DFT Study of the TiO_2 Anatase (100) Surface Doped with Be for Application in DSSCs

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Abstract. Dye-sensitized solar cells (DSSCs) are an innovative photovoltaic technology, characterized by their cost-effectiveness, impressive efficiency, and adaptable structure. Titanium dioxide (TiO_2), especially in its anatase phase, is extensively utilized as a photoanode material because of its advantageous electronic and chemical characteristics. Nonetheless, the broad bandgap of pure TiO_2 restricts its ability to absorb light in the visible spectrum, consequently diminishing its photovoltaic efficiency. This study utilized density functional theory (DFT) to explore the electronic and optical characteristics of the Be-doped (100) anatase TiO_2 surface. The generalized gradient approximation (GGA) employing the Perdew–Burke–Ernzerhof (PBE) functional was applied to characterize the exchange-correlation effects, as executed in the Materials Studio package. The findings demonstrate that the introduction of beryllium into anatase TiO_2 effectively reduces the bandgap, leading to improved absorption in the visible light spectrum. Furthermore, the doped surface demonstrates decreased reflectivity, which is beneficial for enhancing light harvesting in DSSCs. This study illustrates that the incorporation of Be significantly alters the optical and electronic properties of anatase TiO_2, enhancing its potential as a more effective option for dye-sensitized solar cell applications.

Keywords: Anatase TiO_2, (100) surface, beryllium doping, dye-sensitized solar cells, bandgap, density functional theory.

1. Introduction

Solar energy presents a practical approach to addressing the environmental pollution issues caused by excessive fossil fuel consumption and the increasing energy needs resulting from population growth. The utilization of solar cells produces energy in the form of directly usable electricity and eliminates the need for fuel, positioning them as an optimal solution for effectively harnessing this abundant solar energy [1,2]. At present, Silicon solar cells are being utilized and installed on building rooftops to improve energy efficiency, in conjunction with the development of large-scale solar power plants to replace thermal energy sources. While it offers advantages like high photoconversion efficiency (PCE) and a lifespan of over 20 years, it encounters obstacles including limited stability under extended UV exposure, a relatively low open-circuit voltage, and the reliance on expensive or volatile liquid electrolytes, which impede its large-scale commercial implementation. [1].

Dye-sensitized solar cells (DSSCs) present advantages including low manufacturing costs, a variety of dye choices, transparency, versatility, and impressive power conversion efficiency in low-intensity conditions [3-5]. The photocatalyst itself serves as a vital element in photocatalytic systems. Titanium dioxide (TiO_2) serves as a widely used photocatalyst; nonetheless, its application frequently

faces limitations due to its broad band gap energy, which restricts its efficacy to the ultraviolet region of the electromagnetic spectrum. An effective strategy to overcome this limitation involves the sensitization of TiO_2 using dyes that can absorb light within the visible spectrum [6,7]. This research examines the structural, electronic, and optical characteristics of TiO_2 anatase (100) that has been doped with Beryllium.

2. Computational Method

The density functional theory (DFT) calculations were performed using the CASTEP simulation package with the use of generalized gradient approximation (GGA). A kinetic cut-off energy of 650 eV was utilized for the set of plane-wave basis. A 7 x 7 x 3 Monkhorst–Pack mesh was carried out for the integrations over the irreducible Brillouin zone. The convergence of the total energy within 1.0×10^{-6} eV/atom is used to guarantee the accuracy of the calculations. The anatase TiO_2 structure was optimized, from which a (1 0 0) Miller index was cleaved to form a (100) anatase TiO_2 surface. The substitution of doping was performed on (100) anatase TiO_2, whereby one titanium atom at the top layer was replaced by a beryllium atom. The electronic partial density of state and optical properties of the berylium-doped system were calculated.

3. Results and Discussion

3.1. Structural properties

Anatase belongs to the family of TiO_2 polymorphs, which includes rutile and brookite. This investigation involved the optimization of the bulk structure of anatase TiO_2 to confirm the accuracy of the model. The calculations employed k-points and energy cut-off values established through convergence tests, as previously outlined. Geometry optimizations were conducted in a single step using an unconstrained volume to ascertain equilibrium bulk parameters and reference energies. The ground state energy configuration for pure anatase TiO_2 was established by computing the lattice parameters along with their associated minimum energy values.

