Indian Journal of Chemistry
Vol. 57A, January 2018, pp. 34-43

A highly specific heterostructure composed of N-doped TiO_2 anatase nanoparticles and double layer Au for detection of thiophene molecule: A DFT study

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The adsorption of thiophene molecule on the pristine, N-doped and Cu/N codoped TiO_2-supported Au overlayers has been studied using density functional theory calculations, taking into consideration the effects of van der Waals interaction. Thiophene molecule can be adsorbed on both the Au and five-fold coordinated titanium sites of TiO_2 supported Au overlayers. Various adsorption configurations of thiophene over the considered TiO_2 supported Au overlayers are discussed. It is found that with Cu/N codoped nanoparticle as an adsorbent, the adsorption configuration is more stable and consequently the adsorption process is more energetically favorable. The adsorption of thiophene molecule on the N-doped TiO_2 supported Au overlayers is more energetically favorable than the adsorption on the undoped ones. On the Cu/N codoped nanoparticle, the adsorption process is more strongly favored. Thus, Cu/N-codoped system can interact with thiophene molecule more efficiently. The considerable overlaps between the PDOSs of the sulfur and titanium atoms indicate chemical bond forms between these two atoms. These chemical bonds confirm chemisorption of thiophene on the TiO_2 supported Au overlayers. After the adsorption process, the HOMOs are mainly distributed over the adsorbed thiophene molecule. The charge analysis based on Mulliken charges reveals that charge is transferred from the thiophene molecule to the TiO_2 supported Au. This study not only suggests a theoretical basis for adsorption behaviors of thiophene on the TiO_2-supported Au overlayers, but also provides an efficient strategy to design and improve highly efficient sensor devices for thiophene detection.

Keywords: Density functional theory, Thiophene, Titania, Supported gold overlayers, Gold overlayers, Molecular orbitals

TiO_2 is one of the most widely investigated metal oxide semiconductors with exceptional properties such as nontoxicity, strong oxidbillity, unique electronic structure, and long-term thermodynamic stability[1] It has found important applications in numerous fields such as photocatalysis, gas sensor devices, organic dye-sensitized solar cells and air pollution control. [2-5] Three polymorphs of TiO_2 with crystal structure data have been reported in the literature viz., anatase, rutile, and brookite[6]. Of these crystalline forms, the rutile form is found to be the most stable phase. Anatase and brookite have been extensively studied in comparison with the rutile polymorph. As the most favorable and broadly utilized photocatalysts material, the surface area and the quantum confinement effect of TiO_2 are two significant factors that define its properties. Anatase has higher reactivity than the rutile and anatase phases in some other surface processes[8-14]. It has attracted much attention because of its enhanced activity in some photocatalysis reactions such as TiO_2 supported metal particle reactions[15-17]. The main concern associated with TiO_2 is its wide band gap (3-3.2 eV), which greatly affects the photocatalytic activity and optical sensitivity. Due to the wide band gap TiO_2 can only absorb a small portion (3–5%) of the incoming solar light. Various efforts to enhance the photocatalytic activity of TiO_2 have been reported in the past decades including nonmetal doping[8].

It has been demonstrated that gold has less activity than other metals in many reactions. Haruta *et al.*[18] revealed that gold particles can enhance the combustion of CO molecule and promote various catalytic reactions. More recently, there has been a surge of interest in the study of the multicomponent hybrid structures composed of gold particles supported by metal oxides (especially TiO_2).[19-24] Oxide supported gold particles have found applications in some important reactions such as epoxidation of C_3H_6,[25] reduction of NO_x molecules[26]

and dissociation of SO_2 molecule.[27] TiO_2 is considered to be a very suitable candidate to be utilized as support material for gold particles.[28, 29] The interaction between gold nanoclusters and TiO_2 (rutile and anatase) particles have attracted wide attention in the past decades. For example, Vittadini *et al.*[30] examined the adsorption behaviors of gold clusters on the TiO_2 anatase (101) surfaces. The configuration and electronic state of SO_3 molecule adsorbed on Au surfaces have been been investigated by Chikashi *et al.*[31] Molina *et al.*[32] have also conducted a theoretical study of the adsorption of the O_2 and CO_2 on TiO_2 supported gold particles.

A material in the atmosphere which causes harmful effects on the public health and the environment is identified as an air pollutant. A typical air pollutant can be seen in different forms such as solid particles, liquid droplets or gasses. Thiophene is a heterocyclic compound and is considered as one of the most important fuel components. Thiophene molecule generates sulfur containing compounds by combustion, which are characterized as harmful materials participating in the environmental pollution. Since environment protection is a serious issue to the human health, the concentration of sulfur is rigorously controlled by using the appropriate strategies.

