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ORIGINAL RESEARCH PAPER

Exploration of the adsorption of caffeine molecule on the TiO_2 nanostructures: A density functional theory study

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ABSTRACT

The first principles were calculated to study the adsorption behaviors of caffeine molecules on the pristine and N-doped TiO_2 anatase nanoparticles. Both oxygen and nitrogen in the caffeine molecule can react strongly with TiO_2 nanoparticle. Thus, the binding sites were located on the oxygen or nitrogen atom of the caffeine, while the binding site of the TiO_2 nanoparticle occurs on the fivefold coordinated titanium atoms. Counting van der Waals (vdW) interactions showed that adsorption on the N-doped TiO_2 is more favorable in energy than the adsorption on the undoped one that indicates the high sensitivity of N-doped TiO_2 nanoparticles towards caffeine molecules. This condition refers to a dominant effect of nitrogen doping on the adsorption properties of pristine TiO_2. The existence of large overlaps in the PDOS spectra of the oxygen and nitrogen atoms of the caffeine and titanium atom of TiO_2 represent forming Ti-O and Ti-N bonds between them. The results of molecular orbital calculation demonstrate that the HOMOs are strongly localized on the caffeine. Charge analysis based on Mulliken charges reveals a considerable charge transfer from the caffeine to the TiO_2 nanoparticle.

Keywords: *Caffeine; Density Functional Theory; Electronic Properties; Tio2 Nanoparticle*

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INTRODUCTION

Titanium dioxide (TiO_2) is one of the transition metal semiconductors that has been extensively studied. It has outstanding properties, including non-toxicity, chemical stability, abundance and high catalytic efficiency [1-5]. However, pristine TiO_2 can be only activated by ultraviolet light due to its wide bandgap (3 and 3.2 eV for rutile and anatase, respectively), so that it decreases the efficiency of its photocatalytic activity. Doping of TiO_2 can enter energy levels in the bandgap, and efficiently modify its electronic band structure to absorb light in the visible region [6, 7]. Nitrogen doping of TiO_2 improves optical sensitivity and provides conditions for TiO_2 to be responded to the incoming solar light more appropriately.

TiO_2 has been commonly investigated for applications such as photo-catalysis [8], gas sensor devices, heterogeneous catalysis [9] and photovoltaic cells [10]. Over the past few years, researchers paid so much attention to the fundamental principles and crucial practical features of TiO_2 [11-18]. Many researchers from different disciplines have focused on the study of the outstanding properties of TiO_2 nanoparticles. For instance, Liu et al. suggested that nitrogen doping of TiO_2 strengthens the adsorption of toxic gas phase NO molecules by anatase nanoparticles [14]. Recently, it has been revealed that the N-doped TiO_2 anatase nanoparticles react with CO molecules more efficiently than the undoped ones [19]. Furthermore, substituting of nitrogen atom

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into TiO_2 particles enhances its sensing capability in the whole range of applications [20-25]. In addition, the effects of doping of nitrogen atom on the photo-catalytic activity and energy band gap of TiO_2 have been investigated in detail [26-28]

DFT calculations on molecules are based on the Kohn–Sham approach. Thus, two robust and efficient theorems of Hohenberg and Kohn 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 $\rho_0(x,y,z)$; that is, we can calculate any ground state property related to the system under study (e.g., the energy). This can be represented as:

$$\rightarrow E_0[\rho_0(x,y,z)] \quad (1)$$

This relationship means that E_0 is a functional of $\rho_0(x,y,z)$. Then, the first Hohenberg–Kohn theorem states that any ground state property of a molecule is a functional of the ground state electron density function. The second Hohenberg–Kohn theorem says that any trial electron density function will give an energy higher than (or equal to) the true ground state energy. In DFT calculations, the electronic energy from a trial electron density is defined as the energy of the electrons that move under the potential of the atomic nuclei. We can call this nuclear potential as the "external potential" and designate it by v(r). Therefore, the second Hohenberg–Kohn theorem can be specified by the following equation:

$$E_v[\rho_t] \geq E_0[\rho_0] \quad (2)$$

Caffeine is defined as a drug that can affect people in different ways just like any other substance. Consumers understand how caffeine interacts with their bodies in terms of personal health histories. Caffeine is considered to be the most commonly used psychoactive drug in the world. Coffee, soda, and tea are the most common sources of caffeine in the world. A majority of adults use caffeine in their daily life. Of course, many studies have been conducted on the pros and cons of caffeine. However, little research has been done on the potentially injurious effects of caffeine. The risks of suffering from any of the harmful effects of caffeine can be reduced by doing research about how much it is personally being consumed every day. It is also essential to be informed about any pre-existing medical conditions that may contribute to the caffeine's negative effects. This study explored the interaction of caffeine drug with undoped and N-doped TiO_2 anatase nanoparticles. Thus, various adsorption configurations of the caffeine towards the nanoparticles were provided. Electronic properties of adsorption systems were examined in terms of the density of states, and molecular orbitals. Therefore, the study aims at providing a theory basis on how caffeine drug interacts with biocompatible TiO_2 nanoparticles.

COMPUTATIONAL DETAILS AND MODELS

Computational Methods

The Open source Package for Material explorer (OPENMX3.8) [31] was used to calculate Density Functional Theory (DFT) [29, 30]. The pseudo atomic orbitals were utilized as basis sets in the geometry optimizations. The intended 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) [32]. The study used DFT-D2 method developed by Grimme et al. in order to describe the effects of long range van der Waals (vdW) interactions in detail [33]. The convergence criterion of 1.0 × 10-6 Hartree was used for self-consistent field iterations, the criterion was set to 1.0 × 10-4 Hartree/bohr while to calculate energy. Moreover, the crystalline and molecular structure visualization program, XCrysDen [34] were used to display molecular orbital isosurfaces. The Gaussian broadening method was also employed to evaluate electronic DOS. When caffeine interacts with TiO_2 nanoparticle, the adsorption energy was calculated according to the following equation.

$$E_{ads} = E\,(\text{adsorbent} + \text{drug}) - E\,\text{adsorbent} - E\,\text{drug} \quad (3)$$

where E (adsorbent + drug), E adsorbent and E drug are the energies of the complex system, the free TiO_2 nanoparticle without any adsorbed caffeine molecule and the isolated caffeine molecule, respectively. The charge transfer between caffeine molecule and TiO_2 nanoparticle was estimated based on the Mulliken charge analysis.

Modelling of nanoparticles

TiO_2 anatase nanoparticles were modeled by setting a 3×2×1 supercell of pristine TiO_2 anatase.

