# Origin of the type-II band offset between rutile and anatase titanium dioxide: Classical and quantum-mechanical interactions between O ions

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Titanium dioxide is one of the most promising semiconductors for photocatalytic splitting of water for hydrogen. The mixed rutile/anatase system shows even more favorable photocatalytic properties than the pristine ones. Band offset is a key factor that determines the photocatalytic activity of the mixed phase. However, the type of band alignment and the value of the band offset are still under debate both experimentally and theoretically. The difficulty of determining the band offset by commonly used core-level alignment calculation lies in the different symmetry and large lattice mismatch between the two phases. Here, we adopt our recently developed three-step method, which can overcome the lattice mismatch problem, to study the band offset with high accuracy. In the calculation, we used an intermediate phase TiO<sub>2</sub>II to build superlattice models of rutile(101)//TiO<sub>2</sub>II(001) and TiO<sub>2</sub>II(100)//anatase(112) to determine the core-level alignment. Our studies show a type-II, staggered band alignment, with the valence band maximum (VBM) of rutile 0.80 eV above that of anatase, in agreement with recent experimental results. We further analyzed the electronic structure of the two phases, and found that the band offsets of the VBM originate from both the electrostatic interaction and electronic hybridization in rutile and anatase, which contribute 0.36 eV and 0.44 eV, respectively.

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## I. INTRODUCTION

Titanium dioxide  $(TiO_2)$  is widely used in solar cells, photocatalysts, and pigmentations [1–6]. In the past several decades, a tremendous amount of experimental and theoretical research has studied its photoactivity since Fushijima and Honda [7] discovered the photoelectrochemical activity of TiO<sub>2</sub> anodes in 1971. Among the many polymorphs of TiO<sub>2</sub>, rutile, anatase, and brookite are the most common. Rutile and anatase have wide band gaps of 3.03 and 3.20 eV, respectively, which lead to a low absorption efficiency in the solar spectrum [8]. It has been a longstanding puzzle why mixed-phase TiO<sub>2</sub> has better photocatalytic properties than either single-crystal rutile or anatase [9–14]. The reason for the increased reactivity may be attributable to several factors, including charge separation and interfacial charge transfer effects, which come down to the band offset problem.

The physical mechanism between the band offset of rutile and anatase is still unclear, even though large efforts have been made both experimentally and theoretically [15,16]. Through electrochemical impedance analysis, Kavan *et al.* [17] found that the conduction band of anatase is 0.2 eV above that of rutile (type-II rutile), which would cause the transfer of holes from rutile to anatase, as observed in other experiments [18,19]. However, recent x-ray photoelectron spectroscopy (XPS) measurements showed that the conduction band of anatase is 0.2 eV [20] or  $0.6 \sim 0.8$  eV [21] below that of rutile (type-II anatase). Hence, the issue of the band offset between rutile and anatase is still under debate experimentally. A computational approach may clarify this debate, but it is difficult to obtain the band offset between rutile and anatase directly because it has not been possible to construct a heterostructure interface that preserves the bulk structures on both sides of the interface. Various attempts were made to calculate the band offset, such as the branch point energy (BPE) method, the passivated quantum dot (OD) method, electronic potential profiling (EPP) [22-24], the energetics of localized holes or electrons in biphase crystals [25], and quantum-mechanical/molecularmechanical (QM/MM) method [20,26,27]. The BPE method calculates the band offset by sampling the bulk band structure. In QD calculations, large supercells of different phases are built to calculate the band offset by aligning the core-level energy. The EPP method calculates the band offset by measuring the electronic potential of a superlattice, containing over 1000 atoms built with two different phases of  $TiO_2$  [24,28]. QM/MM calculates the band offset by a core-shell model. BPE only considers the bulk properties and discards the interfacial effects, while the other methods face the problem of constructing an interface between two different phases. The band offset between rutile and anatase measured or calculated are all listed in Table I. Up to now, neither the experimental nor the computational results agree with each other, as discussed in a recent article [16].

To definitely clarify the band offset between rutile and anatase, we have combined our newly developed three-step method [29] and the core-level alignment method with a special construction of interface. The core-level alignment method is believed to be a reliable method, which can predict the band offset with high precision [30]. However, this method cannot be directly applied to calculate the band alignment of rutile and anatase because of the difficulty in

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TABLE I. Band offset between rutile and anatase from experiment or calculation.