Herein, our work is focused on the development of novel sensing devices for sulfur removal from sulfur containing compounds. This gives rise to the production of clean fuels with low content of sulfur[33, 34]. An efficient metal oxide based gas sensor should have high sensitivity and response to any toxic material in the atmosphere, low cost manufacture and compatibility with modern electronic devises. Of the most important gas sensors, oxide supported gold nanoparticles have attracted large interest due to their high activity. Therefore, the design and development of hybrid multicomponent structures as sensor materials would be increasingly in demand for protection of environment from any external contaminant. In this regard, we carried out a DFT study of the structural and electronic properties of TiO_2 supported Au overlayers as potentially efficient sensor devices for chemical sensing of thiophene molecule.

Methodology

The first principles electronic structure calculations were carried out within the DFT[35,36] as implemented in the Open source Package for Material eXplorer (OPENMX3.8) code[37] OPENMX is an efficient software package for nano-scale materials simulations based on norm-conserving pseudopotantials and pseudo-atomic localized basis functions[38,39] Localized pseudoatomic orbitals were utilized in the description of wavefunction. The energy cutoff in our calculations was set at 150 Ry. The basis sets were defined based on pseudo-atomic orbitals (PAOs), which were centered on atomic sites. Our considered PAO basis functions include Ti: 3*s*-3*p*-1*d*, Au: 3*s*-3*p*-2*d*-1*f* and O, N: 2*s*-2*p*, within cutoff radii of basis functions set to the values of 7 for Ti, 9 for Au, 5 for O and N (all in Bohrs). The conventional generalized gradient approximation (GGA) parameterized by Perdew-Burke-Ernzerhof (PBE) was set for the exchange-correlation integral approximations[40] The charge exchange between the thiophene molecule and TiO_2 supported Au overlayer was described based on Mulliken population analysis. For optimization of the adsorption configurations of TiO_2 supported Au overlayers with adsorbed thiophene molecules, all atoms of the system are entirely relaxed until the force on each atom is less than 0.01 eV/Å. The size of the simulation box containing pristine TiO_2-supported Au nanoparticles is 20 Å × 20 Å × 30 Å, being larger than the realistic size of the complex system. 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. The adsorption configurations of thiophene on the pristine, N-doped and Cu-N codoped TiO_2 supported Au overlayers were studied in this work. XCrysDen program was used for visualization of the figures presented in this study[41].

Our chosen model of TiO_2 supported Au contained 88 atoms (16 Au, 48 O and 24 Ti atoms). The effects of long range van der Waals (vdW) interactions were taken into account by using Grimme's DFT-D2 approach[42]. The adsorption energy E_{ad}, is calculated as the difference between the total energy of the adsorption system with thiophene molecule $E_{(\text{composite + adsorbate})}$ and the sum of the energies of barely optimized TiO_2 supported Au overlayer $E_{\text{composite}}$ and thiophene molecule $E_{\text{adsorbate}}$. The adsorption energy is defined as follows:

$$E_{ad} = E_{(\text{composite + adsorbate})} - E_{\text{composite}} - E_{\text{adsorbate}} \quad \ldots(1)$$

Based on this equation, the adsorption energies of stable configurations would be negative. The more negative the adsorption energy, the more energy favorable the adsorption configuration.

We have constructed TiO_2 anatase nanoparticle by using a 3×2×1 supercell of TiO_2 anatase available in literature[43, 44]. The size of the studied TiO_2 nanoparticles was chosen following Lei *et al.*[45] and Liu *et al.*[46]. The considered structure of TiO_2 nanoparticle possesses two dangling oxygen atoms, with atomic charge ratio of Ti and O atoms as 1:2. The optimized structure of the pristine TiO_2 nanoparticle (Fig. 1) shows two types of titanium atoms in the crystal structure of TiO_2, viz., 5-fold coordinated (5*f*-Ti) and 6-fold coordinated (6*f*-Ti), as well as two types of oxygen atoms, indicated by 3-fold coordinated (3*f*-O) and 2-fold coordinated (2*f*-O) atoms.[47,48]. TiO_2 supported Au overlayer was constructed using Au nanoparticle placed on the TiO_2 anatase in an appropriate arrangement. The equilibrium structure of the undoped TiO_2-supported Au overlayer is given in Fig. 2.

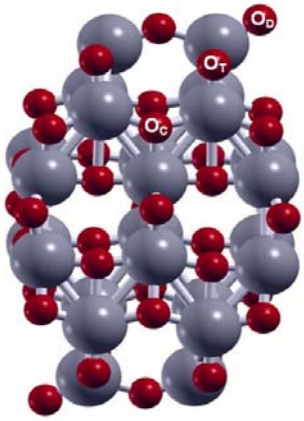

Fig. 1 – Representation of a pristine TiO_2 anatase nanoparticle. Two dangling oxygen atoms were used to set a 1:2 atomic charge ratio between the oxygen and titanium atoms.

