Supporting Information for "Peroxide and superoxide states of adsorbed O_2 on anatase TiO_2 (101) with subsurface defects" by U. Aschauer, J. Chen and A. Selloni

Computational details:

Calculations were performed using the PBE-GGA exchange and correlation functional[1]. Electron-core interactions were described by ultrasoft[2] pseudopotentials, treating O (2s, 2p) and Ti(3s, 3p, 3d and 4s) shells explicitly. A kinetic energy cutoff of 20 Ry was used for the plane-wave basis and a cutoff of 200 Ry for the augmented density. In the GGA calculations the bottom layer was fixed at its relaxed bulk coordinates. All atoms were allowed to move in the GGA+U calculations because of convergence problems caused by relaxation-induced charge localization at the bottom surface. Structures were relaxed using the BFGS algorithm until forces were below 10^{-3} au (~0.05 eV/Å). Due to the large size of the simulation cell (10.26 Å x 11.31 Å x 20.00 Å) reciprocal space sampling could be restricted to the gamma point.

GGA+U lattice constants:

The bulk lattice parameters were optimized both at the GGA and GGA+U levels. A comparison between the two sets of calculations is given below in Table S1.

Table S1: Anatase bulk lattice constants optimized at the GGA and GGA+U level.

	GGA	GGA+U	Difference
a (Å)	3.770	3.795	0.025
c (Å)	9.544	9.555	0.011

The difference between the GGA and GGA+U lattice parameters is quite small. Thus the GGA optimized bulk lattice constants were used for all surface calculations, at both the GGA and GGA+U level.

3 layer vs. 4 layer slab:

In order to check the accuracy of the results obtained with the 3 layer slab, test-calculations using a 4 layer thick slab were performed. Table S2 compares GGA and GGA+U adsorption energies at selected sites of the 4- and 3-layer slabs.

Table S2: Adsorption energies (in eV) at selected sites on the 4 layer slab compared to those on the 3 layer slab at the GGA and GGA+U levels.

GGA, bottom layer fixed		**4 layers**	**3 layers**
	Site 2	-1.25	-1.53
	Site 4	-1.29	-1.47
	Site 5	-1.89	-2.01
GGA+U, bottom layer fixed		**4 layers**	
	Site 4, peroxide	-1.15	
	Site 4, superoxide	-0.75	
GGA+U, bottom layer free		**4 layers**	**3 layers**
	Site 4, peroxide	-1.13	-0.82
	Site 4, superoxide	-0.79	-0.55

The above table shows a reduction (increase) of the computed GGA (GGA+U) adsorption energy when the number of layers is increased from 3 to 4. These features can be related to the character of the HOMO charge density for the clean slab (i.e. before O_2 adsorption), see Figure S1.

