Impurities Effects on the Electronic Structure of Titanium Dioxide

Yuta Aoki and Susumu Saito
Department of Physics, Tokyo Institute of Technology, 2-12-1 Oh-okayama, Meguro-ku, Tokyo 152-8551, Japan
E-mail: y-aoki@stat.phys.titech.ac.jp

Abstract. Effects of substitutional doping of nitrogen to TiO$_2$ are studied within the framework of the density-functional theory (DFT). We compare the total energy and the electronic structure of pristine TiO$_2$ with those of nitrogen-doped TiO$_2$. It is found that the smaller the concentration of doped nitrogen is, the more energy is required for the substitutional doping of the nitrogen atom in both rutile and anatase phases. This result suggests that the doped nitrogen atoms tend to be clustered. A sizable reduction of the photoexcitation energy is also suggested in the rutile structure.

1. Introduction
Titanium dioxide (TiO$_2$) are attracting a wide attention because of its remarkable photocatalytic properties. Especially, photo-induced water decomposition utilizing its photocatalysis [1] is thought to be a potential method for a sustainable hydrogen production using solar light [2].

The mechanism of semiconductor photocatalytic water decomposition is schematically shown in Figure 1. A semiconductor can be excited by the photons with energy equal to or larger than the bandgap $E_g$, and photo-excited electrons and holes are generated in the conduction band and the valence band, respectively. A water decomposition reaction

\begin{equation}
\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2 \tag{1}
\end{equation}

consists of following two half-reactions.

\begin{equation}
\text{H}_2\text{O} + e^- \rightarrow \frac{1}{2}\text{H}_2 + \text{OH}^- \tag{2}
\end{equation}

\begin{equation}
\frac{1}{2}\text{H}_2\text{O} + h^+ \rightarrow \frac{1}{4}\text{O}_2 + \text{H}^+ \tag{3}
\end{equation}

When the redox potential of the reaction (2) $E_{\text{red}}$ is lower than the conduction-band bottom and the redox potential of the reaction (3) $E_{\text{ox}}$ is higher than the valence-band top, photo-excited electron-hole pairs in the semiconductor can initiate the reaction (1). The electronic structure of TiO$_2$ is known to satisfy the above-mentioned requirements.
However, some difficulties still remain in its practical application. One of these difficulties is that the bandgap of TiO$_2$ is so wide that TiO$_2$ only absorbs light with energy of 3.0 eV or larger. This energy is just around the borderline between ultraviolet ray and visible ray although visible ray accounts for as much as around 50 percent of the energy of sunlight [2]. The wide bandgap of TiO$_2$ greatly lowers the solar-to-hydrogen energy conversion efficiency. In order to overcome this difficulty, several kinds of methods to narrow the bandgap are widely studied.

The first successful study of shifting photoresponse into visible spectrum was done by Asahi and co-workers [3]. They investigated the effects of substitutional doping of nitrogen both theoretically and experimentally. They calculated the densities of states (DOSs) of TiO$_2$ with interstitial doping of nitrogen and substitutional doping of nitrogen, fluorine, carbon, sulfur and phosphorus in the anatase structure. The result shows that the nitrogen is the most effective element to narrow the bandgap among the dopants studied. They also prepared nitrogen-doped TiO$_2$ films, which were the mixtures of anatase and rutile phases. These films absorbed the light with the wavelength less than 500 nm, corresponding to the photon energy larger than 2.48 eV.

In the present study, the effects of substitutional doping of nitrogen to TiO$_2$ are studied in more detail within the framework of the density-functional theory (DFT). We compare the total energy of nitrogen-doped TiO$_2$ with that of pristine TiO$_2$ for two representative solid phases of TiO$_2$, rutile and anatase, and for different concentrations of substitution sites. Also, we calculate the electronic structures of nitrogen-doped TiO$_2$ and pristine TiO$_2$ with the rutile structure.

2. Research Objects and Calculational Methods

Our research objects are [TiO$_2$]$_{2n-1}$TiON and [TiO$_2$]$_{2n}$ ($n = 1, 2, 4$) both for rutile and anatase structures. The pre-optimized crystal structures of [TiO$_2$]$_{2n-1}$TiON is shown in Figure 2. It should be noted that $1/4n$ indicates the concentration of substitution sites in these systems.

In the present work, we perform the electronic-structure calculations based on the DFT [4,5] with the local density approximation (LDA) using the Quantum ESPRESSO package [6].

![Figure 2](image-url) The pre-optimized structures of [TiO$_2$]$_{2n-1}$TiON. Sky-blue ball is titanium, red ball is oxygen, and purple ball is nitrogen. (a), (b), and (c) are rutile-structured, and (d), (e), and (f) are anatase-structured materials.
The exchange-correlation functional of Ceperley and Alder [7] parameterized by Perdew and Zunger [8] and the Vanderbilt ultrasoft pseudopotential [9] are used. The energy cutoff for the plane-wave basis is set to be 70 Ry. The structural optimization is performed using the damped dynamics of the Wentzcovitch Lagrangian [10].

