

# First-principles study on local electronic structures and visible light absorption of nitrogen-doped TiO<sub>2</sub> photocatalyst

Junya Senga<sup>1</sup>, Kazuyoshi Tatsumi<sup>2</sup>, Tomoko Yoshida<sup>2</sup>, Shunsuke Muto<sup>2</sup>

<sup>1</sup>Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan

<sup>2</sup>EcoTopia Science Institute, Nagoya University, Nagoya 464-8603, Japan

## Introduction

Anatase-type TiO<sub>2</sub> exhibits a wide band gap of 3.2 eV and its catalytic behavior is activated only under ultraviolet (UV) light irradiation. N-doping was proposed to enhance the visible light photocatalytic activity. We have shown using electron energy-loss and x-ray absorption spectroscopic methods [1] that N<sup>+</sup> implanted into TiO<sub>2</sub> substitutes for oxygen either as (N)o or as (NO<sub>2</sub>)o ((X)o stands for X species occupying the oxygen site). Photocatalytic reactions under visible light suggested that (N)o was a photocatalytic active while (NO<sub>2</sub>)o was not [1]. The present first-principles calculations are intended to qualitatively clarify how the induced (N)o and (NO<sub>2</sub>)o chemical states in TiO<sub>2</sub> enhance the photo-absorption coefficients and excited electron-hole mobilities.

## Theoretical Procedures

Atomic models of the N-doped TiO<sub>2</sub> used here were the same as those in ref. [2]. They were based on the 2x2x1 supercell of the anatase-type TiO<sub>2</sub> unit-cell. We calculated the optical absorption coefficients and band structures by using a first-principles pseudopotential band method (CASTEP code). An exchange-correlation functional of GGA-PBE and a hybrid functional of HSE06 were adopted to the density functional theory.

## Results and Discussion

Figure 1 inset shows the experimental photo-absorption significantly increased with increasing the N<sup>+</sup> irradiation dose. The theoretical spectra calculated with (N)o and (NO<sub>2</sub>)o exhibited significant absorption in the longer-wavelength region compared to the non-doped TiO<sub>2</sub>, being consistent with the experimental result [1].

In the band structures (Figure 2 left) calculated using HSE06 functional, (N)o showed additional two bands (denoted by E<sub>1</sub> and E<sub>2</sub>). E<sub>2</sub> lies over the energy range very close to the top of the valence bands of the non-doped TiO<sub>2</sub>. (NO<sub>2</sub>)o also showed a characteristic band (denoted by E<sub>3</sub>). E<sub>1</sub>, E<sub>2</sub>, and E<sub>3</sub> bands contribute to the visible-light absorption, because they are located in the band gap. E<sub>2</sub> exhibits a relatively larger dispersion compared with E<sub>1</sub> and E<sub>3</sub>. The isosurfaces of their charge densities (Figure 2 right) showed that E<sub>2</sub> was spatially delocalized, while E<sub>1</sub> and E<sub>3</sub> the localized impurity-like states. This theoretical finding is consistent with the experimental claim that (N)o is photo-catalytically active while (NO<sub>2</sub>)o is not, because an electron excited to the localized impurity-like level should be less mobile to the TiO<sub>2</sub> surface where the catalytic reaction occurs. In the poster, theoretical N-K XANES of the N charged defects will be discussed with the experimental results.

