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Carbon monoxide adsorption on cooper doped graphene systems: a DFT study

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The adsorptions of CO on graphene and Cooper (Cu-) doped graphene sysyem are investigated using density functional theory calculation. The optimal adsorption position of CO molecule on graphene surface is determined and the adsorption energies are calculated. CO adsorped on the intrinsic grapheme system is weak physisorption. However, Cu-doped graphene system has strong chemisorption on CO molecule by forming a Cu-CO bond. Meanwhile, the partial densities of state (PDOS) show the orbital hybridizations between CO and Cu-doped grapheme. The adsorbption of CO molecule on Cu doped graphene enhances the DOS intensity near Fermi level, which implies the increase of electrical conductivity in Cu doped graphene. Therefore, Cu doped graphene is expected to be a novel chemical sensor for CO gas.

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1. Introduction

Solid-state gas sensors are renowned for their high sensitivity, which in combination with low production costs and miniature sizes have made them ubiquitous and widely used in many applications, such as in environmental monitoring, control of chemical processes and agriculture and medical fileds [1-2]. There has been a constant pursuit of new and better sensing materials in the past. Existing sensor materials include semiconducting metal oxides [3], silicon based systems [4], conducting polymers [5], carbon nanotubs [6].

Recently, graphene has been demonstrated to be a potential material of highly sensitive gas sensors. It was shown that the increase in graphene charge carrier concentration induced by adsorbed gas molecules can be used to detect rareness gas, even with the possibility of detecting individual molecules. Three excellent properties make graphene possible to be sensitive gas sensor: a) graphene is a strictly two-dimensional material and, as such, has its whole volume exposed to surface adsorbates, which maximizes their effect [7]; b), graphene has much smaller band gap and hance has low Johnson noise even in the limit of no charge carriers[8-9], where a few extra electrons can cause notable relative changes in carrier concentration; c) graphene has few crystal defects [8-10], which ensures a low level of excess noise caused by their thermal switching[11].

Graphene as sensors have been demonstrated to detect many toxic gases molecules, such as NH_3 [12], and CO [13], by determining the sensitive conductance changes of graphene before and after the adsorption of these molecules. Among these toxic gases molecules, CO with high toxicity and flavourless is especially dangerous to environment and health. So, a measurable response to CO at room temperature is vital for the design of sensors. It has been demonstrated that the graphene can be used as gas sensors for detecting small concentration of CO and other gases with high sensitivity at room temperature [13-14]. The results indicate that the sensing mechanism is based on the change in electrical conductivity due to gas molecules adsorbed on the graphene's surface and acting as donors or acceptors. Therefore, in this work, we examine the CO molecule adsorption on the intrinsic graphene and Cu doped graphene sysyems base on first-principles density function theory calculations through investigating the stability, the bonding characteristics, transferred charges between CO and Cu doped graphene sysyem, to reveal the adsorption and detection ability of Cu doped graphene to CO molecule.

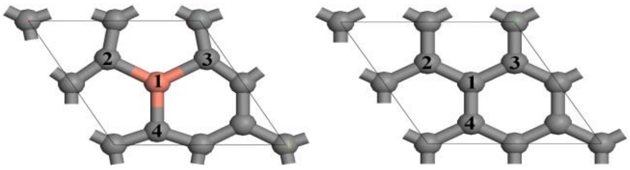
2. Experimental details

All calculations were performed using the density functional theory (DFT) as implemented in the DMol3 code [15-16]. It is well known that the the local density approximation (LDA) overestimates the bond energy Eb and underestimates the equilibrium distances [17]. Thus, the generalized gradient approximation (GGA) was used, which can properly describe the strong Coulomb correction through treating the nonlocality of exchange-correlation [18-20] by using the PBE exchange-correlation function in all of the calculations [21].