Results and Discussion

Adsorption energies and geometries analysis

The adsorption configurations of thiophene on the TiO_2 supported Au overlayers are displayed in Figs 3-7. According to the structure of thiophene and

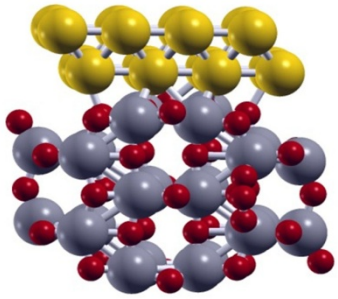

Fig. 2 – Optimized geometry of undoped TiO_2 supported Au overlayer. [The yellow, gray and red balls denote gold, titanium and oxygen atoms, respectively. TiO_2 was demonstrated to an appropriate support material for gold particles].

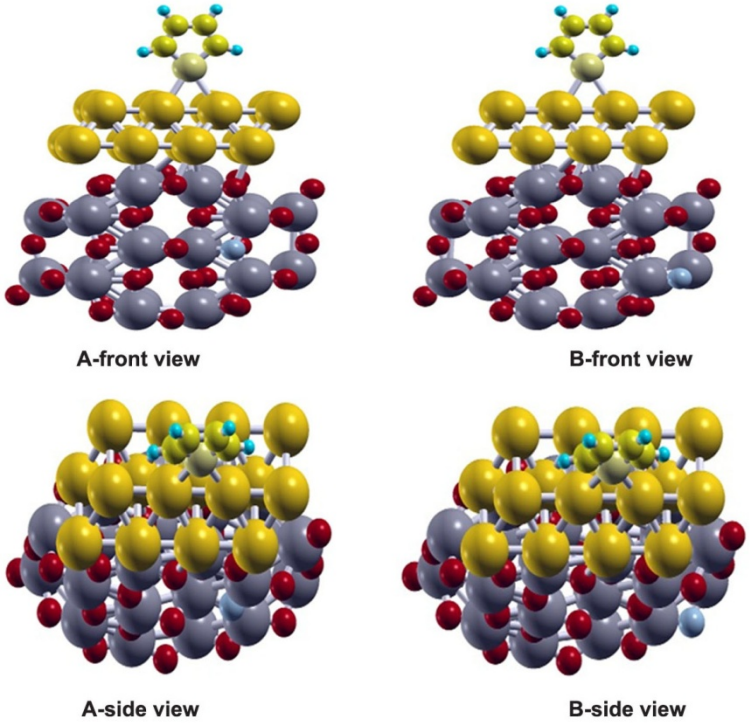

Fig. 3 – Optimized geometry configurations of the thiophene molecule adsorbed on the top Au sites of TiO_2 supported Au overlayers. [(A) Thiophene on the top-Au sites of O_C-substituted nanoparticle, (B) Thiophene on the top-Au sites of O_T-substituted nanoparticle].

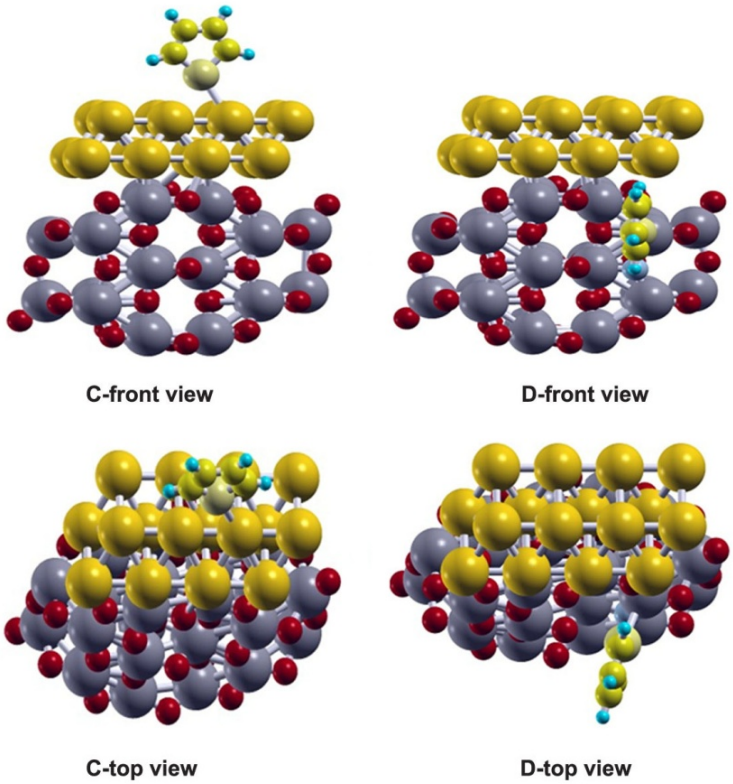

Fig. 4 – Optimized geometry configurations of the thiophene molecule adsorbed on the top Au and titanium sites of TiO_2 supported Au overlayers. [(C) Thiophene on the top-Au sites of pristine nanoparticle, (D) Thiophene on the titanium site of O_C-substituted nanoparticle].