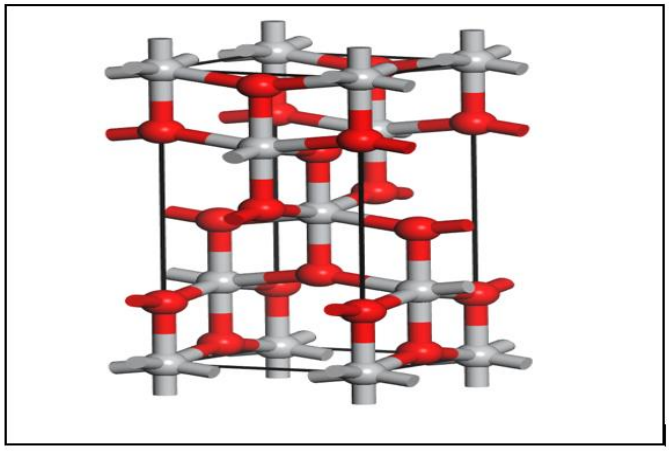


Figure 1. TiO_2 anatase bulk structure

The calculated lattice parameters a, b, and c are presented in Table 1, alongside reported experimental values and earlier theoretical findings for comparison. The calculated results align well with both the experimental findings and the existing literature. The lattice parameters derived in this study align closely with the experimental data, exhibiting deviations of 0.0088% for the a-axis, 0.0088% for the b-axis, and 0.0264% for the c-axis. The observed percentage deviations fall within the range of reasonable and acceptable values for DFT calculations.

The refined structural characteristics of the TiO_2 anatase are presented in Table 1. The parameters presented demonstrate that the computational results achieved align well with both experimental data and other theoretically reported values. The computed discrepancies from the experimental findings align more closely with those documented by Gao *et al* [8].

Table 1: Optimized structural parameters for bulk anatase TiO_2 compared with experimental and previous theoretical results

	EXPERIMENTAL[8]	THIS WORK		LITERATURE[9]	
		Results	Deviation (%)	Results	Deviation (%)
a(Å)	3.7848	3.7760	0.0088	3.7431	0.0417
b(Å)	3.7848	3.7760	0.0088	3.7431	0.0417
c(Å)	9.5124	9.4860	0.0264	9.4812	0.0312

The energy of the anatase TiO_2 bulk structure after optimization was -9913.570370450 eV, for pure anatase TiO_2 (100) surface was -9911.685047841 eV, and for Be-doped anatase TiO_2 was -8704.77733852 eV. The lattice parameters of the surfaces differ from those of the bulk structure; for the bulk structure, a=3.7760, b=3.7760, and c=9.4860, while for the surface they change to a=3.7760, b=9.4860, and c=11.8880

3.2. Electronic Properties

The calculated band gap of pure anatase TiO_2 is around 2.092 eV, which is lower than the experimental value of 3.2 eV, attributed to the underestimation by the GGA functional. The calculated band gap of the cleaved surface TiO_2 anatase (100) is 3.077 eV, which is about 0.985 eV greater than the calculated band gap of pure anatase TiO_2, but it is 0.123 eV smaller than the experimental value (3.2 eV) due to the cleaving of the TiO_2 anatase structure. The determined band gap of Be-doped TiO2 anatase (100) is 2.340 eV, which is roughly 0.737 eV less than that of undoped TiO_2 anatase (100). The Be dopant effectively narrows the band gap while avoiding the formation of isolated states, a feature considered to enhance photocatalytic activity. The findings suggest that the incorporation of Be atoms into the TiO2 surface leads to a reduction in the band gap of TiO_2, consequently shifting its absorption into the visible light spectrum.

Our results regarding beryllium doping align with computational results reported by Ma *et al.* [10], who investigated the doping mechanisms, dopant formation energies, electronic structures, and optical properties for Be, Mg, Ca, Sr, and Ba doped anatase TiO_2. Their results suggested that alkaline earth metal (AEM) dopants shift the valence bands (VBs) to higher energy. Specifically, the dopant-state energies for Ca, Sr, and Ba are quite higher than the Fermi levels, while Be and Mg dopants lead to spin-polarized gap states near the top of the VBs, which is consistent with our findings.

