Supporting Information

Relevance of dispersion and the electronic spin in the DFT+U approach for the description of pristine and defective TiO$_2$ anatase

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I. Geometry Optimization procedure

1. The volume is varied +/-15% from its original volume and 7 deformed structure calculations are performed.
2. ISIF=2 followed by ISIF=4 calculations over the preoptimized structures were performed.
3. With the computed energies at each volume an EOS fitting was performed using a Birch-Murnaghan equation at fourth order as implemented in vaspkit. (See Figure S1 a and c)
4. The equilibrium volume is extracted and used as input for the next set of calculations.
5. For optimizing the a/c ratio with constant volume a maximum physical strain $\epsilon$ is defined as the percent variation of the a/c ratio (i.e. if there is a +/-5% variation in a/c then $\epsilon$ = +/- 0.05), then the a/c of the distorted structure at the maximum physical strain is determined from $(a/c)=(a/c)_{initial} \cdot (1+\epsilon)$. Then 7 distorted structures were computed considering 7 $\epsilon_i$ values through variations of -5% to 5% of the a/c initial value with a step of 1.67%.
6. Then ISIF=2 calculations were computed for each distorted structure and the results of energy vs strain were plotted and fitted to a 4th order polynomial (See figure S1 b and d).

$$E(x) = ax^4 + bx^3 + cx^2 + dx + c$$

with $x=\epsilon$ and the minimum corresponds to the derivative $dE/dx=0$, i.e:

$$0 = 4ax^3 + 3bx^2 + 2cx + d$$

Then by solving the equation we use this new value of $\epsilon_{\text{min}}$ physical strain to compute the a/c ratio and build a new structure, that will be used to optimize the ratio a/c at ISIF=2 with fixed volume followed by ISIF=7 calculation, this final structure is used to reoptimize the volume at a fixed value of the ratio a/c through an EOS fitting as explained next.

7. The step one described previously is repeated by increasing the number of deformed structures for the volume calculations to 9. The procedure is repeated by following steps 2 to 4. Then for the a/c ratio optimization 9 distorted structures were used and steps 5 to 6 were followed.
8. Finally, after completing 4 calculation cycles (1st volume optimization – 1st a/c ratio optimization - 2nd volume optimization – 2nd a/c ratio optimization) the final structure is fully relaxed by ISIF=3 calculation.
9. The convergence between the volume, lattice parameters and energy were checked at each calculation cycle and the final structure is compared to the fully relaxed structure to verify a convergence < 1X10^{-6} Å in the lattice parameters and < 7X10^{-4} eV in the energy.

The convergence data for TiO$_2$ is presented in Table S1.

Ti$_2$O$_3$ geometry optimization was carried out by following a similar procedure as that previously described. However, instead of a/c ratio optimization at constant volume the $\alpha$ angle was optimized at constant volume (see figure S2 b and d). Four calculation cycles were performed (1st volume optimization (see Figure S2 a) – 1st $\alpha$ angle optimization - 2nd volume optimization (see Figure S2 c) – 2nd $\alpha$ angle optimization) the final structure was fully relaxed by ISIF=3 calculation. The convergence data for Ti$_2$O$_3$ is presented in table S2.

The relaxed structure at U$_{n-1}$ is used as a starting structure for the next U$_n$ (u=1,2,3,4) optimization procedure. The initial structures for the TiO$_2$ and Ti$_2$O$_3$ U=0 geometry optimization were taken from Howard et.al.[63] and Straumanis et.al [64], respectively.
Figure S1. PBEsol U=1 Optimization steps until convergence is achieved for the geometry parameters of TiO$_2$. Volume optimization steps (a,c), and a/c optimization calculations (b,d).

Table S1. Convergence data and geometry parameters along each optimization step for TiO$_2$

| Calculation | Step | a(Å)  | c(Å)  | Δa(Å)   | Δc(Å)   | E(eV)    | ΔE(eV)  | Vol(Å$^3$) | ΔVol(Å$^3$) |
|-------------|------|-------|-------|---------|---------|----------|---------|------------|-------------|
| -           | 0    | 3.780 | 9.510 |         |         | 136.268  |         |            |             |
| Vopt1       | 1    | 3.781 | 9.459 | -1.40E-3| -5.05E-2| -111.976 | -5.05E-2| 135.261    | -1.00E+00   |
| 1_a/c       | 2    | 3.779 | 9.455 | -3.01E-4| -5.48E-2| -111.973 | -2.01E-2| 135.078    | -1.19E+00   |
| Vopt2       | 3    | 3.782 | 9.461 | -4.91E-3| -1.11E+0| 2.04E+0  |         | 135.321    | -9.46E-01   |
| 2_a/c       | 4    | 3.777 | 9.466 | -4.36E-2| -1.11E+0| -3.69E+0 |         | 135.082    | -1.18E+00   |
| ISIF=3      | 5    | 3.775 | 9.466 | -2.47E+0| -1.11E+0| 6.46E+0  | -1.18E+0| 135.082    | -1.18E+00   |
Figure S2. PBEsol U=1 Optimization steps until convergence is achieved for the geometry parameters of Ti$_2$O$_3$. Volume optimization steps (a,c), and α angle optimization calculations (b,d).

Table S2. Convergence data and geometry parameters along each optimization step for Ti$_2$O$_3$.

| Calculation | Step | a(Å)       | α(°)        | Δa(Å)      | Δα(°)      | E(eV)    | ΔE(eV)   | Vol(Å$^3$) | ΔVol(Å$^3$) |
|-------------|------|------------|-------------|------------|------------|----------|----------|------------|-------------|
| -           | 0    | 5.4310     | 56.580      |            |            | -104.3219|          |            |             |
| V1opt       | 1    | 5.4381     | 55.264      | 7.1100E-03 | -1.3158E+00| -94.2202 | -1.3158E+00| 101.2000   | -3.1219E+00 |
| Ang1        | 2    | 5.4331     | 55.307      | -5.0000E-03| 4.3200E-02 | -94.2203 | -1.3268E-04| 101.0400   | -1.6000E-01 |
| V2opt       | 3    | 5.4363     | 55.307      | 3.1900E-03 | 0.0000E+00 | -94.2202 | 1.7444E-04 | 101.2167   | 1.7666E-01  |
| Ang2        | 4    | 5.4333     | 55.305      | -3.0300E-03| -2.3000E-03| -94.2204 | -2.2510E-04| 101.0400   | -1.7666E-01 |
| ISIF=3      | 5    | 5.4333     | 55.305      | 0.0000E+00 | 0.0000E+00 | -94.2199 | 4.6883E-04 | 101.0411   | 1.1130E-03  |
# Converged geometries of TiO₂

