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Density functional theory study of the adsorption of toxic large molecules on nitrogen modified TiO_2 anatase nanoparticles

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Abstract

First principles calculations were performed to study the adsorption behaviors of large organic molecules on the pristine and N-doped TiO_2 anatase nanoparticles. Both oxygen and nitrogen in the molecule can react with the TiO_2 nanoparticle strongly. Thus, the binding sites were located on the oxygen or nitrogen atom of the molecule, while on the TiO_2 nanoparticle the binding site occurs on the fivefold coordinated titanium atoms. It was found that the adsorption on the N-doped TiO_2 is more favorable in energy than the adsorption on the undoped one, indicating the high sensitivity of N-doped TiO_2 nanoparticles towards molecule molecules. It means a dominant effect of nitrogen doping on the adsorption properties of pristine TiO_2. The large overlaps in the PDOS spectra of the oxygen and nitrogen atoms of the molecule and titanium atom of TiO_2 represent a forming Ti-O and Ti-N bonds between them.

Keywords: *Molecule; TiO_2 nanoparticle; Electronic properties; Density functional theory*.

Introduction

As one of the most widely studied semiconductor materials, (TiO_2) possesses various advantages in numerous applications because of its particular properties such as non-toxicity, low cost, and high catalytic efficiency [1-4]. Due to the wide band gap (3.2 eV for anatase polymorph), TiO_2 can only absorb a small percentage of the solar spectrum light (UV area). This resulted in a serious limitation of the photocatalytic activity of TiO_2. Thus, effective techniques will be needed to expand the absorption of the incoming light to the visible region. Struggles to recover the photocatalytic activity of TiO_2 catalysts to cover the range of visible light are quite prominent and indispensable. Some research studies have been devoted to the investigation of doping treatments of TiO_2 with metal or non-metal elements. In recent times, the optical sensitivity of TiO_2 was successfully improved using some of the non-metal dopants [5, 6]. This doping pattern presents energy levels in the bandgap, efficiently modifying its band energy.

Asahi and co-workers [7] exhibited that $TiO_{2-x}N_x$, in which oxygen atom was replaced by the nitrogen atom using sputtering methods, shows better photoactivity in the visible spectral range. TiO_2 has been extensively used as a suitable candidate material with a wide range of applications in photo-catalysis [8], gas sensor devices, heterogeneous catalysis [9] and photovoltaic cells [10]. Several experimental and computational studies of TiO_2 have been published, explaining its major importance in environmental remediation and toxicology reduction [11-15].

Recently, Liu *et al.* [16] reported that the N-dopedTiO_2 anatase nanoparticles can interact with toxic NO molecule more capably. Moreover, Liu *et al.* [17] studied the augmented reactivity of N-doped TiO_2 nanoparticles with CO molecules. Performing periodic Hartree–Fock calculations, Fahmi *et al.* [18] exhibited that water can adsorb on the titanium atom and then dissociate to give hydroxyl groups. Nair [19] calculated molecular and dissociative water adsorption energies on TiO_2 (001) using MSINDO-CCM (semi empirical molecular orbital method–cyclic cluster model) computations. Moreover, metal and non-metal doping of TiO_2 particles lead to some enhancements on the sensing ability and adsorption capability [20-22]. The improvements of both adsorption capability and photocatalytic activity induced by non-metal doping and other factors have been examined comprehensively [23-25]. Nevertheless, the effects of doping usage on the optical response and band gap of TiO_2 have been suggested in some studies [26-28].

Heroin molecule has been characterized as an extremely addictive drug, which is largely used by millions of addicts. Most heroin is injected, making further risks for the user, who faces the danger of AIDS or other infection on top of the pain of addiction. This molecule leads to the harmful effects on the brain cells, heart and immune system. It can increase feelings of happiness by changing activity in the limbic system. When the brain experiences such a pleasure feeling, molecule is responsible for creating physical addiction which is typical for molecule addicts. In this work, we studied the adsorption of large molecules on the pristine and N-doped TiO_2 anatase nanoparticles. Different analyses of the adsorption configurations and systems were studied in terms of the bond lengths, density of states, molecular orbitals and Mulliken charge analysis. This work aims at investigating the effect of the doping of nitrogen atom on the electronic properties of TiO_2 nanoparticles with adsorbed molecules.

