A comparative study of structural and electronic properties of formaldehyde molecule on monolayer honeycomb structures based on vdW-DF prospective

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A R T I C L E   I N F O

Article history:
Received 13 November 2015
Received in revised form 21 April 2016
Accepted 3 May 2016
Available online 6 May 2016

Keywords:
vdW-DF
Graphene
h-AlN
h-SiC
Formaldehyde
Sensor

A B S T R A C T

In order to develop the potential applications of monolayer sheets as gas sensors, the adsorption of formaldehyde (H2CO) molecule on graphene, hexagonal silicon carbide (h-SiC) as well as hexagonal aluminum nitride (h-AlN) monolayer sheets have been investigated. In this work we have used the so-called van der Waals density functional (vdW-DF) method. It was found that H2CO molecule adsorption on h-AlN nanosheet had relatively higher adsorption energy and shorter binding distance and finally much more reactive in the adsorption of H2CO compared with the h-SiC and graphene sheets. The density of states (DOS) was calculated and the results show that the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy gap of h-AlN and h-SiC sheets is significantly reduced upon the H2CO adsorption compared to the graphene which leads to an enhancement in the electrical conductivity of respective systems. We have evaluated these findings by well-known Mulliken as well as Hirshfeld and Voronoi charges analyses for aforementioned systems. The purpose of this work is to achieve deep insights into the influence of H2CO molecule on the electronic properties of h-AlN and h-SiC monolayer sheets, and how these effects could be used to design more sensitive gas sensing devices. Based on the DFT calculation results, the h-AlN and also h-h-SiC sheets are anticipated to be potential novel sensor for detecting the presence of H2CO toxic gas.

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1. Introduction

Recently, sensing has been a hot topic in nanomaterial research. Gas sensors are attracting huge attention, due to wide variety of potential applications in environmental, industrial and medical monitoring [1,2] and with high sensitivity, fast response time are required for detection of pollutant and toxic gases [3–6]. These gases are highly toxic for human living and animals since they confine the consumption of oxygen by body tissues [7]. The sensing mechanism for this compound attributes to change of conductivity as a result of the charge transfer between it and target gas. Therefore, we can demonstrate capability of sensor by measuring conductance of change before and after adsorption process. There are several main criteria for efficient and excellent gas sensing system, such as (i) fast response time, (ii) high sensitivity, (iii) selectivity, (iv) temperature independence and, (v) high stability.

Formaldehyde is known as environmental pollutant and is volatile carcinogen and highly toxic which are famous to cause in asthma, dermatitis, hence, it is essential to control and monitor its exposure in both human beings and industrial and its removal from the environment. From the theoretical point of view, a lot of materials, such as ZnO [8], TiO2 [9], SnO2 [10], SiO2 [11], RuO2 [12] and V2O5 [13] have been considered for detecting formaldehyde molecule. The different techniques such as chromatography, spectrophotometry and polarography have been employed to detect formaldehyde [14,15]. Nonetheless, these techniques need expensive and complicated instruments and also are insensitive. Thus, it seems necessary to investigate interaction between formaldehyde molecule and suitable devices such as nanostructured materials which have recently exhibited as potential candidates for toxins agents detecting and sensing. Last decades, several theoretical efforts have been dedicated for expansion of sensitive and rapid methods for analyzing the formaldehyde [16–20]. Owing to this