## 1. TiO₂ PBEsol U=0

| Ti O₂ | 1.00000000000000 | 3.7729692360596809 | 0.0000000000000000 | -0.0000000000000000 |
|-------|------------------|-------------------|-------------------|---------------------|
|       | -0.00000000000000 | 3.7729692360596809 | 0.0000000000000000 | -0.0000000000000000 |
|       | 0.0000000000000000 | -0.0000000000000000 | 9.5561387893009861 |

| Ti O | 4 8 |
|------|----|

Direct

| 0.00000000000000 | -0.00000000000000 | -0.00000000000000 |
|------------------|------------------|------------------|
| 0.50000000000000 | 0.50000000000000 | 0.50000000000000 |
| 0.50000000000000 | 0.50000000000000 | 0.25000000000000 |
| 0.75000000000000 | 0.7076179768386774 |
| 0.2076179618386709 | 0.2076179768386745 |
| 0.4576179768386745 | 0.9576179768386774 |
| 0.5423820231613226 | 0.5423820231613226 |
| 0.0423820531613271 | 0.0423820531613271 |
| 0.2923820231613255 | 0.2923820231613255 |
| 0.7923820231613226 | 0.7923820231613226 |

## 2. TiO₂ PBEsol U=1

| Ti O₂ | 1.00000000000000 | 0.0000000000000000 |

| Direct | -0.0000000000000000 | 0.0000000000000000 |
|--------|-------------------|-------------------|
| 0.50000000000000 | 0.0000000000000000 | 0.9576179768386774 |
| 0.50000000000000 | -0.0000000000000000 | 0.5423820231613226 |
| 0.0000000000000000 | 0.5000000000000000 | 0.0423820531613271 |
| 0.50000000000000 | 0.5000000000000000 | 0.2923820231613255 |
| 0.7923820231613226 | 0.7923820231613226 | 0.7923820231613226 |
3.7871192869247983  0.00000000000000000  0.00000000000000000
0.00000000000000000  3.7871192869247983  0.00000000000000000
0.00000000000000000  0.00000000000000000  9.5668814005190317

Ti  O
4  8

Direct
-0.00000000000000000  0.00000000000000000  -0.00000000000000000
0.50000000000000000  0.50000000000000000  0.50000000000000000
0.00000000000000000  0.50000000000000000  0.25000000000000000
0.50000000000000000  0.00000000000000000  0.75000000000000000
0.00000000000000000  0.00000000000000000  0.2076655252589770
0.50000000000000000  0.50000000000000000  0.7076655102589721
-0.00000000000000000  0.50000000000000000  0.4576655102589722
0.50000000000000000  -0.00000000000000000  0.9576655102589721
0.50000000000000000  -0.00000000000000000  0.5423344897410279
-0.00000000000000000  0.50000000000000000  0.0423345007410251
0.50000000000000000  0.00000000000000000  0.2923344897410278
-0.00000000000000000  0.00000000000000000  0.7923344897410279

3. TiO₂ PBEsol U=2

Ti O2
1.00000000000000000
3.8008914404632632  0.00000000000000000  0.00000000000000000
0.00000000000000000  3.8008914404632632  0.00000000000000000
0.00000000000000000  0.00000000000000000  9.5772813666030334

Ti  O
4  8

Direct
-0.00000000000000000  0.00000000000000000  0.00000000000000000
0.50000000000000000  0.50000000000000000  0.50000000000000000
4. \( \text{TiO}_2 \) PBEsol U=3

\[
\begin{array}{ccc}
-0.0000000000000000 & 0.5000000000000000 & 0.2500000000000000 \\
0.5000000000000000 & 0.0000000000000000 & 0.7500000000000000 \\
0.0000000000000000 & 0.0000000000000000 & 0.2077279904936862 \\
0.5000000000000000 & 0.5000000000000000 & 0.0000000000000000 \\
0.0000000000000000 & 0.0000000000000000 & 0.4577279154936835 \\
0.5000000000000000 & -0.0000000000000000 & 0.9577279154936834 \\
0.5000000000000000 & -0.0000000000000000 & 0.5422720845063166 \\
0.0000000000000000 & 0.0000000000000000 & 0.0422720505063137 \\
0.5000000000000000 & 0.5000000000000000 & 0.0422720505063137 \\
0.0000000000000000 & 0.0000000000000000 & 0.7922720845063166
\end{array}
\]
5. \( \text{TiO}_2 \) PBEsol U=4

\[
\begin{array}{cccc}
0.5000000000000000 & 0.5000000000000000 & 0.2922409125067348 \\
0.0000000000000000 & 0.0000000000000000 & 0.7922409425067369 \\
\end{array}
\]

\begin{align*}
\text{TiO}_2 \\
1.0000000000000000 \\
3.8265186425189275 & 0.0000000000000000 & 0.0000000000000000 \\
0.0000000000000000 & 3.8265186425189275 & -0.0000000000000000 \\
0.0000000000000000 & -0.0000000000000000 & 9.6072785298340868 \\
\end{align*}

\[\begin{array}{cccc}
\text{Ti} & \text{O} \\
4 & 8 \\
\end{array}\]

