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Rh-doped MoSe₂ as a toxic gas scavenger: a first-principles study

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Using first-principles theory, we investigated the most stable configuration for the Rh dopant on a MoSe₂ monolayer, and the interaction of the Rh-doped MoSe₂ (Rh-MoSe₂) monolayer with four toxic gases (CO, NO, NO₂ and SO₂) to exploit the potential application of the Rh-MoSe₂ monolayer as a gas sensor or adsorbent. Based on adsorption behavior comparison with other 2D adsorbents and desorption behavior analysis, we assume that the Rh-MoSe₂ monolayer is a desirable adsorbent for CO, NO and NO₂ storage or removal given the larger adsorption energy (E_{ad}) of -2.00 , -2.56 and -1.88 eV, respectively, compared with other materials. In the meanwhile, the Rh-MoSe₂ monolayer is a good sensing material for SO₂ detection according to its desirable adsorption and desorption behaviors towards the target molecule. Our theoretical calculation would provide a first insight into the TM-doping effect on the structural and electronic properties of the MoSe₂ monolayer, and shed light on the application of Rh-MoSe₂ for the sensing or disposal of common toxic gases.

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1. Introduction

Sensing toxic gases, especially detection of the ones at sub-ppm levels, is quite imperative with respect to environmental standards and agricultural pollution monitoring. In this regard, researchers have always contributed to finding novel sensing materials for potential application as chemical sensors with a rapid response, high sensitivity and low cost. In the past few decades, semiconducting metal oxide nanowire,¹⁻³ carbon nanotube,⁴⁻⁶ and graphene⁷⁻⁹ based sensors have successively caught the attention of researchers, arousing considerable interest from the research community. Nevertheless, they are never satisfied by these achievements, persisting to pursue some new materials that possess more fascinating sensing behavior than the previous ones.

After the successful application of graphene as a gas sensor, scholars have turned their attention to two-dimensional (2D) materials that have large surface-volume ratios and tunable electronic properties due to their unique structural configuration. Materials such as hexagonal boron nitride,¹⁰ antimonene,¹¹ phosphorene¹² and silicene¹³ have become the focus of the sensing field, in order to find candidate materials having the advantages of graphene such as high carrier mobility and strong chemical activity for gas interaction,^{14,15} as well as semiconducting properties. In the meanwhile, group III-V nitrides,

particularly AlN and InN,^{16,17} have been regarded as promising structures for gas sensing,^{18,19} and the experimental breakthrough in the synthesis of InN²⁰ makes it possible to be used as a substitute for graphene with inherent bandgap characteristics.²¹

Very recently, 2D transition metal dichalcogenides (TMDs), especially MoS₂ monolayers,²²⁻²⁴ have attracted much attention as alternative materials to conventional metal oxides for chemical sensing devices. Moreover, surface doping with transition metal (TM) atoms has been demonstrated to provide a monolayer with enhanced adsorption and sensing performance for gas molecules²⁵⁻²⁸ due to the improved chemical activity and electron mobility induced by the TM dopant,²⁹ opening up a novel insight into the sensor family. Other than that, MoSe₂, as a new emerging semiconducting material, has been investigated as well for its application as a sensor. While Late *et al.* first reported the high sensing performance of the MoSe₂ monolayer for ppm-level NH₃ gas,³⁰ Baek *et al.* developed a MoSe₂ multilayer based field-effect transistor for NO₂ detection.³¹ However, the potential applications of MoSe₂ based materials need to be further explored and broadened after their successful synthesis by chemical vapor deposition.³² This inspires us to implement a first-principles calculation to study the adsorption performance of TM-MoSe₂ monolayers towards four industrial exhaust gases including CO, NO, NO₂ and SO₂ to put forward a novel material for toxic gas sensing. Among numerous TM atoms, rhodium (Rh) is the one with strong electron mobility and catalytic performance for gas interaction, previously demonstrated by carbon nanotube,³³ graphene,³⁴ and MoS₂ monolayer systems³⁵ where Rh was proposed as a dopant to functionalize the proposed surfaces. We assumed that it

