

# Control of the Adsorption Behavior of Gas Molecule on Graphene by Strain: First-Principles Calculations for Development of Multi-Gas Selective Sensors

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**Abstract**—Graphene is a promising material for gas sensing because of its unique electrochemical properties. Previous studies have revealed that the adsorption and desorption of gas molecules on graphene were controlled by mechanical strain. In this study, first-principles calculation was applied to the investigation of the effect of tensile and compressive strains on the gas adsorption properties of graphene. It was found that the adsorption energy varied almost linearly with the applied strain due to the change of its electronic band structure and, consequently, it caused the change of the magnitude of the charge transfer between them. Among them, NO<sub>2</sub> exhibited greater strain sensitivity, specifically, its adsorption energy increased by about 70% under compressive strain of 10%. The non-equilibrium green function (NEGF) method was also performed to confirm that the I-V characteristic was changed by the adsorption of gas molecules and strain. Notably, it was found that the change of current was about 14 times larger than that observed in 10%-tensile-strained graphene adsorbed with H<sub>2</sub>O system when no strain was applied. Overall, our results validated that tuning the gas binding behavior of graphene by application of strain is a promising approach for developing multi-gas sensors with high selectivity.

**Keywords**—graphene, gas, strain, first-principles calculation

## I. INTRODUCTION

Recent research suggests that analyzing the gases exhaled by humans can serve as an early indicator of diseases. For instance, individuals with diabetes exhale high levels of acetone (above 1.76 ppm), while healthy people exhale less than 0.8 ppm. Additionally, elevated ammonia levels in breath are linked to kidney disease. It is worth noting that human breath comprises a diverse array of gas molecules, each present at varying concentrations, thereby underscoring the complexity and potential diagnostic value of breath analysis in disease detection [1-2]. In light of these findings, there is a growing need for highly sensitive multi-gas sensors with selectivity to enable continuous monitoring of human health and alleviate the burden on healthcare systems.

Graphene, with its large surface area, high carrier mobility, and exceptional sensitivity to gas molecules, holds significant

promise as a gas sensing material. By leveraging these unique properties, graphene-based sensors can offer enhanced detection capabilities, enabling precise and reliable monitoring of various gases associated with human health conditions [3-6]. Previous research has convincingly demonstrated that the adsorption of molecules onto graphene's surface induces significant changes in its resistance due to electronic charge transfer between the adsorbents and graphene. Notably, Schedin et al. successfully fabricated a highly sensitive graphene gas sensor capable of detecting gas molecules at concentrations as low as 1 part-per-billion [7-8].

Despite these achievements, realizing selectivity in gas sensors remains a formidable challenge, particularly when it comes to differentiating target molecules from complex gas mixtures prevalent in real-world environments. Conventional methods, such as incorporating dopants or introducing defects in graphene, suffer from limitations such as reduced carrier mobility and irreversibility, which restrict their applicability to specific gas molecules [9-12]. Therefore, alternative approaches are needed to enhance the selectivity of graphene-based gas sensors without compromising their performance. To solve this issue, the authors have explored the use of strain to tune the adsorption and desorption of gases on graphene without affecting its high sensitivity. Recent the authors have

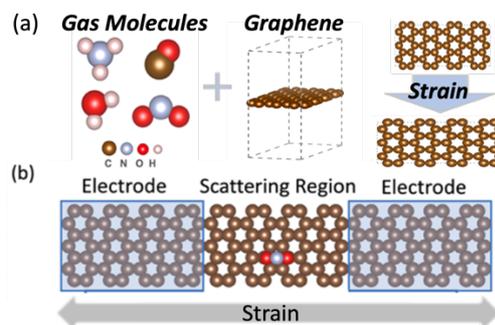


Fig. 1. (a) Atomic model in standard DFT calculation, depicting adsorbent gases and schematic diagram representing the application of uniaxial strain to graphene layer. (b) Illustration of the simulation structure processed with the NEGF method with left and right graphene lead (blue shade region).

shown that the adsorption energy changed significantly with the applied strain, and it was validated by applying cyclic tensile strain to a graphene-based gas sensor on a flexible PDMS substrate [13-14]. The underlying mechanisms of the strain-induced change of gas binding on graphene, however, are not fully clarified yet from the view of electronic level.

In this study, therefore, first-principles calculation combined with the non-equilibrium green function (NEGF) method was used to investigate the effect of strain on the different gas (NH<sub>3</sub>, CO, H<sub>2</sub>O and NO<sub>2</sub>) adsorption behaviour on graphene from equilibrium to transport states. The findings presented in this study shed new light on the modulation of gas adsorption characteristics in graphene through strain engineering. This offers potential avenues to enhance selectivity in graphene-based gas sensors and provides valuable guidance for future experimental investigations.