The unit cell of TiO_2 under study was reported by Wyckoff [35] and taken from the "American Mineralogists Database" webpage [36]. Dimensions of the simulation box in our calculations is 20×15×30 Å3 that is much larger than the nanoparticle size. A vacuum space of about 11.5 Å was set between neighbor particles to avoid the additional interactions between repeated slabs. Two oxygen atoms of pristine TiO_2 (twofold coordinated and threefold coordinated oxygen atoms) were substituted by nitrogen atoms to prepare N-doped nanoparticles. Twofold coordinated oxygen atom was denoted by 2f-O and the threefold one was denoted by 3f-O (middle oxygen) in Fig. 1. In addition, fivefold coordinated and sixfold coordinated titanium atoms were sketched by 5f-Ti and 6f-Ti, respectively [37]. Fig. 2 depicts the schematic structure of caffeine molecule.

RESULTS AND DISCUSSION

Interaction between caffeine and N-doped TiO_2 nanoparticles

Different conformations were simulated for the pristine and N-doped TiO_2 nanoparticle + caffeine, where the caffeine molecule is placed perpendicular to the TiO_2 surface. Six possible adsorption geometries of caffeine towards the nanoparticle were considered in the study. It should be noted that both oxygen and nitrogen atoms of caffeine molecule strongly interact with the fivefold coordinated titanium atom of TiO_2, and the carbon atom does not contribute to the adsorption any longer. The reaction of active sites of caffeine molecule with the fivefold coordinated titanium sites results in a strong binding between nanoparticle and caffeine molecule. Figs. 3 and 4 show dsorption geometries of caffeine molecule on

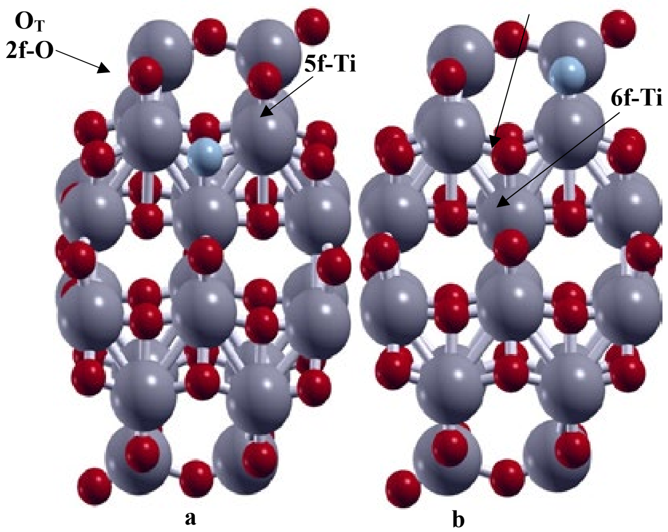

Fig. 1. Optimized N-doped TiO_2 anatase nanoparticles constructed using the 3×2×1 unit cells, colors represent atoms accordingly: Ti in gray, O in red and N in blue.

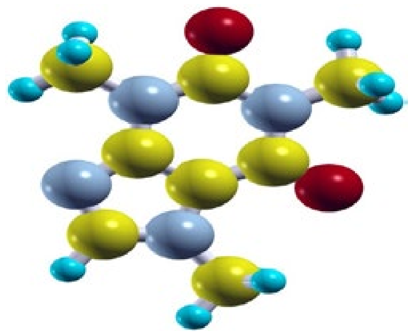

Fig. 2. Representation of the optimized structure of caffein molecule, colors represent atoms accordingly: C in yellow, N in blue, O in red and H in cyan.

the undoped and N-doped TiO_2 nanoparticle, as labeled by adsorption configurations A-F.

Each configuration in the above figures represents that the caffeine molecule was approached to the TiO_2 nanoparticles at different positions. From all configurations, it can be seen that the caffeine molecule was adsorbed either by its nitrogen or oxygen atom to the undercoordinated titanium sites of TiO_2. The nitrogen atom was also substituted into the oxygen vacancy of TiO_2 according to two doping positions. In one doping configuration, a nitrogen atom substitutes an oxygen atom in the OC site of the particle, while the other doping configuration represents the replacement of OT site by nitrogen atom. Table 1 lists the bond lengths for caffeine molecule adsorbed to the TiO_2 nanoparticles. For brevity, we have only reported the newly formed bonds between the drug molecule and nanoparticle. The smaller the bond formed between the nitrogen or oxygen atom of caffeine molecule and the fivefold coordinated titanium atom of TiO_2 nanoparticle (Ti-N, Ti-O), the stronger the interaction between caffeine and TiO_2 anatase nanoparticle.

Further analysis of adsorption energies reveals that the interaction between caffeine molecule and fivefold coordinated titanium site of TiO_2 is strongly favored in terms of energy. Table 1

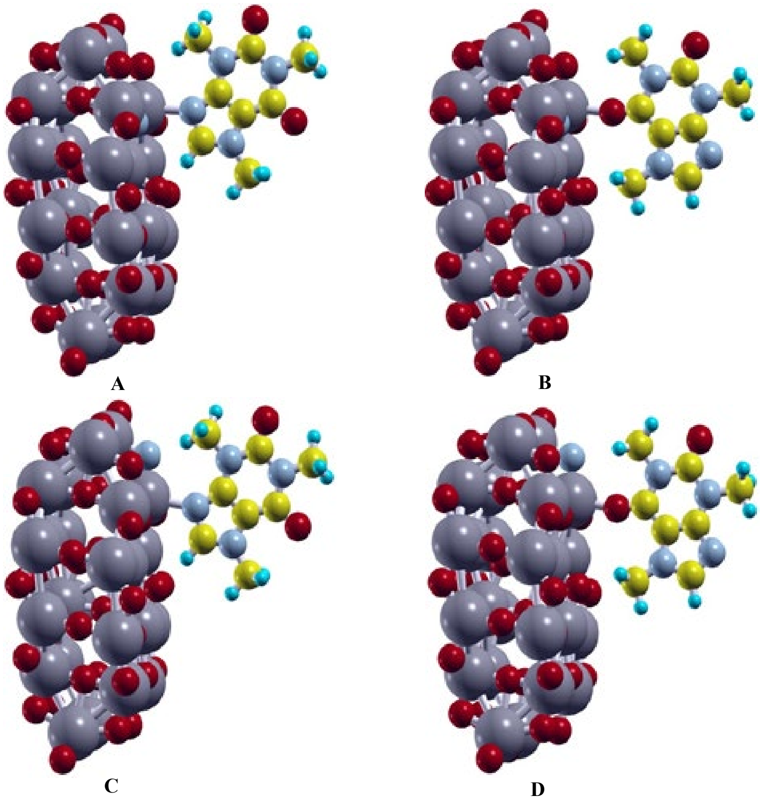

Fig. 3. Optimized geometry configurations of N-doped TiO_2 anatase nanoparticles with adsorbed caffein molecule.

