Computational study of dye adsorption onto Brookite TiO_2 surfaces for the applications in dye sensitized solar cells

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Abstract. The theoretical and computational studies of dye sensitized solar cells (DSSCs) can contribute to a deeper understanding of these type of solar cells. In the current study the density functional theory (DFT) is used to understand the electronic properties of low index brookite (1 0 0) surface doped with ruthenium. The structural optimizations, band structure, and electronic density of states of doped and undoped titanium dioxide (TiO_2) brookite surface was performed using the first-principles calculations based on DFT emplotying a plane-wave pseudopotential method. Two different doping methods which were employed in the current work are, doping by replacement and adsorption. The overlap among the Ruthenium (Ru) 3d, Titanium (Ti) 3d, and Oxygen (O) 2p states enhance photocatalytic activity in the visible light region. The adsorption method shows that an equilibrium position is reached for ruthenium element after optimization. All the methods show that the TiO_2 brookite (1 0 0) surface reduces its band gap after been doped with the ruthenium element. From the two techniques used, the total energy of the doped structures show that they are energetically favorable, with the band gap being reduced to 0.263 eV compared to 2.376 eV of the pure system.

1. Introduction

The escalating costs of crude oil in international markets have created an urgency for utilization of alternative sources of energy. In developing countries like South Africa, efforts are underway to make use of renewable energy as the alternative way of energy production to replace the coal which is deplecting. Several solar plants have been installed in different provinces of South Africa, e.g. Limpopo, Northern Cape, etc. The use of sunlight for energy production is an added advantage to South Africa as a country, as many of its places receive high global solar radiation. Currently, the most useful part of solar spectrum is the visible light which is about 46 % of the sunlight,the other percentage belongs to infrared light 47 % and 5-7 % of the ultra violet light [1,2]. In photovoltaics technologies researchers have put more efforts on improving the efficiency of low cost solar cells which have high photon to energy conversion efficiency, like dye sensitized solar cells, perovskites, polymer, etc [1, 3-5].

In dye sensitized solar cells (DSSCs), the TiO_2 nanostructure used as a semiconductor is a very important component of the solar cell, as it acts as the electron transporter for the efficiency of the solar cell. The dye molecules are adsorbed on its surface, to be used as photon absorber. These molecules adsorbed onto TiO_2 semiconductor are the source of the photocurrent of the solar cell [6-8]. In general the dye sensitizer absorbs the solar radiation, becomes excited and transfers the photoexcited electron to the wide band gap TiO_2 semiconductor layer of nanometer sized particles. The charge hole which is created in the dye after excited state charge injection, is then transferred to a redox couple liquid electrolyte (usually iodine tri iodide) or solid hole conductor.

However, the electron band gap of TiO_2 is relatively large (3.2 eV for anatase, 3.0 eV for rutile and 3.4 eV for brookite) and limit its application in DSSCs [9-12]. To improve the efficiency of the DSSCs, the requirements will be: (i) to reduce the TiO_2 band gap, so that its absorption properties will match the visible solar spectrum, (ii) to modify the sensitizer or dye molecules so that it can absorb on the near infrared spectrum [1,6]. Therefore the modification of different electronic and optical properties of TiO_2 polymorphs (anatase, rutile and brookite) is very important for application in DSSCs and related technologies such as photo-catalyst. Surface doping of TiO_2 polymorphs has been considered as a possible solution to overcome the limitations of using TiO_2 in solar cells [9,10,13]. However, there is still limited on doping of brookite TiO_2 surfaces.

Brookite is one of the structural conformations of titanium dioxide polymorphs. Amongst TiO_2 phases brookite is the least studied TiO_2 photocatalyst due to the difficulties usually encountered in order to obtain it as a pure phase [14]. Experimentally it is difficult to prepare brookite with high purity and large surface area and this is one of the reasons for limited literature on its photocatalytic properties. Despite the difficulties encountered when synthesising pure brookite TiO_2, computer simulation methods have proved to be helpful in studying photocatalytic properties of brookite TiO_2. Thus, density functional theory calculations have shown that the commonly exposed brookite (210) surface is more reactive than anatase (101) surface and might be useful for photocatalytic applications [14]. Li et al. studied the brookite TiO_2 surfaces and showed that the brookite TiO_2 (210) has the same structural building block as anatase TiO_2 (101) [14]. Their findings elaborate that, the differences in surface structure significantly change the reactivity toward adsorption of various molecules, and most importantly, generate highly active sites at the junction between different structural units on brookite TiO_2 (210). The study further suggested that brookite TiO_2 (210) surface exhibits distinct activity, which may be useful in catalytic and photocatalytic applications.

