

# Computational study of TiO<sub>2</sub> Brookite (100), (010) and (210) surface doped with Ruthenium for application in Dye Sensitised Solar Cells

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**Abstract.** Titanium dioxide (TiO<sub>2</sub>) polymorphs are widely used in many energy-related applications due to their peculiar electronic and physicochemical properties. The electronic structures of brookite TiO<sub>2</sub> surfaces doped with transition metal ruthenium have been investigated by ab initio band calculations based on the density functional theory with the planewave ultrasoft pseudopotential method. The generalized gradient approximation (GGA) was used in the scheme of Perdew-Burke-Ernzerhof (PBE) to describe the exchange-correlation functional. All calculations were carried out with CASTEP (Cambridge Sequential Total Energy Package) code in Materials Studio of Accelrys Inc. The surface structures of Ru doped TiO<sub>2</sub> were constructed by cleaving the 1 × 1 × 1 optimized bulk structure of brookite TiO<sub>2</sub>. The results indicate that Ru doping can narrow the band gap of TiO<sub>2</sub>, leading to the improvement in the photoreactivity of TiO<sub>2</sub>, and simultaneously maintain strong redox potential. The theoretical calculations could provide meaningful guide to develop more active photocatalysts with visible light response.

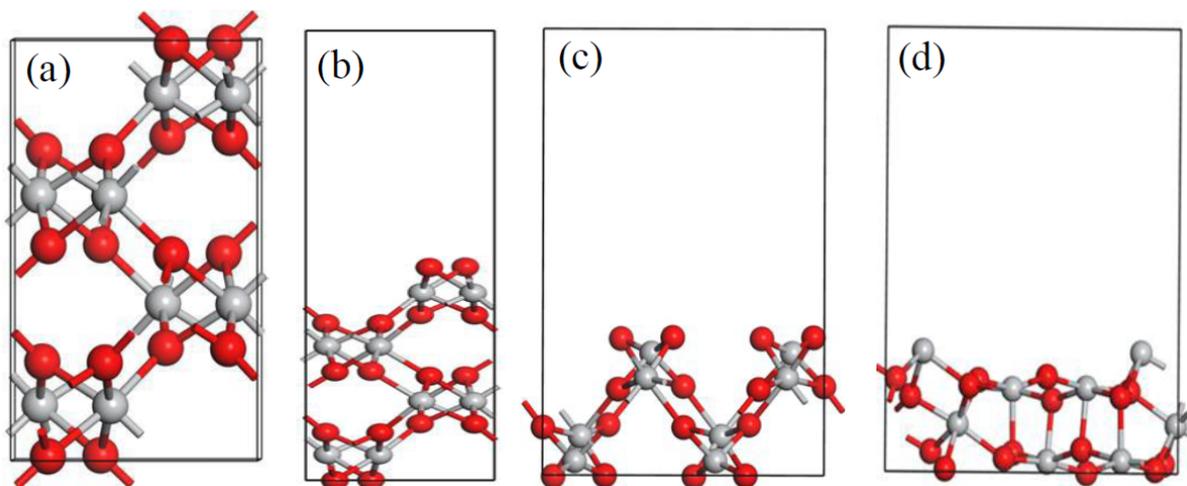
## 1. Introduction

In the last decades, properties for titanium dioxide (TiO<sub>2</sub>) polymorphs have been the subject of many experimental and computational studies, the most common polymorphs being the minerals rutile, anatase, and brookite [1]. A large number of applications of TiO<sub>2</sub> in materials science is, almost without exception, ultimately a result of the facile electron-transfer processes that occur at the interface between the semiconductor and adsorbed molecules [1–7]. When photons are excited, TiO<sub>2</sub> is a good electron and hole donor and can, therefore promote photocatalytic processes at its interface [3]. Its photocatalytic properties, in addition to its abundance, low cost, stability, and low toxicity, are the basis for its use in solar cells [4]. However, brookite is the rarest of the natural occurring TiO<sub>2</sub> polymorphs, and it is the most difficult phase to prepare in the laboratory [1]. As a result, the properties of pure brookite are poorly known. TiO<sub>2</sub> can only show photocatalytic activity under ultraviolet (UV) light irradiation ( $\lambda < 387.5$  nm) that accounts for only a small portion of solar energy (approximately 5%), in contrast to visible light for a major part of solar energy (approximately 45%), but can be photosensitized by the adsorption of chromophores that, when excited, inject electrons into the TiO<sub>2</sub> conduction band [8]. In spite of a large number of publications on pure and doped TiO<sub>2</sub> many aspects of