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

Complex	Ti-N	Ti-O	Adsorption energy		Mulliken Charge
			PBE	DFT-D2	
A	2.43	---	-4.43	-6.20	-0.709
B	---	2.31	-4.31	-6.11	-0.588
C	2.38	---	-3.72	-5.80	-0.533
D	---	2.17	-3.70	-5.81	-0.376
E	2.36	---	-1.18	-2.22	-0.320
F	---	2.13	-1.23	-2.28	-0.325

summarizes the adsorption energies of the most stable configurations.

With regard to the results of this table, it is found that the adsorption of caffeine molecule on the N-doped nanoparticle is more energetically favorable than the adsorption on the pristine one. Thus, the N-doped nanoparticle can strongly interact with caffeine molecule and provide more energy favorable adsorption configurations. The negative sign of adsorption energies indicate the process is exothermic and energy favorable. The higher the adsorption energy of caffeine on the TiO_2, the stronger the interaction between caffeine and TiO_2 nanoparticle. Therefore, the N-doped nanoparticles have higher adsorption ability than the pristine ones, suggesting that the nitrogen doping strengthens the interaction between caffeine and TiO_2 nanoparticle.

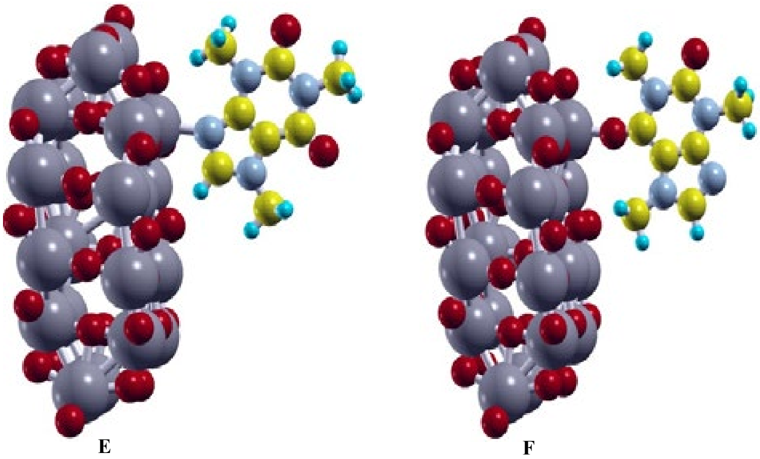

Fig. 4. Optimized geometry configurations of undoped TiO_2 anatase nanoparticles with adsorbed caffein molecule.

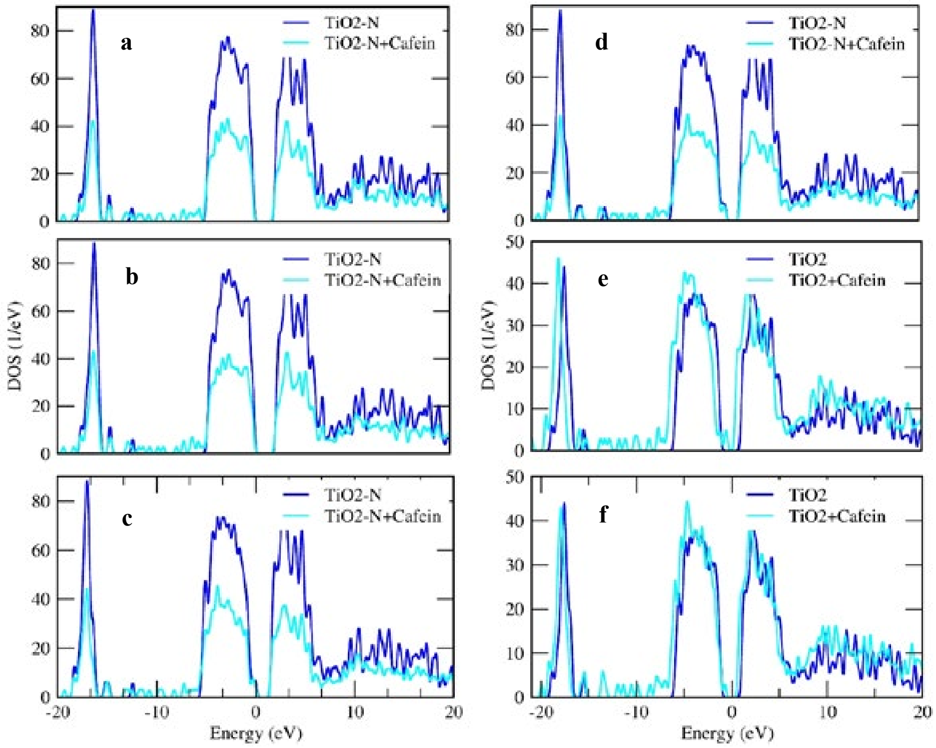

Fig. 5. Density of states for caffein molecule adsorbed on the undoped and N-doped TiO_2 anatase nanoparticles, a: Complex A; b: Complex B; c: Complex C; d: Complex D; e: Complex E; f: Complex F.

According to Table 1, the highest adsorption energy occurs in configuration A, representing that there is a stronger interaction between nitrogen atom of caffeine molecule and titanium atom than the interaction of oxygen atom. In contrast, the lowest adsorption energy belongs to configuration E, which shows the interaction between nitrogen atom of caffeine and pristine TiO_2 nanoparticle is less favorable. Thus, it could be concluded that the nitrogen modified TiO_2 nanoparticle is an ideal material to be utilized for sensing of caffeine molecule.

The adsorption energies are significantly increased when we consider the effects of long range vdW interactions. This indicates the prominent effect of van der Waals interaction during the adsorption of caffeine on the TiO_2 nanoparticles.

Electro

Fig. 5 shows total density of states (TDOS) of the complex systems with the caffeine adsorbed TiO_2 nanoparticles. It represents the differences between DOS of bare nanoparticle and caffeine adsorbed one. are slightly increased by the adsorption of caffeine molecule. These differences include both changes in the energies of the peaks and creation of some small peaks in the DOS of N-doped TiO_2 at lower-lying energies ranging from -13 eV to -7 eV. Consequently, these changes in the DOS states would affect the electronic transport properties of the nanoparticles.

Fig. 6 depicts the projected density of states for caffeine molecule adsorbed on the TiO_2 anatase nanoparticles. Panels (a-f) show the PDOSs for configurations A-F. Significant overlaps between the PDOSs of the interacting atoms (nitrogen or oxygen atom of caffeine molecule and titanium atom of TiO_2) represent the formation of chemical bonds between them. Figs. 7 and 8 show the PDOSs of the nitrogen atom of caffeine molecule, titanium atom and their pertaining d orbitals for configurations A and C, respectively.

