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Adsorption of formaldehyde on graphene and graphyne

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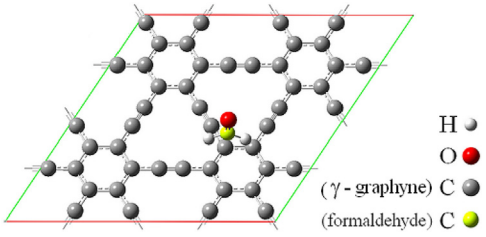
HIGHLIGHTS

- Effect of formaldehyde on electronic properties of graphene and graphyne is studied.
- Formaldehyde is physisorbed on graphene and graphyne.
- Charge is transferred from formaldehyde to graphene and graphyne sheets.
- The n-type semiconductors are obtained via formaldehyde adsorption.
- Graphene and graphyne are proper candidates for formaldehyde detection.

GRAPHICAL ABSTRACT

We have studied adsorption of formaldehyde on graphene and graphyne using density functional theory. The electronic properties of these nanomaterials are sensitive to the presence of formaldehyde.



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ABSTRACT

The adsorption of formaldehyde on graphene and graphyne was investigated to search high sensitivity sensors for detection of formaldehyde. We have used density functional theory to study the effect of formaldehyde on the electronic properties of graphene and graphyne. It is found that formaldehyde is physisorbed on the graphene and graphyne with small binding energy, large binding distance, and small charge transfer. The calculations also indicate that formaldehyde adsorption modifies the electronic properties of semimetallic graphene, α-graphyne, and β-graphyne and semiconducting γ-graphyne. The graphene and graphyne show semiconducting property in the presence of formaldehyde. The effect of formaldehyde on the electronic properties of graphene and graphyne suggests the potential application of these carbon nanomaterials for formaldehyde detection.

1. Introduction

During the last decades, carbon nanostructures such as carbon nanotubes and graphene due to their novel structures and unique properties have attracted tremendous attention and become promising materials for many applications. Recently, the possibility of using these nanomaterials as high sensitivity and selectivity gas sensors has been considered [1–7]. It is found that carbon nanotubes and graphene are highly sensitive to small gases such as NO_2, CO, O_2, NH_3, H_2O, H_2O_2, etc. [1–7]. To promote the performance of gas sensors based on carbon nanomaterials, many modification strategies are developed [8–12]. For instance, carbon nanotubes and graphene have been doped with metals to provide suitable sensors for gas detection [8–12]. It is found that the metal doped carbon nanotubes and graphene are more sensitive than the pure ones for gas detection.

A few years ago, the possibility of using a new allotrope of carbon named graphyne as a highly sensitive gas sensor was demonstrated. As an example, detection of hydrogen peroxide with graphyne based biosensor has been studied [13]. It is shown

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that the electronic properties of graphyne are sensitive to hydrogen peroxide, so graphyne is a proper candidate for hydrogen peroxide detection. Despite the numerous investigations on carbon nanotubes and graphene, study of the graphyne has been less and few works have been presented on the interaction of gases with graphyne.

Formaldehyde (H_2CO) which is known as a common environmental pollutant is highly toxic and volatile. It is reported that formaldehyde gas can cause asthma-like symptoms and induce central nervous system and immunity system damage leading to blindness and respiratory disease [14,15]. Therefore, monitoring and controlling its exposure in both industrial and residential environments are essential. Many efforts have been done to find sensitive methods for formaldehyde detection, including fluorometry, polarography, spectrophotometry, and gas chromatography [16,17]. Meanwhile, theoretical studies were performed to exploit the possibility of using carbon nanostructures such as carbon nanotubes and graphene as gas sensors for detecting formaldehyde [11,12,18–20]. In particular, Chi et al. studied adsorption of formaldehyde on graphene and Al-doped graphene. They found that Al-doped graphene is more sensitive than pure graphene to the presence of formaldehyde [11]. Qin et al. examined the effect of defect–dopant combination upon the strength and stability of formaldehyde adsorption. They showed that graphene with Stone–Wales defect is more sensitive than pure graphene. It is also found that the defect–dopant sheet is more suitable for detection of formaldehyde [12]. The validity of using boron doped single walled carbon nanotube, silicon doped boron nitride nanotube, and BC_2N nanotube to detect formaldehyde has been also studied [18–20]. These results provide new insight to gas sensors for formaldehyde detection. In the present article, we have studied the possibility of using graphyne as sensors for formaldehyde detection using density functional theory (DFT).