	Year	VBO (eV)	CBO (eV)	Туре
	2011 [26]	0.55	0.35	II
	2012 [27]	0	-0.2	Ι
	2013 [20]	0.39~0.47	0.17~0.30	II
Theoretical	2013 [21]	0.63	0.39	II
Results	2014 [22]	0.52	0.22	II
	2014 [23]	0.86~0.90	0.65~0.69	II
	2015 [24]	0.41	0.21	II
	2015 [25]	0.39	0.22	II
	present work	0.80	-	II
	1996 [17]	_	-0.2	Ι
Experimental	2007 [43]	0.2	-	II
Results	2013 [20]	0.39	0.22	II
	2013 [21]	0.60~0.80	-	II

building a supperlattice of the two phases, due to the different symmetry and the large lattice mismatch. In this paper, we solved this problem by adopting a high-pressure phase, TiO<sub>2</sub>II,  $\alpha$ -PbO<sub>2</sub>-like form, as the key intermediate phase, which can match well with both rutile and anatase. The interface between rutile(101)//TiO<sub>2</sub>II(001) and TiO<sub>2</sub>II(100)//anatase(112) can be perfectly formed [31]. With the constructed interface, we apply an accurate three-step method to calculate the band offset between rutile, TiO<sub>2</sub>II and anatase. We found a type-II, staggered band alignment, with the valence band maximum (VBM) of rutile 0.8 eV above that of anatase. Both electrostatic interaction and electronic hybridization are found to contribute to the staggered band offset through both Madelung potential calculations and tight-binding calculations.

#### **II. METHODS**

## A. Core-level alignment method and three-step method for band offset calculation

The core-level alignment method developed by Wei and Zunger is commonly used to calculate the band offset between structures with a small lattice mismatch [30]. Following the procedure used in XPS analysis, one may calculate the valence band offset between two hypothetical compounds L and R by

$$\Delta E_{v}(L/R) = \Delta E_{v,C^{*}}^{R} - \Delta E_{v,C}^{L} + \Delta E_{C,C^{*}}^{L/R} , \qquad (1)$$

where  $\Delta E_{v,C}^{L}$  and  $\Delta E_{v,C^*}^{R}$  are the energy separation from the core level (*C* and *C*<sup>\*</sup>) to the VBM of the corresponding materials, which can be obtained by bulk calculation and  $\Delta E_{C,C^*}^{L/R}$  is the energy difference in core levels of the two materials under a common energy reference, which is calculated using the deep-lying core states from the calculation of an (*L*/*R*) (001) heterojunction supercell. Here, the core level on each side of the heterojunction is assumed to preserve the bulk value, neglecting the influence from the volume deformation to the core level, which is only suitable for systems with negligible lattice mismatch. This method is largely improved by taking account of deformation potentials of energy levels [32,33].

In order to extend this idea to systems with a larger lattice mismatch, we recently proposed a new method, the three-step method [29]. Here, the lattice constants of *L* are denoted as  $(a_1,a_2,a_3)$  and those of *R* are  $(b_1,b_2,b_3)$ . In the first step, *L* is expanded along the [100] direction by  $(b_1 - a_1)/a_1$ , which is denoted as *L'* with lattice constant  $(b_1,a_2,a_3)$ .  $\Delta E_{C,C'}^{L/L'}$  is the core level difference between *L* and *L'*, which is obtained from the calculation of the heterostructure of L/L' along the [100] direction. In the second step, *L''* is constructed from expanding *L'* along [010] by  $(b_2 - a_2)/a_2$ , and the core level difference  $\Delta E_{C,C'}^{L/L'}$  is obtained from the calculation of the heterostructure of the heterostructure of *L'/L''* along the [010] direction. In the third step, the core level difference  $\Delta E_{C,C'}^{L/L'}$ , between *L''* and *R* is obtained from the calculation of the heterostructure of *L'/R* along the [001] direction. With all the three steps, the valence band offset between two compounds *L* and *R* is calculated by

$$\Delta E_{v}(L/R) = \Delta E_{v,C^{*}}^{R} - \Delta E_{v,C}^{L} + \Delta E_{C,C'}^{L'L'} + \Delta E_{C',C^{*}}^{L'/L''} + \Delta E_{C'',C^{*}}^{L''/R}$$
(2)

The derived band offset is accurate in the three-step method without any approximation [29]. It is also worth noting that the calculation procedure is straightforward.

