



Article DFT Calculations of Silver Atom Modified Tungsten Disulfide Monolayer as Promising Sensing Materials for Small Molecular Toxic Gases

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Abstract: In the contemporary context, the significance of detecting harmful gases cannot be overstated, as it profoundly affects both environmental integrity and human welfare. In this study, theoretically, density functional theory was employed to explore the adsorption behavior of three prevalent hazardous gases, namely CO, NO2, and SO2, on silver-atom-modified tungsten disulfide (WS₂) monolayer. The multifaceted analysis encompasses an array of critical aspects, including the adsorption structure, adsorption energy, electron transfer, and charge density difference to unravel the adsorption behavior. Further exploration of electronic properties encompassing band structure, density of states (DOS), and work function was conducted. The ambit of our exploration extends to the desorption properties based on adsorption-free energies. Among these gas molecules, NO_2 stands out with the highest adsorption energy and the most substantial electron transfer. Notably, each of these adsorption processes triggers a redistribution of electron density, with NO₂ exhibiting the most pronounced effect. Furthermore, the adsorptions of CO, NO₂, and SO₂ induce a noteworthy reduction in the band gap, prompting the reconfiguration of molecular orbitals. Additionally, the adsorption of these gases also leads to an increase in the work function of Ag-WS₂ to a different extent. Our investigation of desorption properties uncovers that Ag-WS₂ can adeptly function at ambient temperatures to detect CO and SO₂. However, for NO₂ detection, higher temperatures become imperative due to the necessity for poison removal. The implications of our findings underscore the tremendous potential of $Ag-WS_2$ as a sensing material for detecting these hazardous gases. Our research extends to the broader realm of surface modification of transition metal dichalcogenides and their promising applications in the domain of gas sensing.

Keywords: hazardous gases; Ag doped WS₂ monolayer; DFT; adsorption; gas sensor

1. Introduction

The detection and monitoring of hazardous gases plays a crucial role in safeguarding both the environment and human life [1,2]. The release of environmentally harmful gases from various natural sources, industrial processes, and vehicular emissions poses serious threats to air quality and human health [3–5]. Environmental monitoring is crucial for understanding the impact of hazardous gases on air quality and the ecosystem. The early detection of gas leaks or abnormal gas concentrations in industrial settings can prevent accidents and protect workers' safety. Furthermore, monitoring of air quality in urban areas can aid in implementing timely public health interventions to reduce the adverse effects of pollution on respiratory and cardiovascular health. To address these challenges, researchers have been actively exploring advanced gas sensing technologies, particularly chemical gas sensors, to detect and quantify several hazardous gases [2,6,7].

Currently, significant progress has been achieved in the development of chemical gas sensors for detecting various hazardous gases. These gas sensors enable selective and



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). sensitive detection of specific gas molecules. Furthermore, advances in nanotechnology and materials science have led to the creation of miniaturized, low-power, and cost-effective gas sensors. This, in turn, facilitates their integration into various environmental monitoring systems and wearable devices [8,9]. Typically, gas sensors rely on various sensing materials that exhibit distinct gas-sensing properties. These include metal oxides [2], metal-organic frameworks (MOFs) [10], conductive polymers [7], and two-dimensional (2D) materials like graphene and transition metal dichalcogenides (TMDs) [11]. Among these materials, 2D materials have emerged as promising candidates for gas sensing applications due to their exceptional characteristics. These encompass a high surface-to-volume ratio, impressive mechanical and chemical stability, and the potential for miniaturization [12]. TMDs constitute a group of compounds that display appealing sensing properties for various gases, such as inorganic gases with compact structures and volatile organic compounds (VOC) [13,14]. Unlike graphene, which lacks a bandgap, most TMDs possess an adjustable bandgap of approximately 1~2 eV [15]. WS₂, a well-known TMD, exhibits a high mobility of about 140 cm²V⁻¹S⁻¹ and an excellent on/off ratio of about 1×10^8 [16]. This has led to the innovation of novel field-effect transistors (FET) and optical devices. When WS₂ is employed as a gas sensing material, it often demonstrates p-type semiconductor properties. This implies that when detecting oxidizing gases, its resistance decreases, and vice versa [17]. With these characteristics, WS_2 can differentiate between different gas types by detecting changes in resistance, such as NO_2 and NH_3 [18–20]. However, pristine WS_2 often fails to meet the requirements for sensitivity and selectivity, promoting the application of various modification methods.

