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Theoretical study of the interaction of harmful heroin molecule with N-doped TiO_2 anatase nanoparticles

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ABSTRACT: Density functional theory calculations were carried out to study the interaction of heroin molecule with pristine and N-dopedTiO_2 anatase nanoparticles. The oxygen atom of heroin molecule was found to be the binding site on the heroin molecule. In contrast, the binding site of TiO_2 nanoparticle was positioned over the fivefold coordinated titanium atoms. The results showed that the adsorption energies of heroin on the considered nanoparticles followed the order N-doped TiO_2> pristine (undoped) TiO_2. The N-doped TiO_2 nanoparticle was strongly favored with high sensitivity to heroin detection. Thus, the adsorption of heroin on the N-doped nanoparticle is more favorable in energy than the adsorption on the pristine one.The charge transfers were predicted based on Mulliken population analysis. The electron transfer from heroin to the TiO_2 particles was in the order N-doped TiO_2> pristine (undoped) TiO_2.The significant overlaps in the PDOS spectra of the oxygen atom of heroin and titanium atom of TiO_2 indicate that chemical bond was formed between adsorbate and nanoparticle. After the adsorption process, the electronic density in the highest occupied molecular orbitals was strongly distributed over the adsorbed heroin molecule.These processes eventually lead to the adsorption of heroin on the TiO_2 particles.

Keywords: *Density of states; Density functional theory; Electronic properties; Heroin; Molecular orbital; TiO_2 Nanoparticle*

INTRODUCTION

As an important semiconductor photocatalyst, titania (TiO_2) has some obvious advantages in numerous applications due to its non-toxicity, low price, chemical stability, and high catalytic efficiency (Linsebigler,*et al.*, 1995, Zhang and Lindan, 2003, Erdogan,*et al.*, 2010, Hummatov,*et al.*, 2012). Since TiO_2 has a wide band gap (3.2 eV for anatase polymorph), it can only absorb a small fraction of the solar spectrum energy (ultraviolet region).This leads to a serious restriction of the photocatalytic activity of TiO_2. Thus, efficient strategies would be required to extend the absorption of the incoming solar light to the visible area.Efforts to improve the photocatalytic activity of TiO_2 catalysts to

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cover the range of visible light are quite striking and essential. Some research work is devoted to the application of doping treatments of TiO_2 with metal or non-metal elements. Recently, non-metal-doped TiO_2 was found to be most operative to extend the optical sensitivity of TiO_2 to the visible region(Shah,*et al.*, 2002, Burda,*et al.*, 2003). Doping of TiO_2 can introduce energy levels in the bandgap, effectively amending its band energy to absorb light in the visible region.

Asahi *et al.* (Asahi,*et al.*, 2001) showed that TiO_2-xNx, in which nitrogen was substituted into the oxygen vacancy by sputtering methods, reveals improved photoactivity in the visible spectral range. It has been widely studied for many years as a model metal oxide with a wide range of applications in photo-catalysis (Diebold, 2003), gas sensor devices, heterogeneous catalysis (Han *et al.*, 2009) and photovoltaic cells (Fujishima and Honda, 1972). There are some experimental and theoretical studies with regard to the adsorption processes and surface properties of TiO_2, describing its significant importance in environmental and surface reactions (Onal, *et al.*, 2009, Shi,*et al.*, 2011, Lei,*et al.*, 2010, Beltran, *et al.*, 2008, Tang and Cao, 2011).