Direct

\[
\begin{array}{cccc}
0.0000000000000000 & 0.0000000000000000 & 0.2500000000000000 \\
0.5000000000000000 & 0.5000000000000000 & -0.0000000000000000 \\
-0.0000000000000000 & 0.7500000000000000 & 0.0000000000000000 \\
0.0000000000000000 & 0.0000000000000000 & 0.9577299185869055 \\
0.0000000000000000 & 0.0000000000000000 & 0.5422700814130945 \\
0.5000000000000000 & 0.4565400042869055 & 0.1006000006020945 \\
-0.0000000000000000 & 0.0000000000000000 & 0.2922700814130945 \\
-0.0000000000000000 & 0.0000000000000000 & 0.7922700814130945 \\
\end{array}
\]
6. TiO$_2$ PBEsol U=6

```
Ti O2
1.0000000000000000
3.8509222545303814 0.0000000000000000 0.0000000000000000
0.0000000000000000 3.8509222545303814 -0.0000000000000000
0.0000000000000000 -0.0000000000000000 9.649366076142251
```

```
Ti O
4 8
Direct
-0.0000000000000000 -0.0000000000000000 -0.0000000000000000
0.5000000000000000 0.5000000000000000 0.5000000000000000
-0.0000000000000000 0.5000000000000000 0.2500000000000000
0.5000000000000000 -0.0000000000000000 0.7500000000000000
-0.0000000000000000 0.0000000000000000 0.207655746832124
0.5000000000000000 0.5000000000000000 0.7076553656832130
0.0000000000000000 0.5000000000000000 0.457655146832074
0.5000000000000000 -0.0000000000000000 0.9576553656832130
0.5000000000000000 0.0000000000000000 0.5423446343167870
0.0000000000000000 0.5000000000000000 0.042344813167923
0.5000000000000000 0.0000000000000000 0.292344853167926
0.0 -0.0000000000000000 0.7923446343167870
```
Ti  O
4  8

Direct

0.00000000000000  0.00000000000000  0.00000000000000
0.50000000000000  0.50000000000000  0.50000000000000
0.00000000000000  0.50000000000000  0.75000000000000
0.50000000000000  0.00000000000000  0.20885650799999
0.50000000000000  0.50000000000000  0.70885652300000
0.00000000000000  0.50000000000000  0.45885652300000
0.50000000000000  0.00000000000000  0.95885652300000
0.50000000000000  0.00000000000000  0.29114347699999
0.00000000000000  0.00000000000000  0.79114347699999

8. TiO₂ PBEsol-D3 U=1

Ti  O₂
1.00000000000000
3.7775239944000001  0.00000000000000  0.00000000000000
0.00000000000000  3.7775239944000001  0.00000000000000
0.00000000000000  0.00000000000000  9.46637153630000

Ti  O
4  8

Direct

0.00000000000000  0.00000000000000  0.00000000000000
0.50000000000000  0.50000000000000  0.50000000000000
0.00000000000000  0.50000000000000  0.25000000000000
0.50000000000000  0.00000000000000  0.75000000000000
9. \[ \text{TiO}_2 \ \text{PBEsol-D3 U=2} \]

\begin{verbatim}
Ti  O2
1.00000000000000
  3.790625338000000  0.000000000000000  0.000000000000000
  0.000000000000000  3.790625338000000  0.000000000000000
  0.000000000000000  0.000000000000000  9.480930328399999
Ti  O
4   8
Direct
0.000000000000000  0.000000000000000  0.000000000000000  0.000000000000000  0.500000000000000  0.500000000000000  0.000000000000000  0.000000000000000  0.500000000000000  0.500000000000000  0.000000000000000  0.000000000000000  0.500000000000000  0.500000000000000  0.000000000000000  0.000000000000000  0.500000000000000  0.500000000000000  0.000000000000000  0.000000000000000  0.500000000000000  0.500000000000000  0.000000000000000  0.000000000000000  0.500000000000000  0.500000000000000  0.000000000000000  0.000000000000000  0.500000000000000  0.500000000000000  0.000000000000000  0.000000000000000  0.500000000000000  0.500000000000000  0.000000000000000  0.000000000000000
\end{verbatim}

S11
10. TiO$_2$ PBEsol-D3 U=3

| Ti  | O  |
|-----|----|
| 4   | 8  |

Direct

|   |   |   |
|---|---|---|
| 0.000000000000000 | 0.000000000000000 | 0.000000000000000 |
| 0.500000000000000 | 0.500000000000000 | 0.500000000000000 |
| 0.000000000000000 | 0.500000000000000 | 0.250000000000000 |
| 0.500000000000000 | 0.000000000000000 | 0.750000000000000 |
| 0.000000000000000 | 0.000000000000000 | 0.208921715999999 |
| 0.500000000000000 | 0.500000000000000 | 0.708921611000001 |
| 0.000000000000000 | 0.500000000000000 | 0.458921641000003 |
| 0.500000000000000 | 0.000000000000000 | 0.958921611000001 |
| 0.500000000000000 | 0.000000000000000 | 0.541078388999999 |
| 0.000000000000000 | 0.500000000000000 | 0.041078333000001 |
| 0.500000000000000 | 0.500000000000000 | 0.291078358999996 |
| 0.000000000000000 | 0.000000000000000 | 0.791078388999999 |

11. TiO$_2$ PBEsol-D3 U=4

| Ti  | O  |
|-----|----|
| 4   | 8  |

Ti O2

1.00000000000000

512
12. TiO$_2$ PBEsol-D3 U=6

Ti O$_2$

1.00000000000000

3.8393427294256446 0.0000000000000000 0.0000000000000000
0.0000000000000000 3.8393427294256446 0.0000000000000000
0.0000000000000000 -0.0000000000000000 -9.5641177735926011

Ti O

4 8

Direct

-0.0000000000000000 0.0000000000000000 -0.0000000000000000
Table S3. Optimized geometries for TiO$_2$ with different U values.

| Hubbard U value | PBEsol a(Å) | PBEsol c(Å) | Vol(Å$^3$) | PBEsol-D3 a(Å) | PBEsol-D3 c(Å) | Vol(Å$^3$) |
|-----------------|--------------|--------------|-------------|----------------|----------------|-------------|
| 0               | 3.76         | 9.46         | 133.96      | 3.76           | 9.46           | 133.96      |
| 1               | 3.79         | 9.57         | 137.21      | 3.78           | 9.47           | 135.08      |
| 2               | 3.80         | 9.58         | 138.36      | 3.79           | 9.48           | 136.23      |
| 3               | 3.81         | 9.59         | 139.51      | 3.80           | 9.50           | 137.41      |
| 4               | 3.83         | 9.61         | 140.67      | 3.82           | 9.52           | 138.59      |
| 6               | 3.85         | 9.64         | 143.03      | 3.84           | 9.56           | 140.98      |
| Experimental value | 3.78       | 9.51         | 136.27      | 3.78           | 9.51           | 136.27      |