These figures show the highest overlap between the PDOSs of nitrogen atom and d1 orbital of titanium atom, compared with the other d orbitals. Thus, it can be concluded that the d1 orbital of the titanium highly contributes to the formation of chemical bond with nitrogen atom. Figs. 9 and 10 depict the corresponding PDOSs of the oxygen atom of caffeine molecule, titanium atom and

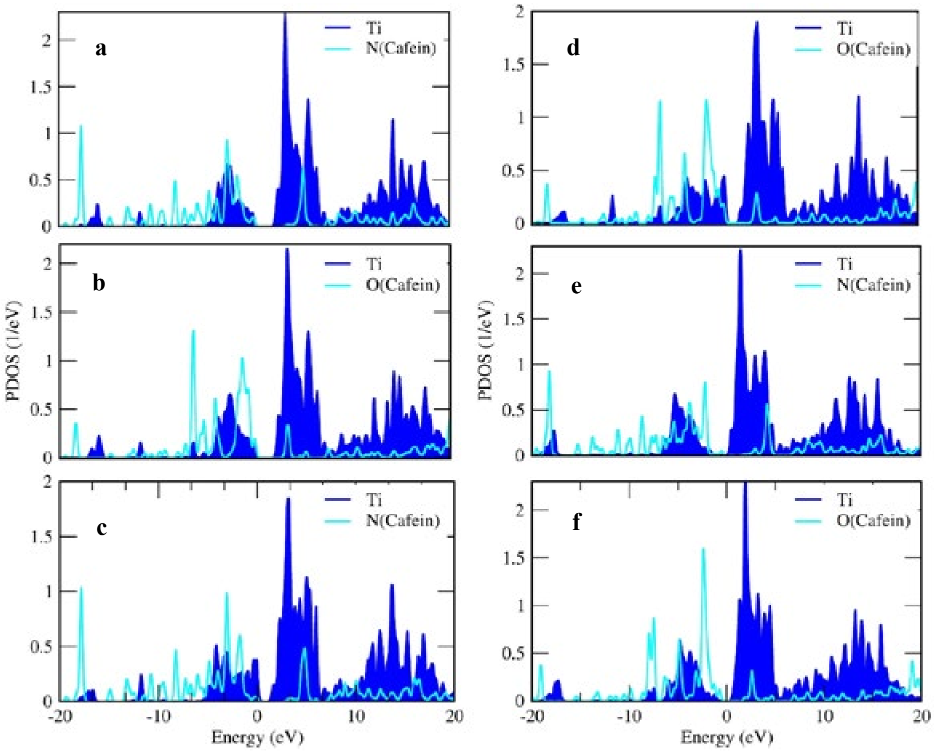

Fig. 6. Projected density of states for caffein molecule adsorbed on the TiO_2 anatase nanoparticles, a: Complex A; b: Complex B; c: Complex C; d: Complex D; e: Complex E; f: Complex F.

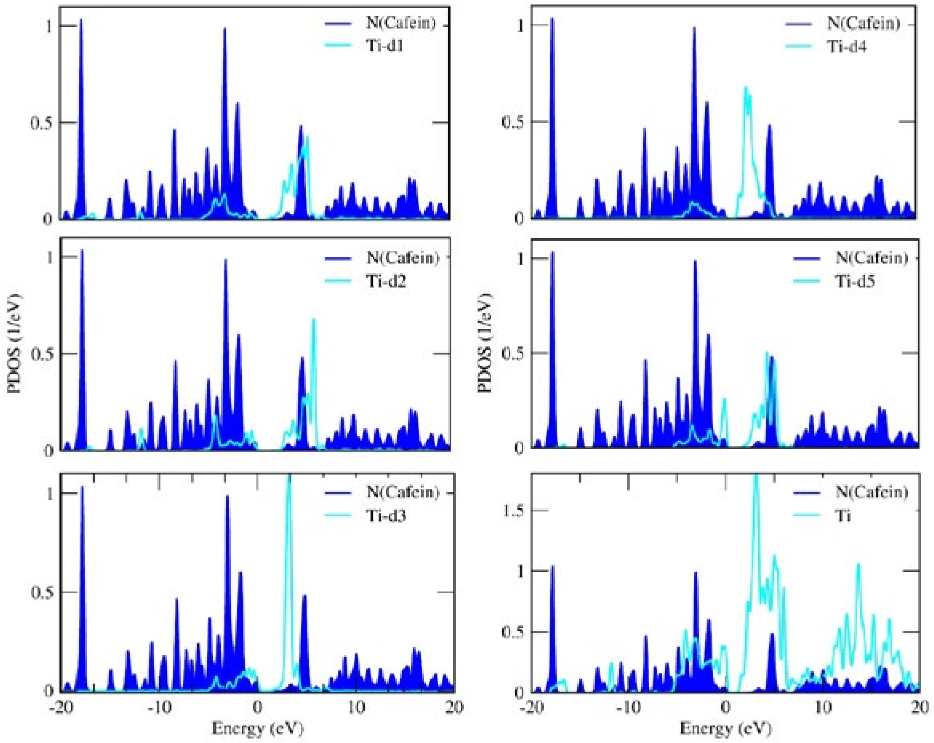

Fig. 7. Projected density of states for the nitrogen atom of the caffein, titanium atom and different d orbitals of the titanium (complex A).