In the theoretical studies by Liu *et al.*(Liu, *et al.*, 2012) it was reported that the N-doped TiO_2 anatase nanoparticles can interact with toxic NO molecule more efficiently.In the study by Liu *et al.* (Liu, *et al.*, 2013) the increased reactivity of N-doped TiO_2 nanoparticles with CO molecules have been addressed. By using periodic Hartree-Fock method, Fahmi*et al.* (Fahmi and Minot, 1994) showed that water can adsorb on the titanium atom and then dissociate to give hydroxyl groups. Nair (Nair, 2004) estimated molecular and dissociative water adsorption energy values on anatase TiO_2 (001) using MSINDO-CCM (semiempirical molecular orbital method–cyclic cluster model) calculations.Moreover, metal and non-metal doping of TiO_2 particles can lead to some improvements on the sensing capability and adsorption ability (Abbasi, *et al.*, 2016, Liu, *et al.*, 2012, Breedon, *et al.*, 2010).The improvements of both adsorption capability and photocatalytic activity caused by non-metal doping and other factors were investigated in detail (Livraghi, *et al.*, 2006, Rumaiz, *et al.*, 2009, Zhao and Liu, 2008). However, the effects of doping treatment on the optical response and band gap of TiO_2 have been explained in some works (Gao, *et al.*, 2009, Zhao, *et al.*, 2011, Landman, *et al.*, 2012). DFT calculations on molecules are based on the Kohn–Sham approach, two robust and efficient Hohenberg and Kohn theorems are provided in order to describe the DFT formalism. The first Hohenberg–Kohn theorem states that all the properties of a molecule in a ground electronic state are calculated using the ground state electron density function, , that is, using we can calculate any ground state property related to the system under study, e.g. the energy.

Heroin is a highly addictive drug, being widely used by millions of addicts around the world. 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. Heroin causes detrimental effects on the brain, heart and immune system. Heroin can increase feelings of happiness by changing activity in the limbic system. When the brain experiences such a pleasure feeling, heroin is responsible for creating physical addiction which is typical for heroin addicts. In this paper, we have investigated the interaction of heroin molecule with undoped and N-doped TiO_2 anatase nanoparticles. The structural and electronic properties of the adsorption configurations were studied in view of the bond lengths, density of states, molecular orbitals and Mulliken charge analysis. The aim of this work is to investigate the effect of nitrogen doping on the electronic structure of heroin adsorbed TiO_2 particles to find suitable sensor material for the adsorption of harmful heroin molecules.

COMPUTATIONAL DETAILS AND MODELS

DFT calculations (Hohenberg and Kohn, 1964, Kohn and Sham, 1965) were carried outusing the Open source Package for Material eXplorer (OPENMX3.8) (Ozaki, *et al.*, 2013). The considered cutoff energy was set to the value of 150 Ry in our calculations. The exchange-correlation energy functional was treated using the generalized gradient approximation (GGA) parameterized by Perdew–Burke–Ernzerhof (PBE) (Perdew and Zunger, 1981).The pseudo atomic orbitals were utilized as basis sets in the geometry opti-

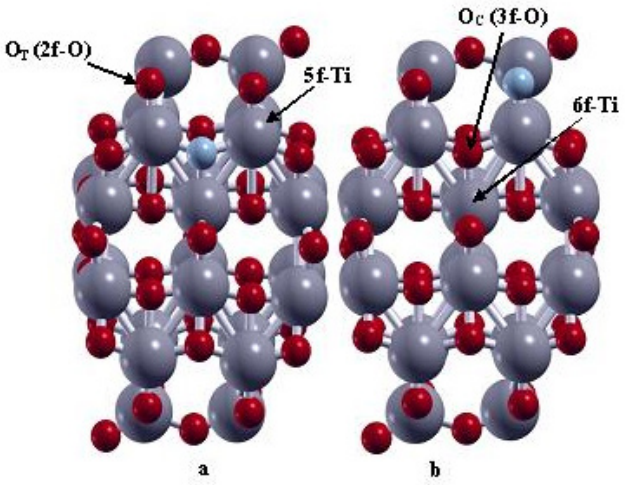


Fig. 1. Optimized N-doped TiO_2 anatase nanoparticles constructed using the 3×2×1 unit cells, colors represent atoms accordingly: Ti in gray, O in red and N in blue.

mizations. To fully describe the effects of long range van der Waals (vdW) interactions, we have employed DFT-D2 method, which was developed by Grimme*et al.* (Grimme, 2006). 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, XCrys Den (Koklj, 2003), was employed for displaying molecular orbital isosurfaces. The Gaussian broadening method for evaluating electronic DOS was used. When heroin interacts with TiO_2 nanoparticle, the adsorption energy was calculated according to the following equation:

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

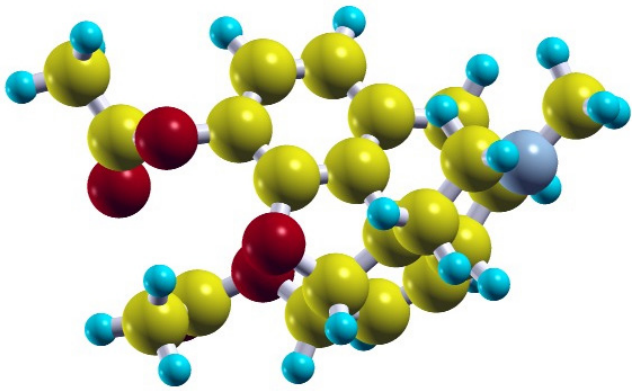


Fig. 2. Representation of the optimized structure of heroin molecule, colors represent atoms accordingly: C in yellow, N in blue, O in red and H in cyan.

where $E_{(adsorbent + adsorbate)}$, E adsorbent and E adsorbateare the energies of the complex system, the free TiO_2 nanoparticle without any adsorbed heroin molecule and the isolated heroin molecule, respectively. The charge transfer between heroin molecule and TiO_2 nanoparticle was estimated based on the Mulliken charge analysis.The considered unit cell of TiO_2 was reported by Wyckoff (Wyckoff, 1963) and taken from "American Mineralogists Database" webpage (Downs, 2014).The size of the simulation box considered in our calculations is 20×15×30 $Å^3$, which is much larger than the size of the particle. The vacuum space was set at 11.5 Å, which is necessary to avoid the interactions between the neighbor particles. 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 Fig.1 with fivefold coordinated and sixfold coordinated titanium atoms sketched by 5f-Ti and 6f-Ti, respectively (Wu, *et al.*, 2013). The schematic structure of heroin molecule is represented in Fig.2.

RESULTS AND DISCUSSION

The interaction of heroin with N-doped TiO_2 nanoparticles

Various conformations were simulated for the pristine and N-doped TiO_2 nanoparticle + heroin, where the heroin molecule is place perpendicular to the TiO_2 surface. Three possible adsorption orientations of heroin molecule with respect to the TiO_2 nanoparticle were considered. Important to note is that the oxygen atom in the heroin 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 heroin molecule adsorbed on the fivefold coordinated titanium site of TiO_2 were studied here. Optimized geometry configurations of heroin molecule on the undoped and N-doped nanoparticles were displayed in Figs. 3 and 4.

These configurations were marked by labels A-C in these Figures. In all cases, the oxygen atom of heroin molecule was found to be the binding site, while on

