Title	First-principles calculation of electronic structure of V-doped anatase TiO ₂
Authors(s)	Long, Run, English, Niall J.
Publication date	2010-08-23
Publication information	Long, Run, and Niall J. English. "First-Principles Calculation of Electronic Structure of V-Doped Anatase TiO ₂ " 11, no. 12 (August 23, 2010).
Publisher	Wiley
Item record/more information	http://hdl.handle.net/10197/2790
Publisher's statement	This is the authors' version of the following article: "First-principles calculation of electronic structure of V-doped anatase TiO ₂ " published in ChemPhysChem, 11 (12): 2606-2611. It is available in its final form at http://dx.doi.org/10.1002/cphc.201000329
Publisher's version (DOI)	10.1002/cphc.201000329

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First-principles calculation of electronic structure of V-doped anatase TiO₂

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The energetic and electronic structures of V-doped anatase TiO₂ have been investigated systematically by the GGA+U approach, including replacement of Ti by V in the absence and presence of oxygen vacancies and the presence of an interstitial site. It was found that V should exist as a V⁴⁺ ion in the replacement of Ti in the anatase lattice, the electron transitions of which to the conduction band from V 3d states are responsible for the experimentally observed visible-light absorption. The influence of V dopant concentration on the electronic and magnetic properties is also discussed, such as the influence of the U value in systems containing oxygen vacancies and spin flip phenomena for interstitial V-doping.

1. Introduction

Titanium dioxide (TiO_2) has attracted intense attention as a promising metal oxide material for application in photocatalysts, water splitting and solar cells because of its unique physical and chemical properties [1, 2], such as high oxidative power, long-term stability, low cost and non-toxicity. However, the large intrinsic band gap of titania (3.2 eV for anatase and 3.0 eV for rutile) leads to activity only under ultraviolet light irradiation and thereby limits its photo-excited electron efficiency. To extend its photon absorption edge to the visible-light region, it is necessary to improve the photocatalytic efficiency, and many experiments have been performed to dope impurity atoms into the TiO_2 lattice in an attempt to narrow the band gap and to improve the efficiency. Both mono- and co-doping by metal and non-metal elements have been reported [3-11].

V-doped TiO_2 semiconductors have also been studied experimentally and theoretically, chiefly because of evidence of ferromagnetism at and above room temperature [12-14]. This makes them potential candidates for dilute magnetic semiconductor (DMS) applications in spintronic devices. In addition, a number of experiments have been carried out to investigate the photocatalytic efficiency of V-doped TiO_2 . For example, Martien et al. reported reduced photoreactivity in TiO_2 doped with V^{5+} via co-precipitation [15], while Choi et al. pointed out that V^{4+} -doped TiO_2 increased photoreactivity [16]. Recent reports from Klosek et al. also indicate that V^{4+} -doped TiO_2 is quite active under visible-light irradiation [17]. Visible absorption in these catalysts is indicative of the excitation of a 3d electron from a V^{4+} center into the TiO_2 conduction band [18]. To the best of our knowledge, there has been no related theoretical work which attempts to rationalize and explain the relationship between electronic structure and photocatalytic activity underlined by these experimental observations. As indicated by two groups [13, 14] standard local density approximation (LDA) calculations for V-doped TiO_2 would produce qualitatively wrong semi-metallic behavior, while DFT+U was found to describe properly semiconductor characteristics, which has also been indicated by Yang et al. of Cr-doped TiO_2 systems [5]. In this work, the electronic structure of V-doped TiO_2 has been studied by the GGA+U method, and it has been confirmed that the GGA+U

approach affords a good description for V 3d state-splitting and for estimation of the band gap of titania.

In this paper, we aim to resolve three main considerations of V-doping in anatase: 1) the energetic feasibility of formation of substitutional and interstitial V ions, 2) the origin of band gap narrowing, and 3) the influence of V dopant concentration on electronic structure.

