

## First-principles study on the structural and electronic properties of double N atoms doped-rutile TiO<sub>2</sub>

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**Abstract.** The electronic structure of rutile TiO<sub>2</sub> doped with double nitrogen atoms is studied by the plane-wave ultrasoft pseudopotential method based on the first-principles density functional theory. It has been used to analyze the effect of three doping positions of double N on the relevant band structure. The calculation demonstrates that there exist additional states in the band gap when doping of the rutile TiO<sub>2</sub> with N atoms, and the gap become narrowing. The results imply that the doped two N atoms in the adjacent position form a more intermediate stable level, and the total energy is the minimum.

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**Key words:** rutile TiO<sub>2</sub>, N-doping, density functional theory

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## 1 Introduction

Due to the Fujisima-Honda effect [1], TiO<sub>2</sub> can effectively degrade pollutants in the air and water after being radiated, and it is also inherently safe, inexpensive and so, it get people's appreciation as a new generation of purification materials. But the band gap of TiO<sub>2</sub> is wider (3.0 eV for rutile type, 3.2 eV for anatase), which makes the light absorption is limited to in the ultraviolet region. In order to improve the efficiency of catalytic activity and conversion, people focus on the changing of the width of the band gap. At present the most important way of improving the width of the gap is doping. Through doping, it forms impurity energy levels and alternation levels. Consequently, it can reduce the direct band gap.

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Zhu and others [2–6] performed metal ions-doping to anatase TiO<sub>2</sub> phase, and thus making the spectrum absorption band edge expanded, which makes the absorption moving to the visible light region. Choi [7] had systematically studied the doping of the majority of transitional metal elements among the periodic table of elements, and analyzed the mechanism of doping by using band structure. It was found that the energy levels of adulterants and the conformation of the d-electrons were the important factors which affected the photo catalytic activity of TiO<sub>2</sub>.

The non-metallic ion (N, C, S and F) doped TiO<sub>2</sub> catalysts, also showed better results in enhancing the capacity to respond to visible light [8]. Asahi [9] employed N replaced the 0.75% of crystal lattice oxygen in the nanocrystals of TiO<sub>2</sub>, and made a kind of replacement O-Doped optical catalyst. It showed a better catalytic effect when the catalyst is under visible light irradiation. Kobayakawa [10] hydrolyzed titanium isopropoxide to getting titanium hydroxide, then heated it with carbamide, made the N-doped TiO<sub>2</sub> based catalyst whose spectral response range was less than 550 nm in the visible light. But at present, the studies of doped rutile-TiO<sub>2</sub>, especially, the study of electrically neutral doping is of less. This is due to, firstly the photocatalytic effect of a single rutile was not as good as anatase [11]. Secondly, the experiment can not determine and analyze accurately and quantitatively the doping and vacancy position.

In fact, the rutile-TiO<sub>2</sub> catalytic degradation of certain contaminants also had quite high photocatalytic activity. Under certain conditions, rutile and anatase particles can synergies [12–14]. Therefore, there is a certain practical needs of rutile phase doping research. At present, for a single nitrogen-doping research has been relatively mature, whereas in the case of many impurity atoms doping, based on the charge compensation mechanism, atoms occupying position will become particularly important. This paper will aim to study the positions of the two N-doped relationship to provide guidance for electrically neutral doping. Based on the density functional theory (DFT) the plane-wave ultrasoft pseudopotential method has been successfully applied to study the electronic structure and dynamical properties for variety of materials [15–21]. In order to reveal more clearly the effect of the impurity elements doped on the rutile-phase TiO<sub>2</sub>, in this paper, we will optimize the N-doped TiO<sub>2</sub> rutile phase geometry, and analyze the double N-doped rutile properties from *ab initio* calculations.

## 2 Computational method

Rutile TiO<sub>2</sub> has a tetragonal crystal structure, with a space group of P42/MNM. In this article, we employed the rutile-phase TiO<sub>2</sub> single-cell and super-cell (2×2×1) models as shown in Fig. 1 (a) and Fig. 1(b), respectively. The super-cell model consists of four single-cell, which acquired along the X, Y-axis. The crystal structure formula is Ti<sub>8</sub>O<sub>16</sub>, The crystal structure of double-N doped TiO<sub>2</sub> formula Ti<sub>8</sub>N<sub>2</sub>O<sub>14</sub> (N doping concentration is 12.5%).