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would be interesting and necessary to investigate the adsorption and sensing behaviors of the Rh-doped MoSe₂ (Rh-MoSe₂) monolayer towards toxic gases to exploit the novel material for toxic gas detection or removal. The results indicate that the Rh-MoSe₂ monolayer possesses quite strong adsorption behavior towards CO, NO and NO₂ molecules that gives rise to chemisorption in these systems, while physisorption could be determined for the Rh-MoSe₂/SO₂ system. Through adsorption behavior comparison with other 2D adsorbents and desorption behavior analysis, we assume that Rh-MoSe₂ is a desirable adsorbent for CO, NO and NO₂ storage or removal while being a good sensing material for SO₂ detection. To the best of our knowledge, this would be the first report investigating the potential application of Rh-MoSe₂ for the removal of four toxic species in a theoretical manner.

2. Computational details

In this work, spin-polarized calculations were implemented in the Dmol³ package³⁶ of Materials Studio. The Perdew–Burke–Ernzerhof (PBE) functional with a generalized gradient approximation (GGA) was employed to deal with the electron exchange and correlation,³⁷ and to obtain the optimized structures. The Grimme method was employed³⁸ for better understanding the van der Waals interaction. We selected double numerical plus polarization (DNP) as the atomic orbital basis set,²⁶ while the DFT semi-core pseudopotential (DSSP) method was employed to dissolve the relativistic effect of the TM atom.³⁹ The *k*-point sample of the Monkhorst–Pack grid was sampled to 5 × 5 × 1 of the Brillouin zone for geometry optimization and to 7 × 7 × 1 for electronic structure calculations.⁴⁰ The energy tolerance accuracy, maximum force, and displacement were selected as 10^{−5} Ha, 2 × 10^{−3} Ha Å^{−1}, and 5 × 10^{−3} Å,⁴¹ respectively. For static electronic structure calculations, a self-consistent loop energy of 10^{−6} Ha, global orbital cut-off radius of 5.0 Å and smearing of 0.005 Ha were employed to ensure the accurate results of total energy.⁴² For basis set superposition errors (BSSE), little impact could be caused in the Dmol³ package,⁴³ and thus we would not analyze it in the following part.

A 4 × 4 × 1 MoSe₂ monolayer supercell including 16 Mo and 32 Se atoms with a vacuum region of 15 Å was established and relaxed to its most stable configuration. A previous report has proved that a 4 × 4 supercell would be large enough to conduct the gas adsorption process while a 15 Å slab would be appropriate to prevent the interaction between adjacent units.⁴⁴ The lattice constant calculated here was 3.30 Å, which is in agreement with other theoretical studies (3.31 Å (ref. 45)).

The adsorption energy (E_{ad}) of each gas adsorption process was calculated by the following equation:²³

$$E_{\text{ad}} = E_{\text{Rh-MoSe}_2/\text{gas}} - E_{\text{Rh-MoSe}_2} - E_{\text{gas}} \quad (1)$$

where the $E_{\text{Rh-MoSe}_2/\text{gas}}$, $E_{\text{Rh-MoSe}_2}$ and E_{gas} represent energies of the adsorbed system, isolated Rh-MoSe₂ and gas molecule, respectively. To analyze the charge transfer (Q_{T}) between the target molecule and adsorbent surface, the Mulliken population

analysis was considered, characterized by the carried electron value by gas molecules after adsorption. Only the most favorable configuration for gas adsorption would be plotted and analyzed in the following parts.

3. Results and discussion

3.1 Geometric and electronic structure of Rh-MoSe₂

We determined Rh atom adsorption onto a bare MoSe₂ monolayer Rh-MoSe₂, where four possible sites were considered, traced as T_H (above the center of the hexagonal ring of MoSe₂), T_{Mo} (at the top of the Mo atom), T_{Se} (at the top of the Se atom) and B_{S-S} (the bridge site between two Se atoms), respectively. The binding energy (E_{b}) for Rh adsorption onto the most favorable doping site is determined through the formula:

$$E_{\text{d}} = E_{\text{Rh-MoSe}_2} - E_{\text{Rh}} - E_{\text{MoSe}_2} \quad (2)$$

where $E_{\text{Rh-MoSe}_2}$, E_{Rh} , and E_{MoSe_2} represent the energies of the Rh-MoSe₂, Rh atom and pure MoSe₂, respectively.

