



# Origin of photocatalytic activity of nitrogen-doped germanium dioxide under visible light from first principles



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## ARTICLE INFO

Available online 9 January 2015

### Keywords:

Electronic structure  
Visible-light photocatalysis  
N-doped GeO<sub>2</sub>  
First-principles

## ABSTRACT

The large intrinsic band gap of GeO<sub>2</sub> hinders its potential application as a photocatalyst under visible-light irradiation. Here, we perform first-principles calculations to investigate the origin of the experimentally observed visible-light photocatalytic activity of GeO<sub>2</sub> induced by N doping. Four possible defects (N-doping, N+H codoping, Ge vacancy and O vacancy) for the redshift of N-doped GeO<sub>2</sub> are tentatively put forward. The lowest formation energy indicates that N+H codoped GeO<sub>2</sub> is the most stable and easiest to form. N-doping at an oxygen site induces gap states, which are made up primarily of N 2p-derived states with some O 2p contributions, and the lowest-energy empty states is in the middle of the gap. For Ge vacancy model, O 2p states form the intermediate band, while Ge 4s orbitals localized in the gap contribute to the impurity level in O vacancy model. These gap levels lead to a reduced effective band gap, which is one of the potential interest for photocatalytic applications. Electronic transitions from these localized states induce a redshift to the visible region of the optical absorption edge. The calculated optical properties for N-doped GeO<sub>2</sub> show a significant visible light absorption at about 400–600 nm, in close agreement with the experimental result. This work indicates that N-doped GeO<sub>2</sub> would be a promising photocatalyst with favorable photocatalytic activity in the visible region.

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## 1. Introduction

Photocatalysis is a promising technology to address problems in chemical synthesis, energy utilization, and environmental remediation [1–4]. The potential for water and air purification by mineralizing of organic pollutants using photocatalysts is particularly appealing. Such photocatalysis depends on capturing photon energy via excitation of electrons from the valence band (VB) to the conduction band (CB) of

appropriate semiconductors, creating an excited electron–hole pair that is then used to promote redox reactions [5,6]. So far, many photocatalysts have been reported already capable of degrading organic pollutants. These photocatalysts are usually solid semiconductors which are (i) able to absorb ultraviolet light (UV) and/or visible light, (ii) chemically and biologically inert and photostable, (iii) inexpensive and (iv) nontoxic. Titania, as a prototypical example, is the most widely used photocatalytic material because it fulfills all of the above requirements as well as exhibits adequate conversion values [7]. Due to its large band gap ( $E_g = 3.0\text{--}3.4\text{ eV}$ ), however, pure TiO<sub>2</sub> only activates under UV irradiation, leaving approximately 95% of the available solar energy unused, which is an inexpensive, renewable energy source, for the excitation

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energy of the photocatalytic processes [8]. This limitation is also for other semiconductors with wide band gaps, such as ZnS [9–11], SrTiO<sub>3</sub> [12], SnO<sub>2</sub> [13], BiOCl [14], and CeO<sub>2</sub> [15].

To optimize the photoactivity of semiconductors with wide band gaps, several research paths have been pursued. Two methodologies, central to current research, consider the extension of the light absorption spectrum to the visible region by cation and/or anion doping, or coupling with other systems to facilitate the electron–hole charge separation process [5]. A large number of experimental and theoretical studies have shown that N doped into substitutional sites of semiconductors, such as TiO<sub>2</sub> [2,16–19], BiVO<sub>4</sub> [20], La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> [21], SrTiO<sub>3</sub> [22], ZnS [23], and CeO<sub>2</sub> [24,25], can reduce band gap and enhance catalytic activity in various reactions performed under visible light irradiation. For examples, using electron paramagnetic resonance (EPR) spectroscopy measurements and density functional theory (DFT) calculations, Livraghi et al. demonstrated that N impurity, giving rise to localized states in the band gap of the TiO<sub>2</sub>, is responsible for visible light absorption with promotion of electrons from the band gap localized states to the CB or to surface-adsorbed electron scavengers [17]. A first-principles screened exchange hybrid DFT with the HSE06 functional calculations on N-doped NiO found that N-doping induces gap states, i.e., the top of the VB is made up of dopant 2p states and the lowest unoccupied states is the empty gap states derived from the dopant, leading to band gap narrowing [26].

More recently, to develop new photocatalysts and based on the consideration of the requirements of chemically and biologically inert and photostable, inexpensive and nontoxic, a novel photocatalyst, N-doped GeO<sub>2</sub>, has been synthesized and studied by Charanpahari et al. [27]. In their experiments, UV–visible absorption analysis shows that N doped into GeO<sub>2</sub> reduces the band gap from 5.6 eV to about 2.75 eV and extends its light absorption to the visible region ( $\lambda < \sim 450$  nm). Particularly, N-doped GeO<sub>2</sub> can degrade Rhodamine B (cationic) and Acid violet 7 (anionic) dyes efficiently from aqueous solutions, and moreover the degradation rates are much higher than those of P25 (TiO<sub>2</sub>) in the visible region. The results indicate that N-doped GeO<sub>2</sub> is a promising photocatalyst for environmental sustainability.