The calculation in this paper is based on the wavelet plane ultrasoft pseudopotential

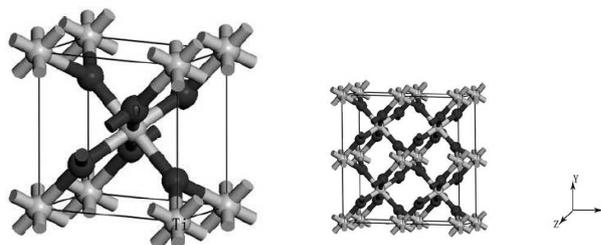


Figure 1: (a) The structure of rutile TiO<sub>2</sub> primitive cell, and (b) The super cell structure of rutile TiO<sub>2</sub> ( $2 \times 2 \times 1$ ).

method. In order to minimize the number of plane waves, we apply ultrasoft pseudopotential to describe the ion-core interaction with the valence electrons. In the reciprocal k-space, the cut-off energy is selected as 300 eV, the generalized gradient approximation (GGA) [22] method was used in the work. The integral calculation of total system energy and charge density which works in the Brillouin zone takes the Monkhorst-Pack scheme to select the k grid as  $2 \times 2 \times 7$ . In the calculation, the involved valence electron configurations are O  $2s^2 2p^4$ , N  $2s^2 2p^3$ , Ti  $3s^2 3p^6 3d^2 4s$ . The calculation was accomplished by employing CASTEP [23] quantum mechanics software package which is based on density functional theory.

### 3 Results and discussion

#### 3.1 Pure rutile lattice constant and electronic structure

Firstly, we carry out structural optimization of TiO<sub>2</sub>, then we obtain the rutile phase TiO<sub>2</sub> lattice constants and energy band structures. The lattice parameters  $a$ ,  $b$  and  $u$  are listed in Table 1, where the experimental data are also included. Apparently, our calculation results are well consistent with the experimental and other simulation results.

Table 1: Comparisons of lattice parameters between calculations and experiment

Lattice parameters	Expt. [24]	This work	Relative error	Other work [25]
$a/\text{nm}$	$0.45929 \pm 0.00005$	0.4594	$2.3950 \times 10^{-4}$	0.4594
$c/\text{nm}$	$0.29591 \pm 0.00003$	0.2959	$3.3794 \times 10^{-5}$	0.2959
$u$	$0.03056 \pm 0.00006$	0.03059	$9.8168 \times 10^{-4}$	0.03059

The rutile TiO<sub>2</sub> band structure and density of states are shown in Fig. 2, the Fermi level has been chosen at zero-point energy, which is shown as dotted line in the figure. The calculated band gap is 2.048 eV, which is less than the experimental value of 3.0 eV, while it matches the band gap of 1.9 eV calculated by Song *et al.* [25]. As we all know that DFT exists a certain degree of bias [25, 26] in the calculation of electronic band structure.

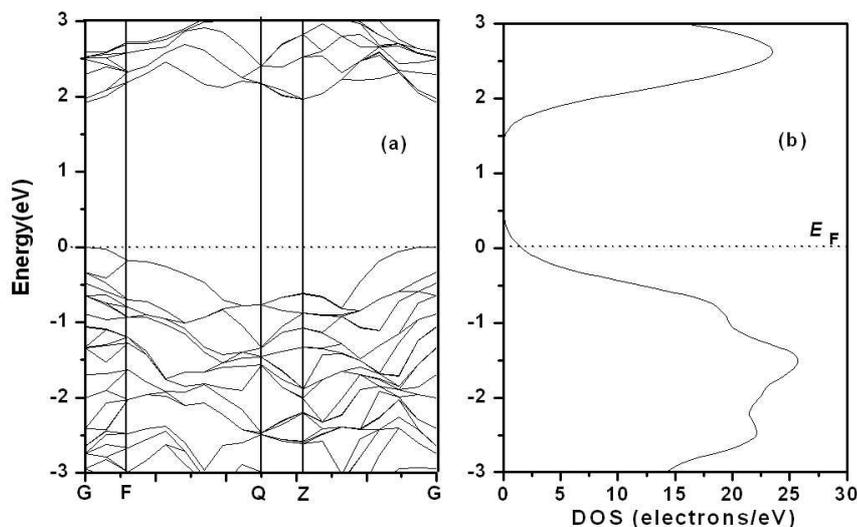


Figure 2: (a) The band structure of rutile  $\text{TiO}_2$ ; (b) The total density of rutile  $\text{TiO}_2$

