

RESEARCH ARTICLE

A First-principles Study of the Interaction of Aspirin with Nitrogen-doped TiO₂ Anatase Nanoparticles

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ARTICLE INFO

Article History:

Received 28 May 2016;

Accepted 7 July 2016;

Publish 19 July 2016

Keywords:

Adsorption

Anatase nanoparticle

Aspirin

DFT

PDOS

TiO₂

ABSTRACT

Objective(s): First-principles calculations have been carried out to investigate the interaction of aspirin molecule with nitrogen-doped TiO₂ anatase nanoparticles using the density functional theory method in order to fully exploit the biosensing capabilities of TiO₂ particles.

Methods: For this purpose, we have mainly studied the adsorption of the aspirin molecule on the fivefold coordinated titanium atom site of the TiO₂ nanoparticles because of the more reactivity of this site in comparison with the other sites. The complex systems consisting of the aspirin molecule positioned toward the undoped and nitrogen-doped nanoparticles have been relaxed geometrically.

Results: The obtained results include structural parameters such as bond lengths and energetic of the systems. The electronic structure and its variations resulting from the adsorption process, including the density of states, molecular orbitals and the Mulliken charge transfer analysis have been discussed. We found that the adsorption of aspirin molecule on the nitrogen-doped TiO₂ nanoparticles is energetically more favorable than the adsorption on the undoped ones.

Conclusions: These results thus provide a theoretical basis and overall understanding on the interaction of TiO₂ nanoparticles with aspirin molecule for applications in modeling of efficient nanomedicine carriers, biosensors and drug delivery purposes.

How to cite this article:

Abbasi A, Jahanbin Sardroodi J. A First-principles Study of the Interaction of Aspirin with Nitrogen-doped TiO₂ Anatase Nanoparticles. *Nanomed Res J*, 2016; 1(2):69-78. DOI: 10.7508/nmrj.2016.02.002

INTRODUCTION

Titanium dioxide has been identified as an important semiconductor metal oxide, which has different applications in many fields such as photocatalysis [1], gas sensor devices, heterogeneous catalysis [2] and photovoltaic cells [3]. This physically well-organized material has involved numerous academic and industrial attentions because of its exceptional properties such as lack of toxicity, chemical stability, large band-gap and

so on. These unique properties make it possible the TiO₂ could be considered as a fascinating material [4-8]. Many academics have investigated some of the important properties of TiO₂ [8-15]. Anatase phase of TiO₂ has a wide band-gap of 3.2eV, and can be utilized only for absorbing a few portion (3-5%) of the incoming solar irradiation. A convenient method to expand the photo-catalytic properties and adsorption abilities of TiO₂ should satisfy the improvements on the behaviors of TiO₂ and be

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utilized in wide range of investigations. Doping of TiO₂ with some non-metal elements such as nitrogen is such a process, which has a reinforcing effect on the activities of TiO₂ [16-19]. N-doped TiO₂ anatase nanoparticles have been studied by numerous researchers over the past years. For example, Liu *et al.* [20] reported that the N-doped TiO₂ anatase can adsorb NO molecules more strongly, compared to the undoped ones. Additionally, doping of TiO₂ nanoparticles with nitrogen atom developed its electronic and structural properties and makes the TiO₂ particle as an effective candidate to be utilized in gas sensor devices [20-25]. Nevertheless, the effects of N-doping on band structure of TiO₂ anatase and the photo-catalytic activity have been investigated in some other works [26, 27]. For exhibiting the enhancements of the efficiency of TiO₂ nanoparticles in the surface phenomena, some researchers have evaluated its electronic properties such as density of states (DOS), band structures and also its structural properties such as bond lengths and adsorption energies [14,19,28]. Density functional theory (DFT) is based not on the wavefunction, but rather on the electron density function, usually named the electron density or charge density, labelled by ρ . This is a probability per unit volume; the probability of finding an electron in a volume element $dx dy dz$. The electron density function is the basis not only of DFT, but of an entire set of methods of regarding and reviewing atoms and molecules, and, unlike the wavefunction, is measurable, e.g. by X-ray diffraction. The electronic density is a function of position only, that is, of just three variables (x, y, z). Today, DFT calculations on molecules are based on the Kohn-Sham approach, the stage for which was set by two theorems suggested by Hohenberg and Kohn. The first Hohenberg-Kohn [24] theorem says that all the properties of a molecule in a ground electronic state are calculated using the ground state electron density function. The second theorem declares that any trial electron density function will give energy higher than (or equal to, if it were exactly the true electron density function) the true ground state energy.

