1. Introduction

Air pollution is still a global challenge, and daily human and industrial activities are the major source of pollution to the environment, also harming human health. H$_2$S is a common environmental pollutant, which is usually produced during the preparation process of petroleum and natural gas.\(^1\) It is a highly toxic gas to human beings at low concentrations and can cause mortalities at high concentrations.\(^2\) Hence, the detection of H$_2$S is a great technological challenge.\(^3\) A promising candidate for gas sensors should possess some advantages such as miniature size, higher sensitivity, and low production cost.\(^4\) Recently, graphene, a two-dimensional and one-carbon-thick material, has attracted significant attention due to its excellent physical and chemical properties since its first synthesis was experimentally achieved in 2004.\(^7\) Graphene exhibits great promise for the application of gas sensing because it possesses a large surface and high reactivity.\(^11\) However, studies suggest that the weak interaction between the adsorbents and graphene and the zero band-gap limit its application in gas detection. To solve this problem, many researchers have focused on improving its reactivity. Several common techniques such as the functionalization using defects\(^18\)–\(^20\) and impurities\(^21\)–\(^23\) have been explored. Different elements are attached to the surface of graphene to alter its electronic properties and chemical reactivity. Thus, a promising material prepared by exposing graphene to hydrogen plasma is graphene, which was first synthesized in 2009 by Elias et al.\(^24\) In graphene, the hydrogen atoms are attached on both sides of graphene, and then, sp$^3$ hybridization in graphene changes to sp$^2$ hybridization.\(^25\) Graphene exhibits unique electronic and magnetic properties and has been explored in recent years in the aspects of science and technology, such as transistor and nanoelectronic designs, hydrogen storage, and bio-sensing.\(^26\)–\(^31\) It is a wide band gap semiconductor and overcomes the restrictions of the non-existence of a band-gap in graphene for some application areas such as gas sensing. Furthermore, its excellent mechanical strength and large surface area predicate its promising application for gas sensing. Islam et al.\(^32\) studied the interaction of graphane towards CH$_4$ molecules, and the results suggested that the H-vacancy and metal-doping significantly enhanced the methane adsorption. Thus, the introduction of an H-vacancy defect and metal-dopants have been successfully attempted to increase the adsorption stability of graphane towards gas molecules.\(^33\)–\(^36\) In our study, we investigated the adsorption properties of H$_2$S molecules on the pure, H-vacancy-defected, and transition-metal (TM)-doped graphane using density functional theory (DFT) calculations. The TM-dopants considered herein were Fe, Co, and Cu. We believe that our study provides useful information for the application based on graphane for gas sensing.

2. Computational methods and model

All the DFT calculations were performed via the Dmol$^3$ code.\(^37\) We used the generalized gradient approximation (GGA) for the exchange-correlation functional, as described by Perdew–Burke–Ernzerhof (PBE).\(^38\) Basiuk et al. reported that the PBE functional along with Grimme dispersion correction could be
suggested as most suitable for theoretical studies of the interaction between molecules and graphene. Therefore, all the results were obtained using the Grimme-corrected PBE functional. We selected DFT semicore pseudopotential (DSSP) as a single effective potential to replace the core electrons. A double numerical plus polarization (DNP) was employed as the basis set. The DNP basis set corresponded to a double-ζ quality basis set with a p-type polarization function to hydrogen and d-type polarization functions added to heavier atoms, which was comparable with the Gaussian 6-31G (d, p) basis set and exhibited a better accuracy.

We applied a 5 x 5 x 1 supercell under the periodic boundary condition on the x and y axes to model the infinite graphene sheet. The vacuum space of 20 Å was set in the direction normal to the sheets to avoid the interactions between periodic images. A 5 x 5 x 1 mesh of k-point and the global orbital cut-off of 5.0 Å were set in the spin-unrestricted calculations. All atoms were allowed to relax. Convergence in energy, force, and displacement were set at 4.54 x 10^-4 eV, 1.09 eV Å^-1, and 0.005 Å, respectively.

