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Chemisorption of NO on Pt-decorated graphene as modified nanostructure media: A first principles study

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ABSTRACT

We used density functional theory calculations (DFT) to search the potential of pristine as well as Pt-decorated graphene sheets as adsorbent/gas sensors for NO by considering the electronic properties of NO on these two surfaces. We found much higher adsorption energy, higher charge transfer, lower connecting distance, and higher orbital hybridizing of NO gas molecule on Pt-decorated graphene than pristine graphene. We used orbital analysis including density of states as well as frontier molecular orbital study for NO-surface systems because of more understanding of the kind of interaction. Our results reveal physisorption of NO on pristine graphene with adsorption energy of −24 kJ mol^{-1} while in contrast much higher adsorption energy of −199 kJ mol^{-1} is achieved upon adsorption of NO on Pt-decorated graphene which is in the range of chemisorption.

1. Introduction

Graphene as a two-dimensional sp^2 connected carbon sheet is an advanced material that has exceptional properties such as high surface-to-volume fraction, little electrical noise, and outstanding transport properties related with its 2D structure [1]. Because of its excellent structural and electronic properties, graphene develops into an interesting candidate for numerous potential uses, such as composites [2] and gas sensors [3,4]. The electronic devices based on graphene, advantage from its outstanding high charge transferring and high stability. Moreover recent researchers have recognized that diverse nanostructures could be carved from graphene surface to construct single electron transistor circuitries [5], which in fact is starting for new manufacture techniques of nanoelectronics. In parallel to carbon nanotubes [6,7], there are lots of experimental and theoretical studies focusing on graphene toward sensing materials [8–10]. Sensors based on graphene can detect the conductivity change upon adsorption of molecules. The change in the conductivity can relate to the alteration in the amount of charge transfer in the graphene affected by adsorbed gas molecules. It has been expected that such devices could detect individual gas molecule [6]. Some topical researches on graphene as gas sensor were reviewed by Mao et al. [11]. They talked about the challenges and opportunities of using these materials toward gas sensor. Graphene is especially subjected to doping and chemical modification but also highly subjected to defects and impurities on its structure. Based on the results of some researches, the most thriving process for increasing the adsorption aptitude of graphene can be achieved by chemical modification using atom doping [12–16]. In our previous reports, we used N-doped graphene and searched its interaction with some boron [17], and SOx compounds [18]. We found this defected graphene could able to increase the adsorption properties of these compounds. In another research work [19] we used Al-doped graphene as an advanced adsorbent for acetyl halide molecules whereas there is low adsorption in the case of pristine graphene. Moreover the application of Al-doped graphene as a gas sensor for some ether molecules was investigated by our team [20] and large sensor ability was found for this modified surface. An adsorbent for NO_2 and N_2O gas molecules was another application of Al-doped graphene [21]. Also we used Al-doped graphene as adsorbent for CO, CO_2 and H_2O molecules [22] and some halomethane molecules [23].

Baby et al. [24] made-up an amperometric glucose biosensor by decoration of Pt and Au nanoparticles on graphene nanosheet. Based on their research, decorated nanoparticles could able to immobilize glucose oxidase by physical adsorption resulting an enhancement in the performance of biosensor.

Giovanni et al. [25] organized some Nobel metal decorated graphene and studied the catalytic potential of hybrid materials. They found that the metal, considerably affects the electrochemical sensing and biosensing performance of resulted sensor. Gutes

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et al. [26] proposed a straightforward and flexible technique for decoration of metal nanoparticles on graphene sheet and then the gas sensing transducer was presented as proof of concept. Subrahmanyam et al. [27] studied on experimental decoration of Ag, Au, Pt and Pd nanoparticles on graphene and found that there is a major charge-transfer interaction between graphene and these metal nanoparticles. They used first-principles calculations to put emphasis on the importance of charge-transfer between the metal nanoparticles and graphene. Lopez et al. had studied the interaction between hydrogen molecules and palladium-doped graphene by using DFT [28]. In their study hydrogen molecules physisorbed weakly on the surface of pure carbon nanostructure while high adsorption in the range of chemisorption is achieved in the case of Pd-decorated graphene. At another research Liu et al. [29] used DFT method for study the adsorption property of hydrogen molecules on titanium decorated graphene. They found that the binding energies of molecular hydrogen could be significantly enhanced by using Ti-decorated graphene.

Since it is proven that chemical simulations give significant information on the concept of different adsorbent–adsorbate systems [30–35] in this research we focused on the first-principles simulation of adsorption of NO gas molecules on the surfaces of pristine as well as Pt-decorated graphene. The gas molecule NO is all of massive practical benefit for industrial as well as environmental applications. It is very poison gas and so there is much need to measure its concentration at ambient situations. To the best of our knowledge there is no study on the adsorption properties of NO on the surface of Pt-decorated graphene. The motivation of this research is to achieve basic insights to the effect of adsorbed NO on the electronic properties of two mentioned graphene sheets.

