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RESEARCH ARTICLE

A theoretical investigation of the interaction of Immucillin-A with N-doped TiO_2 anatase nanoparticles: Applications to nanobiosensors and nanocarriers

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ABSTRACT

Objective(s): Adsorption of IMMUCILLIN-A (BCX4430) molecule on the pristine and N-doped TiO_2 anatase nanoparticles were studied using the density functional theory (DFT) calculations. The adsorption energy analysis indicated that TiO_2+IMMUCILLIN-A complexes including OC-substituted TiO_2 have higher adsorption energy than the complexes with OT substituted TiO_2, thus providing more stable configurations.

Methods: The structural properties including bond lengths, adsorption energies and bond angles were analysed. The electronic structure of the adsorption system were investigated in view of the density of states, molecular orbitals and Mulliken charge analysis.

Results: The results show that, the interaction of IMMUCILLIN-A drug with N-doped TiO_2 nanoparticles is more energetically favorable than the interaction with the pristine ones, suggesting that the N-doped nanoparticles can react with IMMUCILLIN-A drug more efficiently. The Mulliken charge analysis also suggests a charge transfer from IMMUCILLIN-A molecule to the TiO_2 nanoparticle.

Conclusions: Based on obtained results, it can be concluded that the N-doped TiO_2 nanoparticle could be utilized as an efficient candidate for application as highly sensitive nanobiosensors and efficient nanocarriers for IMMUCILLIN-A drugs.

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INTRODUCTION

Titanium dioxide (TiO_2) is one of the most broadly utilized semiconductor photo-catalysts due to its outstanding properties (e.g., high activity, excellent stability, nontoxicity and low cost) [1-3]. TiO_2 can be found in a broad range of applications such as renewable energy, dye sensitized solar cells and environmental protections (sensor devices) [3-6]. TiO_2 exists in three important crystallographic forms: rutile, anatase, and brookite with a wide variety of technological utilizations. The rutile and anatase polymorphs have been extensively studied compared to the brookite form [7]. In the past few years, it has gained great attentions [8, 9] and many experimental or theoretical efforts [10-12]. The wide band-gap of TiO_2 (3-3.2eV) limited its efficiency to interact with the incoming solar light and reduced the absorption of the solar irradiance to a few

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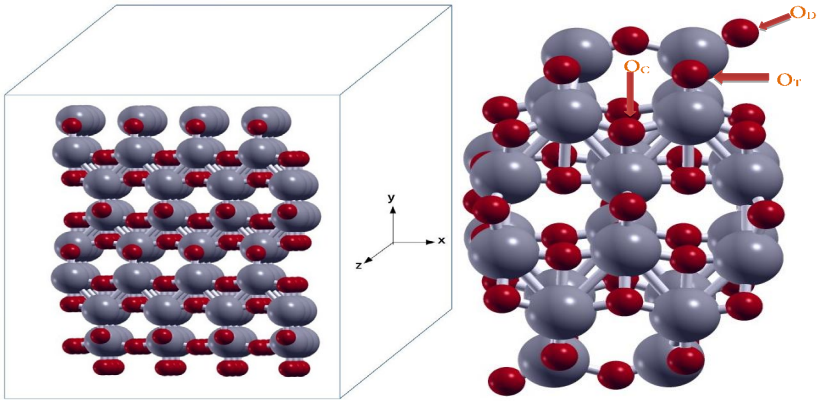
percentage (i.e. 3–5%spectrum) [13, 14]. To rectify the photo-catalytic activity of TiO_2, promising efforts have been done. One of the most important strategies would be a process that could extend the optical response of TiO_2 to the visible area [15-18]. The nitrogen doping of TiO_2 anatase is such a process (non-metal doping), which significantly increases the photo-catalytic activity of TiO_2 [19-23]. Several theoretical studies have previously been investigated to obtain an important insight into the effects of the interaction of gas molecules with the anatase nanoparticles. As an example, Liu et al. [13] showed that the nitric oxide molecule can be strongly adsorbed on the N-doped anatase nanoparticles. Performing DFT calculations, Liu et al. [14] suggested that the N-doped TiO_2 anatase nanoparticles can react with CO molecules more efficiently. Tang et al. [24, 25] reported the insights of density functional calculations of the adsorption of nitrogen oxides on graphene, graphene oxides and Pd-decorated graphene oxides. The interaction of SOx molecules with undoped and N-doped TiO_2 anatase nanoparticles has been also studied in our previous computational works [26, 27]. Density functional theory is developed based on the electron density function, usually named the electron density or charge density. The electron density function is the probability of finding an electron in considered a volume element dxdydz. The electron density function acts as an important quantity of DFT calculations and is based on an overall set of techniques of studying atoms and molecules. Unlike the wavefunction, electron density is measurable, e.g. by X-ray diffraction. The electronic density is determined by relative positions of atoms in the molecules. In other words, it is a function of three spatial variables (x, y, z). Modern DFT calculations on molecules are based on the Kohn–Sham (KS) equations. Also, two important theorems have been suggested by Hohenberg and Kohn. The first Hohenberg–Kohn [28, 29] theorem tells that all the properties of a molecule in a ground electronic state are computed by means of the ground state electron density function. The second theorem suggests that any trial electron density function will generate an energy higher than (or equal to) the true ground state energy.

