

Sensing of Nitrogenous Toxic Gases on X-SnSe₂/SnO₂ Heterostructures by Doping with Rare Earth (X=La, Pr)

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Article

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Abstract

The detection of toxic gases, particularly nitrogenous ones, has a direct impact on human health and safety. This study investigated the adsorption behavior of four nitrogenous gases (NO_2 , NO , NH_3 , and HCN) using density functional theory. These gases were detected using a heterostructure of $\text{SnSe}_2/\text{SnO}_2$ doped with rare-earth elements (La and Pr). Analysis of the results revealed distinct reaction patterns on both heterostructures. For nitrogenous gases containing oxygen, high adsorption energies (E_{ads}), high charge transfer (Q_t), and a high work function were observed, particularly in $\text{Pr-SnSe}_2/\text{SnO}_2$, where the highest values reached -2.75 eV, -0.34 e, and 5.76 eV, respectively, upon adsorption of NO_2 . The results also indicate a significant convergence of these values for both heterostructures upon the adsorption of hydrogen-containing gases. This study demonstrates that $\text{Pr-SnSe}_2/\text{SnO}_2$ is more effective at sensing oxygen-containing gases than hydrogen-containing gases, making it a promising sensor for this class of gases.

1. Introduction

There are many nitrogenous toxic gases that are prevalent in the atmospheric environment, for example, nitrogen dioxide (NO_2), nitric oxide (NO), ammonia (NH_3), and hydrogen cyanide (HCN) [1]. These gases cause atmospheric pollution and present a significant challenge regarding anthropogenic climate change. Moreover, it causes a significant risk to human health and contribute to grave environmental and climatic problems [2, 3]. In general, the nitrogenous toxic gases (NO_2 , NO , NH_3) can derive from vehicular exhaust, industrial emissions, biological metabolism, and agricultural production [4]. Also, HCN can arise from high-temperature decomposition and chemical reactions, which are considered more toxic than other nitrogen gases [5, 6]. Given the significant impact of toxic gases (NO_2 , NO , NH_3 , and HCN), regular observation of their levels is important to protect human health and the environment [7–9].

To preserve human health and safety from these gases, there must be a method available that can monitor and detect these gases with high specificity and sensitivity. Many scientists are actively involved in the search for appropriate materials for gas-sensing applications. Recently, 2D materials have been subject to extensive study and exploration due to their extensive application potential [10–15]. For instance, in 2004, Geim *et al.* found a single-layer grapheme, which was confirmed to be the first stably obtainable 2D material by mechanically exfoliating graphite [16].

Many previous studies have focused on the practical aspects of studying gas sensors based on $\text{SnO}_2/\text{SnSe}_2$ heterostructures. In 2021, Tingting *et al.* developed an $\text{SnO}_2/\text{SnSe}_2$ sensor that detected H_2S gas at room temperature, showing a high response and extreme sensitivity to that temperature [17]. $\text{SnO}_2/\text{SnSe}_2$ was also developed by Xi Li *et al.* in 2023 to detect NO_2 gas at a temperature of 298°C and with the effect of infrared radiation, where this sensor shows a high degree of sensitivity [18]. In 2025, $\text{SnO}_2/\text{SnSe}_2$ was used by Qing Han *et al.* to detect formaldehyde at low temperatures, where SnO_2 nanosheets were coated onto SnSe_2 nanoblocks. This sensor is characterized by high stability, moisture

resistance, and good performance [19]. Also in 2025, Peijiang Cao *et al* used heat-treated SnSe₂ to obtain a range of materials, including SnO₂/SnSe₂ and Au-SnO₂/SnSe₂, and demonstrated that Au-SnO₂/SnSe₂ exhibits outstanding sensing performance for NO₂ gas [20].

Although several studies have investigated the electronic and structural properties of SnSe₂ and SnO₂ individually, studies about the heterostructure formed between these two materials are still limited, mainly regarding the effect of doping and stacking alignment on the efficiency of toxic gas sensing, principally nitrogen-based gases. Also, the relationship between adsorption energy, the possible enhancement of sensor sensitivity and charge transfer still requires detailed investigation using density functional theory (DFT) calculations. This study aims to fill this research gap by investigating the adsorption mechanism and electronic properties of the SnSe₂/SnO₂ heterostructure using DMol³ calculations.

In this study, SnSe₂ is selected to incorporate with SnO₂ to build a heterostructure by using first-principle calculations to verify this conjecture and conduct the theoretical study as sensor materials or adsorbents. Initially, the individual surfaces of SnSe₂ and SnO₂ were constructed and subsequently optimized separately. Thereafter, the SnSe₂/SnO₂ heterostructure surface was built and optimized as well. To enhance the surface sensitivity toward nitrogen-based gases (NO₂, NO, NH₃, and HCN), the heterostructure was doped with La and Pr elements.

2. Computational Details

The calculations in this work were performed based on DFT using the Dmol³ model [21, 22]. We select a 3 × 3 × 1 supercell of both optimized SnSe₂ and SnO₂ to build the heterostructure SnSe₂/SnO₂. In order to avoid the interference between SnSe₂ and SnO₂ surfaces, the vacuum layer in this case is 25 Å. In the computational procedure, the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was employed to accurately account for the effects of electronic correlation and exchange [23, 24]. In addition, the Grimme scheme incorporating the DFT-D method was utilized, as it is crucial for property describing the weak van der Waals forces, which play a fundamental role in studying adsorption processes [25, 26]. For integration of Brillion zone, a k-point mesh of 7×7×1 was used, to perform accurate electronic structure calculations. Also in these calculations to improve the convergence, we used smearing parameter of 0.02 Ha. The global orbital cutoff was 4.6 Å, with energy convergence tolerance of 10⁻⁵ Ha, force convergence tolerance 0.001Ha/Å, and displacement convergence tolerance of 0.005Å. Lastly, we chose the double numerical polarization (DNP) to enhance the reliability and precision of the calculations [27] .

The incorporation of La and Pr atoms on the heterostructure surface was explored through three doping positions to analyze electronic properties and stability: position (P1, P2 and P3), we can see these positions in Fig. 1(b). The formation energy can be written as [28]:

$$E_{form} = E_{x-SnSe_2/SnO_2} - E_{SnSe_2/SnO_2} - E_x \quad (1)$$

where E_{x-SnSe_2/SnO_2} , and E_{SnSe_2/SnO_2} represent the total energies of La-SnSe₂/SnO₂, Pr-SnSe₂/SnO₂, and SnSe₂/SnO₂, respectively, while E_x represents the energies of the individual La/ Pr atoms. The adsorption energy of the heterostructure surface determines whether the gas binds strongly to substrates. We can calculate the adsorption energy by using the following equation [29, 30]:

$$E_{ads} = E_{tot} - E_{hetero} - E_{gas} \quad (2)$$

where E_{tot} , E_{hetero} , and E_{gas} represent the total energy of the doping heterostructure after adsorption, the total energy of the heterostructure before adsorption, and the total energy of the gas atom, respectively. When the absolute value of E_{ads} is high, it refers to a more stable adsorption. We can calculate the charge transfer value (Q_t) between the surface and the adsorbed gas by using the following equation [31]:

$$Q_t = Q_{adsorbed} - Q_{isolated} \quad (3)$$

where $Q_{adsorbed}$ is the charge of the gas after adsorption, and $Q_{isolated}$ is the charge of the gas before adsorption. When the Q_t is negative, that means the electron is transferred from the surface to the gas molecule, but a positive value of Q_t means the electron is transferred from the gas molecule to the surface.

