



Theoretical analysis of band alignment and charge carriers migration in mixed-phase TiO₂ systems

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Abstract

Photocatalysts based on mixtures of rutile and anatase forms of titania usually show a better catalytic performance than each individual component. In order to understand this behavior, several experimental and theoretical approaches have been proposed in the past, looking for an adequate reference frame for aligning energy bands, and arriving sometimes to opposite results. In this work, the theoretical results obtained for the band alignment applying a modified common anion rule for different possibilities of mixed-phase (anatase–rutile) interaction are presented. According to our results, mixed-phase systems involve the transfer of electrons from rutile to anatase and holes from anatase to rutile. This analysis would be applicable to real samples of mixed phase of titania with large particle size. However, for heterogeneous size particulate systems, it is not only necessary to consider the alignment of bands of the bulk system, but also those of the corresponding surfaces. In keeping with the analysis performed, the best mixed systems are those composed by large particles of both polymorphs or by small particles of anatase dissolved in rutile. Our results could explain the disagreement found in the literature regarding the experimental works.

Keywords Mixed-phase titania · Band alignment · DFT · Common anion rule · Heterojunction

1 Introduction

Titania is a promising semiconductor applicable to the development of strategies for photocatalytic environmental remediation and for the generation of alternative energy sources, among other possibilities. Its oxide-reducing capacity is set by the positions of the valence (VB) and conduction (CB) bands, while the band gap (BG) energy determines the ability for activation of this photocatalyst. This oxide is present in different polymorphic forms in nature, being anatase and rutile those with higher catalytic properties. Their structural differences are reflected in their density [1], band structure, exposed surfaces, energy required for activation, kinetics of generated charges, and direct or indirect nature of the BG, among others. Rutile has a relatively wide band

gap of 3.0 eV, while that of anatase is even larger, 3.2 eV. The highest density of rutile could be an important factor in controlling the photoactivity by the diffusing capacity of the charge carriers [2]. Mixed-phase (anatase/rutile) photocatalysts as Degussa P25 generally show higher catalytic activity than pure anatase phase as has been reported in several experimental studies. For example, Ohno et al. found that anatase or rutile phases in pure powder are not efficient for the oxidation of naphthalene, while they are if the titania particles are present as a mixed phase [3, 4].

In photocatalysis, the holes and electrons generated from the excitation semiconductor can migrate to the surface and react with reagents present in the medium, recombine with each other within the bulk or on the surface, or react with a punctual or linear defect. In such migration, electrons and holes generated can meet each other upon the surface of another crystal phase of the oxide or other surface with different coordination of the same phase. The role played by these interfaces represents a potential optimizable point to enhance the catalytic activity of a photocatalyst. One of the biggest problems in predicting the behavior of charge transfer in heterojunctions is the reference frame for aligning energy bands. Specifically, the problem lies in defining whether there is a

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universal energy scale. There are, added to the uncertainty of establishing the possible framework, interfacial chemical interactions in heterovalent systems as well as the influence of different proportions of exposed surfaces, their spatial distribution, and the size and orientation of different monocrystals. Moreover, differences in the coordination of atoms exposed on surfaces cause the appearance of localized states in the BG. There are different possible kinds of interaction between semiconductors depending on the relative widths and locations of their respective bands [5]. For the engineering of photocatalysts involving the presence of interfaces, the different possibilities of alignment between the bands of two semiconductors in contact imply the need to know at least two important parameters; these are: energy difference between the valence bands (ΔE_V) and the energy difference between the conduction bands (ΔE_C) of the semiconductors involved [6].

In order to estimate or predict the semiconductor heterojunction band offsets, several proposals have been implemented. They can be divided essentially into three categories [6]. The first of them is based on the assumption of some empirical rule to put the electronic levels of each phase on a single absolute energy scale. In the second category, the alignment is achieved making an independent calculation of the electronic band structure for each semiconductor and afterward combing these bands relative to a reference level determined by some matching theoretical rule. In the third category of proposals, a self-consistent calculation comprising both each semiconductor and the interface is performed, attaining the detailed electronic structure of the specific heterojunction considered. The first category include: (a) the so-called electron affinity rule, which states that the conduction band offset is given by the difference in the electron affinities of the two heterojunction constituents [7]; and (b) the common anion rule, proposed for compound semiconductors with a common anion, where the position of the semiconductor valence band edge on an absolute energy scale would be determined mainly by the energies of the outermost electrons of this common anion [8]. The last rule can be related to the linear combination of atomic orbitals picture of energy bands for tetrahedrally coordinated semiconductors where the valence band top depends predominantly on the energy of the anion p orbital [9]. Recently, A. Klein outlined that this rule is well followed by II–V semiconductor interfaces and many oxide heterointerfaces [10], taking into account density functional calculations [11] and experimental results [12]. Regarding the second category, we can mention the earlier work of J. Tersoff [13], arguing for the existence of an effective midgap energy level, named as the branching point energy (BPE), that corresponds to the energy in the band gap at which an interface would contain equal conduction and valence band character. This kind of considerations can be applied in principle to any kind of interface.

