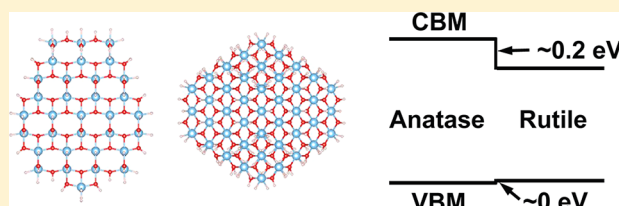


## Calculating Band Alignment between Materials with Different Structures: The Case of Anatase and Rutile Titanium Dioxide

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**ABSTRACT:** A method to calculate the band alignment between materials with different structures using passivated quantum dots is proposed. By using this method, the rutile/anatase titanium dioxide band offset is determined. The valence band maxima of anatase and rutile are close to each other, whereas the conduction band minimum of anatase is found to be about 0.2 eV higher than that of rutile, which is in agreement with the experimental fact that anatase has higher photocatalytic activity. The reliability of this method is further tested on several semiconductors, and reasonable results are obtained for most cases.



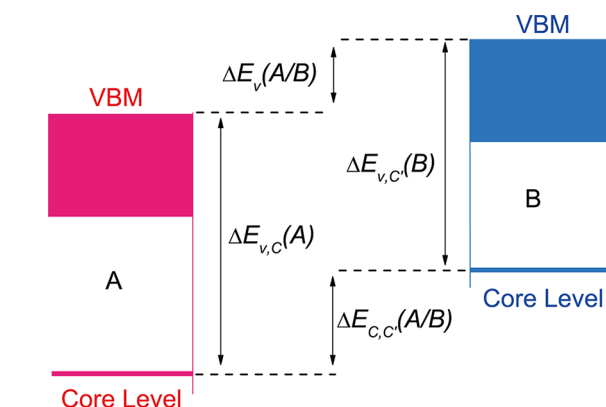
## INTRODUCTION

Band offset between two semiconductor compounds or organic polymers A and B forming a heterostructure is one of the most important parameters in material design and device modeling<sup>1</sup> because it forms a solid-state scale of electronegativity that determines charge transport across the heterojunction interface and chemical activity.<sup>2,3</sup> It also decides the quantum confinement in quantum wells, wires, and dots.<sup>4–6</sup> Furthermore, the absolute alignment of the band edge states determines the dopability of a material.<sup>7</sup> Therefore, it is crucial to be able to predict and understand the chemical trends of the band alignment because it plays an important role in renewable energy applications, such as solar cells and photoelectrochemical water splitting.

Experimentally, to determine the band alignment between different materials, the X-ray photoemission spectroscopy method can be used to measure the core-state energy, which is then taken as an energy reference to determine the energy of other energy levels.<sup>8</sup> Theoretically, a similar scheme is developed, as shown in Figure 1, in which the valence band offset is calculated by<sup>9–11</sup>

$$\Delta E_v(A/B) = \Delta E_{v,C'}(B) - \Delta E_{v,C}(A) + \Delta E_{C,C'}(A/B)$$

Here,  $\Delta E_{v,C}(A)$  and  $\Delta E_{v,C'}(B)$  are the energy separations from the core level to the valence band maximum (VBM) in corresponding bulk materials, which can be obtained from bulk calculations.  $\Delta E_{C,C'}(A/B)$  is the core-level energy difference of the two materials under a common energy reference. Usually,  $\Delta E_{C,C'}(A/B)$  is calculated using the deep-lying core states from both sides of a (A/B) heterostructure and assuming that the core levels on each side of the heterostructure preserve their individual bulk values or with only a constant shift. This approach is proven to work well for numerous systems, such as III–V and II–V semiconductors.<sup>10,11</sup> However, this approach



