

# First Principle Study of the Physical Properties of Platinum (Pt) Decorated Graphene and NH<sub>2</sub> Doped Pt-decorated Graphene; Effect on Hydrogen Storage

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Received June 10, 2019; Revised July 15, 2019; Accepted July 29, 2019

**Abstract** We conducted theoretical investigation of the structural and electronic properties of Pt-functionalized graphene and NH-doped Pt-functionalized graphene, which are shown to be efficient materials for hydrogen storage. Nitrene radical dopant was an effective addition required for enhancing the Pt binding on the graphene sheet. We found that up to three H<sub>2</sub> molecules could be adsorbed by Pt-functionalized graphene with an average binding energy in the range 3.049–1.731 eV. The most crucial part of our work is measuring the effect of nitrene radical on Pt-functionalized graphene. Our calculations predicted that the addition of NH radicals on Pt-functionalized graphene enhance the binding of Pt on graphene, which helps also to avoid the desorption of Pt(H<sub>2</sub>)<sub>n</sub> (n=1-3) complexes from graphene sheet. Our results also predict Pt-functionalized NH-doped graphene is a potential hydrogen storage medium for on-board applications.

**Keywords:** DFT, H<sub>2</sub>, Pt-functionalized graphene, hydrogen storage capacity, NH radical

**Cite This Article:** El Hadji Oumar Gueye, Abdoulaye Ndiaye Dione, Allé Dioum, Baye Modou Ndiaye, Papa Douta Tall, and Aboubaker Chédikh Beye, “First Principle Study of the Physical Properties of Platinum (Pt) Decorated Graphene and NH<sub>2</sub> Doped Pt-decorated Graphene; Effect on Hydrogen Storage.” *American Journal of Nanomaterials*, vol. 7, no. 1 (2019): 30-38. doi: 10.12691/ajn-7-1-4.

## 1. Introduction

The rapidly growing needs of energy can only be fulfilled if the current sources of energy could be replaced with such sources, which are safe, pollution free, abundantly available, cheap, and recyclable. Hydrogen has great potential to be a carrier of energy for future and is a perfect alternative for fossil fuels. Especially for transportation applications, hydrogen is thought to be a clean carrier of energy in fuel cell vehicles. It has the highest energy density of 120 MJ kg<sup>-1</sup>, among all the known fuels. However, even after extensive research of many years, storage of hydrogen is still a hurdle towards the transition to a hydrogen economy. The main problem of using hydrogen as a fuel is its gaseous nature. Therefore, it is crucial and need of the hour to find a practical system to store hydrogen safely with high gravimetric and volumetric density at ambient conditions [1]. A target of 5.5 wt. % has been set by the U.S. Department of Energy (DOE) for on-board storage of H<sub>2</sub> to be met by 2017 [2]. During the past decade, tremendous research has been carried out on solid-state materials for several applications including hydrogen storage for fuel cell powered vehicles despite having problems with kinetics and reversibility [3,4]. Functionalized carbon

nanostructures are considered promising in the context of hydrogen storage. Carbon nanostructures in their pristine form are chemically very inert for their applications in most of the technological fields like hydrogen storage. In order to increase their reactivity many techniques can be adopted. The common technique for functionalizing carbon nanostructures is doping of foreign atoms on the surface or in the interior of the nanostructures. Transition metals (TM) are one of the most studied dopants on carbon nanostructures in the recent past and they have been explored particularly in the pursuit of suitable hydrogen storage media [5,6].

Extensive research shows that suitable hydrogen storage capacity and H<sub>2</sub> adsorption binding energies can be achieved by doping these carbon-based nanomaterials with boron, or aluminum by decorating them with light alkali metals (Li and Na), alkaline earth metals (Ca and Sr), light transition metals (Sc through Ni) and other transition metals anchored on mono vacancies such as Palladium, Platinum, Titanium, Nickel, and Niobium [7-17]. Many researchers have reported the preparation of graphene-supported Pt-based catalysts and that all of them showed enhanced electrocatalytic performance for methanol oxidation [18,19,20]. In order to enhance the sensing effect, graphene were usually functionalized by metal and metal oxides, such as Pd [21,22,23,24], Pt [25,26,27], TiO<sub>2</sub> [27] and SnO<sub>2</sub> [26]. Particularly, Pd or Pt

displays high reactivity for hydrogen sensing, because they can disassociate  $H_2$  molecules even at room temperature [28,29].

