

RESEARCH PAPER

Adsorption of H₂S molecule on TiO₂/Au nanocomposites: A density functional theory study

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ABSTRACT

The adsorption of hydrogen sulfide molecule on undoped and N-doped TiO₂/Au nanocomposites was investigated by density functional theory (DFT) calculations. The results showed that the adsorption energies of H₂S on the nanocomposites follow the order of 2N doped (Ti site) > N-doped (Ti site) > Undoped (Ti site). The structural properties including bond lengths, angles and adsorption energies and electronic properties in view of the projected density of states (PDOSs) and molecular orbitals (MOs) were analyzed in detail. The results indicated that the interaction between H₂S molecule and N-doped TiO₂/Au nanocomposite is stronger than that between H₂S and undoped nanocomposite, suggesting that N-doping helps to strengthen the interaction of H₂S with TiO₂/Au nanocomposite. Mulliken population analysis was conducted to analyze the charge transfer between the nanocomposite and H₂S molecule. Although H₂S molecule has no significant interaction with undoped nanocomposite, it tends to be strongly adsorbed on the N-doped nanocomposite. The results also suggest that the two doped nitrogen atoms in TiO₂ greatly strengthen the adsorption process, being a helpful procedure to help in the design and development of improved sensor devices for H₂S detection.

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INTRODUCTION

Titanium dioxide has aroused motivating interests as a promising semiconductor material because of its unique properties such as non-toxicity, high catalytic efficiency and extensive band-gap [1]. TiO₂ has been largely utilized in different fields such as photo-catalysis, gas sensing, organic dye-sensitized solar cells, water-splitting and removal of air pollutants [2-5]. It is crystallized in three important crystallographic phases namely anatase, rutile, and brookite [6]. The photocatalytic properties of TiO₂ are restricted due to its wide band gap (3.2 eV), which makes the adsorption of the incoming solar light in a negligible percentage (3-5 %). Doping of TiO₂ with some nonmetal

elements such as nitrogen is an appropriate method to extend the optical response of TiO₂ to the visible area [7, 8]. Recently, oxide supported Au nanoparticles have attracted noteworthy attention due to the catalytic activities of these materials at low temperatures [9, 10] for a progressively greater number of oxidation processes. Several experimental studies for excellent activity of Au nanoparticles have been published. Goodman et al. [11] reported size and effects of the band structure, and measured the onset of the reactivity to identify when the Au particles become as tinny as two monolayers so that they are changed from a metallic state to a separated state. Up to now, a great number of DFT calculations of O₂ adsorption

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and CO+O₂ reaction at different Au collections have been published. Hakkinen Landman and co-workers [12] reported the charging of Au particles as an efficient parameter. The adsorption of O₂ and CO₂ and reaction at gold nanoparticle models supported by TiO₂ surfaces have been inspected by first principle studies [13]. Several computational investigations on N-doped TiO₂ anatase with Au nanoparticles have been reported, clarifying nearly the significant electronic and structural properties of these systems. For instance, Liu et al. [14] studied the adsorption of NO molecule on the undoped and N-doped TiO₂ anatase nanoparticles. The increased ability of N-doped TiO₂ anatase nanoparticles for adsorption of toxic NO₂ molecules has been also addressed in our previous computational work [15]. There are a few computational and experimental studies on the adsorption behavior of TiO₂/Au nanocomposites. H₂S molecule has been characterized as a toxic gas and control of the concentration of this injurious molecule is an important subject to public health and environmental protection [16].

In this study, the interactions of H₂S molecules with TiO₂/Au nanocomposites are investigated by DFT computations. We present the DFT results of the complex systems consisting of H₂S molecule located between the TiO₂ anatase nanoparticle and Au monolayer. The electronic structure of the adsorption systems is also analyzed using projected partial density of states (PDOS) and molecular orbital techniques. This work aims to provide an overall understanding on the adsorption behavior of TiO₂/Au nanocomposites as potentially efficient gas sensors for H₂S molecules.

