

ORIGINAL RESEARCH PAPER

TiO₂/Gold nanocomposite as an extremely sensitive molecule sensor for NO₂ detection: A DFT study

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Abstract

First-principles calculations within density functional theory (DFT) have been performed to investigate the interactions of NO₂ molecules with TiO₂/Gold nanocomposites in order to completely exploit the adsorption properties of these nanostructures. Given the need to further comprehend the behavior of the NO₂ molecules positioned between the TiO₂ nanoparticle and Au monolayer, we have geometrically optimized the complex systems consisting of the NO₂ molecule oriented at appropriate positions between the nanoparticle and Au monolayer. The structural properties such as bond lengths, bond angles, adsorption energies and Mulliken population analysis and the electronic properties including the density of states and molecular orbitals have been also analyzed in detail. The results indicate that the interaction between NO₂ and undoped TiO₂-N/Gold nanocomposites is stronger than that between gas molecules and N-doped TiO₂/Gold nanocomposites, which reveals that the pristine nanocomposite can react with NO₂ molecule more efficiently. Therefore, the obtained results also suggest a theoretical basis for the potential applications of TiO₂/Gold nanocomposites in gas sensing, which could help in the developing of novel TiO₂ based advanced sensor devices.

Keywords: Density Functional Theory; TiO₂; NO₂; TiO₂/Gold nanocomposite; Density of States

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INTRODUCTION

Titanium dioxide has fascinated exciting interests as an excellent semiconductor material due to its peculiar properties such as non-toxicity, high catalytic efficiency and extensive band-gap [1]. TiO₂ has been broadly employed in numerous fields such as photo-catalysis, gas sensing, organic dye-sensitized solar cells, water-splitting and removal of air pollutants [2, 3, 4, 5]. It has been found in three important crystallographic phases namely anatase, rutile, and brookite [6]. The

photocatalytic properties of TiO₂ were limited because of its large band gap (3.2 eV) and that's why the TiO₂ only absorbs a minor percentage (3-5 % of the incoming solar light). TiO₂ doping with some nonmetal elements such as nitrogen is a suitable method, which would enhance the optical response of TiO₂ to the visible area and recover its photocatalytic properties [7, 8]. Newly, oxide supported Au nanoparticles have involved significant attention due to the catalytic activities of these materials at small temperatures [9, 10]

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for a progressively greater number of oxidation processes. From the experimental viewpoint, several propositions have been considered for the source of the excellent activity of Au nanoparticles. Goodman *et al.* [11] suggested size and effects of the band structure and measure the onset of the reactivity to look when the Au particles become as tiny as two monolayers at which point they subject to a change from a metallic to a separating state. From the theoretical standpoint, the clarifications of the low-temperature activity of supported Au nanoparticles are also numerous. By now, a number of density functional theory calculations have been published for O₂ adsorption and CO+O₂ reaction at different Au collections. Hakkinen Landman and co-workers [12] HL identified in their calculations the charging of the Au particles as an imperative parameter. With the large number of suggestions for essential parameters accounting for the extraordinary high reactivity of supported Au particles, there are many theoretical investigations, which have been considered for more systems. The adsorptions of the O₂ and CO₂ and reaction at gold nanoparticle models supported by TiO₂ surfaces have been investigated by density functional theory study [13]. However, numerous computational studies of N-doped TiO₂ anatase and Au nanoparticles have been published separately, explaining some of the important electronic and structural properties of these particles. For instance, Liu *et al.* [14] studied the adsorption of NO molecule on undoped and N-doped TiO₂ anatase nanoparticles. Carrying out first-principles calculations, Liu *et al.* suggested that the N-doped TiO₂ anatase nanoparticles can interact with CO molecule more capably compared to the pristine ones [15]. There are a few computational and experimental studies on the adsorption behaviors of TiO₂/Gold nanocomposites. NO₂ molecules have been characterized as toxic gases, which are mainly emitted from power plants and vehicle engines. So, controlling the concentrations of these injurious molecules is a vital subject to public health and environmental protection [16]. In this study, the interaction of NO₂ molecules with TiO₂/Gold nanocomposites has been investigated by DFT computations. We presented here results of calculations of complex systems consisting of NO₂ molecule positioned between the TiO₂ anatase nanoparticle and Au monolayer. The electronic structures of the adsorption systems have been

also analyzed including the projected partial density of states (PDOS) and molecular orbitals. The main aim of this study is to provide a general understanding on the adsorption behaviors of TiO₂/Gold nanocomposites as the effective sensor devices.