**Figure 1.** Illustration of the scheme to calculate the band offset using the core-level reference.

has limitations because, when structures of the two materials are very different, constructing a heterostructure that preserves most of the properties of the pure materials is nearly impossible. One example is titanium dioxide (TiO<sub>2</sub>), which, due to its high photocatalytic activity, high stability, and low cost, is one of the most promising materials for photocatalysis applications, such as H<sub>2</sub> production from water splitting.<sup>12–15</sup> TiO<sub>2</sub> has two main crystal structures, that is, anatase and rutile structures, which have different band alignments and photocatalytic capacities.<sup>3</sup> However, it is difficult to obtain the band offsets between the anatase and the rutile TiO<sub>2</sub> phases because these two structure are very different; thus, it is not possible to construct a heterostructure interface that preserves the bulk

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structures on the two sides of the interface. People have tried to use other methods to calculate the band alignment, such as the one based on the branching point energy (BPE), which is defined as the weighted average of midgap energies over the  $k$ -point meshes.<sup>16</sup> In this approach, only the bulk band structure is needed. Although it has been successfully applied to several systems,<sup>16,17</sup> its validity is still questionable because the number of bands used in such a calculation is not a very well defined quantity, especially when the atomic d band is involved. For example, when dealing with the rutile/anatase system, the BPE method predicts that the conduction band minimum (CBM) of anatase is about 0.35 eV lower than that of rutile.<sup>18</sup> Such an alignment is in opposition to the experimental fact that anatase is more efficient than rutile in photocatalysis<sup>3</sup> since a higher CBM leads to higher electron transfer activity. Hence, the issue of how to calculate the band offset between anatase and rutile TiO<sub>2</sub> is still under debate. In this work, we proposed a method to calculate the band alignment between materials with different structures and show that a correct rutile/anatase band offset can be obtained using this method.

## METHODS

All calculations are performed using the frozen-core projector augmented wave method<sup>19,20</sup> as implemented in the Vienna Ab-initio Simulation Package.<sup>21,22</sup> The local density approximation (LDA) is adopted. Despite the band-gap error, in many cases, the valence band offset calculated by LDA is practically reasonable.<sup>10,11,23</sup> It should also be noted that the proposed approach in this work is general and can be used with methods going beyond LDA. The cutoff energy for plane-wave expansion is 400 eV, and the threshold for structure relaxation is 0.05 eV/Å.

Bulk properties of anatase and rutile are calculated first. The optimized lattice constants are  $a = 3.77$  Å and  $c = 9.44$  Å for anatase, and for rutile,  $a = 4.57$  Å and  $c = 2.92$  Å are obtained. These results are in agreement with experiment.<sup>24</sup> LDA calculations predict an indirect band gap of 1.87 eV for anatase and a direct band gap of 1.68 eV for rutile. Although the band-gap values are severely underestimated, the band-gap difference between anatase and rutile is well-reproduced.<sup>3</sup> The core-level energy is determined by the average of 1s states of one Ti and two O atoms in the bulk. From the bulk calculation, the core level-to-VBM energy separations,  $\Delta E_{v,C}$ , for anatase and rutile can be obtained.

The next issue is to calculate the bulk core-level energy difference,  $\Delta E_{C,C'}$ , between anatase and rutile. Our basic idea is to use quantum dots (QDs). We construct a supercell containing one anatase TiO<sub>2</sub> QD and one rutile TiO<sub>2</sub> QD and do a self-consistent calculation for this supercell. Because the two QDs are in the same supercell, they have the same energy reference, and the core-level energy difference between the atoms in the two QDs can be determined directly. It can be expected that, when the QD is large enough, the center region of the QD would render bulk properties. Therefore, the atoms in the center of the two QDs are almost identical to those in bulk material, and the  $\Delta E_{C,C'}$  can be calculated by the core-level energy difference between these center atoms. In this approach, there is no need to construct a heterojunction; thus, it can be applied to materials with different structures.