Immucillin-A is an antiviral drug, with a wide range of applications in drug delivery systems. It is initially supposed to be an efficient drug for the treatment of Hepatitis C disease. Immucillin-A has been also demonstrated to be an important drug in the treatment of fatal and dangerous filovirus infections such as Ebola virus illness. It also suggests wide-ranging antiviral usefulness in the presence of other RNA virus families, including bunyaviruses, arenaviruses and flaviviruses. The primary tests and experiments of this antiviral drug have been successfully performed on both rodents and monkeys. Important to note is that IMMUCILLIN-A can protect against both Ebola and Marburg viruses. We explain the applicability of the DFT method to investigate the interaction behaviours of IMMUCILLIN-A drugs with TiO_2 nanoparticles to further determine the structural and electronic properties of these nanoparticles. Design of efficient nanosensors and nanocarriers for some important drugs is fundamentally essential task and critical to public health. A nanocarrier is nanoparticle, which has been used as a transport module for another substance, such as a drug. Most broadly used nanocarriers include micelles, carbon-based materials and other substances. Nanocarriers are presently being planned to be utilized in drug delivery purposes. The interaction of IMMUCILLIN-A molecules with N-doped TiO_2 nanoparticles has not been extensively studied. This work aims to supply an overall understanding on the energetics and interaction behaviors of N-doped TiO_2 nanoparticles with important IMMUCILLIN-A drugs in order to obtain efficient nanobiosensors and nanocarriers for IMMUCILLIN-A drugs.

DETAILS OF COMPUTATIONS AND STRUCTURAL MODELS

DFT calculations [28, 29] were carried out as implemented in the Open source Package for Material eXplorer (OPENMX3.8) [30], which has been proven to be an effective software package for nano-scale material simulations based on DFT, norm-conserving pseudopotentials, and pseudo-atomic localized basis functions. Pseudo atomic orbitals centered on atomic sites were employed as basis sets in order to expand the wave functions in a Kohn-Sham (KS) scheme with a cut off energy of 150 Ry. The generalized gradient approximation (GGA) in the Pedrew-Burke-Ernzerhof (PBE) form [31], was used in order to describe the exchange and correlation energy functional.



a b

Fig. 1. (a): Representation of a 3×2×1 supercell of TiO_2 anatase constructed from TiO_2 unit cells along x, y and z directions and (b): Optimized structure of a pristine TiO_2 anatase nanoparticle, OC: central oxygen; OT: twofold coordinated oxygen; OD: dangling oxygen.

The GGA functionals are perfectly local in the mathematical sense: the value of the functional at a given point depends only on information about the density, its gradient, and possibly other information at this very point and is absolutely independent of properties of electron densities at given points. Calling these functionals 'non-local' is only described by the fact that these functionals go beyond the 'local' density approximation and of course the observation that knowledge of the gradients is the first step towards accounting for the inhomogeneity of the real density. The GGA approximation is developed and parametrized by Pedrew-Burke-Ernzerhof. The convergence criterion of energy is set at 10−4 Hartree/bohr. The open-source program XCrysDen [32] was used in order to visualize data such as molecular orbitals. To simulate the interaction behaviours of IMMUCILLIN-A drugs over the TiO_2 anatase nanoparticles, we have geometrically optimized the structure of an IMMUCILLIN-A drug adsorbed on the undoped and N-doped TiO_2 nanoparticles. The adsorption process was examined based on different orientations of IMMUCILLIN-A towards the TiO_2 nanoparticles. The adsorption energy is estimated as follows:

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

Where $E_{(particle+adsorbate)}$ is the total energy of the complex system consisting of the IMMUCILLIN-A molecule adsorbed on the TiO_2 anatase nanoparticle, E particle is the energy of the nanoparticle without any adsorbed molecule, and E adsorbate is that of the free IMMUCILLIN-A drug. The more negative the Ead is, the more energy favorable the adsorbed structure is. A 72 atom TiO_2 anatase nanoparticle was constructed by placing 3×2×1 numbers of TiO_2 unit cells along x, y and z axes, respectively. The unit cell was taken from "American Mineralogists Database" webpage developed by Wyckoff. We have selected the nanoparticle under study based on our previous study [33]. ure 1 (a) shows the structure of the considered supercell of TiO_2 anatase. The optimized structure of pristine TiO_2 nanoparticle was also shown in Figure 1 (b). N-doped TiO_2 anatase nanoparticles were constructed by replacement of twofold coordinated and threefold coordinated oxygen atoms of TiO_2 by nitrogen atoms. OT and OC will be used as generic labels to represent "twofold coordinated oxygen" and "three coordinated oxygen" atoms, respectively. In other words, OT and OC refer to twofold coordinated oxygen and threefold coordinated oxygen atoms of TiO_2. The considered undoped and N-doped anatase nanoparticles were geometrically optimized and then the complex systems including the IMMUCILLIN-A drugs positioned over the TiO_2 nanoparticles were optimized. The interaction of IMMUCILLIN-A drugs on the fivefold coordinated titanium atoms of TiO_2 nanoparticles was extensively investigated in this work. The optimized geometries of the N-doped nanoparticles were displayed in Figure 2.