After optimization, the most stable configuration of Rh-MoSe₂ in line with relevant deformation charge density (DCD) is shown in Fig. 1. One can see that the Rh atom tends to be adsorbed onto the MoSe₂ monolayer through the T_{Mo} site, with three Rh–Se bond lengths of 2.383, 2.383 and 2.354 Å, respectively. The geometry of MoSe₂ undergoes a little deformation after Rh doping due to the binding force of Rh–Se bonds.⁴⁶ The Q_{T} between the Rh dopant and the MoSe₂ monolayer is found to be −0.239 e, indicating that the Rh dopant acts as an electron acceptor while the MoSe₂ monolayer acts as a donor. This is in line with the strong electron withdrawing properties of the Rh atom,³³ thereby leading to high electron localization around the Rh atom. In addition, we can find that the Mo atoms are mainly the electron accepting centers while the Se atoms are the electron donating centers for the optimized Rh-MoSe₂ system.

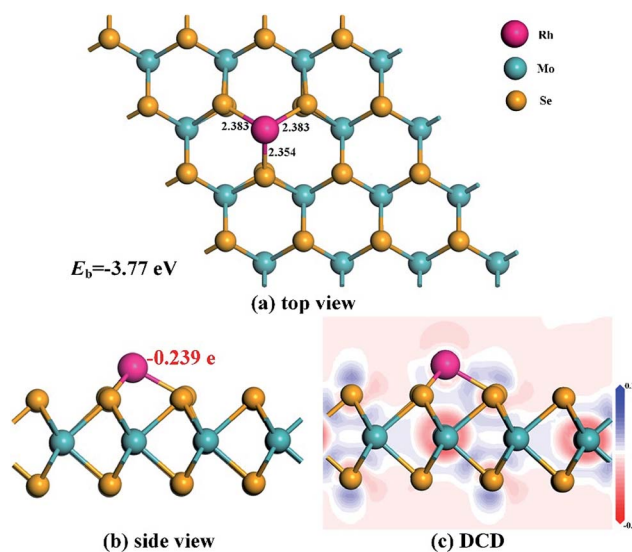


Fig. 1 Geometric structures (a) and (b) and DCD (c) of the Rh-MoSe₂ monolayer. The black values are the atom-to-atom distance while the red value is the electron amount carried by Rh dopant.



To further elucidate the electronic behavior of the Rh doping effect on the MoSe₂ monolayer compared with its pure counterpart, density of states (DOS) analysis is performed, as depicted in Fig. 2. It can be seen in the total DOS distribution of Fig. 2(a) that there is a big band gap near the Fermi level in the DOS curve of intrinsic MoSe₂, confirming its semiconducting properties well. With the doping of the Rh atom, the gap gets narrowed obviously due to the upward shifted Fermi level which was originally identified as the valence band maximum in the Dmol³ package, caused by the Rh contribution. It is interesting to note that the DOS spin up and down of the Rh-MoSe₂ monolayer are shown to be asymmetric in comparison with those in the pure MoSe₂ system that shows good symmetry, which could be ascribed to the total magnetic moment of 1.0 μ_B in this system induced by the Rh dopant. Moreover, due to the electron-donating behavior of the MoSe₂ monolayer that results in an improved effective coulombic potential,⁴⁷ the DOS curve of the Rh-MoSe₂ system is found to left shift towards a lower region consequently compared with that of its intrinsic counterpart. In Fig. 1(b), the DOS of the Rh 4d orbital is largely overlapped with that of the Se 4p orbital, demonstrating strong hybridization of the Rh atom onto the MoSe₂ monolayer. Apart from that, it reveals that the highest occupied molecular orbitals (HOMOs) are mainly located at the Se atom while the lowest unoccupied molecular orbitals are at the Rh atom, which confirms the results of DCD that charge is accumulated around the Rh dopant.⁴⁸

3.2 CO adsorption

Fig. 3 shows the most stable configuration and related DCD for CO adsorption on the Rh-MoSe₂ monolayer. One can see that the C atom is trapped by the Rh dopant with a Rh-C bond length of 1.892 Å after the CO molecule is adsorbed on the