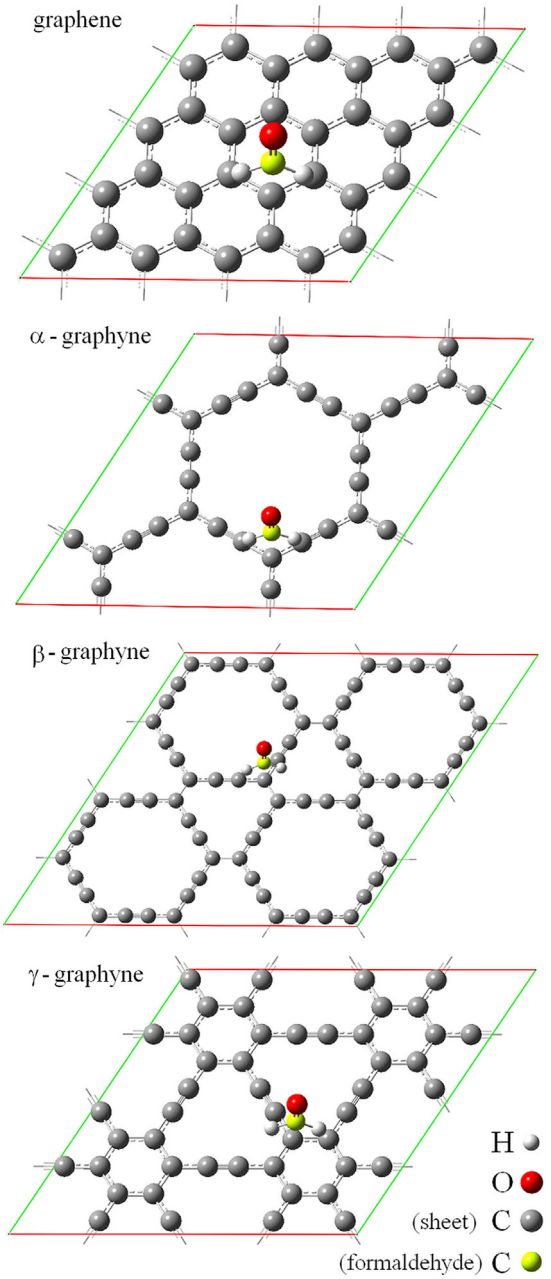

Fig. 1. Adsorption configurations of formaldehyde on graphene, α-graphyne, β-graphyne, and γ-graphyne.

2. Computational details

The simulations are performed by using the OpenMX 3.6 [21] which is based on DFT, within the generalized gradient approximation (GGA) as parameterized by Perdew–Burke–Ernzerhof (PBE) [22]. Compared to local density approximation (LDA), GGA will not lead to a strong bonding of molecules. So, if the calculated molecule is adsorbed on the surface, it will definitely bind in a real system [23–25]. The electronic wave functions are expanded in plane waves with energy cutoff of 100 Ry. The structures are relaxed until residual forces on each atom are smaller than 0.01 eV/Å. The *k*-point is set to 51 points along each high symmetry line in the Brillouin zone. The charge transfer is calculated based on the Mulliken population analysis.

We have considered supercells of graphene with 4×4 unit cells and α-graphyene, β-graphyne, and γ-graphyne with 2×2 unit cells

Table 1
The number of carbon atoms per supercell, dimension of supercell, binding energy, charge transfer from formaldehyde to graphene and graphyne sheets, and energy band gap.

	n_C	$a \times b \times c$ (Å^3)	E_b(eV)	q(e)	E_g(eV)
Graphene	16×2	$9.845 \times 9.845 \times 15.0$	0.29	0.086	0.13
α-graphyne	4×8	$13.9624 \times 13.9624 \times 15.0$	0.36	0.138	0.09
β-graphyne	4×18	$19.0014 \times 19.0014 \times 15.0$	0.45	0.175	0.04
γ-graphyne	4×12	$13.7656 \times 13.7656 \times 15.0$	0.40	0.167	0.39

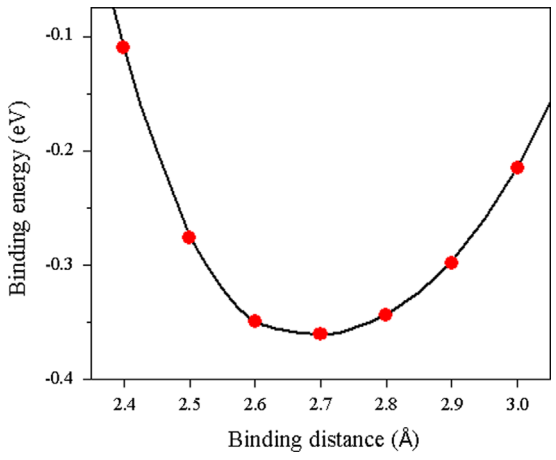

Fig. 2. Binding energy as a function of binding distance for α-graphyne in the presence of formaldehyde.