecies


---------------------------------(110) Bare Slab-----------------------------------------------------

#-------Description of the system-----------------

SystemName          Anatase-slab-110
SystemLabel         Anatase-slab-110

#-------Define structure--------------------------

NumberOfAtoms 72
NumberOfSpecies 2

%block ChemicalSpeciesLabel
1          8          O
2          22         Ti
%endblock ChemicalSpeciesLabel

%block GeometryConstraints
   position 1 2 3 4 9 14
%endblock GeometryConstraints

LatticeConstant 1.  Ang
%block  LatticeVectors
0          0          48.16882104120879
5.352091226800977     0          0
0          -9.514299999999999     0
%endblock

AtomicCoordinatesFormat Ang
%block AtomicCoordinatesAndAtomicSpecies
4.845409210049624     2.4688333333332064    -2.602152213546413    2    Ti
4.845409210049624     0.4888333333332089    -2.602152213546412    1    O
4.845409210049624     -5.066166666666788    -2.602152213546412    1    O
2.169363596649135     -2.2881666666667906   -2.6017986601558185   2    Ti
0.8315175666441874    -1.8901666666667907   -1.26395263015087     1    O
```

| | | | | |
|---|---|---|---|---|
| 0.8315175666441874 | 2.06983333333321 | -1.263952630150869 | 1 | O |
| 2.1693635966491343 | 2.4688333333332073 | 0.07389339985407695 | 2 | Ti |
| 2.1693635966491343 | 0.48883333333321066 | 0.07389339985407695 | 1 | O |
| 2.169363596649135 | -0.30916666666679116 | -2.6017986601558185 | 1 | O |
| 0.8315175666441874 | 0.08983333333320975 | -1.26395263015087 | 2 | Ti |
| 3.507209626654083 | -4.667166666666792 | -1.2639526301508717 | 2 | Ti |
| 3.507209626654083 | -6.6471666666667915 | -1.2639526301508708 | 1 | O |
| 3.507209626654083 | -2.6871666666667915 | -1.2639526301508717 | 1 | O |
| 2.169363596649135 | -4.269166666666792 | -2.6017986601558185 | 1 | O |
| 2.1693635966491343 | -5.066166666666788 | 0.07389339985407695 | 1 | O |
| 0.8311640132535945 | -4.667166666666791 | 1.4120929832496172 | 2 | Ti |
| 0.8311640132535945 | -6.6471666666667915 | 1.4120929832496172 | 1 | O |
| 0.8311640132535945 | -2.6871666666667906 | 1.4120929832496167 | 1 | O |
| 4.845409210049626 | -2.2881666666667906 | 0.07424695324467123 | 2 | Ti |
| 3.5075631800446767 | -1.8901666666667905 | 1.412092983249619 | 1 | O |
| 3.5075631800446767 | 2.069833333333209 | 1.412092983249619 | 1 | O |
| 4.845409210049624 | 2.4688333333332064 | 2.7499390132545667 | 2 | Ti |
| 4.845409210049624 | 0.4888333333332102 | 2.749939013254567 | 1 | O |
| 4.845409210049626 | -0.3091666666667914 | 0.07424695324467123 | 1 | O |
| 3.5075631800446767 | 0.08983333333320931 | 1.4120929832496194 | 2 | Ti |
| 4.845409210049626 | -4.269166666666792 | 0.07424695324467123 | 1 | O |
| 4.845409210049624 | -5.066166666666788 | 2.7499390132545676 | 1 | O |
| 2.169363596649137 | -2.28816666666679 | 2.7502925666451588 | 2 | Ti |
| 0.8315175666441896 | -1.8901666666667907 | 4.088138596650106 | 1 | O |
| 0.8315175666441896 | 2.06983333333321 | 4.088138596650106 | 1 | O |
| 2.169363596649137 | 2.4688333333332064 | 5.425984626655054 | 2 | Ti |
| 2.169363596649137 | 0.4888333333332098 | 5.425984626655053 | 1 | O |
| 2.169363596649137 | -0.3091666666667916 | 2.7502925666451588 | 1 | O |
| 0.8315175666441896 | 0.08983333333320953 | 4.088138596650106 | 2 | Ti |
| 3.507209626654084 | -4.667166666666791 | 4.088138596650106 | 2 | Ti |
| 3.507209626654084 | -6.6471666666667915 | 4.088138596650107 | 1 | O |
| 3.507209626654084 | -2.687166666666791 | 4.088138596650106 | 1 | O |
| 2.169363596649137 | -4.269166666666792 | 2.7502925666451583 | 1 | O |
| 2.169363596649137 | -5.066166666666788 | 5.425984626655053 | 1 | O |
| 0.8311640132535945 | -4.667166666666791 | 6.764184210050596 | 2 | Ti |
| 0.8311640132535945 | -6.6471666666667915 | 6.764184210050597 | 1 | O |
| 0.8311640132535945 | -2.687166666666791 | 6.764184210050596 | 1 | O |
| 4.845409210049624 | -2.28816666666679 | 5.426338180045646 | 2 | Ti |
| 3.5075631800446767 | -1.8901666666667907 | 6.764184210050592 | 1 | O |
| 3.5075631800446767 | 2.069833333333209 | 6.764184210050593 | 1 | O |
| 4.845409210049624 | 2.4688333333332064 | 8.10203024005554 | 2 | Ti |
| 4.845409210049624 | 0.4888333333332098 | 8.10203024005554 | 1 | O |
| 4.845409210049624 | -0.3091666666667914 | 5.426338180045645 | 1 | O |
| 3.5075631800446767 | 0.08983333333320931 | 6.764184210050592 | 2 | Ti |
| 4.845409210049624 | -4.269166666666791 | 5.426338180045646 | 1 | O |
| 4.845409210049624 | -5.066166666666788 | 8.10203024005554 | 1 | O |
| 2.1693635966491343 | -2.28816666666679 | 8.102383793446137 | 2 | Ti |
| 0.831517566644187 | -1.8901666666667907 | 9.440229823451082 | 1 | O |

