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Density functional theory study of the adsorption of NO₂ molecule on Nitrogen-doped TiO₂ anatase nanoparticles

ABSTRACT

A. Rastkar Ebrahimzadeh
M. Abbasi*
J. Jahanbin Sardroodi
S. Afshari

*Molecular Simulation Lab,
Azarbaijan Shahid Madani
University, Tabriz, Iran.*

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Adsorption of NO₂ molecule on pristine and N-doped TiO₂ anatase nanoparticles have been studied using the density functional theory (DFT) technique. The structural properties (such as bond lengths and bond angles) and the electronic properties (such as density of states, band structures and atomic partial charges) have been computed for considered nanoparticles. The results show that, the adsorption of NO₂ molecule on N-doped nanoparticles is more energetically favorable than the adsorption of NO₂ molecule on the pure TiO₂ nanoparticles. However, on the base of the obtained results, the N-doped TiO₂ nanoparticles can be used in NO₂ sensing and removing applications.

Keywords: *Density Functional Theory (DFT); Titanium Dioxide; Nitrogen Dioxide; Mulliken analysis; Density of states; Band structure.*

INTRODUCTION

Titanium dioxide is one of the most important metal oxides semiconductors due to its particular properties such as chemical stability, non-toxicity and low-cost [1-3]. One can see TiO₂ in a various range of applications both in scientific research and industrial applications such as gas sensor devices, semiconductor materials, heterogeneous catalysis, and photocatalysis and so on. In the recent years it has been attracted many scientific attentions [3-11] on the experimental and theoretical research in order to develop TiO₂ related science and industry. The electronic structure of TiO₂ gives it some unique properties and applications, such as its wide band gap (3-3.2eV) and its photocatalytic activity [12-13]. Doping of Titanium dioxide with different nonmetal elements, especially nitrogen, can enhance its photocatalytic activity to the visible region [13-16]. N-doped TiO₂ anatase nanoparticles have attracted many scientific and industrial interests over the past few years. Nitrogen-doping can introduces a hole inside the band-gap of Titanium dioxide, impurity states in the band-gap can increase the photocatalysis rate of Titanium dioxide and oxidize toxic Nitrogen dioxide (NO₂) molecule, and the adsorption of air pollutants on N-doped TiO₂ nanoparticles has not been extensively studied.

* Corresponding author:
Moosa Abbasi
Molecular Simulation Lab,
Azarbaijan Shahid Madani
University, Tabriz, Iran.
Tel +98 4124327500
Fax +98 4124327541
Email M_aygar2010@yahoo.com

In this research, we investigated the adsorption of Nitrogen dioxide molecule on N-doped TiO₂ anatase nanoparticles using the DFT calculations [17-18]. In this study, the adsorption energy, bond length, density of states (DOS), and band structures for pristine and N-doped TiO₂ anatase structures were analyzed [18-22]. Meanwhile, N-doping in Titanium dioxide increases the adsorption energies for doped structures. Furthermore, more NO₂ molecules can be adsorbed on the N-doped nanoparticles in compare with pristine nanoparticles [23-25]. The doping of nitrogen into TiO₂ anatase has a considerable influence on the adsorption energies for TiO₂ anatase nanoparticles which the doping method can acts as an efficient method to remove the air pollutants from the environment via TiO₂ nanoparticles [11,13].

EXPERIMENTAL

Calculation details

All calculations were carried out using the open source package for material explorer (OpenMX3.6) package [26]. Pseudo atomic orbitals (PAO's) have been used as the basis set in order to expand the wave functions in a KS schema with a cutoff energy of 150Ry [18,21]. For modeling the exchange and correlation interactions both of the local density approximation (LDA) together with the Ceperly-Alder (CA) and the generalized gradient approximation together with the Perdew-Burke-Ernzerhof (PBE) were used [16,17]. In the calculations including the electronic relaxation, the residual minimization method with direct inversion in the iterative subspace (RMM-DIIS) was used whereas the convergence criterion of energy was set to 10⁻⁴ Hartree/bohr, and the convergence criterion for self-consistent field calculations was set to 1×10⁻⁶ Hartree.