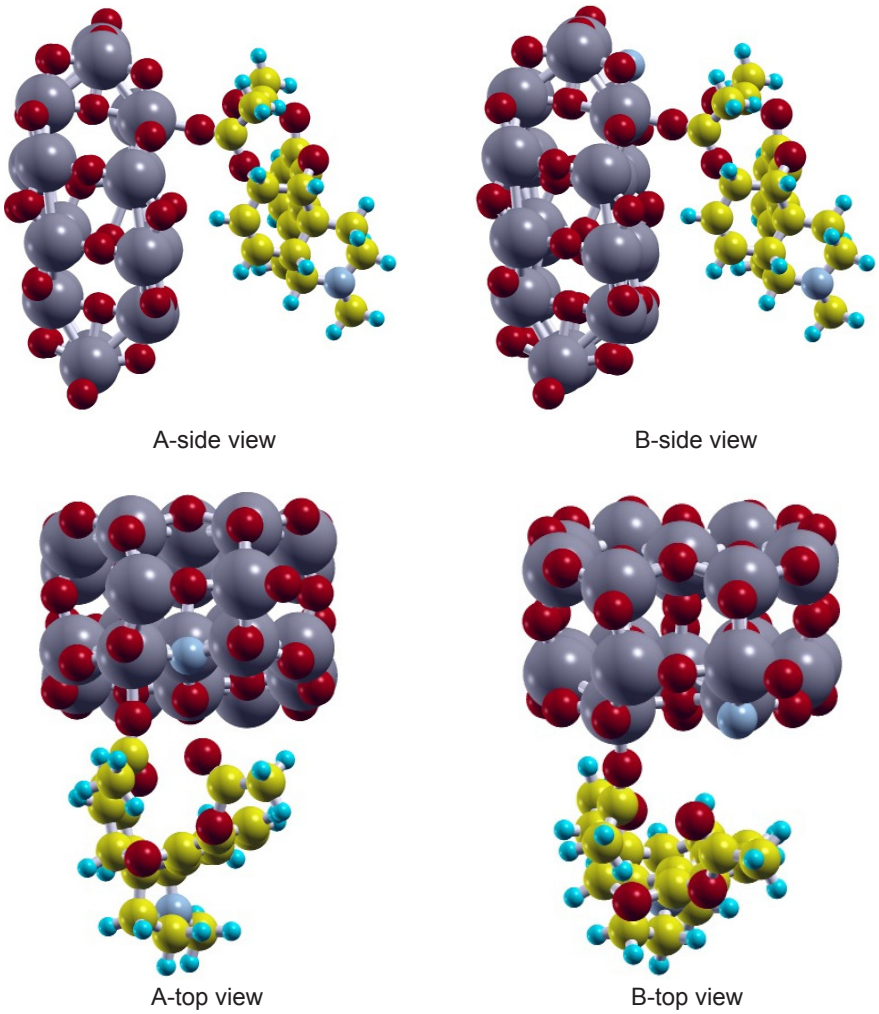


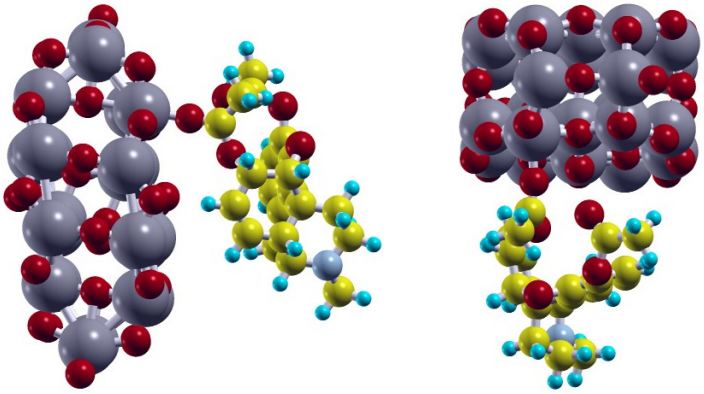
Fig. 3. Optimized geometry configurations of heroin adsorbed N-doped TiO_2 anatase nanoparticles. The oxygen atom of heroin molecule was bound to the fivefold coordinated titanium atom.

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 heroin molecule were listed in Table 1.

For brevity, we have only reported the newly formed bonds between the molecule and nanoparticle. The smaller the distance heroin was positioned towards the TiO_2 nanoparticle after the adsorption process, the stronger the adsorption of heroin on the TiO_2 nanoparticle.The comparison of the results presented in Table 1 indicates that the smallest distance between the oxygen atom of heroin 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 heroin interaction with N-doped (O_C-substituted nanoparticle). In configuration C, heroin molecule interacts with pristine nanoparticle, pro-

Table 1.Bond lengths (in Å), adsorption energies (in eV) and Mulliken charge values for heroin 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



C-side view C-top view

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

viding the lowest distance between the nanoparticle and heroin molecule. By the comparison of the results, we found that the interaction of oxygen site of heroin molecule with fivefold coordinated titanium site of TiO_2 was strongly favored. In order to further describe the behavior of the heroin molecule adsorbed on the