Several effective methods have proven successful in enhancing the sensing properties of WS₂. These methods include the construction of composite structures, such as composites with graphene [21,22], carbon nanotube [23], and metal oxide [24–26], as well as surface modification using transition metal (TM) nanostructures [27,28]. TM nanostructures introduce active sites onto WS₂, and these active sites exhibit varying adsorption and catalytic effects on different gases, thereby contributing to selectivity [29]. Previous theoretical studies have indicated that the adsorption strength of several inorganic molecules on intrinsic WS₂ is relatively weak, with adsorption energies not exceeding 0.42 eV [30–32]. Via the introduction of TM active sites via doping, interactions can be intensified, and the selectivity for specific gases can be achieved. Various research studies have explored the impact of adsorption behavior from TM active sites on different TMDs. Hu et al. conducted a comprehensive study on the adsorption of small molecule gases on TM-atom-doped MoS₂. They discovered that different TM active sites yield varying adsorption strengths and selectivity for small inorganic gases like CO, NO, NO₂, and NH₃ [33]. Through the manipulation of different elements, the adsorption effect of MoTe₂ on CO can be enhanced and differentiated [34]. Similar adjustments in the adsorption effect were also observed for NO₂ adsorption [35]. Jia et al. [36] reported on the adsorption of CO₂, NO₂, and NO on different TM-doped WSe₂. By comparing work functions, they determined that Ag doping is suitable for NO₂ detection. Among the noble metal dopants, Ag stands out as one of the most affordable noble metal options. Furthermore, Ag sites exhibit high reactivity toward the adsorption of small molecules and can lower the operation temperature of the sensors [37]. For instance, Er et al. found that Ag decoration leads to the maximum sensitivity improvement in NH₃ detection compared to other noble metal modifications, including Pt and Au, for the reason that Ag nanoparticles bring higher activity for O_2 decomposition and detect gas molecule adsorption [38]. Moreover, Ag on TMDs belongs to n-type doping and can adjust the electron transfer for modulating the potential barrier. Zhang et al. discussed the sensing performance using Ag-doped MoSe₂ sensing materials, and the sensitivity to H₂S was obviously improved [39]. Kim et al. discovered that Ag nanostructure on WS_2 can enhance the sensitivity as well as recovery performance of NO_2 because of the n-type doping and synergistically catalytic effect [40]. From the above discussion, Ag doping is beneficial to simultaneously improve the electronic structure and catalytic performance for detected gas adsorption and decomposition, and Ag-WS₂

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heterostructure can bring excellent carrier characteristics of optical excitation [41]. Given the limited adsorption behavior and selective detection of several toxic gas molecules on pristine WS₂ and the advantageous of Ag active sites, it is imperative to further investigate adsorption performance, gas sensitivity and selectivity.

In this research, first-principles calculations based on density functional theory (DFT) to investigate the adsorption of three representative hazardous gases (CO, NO₂, and SO₂) on an Ag-doped WS₂ monolayer were employed. Detailed calculations of atomic structures and adsorption parameters were conducted, followed by a comprehensive comparison. Moreover, the alterations in electronic properties before and after adsorption were discussed, and the sensing properties were also evaluated. To summarize, this study offers a theoretical perspective on the sensing properties of modified WS₂. It opens up extensive possibilities for exploring diverse TMDs as sensing materials and varying surface modifications to enhance sensing characteristics.