Structure of nanoparticles

For the N-doped TiO₂ anatase nanoparticles, one nitrogen atom substitutes an oxygen atom as an impurity state in the TiO₂ nanoparticle; impurity state introduces a hole inside the band gap. The empty state generated by doping of nitrogen, may be on the top of the valence band or inside the band gap of TiO₂ anatase. Hole

generated in the particle can oxidize toxic NO₂ molecules during the photocatalysis reaction [11, 13]. The chosen TiO₂ nanoparticles, consisting of 72 atoms, have been made using x-ray crystal structures reported at data base page of American Mineralogists web site [27]. These nanoparticles have been optimized and adsorption of a NO₂ molecule on their surfaces was investigated by computational methods. Equilibrium structures for nanoparticles have been shown in Figure 1 from different views.

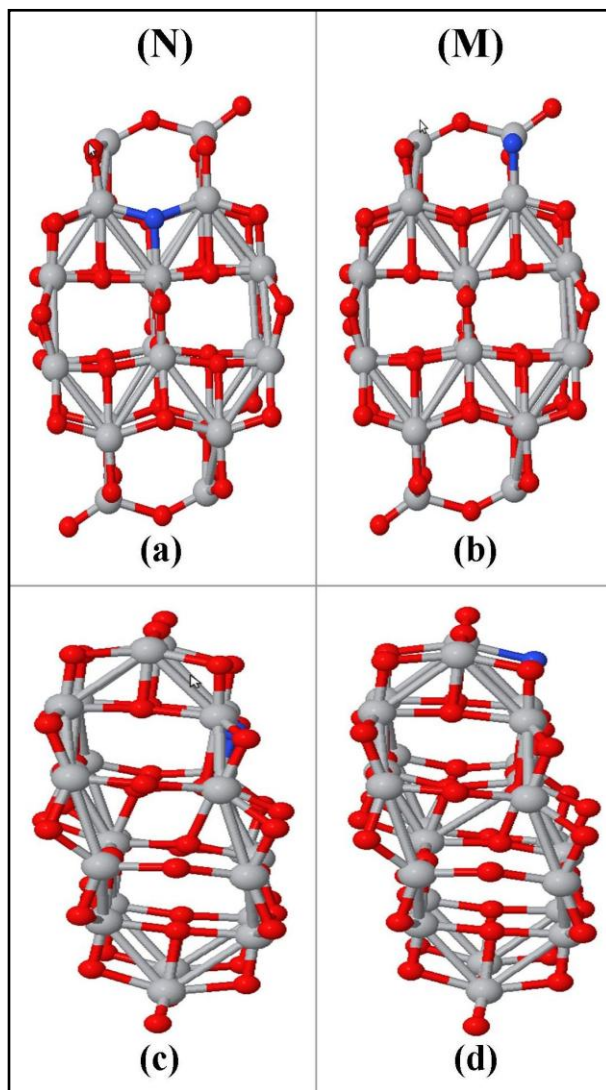


Fig. 1. Front view and side view of the considered 72 atom nanoparticle, (a) Front view of a particle in the position that one Nitrogen atom substitutes an oxygen atom in N position. (c) Side view of it. (b) Front view of a particle in M position. (d) Side view of it.

Two substitutional doping configurations have been considered in this study as a N and M configurations. In N configuration, one nitrogen atom substitutes an oxygen atom in the middle of the particle and in other configuration; one nitrogen atom substitutes an oxygen atom in M position. Both of the two substitutional configurations cause an impurity state inside the band gap or in the top of the valence band (see Figure 1) [14]. The NO₂ molecule can be adsorbed on different surface oxygen atoms, but the adsorption on dangling oxygen atom site is more energetically favorable than the adsorption on the other surface oxygen atom sites [11, 16]. Therefore, the adsorption of NO₂ molecule on dangling oxygen atom of TiO₂ anatase has been widely studied in this work [23]. Equilibrium geometries for adsorption systems (NO₂- adsorbed anatase nanoparticles) were shown in Figure 2.

