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ORIGINAL RESEARCH ARTICLE

A DFT+U Study of the Structural and Electronic Properties of Zinc-Doped Anatase TiO_2 Nanomaterial

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ABSTRACT
This work reports a theoretical study on the structural and electronic properties of the anatase phase of titanium dioxide (TiO_2) within the framework of density functional theory corrected for on-site coulomb interactions in strongly correlated materials (DFT+U). The exchange correlation was described by local density approximation (LDA). The optimized lattice parameters obtained for the pure anatase TiO_2 agree with the experimental data. Our results revealed that, after the zinc doping, the structure didn't change but there was a little expansion in the volume of the pure material. It was found that the doped structure's stability increases as the concentration of the dopant increases, but all the doped structures are stable. However, introducing the zinc dopant has significantly reduced the band gap of the pure anatase by 80.7 %, 80 %, and 78.6 % due to 0.25, 0.5, and 0.75 doping concentrations, respectively. This implies that the band gap energy increases as the doping concentration increases.

INTRODUCTION

Titanium dioxide (TiO_2), also known as titania, is the only naturally occurring oxide of titanium at atmospheric pressure. It exists in three main polymorphs: rutile, anatase, and brookite. However, the brookite phase is very difficult to synthesize compared to the other two, so it is rarely studied (Beltran et al., 2006). Other high-pressure phases of TiO_2 have been reported (Kominami et al., 2000).

However, TiO_2 has been used for many years in various industrial and consumer goods, including paints, coatings, adhesives, paper and paperboard, plastics and rubbers, and printing inks. Subsequently, researchers have proven other potential applications of this material, such as in photocatalysis, dye-sensitized solar cells, sensors, hydrolysis, etc. (Fujishima et al., 1972; Tang et al., 1995; Bai et al., 2014; Al-Attafi et al., 2018; Qing et al., 2019; Sasanka et al., 2021). The excellent chemical stability, low cost, and non-toxicity of TiO_2 are some of the main factors that made it more attractive in the fields mentioned above.

Moreover, despite all the advantages of this material, some challenges still need to be addressed for more diverse applications. The wide band gap of TiO_2 (3.0 eV for rutile and 3.2 eV for anatase TiO_2, respectively) (Daude et al.,1977; Takeshi et al.,2001) has limited its applicability in many fields. The photon absorption of semiconductors depends largely on their band gap energy. A material only absorbs photons when the semiconducting band gap energy is lower than the photon energies. Due to its wide band gap, TiO2 can only generate electron-hole pairs under ultra violet (UV) light. It is well known that solar light consists of only 5 % UV light; a large part of solar energy cannot be utilized (Dantong et al., 2015). Thus, this necessitates extending the light absorption of TiO_2 beyond the UV region.

Because of this, several works were reported theoretically and experimentally using both metal and non-metal dopants in engineering the material's band gaps, thereby extending the light absorption to at least the visible region. Some of the metal dopants used were Ag, Fe, V, Al, Pt, Cu, Cr, and Zn (Lee et al., 2005; Carneiro et al., 2005; Wu and Chen, 2004; Li and Li, 2001; Li and Li, 2002) and non-metals were N, S, C, B (Wu, et al., 2008; Takeshita et al., 2006; Yu et al., 2006; Treschev et al., 2008; Lettmann et al., 2001; Zaleska et al., 2007). However, a lot of density functional theory (DFT) based studies were reported explaining some important properties of TiO_2, which include but are not limited to Electronic band structure and optical properties of TiO_2 (Nura et al., 2019), phase stability in doped TiO_2 (Dorian et al., 2012). Nitrogen-doped TiO_2 was reported using DFT+U (GGA-PBE) formalism. The band gap was reduced by 0.6 eV (Navarra et al., 2022). A 0.89 eV reduction was reported using 5.6 % Cu doping on the (112) anatase TiO_2 surface through the GGA-PBE scheme (Sharma et al., 2023).