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http://dx.doi.org/10.1016/j.apsusc.2016.05.011
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fact that CNTs based sensors can’t detect some gases due to very weak adsorption of gas molecules on the CNTs and inadequate charge transfer between them [21] we have motivated to consider the adsorption of formaldehyde on the other suitable nanostructured materials. Graphene due to its unique structural, mechanical and electronic properties is demonstrated to be an exceptional sensor material because of its following factors: (1) graphene has much smaller band gap energy than CNT, thus it is highly conducive, besides it has limited crystal defects thus it has enormously low Johnson noise [22](2) graphene single atomic layer with high specific surface area (2630 m² g⁻¹) possesses a high adsorption capacity [23]. Zhang et al. studied the adsorption of formaldehyde on pure, Ti-doped and N-doped graphene sheet [24]. Analyses of adsorption energies and density of states (DOS) reveal that doped Ti atom could improve the interaction of harmful gases with graphene. Qin et al. evaluated effects of Stone–Wales (SW) defect on the adsorption of formaldehyde on graphene sheet with or without Al dopant [25]. It was found that graphene with SW defect is more sensitive than that of pristine one for detecting formaldehyde molecule. Compared with Al-doped graphene/H₂CO complex, the binding energy for Al-doped SW defect system can be increased by SW defect. Majidi and Karami studied the adsorption of formaldehyde on graphene and graphene [26]. The results indicated that formaldehyde molecule was physisorbed on the graphene and physisorbed with negligible binding energy, large binding distance, and small charge transfer [27]. We have shown in our previous works that hexagonal-AlN (h-AlN) sheet seems to be superior material for nerve agent adsorption and detection compared to the graphene or h-BN sheet. The objective of this article is to study by density functional theory (DFT) calculations, the potential application of h-AlN and h-SiC monolayer sheets as gas sensors to detect formaldehyde toxic gas. We hope our results may provide new insight into the gas sensors for practical applications.

2. Computational details

The ab initio calculations of the monolayer honeycomb structures and formaldehyde are studied based on the DFT method [28,29], using the SIESTA code [30–32] which solves the standard Kohn–Sham equations and has been demonstrated to be very efficient for large atomic systems. Owing to LDA overestimates the binding energy and underestimates the bonding distance [33], we used generalized gradient approximation (GGA) functional with exchange correlation energy in the form of Perdew–Burk–Ernzerhof (PBE) [34]. The pseudopotentials were constructed using the Troullier and Martins scheme to explain the valence electron interaction with the atomic core [35]. In the simulation, a two-dimensional periodic boundary condition was used for the super-cells with 7.387 Å x 12.788 Å x 30 Å for graphene and 13.731 Å x 7.929 Å x 30 Å for h-AlN and h-SiC sheets. In order to avoid interaction between two layers, the vacuum space is applied about 30 Å. In addition, it is important to consider the nonlocal corrections pertaining to dispersion interactions. Because conventional DFT methods do not describe vdW interactions, we implemented the fully self-consistent vdW-DFT at the GGA theoretical level, with the PBE exchange functional being favorable for calculating vdW interactions [36–40]. For a better description of physical quantities, a high dense Brillouin zone sampling is necessary and the Monkhorst-Pack block was set to 5 x 5 x 1 denser for geometry optimization. It was increased to 15 x 15 x 1 for the determination of the DOS and partial density of states (PDOS). A cutoff energy of 150 Ry was used to represent the charge density. The relaxed atomic structures were obtained by minimizing the total energy using Hellmann–Feynman forces, including Pullay-like corrections. Structural optimizations were performed using the conjugate gradient algorithm until the residual forces were smaller than 0.02 eV Å⁻¹. The valence electrons of all systems were explained by means of a double-ζ pseudoatomic basis set consisting of polarization functions (DZP). The range of those basis functions was controlled by the energy shift parameter, which was set to 0.05 eV.

3. Results and discussion

To evaluate the interaction between formaldehyde and h-AlN, h-SiC and graphene sheets we have first calculated the binding energy (Eₐ) of adsorbed system according to the following equation:

\[ E_b = E_{(G+H₂CO)} - (E_{H₂CO} + E_G) \]  

where \( E_{(G+H₂CO)} \) is the total energy of graphene interacting with the H₂CO and \( E_{H₂CO} \) and \( E_G \) are total energies of relaxed isolated H₂CO and graphene. A negative \( E_b \) corresponds to a stable adsorption structure. The net charge-transfer (Qₜ) from graphene to formaldehyde (vice versa) is calculated by using Mulliken, Hirshfeld and Voronoi population analysis, which is defined as the charge difference between the H₂CO molecule adsorbed on the honeycomb structures and an isolated H₂CO molecule.