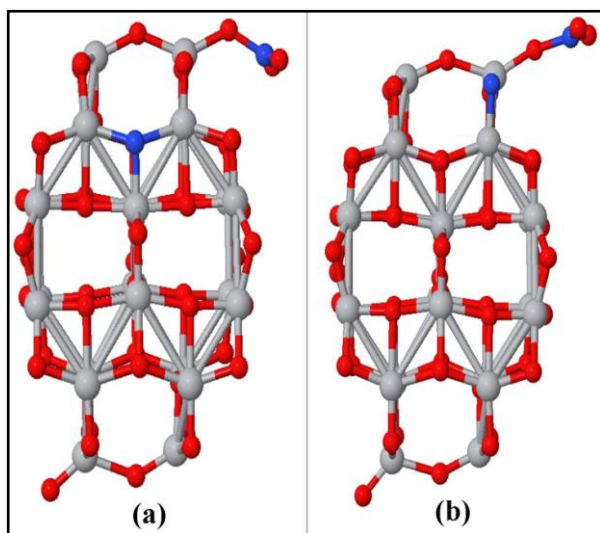


Fig. 2. A NO₂ molecule on a N-doped TiO₂ anatase nanoparticle. (A) Adsorbed NO₂ molecule on a N-doped particle in configuration (N). (B) Same adsorption mechanism in configuration (M).

RESULTS AND DISCUSSION

Adsorption of a NO₂ molecule on a N-doped TiO₂ anatase nanoparticle

- **Geometry optimization**

Adsorption of a NO₂ molecule on N-doped anatase nanoparticles in two substitutional configurations were considered in this section as shown in Figure 2, After the adsorption, two

important bonds were formed between the adsorbed molecule and nanoparticle which have been represented as a Ti-O and newly-formed N-O bond. The Ti-O bond was formed between the oxygen atom of the NO₂ molecule and titanium atom of the nanoparticle, while the N-O bond was formed between the nitrogen atom of the NO₂ molecule and oxygen atom of the nanoparticle [13, 16]. After the adsorption, the O-N-O bond angle of NO₂ molecule decreases to 129.4° while the experimental value is about 134.3°.

The adsorption energy of the studied systems has been evaluated from the following equation:

$$E_{\text{ad}} = E(\text{nanoparticle} + \text{NO}_2) - E(\text{nanoparticle}) - E(\text{NO}_2)$$

The values of adsorption energies were listed as Table 1. This table shows that the adsorption energy values for N-doped nanoparticle are more negative than pristine nanoparticle. From this point of view and neglecting entropy change effects we can deduce that adsorption of a toxic NO₂ molecule on a N-doped particle is more energetically favorable than the adsorption on a pristine nanoparticle [11, 24]. Table 2 has been contained the length for dangling Ti-O bond, N-O bond of the adsorbed NO₂ molecule, newly-formed N-O bond and Ti-N bond in before and after the adsorption for comparison with the experimental values taken from ref. [11,12]. The reported results show that the adsorption of NO₂ causes the stretching the dangling Ti-O bond and the N-O bond of the adsorbed NO₂ molecule. These variations of bond lengths are due to the moving of electronic density from the old bonds to the newly-formed bonds between adsorbent and adsorbed molecule [11].

Table 1. Adsorption energy for a NO₂ molecule on an anatase nanoparticle. (Unit in eV.)

Type (N-doped)	E _{ad} (LDA)	E _{ad} (GGA)
doped(A)	-5.278	-5.249
doped(B)	-5.984	-5.685

Table 2. Bond length of a NO₂ molecule adsorbed on a TiO₂ anatase nanoparticles. Unit in Å

Type	Ti-O	Ti-N	N-O (NO ₂)	newly-formed N-O
(A)	1.86	1.92	1.26	1.57
(B)	1.85	1.80	1.29	1.50
Experimental	1.947	2.01-2.11	1.20	-