GeO<sub>2</sub>, a n-type semiconductor, has been extensively used in optoelectronics, electro-optical modulators, piezoelectric, glass material, lithium-ion batteries, optical-fiber material, nonlinear-optical applications, and optical waveguide materials due to its excellent properties, such as, higher electron mobility, higher hole mobility, high refractive index, and good optical transparency [28–34]. N doping expands the application area of GeO<sub>2</sub>—as a candidate photocatalyst. The mechanism, however, on the photocatalytic activity of N-doped GeO<sub>2</sub> has not yet been unraveled. An aspect of its photocatalytic activity that has been neglected is the possible role of native point defects in GeO<sub>2</sub>, which always exist. Moreover, an unintentionally doped impurity, such as H, is ubiquitous and regarded as a potential donor in oxides. In addition, precursors for synthesizing GeO<sub>2</sub> usually contain H, and they are possibly left in the bulk phase. Therefore, it is also worth investigating the influence of native defects and interstitial H in N-doped GeO<sub>2</sub> on its photoactivity.

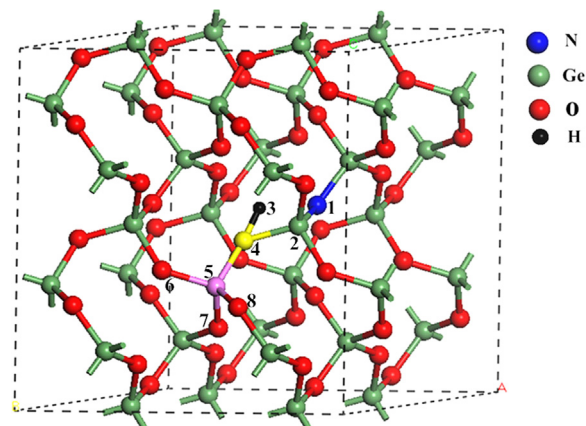
In this work, to obtain microscopic insight into the effect of N-doping on its visible-light photocatalytic activity, we

explore the geometric, electronic, and optical properties of the GeO<sub>2</sub> structure with and without N doping, together with possible interstitial H as well as Ge and O vacancies systematically by means of the first principles DFT calculations. Four different models, N-doping, N+H codoping, O vacancy, and Ge vacancy, are considered to probe the possible reasons. The results show that doping with N introduces new dopant-derived states into the band gap of the oxide, which may be beneficial for narrowing the band gap of GeO<sub>2</sub>, providing a solid basis for the rationalization of the experimentally observed redshift in photoactivity and visible-light photocatalytic activity. From the results it can be proposed that the N-doped GeO<sub>2</sub> can be candidates for photocatalyst.

## 2. Theoretical model and computational details

At room temperature GeO<sub>2</sub> is a white powder or colorless crystals and it exists in three stable forms: the rutile tetragonal structure (P4<sub>2</sub>/mmm, D<sub>4h</sub><sup>14</sup>), the trigonal structure of a-quartz (P3<sub>1</sub>21 D<sub>3</sub><sup>4</sup>, and the amorphous glass [29,35–37]. Here, we choose the a-quartz GeO<sub>2</sub> found in prepared samples. A 2 × 2 × 2 supercell (72 atoms) is chosen to simulate N-doped GeO<sub>2</sub> structure. Four different models are considered: N<sub>0</sub>-GeO<sub>2</sub> (N atom substituting lattice O atom), N<sub>0</sub>+H<sub>1</sub>-GeO<sub>2</sub> (an O atom is replaced by a N atom, and one H atom, as an interstitial atom, is bonded to O atom), V<sub>Ge</sub>-GeO<sub>2</sub> (a Ge atom is removed from pure GeO<sub>2</sub>), and V<sub>O</sub>-GeO<sub>2</sub> (an O atom is removed from pure GeO<sub>2</sub>). It should be pointed out that, for the N<sub>0</sub>+H<sub>1</sub>-GeO<sub>2</sub> model, the doping N atom is to substitute O atom in the center of the 2 × 2 × 2 supercell, while the H impurity (labeled 3 in Fig. 1) is placed at the closest position to the substitutional N atom (labeled 4 in Fig. 1). This is because that total energy calculations reveal that this kind of codoped atoms exhibit a strong tendency to form a pair occupying neighboring lattice sites.

The calculations are performed using the CASTEP [38] code based on first-principles DFT. The exchange and correlation interactions are modeled using the Local Density Approximation (LDA) with the CA-PZ functional. As



**Fig. 1.** Lattice structure of GeO<sub>2</sub> (2 × 2 × 2 supercell with 72 atoms). Ge atoms are in green, O atoms are in red, H atom is in black and N is in blue (No. 4 atom is O atom and No. 5 atoms is Ge atom). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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