```
0.831517566644187     2.069833333333209     9.440229823451082     1     O
2.1693635966491343    2.4688333333332064    10.77807585345603     2     Ti
2.1693635966491343    0.48883333333320933   10.77807585345603     1     O
2.1693635966491343    -0.3091666666667916   8.102383793446135     1     O
0.831517566644187     0.08983333333320953   9.440229823451082     2     Ti
3.507209626654082     -4.667166666666791    9.440229823451084     2     Ti
3.507209626654082     -6.6471666666667915   9.440229823451084     1     O
3.507209626654082     -2.687166666666791    9.440229823451084     1     O
2.1693635966491343    -4.269166666666792    8.102383793446137     1     O
2.1693635966491343    -5.066166666666788    10.77807585345603     1     O
0.8311640132535945    -4.667166666666792    12.11627543685157     2     Ti
0.8311640132535945    -6.647166666666791    12.11627543685157     1     O
0.8311640132535945    -2.6871666666667915   12.11627543685157     1     O
4.845409210049624     -2.2881666666667906   10.778429406846623    2     Ti
3.507563180044676     -1.8901666666667902   12.116275436851573    1     O
3.507563180044676     2.06983333333321      12.116275436851573    1     O
4.845409210049624     -0.30916666666679116  10.778429406846623    1     O
3.507563180044676     0.0898333333332102    12.116275436851573    2     Ti
4.845409210049624     -4.269166666666791    10.778429406846625    1     O
%endblock AtomicCoordinatesAndAtomicSpecies


--------------------------------(100) 1x2 Slab with 2x3 Graphene---------------------------------

#-------Description of the system-----------------

SystemName          An-Gr-slab-100
SystemLabel         An-Gr-slab-100

#-------Define structure--------------------------

NumberOfAtoms 52
NumberOfSpecies 3

%block ChemicalSpeciesLabel
1          6          C
2          8          O
3          22         Ti
%endblock ChemicalSpeciesLabel

%block GeometryConstraints
   position 31 32 33 34 35 36
%endblock GeometryConstraints

LatticeConstant 1.  Ang
%block  LatticeVectors
10.2397977905076        0.          0.
0.          3.7846644884748         0.
```