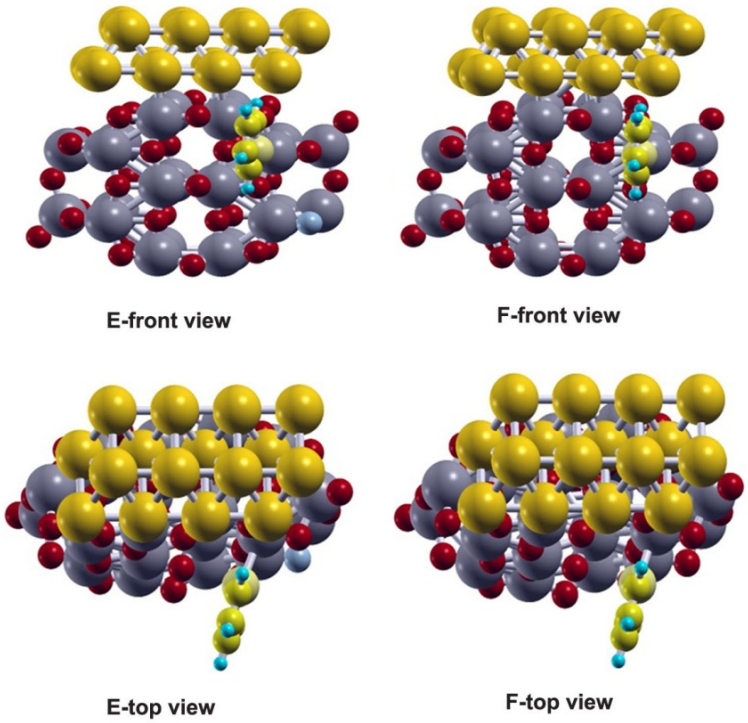

Fig. 5 – Optimized geometry configurations of the thiophene molecule adsorbed on the titanium sites of TiO_2 supported Au overlayers. [(E) Thiophene on the titanium site of O_T-substituted nanoparticle, (F) Thiophene on the titanium site of pristine nanoparticle].

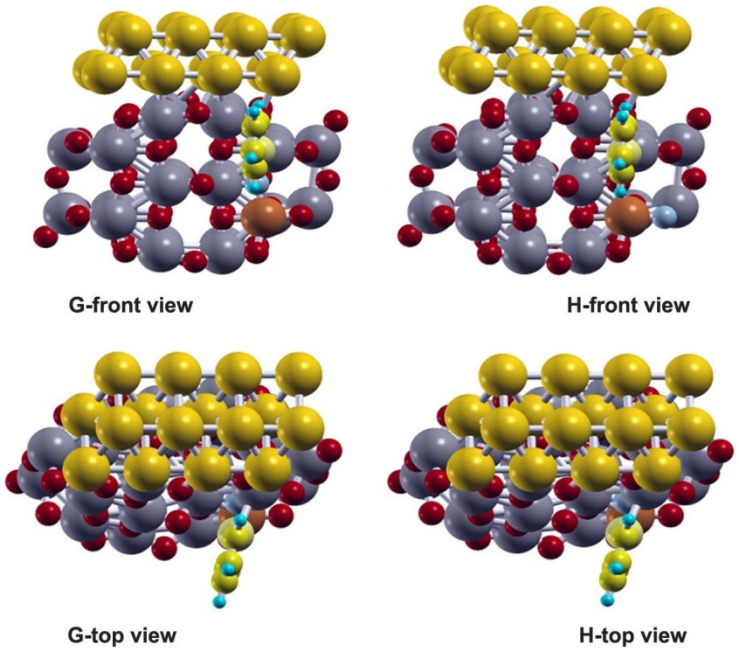

Fig. 6 – Optimized geometry configurations of the thiophene molecule adsorbed on the titanium sites of Cu-doped and Cu/N codoped TiO_2 supported Au overlayers. [(G) Thiophene on the top-Au sites of pristine nanoparticle, (H) Thiophene on the side-Au sites of pristine nanoparticle].

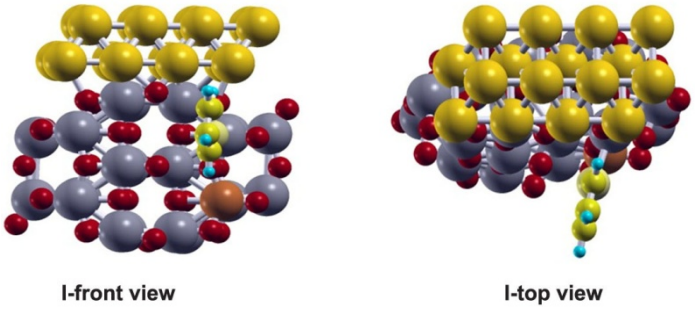

Fig. 7 – Optimized geometry configurations of the thiophene molecule adsorbed on the titanium sites of Cu-doped TiO_2 supported Au overlayers.