Experimental studies have shown that it is possible to use perfluorophenyl-azide to generate nitrene radicals and immobilized graphene on silicon wafers as reported in reference [30]. Despite the interesting influence that nitrene radical had on graphene [31], theoretical investigation of Pt-functionalized NH-doped graphene for hydrogen uptake have not yet been addressed. It therefore is important to determine the effectiveness of Pt- functionalized graphene and Pt- functionalized NH-doped graphene for hydrogen storage. Motivated by the challenge to develop hydrogen storage materials for practical applications, the aim of this work is to provide a detailed description of the interactions of  $H_2$  with both Pt-functionalized and NH-doped Pt-functionalized graphene surfaces. To achieve this goal, we performed first-principles calculations based on density functional theory (DFT) for a systematic study of the geometric stability and hydrogen storage capacity of Pt-functionalized graphene and NH-doped Pt-functionalized graphene. First, Pt-functionalized graphene was investigated. Next, the hydrogen adsorption of Pt-functionalized was evaluated. Finally, we investigated the effect of NH radical on Pt-functionalized graphene.

## 2. Computational Method

We performed calculations based on Density Functional Theory (DFT) using DMol3 codes as implemented on Material Studio 7.0 with the atomic orbitals developed by B.Delley as the basis sets [32,33]. The exchange correlation interaction between electrons is described using (local density approximation) (LDA) with the Perdew Wang correlation [34] throughout this paper. It is well known that, the LDA method predicts notably higher binding energy compared to (generalized gradient approximation) (GGA) method [35,36]. Some researchers have predicted that relativistic effects should be considered for DFT calculations for a transition metal [37,38]. So we chose the all-electron with relativistic correction core treatment method and the numerical double numerical plus polarization basis set (DNP), which has shown accurate results [39,40]. The energy minimization was done with the convergence tolerance energy of 1.0 10<sup>-6</sup> Ha. All positions of the atoms were relaxed such that the force on each atom was less than 0.002 Ha/Å. The Brillouin zone was sampled using 5 x 5 x 1 Monkhorst-Pack mesh of special k-points [41]. We chose 4.5 Å as the real space global orbital cutoff radius. To improve the convergence, thermal smearing was set to 0.005 Ha. To model the graphene sheets, a supercell containing 50 atoms with periodic boundary conditions along the x and y-axes was used. The optimized lattice parameters of the supercell were a = b = 12.30Å and c = 30 Å (a, and b are the distances in the plane of graphene, and c is the distance between two adjacent graphene sheet selected to avoid any interaction between periodic images).

The binding energy of the Platinum atom on graphene was calculated as:

$$E_b = -\left[E_{gra+Pt} - (E_{grap} + E_{Pt})\right] \quad (1)$$

where,  $E_{gra+Pt}$  is the total energy of the graphene sheet with Platinum (Pt) decoration,  $E_{grap}$  is the total energy of the pristine graphene sheet,  $E_{Pt}$  is the total energy of a free Pt atom.

The binding energy of the Platinum atom on graphene doped with nitrene (NH) was calculated as:

$$E_b = -\left[E_{grap+NH+Pt} - (E_{grap+NH} + E_{Pt})\right] \quad (2)$$

where,  $E_{grap+NH+Pt}$  is the total energy of the graphene sheet with Platinum (Pt) decoration, and NH doping  $E_{grap+NH}$  is the total energy of the graphene doped with Nh,  $E_{Pt}$  is the total energy of a free Pt atom.

The adsorption energy of the Hydrogens atom on graphene decorated with Pt was calculated as:

$$E_{ad} = -\left[E_{grap+Pt+nH_2} - (E_{grap+Pt} + nE_{H_2})\right] / n \quad (3)$$

where,  $E_{grap+Pt+H_2}$  is the total energy of the graphene sheet with Pt)decoration and  $H_2$  adsorbed,  $E_{grap+Pt}$  is the total energy of the graphene decorated with Pt,  $E_{H_2}$  is the total energy of a free  $H_2$  molecule.