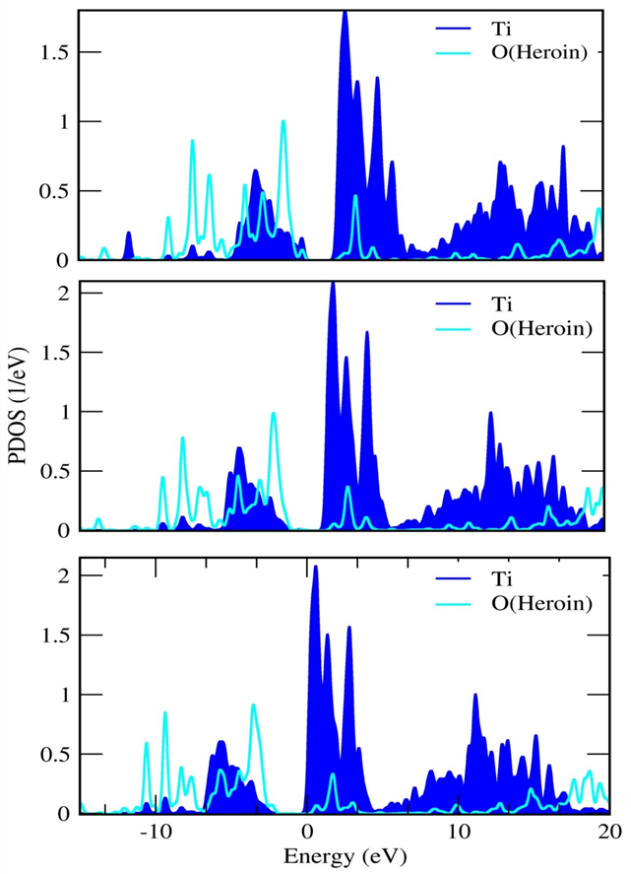


Fig. 5. Projected density of states for heroin molecule adsorbed on the TiO_2 anatase nanoparticles, a: configuration A; b: configuration B; c: configuration C.

TiO_2 nanoparticle, we calculated the adsorption energies of the most stable configurations (see Table 1).

The results of this Table indicate that heroin adsorption on the N-doped TiO_2 nanoparticle is more energetically favorable than the adsorption on the pristine one. Therefore, the N-doped nanoparticle strongly reacts with heroin molecule. It is worth noting that the large adsorption energy gives rise to a strong binding between the TiO_2 and heroin molecule. As can be seen from Table 1, the highest adsorption energy occurs in configuration A, representing that the interaction of oxygen atom of heroin 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 heroin molecule. Moreover, the adsorption of heroin 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 heroin 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 heroin on the considered nanoparticles.

Electronic structures

The projected density of states for heroin molecule adsorbed on the TiO_2 anatase nanoparticles were