3. Results and Discussion

3.1. Geometrical Structures of Gas Molecules, and Heterostructures

We will study the geometric structures of the gases under study, including nitrogenous toxic gases such as NO₂, NO, NH₃, and HCN, are depicted in Fig. 1(a). These gases exhibit different characteristics. One of the most important structural properties of these gases is that they are polyatomic molecules, and this polyatomic structure directly affects their thermal behavior. Its geometric structure ranges from linear for NO to curved for NO₂ and HCN gases and then polymorphic for NH₃, where the attractive forces between the molecules influence these shapes. All these gases have covalent bonds and possess free electrons, except for HCN, which does not have free electrons. The presence of these electrons facilitates charge transfer, thereby affecting the adsorption energy (see Fig. 3).

From Fig. 1(c), we observe that SnSe₂ is the upper layer, while SnO₂ is the lower layer. The distance between the two layers is measured in angstroms and has a value of 3.532Å. The lattice constants of SnSe₂, SnO₂, and SnSe₂/SnO₂ are a = b = 3.84, 3.23 and 3.53Å, respectively, which is consistent with the Ref. [32]. We doped the SnSe₂/SnO₂ with La and Pr atoms. This doping has been studied in three positions. The first position (P1): the impurity atom is located above the lower Se atom and bonded to

the three Sn atoms, the second position (P2): the impurity atom is located above the Sn atom and bonded to the three Se atoms and the third position (P3): the impurity atom is located above the upper Se atom, as shown in Fig. 1(b). We chose the position (P1) that has the most stability (binding energies of La-SnSe₂/SnO₂ and Pr-SnSe₂/SnO₂ are - 15.99098 eV and - 15.76080 eV, respectively) as shown in Fig. 1(d and e), i.e., (most binding energy), see Table 1.

Figure 1(f-h) exhibits the band structure of SnSe₂, SnO₂, and SnSe₂/SnO₂ heterostructure. To compare the electronic properties of SnSe₂ and SnO₂ monolayer with those of SnSe₂/SnO₂ heterostructure by using the band structure, we find that the direct band gap (indirect band gap) for SnSe₂ (SnO₂) is 0.717 (2.75) eV, respectively, which are corresponding to those in Ref. [32]. While for SnSe₂/SnO₂ heterostructure we observe overlap of the valence band with the conduction band, meaning the band gap is zero, this result is corresponding to Ref. [19].

Figure 1(i) illustrates the total density of states (TDOS). The bottom band width reflects the electron's ability to participate in bonds: that is, the larger the bottom band width, the more strongly the atomic orbital is stretched, and the greater the electron's ability to participate in bond [33]. Figure 1(j) illustrates the electron bonding in different orbitals of three elements, which represents the partial density of states (PDOS), the valence band part at -8eV to 0eV is mainly the 2p state contribution of oxygen, 3d for Se and 4d for Sn, the highest contribution is made by oxygen at -1 eV. In the conduction band from 0eV to 3eV, the PDOS has a similar contribution to all elements. These spectra are similar of those in Ref. [19].

Table 1
Binding energy values for SnSe₂/SnO₂ doping by La and Pr
in three positions.

Heterostructure	P1 (eV)	P2 (eV)	P3 (eV)
La-SnSe ₂ /SnO ₂	-15.99098	-9.54419	-15.99077
Pr-SnSe ₂ /SnO ₂	-15.76080	-15.58487	-15.75969

3.2 Adsorption of Gases on Heterostructure

In this section, we will give an analysis of the geometric structures of La-SnSe₂/SnO₂ and Pr-SnSe₂/SnO₂ after absorbing the gases from it (see Fig. 2). Table 2 gives the parameters of the structure, including angles and bond lengths for NO₂, NO, NH₃, and HCN.

NO₂ adsorption on La-SnSe₂/SnO₂ and Pr-SnSe₂/SnO₂ discloses distinct interactions (see Fig. 3 and Table 2). On La-SnSe₂/SnO₂, the N-O bond length after adsorption is 1.214 Å, with an angle O-N-O of 119.267°, and (E_{ads}) adsorption energy is -2.46 eV, indicating chemisorption. In this case, the adsorption distance (D) is 2.55 Å, and the charge transfer (Q_t) is -0.31 e. In comparison, on Pr-SnSe₂/SnO₂, the N-O bond length increases to 1.288 Å. Angle of O-N-O is 113.446°, with increasing in adsorption energy (E_{ads}) to -2.75 eV, this means a high adsorption value in the presence of Pr, resulting

in a distance of adsorption (D) of 2.45 Å by presence of Pr, we can consider the adsorption to be close to the presence of La, and charge transfer (Q_t) of -0.34 e.

Table 2: Geometric parameters of gas molecules NO₂, NO, NH₃ and HCN after adsorption on La-SnSe₂/SnO₂ and Pr-SnSe₂/SnO₂, bond lengths and angles measured with units Å and θ° , respectively.

Gas	Adsorbed on La-SnSe ₂ /SnO ₂			Adsorbed on Pr-SnSe ₂ /SnO ₂		
NO₂	Se-La	N-O	Angle NO ₂	Se-Pr	N-O	Angle NO ₂
	2.863	1.214	119.267	2.854	1.288	113.446
	2.881	1.337		2.873	1.291	
	2.905			2.877		
NO	Se-La	N-O		Se-Pr	N-O	
	2.861	1.194		2.836	1.195	
	2.868			2.840		
	2.869			2.858		
NH₃	Se-La	N-H	Angle NH ₃	Se-Pr	N-H	Angle NH ₃
	2.800	1.025	105.868	2.774	1.025	106.153
	2.807	1.026	106.420	2.781	1.026	106.261
	2.820	1.026	106.513	2.782	1.026	106.313
HCN	Se-La	H-C	Angle HCN	Se-Pr	H-C	Angle HCN
	2.821	1.076	179.963	2.807	1.076	179.355
	2.829	C-N		2.807	C-N	
	2.832	1.178		2.810	1.178	

The adsorption of NO on La-SnSe₂/SnO₂ and Pr-SnSe₂/SnO₂ shows a clear difference in the adsorption distance (see Fig. 3 and Table 2). On La-SnSe₂/SnO₂, the adsorption of NO gives an adsorption distance (D) of 2.44 Å, charge transfer (Q_t) of -0.16 e, and adsorption energy (E_{ads}) of -1.94 eV. This refers to chemisorption with a bond length N-O of 1.194 Å. On Pr-SnSe₂/SnO₂, we observe an adsorption distance (D) of 2.33 Å, high adsorption energy (E_{ads}) of -2 eV, and a bond length N-O is 1.195 Å, with a slight increase in charge transfer (Q_t) of -0.17 e. Comparing adsorption energies reveals distinct adsorption patterns for both heterostructure, but the most important factor is the presence of Pr.