2. Computational methodology

We have used *ab initio* band-structure and total energy methods, implemented in the Vienna *Ab initio* Simulation Package (VASP) [19, 20], to study the geometric and electronic properties of V-doped anatase. Two supercells, containing 48 and 108 atoms, were used to compare the effects of V doping concentration (2.1 and 0.9 at %, respectively) on electronic structure. The projected augmented wave (PAW) method was chosen to represent electron-ion interactions [19]. The exchange-correlation interactions were handled by the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) approach [21]. The Brillouin-zone integration was performed on a well-converged $4 \times 4 \times 4$ and $2 \times 2 \times 2$ Monkhorst-Pack k -point meshes [22] for the 48- and 108-atom supercells, respectively, in the case of geometry optimization, and a $4 \times 4 \times 4$ k -point mesh was used to calculate the density of states using tetrahedron method with Blöchl corrections. The plane wave cut-off energy was set to 400 eV. Both the atomic positions and lattice parameters were optimized using the GGA method until the atomic forces were smaller than 0.01 eV/Å. To account for strongly correlated interactions of the d shells, the DFT+U method was used to calculate the electronic properties, and on-site effective U ($U = U' - J$) parameters, introduced by Dudarev et al. [23], were applied to Ti 3d and Cr 3d electrons. Our previous work has shown that this method affords a good description for both geometric and electronic structures [7-9], and this has also been found by Yang et al. [5].

3. Results and Discussions

3.1 Formation Energies

It is necessary to clarify as to whether the V dopant would exist as a substitutional or interstitial impurity in the anatase lattice. One V ion located at the host Ti site with and without an adjoining oxygen vacancy is denoted by V@Ti and V@Ti-O_v, respectively. V_{in} is used to represent if the V ion locates at the interstitial site. The models were shown in Figure 1. Here, we used different origin in Figs 1(a) and 1(b) for eyes. To evaluate the relative difficulty for the incorporation of V dopants into host lattice, the formation energies were calculated, which can also determine the relative stability of the doped systems. The formation energies of substitutionally doped V with and without oxygen vacancies, and of interstitially doped V, were calculated by eqns. (1), (2), and (3) respectively:

$$E_{form} = E(doped) - E(undoped) - \mu_V + \mu_{Ti} \quad (1)$$

$$E_{form} = E(doped) - E(undoped) - \mu_V + \mu_{Ti} + \mu_O \quad (2)$$

$$E_{form} = E(doped) - E(undoped) - \mu_V \quad (3)$$

where $E(doped)$ and $E(undoped)$ represent the total energies for pure and undoped anatase, respectively. The formation energies for the different doped systems were considered in this work as a function of the oxygen chemical potential (μ_O), which is a parameter that characterizes the oxygen environment during synthesis [24, 25]. The environment acts as a reservoir, which can give or take any amount of oxygen without changing its temperature and pressure [26]. Low and high values of μ_O correspond to O-poor and -rich conditions, respectively. By referencing μ_O to the energy of an O atom in an O₂ molecule ($\mu_O = \frac{1}{2}\mu(O_2) + \mu'_O$), we take $-4\text{eV} \leq \mu'_O \leq 0\text{eV}$, where the value $\mu'_O = 0$ corresponds to the O-rich limit, whereas $\mu'_O = -4\text{eV}$ is approximately half the enthalpy of formation of anatase (our calculated value is 9.98 eV in comparison to an experimental value of 9.8 eV) [27]. The chemical potential of a Ti atom, μ_{Ti} , was calculated from $\mu_{Ti} = \mu(TiO_2) - 2\mu_O$. The chemical potential for V (μ_V), was fixed and calculated from the

formula $\mu_v = \mu(\text{VO}_2) - \mu(\text{O}_2)$. The calculated formation energies for a 48-atom supercell have been plotted in Figure 2 (solid line), which suggest the following: 1) the replacement of Ti by V is energetically favorable under O-rich (Ti-poor) growth conditions without an oxygen vacancy, although the formation energies are comparatively large under Ti-rich (O-poor) growth conditions; 2) the introduction of V into Ti sites is energetically unfavorable in terms of concomitant creation of an oxygen vacancy; 3) the formation energies are always high for interstitial placement of V into the TiO_2 lattice regardless of growth conditions. Therefore, it is expected that V should be substituted for Ti ions in TiO_2 lattice. To confirm these energy results, the 108-atom supercell was used to calculate the formation energies of the defective systems and the results have been plotted in Figure 2 (dotted line), which indicates clearly that the energy difference between the two differently sized supercells is very small. Therefore, our calculated energy results are reliable for V-doped TiO_2 systems.