Aspirin or acetylsalicylic acid (ASA), is a medication, which has been utilized to treat pain, fever, and inflammation. Aspirin at lower doses has also been considered to help inhibit heart attacks and blood clotting in people who are of the

subject of great risk of emerging blood clots.[29] Aspirin could be applied as an effective material in preventing certain types of cancer, particularly colorectal cancer. The stability of drugs in the presence of solid additives has attracted substantial consideration in the field of pharmaceuticals. Aspirin is a drug that hydrolyses to salicylic acid and acetic acid in the vicinity of moist media or water. In this research, the interaction of aspirin molecule with N-doped TiO₂ anatase nanoparticles was investigated using the DFT computations. The electronic and structural properties of the considered non-adsorbed and adsorbed structures and the adsorption energies in adsorbed complexes were computed and analyzed. Moreover, the effects of doping of nitrogen on total density of states (DOS) and band structure of TiO₂ were investigated in detail.

COMPUTATIONAL DETAILS

Methods of computations

All of DFT calculations [30,31] have been performed using the Open source Package for Material eXplorer (OPENMX) version 3.7 [32] which has been verified to be a well-organized package for simulation of large atomic systems, specially solid state substrates. The same outer electrons of Ti atom were considered as valence electrons in the self-consistent field iteration. Pseudo atomic orbitals (PAO's) centered on atomic sites have been used as basis sets in order to expand the wave functions in a KS schema with a cutoff energy of 150 Ry (Rydberg) [32, 33]. Pseudo atomic orbitals were generated via the basis sets (two-s, two-p, one-d) for Ti atom, two-s and two-p for O, N and C atoms and two-s for H atom according to the cutoff radii set to the values of 7 for Ti, 5.5 for H, 5 for O and N and 4.5 for C (all in Bohrs) in generation by a confinement scheme. The cutoff radius (a.u.) is an important parameter for the generation of pseudopotentials. Although an optimum cutoff radius is determined so that the generated pseudopotentials has a smooth shape without distinct kinks and a lot of nodes, however, the selection includes somewhat an empirical factor. The accuracy and efficiency of the calculations can be controlled by two parameters: a cutoff radius and the number of basis functions. In general, one can get the convergent results by increasing the cutoff radius and the number of basis functions. However,

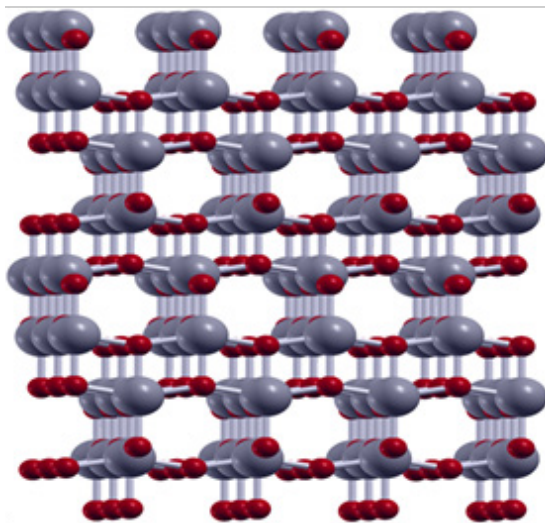


Fig. 1. A 3×2×1 supercell of TiO₂ anatase. Colors represent atoms accordingly: Ti in gray and O in red

it is noted that the use of a large number of basis orbitals with a large cutoff radius requires an extensive computational resource such as memory size and computational time [33]. The generalized gradient approximation functional (GGA) in the Pedrew-Burke-Ernzerhof (PBE) form, which treat the exchange correlation in an approximate manner was used in the calculations [34]. An efficient open-source program (XCrysDen), which is a crystalline and molecular structure visualization program [35] was utilized in display of isosurfaces such as molecular orbitals, contours and other Figures present in this study. The adsorption energy was calculated via the following formula:

$$E_{ad} = E_{(particle+drug)} - E_{particle} - E_{drug} \quad (1)$$

Where $E_{(particle+drug)}$, $E_{particle}$ and E_{drug} are the energies of the complex system, the free TiO₂ nanoparticle without any adsorbed molecule and the free aspirin molecule in a non-adsorbed state respectively. The more negative the E_{ad} is, the more energy favorable the adsorbed structure is.