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In particular, zinc ion (zn^{2+}) has been reported to be one of the best dopants in TiO_2 due to its low cost, provision of excess negative charge carriers, and low empty trap states (Meesombad et al., 2021). In addition to this, among all the transition metal ions, Zn^{2+} gives more effective doping with TiO_2 because ionic radii of Zn^{2+} (0.74 Å) and Ti^{4+} ion (0.75 Å) are almost the same (Rauf et al., 2011). Therefore, the Zn^{2+} ion can readily replace the Ti^{4+} ion in the TiO_2 lattice without altering the crystal structure (Aware and Jadhav, 2016). Recently, increasing interest has been in doping TiO_2 nanostructured with zn^{2+} ion. Zinc-doped TiO_2 nanoparticles were reported using the solution combustion technique, narrower band gaps and slight particle refinement were observed in the nanoparticles with higher Zn concentration (Meesombad et al., 2021). However, a Zn-doped TiO2 film's higher photocatalytic activity compared with the undoped sample was reported using an acidic oxidation method and heat treatment process (Tuncay et al., 2022). Other DFT works reported a slight decrease in the band gap of the pure anatase TiO_2 due to zinc doping (Othmen et al., 2021; Vivak et al., 2023).

However, despite all these, most of the theoretical works use the conventional DFT- which has been characterized by having a typical problem of underestimating the electronic band gaps of materials. One of the best methods of relieving this problem of the conventional DFT is by employing the DFT plus Hubbard correction U (DFT+U) method in strongly correlated systems.

Therefore, this work is centered on investigating the effect of zinc doping on the structural and electronic properties of anatase TiO_2 within the framework of DFT+U formalism.

MATERIAL AND METHOD

Computational Method

The calculations were performed on the conventional cells of anatase TiO_2 using first principle calculation based on density functional theory plus Hubbard correction (DFT+U) as implemented in the QUANTUM ESPRESSO simulation package (Paola et al., 2009). We chose Hubbard value U = 7 eV - which gave the band gap close to the experimental value. The local density approximation (LDA) parameterization of Perdew and Zunger (PZ) was employed in describing the exchange-correlation potential for both the undoped and doped structures. The plane wave basis sets with the maximum kinetic energy cut-off of 340 eV were used to expand the wave functions. The electron-ion core interaction was treated by ultrasoft pseudopotentials for Ti ($3s^2\ 3p^6\ 4s^2\ 3d^2$), O ($2s^2\ 2p^4$) and Zn ($3s^2\ 3p^6\ 4s^2\ 3d^{10}$) valence orbitals as were all obtained in the pseudopotential files. The Brillouin zone integration was performed using the Monkhorst-Pack scheme (Monkhorst and Pack, 1976) with $6 \times 6 \times 6$ k-points grids.

The cell dimensions and atomic positions were fully relaxed for all calculations using the Broyden-Fletcher-Golfarb-Shannon (BFGS) algorithm until the forces acting on the atoms approached a zero value. The calculated electronic densities of states were found using denser k-point mesh.

The conventional cell used in the work has 12 atoms: 4 Ti atoms and 8 oxygen atoms. The substitutional doping was carried out at the Ti-atomic site. Thus, replacing one of the four Ti atoms with one Zn atom corresponds to 25% Zn doping (x=0.25), replacing two Ti atoms with two Zn atoms corresponds to 50% Zn doping(x=0.5), and three Ti atoms replaced by three Zn atoms corresponds to 75% Zn doping (x=0.75).

RESULTS AND DISCUSSION

Structural Properties

The anatase phase of TiO_2 exhibits a tetragonal crystal structure with space group I4/amd, as shown in Figure 1 below.