#### B. Calculation details for electronic structure

In this work, our studies are based on the density functional theory (DFT) method for structural relaxation and electronic structure calculation. The ion-electron interaction is treated by the projector augmented-wave (PAW) technique [34], as implemented in the Vienna *ab initio* simulation package (VASP) [35]. The exchange-correlation potential is treated using the Perdew-Burke-Ernzerhof (PBE) [36] functional. The basis set cutoff is 500 eV. The *k* mesh is generated by the Monkhorst-Pack scheme [37], and the density of *k* points is approximately  $0.04 \text{ Å}^{-1}$ . Our calculations predict the lattice constants for the rutile and anatase within 3% difference from experimental results (Table S1 in the Supplemental



FIG. 1. Bulk phase structures for (a) rutile, (b) anatase, and (c)  $TiO_2II$  and heterostructures for (d)  $rutile(101)//TiO_2II(001)$  and (e)  $TiO_2II(100)//anatase(112)$ . Gray (or blue) and red spheres represent Ti and O atoms, respectively.

Material [38]). The Brillouin zones for rutile and anatase are plotted in Fig. S1 [38]. The Madelung potential is calculated by means of the Ewald summation using the general utility lattice program (GULP) [39]. Maximally localized Wannier functions [40,41] are employed to calculate the hopping parameters between the Ti d orbitals and O p orbitals. When constructing the Wannier functions, we considered five 3dorbitals for each Ti atom and three 2p orbitals for each O atom. Since there are two Ti atoms and four O atoms in the primitive cell of both rutile and anatase, there are 22 Wannier functions in total. The PBE wave function is used as the input. The Wannier functions are well localized, and the O p orbitals of both rutile and anatase are plotted in Fig. S2 [38].

# **III. RESULTS AND DISCUSSION**

The difficulty of building a computational superlattice between rutile and anatase lies in the different symmetry and large lattice mismatch between the two phases, however,



FIG. 2. (a) The model for calculating the valence band offset between *R* and *R'* phases using the three-step method. In the first step, we expand the lattice constant *a* to *a'*, and a heterostructure is built along the [100] direction to calculate the core level difference. In the second and third step, the lattice constants *b* and *c* are expanded successively. (b) Schematic alignment procedure used to calculate the natural valence band offsets for rutile, anatase and TiO<sub>2</sub>II. The valence band offsets of *R*/*R'* and *A*/*A'* are calculated by the three-step method while *R'*/II and *A'*/II are calculated by core-level alignment. The top of the rectangle corresponds to the energy level of the VBM of the TiO<sub>2</sub> phases, which are also indicated on the rectangle. The VBM of TiO<sub>2</sub>II is set as 0 eV. (c) Valence and conduction band alignment mechanisms for rutile/anatase interface. The arrows indicate the flow of electrons (holes) in the conduction band (valence) band.

TiO<sub>2</sub>II (II) was recently found to form a perfect interface with either rutile or anatase [31], allowing a defect-free superlattice of *R*/II and *A*/II. Before constructing the interface, the structures of rutile, anatase and TiO<sub>2</sub>II are optimized by PBE calculation. The optimized crystal structures are plotted in Figs. 1(a)–1(c). The rutile (101) surface has a cell size of  $4.62 \text{ Å} \times 5.48 \text{ Å}$ , which we change to  $4.58 \text{ Å} \times 5.59 \text{ Å}$  (*R'* phase) to match the TiO<sub>2</sub>II (001) surface, and construct a heterostructure of rutile (101)/TiO<sub>2</sub>II(001) [*R'*(101)/II(001)] [Fig. 1(d)]. The anatase (112) surface has a cell size of  $5.37 \text{ Å} \times 5.58 \text{ Å}$ , which we adjust to  $4.93 \text{ Å} \times 5.59 \text{ Å}$  (*A'* phase) to match the TiO<sub>2</sub>II (100) surface and construct anatase (112)/TiO<sub>2</sub>II(100) [*A'*(112)/II(100)] [Fig. 1(e)]. All the heterostructure models we built are electrically neutral and stoichiometric.