3.2 Electronic Structure

It is well known that standard DFT calculations underestimate the band gap of undoped anatase owing to shortcomings in the GGA method. However, the DFT + U approach can improve results significantly through placing on-site interactions U to describe the strong Coulomb interaction between the Ti 3d electrons. Here $U = 5.8$ eV was applied to Ti 3d electrons [5] and produced a band gap of 3.0 eV. It should be noted that the band gap is sensitive to the U value in the DFT +U calculation, and it must be used with care. A variety of U values were tested to evaluate its effect on V 3d states 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0 eV, and it was found that $U = 5.0$ eV can describe correctly the electronic structure of the V-doped 48-atom TiO_2 supercell with and without oxygen vacancy (see Supporting Information for further details).

3.2.1 Substitutional V replacement of Ti with and without an oxygen vacancy

The calculated band gap of undoped anatase was 3.0 eV, as shown in Fig. 3(a), which agrees well with the experimental value of 3.20 eV due to partial correction by DFT+U of the band gap problem. The calculated band structures of V@Ti and V@Ti- O_v are displayed in Figs. 3(b)-3(c), respectively (with black line for down-spin

and red line for up-spin). The dashed lines represent the Fermi level, E_F . This implies that states below E_F are occupied and those above E_F are unoccupied. Here, we have aligned the energy levels of the defective cell with the valence band maximum (VBM) of pure bulk TiO_2 . For V-doped TiO_2 (V@Ti), one Ti ion was replaced by one V ion, extending the host band gap to about 3.1 eV, as shown in Fig. 3(b), which is 0.1 eV larger than the pure case (3.0 eV). The isolated states are located above the VBM and resonate with conduction band minimum (CBM) of TiO_2 and the gap is about 2.55 eV, measured between the occupied and unoccupied states. The gap narrowing is about 0.45 eV relative to pure TiO_2 (3.0 eV). Therefore, V-doped anatase can extend the adsorption edge to the visible light region in the presence of V^{4+} ions in the lattice with electron transitions from V 3d states to the host CBM, which serves to explain well the experimental finding that V-doped TiO_2 is quite active under visible-light irradiation in the range of 2.5-2.7 eV [17]. To examine the influence of the oxygen vacancy on the electronic structure of V-doped TiO_2 , one oxygen atom was removed from the V-doped TiO_2 system (V@Ti-O_v) and the calculated band structure is shown in Fig. 3(c). There appear to be several impurity energy levels located in the middle of the gap as well as below the host CBM. Three are occupied and one is unoccupied. The host band gap is about 2.74 eV, which is about 0.26 eV smaller than that of pure TiO_2 . Furthermore, the gaps are reduced substantially between the occupied and unoccupied levels. Both serve to extend the adsorption edge into the visible-light region. However, the unoccupied energy level from the Ti^{3+} orbital not only benefits for gap narrowing, but also traps photo-excited electrons, which depend on competition between the carrier lifetimes and electron transfer timescales.

To explore further the origin of band gap narrowing of substitutionally V-doped TiO_2 , the calculated density of states (DOS) and projected DOS (PDOS) have been plotted in Fig. 4. For the V@Ti case, the V3d states are split in spin-up and spin-down gap states and located at the band gap, as displayed in Fig. 4(b). The Fermi level E_F is above the V3d spin-up states, indicating an insulating state, while in the PDOS (cf. Fig. 4(b')) are located at the CBM, showing that the splitting of V 3d occupied and unoccupied states is well described by the GGA+U method. Here, electrons excited from the host VBM to unoccupied e_g states and to the host CBM are responsible for

visible-light absorption. As shown in Fig. 4 (b'), the PDOS shows clearly the V3d splitting behavior. The D2d symmetry results in three-fold degenerate t_{2g} states (d_{xy} , d_{xz} , and d_{yz}) and two-fold degenerate e_g states ($d_{x^2-y^2}$ and d_{z^2}), which is typical behavior for splitting of a transition metal cation, *i.e.*, V^{4+} ($3d^14s^0$). In particular, the up-spin d_{xy} states are occupied and up- and down-spin d_{xz} , d_{yz} and e_g states are unoccupied, leading to each V dopant at a Ti site having a magnetic moment of 1.0 μ_B and confirming further the V cation as a V^{4+} state.