We analyzed the adsorption of H₂S on hydrogenated graphene (HG). The adsorption energy was obtained from the expression

\[ E_{\text{ads}} = E(\text{H}_2\text{S/HG}) - E(\text{HG}) - E(\text{H}_2\text{S}) \]

Fig. 1 The optimized structures of (a) HG, (b) VHG, (c) FeVHG, (d) CoVHG, and (e) CuVHG.
where $E(H_2S/HG)$ is the total energy of the $H_2S$ molecule adsorbed on hydrogenated graphene, $E(HG)$ is the total energy of the HG, and $E(H_2S)$ is the total energy of a free $H_2S$ molecule.

3. Results and discussion

3.1 Structures of HG, VHG, FeVHG, CoVHG, and CuVHG

First, we discussed the geometries of pure graphene (HG) and H-vacancy-defected graphene (VHG), and the optimized structures are presented in Fig. 1. The bond lengths of C–H and C–C in the HG configuration were 1.109 Å and 1.496 Å, respectively, which were consistent with those reported in previous studies.\(^{42}\) Pure graphene was a nonmagnetic semiconductor with a wide gap, which was 3.69 eV as obtained from our calculated results. The gap value was in agreement with the literature, and the little difference was due to the selection of the calculated parameters.\(^{25,42,43}\) After introducing the H-
vacancy defect, the Cv atom, which lost an H atom, was labeled in Fig. 1b. The bond lengths of Cv and the adjacent C atoms were 1.469 Å.

Second, we considered the configuration of VHGs doped with Fe (FeVHG), Co (CoVHG), and Cu (CuVHG). Due to the presence of the H-defect in graphane, the vacancy offered a reactive site to craft adsorbents. Therefore, we introduced the transition-metal (TM) atoms to the vacancy site. The TM-dopants also prefer to congruously disperse on the graphane surface, which was due to fact that the binding energies were larger than the cohesive energies. The binding energies for the dopants were 3.80 eV, 3.06 eV, and 3.95 eV. Furthermore, the bond lengths of Fe–Cv, Co–Cv, and Cu–Cv were 2.024 Å, 1.977 Å, and 1.967 Å, respectively. The optimized structures were also obtained and are shown in Fig. 1.

To explore the effect of transition-metal dopants on the electronic and magnetic properties of graphane, we performed the density of states (DOS) calculations, as shown in Fig. 2. As shown in Fig. 2a, HG was nonmagnetic and exhibited a wide band gap. However, the H-vacancy released the p electron on the Cv atom and formed a localized state. In our results, VHG exhibited a net magnetic moment of 1 μB. As shown in Fig. 2b, the DOS of the Cv-p orbital split into a spin-up and a spin-down peak around the Fermi level, which revealed that the unpaired electrons of Cv induced a half-metallic behavior. Moreover, the band gap of VHGs decreased to 1.70 eV. Therefore, VHG was expected to exhibit higher reactivity to interact with the adsorbents as compared to pure graphane.

For the cases of VHGs decorated with the TM atoms, there was strong hybridization between the Cv–2p and TM–3d orbitals (Fig. 2c–e). Transition-metal atoms are well known for their magnetic properties. In the case of FeVHG, the Fe–3d orbital exhibited obvious net magnetic moments. For the cases of CoVHG and CuVHG, the magnetic properties disappeared due to the formation of chemical bonds between the dopants and the Cv atoms. In general, the introduction of TM-dopants contributed to the DOS around the Fermi level, and the resulting compounds exhibited higher sensitivity to absorb molecules.