the results obtained from our calculations, there are two possible adsorption geometries of thiophene on the considered TiO_2 supported Au overlayers: (1) Adsorption on the top Au sites, wherein thiophene positioned toward the top Au sites, and coordinated to the Au sites by its active sulfur atom, and, (2) Adsorption on the five-fold coordinated titanium sites, wherein thiophene moves toward the titanium sites of the TiO_2 supported Au, forming strong chemical bonds. Configurations A and B in Fig. 3 represent the interaction of thiophene with N-doped TiO_2 supported Au overlayers, whereas configuration C shows the interaction between thiophene and pristine system. In contrast, configurations D-F represent the interaction of thiophene with five-fold coordinated titanium sites. We have also considered the adsorption of thiophene on the titanium sites of Cu/N codoped TiO_2 supported Au overlayers. The relevant adsorption configurations are shown in Figs 6 and 7. The results suggest that only sulfur atom of the thiophene molecule interacts with the TiO_2 supported Au nanoparticle, while the carbon atom does not contribute to the adsorption anymore.

Adsorption energies of thiophene molecule on the pristine, N-doped and Cu/N codoped TiO_2 supported Au overlayers were listed in Table 1. In can be seen that the adsorption energies follow the order: Cu/N codoped TiO_2 supported Au nanoparticle > N-doped

Table 1 – Adsorption energies (in eV) and Mulliken charges for thiophene molecule adsorbed on the TiO_2 supported Au overlayers

Config.	Adsorption energy (eV)		Mulliken charge
	PBE	DFT-D2	
A	-4.75	-7.76	-0.165
B	-4.16	-7.22	-0.167
C	-3.62	-6.58	-0.156
D	-4.77	-7.76	-0.201
E	-4.17	-7.20	-0.189
F	-3.90	-7.02	-0.189
G	-5.07	-8.06	-0.182
H	-5.06	-8.04	-0.175
I	-4.76	-7.68	-0.175

nanoparticle > pristine (undoped) nanoparticle. Thus, the adsorption of thiophene on the Cu/N codoped nanoparticle is stronger than the adsorption on the N-doped one. Both N-doped and Cu/N codoped nanoparticles have higher adsorption energy than the undoped ones, representing that the N-doped and Cu/N codoped nanoparticles can interact with thiophene more strongly. In contrast, the undoped nanoparticle has a weak mutual interaction with thiophene molecule. Of the pristine, N-doped and Cu/N codoped nanoparticles, the adsorption on the Cu/N codoped nanoparticle is the most energetically favorable process. In fact, the order of energy favorability is as follows: Cu/N codoped nanoparticle > N-doped nanoparticle > pristine nanoparticle.

For thiophene adsorption on both Au and titanium sites, it was found that the adsorption on the O_C-substituted nanoparticle is more favorable in energy than the adsorption on the O_T-substituted one. By considering these results, it can be concluded that the Cu/N codoped TiO_2 supported Au overlayer would be a promising sensor for thiophene detection in the environment. This is due to the fact that the adsorption energy of Cu/N codoped nanoparticle is more negative than that of N-doped and undoped nanoparticles. We have also corrected the adsorption energies by including van der Waals interactions in our calculations. The adsorption energies obtained from DFT-D2 methods are considerably increased when the effects of vdW interactions were taken into account. This is consistent with the previous study of Tamijani *et al.*[49] that reported the results of the adsorption of noble-gas atoms on the TiO_2 (110) surface based on van der Waals corrected DFT approach and revealed the increase in the adsorption energies caused by vdW interactions. Therefore, the vdW interactions were dominant during the adsorption of thiophene on the TiO_2 supported Au overlayers.

Charge population analysis

Mulliken population analysis was performed to reveal the charge distribution of the atoms in the system under investigation. In order to further examine the adsorption of thiophene molecule on the pristine and doped TiO_2 supported Au overlayers, the charge transfers between thiophene molecule and nanoparticle were analysed (Table 1). The charge transfer induced by thiophene adsorption was evaluated based on the following equation:

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

where Q_j is the value of Mulliken charge of particle j. The subscript "j" denotes the TiO_2 supported Au nanoparticle or thiophene molecule. The charge difference, ΔQ_j, represents the net charge exchange between the thiophene molecule and nanoparticle.

Based on charge analysis, we found that the electron charges were shifted from thiophene molecule to the TiO_2 supported Au nanoparticle. For example, configuration A represents a substantial charge transfer of about -0.165 $|e|$ (e is the electron charge) from the thiophene molecule to the TiO_2 supported Au, indicating that thiophene donates electrons to the nanoparticle.