The adsorption energy of the Hydrogens atom on graphene decorated with Pt and NH was calculated as:

$$E_{ad} = -\left[E_{grap+NH+Pt+nH_2} - (E_{grap+NH+Pt} + nE_{H_2})\right] / n \quad (4)$$

where,  $E_{grap+NH+Pt+H_2}$  is the total energy of the graphene sheet with Pt and NH decoration and  $H_2$  adsorbed,  $E_{grap+NH+Pt}$  is the total energy of the graphene decorated with Pt and,  $E_{H_2}$  is the total energy of a free  $H_2$  molecule.

## 3. Hydrogen Adsorption on Platinum (Pt)

### 3.1. Atomic and Molecular Configuration

**Table 1. Values of adsorption energy of  $H_2$  on Pt ( $E_{ads}$ ) distance between H ( $d_{H-H}$ ) and distance between Pt and H ( $d_{Pt-H}$ )**

PtH <sub>2</sub>	$E_{ads}$ (eV)	$d_{H-H}$ (Å)	$d_{Pt-H}$ (Å)
Atomic	1.048	3.265	1.633
Molecular	3.560	2.038	1.505

First, we have studied two configurations, an atomic configuration (At) and a molecular configuration (Mol) to see the most stable. The binding energies are respectively 1.048eV and 3.560eV for At and Mol, as shown in Table 1. This is in agreement with the results found in the literature [42]. Therefore, we notice that the Molecular configuration is the most stable configuration. However, for the two configuration, we are witnessing a dissociation of the  $H_2$  molecule when it is bound to platinum. The inter-atomic distance between Pt-H are respectively 1.633 Å, 1.505 Å for At and Mol configuration. The interatomic distance H-H are respectively 3.265Å and 2.038Å respectively for At and Mol. Thus, we see that there isn't the formation of Kubas, which is in agreement with the literature.

Thus, in the rest of our study, we will only focus on the Mol configuration since it is more stable.

### 3.2. Hydrogen Adsorption on Molecular Configuration

Then we studied the number of hydrogen atoms that Pt could adsorb in the molecular configuration.

We note that the addition of H<sub>2</sub> causes a decrease of the adsorption energy. We have 3.560 eV, 2.414 eV, 2.237 eV and 1.753 eV respectively for H<sub>2</sub>, 2H<sub>2</sub> and 4H<sub>2</sub>. We note that Pt can make covalent bonds with hydrogen up to 4H<sub>2</sub>, beyond that there is a phenomenon of physisorption. Similarly, as the Table 2 shows, there is no formation of kuba complex because the lowest distances between H are greater than 0.768 except for the case of 5H<sub>2</sub> for the fifth H<sub>2</sub>. We also see that the adsorption energy decreases as the number of H<sub>2</sub> increases.

**Table 2. Adsorption energies (E<sub>ads</sub>) of H<sub>2</sub> molecules on Pt atom along with their equilibrium distances between H-H atom (d<sub>H-H</sub>) and Pt and H atoms (d<sub>Pt-H</sub>)**

n: number of H <sub>2</sub>	E <sub>ads</sub> (eV)	d <sub>H-H</sub> (Å)	d <sub>Pt-H</sub> (Å)
2	3.560	2.038	1.505
4	2.414	1.548	1.272
6	2.237	1.567	0.947
8	1.753	1.546	0.944