its optical and electronic properties and their modifications after doping still remain unclear. In particular, a key problem of selecting proper impurities to meet particular requirements for future applications is related to the location of the impurity's energy levels with respect to the band structure of a particular host [9,10]. Consistent analysis of the changes induced by impurities implies a detailed comparison of the calculated properties of the undoped and doped materials [8,10,11]. Such an approach is used in the present work, whereby first principle method is employed to calculate structural and electronic properties of brookite  $\text{TiO}_2$  surfaces for both pure and Ru-doped systems.

## 2. Structures

Brookite, which is the third natural form together with rutile and anatase polymorphs of  $\text{TiO}_2$ , has a complex structure. It has eight formula units in the orthorhombic cell with space group  $Pbca$ . Brookite formation may be pictured as the joining of distorted  $\text{TiO}_6$  octahedral sharing three edges. The surface structures of brookite have been modelled by cleaving the optimized  $\text{TiO}_2$  brookite bulk structure and constructing slab models. The relaxation of these surfaces has been taken into account by optimizing all of the slabs. This study explores the low index (100) and (010) surfaces for the brookite phase and (210) surface. The (100) and (010) surfaces are represented by 12 atoms while the (210) surface is composed of 24 atoms. A schematic representation of the three low-index surfaces is depicted in Figure 1. The truncation of the octahedral renders different coordination combinations for the outermost titanium cations. Depending on the slice of the brookite surface, the (010) and (010) surfaces may be either oxygen- or titanium terminated, the oxygen-terminated surfaces are found to be the most stable surfaces. Hence, only the oxygen-terminated surfaces are considered in this study. The band structures of the studied surface slab models (100), (010), and (210) surfaces, in addition to the first Brillouin zone with the high symmetry points present a direct gap, as in the bulk.



**Figure 1.** Theoretical models. (a) bulk  $\text{TiO}_2$  brookite, (b) (100)  $\text{TiO}_2$ , (c) (010)  $\text{TiO}_2$  and (d) (210)  $\text{TiO}_2$  surfaces.

## 3. Computational Method

The structural optimizations, band structure, and electronic density of states of doped and undoped brookite  $\text{TiO}_2$  (100), (010) and (210) surfaces were performed using the first-principles

calculations based on density functional theory (DFT) using a plane-wave pseudo-potential method. The surfaces structures of transition metal ruthenium-doped  $\text{TiO}_2$  were constructed by cleaving the  $1 \times 1 \times 1$  optimized bulk structure of brookite  $\text{TiO}_2$  with one Ti atom being replaced by Ru atom. We used the generalized gradient approximation (GGA) in the scheme of Perdew-Burke-Ernzerhof (PBE) to describe the exchange-correlation functional. All calculations were carried out using CASTEP (Cambridge Sequential Total Energy Package) code in Materials Studio of Accelrys Inc [12]. The Monkhorst-Pack scheme k-point grid sampling was set as  $4 \times 4 \times 2$  for the irreducible Brillouin zone and the cut-off potential energy of plane waves was set to 650 eV. The convergence criteria for structural optimization were set to be medium quality with the tolerance for the self-consistent field (SCF), energy, maximum force, and maximum displacement of  $2 \times 10^{-6}$  eV/atom,  $2 \times 10^{-5}$  eV/atom, 0.05 eV/Å and  $2 \times 10^{-3}$  Å, respectively. The doping criteria considered was to replace one titanium atom at the top of the surface with Ru.

