Electronic Structure of Vanadium-Doped TiO$_2$ of Both Anatase and Rutile Based on Density Functional Theory (DFT) Approach

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ABSTRACT

Study of the theoretical approach to calculate the band structure and density of states (DOS) of vanadium-doped TiO$_2$ of both anatase and rutile have been done. The first-principle calculations were done using supercell (2x1x1) method. The first-principle calculation of V-doped TiO$_2$ of both anatase and rutile were analyzed by density-functional theory (DFT) with generalized gradient approximation from Perdew-Burke-Ernzerhof (GGA+PBE), Perdew-Wang’s 1991 (GGA+PW91) and local density approximation (LDA) for exchange-correlation functionals. The calculation of electronic structures show that the V-doped TiO$_2$-anatase with high concentration (7.93%) in 24 atoms are direct- and indirect-gap semiconductor, whereas the V-doped TiO$_2$-rutile with high concentration (15.79%) in 12 atoms is direct-gap semiconductor. The V-doped TiO$_2$ of both anatase and rutile produce the intermediate bands in the upper states. The V-doped anatase produces intermediate band, which is 2.05, 2.04, 2.06 eV above the valence band for GGA+PBE, GGA+PW91 and LDA, respectively. Meanwhile the V-doped rutile produces-intermediate band, which is 1.76, 1.82, 1.74 eV above the valence band for GGA+PBE, GGA+PW91 and LDA, respectively.

Keywords: anatase, band-gap DFT, electronic structure, rutile.

INTRODUCTION

Titanium dioxide or titania (TiO$_2$) is a n-type semiconductor. It has eleven different structure phases (allotrop). In nature, TiO$_2$ has three kinds of crystal structure: anatase, rutile and brookite. Anatase and rutile are the two most stable forms and are both produced on an industrial scale. Anatase phase is a TiO$_2$ polymorph which is less stable than rutile phase, but more efficient than rutile for several applications, including photocatalysis (Zhang et al., 2016; Muctuma et al., 2015), antibacterial activity (Galkina et al., 2014; Huang et al., 2000; Maness et al., 1999), and dyesensitized solar cells (Grätzel, 2005; Grätzel, 2004). In all these applications, surface properties are of major importance.
However, such potential applications are seriously limited by the intrinsic wide energy gaps of TiO$_2$, which confine the advantages of the TiO$_2$ phases to be viable only under ultraviolet (UV) radiation.

Many attempts have been made to improve the photocatalytic performance of TiO$_2$ under visible-light irradiation, such as through transition metal (V, Mn, Fe, Cu, Ce, W, Cr, Co, Ag, etc.) (Al-Hartomy, 2014; Chang and Liu, 2014; Yang et al., 2014; Zhang et al., 2013; Tian et al., 2012; Thuy et al., 2012; Liu et al., 2009) and non-metal doping (N, C, S, etc.) (Zhao et al., 2013; Dong et al., 2008; Zhao et al., 2008; Yang et al., 2007), noble metal deposition on TiO$_2$ surfaces (Ma et al., 2014; Wang et al., 2008), semiconductor coupling (Hoyer and Weller, 1994), inorganic sensitizing (Hu et al., 2006) and organic dye sensitizing (Tan and Wu, 2006). The most promising method to reduce the effective band gap of TiO$_2$ is through the doping of impurities into the TiO$_2$ lattice to modify its electronic structure. Especially in recent years, a number of attempts have been made to improve the visible-light absorption of TiO$_2$ both with transition metal (V, Mn, Fe, Cu, Ce, W, Cr, Co, Ag, etc.) and non-metal dopants (N, C, S, etc.) to modify the electronic structure and improve the photocatalytic reaction efficiency which was strongly influenced by the recombination rate of photo-generated electrons and holes.

Theoretical investigations have also been carried out to study the energy band structures of TiO$_2$ phases including anatase and rutile. The rutile phase, which is the most stable form of TiO$_2$, exhibits a direct band structure of 3.0 eV (Grant, 1959), while the band structure of the metastable anatase phase is indirect band structure of 3.2 eV in nature (Tang et al., 1994). Some studies have also been made by several groups to introduce vanadium metal which can improve the photocatalytic activity of TiO$_2$ and extend its optical absorption to the visible-light region.