COMPUTATIONAL METHODS

Density functional theory

Density functional theory (DFT) calculations [17, 18] were performed using Open source Package for Material eXplorer (OPENMX) ver. 3.7 [19], which has been confirmed to be an effective software package for simulating the nanoscale materials specially solid state and crystalline materials [20, 21]. The cutoff energy of 150 Rydberg is considered regarding the energetics of the complex system. The considered pseudo atomic orbitals (PAOs) were made by using a basis set (of 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, (three-s and three-p) for S atom within cutoff radii set to the values of 7 for Ti, 9

for Au, 5 for O and N, 8 for S (all in Bohrs). The generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof form (PBE) was utilized for exchange–correlation energy functional [22]. The relaxation of all atoms of the nanocomposites were set in the geometry optimization process. The selected pristine and N-doped nanocomposites are positioned in a 20 Å × 20 Å × 30 Å box, which is much greater than the size of the composites. The open-source program XCrysDen [23] was employed for visualizing data such as molecular orbitals. In the simulation box, 86 atoms (14 Au, 48 O and 24 Ti atoms) of undoped or N-doped TiO₂ nanoparticle with Au structure were contained. The adsorption energy of gas molecules adsorbed on the TiO₂/Au nanocomposite is determined as follows:

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

where $E_{(composite + adsorbate)}$ is the total energy of the adsorption system, $E_{composite}$ is the energy of the TiO₂/Au nanocomposite, and $E_{adsorbate}$ is the energy of isolated gas molecule. 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/Au nanocomposites

The TiO₂ anatase nanoparticles containing 72 atoms were constructed by putting 3×2×1 numbers of TiO₂ unit cells along x, y and z axis, respectively. The unit cell is available at “American Mineralogists Database” webpage [24] and was reported by

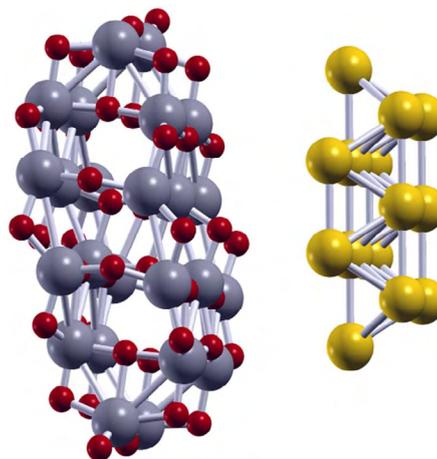


Fig. 1. Optimized geometry of the considered TiO₂/Au nanocomposites constructed from anatase nanoparticle and Au nanoparticle.

Wyckoff [25]. Two appropriate oxygen atoms of TiO_2 nanoparticle were replaced by nitrogen atoms to model the N-doped particles. Two dangling oxygen atoms were considered in the nanoparticle to set a 1:2 charge ratio. The vacuum spacing with the thickness of 11.5 Å was considered between the adjacent particles. Also, a gold structure consisting of 14 Au atoms was constructed in this work and coupled with TiO_2 nanoparticle to model the TiO_2/Au nanocomposites. The 86-atoms TiO_2/Au nanocomposite positioned into a great cubic supercell is shown in Fig. 1. Gas-phase H_2S has a trigonal planar geometry with H-S bond length of 1.34 Å and H-S-H bond angle of 92.1°, based on GGA method. The optimized geometries of the N-doped TiO_2/Au nanocomposites are also displayed in Fig. 2.

RESULTS AND DISCUSSION

Structural and energetics aspects

The interaction of H_2S molecule between TiO_2/Au nanocomposites is shown in Fig. 3, as labeled by types A-E adsorption complexes. It was found

that the interaction of H_2S with TiO_2 nanoparticle is more favorable in energy than that with Au nanoparticle, suggesting that the H_2S molecule is more preferentially adsorbed on the TiO_2

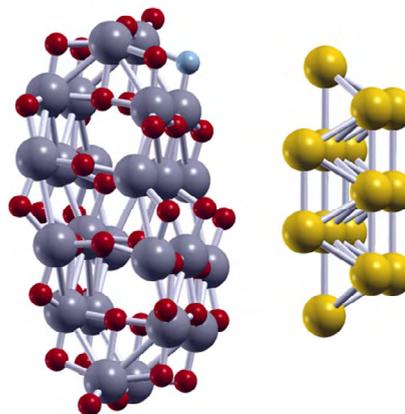


Fig. 2. Optimized geometries of two types of N-doped TiO_2/Au nanocomposites. The light yellow, dark yellow, gray, red, cyan and blue balls denote sulfur, gold, titanium, oxygen, hydrogen and nitrogen atoms, respectively.