High degree of convergence in adsorption energy when NH_3 is adsorbed. On $\text{La-SnSe}_2/\text{SnO}_2$, NH_3 adsorption results in a distance of adsorption (D) of 2.82 Å, the adsorption energy (E_{ads}) is -1.34 eV, with charge transfer (Q_t) of 0.19 e, indicative of chemisorption, and the average bond length N-H is 1.026 Å, the average of angles is 105.868°. While on $\text{Pr-SnSe}_2/\text{SnO}_2$, the adsorption energy (E_{ads}) is -1.33 eV when the adsorption distance (D) is 2.76 Å, it is very clear that the adsorption energy decreases with decreasing adsorption distance, with decreasing charge transfer (Q_t) to 0.18 e, while the bond length remains at the same values with a slight increase in angle to 106.153°. From observing the charge transfer values for the two heterostructures as well as the adsorption energies, we conclude that it is a strong chemisorption, but $\text{La-SnSe}_2/\text{SnO}_2$ is slightly superior due to the presence of La.

There is a high degree of similarity in the bonding properties when HCN is adsorption onto $\text{La-SnSe}_2/\text{SnO}_2$ and $\text{Pr-SnSe}_2/\text{SnO}_2$ (see Fig. 3 and Table 2). An adsorption distance (D) and energy (E_{ads}) of HCN gas are 2.61 Å and -1.07 eV, respectively. It is clear that a chemisorption and charge transfer of 0.015 e, and bond length of (H-C and C-N) about (1.076 and 1.178) Å respectively, and maintaining a linear configuration (angle H-C-N = 179.963°). On the other hand, HCN adsorption on $\text{Pr-SnSe}_2/\text{SnO}_2$ shows a distance of adsorption (D) of 2.54 Å, a charge transfer of 0.45 e, an adsorption energy of -1.07 eV, and a bond length maintained at the same value with a slight decrease in angle to 179.355°.

According to Fig. 3, the relation between adsorption distance (D), adsorption energy (E_{ads}), and charge transfer (Q_t) shows a strong interdependence for the behavior of adsorption of gas on $\text{La-SnSe}_2/\text{SnO}_2$ heterostructure. A shorter adsorption distance is associated with a higher adsorption energy (i.e., more negative adsorption energy), indicating a stronger interaction between the gas and the surface. This nearness facilitates greater charge transfer (Q_t), reflecting this behavior, significant electron exchange between the surface and adsorbed gases.

In order to compare our results with those of previous practical and theoretical studies, we have included Table 3, which illustrates the significance of our results and the high values of adsorption energies and charge transfer, which reinforces the important role of our improved heterostructures in supporting gas sensors.

Table 3
Comparison of the sensing characteristics of some toxic nitrogen gas sensors.

Substrate	Gas	$E_{\text{ads}}(\text{eV})$	$D(\text{\AA})$	$Q_t(\text{e})$	Ref.
Pd-WS ₂ /MoS ₂	NO	-0.854	2.06	0.06	
	NO ₂	-0.848	2.54	-0.19	
	NH ₃	-1.12	2.35	0.21	[34]
SnO ₂ /SnSe ₂	NO ₂	-0.323	2.98	-0.027	[20]
SnO ₂ /SnSe ₂	NO ₂	-0.211	/	/	[18]
Pt-WS ₂ /WSe ₂	NO	-1.881	1.842	-0.05	
	NO ₂	-1.594	1.366	-0.29	[35]
Nb ₂ CO ₂ /GaN	NO ₂	-1.081	2.940	0.027	
	NH ₃	-1.739	2.057	0.229	[36]
Pt-WS ₂ /SiC	NO ₂	-1.02	2.041	-0.24	[37]
La-SnSe ₂ /SnO ₂	NO	-1.94	2.44	-0.16	
	NO ₂	-2.46	2.55	-0.3	
	NH ₃	-1.34	2.82	0.19	
	HCN	-1.07	2.61	0.015	This work
Pr-SnSe ₂ /SnO ₂	NO	-2	2.33	-0.17	
	NO ₂	-2.75	2.45	-0.34	
	NH ₃	-1.33	2.76	0.18	
	HCN	-1.07	2.54	0.01	This work

3.3 Density of states

3.3.1 Total Density of States

The adsorption of NO₂ on La-SnSe₂/SnO₂, as shown in Fig. 4(a1), reveals that the TDOS curve shifts upward at -18eV, -8eV, and 2eV, indicating an interaction between NO₂ and the heterostructure. This interaction leads to noticeable changes in the electronic structure.

In the case of Pr-SnSe₂/SnO₂, shown in Fig. 4(a2), the TDOS curve exhibits an upward shift across almost all energy levels. In particular, the pronounced peak near 1 eV, close to the Fermi level, suggests a strong interaction between NO₂ and Pr-SnSe₂/SnO₂, which can be attributed to the presence of Pr.

In Fig. 4(b1) and Fig. 4(b2), the TDOS for NO adsorption on La-SnSe₂/SnO₂ and Pr-SnSe₂/SnO₂ heterostructures are presented, respectively. For the NO/ La-SnSe₂/SnO₂ system, slightly increasing in the TDOS peaks at approximately - 18 eV and 0 eV, together with a small rightward shift near - 7 eV, indicate a weak interaction between the NO molecule and the heterostructure surface. In contrast, the TDOS of the NO/Pr-SnSe₂/SnO₂ system exhibits noticeable rightward shifts at around - 19.5 eV and - 6.5 eV, along with the appearance of a peak close to the Fermi level. These changes suggest a stronger electronic interaction between NO and Pr-SnSe₂/SnO₂ compared with La-SnSe₂/SnO₂.

For NH₃ adsorption, as shown in Fig. 4(c1) and Fig. 4(c2), the TDOS spectra exhibit nearly identical behavior before and after adsorption for both heterostructures, indicating minimal influences of NH₃ on the electronic structure. Only slight variations are observed around - 18 eV for La-SnSe₂/SnO₂ and - 19 eV for Pr-SnSe₂/SnO₂, which reflects weak interaction between NH₃ molecules and the surfaces.

Finally, for HCN adsorption, Fig. 4(d1) shows that the TDOS of La-SnSe₂/SnO₂ undergoes only minor changes at approximately - 17.5 eV, -8 eV, and 1 eV, indicating weak adsorption behavior. Meanwhile, Fig. 4(d2) reveals the appearance of a very small peak near - 19 eV for the Pr-SnSe₂/SnO₂ system, suggesting a limited electronic interaction after HCN adsorption.

3.3.2 Partial Density of States

Figure 5 represents the PDOS of La-SnSe₂/SnO₂ and Pr-SnSe₂/SnO₂ heterostructure adsorbing (NO₂, NO, NH₃, and HCN). In La-SnSe₂/SnO₂ (Fig. 5(a1)), the adsorbed NO₂ gas molecules are shown. The orbital overlaps are experimental between La-5d orbitals and O-2p and N-2p orbitals, with energies ranging from - 7 eV to -6 eV and to 2.5 eV, and show increased intensity near the Fermi level. Figure 5(b1) shows adsorbed NO gas molecules; an overlap between the O-2p, N-2p, and La-5d orbitals is observed around - 7 eV, as well as at the Fermi level, indicating hybridization between these orbitals. In Fig. 5(c1), an orbital overlap is observed at approximately - 5.5 eV between La-5d and N-2p, which signifies the formation of a chemical bond between these two atoms. This bonding interaction implies that the adsorption of NH₃ is relatively weak, attributable to the limited extent of orbital hybridization involved. In Fig. 5(d1), there is an overlap between H-1s, C-2p, N-2p and La-5d at -7 eV. The La-related band gradually increases toward higher energy. It reaches a maximum at 1 eV, where it again overlaps with other states to form a chemical bond, providing evidence of HCN adsorption.

