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ORIGINAL RESEARCH PAPER

Van der Waals corrected DFT study on the adsorption behaviors of TiO_2 anatase nanoparticles as potential molecule sensor for thiophene detection

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ABSTRACT
Density functional theory investigations were conducted in order to study the effects of the adsorption of thiophene on the structural and electronic properties of TiO_2 anatase nanoparticles. The ability of pristine and N-doped TiO_2 anatase nanoparticles to recognize toxic thiophene was surveyed in detail. It was found that thiophene molecule is chemisorbed on the N-doped anatase nanoparticles in S site geometries with large adsorption energy and small distance. By including van der Waals (vdW) interactions between thiophene molecule and TiO_2, we found that the adsorption on the N-doped TiO_2 is energetically more favorable than the adsorption on the pristine one, suggesting that the nitrogen doping can energetically facilitate the thiophene adsorption on the N-doped nanoparticle. The order of adsorption energy is Parallel(S site)>Perpendicular(S site)>Perpendicular (H site). The interaction between thiophene and N-doped TiO_2 can induce substantial variations in the HOMO/LUMO molecular orbitals of the nanoparticle, changing its electrical conductivity, which is helpful for designing the novel sensor and remover devices. Charge analysis based on Mulliken charges reveals that charge is transferred from thiophene molecule to TiO_2 nanoparticle.

Keywords: *Thiophene; TiO_2; Electronic properties; Density functional theory.*

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INTRODUCTION

Titanium dioxide (TiO_2) has been characterized as a most widely used photocatalytic material, which has various applications in photo-catalysis [1], gas sensor devices, heterogeneous catalysis [2] and photovoltaic cells [3]. Owing to some outstanding properties such as non-toxicity, chemical stability, abundance and high catalytic efficiency, it has attracted numerous scientific attentions in the recent years. These unique properties of TiO_2 make it very interesting material to be utilized in many fields of science and research [4-8]. Numerous attempts have been done to cover all theoretical aspects of TiO_2 related science and technology including fundamental principles and crucial practical features of it [8-15]. The photocatalytic activity of TiO_2 has been restricted due to its relatively wide band gap, which decreases the absorption of the incoming solar irradiation. One convenient solution to enhance the optical response of TiO_2 is the doping of TiO_2 with some non-metal elements such as nitrogen [16-18]. Several computational studies of N-doped TiO_2 nanoparticles have been suggested by different researchers. For example, Liu *et al.* reported that the N doping can facilitate the adsorption of nitric oxide on TiO_2 anatase nanoparticles [14]. Recently, it has been revealed that the N-doped TiO_2

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anatase nanoparticles react with CO molecules more efficiently, compared to the undoped ones [19]. Moreover, the nitrogen doping of TiO_2 nanoparticles makes it possible to apply TiO_2 as an efficient sensor material, altering its electronic and structural properties [20-25]. Nevertheless, the impacts of N-doping on the photo-catalytic activity and therefore the energy gap of TiO_2 have been inspected in some other works [26, 27]. In order to reveal the enhancement of the efficiency of TiO_2 nanoparticles in the adsorption processes some researchers have analyzed its electronic properties such as density of states (DOS), Mulliken population analysis and also its structural properties such as bond lengths and adsorption energies [14, 19, 28]. A material in the atmosphere which causes harmful effects on the public health and the environment is identified as an air pollutant, which can have different forms such as solid particles, liquid droplets or gasses. Thiophene is a heterocyclic compound and is one of the main constituents of fuel. The combustion of thiophene molecule leads to the production of sulfur containing compounds, which are characterized as harmful materials and can participate to the environmental pollution. Since environment protection is a serious subject to the public health, the concentration of sulfur is severely controlled by using the appropriate methods. Hence, the removal of sulfur from sulfur containing compounds especially thiophene is a major point, which facilitates the production of clean fuels with low content of sulfur atom [29-32]. An admirable gas sensor should have high sensitivity to the anticipated poisonous material, as well as extensive variety of application and low price fabrication. Solid state sensors such as TiO_2 anatase nanoparticles are well-known and broadly used materials for recognition of harmful molecules in the atmosphere due to their unique response to the air pollutants. It has been mentioned that the N-doped TiO_2 can be classified as an efficient candidate for detecting different molecules. In this research, we studied the sensitivity of both undoped and N-doped TiO_2 anatase nanoparticles for interaction with harmful thiophene molecule. We provided various adsorption configurations of the thiophene with respect to the nanoparticles. The adsorption energies, electronic properties including the total and projected density of states, the structural properties and the charge transfer analysis of the considered non-adsorbed and adsorbed structures in adsorbed complexes were computed and analyzed. It can be concluded that the electronic properties of TiO_2 anatase nanoparticle, are strongly changed by the adsorption of thiophene. This work is devoted to supply a theoretical basis for the design and manufacture of effective TiO_2 based sensor devices for thiophene detection.

COMPUTATIONAL DETAILS AND MODELS

Computational Methods

Density Functional Theory (DFT) calculations [33, 34] were carried out using the Open source Package for Material eXplorer (OPENMX) ver. 3.8 [35], being a well-organized software package for nano-scale materials simulations based on DFT, PAO basis functions and VPS pseudopotentials. Pseudo atomic orbitals were utilized as basis sets in the geometry optimizations. The considered cutoff energy was set to the value of 150 Rydberg in our calculations [34]. The PAO's were constructed through the basis sets (3-s, 3-p, 1-d) for the titanium atom, (2-s and 2-p) for the oxygen, carbon and nitrogen atoms, (2-s) for the hydrogen atom and (3-s and 3-p) for the sulfur atom with the chosen cutoff radii of 7 for the titanium, 5 for the oxygen, carbon, nitrogen and hydrogen atoms and 8 for sulfur atom (all in bohrs). The exchange-correlation energy functional was described using the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof form (PBE) [36]. The van der Waals interactions were examined using the DFT-D2 method. The convergence criteria for self-consistent field iterations and energy calculation were set to the values of 1.0×10^{-6} Hartree and 1.0×10^{-4} Hartree/bohr, respectively. For the geometry optimization, 'Opt' is used as the geometry optimizer, which is a robust and efficient scheme. The crystalline and molecular structure visualization program, XCrysDen [37], was employed for displaying molecular orbital isosurfaces. The Gaussian broadening method for evaluating electronic DOS was used. For the adsorption of thiophene molecules on the TiO_2/MoS_2 nanocompopsite. The adsorption energy was calculated by using the following formula:

$$E_{ad} = E\,(_{particle + adsorbate)} - E_{particle} - E_{adsorbate} \qquad (1)$$

where $E_{(particle + adsorbate)}$, $E_{particle}$ and $E_{adsorbate}$ are the energies of the complex system, the free TiO_2 nanoparticle without any adsorbed molecule and the free thiophene molecule in an non-adsorbed state respectively. The charge transfer between the thiophene molecule and the nanoparticles

was evaluated using the Mulliken charge analysis, which is based on the difference of the charge concentration on thiophene before and after the adsorption process.