For the $V@Ti-O_v$ case, the DOS and PDOS are displayed in Figs. 4(c) and 4(c'). The occupied V 3d states are fully spin-polarized and are situated in discrete bands in the band gap about 1.5 and 1.78 eV above the host VBM. The PDOS (cf. Fig. 4(c')) shows that both the V3d and Ti3d orbitals contribute to the occupied states while the unoccupied state below the CBM originate from the Ti 3d orbital due to Ti^{4+} reduction to Ti^{3+} arising from the removal of one oxygen atom. Here, the V3d and Ti3d spin-polarization induce a total magnetic moment of 3.0 μ_B per supercell and 2.0 μ_B on V ions. This indicates that the adjacent oxygen vacancy of the VO_5 structure requires that the V ion releases an electron to keep the semiconductor behavior of the TiO_2 . Therefore, the electron configuration on the V ion should be V^{3+} ($3d^24s^0$).

To investigate the influence of doping concentration on the electronic and magnetic structures of substitutionally V-doped TiO_2 with and without an oxygen vacancy, we calculated the band structure, DOS and PDOS of the two cases with the 108-atom supercell with $U = 5.0$ eV, and these are shown in Figs. 5 and 6, respectively. It was found that the electronic behavior of $V@Ti$ is similar with the results of 48-atom supercell (cf. Fig. 5(b) and Fig. 6(b)). However, the band gap is only 2.30 eV, and the narrowing is about 0.7 eV vis-à-vis pure anatase. This implies that substitution by V of Ti can narrow the band gap significantly with a suitable doping concentration rather than a higher doping level. At the same time, here the total magnetic moment and magnetic moment on V ions are identical to those for the higher V concentration in the 48-atom supercell. On the other hand, although the band structure (cf. Fig. 5(c)) shows a similar band gap of 2.72 eV and impurity energy level locations with the 48-atom supercell in the $V@Ti$ system with an oxygen vacancy (cf. Fig. 3(c)), it is only the d_{yz} states of V 3d electrons in the spin-up polarized state which locate in the

forbidden gap (cf. Fig 6(c)). Increasing U up to 6.0 eV, results in splitting V 3d t_{2g} (d_{xy} , d_{yz}) states in the band gap (not shown here). Therefore, it is possible that a smaller U , such as 5.0 eV, does not describe the electronic structure of the interplay between V dopant and an oxygen vacancy at lower V doping concentrations.

3.2.2 Interstitial V Doping

Owing to the small ionic radius of the V cation (0.58 Å for V^{4+} and 0.54 Å for V^{5+}) [27], interstitially V doped-TiO₂ (V_{in}) was also considered. Here, a magnetic moment on the V ion of 2.5 μ_B and a total magnetic moment of 1.0 μ_B were found with $U = 5.0$ eV. This is a strange finding, because the total magnetic moment induced by one interstitially placed V should be 5.0 μ_B in the TiO₂ lattice. One possible explanation may be that higher V doping concentration induced spin flip of the adjacent Ti ion, and this is proven by consideration of the spin-density, as displayed in Fig. 7. Yellow and blue represent the spin-up and spin-down spin-density, respectively. This shows that the Ti ion spin is of the opposite direction compared to the V ion. To investigate the influence of doping concentration on the magnetic properties, the interstitially doped 108-atom supercell was optimized, and it was found that the total magnetic moment was 5.0 μ_B (with 2.5 μ_B on V ion), so that spin-polarization on the adjacent Ti ions are of the same direction. The spin-density result was also confirmed, as displayed in Fig. 7 and which indicates clearly that V and Ti have the same spin-polarization orientation. Here, in the 48-atom supercell, the V dopant and adjacent O atoms form five V-O bonds (cf. Fig. 1b), one of the bonds is 1.950 Å along z-axis, two of them are 2.064 Å along y-axis and the remaining two are 1.905 Å along x-axis, the distances between the V dopant and the nearest Ti atoms are 2.665 Å, indicating the interstitial V forms a very symmetrical structure. On the other hand, in the 108-atom supercell, the corresponding five V-O bond lengths are 1.944, 2.042, 2.042, 1.906, 1.906 Å, respectively. The distances between V dopant and two nearest Ti atoms are 2.661 Å. The geometrical parameter close to each other in 48-atom and 108-atom supercell, which implies that spin flip is not from structure distortion. Therefore, the increasing V concentration will lead to spin flip and serve to decrease the magnetic moment of interstitially doped TiO₂.