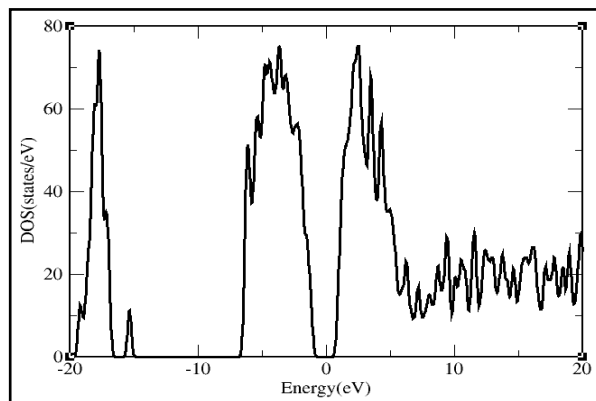
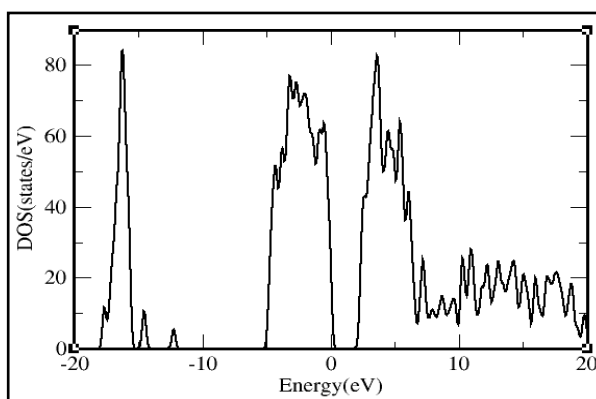
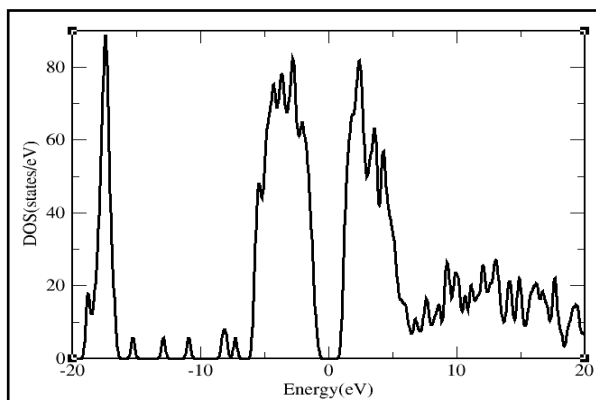
- **Mulliken population analysis**

The mulliken charge analysis is the most common population analysis method, in the mulliken analysis half of the overlap population was devoted to each atomic orbital, giving the overall population of each atomic orbital. One can sum all the populations for all the orbitals on an individual atom, and then subtract the nuclear charge and finally obtain the partial charge on each atom [14]. In this research, the calculated partial charges are -0.3911, -0.072 and +1.281 for each O, N and Ti atoms respectively.

Density of states (DOS) analysis

The density of states describes the number of available states per distance of energy at each energy state which can be occupied by electrons [18]. A great DOS at a given energy state means that there are numerous available states for occupation by electrons, while a DOS of zero represents that there are no states can be occupied by electrons [20, 21]. N-doping in TiO₂ anatase increases the states for occupation by electrons due to the impurity states which have been introduced inside the band gap of the particle. So the N-doped TiO₂ anatase has a more available state than the pristine (undoped) particle and can acts as a strong semiconductor. Consequently, the doping of nitrogen in the TiO₂ as an impurity state introduces a hole inside the particle and leads to the narrowing of the band gap of TiO₂ anatase. As a result, the N-doped TiO₂ anatase has a high photocatalytic activity than the undoped TiO₂ anatase [14, 16]. The reason can be ascribed to the narrowing of band gap for N-doped TiO₂ anatase which causes shifting of the adsorption edge of N-doped TiO₂ to the lower energy (higher wavelength) [16, 22]. The

DOS plots for optimized structures of pristine TiO₂, N-doped TiO₂ and NO₂ adsorbed structures have been shown in Figures 3, 4 and 5 respectively.

**Fig. 3.** DOS for a 72 atom pristine TiO₂ anatase nanoparticle.**Fig. 4.** DOS for N-doped 72 atom TiO₂ anatase nanoparticle**Fig. 5.** DOS for NO₂ adsorbed N-doped TiO₂ anatase nanoparticle.