The density of states (DOS) quantifies the number of accessible states per unit energy at each energy level that electrons can occupy. A substantial density of states at a specific energy level indicates a multitude of accessible states for electron occupancy, whereas a density of states of zero signifies the absence of available states. Figures 2 and 3 present the electronic energy density of states for the bulk structure of TiO_2 anatase, the TiO_2 anatase (100) surface, and the Be-TiO_2 anatase (100) surface, respectively.

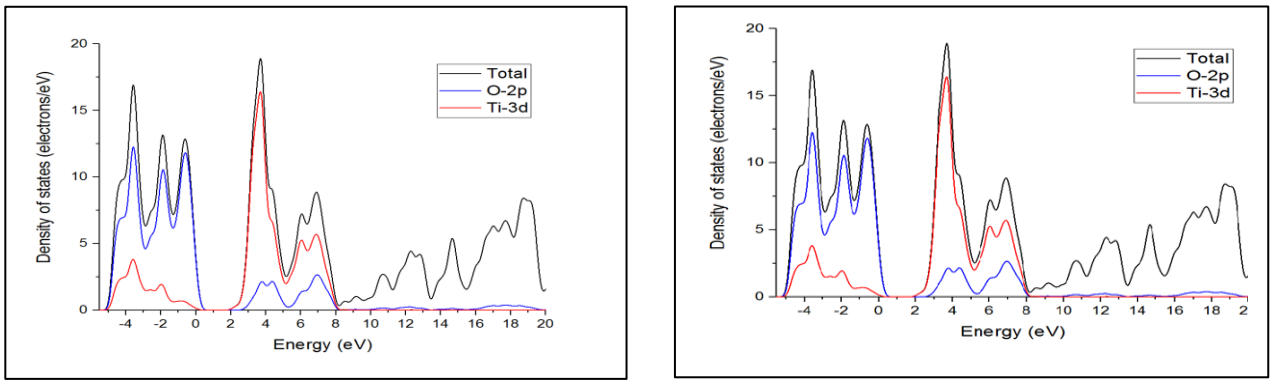


Figure 2. Partial Density of states of TiO_2 anatase bulk structure and pure TiO_2 anatase (100)

Figures 4 illustrate that the Be-doped anatase TiO_2 (100) surface enhances the availability of states for electron occupation, attributed to the introduction of Be impurity states within the band gap. The introduction of an impurity state in the Be-doped TiO_2 anatase (100) surface results in the formation of a "hole" within the particle, which contributes to the narrowing of the TiO_2 anatase band gap. In the un-doped scenario, the valence band of TiO_2 anatase is mainly formed from O-2p orbitals, while the conduction band is predominantly made up of Ti-3d orbitals..

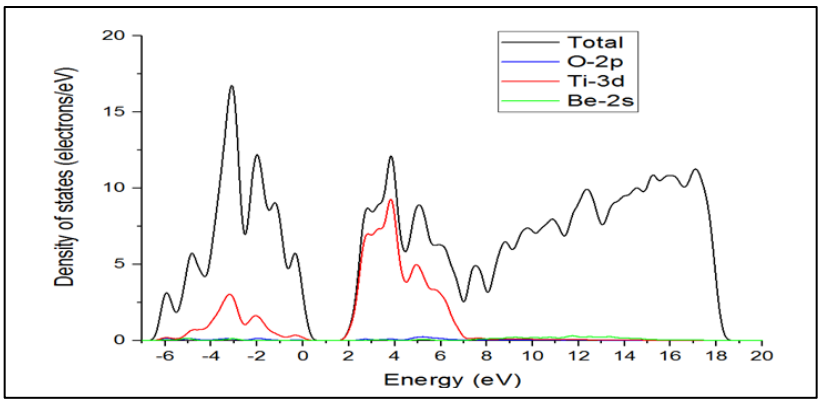


Figure 3. Density of states of Be-doped TiO_2 anatase (100)

For the doped system, the s orbital of the alkaline earth metal (Be) hybridizes with the p orbital, generating coordination fields that interact with the nearest oxygen atoms. The orbital resonance between oxygen and beryllium suggests the formation of a Be-O bond. The valence band of the doped system contains the hybridized orbitals of Be, and the conduction band includes the s-p orbital of Be. These findings are supported by Ma *et al.* [10], who reported that in doped cases, the s orbitals of AEMs hybridize with p (for Be and Mg) or p-d orbitals (for Ca, Sr, Ba) through the promotion of s electrons to p and d orbitals, creating coordination fields that interact with the nearest oxygen atoms. They also reported that the band shifts in Be and Mg-doped cases are very small, while Ca, Sr, and Ba dopants induce an elevation of VBs and generate dopant states in the gap for Ca and Ba-doped cases.