Modelling of nanoparticles

We have constructed the TiO_2 anatase nanoparticles by setting a 3×2×1 supercell of pristine and N-doped TiO_2 anatase. The considered unit cell of TiO_2 was reported by Wyckoff [38], which was chosen from "American Mineralogists Database" webpage [39]. The chosen supercell of TiO_2 anatase was shown in Fig. 1. The size of the simulation box considered in our calculations is 20×15×30 $Å^3$, being much larger than the nanoparticle size. A vacuum space of 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 is denoted by 2f-O and threefold by 3f-O (middle oxygen) in Fig. 2 with fivefold coordinated and sixfold coordinated titanium atoms sketched by 5f-Ti and 6f-Ti, respectively [40]. The schematic structures of thiophene molecule is represented in Fig. 3. The thiophene molecule is positioned in parallel and perpendicular geometries with respect to the optimized undoped and N-doped nanoparticles. The complex system optimization reveals that the sulfur atom of thiophene molecule preferentially interacts with fivefold coordinated titanium atom of nanoparticle and is close to the surface titanium site. It means a higher activity of sulfur atom of thiophene, compared to the other atoms.

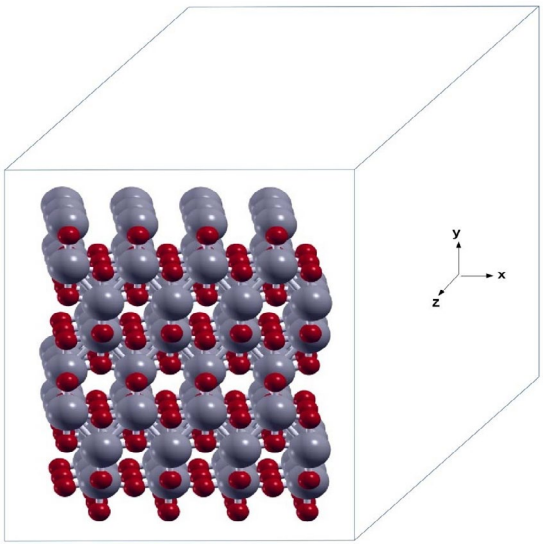

Fig. 1. Representation of a 3×2×1 supercell of TiO_2 anatase constructed from TiO_2 unit cells along x, y and z directions.

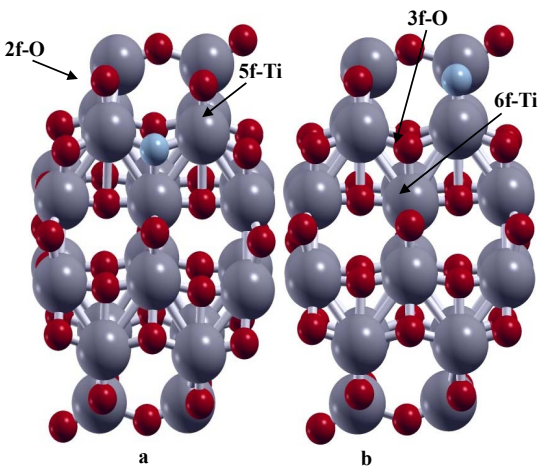

Fig. 2. Optimized N-doped TiO_2 anatase nanoparticles constructed using the 3×2×1 unit cells, colors represent atoms accordingly: Ti in gray, O in red and N in blue.

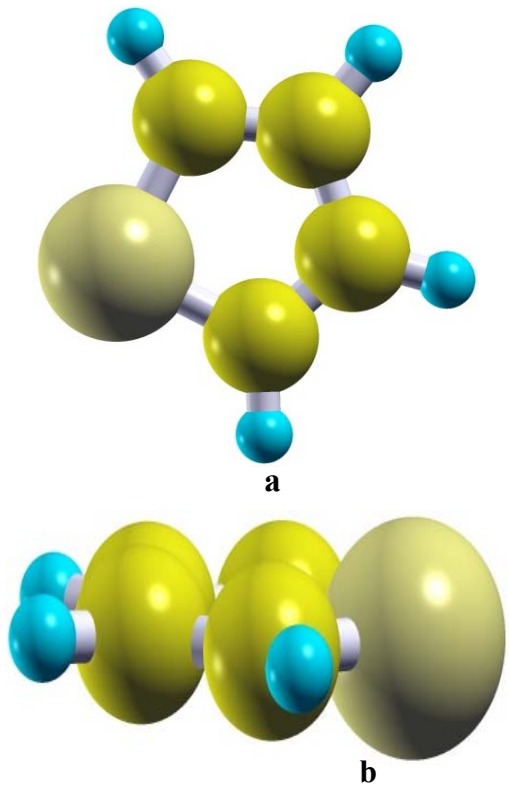

Fig. 3. Representation of the optimized structure of thiophene molecule, (a): front view and (b): lateral view. Colors represent atoms accordingly: S in light yellow, C in dark yellow and H in cyan.

RESULTS AND DISCUSSION

Structure parameters and adsorption energies

According to the structure of thiophene, the thiophene molecule was adsorbed on the fivefold coordinated titanium site of TiO_2 nanoparticles in two possible adsorption geometries. In one geometry, the thiophene molecule was placed vertically (perpendicular geometry) towards the nanoparticle and the other is that thiophene was put horizontally (parallel geometry). Adsorption geometries of thiophene molecule on the optimized TiO_2 nanoparticle are displayed in Fig. 4. This Figure includes the thiophene-adsorbed complexes named A-I for the perpendicular and parallel configurations. Each complex of Fig. 4 differs in substituted oxygen atom of TiO_2 nanoparticle and the relative orientation of thiophene molecule with respect to the nanoparticle from the others. For example, complex A tells the perpendicular orientation of thiophene towards the O_C-substituted nanoparticle. The optimized values of some bond lengths before and after the adsorption on the nanoparticle were listed in Table 1. The bond lengths include the newly formed Ti-S bond, T-O bond and C-S bond of thiophene molecule. The results indicate that the C-S bond of thiophene molecule and Ti-O bonds of TiO_2 nanoparticle are stretched after the adsorption process. These elongations in the bond lengths are mostly attributed to the transfer of electronic density from Ti-O bond of TiO_2 and C-S bond of the adsorbed thiophene molecule to the newly formed Ti-S bond between TiO_2 nanoparticle and thiophene molecule. The smaller bond formed between the sulfur atom of thiophene molecule and the titanium atom of nanoparticle (Ti-S), has stronger interaction between thiophene and TiO_2 anatase nanoparticle. Adsorption energy analysis

