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DFT Study of Nitrous Oxide Adsorption on the Surface of Pt-Decorated Graphene

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In the present study we search potential of Pt-decorated graphene (PtG) as a new nanostructure adsorbent for nitrous oxide (N_2O) using density functional theory (DFT). After fully relaxation of different possible orientations of N_2O -PtG complex, we distinguished two optimized configurations for this system; 1- terminal N-side of gas is oriented towards Pt so that the molecule axis is perpendicular to the surface (P1), and 2- O-side of the molecule is closing to Pt while the axis of molecule has an angular configuration to the surface (P2). Our results showed high adsorption of N_2O on PtG, however there is a significant difference between the value of adsorption for P1 compared to that for P2 (-113.6 (-88.7 BSSE) vs. -41.2 (-32.0 BSSE) kJ mol^{-1}). Results of the charge analyses revealed interesting net charge transfer; the direction of charge is from N_2O to PtG for P1 configuration and the reverse is found for P2.

Keywords: Nitrous oxide, Pt-decorated graphene, Nanostructure adsorbent, DFT, HOMO

INTRODUCTION

Nitrous oxide (N_2O) turns into nitric oxide (NO) within reaction with oxygen atoms, and produces NO which reacts with O_3 , so it is a major naturally occurring controller of stratospheric O_3 . Moreover, N_2O is known as one of the most important greenhouse and pollutant gases. Over a 100-year period, its impact calculated is 265-310 times more than that for CO_2 (per unit mass) [1]. So, identifying the concentration of N_2O is an important task from different viewpoints, such as designing sensitive sensors.

Owing to wonderful electronic structure of graphene, it has been widely used as gas sensor for different analytes [2, 3]. Some research works on graphene as gas sensor have been listed and compared by Mao *et al.* [4]. They discussed the potential of graphene as a gas sensor in various applications.

It is well-known that the adsorbent capability of graphene could be enhanced predominantly by modification of its surface using doped or decorated atoms [5-8]. In our recent study, we documented the potential of N-doped

graphene in interaction with boron [9], SO_x [10] and CO [11].

Based on our previously results, N-doped graphene could increase the adsorption ability of graphene. Moreover, our group reported diverse uses of Al and B-doped graphene sheets [12-19]. The increase in the value of adsorption of different analytes on graphene sheets upon doping of surface by Al or B atom has been well discussed in the literature.

A new way to enhance the adsorption ability of graphene is metal decoration. Upon decoration, single atom situates on high surface area of carbons. It leads to addition of new re-bonding per metal atom with releasing significant energy, resulting in more stability of single atom decorated structure with bulk atoms decorated structure [20]. There are different experimental methods for single atom decoration on graphene. As an example, Wang *et al.* [21] pointed out that a two-step process is a well-ordered method to stabilize single atoms on graphene. Different metals such as Pt, Co and In, have been effectively decorated on graphene in the single-atom form.

Recently, our group investigated the adsorption of NO molecule on the surface of PtG [22]. We found very high

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NO adsorption on this modified surface while there is a weak adsorption on pristine graphene. In parallel, we used PtG as an ideal adsorbent for C₂H₂ and C₂H₄ molecules [23], MeOH and EtOH [24], SO₂ and O₃ [25] and NH₃ and CH₄ [26].

The adsorption of N₂O on the surface of pristine and Al-doped graphene has been recently investigated by our group [14]. We found that N₂O adsorption on pristine graphene is associated with releasing low value of energy (physisorption), while Al-doped graphene showed much higher value of energy. Despite the high adsorption of N₂O on Al-doped graphene, looking for some other adsorbents with higher potential of N₂O adsorption is of great topic. In the present study, we have selected PtG sheet for further investigation, since we are sure about the potential of PtG as an adsorbent for other analytes. Moreover, to the best of our knowledge, there is no reported study on the adsorption properties of N₂O on this mentioned surface. Here, we aim to establish the potential of PtG as a new adsorbent for N₂O molecule by using density functional theory (DFT).