The doping mechanism of different materials can be evaluated easily by electronic structure and related properties calculations. In this paper, we report our investigation of doping brookite TiO_2 (1 0 0) surface with ruthenium as a photocatalyst for application in DSSCs. Density functional theory method is used to calculate the band structures and densities of states (DOS) near the Fermi energy for doped brookite (1 0 0) surface. The discussion is focused on how the electronic properties of this system changes when doped (atom replacement and adsorption) with ruthenium metals.

2. Computational Method

Brookite has an orthorhombic crystalline structure with a unit cell described by the space group (Pbca). The structure is composed of octahedra, each with a titanium atom at its center and oxygen atoms at its corners [15]. In the current study the brookite TiO_2 (1 0 0) surface doped with ruthenium is investigated. The study is geared towards the engineering of the brookite TiO_2 band gap which is higher and need to be tuned to adsorp in the visible spectrum for application in DSSCs. All results computed are based on first principle method, DFT using

Table 1. Optimized structural parameters for bulk brookite TiO_2 compared with experimental and previous theoretical results.

	Experimental [18]	This work		Literature [9]	
		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

CASTEP code implemented in Materials Studio package [16, 17]. The structural optimizations, band structure, and electronic density of states for doped and undoped brookite TiO_2 (100) are performed using the generalized gradient approximation (GGA) in the scheme of Perdew-Burke-Ernzerhof (PBE) describing the exchange-correlation functional. The convergence criteria for structural optimization were set to be of medium quality with the tolerance for the self-consistent field (SCF), energy, maximum force, and maximum displacement of $2x10^{-6}$ eV/atom, 0.05 eV/Å and $2x10^{-3}$ Å, respectively. The cut-off energy selected was 650 eV and Monkhorst-Pack scheme k-point grid sampling was set as 4x4x2 for the irreducible Brillouin zone. Two approaches were considered for ruthenium doping, i.e., replacement of one Ti atom with one Ru1 atom and adsorption of one Ru atom adjacent to Ti atom. Various distances between ruthenium atom and adjacent titanium atom were considered and they ranged from 1 to 4 Å, with a 0.5 Å interval.

3. Results and discussions

The theoretical computer simulation techniques are able for determination of the stability and structure properties of materials under conditions that are difficult to reproduce in the laboratory. The optimized structural properties of doped brookite (1 0 0) surface were calculated and are listed in Table 1. The listed parameters show that our computational results obtained are in good agreement with the experimental and other theoretical literature. The calculated deviations from the experimental results are in better agreement compared to those reported by Beltran et al. [9]. In particular, our models produced better values for lattice parameters a and c, with b producing same results.

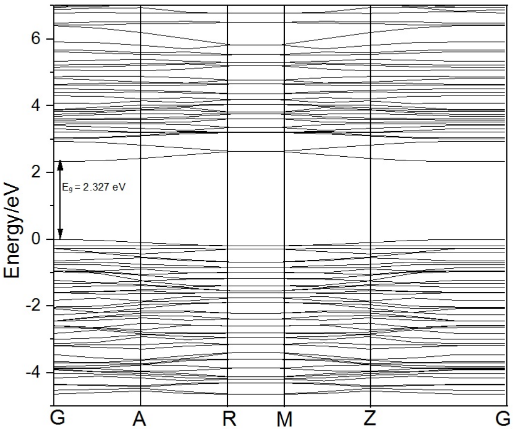

Figure 1. Calculated energy band gap curves for the bulk structure of (1 0 0) TiO_2 surface.