On the other hand, the models corresponding to the third category of proposals to study the semiconductor heterojunctions are constrained to a very specific design of the interface and generalizations are not direct.

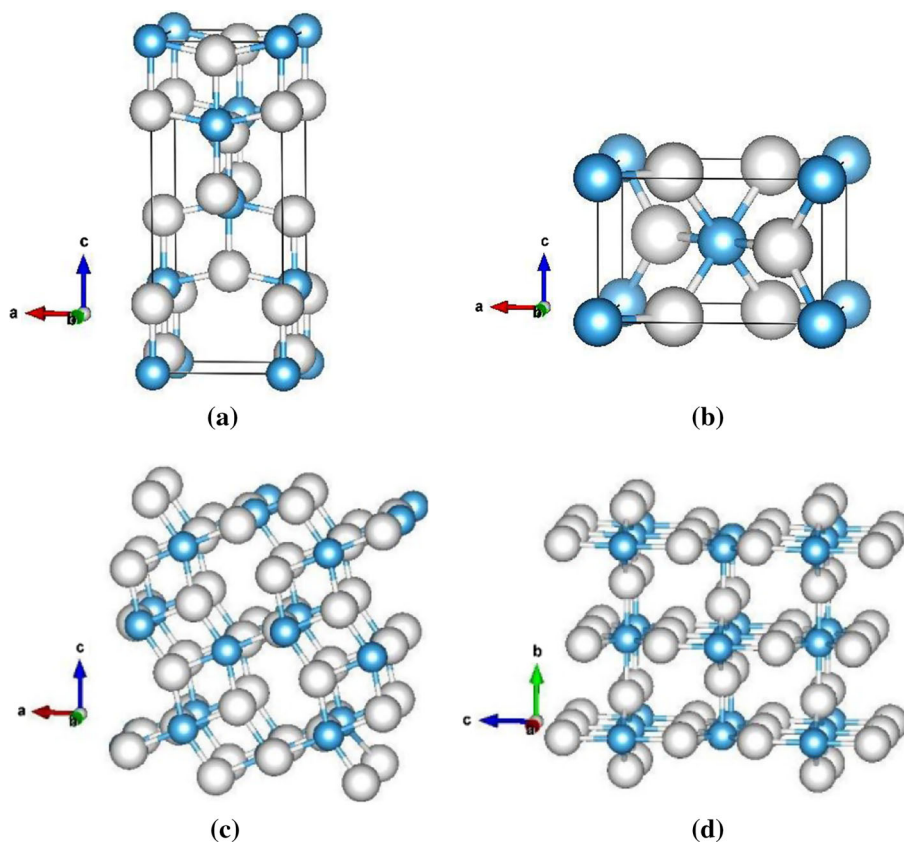
Among the theoretical and experimental works previously published on the alignment of TiO₂ bands, different proposals were found, with contradictory results. For certain research groups [14–18], the electrons would accumulate on the anatase structure, while the holes would do so on the rutile phase. Particularly, in the work of Scaloni et al. [17] these authors have demonstrated through a combination of simulation techniques and X-ray photoemission experiments that anatase shows the higher electron affinity. On the other hand, other works [19–21] propose a movement of electrons and holes favored in the opposite direction, that is to say, from anatase to rutile. We can mention in particular the work of Shen et al. [19], who studied anatase, rutile, and anatase–rutile mixed-phase TiO₂ with time-resolved mid-IR (TR-MIR) spectroscopy, indicating that electron transfer takes place in the anatase–rutile phase junction of mixed-phase TiO₂ and accumulates on the rutile phase. The different conclusions may be due to—besides the different models used for the study of the band alignment—variables such as particle size, presence of nanoparticles, nature of the mixtures, surface areas in contact, defects in polymorphs in contact and crystalline orientations.

In this work, the theoretical results obtained for the band alignment based on a modified common anion rule for different possibilities of mixed-phase (anatase–rutile) interaction are considered with the idea to clarify previous published results and provide useful information for the construction of the desired heterojunction in order to control the migration of charge carriers.