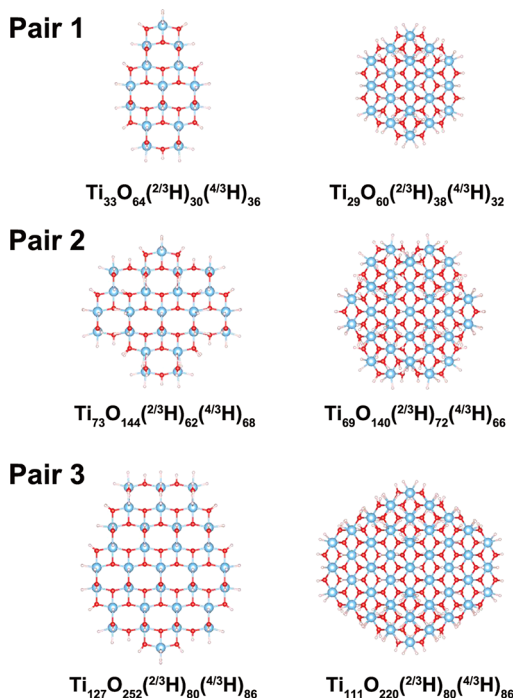
For QD calculations, an important issue is how to deal with the surface dangling bonds. To model an ideal QD, the dangling bonds should be passivated properly. A scheme to use pseudohydrogen atoms <sup>2</sup>H with a fractional nuclear charge  $Z$  to

mimic the passivation of the QD has been suggested recently.<sup>25,26</sup> It is found that such a scheme, which can remove the surface states of the QD, works quite well. The fractional nuclear charge  $Z$  of the pseudohydrogen atoms used is determined by the valence and coordination number of the atoms in different material. In both anatase and rutile TiO<sub>2</sub>, Ti atoms are in a +4 valence state with 6-fold coordination, while O atoms are in a -2 valence state with 3-fold coordination. Each Ti (O) atom contributes (receives) 2/3 electron to (from) each O (Ti) atom. Therefore, a pseudohydrogen with  $Z = 2/3$  (<sup>2/3</sup>H) should be used to passivate O dangling bonds as O needs  $(2/3) \times 3 = 2$  electrons to satisfy the octet rule, while the pseudohydrogen with  $Z = (2 - 2/3) = 4/3$  (<sup>4/3</sup>H) should be used to passivate Ti dangling bonds since two electrons are needed to form a H 1s closed shell. On the basis of these considerations, we construct anatase and rutile QDs as follows: First, a near spherical QD with radii of  $r$  and a Ti atom fixed in the center is cut out from optimized bulk structure. Next, on the basis of a previous molecular dynamics simulation,<sup>27</sup> the Ti atoms with more than two dangling bonds, as well as the O atoms with more than one dangling bond, are removed from the QD. Finally, the surface O atoms are passivated using <sup>2/3</sup>H, and the surface Ti atoms are passivated using <sup>4/3</sup>H. To ensure that the bulk properties are maintained, during the structure relaxation, the Ti and O atoms are fixed at their corresponding bulk positions, while only H atoms are allowed to relax. Such a relaxation scheme makes it possible to use relatively small QDs to achieve the convergence in the calculated core-level difference, since the core-level energy is sensitive to the local environment of atoms. A sufficient vacuum layer (larger than 15 Å) is used to avoid interaction between the QDs.