In order to analyze their electronic properties, the DOS and PDOS of interstitially doped 48- and 108-atom TiO₂ supercells were calculated and are shown in Figs. 4 (d) and 6 (d). For the 48-atom system, the V 3d electrons were split into three occupied states with two spin-up d_{xy} and d_{xz} orbital and one spin-down d_{yz} orbital, as well as splitting of Ti 3d electrons, leading to a total magnetic moment of 1.0 μ_B because the polarized Ti ion has the opposite spin relative to the V ion. On the other hand, for the interstitially doped 108-atom supercell, two of the three V 3d t_{2g} states (d_{xz} , d_{yz}) as well as Ti 3d states are split into occupied spin-up states, leading to a total magnetic moment of 5.0 μ_B . To check clearly possible electron transitions, the band structures of the interstitially doped 48- and 108-atom supercells are shown in Figs. 3(b) and 5(b) (black line for down-spin and red line for up-spin). Three occupied impurity levels were in the band gap due to spin-splitting of V3d and Ti 3d orbitals, resulting in a substantially smaller gap to the host CBM. The host band gap is about 2.45 eV and 2.58 eV for the interstitially doped 48- and 108-atom supercells, respectively, and the gap narrowing is about 0.55 and 0.42 eV vis-à-vis pure anatase. Clearly, interstitial V-doping in TiO₂ can enhance visible-light adsorption without electron traps because all impurity levels are occupied. In addition, the Fermi level is located just below the CBM and thereby shows *n*-type conduction characteristics, which may be of use in the fabrication of transparent conducting films and for electrode materials in solar cells.

4. Conclusions

Substitutionally and interstitially V-doped TiO₂ have been investigated by first-principles DFT calculations in the framework of the GGA+U approach, involving V@Ti, V@Ti-O_v and V_{in} models. By analyzing the geometrical structure, the formation energies, and the electronic structure, the following conclusions can be obtained:

I) Under O-rich growth conditions, the formation energies are in the order V@Ti < V@Ti-O_v < V_{in} and V@Ti is the most energetically favorable doping configuration under O-rich growth conditions.

II) Substitutionally doped anatase (*i.e.*, V⁴⁺ (3d¹4s⁰)) should be responsible for

experimentally reported visible-light photocatalytic activity [17] along with electron transition from V 3d states to the conduction band. The gap narrowing decreases with increasing V doping concentration.

III) In substitutionally doped anatase with an oxygen vacancy, the V ion should exist as V^{3+} ($3d^24s^0$) owing to the 3.0 μB magnetic moment induced by spin-polarized V 3d states in the gap. For interstitially doped anatase, spin flip phenomenon originate from higher V doping levels, and this can also be used in transparent conducting films due to *n*-type conductivity.

IV) Electronic and magnetic properties are sensitive to doping concentration and the Hubbard parameter *U* in presence of a V/oxygen vacancy complex defect and interstitial V dopant.

Acknowledgements

This work was supported by the Irish Research Council for Science, Engineering and Technology (IRCSET). The authors thank the Irish Centre for High End Computing and Science Foundation Ireland for the provision of computational resources.

References

- (1) A. L. Linsebiger, G. Q. Lu, J. T. Yates, *Chem. Rev.* **1995**, 95, 725.
- (2) A. Fujishima, K. Honda, *Nature (London)* **1972**, 28, 37.
- (3) R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science* **2001**, 293, 269.
- (4) T. Umebayashi, Y. Yamaki, H. Itoh, K. Asai, *Appl. Phys. Lett.* **2002**, 81, 454.
- (5) K. S. Yang, Y. Dai, B. B. Huang, *Chem. Phys. Chem.* **2009**, 10, 2327.
- (6) J. M. Herrmann, J. Disdier, P. Pichat, *Chem. Phys. Lett.* **1984**, 108, 618.
- (7) R. Long, N. J. English, *Chem. Mater.* **2010**, 22, 1616.
- (8) R. Long, N. J. English, *J. Phys. Chem. C* **2009**, 113, 8373.
- (9) R. Long, N. J. English, *Chem. Phys. Lett.* **2009**, 478, 175.
- (10) K. Obata, H. Irie, K. Hashimoto, *Chem. Phys.* 2007, 339, 124.
- (11) Y. Q. Gai, J. B. Li, A. S. Li, J. B. Xia, S. H. Wei, *Phys. Rev. Lett.* **2009**, 102, 036402.
- (12) N. H. Hong, J. Sakai, A. Hassini, *Appl. Phys. Lett.* **2004**, 84, 2602.