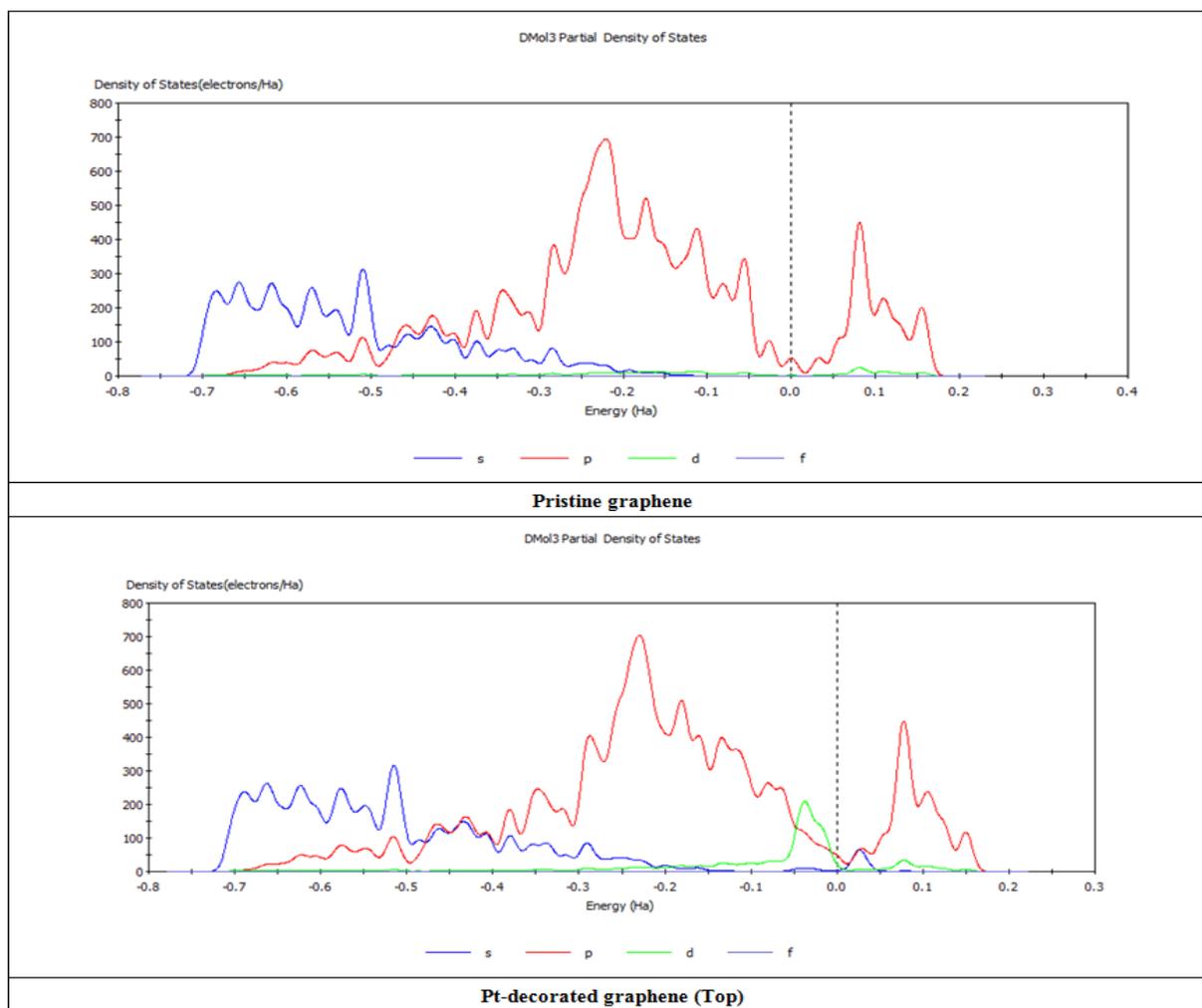
## 4. Pt decoration on Graphene

Since the aim of this study is to evaluate the effect of the presence of Pt atom on graphene upon H<sub>2</sub> adsorption, the binding of Pt atom at three high symmetry points on graphene was studied to determine the stable location of Pt atom on graphene. The symmetry points are the bridge (B) site above the center of a carbon-carbon bond, the top (T) site directly above a carbon atom and the hollow (H) site above of a hexagon ring.