III. Converged geometries of Ti$_2$O$_3$

1. Ti$_2$O$_3$ PBEsol U=0

Ti$_4$O$_6$

1.0000000000000000

5.4642519917672097  0.0013344319898459  0.0009107456149114

3.1343915680578145  4.4758955648586687  0.0009107456147785

3.1343915680578012  1.6320471772754752  4.1677408685983188

Ti  O
4  6

Direct
0.3454939964066505  0.34549410240666522  0.3454941514066527
0.1545058835933538  0.1545058735933530  0.1545058465933472
0.6545054145933470  0.6545057235933477  0.6545060455933530
0.8454945104066504  0.8454939934066467  0.8454941644066502
0.938127928058702  0.5618719931941275  0.249999489999993
0.5618718761941285  0.2500000349999993  0.9381279568058684
0.2500000104000015  0.9381278468058735  0.5618720221941264
0.0618719721941293  0.4381277678058705  0.7500001339999969
0.4381283880586868  0.749999389999985  0.0618719811941265
0.7500000100000017  0.0618719981941315  0.4381278298058685

2.  \( \text{Ti}_2\text{O}_3 \) PBEsol U=1

\text{Ti4 O6}
1.0000000000000000
5.4581862984483136  0.0004643471059587  0.0003188020878418
3.0610642566751234  4.5190356825129410  0.0003188020879977
3.0610642566751234  1.6239081019411896  4.2171798726059277

\text{Ti O}
4  6

Direct
0.343700133189599  0.3437006083189602  0.3437003373189626
0.1562995956810355  0.1562996046810398  0.1562996026810396
0.6562999316810348  0.6562999756810385  0.6562994016810336
0.8437003593189644  0.8437006203189611  0.8437006903189669
0.9352501198109636  0.5647498731890394  0.2499999209999970
0.5647500341890349  0.2499998400000010  0.9352498258109606
0.2499998850000011  0.9352504138109666  0.5647499251890366
0.0647502771890374  0.4352498778109647  0.7500002170000002
3. \( \text{Ti}_2\text{O}_3 \) PBEsol U=2

\[
\begin{array}{c}
\text{Ti}_4\text{O}_6 \\
1.00000000000000 \\
5.4581862984483136 \quad 0.0004643471059587 \quad 0.0003188020879977 \\
3.0610642566751234 \quad 4.5190356825129410 \quad 0.0003188020879977 \\
3.0610642566751234 \quad 1.6239081019411896 \quad 4.2171798726059277 \\
\text{Ti} \quad \text{O} \\
4 \quad 6 \\
\text{Direct}
\end{array}
\]

4. \( \text{Ti}_2\text{O}_3 \) PBEsol U=3

\[
\begin{array}{c}
\text{Ti}_4\text{O}_6 \\
0.3437001333189599 \quad 0.3437006083189602 \quad 0.3437003373189626 \\
0.1562995956810355 \quad 0.1562996046810398 \quad 0.1562996026810396 \\
0.6562999316810348 \quad 0.6562999756810385 \quad 0.6562994016810336 \\
0.8437003593189644 \quad 0.8437006203189611 \quad 0.8437006903189669 \\
0.9352501198109636 \quad 0.5647498731890394 \quad 0.249999920999970 \\
0.5647500341890349 \quad 0.2499998400000010 \quad 0.9352498258109606 \\
0.2499998850000011 \quad 0.9352504138109666 \quad 0.5647499251890366 \\
0.0647502771890374 \quad 0.4352498778109647 \quad 0.7500002170000002 \\
0.4352499328109657 \quad 0.7500004070000017 \quad 0.0647501121890344 \\
0.7500004540000020 \quad 0.0647501801890400 \quad 0.4352497858109642
\end{array}
\]
1.00000000000000
5.4399007184043562 -0.0016528807938532 -0.0011411752877801
2.9848474874807880  4.5478795096712599 -0.0011411752875760
2.984846284518750  1.6107055053492030  4.2530956146294567

Ti  O
4   6

Direct
0.3427942868178331  0.3427945928178371  0.3427944398178351
0.1572055691821691  0.1572054591821671  0.1572055581821647
0.6572059871821683  0.6572057781821687  0.6572054711821682
0.8427944568178329  0.8427946828178303  0.8427951138178340
0.9343294244215328  0.5656707495784674  0.2499998999999988
0.5656712935784698  0.2499996940000031  0.9343287934215267
0.249998669999997  0.9343289934215291  0.5656712285784680
0.0656715295784681  0.4343285984215283  0.7500005189999968
0.4343287954215268  0.7500003870000000  0.0656713435784740
0.749999269999975  0.0656713415784739  0.4343287104215304

5.      Ti2O3 PBEsol U=4

Ti4 O6
1.00000000000000
5.4334430732223202 -0.0007976099546275 -0.0005531206441553
2.9315567769540056  4.5747436135183728 -0.0005531206442028
2.9315583091404851  1.6029634969998634  4.2847145148939241