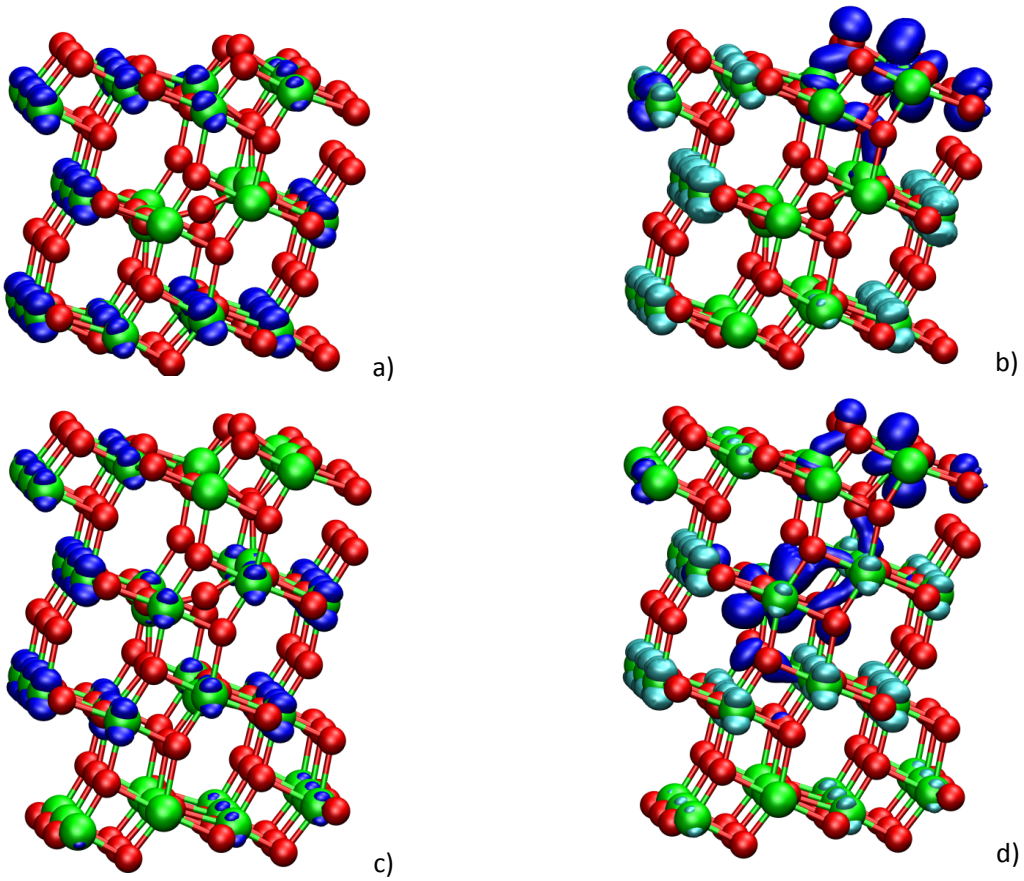

Figure S1: a) and c): HOMO charge density computed at the GGA level for the clean reduced slab with 3 and 4 layers, respectively; b) and d) : HOMO charge density computed at the GGA+U level for the clean reduced slab with 3 and 4 layers, respectively.

Due to the delocalized character of the HOMO at the GGA level, an increase of the number of layers in the slab results in less charge at each of the surface Ti_{5c} sites and thus in a reduced adsorption energy. As the relative stability of the different adsorption sites does not change significantly when going from a three to a four layer slab, the three layer slab represents a reasonable trade-off between accuracy and computational cost at the GGA level.

At the GGA+U level, the localization of the defect states changes with the thickness of the slab. The HOMO is localized mainly at the surface site 5 for a 3 layer slab whereas it localized on both site 5 and in the subsurface, near the defect, with 4 layers. The electronic densities of states (DOS) for the clean 3 and 4 layer slabs calculated at the GGA+U level are however very similar, see Figure S2.

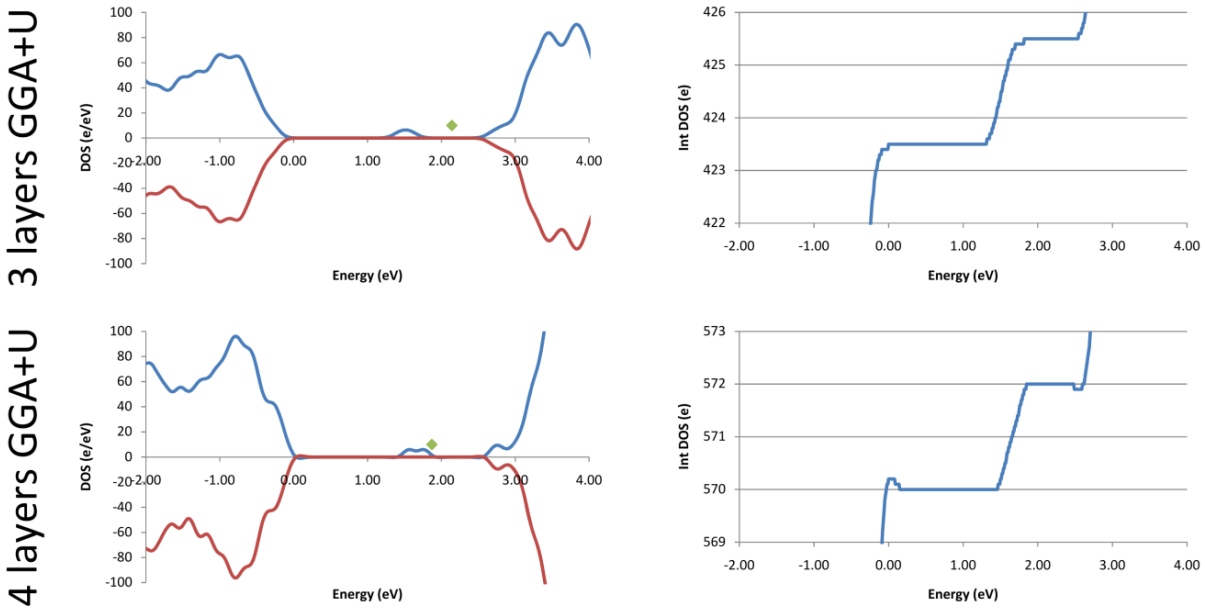

Figure S2: Density of states and integrated density of states for the clean 3 layer and 4 layer slabs at the GGA+U level. The green symbol indicates the Fermi energy.

References

1 J. P. Perdew, K. Burke and M. Ernzerhof, *Physical Review Letters*, 1996, **77**, 3865-3868.

2 D. Vanderbilt, *Physical Review B*, 1990, **41**, 7892-7895.