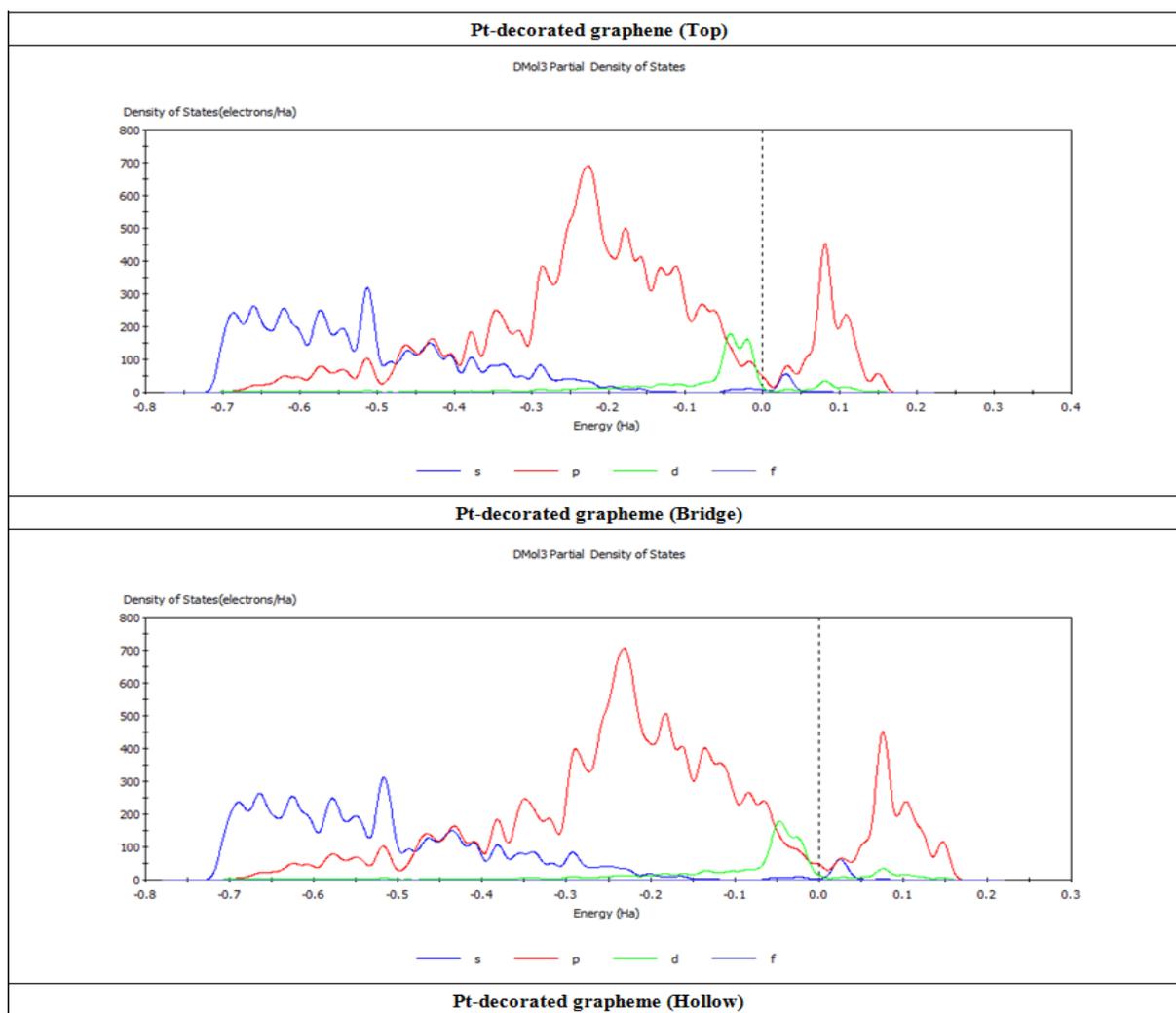
**Table 3. Values of binding energie (E<sub>bind</sub>), d<sub>C-Pt</sub> of Pt atom to pristine graphene at three adsorption sites (T, B, and H)**

Configuration	E <sub>bind</sub> (eV)	d <sub>C-Pt</sub> (Å)
Top	2.351	1.969
Bridge	2.611	2.037
Hollow	2.461	1.986

We note, as Table 3 shown, that the bridge configuration has the largest E<sub>b</sub> with 2.611 eV followed by Hollow with 2.461 eV then Top configuration with 2.351 eV. We also see that the Pt-C distance is greater in the Bridge configuration with a value of 2.037 Å, followed by the Hollow configuration with 2.031 Å and then the Top configuration with 1.967 Å as shown in the table. These results are in agreement with the literature [43,44].