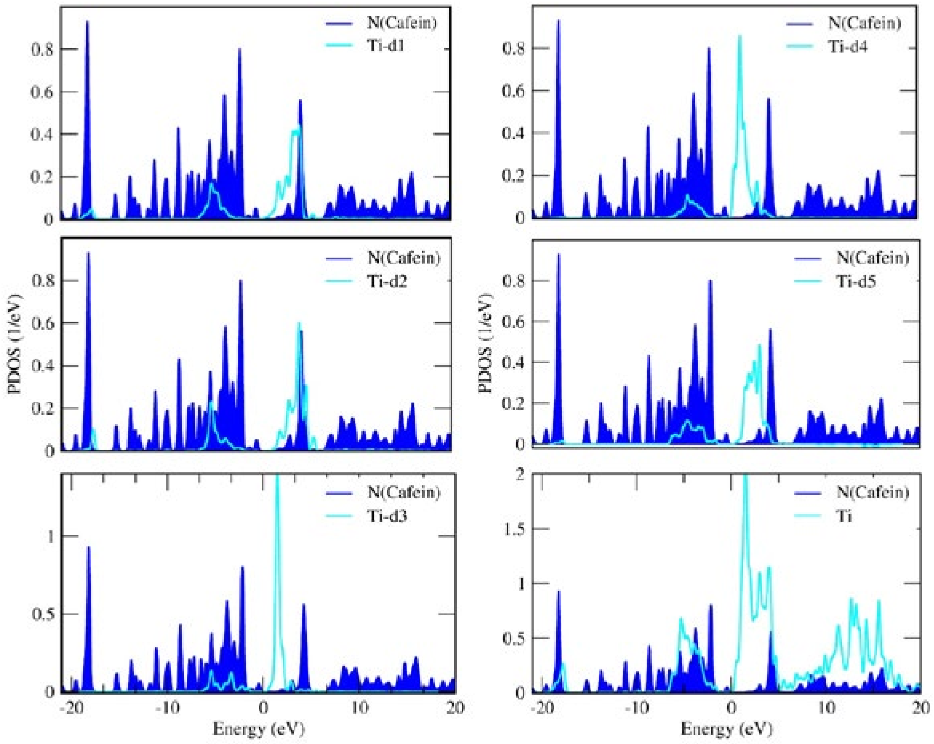

Fig. 8. Projected density of states for the nitrogen atom of the caffein, titanium atom and different d orbitals of the titanium (complex C).

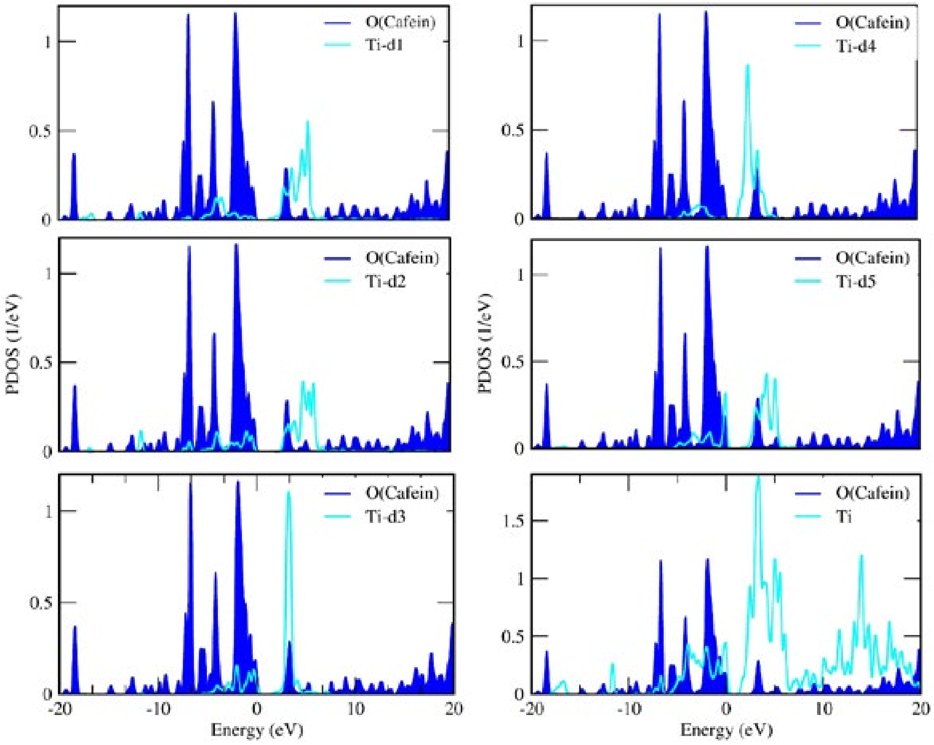

Fig. 9. Projected density of states for the oxygen atom of the caffein, titanium atom and different d orbitals of the titanium (complex B).

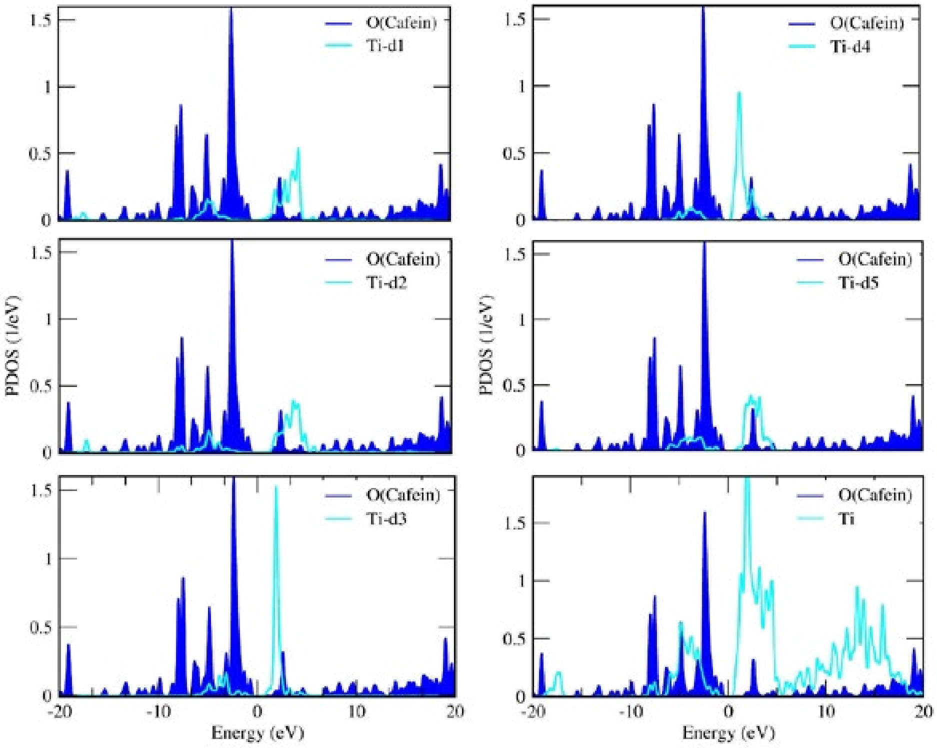

Fig. 10. Projected density of states for the oxygen atom of the caffein, titanium atom and different d orbitals of the titanium (complex D).

different d orbitals, which suggests considerable overlaps between the PDOSs of the oxygen atom of caffeine and d2 orbital (configurations B and D).

Figs. 11 and 12 show the isosurfaces of HOMOs and LUMOs for caffeine molecule adsorbed on the TiO_2 anatase nanoparticles. It is notable that the HOMOs of the adsorption systems are dominant at the whole surface of caffeine molecule, whereas the electronic density in the LUMOs seems to be distributed over the TiO_2 nanoparticle.