## 4. Results and discussions

### 4.1. Structural optimization

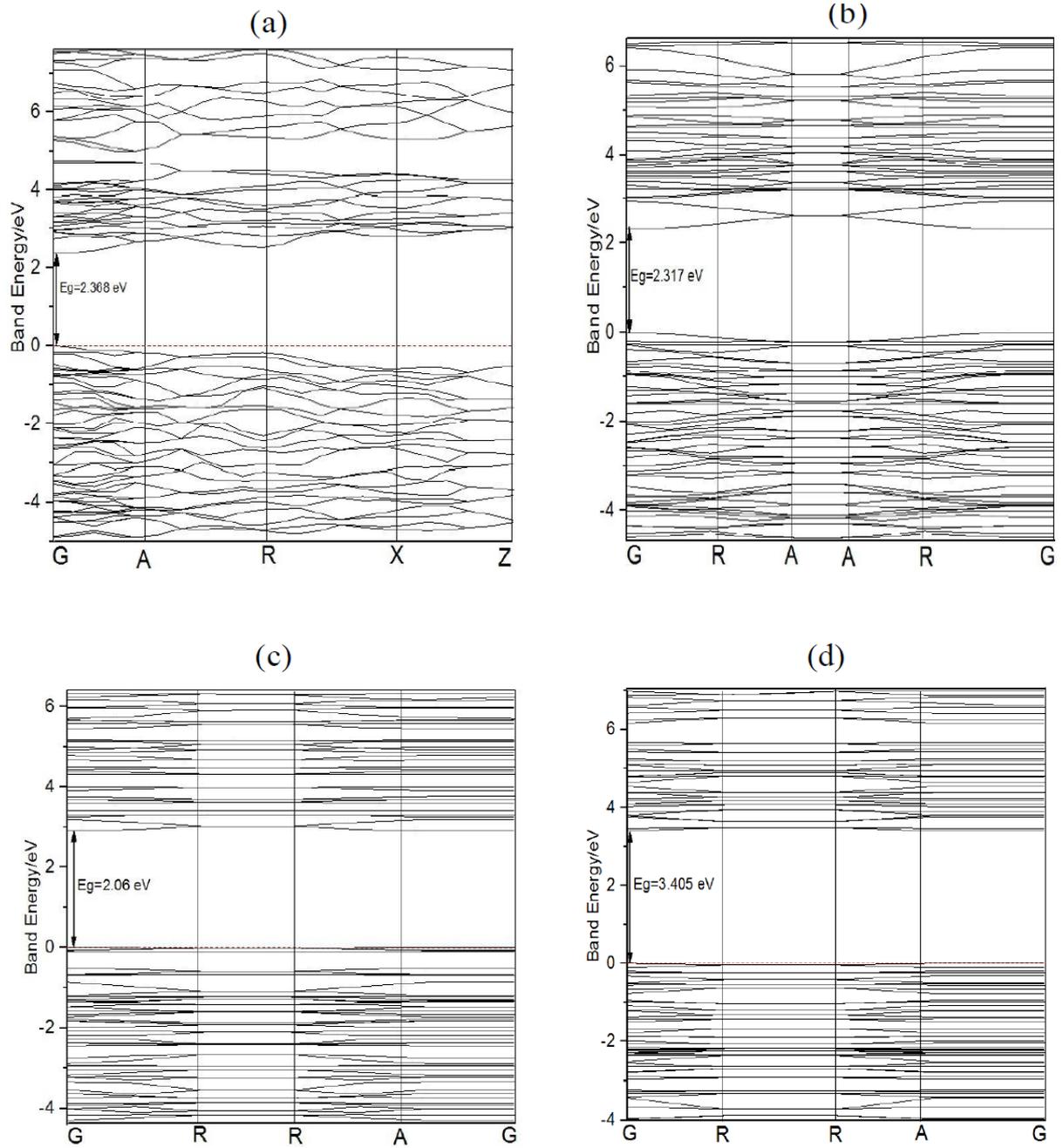
The optimized structures of doped and un-doped brookite  $\text{TiO}_2$  were calculated to find the lattice parameters with the lowest energy. Table 1, shows the lattice parameters a, b and c of the current work, which are compared with the reported experimental values and previous theoretical results. It can be observed that our calculated results are in agreement with both the experimental and reported theoretical results [13]. The lattice parameters obtained in this work are comparable to the experimental data, with deviation of 0.1967% along the a-axis, 0.203% along the b-axis and 0.196% along the c-axis. In comparison with the previous theoretical results reported in [14], the calculated results are more accurate, and thus validating the starting models and method used.