On the other hand, the PDOS of the Pr-SnSe₂/SnO₂ when adsorbing the four toxic gases (NO₂, NO, NH₃, and HCN) respectively, shows an almost perfect overlap for the four plots (a2, b2, c2, and d2), with noticeably higher intensity compared to the PDOS of La-SnSe₂/SnO₂. The PDOS values range from

approximately 18 to 22 electrons/eV near the Fermi level, indicating the high sensitivity of this surface to these gases.

3.4. Recovery Time

We show the relation between desorption energy and recovery time of La-SnSe₂/SnO₂ and Pr-SnSe₂/SnO₂ at three temperatures (298K, 398K, 498K). A long recovery time is associated with a strong interaction [38]. We can calculate recovery time by using the following relation [39]:

$$\tau = v^{-1} \exp \left(-\frac{E_{ads}}{kT} \right) \quad (4)$$

Where v represent the frequency (10^{12} s^{-1}), T is the temperature and k is the Boltzman constant ($8.62 \times 10^{-5} \text{ eV/K}$). The higher desorption energy leads to more negative adsorption energy (E_{ads}) values and leads to a longer recovery time in the desorption process.

Figure 6(a) shows the recovery time of four toxic gases (HCN, NH₃, NO, and NO₂) adsorbed on the La-SnSe₂/SnO₂ heterostructure at three temperatures (298K, 398K, 498K). It is clear that the x-axis in Fig. 6(a) represents the temperatures and also shows that the recovery time decreases with increasing temperature. At the same time, the y-axis represents the recovery time, which follows the sequence HCN<NH₃<NO<NO₂. At (298K), which represents room temperature, the recovery time of NO₂, NO, NH₃, and HCN is very high, maybe several months, and this represents a considerable challenge because of the significant potential of material adsorption of these gases at low temperatures. At high temperature (498K), we get contrast; the recovery time of NH₃ is (37 s). Regarding the recovery time of HCN at same temperature, which is equal (0.07 s), these results lead to high efficiency of desorption. The short recovery time indicates that the gas sensor of La-SnSe₂/SnO₂ heterostructure is a good choice for repeated use.

Figure 6(b) is identical to Fig. 6(a) in terms of axes, and the four toxic gases are arranged in the same order, but the surface used is Pr-SnSe₂/SnO₂. Using this heterostructure, we observe a significant increase in the recovery times of NO₂ and NO at all temperatures compared to La-SnSe₂/SnO₂. At (298K), the desorption of NH₃, NO, and NO₂ gases from Pr-SnSe₂/SnO₂ heterostructure is difficult because of the high value of recovery time. But at high temperature (498K), the recovery time of NH₃ is equal (30 s), and this indicates a high efficiency of desorption. At the same time, the recovery time of HCN is equal to 0.07s, at same temperature. The short recovery times indicates that Pr-SnSe₂/SnO₂ is a good sensor for NH₃ and HCN at 498K.

Finally, comparing the results of the recovery time of La-SnSe₂/SnO₂ heterostructure and Pr-SnSe₂/SnO₂ heterostructure, we find that both surfaces are sensing (NH₃, NO₂, NO, and HCN) gases at low and high temperatures, but the best results are in (NH₃, HCN), making it an ideal gas sensor.

3.5 Work Function

High sensitivity is essential for a high-quality sensing material, as it depends entirely on the work function, which in turn depends on the material's electronic properties [40]. The work function is expressed by the energy threshold that enables the electron to be freed from the surface of the material. This energy enables the electron to move from the Fermi level to vacuum level, which controls the electrostatic potential. It depends entirely on charge transfer. The work function can be calculated from the following relationship [41]:

$$\phi = E_{vac} - E_f \quad (5)$$

Where E_{vac} represents the vacuum level and E_f represents Fermi level.

Figure 7 shows the work function of the both systems, La-SnSe₂/SnO₂ and Pr-SnSe₂/SnO₂, before and after adsorption of the four toxic gases (NO₂, NO, NH₃, and HCN). In the Pr-SnSe₂/SnO₂ heterostructure, after the adsorption of NO₂ and NO gases, we note that the magnitude of the work function for NO₂ and NO gases is 5.76eV and 5.46eV, respectively, which are higher than those of La-SnSe₂/SnO₂ for the same two gases, which are 5.74eV and 5.41eV, respectively.

These results show that the work function of Pr-SnSe₂/SnO₂ is the highest of NO₂ and NO gases, i.e., greatest gas sensing and charge transfer, which supports the results we obtained previously. The work function for the gases NH₃ and HCN on La-SnSe₂/SnO₂ is 4.32eV and 4.65eV, respectively, which is greater than those of its counterpart on Pr-SnSe₂/SnO₂. These changes in the work function, along with previous results, lead us to conclude that Pr-SnSe₂/SnO₂ is a promising material for oxygen-containing gas sensors. At the same time, La-SnSe₂/SnO₂ is a promising material for hydrogen-containing gas sensors.

4. Conclusion

In this work, using the DFT method, we were able to detect and sense toxic nitrogen gases on a heterostructure SnSe₂/SnO₂ surface doped with rare earth (La and Pr). This doping is very important for making sensors more effective and efficient at detecting toxic gases, especially nitrogenous gases. The results show a difference in the sensitivity of the two surfaces to the four toxic gases (NO₂, NO, NH₃, and HCN). We observe that the Pr-SnSe₂/SnO₂ heterostructure is more sensitive to nitrogenous gases containing oxygen, as clearly demonstrated by the adsorption energies and charge transfer. This indicates a stronger reaction and greater stability when using this heterostructure. However, in the case of nitrogen gases containing hydrogen, and through adsorption energies and charge transfer, we find that La-SnSe₂/SnO₂ is more sensitive, but only slightly, compared to Pr-SnSe₂/SnO₂, indicating that this surface is more effective and sensitive to NH₃ and HCN gases. Regarding the recovery time, we observe that Pr-doped SnSe₂/SnO₂ has a faster recovery time for NO₂ and NO gases compared to the La-doped

SnSe₂/SnO₂. Conversely, La-doped SnSe₂/SnO₂ exhibits a faster recovery time for NH₃ and HCN gases than its Pr-doped counterpart.

Finally, our work illustrates the significance of obtained results compare with previous studies, which reinforces the important role of our improved heterostructures in supporting nitrogenous toxic gas sensors.

Declarations

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Author Contribution

W.R. design of study and drafting the manuscript. L. A. Revising the manuscript critically for important intellectual content and approval of the version of the manuscript to be published.

Data Availability

All data generated or analysed during this study are included in this published article.