2. Methods

The spin-restricted DFT calculations were performed using the DMol³ module [42]. The exchange-correlation function was evaluated approximately using the Perdew–Burke–Ernzerhof (PBE) method, derived from the generalized gradient approximation (GGA) [43]. The cutoff radius for all the structures was set to 5.0 Å. The DFT semi-core pseudopotential (DSSP) was utilized to handle core electrons, and the double numerical polarization (DNP) basis set was employed for valence electrons. For periodic WS₂ structures, a Monkhorst–Pack k point grid of $10 \times 10 \times 1$ was used [44]. Given the weak interactions associated with gas adsorption, the long-range forces were accounted for using the Tkatchenko-Scheffler dispersion correction [45]. Convergence in the geometric optimization process was considered achieved when the energy difference reached 10^{-6} Ha (1 Ha = 27.21 eV), the maximum force reached 0.001 Ha/Å, and the maximum displacement of all atoms reached 0.005 Å. To prevent interlayer interactions, a vacuum slab of 15 Å was incorporated along the *z*-axis. The WS₂ supercell was constructed using a 4×4 super cell arrangement. To obtain the Ag-doped WS₂ monolayer, one S atom was replaced by an Ag atom, with Ag forming bonds with three adjacent W atoms. The adsorption energy (E_{a-Ag}) of the Ag atom on the defective WS₂ was:

$$E_{a-Ag} = E_{Ag-WS_2} - E_{WS_2 \text{ with } S \text{ vacancy}} - E_{Ag \text{ atom}}$$
(1)

where E_{Ag-WS2} , E_{WS2} with S vacancy, and $E_{Ag atom}$ represent the total energy of Ag-WS₂ monolayer, WS₂ monolayer with one S vacancy, and one isolated Ag atom. In order to obtain the adsorption strength of one gas molecule (CO, NO₂, and SO₂) on Ag-WS₂, the adsorption energy can be obtained by:

$$E_a = E_{\text{Ag-WS}_2/\text{gas}} - E_{\text{Ag-WS}_2} - E_{\text{gas}}$$
(2)

where $E_{Ag-WS_2/gas}$ and E_{gas} are the total energy of Ag-WS₂ after one gas molecule adsorption and the isolated gas molecule. All the charge calculations were based on Hirshfeld analysis [46]. The charge transfer (Q_t) of gas adsorption was:

$$Q_{\rm t} = Q_{\rm ads-gas} - Q_{\rm iso-gas} \tag{3}$$

where $Q_{ads-gas}$ and $Q_{iso-gas}$ are the charges of the adsorbed gas molecule and isolated molecule. From the formula, it is found that the negative value indicates the role of the electron acceptor of the gas molecule and vice versa. The charge density difference (CDD) can be calculated as:

$$\Delta \rho = \rho_{\rm Ag-WS_2/gas} - \rho_{\rm Ag-WS_2} - \rho_{\rm gas} \tag{4}$$

where $\rho_{Ag-WS_2/gas}$, ρ_{Ag-WS_2} , and ρ_{gas} are the electron density of Ag-WS₂ monolayer after adsorption, Ag-WS₂ monolayer before adsorption, and isolated molecule, respectively.

Considering the sensing properties, the work functions (Φ) of Ag-WS₂ before and after adsorption was calculated as follows:

$$\Phi = E_{\text{vacuum}} - E_{\text{Fermi level}} \tag{5}$$

where E_{vacuum} and $E_{\text{Fermi level}}$ are the energy of vacuum level and Fermi level of Ag-WS₂ before or after adsorption.