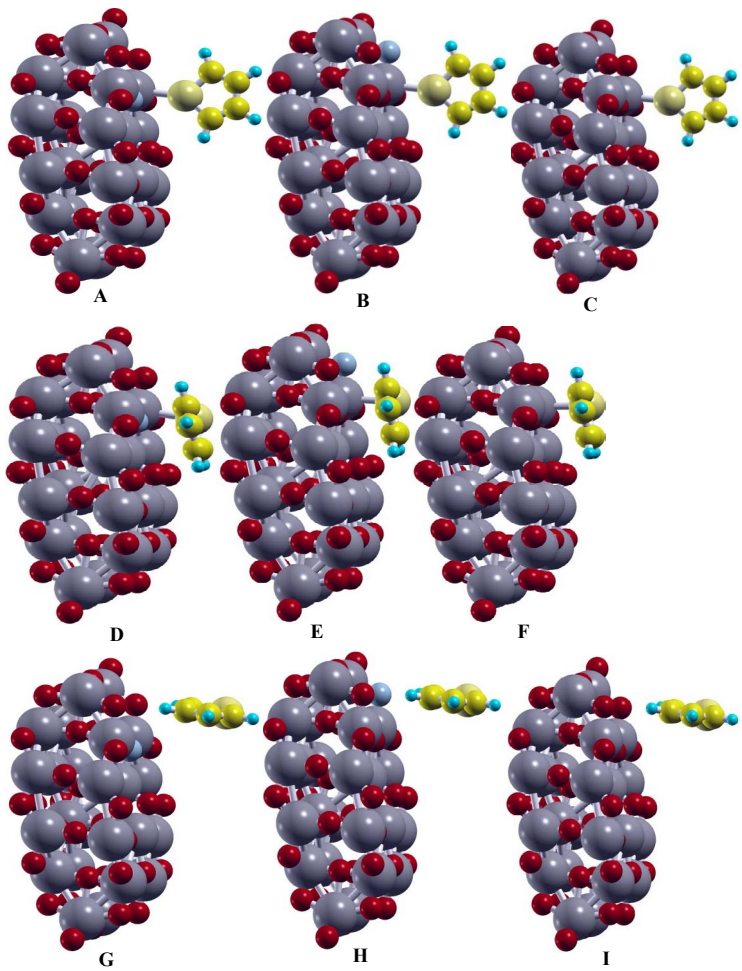

Fig. 4. Optimized geometry configurations of TiO_2 anatase nanoparticles with adsorbed thiophene molecule.

reveals that the thiophene molecule is preferentially adsorbed on the fivefold coordinated titanium site of nanoparticle through its sulfur atom rather than its carbon and hydrogen atoms. The bond lengths relevant to the perpendicular (H-site) configurations were also listed in Table 2. The adsorption energies of the most stable configurations were tabulated in Table 3. These results indicate that the adsorption of thiophene molecule on the N-doped nanoparticle is more energetically favorable than the adsorption on the undoped one. The higher adsorption energy and small adsorption distance indicate chemisorption of thiophene molecule on the nanoparticles. O_C-substituted nanoparticle adsorbs the thiophene molecule more efficiently, compared to the O_T-substituted one. Therefore, the N-doped nanoparticles have higher sensing capabilities than the pristine ones, suggesting that the N-doping strengthens the adsorption of thiophene on the TiO_2 nanoparticle. The more negative the adsorption energy, the higher tendency for adsorption, and consequently more stable adsorption geometry. As can be seen from Table 3, all the calculated adsorption energies are considerably increased when the vdW interactions are taken into account. Therefore, the adsorption energies of thiophene molecule on the undoped and nitrogen-doped TiO_2 nanoparticles becomes higher when the vdw interactions are included, suggesting the significant domination of vdw interactions during the adsorption process. The improvement of both adsorption energy and structural properties of the adsorption of thiophene on TiO_2 resulted from N-doping reveals that the N-doped TiO_2 can be successfully used for removal of the toxic thiophene molecules from the environment. The nitrogen doping effect on the improvement of the adsorption ability of TiO_2 nanoparticles for adsorption of CO molecule has been recently discussed by Liu *et al.* [19].

Table 1: Bond lengths (in Å) for a thiophene molecule adsorbed on the TiO_2 anatase nanoparticles.

Complex	Ti-N	Ti-O	Newly-formed Ti-S	C-S
Perpendicular	---	---	---	---
A	---	1.76	2.73	1.83
B	1.79	---	2.73	1.81
C	---	1.73	2.72	1.81
Parallel (S site)	---	---	---	---
D	---	1.74	2.82	1.85
E	1.79	---	2.72	1.82
F	---	1.73	2.76	1.82
Non-adsorbed	1.76	1.73	---	1.79

Table 2: Bond distances (in Å) for a thiophene molecule adsorbed on the TiO_2 anatase nanoparticles in perpendicular (H site) adsorption configuration.

Complex	O-H1	O-H2	N-H1	C-H1	C-H2	Ti-O	Ti-O	Ti-N
G	2.33	2.50	---	1.10	1.10	1.76	1.84	---
G	---	2.52	2.30	1.10	1.10	1.78	---	1.80
I	2.43	2.56	---	1.09	1.10	1.74	1.81	---
Non-adsorbed	---	---	---	1.04	1.04	1.73	1.73	1.76

Table 3: Adsorption energies (eV) and Mulliken charges (e) for a thiophene molecule adsorbed on the TiO_2 anatase nanoparticles.

Complex	Mulliken charge	Adsorption energy	
		PBE	DFT-D2
Perpendicular (S site)			
A	-0.448	-3.60	-9.20
B	-0.282	-3.06	-8.90
C	-0.214	-0.61	-3.80
Parallel (S site)			
D	-0.711	-4.24	-10.08
E	-0.452	-3.57	-9.60
F	-0.457	-1.17	-5.30
Perpendicular (H site)			
G	-0.145	-3.22	-9.45
H	-0.253	-2.85	-8.60
I	-0.033	-0.19	-3.10

Electronic structures

Fig. 5 displays the total density of states (TDOS) for the non-adsorbed thiophene molecule. This figure represents that the energy gap between the HOMO and the LUMO levels is about 3.8 eV for the thiophene molecule. The TDOS of the complex systems containing TiO_2+Thiophene couples were displayed in Fig. 6 and 7, which shows that the differences between DOS of doped and undoped TiO_2 are increased by adsorption of thiophene. 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 the energy values ranging from -8 eV to -15 eV. So, these variations in DOS states would affect the electronic transport properties of the nanoparticles and this feature can be beneficial for sensing of thiophene by TiO_2 nanoparticles. The titanium and sulfur

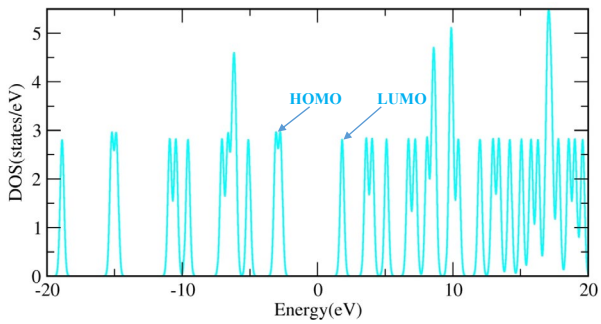

Fig. 5. Total density of states for thiophene molecule before the adsorption process.