```
12.5894251284228        0.        31.6500376532004
%endblock

AtomicCoordinatesFormat Ang
%block AtomicCoordinatesAndAtomicSpecies
-4.858687785846301    -0.9472949671206      -4.4680134982707      3    Ti
-6.898953540853502    -0.947480899953       -4.2707157264891      2    O
-5.2294505470431005   0.9447872663669998    -4.3205353162083      2    O
-1.8341353408875003   -0.9911290254222      -3.5014941140823      3    Ti
-1.720944968801101    0.9312125057969998    -4.2047132198211      2    O
3.1711223484632995    0.9447872663669998    -3.5889474310515004   3    Ti
1.3653988664168994    0.9434070847194       -3.0937252901751      2    O
-0.10959863125470104  -0.9472949671206      -4.3202475658251      2    O
0.261164129412899     0.9447872663669998    -4.4677257478875      3    Ti
-3.462234201919501    -0.9006953921742      -0.9400601222018996   3    Ti
-5.235155914159501    -0.9100260116094001   -0.3422534689034995   2    O
-1.4926243033779008   -0.9805253815182      -1.8348095029382998   2    O
-3.674704457337901    -0.9300120084822      -3.1349438896671      2    O
-3.778417913178301    0.9798708767190001    -1.0560793619942999   2    O
-0.44602147479750043  -0.9878386450422      0.023769644264100442  3    Ti
-0.10595194263150054  0.9215547312174       -0.3117414215475005   2    O
3.5766228814616996    0.9595719062034003    -1.9259866627155002   2    O
4.673149933185299     0.9897899766090004    0.018441587751299338  3    Ti
2.7895983306680994    0.9481736325137997    0.46651799335050015   2    O
1.3320605550188993    -0.9497139503754      -1.0511804258235      2    O
1.6583105795528992    0.9857767730622       -0.9410244352046999   3    Ti
-2.041707540194701    -0.9001998932178      2.6666242398117       3    Ti
-3.807811071915901    -0.9072715965222      3.4815780254997       2    O
-0.08244296133990048  -0.985150353495       1.7079995728844999    2    O
-2.3385489856323005   -0.915422577825       0.4863979575945008    2    O
-2.4204992190099004   0.9828354752286002    2.5298195221845       2    O
0.9038555252768992    -0.9928544926062001   3.6403889943393013    3    Ti
1.3132242250364992    0.9109185997254001    3.4939330779716995    2    O
5.034133964792099     0.9771721916837999    1.6924446073017005    2    O
6.052108117484099     0.9903091286886001    3.716331639772501     3    Ti
4.191090908837699     0.9124285422714       4.036887397689299     2    O
2.6765887073708994    -0.9763011869898001   2.5033445140724995    2    O
3.085591837887299     0.8991998605085998    2.6692044681897       3    Ti
1.6260366602864993    -1.117618035807       5.284176446070901     2    O
-0.9159883474119006   -0.899150966427       4.0371068474037       2    O
6.743821576440899     1.0193972676593996    5.3192306646549       2    O
-1.1705796112310458   -1.2614781146972978   8.3192306568492       1    C
0.10934011715633707   -0.6307725351542043   8.319230650498799     1    C
0.10934041010501172   0.6307729708023173    8.319230660553599     1    C
-1.1705793960369726   1.2614776790491846    8.319230690718        1    C
1.3892585762819856    -1.2614781146972978   8.3192306568492       1    C
2.669178304669368     -0.6307725351542043   8.319230650498799     1    C
2.669178597618043     0.6307729708023173    8.319230660553599     1    C
```

```
1.3892587914760588   1.2614776790491846   8.319230690718      1   C
3.949096763795017    -1.2614781146972978  8.3192306568492     1   C
5.229016492182399    -0.6307725351542043  8.319230650498799   1   C
5.2290167851310745   0.6307729708023173   8.319230660553599   1   C
3.94909697898909     1.2614776790491846   8.319230690718      1   C
6.5089349513080474   -1.2614781146972978  8.3192306568492     1   C
7.788854679695431    -0.6307725351542043  8.319230650498799   1   C
7.788854972644106    0.6307729708023173   8.319230660553599   1   C
6.508935166502122    1.2614776790491846   8.319230690718      1   C
%endblock AtomicCoordinatesAndAtomicSpecies


---------------------------------(101) 1x1 Slab with 1x4 Graphene---------------------------------

#-------Description of the system-----------------

SystemName          Anatase-slab-101
SystemLabel         Anatase-slab-101

#-------Define structure--------------------------

NumberOfAtoms 52
NumberOfSpecies 3

%block ChemicalSpeciesLabel
1          6          C
2          8          O
3          22         Ti
%endblock ChemicalSpeciesLabel

%block GeometryConstraints
   position 1 3 6 8 9
%endblock GeometryConstraints

LatticeConstant 1.  Ang
%block  LatticeVectors
10.2397977905076       0.          0.
0.          3.7846644884748         0.
12.5894251284228       0.          31.6500376532004
%endblock

AtomicCoordinatesFormat Ang
%block AtomicCoordinatesAndAtomicSpecies
-4.858687785846301   -0.9472949671206      -4.4680134982707    3   Ti
-6.898953540853502   -0.947480899953       -4.2707157264891    2   O
-5.2294505470431005  0.9447872663669998    -4.3205353162083    2   O
-1.8341353408875003  -0.9911290254222      -3.5014941140823    3   Ti
-1.720944968801101   0.9312125057969998    -4.2047132198211    2   O
```