COMPUTATIONAL METHOD

B3LYP density functional was used for relaxation of free PtG and PtG-N₂O sheets with split basis sets (for all atoms, 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 [27].

The 6-31G(d,p) basis set is good for general calculations, besides the B3LYP density functional has been known appropriate for nano-structure studies [22-26]. Charge analyses, density of states (DOS), energy of the lowest unoccupied molecular orbital (LUMO), energy of the highest occupied molecular orbital (HOMO), and the HOMO-LUMO energy gap (E_g) have been entirely calculated using above-mentioned basis set.

The value of adsorption energy (E_{ads}) upon adsorption of N₂O on PtG was calculated using Eq. (1):

$$E_{\text{ads}}(\text{PtG}) = E_{\text{PtG-N}_2\text{O}} - (E_{\text{PtG}} + E_{\text{N}_2\text{O}}) \quad (1)$$

where E_{PtG-N₂O} corresponds to the adsorbed system of PtG, E_{PtG} corresponds to the isolated PtG and E_{N₂O} corresponds to the isolated N₂O, respectively. For all adsorption systems,

these calculated adsorption energies were modified based on the Eq. (2).

$$E_{\text{ads, CP}} = E_{\text{ads}} - E_{\text{BSSE}} \quad (2)$$

where E_{ads, CP} is counterpoise corrected adsorption energy of the related complexes and E_{BSSE} is the energy corresponding to the basis set superposition error.

RESULT AND DISCUSSIONS

A supercell of 4 × 4 graphene (12.30 × 12.30 × 16 Å) including one Pt atom was used as the surface of interaction (see Fig. 1). There is no interaction between graphene sheets of neighboring supercells because the z-axis (16 Å) of this supercell is big enough.

There are three potential sites for Pt decoration (see Fig. 1): top site (straightly above a C atom), bridge site (the middle of a C-C bond), and hollow site (at the center of a hexagon). We documented in our recent publications [22-26] that bridge site of graphene is the most energetically favorable position for decoration of Pt, so we placed the Pt atom on this site and let this initial configuration be optimized at the above-mentioned basis set/functional to create relaxed PtG sheet.

It should be mentioned that adsorption properties of N₂O on the surface of pristine graphene as well as corresponding optimized structure have been studied and well discussed [14]. Accordingly, we reported very weak adsorption of N₂O on pristine graphene (-0.11 kJ mol⁻¹). So, in the present work, we just focused on N₂O adsorption on the surface of PtG.

We examined all possible initial configurations to find the most stable configurations of N₂O on PtG. N₂O was situated on top of Pt in different ways: firstly, the middle N-N-O axis has a parallel configuration with respect to the surface. Secondly, each terminal side of molecule (N or O) was placed on top of Pt, individually, so that the N-N-O axis has vertical configuration with respect to the surface. Among three initial configurations, the optimized structures were found in two forms; P1 which is shown in Fig. 2 top and P2 which is shown in Fig. 2 down.

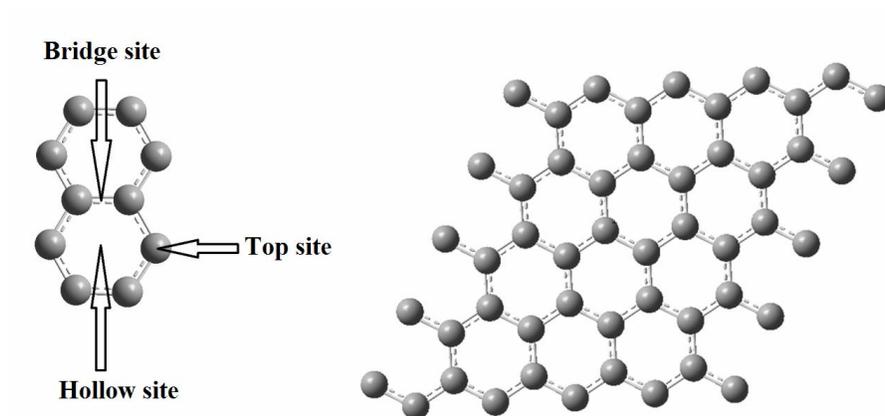


Fig. 1. A supercell of graphene (right) and three possible adsorption sites for decoration of Pt (left).