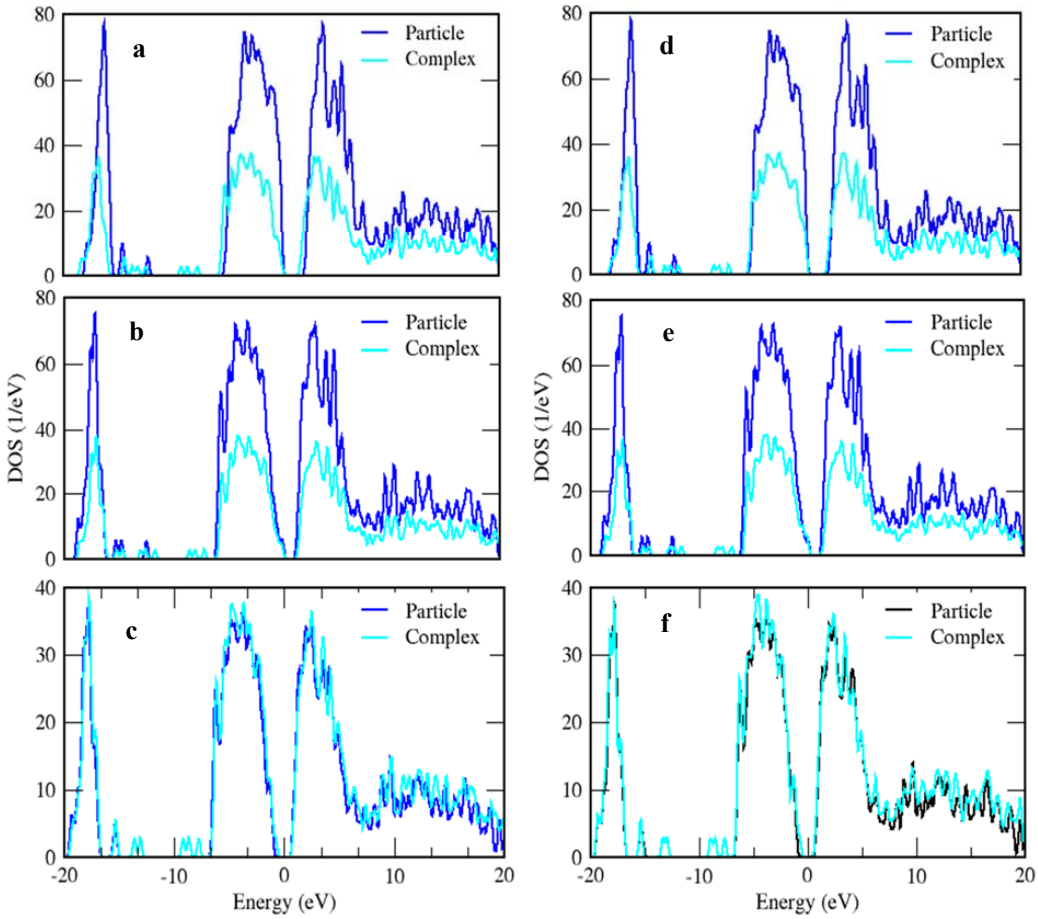

Fig. 6. Density of states for the adsorption of a thiophene molecule on the TiO_2 anatase particles, a: A complex; b: B complex; c: C complex; d: D complex; e: E complex; f: F complex.

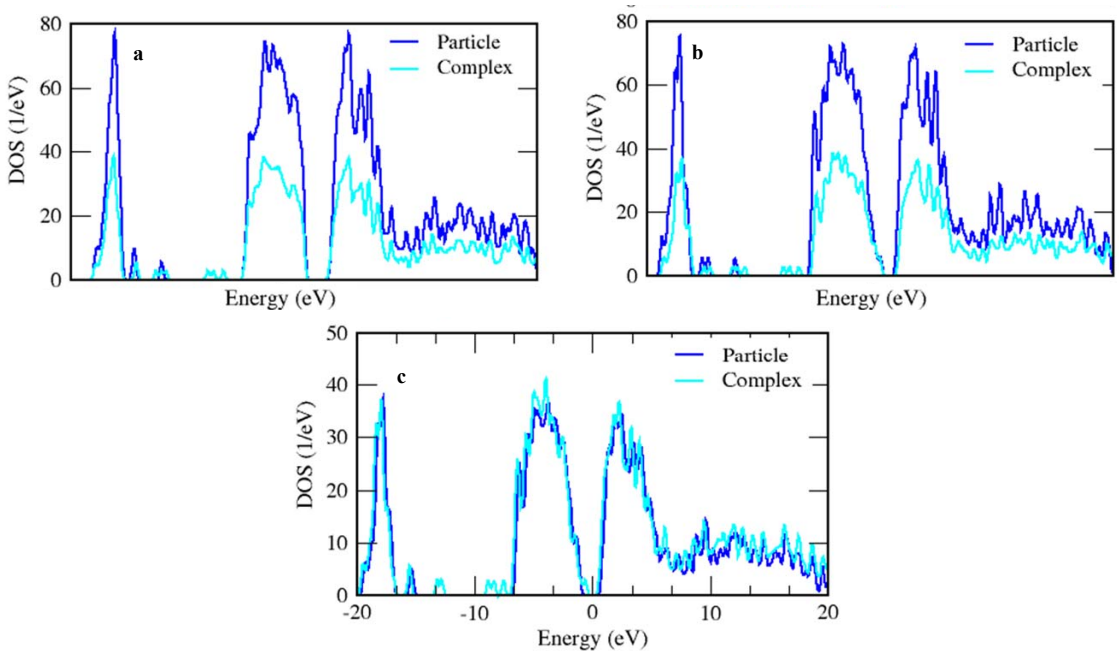

Fig. 7. Density of states for the adsorption of a thiophene molecule on the TiO_2 anatase particles, a: G complex; b: H complex; c: I complex.