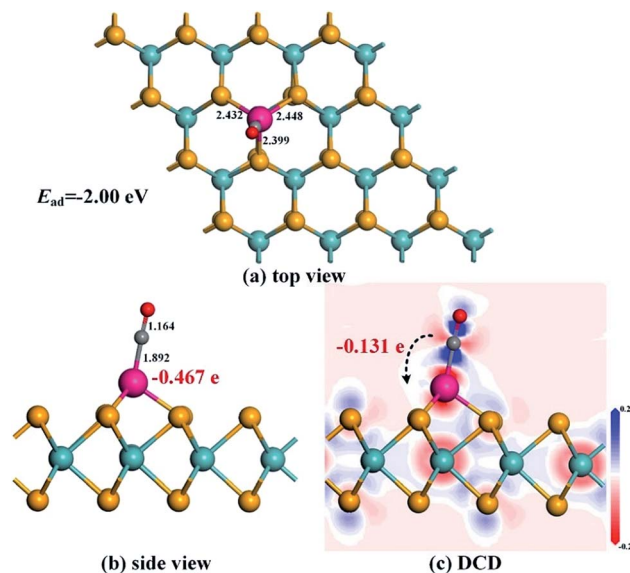


Fig. 3 Adsorption configuration (a) and (b) and DCD (c) of the Rh-MoSe₂/CO system.

surface. It would be worth noting that such a value of atom-to-atom distance is even shorter than the sum of the corresponding covalent radii (2.00 Å for Rh-C⁴⁹) indicating some chemisorption in this system.⁵⁰ In fact, the large enough E_{ad} of -2.00 eV here could not only confirm the strong adsorption performance of Rh-MoSe₂ towards the CO molecule, but also indicate its chemical nature with strong spontaneity for this interaction. In the meanwhile, three Rh-Se bonds, after CO adsorption, are elongated to 2.432, 2.448 and 2.399 Å, respectively, and the C-O bond of the CO molecule is prolonged to 1.164 Å from 1.142 Å in an isolated molecule. These findings suggest the activation behavior for the CO molecule when interacted with the

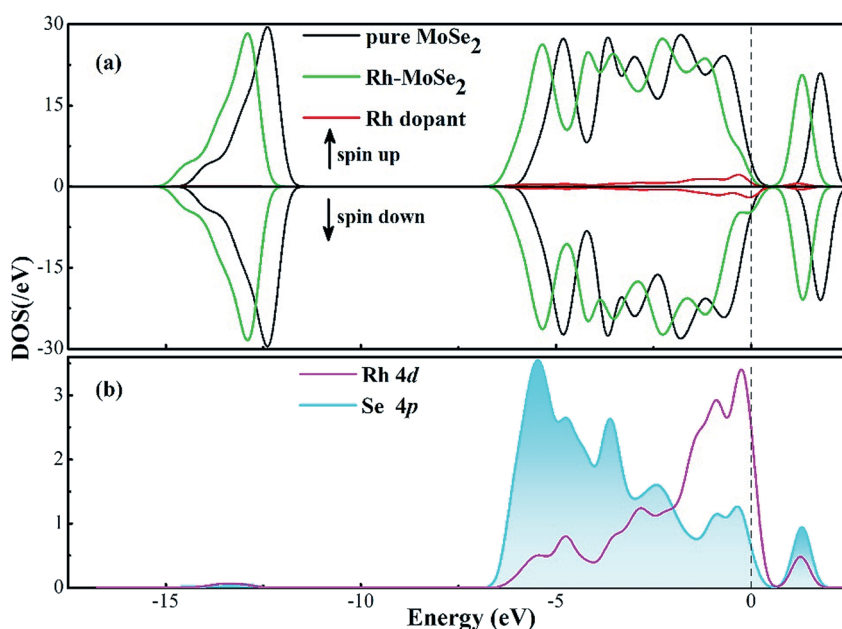


Fig. 2 DOS distribution of Rh-MoSe₂. The dashed line is the Fermi level.