Ti  O
4   6

Direct
0.3424327826993722  0.3424330126993699  0.3424330096993732
6. \( \text{Ti}_2\text{O}_3 \) PBEsol U=6

\[
\begin{align*}
\text{Ti}_4 \text{O}_6 \\
1.00000000000000 \\
5.4363960045795681 & \quad 0.0022380481373034 & \quad 0.0015626690242016 \\
2.8593052092985305 & \quad 4.6237193088848283 & \quad 0.0015626690238983 \\
2.8593067570147030 & \quad 1.594440122869035 & \quad 4.340106236304312 \\
\text{Ti} & \quad \text{O} \\
4 & \quad 6 \\
\text{Direct} \\
0.3424307268039963 & \quad 0.3424309358039958 & \quad 0.3424309688039950 \\
0.1575691641960054 & \quad 0.1575690691960082 & \quad 0.1575692151960061 \\
0.6575696441960095 & \quad 0.657569211960052 & \quad 0.6575690691960081 \\
0.8424308468039921 & \quad 0.8424313178039919 & \quad 0.8424312648039911 \\
0.9348931415645642 & \quad 0.5651069104354330 & \quad 0.2499998990000023 \\
0.5651074574354321 & \quad 0.249999829999986 & \quad 0.9348928205645625 \\
0.2499997039999968 & \quad 0.9348926075645626 & \quad 0.5651077334354336 \\
0.0651075054354363 & \quad 0.4348924655645648 & \quad 0.7500008020000024 \\
0.4348928515645612 & \quad 0.7500003239999984 & \quad 0.0651075564354370 \\
0.7500001619999992 & \quad 0.0651074684354368 & \quad 0.4348927465645632
\end{align*}
\]
7. \( \text{Ti}_2\text{O}_3 \) PBEsol-D3 U=0

\( \text{Ti}_4 \text{O}_6 \)

\[
\begin{array}{ccc}
1.000000000000000 & 0.000000000000000 & 0.000000000000000 \\
5.4294943809999996 & 0.000000000000000 & 0.000000000000000 \\
3.1133676909000001 & 4.4481851199999997 & 0.000000000000000 \\
3.1133676909000001 & 1.6211002499999997 & 4.1422680786999999 \\
\end{array}
\]

Direct

\[
\begin{array}{ccc}
0.3456154570000001 & 0.345615630000003 & 0.345615630000003 \\
0.154384423000003 & 0.154384385999997 & 0.154384385999997 \\
0.6543839539999965 & 0.6543842629999972 & 0.6543842629999972 \\
0.84561597100000009 & 0.8456156250000006 & 0.8456156250000006 \\
0.9375987129999999 & 0.5624011729999978 & 0.249999489999993 \\
0.5624010559999988 & 0.250000034999993 & 0.9375987769999981 \\
0.2500001040000015 & 0.9375986670000032 & 0.5624012019999967 \\
0.0624011519999996 & 0.4375986499999982 & 0.7500001339999969 \\
0.4375992089999983 & 0.7499993899999985 & 0.0624011609999968 \\
0.7500000200000017 & 0.0624011780000018 & 0.4375986499999982 \\
\end{array}
\]

8. \( \text{Ti}_2\text{O}_3 \) PBEsol-D3 U=1

\( \text{Ti}_4 \text{O}_6 \)

\[
\begin{array}{ccc}
1.000000000000000 & 0.000000000000000 & 0.000000000000000 \\
5.42432928090000003 & 0.000000000000000 & 0.000000000000000 \\
3.0416944504000001 & 4.49126296459999997 & 0.000000000000000 \\
3.0416944504000001 & 1.6136323342000001 & 4.1913761114000003 \\
\end{array}
\]

S19
9. Ti₂O₃ PBEsol-D3 U=2

Ti₄O₆

1.00000000000000
5.4243292809000003  0.0000000000000000  0.0000000000000000
3.0416944504000001  4.4912629645999997  0.0000000000000000
3.0416944504000001  1.6136323342000001  4.1913761114000003

Ti  O

4   6

Direct

0.3438728029999965  0.3438732779999967  0.3438730069999991
0.1561269259999989  0.1561269350000032  0.1561269330000030
0.6561272619999983  0.6561273060000019  0.6561267319999970
0.8438730499999991  0.8438733099999993  0.8438733030000023
0.9346486880000029  0.5653512820000017  0.2499999209999970
0.5653514660000027  0.2499998930000018  0.9346483639999974
0.2499999140000000  0.9346490579999980  0.5653513869999998
0.0653517590000021  0.4346484360000034  0.7500001599999970
0.4346484710000027  0.7500004070000017  0.0653515739999975
0.7500004640000029  0.0653516530000005  0.4346482959999989
|                  | 0.2499999140000000 | 0.9346490579999980 | 0.5653513869999998 |
|------------------|---------------------|---------------------|---------------------|
|                  | 0.0653517590000021 | 0.4346484360000034 | 0.7500001599999990 |
|                  | 0.4346484710000027 | 0.7500004070000017 | 0.0653515739999975 |
|                  | 0.7500004640000029 | 0.0653516530000005 | 0.4346482959999989 |

10. \( \text{Ti}_2\text{O}_3 \) PBEsol-D3 U=3

|                  | 10.00000000000000 |
|------------------|-------------------|
|                  | 5.4080031974775018 | -0.0130688330168708 | -0.0090055760720658 |
|                  | 2.9796361468976977 | 4.5131405707170336 | -0.0090055760721928 |
|                  | 2.9796350979098336 | 1.5986109013787804 | 4.2205387941581103 |

| Ti        | O             | 4 | 6 |
|-----------|---------------|---|---|
| Direct    |               |   |   |
| 0.3430037870810937 | 0.3430040920810941 | 0.3430038890810951 |
| 0.1569960909189033 | 0.1569959789189012 | 0.1569960689189015 |
| 0.6569965129189028 | 0.6569963429189030 | 0.6569959429189054 |
| 0.8430039500810964 | 0.8430042160810971 | 0.8430045120811003 |
| 0.9335776354012127 | 0.5664225365987873 | 0.2499998870000013 |
| 0.5664231265987864 | 0.2499997629999982 | 0.9335769124012133 |
| 0.2499999560000035 | 0.9335772484012127 | 0.5664229775987847 |
| 0.0664233025987867 | 0.4335768724012171 | 0.7500004529999984 |
| 0.4335770154012183 | 0.7500004429999976 | 0.0664231175987820 |
| 0.7499999939999995 | 0.0664231265987863 | 0.4335769114012168 |

11. \( \text{Ti}_2\text{O}_3 \) PBEsol-D3 U=4
Ti4 O6
1.00000000000000
5.4005017281000001  0.0000000000000000  0.0000000000000000
2.9144510441000002  4.5465804761999999  0.0000000000000000
2.9144525576000002  1.5936101455000000  4.2581441859000000
Ti  O
4   6
Direct
0.3426854120000016  0.3426856789999988  0.3426856230000013
0.1573144780000035  0.1573144030000009  0.1573145119999992
0.6573149049999987  0.6573146969999968  0.6573143379999991
0.8426855829999980  0.8426859799999992
0.3517274588797734  0.3517278208797749  0.3517279588797721