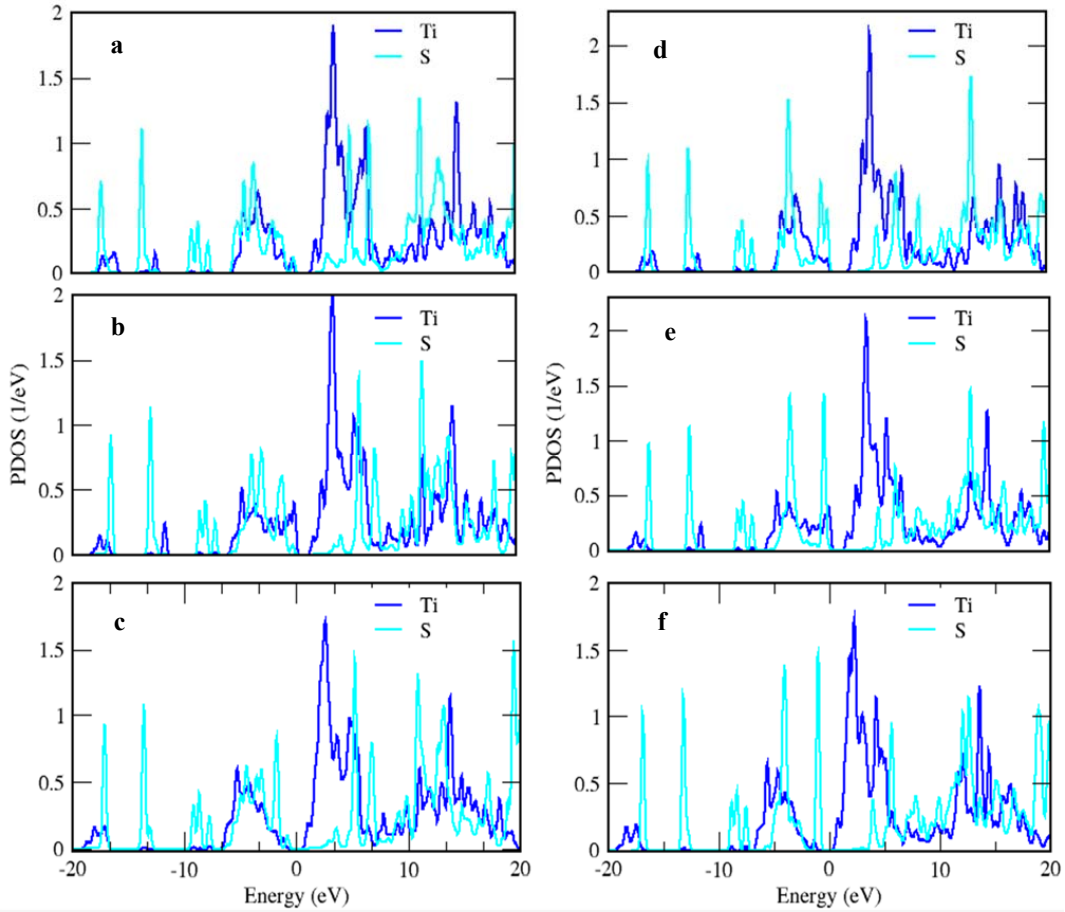

Fig. 8. Projected density of states for the adsorption of thiophene molecule on the TiO_2 anatase nanoparticles, a: A complex; b: B complex; c: C complex; d: D complex; e: E complex; f: F complex.

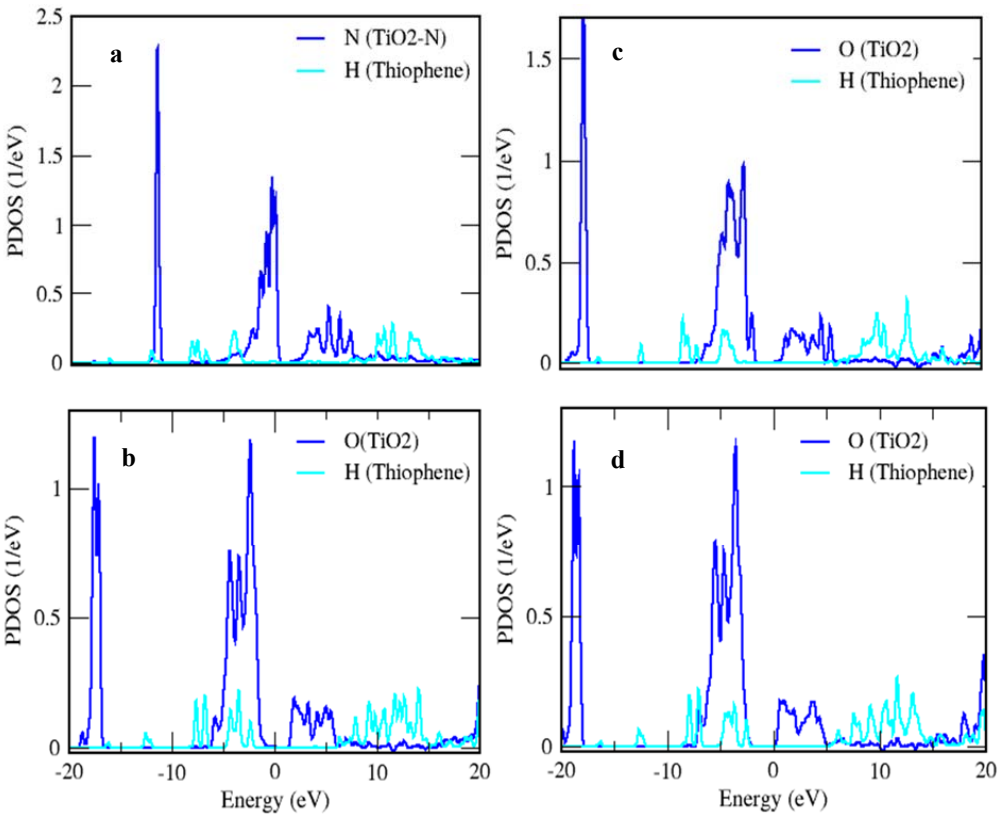

Fig. 9. Projected density of states for the adsorption of thiophene molecule on the TiO_2 anatase nanoparticles, a: H complex; b: H complex; c: G complex; d: G complex.