Double numerical plus polarization (DNP) atomic orbitals were taken as basic sets [21], and DFT semicore pseudopotentials (DSPP) treatment was implemented to consider the relativistic effects [22], as the relativistic effects play an important role in the chemical and physical properties of molecules containing heavier elements. To ensure that the results of the calculations are comparable, identical conditions are employed for the isolated CO molecule, the Cu doped graphene and the total adsorbed system of CO on Cu doped graphene. The k-point was set to 6×6×2 for all slabs. Full structural optimizations were obtained with symmetry constraints using a convergence tolerance of energy of 2.0×10^{-5} hartree (1 hartree = 27.2114 eV), force of 0.004 hartree $Å^{-1}$ and displacement of 0.005 Å. Three-dimensional periodic boundary condition is taken and C-O bond length is set to $l_{C–O}$ =1.13 Å, which is consistent with the experimental results [23]. For graphene, a single layer 2×2 supercell with a vacuum width of 12 Å above is constructed, which ensures that the interaction between repeated slabs in a direction normal to the surface is small enough. Increasing the vacuum width will greatly increase the computation expense although it has only negligible consequence on the results obtained. For comparison, identical simulation parameters were employed in all simulations.

3. Results and discussion

To evaluate the interaction between CO gas molecule and adsorption graphene surface, the binding energy (E_b) of adsorbed systems, which is defined as $E_b = E_{CO+graphene} - (E_{graphene} + E_{CO})$ where $E_{CO+graphene}$, $E_{graphene}$ and E_{CO} denote the total energy of CO molecule adsorption on intrinsic or Cu-doped graphene system, isolated graphene or Cu-doped graphene and a CO molecule, respectively. A negative E_b corresponds to a stable adsorption structure. Fig. 1 (a) shows the optimized structural model of a 2×2 graphene. When one C atom in the site 1 is substituted by Cu atom, the Cu atom forms three bonds with the nearest C atoms at sites 2, 3, and 4, as shown in Fig. 1 (b), and the doping concentration of Cu in graphene is 12.5 at % with the additional constraint that there is only one Cu atom per graphene hexagonal ring to avoid Cu atoms clustering on grapheme [24]. The bond length between Cu and neighboring C (l_{Cu-C}) is 1.86 Å, which is very similar to the literature data (1.83 Å) [25].



(a) (b)

Fig. 1. Optimized configurations of graphene (a) and Cu-doped graphene (b), where one Cu atom dopes in site 1, and sites 2, 3, and 4 are C atoms near the doped Cu atom, gray and light red spheres are denoted as C and Cu, respectively.

For CO adsorption on the above described graphene, there are two highly symmetric adsorption configurations of CO molecule residing either parallel or perpendicular to the graphene surface. These configurations are similar to the cases of of NO adsorption on carbon nanotube [26]. Corresponding to these two cindiguratuons, there are twelve possible binding sites for CO adsorbed on grapheme. The most stable configuration can be determined by comparing the calculated adsorption parameters. The largest bind energy is $E_b = -0.016$ eV and the shortest distance between CO and the nearest C atom is d=3.768 Å among the twelve possible configutations, both of them correspond to the confifuration shown in Fig. 2 (a), which is therefore confirmed to be the stable configuration. This small bind energy value indicates that there is no chemical bond between CO and the C atom on site 1, i.e., it is in fact a physical adsorption through van der Waals interaction between them.

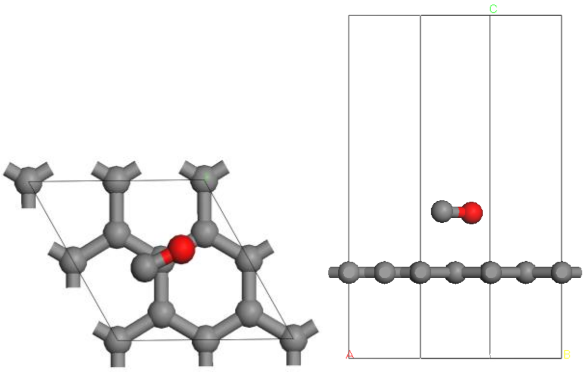


Fig. 2(a). The preferred configurations of a CO molecule adsorption on graphen. Top and below images show the top and side view, respectively.