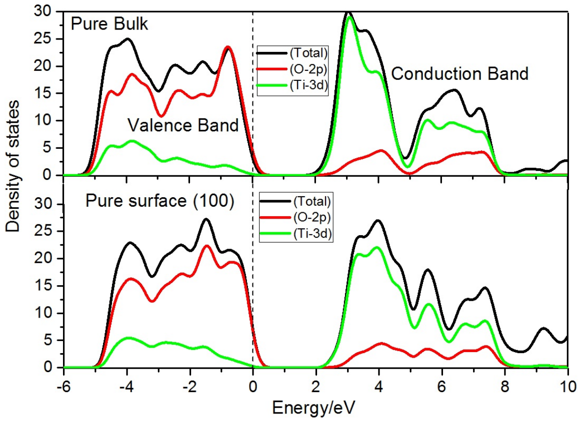

Figure 2. Calculated density of state of bulk and pure TiO_2 (1 0 0) brookite surface.

In order to conveniently investigate the electronic structures of Ru-doped brookite TiO_2, we set the same k-points mesh to sample the first Brillouin zone for pure and Ru-doped models. Figure 1, shows the band gap structure of pure (1 0 0) TiO_2 surface. It can be observed from Figure 1, that the band gap is calculated to be 2.327 eV, which is less than the experimental results of 3.2eV. It is well known that GGA tends to underestimate the band gap due to the choice of the exchange correlation energy. The valence band of pure TiO_2 surface consists of 2p states of oxygen (O) and 3d state of titanium (Ti). The conduction band is dominated by Ti 3d states and is illustrated in Figure 2. The conduction band minimum (CBM) and the valence band maximum (VBM) are located at G, which illustrate that the brookite TiO_2 can be considered as a direct band gap semiconductor.

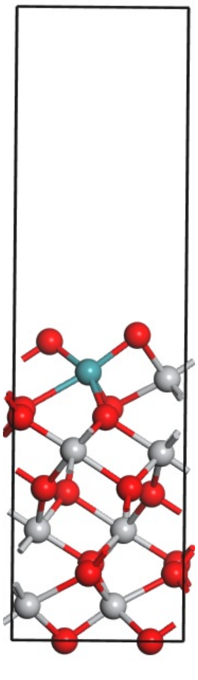

Figure 3. Atomic structure of brookite TiO_2 surface doped with ruthenium element

3.1. Substitutional doping

Figure 3 shows the doped TiO_2 (1 0 0) surface with Ti atom at the top of the surface being substituted by Ru atom. The density of state for the doped system are presented in Figure 4. The doped surface showed that the 3d orbitals for Ru atom generate a coordination fields to interact with the nearest O. The decrease in the band gap as shown in Figure 5, illustrates that there is a shift in the absorbance of the doped TiO_2 to visible spectrum.

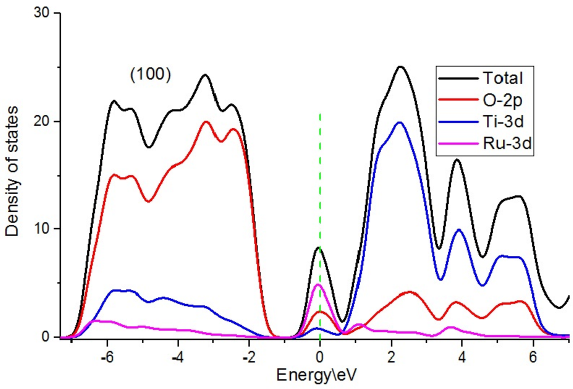

Figure 4. Calculated density of state of doped TiO_2 (1 0 0) brookite surface by substitution of one Ti atom.