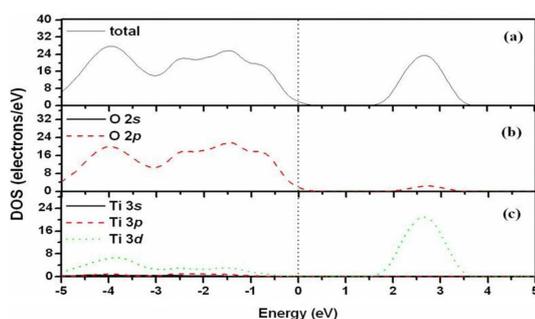


Figure 3: The partial and total density of states: (a) rutile  $\text{TiO}_2$ , (b) O, (c) Ti

Fig. 3 provides partial density of states (PDOS) diagram for pure rutile  $\text{TiO}_2$ , it can be seen that the valence band of rutile  $\text{TiO}_2$  at the vicinity of the Fermi level mainly provided by the O atom  $2p$  orbital, while the conduction band mainly provided by the Ti atom  $3d$  orbital. Therefore, this article now will focus on the examining the doped N atoms effects on the O atom  $2p$  orbitals and the Ti atom  $3d$  orbitals. Based on the above calculation of pure rutile, we can determine that the calculation method is suitable for doped  $\text{TiO}_2$  System.

### 3.2 The geometric structure of double N atoms doped rutile $\text{TiO}_2$

For comparison, we also optimized a single N atom doped rutile structure, then we obtained its geometric structure and electronic properties. Fig. 4 is the models of geometry diagram about one N atom and two N atoms doped  $\text{TiO}_2$  on different positions. By op-

timizing the geometries, then we calculated the total energy, energy band gap and the distances between the two impurity N atoms, the related parameters are listed in Table 2.

For the two N atoms doped  $\text{TiO}_2$ , for convenience, in this article, we take a Ti atom as the benchmark calibration, in the three models of two N atoms doped structure, the N atoms in the same position are labeled N1, N atoms changes in position are written as N2. Through geometry optimization, it can be found that when the two doped N atoms has a minimum distance (the minimum is 0.2546 nm), the structure has the lowest energy, with the highest stability. This indicates that if N atoms doped in rutile  $\text{TiO}_2$ , it will take the nearest neighbor occupancy mode. By comparing Fig. 4 and Fig.1 (b) we find that doping will result in different levels of local deformation. Comparing the data in Table 2, it seems that when the locations of N atoms are in the adjacent position, the two doped N atoms will affect one another.

Considering N atom has one electron less than O atom, the two N atoms in the adjacent position can share electrons more easily, and then reach a steady state, from the optimized model in Fig. 4 (b), we also found that if two N atoms are close to each other, the N-N bond has the shortest distance, the structural optimization parameters are consistent with the above analysis.

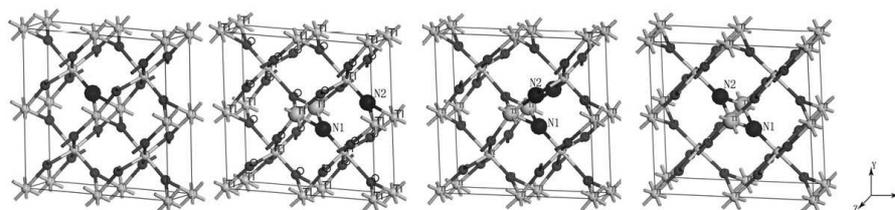


Figure 4: The structures of single N-doped and double N-doped rutile  $\text{TiO}_2$ . (a) single N-doped  $\text{TiO}_2$ ; (b) Model A of double N doped- $\text{TiO}_2$ ; (c) Model B of double N-doped  $\text{TiO}_2$ ; (d) Model C of double N doped- $\text{TiO}_2$ .