Details of calculations

Density functional theory calculations [29, 30] were performed with the open Source Package for Material explorer (OPENMX3.8) [31]. The considered cutoff energy was set at 150 Ry in our calculations. The exchange-correlation energy was described using the generalized gradient approximation (GGA) in the formalism of Perdew–Burke–Ernzerhof (PBE) [32]. The pseudo atomic orbitals were utilized as basis sets. To completely investigate the effects of long range van der Waals (vdW) interactions, we have employed DFT-D2 method, developed by Grimme *et al.* [33]. For self-consistent field iterations, the convergence criterion of 1.0×10^{-6} Hartree was used, while for energy calculation the criterion was set to 1.0×10^{-4} Hartree/bohr. The crystalline and molecular structure visualization program, XCrysDen [34], was employed for displaying molecular orbital isosurfaces. The Gaussian broadening method for evaluating electronic DOS was used. When molecule interacts with TiO_2 nanoparticle, the adsorption energy was calculated according to the following equation.

$$E_{ad} = E_{(adsorbent+\ adsorbate)} - E_{adsorbent} - E_{adsorbate} \quad (1)$$

Where $E_{(adsorbent\ +\ adsorbate)}$, $E_{adsorbent}$ and $E_{adsorbate}$ are the energies of the complex system, the free TiO_2 nanoparticle without any adsorbed molecule and the isolated molecule, respectively. The charge transfer between molecule and TiO_2 nanoparticle was estimated based on the Mulliken charge analysis.

We have taken the unit cell of TiO_2 from the data reported by Wyckoff [35] at the “American Mineralogists Database” webpage [36]. The size of the simulation box considered in our calculations is $20\times15\times30$ Å^3, which is much larger than the size of the particle. Two oxygen atoms of pristine TiO_2 (twofold coordinated and threefold coordinated oxygen atoms) were substituted by nitrogen atoms, leading to the N-doped nanoparticles. Twofold coordinated oxygen atom is denoted by 2f-O and threefold by 3f-O (middle oxygen) in Figure 1 with fivefold coordinated and sixfold coordinated titanium atoms sketched by 5f-Ti and 6f-Ti, respectively[37].The optimized structure of the adsorbing molecule was shown in Figure 2.

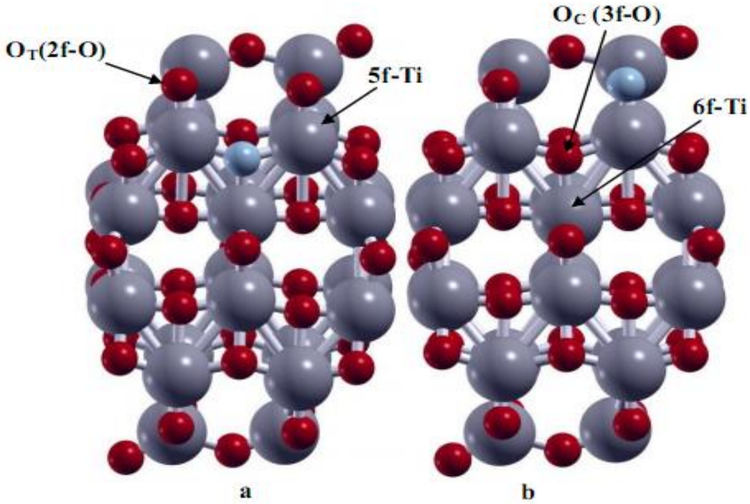


Figure 1. Optimized structures of the N-doped TiO_2 anatase nanoparticles, colors represent atoms accordingly: Ti in gray, O in red and N in blue.

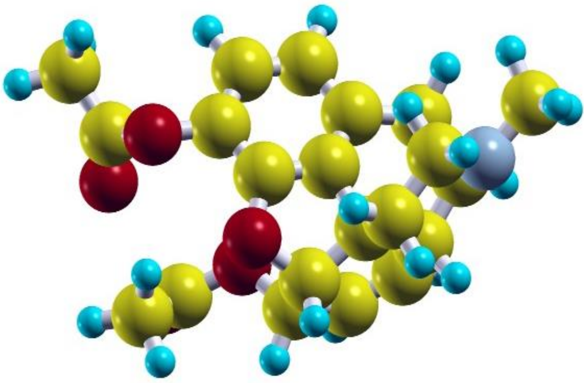
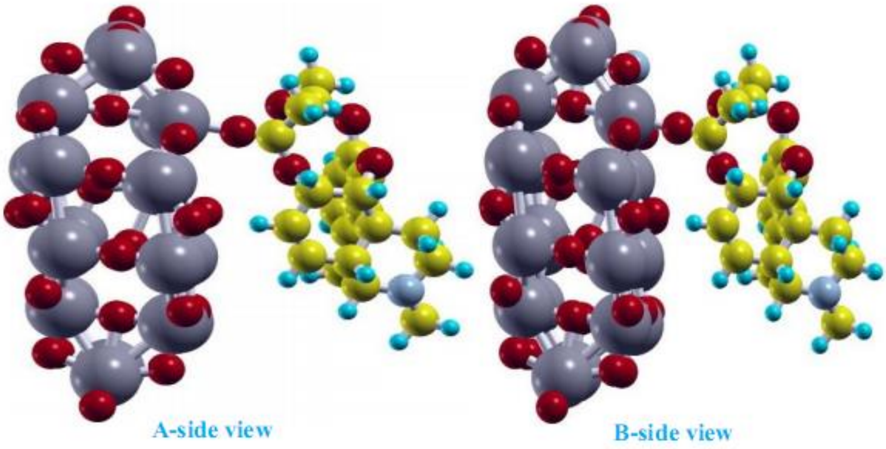


Figure 2. Optimized structure of the adsorbing molecule, colors represent atoms accordingly: C in yellow, N in blue, O in red and H in cyan.