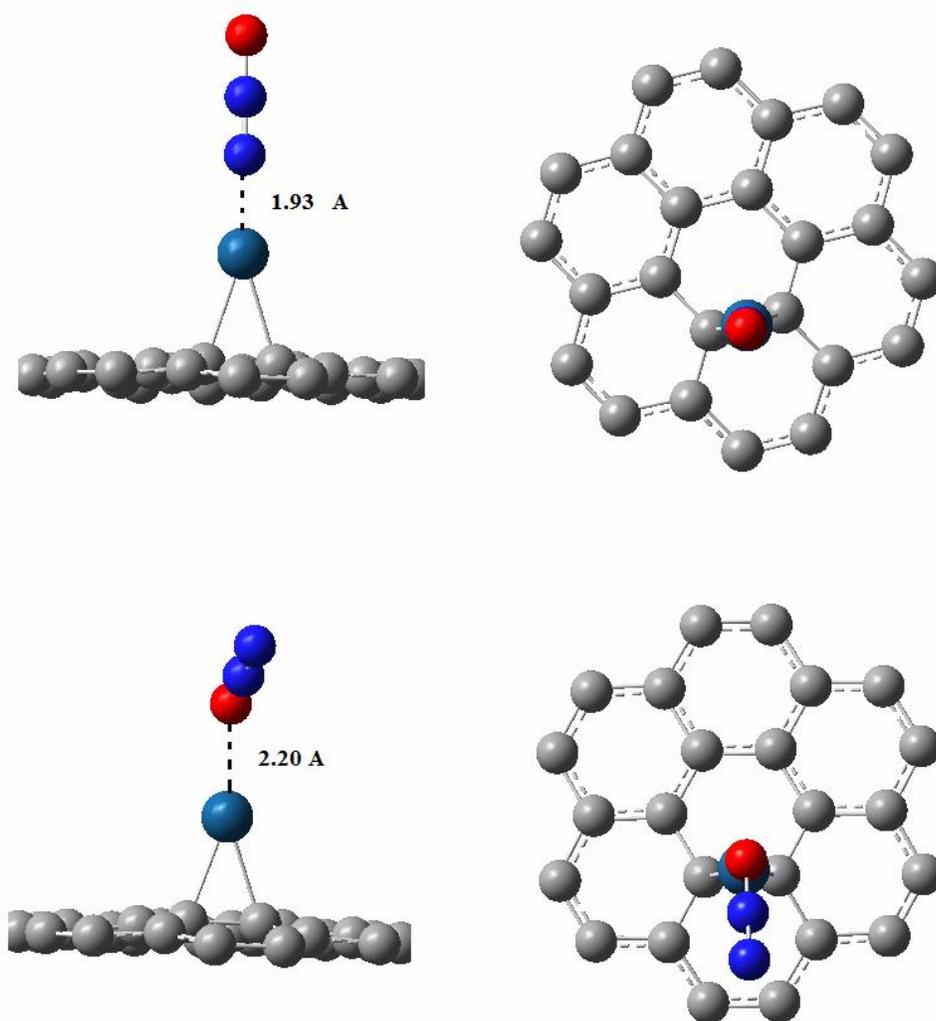


Fig. 2. Side view (left) and top view (right) of some parts of the relaxed structure of adsorbed N_2O in P1 and P2 positions.