Pure TiO$_2$ is a wide band-gap semiconductor with the O $p$ band filled and the Ti-$d$ band empty. When a V atom replaces a Ti atom the resulting system is metallic because of the lack of two electrons necessary to fill up the O $p$ band (Wang et al., 2014; Peng et al., 2014). Thus, it can be expected that V-incorporation in TiO$_2$ can result in some unusual optical transitions and the optical absorption in the visible range. Two type of the doping of vanadium in the TiO$_2$ lattice are substitutional (Islam et al., 2015; Wang et al., 2014) and interstitial (Kokorin et al., 2016). The electronic properties of vanadium-doped rutile TiO$_2$ are investigated theoretically with a Hartree-Fock/DFT hybrid approach by Islam et al. (2015). They used supercells (Ti$_{16}$O$_{32}$, Ti$_{32}$O$_{64}$, and Ti$_{54}$O$_{108}$) as models of the doped rutile TiO$_2$. In the present study, we considered substitutional doping of V$^{4+}$ in both anatase and
rutile phases. The electronic properties of V$^{4+}$-doped TiO$_2$ of anatase (Ti$_7$VO$_{16}$) and rutile (Ti$_3$VO$_8$) have been investigated using the (2x1x1) supercell model by using the first-principles calculation based on density-functional theory (DFT). This is essential for a proper understanding of the material itself and also of the processes used for its production on an industrial.

**METHODS**

All calculations presented are based on density-functional theory (DFT). Kohn-Sham density functional theory calculations are performed with the density functional theory (DFT) using the local density approximation (LDA) (Kohn and Sham, 1965) and generalized gradient approximation (GGA) proposed by Perdew-Burke-Ernzerhof (GGA+PBE) (Perdew et al., 1996), Perdew and Wang’s 1991 (GGA+PW91) (Perdew et al., 1992) for the exchange correlation potential. The electronic properties of V-doped TiO$_2$ of both anatase and rutile phases have been investigated using the (2x1x1) supercell model as implemented within ADF-BAND package of version 2014.10 (SCM, 2014). The substitutional method has been taken into account in this paper. The V atoms are used to substitute Ti atom in TiO$_2$, because atom radius of V are larger than the O atom. The doped TiO$_2$ systems form the configurations of V$^{4+}$-doped TiO$_2$ of anatase (Ti$_7$VO$_{16}$) and rutile (Ti$_3$VO$_8$).

The unit cell of TiO$_2$ in anatase, rutile and (2x1x1) supercell model considered in this study are shown in Figure 1a, 1b, 2a, and 2b. The ideal anatase TiO$_2$ has a tetragonal structure with the space group I4$_1$/amd, which contains four titanium atoms and eight oxygen atoms in unit cell. The cell parameters are $a = b = 3.785$ Å and $c = 9.514$ Å (Weirich et al., 2000). The structure of anatase can be described in terms of chains of TiO$_2$ octahedra. Each Ti$^{4+}$ ion is surrounded by an octahedron of six O$^{2-}$ ions. Our model consists of two unit cells stacked along the $a$-axes, where one Ti atom is substituted by a 3$d$ transition V atom. The (2x1x1) supercell model of V-doped anatase phase contains 24 atoms, in this way the structure of Ti$_7$VO$_{16}$ is obtained. The atomic percentage of the impurity was found to be 7.93 at% (Figure 1b).

The rutile structure belongs to the tetragonal crystal system (space group P4$_2$/mmn), and the lattice parameters are $a = b = 4.594$ Å and $c = 2.958$ Å (Swope et al., 1995). The (2x1x1) supercell model of V-doped rutile phase is composed of 12 atoms, which
correspond to Ti$_{(1-x)}$V$_x$O$_2$ (x = 0.25), in this way, the structure of Ti$_3$VO$_8$ is obtained. The atomic percentage of the impurity was found to be 15.79 at % (Figure 2b).

![Figure 1. Models for calculation, (a) unit cell of anatase and (b) structure of (2x1x1) supercell model of V-doped anatase containing 24 atoms (Ti$_7$VO$_{16}$)](image)

![Figure 2. Models for calculation, (a) unit cell of rutile and (b) structure of (2x1x1) supercell model of V-doped rutile containing 12 atoms (Ti$_3$VO$_8$)](image)

**RESULTS**

**Band Structure and Density of State (DOS) of V-doped Anatase**

The V-doped anatase band structure along the direction of the brillouin zone high symmetry point is as in Figure 3. Figure 3 shows the top of valence band which approximately locates near the k-point = 1, and the bottom of the conduction band which locates at the k-point = 1 or k-point = 16. This means that TiO$_2$ with V-doped anatase TiO$_2$ structure is direct and indirect-gap semiconductor.