```
3.1711223484632995 0.9447872663669998 -3.5889474310515004 3 Ti
1.3653988664168994 0.9434070847194 -3.0937252901751 2 O
-0.10959863125470104 -0.9472949671206 -4.3202475658251 2 O
0.261164129412899 0.9447872663669998 -4.4677257478875 3 Ti
-3.462234201919501 -0.9006953921742 -0.9400601222018996 3 Ti
-5.235155914159501 -0.9100260116094001 -0.3422534689034995 2 O
-1.4926243033779008 -0.9805253815182 -1.8348095029382998 2 O
-3.674704457337901 -0.9300120084822 -3.1349438896671 2 O
-3.778417913178301 0.9798708767190001 -1.0560793619942999 2 O
-0.44602147479750043 -0.9878386450422 0.023769644264100442 3 Ti
-0.10595194263150054 0.9215547312174 -0.3117414215475005 2 O
3.5766228814616996 0.9595719062034003 -1.9259866627155002 2 O
4.673149933185299 0.9897899766090004 0.018441587751299338 3 Ti
2.7895983306680994 0.9481736325137997 0.46651799335050015 2 O
1.3320605550188993 -0.9497139503754 -1.0511804258235 2 O
1.6583105795528992 0.9857767730622 -0.9410244352046999 3 Ti
-2.041707540194701 -0.9001998932178 2.6666242398117 3 Ti
-3.807811071915901 -0.9072715965222 3.4815780254997 2 O
-0.08244296133990048 -0.985150353495 1.7079995728844999 2 O
-2.3385489856323005 -0.915422577825 0.4863979575945008 2 O
-2.4204992190099004 0.9828354752286002 2.5298195221845 2 O
0.9038555252768992 -0.9928544926062001 3.6403889943393013 3 Ti
1.3132242250364992 0.9109185997254001 3.4939330779716995 2 O
5.034133964792099 0.9771721916837999 1.6924446073017005 2 O
6.052108117484099 0.9903091286886001 3.716331639772501 3 Ti
4.191090908837699 0.9124285422714 4.036887397689299 2 O
2.6765887073708994 -0.9763011869898001 2.5033445140724995 2 O
3.085591837887299 0.8991998605085998 2.6692044681897 3 Ti
1.6260366602864993 -1.117618035807 5.284176446070901 2 O
-0.9159883474119006 -0.899150966427 4.0371068474037 2 O
6.743821576440899 1.0193972676593996 5.3192306646549 2 O
-0.8533690016185562 -1.783999458441761 8.3192306568492 1 C
0.33591908807383986 -0.8920470739875356 8.319230650498799 1 C
0.3359193602786994 0.8920476900870054 8.319230660553599 1 C
-0.8533688016624636 1.7839988423422912 8.319230690718 1 C
1.5252059983814439 -1.783999458441761 8.3192306568492 1 C
2.71449408807384 -0.8920470739875356 8.319230650498799 1 C
2.7144943602786995 0.8920476900870054 8.319230660553599 1 C
1.525206198337537 1.7839988423422912 8.319230690718 1 C
3.903780998381444 -1.783999458441761 8.3192306568492 1 C
5.09306908807384 -0.8920470739875356 8.319230650498799 1 C
5.093069360278699 0.8920476900870054 8.319230660553599 1 C
3.9037811983375366 1.7839988423422912 8.319230690718 1 C
6.282355998381444 -1.783999458441761 8.3192306568492 1 C
7.471644088073841 -0.8920470739875356 8.319230650498799 1 C
7.471644360278701 0.8920476900870054 8.319230660553599 1 C
6.282356198337537 1.7839988423422912 8.319230690718 1 C
%endblock AtomicCoordinatesAndAtomicSpecies
```

```
---------------------------------(001) 2x1 Slab with 3x1 Graphene---------------------------------

#-------Description of the system-----------------

SystemName          Anatase-slab-001
SystemLabel         Anatase-slab-001

#-------Define structure-------------------------
NumberOfAtoms 84
NumberOfSpecies 3

%block ChemicalSpeciesLabel
1          6          C
2          8          O
3          22         Ti
%endblock ChemicalSpeciesLabel

%block GeometryConstraints
   position 1 4
%endblock GeometryConstraints

LatticeConstant 1.  Ang
%block  LatticeVectors
7.5693289769496         0.          0.
0.          3.7846644884748         0.
0.          0.          85.6324217417508
%endblock