Table 1. Adsorption Energy (E_{ads}) and Orbital Characteristic: E_{HOMO} , E_{LUMO} , Energy of Fermi Level (E_{FL}), HOMO-LUMO Energy Gap (E_{g}), and the Equilibrium Distance (d_{e}) for all Systems

System	E_{HOMO} (ev)	E_{FL} (ev)	E_{LUMO} (ev)	E_{g} (ev)	Q_{NBO} (e) of adsorbate	Q_{NBO} (e) of Pt	d_{e} (\AA)	E_{ads} (kJ mol^{-1})
N_2O	-9.31	-4.91	-0.52	8.79	-	-	-	-
Isolated PtG	-5.00	-3.79	-2.58	2.42	-	+0.132	-	-
PtG- N_2O (1)	-5.22	-3.47	-1.73	3.49	-0.173	+0.078	1.93	-113.6 (-88.7) ¹
PtG- N_2O (2)	-4.90	-3.34	-1.79	3.11	+0.091	-0.046	2.20	-41.2 (-32.0) ¹

Adsorption of N_2O on PtG corresponds to releasing energies of -113.6 (-88.7 BSSE) and -41.2 (-32.0 BSSE) kJ mol^{-1} for P1 and P2, respectively. The adsorption value of N_2O on PtG in both configurations are much higher compared to that reported for pristine graphene (-1.1 kJ mol^{-1}) [15]. Interestingly, these values are also much higher compared to those of on Al-doped graphene (-22.7 (BSSE) kJ mol^{-1}) reported in our previous study [14]. So, we can conclude that the adsorption property of graphene could be significantly improved by Pt decoration rather than Al doping.

The nearest distances of adsorbent-adsorbate are found to be 1.93 and 2.20 \AA for P1 and P2 configurations, respectively, which are completely shorter compared to those on pristine graphene (4.04 \AA) [14]. Moreover, the distance in P1 configuration is noticeably shorter compared to what was reported by using Al-doped graphene (2.18 \AA) [14]. Interestingly, differences in the adsorbent-adsorbate distances are in accordance to their differences in the value of adsorption energy.

We can conclude that the interaction of N_2O (in P1 and P2) corresponds to the chemisorption region. These extensive higher values of N_2O adsorption on PtG than those on PG are a result of high interaction between Pt...N and Pt...O upon interaction of N_2O in positions 1 and 2, respectively.

We have investigated the net charge transfer of systems using natural bond orbital (NBO). The data are listed in Table 1. The net charge transfer for N_2O adsorption for P1

is calculated to be -0.173 e while reverse is found for P2 (+0.091). This matter points out to the ability of PtG as a n-type or p-type semiconductor at the same time which can be confirmed by considering the change in the local charge of Pt from +0.132 e at its isolated mode to +0.078 e and -0.046 e upon adsorption of N_2O at P1 and P2 configurations, respectively.

These results emphasize that the adsorption of N_2O significantly changes the electronic structure of PtG, and suggest the potential of PtG as a good sensor for this analyte.

Figure 3 shows the HOMO-LUMO outlooks for pristine and PtG along with PtG- N_2O complexes at P1 and P2 configurations. As seen in Fig. 3, the HOMO of PG is mostly restricted on the C-C bonds whereas the LUMO is situated on the conflicting site. After Pt is decorated on graphene, both HOMO and LUMO relocate on Pt atom which results in more reactivity of PtG compared to PG. Additionally, the result of NBO analyses showed that the carbon neighbors of Pt have negative charges owing to their high electron affinity and result in a reduce (+0.132 e) in the electron density of Pt (based on NBO charge analysis).