For the adsorption of CO molecule on the Cu-doped graphene system (Fig. 1 (b)), there are also twelve possible adsorption sites similar to them of CO adsorption on intrinsic graphene. For these twelve possible configurations, their bond energy E_b and the distance between the C atom in CO molecule and Cu atom in the doped graphene (d values) are calculated and listed in Table 1. By comparion these parameters, the most favorable position of CO molecule on Cu-doped graphene is determined to be the configuration of CO⊥graphene ring on Cu doped site with O atom upward, i.e., forming a Cu-C bond, which gives the largest bond energy of $E_b = -7.323$ eV and the shortest bond distance of d=1.856 Å, as shown in Fig. 2 (b). Table 2 is the summary of results for the most stable relaxed structure of CO adsorption on intrinsic graphene and Cu doped graphene. As shown in Table 2, the Cu–C bond length was elongated compare with the C-C bond length. This results in a protruding of Cu atom from graphene sheet and causes slight distortion of the hexagonal structures adjacent to the Cu atom.

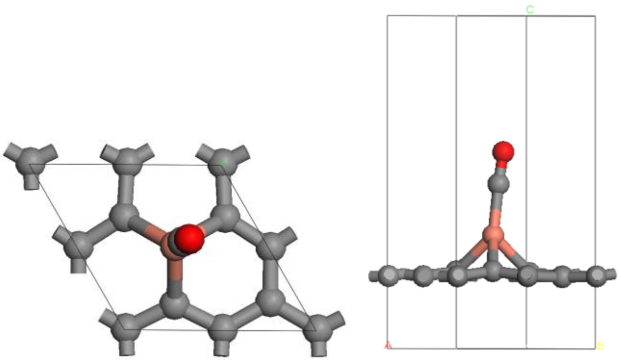


Fig. 2(b). The preferred configurations of a CO molecule adsorption on Cu doped graphene. Top and below images show the top and side view, respectively.

Table 1. The binding energy (E_b) and the distance (d) of CO above the Cu doped graphene surface of a CO molecule adsorping on Cu-dpoed grapheme with twelve possible configurations.

Initial binding configuration		Cu-doped graphene	
		E_b (eV)	d (Å)
CO‖ graphene	T–B–T	-7.150	1.882
	T–H–T	-6.894	1.891
	H–T–H	-6.317	3.442 [a]
	H–B–H	-6.430	3.041 [a]
	B(C atom)–T–H	-6.479	3.076 [a]
	B(O atom)–T–H	-6.226	3.058 [a]
CO⊥graphene	(O atom upward)	-7.323	1.856
	B(O atom upward)	-6.151	1.858
	H(O atom upward)	-7.157	1.871
	T(C atom upward)	-6.475	3.786 [a]
	(C atom upward)	-6.476	3.877 [a]
	H(C atom upward)	-6.477	4.864 [a]

[a] Binding distance between CO gas molecule and graphene layer.
[b] Bond length of Cu and C atom in CO gas molecule.T, B, and H denote top site of C atoms, bridge site of C–C bond, and hollow site of carbon hexagon, respectively.

Table 2. Summary of results for the most stable relaxed structure of CO adsorption on intrinsic graphene and Cu doped graphene.

Configuration	Bond	Bond length l (Å)	Q[a](e)
CO-intrinsic graphene Fig.2(a)	C1–C2 C1–C3 C1–C4	1.426 1.426 1.426	0.001
CO-Cu-doped graphene Fig.2(b)	Cu1–C2 Cu1–C3 Cu1–C4	1.860 1.860 1.878	0.184

[a] Charge transferred from graphene sheet to CO molecule.

To further understand the enhancement effect of the doped Cu on the CO adsorption, the PDOS of the adsorbed CO, the doped Cu, and the graphene in both intrinsic and Cu-doped graphene systems are calculated and shown in Fig. 3. Fig. 3(a) shows the PDOS of CO/graphene system. The main peaks of CO are located at -6.16 and 3.08 eV. However, the main peaks of graphene are located at 9.78, 10.83 and 13.55 eV. There is nearly no interaction between CO molecule and graphene as no hybridization of electrons between them, which interprets why E_b is small. Therefore, intrinsic graphene may not be a good material to adsorb CO molecules, similar to that of H_2CO adsorption on carbon nanotube [15]. While for the CO/Cu-doped-graphene system shown in Fig. 3(b), the main peaks of CO are located at -10.38, 7.52, and 1.71 eV, respectively. The bands of CO interact with both the doped Cu and the grapehene simultaneously at the positions indicated by the dashed lines, showing a strong interaction between CO and the Cu-doped graphene where E_b is the largest. In addition, the doped Cu changes the electronic structures of both CO and the graphene, and their PDOSs shift toward the lower energy range. This suggests that the CO/Cu-doped-graphene configuration is a much more stable system.