RESULTS AND DISCUSSION

Bond lengths and bond angles

The interaction of IMMUCILLIN-A drug on the undoped and N-doped TiO_2 nanoparticles was

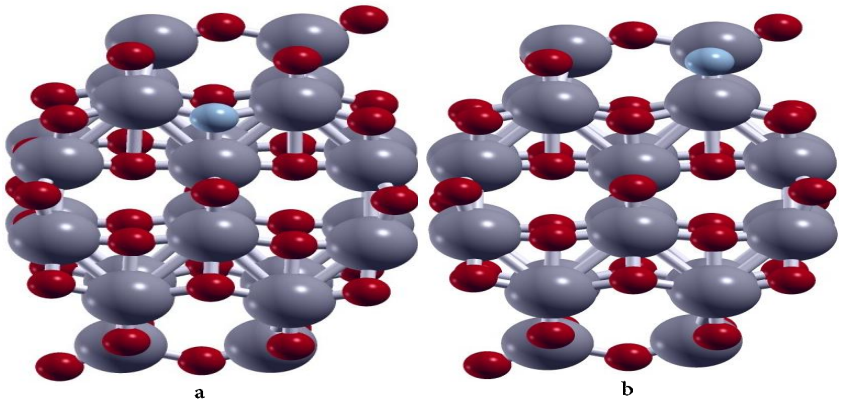


Fig. 2. Representation of the optimized N-doped TiO_2 anatase nanoparticles; (a): OC-substituted nanoparticle. (b): OT-substituted one.

examined on different possible configurations. Optimized structure of IMMUCILLIN-A drug was represented in Figure 3. For All configurations, the oxygen atom of IMMUCILLIN-A is preferentially adsorbed on the fivefold coordinated titanium site of TiO_2 nanoparticle. These configurations contain IMMUCILLIN-A drugs adsorbed on the N-doped, 2N-doped and undoped nanoparticles. Figure 3 also represents the optimized geometry configurations of IMMUCILLIN-A drugs adsorbed on the TiO_2 nanoparticles. Each complex in this figure differs in the substituted oxygen atom of TiO_2 nanoparticle from the others. The most stable adsorption configurations were considered in this work. Configuration A shows the relative orientation of IMMUCILLIN-A molecule on the OC-substituted TiO_2 nanoparticle, whereas configuration B represents the orientation of the drug towards the OT-substituted nanoparticle. The interaction of IMMUCILLIN-A with 2N-doped nanoparticle was displayed in configuration C. Figure 3 also contains one configuration for the IMMUCILLIN-A drug adsorbed on the undoped nanoparticle. The optimized values of some bond lengths before and after the adsorption on the nanoparticle are listed in Table 1. These bond lengths include Ti-O bond of TiO_2 nanoparticle, nearest C-O bond of IMMUCILLIN-A molecule and the newly-formed Ti-O bond between the titanium atom of nanoparticle and oxygen atom of IMMUCILLIN-A. It was found that the Ti-O bond of nanoparticle and C-O bond of IMMUCILLIN-A molecule are elongated after the adsorption process. These elongations in the bond lengths are most likely due to the transfer of electronic density from Ti-O bond of TiO_2 and C-O bond of the adsorbed molecule to the newly formed Ti-O bond between the IMMUCILLIN-A and TiO_2 nanoparticle. Thus, the C-O bond of the IMMUCILLIN-A molecule was stretched and weakened after the adsorption. The smaller the bond formed between the oxygen atom of IMMUCILLIN-A and the fivefold coordinated titanium atom of nanoparticle (Ti-OIMMUCILLIN-A), the stronger the interaction of IMMUCILLIN-A drugs with TiO_2 nanoparticles.

Adsorption Energies

The adsorption of IMMUCILLIN-A drug on the fivefold coordinated titanium atoms of TiO_2 nanoparticles was found to be the most stable adsorption configuration, from the energy point of view. The adsorption energies for IMMUCILLIN-A molecule adsorbed on the undoped and N-doped TiO_2 anatase nanoparticles were listed in Table 2.