2. Computational method

To optimization and calculation of adsorption energy of NO on pristine graphene, we utilized 6-31G(d,p) basis set by applying BLYP density functional including a version of Grimme's D3 dispersion model [36]. In contrast fully geometry optimization of Pt-decorated graphene sheets in the present and absence of NO molecule were performed using B3LYP density functional with split basis set (for all atom except Pt the basis set was 6-31G (d,p), for Pt atom the basis set was lanl2dz) as implemented in Gaussian 09 suite of program [37]. It should be noted that our initial optimization for adsorption of NO molecule on Pt-decorated graphene has been done using 3-21G(d)/lanl2dz basis set (for all possible configurations) to recognize the most stable configurations. Moreover these relaxed structures were subjected to optimization at stronger basis set. The 6-31G(d,p) basis set is good for general calculations on medium to huge molecules, moreover the B3LYP density functional has been known suitable for nanostructure studies [17–20].

Calculations of charge analysis, density of states (DOS), the energy of lowest unoccupied molecular orbital (LUMO), the energy of highest occupied molecular orbital (HOMO), and the HOMO–LUMO energy gap (E_g) have been done using above-mentioned basis set. The charge transferring between NO molecule and the surface of pristine as well as Pt-decorated graphene was calculated from the difference in its charge concentration before and after adsorption. These calculations have been done by natural bond orbital (NBO) analysis.

The adsorption energies E_{ads} between the analyte and pristine graphene (PG) as well as Pt-decorated graphene (PtG) are defined as Eqs. (1) and (2) respectively:

$$E_{ads}(\mathrm{PG}) = E_{\mathrm{PG-NO}} - (E_{\mathrm{PG}} + E_{\mathrm{NO}}) \quad (1)$$

$$E_{ads}(\mathrm{PtG}) = E_{\mathrm{PtG-NO}} - (E_{\mathrm{PtG}} + E_{\mathrm{NO}}) \quad (2)$$

where the $E_{\mathrm{PG\text{-}NO}}$ and $E_{\mathrm{PtG\text{-}NO}}$ correspond to the adsorbed systems of pristine graphene and Pt-decorated graphene, E_{PG} and E_{PtG} correspond to the isolated pristine graphene and Pt-decorated graphene and then E_{NO} corresponds to the isolated analyte (NO), respectively. Because of poor adsorption on pristine graphene we did not calculate the counterpoise corrected energy in the case of pristine graphene but for Pt-decorated graphene this energy for different analyte was calculated based on Eq. (3).

$$E_{\mathrm{PtG,CP}} = E_{ads}(\mathrm{PtG}) - E_{\mathrm{BSSE}} \quad (3)$$

which $E_{\mathrm{PtG,\ CP}}$ is counterpoise corrected adsorption energy of related complexes and E_{BSSE} is basis set superposition errors energy. We should consider that all energies of the equations relate to equivalently relaxed minimum energy structures.

3. Result and discussions

We used a supercell of 4 × 4 graphene (12.30 Å × 12.30 Å × 16 Å) including 50 carbon atoms (see Fig. 1, left). The *z*-axis (16 Å) of this supercell is big sufficient so that there is no interaction between graphene sheets of nearby supercells.

For decoration of Pt on graphene sheet, there are 3 adsorption sites: the bridge site at the middle of a C–C bond, the top site straight above a C atom and the hollow site at the center of a hexagon (see Fig. 1). It has been reported by Ganji et al. [38] that the adsorption of Pt atom on the bridge site (middle of a C–C bond) has the most stability than the two other positions, our study confirms this claim, so we considered this position as the most favorable location of Pt on graphene and afterward let the system to be relax at aforementioned basis set.

We portrayed density of states (DOS) as well as HOMO–LUMO distributions for pristine and Pt-decorated graphene sheets in order to observe the changing in the electronic structure of graphene caused by decoration of Pt. As shown in Fig. 2, the HOMO of PG is largely localized on the C–C bonds and its LUMO on the conflicting site. After Pt decoration on graphene, both HOMO and LUMO largely shift on Pt atom which corresponds to the reducing in the gap of energy (E_g) for about 0.507 eV (see the DOSs in Fig. 2). One can concluded that this reduce in the E_g causes to the more reactivity of Pt-decorated graphene than pristine graphene. Additionally the charge distribution of relaxed graphene before and after Pt decoration was calculated by natural bond orbital (NBO) analysis. By comparing the charge distribution of isolated pristine and Pt-decorated graphene sheets, which listed in Table 1, one can concludes that the C-atoms neighboring Pt atom catches electrons because of their high electron attraction and result a reduce in the electron density (+0.132 e^-) around Pt atom so cause to increase in the reactivity of Pt-decorated graphene toward gas adsorption.

One can images diverse position configurations for adsorption of NO on pristine graphene. Based on our preliminary research on different configurations, the value of physisorption energy for different configurations was not high in the case of pristine graphene. Relaxation in all positions reveals weak adsorption (in the range of physisorption) of NO on pristine graphene.

As input file we made the most stable configuration of pristine graphene–NO complex reported by Zhang et al. [39] and allowed it to be relax at 6-31G(d,p) basis set including BLYP-D3 function. Fig. 3 shows some parts of side and top views of relaxed structure of pristine graphene–NO system. This relaxed structure associates the adsorption energy of −24.1 kJ mol^{-1} and molecule–surface distance of 2.53 Å. This result is in accordance to the earlier report about adsorption of NO on carbon nanotube [40] and also on graphene [39] with the energy of −0.3 eV (or −28.9 kJ mol^{-1}) and the distance of 2.43 Å.