Electronic band structure analysis

The substitutional N-doped TiO₂ anatase represents p-type characteristics which can also exist in semiconductors. The valence band of pristine TiO₂ essentially consists of the 2p, 2s states of oxygen and 3d states of titanium [25]. While in the N-doped case, impurity state includes the N 2p states, and the valence band consists of the 2p states of nitrogen and oxygen atoms and conduction band consists of 3d states of titanium. Due to the interaction between N 2p and Ti 3d states, electrons of the localized N 2p states can be transferred to the conduction band [13-16]. Furthermore, the rate of the electron transferring from the valence band to the conduction band has been enhanced. Because the band gap for N-doped TiO₂ anatase is narrower than that of undoped TiO₂. This also resulted in a high photocatalytic activity of the N-doped anatase TiO₂. Since the nitrogen has a one less electron than the oxygen, replacement of one nitrogen atom with oxygen atom causes a single acceptor, and this can be resulted in the acceptor N 2p state [19,20], lied above the valence band maximum (VBM) of TiO₂ anatase [16,18]. The electronic band structure plots for undoped and N-doped TiO₂ anatase were shown in Figures 6 and 7 respectively. The band gap for N-doped TiO₂ is narrower than that of pristine TiO₂ anatase due to the hybridization of N 2p states with O 2p states [14-18]. For undoped anatase, the band gap is about 2.16 eV, which is lower than the experimental result of 3.2 eV, this difference of the calculated band gap from the experimental value can be due to the selection of exchange-correlation energy [13]. For the undoped case, the top of the valence band and bottom of the conduction band lies at different points [17, 18, 25], exhibiting that TiO₂ with anatase form has an indirect band gap.

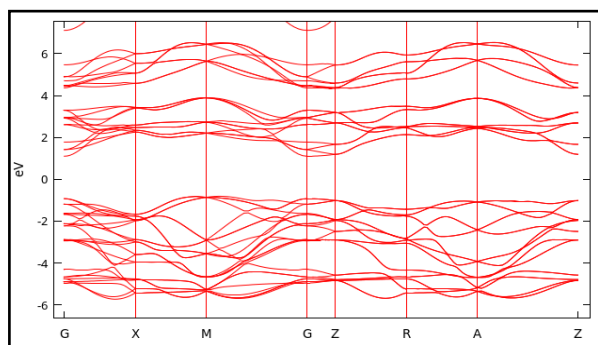


Fig. 6. Band structure for pristine (undoped) anatase TiO₂.

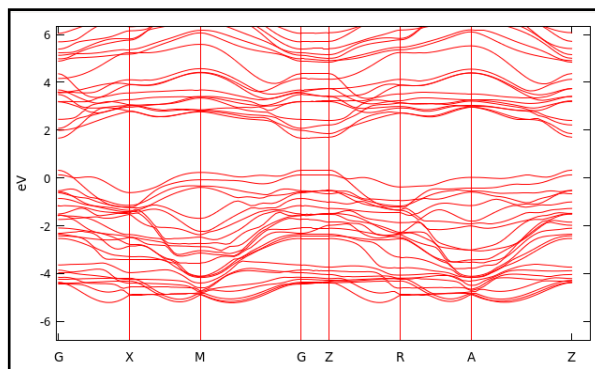


Fig. 7. Band structure for N-doped TiO₂ anatase.

CONCLUSIONS

The adsorption of a NO₂ molecule on 72 atom N-doped TiO₂ anatase nanoparticles has been investigated using the (DFT) calculations. At the first, the considered structures of undoped and N-doped nanoparticles were optimized and then the nanoparticles including the adsorbed NO₂ molecule were geometrically optimized. After the adsorption, the length for the dangling Ti-O bond and N-O bond of the NO₂ molecule were increased due to the moving of electrons from the dangling Ti-O bond and N-O bond to the newly-formed N-O bond between the adsorbed NO₂ molecule and particle. Furthermore, from the obtained results of adsorption evaluation, we can found that the using of nitrogen dopant in the TiO₂ anatase resulted in an increment of adsorption energy, compared to the undoped nanoparticle. This means that the adsorption of a NO₂ molecule on a N-doped particle can be easily occurred. So N-doped nanoparticles have a more efficiency to adsorb toxic NO₂ molecules on their surfaces and control the air pollution during the adsorption processes. Electronic structure analysis of the considered structures exhibits that the band gap of the N-doped TiO₂ anatase is narrower than that of undoped TiO₂ due to the hybridization of N 2p states with O 2p states. For the N-doped nanoparticles, the adsorption of a NO₂ molecule on a different surface oxygen atom sites can take place, but the adsorption on dangling oxygen atom site is more energetically favorable than the adsorption on other surface oxygen atoms [11].

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