Table 1. Bond lengths (in Å) for IMMUCILLIN-A drug adsorbed on the considered TiO_2 anatase nanoparticles.

Complex	Ti-O(before)	Ti-O(after)	Ti-N(before)	Ti-N(after)	C-O(before)	C-O(after)	Ti-O $_{IMMUCILLIN-A}$
A	1.73	1.75	---	---	1.42	1.47	2.47
B	---	---	1.73	1.78	1.42	1.49	2.36
C	---	---	1.73	1.81	1.42	1.50	2.11
D	1.73	1.75	---	---	1.42	1.50	2.26

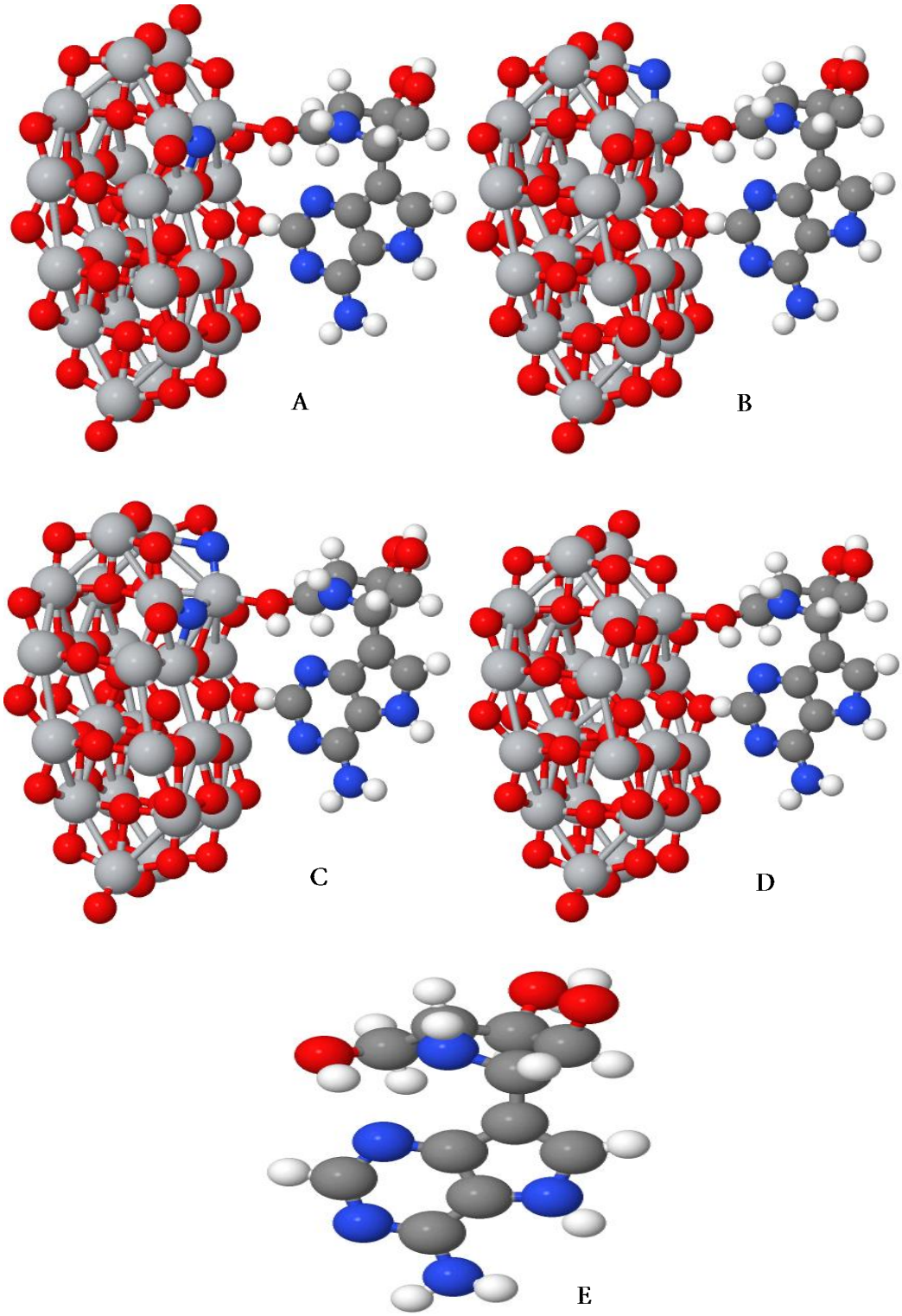


Fig. 3. Optimized geometry configurations of IMMUCILLIN-A drugs adsorbed on the undoped and N-doped TiO_2 anatase nanoparticles. Colours represent atoms accordingly, Ti in grey, O in red, N in blue and H in white. (A): drug adsorbed on the OC-substituted nanoparticle; (B): drug adsorbed on the OT-substituted nanoparticle; (C): drug adsorbed on the OC, T-substituted nanoparticle (2N-doped); (D): drug adsorbed on the undoped nanoparticle; (E): IMMUCILLIN-A drug.