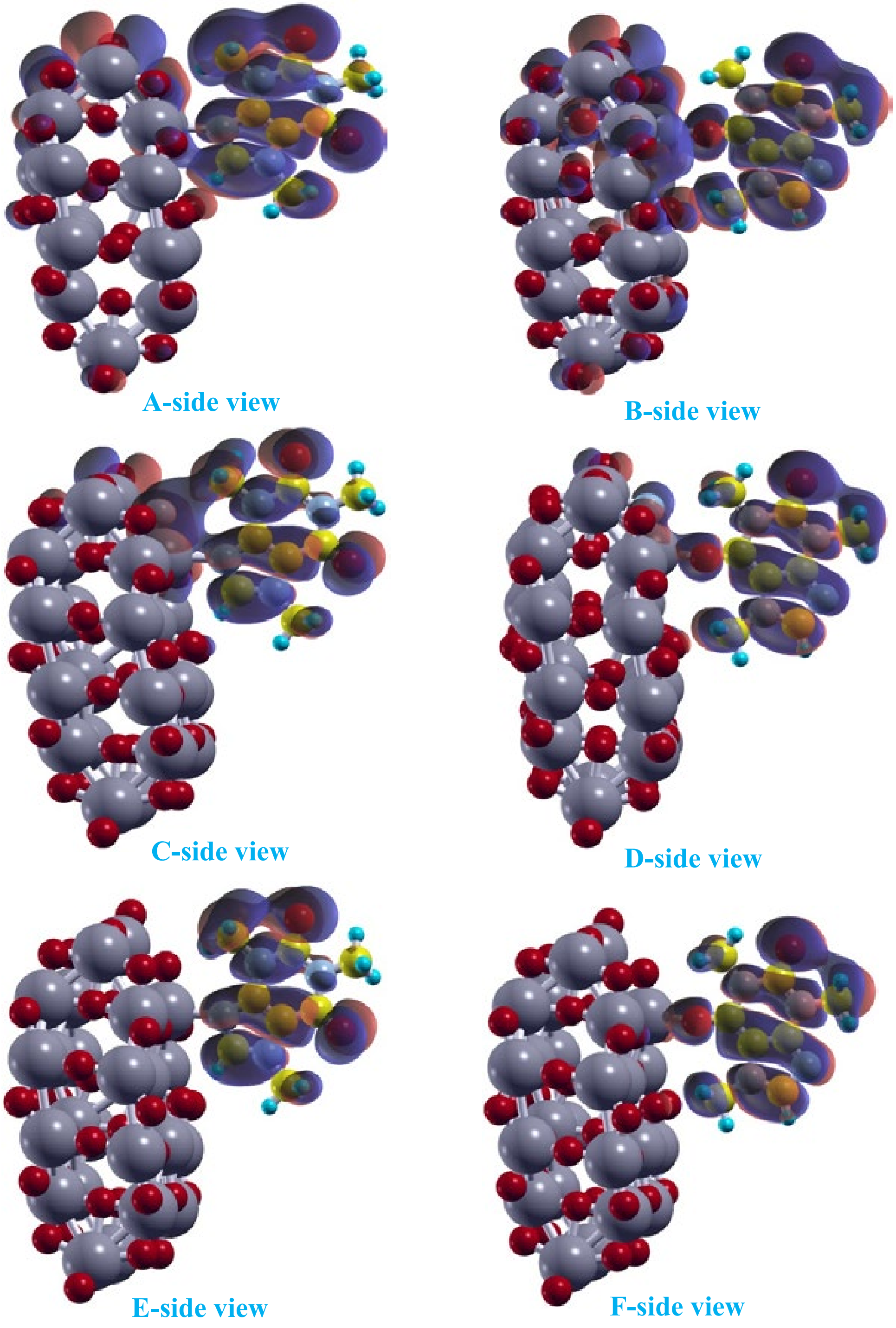
A-side view
B-side view
C-side view
D-side view
E-side view
F-side view

Fig. 11. The isosurfaces of HOMO molecular orbitals of caffein molecule adsorbed on the considered TiO_2 nanoparticles.

Concentration of electronic density on the adsorbed caffeine molecule indicates that the electronic density of adsorption configurations was affected by adsorption of caffeine molecule. This feature of electronic density (especially HOMO) would be useful in the design and development of efficient nanosensors for caffeine drug. We have also calculated the total electron densities and Kohn-Sham potentials for the adsorption complexes under study. These results are in accordance with

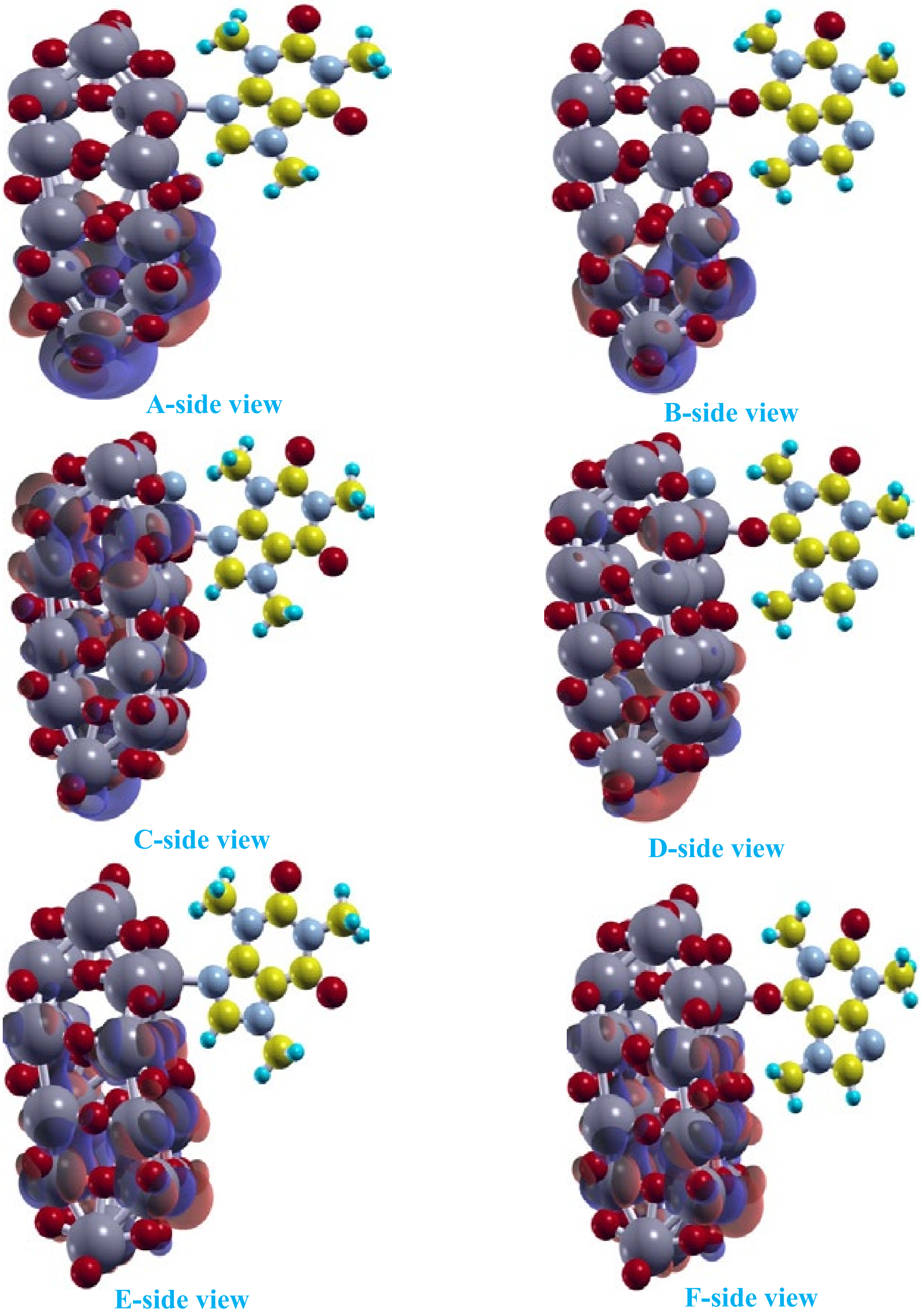
A-side view
B-side view
C-side view
D-side view
E-side view
F-side view