Models of nanoparticles

The studied TiO₂ anatase nanoparticles were modeled via setting a 3×2×1 supercell of TiO₂ anatase along x, y and z axis, respectively. The constructed supercell has been shown in Fig. 1. The unit cell was taken from “American Mineralogists Database” webpage [36] and reported by Wyckoff [37]. The schematic geometric structure of TiO₂ anatase has been displayed in Fig. 2. N-doped TiO₂

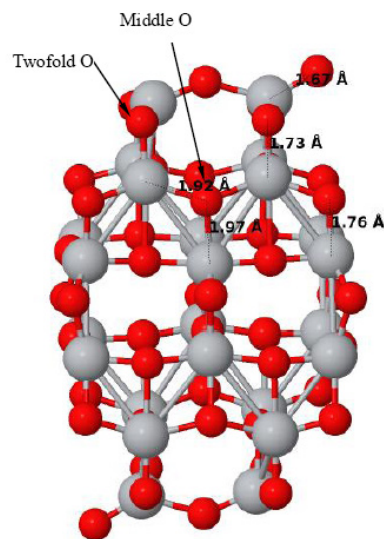


Fig. 2. Optimized geometry of the pristine TiO₂ anatase nanoparticle with bond length results

anatase nanoparticles were constructed by replacement of two surface oxygen atoms by nitrogen atoms. The substitution of oxygen atom by nitrogen atom in the TiO₂ nanoparticle leads to the introducing of a hole in the particle.

The generated empty state (hole) can be observed either on the top of the valence band or mixed inside the band gap of TiO₂ [20]. In one doping configuration, a nitrogen atom substitute an oxygen atom in the middle (3f-O substitution site) of the particle and the other is a nitrogen atom substitute an oxygen atom at 2f-O position. The chosen N-doped nanoparticles were separately optimized to obtain the energy minimized and stable structures for studying the adsorption behaviors of complex systems. The substituted oxygen atoms were found that to be of great importance in calculating and obtaining the optimum parameters of TiO₂. The reason is that the crystal structure of TiO₂ anatase includes two types of oxygen atoms (twofold coordinated oxygen atom, 2f-O, and threefold coordinated oxygen or middle oxygen, 3f-O) and the modification of TiO₂ nanoparticle through substituting these representative oxygen atoms by other atoms has a significant effect on the structural and energetic properties of TiO₂. These effects also comprise the variations in the electronic DOS or appearing and changing of some new bands in the electronic band structure. The aspirin adsorbed complexes were made by the help of the geometrically optimized N-doped nanoparticles.

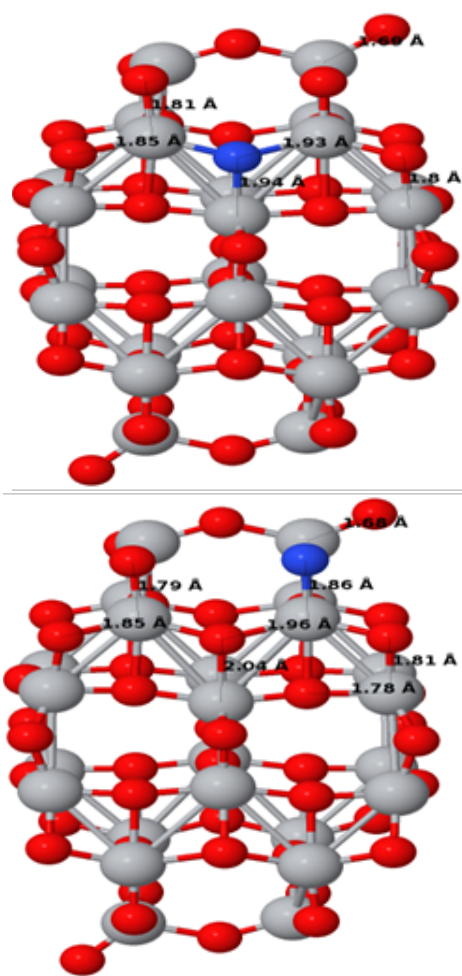


Fig. 3. Optimized geometry structures of two types of N-doped TiO₂ anatase nanoparticles corresponding to two doping configurations. The larger gray spheres are Ti atoms and the small red and blue ones represent O and N atoms, respectively.

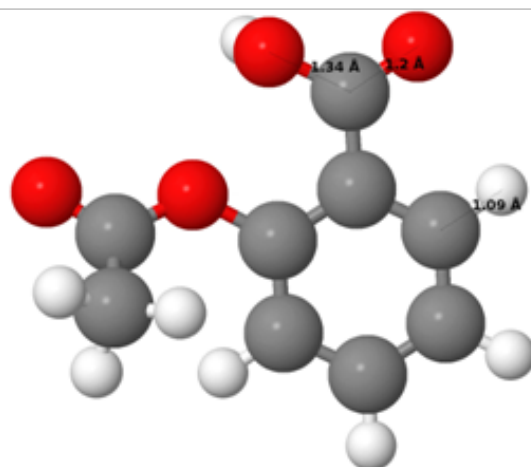


Fig. 4. Structure of the aspirin molecule before the adsorption process with bond length results. Colors represent atoms accordingly: C in gray, O in red and H in white

N-doped nanoparticles were displayed in Fig. 3 from the front view. We investigated the adsorption on the active fivefold coordinated titanium sites of the considered TiO₂ anatase nanoparticles due to their relatively high activity in adsorption process in comparison with the other oxygens. Moreover, the structure of aspirin molecule has been illustrated before the adsorption (Fig. 4).