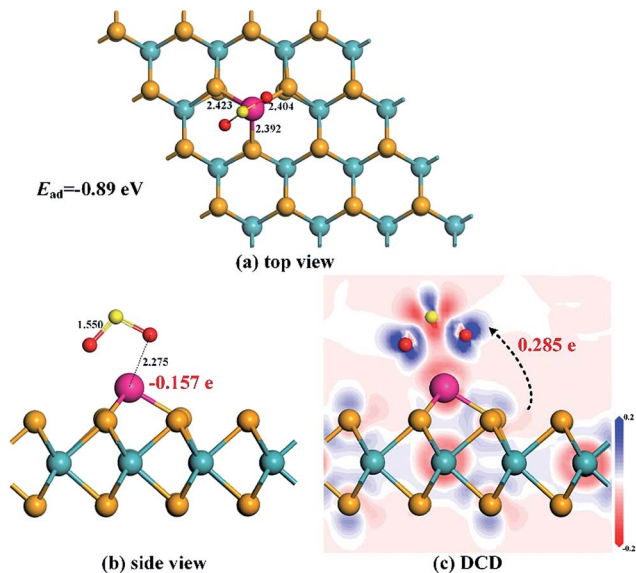


Fig. 9 Adsorption configuration (a) and (b) and DCD (c) of the Rh-MoSe₂/SO₂ system.

the Rh-MoSe₂/SO₂ system. The tiny prolongation for Rh–Se bonds inner Rh-MoSe₂ to 2.423, 2.404 and 2.392 Å, along with S–O bond inner SO₂ to 1.550 Å by 0.019 Å can confirm the weak binding force between the Rh dopant and the SO₂ molecule as well. The E_{ad} obtained here is -0.89 eV and the Mulliken population analysis shows a Q_{T} of 0.285 e from the Rh-MoSe₂ monolayer to the SO₂ molecule. All these findings suggest physisorption for SO₂ adsorption on the Rh-MoSe₂ monolayer.⁵¹

DOS distributions shown in Fig. 10 could give a clear explanation for the electronic behavior in this system. The novel peaks around -11.5 and -7 and the Fermi level in total DOS of the adsorbed system are from the contribution of the adsorbed SO₂ molecule that is somewhat activated after adsorption. At the same time, the overlaps between DOS of Rh 4d and O 2p orbitals, although not as large as the NO₂ system, prove the orbital interaction, to some extent, between the Rh dopant and the SO₂ molecule.

3.6 Application of Rh-MoSe₂ to toxic gas scavenging

We first investigated the potential application of Rh-MoSe₂ as a resistance-type sensor for these gases. According to our previous analysis, it could be found that the Rh-MoSe₂ monolayer has quite strong adsorption performance for three species namely CO, NO and NO₂ molecules, giving rise to chemisorption in these systems, while having relatively weaker performance towards SO₂ adsorption that gives rise to physisorption instead. In other words, it would be difficult for these three gas molecules to desorb from the Rh-MoSe₂ monolayer once they are adsorbed onto the surface, except for the SO₂ molecule which may be desorbed through annealing at high temperature or irradiation with ultraviolet light.^{50,54}

To confirm this assumption, the recovery time (τ) analysis based on transition state theory and van't-Hoff-Arrhenius expression⁵⁵ was implemented, and expressed as:

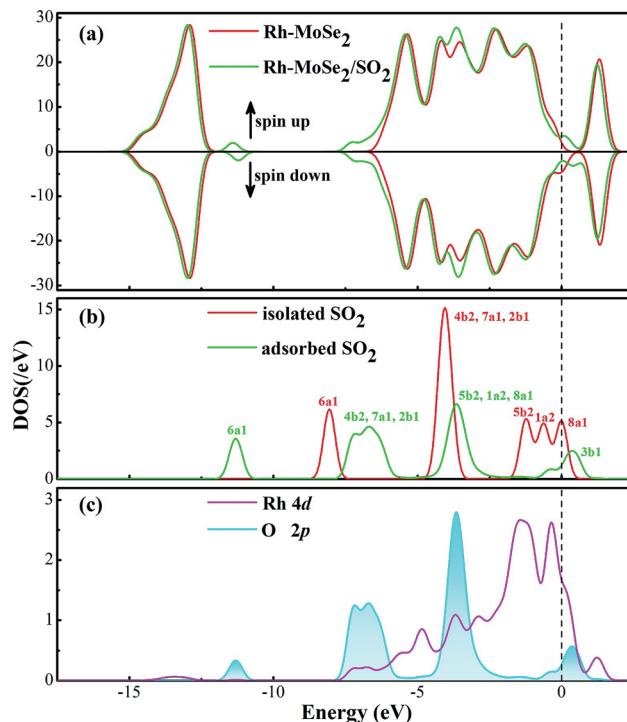


Fig. 10 DOS distribution of the Rh-MoSe₂/SO₂ system. The dashed line is the Fermi level.

$$\tau = A^{-1}e^{(-E_a/K_B T)} \quad (3)$$

where A is the attempt frequency determined as 10^{12} s^{-1} according to a previous report,⁵⁶ T is the temperature and K_B is the Boltzmann constant ($8.318 \times 10^{-3} \text{ kJ (mol K)}^{-1}$). Given the inverse processes between adsorption and desorption, we assume the value of E_{ad} as the potential barrier (E_a) for desorption. It would be obvious that a larger E_{ad} would lead to a harder process for gas desorption, and the increase of temperature can accelerate that process effectively. According to the obtained E_{ad} in our calculations as shown in Table 1, we plotted the recovery time for the desorption of various gases at various temperatures as portrayed in Fig. 11. One can conclude that CO, NO and NO₂ desorption from the Rh-MoSe₂ monolayer would be extremely unrealistic at room temperature, and even at 798 K, it would take more than 4 hours for NO desorption from the surface. Although remarkably enhanced behavior for CO and NO₂ desorption could be achieved at 798 K, the considerable heat loss and the safety of the devices would be another issue. Therefore, it would be inappropriate to use the Rh-MoSe₂ monolayer as the sensing material for CO, NO or NO₂ detection, because the one-off operation for gas sensors would be a waste of money and reduce work-efficiency. On the other hand, we assume that Rh-MoSe₂ is suitable for SO₂ sensing given its good adsorption performance for detection and desorption performance with appropriate recovery time at ambient temperature for recycle use. Moreover, the sensing mechanism of the Rh-MoSe₂ monolayer towards SO₂ would be dependent on the increased conductivity due to the narrowed energy gap from 1.033 eV for the isolated Rh-MoSe₂ monolayer to 0.227 eV for the SO₂ system⁵⁷ as seen in Table 1.



Table 1 Adsorption parameters for various Rh-MoSe₂/gas systems

Gas systems	E_{ad} (eV)	D (Å)	Q_{T} (e)	E_{g} (eV)
CO	-2.00	1.892	-0.131	0.202
NO	-2.56	1.911	0.322	1.210
NO ₂	-1.88	2.113	-0.361	0.520
SO ₂	-0.89	2.275	0.285	0.227

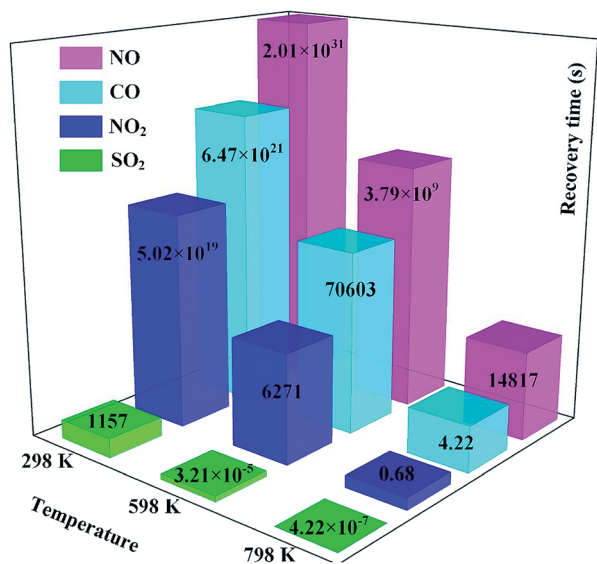
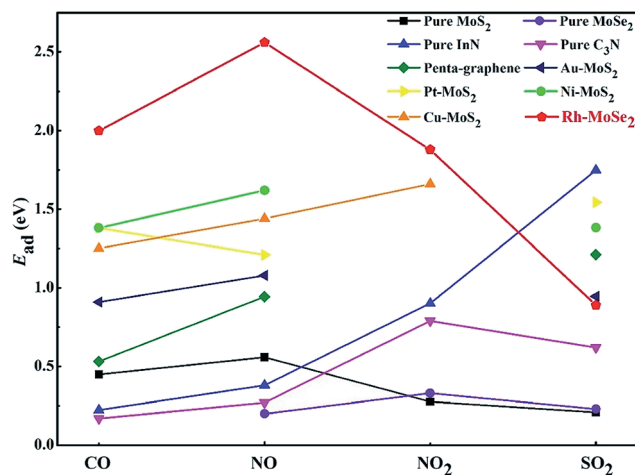