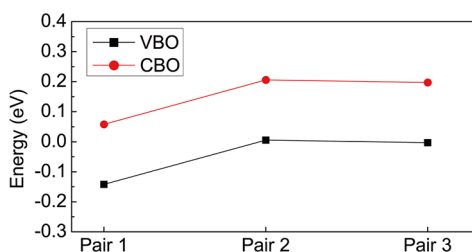
## RESULTS AND DISCUSSION

To explore how the sizes of the QDs affect the calculated band offset, we construct three pairs of anatase and rutile QDs, as seen in Figure 2. The sizes of QDs are different in different pairs. The first pair contains an anatase Ti<sub>33</sub>O<sub>64</sub>(<sup>2/3</sup>H)<sub>30</sub>(<sup>4/3</sup>H)<sub>36</sub> and a rutile Ti<sub>29</sub>O<sub>60</sub>(<sup>2/3</sup>H)<sub>38</sub>(<sup>4/3</sup>H)<sub>32</sub>, the second pair contains an anatase Ti<sub>73</sub>O<sub>144</sub>(<sup>2/3</sup>H)<sub>62</sub>(<sup>4/3</sup>H)<sub>68</sub> and a rutile Ti<sub>69</sub>O<sub>140</sub>(<sup>2/3</sup>H)<sub>72</sub>(<sup>4/3</sup>H)<sub>66</sub>, and the third pair contains an anatase Ti<sub>127</sub>O<sub>252</sub>(<sup>2/3</sup>H)<sub>80</sub>(<sup>4/3</sup>H)<sub>86</sub> and a rutile Ti<sub>111</sub>O<sub>220</sub>(<sup>2/3</sup>H)<sub>80</sub>(<sup>4/3</sup>H)<sub>86</sub>. The reasonableness of the choice of QDs can be further confirmed by the electron counting based on the oxidation numbers. In the QDs, the valence states are +4 for Ti, -2 for O, +1 for <sup>2/3</sup>H, and -1 for <sup>4/3</sup>H. Taking the anatase Ti<sub>33</sub>O<sub>64</sub>(<sup>2/3</sup>H)<sub>30</sub>(<sup>4/3</sup>H)<sub>36</sub> as an example, such oxidation numbers lead to 292 occupied levels (64 O<sup>2-</sup> and 36 H<sup>-</sup>). The number of electrons in this QD is also 292, which validates the occupancy. In the calculations, the average energy of 1s states of one Ti and two O atoms in the center of the QD is taken as the core-level energy and is used to predict the band offset. The calculated band offset using different QD pairs are shown in Figure 3. The conduction band offset (CBO) is obtained according to the calculated valence band offset (VBO) and the experiment band-gap values (3.2 and 3.0 eV for anatase and rutile, respectively<sup>3</sup>). It can be seen that the results converge to a constant when the sizes of the used QDs increase. This is consistent with the expectation that, when the QD is sufficiently large, the center region will render bulk properties. For different systems, the QD size should be carefully tested to ensure converged results.

In contrast to the conclusion in ref 18, our results suggest that the rutile/anatase VBO is close to zero, while the rutile/



**Figure 2.** Schematic of the three QD pairs used to calculate the rutile/anatase band offset. Pair 1: anatase  $\text{Ti}_{33}\text{O}_{64}(\frac{2}{3}\text{H})_{30}(\frac{4}{3}\text{H})_{36}$  and rutile  $\text{Ti}_{29}\text{O}_{60}(\frac{2}{3}\text{H})_{38}(\frac{4}{3}\text{H})_{32}$ . Pair 2: anatase  $\text{Ti}_{73}\text{O}_{144}(\frac{2}{3}\text{H})_{62}(\frac{4}{3}\text{H})_{68}$  and rutile  $\text{Ti}_{69}\text{O}_{140}(\frac{2}{3}\text{H})_{72}(\frac{4}{3}\text{H})_{66}$ . Pair 3: anatase  $\text{Ti}_{127}\text{O}_{252}(\frac{2}{3}\text{H})_{80}(\frac{4}{3}\text{H})_{86}$  and rutile  $\text{Ti}_{111}\text{O}_{220}(\frac{2}{3}\text{H})_{80}(\frac{4}{3}\text{H})_{86}$ .

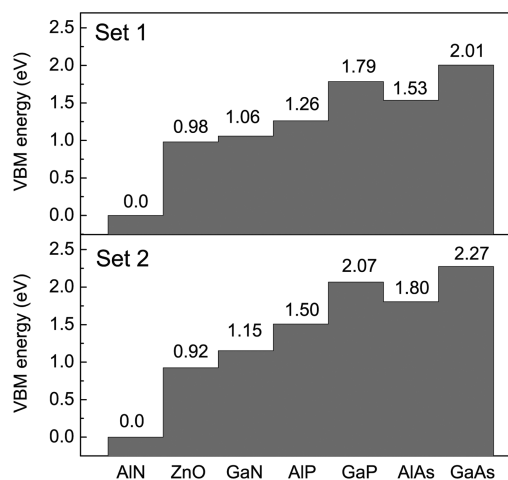


**Figure 3.** Calculated rutile/anatase VBO and CBO using different QD pairs. Pair 2 is found to be sufficient to converge the results. The CBO is deduced from the calculated VBO and the experimental band-gap values. Positive values indicate that the CBM or VBM of anatase is higher than that of rutile.