3. Results

3.1. Structure, Electronic Properties and Stability of Ag Doped WS₂ Monolayer

Firstly, the supercell of the pristine WS₂ monolayer was optimized. The optimized lattice parameters of the 4 × 4-size WS₂ supercell were found to be 12.76 Å, with a W-S bond length of 2.43 Å. These results are in good arrangement with previous studies (which reported 6.37 Å for a 2 × 2-sized supercell) [47]. For the Ag-WS₂ structure, an S vacancy was introduced, and this vacancy was then substituted with an Ag atom. The optimized structure of the WS₂ monolayer, WS₂ with a single S vacancy, and the Ag-WS₂ monolayer are depicted in Figure 1. The Ag atom is positioned between three W atoms and forms bonds with them. The calculated bond length for the Ag-W is 2.84 Å, which is greater than the W-S bond length. Consequently, the Ag atom extends beyond the S plane. Furthermore, the adsorption energy of Ag on the defective WS₂ monolayer is determined to be 2.31 eV, indicative of an exothermic process. Additionally, following adsorption on the S vacancy, the Ag atom carries a positive charge of +0.25 eV. As illustrated by the CDD configurations in Figure 2a, an electron depletion region forms above the Ag atom, while electrons tend to accumulate around three Ag-W bonds. This phenomenon also underscores the transfer of electrons from Ag to the WS₂ monolayer.



Figure 1. The optimized structures of perfect, defect, and Ag-doped WS₂ monolayer: (**a**) pristine WS₂ monolayer; (**b**) WS₂ monolayer with one S vacancy; (**c**) Ag-doped WS₂ monolayer.

Regarding the electronic properties of both pristine and Ag-doped WS₂ monolayers, the band structures are depicted in Figure 2(b1,b2). The pristine WS₂ exhibits a band gap of 1.85 eV based on the PBE method, aligning closely with previous research findings (ranging from 1.80 eV to 1.85 eV) [47,48]. It is generally recognized that the PBE method may underestimate the band gap [49]; however, this study mainly focused on the relative change of the gap value after different gas adsorption. Additionally, considering the computational efficiency, this study still used PBE to evaluate the band gap change for gas detection. Upon Ag doping, several bands emerge between the valence and conductive states, leading to a reduction in the band gap to 1.28 eV. For a comprehensive examination of the new bands, the density of states (DOS) is illustrated in Figure 2(c1,c2). In the total DOS (TODS) of Ag-WS₂, a distinct peak is present above 0 eV. However, the peak originating from Ag 4d orbitals is notably smaller. Conversely, examining the DOS of one of the adjacent W atoms, the peak is attributed to W 5d orbitals. Thus, the introduction of the Ag atom noticeably alters the W 5d orbitals, leading to observable hybridization above 0 eV between Ag 4d and W 5d orbitals. This hybridization indicates chemical interactions between Ag and W atoms and serves as the rationale behind the reduction in the WS₂ band gap. Furthermore, an evaluation of thermal stability is also conducted. Molecular dynamic (MD) simulations were performed under a constant temperature and constant volume (NVT) canonical ensemble at 500 K, covering a duration of 5000 fs (with intervals of 2 fs) of 2500 steps. The outcomes are presented in Figure 2(d1,d2), affirming the structural integrity of the Ag-WS₂ monolayer with no apparent bond breakage. The total energy of the structure remains within a reasonable range. Consequently, the MD results substantiate the thermal stability of the Ag-WS₂ monolayer.



Figure 2. Electronic properties and stability of Ag-WS₂: (**a**) CDD of Ag-WS₂ (the isosurface is 0.01 e/Å^3 , and the pink and yellow represent the electron accumulation and depletion region, respectively); (**b1**,**b2**) band structure of pristine WS₂ monolayer and Ag-doped WS₂ monolayer; (**c1**,**c2**) DOS of Ag-WS₂, and atomic orbitals of Ag and one of the adjacent W atoms; (**d1**,**d2**) thermal stability of Ag-WS₂ monolayer at 500 K.

