SUPPORTING INFORMATION

Electronic and structural properties of antibacterial Ag-Ti-based surfaces: an ab initio theoretical study

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1. Structural and Electronic properties of anatase and rutile Ti_2O

The structural and electronic properties of the TiO_2 bulk system, such as the lattice constants and the electronic density of states (EDOS), were evaluated for both phases as the first step towards understanding this material and validating the quality of our techniques in reproducing its basic characteristics. Both rutile and anatase crystals exhibit tetragonal unit cells along with two lattice constants (a and c). The two TiO_2 structures have two lattice constants (a and c); the rutile has prismatic features while the anatase shows di-pyramidal habits. In this work, the brookite orthorhombic structure was not considered, since it is less stable than rutile and anatase. In order to evaluate the DFT lattice constants (a and c) of rutile and anatase unit cells, we performed a series of total energy minimization on a 2d grid in space varying a and c. The minimum total energy of these 3d curves corresponds to the preferred a and c lattice constants. It is important to check our approach and compare our ab initio data on the basic structural property like the lattice constant compared to previous theoretical and experimental data. The current VASP PBEGGA Rutile α lattice constant 4.614Å (4.65 Å with siesta) are in line witqh GGA-PBE (4.64 Å, 4.67 Å), PWGGA (4.63 Å) and QEspresso-PBEGGA (4.62 Å) while the c lattice constant (2.97 Å VASP and 3.00 Å Siesta) agree with GGA-PBE (2.99Å, 2.97 Å), PWGGA (2.98 Å) and QEspresso-PBEGGA (2.977 Å) [52 and references there in].Similar good agreement is also observed for the anatase α lattice constant 3.78 Å VASP and 3.85 Å with Siesta are in line with GGA-PBE (3.83Å, 3.8 Å), HF 3.76 Å) and QEspresso-PBEGGA (3.785 Å) while the c lattice constant (9.64 Å VASP and 9.65 Å Siesta) agree with GGA-PBE (9.62Å, 9.67 Å), HF (9.85 Å) and QEspresso-PBEGGA (9.51 Å) [52].

Concerning the electronic properties, it is known that both rutile and anatase are semiconductors, however, the present and available in the literature DFT and HF calculations of the Energy band gap (Egap) underestimate it by 1-1.5eV as expected [ ] due to the delocalization error [53-54] from the corresponding experimental values 3.03 eV for rutile, 3.2 eV for anatase and 3.4 eV for amorphous [52]. In particular, the current VASP PBEGGA Rutile band gap is 1.78eV in line with GGA-PBE (1.73eV and 1.85eV), PWGGA (1.9eV), LDA (1.78eV) and QEspresso-PBEGGA (1.8eV) [52]. In addition, the present work VASP

PBEGGA Anatase band gap (2.14eV) is also in agreement with GGA-PBE (2.02 eV and 2.25 eV), LDA (2.04 eV) and QEspresso-PBEGGA (2.1 eV) [52]. The electronic density of states (EDOS) is the basic electronic property of any material that is an outcome of the Density functional theory calculation. The total EDOS of this work using both VASP and SIESTA are in line with the available in the literature DFT EDOSs of TiO_2 (Anatase, Rutile and an disorder 192-atom crystal model) [52] depict a broad valence band from -6 eV up to the Fermi level and a conductance band of approximately 2 eV.