12.  Ti2O3  PBEsol-D3 U=6

Ti4 O6
1.00000000000000
5.6212257256375500 -0.0003204180604673 -0.0002179030404288
3.2663941973264299  4.5748018822344862 -0.0002179030404364
3.2663936431801330  1.6812220375613252  4.2546795023393162
Ti  O
4   6
Direct
0.3517274588797734  0.3517278208797749  0.3517279588797721

522
Table S4. Optimized geometries for Ti$_2$O$_3$ with different U values.

| Method Hubbard U value | Method PBEsol a(Å) | α(°) | Vol(Å$^3$) | Method PBEsol-D3 a(Å) | α(°) | Vol(Å$^3$) |
|------------------------|--------------------|------|------------|------------------------|------|------------|
| 0                      | 5.46               | 54.98| 100.04     | 5.43                   | 55.01| 100.04     |
| 1                      | 5.43               | 55.01| 101.90     | 5.43                   | 55.31| 101.04     |
| 2                      | 5.46               | 55.88| 104.01     | 5.42                   | 55.89| 102.11     |
| 3                      | 5.44               | 56.74| 105.26     | 5.41                   | 56.71| 103.33     |
| 4                      | 5.43               | 57.36| 106.52     | 5.40                   | 57.34| 104.55     |
| 6                      | 5.44               | 58.24| 109.04     | 5.40                   | 58.29| 107.02     |
| Experimental value     | 5.43               | 56.58| 104.32     | 5.43                   | 56.58| 104.32     |

IV. Calculation parameters

INCAR TiO$_2$ U=3
Full optimization after preoptimization by following the procedure described in section I.

# Basic setup:
ISPIN = 2
ISTART = 1
ICHARG = 1

# Accuracy controls:
PREC = Accurate
# Electronic loop controls:
ALGO = Fast
EDIFF = 0.000001
ENCUT = 600
NELM = 200
NELMIN = 5
NELMDL = -10
MAXMIX = -100
ISMEAR = 0
SIGMA = 0.05

# Relaxation control:
IBRION = 1  # Conjugate gradients
NSW = 50
ISIF = 3  # Ions
EDIFFG = -0.01

# Properties:
LCHARG = .TRUE.
LWAVE = .TRUE.
LELF = .FALSE.
LVTOT = .FALSE.
LVHAR = .FALSE.
GGA = PS
LDAU = .TRUE.

# HUBBARD
LDAUU = 3.00 0.00
LDAUJ = 0.00 0.00
LDAUL = 2 -1
LDAUPRINT = 1
LMAXMIX = 4
LASPH = .TRUE.

V. TiO2 (001) anatase surface

Ti O
1.00000000000000
15.2136999999999993 0.000000000000000 0.0000000000000000
0.0000000000000000 15.2136999999999993 0.0000000000000000
0.0000000000000000 0.0000000000000000 29.0000000000000000

