Investigation Adsorption Mechanism of Methane Gas in Graphene and Copper Doped Nano-ribbon Using Density Function Theory

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Abstract. In this study, density function theory was used to evaluate geometrical and electronic properties for pure and doped system as well as adsorption energy. Pure graphene nano-ribbon appeared in plane surface during adsorption energy to have low sensitivity to methane gas. Its energy gap changed only in distance 1A because of the chemical adsorption. Doping mechanism enhanced the proprieties of graphene nano-ribbon. In geometrical structure, copper (Cu) atom stretching the nano system and it is a sign of modification. Additionally, energy gap was decreasing by doped in transition metal atom and become opening. Adsorption energy of doped system was higher than pure nano-ribbon. It was noticed that the doped transition metal enhanced the sensitivity of the system 6 times greater than pure graphene nano-ribbon. Doping graphene nano-ribbon by copper atom revealed to be a key to design chemical and physical gas sensor for methane gas.

1. Introduction

Graphene as a two-dimensional connected carbon sheet is an excellent material that has exceptional properties such as superior surface to volume fraction, little electrical noise and outstanding transport properties[1]. Graphene has more superior efficiency in addition to its unique two-dimensional structure and has unique chemical properties such as outstanding electrical, optical and mechanical properties. Due to its excellent properties, graphene has been commonly used in a number of ways, such as energy generation, spintronics and field effects transistor (FET)[2]. Graphene has also been proven to have possible uses in detection molecules, both experimental and theoretical methods. Graphene could be employed as a novel material for adsorption and desorption due to its low dimensions and wide surface area process [3]. Graphene is a zero band gap semiconductor with its valence and conduction bands touching in corner of the Brillion zone in called Dirac points [4]. However many theoretical and experimental studies showed that graphene has weak physical adsorption of most gas molecule[5]. Therefore, researchers utilized many mechanisms such as defect vacancy and doped graphene by metal atom[6]. Graphene doped by metal atom led to significant structural and electronic properties, also electrical conductivity and chemical reactivity during adsorption process to detection small gas
molecule[7]. It is noteworthy that doped graphene by metallic atom creates modifications process without damaged one atom thick of it[8]. Many studies showed that the introduction of defect or doped metallic atom in graphene will modify the charge transfer strength between it and gas molecule adsorbed, also enhance sensitivity and selectivity of gas-based sensor[9]. Gas sensing was important environmental issue for hazard toxic gases molecule. Thus, this study is mainly focused on used different nano-system for detection methane gas.

2. Theoretical background

In order to investigate the electron systems’ electronic structure, density functional theory (DFT) is employed for this purpose which is widely used quantum mechanical method in physics and chemistry. DFT usually applied to evaluate the ground-state properties of metals semiconductors as well as insulators. Furthermore, DFT is a useful method in physics and chemistry computational [10]. Historically, in 1927, the starting point for the theory of density was the Thomas-Fermi model. They defined the energy of an atom by representing its kinetic energy as a function of electron density, combining this with the classic expressions for interactions among nuclear-electron and electron-electron, which can also be defined in terms of electron density [11, 12]. The DFT focuses on the much simpler electron density $\rho(r)$. DFT’s central concepts are dependent on ground state energy. Others ground state electronic properties are determined uniquely by the density of the electrons [13, 14]. However, the exact ground conditions of the system correlates to the electronic density for minimal total energy.

3. Materials and Research Aim

(GNR), (Cu-GNR) and $\text{CH}_4$. DFT method was used to computed structural, electronic and adsorption energy for pure and doped graphene by Cu atom. The aim of present study is design sensor for toxic gas. The equations below were used in the study.

Adsorption energy = $(E_{\text{gas}}+E_{\text{ribbon}})-E_{(\text{gas}+\text{ribbon})}$[15]

Where $E_{\text{gas}}$ total energy for adsorption gas, $E_{\text{ribbon}}$ is total energy for nano-system and $E_{(\text{gas}+\text{ribbon})}$ is total energy for adsorption system.

Energy gap=$E_{\text{LUMO}}-E_{\text{HOMO}}$ [16]

4. Result and discussion

4.1. Geometrical proprieties

Geometrical characteristics summarized on bond length and angle between atoms computed for graphene nano-ribbon when toxic gas molecule absence. Fig. 1 lists the geometry structure for pure graphene nano-ribbon. Bond lengths for C-C, C=C, C=C (aromatic) and C-H are (1.4555), (1.3661), (1.4305) and (1.0859), respectively [15]. Angles between atoms listed for (C--C--C) and (C=C-H) are 120.232 and 119.922 degree, respectively[15]. For doped nano-ribbon, Fig. 2 illustrated a geometrical structure for G-Cu nano-ribbon. Bond length between carbon-carbon for all type’s agreement with previous study [16]. The bond length between Cu-C are varies between 1.8427-1.8672 Å. Computed bond length for metal-carbon was agreement with study [16]. The angle between carbons atoms are agreement with past section also. Bond angel between Cu atom and three neighbor atoms are 85.3641-103.7705 degree. Bond angle for system under study agreement with [17]. Also that clear copper atoms stretching structure of graphene nano-ribbon because the radius of it greater than carbon radius [18].
4.2. Adsorption energy

In this section, study adsorption energy for pure graphene nano-ribbon compared with doped system. For pure system CH$_4$ gas molecule reaction with graphene is low activity. The absolute energy value increasing from zero to 2 eV at distance $4 \sim 1.5$ Å all these distances refer to physical adsorption. Chemical adsorption appears only when bonds formed between H related to gas with C of graphene nano-ribbon. For doped system CH$_4$ has adsorption energy greater than pure nano-ribbon, modification of interaction process was clear. In addition, findings indicated that G-Cu system sensing CH$_4$ gas for all distance. Finally, results indicated that G-Cu system has high sensitivity for CH$_4$(doped) $>$ CH$_4$(pure). Table 1 listed the values of adsorption energy and Figure 2 showed the curves of adsorption energy measured in eV unit.