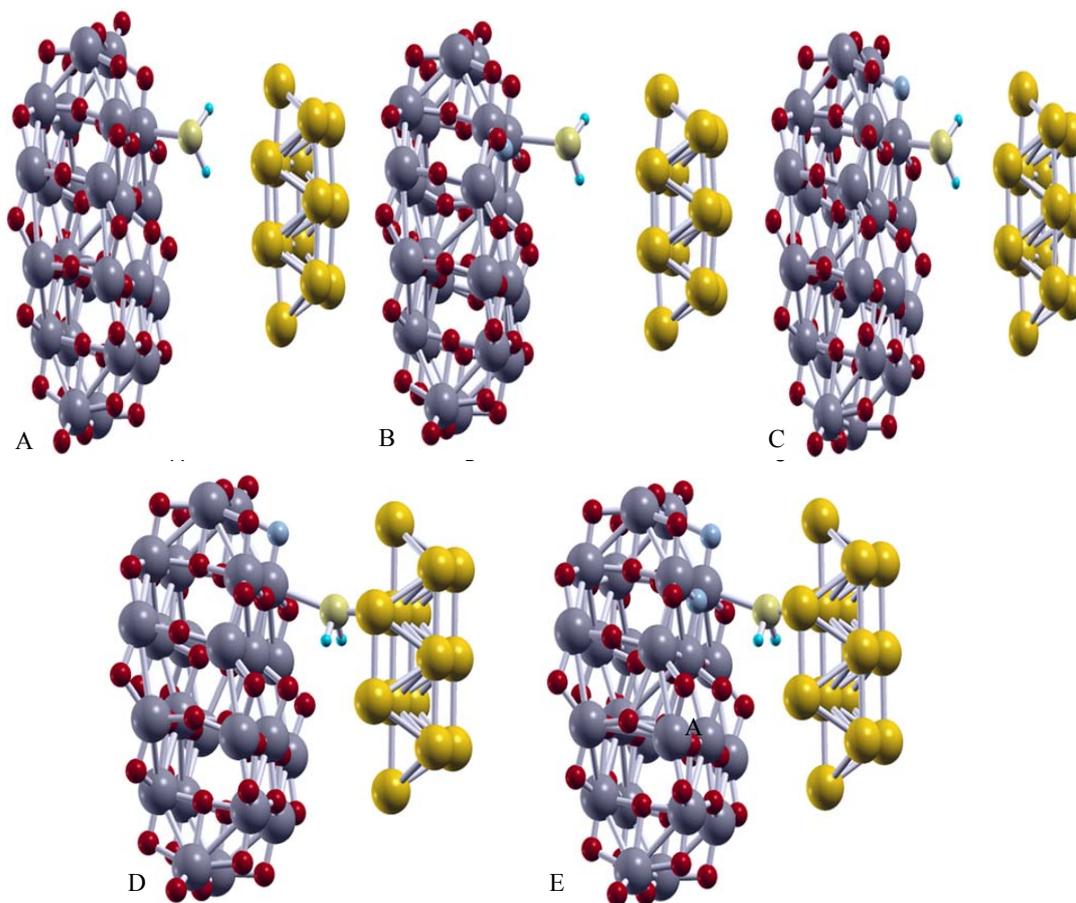


Fig. 3. Optimized geometry configurations of the interaction of H_2S molecule with TiO_2/Au nanocomposites.

nanoparticle rather than Au nanoparticle. The reason may be due to the calculated adsorption energies and molecular orbital results of the complex systems. In configuration A, H₂S molecule interacts with pristine nanocomposite, while configurations B and C show the H₂S molecule adsorbed on the N-doped nanocomposites. Configuration D presents the H₂S interaction with two contacting points from both Au and TiO₂ nanoparticles. In configuration E, one H₂S molecule is adsorbed on the two N-doped nanocomposite. Table 1 lists the lengths for H-S bonds of the adsorbed H₂S molecule and the newly-formed Au-S, Ti-S bonds, as well as H-S-H bond angles before and after the adsorption process. The results of this table indicate that

the H-S bonds of the adsorbed H₂S molecule are stretched after the adsorption process. The reason is that the electronic density is transferred from the Au-Au, Ti-O and H-S bonds to the newly-formed bonds in the middle of the nanocomposite and adsorbate molecule. The H-S-H bond angle of the H₂S molecule was increased after the adsorption. This increase could be mostly attributed to the formation of a new bond and therefore transferring the electronic density from the old bonds of nanocomposite and adsorbed H₂S molecule to the newly-formed bonds. This formation of new bond also increases the p characteristics of bonding molecular orbitals of sulfur in the H₂S molecule. The adsorption energy values for nanocomposites