AtomicCoordinatesFormat Ang
%block AtomicCoordinatesAndAtomicSpecies
-2.838376093681799    -0.9460553148417      -13.8265747135068     3        Ti
-0.9461738873789991   -0.9461808056253      -11.370864959126399   3        Ti
-0.946118919374999    -0.9461728020045      -9.4854187740396      2        O
-0.9462938601941993   -0.9460553148417      -13.427557371606      2        O
-2.838550480428599    -0.9461807235993      -11.931042264304798   2        O
-0.946227754646999    0.9461615619435       -11.083693519668      2        O
-2.838500834059799    -0.9461800123545001   -4.3907088105048      3        Ti
-2.838517366796999    0.9461542796222997    -4.7322807012516      2        O
-2.838484886617799    0.9461629172247001    -8.7191633763192      2        O
-0.9461691129365994   0.9461532201639       -9.074785205312399    3        Ti
-0.9461562353837993   0.9461505641090999    -7.103008138043999    2        O
-2.838476125711799    -0.9461790777873      -6.3601551994764      2        O
-2.8385008478189993   0.9461518839339       -6.5918287490916      3        Ti
-0.9461693759489989   -0.9461801753481001   -1.99909661637        3        Ti
-0.9461698083053989   -0.9461725151781001   -0.027013878947999892 2        O
-0.9461737497869991   -0.9461700496353      -4.0616276374128      2        O
```

| | | | | |
|---|---|---|---|---|
| -2.838505562461799 | -0.9461796075165001 | -2.4614765771988 | 2 | O |
| -0.9461775023441992 | 0.9461565382479 | -1.6220193513383998 | 2 | O |
| -2.838502221092999 | -0.9462048979845 | 5.1891055782972 | 3 | Ti |
| -2.838477574661399 | 0.9461288907231002 | 4.7950933380252 | 2 | O |
| -2.838506193797399 | 0.9461693253075001 | 0.8354945262804 | 2 | O |
| -0.9461690526077988 | 0.9461521792274998 | 0.5006474122524001 | 3 | Ti |
| -0.9461783157245991 | 0.9461304338703 | 2.4261301492512 | 2 | O |
| -2.838538246912199 | -0.9461984973105001 | 3.17291475858 2 | O | |
| -2.838501726290999 | 0.9461513213942998 | 2.8965690037032 | 3 | Ti |
| -0.946167439606199 | -0.9461805595473 | 7.47792642219 3 | Ti | |
| -0.9460639450205992 | -0.9461757078416999 | 9.4142922386856 | 2 | O |
| -0.9461638892033992 | -0.9461943547329 | 5.4619987937424 | 2 | O |
| -2.838504846454199 | -0.9461900015337 | 7.0821261675275995 | 2 | O |
| -0.9462238412129991 | 0.9461471100206997 | 7.809030043684801 | 2 | O |
| -2.838517489571399 | 0.9465969670647001 | 14.229164369792402 | 2 | O |
| -2.8384442313569993 | 0.9462087163095003 | 10.212140488502401 | 2 | O |
| -0.9461696188517994 | 0.9461511912111 | 9.8710358046216 | 3 | Ti |
| -0.9461414241341992 | 0.9460288105359 | 11.840087120391601 | 2 | O |
| -2.838442243152599 | -0.9462304001325 | 12.676038933919202 | 2 | O |
| -2.838506089015799 | 0.9461249069055 | 12.378520694072401 | 3 | Ti |
| 0.9462883947930005 | -0.9460553148417 | -13.8265747135068 | 3 | Ti |
| 2.8384906010958004 | -0.9461808056253 | -11.370864959126399 | 3 | Ti |
| 2.8385455690998014 | -0.9461728020045 | -9.4854187740396 | 2 | O |
| 2.8383706282806007 | -0.9460553148417 | -13.427557371606 | 2 | O |
| 0.9461140080462012 | -0.9461807235993 | -11.931042264304798 | 2 | O |
| 2.8384367338278014 | 0.9461615619435 | -11.083693519668 | 2 | O |
| 0.9461636544150012 | -0.9461800123545001 | -4.3907088105048 | 3 | Ti |
| 0.9461471216778006 | 0.9461542796222997 | -4.7322807012516 | 2 | O |
| 0.946179601857001 | 0.9461629172247001 | -8.7191633763192 | 2 | O |
| 2.838495375538201 | 0.9461532201639 | -9.074785205312399 | 3 | Ti |