Figure 4 gives the partial and total density of states (DOS) of V-doped anatase within GGA+PBE, GGA+PW91 and LDA using the (2x1x1) supercell method. The valence band of V-doped TiO$_2$-anatase mainly consists of the 2p, 2s states of O and 3d states of V and Ti. The upper valence bands show a strong hybridization between 2p orbitals from O atoms and 3d orbitals from V and Ti atoms. The top of the valence bands was dominated by the O 2p orbitals, while the conduction bands, especially the bottom, contain significant contributions from the V 3d and Ti 3d orbitals. It is obvious from anatase model in Figure 1b that the doped V 3d orbitals substantially contributed to the valence bands and the impurity bands. The Ti 3d and V 3d states give rise to some bands in the energy range from 4.00 to 11.00 eV. The lowest conduction band is dominated by V 3d
states. Meanwhile, the hybridization among the V 3d, Ti 3d and O 2p levels at the valence band can be observed as in Figure 4. In the uppermost valence band, the O 2p states are predominantly found between -2.50 to 2.50 eV, while the O 2s states appear in the range from -15.00 to -13.00 eV.

![Figure 3](image3.png)

**Figure 3.** The band structure of V-doped anatase within GGA+PBE, GGA+PW91 and LDA using the (2x1x1) supercell method.

![Figure 4](image4.png)

**Figure 4.** The corresponding total-density of state (t-DOS, black line) and partial-density of state (p-DOS, blue, yellow and red line) of V-doped anatase within GGA+PBE, GGA+PW91 and LDA using the (2x1x1) supercell method.
The V 3d states in V-doped TiO$_2$-anatase have been observed in the energy range from 2.00 to 3.00, 2.50 to 3.50 and 2.75 to 3.75 eV. The O 2s states have slightly shifted to low energy range. V-incorporation atom induces the increasing $p$ states in the top of valence band. The valence band mainly consists of the 2$p$, 2$s$ states of O and 3$d$ states of V and Ti. In this early calculations, the V-doped anatase with 7.93% in 24 atoms produced upper states, and it was 2.05, 2.04, 2.06 eV above the valence band and 0.48, 0.54 and 0.47 eV below the conduction band for GGA+PBE, GGA+PW91 and LDA, respectively (Figure 5), which are suitable with the experimental value of V-doped TiO$_2$-anatase with high concentration (4.17%) in 24 atoms, and it was 1.82 eV above the valence band (Wang et al., 2014). The band gaps of the V-doped anatase from this research have a much smaller value than the band gap un-doped TiO$_2$ (anatase) calculation using LDA method that is equal to 2.59 eV (Sutrisno and Sunarto, 2014).

**Figure 5.** The Intermediate band of V-doped anatase with 7.93% in 24 atoms produced upper states within GGA+PBE, GGA+PW91 and LDA using the (2x1x1) supercell method.

In the uppermost valence band, O 2$p$ states are predominantly found between -4.50 and 1.00 eV, while O 2$s$ states appear in the range from -15.0 to -13.0 eV. The V 3$d$ states give rise to some bands in the energy range from 4.00 to 5.00 eV, meanwhile the Ti 3$d$ states are predominantly found between 5.00 to 10.00 eV. As Wang et al. (2014) clarified for V-doped TiO$_2$-anatase, the D$_{4h}$ symmetry caused the three-fold degenerate $t_{2g}$ (3$d_{xy}$, 3$d_{xz}$, and 3$d_{yz}$) and two-fold degenerate $e_g$ (3$d_{x^2-y^2}$ and 3$d_z$) of a transition metal cation to further split; the $t_{2g}$ split into a two-fold degenerate levels of both 3$d_{yz}$ and 3$d_{xz}$ and a level of 3$d_{xy}$ while the $e_g$ split into two levels of 3$d_{x^2-y^2}$ and 3$d_z$.

**Density of State (DOS) and Band Structure of V-doped Rutile**

Band structure and density of states (DOS) V-doped TiO$_2$-rutile within GGA+PBE, GGA+PW91 and LDA using (2x1x1) supercell method are performed in the configuration of Ti$_3$VO$_8$, which is presented in Figure 6 and 7, respectively. In Figure 6, the top of valence band approximately locates near the k-point = 1 and the bottom of the conduction band locates at the k-point = 1; this means that V-doped rutile structure is a direct-gap semiconductor. The valence band of V-doped TiO$_2$-rutile mainly consists of the 2$p$, 2$s$
states of O and 3d states of V and Ti. The upper valence bands showed a strong hybridization between 2p orbitals from O atoms and 3d orbitals from V and Ti atoms.