3.2. Adsorption of CO, NO₂, and SO₂ on Ag-WS₂ Monolayer

Adsorption studies involving CO, NO₂, and SO₂ molecules on Ag-WS₂ were conducted using the Ag atom as the active adsorption site. Various adsorption directions were considered for different molecules. For diatomic molecules, such as CO, the adsorption direction options included C downward and O downward. For symmetrical triatomic molecules (NO₂ and SO₂), two directions were examined: central atom downward and edge atom downward. Following complete geometric optimization, four adsorption configurations with the minimum total energy were identified. These adsorption parameters are presented in Table 1, and the corresponding configurations are illustrated in Figure 3. For NO₂ adsorption, only the O downward configuration with higher adsorption energy was analyzed in greater detail. Concerning CO adsorption on the Ag-WS₂ monolayer, the CO molecule was observed to be nearly perpendicular to the surface, with C facing downward, as shown in Figure 3a. The calculated adsorption energy was approximately -0.73 eV. The distance between the Ag and C atoms measured 2.13 Å, significantly smaller than the

sum of van der Waals radii of the Ag and C atoms (1.72 Å and 1.70 Å, respectively) [50]. This phenomenon suggests the potential formation of a newly formed Ag-C chemical bond after CO adsorption. Hirshfeld analysis indicated that CO loses 0.08 e and gains a positive charge during the adsorption process, implying that CO functions as an electron donor. Upon NO₂ adsorption, two configurations were identified. The O downward configuration exhibits a calculated adsorption energy of -1.40 eV, while the N downward configuration displayed an adsorption energy of -1.11 eV. In comparison, NO₂ demonstrated a preference for adsorption on the Ag site, with O facing downward, as depicted in Figure 3b. This study focused solely on adsorption configurations with higher adsorption energies for NO₂. The distance between Ag and O was measured at 2.34 Å, also smaller than the sum of van der Waals radii of Ag and O atoms (1.72 Å and 1.52 Å, respectively) [50], indicating potential chemical interactions between NO_2 and the Ag atom. During this process, NO_2 accepted 0.40 electrons from the Ag-WS2 monolayer, resulting in a negatively charged identity. Regarding SO_2 adsorption, one O atom within the SO_2 molecule displayed an affinity for proximity to the Ag atom. This configuration exhibited an adsorption energy of -0.69 eV and an adsorption distance (Ag-O) of 2.30 Å, which is smaller than the sum of van der Waals radii of Ag and O atom. Similar to NO₂, SO₂ acted as an electron acceptor, involving an electron transfer of 0.20 e.

Table 1. Adsorption energy, electron transfer, and adsorption distance of three hazardous gas molecules on Ag-WS₂ monolayer.

Adsorption Configurations	E_a (eV)	Q_{t} (e)	Adsorption Distance (Å)
Ag-WS ₂ -CO	-0.73	+0.08	2.13 (Ag-C)
Ag-WS ₂ -NO ₂ (N downward)	-1.11	-0.35	2.21 (Ag-N)
$Ag-WS_2-NO_2$ (O downward)	-1.40	-0.40	2.34 (Ag-O)
Ag-WS ₂ -SO ₂	-0.69	-0.20	2.30 (Ag-O)



Figure 3. Adsorption configurations of CO, NO₂, and SO₂ on Ag-WS₂ monolayer: (**a**) CO on Ag-WS₂ monolayer; (**b**) NO₂ on Ag-WS₂ monolayer ($E_a = -1.40 \text{ eV}$); (**c**) SO₂ on Ag-WS₂ monolayer.

To investigate the electron density contribution, the CDD maps of the three molecules on Ag-WS₂ are depicted in Figure 4. In the case of CO adsorption, electron accumulation manifests below and around the C atom within CO, while electron depletion is observed just above the Ag atom and around the O atom within CO. Notably, the electron movement within CO aligns with the direction of electron transfer. Upon NO₂ adsorption, an electron accumulation region emerges above the N atom. Prominently, a distinct accumulation region surrounds the NO₂ molecule, indicating its role as an electron acceptor. This same pattern is observed for SO₂ adsorption, where conspicuous electron accumulation regions are evident around S and O atoms. Consequently, both NO₂ and SO₂ are negatively charged after adsorption.