projected DOSs (Ti-PDOS and S-PDOS) for perpendicular and parallel (S site) configurations were shown in Fig. 8 as panels (a-f). The large overlap between the PDOSs of titanium and sulfur atoms reveals that the new Ti-S bond forms between the titanium atom of nanoparticle and sulfur atom of thiophene. The corresponding PDOSs for the perpendicular (H site) configuration were also shown in Fig. 9, which indicates a lower overlap between the PDOS of oxygen atoms of TiO_2 nanoparticle and hydrogen atoms of thiophene molecule. This implies that there is a weak mutual interaction between hydrogen atoms of thiophene and oxygen atoms of nanoparticle. The PDOSs of the titanium and sulfur atoms and their pertaining d orbitals were presented in Fig. 10 for complex A. This figure shows the highest overlap between the PDOSs of sulfur atom and d^1 orbital of titanium atom, compared with the other d orbitals. This is probably due to the higher contribution of d^1 orbital of titanium atom in chemical bond formation with sulfur atom. Fig. 11 contains the HOMO and LUMO orbitals of the thiophene molecule before the adsorption process. Interestingly, the HOMO of thiophene is dominant at the middle of C-C and C-H bonds as shown in Fig. 11, whereas the electronic density in the LUMO of thiophene seem to be distributed over the whole thiophene molecule. Figs. 12 and 13 show the HOMO and LUMO molecular orbitals of the TiO_2 nanoparticles with adsorbed thiophene molecule, respectively. As shown in these figures, the HOMOs are strongly distributed over the thiophene molecule, whereas the LUMOs are dominant at the TiO_2 nanoparticle. The higher accumulation of the electronic density at the thiophene molecule depicted in the HOMO orbitals is a good electronic reason taken into account for the transfer of the electronic density from the thiophene molecule to the TiO_2 nanoparticle. Fig. 14 represents the spin polarized density of states of TiO_2+Thiophene couples with the distribution of spin densities shown in Fig. 15. It can be seen that the magnetization is mainly located on the thiophene molecule. As a matter of convenience, we presented the spin polarized DOSs and plots for two complexes only. The difference electron densities measured from atomic density for the thiophene molecule adsorbed on

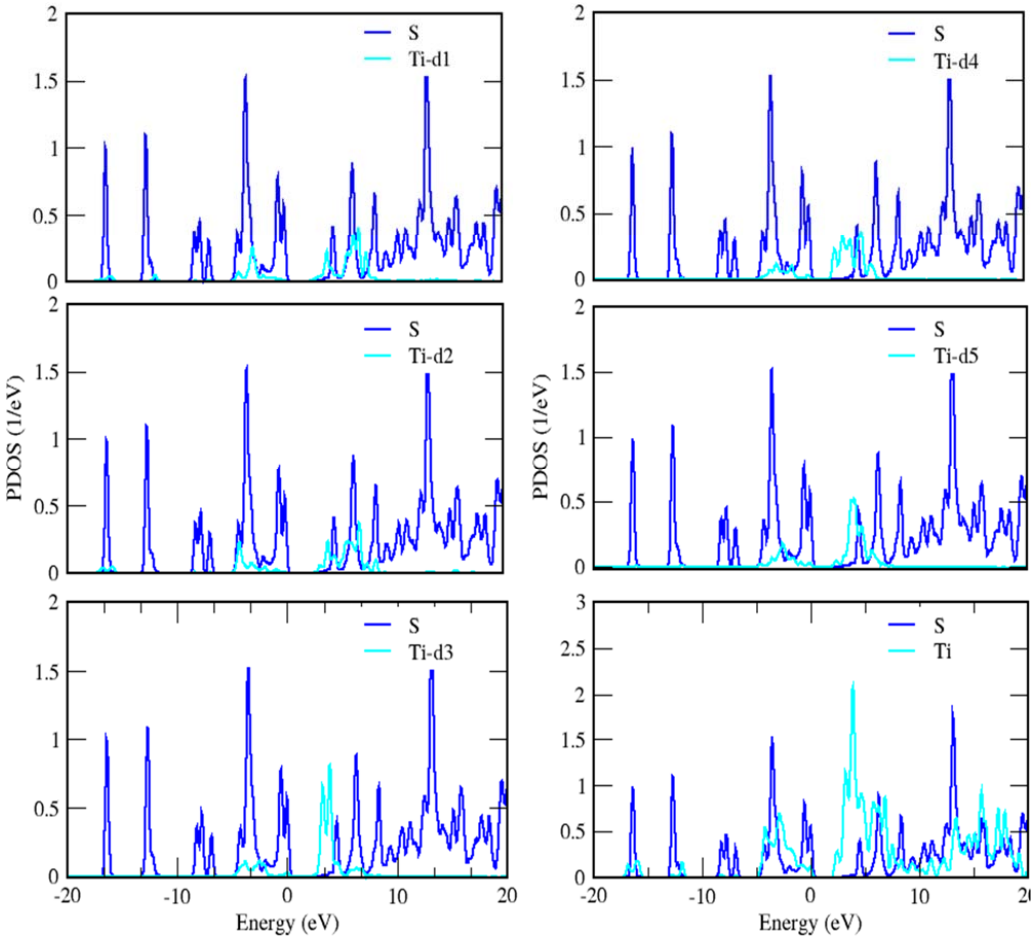

Fig. 10. Projected density of states for the sulfur atom of thiophene, titanium atom and different d orbitals of titanium.

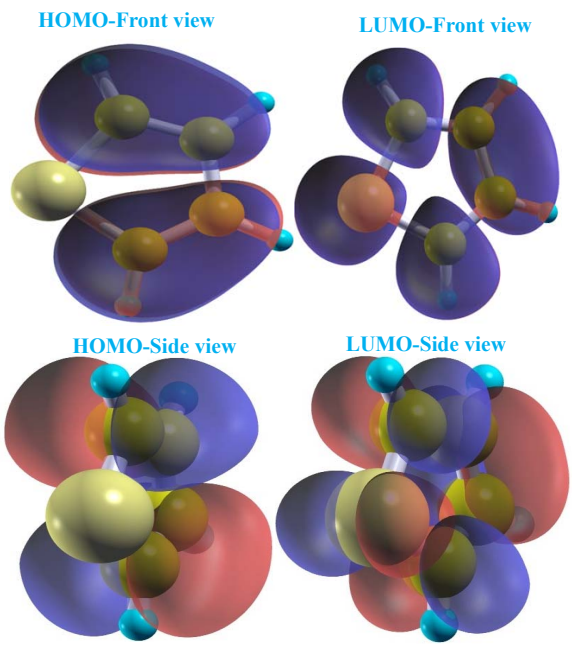

Fig. 11. HOMO and LUMO orbitals of a thiophene molecule in both front and side views.