## II. CALCULATION DETAILS

### A. Standard DFT Calculation

All Density Functional Theory (DFT) calculations were performed using the VASP (Vienna Ab initio Simulation Package) code. The electron-electron interactions were treated with Projector-Augmented Wave (PAW) pseudopotentials, an advanced approach that enhances the efficiency of DFT calculations [15]. The Perdew-Burke-Ernzerhof (PBE) function under the generalized gradient approximation (GGA) was utilized to calculate the exchange-correlation energy resulting from the electron-electron interaction. To ensure convergence, a plane wave cut-off energy of 500 eV was employed. During the geometrical optimization, the Brillouin zone was sampled using a  $4 \times 4 \times 1$  Monkhorst-Pack k-mesh grid. In order to obtain the accurate energy, a denser k-mesh grid ( $12 \times 12 \times 1$ ) was applied during the self-consistent calculation. The tolerance for energy convergence was  $10^{-5}$  eV, while atomic positions were optimized until the maximum force in every atom was smaller than 0.01 eV/Å. As for the analytical model, as shown in Fig. 1(a), a rectangular shape graphene super cell consisting of 48 carbon atoms were used as sensing material while four different gas molecules (NH<sub>3</sub>, CO, H<sub>2</sub>O, and NO<sub>2</sub>) were selected as adsorbents.

### B. Transport Calculation

The NEGF method was used to investigate electrons transport through the graphene sheet before and after gas physisorption under strains by using TranSIESTA code [16]. As illustrated in Fig. 1(b), the device structure consisted of a graphene right electrode, a scattering region, and a graphene left electrode. The left and right electrodes each contained 48 carbon atoms and were considered to couple directly only via the center scattering region. The conductivity of a nanoscale conductor is the sum of all the transmission possibilities possessed by an electron propagating with an energy equal to the chemical potential. Therefore, the conductance can be expressed as follow:

$$G(\mu) = G_0 \sum_n T_n(\mu) \quad (1)$$

where the unit of quantum conductance, represented by  $G_0$ , is equal to  $2e^2/h$ ,  $T_n$  is the transmission eigenvalues of the channel. As for the current flowing through the scattering region was calculated based on Landauer-Buttiker formula:

$$I(V_b) = G_0 \int_{\mu_L}^{\mu_R} T(E, V_b) dE \quad (2)$$

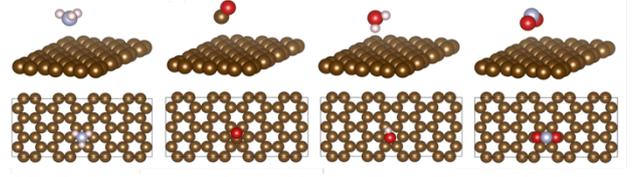


Fig. 2. Optimized adsorption structure for pristine graphene adsorbing with one NH<sub>3</sub>, CO, H<sub>2</sub>O and NO<sub>2</sub> molecule, respectively.

TABLE I. CALCULATED DETAILS

System	Distance/Å	Adsorption energy /meV	Charge transfer/e <sup>-</sup>
NH <sub>3</sub> +G	3.7052	-23.9523	-0.0075
CO+PG	3.7700	-12.8704	-0.0008
H <sub>2</sub> O+PG	3.4371	-30.3687	0.0082
NO <sub>2</sub> +PG	3.6897	-145.4457	0.1807

<sup>a</sup>. The negative value of charge transfer represents the electrons were transferred from gas to graphene while the positive value represents the opposite transportation direction.

where the transmission probability  $T$  is dependent on the incident energy  $E$  of electrons, as well as the potential bias  $V_b$ . The electrochemical potential difference between left and right electrodes is given by  $eV_b = \mu_L - \mu_R$ .

## III. RESULTS AND DISCUSSIONS

### A. Gas adsorption on pristine graphene (PG)

Prior to investigating the impact of strain on gas adsorption behavior, we initially examined the energetically favorable gas adsorption structures on PG without strains. The optimized gas adsorption structures are illustrated in Fig. 2. It is evident that the most stable configuration for water molecule adsorption on PG occurs when the hydrogen atom of the H-O bond is oriented towards the hollow site on the PG surface. Similarly, NH<sub>3</sub> exhibits the most stable adsorption when the N atom of ammonia is near the PG surface. Furthermore, we observed that CO undergoes a slight rotation, with the carbon atom of the C-O bond pointing towards the PG surface. Lastly, the most favorable configuration for NO<sub>2</sub> molecule adsorption involves the N-O bond directed towards the graphene surface. To obtain more quantitatively evaluation, we calculated the adsorption energy as following equation:

$$E_{ad} = E_{Graphene+Gas} - E_{Graphene} - E_{Gas} \quad (3)$$

where the  $E_{Graphene+Gas}$  represents the free energy of adsorption system and  $E_{Graphene}$ ,  $E_{Gas}$  represent the energy of isolated graphene and gas molecule individually. Furthermore, to assess the electron transport between graphene and gas molecules, we utilized the Bader charge analysis method using the code developed by G. Henkelman's group [17-18]. Comprehensive calculation results, including adsorption energy, equilibrium distance, and charge transfer, are summarized in Table 1. It is observed that the calculated equilibrium distances for these four systems range between 3 to 4 Å, indicating that the gas molecules are connected to the PG surface via weak van der Waals interactions. Additionally, based on the calculated charge transfer, NH<sub>3</sub> and CO were identified as donor-type molecules, while H<sub>2</sub>O and NO<sub>2</sub> exhibited acceptor-type behaviour upon adsorption onto the PG surface. These findings are consistent with previous

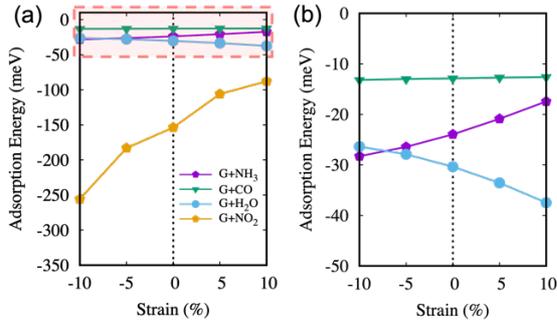


Fig. 3. Relationship between adsorption energy on graphene and the applied strain, with positive values in the x-axis representing present tensile strain and negative values representing compressive strain.

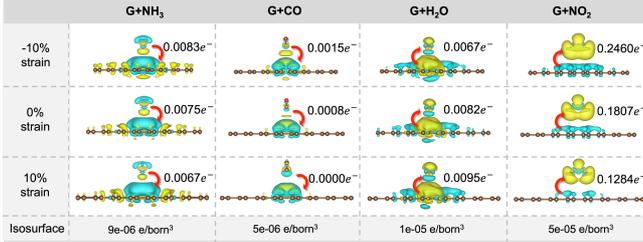


Fig. 4. Charge density difference (CDD) for each gas adsorption system under -10%, 0% and 10% strained graphene surface.

experimental and computational results, confirming the validity of our calculations [8, 19].

### B. Variation of Adsorption Behavior with Strain

Subsequently, we applied different uniaxial tensile and compressive strains along the armchair direction of the graphene surface to investigate their impact on gas adsorption behaviors. The findings, presented in Fig. 3(a), demonstrate a distinct linear relationship between the adsorption energy and strains. Particularly,  $\text{NO}_2$  exhibits the highest strain sensitivity compared to the other gases ( $\text{NH}_3$ ,  $\text{CO}$ , and  $\text{H}_2\text{O}$ ). Under 10% tensile strain, the adsorption energy of  $\text{NO}_2$  decreased from -145 meV to -81 meV, whereas under 10% compressive strain, it increased from -145 meV to -264 meV. Upon closer examination of the other three gases, as shown in Fig. 3(b), it was observed that each gas specie presents individual strain responses. Specifically, for  $\text{CO}$ , neither tensile nor compressive strains significantly altered its gas sensing properties. In the case of  $\text{NH}_3$ , compressive strain led to an increase in bonding, while for  $\text{H}_2\text{O}$ , the adsorption energy was higher under tensile strain.

To gain deeper insights into the impact of strain on adsorption behavior, we performed an analysis of Bader charge transfer and Charge Density Difference (CDD). This analysis aimed to provide an understanding of the strain-induced changes of adsorption behavior from the view of charge transfer. The calculated results were depicted in Fig. 4, where the regions of electron accumulation were indicated by yellow color and electron depletion was indicated by blue color. It is well-established in previous studies that the extent of charge transfer between gas molecules and graphene significantly influences the adsorption energy. Specifically, a larger charge transfer corresponds to a stronger interaction and higher adsorption energy [7,8,20]. Consistently with this assumption, we found that  $\text{NO}_2$  exhibits the highest strain response, displaying a significant change in charge transfer