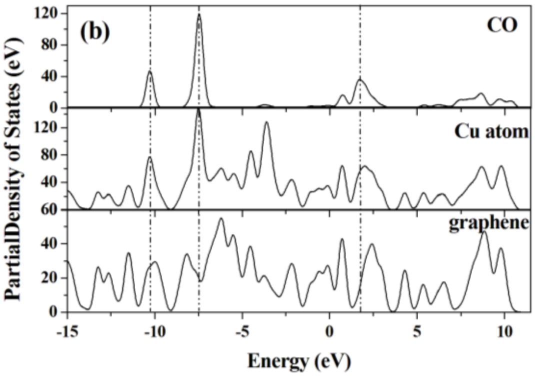


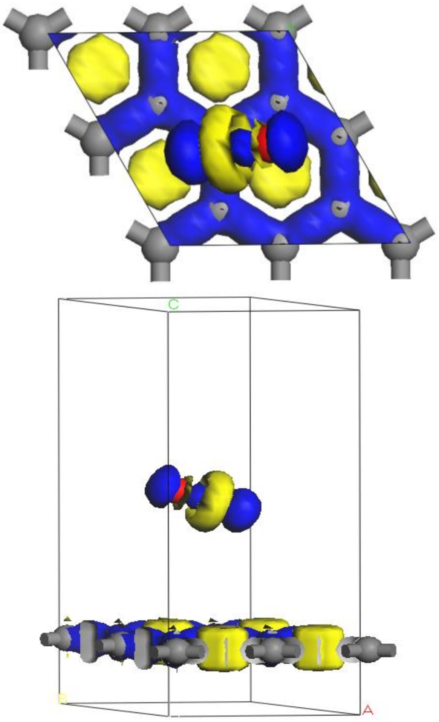
Fig. 3. The PDOS of CO and graphene in a CO molecule adsorped gragene system (a), and the PDOS of CO, Cu atom and grapheme of a CO molecule adsorped on Cu doped grapheme (b). Fermi level is set at 0.

Table 3 summarizes the present calculation results in comparison with the relative literature results [7, 13, 27, 28]. It can be seen that only weak physisorption of CO adsorbing on either graphene or SWCNT, with an adsorption energy much smaller than unit. When doped with metallic atom (Al, Cu or Pd), the adsorption of CO on either graphene or SWCNT becomes a chemisorption with adsorption energy larger than unit. So doping metallic atom is a useful way to improve the adsortion property of nano carbon material to CO. Among the adsortion systems shown in Table 3, the Cu-doped graphene is energetically favorable for CO adsorption with the maximum adsortion energy and the shortest bond length between C in CO and Cu atoms. So, Cu-doped graphene system is an advantageous system for stable CO adsorption among the listed undoped and metal atom doped nano carbon material systems.

Table 3. Comparison of calculated binding energy (E_b), net electron transfer (Q) and the distance (d) of CO above the adsorption system among different nano carbon matetials.