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Figures

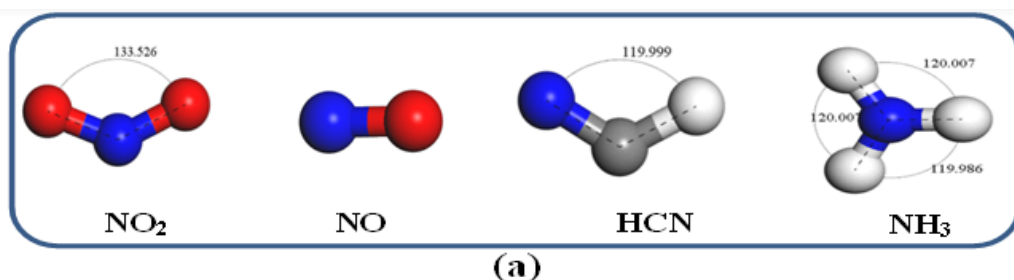
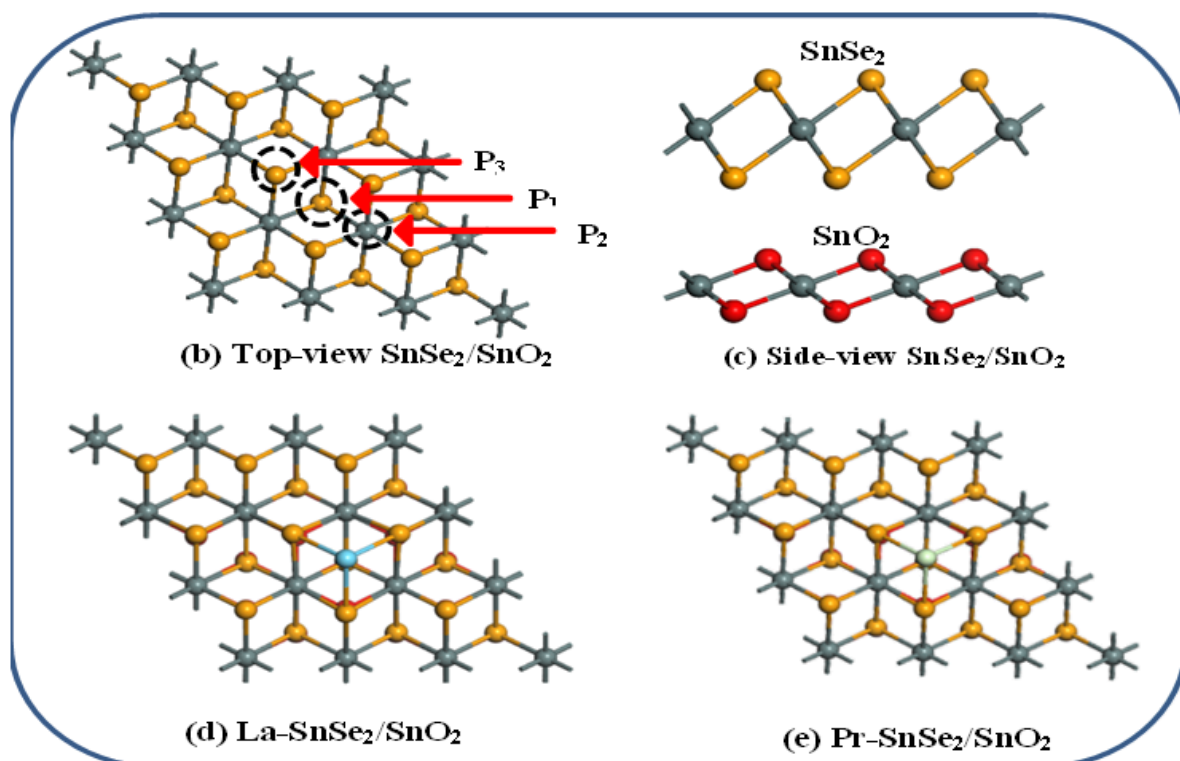
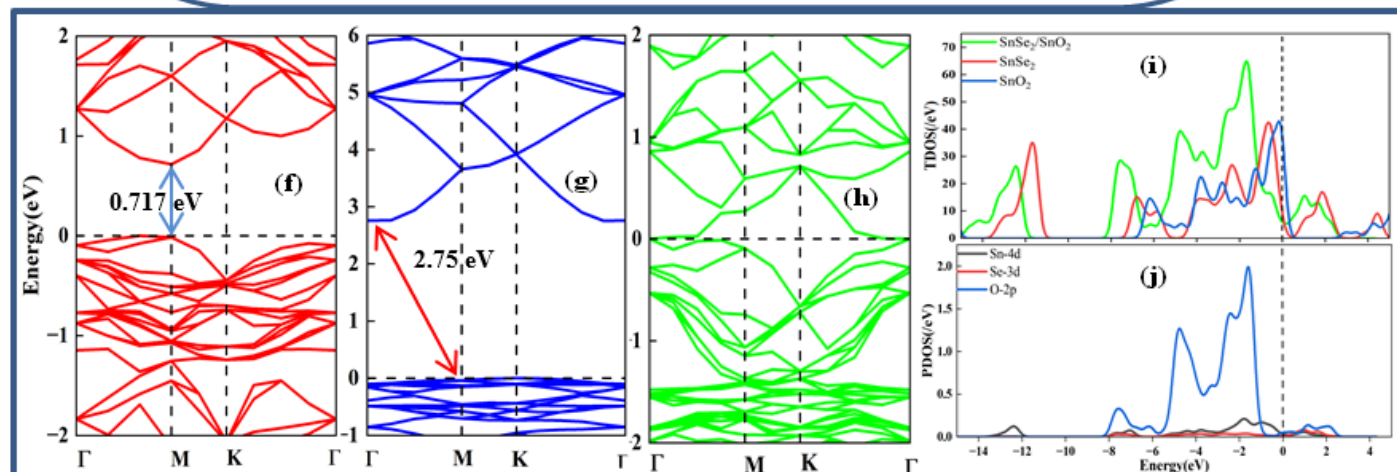


Figure 1

(a) Nitrogenous Toxic Gases: NO₂, NO, HCN and NH₃, (b) and (c) represent the top and side-view of SnSe₂/SnO₂ heterostructure, respectively, (d) and (e) represent SnSe₂/SnO₂ doping with La and Pr, respectively. (f), (g) and (h) represent band structure of SnSe₂, SnO₂ and SnSe₂/SnO₂, respectively. (i) and (j) represent the TDOS and PDOS of SnSe₂/SnO₂.