Figure 4. CDD configurations and the projection curve of Z-direction of CO, NO₂, and SO₂ on Ag-WS₂ monolayer: (**a**) CO on Ag-WS₂ monolayer; (**b**) NO₂ on Ag-WS₂ monolayer; (**c**) SO₂ on Ag-WS₂ monolayer (the isosurface is 0.01 e/Å^3 , and the pink and yellow represent the electron accumulation and depletion region, respectively).

3.3. Electronic Properties of Ag-WS₂ Monolayer after Gas Adsorption

To compare the electronic properties of Ag-WS₂ before and after adsorption, the calculations of the band structure and DOS after adsorption were conducted, as shown in Figure 5. It is evident that all gas adsorptions result in a reduction in the band gap, as illustrated in Figure 5a,d,g. The calculated band gaps are 1.19 eV, 1.06 eV, and 0.96 eV for CO, NO₂, and SO₂ adsorption, respectively. Notably, both NO₂ and SO₂ adsorptions lead to band rearrangements around 0 eV. Specifically, NO₂ adsorption introduces a new band at 0 eV, contributing to the reduction in bandgap. Conversely, SO_2 adsorption presents a distinct scenario where the new bands form below the conduction band. Additionally, alterations in the morphology of these two curves of new bands are also observed. For an in-depth analysis of the changes in bandgap and a thorough investigation of the molecular orbitals before and after adsorption, the TDOS of Ag-WS₂ after adsorption and the molecular orbitals of CO, NO_2 , and SO_2 are shown in Figure 5b,e,h. Isolated CO exhibits occupied 5σ molecular orbitals and unoccupied $2\pi^*$ [51]. Following adsorption, the previously occupied 5σ orbitals nearly vanish, and the $2\pi^*$ orbitals exhibit a flattened profile with unoccupied characteristics. This observation supports the notion that CO loses electrons upon adsorption. Isolated NO₂ displays an asymmetric DOS, implying inherent magnetism before adsorption [52]. Upon adsorption, the PDOS of NO₂ becomes symmetric. The $3\pi^*$ orbitals, which were partly occupied before adsorption, undergo a leftward shift and become nearly fully occupied after adsorption. In contrast, for SO_2 , the 3b orbitals are entirely unoccupied before adsorption [53]. However, after adsorption, these orbitals experience partial occupation. This molecular orbital analysis underscores the transition of certain orbitals within NO_2 and SO_2 from an unoccupied to an occupied state, providing evidence that they function as electron acceptors during the adsorption process.

The chemical interactions were investigated via the calculation of atomic orbitals of Ag and atoms within molecules. Upon CO adsorption, overlapping states are discernible above 0 eV, indicating unoccupied orbitals. Consequently, the chemical interactions manifest within the vacant atomic orbitals of Ag 4d and C 2p (within CO). However, minimal chemical interactions are observed within the occupied orbitals. Regarding NO₂ adsorption, hybridization between Ag 4d and O 2p (in NO₂) is evident around energy levels of approximately -7 eV, -6 eV, -1.5 eV, and -0.5 eV. These orbitals are all occupied, highlighting the prevalence of chemical interactions within occupied atomic orbitals of Ag 4d and O 2p (in NO₂). In the case of SO₂ adsorption, hybridizations occur within the energy range of about -7.5 eV to -6 eV, in proximity to -3 eV, and around +0.6 eV. Consequently, both occupied and unoccupied orbitals display chemical interactions. In essence, all three molecules exhibit chemical interactions with Ag atoms, with hybridization occurring across both occupied and unoccupied orbitals for different molecules.