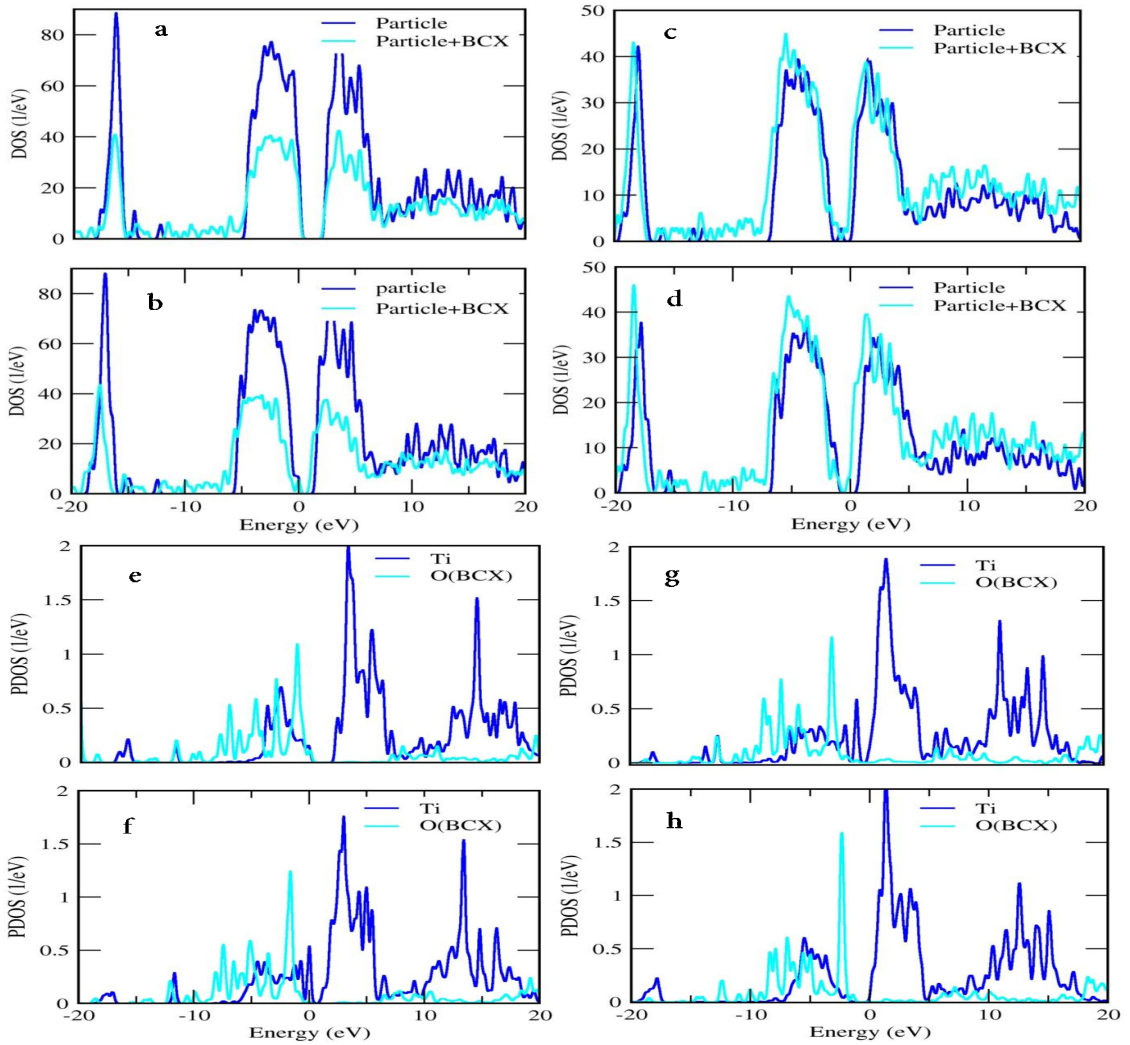


Fig. 4. Total and projected density of states for the considered systems consisting of the IMMUCILLIN-A molecule adsorbed on the N-doped TiO_2 anatase nanoparticles in before and after the adsorption process, (a, e) Configuration A; (b, f) Configuration B; (c, g) Configuration C; (d, h) Configuration D.