Electronic structures

In order to highlight the electronic interactions between TiO_2 supported Au overlayer and thiophene molecule, we calculated the projected density of states (PDOSs) for the adsorption configurations of thiophene on the considered nanoparticles. Figure 8 shows the PDOSs for thiophene molecule adsorbed on the TiO_2 supported Au overlayers. Panels (a-f) show the PDOS spectra for configurations D-I, respectively. For all panels, we can see that the PDOSs of the sulfur atom of the thiophene molecule and titanium atom of the nanoparticle have significant overlaps in some energy levels. From these overlaps between the PDOSs of the interacting atoms, we can see that the sulfur atom forms a chemical bond with the fivefold coordinated titanium atom of the nanoparticle. Therefore, the sulfur atom of the thiophene molecule coordinated to the titanium atom, indicating that thiophene strongly interacts with TiO_2 supported Au overlayer. It should be noted that all configurations presented in this study provide a double contacting point between the nanoparticle and thiophene molecule.

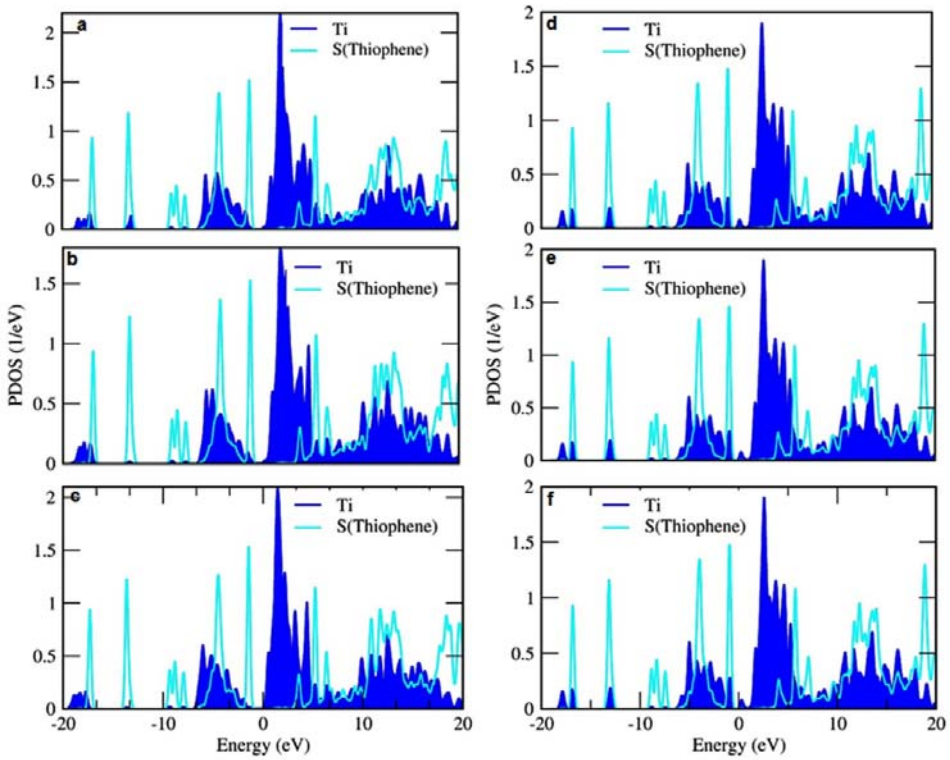

Fig. 8 – PDOSs of the titanium and sulfur atoms for thiophene molecule adsorbed on the TiO_2 supported Au overlayers, (a) configuration D; (b) configuration E; (c) configuration F; (d) configuration G; (e) configuration H; (f) configuration I.