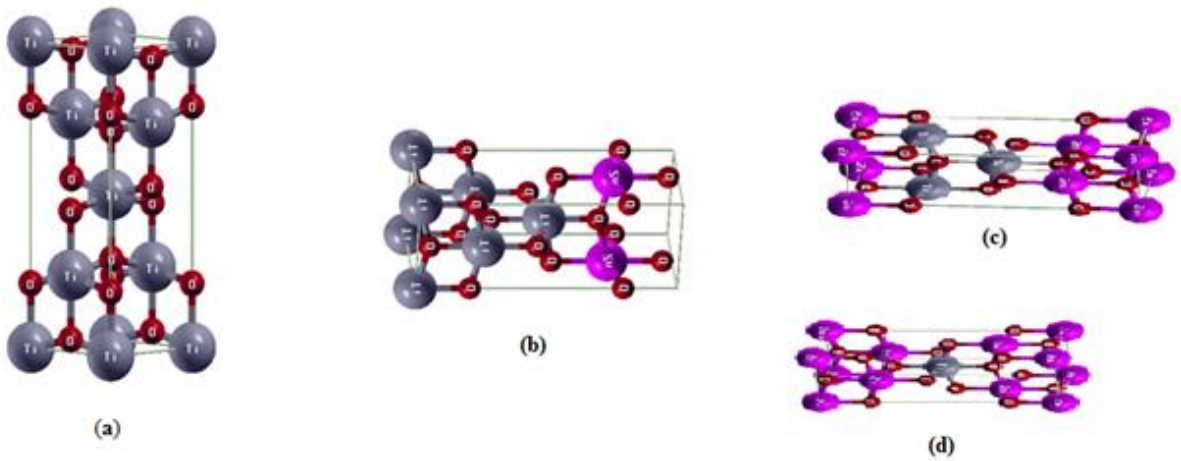

Figure 1: LDA + U Optimized Crystal Structures of **(a)** Pure Anatase TiO_2 **(b)** 25 % Zn Doped TiO_2 **(c)** 50 % Zn Doped TiO_2 **(d)** 75 % Zn Doped TiO_2

The optimized lattice parameters of the pure and doped models were calculated and shown in Table 1 below. It can be seen that the calculated lattice parameters of the pure anatase TiO_2 were in reasonable agreement with the experimentally reported data (Howard et al., 1991; Pascual et al., 1978). The percentage differences between the experimental data and our results were 1.79 % and 2.06 % for the lattice constants *a* and *c,* respectively. This has shown the reliability of the adopted method.

However, after the 25 % zinc doping, the lattice parameters were slightly decreased by 0.5 % and 0.1 % for *a* and *c* respectively. The little reduction of the lattice constants may be due to the imbalance of charges and slight variations of ionic radii of Zn^{2+} and Ti^{4+} ions. On the other hand, the unit cell volume was expanded by 0.74 %. This slight unit cell volume expansion after doping is similar to other theoretical reported work (Hao et al., 2017). Our calculation results revealed that, the other two doping models (50 % and 75 % zinc doping) have the same lattice parameters and unit cell volumes with 25 % zinc doping. This implies that a change in concentration of the dopant doesn't alter the lattice parameters or the unit cell volume.

To investigate the stability of the zinc-doped structures, we calculated the dopant formation energies of the zinc atom using equation (1) (Zhang *et al.*, 2007). The dopant formation energy in this context is defined as the energy required to insert one zinc atom with a chemical potential μ_{Zn} into the cell after removing one titanium atom with chemical potential μ_{Ti} from the same position (Dorian *et al.*, 2012).

$$E_f = E_{doped} - E_{undoped} + \mu_{Ti} - \mu_{Zn} \quad (1)$$

Where, E_{doped} is the DFT+U total energy of the zinc-doped TiO_2, $E_{undoped}$ is the DFT+U total energy of the pure TiO_2, μ_{Ti} is the chemical potential per atom of titanium bulk crystal and μ_{Zn} is the chemical potential per atom of zinc bulk crystal. Following common practice (Zhang *et al.*, 2007), the chemical potentials are calculated as the DFT total energy per atom in the bulk systems. The calculated dopant formation energies of the doped systems are shown in Table 1. All three doped structures are stable due to the possession of negative formation energies. However the 75 % zinc-doped structure has the lowest dopant formation energy and thus the most stable.

Electronic Properties

The band gap values obtained for the pure and doped TiO2 models (in this work) are compared with other DFT-reported studies, as shown in Table 2 below. It can be seen that the type of exchange-correlation approximation used greatly affects the band gap. However, the results obtained in the present work give the smallest band gap values for the doped systems compared to conventional DFT reported works.

Table 1: The LDA+U optimized lattice constants, dopant formation energies, and unit cell volumes of pure anatase TiO_2 and its zinc-doped models.