These results indicate that the interaction of IMMUCILLIN-A molecule with the N-doped nanoparticles is more favorable in energy than the interaction with the undoped ones. N-doped nanoparticles have higher adsorption ability than the undoped ones and can be effectively utilized as nanocarriers for the IMMUCILLIN-A drugs. The reason can be easily checked using the data provided in Table 2, representing that the N-doped nanoparticles (configurations A, B and C) have higher (more negative) adsorption energy than the undoped ones (configuration D). The adsorption energy of OC-substituted nanoparticle (configuration A) is higher than that of OT-substituted one (configuration B), indicating that the OC-substituted nanoparticle can interact with IMMUCILLIN-A drugs more

Table 2. Adsorption energies (in eV) and charge transfers based on Mulliken charges (in |e|) for IMMUCILLIN-A drug adsorbed on the considered TiO_2 anatase nanoparticles.

Complex	E_{ads}	ΔQ
A	-4.80	-0.84
B	-4.03	-0.53
C	-4.84	-0.86
D	-1.32	-0.34

strongly. On the other hand, the adsorption on the 2N-doped nanoparticle (configuration C) is more energetically favorable than the adsorption on the N-doped one, implying that the 2N-doped nanoparticle reacts with IMMUCILLIN-A drug more efficiently. It reveals a dominant effect of nitrogen doping during the adsorption process. The higher adsorption energy of configuration C in comparison with the other configurations is in reasonable accordance with the lowest distance of IMMUCILLIN-A with respect to the nanoparticle (see Table 1). The more negative the adsorption energy, the higher tendency for adsorption, and consequently stronger adsorption. The obtained results show that the nitrogen doping strengthens the interaction of IMMUCILLIN-A with TiO_2 anatase nanoparticles.

Electronic structures

Total density of states (TDOSs) for bare TiO_2 nanoparticles and the complex systems composed of IMMUCILLIN-A and N-doped TiO_2 particles are shown in Figure 6. Panels (a-d) display the TDOSs for configurations A-D, respectively. The differences include some small peaks at the energy values ranging from -8 eV to -12 eV. The comparison of the TDOSs of studied systems before and after the adsorption process show that the differences between DOS of bare nanoparticles and complex systems are increased by the adsorption of IMMUCILLIN-A. This figure indicates an appearance of small peaks in the DOS of N-doped particles and changes in the energies of the states to the lower values. The appearance of new peaks in the DOS spectra is due to the doping of nitrogen