RESULTS AND DISCUSSION

Bond lengths and bond angles

Studied formaldehyde molecule has been adsorbed on the fivefold coordinated titanium site of TiO₂ from two orientations relative to TiO₂ nanoparticles. In one orientation, aspirin's oxygen was laid toward the nanoparticle in parallel orientation (orientation 1) and in other it was located perpendicularly with respect to the nanoparticle resulting in the adsorption on the nanoparticle with slightly distortion but with the same orientation (orientation 2). These interactions both include N-doped nanoparticles in the middle oxygen position and N-doped ones in the twofold coordinated oxygen atom sites. Fig. 5 represents the considered TiO₂-aspirin complexes in parallel configuration optimized using the DFT method. This Figure includes the aspirin-adsorbed complexes named A to C for the adsorption in the parallel configuration. Each complex of Fig. 5 differs in substituted oxygen atom of TiO₂ nanoparticle and/or adsorbed aspirin positioning from the others. For instance, complex A was made from OC-substituted TiO₂ nanoparticle and aspirin molecule with parallel arrangement towards the nanoparticle (orientation 1). The undoped TiO₂ interacts with aspirin molecule in both configurations. The optimization of the complexes formed from the aspirin orientation with carbon atom towards the nanoparticle leads to the complexes with lower degree of stability and favorability. Then, the most favorable configurations (namely parallel and perpendicular) have been studied in this work. Fig. 6 also presents three configurations for perpendicular adsorptions of aspirin on the nanoparticle, which have been denoted by D to F complex types. It has been found that the perpendicular interaction of aspirin with nanoparticles results in the most stable configurations, compared to the parallel orientation of aspirin. The optimized values of some bond

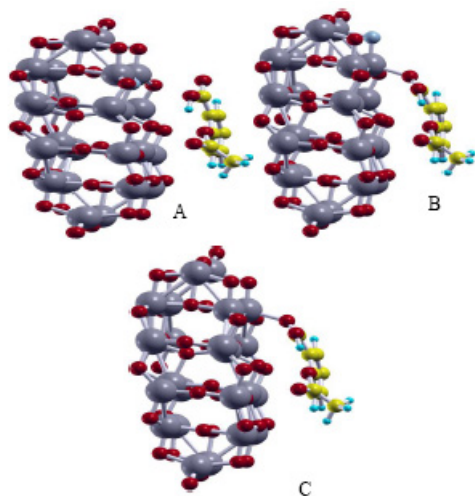


Fig. 5. Optimized TiO₂-Aspirin complexes with parallel adsorption configurations. Colors represent atoms accordingly: Ti in gray, O in red, N in blue, C in yellow and H in cyan.

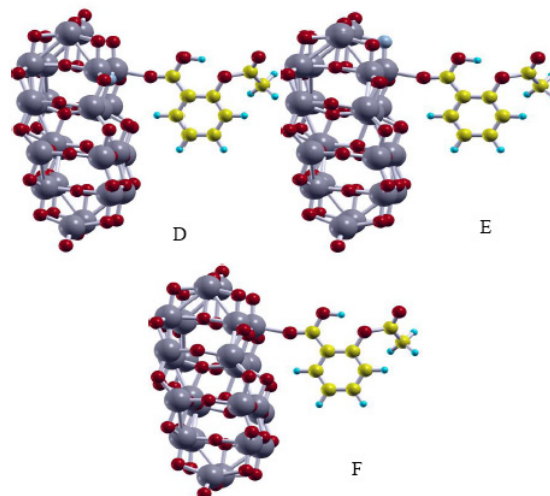


Fig. 6. Optimized TiO₂-Aspirin complexes with perpendicular adsorption configurations.

lengths before and after the adsorption on the nanoparticle have been listed in table 1. The bond lengths given in this table are included Ti-O bond of TiO₂ nanoparticle, nearest C-O bond of aspirin molecule and newly-formed Ti-O bond between titanium atom nanoparticle and nearest oxygen atom of aspirin. The results of this table show that the Ti-O bond and C-O bond of aspirin molecule are stretched after the adsorption process. These variations of the bond lengths are mostly due to the transfer of electronic density from Ti-O bond of TiO₂ and C-O bond of the adsorbed aspirin molecule to the newly formed Ti-O bond at the interface of aspirin molecule and TiO₂ anatase nanoparticle. Therefore, the C-O bond of the aspirin molecule is weakened after the adsorption. The smaller the bond formed between the oxygen atom of aspirin molecule and the fivefold