COMPUTATIONAL METHODS

Density functional theory

Density Functional Theory (DFT) calculations [17, 18] were performed with the Open source Package for Material eXplorer (OPENMX) ver. 3.7 [19], being an efficient software package for nano-scale materials simulations based on DFT, norm-conserving pseudopotentials, and pseudo-atomic localized basis functions [20, 21]. Pseudo atomic orbitals (PAO's) were used as basis sets. In the calculations related to the energetics of the system, the cutoff energy of 150 Rydberg is considered, which is demonstrated to be the most important criterion related to the computational effort and accuracy. The employed PAO's were generated by using the basis sets (tree-s, three-p, one-d) for Ti atom, (three-s, three-p, two-d, one-f) for Au atom, (two-s and two-p) for O and N atoms, within cutoff radii set to the values of 7 for Ti, 9 for Au, 5 for O and N (all in Bohrs). As an exchange-correlation energy functional approximation, the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof form (PBE) was utilized [22]. The convergence criteria of the self-consistent field (SCF) and energy calculation have been set to the values of 1.0×10^{-6} Hartree and 1.0×10^{-4} Hartree/bohr, respectively. In the course of geometry optimization, 'Opt' is used as the geometry optimizer, which is a robust and efficient scheme. All atoms of the considered nanocomposites were allowed to relax. The chosen pristine and N-doped nanocomposites are placed in a 20 Å × 20 Å × 30 Å box, which is much bigger than the size of the composites. The thickness of the vacuum spacing is 11.5 Å, which is essential for reducing the interaction between the nearest particles according to the periodic boundary conditions. The open-source program XCrysDen [23] was employed for picturing data such as molecular orbitals and to prepare the Figures considered in this study. The box considered in these computations contains 86 atoms (14 Au, 48 O and 24 Ti atoms) of undoped or N-doped TiO₂ nanoparticle with Au surface. The Gaussian broadening method for evaluating

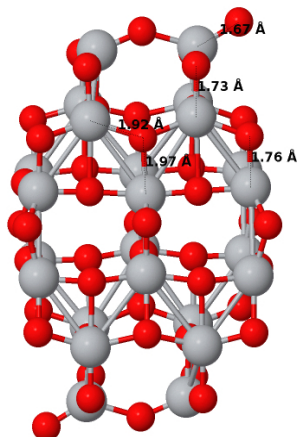


Fig. 1. Optimized geometry of a 72 atom TiO₂ anatase nanoparticle with bond length results prepared from 3×2×1 unit cells.

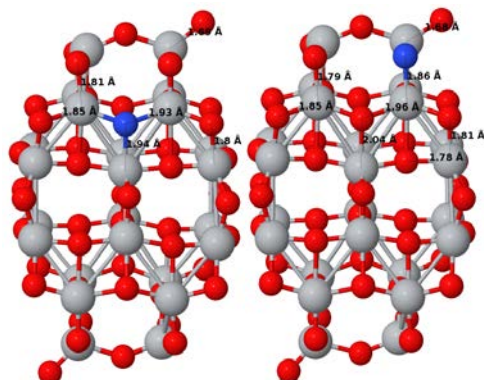


Fig. 2. Optimized N-doped TiO₂ anatase nanoparticles. The larger gray spheres are Ti atoms and the small red and blue ones represent O and N atoms, respectively.

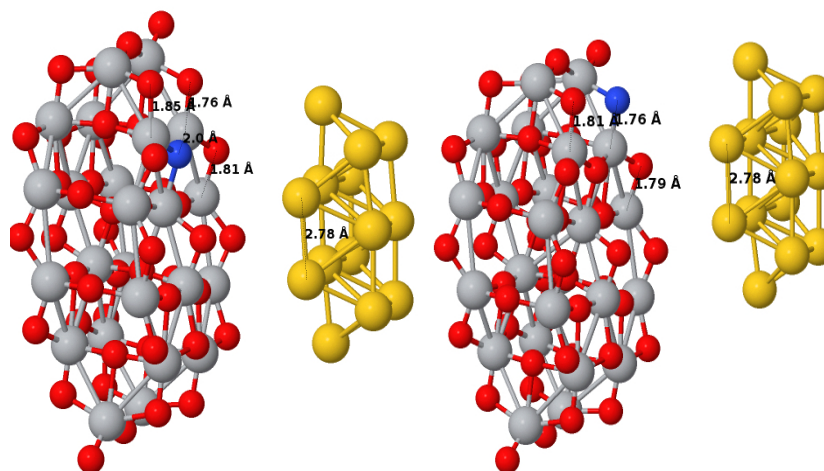


Fig. 3. Optimized geometries of two types of N-doped TiO₂/Gold nanocomposites. The yellow, gray, red and blue balls denote gold, titanium, oxygen and nitrogen atoms, respectively.