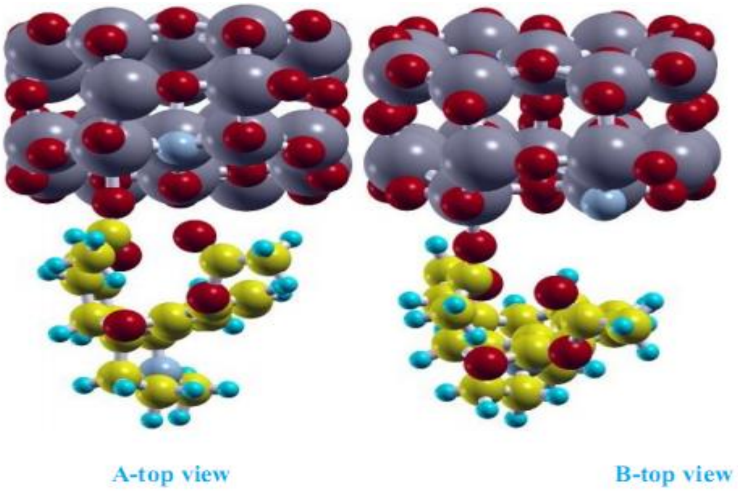
Results and discussion

The interaction of molecule with N-doped TiO_2 nanoparticles

Various conformations were simulated for the pristine and N-doped TiO_2 nanoparticle + molecule, where the molecule molecule is place perpendicular to the TiO_2 surface. Three possible adsorption orientations of molecule with respect to the TiO_2 nanoparticle were considered. Important to note is that the oxygen atom in the molecule reacts with TiO_2 nanoparticle more strongly. In contrast, the nitrogen and carbon atoms do not interact with the nanoparticle. Thus, the most stable configurations of molecule adsorbed on the fivefold coordinated titanium site of TiO_2 were studied here. Optimized geometry configurations of molecule on the undoped and N-doped nanoparticles were displayed in Figures 3 and 4.

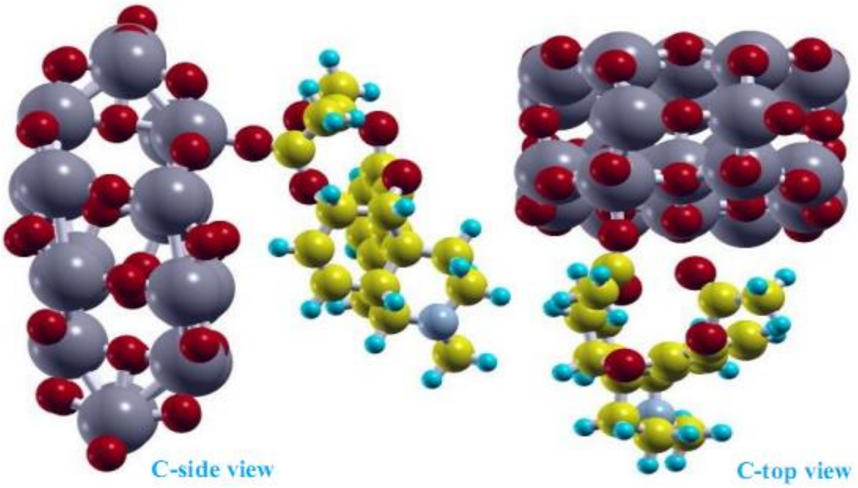


A-side view B-side view



A-top view B-top view

Figure 3. Optimized geometry configurations of molecule adsorbed N-doped TiO_2 anatase nanoparticles. The oxygen atom of molecule was bound to the fivefold coordinated titanium atom.



C-side view C-top view

Figure 4. Optimized geometry configurations of molecule adsorbed undoped TiO_2 anatase nanoparticles. The oxygen atom of molecule was bound to the fivefold coordinated titanium atom.

These configurations were marked by labels A-C in these figures. In all cases, the oxygen atom of molecule was found to be the binding site, while on the TiO_2 nanoparticle, the binding site was located on the fivefold coordinated titanium atom.

The bond lengths for the newly-formed Ti-O bonds between the TiO_2 and molecule were listed in Table 1.

Table 1. Bond lengths (in Ǻ), adsorption energies (in eV) and Mulliken charge values for molecule adsorbed on the TiO_2 anatase nanoparticles.