coordinated titanium atom of nanoparticle (Ti-O), the more powerful the adsorption of aspirin on TiO₂ anatase nanoparticle. As can be seen from Table 1, although the configuration B has the smaller newly formed Ti-O bond length than the configuration A (2.14 Å versus 2.20 Å), it has the higher adsorption energy than the configuration A (-3.53 eV versus -3.45 eV). Since higher adsorption energy gives rise to a strong binding between adsorbate and the nanoparticle, we can see that there is a stronger interaction between aspirin and TiO₂ nanoparticle in configuration B compared to the interaction in configuration A. Also the adsorption energy of configuration D is higher than that of configuration E (while configuration D has the lower Ti-O bond length than the configuration E), which indicates a strong interaction between aspirin and nanoparticle in

Table 1. Bond lengths (in Å), adsorption energies (in eV) and Mulliken charge results for the interaction of aspirin with TiO₂ anatase nanoparticles.

Complex	Ti-O	Ti-N	C-O	Newly-formed Ti-O	E _{ad} (eV)	Q(e)
A	1.80	---	1.28	2.20	-3.45	+0.48
B	---	1.80	1.28	2.14	-3.53	+0.55
C	1.73	---	1.28	2.15	-1.18	+0.54
D	1.76	---	1.28	2.12	-3.99	+0.69
E	---	1.82	1.28	2.19	-3.86	+0.73
F	1.73	---	1.27	2.18	-1.21	+0.72

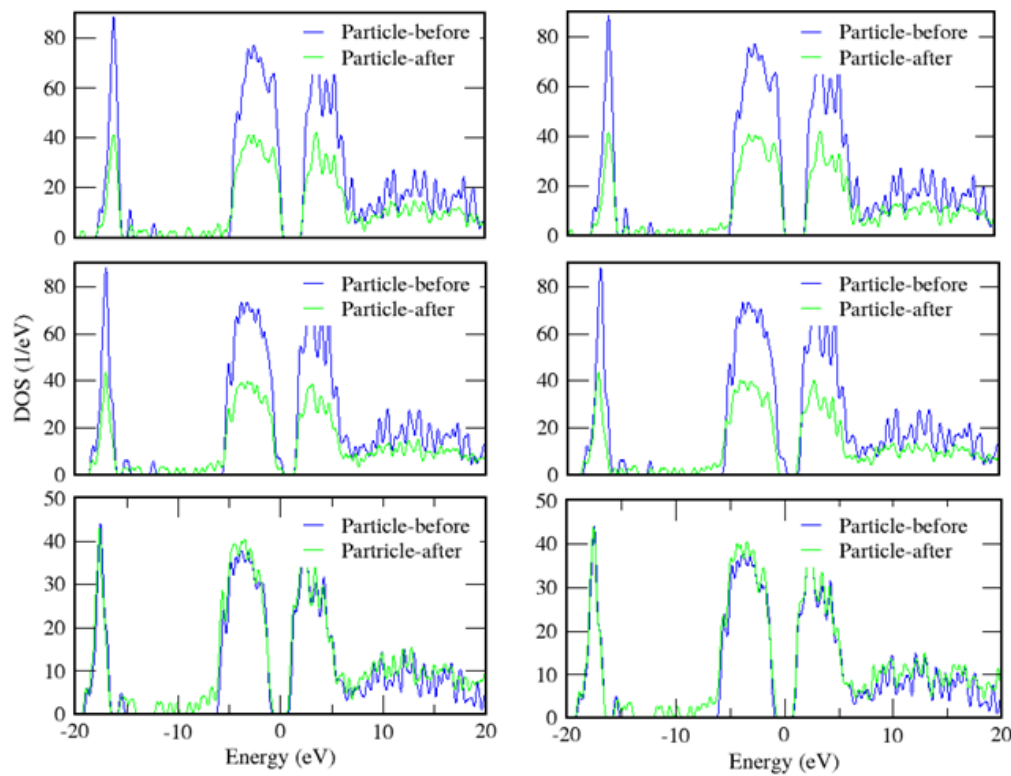


Fig. 7. DOS for the adsorption of aspirin molecule on the undoped and N-doped nanoparticle before and after the adsorption process, a: A complex, b: B complex, c: C complex, d: D complex, e: E complex and f: F complex.

configuration D. On the other hand, lower Ti-O distance in configuration B in comparison with configuration A corresponds to the higher value of Mulliken charge transferred from TiO_2 to aspirin. This increasing of the charge transfer could be a useful feature for sensing of aspirin molecule by TiO_2 nanoparticle.