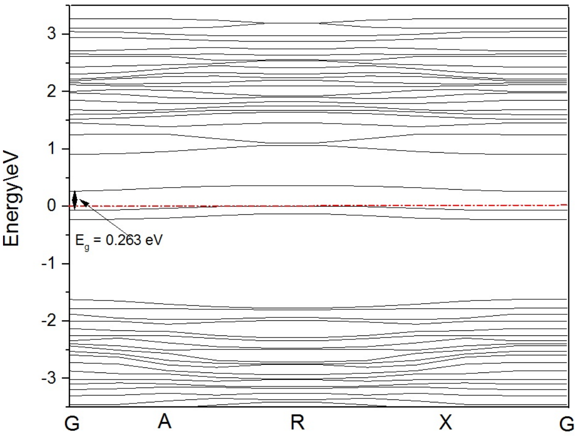

Figure 5. Calculated energy band gap curves of the doped (1 0 0) brookite TiO_2 surface by substitution of one Ti atom

3.2. Adsorption

The procedure followed during the dye uptake in dye sensitized solar cell is of dipping the TiO_2 nano particle film into the solution of the dye molecules. In this paper, we mimic the adsorption of the dye molecules in DSSCs, by adsorbing the ruthenium atom by placing it onto TiO_2 surface. The Ru atom is placed adjacent the Ti atom at the top of the surface at various distances as shown in Figures 6 and 7. The pictures show doped surfaces before and after optimization with the variation of Ru atomic displacement. The two figures depict that after optimization of the doped surface, Ru atom prefers to bond with Ti at an average distance of 2.21 Å. When Ru is placed closer (1 to 2 Å) to the surface it moves away from the surface to a distance of 2.21 Å. And when is placed away (2.5 to 4 Å) from Ti atom it moves closer to the surface to an average bond distance of 2.21 Å. The calculated bond distances are summarised in Table 2.

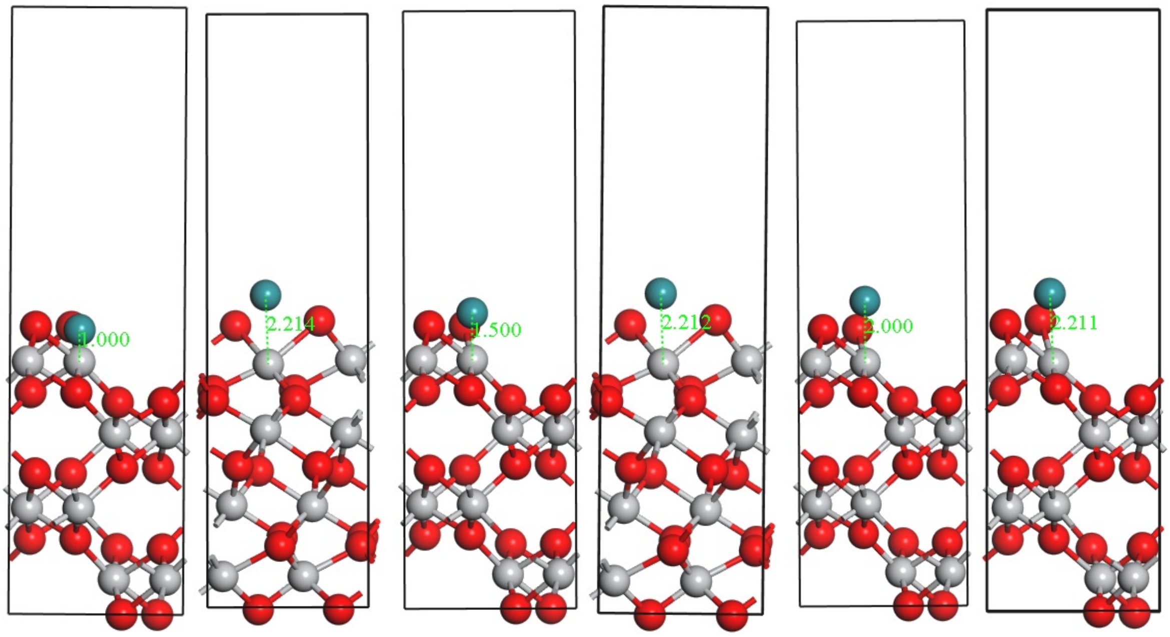

Figure 6. Atomic structure of brookite TiO_2 doped at the distance of 1−2 Å before and after optimisation (the distances are illustrated on the figures).