2 Computational methods

The calculations were performed using the VASP [22] code within the formalism of the functional density theory with the inclusion of the Hubbard coefficient (DFT+U) acting on the 3d states of Ti. In particular, the Dudarev [23] approximation implemented in the code was used. A value of 8 eV was carefully optimized to correctly represent band gap width (BG), obtaining a value of 3.21 eV for anatase (experimental 3.2 eV) and 2.61 eV for rutile (experimental 3.0 eV) [24]. This value has been previously used by our group with excellent results [25, 26]. The projector-augmented wave scheme (PAW) was used to describe the inner cores [27]. Electron exchange and correlation effects were described by using the generalized gradient approach (GGA) using the functional proposed by Perdew–Wang (PW91) [28]. In order to evaluate the magnetic properties of the systems, calculations were performed at the spin-polarized level. The energy convergence

Fig. 1 Ball and stick model of anatase (a) and rutile (b) crystal structures; the anatase $\text{TiO}_2(101)$ surface and the rutile $\text{TiO}_2(110)$ surface are represented in c and d, respectively. The oxygen and titanium atoms are represented by white and light blue spheres, respectively (Color figure online)



criterion used was 0.1 meV. The basis of plane waves for the electrons of the elements involved was generated considering 4 electrons for the Ti ($3d^34s^1$) and 6 electrons for the O ($2s^22p^4$). The Kohn–Sham one-electron wave functions were expanded on the basis of plane waves with optimized cutoff energy of 400 eV for kinetic energy. The bulk systems (Fig. 1a and b) were modeled using $15 \times 15 \times 15$ k-points according to the Monkhorst–Pack scheme [29]. The $\text{TiO}_2(101)$ and $\text{TiO}_2(110)$ surfaces (Fig. 1c, d) were modeled using 3-layer slabs of titanium and oxygen atoms. The periodic supercells used were $(2 \times 2 \times 1)$ with a grid of $5 \times 5 \times 1$ k-points for anatase (101) and $(2 \times 1 \times 2)$ with $7 \times 1 \times 5$ k-points for rutile (110), respectively. During the structural optimization, the bottom two layers were fixed at their bulk positions, whereas the top layer was allowed to relax.

The respective optimized cell parameters are: $a = b = 3.95 \text{ \AA}$ and $c = 9.76 \text{ \AA}$ for anatase bulk, $a = b = 4.73 \text{ \AA}$ and $c = 3.10 \text{ \AA}$ for rutile bulk. In the case of the surface, the values optimized for $\text{TiO}_2(101)$ are $a = 5.44 \text{ \AA}$, $b = 3.78 \text{ \AA}$, and $c = 25.64 \text{ \AA}$ with a vacuum of 13.21 \AA and for $\text{TiO}_2(110)$ $a = 3.10 \text{ \AA}$, $b = 26.25 \text{ \AA}$ (includes a vacuum of 17.07 \AA) and $c = 6.69 \text{ \AA}$. For the cases presented with oxygen vacancy (V_o), a single atom of oxygen was removed from the surface.

The respective electronic density of states (DOS) of all systems was evaluated, and the charges of the ions were obtained using the Bader’s analysis [30]. The energy scales of

rutile and anatase were aligned considering the bottom of the valence band formed predominantly by oxygen 2p orbitals.

A concept that arises from the study of the topology of band structures is the idea of effective mass (m^*) or effective tensor mass, which plays an important role in determining the dynamics of electrons near anisotropic minima (or electronic holes near anisotropic maxima). The effective tensile mass is defined as:

$$[\mathbf{m}^*(\mathbf{k})]_{ij} = \pm \frac{1}{\hbar^2} \left[\frac{\partial^2 \varepsilon(\mathbf{k})}{\partial k_i \partial k_j} \right]^{-1}, \quad (1)$$

where the + or – sign depends on whether \mathbf{k} is close to a maximum of the valence band (hollow) or a minimum of the conduction band (electron). The values of effective mass for anatase and rutile are presented in Sect. 3.3.

Regarding the alignment of different mixed-phase TiO_2 systems, a procedure based on a modified common anion rule was followed. In the standard application of this rule, the valence band tops are aligned. This method gives good results for many oxide heterointerfaces [10]. Nevertheless, recently it was observed that in the case of TiO_2 anatase/rutile interface, a more convenient description is obtained imposing the alignment of deeper levels [14]. In the proposal employed in the present work, the valence band bottoms are taken as the levels to be aligned.

3 Results and discussion

3.1 Alignment of bands in the titania with mixed-phase anatase–rutile

The results obtained for the alignment of bands of rutile and anatase bulk by the presence of common anion are shown in Fig. 2. The values are in agreement with the experimental electronic affinities of rutile, 4.9 eV, and of anatase, 5.1 eV, obtained by electronic photoemission microscopy of anatase films embedded in rutile nanocrystals [31] and with the calculated ionization potentials for rutile (7.83 eV) and for anatase (8.30 eV) by the Scanlon group [17]. Both values imply that the rutile has a smaller tendency than the anatase to attract electrons and consequently a lower energy of ionization. This conclusion would be further supported by the values of Bader charges obtained for Ti atoms, being $2.733e$ for rutile and $2.748e$ for anatase. The contact between Ti ions of different structures would imply a charge transfer from the rutile structure to that of the anatase polymorph.