Table 2: The total energy and band gaps of rutile and four kinds of N-doped rutile  $\text{TiO}_2$  and the bond distance between the two doped N-N

	Final free energy (eV)	Energy gaps (eV)	Atomic distance of N-N (nm)
$\text{Ti}_8\text{O}_{16}$	-19890.0596	2.048	/
$\text{Ti}_8\text{O}_{15}\text{N}$	-19678.9163	1.553	/
Model A	-19552.3673	1.63	0.3377
Model B	-19552.8169	1.24	0.2546
Model C	-19552.2915	1.28	0.2715

### 3.3 The electronic structure of double N doped rutile $\text{TiO}_2$

The band structure for the three models of double N-doped rutile  $\text{TiO}_2$  are shown in Fig. 5. Comparing the results shown in Fig. 5 and Fig. 2 (a), we can find that the band

gaps of doped  $\text{TiO}_2$  have significant difference, and the calculated band gaps are listed in Table 2. The adulterant N atoms replacing O atoms which evidently makes the band gap reduced, the value has been reduced 0.2-0.6 eV compared to the undoped rutile  $\text{TiO}_2$  band gap. When the two impurity atoms take next-next nearest neighbor (Model A), the conduction band almost has not moved, and the valence band moved a little upwards to achieve the purpose of reducing the band gap. When the two impurity atoms occupy the neighbor (Model C) and sub-neighbor (Model B) position, the conduction band move to the low-energy level, while the valence band move to the high-energy-level mobile, so the band gap was reduced. The band gap of the a single N doped rutile structure has a width of 1.553 eV, but the width of the band gap of the double N atoms doped rutile changed with the distance of the two impurity atoms. From Table 2 we can clearly see that when the impurity atoms occupying the nearest neighbor position, the band gap is minimum; and the band gap width will increase while the distance between two impurity atoms increase. When the two impurity atoms are spaced 0.3377 nm, the band gap of double N atoms doped rutile will be larger than the single-N atoms doped rutile. Overall, through the introduction of N impurities, the band gap of the energy band has significantly reduced. When the double N atoms occupying the nearest position, the band gap of the energy band is smaller than that of single N-doped rutile, theoretically speaking, double N-doping can enhance the photocatalytic efficaciously.

Fig. 6 shows the impurity atoms and Ti atoms sub-state density of state map. We can find that N1  $2p$  orbital was located in the middle of the band gap, indicating that it can change the band gap well by introducing into atom N. In the Model A, N1 atom gets a higher DOS near Fermi energy, its band gap is 1.695 eV. In the Model B, N1 atom gets a flat DOS near Fermi energy, its band gap is 1.286 eV. In the Model C, the band gap is 1.239 eV. The three groups of data accord with those of the total DOS, and in the Model

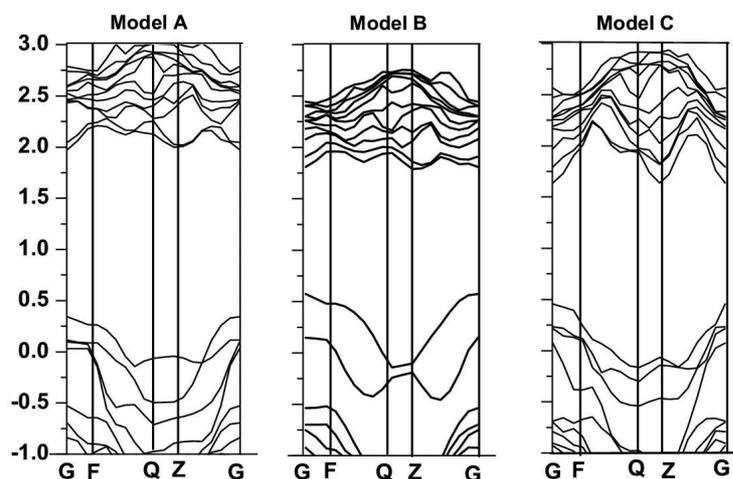


Figure 5: The band structures of three models of double N-doped rutile  $\text{TiO}_2$