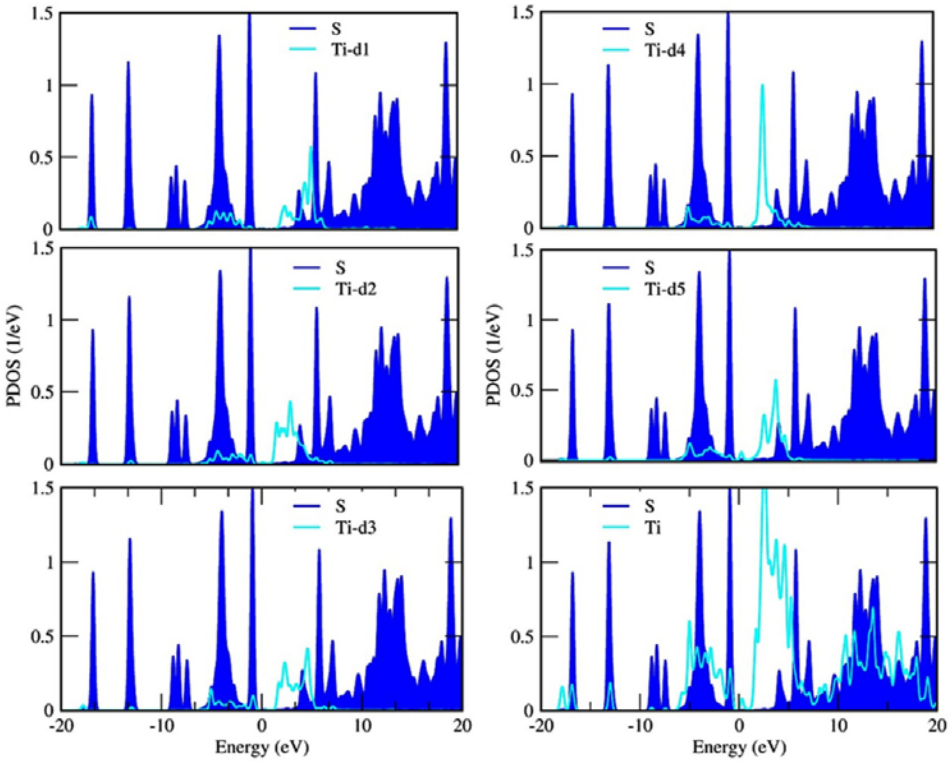

Fig. 9 – PDOSs of the sulfur atom of thiophene, titanium atom and five *d* orbitals of the titanium for thiophene molecule adsorbed on the TiO_2 supported Au overlayers (configuration D).

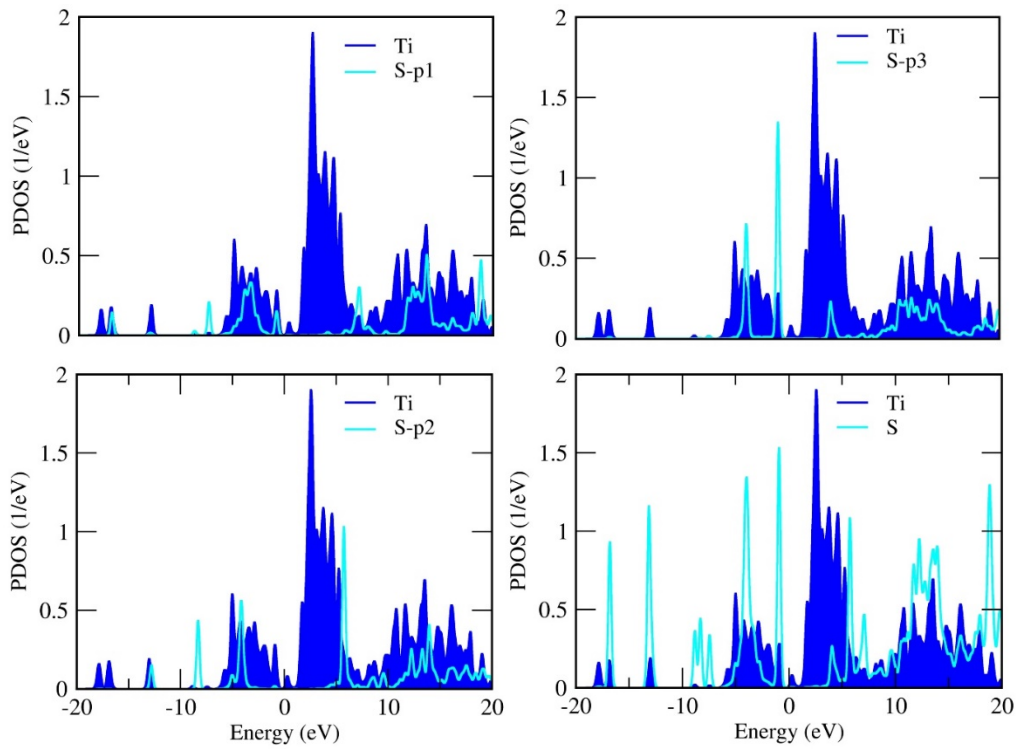

Fig. 10 – PDOSs of the titanium atom, sulfur atom of thiophene, and three *p* orbitals of the sulfur for thiophene molecule adsorbed on the TiO_2 supported Au overlayers.

We also calculated the PDOSs of the different *p* and *d* orbitals of the titanium and sulfur atoms. The relevant PDOSs were displayed in Figs 9 and 10. Figure 9 shows the PDOSs of the sulfur atom of the thiophene molecule and five *d* orbitals of the titanium atom. As can be seen, there is a large overlap between the PDOSs of the sulfur atom and d^1 orbital of the titanium atom. The PDOSs of the three *p* orbitals of the sulfur atom and the titanium atom, representing higher overlaps between the PDOSs of the titanium atom with p^1 orbital of the sulfur atom are displayed in Fig. 10. This indicates that the titanium atom has a significant mutual interaction with the p^1 orbital of the sulfur atom.