electronic DOS is used. A 21×21×21 Γ -centered k-point mesh is used in the calculations associated with the electronic DOS. The adsorption energy of gas molecules adsorbed on the TiO₂/Gold nanocomposite is evaluated using the following formula:

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

where $E_{(composite + adsorbate)}$ is the total energy of the adsorption system, $E_{composite}$ is the energy of the TiO₂/Gold nanocomposite, and $E_{adsorbate}$ is the energy of isolated gas molecules. According to this definition, the adsorption energies of stable configurations are negative; the more negative the adsorption energy, the more energy favorable the complex system.

Modeling TiO₂/Gold nanocomposites

The considered TiO₂ anatase nanoparticles containing 72 atoms were made by setting 3×2×1 numbers of TiO₂ unit cells along x, y and z axis, respectively. The unit cell was taken from "American Mineralogists Database" webpage [24] and was reported by Wyckoff [25]. Fig. 1 displays the optimized geometry of a 72 atom TiO₂ anatase nanoparticle prepared from 3×2×1 unit cells. Two suitable oxygen atoms of TiO₂ nanoparticle were substituted by nitrogen atoms to construct the N-doped particles. In one doping configuration, a nitrogen atom substitutes an oxygen atom in the middle of the particle and the other configuration characterizes the replacement at twofold coordinated oxygen position. The optimized geometries of the N-doped TiO₂ anatase nanoparticles were shown in Fig. 2.

Moreover, the coupled structures of N-doped TiO₂ and Au nanoparticle were presented in Fig. 3. The crystal model of TiO₂ anatase nanoparticle contains two types of titanium atoms, referred to as five-fold (5f-Ti) and six-fold (6f-Ti), as well as two types of oxygen atoms, specified by three-fold (3f-O) and two-fold (2f-O) O atoms. Generally, the 2f-O and 5f-Ti atoms are more reactive than the 3f-O and 6f-Ti atoms due to the undercoordination in 2f-O and 5f-Ti atoms. Fig. 4 shows the structure of the considered pristine Au monolayer. A gold structure consisting of 14 Au atoms has been inspected in this study and coupled with TiO₂ nanoparticle in order to model a TiO₂/Gold nanocomposites. The 86 atom TiO₂/Gold nanocomposite placed in a large cubic supercell has been represented in Fig. 5.

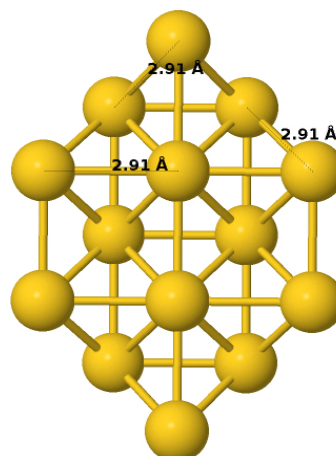


Fig. 4. Optimized geometry of an Au monolayer structure with bond length results.

RESULTS AND DISCUSSION

Bond lengths, angles and adsorption energies

The interaction of NO₂ molecule between TiO₂/Gold nanocomposites has been also shown in Fig. 6 as named by types A-C adsorption configurations. Adsorption on the Au nanoparticle is found to be more energetic than the adsorption on the TiO₂ nanoparticle. The reason can be easily checked using the calculated adsorption energies and molecular orbital results. At the interface of the adsorption complex, the NO₂ molecule preferentially interacts with the Au nanoparticle, being mostly attributed to the higher activity of this nanoparticle in adsorption processes. Unlike Au nanoparticle, TiO₂ nanoparticle does not interact with NO₂ molecule due to its lower activity in the composite structures during the adsorption process. In configurations A and B, NO₂ molecule interacts with nitrogen doped nanocomposite and the other configuration contains the NO₂ molecule