Complex	Ti-O	Adsorption energy		Mulliken Charge
		PBE	DFT-D2	
A	2.13	-4.64	-6.24	-0.612
B	2.17	-4.42	-6.14	-0.546
C	2.31	-3.82	-5.86	-0.524

For brevity, we have only reported the newly formed bonds between the molecule and nanoparticle. The smaller the distance was positioned towards the TiO_2 nanoparticle after the adsorption process, the stronger the adsorption of molecule on the TiO_2 nanoparticle. The comparison of the results presented in Table 1 indicates that the smallest distance between the oxygen atom of molecule and titanium atom of TiO_2 was occurred in configuration A, whereas the largest distance belongs to configuration C. This indicates that the strongest adsorption occurs in configuration A, representing molecule interaction with N-doped (O_C-substituted nanoparticle). In configuration C, molecule interacts with pristine nanoparticle, providing the lowest distance between the nanoparticle and molecule. By the comparison of the results, we found that the interaction of oxygen site of molecule with fivefold coordinated titanium site of TiO_2 was strongly favored. In order to further describe the behavior of the molecule adsorbed on the TiO_2 nanoparticle, we calculated the adsorption energies of the most stable configurations (see Table 1).

The results of this table indicate that molecule adsorption on the N-doped TiO_2nanoparticle is more energetically favorable than the adsorption on the pristine one. Therefore, the N-doped nanoparticle strongly reacts with molecule. It is worth noting that the large adsorption energy gives rise to a strong binding between the TiO_2 and molecule. As can be seen from Table 1, the highest adsorption energy occurs in configuration A, representing that the interaction of oxygen atom of molecule with titanium atom is stronger than the same interaction in other configurations. The lowest adsorption energy belongs to configuration C, which shows the interaction of pristine nanoparticle with molecule. Moreover, the adsorption of molecule on the O_C-substituted TiO_2 is more favorable in energy than the adsorption on the O_T-substituted one. By considering these results and analyzing adsorption systems, we concluded that the nitrogen modified TiO_2 nanoparticle is an ideal material to be utilized for sensing of molecule.

It should be also noted that the adsorption energies from DFT-D2 method are considerably larger than those of PBE method, representing the dominant effect of long range van der Waals interaction during the adsorption of molecule on the considered nanoparticles.

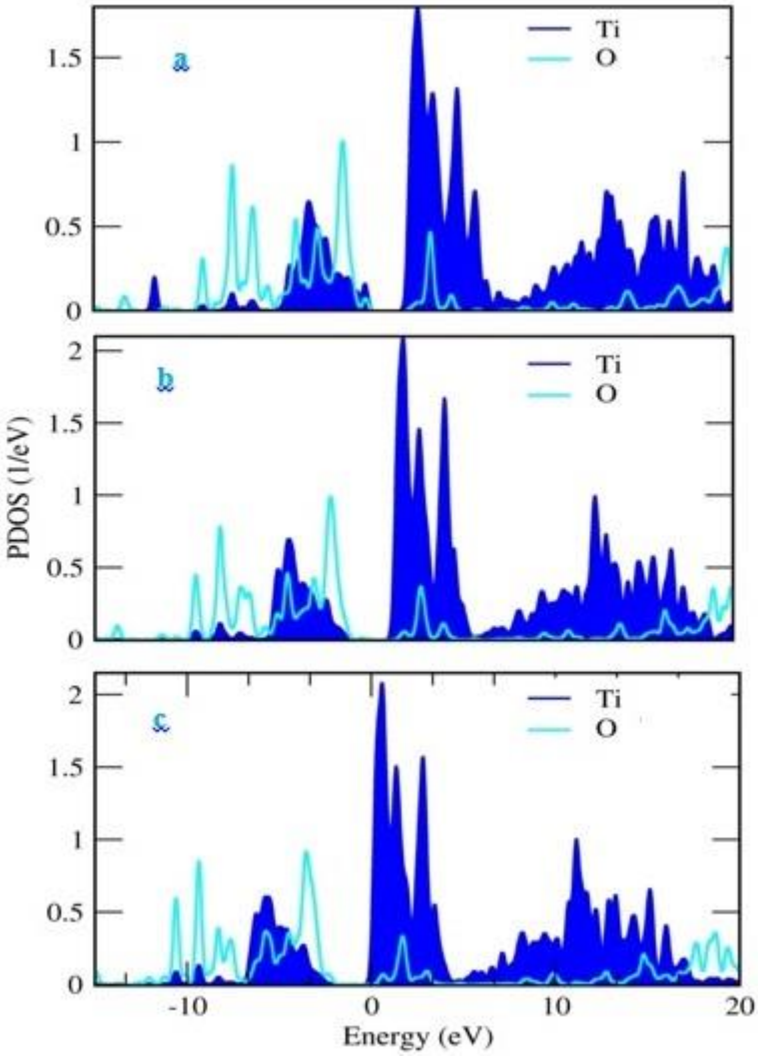


Figure 5. Projected density of states for molecule adsorbed on the TiO_2 anatase nanoparticles, a: configuration A; b: configuration B; c: configuration C.