In addition, the molecular orbital calculations were also conducted to further analyze the electronic density distribution for the considered adsorption configurations. Figure 11 displays the HOMO and LUMO for isolated thiophene molecule along with the corresponding DOS spectra (before the adsorption). Interestingly, the HOMO of thiophene is dominant at the middle of C-C and C-H bonds as shown in Fig. 11, while the electronic density in the LUMO of thiophene seems to be distributed over the entire thiophene molecule. The isosurfaces of HOMOs and

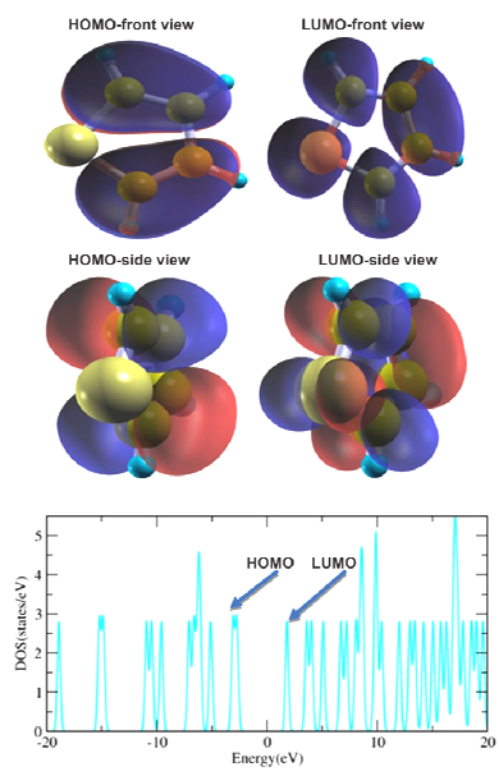

Fig. 11 – HOMO-LUMO isosurfaces and total density of states of an isolated thiophene molecule.

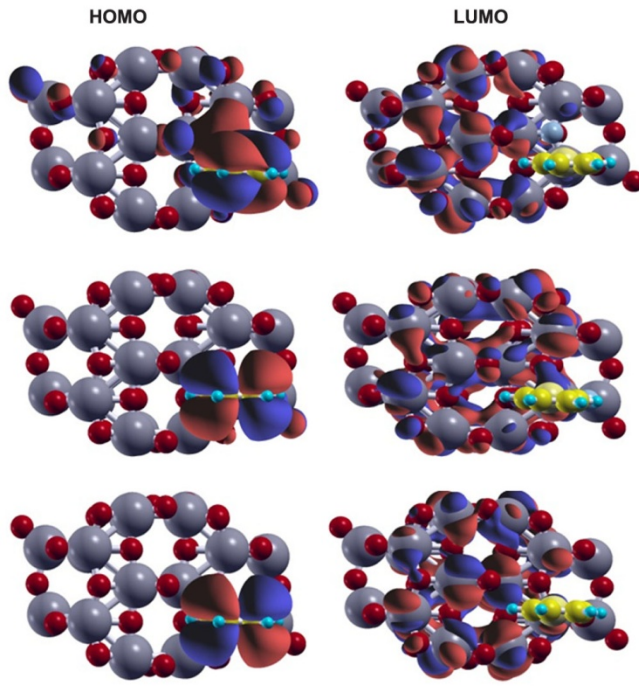

Fig. 12 – Isosurfaces of HOMOs and LUMOs for the adsorption systems of thiophene with the studied nanoparticles.

LUMOs for thiophene molecule on the considered TiO_2 supported Au overlayers (After the adsorption) are represented in Fig. 12. As can be seen from this figure, the electronic density in the HOMOs were mainly distributed over the adsorbed thiophene molecule, while the LUMOs were contributed largely by the TiO_2 nanoparticle. This contribution of the HOMOs of the adsorption configurations by thiophene molecule shows that the adsorption of thiophene influences the electronic density distribution over the adsorption systems and this feature can be useful for chemical sensing of thiophene by TiO_2 supported Au overlayers.

Conclusions

In this study, we have carried out a systematic study of the adsorption behavior of thiophene on the pristine, N-doped and Cu/N codoped TiO_2 supported Au overlayers by density functional theory calculations. We have considered thiophene adsorption on both Au and fivefold coordinated titanium sites of the nanoparticle. It was found that the thiophene molecule interacts with TiO_2 supported Au overlayer by its active sulfur atom, providing double contacting point at the interface region. The order of adsorption energy is: Cu/N codoped TiO_2 supported Au > N-doped nanoparticle > pristine (undoped) nanoparticle, which in turn reflects the order of configuration stability. The results also indicate that the interaction of thiophene molecule with N-doped TiO_2 supported Au overlayer is energetically more favorable than the interaction with pristine (undoped) one. On the Cu/N codoped TiO_2 supported Au overlayer, the adsorption of thiophene is more strongly favored from the energy point of view. Thus, Cu/N codoping is favorable for the interaction of thiophene with TiO_2 supported Au overlayers, indicating that N-doped and Cu/N codoped systems are promising materials for sensor devices for chemical sensing of thiophene in the environment. Mulliken population analysis reveals a substantial charge transfer from the thiophene molecule to the TiO_2 supported Au to overlayer. After thiophene is adsorbed, the PDOSs of the interacting atoms show considerable overlap, indicating the formation of chemical bond between the thiophene molecule and nanoparticle. Molecular orbital analysis indicates that the HOMOs of the adsorption configurations were mainly distributed over the adsorbed thiophene molecule.

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