The results obtained here locate both rutile bands above the anatase bands. The difference between valence bands (ΔE_V) obtained in our representation is 0.77 eV and between conduction bands (ΔE_C) is 0.17 eV. Then, considering the previous proposals for mixed bulk phase anatase–rutile heterojunctions, our results sustain that electrons accumulate on anatase and holes on rutile. Indeed, our results are in good agreement with those found by Pfeifer and his group [14]. They obtained experimentally using photoelectron XPS spectroscopy an energy difference of 0.7 eV for the valence bands and 0.5 eV for the conduction bands. Both values are in good agreement with the theoretical results of 0.63 eV for the valence bands and 0.39 eV for the conduction bands published by the same group. The values theoretically obtained by the Deák group are 0.55 eV for the valence bands and 0.35 eV for the conduction bands [16]. The work of Ming-Gang and collaborators [15] reports values of 0.52 eV and 0.22 eV, respectively.

The studies of electronic paramagnetic resonance (EPR) of Hurum [32] allow to determine the electrons transfer from rutile to anatase. This transfer implies a greater activity of the mixed systems by two mechanisms. One based on the greater efficiency in the absorption at smaller wavelengths since the BG of the rutile is 0.2 eV smaller than the one of anatase. This author attributes to this characteristic the name of “antenna function.” The second one is based on the transfer of electrons generated in rutile to anatase, called “reservoir tank function.” The separation of the charges leads to the increase in the half-life of the latter due to the smaller hollow electron recombination as a consequence of the band bending (see Sect. 3.3).

In a recently published paper, Nosaka et al. [33] explained the different results obtained between experimental and theo-

retical studies taking into account the existence of an indirect BG for anatase and the consideration of different VB widths due to the greater interaction between atomic orbitals in rutile. This paper proposes, revising and reconsidering the literature, an alignment concordant with the one proposed in the present work.

3.2 Influence of particle size on the band alignment

It is important to note that the morphology of small titania particles has an influence on the synergism between the anatase and rutile interfaces. The control in the growth of the crystal can be fundamental to favor the development of a certain phase, the size and the crystallinity, and the surface of the catalyst. The possibilities of distribution of the different phases among themselves, nature of the polymorph, quantity and nature of exposed surface, monocrystal orientations, for example, are extremely vast and highly dependent on the conditions of synthesis of the samples implying different catalytic behaviors.

Unlike previous theoretical works, this paper analyzes different possibilities of alignment considering the variety of situations obtained as a result of the application of different experimental techniques, such as phase mixture of homogeneous/heterogeneous particles size or small particles of similar size. Table 1 summarizes and schematizes the different possibilities of alignment using the common anion rule.

The change of coordination of the exposed atoms in surfaces causes the appearance of states located in the BG. The presence of these states, which is dependent on the exposed surfaces, interacts with the VB and CB, introducing new factors that make the analysis of the direction of flux of holes and electrons more complex. Each surface, even within the same polymorph, presents a certain coordination that favors the formation of specific defects, reconstructions, work function differences, modifications of the atomic charges with respect to the bulk and differences in the proper electronic structure. Each of the mentioned factors has a direct influence on the photocatalyst chemical activity.

The different energies associated with the creation of surface defects such as vacancies in anatase $\text{TiO}_2(101)$ and rutile $\text{TiO}_2(110)$ have been studied in the past, and the results predict a considerable variation in the formation of vacancies in both surfaces. The vacancies are much more stable in the rutile structure [36]. A possible explanation for the different photocatalytic activities between anatase (101) and anatase (001) was proposed by Zawadzki et al. [37]. In their work, they combined theoretical calculations with experimental data of transient absorption spectroscopy (TAS), indicating that this observation could be due to the different behavior of the holes in the surface and subsurface of both polymorphs.

The alignment of surfaces without defects differs from that of defective surfaces because the presence of defects has

Fig. 2 Alignment of the TiO₂ bulk according to common anion rule. The light blue curve corresponds to the DOS of anatase, and the violet curve corresponds to the DOS of rutile. In the diagram of the right panel, the process of transfer of charge is illustrated (Color figure online)