- (13) Y. Wang, D. J. Doren, *Solid State Commun.* **2005**, *136*, 142.
- (14) X. S. Du, Q. X. Li, H. B. Su, J. L. Yang, *Phys. Rev. B* **2006**, *74*, 233210.
- (15) S. T. Martin, C. L. Morrison, M. R. Hoffmann, *J. Phys. Chem.* **1994**, *98*, 13695.
- (16) W. Choi, A. Termin, M. R. Hoffmann, *J. Phys. Chem.* **1994**, *98*, 13669.
- (17) S. Klosek, D. Raftery, *J. Phys. Chem. B* **2001**, *105*, 2815.
- (18) K. Mizushima, M. Tanaka, A. Asai, S. Iida, *J. Phys. Chem. Solids* **1979**, *40*, 1129.
- (19) P. E. Blöchl, *Phys. Rev. B* **50**, 17953, 1994.
- (20) G. Kresse, J. Furthmüller, *Phys. Rev. B* **54**, 11169, 1996.
- (21) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865, 1996.
- (22) H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* **13**, 5188, 1976.
- (23) S. L. Dudarev, G. A. Botton, S. Y. Savarsov, C. J. Humphreys, A. P. Sutton, *Phys. Rev. B* **1998**, *57*, 1505.
- (24) N. C. Wilson, I. E. Grey, S. P. Russo, *J. Phys. Chem. C* **2007**, *111*, 10915.
- (25) C. Di. Valentin, G. Pacchioni, A. Selloni, *Chem. Mater.* **2005**, *17*, 6656.
- (26) K. Reuter, M. Scheffler, *Phys. Rev. B* **2001**, *65*, 035406.
- (27) *CRC Handbook of Chemistry and Physics*, 87th ed.; Lide, D. R., Ed.; Taylor & Francis: London, 2006. (a) Section 5: Standard Thermodynamics Properties of Chemical Substances, 5-17 Enthalpy of Formation; (b) Section 12: Properties of Solids 12-12 Ionic Radii in Crystal.

Figure captions

Figure 1 Structures for (a) V@Ti and (b) V_{in} constructed from the 48-atom anatase supercell. The gray and smaller red spheres represent Ti and O atoms, respectively, and the dark sphere denotes the V atom. The x , y and z axis are along the crystallographic a , b , and c directions, respectively.

Figure 2 Formation energies (eV) E_{form} as a function of the oxygen chemical potential for 48- and 108-atom supercells (solid and dotted lines, respectively) with V@Ti, V@Ti-O_v, and V_{in}.

Figure 3 Band structure of V-doped 48-atom supercell for (a) pure, (b) V@Ti, (c) V@Ti-O_v, and (d) V_{in}. The top of the valence band for pure anatase is taken as the reference level. The black lines are for spin-down and red lines for spin-up states. The dashed lines represent the Fermi level, E_F .

Figure 4 DOS (A) and corresponding PDOS (B) for V-doped 48-atom anatase. The top of the valence band for pure anatase is taken as the reference level. The dashed lines represent the Fermi level, E_F .

Figure 5 Band structure of V-doped 108-atom supercell for (a) pure, (b) V@Ti, (c) V@Ti-O_v, and (d) V_{in}. The top of the valence band for pure anatase is taken as the reference level. The black lines are for spin-down and red lines for spin-up states. The dashed lines represent the Fermi level, E_F .

Figure 6 DOS (A) and corresponding PDOS (B) for V-doped 108-atom anatase. The top of the valence band for pure anatase is taken as the reference level. The dashed lines represent the Fermi level, E_F .

Figure 7 Spin-density for V_{in} in 48- and 108-atom supecells with $U = 5.0$ eV. Yellow and blue represent the spin-up and spin-down spin-density, respectively.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

48-atom with $U = 5.0$ eV

108-atom with $U = 5.0$ eV

Figure 7