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# Adsorption of formaldehyde molecule on Stone–Wales defected graphene doped with Cr, Mn, and Co: A theoretical study

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ABSTRACT

Adsorption of $H_2CO$ molecule on Cr, Mn and Co doped Stone–Wales defected graphene were theoretically studied using density functional theory (DFT) method. It was found that $H_2CO$ molecule had no considerable interaction with perfect or SW-defected graphene, but the presence of Stone–Wales defect in graphene enhanced the adsorption of $H_2CO$, which exhibited larger binding energy and smaller bond distance. Chemisorptions were observed on the transition metal (TM) atoms (Cr, Mn and Co) doped structures. Compared with TM-doped perfect graphene, the binding energy of $H_2CO$ molecule on TM-doped defective graphene can be enlarged by the introduction of SW-defect. The density of states (DOS) showed that the contribution of hybridization between O atom of $H_2CO$ molecule and transition metal atom is mainly from the p or d orbitals. Furthermore, adsorption of $H_2CO$ affected the electronic conductance of the Cr and Mn doped defective graphene, which can be seen signal of gas sensor. It is expected that the results could provide useful information for the design of $H_2CO$ sensing devices.



## 1. Introduction

Graphene, a two-dimensional (2D) sheet of carbon atoms, has attracted considerable interest since it was discovered experimentally in 2004 [1–5]. Stankovich et al. have accomplished a valuable technique to prepare graphene sheet as extensive production usage [6]. Recently, graphene has been demonstrated as gas chemical sensors for detecting many molecules. Schedin et al. reported that graphene was highly sensitive to $NO_2$, $NH_3$, CO, and $H_2O$ [7], and it was found that graphene was a low-noise material electronically which made it a promising candidate for chemical detectors and other applications, such as local probes sensitive to the magnetic field, external charge, and mechanical strain. Meanwhile, theoretical investigations using density functional theory (DFT) method are also performed to explore such applications. For example, Dai et al. studied the adsorption of some common types of gas molecule on B-, N-, Al- and S-doped graphene theoretically [8]. Ao et al. found that the Al-doped graphene had relatively high sensitivity to CO molecule [9]. These indicate that the inducing of impurity may affect the sensitivity of graphene significantly. Transition-metal atoms doped carbon-based nanoscale structure has been widely investigated in theory and shown experimentally to form various structures, which can be manipulated to present new phenomena and show the different and interesting magnetic properties [10–13]. Dai et al. studied the oxygen molecule adsorbing on graphene with B, Al, N, Si, P, Cr, Mn doped, and the spin density showed that the adsorption changes the magnetic properties of Mn and Cr doped configurations [14]. However, graphene usually suffers from diversified topological defects during its growth. A great number of experiments and theories have demonstrated that the existence of various defect [15,16], such as vacancies [1], Stone–Wales (SW) defect [17], Octagon-pentagon pair defect [18], inverse Stone–Wales (ISW) defect [19], pentagon-heptagon pair defect [20] in the carbon nanostructures, which produce a significant influence on the mechanical [21] and electronic properties [22,23] and exhibit to be useful to achieve some desired functionalities. SW-defect acts as a typical topological defect consisting of two pairs of five-member and seven-member rings. Roh et al. investigated the adsorption of alkanethiol molecule on the carbon nanotubes and found that the active adsorption sites might be SW defects [24]. Akdim et al. reported the adsorption of ozone on carbon nanotubes with SW-defect and the results suggested that the adsorption on defected CNTs was stronger than perfect one [25]. These investigations imply that the defect is the key to understand and explore the adsorption of gas molecule on the graphene sensors.

$H_2CO$ is known as a common environmental pollutant and has highly toxicity and volatility [26]. So it is very important to control and monitor its exposure in both industrial and residential

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environment. Many methods such as gas chromatography, polarography and fluorometry [27,28] have been used for detecting $H_2CO$ molecules. Recently, using DFT calculations, Xian Qin et al. studied the adsorption of $H_2CO$ on Al-doped SW-defect graphene and found that it was more sensitive than perfect graphene [29]. Siamak et al. studied the $H_2CO$ adsorption on vacancy defected boron nitride nanosheets, and the results show that the existence of vacancy enhances the adsorption energy [30]. In this paper, we present a detailed investigation on the combination effects of SW defects and TM-doped (Cr, Mn and Co), on the sensitivity of graphene system to $H_2CO$ based on DFT. It is respected that the results may afford new insight to gas sensors for graphene applications.

## 2. Calculation methods and model

All the DFT spin-unrestricted calculations have been carried out by using the Dmol$^3$ code. It is widely known that calculations limited at the local density approximation (LDA) tend to overestimate bond energy and underestimate equilibrium distance. In contrast to LDA, the uniform generalized gradient approximation (GGA) tends to improve total energy, atomization energy, and energy barrier. Generally, it yields chemical bonds slightly longer and weaker than LDA, an effect that corrects LDA predictions [31,32]. Accordingly, GGA with Perdew–Burke–Ernzerhof (PBE) function was selected to describe the exchange–correlation interaction, which has been adopted to describe the interaction between molecules and graphene successfully. The DFT semicore pseudopotential (DSSP) core treatment was employed for relativistic effects with double numerical basis set plus polarization functions (DNP). In addition, convergence in energy, force, and displacement were set $2 \times 10^{-5}$ Ha, 0.002 Ha/Å, and 0.005 Å, respectively.