**Figure 1a.** Partial density of state of pristine graphene and Pt-decorated graphene (Top)



**Figure 1b.** Partial density of state of pristine graphene and Pt-decorated graphene (Bridge and Hollow)

To better understand the principle of charge transfer, we performed the Mulliken charge analysis. The charge of the Pt for the configurations T, B and H being respectively 0.053e, 0.045e, 0.060. The charges carried by the carbons directly linked to the Pt are for the top -0.244e, for the bridge -0.221e and -0.221e and -0.162e for the Hollow. Thus, we see that for the three configurations the Pt played the role of donor while the graphene played the role of acceptor. The study of the DOS (Cf Figures 1a, b) shows a shrinkage of the band at the Fermi level, which is due as shown by the Mulliken charge analysis to the electron transfer from the Pt atom to the graphene sheet.

## 5. Hydrogen Adsorption on Pt Decoration Graphene

### 5.1. Hydrogen Adsorption on Top, Bridge and Hollow

We study here the hydrogen adsorption process on the Pt-decorated graphene for the three configurations (Top, Bridge and Hollow). For the different configurations (Top, Bridge and Hollow) we notice that unlike the Pt alone on the graphene, the H<sub>2</sub> adsorption is stronger for the Top

configuration followed by the Hollow configuration and then the bridge configuration. However, even if there is no covalent bond, we see an electron transfer as shown by the electron density on Figure. 2. The E<sub>ad</sub> are respectively 3.049eV, 2.939eV and 2.791eV for the Top, Hollow and Bridge as given in table. The distance C-Pt being respectively 2,384, 2,360 and 2,354 for Top, Bridge and Hollow. We notice that the C-Pt distances are higher than for the Pt alone, which is quite logical.

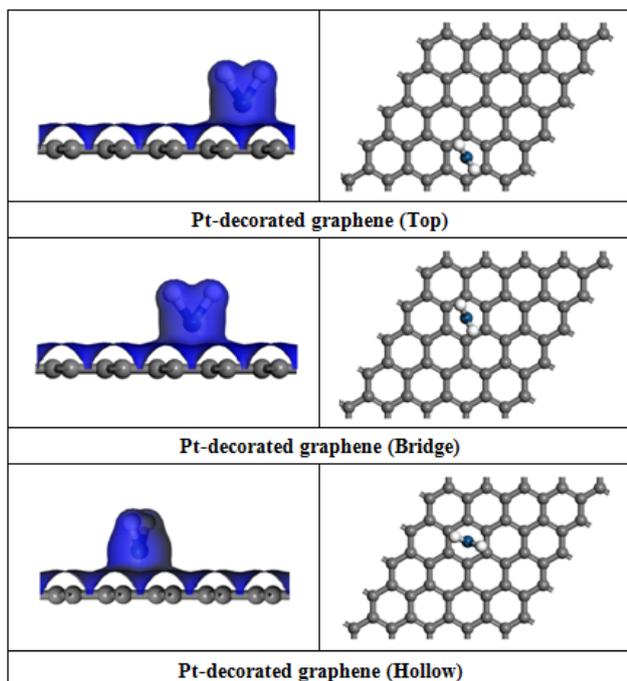
**Table 4.** Adsorption energies (E<sub>ad</sub>) of one H<sub>2</sub> molecules in graphene functionalized with Pt atoms (Top, Bridge, Hollow) along with their equilibrium distances between H-H atom (d<sub>H-H</sub>), Pt and C atom (d<sub>C-Pt</sub>) and Pt and H atoms (d<sub>Pt-H</sub>)

	E <sub>ads</sub> (eV)	d <sub>C-Pt</sub> (Å)	d <sub>Pt-H</sub> (Å)	d <sub>H-H</sub> (Å)
Top	3.049	2.384	1.538	1.845
Bridge	2.791	2.360	1.536	1.839
Hollow	2.939	2.354	1.536	1.842

Similarly, by comparing the distances Pt-H with the distance of the PtH<sub>2</sub> alone we notice an increase in the Pt-H distance with respectively 1.538 Å, 1.536 Å and 1.536 Å for the T, B and H. This is quite logical because of the addition of a Pt interaction with the graphene resulting to a reduction of the interaction with the H<sub>2</sub> then an increase of the Pt-H distance. Likewise, for the PtH<sub>2</sub>,

we observe a dissociation of the  $H_2$  as shown by the distances H-H (see table).

In the following, we have studied for the Top configuration the number of  $H_2$  that the Pt-decorated graphene can adsorb.