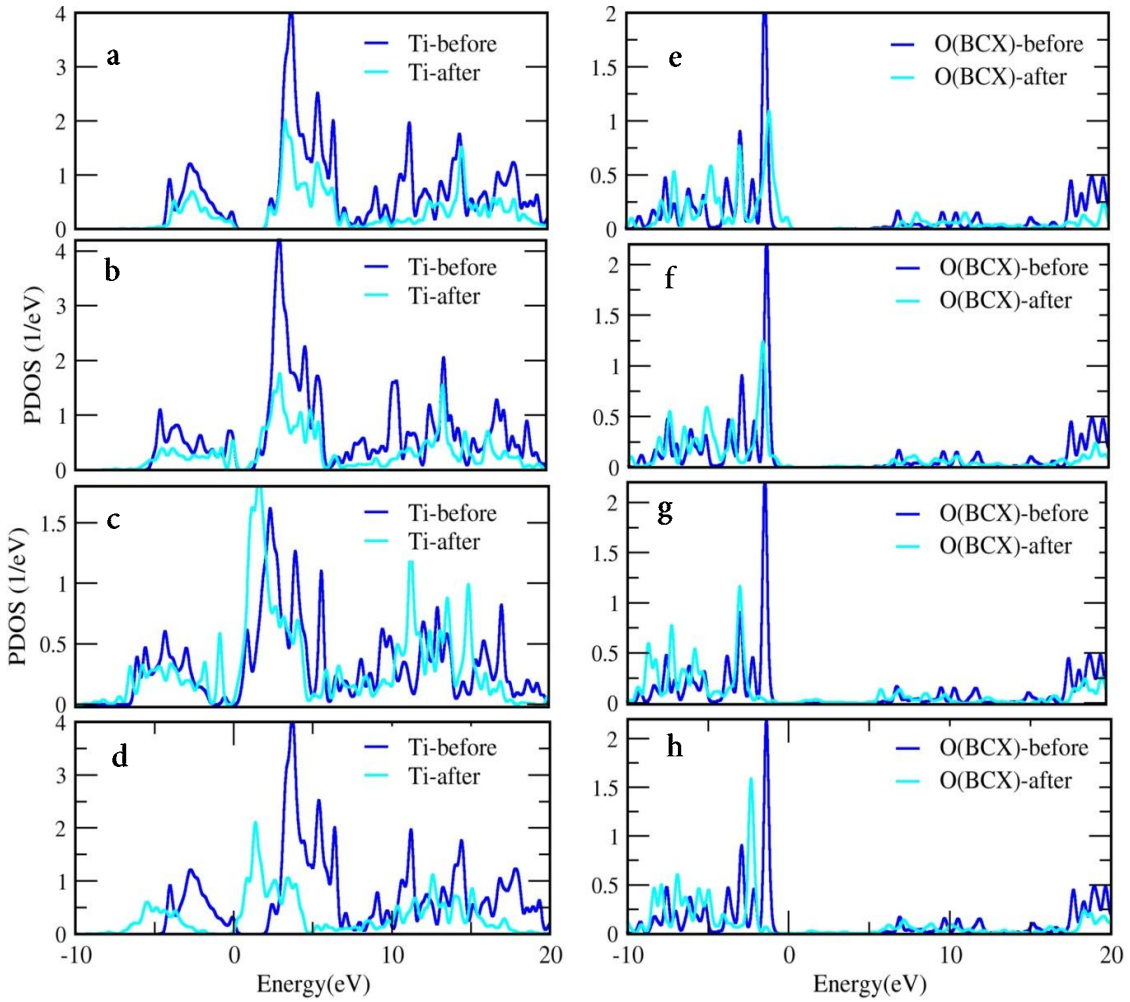


Fig. 5. PDOS for the adsorption of IMMUCILLIN-A molecule on the N-doped nanoparticles before and after the adsorption process, (a, e) Configuration A; (b, f) Configuration B; (c, g) Configuration C; (d, h) Configuration D

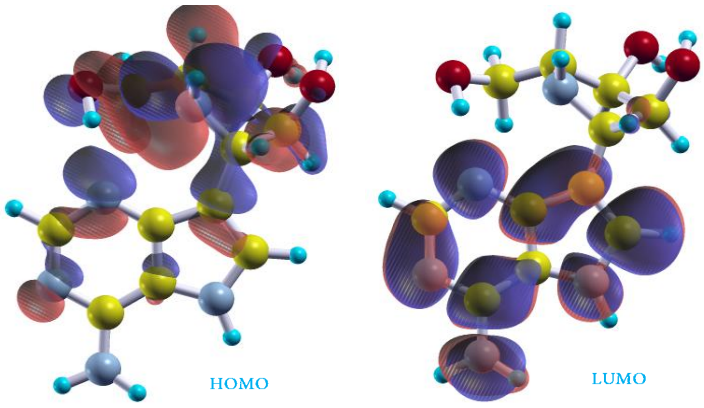


Fig. 6. The isosurfaces of HOMO (left) and LUMO (right) molecular orbitals of bare IMMUCILLIN-A molecule, where |0.02| was used as an isovalue of the molecular orbital.

impurity and the adsorption of IMMUCILLIN-A drug on the considered nanoparticles. Therefore, these variations in energies of the DOS spectra would affect the electronic transport properties of the TiO_2 nanoparticles, thus being a helpful feature for sensing of IMMUCILLIN-A by TiO_2 nanoparticles. The projected density of states for oxygen atom of IMMUCILLIN-A and fivefold coordinated titanium atom of TiO_2 are shown in Figure 4. The large overlaps between the PDOSs of oxygen and titanium atoms reveal that the titanium atom of nanoparticle and oxygen atom of IMMUCILLIN-A form a chemical bond after the adsorption process. It suggests that the IMMUCILLIN-A molecule chemisorbs on the TiO_2 nanoparticle. Figure 5 presents the titanium and oxygen projected DOSs before and after the adsorption process. A closer inspection shows a negligible discrepancy between the PDOS spectra, and the biggest difference is the creation of some peaks in the DOSs of particles after the adsorption process. The HOMO and LUMO molecular orbitals for bare IMMUCILLIN-A molecule are shown in Figure 6. Figure 7 displays the molecular orbitals for TiO_2+IMMUCILLIN-A complexes. This Figure represents that the LUMOs are dominant at the TiO_2 nanoparticles, whereas the electronic densities in HOMOs seem to be distributed over the IMMUCILLIN-A drugs. In order to fully describe the charge transfer between the IMMUCILLIN-A and TiO_2 nanoparticle, the Mulliken population analysis was conducted in this work. For complex A, Mulliken charge analysis reveals a charge transfer of about -0.84 |e| (e, the electron charge) from the IMMUCILLIN-A drug to the TiO_2 nanoparticle, implying that TiO_2 acts as an electron acceptor. This charge transfer is expected to make variations on the conductivity of the system. The charge transfer provides a useful insight to help in development of efficient nanobiosensors and nanocarriers for IMMUCILLIN-A drugs.