Figure 5. Electronic properties of CO, NO₂, and SO₂ on Ag-WS₂ monolayer: (**a**) band structure of CO on Ag-WS₂ monolayer; (**b**) TDOS of CO on Ag-WS₂ monolayer and molecular orbitals of CO before and after adsorption; (**c**) atomic orbitals of Ag 4d in Ag-WS₂ and C 2p in CO; (**d**) band structure of NO₂ on Ag-WS₂ monolayer; (**e**) TDOS of NO₂ on Ag-WS₂ monolayer and molecular orbitals of NO₂ before and after adsorption; (**f**) atomic orbitals of Ag 4d in Ag-WS₂ and 2p orbitals of one O atom in NO₂; (**g**) band structure of SO₂ on Ag-WS₂ monolayer; (**h**) TDOS of SO₂ on Ag-WS₂ monolayer and molecular orbitals of SO₂ before and after adsorption; (**i**) atomic orbitals of Ag 4d in Ag-WS₂ and 2p orbitals of Ag 4d in Ag-WS₂ monolayer and molecular orbitals of SO₂ before and after adsorption; (**i**) atomic orbitals of Ag 4d in Ag-WS₂ and 2p orbitals of Ag 4d in Ag-WS₂ monolayer and molecular orbitals of SO₂ before and after adsorption; (**i**) atomic orbitals of Ag 4d in Ag-WS₂ monolayer and molecular orbitals of SO₂ before and after adsorption; (**i**) atomic orbitals of Ag 4d in Ag-WS₂ and 2p orbitals of Ag 4d in Ag-WS₂ and 2p orbitals of SO₂ before and after adsorption; (**i**) atomic orbitals of Ag 4d in Ag-WS₂ and 2p orbitals of the bottom O atom in SO₂.

3.4. Sensing Properties Evaluation

In the current state, resistance-type gas sensors have gained extensive utilization [54]. The resistance is closely linked to the band structure. When the band gap narrows, electrons are more readily excited to the conduction band, resulting in an increase in resistance. The relative conductivity can be assessed as follows [55]:

$$\sigma \propto e^{\left[-E_{\rm gap}/(2k_B T)\right]} \tag{6}$$

where E_{gap} , k_B , and T represent the bandgap, Boltzmann's constant (8.62 × 10⁻⁵ eV/K), and the temperature in Kelvin (K), respectively. The Ag-WS₂ monolayer processes a bandgap of 1.28 eV. Following adsorption, the band gap experiences varying degrees of reduction. Consequently, the resistance diminishes for all three gas adsorptions. Furthermore, a larger adsorption energy corresponds to a greater adsorbing capacity [56]. However, despite SO₂ adsorption causing the most substantial decrease in the band gap, it is noteworthy that NO₂ exhibits the highest adsorption energy. As a result, distinguishing between the changes in resistance caused by NO₂ and SO₂ becomes challenging.

To overcome this limitation, the work function of Ag-WS₂ was calculated. This parameter can be measured using the Kelvin probe method. Simplifying the experimental approach, the metal–insulator–semiconductor (MIS) capacitors can effectively reflect changes in the work function [57]. According to Formula (5), the results of the work function calculations are depicted in Figure 6. Before adsorption, the work function of Ag-WS₂ stands at 4.80 eV. After the adsorption of the three different gases, the work function undergoes distinct degrees of augmentation. The smallest change in the work function is observed after CO adsorption, leading to an increase in value to 4.88 eV. However, the work function experiences a remarkable elevation following NO₂ adsorption, reaching 5.50 eV. Concerning SO₂, this value becomes 5.19 eV. For the sensing scheme of Ag-WS₂, the MIS-based gas sensor is shown in Figure 7. The operating principle of hybrid suspended gate FET (HSGFET) is that the change of work function results in a shift of the gate voltage [57–60]. Therefore, the maximum increase in the work function of Ag-WS₂ after NO₂ detection results in the change of the gate voltage at the greatest extent. In summary, among the three types of gases, NO₂ causes the most substantial enhancement in the work function, aligning with its higher adsorption energy and adsorption capacity. Consequently, if Ag-WS₂ operates as a work function-based gas sensor, it exhibits the most pronounced response to NO₂ compared to the other two gases at the same concentration.



Figure 6. Work function of Ag-WS₂ monolayer before and after CO, NO₂, and SO₂ adsorption.



Figure 7. Assumed work function-based gas sensor of Ag-WS₂ using HSGFET structure.