| 2.838508253091001 | 0.9461505641090999 | -7.103008138043999 | 2 | O |
| 0.9461883627630008 | -0.9461790777873 | -6.3601551994764 | 2 | O |
| 0.9461636406558012 | 0.9461518839339 | -6.5918287490916 | 3 | Ti |
| 2.8384951125258016 | -0.9461801753481001 | -1.99909661637 | 3 | Ti |
| 2.838494680169401 | -0.9461725151781001 | -0.027013878947999892 | 2 | O |
| 2.8384907386878004 | -0.9461700496353 | -4.0616276374128 | 2 | O |
| 0.9461589260130006 | -0.9461796075165001 | -2.4614765771988 | 2 | O |
| 2.8384869861306004 | 0.9461565382479 | -1.6220193513383998 | 2 | O |
| 0.9461622673818009 | -0.9462048979845 | 5.1891055782972 | 3 | Ti |
| 0.9461869138134005 | 0.9461288907231002 | 4.7950933380252 | 2 | O |
| 0.9461582946774008 | 0.9461693253075001 | 0.8354945262804 | 2 | O |
| 2.8384954358670007 | 0.9461521792274998 | 0.5006474122524001 | 3 | Ti |
| 2.838486172750201 | 0.9461304338703 | 2.4261301492512 | 2 | O |
| 0.9461262415626011 | -0.9461984973105001 | 3.17291475858 2 | O | |
| 0.9461627621838011 | 0.9461513213942998 | 2.8965690037032 | 3 | Ti |
| 2.8384970488686014 | -0.9461805595473 | 7.47792642219 3 | Ti | |
| 2.8386005434542008 | -0.9461757078416999 | 9.4142922386856 | 2 | O |
| 2.8385005992714007 | -0.9461943547329 | 5.4619987937424 | 2 | O |

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0.9461596420206013   -0.9461900015337      7.0821261675275995  2   O
2.8384406472618013   0.9461471100206997    7.809030043684801   2   O
0.946146998903401    0.9465969670647001    14.229164369792402  2   O
0.9462202571178007   0.9462087163095003    10.212140488502401  2   O
2.8384948696230006   0.9461511912111       9.8710358046216     3   Ti
2.8385230643406003   0.9460288105359       11.840087120391601  2   O
0.9462222453222009   -0.9462304001325      12.676038933919202  2   O
0.946158399459001    0.9461249069055       12.378520694072401  3   Ti
-7.928584434363832   -1.783999458441761    17.2291643619867    1   C
-4.757149528517441   -0.8920470739875356   17.2291643556363    1   C
-4.757148802637817   0.8920476900870054    17.2291643656911    1   C
-7.928583901147584   1.7839988423422912    17.2291643958555    1   C
-1.5857177676971643  -1.783999458441761    17.2291643619867    1   C
1.585717138149227    -0.8920470739875356   17.2291643556363    1   C
1.5857178640288518   0.8920476900870054    17.2291643656911    1   C
-1.5857172344809163  1.7839988423422912    17.2291643958555    1   C
4.757148898969503    -1.783999458441761    17.2291643619867    1   C
7.9285838048158945   -0.8920470739875356   17.2291643556363    1   C
7.928584530695519    0.8920476900870054    17.2291643656911    1   C
4.757149432185751    1.7839988423422912    17.2291643958555    1   C
%endblock AtomicCoordinatesAndAtomicSpecies

---------------------------------(110) 1x1 Slab with 2x2 Graphene---------------------------------

#-------Description of the system-----------------

SystemName          Anatase-slab-110
SystemLabel         Anatase-slab-110

#-------Define structure--------------------------

NumberOfAtoms 88
NumberOfSpecies 3

%block ChemicalSpeciesLabel
1         6         C
2         8         O
3         22        Ti
%endblock ChemicalSpeciesLabel

%block GeometryConstraints
   position 1 2 3 4 9 14
%endblock GeometryConstraints

LatticeConstant 1.  Ang
%block  LatticeVectors
5.3523238488048         0.          0.
0.          9.5147135267436         0.
```