To find the most stable configuration of H₂CO molecule adsorbed on h-AlN nanosheet, the H₂CO molecule is initially located at various positions above a hexagonal honeycomb sheet with different orientations. Before adsorption process, an optimization was applied to both H₂CO molecule and h-AlN nanosheet. For the H₂CO/h-AlN complex, we considered various possible adsorption configurations including of the O, C and H atoms of H₂CO molecule approaching to the Al atom (Al site) and N atom (N site) of the h-AlN nanosheet with the H₂CO molecular axis being parallel and perpendicular to the surface. Four possible binding sites for the adsorbed H₂CO molecule on h-AlN nanosheet were considered as initial structures. (1) O atom of H₂CO is located on the hollow site above the center of hexagon (A₁). (2) O and H atoms of H₂CO are located above the Al and N atoms, respectively, with parallel orientation (A₂). (3) Two hydrogen atoms of H₂CO molecule are located above the two N atoms of h-AlN nanosheet with perpendicular orientation (A₃). (4) O atom of H₂CO is placed above the Al atom of h-AlN nanosheet with perpendicular orientation (A₄).

It is necessary to find the stable adsorption configuration of H₂CO molecule on the h-AlN nanosheet. After full structural relaxation, the most stable configurations are identified by comparing the obtained energies of optimized configurations from the different initial states. The binding energies of all configurations are calculated, compared and presented in Table 1. From Table 1, we can learn that the O atom of H₂CO molecule is adsorbed on Al atom of h-AlN sheet with high binding energy compared with the other considered configurations where the H or C atom was close to the nanosheet. The configuration where O atom was close to surface has the most stable adsorption. In the following, we will limit the following investigation on the energetically most stable configuration.

As shown in Fig. 1 the binding energy has the lowest value when the binding distance is about 2.109 Å. The binding distance is defined as the nearest distance between the O atom of H₂CO and the Al atom of h-AlN nanosheet. The C–H bond length and bond angle of H–C–H and two H–C–O in pure H₂CO are 1.10 Å, 116.3°, 121.8° and 121.8°, respectively, which are in good agreement with the experimental values [41]. However, our results show that these were changed to 1.01 Å, 120.46°, 119.37° and 120.17°, respectively, in the adsorbed form. In addition, the Al–N bond length in h-AlN sheet is altered from around 1.83–1.85 Å. It should be noted that the N–Al–N angles in the h-AlN nanosheet are very close to 120° but, after the adsorption phenomenon it varies to a lower value as
shown in Fig. 1. The noticeable adsorption energy and small binding distance and deformation of the system structure all indicate that there is strong interaction between the H₂CO molecule and the h-AlN nanosheet (chemisorption process).

We next evaluate the adsorption of the formaldehyde molecule on the h-SiC nanosheet. Several initial configurations for the interacting molecules with various active sites were considered as in the case of h-AlN/formaldehyde and similar calculations procedures have been performed for the systems under consideration. More detailed information from the simulation of the H₂CO/h-SiC systems, consisting of values of binding energy, equilibrium H₂CO/h-SiC sheet distance are calculated, compared and listed in Table 1. It was found that O atom of H₂CO molecule prefers to be attached to the Si atom of the h-SiC surface while H atom was placed close to the C atom of the sheet as shown in Fig. 1(b). The calculated binding energy for the energetically favorable H₂CO/h-SiC complex was determined to be −0.42 eV. Adsorption process has influence on the structure geometries of H₂CO molecule. The changes of bond length and bond angles are shown in Fig. 1(b). It is worth noted that interaction between H₂CO molecule and h-SiC sheet is weaker than the h-AlN one.

To understand the adsorption behavior of formaldehyde molecule on the graphene sheet, the gas molecule investigated is initially placed at various positions above a graphene sheet with different orientations namely: (1) H atom of formaldehyde is located above the C atom of graphene with perpendicular orientation (G₁), (2) H atom of formaldehyde is placed hollow site the C atom of graphene with perpendicular orientation (G₂), (3) O–C bond length of formaldehyde is located top of the graphene with perpendicular orientation (G₃), (4) O–C–H bond length of formaldehyde is parallel with C atom of graphene (G₄). (5) Both of O and H atoms of formaldehyde are located hollow site of graphene with parallel orientation (G₅). (6) O atom of formaldehyde is placed hollow site of graphene with perpendicular (G₆). After full relaxation, the most stable configurations are identified by comparing the energies of optimized configurations as shown in Table 1.