S/N	TiO_2 Models	Lattice Constants (Å)	Exp. lattice Constants(Å) (Howard et al.,1991; Pascual et al.,1978)	Dopant Formation Energy(E_f) (eV)	Unit Cell Volume (Å^3)
1	Pure Anatase TiO_2	a=b=3.717,c=9.3177	a=b = 3.7850, c = 9.5140	-	128.75
2	$Ti_{1-x}Zn_xO_2$(x=0.25)	a=b=3.698,c=9.3068	-	-10.53	129.70
3	$Ti_{1-x}Zn_xO_2$(x=0.50)	a=b=3.698,c=9.3068	-	-140.57	129.70
4	$Ti_{1-x}Zn_xO_2$(x=0.75)	a=b=3.698,c=9.3068	-	-270.87	129.70

Table 2: Comparison between this work and other DFT works reported regarding the materials, type of exchange-correlation approximation (X-C) used, band gaps, and band gap reductions.

S/N	Material/Model	X-C Used	Band-gap (eV)	Band-gap Reduction (eV)	References
1	Pure TiO_2	LDA + U	2.90	-	This work
2	25% Zn doped TiO_2	LDA + U	0.56	2.34	This work
3	50% Zn doped TiO_2	LDA + U	0.58	2.32	This work
4	75% Zn doped TiO_2	LDA + U	0.62	2.28	This work
5	Pure TiO_2	GGA	2.12	-	Vivek et al., 2023
6	6.5% Zn doped TiO_2	GGA	1.73	0.39	Vivek et al., 2023
7	Pure TiO_2	GGA + U	2.87	-	Vivek et al., 2023
8	6.5% Zn doped TiO_2	GGA + U	2.60	0.27	Vivek et al., 2023
9	Pure TiO_2	LDA	2.25	-	Othmen et al., 2021
10	2 % Zn doped TiO_2	LDA	2.24	0.01	Othmen et al., 2021
11	4% Zn doped TiO_2	LDA	1.94	0.31	Othmen et al., 2021
12	6% Zn doped TiO_2	LDA	1.86	0.39	Othmen et al., 2021

Figure 2(a) shows the DOS plot for the pure anatase TiO_2. It can be seen that there are more states in the valence band than in the conduction band. The calculated DOS is zero between 7.04 eV and 9.95 eV, which is the forbidden gap. Thus, the calculated band gap energy of the pure anatase TiO_2 is 2.9 eV. This value is close to the experimental value of 3.2 eV (Daude et al., 1977; Takeshi et al., 2001) and exceeded the theoretical values of 1.94 eV and 2.07 eV (Landman et al.,2012; Nura et al., 2019).

Figure 2(b) displays the DOS of the 25 % zinc-doped TiO_2. No states are available for occupation in the interval 5.54 eV to 6.10 eV; hence, the band gap is 0.56 eV. This is equivalent to an 80.7 % reduction compared to pure material. As shown from the plot, more states were introduced especially to the valence band.

However, the DOS plot of 50 % zinc-doped TiO_2 is shown in Figure 2(c). The zero states were observed between 4.88 eV and 5.45 eV. The calculated band gap of the material is 0.58 eV, which corresponds to an 80 % reduction compared to that of the pure anatase TiO_2.

Figure 2(d) reveals the DOS of the 75 % zinc-doped material. Like other doped models, more states were contributed to the valence band. The calculated band gap is 0.62 eV, meaning that the pure anatase TiO2 band gap was reduced by 78.6 %.

The 25 % zinc doping has the lowest band gap with the 75 % doping model having the highest. This implies that the band gap energy increases as the doping concentration increases.