Table 1. Bond lengths (in Å), bond angles (in degrees), adsorption energies (in eV), and Mulliken charge values of H₂S molecule adsorbed on the TiO₂/Au nanocomposites.

Complex type	Ti-S	Au-S	S-H1	S-H2	H-S-H	ΔE _{ad}	ΔQ
A	2.72		1.41	1.42	95.1	-2.10	-0.337
B	2.80		1.41	1.42	94.6	-2.01	-0.302
C	2.72		1.41	1.42	95.4	-2.02	-0.310
D	2.80	2.57	1.42	1.46	97.2	-2.22	-0.524
E		2.50	1.43	1.52	98.4	-2.32	-0.555
Non-adsorbed			1.34	1.34	92.1		

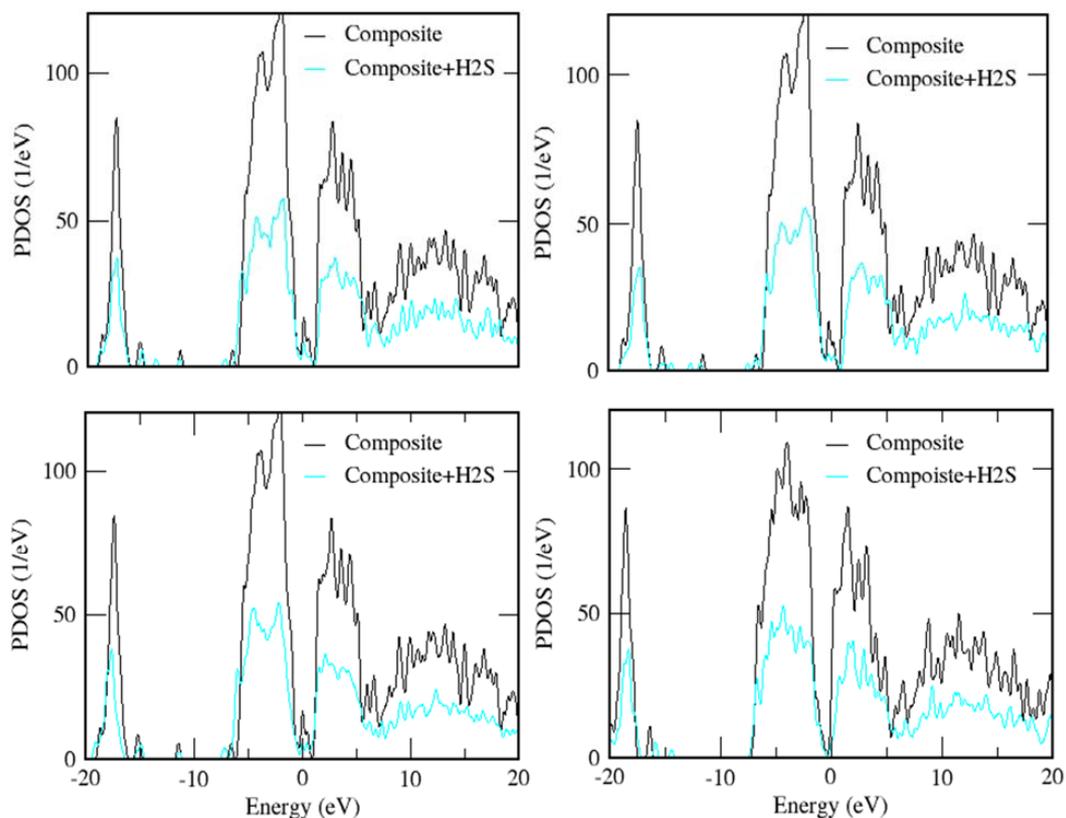


Fig. 4. DOS for the pristine and N-doped TiO₂/Au nanocomposites. a: Complex A; b:Complex B; c: Complex C and d: Complex E.

are reported in Table 1. Adsorption on the N-doped nanocomposite is found to be energetically more favorable than the adsorption on the undoped one, which means that the N doping has an activating role on the adsorption of H₂S. In other words, N-doped nanocomposite can react with H₂S molecule more efficiently. Also, two doped nitrogen atoms make the interaction of H₂S on the nanocomposite very strong, compared to the one N-doped nanocomposite. It suggests that the adsorption on the two N-doped nanocomposite is energetically more favorable than that on the N-doped nanocomposite.