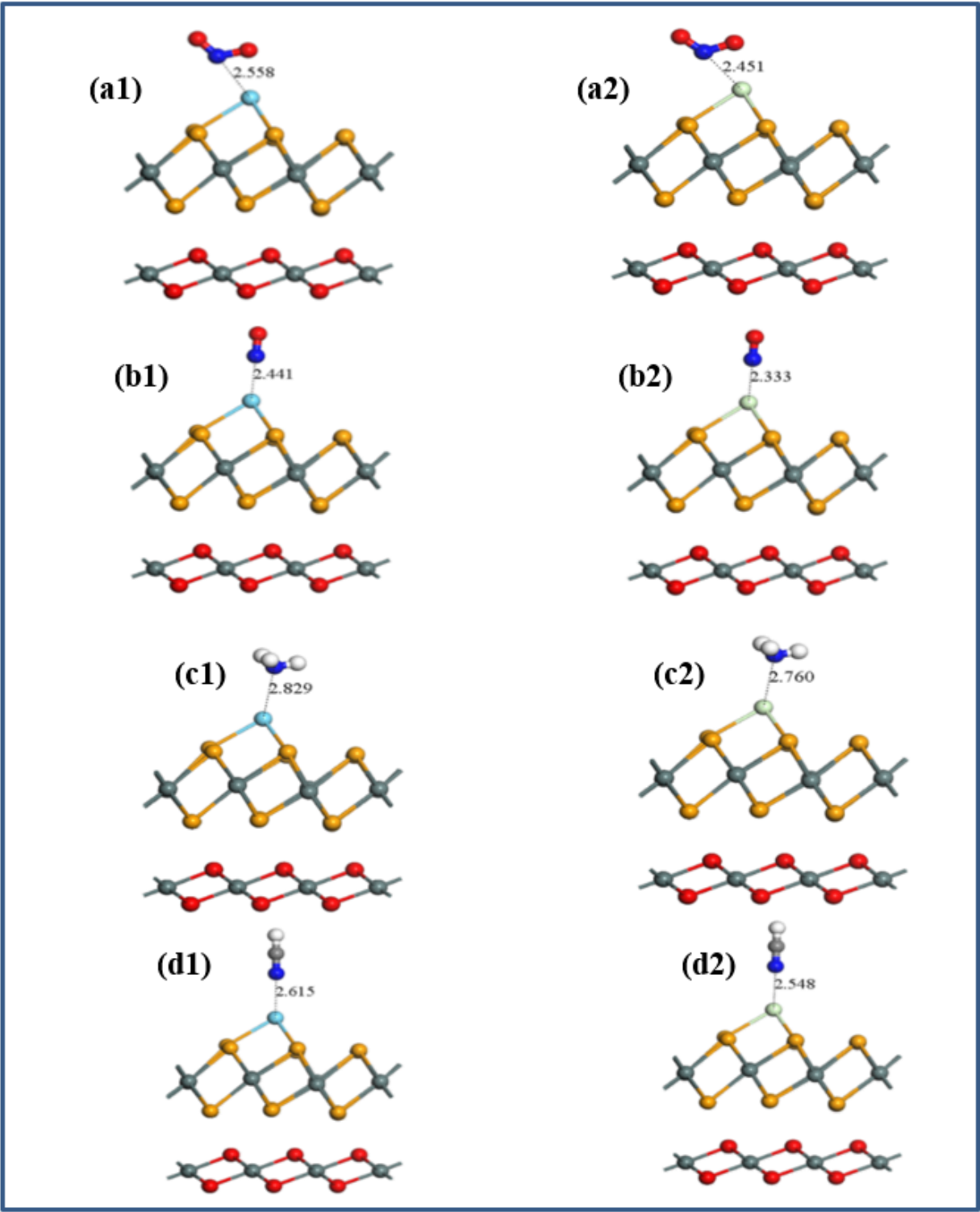


Figure 2

Structure of gas molecules: (a1) NO₂, (b1) NO, (c1) NH₃, and (d1) HCN adsorbed on La-SnSe₂/SnO₂, (a2) NO₂, (b2) NO, (c2) NH₃, and (d2) HCN adsorbed on Pr-SnSe₂/SnO₂.

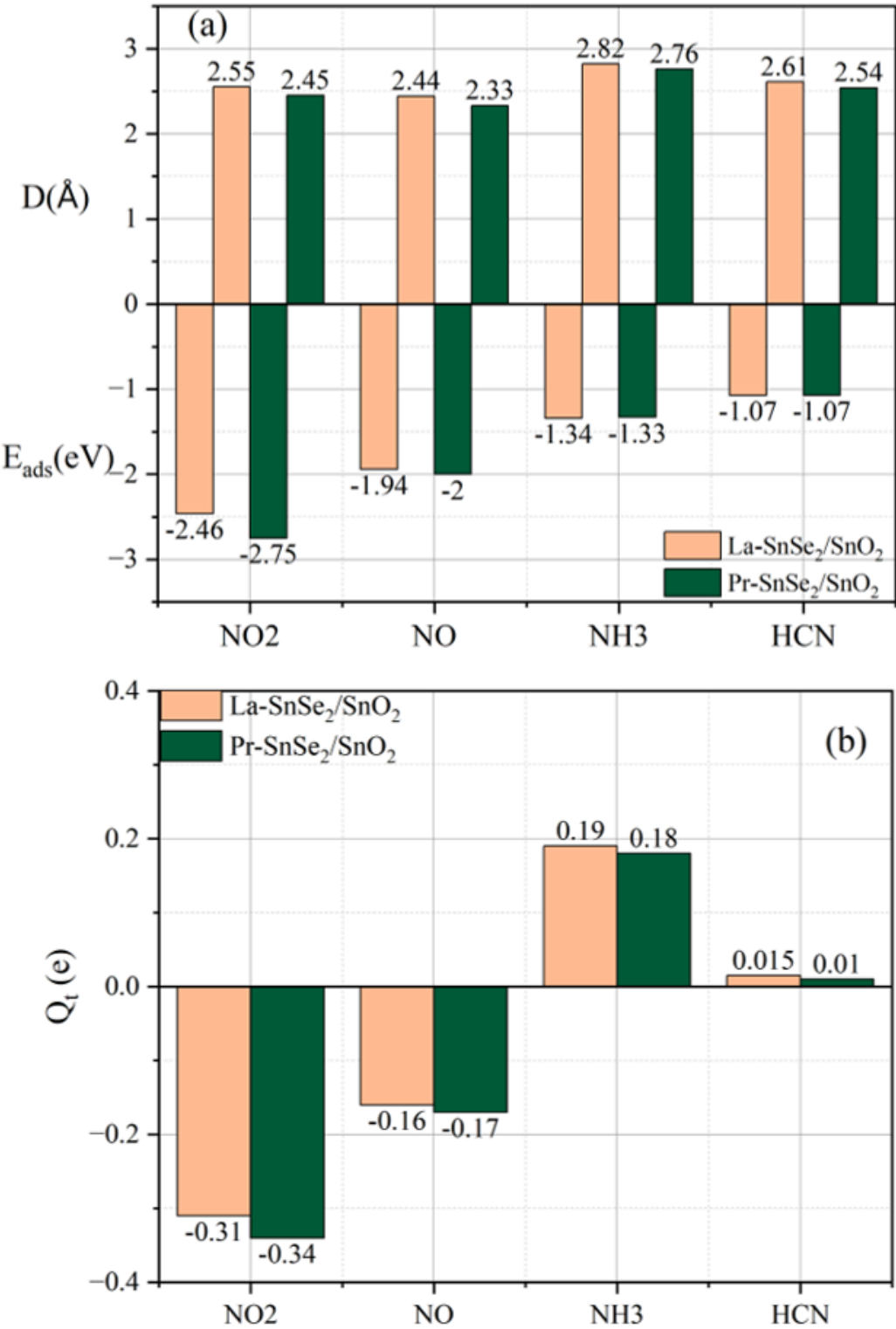


Figure 3

Adsorption characteristics of gas molecules on La-SnSe₂/SnO₂ and Pr-SnSe₂/SnO₂. (a) Adsorption distance (D in Å) and adsorption energy (E_{ads} in eV) and (b) charge transfer (Q_t in e). Data are provided for NO₂, NO, NH₃ and HCN.