The HOMO and LUMO of adsorbed systems for complexed PtG are shown in Fig. 3 and the data are listed in Table 1. Comparing the HOMO-LUMO distributions in free PtG with those of adsorbed N_2O (P1 and P2) indicates that the distribution of both HOMO and LUMO is affected by adsorbate, however the greatest impact is concentrated on the case of P1 compared to P2, as expected by their

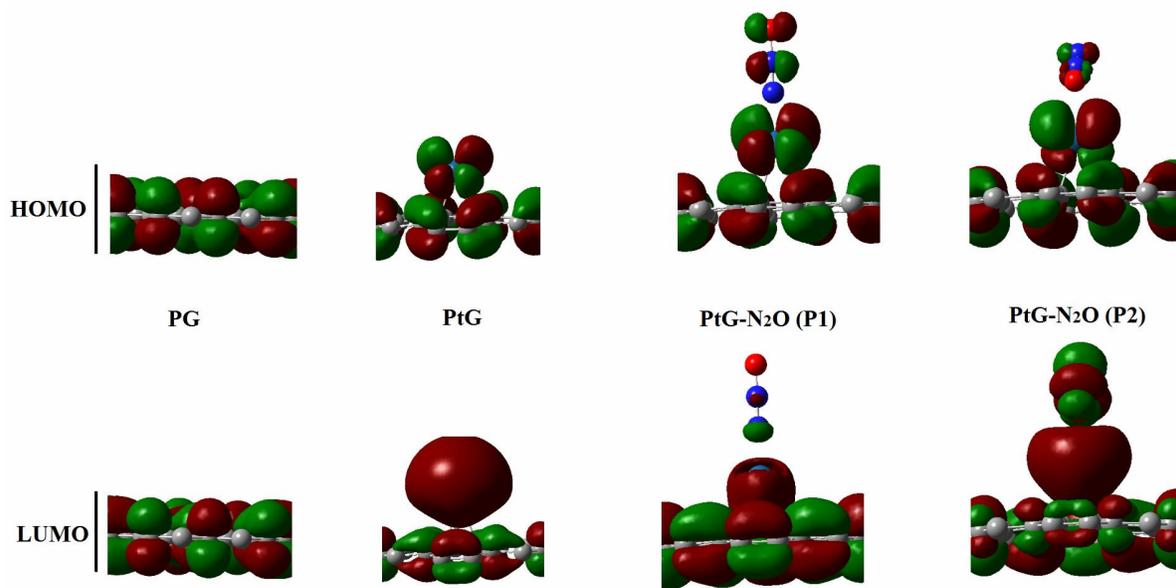


Fig. 3. HOMO and LUMO distributions of different systems.