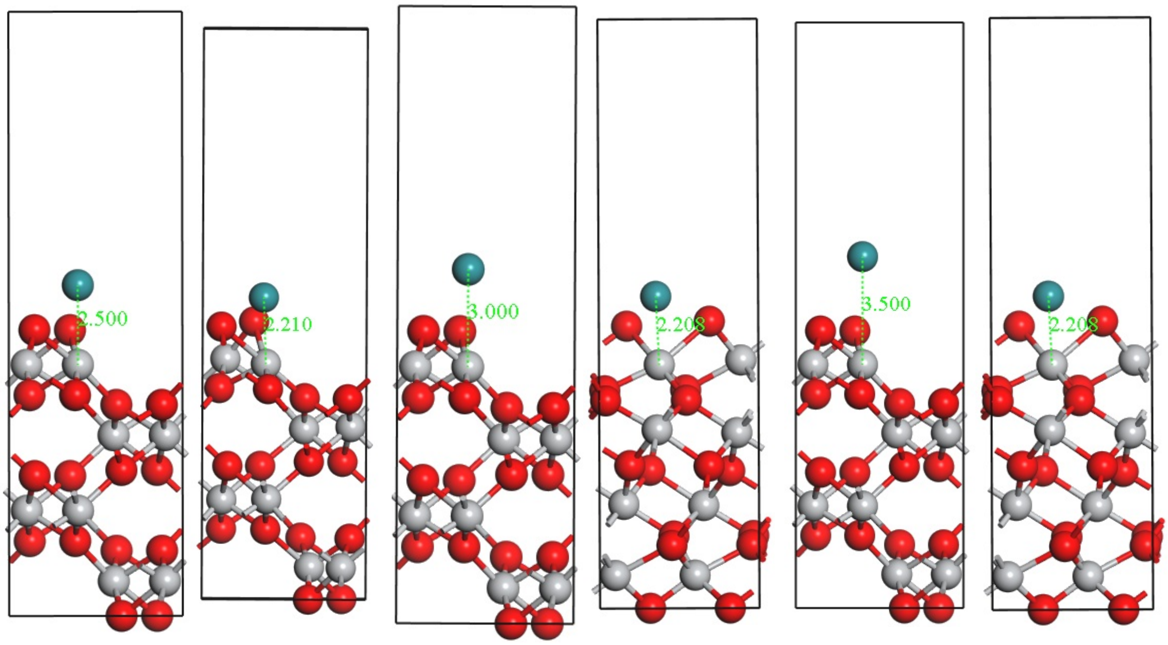

Figure 7. Atomic structure of brookite TiO_2 doped at the distance of 2.5 − 3.5 Å before and after optimisation (the distances are illustrated on the figures).

Figure 8 illustrates calculated energy band gap as a function of Ru position adsorbed on brookite surface. The band gap is defined as the separation between the VBM and CBM. The

Table 2. Final energy of optimized structural parameters for TiO_2 brookite (100) surface as the distance is varied.

Before relaxation (Å)	After relaxation (Å)	Total energy (eV)
1.00	2.214	-517571
1.50	2.212	-517567
2.00	2.211	-517567
2.50	2.210	-517567
3.00	2.208	-517560
3.50	2.211	-517565
4.00	2.209	-517565

calculated band gap at various Ru positions is found to be an average of 2.70 eV, which is in agreement with reported results by Mo et al [19]. However, both energy band gaps are underestimated compared to the experimental value of 3.4 eV [20]. It can be observed that the band gap varies slightly as Ru distance is varied. The lowest total energy of the system was obtained to be -517571 eV and corresponding to Ru adsorbed at 0.5 Å from Ti atom.

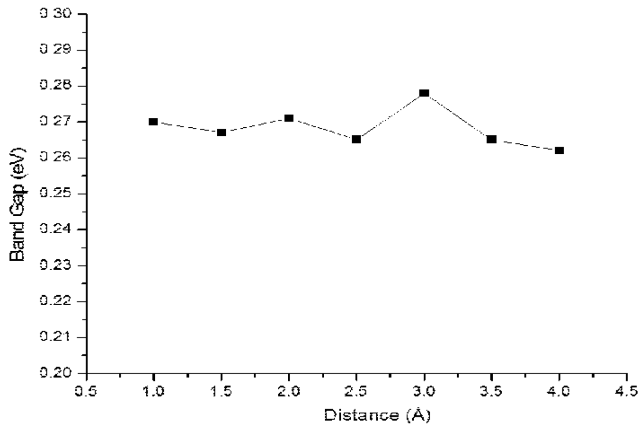

Figure 8. Dependency of the band gap on the doping distance of the ruthenium element