### 3.2 Adsorption of H₂S on HG and VHGs

Herein, we explored the adsorption of H₂S on HG and VHGs. According to the geometric symmetry of configuration, there were three initial adsorption structures: the H atom of the H₂S molecule close to the graphane surface with the H–S bond parallel to graphane, the H atom of the H₂S molecule close to the graphane surface with the H–S bond perpendicular to graphane, and the S atom of the H₂S molecule close to the graphane surface. After full relaxation, the calculated results indicated that the S atom of the H₂S molecule close to the graphane was the most stable adsorption structure. We performed the most stable optimized configurations of H₂S/HG and H₂S/VHG, as shown in Fig. 3. Moreover, the corresponding parameters describing the adsorption configurations are summarized in Table 1.

As shown in Table 1, the E_{ads} of H₂S/VHG was −0.05 eV, which was larger than that of H₂S/HG showing a value of −0.02 eV. The enhancement of adsorption stability suggested that the presence of the H-vacancy improved the sensitivity of graphane to absorb the H₂S molecule. The distances between the S atom of the H₂S molecule and the graphane surface (HG and VHGs) were 3.299 Å and 4.120 Å, respectively. Moreover, the band gaps of the adsorption complexes were obtained. The E₆ of HG and VHGs was 3.69 eV and 1.70 eV, which changed to 3.58 eV and 1.66 eV, respectively. The weak interaction with the H₂S molecule did not induce an obvious change in the band gaps of

![Fig. 3](image-url) The optimized structures of (a) H₂S/HG and (b) H₂S/VHG.
the graphane substrate. Moreover, we calculated the charge transfer of the H$_2$S molecule to graphane. The $Q$ of H$_2$S/VHG was 0.007 e. The small adsorption energy, large bond distance, and low charge transfer showed that the adsorption of H$_2$S was due to physisorption.

### 3.3 Adsorption of H$_2$S on FeVHG, CoVHG, and CuVHG

Herein, we investigated the adsorption of H$_2$S on FeVHG, CoVHG, and CuVHG. As stated in Section 3.2, we set the initial adsorption structure with the S atom close to the dopants. After optimization, the adsorption configurations were obtained, as shown in Fig. 4. Furthermore, the corresponding parameters are summarized in Table 2. The adsorption complex of H$_2$S/CoVHG exhibited maximum stability, of which the adsorption energy was $-1.50$ eV. Compared with the adsorption of H$_2$S on HG and VHG, the $E_{\text{ads}}$ was enlarged by the introducing of dopants (Fe, Co, and Cu). After interaction with H$_2$S, the bond lengths of dopant-C$_\text{v}$ were elongated such as the $d_{\text{Fe-Cv}}$ changed from 2.224 Å to 2.247 Å. According to the Mulliken analysis results, the $Q$ of H$_2$S/CoVHG was the highest with the value of 0.302 e. In the adsorption process, the electrons transferred from the H$_2$S molecule to the graphane substrate. The large adsorption energy and high charge transfer indicated that the introduction of dopants improved the sensitivity to the H$_2$S molecule and the adsorptions on VHG doped with dopants (Fe, Co, and Cu) were via chemisorption.

In our calculated results, the band gaps of FeVHG, CoVHG, and CuVHG were 0.97 eV, 1.26 eV, and 2.33 eV, respectively. The adsorption of the H$_2$S molecule induced a decrease of band gaps. In the case of H$_2$S/FeVHG, the $E_g$ was smaller by about 0.2 eV than that of FeVHG. As is well-known, the change in the $E_g$ of the structures induces the electric conductivity change of graphane according to the following equation:  

$$\sigma \propto \exp \left( \frac{-E_g}{2kT} \right)$$

where $\sigma$ is the electric conductivity of the configurations, $k$ is the Boltzmann’s constant, and $T$ is the thermodynamic temperature. Therefore, the change of electric conductance of the graphane substrate by the adsorption of the H$_2$S molecule can be seen as a signal to detect H$_2$S gas.

### 3.4 Electronic and magnetic properties

To deeply understand the effect of H-vacancy and dopants on the adsorption of H$_2$S, we performed the spin polarized density of states (PDOS) of adsorption complexes, as shown in Fig. 5–9. As shown in Fig. 5 and 6, the DOS of H$_2$S/HG and H$_2$S/VHG were similar to those of HG and VHG (Fig. 2a and b). From the PDOS of the H$_2$S molecule, we can see that there was very little interaction between the HG (VHG) sheet and the H$_2$S molecule.