Fig. 12. The isosurfaces of LUMO molecular orbitals of caffein molecule adsorbed on the considered TiO_2 nanoparticles.

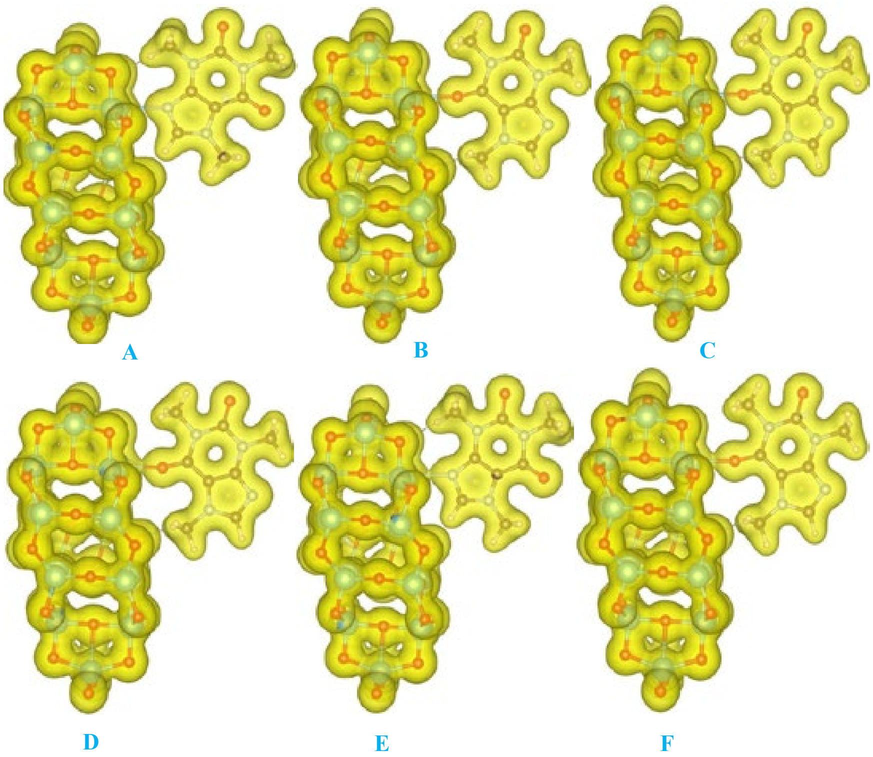

Fig. 13. Isosurface plots of the total electron density for caffein molecule adsorbed on the TiO_2 anatase nanoparticles.

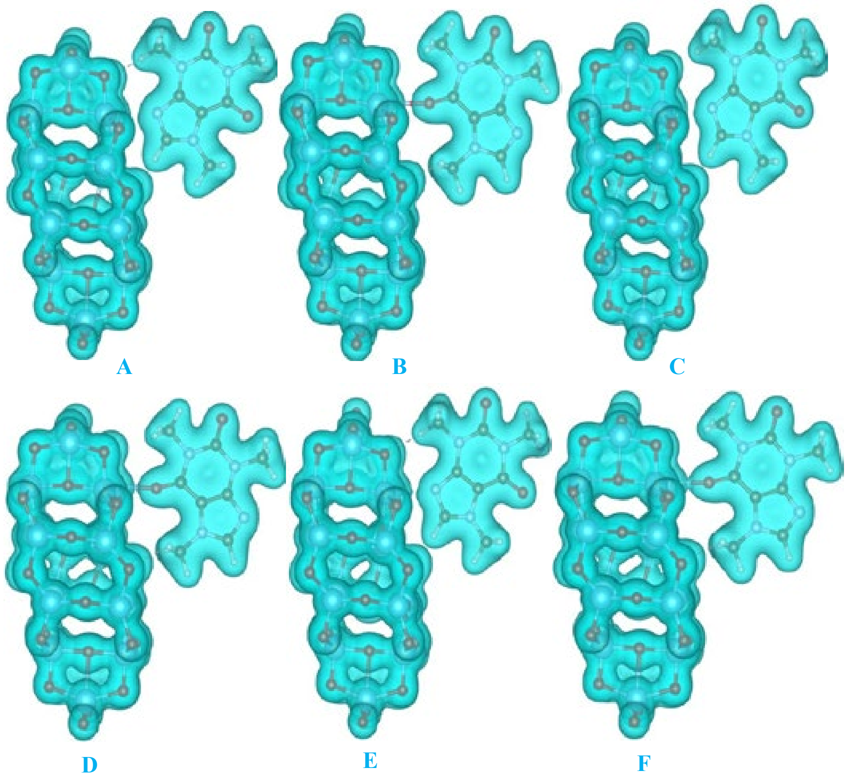

Fig. 14. Isosurface plots of Kohn-Sham potentials excluding the nonlocal potential for up-spin in a Gaussian cube format.

the molecular orbital calculations. Fig. 13 shows the calculated total electron densities, while Fig. 14 depicts the Kohn-Sham potentials for caffeine adsorbed TiO_2 nanoparticles. According to Fig. 13, the electron density was distributed between the newly formed Ti-N and Ti-O bonds, representing the formation of chemical bonds. This can be clearly understood form Fig. 14, which indicates the potential distribution of the studied systems. To further analyze the charges exchange between TiO_2 nanoparticle and caffeine molecule, we have performed charge analysis based on Mulliken charges. The results indicate that caffeine adsorption induces a noticeable charge transfer of about -0.709 e from caffeine to the TiO_2 nanoparticle for configuration A. This implies that the caffeine molecule behaves as a charge donor after the adsorption process. According to Table 1, the highest value of charge transfer was estimated for configuration A, whereas the lowest charge transfer belongs to configuration E, in accordance with the variations of adsorption energies.