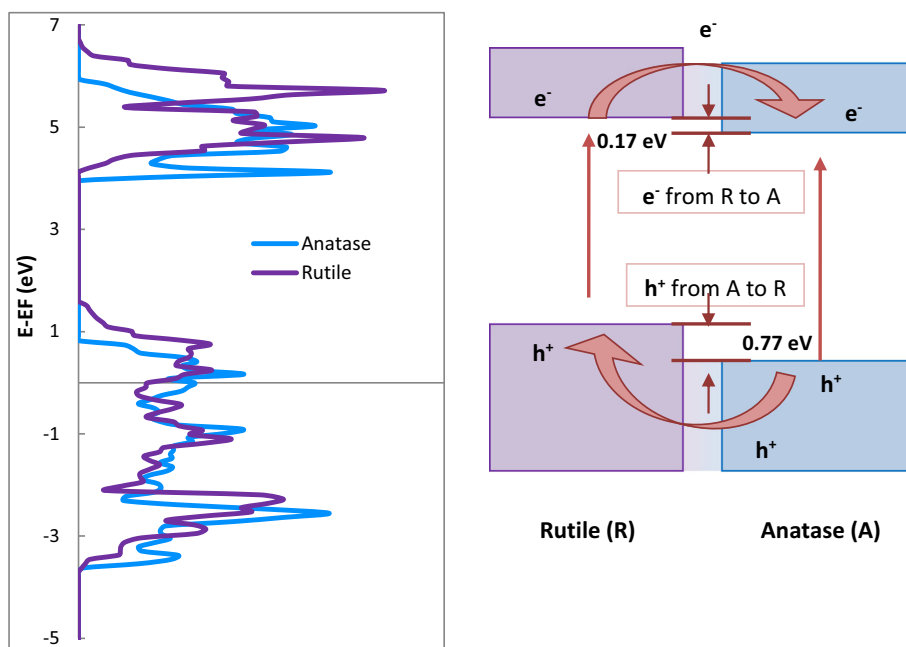





Table 1 Different possibilities of alignment using the common anion rule. Schemes of different anatase (in blue)/rutile (in violet) interfaces junction in mixed-phase TiO₂ are provided (Color figure online)

Experimental samples	Theoretical modeling of alignment	Example [references]
Homogeneous distribution of large grains	Bulk DOS of both polymorphs	[34] 
Small particles of one polymorph immersed in the other's matrix	Small particles: DOS of the more stable surface matrix; bulk DOS	[32] 
Homogeneous distribution of small particles	DOS of the most stable surfaces of both polymorphs	[35] 

The references given are examples of structures observed experimentally

a direct effect on the electronic structure. Neither is aligned in the same way bulk and surfaces, and when the difference in the size of the particles studied is very large this fact must be taken into account. The differences in the structures of bands of different surfaces would explain their differences in reactivity. It is therefore important to consider the importance of anisotropy in the alignment between bands. Recent investigations with absorption–excitation infrared spectroscopy show that the relative position of the bands of anatase and rutile and the consequent mobility of charges depend on the size

of the polymorphic phases involved and can be controlled by dynamic factors [38].

The catalytic reactions are essentially surface dependent, although the effect of bulk structure is important in the photonic process as it affects the excitation and charge transfer mechanisms. For studying the photocatalytic reactions, it is necessary to differentiate between the effects in the bulk and those in the surface.

For large areas of a given polymorph with small clusters immersed within the other polymorph, it could be assumed that the most appropriate alignment would be the bulk of the

Table 2 Energy differences between the CB minima (ΔE_C) and VB maxima (ΔE_V) for the indicated systems. Differences were calculated in such a way to always obtain positive values

Systems aligned	ΔE_V (eV)	ΔE_C (eV)
R/A	0.77 – A/R	0.17 – R/A
A/R(110)	1.17 – A/R	0.03 – A/R
R/A(101)	0.80 – A/R	0.05 – R/A
A(101)/R(110)	1.20 – A/R	0.10 – A/R
A(101)+V _O /R(110)+V _O	0.37 – A/R	0.66 – A/R
A(101)/R(110)+V _O	1.21 – A/R	0.10 – A/R

A anatase bulk, R rutile bulk, V_O oxygen vacancy. A(101) and R(110) are the corresponding surfaces of anatase and rutile phases of titania, respectively. The letters indicate where the electrons (CB)/holes (VB) come from and where they go

first with the more stable surface of the second. In highly heterogeneous structures and small domains, the best alignment could be assumed to be between surfaces, whereas for large domains in contact with each other with little space for relaxation between the grain boundaries it could be assumed that the best alignment would be the bulk alignment.

From the hypotheses presented in the previous paragraph, the results of alignment obtained for the different possibilities are presented in Table 2. They are: anatase bulk and rutile (110) surface (A/R(110)), rutile bulk (R) and anatase (101) surface (R/A(101)), pure anatase and rutile (A(101)/R(110)) surfaces, both surfaces with oxygen vacancies (V_O) (known as reduced surfaces) (A(101)+V_O/R(110)+V_O) and anatase (101) with rutile (101) with oxygen vacancies (A(101)/R(110)+V_O).