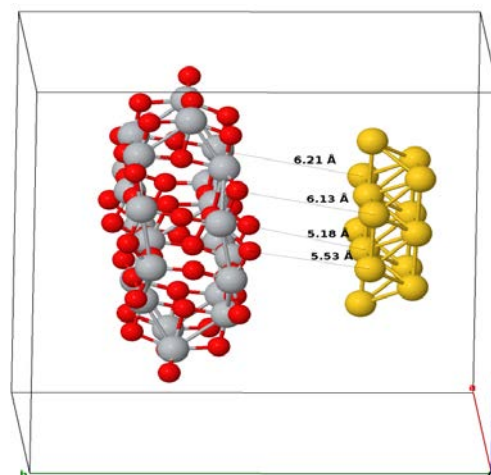


Fig. 5. Optimized geometry of the considered TiO₂/Au nanocomposites constructed from anatase nanoparticle and Au monolayer.

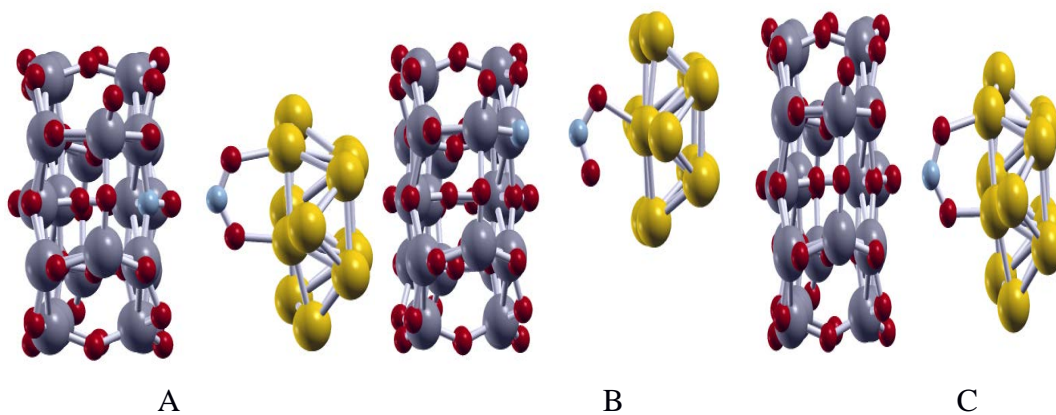


Fig. 6. Top view of the optimized geometry configurations of the interaction of NO₂ molecule with TiO₂/Gold nanocomposites. The NO₂ molecule is preferentially adsorbed on the Au particle surface.

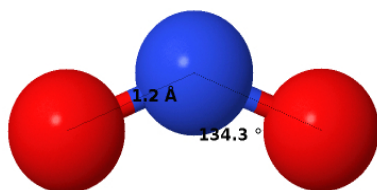


Fig. 7. Structure of NO₂ molecule before the adsorption process (Non-adsorbed state).

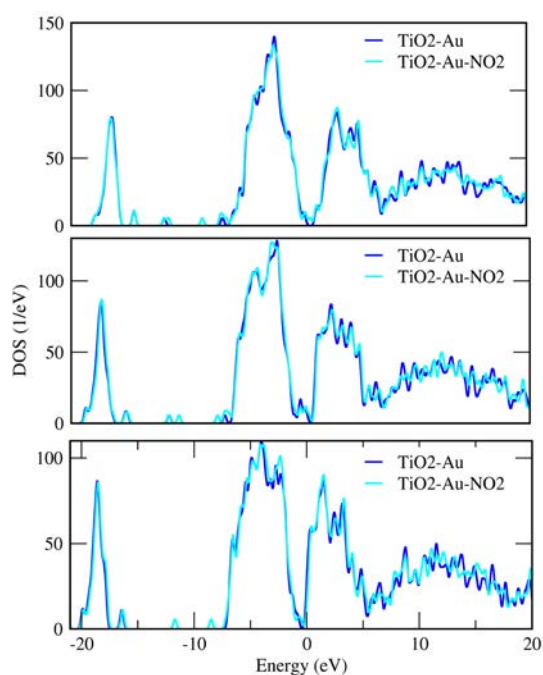


Fig. 8. DOS for the pristine and two types of N-doped TiO₂/Gold nanocomposites. a: A complex; b: B complex and c: C complex. The Fermi energy is set to zero denoted by orange solid line.