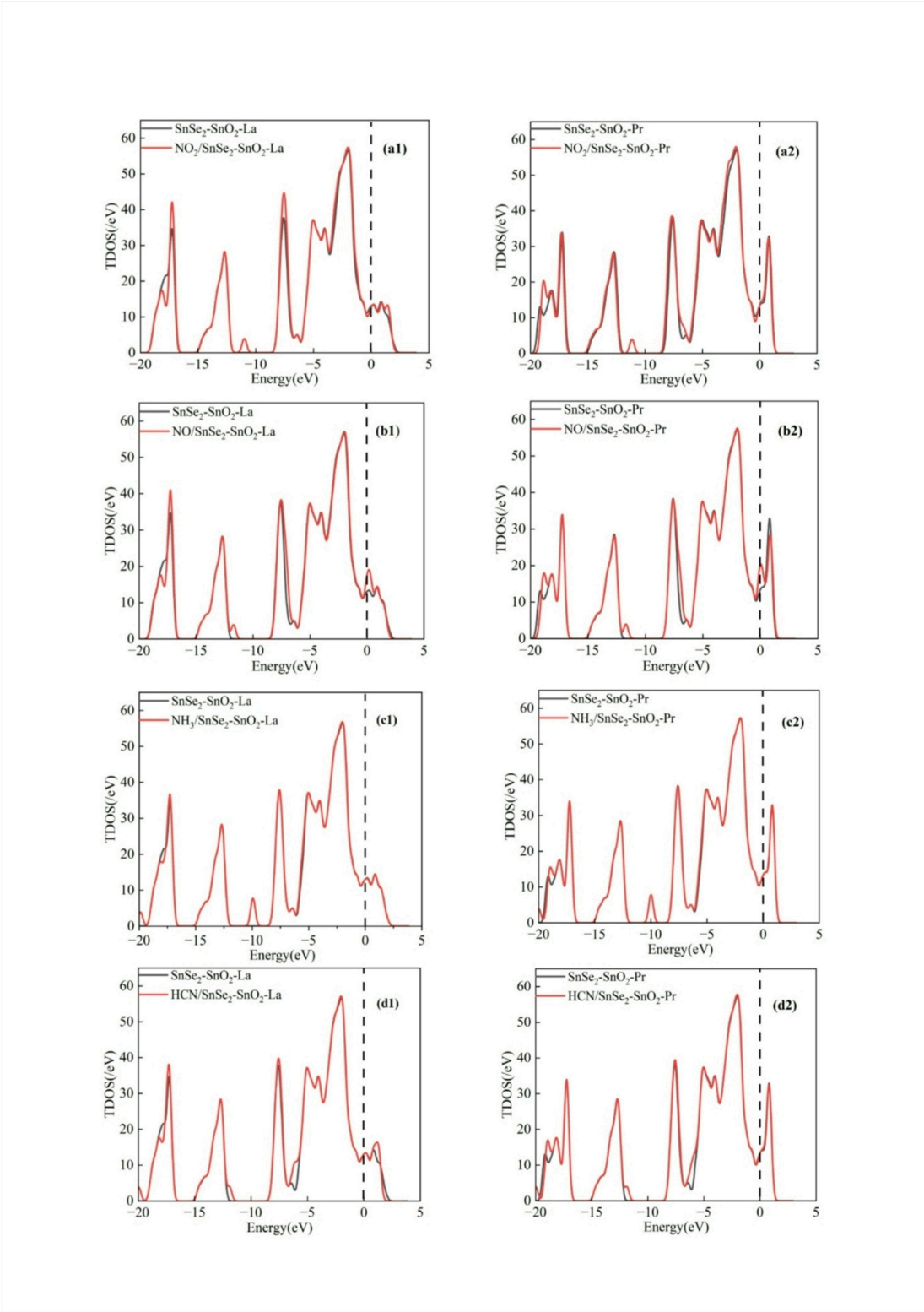


Figure 4

TDOS of La- SnSe₂/SnO₂ when adsorption (a1) NO₂ (b1) NO (c1) NH₃ and (d1) HCN, also for Pr- SnSe₂/SnO₂ when adsorption (a2) NO₂ (b2) NO (c2) NH₃ and (d2) HCN.

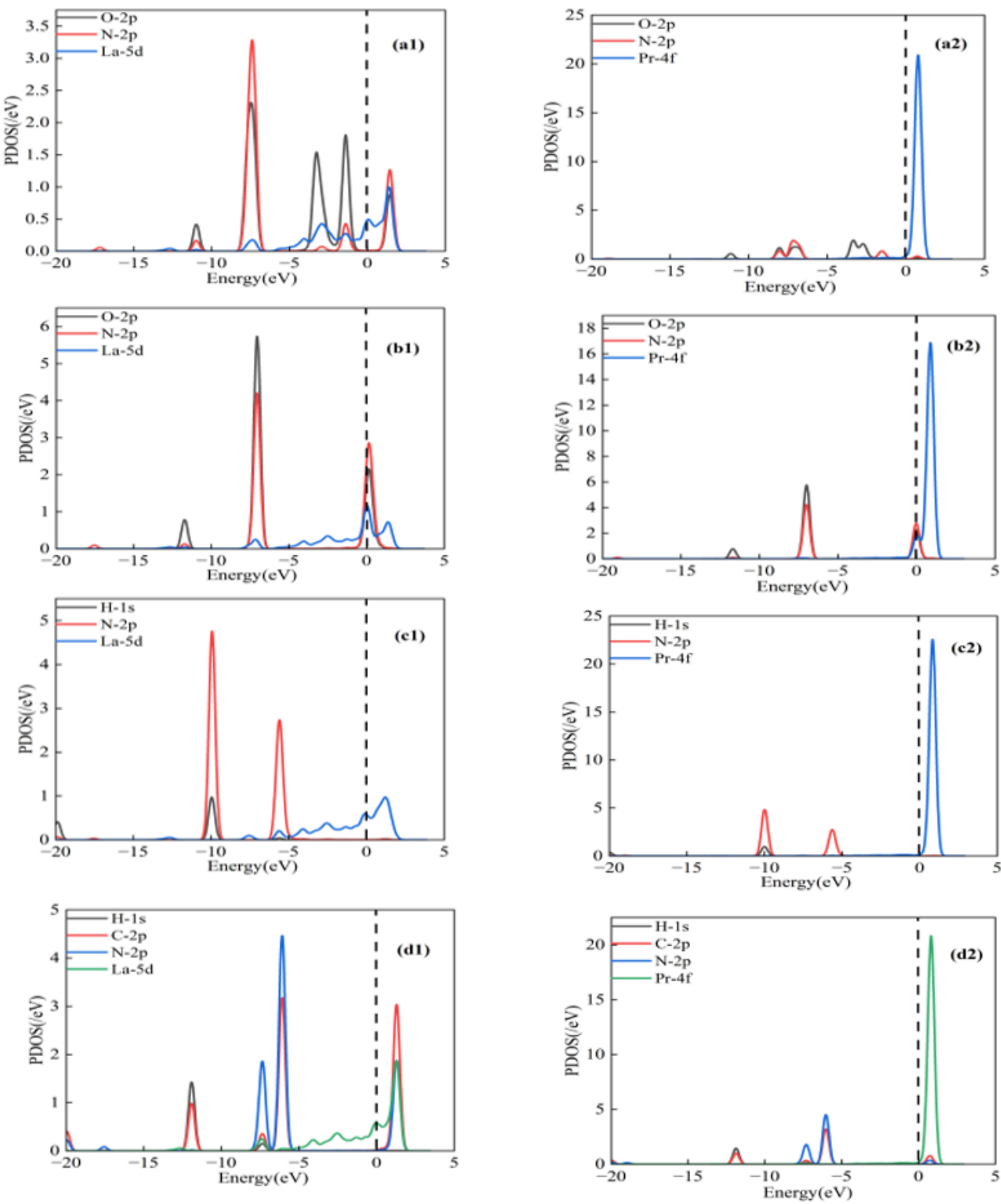


Figure 5

PDOS of La-SnSe₂/SnO₂ when adsorption (a1) NO₂ (b1) NO (c1) NH₃ and (d1) HCN, also for Pr- SnSe₂/SnO₂ when adsorption (a2) NO₂ (b2) NO (c2) NH₃ and (d2) HCN.