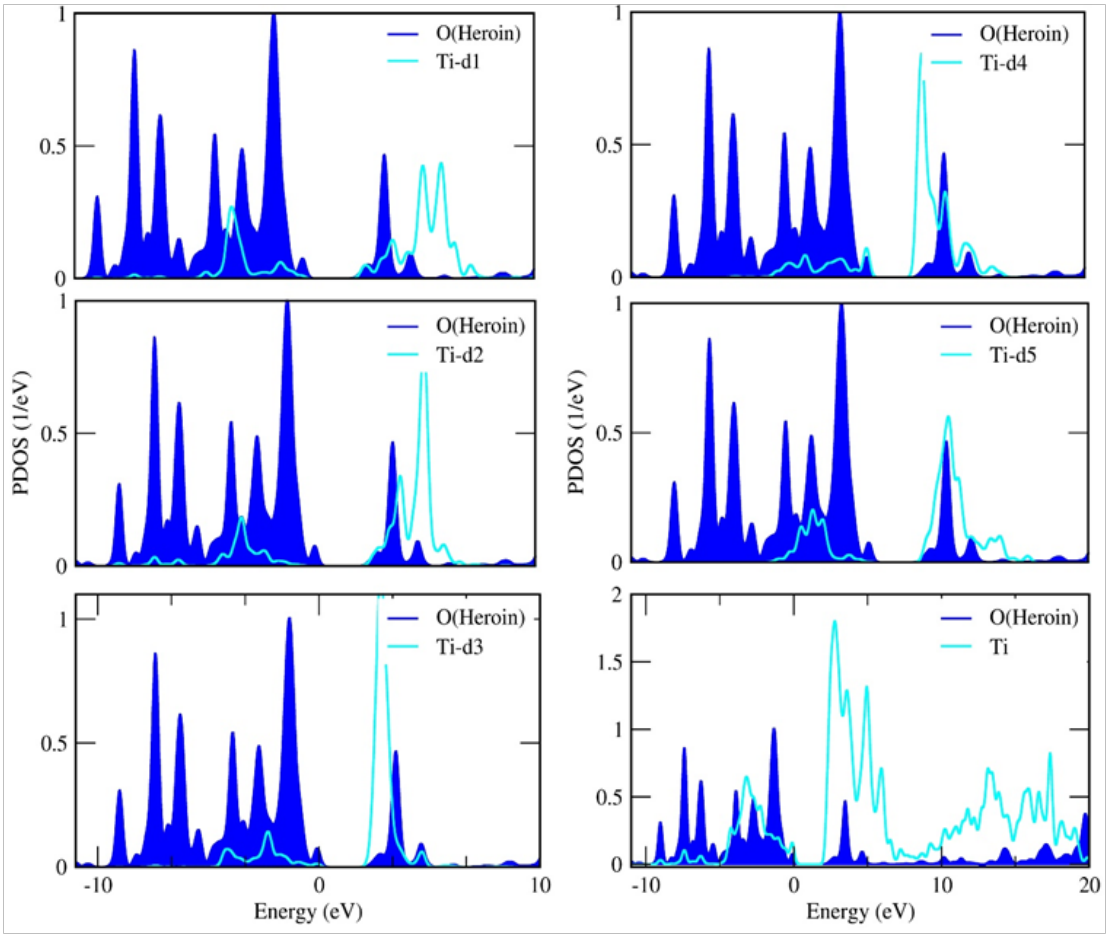


Fig. 6.Projected density of states for the oxygen atom of the heroin, titanium atom and different d orbitals of the titanium (configuration A).

displayed in Fig.5. Panels (a-c) show the PDOSs for configurations A-C, respectively. The substantial overlaps between the PDOSs of the oxygen atom of heroin molecule and titanium atom of TiO_2 represent the formation of chemical Ti-O bond between them. This formation of chemical bond at the interface region confirms that heroin molecule was chemisorbed 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 heroin molecule was strongly adsorbed on the N-doped nanoparticle, compared to the undoped one. The PDOSs of the oxygen atom of heroin molecule, titanium atomand five d orbitals of the titanium were shown in Figs.6 and 7 for configurations A and B, respectively.

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

To better describe the electronic density distribution over the heroin adsorbed TiO_2 complexes, we calculated the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) for the considered systems. Fig. 8 displays the HOMO and LUMO diagrams for isolated heroin molecule.

The electronic density in the HOMO exhibit dominant distribution on the whole heroin molecule. Figs. 9 and 10 show the isosurfaces of HOMOs and LUMOsfor heroin molecule adsorbed on the TiO_2 anatase nanoparticles.

Fascinatingly, the HOMOs of the complex systems were dominant at the whole heroin molecule, whereas the electronic density in the LUMOs seem to be distributed over the TiO_2 nanoparticle. Thus, the electronic structure of the TiO_2 nanoparticle was influenced