Electronic structures

For molecule adsorption on the TiO_2 anatase nanoparticles, the projected density of states was shown in Figure 5. Panels (a-c) display the PDOSs for configurations A-C, respectively. The considerable overlaps between the PDOSs of the oxygen atom of molecule and titanium atom of TiO_2 denote the formation of chemical Ti-O bond between them. This chemical bond formation approves the chemical adsorption of molecule on the TiO_2 nanoparticle.

As can be seen from this figure, panels (a, b) exhibit higher overlaps between the PDOSs of the oxygen and titanium atoms than panel (a), representing that molecule was strongly adsorbed on the N-doped nanoparticle, compared to the undoped one. The PDOSs of the oxygen atom of molecule, titanium atom and five d orbitals of the titanium were shown in Figures6 and 7 for configurations A and B, respectively.

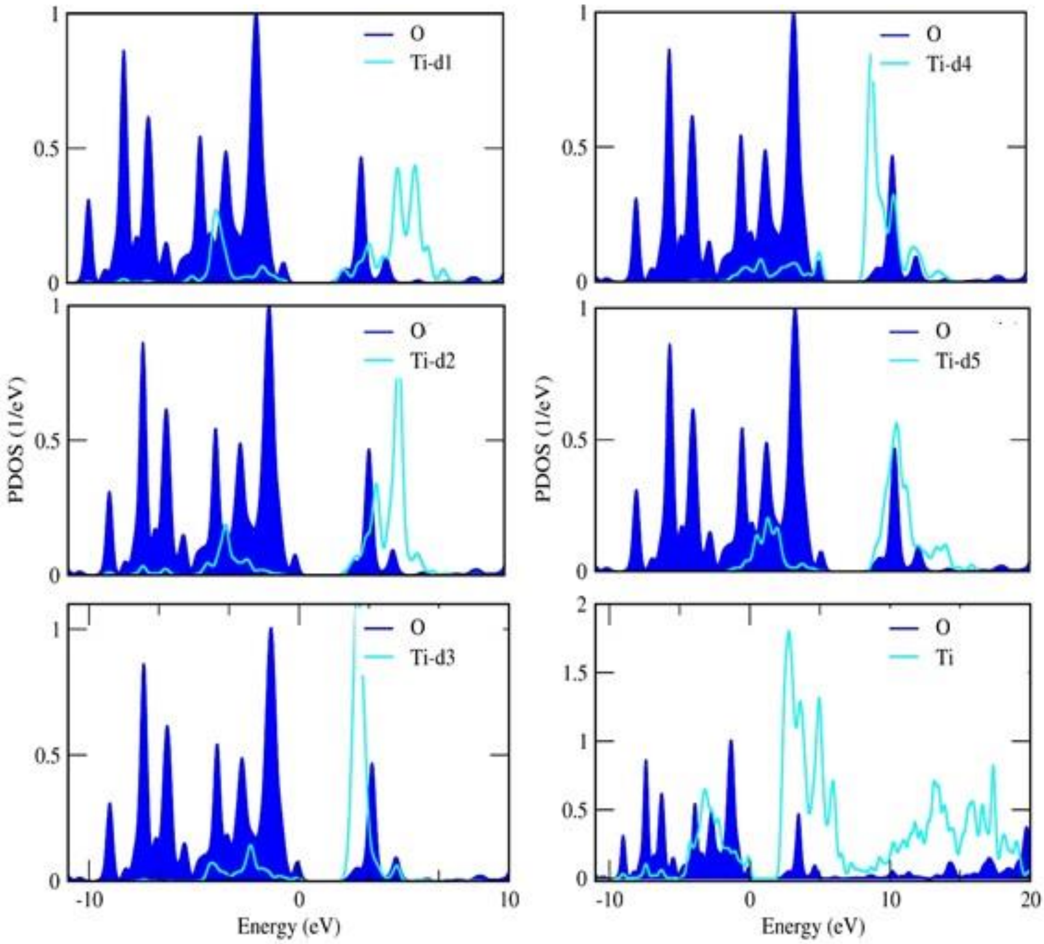


Figure 6. Projected density of states for the oxygen atom of the molecule, titanium atom and different d orbitals of the titanium (configuration A).

There are high overlaps between the PDOSs of the oxygen atom of molecule and d^2 orbital of the titanium atom, indicating effective mutual interaction between them.