In the case of H$_2$S/FeVHG, instead of the two spin-up peaks of the 3d orbital in FeVHG, there was a sharp peak through the Fermi level. Furthermore, we found that a strong hybridization occurred between the Fe-3d and C$_\text{v}$-2p orbitals around the Fermi level, which indicated that a chemical bond formed between the Fe and C$_\text{v}$ atoms. For the configuration of H$_2$S/CoVHG, the spin-up and spin-down of the Co-3d orbitals mismatched and induced a magnetic moment, which resulted from the adsorption of H$_2$S. There were overlaps between the DOS of Co-3d and S-2p orbitals, which varied from $-1.8$ eV to $-1.5$ eV. The strong hybridization explained the strong

![Fig. 4](image)

**Fig. 4** The optimized structures of (a) H$_2$S/FeVHG, (b) H$_2$S/CoVHG, and (c) H$_2$S/CuVHG.

### Table 2 Summary of the results for the H$_2$S molecule adsorbed on metal atom doped H-vacancy defected graphane. The properties listed are as follows: the distance between the H and S atom of the H$_2$S molecule ($d_{\text{H-S}}$), the angle of the H$_2$S molecule (\(\alpha\)), the distance between the S atom of H$_2$S and metal-dopant ($d_{\text{S-dopant}}$), the distance between the C$_\text{v}$ atom and metal-dopant ($d_{\text{C-dopant}}$), the adsorption energy ($E_{\text{ads}}$), the band gap ($E_g$) of the adsorption system, and the charge transfer of the H$_2$S molecule ($Q$).

| System           | $d_{\text{H-S}}$ (\(\AA\)) | \(\alpha\) (°) | $d_{\text{S-dopant}}$ (\(\AA\)) | $d_{\text{C-dopant}}$ (\(\AA\)) | $E_{\text{ads}}$ (eV) | $E_g$ (eV) | $Q$ (e) |
|------------------|-----------------------------|----------------|-------------------------------|-------------------------------|----------------|-------------|--------|
| H$_2$S/FeVHG     | 1.370–1.371                 | 90.45          | 2.247                         | 2.047                         | $-0.93$         | 0.75        | 0.058  |
| H$_2$S/CoVHG     | 1.369–1.371                 | 90.36          | 2.221                         | 1.995                         | $-1.50$         | 1.10        | 0.170  |
| H$_2$S/CuVHG     | 1.363–1.363                 | 91.71          | 2.220                         | 1.966                         | $-0.88$         | 2.12        | 0.302  |
affinity of CoVHG towards the H$_2$S gas molecule. As above-mentioned, the contribution of the 3d orbital of dopants to the DOS around the Fermi level improved the reactivity of graphane and the strong interaction between the dopants and molecules was responsible for the increase in the adsorption energy.
4. Conclusions

In summary, we explored the adsorption of the H$_2$S molecule on the surface of pure graphite, and H-vacancy-defected and transition-metal-doped graphene. First, we investigated the effect of the H-vacancy and dopants on the geometric structure and electronic properties of graphene. Our results revealed that the states of C$_v$ and dopants were available near the Fermi level and improved the reactivity of the graphene substrate. Furthermore, the C$_v$ atom exhibited a half-metallic behavior. Second, we calculated the adsorption energy, bond length, band gap, and charge transfer for the adsorption systems. The results suggested that the H-vacancy and dopants enhanced the adsorption stability of H$_2$S on the graphene surface. Furthermore, the PDOS results indicated that there was a strong hybridization between the C$_v$-$\sigma$ orbital and the dopants. Based on these results, it can be concluded that TM-doped graphene is capable of becoming a new sensor for H$_2$S molecules. We believe that our results can provide useful information towards the applications based on graphene.

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