Table 1. Bond lengths (in Å) for and angles (in degrees) of NO₂ molecule adsorbed on TiO₂/Gold nanocomposites.

Type of complex	Au-O1	Au-O2	N-O1	N-O2	O-N-O
A	2.21	2.29	1.31	1.32	121.5
B	2.36	---	1.30	1.33	116.6
C	2.23	2.39	1.31	1.33	119.9
Before adsorption	---	---	1.19	1.19	134.3

Table 2. Adsorption energy and Mulliken charge values for NO₂ molecule adsorbed on TiO₂/Gold nanocomposites.

Type of complex	Adsorption energy (eV)	Mulliken charge (e)
A	-2.10	+0.0038
B	-1.96	+0.118
C	-2.32	+0.145

adsorbed on the pristine nanocomposite. The adsorption of NO₂ molecule on the nanocomposite in configuration C leads to the most stable complex from the energetic viewpoint, compared to the other complexes. Table 1 included the lengths for N-O bonds of the adsorbed NO₂ molecule and the newly-formed Au-O and O-N-O bond angles before and after the adsorption process. The results of this table indicate that the N-O bonds of the adsorbed NO₂ molecule are stretched after the adsorption due to the transference of electronic density from the old Au-Au and N-O bonds to the newly-formed Au-O bonds between nanocomposite and NO₂ molecule. The structure of NO₂ molecule before the adsorption process has been displayed with bond length and bond angle results in Fig. 7. The O-N-O bond angle of the NO₂ molecule after the adsorption on the considered nanocomposites was decreased. This decrease could be mostly ascribed to the formation of new bond and therefore transferring the electronic density from the old bonds of nanocomposite and adsorbed NO₂ molecule to the newly-formed bonds, which makes the weakening of the N-O bonds of NO₂ molecule [14, 15]. This formation of new bond also increases the p characteristics of bonding molecular orbitals so that the *sp*² hybridization of nitrogen in the NO₂ molecule becomes *near-sp*³. The adsorption energy values for nanocomposites have been reported in table 2. Adsorption on the undoped nanocomposite is found to be energetically more favorable than the adsorption on the N-doped ones, which means that the N doping has a deactivating role on the adsorption of NO₂ on Au particles at the interface of TiO₂/Gold nanocomposites. In other words, pristine nanocomposite can react with NO₂ molecule more efficiently. The adsorption energy of configuration C is about -2.32 eV, suggesting the most energy favorable adsorption configuration in comparison with the other configurations.

Electronic structures

Fig. 8 presents the total density of states (TDOS) for pristine and two types N-doped TiO₂/Gold nanocomposites before and after the adsorption process. This figure shows that a small peak was created in the DOS of N-doped nanocomposite at the energy values close to -12 eV. The Fermi energy is set to zero denoted by orange solid line in Fig. 8. The TDOS of nanocomposites only exhibit small differences in comparison with the isolated