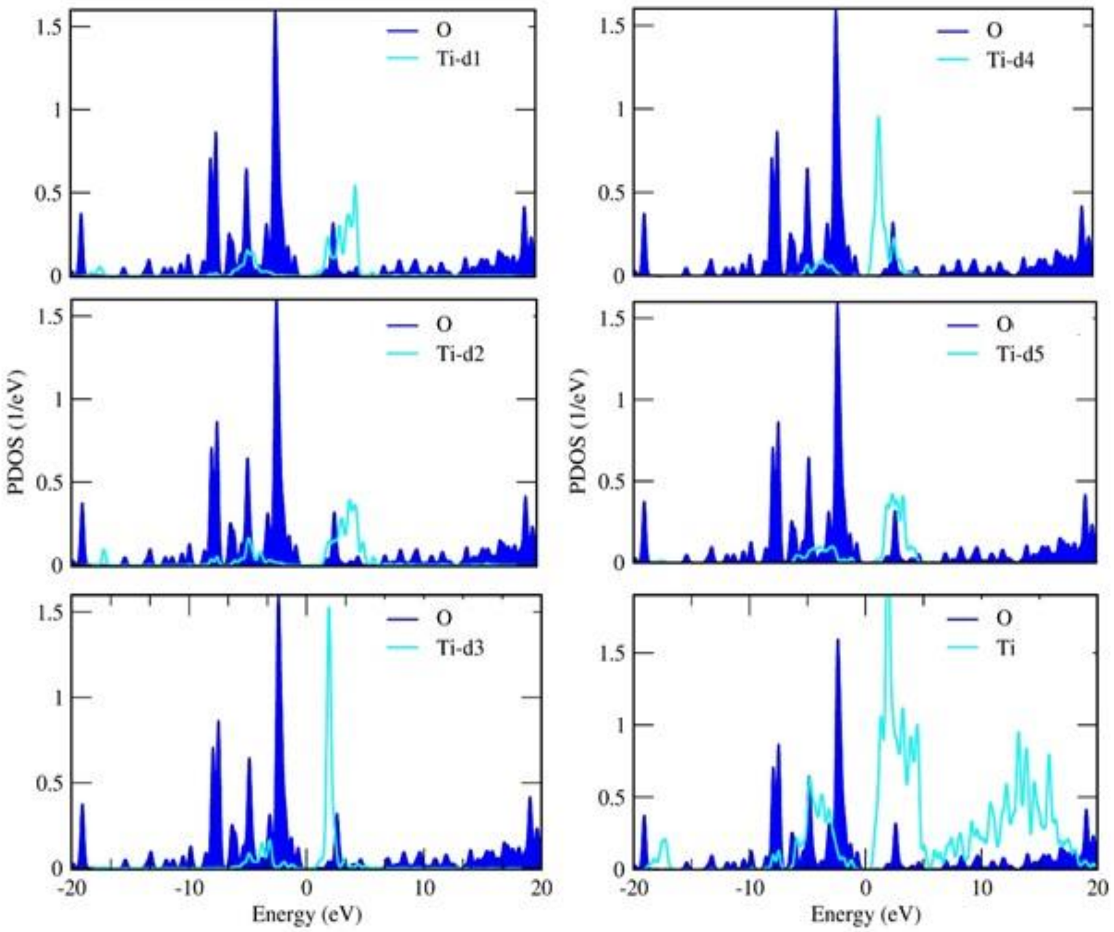


Figure 7. Projected density of states for the oxygen atom of the molecule, titanium atom and different d orbitals of the titanium (configuration B).

In order to further investigate the electronic density distribution on the TiO_2 complexes with adsorbed molecule molecules, we have presented the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) for the considered systems. Figure 8 displays the HOMO and LUMO diagrams for isolated molecule.

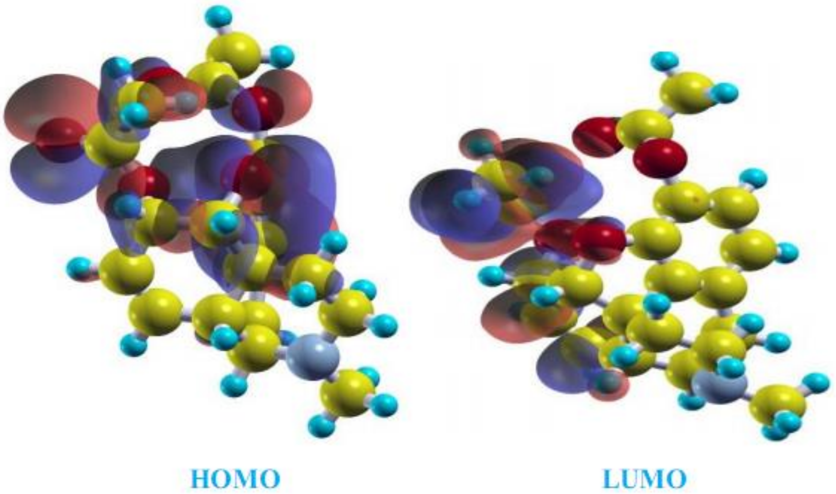


Figure 8. The isosurfaces of HOMO and LUMO of molecule in non-adsorbed state.