The total density of states (TDOS) and partial density of states (PDOS) of Ru-adsorbed onto brookite TiO_2 are shown in Figure 9. The TDOS shape of Ru-doped TiO_2 becomes broader than that of pure TiO_2, which indicates that the electronic non locality is more obvious, owing to the reduction of crystal symmetry. The Ru 3d states are somewhat delocalized, which contributes to the formation of impurity energy levels (IELs) by hybridizationg 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 the separation of photogenerated electronhole pairs, as well as in favour of the migration of photoexcited carriers and the process of photocatalysis. The Fermi level in the case of the Ru doping shift from the top of the valence band to the bottom of the conduction band, which is normally attributed to the n type doping. Significant reduction in the band gap is noted and this tends to enhance absorption of the brookite TiO_2 to visible light spectrum.

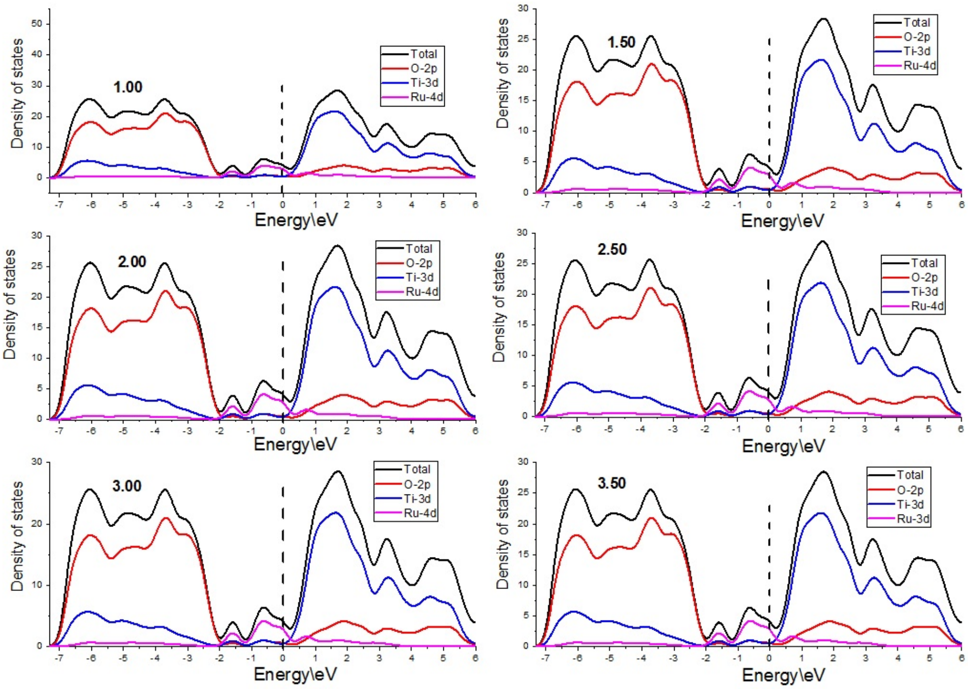

Figure 9. Calculated density of state of doped (1 0 0) brookite TiO_2 surface at different distance as illustrated.

4. Conclusion

First principle calculations were performed successfully in order to investigate the structural and electronic properties of substitutional and adsorbed Ru doped TiO_2 (1 0 0) brookite surface. The calculated lattice parameter are in good agreement with experimental results. The two approaches employed in the study revealed that doping brookite TiO_2 with ruthenium narrow the energy band gap. The decrease in the band gap renders the electronic transfer from valence band to conduction band easier. These decreases in electron transition energy from the valence band to conduction band may be responsible for the visible light absorption. The simulated results showed that doping of TiO_2 semiconductor can improve the efficiency of DSSCs, as the TiO_2 band gap has shifted to absorb on the visible spectrum.

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