3.3. Optical properties

Figure 5 displays the reflectivity spectra of bulk anatase TiO_2, pure anatase TiO_2 (100) surface, and Be-doped anatase TiO_2 (100) surface across a wavelength range of approximately 0 – 2000 nm. The Be-doped surface exhibits significantly reduced reflectivity in both the ultraviolet (UV) and infrared (IR) regions compared to the undoped systems. However, in the visible region, the Be-doped surface shows higher reflectivity than the pure surface. This enhancement may be attributed to the presence of Be impurity states, which alter the surface's electronic structure and optical response.

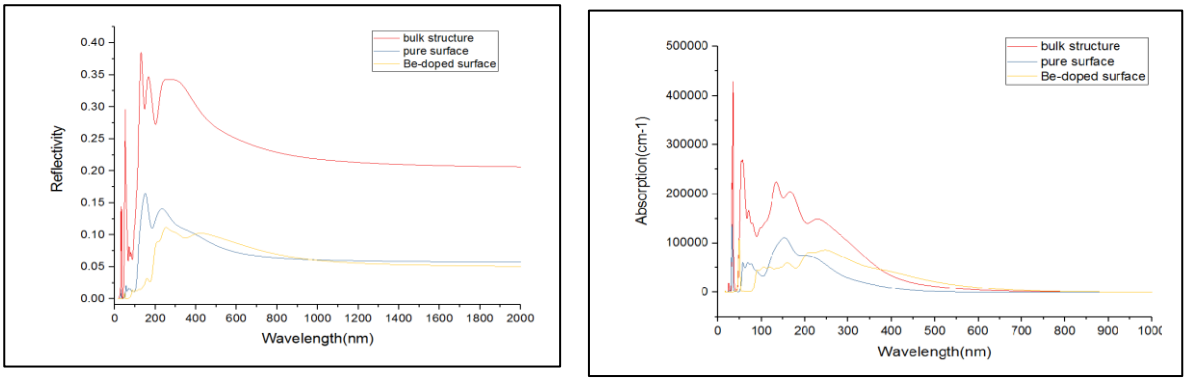


Figure 5. Reflectivity and Absorption for bulk TiO_2 bulk structure, pure anatase TiO_2 (100) surface and Be- doped anatase TiO_2 (100) surface.

The absorption spectrum, presented in Figure 5, provides insights into the light-harvesting capabilities of the materials. The absorption onset is used to estimate the optical band gap. Notably, the Be-doped anatase TiO_2 exhibits enhanced absorption in the visible and near-infrared regions. This can be attributed to the dopant-induced states within the band gap, which facilitate sub-bandgap optical transitions. It is important to note that the electronic band gap differs from the optical band gap, which considers excitonic and many-body interactions. The presence of Be dopants effectively narrows the optical band gap, enabling better absorption of solar radiation.