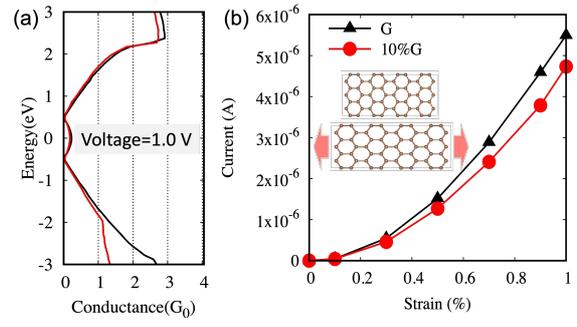


Fig. 5. Strain-induced change of I-V characteristics of graphene

TABLE II. CALCULATED CURRENT WITH VOLTAGE EQUALS TO 1.0 V

Strain	Current		
	$I(\text{Graphene}) / \mu\text{A}$	$I(\text{Graphene}+\text{H}_2\text{O}) / \mu\text{A}$	$\Delta I / \text{nA}$
0%	5.4385	5.4398	1.3
10%	4.7228	4.7410	18.2

with applied strain. The trends observed in the charge transfer align with the corresponding adsorption energy, as a greater charge transfer indicates a stronger interaction and higher adsorption energy. On the other hand,  $\text{CO}$  and  $\text{NH}_3$  exhibit similar trends to the adsorption energy, with  $\text{CO}$  showing low sensitivity to strain and  $\text{NH}_3$  exhibiting an opposite trend compared to  $\text{H}_2\text{O}$ . These findings are consistent with our previous observations regarding the strain-induced changes in gas adsorption energy. And the distinct linear strain sensitivity exhibited by each gas molecule further emphasizes the potential for selective detection through strain modulation.

### C. Strain Dependence of Transport Properties of Graphene and Its Gas Sensing Properties

To evaluate the effect of strain on the transport properties of graphene and its gas sensing properties, we calculated the current-voltage (I-V) characteristics of isolated graphene at first. The calculated results are shown in Fig. 5(a), where it can be observed that the tensile strain leads to a decrease in the electrical conductivity of graphene. This behavior can be attributed to the mechanical strain that moves the Dirac cone of graphene in reciprocal space, leading to a decrease in the density of electronic states around Fermi level [21]. The calculated I-V characteristics of pristine graphene and graphene subjected to a 10% tensile strain, as depicted in Fig. 5(b). The results clearly demonstrate that, under the same external voltage, the current passing through the strained graphene is reduced in comparison to the 0% strain condition. This behavior can be attributed to the following explanation based on Eq. (2). It is well-known that the current flowing through the central scattering region is described as the integration of the conductivity. Therefore, considering the effect of strain on the conductivity of graphene, we can infer that the reduction in current can be attributed to the decrease in the conductivity of the strained graphene, which in turn leads to a lower number of carriers and an overall decrease in the current.

After examining the I-V characteristics of isolated graphene, we expanded to investigate the adsorption behavior of gas molecules, specifically focusing on the adsorption of water molecules on graphene. Table I provides a summary of the currents before and after the adsorption of water molecule

on the graphene surface, considering the presence and absence of a 10% tensile strain, while maintaining an external bias voltage of 1.0 V. It can be found that under the 0% strain condition, the adsorption of water molecule caused a small change in the current through the graphene surface, with a measured value of only 1.3 nA. When a 10% tensile strain was applied, the current passing through the strained graphene surface alone exhibited a substantial increase, reaching 4.7228  $\mu$ A. In the case of the strained gas adsorption system, the current further increased to 4.7410  $\mu$ A. Previous experimental work has indicated that the change in current is closely linked to the sensitivity of fabricated gas sensors [7]. Therefore, the significant increase in current difference (approximately 14 times) suggests that the application of appropriate strain can improve the sensitivity of sensors to specific gas species. These findings align well with the earlier calculation results using standard DFT methods, which predicted an increased charge transfer between water molecules and the graphene surface under tensile strain, leading to enhanced adsorption energy. Taken together, these results suggest that mechanical strain can effectively modulate the interaction between adsorbed gas molecules and the graphene surface, highlighting the potential of strain engineering in tuning gas adsorption properties.

#### CONCLUSIONS

In conclusion, this study investigated the effect of tensile and compressive strains on the gas adsorption properties of graphene using first-principles calculations. The key findings can be summarized as follows:

1. The adsorption energy of various gas molecules on graphene varied linearly with the applied strain. Notably, NO<sub>2</sub> exhibited significant strain sensitivity, with a 70% increase in adsorption energy under a compressive strain of 10%.
2. Each gas species responded differently to strain. CO showed negligible changes in gas sensing properties under both tensile and compressive strains. NH<sub>3</sub> bonding increased under compressive strain, while H<sub>2</sub>O adsorption energy was higher under tensile strain.
3. The observed changes in charge transfer due to strain were consistent with previous findings on gas adsorption behavior, reinforcing the understanding of the underlying mechanisms.
4. The NEGF method revealed a substantial impact of gas adsorption and strain on the I-V characteristics. The change in current was approximately 14 times larger in the strained graphene system with gas adsorption compared to the 10%-tensile-strained graphene adsorbed with H<sub>2</sub>O under no strain.

Overall, these findings highlight the potential of strain engineering in developing highly selective multi-gas sensors based on graphene. By modulating strain, the sensitivity and selectivity of graphene-based gas sensors can be enhanced, opening up new possibilities for their application in various gas detection scenarios.

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