The interaction between the H₂CO molecule and graphene are weaker than those between H₂CO molecule and h-SiC and h-AlN nanosheets as shown in Table 1. Form Table 1, we can learn that the H₂CO molecule is physisorbed on graphene sheet with small binding energy −0.231 eV and large binding distance 3.070 Å. The calculated binding energies (Eᵣ), the distances between O atom of H₂CO molecule, the closest C atom of graphene and the equilibrium H₂CO/graphene system distance were summarized in Table 1. It is worth mentioning that, the bond length C–C and C–C–C angles

![Diagram](image-url)

**Fig. 1.** Schematic view of the energetically favorable configurations of formaldehyde adsorbed on the (a) h-AlN nanosheet (b) h-SiC nanosheet (c) graphene. H atoms are shown in white, Al atoms are shown in pink, C atoms are shown in grey, Si atoms are shown in yellow, N atoms are shown in blue and O atoms are shown in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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in graphene sheet is remains nearly unchanged after adsorption phenomenon as shown in Fig. 1(c). The small binding energy and large binding distance values indicate that H$_2$CO molecule undergoes physical adsorption on graphene due to weak vdW interaction between them while there is strong interaction in the case of h-SiC and h-AlN nanosheets.

Furthermore, to investigate the change of electronic structures in monolayer sheets caused by the adsorption of H$_2$CO molecule, the charge transfer between two interacting entities was calculated by Mulliken [42,43], Hirshfeld [44], and Voronoi [45] methods. As listed in Table 2, based on the Mulliken population, 0.01 e, 0.12 e and 0.02 e have been transferred from h-AlN, h-SiC and graphene nanosheets to H$_2$CO molecule, respectively. Owing to the Mulliken’s approach to judge values of partial atomic charge are not realistic [46], we also used the Hirshfeld and Voronoi methods which are more reliable than Mulliken method [47]. The obtained results of respectively Voronoi and Hirshfeld methods propose that 0.29 e and 0.21 e are transferred from h-AlN nanosheet to H$_2$CO molecule which is consistent with the finding of strong binding energy. The results reveal that the H$_2$CO molecule behaves as an acceptor and h-AlN nanosheet acting as a donor entity. The partial atomic charge however indicates that Al atom loses 0.06 e (0.07 e) and O atom acquires 0.15 e (0.12 e) by means of Voronoi (Hirshfeld) analysis. Oxygen atom of H$_2$CO molecule owing to high electronegativity has strong ability to obtain charge and behaves as an acceptor grabbing charge from the Al atom, which shows that charge transfer was happen from h-AlN nanosheet to H$_2$CO molecule. The same analysis is carried out for h-SiC and graphene based on Voronoi and Hirshfeld methods. According to obtained results by these methods it was found that 0.22 and 0.18 e are transferred from h-SiC sheet to H$_2$CO molecule (see Table 2). The results show also that graphene sheet gains electrons and H$_2$CO molecule loses electrons during the adsorption process.

To deeply understand the electronic properties of these systems, the density of states (DOS) for the pure monolayer sheets, pure H$_2$CO molecule and H$_2$CO molecule adsorbed on the monolayer nanosheets were obtained and analyzed (see Fig. 2). The Fermi level was set at zero and drawn and simultaneously electrical conductivity of the nanosheet should induce some change by charge transfer as H$_2$CO molecules adsorbed on the nanosheet surface. As depicted in Fig. 2(a), it was found that when H$_2$CO molecule is adsorbed on the h-AlN nanosheet, there is strong interaction between H$_2$CO molecule and h-AlN nanosheet. Our calculation results showed that when the H$_2$CO molecule is strongly adsorbed on the h-AlN, the Fermi level of the h-AlN was increased from -4.48 to -4.89 eV due to the strong interaction. In addition, the

<table>
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<th>Voronoi (e)</th>
<th>Hirshfeld (e)</th>
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Fig. 2. Comparison between the density of states (DOS) for (a) pure h-AlN nanosheet, H$_2$CO/h-AlN, pure H$_2$CO (b) pure h-SiC nanosheet, H$_2$CO/h-SiC, pure H$_2$CO, (c) pure graphene, H$_2$CO/graphene, pure H$_2$CO. (d) Calculated partial density of states (PDOS) for O and Al atom of H$_2$CO/h-AlN system. The Fermi level is located at zero.
band gap \( (E_g) \) of the system sharply decreases by 1.87 eV \( (E_g \) value was decreased from 3.420 to 1.554 eV) in the adsorbed form and it becomes more semiconductor like with a decrease in the DOS near the Fermi level.