In Figure S.1 and S.2, the atomic projected electronic density of states (PDOS) reveals that oxygen is mainly responsible for the highest occupied states that are close to the Fermi level, while titanium occupies mostly the energies from -6 eV to -4 eV. The unoccupied states are primarily due to titanium. The states close to the Fermi level are mainly due to oxygen $2p_z$ and titanium 3d. In the insets of Figures 5 and 6, selective wavefunctions are shown. In the case of rutile, the WF at -5.69 eV is due to Ti3d–02p hybridizations, while that closer to the Fermi level (-2.35 eV) has O2p–O2p antibonding features. Above the Fermi level, the rutile WF is mainly due to Ti3d non-bonded orbitals. Similar behaviour is observed in the anatase WFs, where the states close to -4 eV are due to Ti–O hybridizations (in the inset, the WF at -4.2 eV has Ti3deg–Ti3deg directional bonding, where the O 2p electrons participate), the states close to Fermi are due to O 2p, and above the Fermi, the Ti orbitals are dominant. Consequently, any doping or coating that is meant to change the band gap must be designed in order to create hybrid bonds with these orbitals. Summarizing, both VASP and SIESTA DFT calculations used in this work satisfactorily reproduce the TiO_2 basic structural and electronic properties for both rutile and anatase in line with previous theoretical and experimental data.
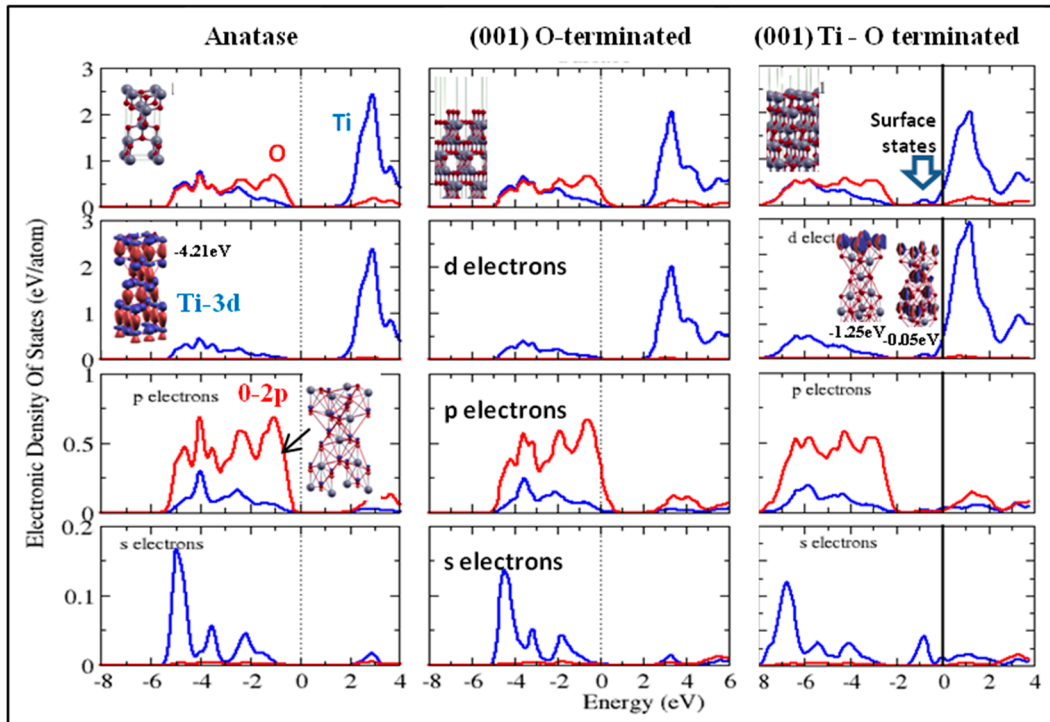

Figure S.1. Electronic features of TiO_2 anatase and oxygen and Ti–O-terminated anatase (001) surfaces along with selective wavefunctions.