Figure 6. The band structure of V-doped rutile within GGA+PBE, GGA+PW91 and LDA using the (2x1x1) supercell method.

Figure 7. The corresponding total-density of state (t-DOS, black line) and partial-density of state (p-DOS, blue, yellow and red lines) of V-doped rutile within GGA+PBE, GGA+PW91 and LDA using the (2x1x1) supercell method.

The V-doping can induce the upper states in band gap, which are mainly composed of the 3d and 2p electronic states. From the results of DOS of V atoms in Figure 7, the 3d electronic states are mainly attributed to the V, while the p electronic states are due to the
O 2p states. These results are consistent with the previous experimental and theoretical results (Prasai et al., 2012; Mo et al., 1995). In this early calculations, the V-doped rutile with 15.79% in 12 atoms produced upper states, and it was 1.76, 1.82, 1.74 eV above the valence band and 0.41, 0.39, 0.41 eV below the conduction band for GGA+PBE, GGA+PW91 and LDA, respectively (Figure 8). These midgap electronic states may induce some visible optical transition. Meanwhile, the p and d states have been observed in the energy range of 7-9 eV at the bottom of valence band due to the doping of V. These p and d states are similar to the midgap states. To the V-doped TiO2-rutile, it is observed that the 3d states of Ti mainly appear at the valence band, particularly, dominated at the top and bottom of valence band. Thus, the enhanced d states of V-doped TiO2-rutile at the uppermost valence band are due to the V-dopant, which is consistent with the previous theoretical results. Even in the high concentration doping (Ti3VO8) system, the V 3d states also located above the valence band using GGA+PBE, GGA+PW91 and LDA method. The increasing d electronic states of V-doped TiO2-rutile at the uppermost valence band lead to the band gap narrowing. The valence band mainly consists of the 2p, 2s states of O and 3d states of V and Ti. In the uppermost valence band, O 2p states were predominantly found between -19.00 and -13.00 eV, while O 2s states appear in the range from -32.00 to -28.00 eV. The V 3d states give rise to some bands in the energy range from -13.00 to -12.00 eV, meanwhile The Ti 3d states were predominantly found between -9.00 to -5.00 eV. The calculated minimum band gaps of GGA+PBE, GGA+PW91 and LDA are about 1.74, 1.79 and 1.78, eV respectively, which are less than the experimental value of undoped TiO2-rutile of 3.00 eV (Grant, 1959). The band gaps of the V-doped anatase from this research have smaller value than the band gap of un-doped TiO2 (rutile) generated from the calculated using LDA method of 1.67 eV (Sutrisno and Sunarto, 2014).

Figure 8. The Intermediate band of V-doped rutile with 15.79% in 12 atoms produced upper states within GGA+PBE, GGA+PW91 and LDA using the (2x1x1) supercell method.
CONCLUSION

The first-principle calculation of V-doped TiO$_2$ of both anatase and rutile were analyzed by using density-functional theory (DFT) with generalized gradient approximation from Perdew-Burke-Ernzerhof (GGA+PBE), Perdew-Wang’s 1991 (GGA+PW91) and local density approximation (LDA) for exchange-correlation functionals. The calculation of electronic structures show that the V-doped TiO$_2$-anatase with high concentration (7.93%) in 24 atoms are direct- and indirect-gap semiconductor, whereas the V-doped TiO$_2$-rutile with high concentration (15.79%) in 12 atoms is direct-gap semiconductor. The V-doped TiO$_2$ of both anatase and rutile produce the intermediate bands in the upper states of band gap. The calculated band gaps of V-doped TiO$_2$-anatase from GGA+PBE, GGA+PW91 and LDA are 2.05, 2.04, 2.06 eV above the valence band and 0.48, 0.54 and 0.47 eV below the conduction band, respectively. The V-doped TiO$_2$-rutile produces intermediate band, which are 1.76, 1.82, 1.74 eV above the valence band and 0.41, 0.39, 0.41 eV below the conduction band for GGA+PBE, GGA+PW91 and LDA, respectively.

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