0. 0. 48.1709146371264
%endblock

AtomicCoordinatesFormat Ang
%block AtomicCoordinatesAndAtomicSpecies

| | | | | |
|---|---|---|---|---|
| 2.046025407577199 | 4.3708919192274 | -7.390829857690649 | 3 | Ti |
| 2.046025407577199 | 2.3908058610618 | -7.390829857690649 | 2 | O |
| 2.046025407577199 | -3.1644355798734 | -7.390829857690649 | 2 | O |
| -0.6301365168252007 | -0.3863148379062 | -7.390476289115849 | 3 | Ti |
| -2.001746453775601 | -0.11724705261780022 | -6.205906423375049 | 2 | O |
| -1.9511730107184007 | 4.0691931745458 | -6.18726628000425 | 2 | O |
| -0.6807249986880008 | 4.341427935537 | -4.67730007876425 | 3 | Ti |
| -0.6951365202432007 | 2.4142683553086 | -4.66507670712825 | 2 | O |
| -0.6301365168252007 | 1.592771176731 | -7.390476289115849 | 2 | O |
| -2.0149080282156007 | 1.9989159869153998 | -6.14587604454705 | 3 | Ti |
| 0.6612403994699991 | -2.7585207711222006 | -6.14589120453945 | 3 | Ti |
| 0.6745921424591992 | -4.8746091664662 | -6.205864817141849 | 2 | O |
| 0.7248597089747992 | -0.6880842429594001 | -6.18722981706585 | 2 | O |
| -0.6301365168252007 | -2.3674009396002003 | -7.390476289115849 | 2 | O |
| -0.6424825485540007 | -3.2267781525714003 | -4.67640058164825 | 2 | O |
| -2.0183795235912005 | -2.7572472444426 | -3.34834088086785 | 3 | Ti |
| -2.0256807631620006 | -4.7868446338565995 | -3.3706344469318497 | 2 | O |
| -1.9777723765968007 | -0.7820049215958003 | -3.3809756436214498 | 2 | O |
| 1.9954434703308 | -0.41594620702740004 | -4.6772745332218495 | 3 | Ti |
| 0.6505553148611991 | -0.02947965333180025 | -3.37064562681105 | 2 | O |
| 0.6983262390803993 | 3.9752209052597998 | -3.38092134399705 | 2 | O |
| 1.9953836384495993 | 4.340499752605799 | -2.00182453893345 | 3 | Ti |
| 1.99181097591 | 2.382378719385 | -1.99403119204905 | 2 | O |
| 2.0335741470743995 | 1.5306253018518 | -4.67668967090745 | 2 | O |
| 0.6577731297563991 | 2.000115827787 | -3.3483324644710497 | 3 | Ti |
| 1.9811379168419991 | -2.3429868220373997 | -4.6650499782946495 | 2 | O |
| 2.015503833562799 | -3.1814660841810003 | -1.9941461670994496 | 2 | O |
| -0.6807797941728007 | -0.41685542343060034 | -2.00182313496585 | 3 | Ti |
| -2.020824709654801 | -0.004211257205400054 | -0.6709981075234497 | 2 | O |
| -2.006800193118001 | 3.9606275839242 | -0.6698305732534502 | 2 | O |
| -0.6807457676712008 | 4.3409966793437995 | 0.675797732978551 | 3 | Ti |
| -0.6781279269324005 | 2.3808804398778 | 0.6778752938569506 | 2 | O |
| -0.6606145837200006 | 1.5759217022178 | -1.9941639270514497 | 2 | O |
| -2.018835727860001 | 2.0000366637006 | -0.66377346065625 | 3 | Ti |
| 0.6573247047275994 | -2.7573183371706005 | -0.6637740237250505 | 3 | Ti |
| 0.6552870227735994 | -4.7615753968314 | -0.67100748865185 | 2 | O |
| 0.6694351059227994 | -0.7967167752641999 | -0.6698747551030495 | 2 | O |
| -0.6844396164816007 | -2.3749211446673995 | -1.9939430749570497 | 2 | O |
| -0.6713756048244006 | -3.174627129387 | 0.6783575718097508 | 2 | O |
| -2.0188197888852004 | -2.7569937179526 | 2.01357139879455 | 3 | Ti |
| -2.0155820226276004 | -4.7586971367726 | 2.0178476729533505 | 2 | O |
| -2.0132510786724005 | -0.7931151898277999 | 2.01777281602575 | 2 | O |
| 1.9954161466763995 | -0.4163597498381999 | 0.6757981833277507 | 3 | Ti |

```
0.6605882065103992 -0.0013409690154000398 2.0178319234321505 2 O
0.6628960413599994 3.9642451665474 2.0177873145181495 2 O
1.9953188363219994 4.340913201219 3.35882758799175 3 Ti
1.9955687743067996 2.378279681715 3.354385832463749 2 O
2.004790097007599 1.5827318314877998 0.6783415000057502 2 O
0.6573420863015991 2.0003638019106 2.01357158454375 3 Ti
1.9980070019196 -2.3764783273098002 0.6778972207297507 2 O
2.009471953750799 -3.1648396214274 3.3580756567081496 2 O
-0.6808430319852006 -0.4164435015593999 3.3588267285709508 3 Ti
-2.0074961318664006 0.020522160056999805 4.733065437944551 2 O
-2.005552362802801 3.9452851746966 4.72743614597415 2 O
-0.6807921546972007 4.3415252548878005 6.15545176562295 3 Ti
-0.7190302696248008 2.2924879638402 6.087824998095749 2 O
-0.6666888397512007 1.5925153667429999 3.3580611841465506 2 O
-2.018041489153201 2.0013060721458 4.682650217749349 3 Ti
0.6581200769807993 -2.7560505152670007 4.68265088030775 3 Ti
0.6686633344019994 -4.7368326757038 4.733079719464949 2 O
0.6706194724571994 -0.8120683825170003 4.727419489933351 2 O
-0.6805958802384007 -2.3790737347314 3.3543871136569505 2 O
-0.6575937180204008 -3.0675211999025995 6.05890930741215 2 O
-2.0164708547760006 -2.755943934387001 7.23654703470615 3 Ti
-1.8900669746784007 -4.6028190319062 7.491068540305352 2 O
-2.0991719594496008 -0.9440011584654 7.498901302534951 2 O
1.9953701343239993 -0.41583250840740016 6.155451902156551 3 Ti
0.7860865539659994 0.1545269926745998 7.49105145931695 2 O
0.5769800117591997 3.813345899643 7.4989164249541505 2 O
2.0186074095179993 1.6898371269905998 6.058937586801751 2 O
0.6596924947619995 2.0014117904298 7.236546507622951 3 Ti
1.9570916504327993 -2.4648723417318 6.08786239030935 2 O
-2.007034674573426 -3.964264156647444 10.49891641714845 1 C
-0.6690112044323608 -3.1714616602216474 10.49891641079805 1 C
-0.6690108981848724 -1.5856877921648191 10.498916420852849 1 C
-2.007034449610318 -0.7928863909660913 10.49891645101725 1 C
-2.007034674573426 0.7928858433525563 10.49891641714845 1 C
-0.6690112044323608 1.5856883397783528 10.49891641079805 1 C
-0.6690108981848724 3.1714622078351815 10.498916420852849 1 C
-2.007034449610318 3.964263609033909 10.49891645101725 1 C
0.6690109388270629 -3.964264156647444 10.49891641714845 1 C
2.007034408968128 -3.1714616602216474 10.49891641079805 1 C
2.0070347152156165 -1.5856877921648191 10.498916420852849 1 C
0.669011163790171 -0.7928863909660913 10.49891645101725 1 C
0.6690109388270629 0.7928858433525563 10.49891641714845 1 C
2.007034408968128 1.5856883397783528 10.49891641079805 1 C
2.0070347152156165 3.1714622078351815 10.498916420852849 1 C
0.669011163790171 3.964263609033909 10.49891645101725 1 C
%endblock AtomicCoordinatesAndAtomicSpecies
```