When small rutile particles are immersed in an anatase structure, the system could be analyzed by aligning the electronic structures of bulk anatase and rutile surface (110) as the case presented A/R(110) in Table 2. The corresponding alignment is pictured in Fig. 3a. In this situation, the theoretical result obtained is that the holes would concentrate on the rutile particles as well as the electrons.

For the R/A(101) system, the excited electrons in the CB of the rutile bulk migrate to the surface of the anatase, but the holes mobilize from the surface of the anatase to the bulk of rutile (Fig. 3b). This would benefit the reduction reactions on anatase nanoparticles supported on a rutile phase.

When the pure surfaces of anatase and rutile (A(101)/R(110)) are aligned (Fig. 3c), the energy differences between the valence bands would indicate that the holes are transferred from the anatase surface to the rutile surface. On the other hand, from the relative locations in the alignment for conduction bands it would be expected that the electrons would migrate from the anatase (101) surface to the rutile (110) surface. This would make mixed systems with high rutile content good oxidants and reducers simultaneously.

When the interface of our mixed titania catalyst is such that the band alignment occurs between the reduced surfaces of both polymorphs (A(101)+V_O/R(110)+V_O), the transfer of holes and electrons is from anatase surface to rutile surface (Fig. 4a).

The systems constituted by small particles most likely to be formed are those with pure anatase surfaces and reduced rutile surfaces (A(101)/R(110)+V_O). In this case, the analysis of the band alignment (Fig. 4b) would indicate that the direction of transfer of electrons and holes is from the anatase surface to the rutile surface. In principle, electrons and holes would be concentrated in the same polymorph.

In the considered case of alignment between small particles of rutile immersed in anatase (see Table 2 A/R(110) and A(101)/R(110)), it is observed that the transfer of electrons and holes would have the anatase-to-rutile direction. This conclusion is different from that observed against the alignment of bulk structures and could partially explain the different experimental results published in the literature. In addition, in each case analyzed for band alignment between surfaces, different states in the energy gap can be observed that could participate in both the separation and the annihilation of charges. The way in which these defect states are involved in the alignment is unclear, although it could be assumed that the holes transferred from VB from anatase to rutile could be transferred back to those gap states. A possible explanation of the direction of the charge carriers migration could be due to the holes generated in anatase would be favored in their migration toward the rutile (110) surface since in the last surface the vacancies are more stable and the holes would be attracted toward them. On the other hand, the sub-coordinated Ti of this surface (in greater number than in anatase TiO₂(101)) would attract the electrons. These observations would reinforce the hypothesis that between aligned surfaces the transfer of holes and electrons is from anatase to rutile titania.

3.3 Band bending in anatase and rutile

It is known that the charge carriers in anatase have longer lifetimes than in rutile. The measurements made by the microwave photoconductivity time-solved (TRMC) method in samples of anatase and rutile powders have been used as a tool for investigating the lifetimes of charge carriers in TiO₂ [39]. The experimental evidence from the work of Colbeau and his group would indicate that the absorption of UV light in rutile powders leads to the excitation of electrons and holes that disappear very quickly by recombination. Consequently, for this polymorph, illumination leads mainly to the conversion of light into heat. Thus, they explain that the probability of light-induced photocatalysis reactions is less probable to occur in rutile phase than in anatase. However, the long decay of TRMC in anatase powder indicates the availability of elec-