CONCLUSIONS

The adsorption behaviors and geometry configurations of IMMUCILLIN-A on the fivefold coordinated titanium atoms of undoped and N-doped TiO_2 anatase nanoparticles were investigated using the DFT calculations. The results indicate that the interaction of IMMUCILLIN-A with TiO_2 nanoparticles gives rise to an increase in the Ti-O bond of TiO_2, as well as C-O bond of IMMUCILLIN-A, thus making the interaction of IMMUCILLIN-A on the TiO_2 nanoparticle stronger. Adsorption energy analysis shows that the N-doped nanoparticles have a higher efficiency to interact with IMMUCILLIN-A molecule, compared to the pristine ones. The density of states for pristine and N-doped TiO_2 were also presented before and after adsorption and the effect of adsorption of IMMUCILLIN-A on these properties were discussed in detail. The results suggest that N-doped TiO_2 can be used for sensing of IMMUCILLIN-A drug. The interaction of IMMUCILLIN-A over the N-doped TiO_2 nanoparticles is energetically more favorable than the interaction over the undoped ones.

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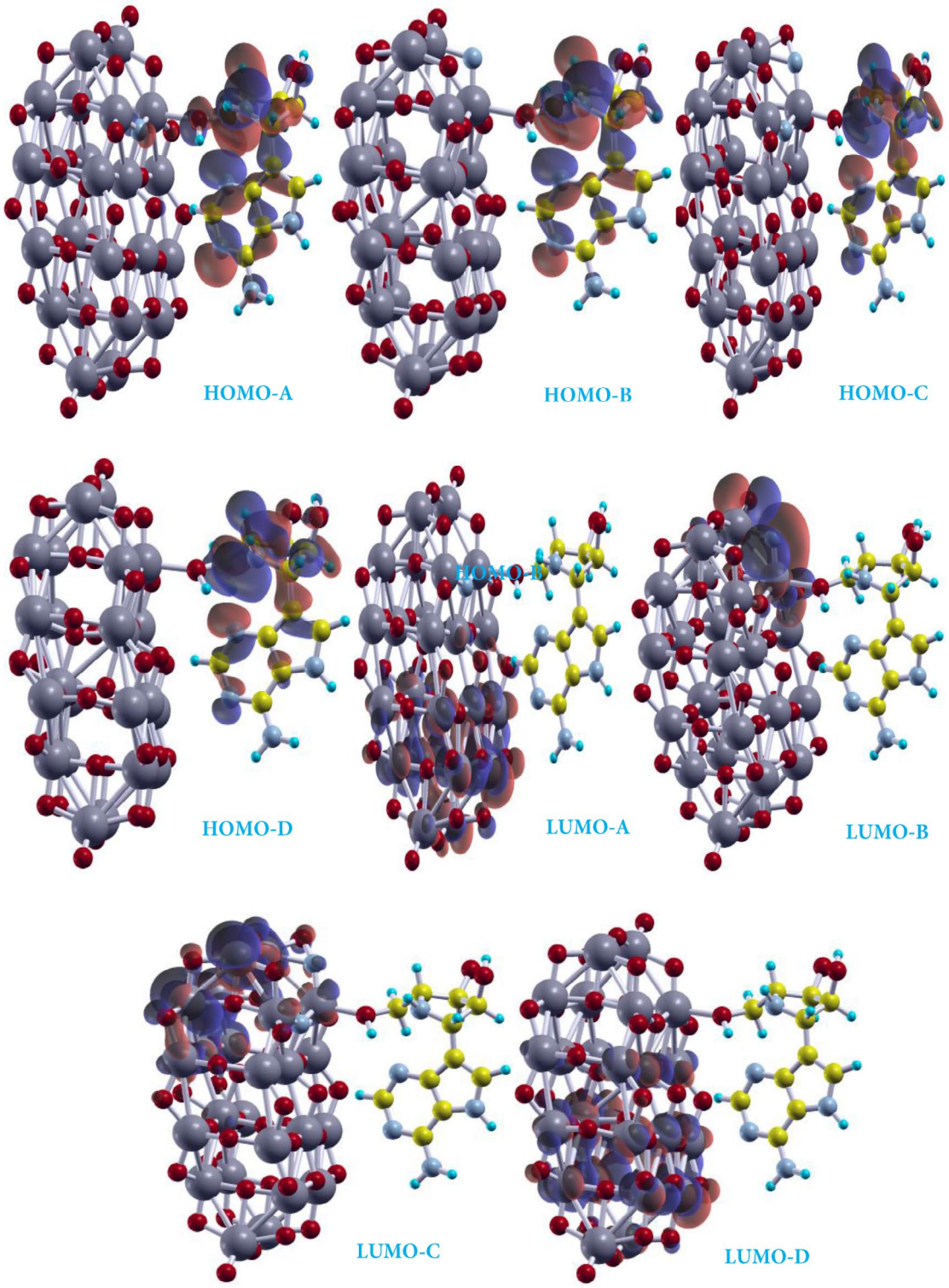

Figure 7. The isosurfaces of HOMO and LUMO molecular orbitals of TiO2-IMMUCILLIN-A adsorption configurations for complexes A-D. Labels A-D refer to the adsorption configurations shown in Figure 3 and HOMO and LUMO mean the highest occupied and the lowest unoccupied molecular orbitals.

CONFLICT OF INTEREST

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

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