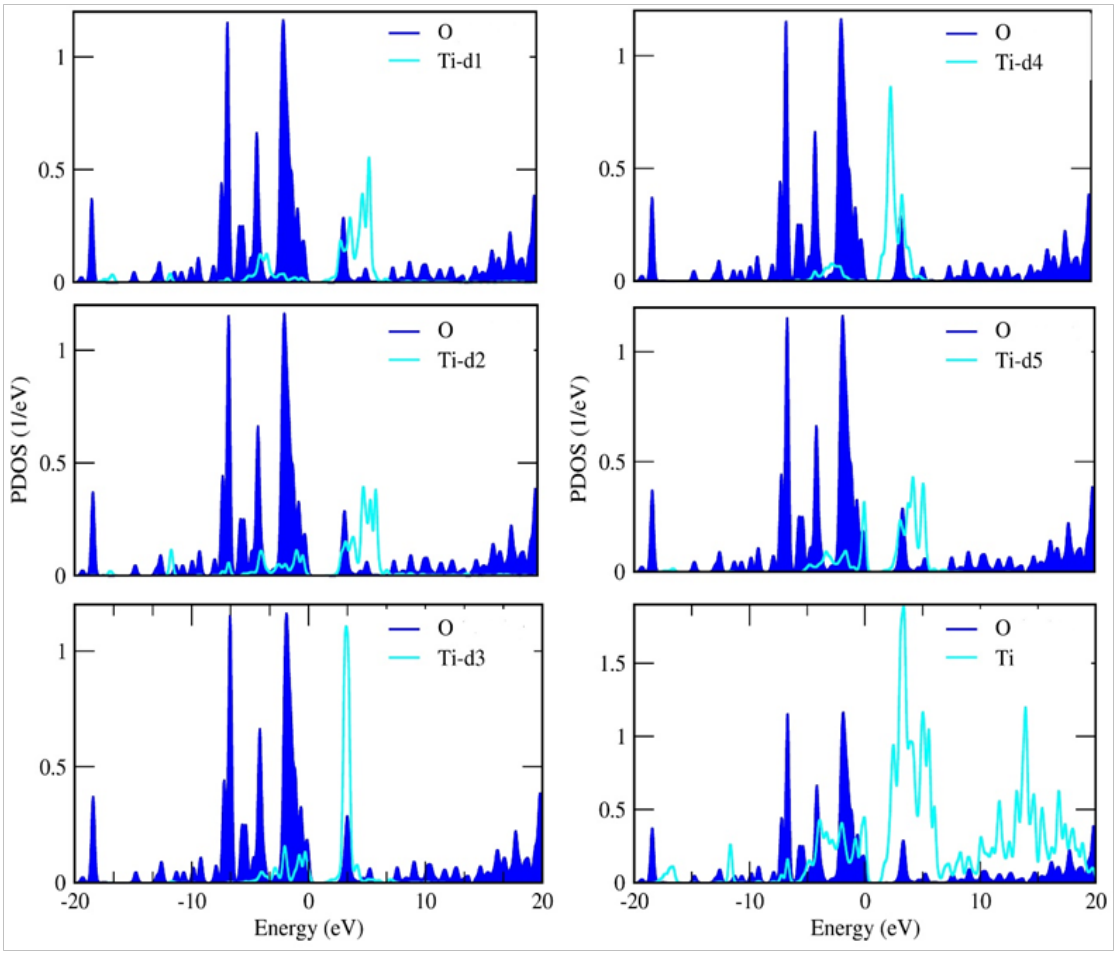
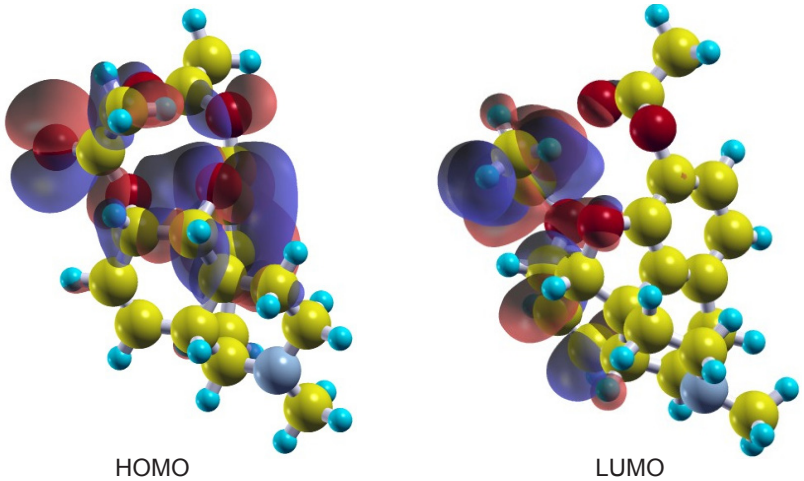


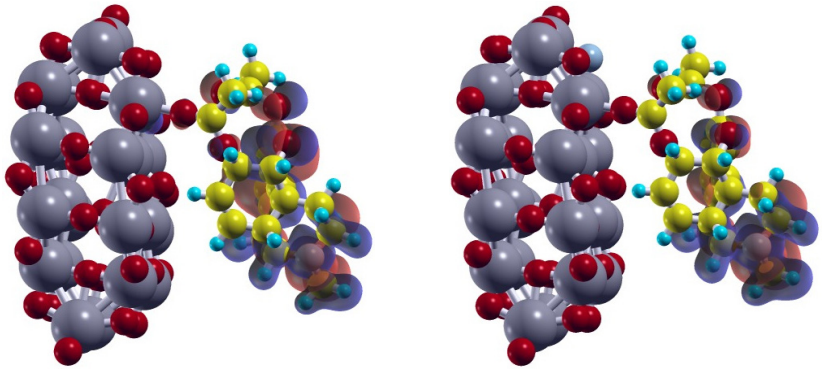
Fig. 7. Projected density of states for the oxygen atom of the heroin, titanium atom and different d orbitals of the titanium (configuration B).

by the adsorption of heroin molecule. In the HOMO isosurfaces of the adsorption systems, we can see a main contribution from the adsorbed heroin molecule rather than TiO_2 nanoparticle, implying that heroin adsorption has considerable effect on the distribution of electronic densities. We have also estimated the values of charge transfer between the heroin molecule and TiO_2 nanoparticle.