**Figure 2.** Optimized structures and electron density of Pt-functionalized graphene sheet with Pt atom at bridge (B), top (T) and hollow (H) sites with one  $H_2$  molecule. Here blue balls represents Pt, with balls represents H and grey balls carbons atoms of graphene

## 5.2. Hydrogen Adsorption on Top Pt-decorated Graphene

In this part, we reported on the adsorption of  $H_2$  molecules on Top Pt-functionalized  $4 \times 4$  graphene. The computational results presented below show that Pt-functionalized flat graphene sheets may bind up to three  $H_2$  molecules per Pt atom to reach saturation. We observed that when three  $H_2$  molecules are bonded, one additional  $H_2$  molecule breaks the connection between Pt atom and graphene. We observed that the stability of the  $Pt(H_2)_n$  on graphene was decreasing when the number of hydrogen molecules adsorbed on it was increasing. Table 5 summarizes the binding energy of  $H_2$  on Pt-functionalized graphene as the number of  $H_2$  molecules increased along with, the average equilibrium parameters. For simplicity we denote the average distance between Pt and H atoms ( $d_{Pt-H}$ ), between H-H atoms ( $d_{H-H}$ ) and the relative distance of Pt atoms to the nearest carbon atom ( $d_{C-Pt}$ ).

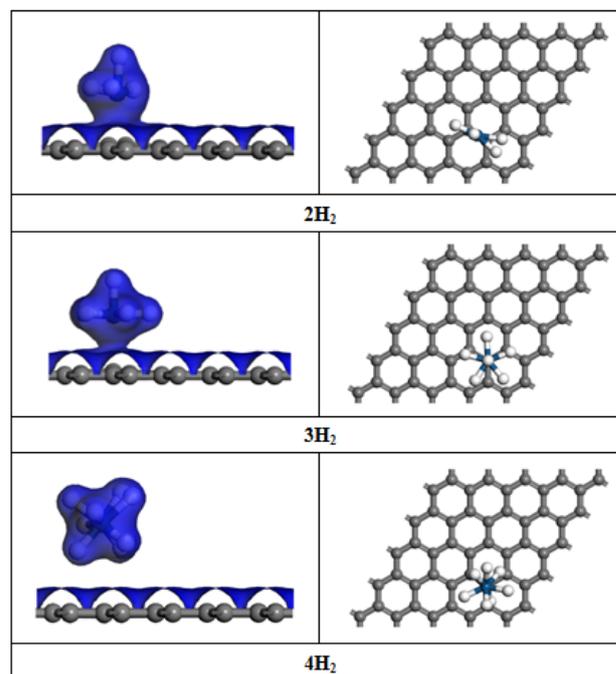
**Table 5.** Adsorption energies ( $E_{ad}$ ) of  $H_2$  molecules in graphene functionalized with Pt atoms (Top) along with their equilibrium distances between H-H atom ( $d_{H-H}$ ), Pt and C atom ( $d_{C-Pt}$ ) and Pt and H atoms ( $d_{Pt-H}$ )

	$E_{ads}(eV)$	$d_{C-Pt}(\text{Å})$	$d_{Pt-H}(\text{Å})$	$d_{H-H}(\text{Å})$
2	3.049	2.384	1.538	1.845
4	1.843	2.377	1.536	0.943
6	1.731	2.523	1.864	1.514

We then analyzed the successive addition of  $H_2$  molecules to Pt-functionalized graphene. Figure 3 represents the optimized structure for different numbers of  $H_2$  molecules to illustrate the saturation adsorption capacity of  $H_2$  on Pt-functionalized graphene.

The first  $H_2$  molecule is adsorbed with a binding energy of  $-3.049eV$  on Pt-G. We also observed that the average distance between Pt atom and hydrogen atoms ( $d_{Pt-H}$ ) was  $1.536\text{Å}$ , and the bond length ( $d_{H-H}$ ) was equal to  $1.514\text{Å}$ . The first three  $H_2$  molecules were strongly adsorbed on the Pt atom as shown in Figure 3.