Adsorption Energies

The adsorption energies for the undoped and N-doped TiO_2 anatase nanoparticles have been tabulated as table 1 as the Eads reported results. These results show that the adsorption of aspirin molecule on the N-doped nanoparticle is energetically more favorable than the adsorption on the pristine one. It means that the N-doped nanoparticle interacts with aspirin molecule more effectively in comparison with the undoped one. In both adsorption configurations, the N-doped complexes have been clarified as the most stable ones from the energetics point of view. For parallel configuration, the calculated adsorption energy of complex B is more negative (higher) than that of complex A, suggesting the more stability of this

complex. The calculated adsorption energy of complex D in perpendicular configuration is higher than that of complex E, which indicates that the complex D interacts with the molecule strongly. These results indicate that the N-doping could strengthen the interaction of aspirin over the TiO_2 anatase nanoparticles. The improvement of both adsorption energy and structural properties of the adsorption of aspirin on TiO_2 nanoparticles resulted by N-doping proposes us that the TiO_2 can be used for sensing of aspirin molecule. The increasing of efficiency of the TiO_2 nanoparticles by the doping of nitrogen atom is an effective property to help in the development of more efficient and consequently more demanding biosensors for aspirin detection.

Electronic structures

Fig. 7 displays the total density of states (TDOS) for the interaction of pristine and the N-doped anatase TiO_2 particles with aspirin molecule in both configurations before and after the adsorption process. The biggest difference is the creation a small peak in the DOS of N-doped TiO_2 at the

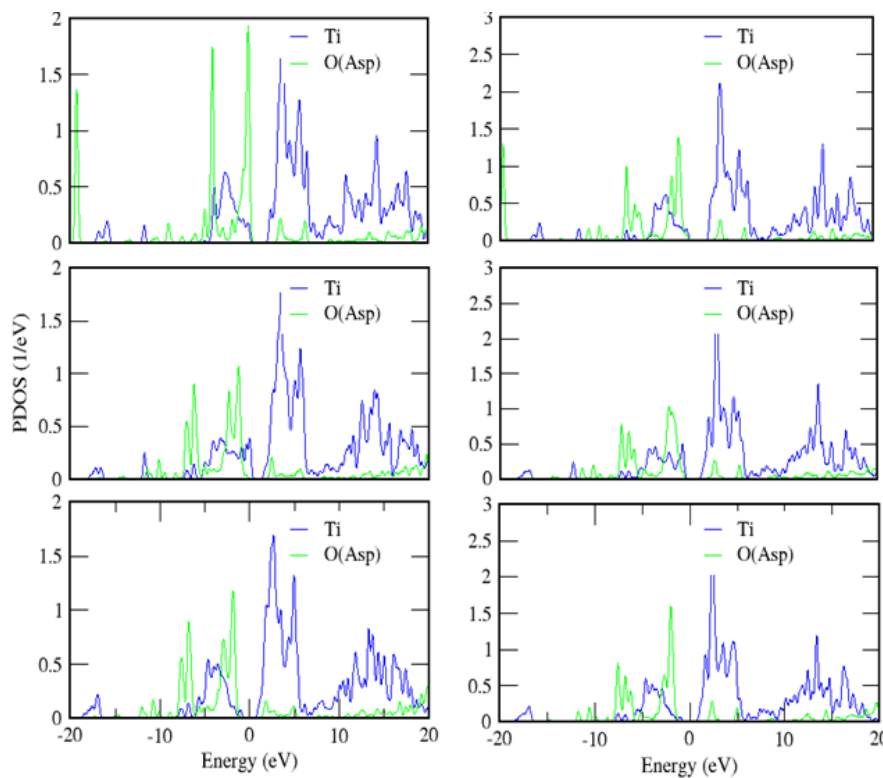


Fig. 8. PDOS for the adsorption of aspirin molecule on the N-doped nanoparticles, a: A complex, b: B complex, c: C complex, d: D complex, e: E complex and f: F complex.

energy values close to -12 eV. Fig.7 also presents a comparison of the DOS of N-doped particles (panels' a-f) before and after the adsorption for clear comparison. These panels show that the DOSs of N-doped particles before and after the adsorption have small differences with each other. The whole DOSs of studied systems show that the differences between DOS of doped and undoped TiO₂ are increased by adsorption of CH₂O. These variations are comprised both growing shift of energies of peaks and formation of some peaks in the DOS of the pristine TiO₂. These impacts are also included of small shifts in energies of the states and generating some small peaks at energies between -5 to -15 eV. A closer inspection of this Figure reveals that the adsorption process changes the energies of the states and the density of the states. So, these changes in energy gap of DOS would affect the electronic transport properties of the nanoparticles and this feature can be beneficial for sensing of aspirin by TiO₂ nanoparticles. The projected density of states (PDOSs) and key molecular orbitals (HOMOs, LUMOs) were computed to additional analysis the aspirin adsorption on TiO₂

nanoparticles. The titanium and oxygen projected DOSs (Ti-PDOS and O-PDOS) after the adsorption were shown in Fig. 8 as panels (a-c for parallel configuration) and (d-f for perpendicular configuration) respectively. These panels indicate the bond formation between the titanium atom of nanoparticle and oxygen atom during the adsorption process. The large overlap between the PDOS of these two atoms is a good electronic reason which could take into account for the formation of chemical bond. It means that the