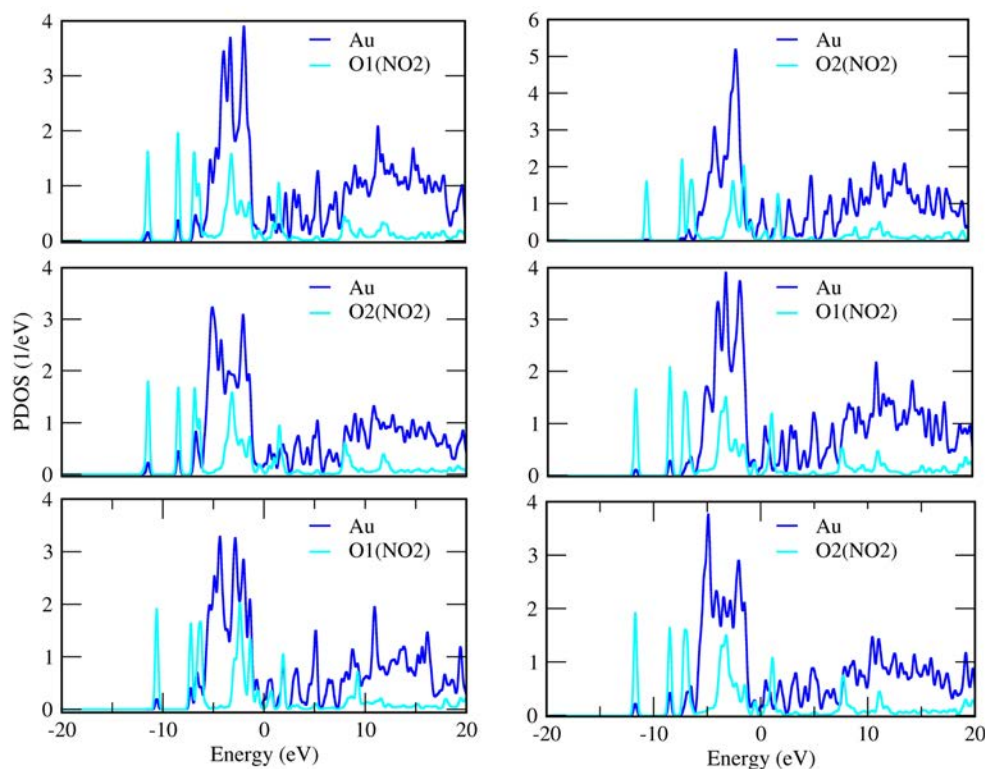


Fig. 9. PDOS for the adsorption complexes of TiO₂/Gold nanocomposites, a: A complex; b: A complex; c: B complex; d: B complex; e: C complex; f: C complex.

non-adsorbed nanocomposites. These differences are included both shifting of energies of the peaks and appearing some peaks in the DOS of the considered systems. However, these changes in energy of the states would affect the electronic transport properties of the nanocomposites and this feature can be useful for designing and manufacturing NO₂ sensors in the adsorption process. The projected partial density of states (PDOS) for the interaction of NO₂ molecule with TiO₂/Gold nanocomposites have been displayed in Fig. 9 (a-f). Panels (a, b) present the PDOS of the oxygen atom of NO₂ molecule and the Au atom for configuration A. The large overlap between the PDOS of these two atoms shows that the oxygen atom of NO₂ molecule forms a chemical bond with the Au atom of nanocomposite, suggesting the effective interaction of NO₂ molecule from this site. The PDOSs for NO₂ interaction with nanocomposite in other two configurations have been also presented as panels (c-d and e-f), which indicates a high overlap between the PDOS of oxygen atom of NO₂ molecule and the Au atom

of nanocomposite. Fig. 10 (a-f) shows the PDOS of the Au atom before and after the adsorption on the considered nanocomposites, which also suggests a shifting of the PDOS of Au atom to the lower energy values. To fully analyze the charge transfer in the course of adsorption process, the isosurfaces of HOMO and LUMO molecular orbitals for NO₂ adsorption on the nanocomposites have been shown in Fig. 11, which suggests that the HOMO is mainly localized on the TiO₂ particle, whereas the LUMO is strongly localized on the Au particle. For brevity, the isosurfaces for one configuration have been only given.

Mulliken Charge Analysis

To further explain the charge transfer between NO₂ molecule and TiO₂/Gold nanocomposites, we report in table 2 the partial charge values based on Mulliken charge approach. The charge difference for the particle *i* after and before adsorption, was evaluated using the following formula:

$$\Delta Q_i = Q_{i(\text{in complex})} - Q_{i(\text{in vacuum})} \quad (2)$$

where Q_i is the value of Mulliken charge of

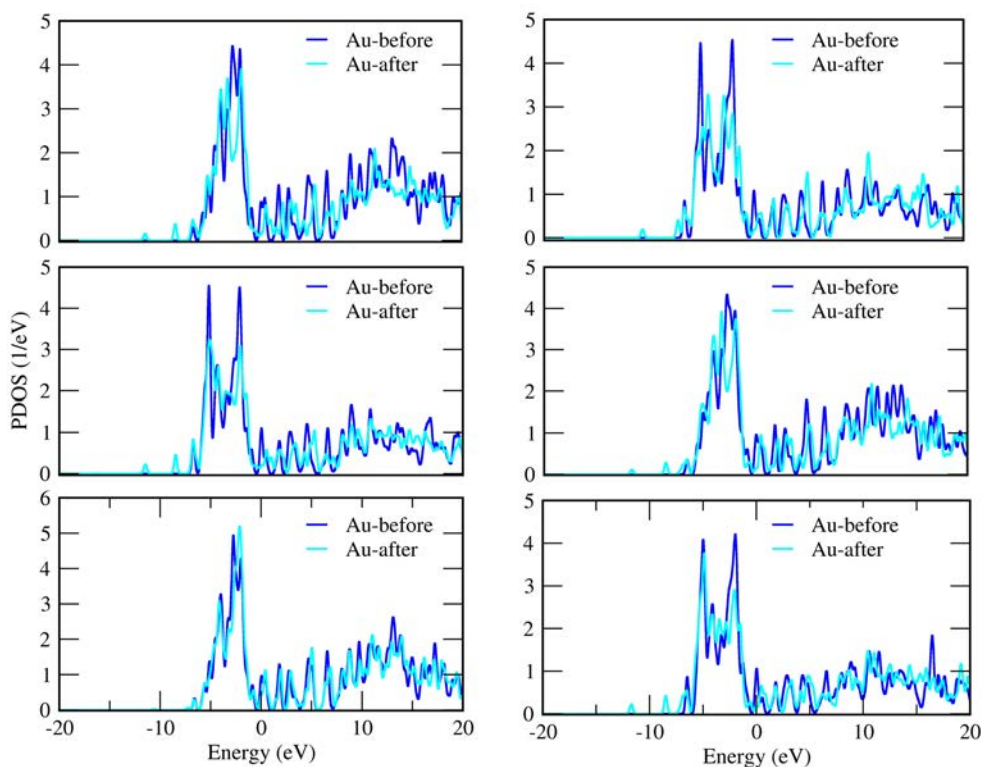


Fig. 10. PDOS for the adsorption complexes of TiO₂/Gold nanocomposites in before and after the adsorption process, a: A complex; b: A complex; c: B complex; d: B complex; e: C complex; f: C complex.

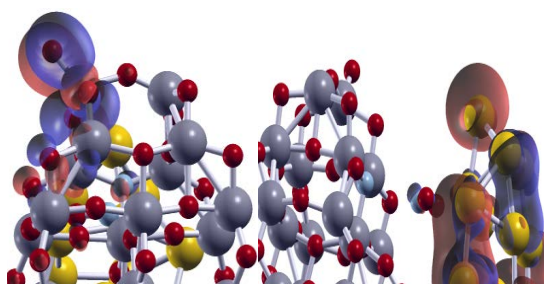


Fig. 11. The isosurfaces of HOMO and LUMO molecular orbital of the NO₂ molecule adsorbed on the TiO₂/Gold nanocomposites

the *i*. Subscript "i" symbolizes the TiO₂/Gold nanocomposites or NO₂ molecule. The charge difference, ΔQ_i , is a measure of the amount of charge transferred to, or, from the considered nanocomposites from, or, to the NO₂ molecule. Our charge analysis indicates that NO₂ adsorption induces a comparatively considerable charge transfer (about -0.145 *e*) from nanocomposite to NO₂ for configuration C, suggesting that NO₂ behaves as an electron acceptor. The calculated Mulliken charge values for complexes A and B

(N-doped systems) are about +0.0038 and +0.118 *e* respectively, which indicate a lower charge transfer from nanocomposite to the NO₂ molecule, compared to the pure (undoped) system. This means that the N doping reduces the efficiency of the charge transfer. Also, it is revealed that the charge transfer causes changes on the conductivity of the system. This could be an operative property to help in the design of novel TiO₂-based sensor devices for NO₂.

CONCLUSIONS

Density functional theory calculations have been carried out to investigate the interaction of NO₂ molecules with undoped and N-doped TiO₂/Gold nanocomposites to completely comprehend the sensing properties of these nanocomposites in adsorption processes. The results indicate that the adsorption of NO₂ molecule causes the stretching of the N-O bonds of the adsorbed NO₂ molecule. The bond angles of the NO₂ molecule after the adsorption process are lower than those in the gas phase state, being attributed to the transference of the electronic density from the Au bonds of nanocomposite and the N-O bonds

of NO₂ molecule to the newly-formed bond at the interacting point. The results also suggest that the undoped nanocomposites have a higher capability to interact with toxic NO₂ molecule, compared to the N-doped ones. The variations in the electronic structure and adsorption energies are found to be responsible for changing the conductivity of the system. Our reported results thus suggest a theoretical basis for the potential application of TiO₂/Gold hybrid nanostructures as gas sensors for main air pollutants such as NO₂ 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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