The same analysis is carried out for stable the \( \text{H}_2\text{CO}/\text{h-SiC} \) sheet system. By detecting the conductivity change of the \( \text{H}_2\text{CO}/\text{h-SiC} \) sheet system before and after the adsorption phenomenon of \( \text{H}_2\text{CO} \) molecule, the existence of \( \text{H}_2\text{CO} \) toxic gas can be detected sensitively. The obtained results show that considerable changes occur in DOS spectra of \( \text{h-SiC} \) sheet and \( \text{H}_2\text{CO}/\text{h-SiC} \) system as shown in Fig. 2(b). On the other hand, the difference in the Fermi levels of the \( \text{h-SiC} \) sheet \( (E_f = -4.067 \text{ eV}) \) and \( \text{H}_2\text{CO}/\text{h-SiC} \) sheet system \( (E_f = -4.585 \text{ eV}) \) clearly demonstrate that charge transfer occurs between the \( \text{h-SiC} \) sheet and \( \text{H}_2\text{CO} \) molecule during the adsorption process. It was revealed that there is charge transfer between \( \text{H}_2\text{CO} \) molecule and \( \text{h-SiC} \) nanosheet which is reflected high adsorption energy.

To verify the influence of the adsorption of \( \text{H}_2\text{CO} \) molecule on the graphene sheet density of states (DOSs) spectra with and without adsorbed \( \text{H}_2\text{CO} \) molecule were calculated as shown in Fig. 2(c). As shown in the figure it was found that the DOS spectra at the Fermi level has no noticeable change and DOS spectra of \( \text{H}_2\text{CO}/\text{graphene} \) system is very similar to pure graphene. Thus, the small adsorption energy, long binding distance and little charge transfer indicate that graphene are not suitable for sensing \( \text{H}_2\text{CO} \) molecule.

To further clarify the adsorption processes of \( \text{H}_2\text{CO}/\text{h-AlN} \) complex as energetically most stable system, the partial density of states (PDOSs) of the Al and O atoms (before adsorption) are calculated and represented in Fig. 2(d). According to the PDOS analysis, the O-2p orbital contributes to both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) states while the Al-3p contributes only to the HOMO state. This indicates that Al atom tends to give electrons while O atom can achieve or give electrons, respectively, due to its high electronegativity and lone pairs electrons.

Further insight can be achieved from total electron density maps of the electronic densities. The isosurface plots of HOMO/LUMO as well as total electron density on the \( \text{H}_2\text{CO}/\text{monolayer} \) sheet are shown in Fig. 3. It was found from the figure that densities of the HOMO state are localized on the \( \text{h-AlN} \) nanosheet while densities of the LUMO are located on the \( \text{H}_2\text{CO} \) molecule. The significant overlap of electron clouds between the \( \text{H}_2\text{CO} \) molecule and \( \text{h-AlN} \) nanosheet was observed from the total electron density calculation (see Fig. 3(c)). We next consider the same analysis on the \( \text{H}_2\text{CO}/\text{h-SiC} \) and \( \text{H}_2\text{CO}/\text{graphene} \) systems. It was found that densities of the HOMO are localized on the \( \text{h-SiC} \) nanosheet and the LUMO are localized on the \( \text{H}_2\text{CO} \) molecule while both of densities of the HOMO and LUMO are localized on the graphene sheet as shown in Fig. 3(g) and (h).

The negligible overlapping of electron clouds between the \( \text{H}_2\text{CO} \) molecule and \( \text{h-SiC} \) and graphene nanosheets were observed Fig. 3(f) and (i). Nevertheless, unlike \( \text{h-SiC} \) and \( \text{h-AlN} \) nanosheets, there is no evidence of hybridization between the \( \text{H}_2\text{CO} \) molecule and graphene nanosheet and does not have noticeable influence on the electronic structure of the graphene sheet (see Fig. 2(c)). The result shows that graphene remain nearly unchanged by physisorption process of the \( \text{H}_2\text{CO} \) molecule and the conductivity change is hardly observable. The change in electro-conductivity of the graphene is a key process in the sensor industry [48]. It is famous that \( E_g \) is a crucial factor for determining the electrical conductivity of graphene system which refers to the energy difference between valance level (HOMO) and the conduction level(LUMO) in insulator and semiconductor by the following relation [49]:

\[
\sigma \propto \exp(-E_g/2KT)
\]