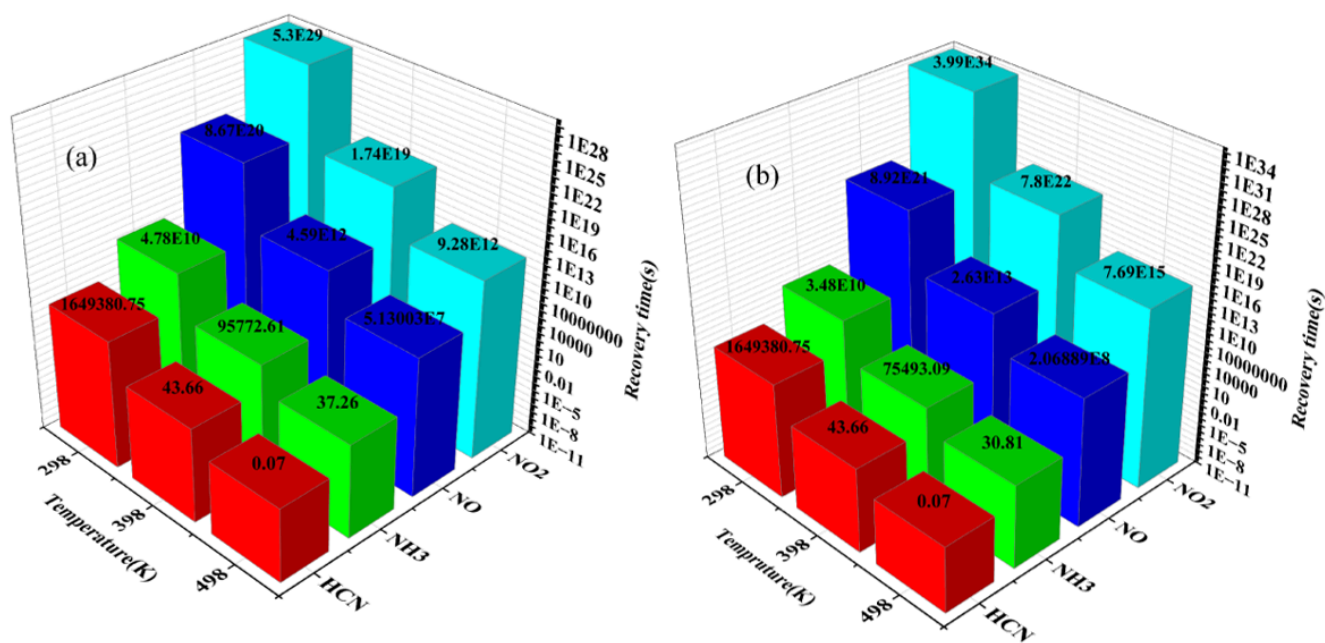


Figure 6

(a) The recovery time of HCN, NH₃, NO and NO₂ and on La-SnSn₂/SnO₂ heterostructure, (b) the recovery time of HCN, NH₃, NO and NO₂ on Pr-SnSe₂/SnO₂ heterostructure.

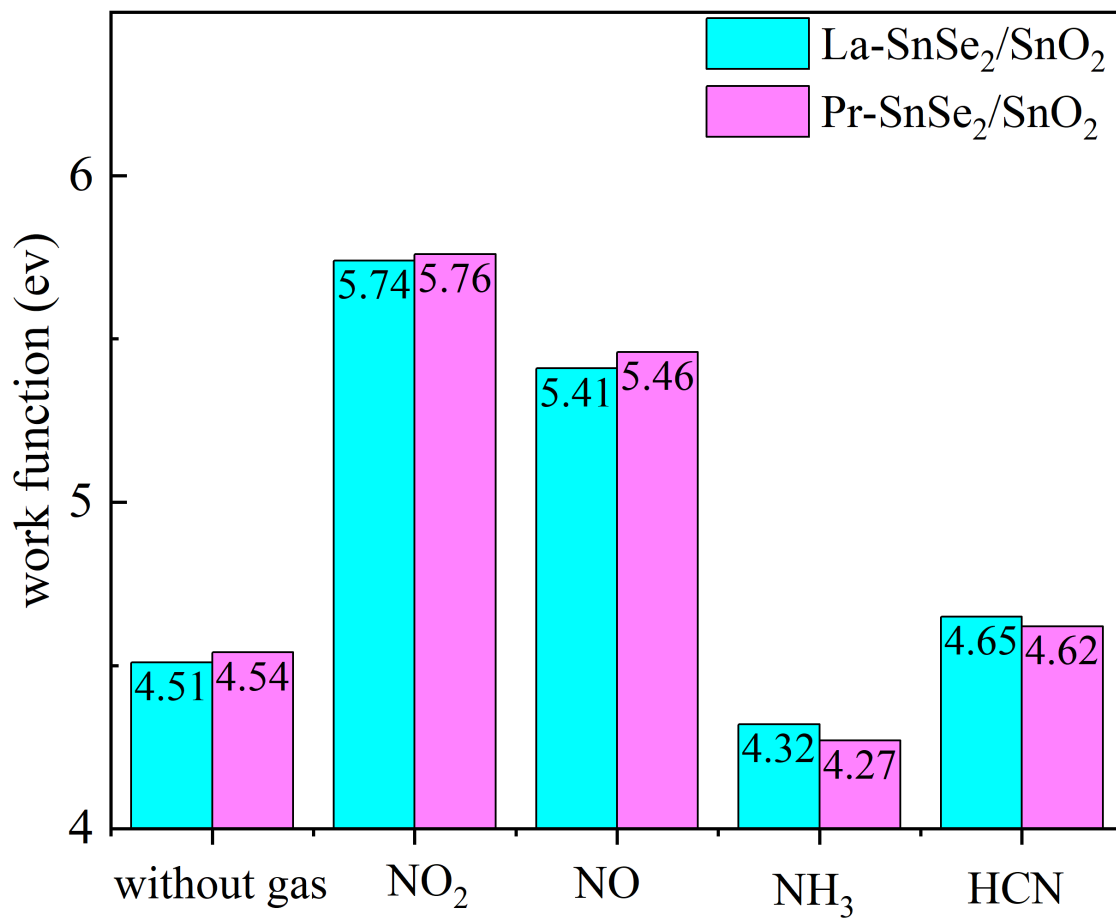


Figure 7

The work function of La-SnSe₂/SnO₂ and Pr-SnSe₂/SnO₂ heterostructures before and after the adsorption of nitrogenous gases.