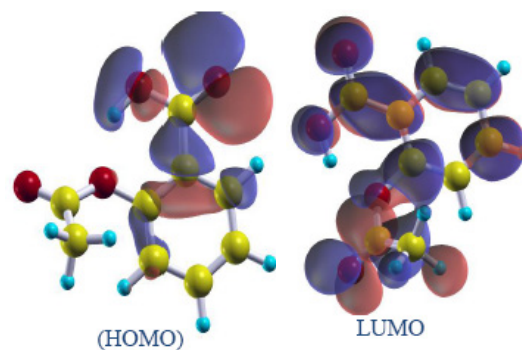


Fig. 9. The isosurfaces of HOMO and LUMO molecular orbitals for isolated non-adsorbed aspirin molecule.

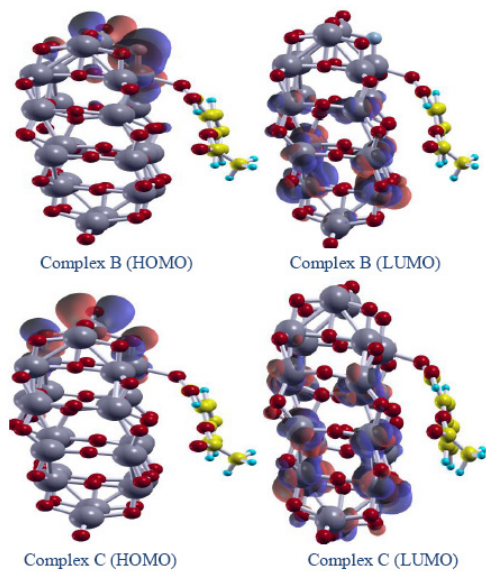


Fig. 10. The isosurfaces of HOMO and LUMO molecular orbitals of the studied systems consisting of the aspirin molecule adsorbed on the TiO₂ nanoparticles for parallel configuration. The orange and blue colors represent the positive and negative value areas respectively.

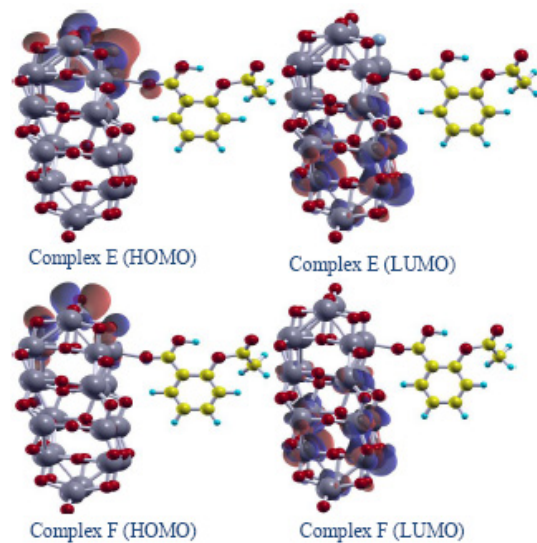


Fig. 11. The isosurfaces of HOMO and LUMO molecular orbitals of the studied systems consisting of the aspirin molecule adsorbed on the TiO₂ nanoparticles for perpendicular configuration. The orange and blue colors represent the positive and negative value areas respectively.

aspirin molecule is chemisorbed on the nanoparticle in most stable configurations. Fig. 9 has been contained the isosurfaces of HOMO and LUMO molecular orbitals of the isolated non-adsorbed aspirin molecule respectively. The isosurfaces of molecular orbitals for TiO₂/aspirin complexes have been also shown for two complexes of both parallel and perpendicular configurations (Figs 10 and 11). These Figures show that the HOMO's and LUMO's are mainly localized on the TiO₂ nanoparticle and the aspirin molecule describes a negligible state of localization. We have also investigated the band structures for pristine and N-doped TiO₂ anatase. The computed band structures are represented as Fig. 12 (Top and Down) for pristine and N-doped TiO₂ respectively. One can see from Fig. 12 that the valence band of pristine TiO₂ mainly includes the 2p states of oxygen while the conduction band mainly consists of 3d states of titanium. Band structures for the considered N-doped TiO₂ contained an impurity state as the 2p states of nitrogen inside the band-gap, and the valence band consists of the mixed 2p states of oxygen and 2p states of nitrogen while the conduction band was mainly composed of 3d states of titanium 26. Due to the interaction between nitrogen's 2p and titanium's 3d states, electrons of the nitrogen's 2p states would be transferred to the conduction band