## References

[1] T. Yoshida et al., *Trans. Mater. Res. Soc. Japan* **33** (2008) 339-344

[2] R. Asahi et al., Chemical Physics **339** (2007) 57-63

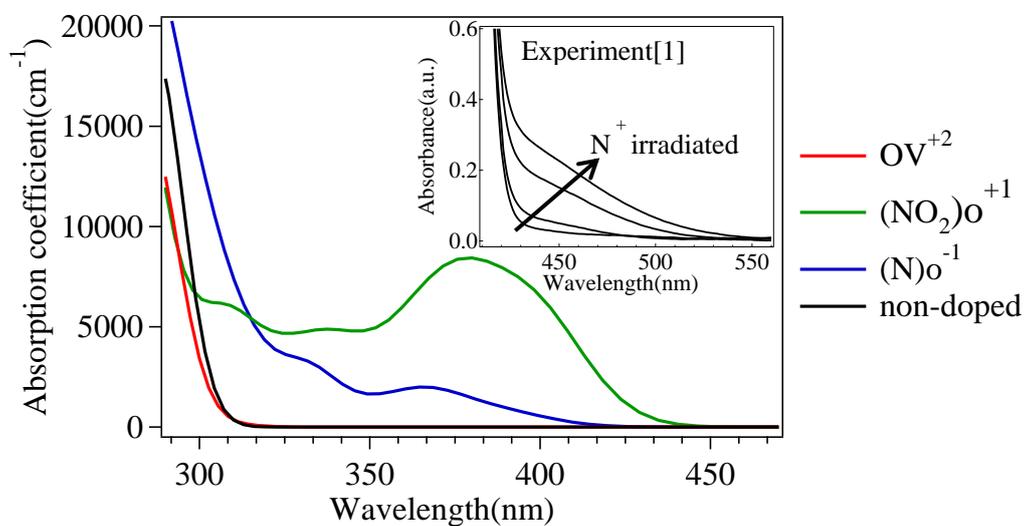


FIG 1. Calculation result of optical absorption spectra.

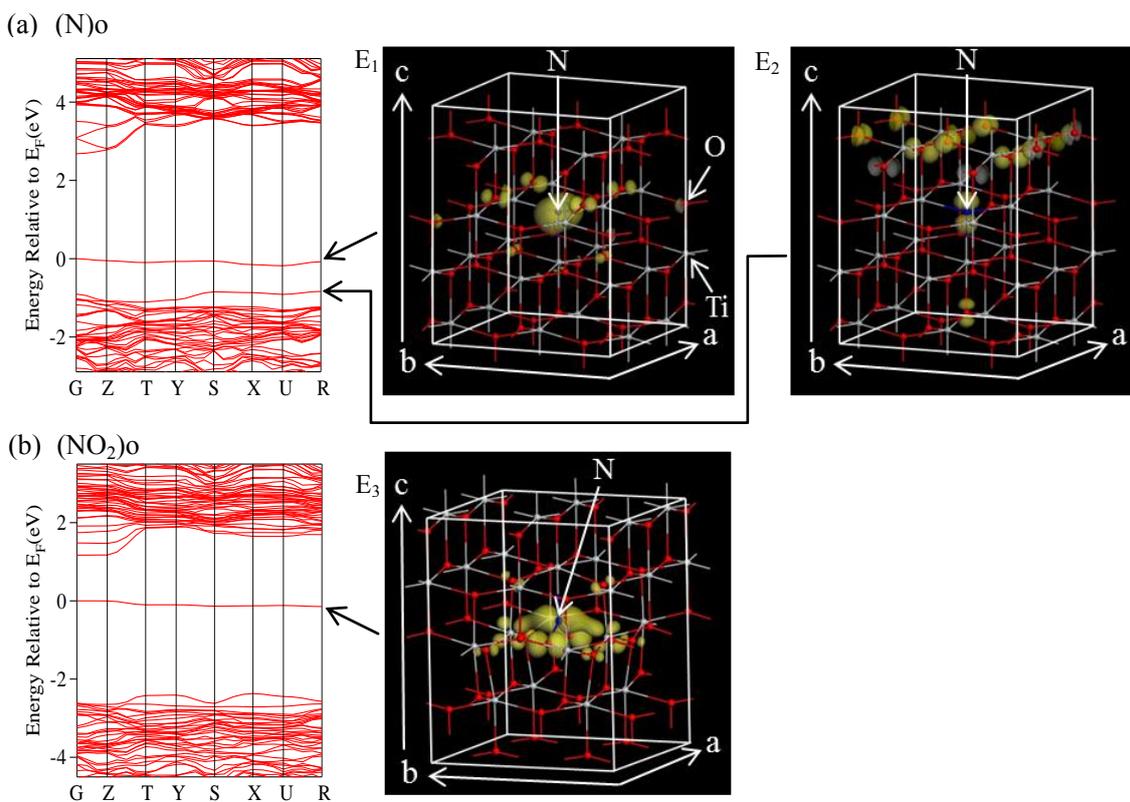


FIG 2 Band structures (left) and isosurfaces of charge densities (right). Fermi levels were taken as zero of the vertical axes.