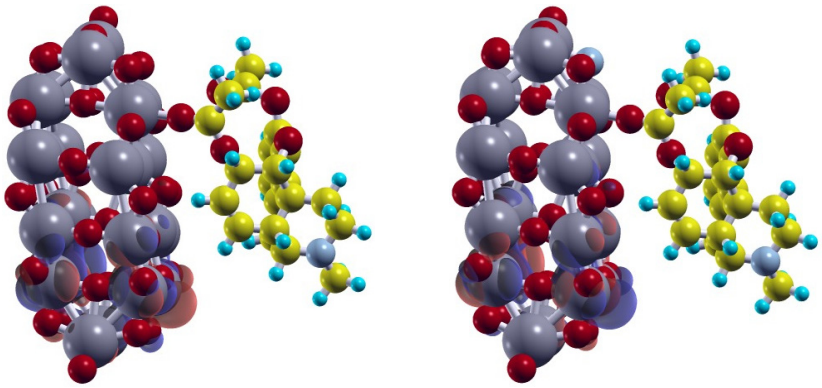


HOMO LUMO

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



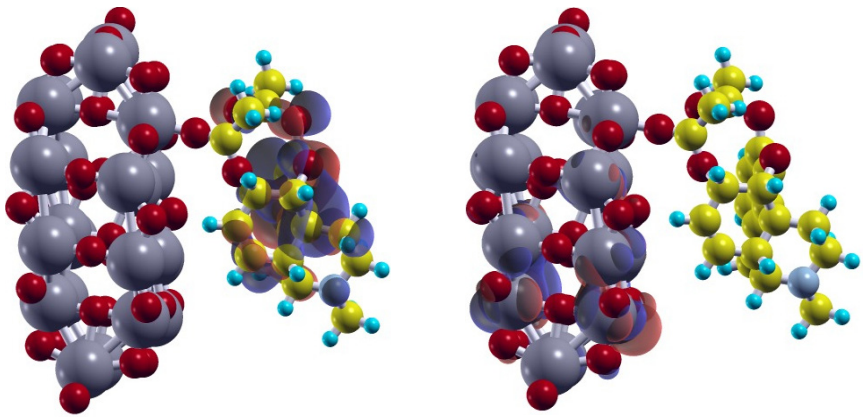
HOMO-A HOMO-B



LUMO-A LUMO-B

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

The obtained results were listed in Table 1. As a matter of convenience, we have discussed the charge exchange for one configuration only. For adsorption type A, we can see a remarkable charge transfer of about -0.612 |e| (e, the electron charge) from heroin molecule to the TiO_2 nanoparticle, representing that heroin acts as a charge donor. The highest value of charge transfer occurs in configuration A, whereas the lowest charge transfer belongs to configuration C, which is in reasonable agreement with higher adsorption energy of configuration A in comparison with configuration C.



HOMO-C LUMO-C

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

CONCLUSIONS

The adsorption ofheroinmolecule on the pristine and N-doped TiO_2 anatase nanoparticles were investigated by use of DFT calculations. The perpendicular adsorption configuration of heroin on the TiO_2 nanoparticle were considered. The oxygen atom of the heroin molecule was found to be strongly coordinated to the five-fold coordinated titanium atoms. The interaction of heroin molecule with N-doped TiO_2 is more energetically favorable than the interaction with undoped ones, representing that the N-doped nanoparticle strongly reacts with heroin molecule. We have analyzed the density of states, Mulliken population and molecular orbitals for the adsorbed systems.The projected density of states of the oxygen atom of heroin molecule and titanium atom of TiO_2 represent substantial overlaps between these atoms and consequently formation of chemical Ti-O bonds. After the adsorption, the HOMOs of the whole complex system were mainly distributed on the adsorbed heroin molecule. Thus the sensitive electronic structure, as well as the revealed high activity to heroin adsorption suggest the potential of TiO_2 nanoparticle for high sensitive detection to heroin molecule. Further Mulliken charge analysis quantitatively presents the donation of electrons from the adsorbed heroin molecule to the TiO_2 particle.

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