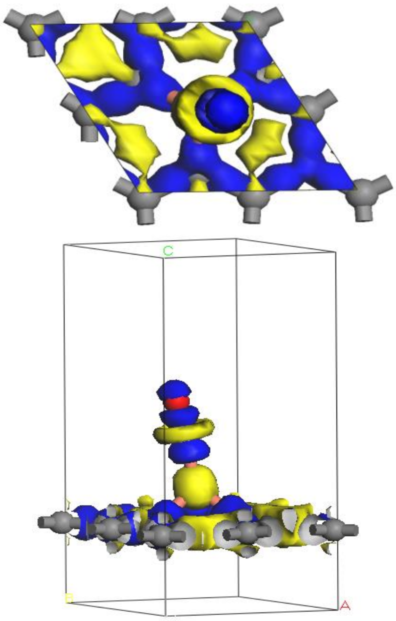
Configuration	E_b (eV)	Q^a (e)	d (Å)
CO-Cu-doped graphene (this work)	−7.323	0.184	1.860^b
CO-Al-doped graphene[13]	−4.979	0.027	1.961^b
CO-Al-doped SWCNT[27]	−1.280	0.004	2.010^c
CO-Pd-doped SWCNT[28]	−1.780	0.175	1.907^b
CO- SWCNT[26]	-0.257	0.018	2.837
CO- graphene[7]	0.014	0.013	3.740

To investigate the changes of electronic structures in graphene caused by the adsorption of CO molecule, electron density difference $\Delta\rho$ is calculated, $\Delta\rho$ is defined as $\Delta\rho=\rho_{\text{CO+graphene}}-\rho_{\text{graphene}}-\rho_{\text{CO}}$ in which $\rho_{\text{CO+graphene}}$, ρ_{graphene} and ρ_{CO} denote electron density of the intrinsic or Cu-doped graphene with CO adsorption, isolated graphene or Cu-doped graphene and a CO molecule, respectively. So, $\Delta\rho$ represents the variation of charge density during this adsorption process. The electronic density differences of energy favorable intrinsic and Cu-doped graphene with CO adsorptions are shown in Fig. 4, where the blue and yellow regions represent the areas of electron accumulation and the area of electron loss, respectively. Fig.4 (a) indicates that the bonds both in the intrinsic graphene and CO are of covalent nature because the preferential electron accumulation sites are mainly located within the bond rather than heavily centered on a particular atom. Physisorption of CO on the intrinsic graphene does not alter the electron distribution of both CO molecule and graphene, implying the weak bonding characteristics. It is discernable that electronic polarization is induced by the preferential accumulation of electrons on O in CO molecules. While the chemisorption of CO on Cu doped graphene can be seen from Fig. 4 (b). In this case, the adsorption of CO on Cu doped graphene leads to significant electron transfer from Cu doped graphene to CO molecule, where Cu atom loses electrons while O and C atom of CO molecule gain electrons. Furthermore, to investigate the changes of electronic structures in graphenes caused by the physi- or chemisorption of CO molecule, the net electron transfer (Q) from either the intrinsic or the Cu doped graphene to the polar CO molecules was calculated based on Mulliken analysis [23]. As listed in Table 2 and Table 3, the Q value of 0.184e indicates that CO molecule share a small part of electron with Cu-doped graphene system, to form stable chemsorption, while the very small Q value of 0.001e for CO molecule adsorption on graphene implies that there is nerely no electron transfer from grapheme to CO molecule.



(a)

Fig. 4(a). The electronic density difference isosurfaces for the CO–graphene system with preferred configuration. The blue region shows the electron accumulation, while the yellow region shows the electron loss.



(b)

Fig. 4(b). The electronic density difference isosurfaces for the CO–Cu doped graphene system with preferred configuration. The blue region shows the electron accumulation, while the yellow region shows the electron loss.