Table 1. Values of adsorption energy for system under study measured in eV unit

| D (Å) | Pure nano-ribbon | Doped nano-ribbon |
|-------|------------------|-------------------|
| 1     | -7.3088          | -45.2869          |
| 1.5   | -2.1496          | -6.6194           |
| 2     | -0.5278          | -1.2320           |
| 2.5   | -0.1034          | -0.4476           |
| 3     | -0.01360         | -0.4187           |
| 3.5   | 0.001532         | -0.4676           |
| 4     | 0.002721         | -0.4974           |
4.3. Energy gap

Energy gaps depend on difference energy between HOMO and LUMO value. Results in Table 2 showed that energy gap decreased when interaction increasing, this is suggested to take place because of gas molecule approaches the surface and Van Der Waals formations. Moreover, result revealed that when energy gap decreased in distance near surface of the graphene, the nano-ribbon has high stability [19]. Results showed that for distance far from surface energy gap for adsorbed systems remain at pristine graphene nano-ribbon energy gap, in other hand increasing in energy gap ability of sensing for gases decreased [20]. Energy gap of doped nano-ribbon CH$_4$ small compared with pure system. Appear energy gaps in this phase because attractive force between CH$_4$ and surface of nano system. Energy gap in doped nano-ribbon and during adsorption mechanism remain opening. Results show that CH$_4$ have high reactivity with system under study compared with pure system [21]. Fig. 3 represent energy gap curves for system under study.

### Table 2. Values of energy gap for systems under study in eV unit.

| D (A) | Pure nano-ribbon | Doped nano-ribbon |
|-------|------------------|-------------------|
| 1     | 2.086            | 1.218             |
| 1.5   | 2.477            | 1.243             |
| 2     | 2.524            | 1.137             |
| 2.5   | 2.532            | 1.093             |
| 3     | 2.533            | 1.087             |
| 3.5   | 2.533            | 1.087             |
| 4     | 2.532            | 1.087             |
| Pure nano-ribbon | 2.533 |                  |
| Doped nano-ribbon | 1.535 |                  |
4.4. FT-IR spectroscopic

In this section study (FT-IR) spectroscopic to determine functional group for graphene before and after adsorption with gas molecule. FT-IR spectroscopy is important tool to determine chemical adsorption by appear the radical of gas adsorbed on surface of graphene nano-ribbon, it calculated using DFT at basis set 6-31G with hybrid function B3LYP. Pure graphene FT-IR analysis for C-H bond appears at 3213 cm$^{-1}$ in stretching vibration mode$^{[22]}$, C-H a skew-symmetric appears on 3192 cm$^{-1}$ of methylene group$^{[22]}$, methylene group appear at 1351 cm$^{-1}$ region of FT-IR spectrum approximately from 1349 cm$^{-1}$ for study$^{[22]}$. For CH$_4$ adsorbed in pure graphene nano-ribbon, appear new region at wave number (810-828) cm$^{-1}$ and 1458 cm$^{-1}$ resulting from contacted methane molecule on surface of graphene ribbon. For doped nano-ribbon, C-Cu peak appear in very low intensity and wave number was 511 cm$^{-1}$ and this value agreement with previous study in $^{[23]}$. Carbon metal absorption spectra vary between 350-630 cm$^{-1}$$^{[24]}$. CH$_4$ appear many types of peak related to direction of methane gas. Three new peak appear in spectrum are 1820, 3010 and 3115 cm$^{-1}$ respectively related to CH$_4$ adsorption $^{[24]}$. This result proved adsorption of methane gas more acceptable than pure graphene nano-ribbon. Methane can be detecting by this system in all state, in other hand in rest and active state. Also, adsorption process explains that have high effect on carbon metal absorption peaks. Figs. 4 and 5 represent FT-IR spectra for pure and doped nano-ribbon respectively.

![Fig.3. curves of energy gap for adsorption systems.](image-url)
5. Conclusions

Pure and doped nano ribbon have good relaxation structure, bond length and angle between them has agreements with experimental results. Doped in copper transition metal medicated electronic, structural and spectral properties of pure graphene nano-ribbon. Methane gas molecule adsorption in pure graphene nano-ribbon was very weak in two types of adsorption, but in doped system result show have high interactivity compared with pure system and kinds of adsorption mechanism. FT-IR spectroscopic used to determine free radical of adsorption gases, doped nano-ribbon sense methane gas in all phases and this result proves that system has high sensitivity compared with pure graphene nano-ribbon.
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