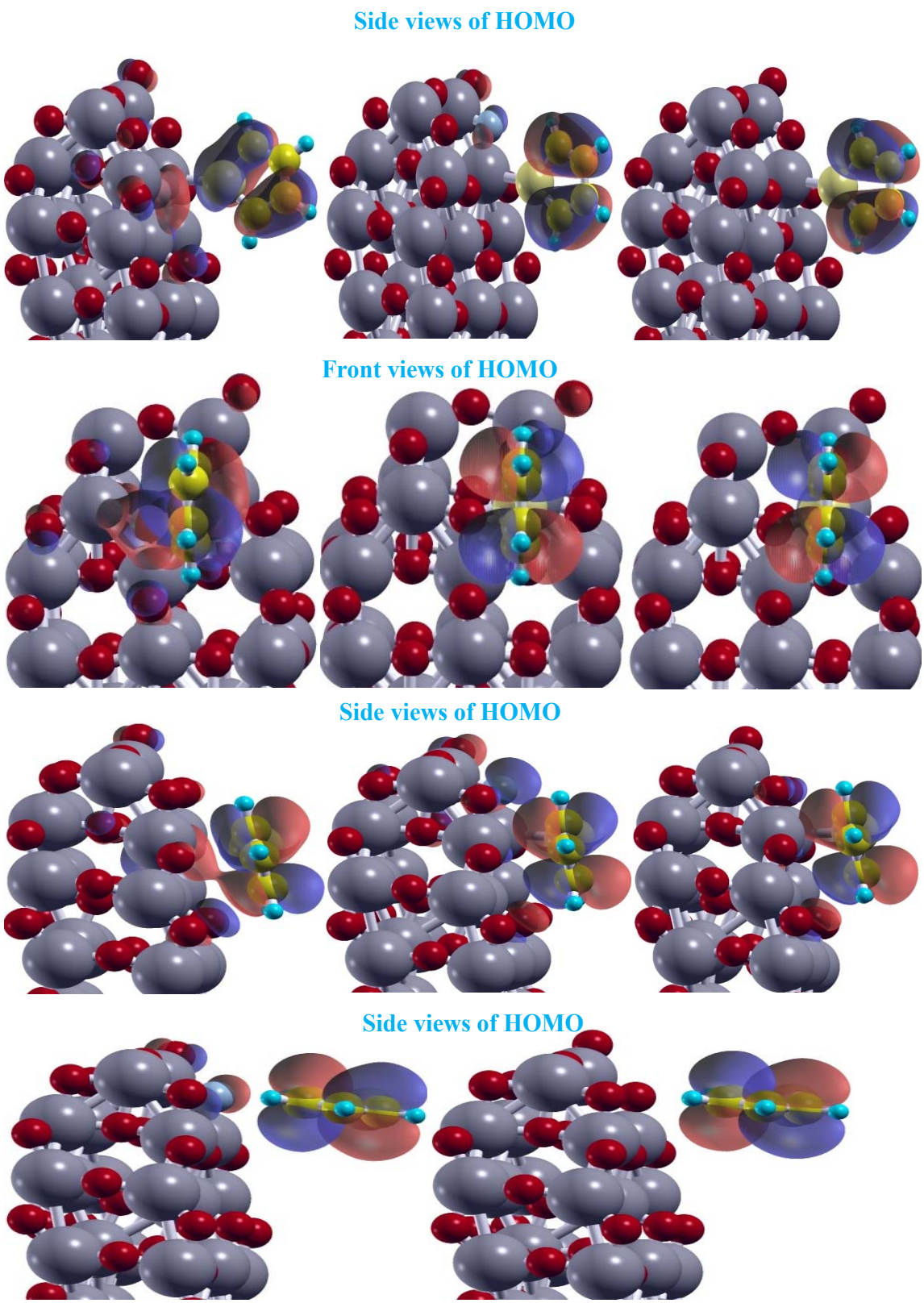

Fig. 12. The isosurfaces of HOMO molecular orbitals of thiophene molecule adsorbed on the considered nanoparticles.

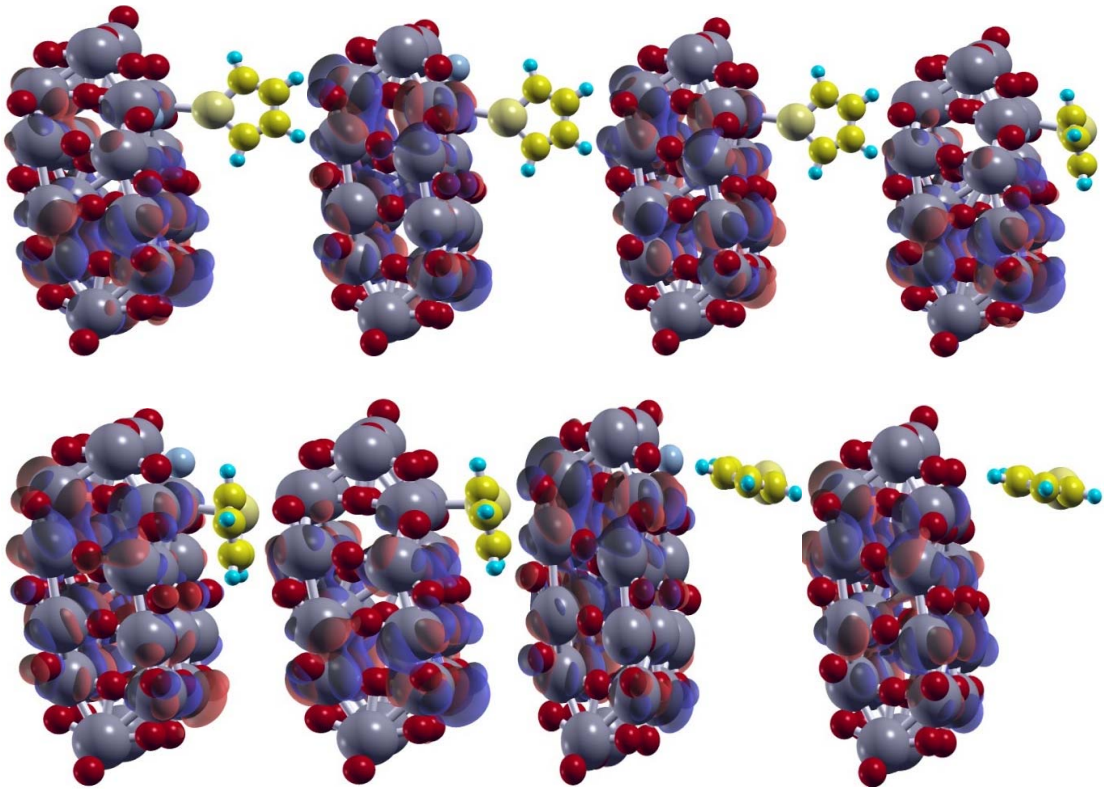

Fig. 13. The isosurfaces of LUMO molecular orbitals of thiophene molecule adsorbed on the considered nanoparticles