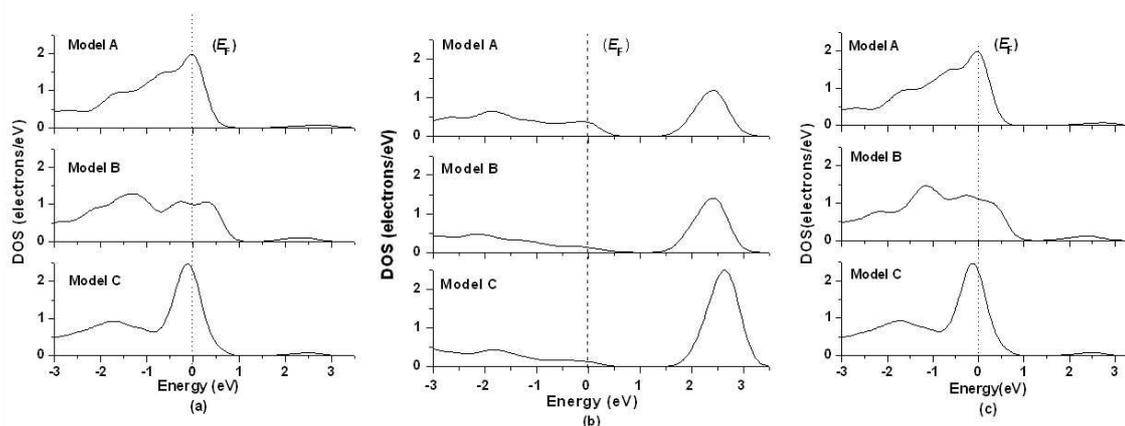


Figure 6: The partial density of states for three models of double N-doped rutile  $\text{TiO}_2$ : a) for N1  $2p$  states, b) for Ti  $3d$  states, c) for N2  $2p$  states.

B, near the Fermi energy, it has a platform of plateau, which is easier to improve the visible light catalytic in theory. From Fig. 6 (b) we can see that the three kinds of doped models have certain impact on Ti atom's valence band. The valence band will have a certain extension to the high energy level, and the effect to the conduction band is less prominent, the conduction band width and the lower limit do not change significantly. Non-metallic atom doping will achieve the purpose of changing the band gap not by changing the electronic structure of metal atoms. Certainly, the metal ion doping may be changed by changing the lower limit of the conduction band and it also can achieve different effects [27]. Finally, when comparing Fig. 6 (c) with Fig. 6 (a), we find that the sub-density of the two impurity atoms does not have much difference among the three models. The band gap produced by N1 atom in Model C is slightly smaller than the band gap produced by N2 atom. By comparing the bond lengths of Ti-N1 and Ti-N2, we find that they are both 0.2013 nm. the Ti-N1-Ti bond angle is  $95.171^\circ$ , while the Ti-N2-Ti bond angle is  $95.169^\circ$ . It means, when N atom is a little away from Ti atoms, then its band gap will be larger. From the optimized model in Fig. 4 (b), we also found that two atoms are close to each other, which can explain that Model B is not only has a smaller band gap, but also has a more stable structure. Thus, in considering further study of electric neutral doping, we will take model B as a foundation to carry out the research of electrical neutral doping by vacant doping.

## 4 Conclusion

By employing the first-principles density functional theory, we study the geometry and electronic structure of the double-N atoms doped  $\text{TiO}_2$  rutile phase. During the computa-

tional processes, we considered three possible doping models and we had implemented geometry optimization. It is found that when the two nitrogen impurity atoms occupied the two adjacent B model, it has the most stable position. From the band structure and the density of states analysis, it is observed that, pairs of N atoms doped TiO<sub>2</sub> induced impurity level appears in the band gap and the band gaps of the three models have been reduced. When the impurity atoms occupy the nearest adjacent positions, the band gap is minimum, indicating that it can enhance the catalytic activity of light. As the distance between two impurity atoms increases, the band gap will gradually become larger.

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