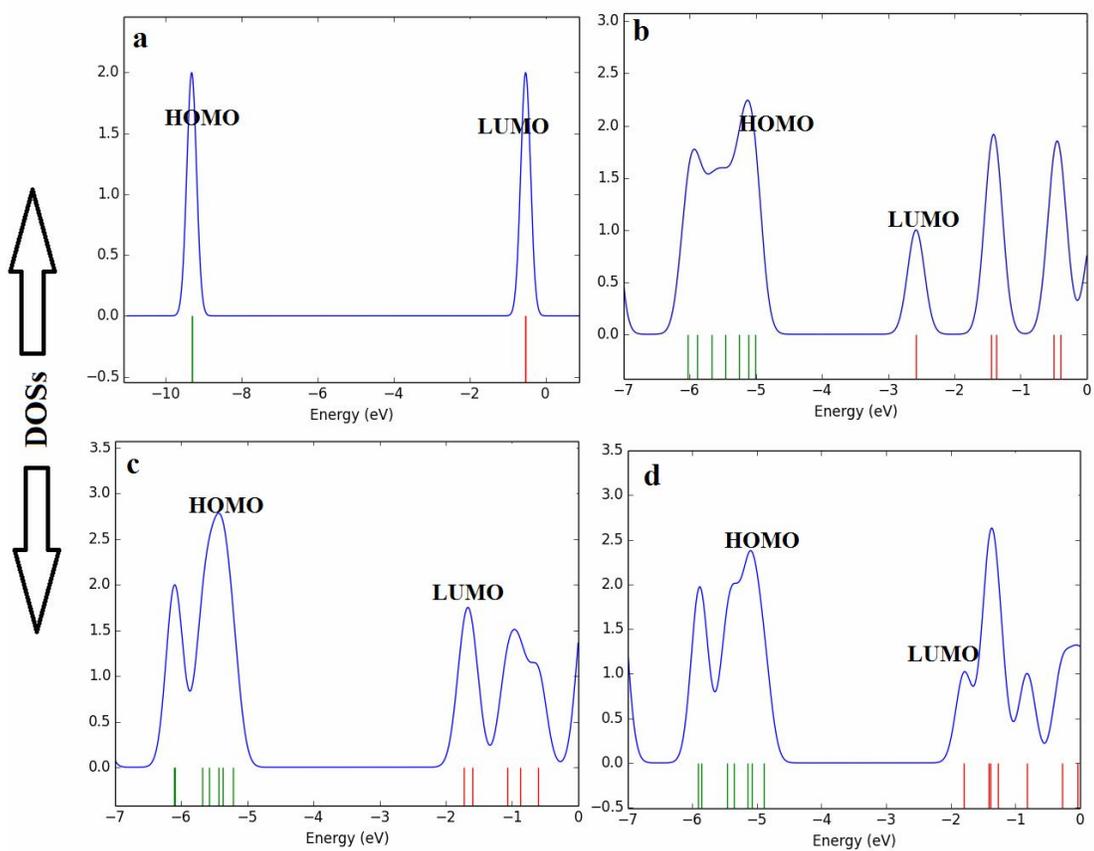


Fig. 4. DOSs for free N_2O (a), free PtG (b), PtG- N_2O (position 1) (c), and PtG- N_2O (position 2) (d).

difference in the value of adsorption energy. It is obvious that in the case of P1 adsorption, the HOMO redistributes somewhat on N₂O, however the major change occurs in redistribution of LUMO while the density of charge on Pt is reduced upon adsorption. In the case of P2, the HOMO and LUMO of PtG are not major affected by adsorption, as seen in Fig.3. These results are quite in accordance to the results of charge analyses.

By considering the data of Table 1, upon adsorption of N₂O we can see a decrease and an increase in the HOMO of system from -5.00 eV for isolated PtG to -5.22 and -4.90 eV, for P1 and P2, respectively. Moreover, it can be seen that the LUMO of system increases from -2.58 eV to -1.73 and -1.79 eV, in the same order. These changes are correspond to the increase in the E_g (E_{HOMO}-E_{LUMO}) of system from 2.42 eV for isolated PtG to 3.49 and 3.11 eV for adsorbed systems in P1 and P2, respectively.

To deep understanding the electronic property of PtG upon adsorption of N₂O, the DOS for all systems in free and complexed forms was depicted close to the Fermi level (see Fig. 4). The DOS of free N₂O (Fig. 4a) has a big E_g (8.79 eV), indicating its stability in free form. Comparing the DOS of free PtG to those for PtG- N₂O complexes (Fig. 4b, c, and d) we can find significant changes in locations of both HOMO and LUMO, so that the E_g of each system increases significantly upon adsorption of N₂O. This increase is much more pronounced at P1 compared to P2. It should be kept in mind that any increase in the E_g corresponds to an increase in the stability of system upon adsorption [28-32].

CONCLUSIONS

The potential of PtG as a nanostructure adsorbent for N₂O was investigated through searching different geometries of adsorbed analyte. We calculated the relaxed energy of each system and then we used orbital descriptions, density of states as well as charge analyses for two different positions. We notified that the adsorption in P1 changes the electronic structure of system more than P1. Our results confirm that Pt decoration on graphene greatly enhances the potential of graphene as an ideal adsorbent towards interaction with N₂O. The NBO charge analysis revealed reverse direction of charge transfer for P1

compared to P2 which corresponds to the n-type or p-type property of PtG semiconductor.

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