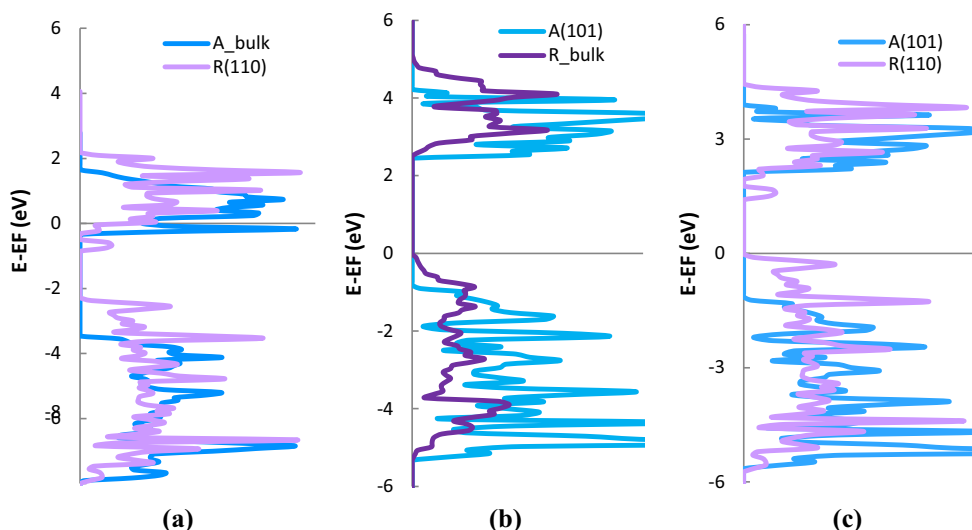
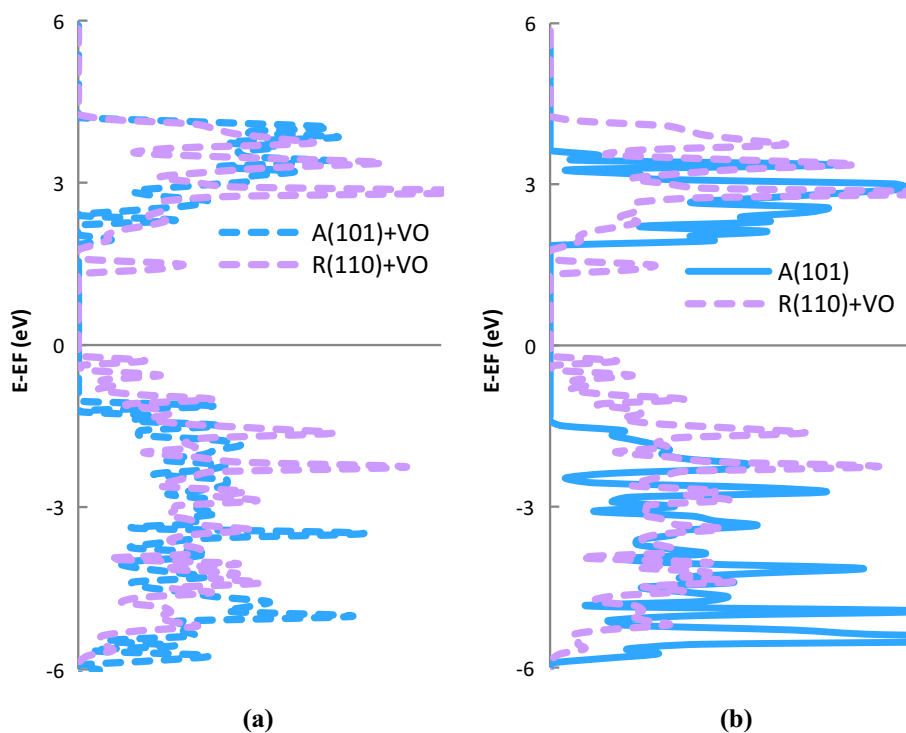


Fig. 3 **a** Alignment of the bands of anatase bulk (blue) and those of rutile (110) surface (lilac) according to common anion rule. **b** Alignment of the bands anatase (101) surface (blue light) and those of rutile bulk (violet) according to common anion rule. **c** Alignment of bands of pure anatase (101) surface (blue light) and rutile (110) surface (lilac) according to common anion rule (Color figure online)

Fig. 4 **a** Alignment by common anion of bands of anatase (101) surface with an oxygen vacancy (blue light) and rutile (110) surface with an oxygen vacancy (lilac). **b** Alignment of the bands of pure anatase surface (light blue) and rutile (110) surface with an oxygen vacancy (lilac) according to common anion rule (Color figure online)



trons for catalytic reactions, while excess holes are trapped at the surface. This relationship would explain in part why anatase is the most favorable TiO_2 structure for photocatalysis in pure samples. This higher rate of reconversion of light into heat for rutile is reflected in the lower specific heat of this one from the 200 K of temperature. The obtained values using Phonopy [40] are 51.09 J/K.mol for rutile and 55.30 J/K.mol

for anatase at 300 K similar to the experimental values of 54.13 J/K.mol and 54.62 J/K.mol, respectively [41].

These different half-lives of the charges generated between anatase and rutile have been explained by a difference in the band bending of both polymorphs [42] using the non-lens transient heterodyne detection (LF-HD-TG) technique; they studied the dynamics of charge carriers in anatase and rutile films made from TiO_2 nanoparticles. The decay of