A $5 \times 5$ supercell with a periodic boundary condition along the x–y plane was employed to model the infinite graphene sheet. The vacuum space was set with 25 Å in the $z$ direction, which was enough large to avoid the interactions between periodic images. A $5 \times 5 \times 1$ mesh of $k$-points was used to represent the Brillouin zone for all calculation models. A real-space global orbital cutoff radius 5.0 Å and a smearing point of 0.002 Ha were chosen to ensure high-quality results in all calculations. The binding energies of $H_2CO$ molecule on graphene are calculated using the following equation:

$$E_b = E(\text{total}) - E(\text{sheet}) - E(H_2CO)$$

where $E$ (total), $E$ (sheet), and $E$ ($H_2CO$) are the total energies of relaxed graphene with an absorbed $H_2CO$ molecule, the isolated graphene sheet and the isolated $H_2CO$ molecule.

## 3. Results and discussion

The Stone–Wales defect was formed by rotating the carbon bond dimmer in the hexagonal network by 90°, and the optimized geometry structure of graphene with SW defect (SWG) was shown in Fig. 1a. It was found in this work the rotated C–C bond were more or less compressed and stretched. In particular, the rotated bond was changed from 1.42 Å to 1.34 Å, which accorded with the results of Ma et al. [33]. For examining the main effect of TM atoms (Cr, Mn, and Co) doped on the adsorption process, a substitution of TM atoms for C atom was selected and evaluated in present calculation. Considering the symmetry of SW-defect, five doping sites were examined and labeled in Fig. 1b. The calculated results showed that the Cr, Mn, and Co atoms all preferred to occupy the site of C2. As to various possible adsorption geometries including the C, O and H atoms of $H_2CO$ molecule close to the CNTs, Mei Chi et al. reported that the initial structure with O atom close to the doped system had the most salability after adsorbed [32]. Therefore, the adsorption configurations when the O atom closed to the C1 atom (or TM atoms) were taken into account.

### 3.1. Adsorption of $H_2CO$ on the PG and SWG

We first discussed the adsorption of $H_2CO$ on PG (perfect graphene) and SWG (Stone–Wales defected graphene) without TM atoms doped. The $H_2CO$ molecule was residing perpendicular to the surface of graphene in initial structures as shown in Fig. 1b. The calculated binding energy ($E_b$), the distance between O atom of $H_2CO$ molecule and the closest C atom of graphene (D), and the charge transfer from the graphene to the $H_2CO$ molecule (Q) were listed in Table 1. The $E_b$ of SWG was −0.139 eV which was larger than that of PG. The results indicated that the presence of SW defect increased the sensitivity of graphene for detecting $H_2CO$ molecule, which well agreed with the result reported by Qin and co-workers [29]. The distance (D) of the SWG (3.135 Å) was smaller than that of PG (3.319 Å), but they were too long to form any chemical bonds. As shown in Table 1, the two structures have a small Q values, confirming the weak interaction between the graphene and the $H_2CO$ molecule. From the above, it was obtained that the SWG was more sensitive to the $H_2CO$ gas than PG, but the

**Table 1**
The binding energy ($E_b$), the distance between O atom and the closest C atom (D), and the charge transfer (Q) of $H_2CO$ molecule.

| Configuration | $E_b$ (eV) | D (Å) | Q (e) |
|---|---|---|---|
| PG | −0.091 | 3.319 | −0.024 |
| SWG | −0.139 | 3.135 | −0.047 |

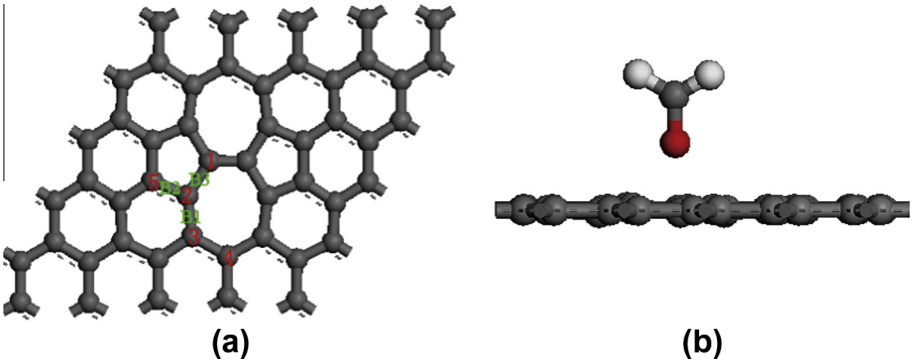


**Fig. 1.** The optimized structures of (a) SW defected graphene and (b) the initial structure of a $H_2CO$ molecule absorbing on the SW-graphene.