**Table 1.** Optimized structural parameters for bulk brookite  $\text{TiO}_2$  compared with experimental and previous theoretical results

	Experimental [13]	This work		Literature [14]	
		Results	Deviation % %	Results	Deviation % %
a(Å)	9.184	9.166	0.196	9.157	0.294
b(Å)	5.447	5.436	0.202	5.430	0.202
c(Å)	5.145	5.135	0.195	5.122	0.448

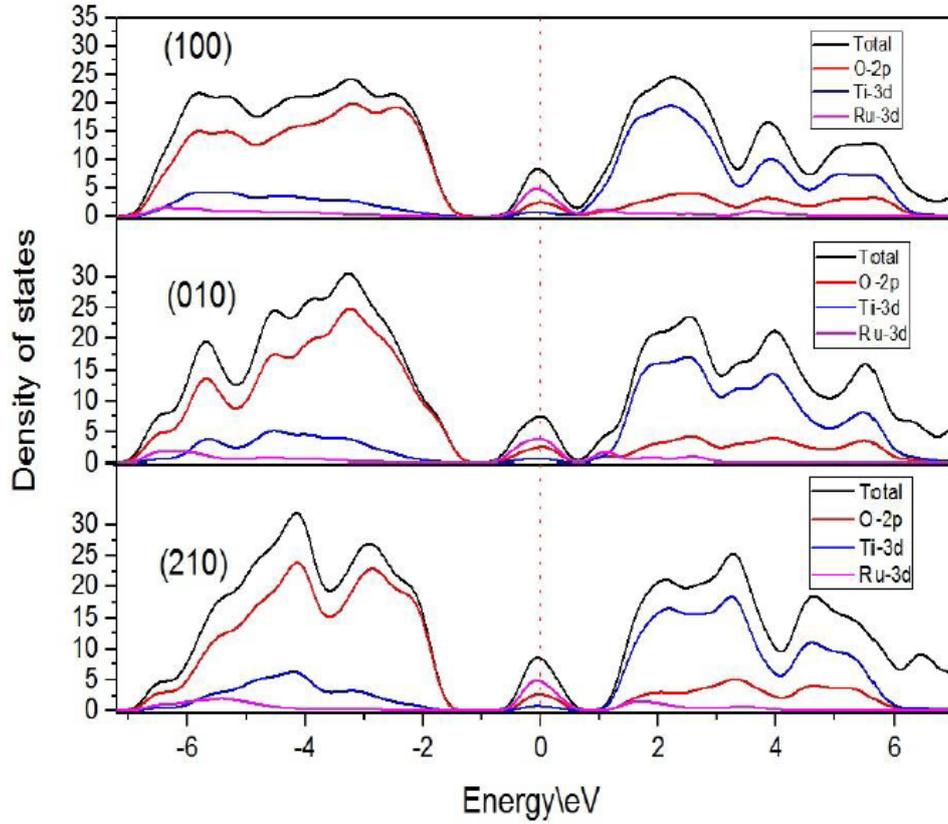
### 4.2. Electronic properties

In order to conveniently investigate the electronic structures of Ru-doped brookite  $\text{TiO}_2$  surfaces, we set the same k-points mesh to sample the first Brillouin zone for pure and doped systems. An energy band gap of 2.386 eV was obtained for the bulk brookite structure and is shown in Figure 2(a). Both the conduction band minimum (CBM) and the valence band maximum (VBM) are located at G. Thus, the brookite  $\text{TiO}_2$  can be considered as a direct band gap semiconductor. But is underestimated compared with the experimental value of 3.23 eV, due to the limitation of DFT: the discontinuity in the exchange correlation potential is not taken into account within the framework of DFT. However, our discussions about energy gap will not be affected because only the relative energy changes are of concern. The upper valence band, VB, lying in the range of 2.1-4.2 eV consists of O 2p orbitals hybridized with Ti 3d orbitals as illustrated in Figure 2. The band structures of the studied surface slab models (100), (010), and (210) surfaces, in addition to the first Brillouin zone with the high symmetry points present a direct band gap, as in the bulk. The corresponding values are 2.317, 2.080 and 3.405 eV for (100), (010), and (210) surfaces, respectively. The lower value of band gap energy for the (010)



**Figure 2.** The energy band structures of (a) bulk brookite TiO<sub>2</sub>; (b) (100) TiO<sub>2</sub>; (c) (010) TiO<sub>2</sub> and (d) (210) TiO<sub>2</sub> surfaces. The dashed line indicates the Fermi level.

surface can be attributed to the minor stabilization of the Fermi energy showing the most flat VB topology. After doping with Ru all the surfaces present a direct gap, as in the bulk (the bottom of the CB and the top of the VB are located at G). The band gaps for the TiO<sub>2</sub> brookite surfaces (100), (010) and (210) after doping with Ru are determined as 0.256 eV, 0.275 eV and 0.177 eV, respectively. The lower value of band gap energy for the (210) surface can be attributed to the minor stabilization of the Fermi energy showing the most flat VB topology. The total density