Electronic structures

Fig. 4 presents the total density of states (TDOS) for pristine and two types of N-doped TiO₂/Au nanocomposites before and after the adsorption process. The TDOS of nanocomposites only exhibit small differences in comparison with the isolated

non-adsorbed nanocomposites. These differences included both small shifts in the energies of the peaks and presence of some peaks in DOS of the considered systems. However, these variations in energy of the states would affect the electronic transport properties of the nanocomposites and this feature can be beneficial for engineering H₂S sensors. The projected density of states (PDOS) for the interaction of H₂S molecule with TiO₂/Au nanocomposites are displayed in Fig. 5. Panels (a, b) present the PDOS of the H₂S sulphur atom of H₂S molecule and the titanium atom of TiO₂ nanoparticle for the configurations A and B. The great overlaps between the PDOS of these two atoms show that the sulphur atom of H₂S molecule forms a chemical bond with the titanium atom of nanocomposite. The PDOS for configurations C, D and E are represented in panels (c-d and e-f), indicating high overlaps between the PDOS of sulphur atom of H₂S molecule and the Ti and Au

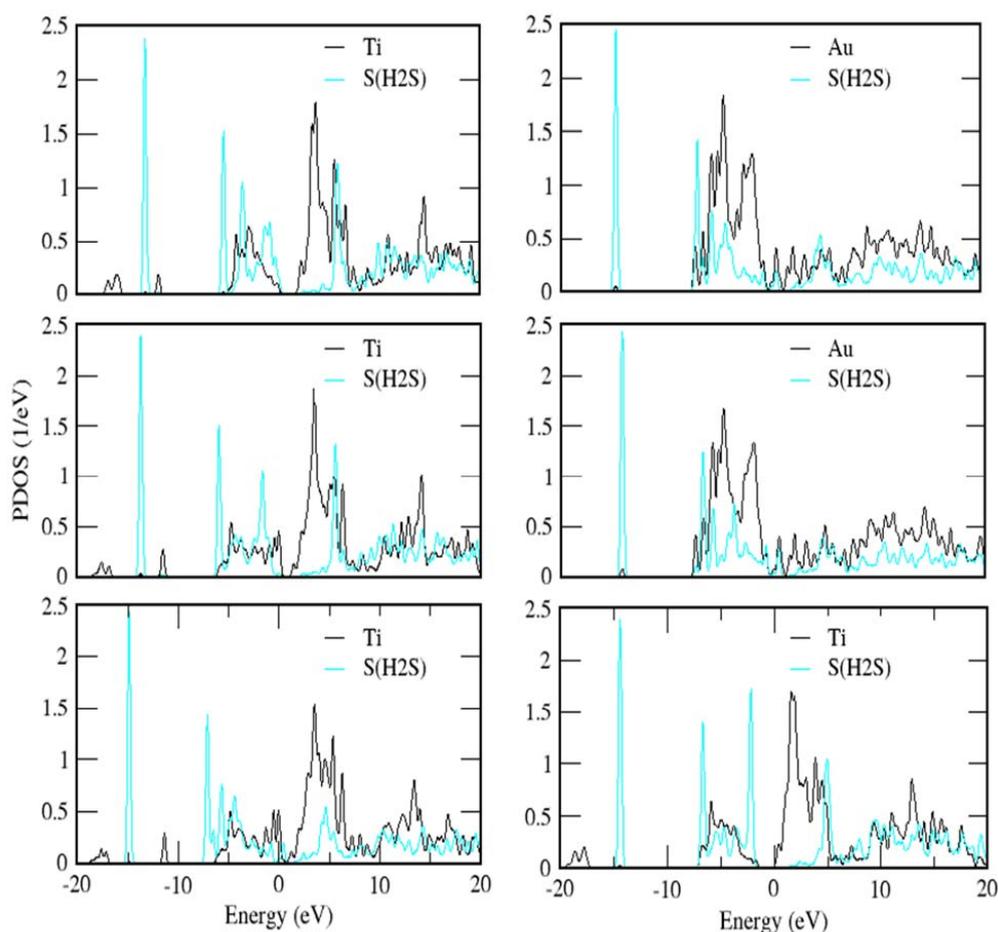


Fig. 5. PDOS for the adsorption complexes of H₂S molecule on TiO₂/Au nanocomposites, a: Complex A; b: Complex B; c: Complex C; d: Complex E; e: Complex D and f: Complex D.

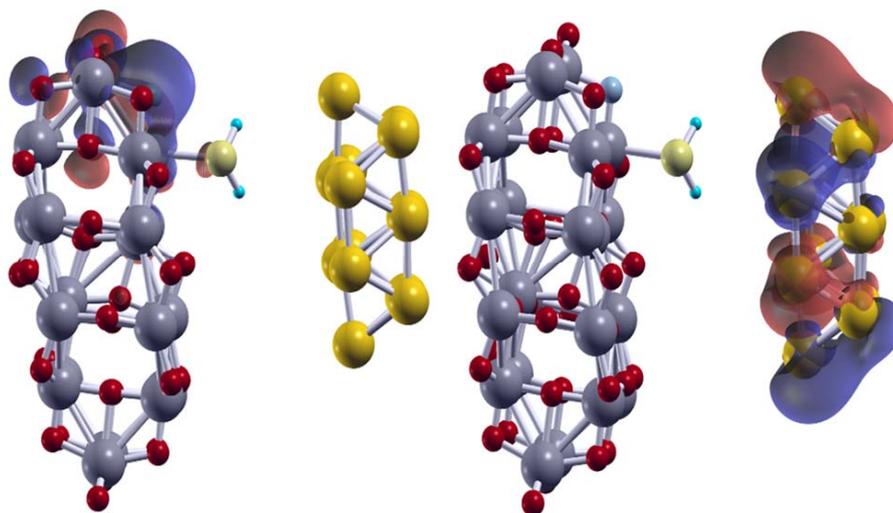


Fig. 6. The isosurfaces of HOMO and LUMO molecular orbitals for H₂S molecules adsorbed on the TiO₂/Au nanocomposites.

atoms of nanocomposite. These overlaps of the PDOS spectra declare that chemical bond is formed after the adsorption of H₂S molecule. The isosurfaces of HOMO and LUMO molecular orbitals for H₂S adsorption on the nanocomposites are shown in Fig. 6, indicating that the HOMO is greatly localized on the