The properties of any material are altered when moving to surfaces, thin films or nanowires and nanoclusters. Aiming to reveal a difference in the TiO_2 band gap that might allow us to tune the performance of devices, we considered a free-standing thin film of anatase (001). We used the equilibrium lattice constants of anatase (a=3.78 Å and c=9.639 Å) that were in excellent agreement with other theoretical and experimental data [52]. The thin film of anatase (001) was created by keeping the periodic boundary conditions only in the in-plane directions, thus creating two terminated layers (one with oxygen atoms and another with titanium atoms) and performing energy minimization and atomic relaxation. We used four k-point meshes 3x3x1, 6x6x1, 9x9x1 and 12x12x1 to improve our statistics. In Figure S.1 and Figure S.2, the bulk anatase and rutile electronic density of states (EDOS) are in very good agreement with other studies [52 and references therein]. The results on the thin film of anatase (001) for the -point mesh of 991, show a filling of the bulk anatase band gap. The occupied thin film states have similar features to the anatase bulk EDOS, while a broadening of the valence band is observed. It should be noted that although such a thin film might be unstable in experimental conditions, it could be formed on our devices as the ontop oxide layer on pure titanium metallic diodes. The thin film EDOS features might be an upper limit of how far we could tune the electron band gap or the electronic properties of our system by decreasing the width of the oxide coat layer.

2. Anatase (001) and Rutile (001) surfaces

Material surfaces are critical, since they directly interact with the environment while their properties usually differ from the bulk ones and depend on their crystalline orientation. Therefore, several studies have been performed concerning the properties of anatase and rutile (001) and (110) surfaces. In this report, we focus on the electronic properties of rutile(001) and anatase(001). The (001) surfaces were created using 1x1x10 rutile unit cells along the [001] direction and 1x1x4 anatase unit cells, keeping the periodic boundary conditions only in the in-plane directions using a 10x10x1 k-point mesh, thus creating several terminated layers (with oxygen atoms and/or with titanium–oxygen atoms). The surface supercell length along the z axis should be big enough to achieve bulk behaviour in the middle of the box. For all cases, energy minimizations were performed resulting in atomic relaxation, especially at the surface layer.

The surface contraction or expansion is estimated through the calculations of the relative relaxed positions which offers the alteration of the interlayer distances compared to the bulk. For both cases, the surface layer shows contraction followed by expansion of the second layer in line with the β-TiNb(110) surface. Titanium atoms almost reach the perfect interatomic bulk distance in the middle of the supercell while the oxygen atom RR, although decreasing, does not converge to the bulk values. Moreover, the -6% contraction of the Ti surface atoms and +15 expansion of the oxygen second-layer atoms offers an almost rippled surface layer with titanium–oxygen features. In Figure 5, the anatase EDOS of the bulk system is altered in the presence of surfaces. In the case of the titanium surface layer, new surface states are presented due to Ti inside the band gap that is clearly presented in the third column of the Ti surface atom EDOS. In these surface states close to the Fermi level, the Ti 3d are dominant, while the 3p and 4s orbital