**Figure 3.** The TDOS and PDOS of the doped  $\text{TiO}_2$ . The red dashed line represents the position of the Fermi level.

of states (TDOS) and partial density of states (PDOS) of Ru-doped brookite  $\text{TiO}_2$  are shown in Figure 3, which were drawn using Origin Lab software [15]. The TDOS shape of doped  $\text{TiO}_2$  becomes broader than that of pure  $\text{TiO}_2$ , which indicates that the electronic nonlocality is more obvious, owing to the reduction of crystal symmetry. The 3d or 4d states of Ru are somewhat delocalized, which contributes to the formation of impurity energy levels (IELs) by hybridizing with O 2p states or Ti 3d states. Such hybrid effect may form energy levels in the band gap or hybrid with CBM/VBM, providing trapping potential well for electrons and holes. It gives a contribution to separation of photogenerated electron-hole pairs, as well as in favour of the migration of photoexcited carriers and the process of photocatalysis. The decrease in the band gap attribute to the fact that  $\text{TiO}_2$  band gap can be engineered to absorb light in visible region of the spectrum. The reduction in energy band gap could possibly increase the efficiency of the solar cell when  $\text{TiO}_2$  is used.

## 5. Conclusions

First principle calculations based on the density functional theory were performed successfully to understand the effect of doping brookite (100), (010) and (210)  $\text{TiO}_2$  surfaces. The structural and electronic properties of Ru doped on different surfaces were fully investigated. The energy band gaps for various surfaces doped with ruthenium are predicted and Ru doped (210) surface showed a good redshift found to have lowest energy band gap as compared to other surfaces. The analysis of the electronic structure for the studied surfaces of brookite revealed that all the

surfaces have a direct band gap. The findings of this comprehensive study on brookite TiO<sub>2</sub> surfaces shed insights and probe further investigation on defect properties, impurities, thin films, surfaces, and interfaces of TiO<sub>2</sub> system, particularly brookite polymorph.

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