anatase CBO is about 0.2 eV, with the CBM of anatase being higher. Such a band alignment can be easily understood. In both anatase and rutile, Ti is in a +4 valence state and O is in a -2 valence state. Moreover, local environments of Ti or O atoms are similar, which can be described as chains of distorted  $\text{TiO}_6$  octahedra, indicating that the Ti–O bonding characters in anatase and rutile are similar. It has been shown previously that the VBO between structures that have similar bonding characters (such as zinc-blende (ZB) and wurtzite (WZ)) is close to zero. For example, the VBO of ZB and WZ ZnO is found to be only 0.037 eV.<sup>28</sup> Therefore, the similar local environments in anatase and rutile would lead to a small VBO. As the rutile/anatase VBO is small, their band-gap difference will mainly affect the position of the CBM, resulting in a 0.2 eV CBO. This conclusion is further supported by the fact that anatase exhibits higher photocatalytic activity than rutile.<sup>3</sup>

To further check the performance of the QD method, we have calculated the valence band alignment of several

semiconductors in zinc-blende structures. Two QD sets with different sizes are used to see the size effect, namely,  $\text{A}_{43}\text{X}_{44}(\frac{Z}{2}\text{H})_{40}(\frac{Z'}{2}\text{H})_{36}$  (Set 1) and  $\text{A}_{79}\text{X}_{68}(\frac{Z}{2}\text{H})_{28}(\frac{Z'}{2}\text{H})_{72}$  (Set 2), where A and X represent a cation and anion, respectively. The fractional charge Z and Z' are determined according to the discussion above. For III–V semiconductors,  $\frac{3}{4}\text{H}$  and  $\frac{5}{4}\text{H}$  are used, whereas for II–VI semiconductors,  $\frac{1}{2}\text{H}$  and  $\frac{3}{2}\text{H}$  are used. The results are shown in Figure 4. It is found that the



**Figure 4.** Valence band alignment of several semiconductors in zinc-blende structures calculated by the QD method. Two QD sets:  $\text{A}_{43}\text{X}_{44}(\frac{Z}{2}\text{H})_{40}(\frac{Z'}{2}\text{H})_{36}$  (Set 1) and  $\text{A}_{79}\text{X}_{68}(\frac{Z}{2}\text{H})_{28}(\frac{Z'}{2}\text{H})_{72}$  (Set 2) are used.

transitivity rule works well; that is, the AX/BY VBO can be deduced from AX/CZ and CZ/BY VBOs. The maximum error is in the order of a few tens of millielectronvolts according to our test. In most cases, the method gives reasonable results. For example, the calculated VBOs of AlN/GaN (~1.1 eV), AlP/GaP (~0.5 eV), and AlAs/GaAs (~0.5 eV) are consistent with previous experimental and theoretical studies.<sup>10,11,29–31</sup> For ZnO/GaN, there are several VBO values reported, such as 0.8 eV in ref 32 and 0.13 eV in ref 33. The calculated ZnO/GaN VBOs here are 0.08 eV (Set 1) and 0.23 eV (Set 2). It can be also seen that, from Set 1 to Set 2, the size effect is small in systems with small size and chemical differences, such as AlAs/GaAs and AlP/GaP, but is large in other systems with large size or chemical differences, such as ZnO/GaN. In these later cases, larger QDs should be used. Despite the size convergence problem, the sign of the VBO is correct in these systems, and the calculated results are reasonable. In general, the QD method works fine for most systems tested here.

## CONCLUSIONS

In summary, we proposed a method to calculate the band alignment using quantum dots, without the necessity to construct a coherent heterostructure. This is very useful for studying the band alignment between systems with very different crystal structures. Correct rutile/anatase  $\text{TiO}_2$  band alignment is obtained through this method, with the CBM of anatase being about 0.2 eV higher than that of rutile, which is in agreement with experiment. Further tests on several semiconductor materials show that this method gives reasonable results.

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## Notes

The authors declare no competing financial interest.

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