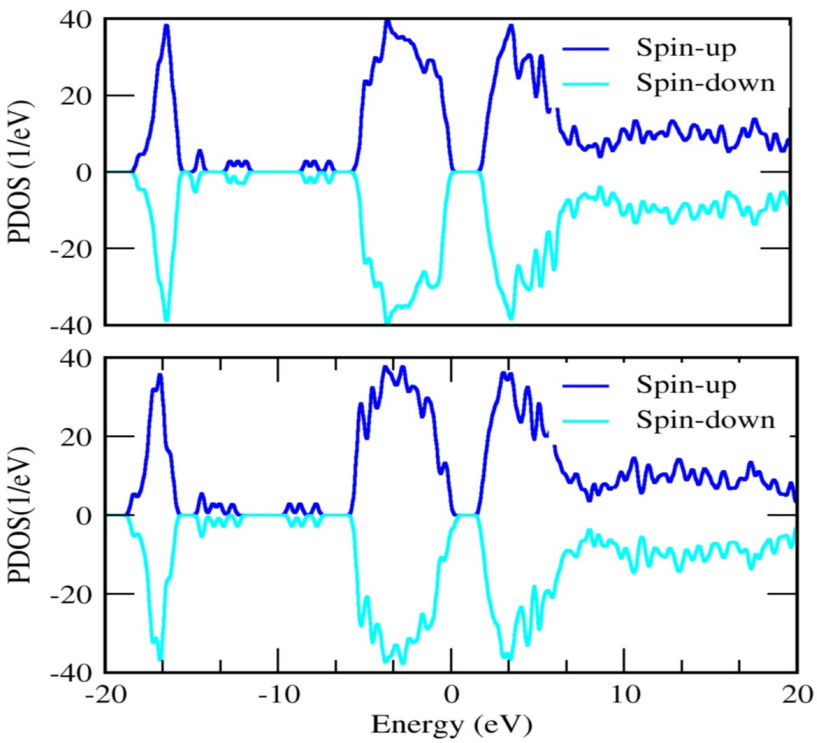

Fig. 14. Spin polarized density of states for the thiophene adsorption on the considered nanoparticles.

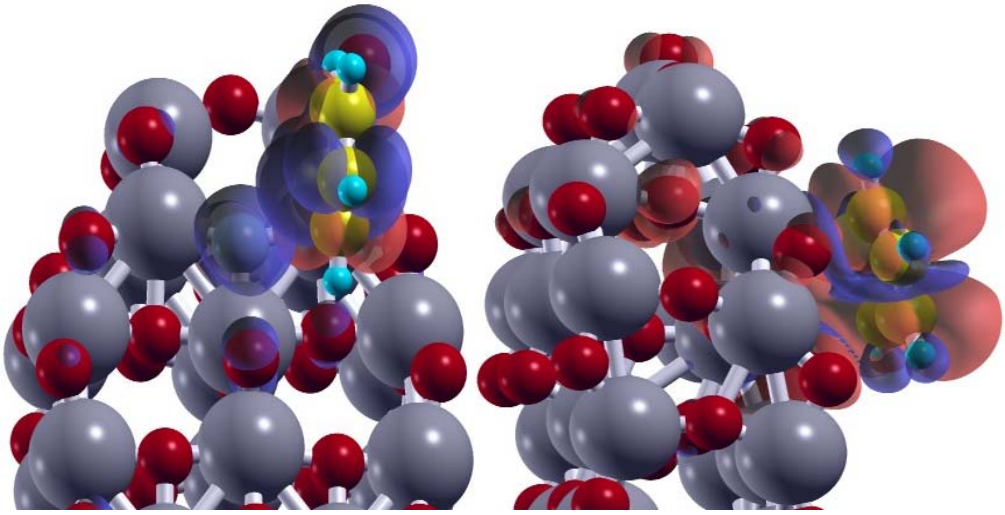

Fig. 15. Spin distribution density plots for the thiophene adsorption on the considered nanoparticles.

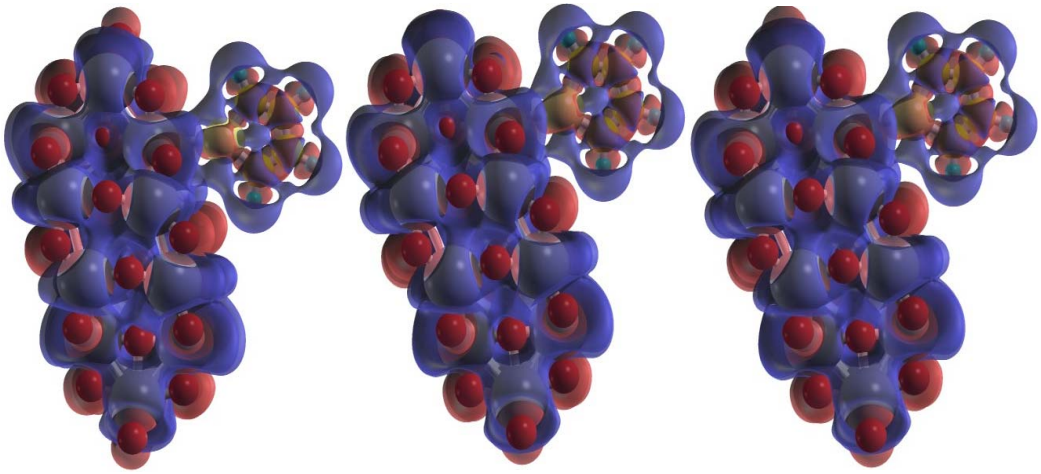

Fig. 16. The difference electron density measured from atomic density for the thiophene molecule adsorbed on the TiO2 nanoparticles.

the TiO_2 nanoparticles were displayed in Fig. 16. This figure shows the electronic density both on the nanoparticle and the thiophene molecule for clear comparison between the densities. To further analyze the charge transfer between nanoparticle and thiophene molecule, we reported the Mulliken charge values in Table 3. Our analysis of the charge transfer results indicates that thiophene adsorption induces a significant charge transfer of about -0.448 e from thiophene to the TiO_2 nanoparticle for configuration A, suggesting the donor property of thiophene molecule in reaction with TiO_2 nanoparticle. This would be an effective property to help in the development of efficient sensor and remover devices for thiophene detection in the environment.

CONCLUSIONS

In this letter, we have carried out density functional theory calculations on structural and electronic properties of undoped and N-doped TiO_2 anatase nanoparticles. The results reveal that the N-doped nanoparticles are more energetic than the undoped ones and can react with thiophene molecules more efficiently. With vdw interactions counted in calculations, it was found that the thiophene molecule is preferentially chemisorbed on the fivefold coordinated titanium site of TiO_2 nanoparticle. Parallel (S site) adsorption geometries are more stable than the perpendicular ones. The order of adsorption energy is calculated to be Parallel(S site)>Perpendicular(S

site)>Perpendicular (H site). We have also commented on the electronic properties of the studied systems including the DOS and molecular orbital plots in order to understand the electron transport phenomena. The obtained results indicate that the N-doped anatase nanoparticles are more active than the undoped ones. The N doping yields an increased affinity for TiO_2 nanoparticles to interact with thiophene molecules in the environment, being an efficient property to be utilized in sensing and removing applications. Our calculated results thus suggest a theoretical basis for the N-doped TiO_2 nanoparticles to be effectively employed in manufacturing the efficient sensor devices for thiophene recognition in the environment.

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CONFLICT OF INTEREST

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

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