3. Energetics
In the present work, we compare the relative tendencies for the nitrogen substitution to occur in different crystalline geometries with different nitrogen concentrations. So, we compare the energies required for nitrogen substitution per nitrogen atom both for rutile and anatase structures in different nitrogen concentrations, with respect to the highest nitrogen concentration case considered for the rutile structure in the present work (n = 1). Assuming that the doped nitrogen atoms are derived from nitrogen molecules and the replaced oxygen atoms desorb as oxygen molecules, the relative energies required for nitrogen substitution is given by \( \Delta \varepsilon_n - \Delta \varepsilon_1 \) (rutile) where

\[
\Delta \varepsilon_n = E([\text{TiO}_2]_{2n-1}\text{TiON}) - E([\text{TiO}_2]_{2n})
\]

Here, each \( E \) is the total energy of the structural unit given in the parenthesis. The value to be compared \( \Delta \varepsilon_n - \Delta \varepsilon_1 \) (rutile) is, on the other hand, equal to \( \Delta \varepsilon_n - \Delta \varepsilon_1 \) (rutile) where

\[
\Delta \varepsilon_n = E([\text{TiO}_2]_{2n-1}\text{TiON}) - E([\text{TiO}_2]_{2n}).
\]

Therefore, \( E(\text{O}_2) \) and \( E(\text{N}_2) \) are not necessary for the present purpose.

The result is shown in Figure 3. It is found that the smaller the concentration of substitution sites is, the more energy is required for substitution per atom in both rutile and anatase phases. This suggests that, when a certain number of nitrogen atoms are doped into TiO_2, the doped nitrogen atoms should tend to be concentrated in small domains. This "clustering" is known to take place in doping into semiconductor device materials, and is attracting more attentions since it can become a serious obstacle in the future nanometer-scale technology [11–13]. Also, the present result suggests that it is easier to dope nitrogen atoms into rutile than into anatase.

4. Electronic Structure
We also calculate the electronic structure of pristine TiO_2 rutile and that of rutile-structured TiO_2 TiON (Figure 4). Here, the optimized geometry of rutile-structured TiO_2 TiON is primitive monoclinic while that of the pristine TiO_2 is primitive tetragonal. However, symmetry-point names usually used for primitive monoclinic Brillouin zones are used for the corresponding symmetry points of the primitive tetragonal Brillouin zones (Figure 4(a)) in order to compare directly their electronic structures.

As for rutile-structured TiO_2 TiON, the bottom of the original conduction band and the top of the original valence band are on the A point and on the \( \Gamma \) point, respectively, and the gap is 1.11 eV. However, since TiO_2 TiON has odd-numbered electrons per unit cell, it should possess the metallic band structure and the Fermi level is not within the fundamental gap anymore. Therefore, the energy difference between the conduction-band bottom and the Fermi energy is also important to discuss photoexcitation. It is found that the energy difference between the conduction bottom and the Fermi level is 2.02 eV. This value should be compared not to the
Figure 4. Electronic band structure of (TiO$_2$)$_2$ rutile (a) and rutile-structured TiO$_2$TiON (b). (a): The valence top is taken as zero. (b): The Fermi level is taken as zero.

LDA fundamental-gap value of rutile (1.85 eV) but to the experimental bandgap value of 3.0 eV [14], because the LDA gives electronic structures of metallic systems quantitatively well while it underestimates the bandgap values of insulators and semiconductors [15, 16]. Therefore, the present result suggests that the photoexcitation energy reduces by 0.98 eV with nitrogen doping.

5. Summary and Conclusion
We have compared the total energy and the electronic structures between nitrogen-doped TiO$_2$ and pristine TiO$_2$ both for rutile and anatase structures. The calculations have been based on the DFT with the LDA using the ultrasoft pseudopotential. Result suggest that the doped nitrogen atoms may tend to be clustered. In addition, it is shown that the conduction-band bottom shifts from the Γ point to the A point, and the photoexcitation energy can reduce considerably with nitrogen substitutional doping.

Acknowledgements
Numerical calculations were mainly performed on TSUBAME 2.0 at the Global Scientific Information and Computing Center, Tokyo Institute of Technology. We also acknowledge the financial supports from the Global Center-of-Excellence Program by Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT) through the Nanoscience and Quantum Physics Project of Tokyo Institute of Technology, and the Elements Science and Technology Project by MEXT.

References
[1] Fujishima A and Honda K 1972 *Nature* **238** 37
[2] Ni M, Leung M K H, Leung D Y C and Sumathy K 2007 *Renew. Sust. Energy. Rev.* **11** 401
[3] Asahi R, Morikawa T, Ohwaki T, Aoki K and Taga Y 2001 *Science* **293** 269
[4] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864
[5] Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
[6] Giannozzi P et al. 2009 *J. Phys.: Condens. Matter* **21** 395502
[7] Ceperly D M and Alder B J 1980 *Phys. Rev. Lett.* **45** 566
[8] Perdew J P and Zunger A 1981 *Phys. Rev. B* **23** 5048
[9] Vanderbilt D 1990 *Phys. Rev. B* **41** 7892
[10] Wentzcovitch R M 1991 *Phys. Rev. B* **44** 2358
[11] Chadi D J et al. 1997 *Phys. Rev. Lett.* **79** 4834
[12] Kim Y S, Lee E C and Chang K J 2003 *Phys. Rev. Lett.* **91** 125503
[13] Mueller D C and Fichtner W 2004 *Phys. Rev. B* **70** 245207
[14] Kavan L, Grätzel M, Gilbert S E, Klemenz C and Scheel H J 1996 *J. Am. Chem. Soc.* **118** 6716
[15] Wang C S and Pickett W E 1983 *Phys. Rev. Lett.* **51** 597
[16] Perdew J P and Levy M 1983 *Phys. Rev. Lett.* **51** 1884