CONCLUSIONS

This study dealt with the interaction between caffeine drug and pristine N-doped TiO_2 anatase nanoparticles using density functional theory calculations. Various adsorption models of caffeine on the nanoparticles under study were examined in detail. Both oxygen and nitrogen atoms of the caffeine molecule can interact with the fivefold coordinated titanium atom. The calculations predict that caffeine presents a stronger interaction with TiO_2 nanoparticles containing doped nitrogen atom rather than with pristine or undoped nanoparticles. The interaction between caffeine molecule and N-doped TiO_2 is more energetically favorable than the interaction with the undoped ones. This condition represents that the N-doped nanoparticle is strongly favored. The adsorption energies for caffeine molecule are significantly increased by including vdW interactions. The projected density of the states of oxygen and nitrogen atoms of caffeine 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 caffeine molecule. Thus, nitrogen doping into TiO_2 particle strengthens the interaction between caffeine and TiO_2 nanoparticle. The resulting systems suggest that TiO_2 anatase, in nitrogen modified form, can be used as caffeine sensor due to the sensitivity of the electronic properties around the Fermi energy to the presence of caffeine drug.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES

1. A. L. Linsebigler, G. Lu and J. T. Yates. J. Chem. Rev., 95, 735 (1995).
2. C. Zhang and P. J. D. Lindan. J. Chem. Phys. Letts., 373, 15 (2003).
3. R. Erdogan, O. Ozbek, and I. Onal. J. Surf. Sci., 604, 1029 (2010).
4. R. Hummatov, O. Gulseren, E. Ozensoy, D. Toffoli, and H. Ustunel. J. Phys. Chem. C. 116, 6191 (2012).
5. A. Fahmi and C. A. Minot. Surf. Sci., 304, 343 (1994).
6. S. I. Shah, W. Li, C. P. Huang, O. Jung, and C. Ni, Proc. Natl. Acad. Sci. U.S.A. 99, 6482 (2002).
7. W. Li, A. I. Frenkel, J. C. Woicik, C. Ni, and S. I. Shah, Phys. Rev. B. 72, 155315 (2005).
8. U. Diebold. Surf. Sci. Reports, 48, 53 (2003).
9. F. Han, V. S. R. Kambala, M. Srinivasan, D. Rajarathnam and R. J. Naidu. Applied Catalysis A: General, 359, 25 (2009).
10. A. Fujishima and K. Honda. Nature. 238, 37 (1972).
11. I. Onal, S. Soyer, and S. Senkan. Surf. Sci., 600, 2457 (2009).
12. W. Shi, Q. Chen, Y. Xu, D. Wu and C. F. Huo. J. Solid State Chem. 184, 1983 (2011).
13. Y. Lei, H. Liu and W. Xiao. Modelling Simul. Mater. Sci. Eng., 18, 025004 (2010).
14. A. Beltran, J. Andres, J. R. Sambrano, and E. Longo. J. Phys. Chem. A. 112, 8943 (2008).
15. S. Tang and Z. Cao. J. Chem. Phys., 134, 044710 (2011).
16. J. Liu, Q. Liu, P. Fang, C. Pan and W. Xiao. Appl. Surf. Sci., 258, 8312 (2012).
17. A. Abbasi, J. J. Sardroodi, and A. R. Ebrahimzadeh. J. Theor. Comput. Chem., 14, 1 (2015).
18. H. Irie, Y. Watanabe and K. Hashimoto. J. Phys. Chem. B. 107, 5483 (2003).
19. J. Liu, L. Dong, W. Guo, T. Liang, and W. Lai. J. Phys. Chem. C. 117, 13037 (2013).
20. A. Abbasi, J. J. Sardroodi and A. R. Ebrahimzadeh. Can. J. Chem., 94, 78 (2016).
21. S. Livraghi, M. C. Paganini, E. Giamello, A. Selloni, C. D. Valentin and G. Pacchioni. J. Am. Chem. Sci., 128, 15666 (2006).
22. H. Liu, M. Zhao, Y. Lei, C. Pan and W. Xiao. J. Comput. Mater. Sci., 15, 389 (2012).
23. M. Breedon, M. Spencer and I. Yarovsky. J. Phys. Chem. C. 114, 16603 (2010).

24. A. K. Rumaiz, J. C. Woicik, E. Cockayne, H. Y. Lin, G. H. Jaffari and S. I. Shah. Appl. Phys. Letts., 95, 262111 (2009).
25. Z. Zhao and Q. Liu. Journal of Physics D: Applied Physics, 41, 085417 (2008).
26. H. Gao, J. Zhou, D. Dai and Y. Qu. J. Chem. Eng. Technol., 32, 867 (2009).
27. D. Zhao, X. Huang, B. Tian, S. Zhou, Y. Li and Z. Du. Appl. Phys. Letts., 98, 115 (2011).
28. M. Landmann, E. Rauls and W. G. Schmidt. Journal of Physics: Condensed Matter. 24, 195503 (2012).
29. P. Hohenberg and W. Kohn. J. Phys. Rev., 136, B864 (1964).
30. W. Kohn and L. Sham. J. Phys. Rev., 140, A1133 (1965).
31. The code, OPENMX, pseudoatomic basis functions, and pseudopotentials are available on a web site 'http://www.openmxsquare.org'.
32. J. P. Perdew, K. Burke and M. Ernzerhof. J. Phys. Rev. Letts. 78, 1396 (1997).
33. S. Grimme. J. Comput. Chem., 27, 1787 (2006).
34. A. Koklj. J. Comput. Mater. Sci., 28, 155 (2003).
35. R. W. G. Wyckoff. Crystal structures, Second edition. Interscience Publishers, USA, New York, (1963).
36. Web page at: http://rruff.geo.arizona.edu/AMS/amcsd.
37. C. Wu, M. Chen, A. A. Skelton, P. T. Cummings and T. Zheng. ACS Appl. Mat Interfaces. 5, 2567 (2013).