The HOMO of the adsorption system represents that the distribution was dominantly occurred on the whole molecule. Figures 9 and 10 show the isosurfaces of HOMOs and LUMOs for molecule adsorbed on the TiO_2 anatase nanoparticles.

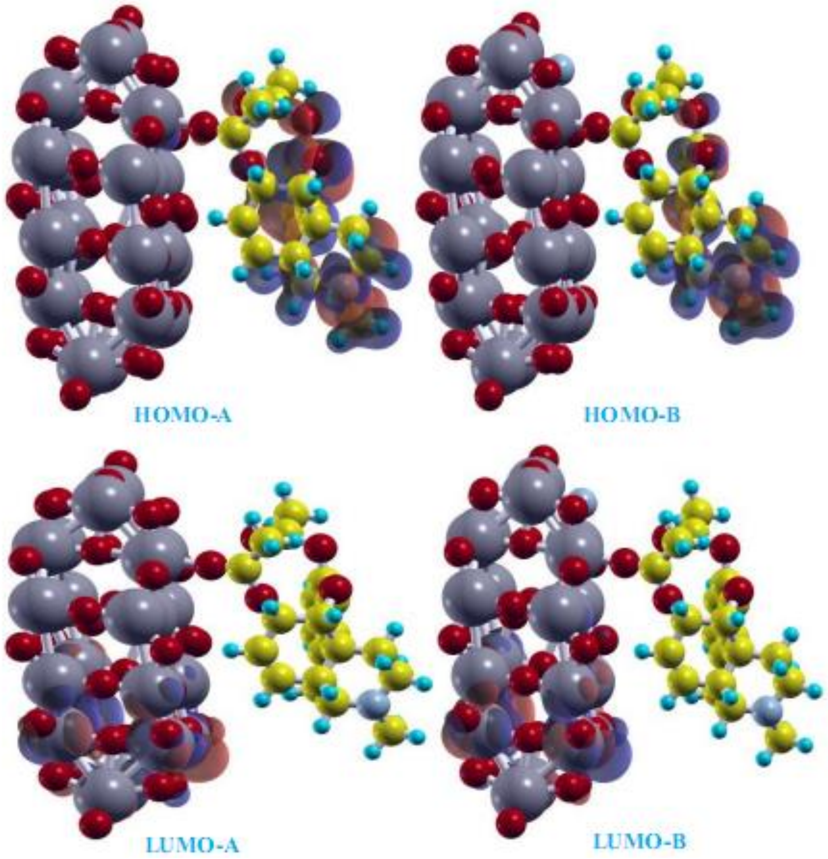


Figure 9. The isosurfaces of HOMOs and LUMOs for molecule adsorbed N-doped TiO_2 anatase nanoparticles. After the adsorption process, the electronic density was distributed over the adsorbed molecule.

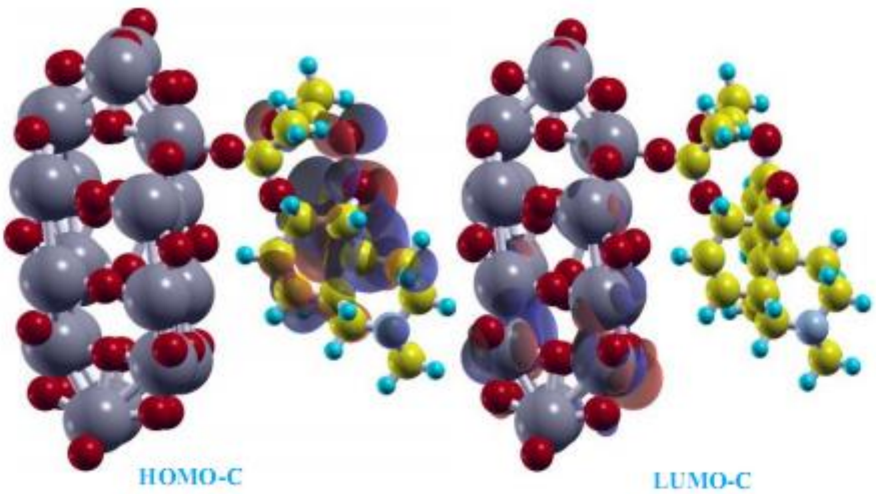


Figure 10. The isosurfaces of HOMOs and LUMOs for molecule adsorbed undoped TiO_2 anatase nanoparticles. After the adsorption process, the electronic density was distributed over the adsorbed molecule.

Interestingly, the HOMOs of the complex systems were high on the adsorbed molecule, whereas the electronic density in the LUMOs shows a major distribution on the nanoparticle. Consequently, the electronic structure of the TiO_2 nanoparticle was significantly affected upon molecule adsorption. The HOMO isosurfaces of the adsorption systems indicate that the main contribution was resulted from the adsorbed molecule rather than TiO_2 nanoparticle, suggesting that molecule adsorption has substantial effect on the electronic density variation.