To better understand the electronic properties of these intrinsic and Cu-doped graphene systems, we also calculated the electronic densities of states (DOS) for the intrinsic and Cu-doped graphene and the DOSs of these two systems with CO adsorbing on. As shown in Fig. 5 (a), grapheme is in fact a semiconductor with a small band gap near its Fermi level. The DOSs of graphene and CO adsorped graphene (Fig. 5 (a) and (c)) present nearly no difference, i.e., the physisorption of CO on graphene does not alter the electron distribution for both CO molecule and graphene. However, it is seen from Fig. 5(b) that Cu doping makes the band gap near Fermi level almost disappears and a possible charge transfer from Cu to graphene according to the Mulliken charge population analysis, which suggests that Cu-doped graphene becomes to a weak conductor. While for the Cu-doped graphene after the adsorption of a CO molecule, as shown in Fig. 5(d), the band gaps near Fermi level completely disappear and the DOS intensity in this region is enhanced, which indicates that the Cu-doped graphene with adsorption of a CO molecule has become a conductor. When the graphene interacts with a CO molecule, a large charge transfer occurs not only from Cu to graphene, but also from Cu-doped graphene system to CO molecule, which dramatically changes the conductance of the graphene and makes the Cu-doped graphene becomes an evident conductor. Thus, the chemisorbed CO on the Cu doped graphene will give rise to an increase in the electrical conductivity of the doped graphene layer. By detecting the current or resistance change of the Cu doped graphene systems before and after the adsorption of CO, the presence of CO molecule can be detected sensitively. Therefore, Cu doped graphene should be a promising sensor material for both adsorbing and detecting CO molecules.

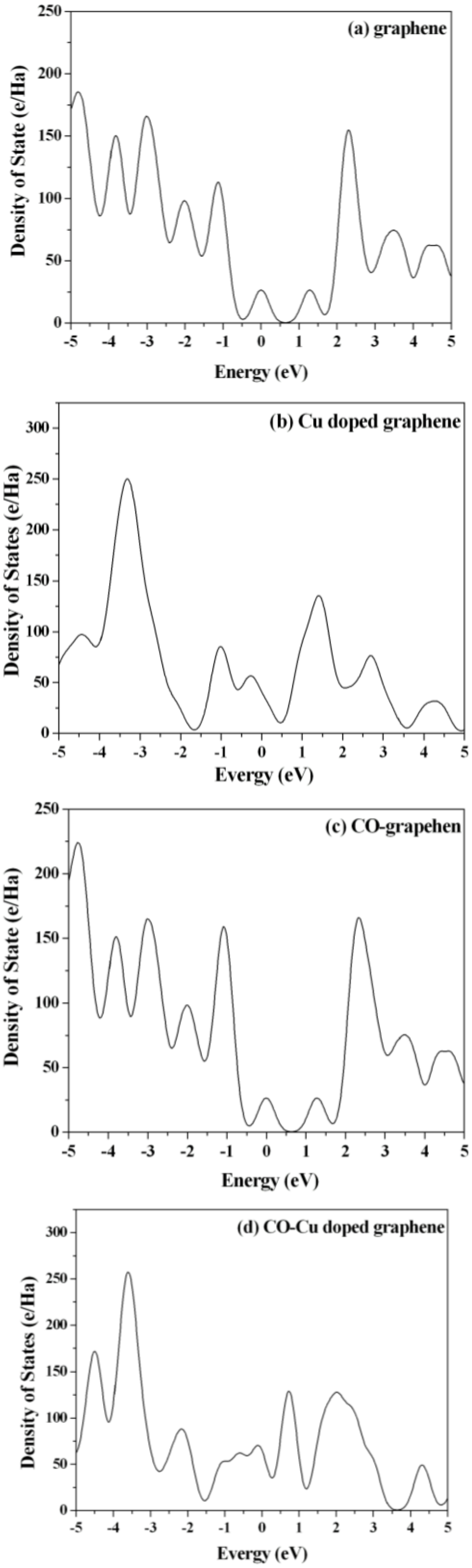


Fig. 5. Calculated electronic density of states (DOSs) for the intrinsic raphene (a), Cu doped graphene (b), CO–graphene system with preferred configuration (c), and CO–Cu doped graphene system with preferred configuration (d).

4. Conclusions

With DFT calculations, the adsorption of CO on Cu-doped graphene has been investigated. Detailed analysis of the structural and electronic properties of optimized configurations has been performed. The most favorable configurations of CO molecule on Cu-doped graphene with large binding energies is CO⊥graphene ring on Cu doped site with O atom upward. Our results reveal that CO molecule has strong interaction with Cu-doped graphene, forming a Cu-C bond that introduces a large charge transfer after adsorption and shallow acceptor state has been introduced in the system. As a result, the electronic conductance is increased. Therefore, Cu-doped graphene would be more suitable for the adsorbtion and detection of CO molecules.

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