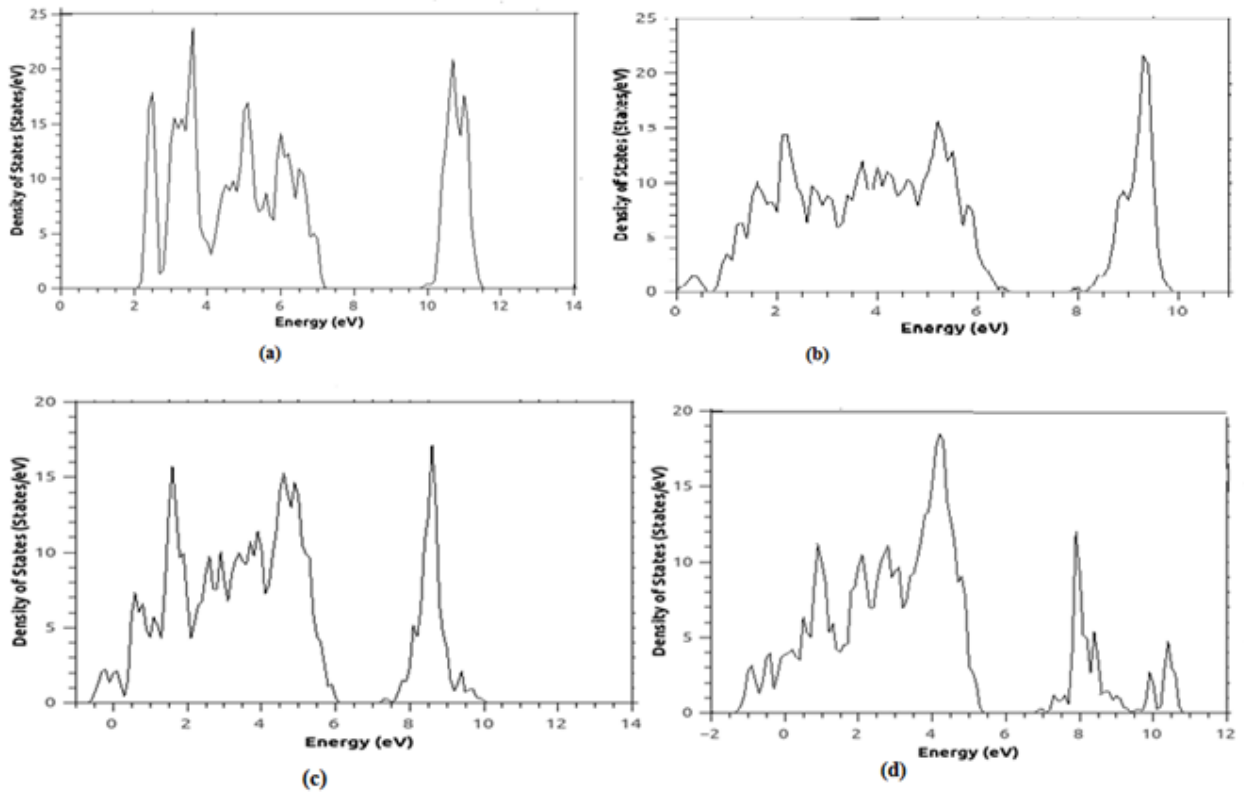

Figure 2: Density of States (DOS) plots of the**: (a)** Pure anatase TiO_2 **(b)** 25 % Zn Doped TiO_2 **(c)** 50 % Zn Doped TiO_2 **(d)** 75 % Zn Doped TiO_2

Therefore, it can be predicted that zinc doping significantly narrows the band gap of the pure anatase TiO_2 in agreement with the experimental findings and other DFT works (Meesombad et al., 2021; Othmen et al., 2021; Vivek et al., 2023).

CONCLUSION

This paper reported the first principle study on the structural and electronic properties of anatase titanium dioxide (TiO2) based on density functional theory plus Hubbard corrections (DFT+U).

Firstly, about the structural properties, the optimized lattice parameters of the pure anatase TiO_2 agreed with the experimental values. There was no structural transition after the zinc doping, only that the pure material suffered a slight expansion in its volume. We found out that all the doped structures are stable with the 75 % zinc doped model being the most stable.

Secondly, zinc doping has significantly decreased the band gap of the pure anatase TiO2 on the electronic properties. The 25 % zinc doping has the lowest band gap with the 75 % doping model having the highest. However, more states were also contributed after the doping especially in the valence band.

Conclusively, based on the results obtained, it can be predicted that the zinc-doped TiO_2 nanomaterial may be considered a very good candidate in photocatalysis and photovoltaic applications, among others.

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