also contribute. It should be noted that the oxygen second-layer atoms relax really close to the Ti surface atoms due to the high contraction of the surface layer that can be considered as an almost mixed Ti–O-terminated layer. In contrast, in the (001) surface with oxygen termination, the energy band gap isnot markedlyaffected, and an absence of surface states at the Fermi level is observed. The oxygen surface atoms follow the behaviour of the bulk ones. In general, the bulk peak around -17eV due to oxygen atoms is depicted in all cases, as well as the broad valence band from -5 eV until the Fermi level. In Figure 5, we present the anatase electronic density of states for both oxygen and titanium–oxygen-terminated (001) surfaces. The anatase band gap is 2.08eV at the Γ-kpoint comparable to 2.02-2.25eV of previous theoretical calculations, while it is underestimated in the experimental data (3.2eV) [52]. The oxygen-terminated surface is energeticallyfavoured compared to the Ti- terminated. The occupied wavefunctions close to the Fermi level aremainly due to oxygen 2p orbitals for both anatase and oxygen-terminated (001) faces comparable to the rutile phase. Although unfavoured, the presence of titanium at the surface layer introduces new degenerate electron surface states inside the band gap, showing dangly bonds that could be interesting for further metal or semiconductor deposition aiming to create a material with a tunable band gap. The surface energy of Ti (-O)-terminated anatase (001) is 0.974 eV/$\mathring{A}^2$ while the oxygen-terminated anatase is 0.784 eV/$\mathring{A}^2$, resulting in the titanium (-oxygen)-terminated as the energetically favoured. Nevertheless, in reality, both terminations might coexist. The partial EDOS and selective wavefunctions were also calculated for the case of rutile(001). In Figure 6, we present the electronic density of states (total and d, p, s partial) of titanium and oxygen atoms for bulk rutile and the Ti–O terminated rutile (001). The band gap of rutile at Γ--point is 1.74eV standing in the energy range of previous theoretical calculations 1.73 – 1.9 eV [52], underestimated against the experimental 3.03eV band gap.
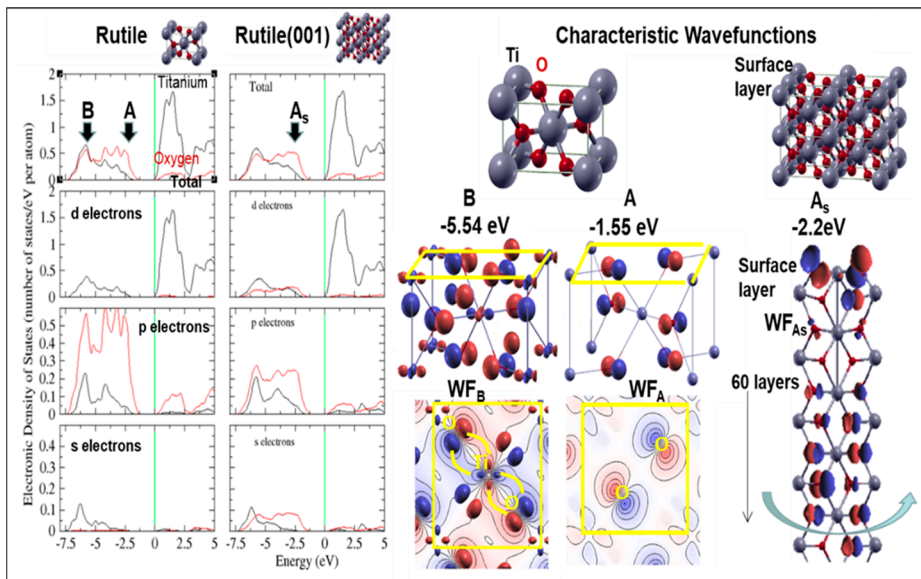

Figure S.2. Electronic features ofTiO$_2$ rutile and rutile (001) surface.

The presence of the Ti–O rutile (001) surface further reduces the band gap to 1.69 eV as expected. Both Ti and O atoms contribute to the wide energy band from -7.5 eV up to -2.0 eV, mainly with their Ti 3d

and O 2p electrons. The electronic features around -5.7 eV (state named B) show an overlap peak in the PDOS of Ti and O atoms, while in the wavefunction (WF$_B$), both Ti 3d and O 2p orbitals are visible. In the contour WF plot projected in the centre of the rutile unit cell, the Ti central atom 3deg orbital lobe forms direction hybridizations with the two nearest neighbour O atoms and their 2 p orbitals, as depicted in Figure S2 with dashed lines. In contrast, at the highest occupied state at -2.4 eV, the main contribution in the PDOS is O, as also depicted in the 3D wavefunction plot (WF$_A$). In the WF$_A$ contour plot, the two oxygen 2p electrons present anti-bondingfeatures.

Similar behaviour is observed in the rutile (001) system, where the states close to the Fermi level reveal O 2p occupation, mainly at the system's bulk O atoms starting at -1.42eV. The As state at -2.22 eV is localized at the oxygen surface atoms that are not bonded and are almost vertically aligned to the surface layer presented dangly bonds, therefore enhancing the surface reactivity. The calculated rutile surface energies are 0.12 eV/Å^2 for the Ti–O-terminated layer and 0.32eV/Å^2 for the oxygen-terminated surface layer. Concluding for all cases, the cases of Ti-rich surfaces reduce the TiO_2 bulk band gap due to the introduction of new surface states close to the Fermi level.