Another aspect that requires consideration is the recovery property. When a gas sensor is exposed to an atmosphere containing the target gases, these gas molecules are adsorbed onto the active sites of the sensing material, initiating subsequent surface reactions. Once the detected gas is eliminated, the adsorbed molecules will desorb from the active site. A more challenging desorption process results in a poorer recovery property. It's important to note that desorption is the reverse process of adsorption. In this study, all the adsorption processes are exothermic, meaning that desorption is an endothermic process. The energy barrier required for desorption corresponds to the absolute value of the adsorption energy. Drawing on the Van 't Hoff Arrhenius expression derived from transition state theory, the relative desorption time can be estimated using the following formula [61,62]:

$$\tau = A^{-1} e^{\left(-E_a/k_B T\right)} \tag{7}$$

where *A* and *E*_a denote the apparent frequency and adsorption energy. From the previous research, *A* is approximately 10^{12} s^{-1} [61,62]. The evaluation of desorption times from 300 K to 700 K is shown in Figure 8.



Figure 8. Desorption time of CO, NO₂, and SO₂ on Ag-WS₂ monolayer at different working temperatures.

At a temperature of 300 K, the desorption time of NO₂ is the longest, extending beyond 10^{11} s. In contrast, the desorption times of CO and SO₂ are significantly shorter, approximately 2 s and 0.39 s, respectively. This implies that the Ag-WS₂ monolayer is well-suited for detecting CO or SO_2 at room temperature. However, in environments containing NO₂, there exists the possibility of NO₂ molecules poisoning the Ag sites. To prevent this phenomenon, elevating the temperature becomes necessary. Around 500 K, the desorption time of NO_2 is reduced to about 100 s. This reduction indicates that the Ag-WS₂ monolayer is less susceptible to poisoning at this temperature or even higher temperatures. Therefore, the $Ag-WS_2$ monolayer proves more suitable for operation at elevated working temperatures when detecting NO₂. Taking into account selectivity, if the working temperature is raised to about 500 K, CO and SO₂ are more likely to desorb from the Ag sites. Thus, the Ag-WS₂ monolayer exhibits favorable selectivity for NO₂ detection at higher working temperatures. On the other hand, when operating at room temperature and detecting target gases containing only CO and SO₂, the Ag-WS₂ monolayer's heightened sensitivity to SO_2 , owing to the larger change in work function caused by SO_2 adsorption, makes it more selective toward SO₂.

4. Conclusions

This study delves into the adsorption behavior and chemical interactions of three hazardous gases, CO, NO₂, and SO₂, on an Ag-atom-doped WS₂ monolayer, employing DFT calculations. Various parameters pertinent to adsorption behavior, such as adsorption energy and electron transfer, were computed and subsequently compared. To gain deeper insights into the electronic and sensing properties, the band structure, DOS, work function, and desorption behavior were scrutinized. The main conclusions are as follows:

- (1) NO₂ adsorption is characterized by the highest adsorption energy and electron transfer of -1.40 eV and -0.40 eV, and the CDD analysis illustrates alterations in electron density after adsorption, with NO₂ adsorption leading to the most significant electron redistribution.
- (2) The band gap of Ag-WS₂ experienced reductions from 1.28 eV to 1.19 eV, 1.06 eV, and 0.96 eV for CO, NO₂, and SO₂, respectively, causing diverse modifications in the states of the adsorbed molecule's molecular orbitals. Chemical interactions manifest through the hybridization of atomic orbitals of Ag and atoms within gas molecules.

- (3) The work functions elevation for all three adsorptions, with NO₂ displaying the most pronounced increase from 4.80 eV to 5.50 eV.
- (4) Desorption properties reveal that the Ag-WS₂ monolayer is well-suited for detecting CO and SO₂ at mild or room temperatures, while higher working temperatures are preferable for NO₂ detection.

This investigation provides a theoretical foundation for enhancing gas sensing properties in various domains via surface modification of TMDs.

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