

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

Zhong-Liang Zeng<sup>a,b</sup>, Guang Zheng<sup>a,b,\*</sup>, Xi-Cheng Wang<sup>a,b</sup>,  
Kai-Hua He<sup>a,b</sup>, Qi-Li Chen<sup>a,b</sup>, Li Yu<sup>a,b</sup>, and Qing-Bo Wang<sup>a,b</sup>

<sup>a</sup>College of Maths and Physics, China University of Geosciences, Wuhan 430074, China

<sup>b</sup>Institute of Materials Modelling and Computational Physics, China University of Geosciences, Wuhan 430074, China

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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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\*Corresponding author. *Email address:* mzheng88@gmail.com (G. Zheng)

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