# Appendix C

MATHEMATICA SCRIPT FOR WULFF PLOTS

```
OnPlane[p_, pp_, pn_] := If[Abs[(p - pp).pn] < 0.001 p.p, True, False]
OrderClockwise[ps_, d_] := Block[{c, v1, v2, v3, ang, ord, dn, ac, npnts}, npnts = Dimensions[ps][[1]]; c = Mean[ps];
   v1 = ps[[1]] - c; v1 /= Sqrt[v1.v1]; dn = d/Sqrt[d.d];
   ang = Join[{0}, Table[v2 = ps[[i]] - c; v2 /= Sqrt[v2.v2]; v3 = dn.Cross[v1, v2]; ac = ArcCos[v1.v2] // N;
      ac + UnitStep[-v3] (2 π - 2 ac), {i, 2, npnts}]];
   ps[[Ordering[ang]]]];
PolygonArea[ps_, d_] := Block[{pso, nd, A, np},
  np = Dimensions[ps][[1]];
  If[np > 2, nd = d/Sqrt[d.d]; pso = OrderClockwise[ps, nd];
   pso = Append[pso, pso[[1]]];
   A = 1/2 Sum[Cross[pso[[i]], pso[[i + 1]]].nd, {i, np}], 0]]

wulff[facets_, γ_, lpsub_, db_] :=
 Block[{nv, nf, unv, pts, pc, nnp, np, ppf, naf, npf, tabP, tabE, ps, plts = {0, 0, 0}, EperVol23, A, vol, en},
  nv = Table[facets[[i]].rv /. lpsub // N, {i, Dimensions[facets][[1]]}];
  nf = Dimensions[nv][[1]];
  unv = Table[nv[[i]]/Sqrt[nv[[i]].nv[[i]]], {i, nf}];
  (* Find triples of non-parallel planes and their common point also plot them to check things are OK *)
  pts =
   Flatten[
    Table[If[Det[unv[[{i, j, k}]]] ≠ 0,
      pc = (γ[[i]] Cross[unv[[j]], unv[[k]]] + γ[[j]] Cross[unv[[k]], unv[[i]]] + γ[[k]] Cross[unv[[i]], unv[[j]]]) /
        Det[unv[[{i, j, k}]]];
      {{i, j, k}, pc}, ## &[], {i, 1, nf - 2}, {j, i + 1, nf - 1}, {k, j + 1, nf}], 2];
  nnp = Dimensions[pts][[1]]; If[db, Print[nnp]];
  If[db, Block[{d, v, tab, hs = 0.5, sr = 0.1},
    tab = Table[v = pts[[i, 2]]; d = Sqrt[v.v]; {Hue[d hs], Sphere[v, 0.1]}, {i, nnp}];
    Print[Graphics3D[tab, PlotRange → All]]];

  (* Find the subset of points that are right at the box boundary *)
  np = Table[If[Product[UnitStep[(γ[[j]] unv[[j]] - 0.999 pts[[i, 2]]).unv[[j]]], {j, nf}] > 0.1, pts[[i]], ## &[]],
     {i, Dimensions[pts][[1]]}] // N;
  If[db, Block[{tab, nnnp, v, d, hs = 0.5, sr = 0.1}, nnnp = Dimensions[np][[1]];
    tab = Table[v = np[[i, 2]]; d = Sqrt[v.v]; {Hue[d hs], Sphere[v, 0.1]}, {i, nnnp}];
    Print[Graphics3D[tab]]];
  (* For each facet find the boundary corners that sit on the plane *)
  ppf = Table[Table[(*Print[{np[[i,2]],γ[[j]] unv[[j]],unv[[j]],OnPlane[np[[i,2]],γ[[j]] unv[[j]],unv[[j]]]//N];*)
     If[OnPlane[np[[i, 2]], γ[[j]] unv[[j]], unv[[j]]], i, ## &[]], {i, Dimensions[np][[1]]}], {j, nf}];

  naf = Dimensions[ppf][[1]];
  tabP = Table[If[Dimensions[ppf[[i]]][[1]] > 2, ps = OrderClockwise[np[[ppf[[i]], 2]], unv[[i]]]; Polygon[ps], ## &[]], {i, nf}];
  tabE = Table[If[Dimensions[ppf[[i]]][[1]] > 2, ps = OrderClockwise[np[[ppf[[i]], 2]], unv[[i]]]; Line[Append[ps, ps[[1]]]],
     ## &[]], {i, nf}];
  plts[[1]] = Graphics3D[{Thick, DBlue, tabE}, Boxed → False];
  plts[[2]] = Graphics3D[{tabP}, Boxed → False];
  plts[[3]] = Graphics3D[{Opacity[0.2], Blue, tabP}, Boxed → False];
  Print[GraphicsRow[plts, ImageSize → 800]];

  A = Table[PolygonArea[np[[ppf[[i]], 2]], unv[[i]]], {i, nf}];
  vol = 1/3 Table[A[[i]] γ[[i]], {i, nf}];
  en = Sum[γ[[i]] A[[i]], {i, nf}];
  EperVol23 = en/Total[vol]^(2/3);
  {EperVol23, A/Total[vol]^(2/3)}
 ]
```