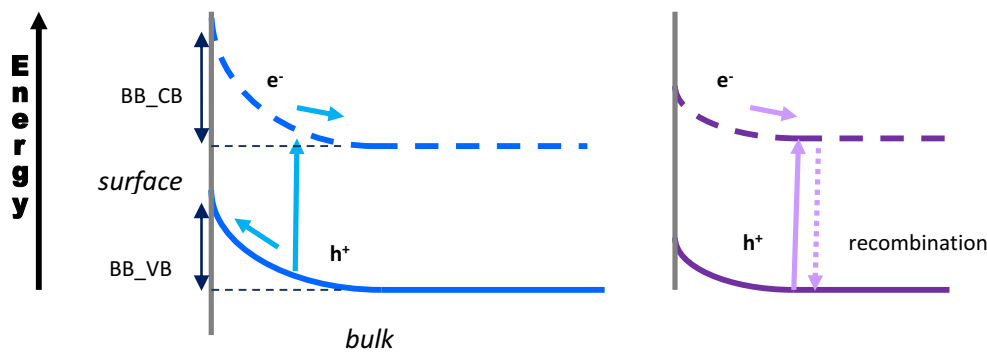


Fig. 5 Band bending of anatase (left) and rutile (right). The conduction bands are drawn in broken lines, and the valence bands are drawn in continuous lines

the concentrations of photoexcited holes in TiO₂ films can be directly measured by this technique, since the effective mass of the holes (m_h^*) is much greater than that of the electrons (m_e^*). These authors suggest that the relaxation of holes in anatase occurs through first-order kinetics with very short capture times, while in rutile these times are 100-fold longer. According to these authors, the differences in the relaxation processes of photogenerated holes between anatase and rutile were found to be independent of the size of the studied TiO₂ particle. In this work, they consider that one possibility to account for the observed differences would be the dissimilar curvatures of the bands. It is suggested that anatase has an inherently curved surface band that spontaneously forms in a deeper region with a more pronounced potential as compared to rutile. The dielectric constant of anatase (31) is much lower than that of rutile (173) [43]. This causes a much more pronounced bending of the surface band. Hence, many more photoexcited holes can be rapidly transported to the surface and trapped by the surface states. If this hypothesis is true, then the process of rapid capture of holes in TiO₂ anatase is an important reason for the rapid separation of charges, and therefore in part would explain the high photocatalytic activity of TiO₂ anatase. Contradictory values of effective mass have been reported [44, 45]. One of the parameters to estimate the mobility of charges is the effective mass (m^*). Rutile is generally reported to have a greater effective mass than for anatase. Even more, a strong anisotropy has also been observed in the reported values of rutile. The lower effective mass of the charges generated in the anatase results in a greater mobility, which would provide another factor to the explanation of the greater activity of anatase with respect to that of rutile. According to our calculations, the m_e^* is 0.317 for anatase in the direction $Z-\Gamma$ and 0.083 for rutile in the direction $\Gamma-X$, while the m_h^* is 0.061 for anatase and 0.171 for rutile in the same directions.

The band bendings of anatase and rutile titania are analyzed. For that purpose, the bands of anatase bulk and its (101) reduced surface and those of rutile bulk and its (110) reduced

surface have been aligned considering a common Fermi level. The reason for using the densities of the states of reduced surfaces is to be able to compare with experimental results. The corresponding band bending (BB) values obtained for anatase are 1.88 eV (BB_CB) and 2.20 eV (BB_VB), where BB_CB and BB_VB correspond to the energy differences between the bottom of the CB and the top of the VB of the bulk and the corresponding reduced surfaces, while for rutile are 0.73 eV (BB_CB) and 0.36 eV (BB_VB). Of these results, it follows that for anatase phase as well as for rutile one the photogenerated holes in the bulk are transferred to the surface, but in the case of anatase the electrons present greater difficulty to access because of the greater band bending that presents this polymorph. However, this allows a more efficient separation of charges than in the rutile where the holes that access the surface easily recombine with the electrons of the bulk [46] as it is shown in Fig. 5.

This theoretical conclusion agrees with the experimental results obtained by Luttrell's group [45]. These authors evaluated the photocatalytic activity related to the thickness of TiO₂ films and concluded that the transport of charges generated in the bulk depth of the sample to the surface is much more effective in anatase than in rutile.

4 Conclusions

Different possibilities of interaction in the alignment of bands were studied regarding the alignment of bands in the anatase–rutile systems. According to the obtained results, the charge transfer is sensitively dependent on the interfaces generated, which in turn is related to the different proportions of the polymorphs and the size of the particles considered in the mixture. In particular, mixed-phase systems involve the transfer of electrons from rutile to anatase and holes from anatase to rutile. This analysis would be applicable to real samples of mixed phase of titania with large particle size. However, for heterogeneous size particulate systems, it is

not only necessary to consider the alignment of bands of the bulk system, but also those of the corresponding surfaces. For example, the alignment of pure surfaces differs from that of defective surfaces due to the different electronic structure in the latter case coming from the generation of states in the energy gap.

In relation to the analysis performed, the best mixed systems to improve its oxide-reducing capacity by increasing the lifetime of the generated charges are those composed by large particles of both polymorphs or by small particles of anatase dissolved in rutile. Our results provide information for the design of different possible mixed anatase–rutile heterojunctions, based all of them on the same theoretical background, which will be of usefulness for the experimentalists.

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