TiO₂ nanoparticle, whereas the LUMO is mainly localized on the Au nanoparticle. To further describe the charge transfer between H₂S molecule and TiO₂/Au nanocomposites, in Table 1, we report 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 the particle(s) *i*. Subscript “*i*” denotes the TiO₂/Au nanocomposites or H₂S molecule. For complex E, the calculated charge value of nanocomposite is about -0.555 *e* and that of H₂S adsorbate is +0.555 *e*, suggesting that H₂S behaves as an electron acceptor. It was found that the charge transfer makes changes on the conductivity of the system.

CONCLUSIONS

In order to investigate the interaction of H₂S molecules with undoped and N-doped TiO₂/Au nanocomposites, we have carried out density functional theory calculations. The results indicate that the adsorption of H₂S molecule causes the elongation of the H-S bonds of the adsorbed H₂S molecule. The bond angles of the H₂S molecule

after the adsorption process are larger than those in the gas phase state, being attributed to the transfer of the electronic density from the Ti-O bonds of TiO₂ nanoparticle and Au-Au bonds of Au nanoparticle, as well as the H-S bonds of H₂S molecule to the newly-formed bond at the contacting point. The results also suggest that the N-doped nanocomposites have a higher capability to interact with harmful H₂S molecule, compared to the undoped ones. The variations in the electronic structure and adsorption energies were found to be responsible for changing the conductivity of the system. Our reported results thus provide a theoretical basis for the possible application of TiO₂/Au hybrid nanostructures as gas sensors for main air pollutants such as H₂S in the environment.

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CONFLICT OF INTERESTS

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

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