Fig. 3. The calculated orbital localized (a) HOMO (b) LUMO (c) total density of \( \text{H}_2\text{CO}/\text{h-AlN} \) system and (d) HOMO (e) LUMO (f) total density of \( \text{H}_2\text{CO}/\text{h-SiC} \) system and (g) HOMO (h) LUMO (i) total density of \( \text{H}_2\text{CO}/\text{graphene} \) system. (Red and green colors denote the negative and positive signs of the wave function). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
where $\sigma$ is electrical conductivity, $K$ is Boltzmann’s constant ($8.62 \times 10^{-5}$ eV/K) and $T$ is the temperature. However, in energetically favorable configuration of H$_2$CO/graphene system, the $E_g$ is rarely changed from 2.479 eV in pristine graphene to 2.211 eV by the physisorption process, indicating that the graphene sheet is not sensitive to H$_2$CO molecule, while for H$_2$CO/h-SiC nanosheet system is varied from 2.545 eV in pure h-SiC nanosheet to 1.212 eV. In the following the frontier energy gap decreases and the electrical conductivity of h-SiC nanosheet is enhanced (see Table 3). Compared to pure graphene, the h-SiC nanosheet have stronger interaction with the H$_2$CO molecule and can provide more sensitive signal for H$_2$CO sensing. Therefore, the h-SiC nanosheet has a good sensitivity to H$_2$CO molecule detection and also it can be effectively adsorbed on the h-SiC nanosheet.

The same calculation is carried out for h-AlN/H$_2$CO system. As cited in Table 3, the $E_g$ decreases from 3.420 eV in pristine h-AlN nanosheet to 1.554 eV after adsorption process. According to above equation, the smaller $E_g$ values lead to the higher electrical conductivity at the given temperature. The significant change (around 54.56%) in $E_g$ value reveals the high sensitivity of the electronic properties of h-AlN nanosheet toward the adsorption of H$_2$CO molecule. It has been previously indicated that this occurrence may be owing to charge transfer and geometry deformation [50]. It is worth mentioning that strong interactions are one of the most important factors for sensor industry owing to it entails that desorption of the adsorbate molecule could be durable and the device may suffer from long recovery times [51]. If $E_{ad}$ is considerably increased, much longer recovery time is anticipated based on transition state theory:

$$\tau = \exp(\frac{E_{ad}}{k_B T})$$

where $\tau$ is recovery time, $T$ is the temperature, $K$ is Boltzmann’s constant and $k_B$ is the attempt frequency. According to above equation, more negative $E_{ad}$ values will delay recovery time in an exponential manner. The adsorption energy of H$_2$CO molecule on the h-AlN nanosheet is not too large to inhibit recovery of h-AlN nanosheet. Thus, it will possess short recovery time and suitable for H$_2$CO detection [52].

### 4. Conclusion

To summarize, we report DFT with vdW simulation of the interaction between H$_2$CO molecule and different kinds of honeycomb monolayer structure. Detailed analysis of the geometrical structures and electronic properties of energetically favorable configurations were performed. We found that the h-AlN nanosheet was more sensitive to adsorb H$_2$CO molecule compared the graphene and h-SiC nanosheet. The electronic properties and geometric structures of h-AlN/H$_2$CO present dramatic changes after the adsorption of H$_2$CO molecule. The energy gap of h-AlN nanosheet is significantly reduced upon the adsorption of H$_2$CO molecule (about 54.56%) compared graphene and h-SiC nanosheet, thus leading to the increase in electrical conductivity reveal that the high sensitivity of the electronic properties of h-AlN nanosheet toward the adsorption of H$_2$CO molecule. All results above confirm that chemisorption takes place between h-AlN nanosheet and H$_2$CO molecule in adsorbed form. Thus we propose h-AlN nanosheet would be a promising candidate to detect the H$_2$CO molecule.

The current results supplied not only insightful information about the adsorption of H$_2$CO molecule in different monolayer with various sites and orientations but also revealed suitable applications of h-AlN nanosheet as gas sensor for sensing H$_2$CO molecule. We hope our results will be helpful for the application of h-AlN nanosheet for chemical sensor to detect H$_2$CO molecule.

### References