From this superlattice, we calculated the band offset step by step by using both the core-level alignment method and the three-step method. The band offsets of R'/II and A'/IIwere calculated by core-level alignment using Eq. (1) [30], and are denoted as  $\Delta E_v(R'/II)$  and  $\Delta E_v(II/A')$ , respectively. The valence band offset between R and R' (A and A') was calculated by the three-step method [29]. The models of how rutile changes from R to R' are built according to the steps in Fig. 2(a) (A to A' in Fig. S3 [38]), and the core level alignment is denoted as  $\Delta E_v(R/R')$  for rutile and  $\Delta E_v(A/A')$  for anatase. The computational progress is schematically shown in Fig. 2(b), where the VBM of TiO<sub>2</sub>II is set as 0 eV. The results of core-level alignment calculations for  $\Delta E_v(R'/II)$ and  $\Delta E_{\nu}(\Pi/A')$ , are 0.69 eV and 0.17 eV, respectively. The three-step method yields that  $\Delta E_v(R/R')$  is -0.16 eV and  $\Delta E_v(A/A')$  is -0.10 eV. All the band offsets calculated by the core-level alignment method or the three-step method satisfy the transitivity relation, which means that if the band offsets of A/B and A/C are known, then that of B/C can be calculated by subtracting A/B from A/C. Finally we obtain the band



FIG. 3. (a) Comparison of the electronic density of states of rutile and anatase calculated by the PBE functional. The VBM is marked by a dashed gray line, and the VBM of anatase is 0.8 eV below that of rutile. (b) The number versus distance of neighbor atoms centered on an O atom in rutile and anatase. The gray and red triangles point out the nearest Ti atoms and the second-nearest O atoms, respectively.

offset between rutile and anatase by:

$$\Delta E_v(A/R) = \Delta E_v(R/R') + \Delta E_v(R'/II) + \Delta E_v(II/A') + \Delta E_v(A/A').$$
(3)

We conclude that the valence band edge of rutile lies about 0.80 eV above that of anatase. Based on the general consensus that the band gaps of rutile and anatase are 3.03 and 3.20 eV respectively [20], the conduction band offset of rutile is about 0.6 eV above that of anatase. The band offset between rutile and

anatase TiO<sub>2</sub> is shown in Fig. 2(c). This staggered type-II band offset would favor the transfer of photogenerated electrons from rutile to anatase, and the transfer of holes from anatase to rutile. Our result supports the very recent experimental work conducted by Pfeifer *et al.* [21] with VBM of rutile 0.7  $\pm$  0.1 eV above that of anatase.

It is interesting to understand why there is a 0.80 eV band offset between rutile and anatase, so we looked into the electronic structure properties of rutile and anatase. According to the common anion rule alignment [42], the valence band offset should be small between oxides, except the case where



FIG. 4. The tight-binding band structure of rutile and anatase. The band structure of rutile and anatase with only the nearest Ti-O interaction are plotted in (a) and (c) as a green line, respectively. The band structure of rutile and anatase with both the nearest Ti-O and second nearest O-O interactions are plotted as red dots in (b) and (d), respectively. The PBE band structures are shown for comparison in (b) and (d) as a black line. (e) Schematic illustration of the VBM shift of rutile and anatase. If only electrostatic interaction is considered, the VBM of rutile shifts 0.36 eV compared to anatase due to the Madelung potential, which is illustrated as a blue line. If electronic hybridization is added, the widenings of the VBMs of rutile and anatase are 5.72 eV and 4.84 eV, respectively, and the green curve and red curve represent the band including the first-nearest interaction only and include both nearest and second-nearest interaction. Both the contributions from electrostatic interaction and electronic hybridization result in a total offset of 0.80 eV.

cation orbitals contribute to the valence band. However, from the results of DFT calculations [Fig. 3(a)], the valence band edge is dominated by O 2p. The valence parts of DOS are similar among rutile and anatase, except that there is a long tail,  $\sim 0.8 \text{ eV}$ , at the top of the valence band of rutile.