Fig. 11 Recovery time for four species at various temperatures.

Second, the large E_{ad} in CO, NO and NO₂ systems allows the excellent performance of Rh-MoSe₂ as a gas adsorbent for their storage or removal from specific environments. For this purpose, we summarize in Fig. 12 the calculated E_{ad} values of recently reported 2D adsorbents for four gases, in order to find out whether Rh-MoSe₂ could be an alternative for scavenging toxic gases. From the figure, we can find that the Rh-MoSe₂ monolayer possesses better adsorption performance for CO, NO and NO₂ molecules compared with the pure MoSe₂ monolayer,²³ the pure MoSe₂ monolayer,⁵⁸ pure InN,¹⁹ pure C₃N,⁵⁷ pure penta-graphene,⁵⁹ and some other TM-doped MoS₂ monolayers.^{22,40,60,61} That is to say, the Rh-MoSe₂ monolayer has strong potential to be an adsorbent candidate for CO, NO or NO₂ storage and removal. Conversely, it is not a desirable SO₂ adsorbent due to its weaker performance than pure InN,¹⁹ penta-graphene,⁵⁹ the Au-MoS₂ monolayer,⁴⁰ the Pt-MoS₂ monolayer⁴⁰ and the Ni-MoS₂ monolayer,⁶⁰ although it has better performance than the pure MoS₂ monolayer,²³ the pure MoSe₂ monolayer⁵⁸ and pure C₃N,⁵⁷ except for the Cu-MoS₂ monolayer which is not studied for SO₂ adsorption in ref. 22 and 61. In addition, we would introduce the application of borophene as a potential SO₂ adsorbent given its strong ability and capacity whereby up to seven SO₂ molecules could be chemisorbed on its one side, with a weight percentage of 82.88%, for SO₂ adsorption.⁶²

Fig. 12 E_{ad} comparison of Rh-MoSe₂ for four species with recent reports.

4. Conclusions

In this work, we implemented a first-principles theory to study the adsorption performance of the Rh-MoSe₂ monolayer towards four toxic gases, including CO, NO, NO₂ and SO₂. Desorption behavior analysis and adsorption behavior comparison with other 2D materials towards these four species were conducted in order to exploit the potential application of our proposed monolayer. The results indicated that the Rh-MoSe₂ monolayer possesses quite strong adsorption behavior towards CO, NO and NO₂ molecules that gives rise to chemisorption in these systems, while physisorption could be determined for the Rh-MoSe₂/SO₂ system. In that regard, based on the adsorption behavior comparison with other adsorbents and desorption behavior analysis, we assume that Rh-MoSe₂ is a desirable adsorbent for CO, NO and NO₂ storage or removal while it is a good sensing material for SO₂ detection. Our theoretical calculation would provide a first insight into the TM-doping effect on the structural and electronic properties of the MoSe₂ monolayer, and shed light on the application of Rh-MoSe₂ for the sensing or disposal of common toxic gases.

Author contributions

Xiaoxing Zhang conceived and designed the research, Hao Cui performed the research and wrote this manuscript while Guozhi Zhang and Ju Tang helped analyze the data.

Conflicts of interest

There are no conflicts to declare.

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