Ti O
64 128

Selective dynamics

Direct
0.0000000000000000 0.0000000000000000 0.275053231379594 T T T
0.0000000000000000 0.249998170000026 0.275053231379594 T T T
0.0000000000000000 0.49999633999981 0.275053231379594 T T T
-0.0000000000000000 0.74999449999971 0.275053231379594 T T T
0.249998170000026 -0.0000000000000000 0.275053231379594 T T T
0.249998170000026 0.249998170000026 0.275053231379594 T T T
0.249998170000026 0.49999633999981 0.275053231379594 T T T
0.249998170000026 0.74999449999971 0.275053231379594 T T T
0.49999633999981 0.0000000000000000 0.275053231379594 T T T
0.49999633999981 0.249998170000026 0.275053231379594 T T T
0.49999633999981 0.49999633999981 0.275053231379594 T T T
0.49999633999981 0.74999449999971 0.275053231379594 T T T
0.74999449999971 -0.0000000000000000 0.275053231379594 T T T
0.74999449999971 0.249998170000026 0.275053231379594 T T T
0.74999449999971 0.49999633999981 0.275053231379594 T T T
0.74999449999971 0.749999499999971 0.275053231379594 T T T
0.124999970999995 0.124999970999995 0.1119448770623885 T T T
0.124999970999995 0.3749997250000021 0.1119448770623885 T T T
| x1  | y1  | z1   | label1 | label2 | label3 |
|-----|-----|------|--------|--------|--------|
| 0.124999907999995 | 0.4999996339999981 | 0.1944816089138053 | T | T | T |
| 0.124999907999995 | 0.7499994499999971 | 0.1944816089138053 | T | T | T |
| 0.3749997250000021 | -0.0000000000000000 | 0.1944816089138053 | T | T | T |
| 0.3749997250000021 | 0.2499981700000026 | 0.1944816089138053 | T | T | T |
| 0.3749997250000021 | 0.7499944999999971 | 0.1944816089138053 | T | T | T |
| 0.6249995419999976 | 0.0000000000000000 | 0.1944816089138053 | T | T | T |
| 0.6249995419999976 | 0.2499981700000026 | 0.1944816089138053 | T | T | T |
| 0.6249995419999976 | 0.4999963399999981 | 0.1944816089138053 | T | T | T |
| 0.6249995419999976 | 0.7499994499999971 | 0.1944816089138053 | T | T | T |
| 0.8749993590000003 | -0.0000000000000000 | 0.1944816089138053 | T | T | T |
| 0.8749993590000003 | 0.2499981700000026 | 0.1944816089138053 | T | T | T |
| 0.8749993590000003 | 0.4999963399999981 | 0.1944816089138053 | T | T | T |
| 0.8749993590000003 | 0.7499944999999971 | 0.1944816089138053 | T | T | T |
| 0.0000000000000000 | 0.0000000000000000 | 0.0167046872410026 | F | F | F |
| 0.0000000000000000 | 0.2499981700000026 | 0.0167046872410026 | F | F | F |
| 0.0000000000000000 | 0.4999963399999981 | 0.0167046872410026 | F | F | F |
| 0.0000000000000000 | 0.7499944999999971 | 0.0167046872410026 | F | F | F |
| 0.2499981700000026 | 0.0000000000000000 | 0.0167046872410026 | F | F | F |
| 0.2499981700000026 | 0.2499981700000026 | 0.0167046872410026 | F | F | F |
| 0.2499981700000026 | 0.4999963399999981 | 0.0167046872410026 | F | F | F |
| 0.2499981700000026 | 0.7499944999999971 | 0.0167046872410026 | F | F | F |
| 0.4999963399999981 | 0.0000000000000000 | 0.0167046872410026 | F | F | F |
| 0.4999963399999981 | 0.2499981700000026 | 0.0167046872410026 | F | F | F |
| 0.4999963399999981 | 0.4999963399999981 | 0.0167046872410026 | F | F | F |
| 0.4999963399999981 | 0.7499944999999971 | 0.0167046872410026 | F | F | F |
| 0.7499944999999971 | 0.0000000000000000 | 0.0167046872410026 | F | F | F |
| 0.7499944999999971 | 0.2499981700000026 | 0.0167046872410026 | F | F | F |
| 0.7499944999999971 | 0.4999963399999981 | 0.0167046872410026 | F | F | F |
| 0.7499944999999971 | 0.7499944999999971 | 0.0167046872410026 | F | F | F |
| 0.124999079999995 | 0.124999079999995 | 0.1803623868732818 | T | T | T |
| 0.124999079999995 | 0.3749997250000021 | 0.1803623868732818 | T | T | T |
| x1  | y1  | z1  | x2  | y2  | z2  | x3  | y3  | z3  | x4  | y4  | z4  | x5  | y5  | z5  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 0.124999907999995 | 0.6249995419999976 | 0.1803623868732818 | T | T | T | 
| 0.124999907999995 | 0.8749993590000003 | 0.1803623868732818 | T | T | T | 
| 0.3749997250000021 | 0.124999907999995 | 0.1803623868732818 | T | T | T | 
| 0.3749997250000021 | 0.3749997250000021 | 0.1803623868732818 | T | T | T | 
| 0.3749997250000021 | 0.6249995419999976 | 0.1803623868732818 | T | T | T | 
| 0.3749997250000021 | 0.8749993590000003 | 0.1803623868732818 | T | T | T | 
| 0.6249995419999976 | 0.124999907999995 | 0.1803623868732818 | T | T | T | 
| 0.6249995419999976 | 0.3749997250000021 | 0.1803623868732818 | T | T | T | 
| 0.6249995419999976 | 0.6249995419999976 | 0.1803623868732818 | T | T | T | 
| 0.6249995419999976 | 0.8749993590000003 | 0.1803623868732818 | T | T | T | 
| 0.0000000000000000 | 0.124999907999995 | 0.0985879896550017 | F | F | F | 
| 0.0000000000000000 | 0.3749997250000021 | 0.0985879896550017 | F | F | F | 
| 0.0000000000000000 | 0.6249995419999976 | 0.0985879896550017 | F | F | F | 
| 0.0000000000000000 | 0.8749993590000003 | 0.0985879896550017 | F | F | F | 
| 0.2499998170000026 | 0.124999907999995 | 0.0985879896550017 | F | F | F | 
| 0.2499998170000026 | 0.3749997250000021 | 0.0985879896550017 | F | F | F | 
| 0.2499998170000026 | 0.6249995419999976 | 0.0985879896550017 | F | F | F | 
| 0.2499998170000026 | 0.8749993590000003 | 0.0985879896550017 | F | F | F | 
| 0.4999996339999981 | 0.124999907999995 | 0.0985879896550017 | F | F | F | 
| 0.4999996339999981 | 0.3749997250000021 | 0.0985879896550017 | F | F | F | 
| 0.4999996339999981 | 0.6249995419999976 | 0.0985879896550017 | F | F | F | 
| 0.4999996339999981 | 0.8749993590000003 | 0.0985879896550017 | F | F | F | 
| 0.749994499999971 | 0.124999907999995 | 0.0985879896550017 | F | F | F | 
| 0.749994499999971 | 0.3749997250000021 | 0.0985879896550017 | F | F | F | 
| 0.749994499999971 | 0.6249995419999976 | 0.0985879896550017 | F | F | F | 
| 0.749994499999971 | 0.8749993590000003 | 0.0985879896550017 | F | F | F | 
| 0.124999907999995 | 0.0000000000000000 | 0.2624964526750593 | T | T | T | 
| 0.124999907999995 | 0.2499998170000026 | 0.2624964526750593 | T | T | T |
| X1 | Y1 | Z1 | Condition1 | Condition2 | Condition3 |
|----|----|----|------------|------------|------------|