To find the origin of the tail, we first examined the structural difference between rutile and anatase. We analyzed the characteristics of the structures by counting the number versus distance of neighbor atoms centered on an O atom, which is plotted in Fig. 3(b). (The detailed difference in the O local environment between rutile and anatase is shown in Fig. S4 [38].) The nearest-neighbor atoms of O in both phases are three Ti atoms, with nearly identical bond lengths. The structural difference comes largely from the second nearest, O atoms. There are 11 second-nearest O atoms surrounding an O atom in rutile while there are only 10 in anatase. The local structural difference may induce twofold contributions to the band alignment: electrostatic interaction and electronic hybridization.

The electrostatic contribution to the band offset, which is the Coulomb interaction between Ti and O atoms, was calculated by Ewald summation. The calculation showed that the Madelung electrostatic potential of O atoms are 25.79 eV and 26.15 eV in rutile and anatase, respectively (note that a smaller electrostatic potential suggests a higher electronic level). This makes the center of the O 2*p* valence bands in rutile higher by 0.36 eV compared to anatase. Our result is close to that of Scanlon *et al.* [20], which is calculated using the polarizable shell model. The difference in Madelung potential is because that the O<sup>2–</sup> ion in rutile has more neighboring O<sup>2–</sup> ions than that of anatase.

The band offset cannot be fully accounted for by considering only the Madelung potentials. The remaining contribution is caused by electron hybridization. A clue is that the O 2pband in rutile has a larger bandwidth than that in anatase [see the DOS plot in Fig. 3(a)]. Although the nearest-neighbor environment of O in both phases is similar, the secondnearest neighbors are obviously different. We studied the electronic hybridization strength of both phases by calculating the hopping parameters using maximally localized Wannier functions [40,41]. Based on the hopping parameters between orbitals, including O 2p and Ti 3d of rutile and anatase in the Supplemental Material [38], we constructed the tight-binding band structure with only Ti-O interactions and with both O-O and Ti-O interactions. When we consider the nearest Ti-O interactions only, the band structures of rutile and anatase are evidently different from the PBE band structure [Figs. 4(a) and 4(c). In this case, we find that the bandwidths of O 2p bands in rutile and anatase are 4.09 eV and 3.67 eV, respectively. When we consider both the nearest Ti-O and O-O interaction, the band structures are substantially improved, especially the VBMs of rutile and anatase fit well with the PBE band structure [Figs. 4(b) and 4(d). Importantly, the O-O interaction makes the bandwidths (5.72 eV and 4.84 eV in rutile and anatase, respectively) of O 2p bands wider in both phases. Therefore, the bandwidth of 2p bands in rutile is larger by 0.88 eV than that in anatase mainly due to the O-O interaction.

With our above results, we are now in position to fully understand the origin of the band offset between rutile and anatase. First we align the center of the O 2p orbitals according the Madelung potential of O atoms so that the center of the O 2p bands in rutile is 0.36 eV above that in anatase, as illustrated by blue lines in Fig. 4(e). Then we add the electronic hybridization. If the O-O interaction is considered, the bandwidth of rutile will be 0.88 eV wider than that of anatase, which contributes 0.44 eV to the band offset, as illustrated by the red curve in Fig. 4(e). Both electrostatic interaction and electronic hybridization contribute to the rise of the VBM of rutile, and the total effect gives a band offset of 0.80 eV.

# **IV. CONCLUSION**

We propose a strategy to calculate the band offset between rutile and anatase through an intermediate phase TiO<sub>2</sub>II by combing the core-level alignment method with the threestep method. The result reveals a staggered energy band alignment, with the VBM of rutile about 0.80 eV above that of anatase, which is supported by the very recent experimental data [21] with the VBM of rutile  $0.7 \pm 0.1$  eV above that of anatase. By further analyzing crystal structure and electronic structure, we found that the band alignment is originated from both the electrostatic interaction and electronic hybridization, contributing 0.36 eV and 0.44 eV, respectively. Understanding the origins of the staggered band offset may lead to new ways to manipulate the interface to further improve the efficiency of TiO<sub>2</sub>-based photocatalysis.

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