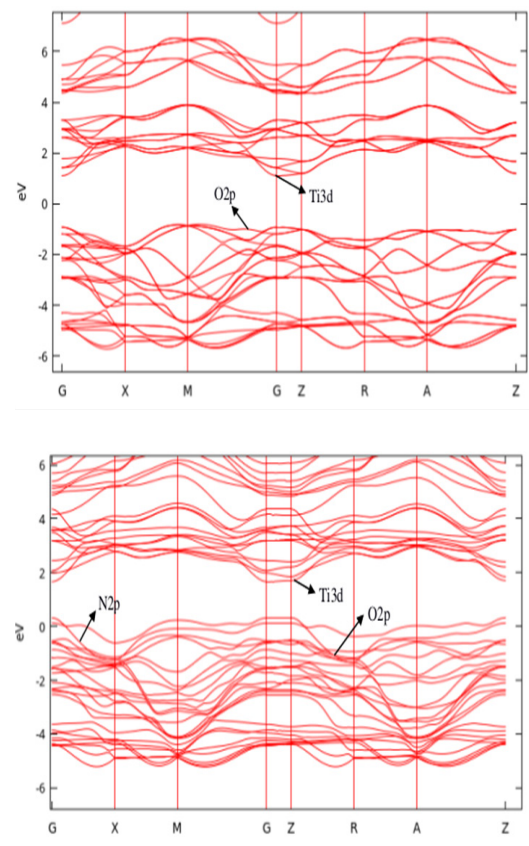


Fig. 12. Band structures of considered TiO₂, a: pure and b: N-doped.

more easily in comparison to the pristine TiO₂. In addition, the increasing the rate of the electron transfer from the valence band to the conduction band extends photo-catalytic activity of the N-doped TiO₂ to the low-energy region, again, in comparison with the undoped one [21, 23]. Further analysis of the band structures and total density of states shows that the band-gap for N-doped TiO₂ at Γ point is much narrower than that of undoped one. It is probably due to the mixing of nitrogen's 2p states with oxygen's 2p states in the N-doped TiO₂.

Charge transfer analysis

To further explain the charge transfer between aspirin molecule and TiO₂ nanoparticle, we report in table 1 the charge analysis based on Mulliken charges. The charge difference for the particle j after and before adsorption was calculated using the following equation:

$$\Delta Q_j = Q_j \text{ (in complex)} - Q_j \text{ (in vacuum)} \quad (2)$$

Where Q_j is the value of Mulliken charge of the j. Subscript "j" signifies the TiO₂ nanoparticle or aspirin molecule. The charge difference, ΔQ_j , is a measure of the amount of charge transferred to, or, from the studied nanoparticles from, or, to the aspirin molecule. For example, the computed charge value for TiO₂ nanoparticle in configuration A is about +0.48 e and that of aspirin molecule is -0.48 e. This means that TiO₂ nanoparticle acts as an electron donor to aspirin molecule. In other words, aspirin molecule accepts electrons from TiO₂. This could be an effective property to help in the designation and improvement of TiO₂-based biosensors for aspirin recognition.

CONCLUSIONS

We studied the adsorption energy and geometry configurations of aspirin on the fivefold coordinated titanium atom of undoped and two types of N-doped TiO₂ anatase nanoparticles using first-principles DFT calculations. The results indicate that the interaction of aspirin molecule with nanoparticles causes the stretching of the Ti-O bond of TiO₂, as well as C-O bond of aspirin, leading to the bond lengths of aspirin molecule getting smaller. Analyzing of the adsorption energies shows that the N-doped nanoparticles have a higher efficiency to interact with aspirin molecule, compared to the pristine TiO₂. The

density of states for pristine and N-doped TiO₂ have been also presented before and after adsorption and the effect of adsorption of aspirin on these properties have been discussed and it was suggested that TiO₂ can be used for sensing of aspirin. The interaction of aspirin over the N-doped nanoparticles is energetically more favorable than the interaction over the undoped ones. The band structure calculations suggest that the band gap of N-doped TiO₂ is narrower than that of pristine one, resulting in the improvements on the capabilities of TiO₂. Based on the obtained results, it can be inferred that the N-doped nanoparticles have higher adsorption ability than the undoped ones.

ACKNOWLEDGEMENT

This work has been supported by Azarbaijan Shahid Madani University.

CONFLICTS OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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