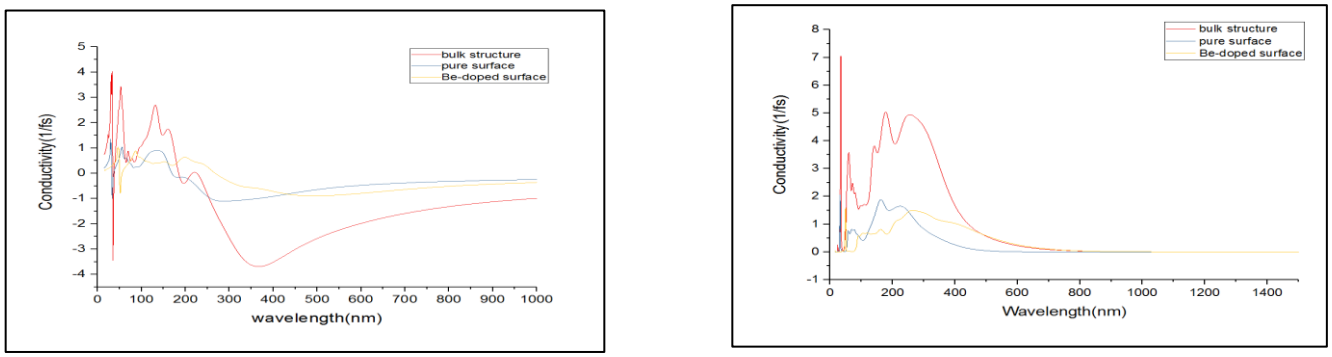
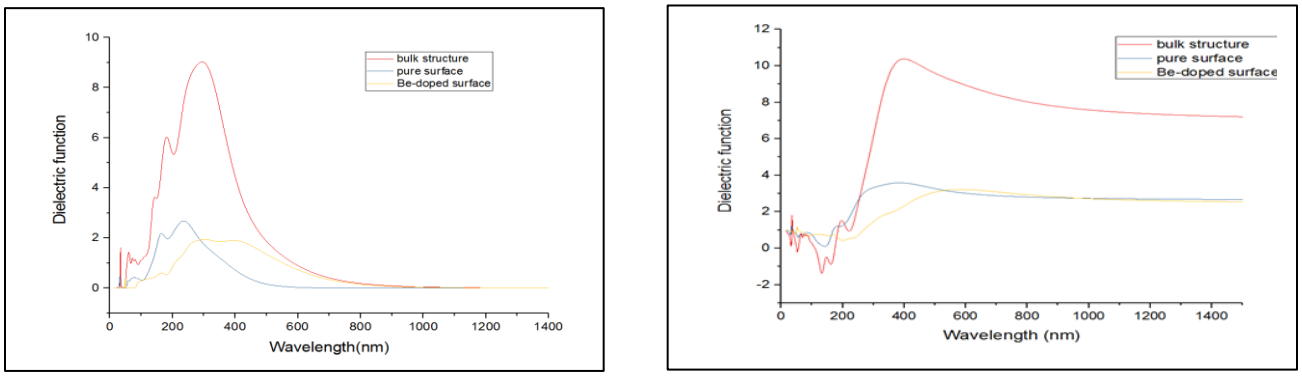


Figure 6. Conductivity for bulk TiO_2 bulk structure, pure 100 anatase TiO_2 surface and Be-doped 100 anatase TiO_2 surface.

Figure 6 shows the imaginary part of the optical conductivity and the real part. Optical conductivity relates to how the material responds to time-varying electric fields, linking current density to the applied electric field across different frequencies. These results indicate that the Be-doped anatase TiO_2 surface can conduct under optical excitation across a broader wavelength range, supporting its potential for improved photo-induced charge transport. The imaginary part of the dielectric function, $\iota\xi_2(\omega)$,

which reflects electronic transitions from occupied to unoccupied states induced by photons, and it is derived from the electronic band structure. The real part, $\xi_1(\omega)$, calculated using the Kramers–Kronig relation $\xi(\omega) = \xi_1(\omega) + \iota\xi_2(\omega)$ accounts for the material's polarizability and refractive behaviour



Figures 7. The imaginary and real parts of the dielectric function, respectively.

The Be-doped TiO_2 surface shows a lower imaginary dielectric response compared to the bulk and pure surface at 57 nm to 700nm, suggesting reduced transition probabilities at higher photon energies. The real part is also smaller in the visible and IR regions for the Be-doped surface, indicating reduced refractive behaviour. The presence of impurity states (introduced by Be atoms) enhances electron transport by reducing the band gap and facilitating easier excitation of electrons. These excited electrons can contribute more efficiently to the photocurrent in solar applications like Dye-Sensitized Solar Cells (DSSCs).

4. Conclusion

Beryllium-doped anatase TiO_2 (100) surface has been successfully studied using first-principles density functional theory. The structural, electronic, and optical properties of the anatase TiO_2 bulk structure, pure (100) anatase TiO_2 surface, and doped surface were calculated. Suitable energy cut-off (650 eV) and k-points (7 x 7x 3) were deduced from convergence test calculations. The calculated results demonstrate that Be-doping can improve the photocatalytic performance of the anatase TiO_2 (100) surface. Specifically, the Be dopant narrows the band gap of anatase TiO_2 (100), shifting the absorption spectrum to the visible range, which enables the solar cell to absorb more photons. The Be-doped anatase TiO_2 (100) shifts the absorption to longer wavelengths, improves optical absorbance, limits reflectance in the visible light and near-infrared (IR) regions, and reduces the band gap of anatase TiO_2, leading to an improvement in dye-sensitized solar cells.

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