| 0.124999907999995 | 0.499996339999981 | 0.2624964526750593 | T | T | T |
| 0.124999907999995 | 0.749994499999971 | 0.2624964526750593 | T | T | T |
| 0.3749997250000021 | -0.0000000000000000 | 0.2624964526750593 | T | T | T |
| 0.3749997250000021 | 0.249998170000026 | 0.2624964526750593 | T | T | T |
| 0.3749997250000021 | 0.499996339999981 | 0.2624964526750593 | T | T | T |
| 0.3749997250000021 | 0.749994499999971 | 0.2624964526750593 | T | T | T |
| 0.6249995419999976 | -0.0000000000000000 | 0.2624964526750593 | T | T | T |
| 0.6249995419999976 | 0.249998170000026 | 0.2624964526750593 | T | T | T |
| 0.6249995419999976 | 0.499996339999981 | 0.2624964526750593 | T | T | T |
| 0.6249995419999976 | 0.749994499999971 | 0.2624964526750593 | T | T | T |
| 0.8749993590000003 | 0.0000000000000000 | 0.2624964526750593 | T | T | T |
| 0.8749993590000003 | 0.249998170000026 | 0.2624964526750593 | T | T | T |
| 0.8749993590000003 | 0.499996339999981 | 0.2624964526750593 | T | T | T |
| 0.8749993590000003 | 0.749994499999971 | 0.2624964526750593 | T | T | T |
| 0.124999907999995 | -0.0000000000000000 | 0.1260453038172506 | T | T | T |
| 0.124999907999995 | 0.249998170000026 | 0.1260453038172506 | T | T | T |
| 0.124999907999995 | 0.499996339999981 | 0.1260453038172506 | T | T | T |
| 0.124999907999995 | 0.749994499999971 | 0.1260453038172506 | T | T | T |
| 0.3749997250000021 | -0.0000000000000000 | 0.1260453038172506 | T | T | T |
| 0.3749997250000021 | 0.249998170000026 | 0.1260453038172506 | T | T | T |
| 0.3749997250000021 | 0.499996339999981 | 0.1260453038172506 | T | T | T |
| 0.3749997250000021 | 0.749994499999971 | 0.1260453038172506 | T | T | T |
| 0.6249995419999976 | -0.0000000000000000 | 0.1260453038172506 | T | T | T |
| 0.6249995419999976 | 0.249998170000026 | 0.1260453038172506 | T | T | T |
| 0.6249995419999976 | 0.499996339999981 | 0.1260453038172506 | T | T | T |
| 0.6249995419999976 | 0.749994499999971 | 0.1260453038172506 | T | T | T |
| 0.8749993590000003 | 0.0000000000000000 | 0.1260453038172506 | T | T | T |
| 0.8749993590000003 | 0.249998170000026 | 0.1260453038172506 | T | T | T |
| 0.8749993590000003 | 0.499996339999981 | 0.1260453038172506 | T | T | T |
| 0.8749993590000003 | 0.749994499999971 | 0.1260453038172506 | T | T | T |
| -0.0000000000000000 | 0.124999907999995 | 0.291658020161817 | T | T | T |
| 0.0000000000000000 | 0.3749997250000021 | 0.291658020161817 | T | T | T |
| x1  | x2  | y1  | T | T | T |
|-----|-----|-----|---|---|---|
| 0.0000000000000000 | 0.6249995419999976 | 0.2916580201061817 | T | T | T |
| -0.0000000000000000 | 0.8749993590000003 | 0.2916580201061817 | T | T | T |
| 0.249998170000026 | 0.1249999079999995 | 0.2916580201061817 | T | T | T |
| 0.249998170000026 | 0.3749997250000021 | 0.2916580201061817 | T | T | T |
| 0.249998170000026 | 0.6249995419999976 | 0.2916580201061817 | T | T | T |
| 0.249998170000026 | 0.8749993590000003 | 0.2916580201061817 | T | T | T |
| 0.4999963399999981 | 0.1249999079999995 | 0.2916580201061817 | T | T | T |
| 0.4999963399999981 | 0.3749997250000021 | 0.2916580201061817 | T | T | T |
| 0.4999963399999981 | 0.6249995419999976 | 0.2916580201061817 | T | T | T |
| 0.4999963399999981 | 0.8749993590000003 | 0.2916580201061817 | T | T | T |
| 0.7499994499999971 | 0.1249999079999995 | 0.2916580201061817 | T | T | T |
| 0.7499994499999971 | 0.3749997250000021 | 0.2916580201061817 | T | T | T |
| 0.7499994499999971 | 0.6249995419999976 | 0.2916580201061817 | T | T | T |
| 0.7499994499999971 | 0.8749993590000003 | 0.2916580201061817 | T | T | T |
| 0.1249999079999995 | 0.1249999079999995 | 0.0436137220689972 | F | F | F |
| 0.1249999079999995 | 0.3749997250000021 | 0.0436137220689972 | F | F | F |
| 0.1249999079999995 | 0.6249995419999976 | 0.0436137220689972 | F | F | F |
| 0.1249999079999995 | 0.8749993590000003 | 0.0436137220689972 | F | F | F |
| 0.3749997250000021 | 0.1249999079999995 | 0.0436137220689972 | F | F | F |
| 0.3749997250000021 | 0.3749997250000021 | 0.0436137220689972 | F | F | F |
| 0.3749997250000021 | 0.6249995419999976 | 0.0436137220689972 | F | F | F |
| 0.3749997250000021 | 0.8749993590000003 | 0.0436137220689972 | F | F | F |
| 0.6249995419999976 | 0.1249999079999995 | 0.0436137220689972 | F | F | F |
| 0.6249995419999976 | 0.3749997250000021 | 0.0436137220689972 | F | F | F |
| 0.6249995419999976 | 0.6249995419999976 | 0.0436137220689972 | F | F | F |
| 0.6249995419999976 | 0.8749993590000003 | 0.0436137220689972 | F | F | F |
| 0.8749993590000003 | 0.1249999079999995 | 0.0436137220689972 | F | F | F |
| 0.8749993590000003 | 0.3749997250000021 | 0.0436137220689972 | F | F | F |
| 0.8749993590000003 | 0.6249995419999976 | 0.0436137220689972 | F | F | F |
| 0.8749993590000003 | 0.8749993590000003 | 0.0436137220689972 | F | F | F |
| -0.0000000000000000 | 0.0000000000000000 | 0.2082683807298407 | T | T | T |
| -0.0000000000000000 | 0.2499981700000026 | 0.2082683807298407 | T | T | T |
VI. Geometries comparison

Figure S3. Geometries comparison between U=0 and U=3 optimized geometries for cobalt and yttrium interstitially doped (a and b, respectively) TiO$_2$ (001) anatase surface. The substitutional Co and Y doped structures are shown in c and d. Red in the color gradient and in the TiO$_2$ surface shows the highest change in the bond distances.
VII. CO₂ adsorption energy over the TiO₂(001) anatase surface

Figure S4. Adsorption of a CO₂ molecule over a TiO₂ (001) surface, some geometry parameters are presented.

The adsorption energy ($E_{\text{ads}}$) of a CO₂ molecule over a TiO₂ (001) surface was computed at PBEsol-D3(BJ) with U=3 in a similar configuration as that reported by Araujo et al.¹ The adsorption energy is in agreement with that previously reported by Araujo et al.¹ and Huygh et al.²

VIII. DOS plot of the pristine TiO₂(001) anatase

Figure S5. Density of states plot of the TiO₂ (001) anatase pristine surface.

References

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