In addition, the charge transfer values between the adsorbent and adsorbed molecule were estimated in this work. The results were summarized in Table 1. For brevity, we have presented the charge transfer report for one configuration only. In the case of complex A, there is a considerable charge transfer of about -0.612 |e| (e, the electron charge) from molecule to the TiO_2 nanoparticle, indicating that molecule behaves as a charge donor. The maximum value of charge transfer arises from configuration A, whereas the lowest charge transfer belongs to configuration C, in reasonable agreement with higher adsorption energy of configuration A in comparison with configuration C.

The charge density difference calculations were also performed in this study in order to further examine the electronic structure of the adsorption system. It can be seen Figure 11 that the charge was dominantly accumulated on the adsorbed molecule.

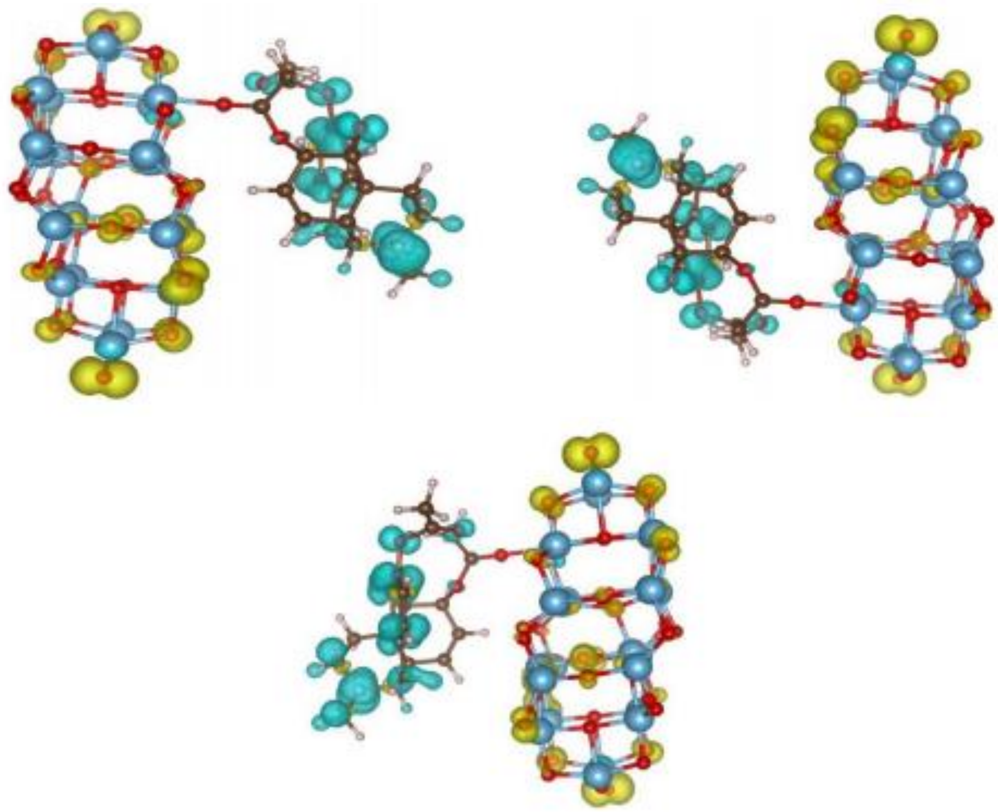


Figure 11. Isosurface plots of electron charge density difference for molecule adsorbed on the N-doped TiO_2 anatase nanoparticles.

Conclusions

In this paper, the interaction of molecule drug with pristine and N-doped TiO_2 anatase nanoparticles were investigated using density functional theory calculations. Various adsorption models of molecule on the considered nanoparticles were examined in detail. The calculations predict that molecule presents a stronger interaction with TiO_2 nanoparticles containing doped nitrogen atom rather than with pristine or undoped nanoparticles. The interaction of molecule with N-doped TiO_2 is more energetically favorable than the interaction with undoped ones, representing that the N-doped nanoparticle is strongly favored. By the inclusion of vdW interactions, the adsorption energies for molecule are considerably increased. The projected density of states of the oxygen and nitrogen atoms of molecule and titanium atom of TiO_2 represent considerable overlaps between these atoms and consequently formation of chemical Ti-O and Ti-N bonds at the interface region. After the adsorption, the HOMOs of the adsorption systems were mainly distributed on the adsorbed molecule. Thus, nitrogen doping into TiO_2 particle, strengthens the interaction between molecule and TiO_2 nanoparticle. The distribution of charge electron densities represents that the charges were accumulated on the adsorbed molecule.

Acknowledgement

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