The  $E_{ad}$  energies varied between  $3.049 - 1.731eV$ , the average  $d_{H-H}$  was between  $0.943 - 1.514\text{Å}$ , the average  $d_{Pt-H}$  ranged between  $1.536 - 1.864\text{Å}$  and the  $d_{Pt-C}$  was between  $2.377 - 2.523\text{Å}$  as shown in Table 5. The  $d_{Pt-H}$  were between  $1.536 - 1.864\text{Å}$  as shown in Table 3, which were in good agreement with distances reported in the literature [42,44]. We found that Pt-graphene achieved saturation with three adsorbed molecules, as after adding one more  $H_2$  molecule a weak physisorption was observed with  $d_{Pt-C}$  of  $3.769\text{Å}$  for the  $H_2$  molecule. Our results showed that metal functionalized graphene play an important role crucial factor in the  $H_2$  storage capacity when compared to  $H_2$  adsorption on pristine graphene as reported in the early literature [45,46,47].



**Figure 3.** Optimized structures and electron density of Pt-functionalized graphene sheet with Pt atom at top (T) with one to four  $H_2$  molecules

## 6. NH doped Pt Decorated Graphene

We next focused on the effect of nitrene radical-doped single-sided Pt-functionalized graphene for hydrogen storage. A number of theoretical papers focus on NH-doped graphene and its properties. Pablo et al. used nitrene radical to tune the optical properties of graphene [31]. Kutana et al report that when NH groups are attached to graphene, the C-C bonds are broken inducing a strong

local deformation on the graphitic structure [48]. Motivated by the transformation effects of these groups on carbon-based materials, we found it crucial to know their reactivity in the presence of Pt-functionalized graphene for hydrogen storage. We carried out the calculations in two parts: First, we doped one NH radical on Pt functionalized graphene on a single-sided in order to determine the most favourable site for the NH radical. Second, we investigated the effect of the nitrene radical on the successive  $H_2$  adsorption. We placed NH radical on three different site as show in Figure 4 (A, B and C) in order to check the most favorable site. Tableau 3 show the binding energy ( $E_b$ ), the distance between Pt atom and the nearest carbon atom ( $d_{C-Pt}$ ).

In Table 6 we notice that with the addition of NH  $E_b$  increases for the three configurations (Top, Bridge and Hollow). With a bigger  $E_b$  for the C Top. We also note that as for platinum only the most stable configuration in terms of  $E_b$  is the Top configuration. Similarly, as shown in table and in Figure 4, we observe for certain configurations a covalent bond between the Pt-N which tends to avoid the dissociation of the Pt as we will see in part 9.

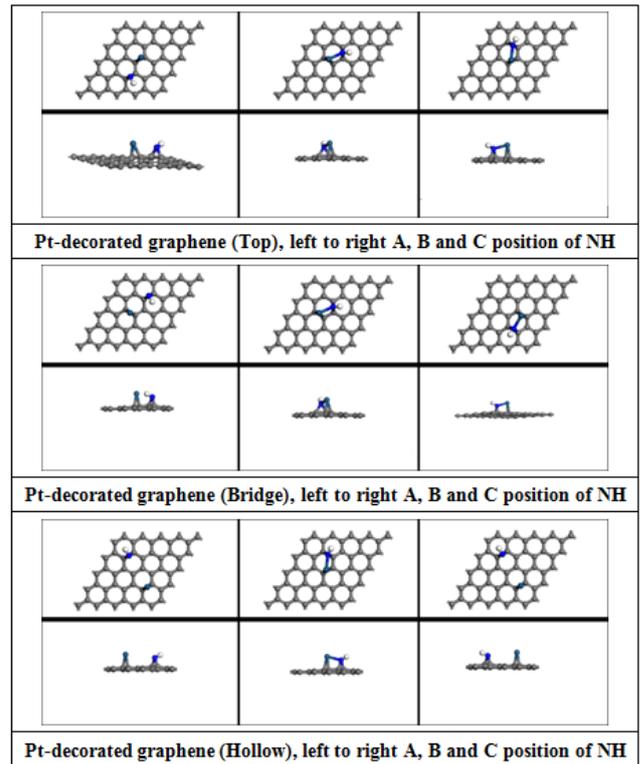
**Table 6. Values of binding energie ( $E_{bind}$ ),  $d_{C-Pt}$  of Pt-decorated graphene at three adsorption sites (T, B, and H) doped with NH in three different positions (A, B and C)**

	$E_{bind}(eV)$	$d_{C-Pt}(\text{\AA})$
A Top	2.724	2.026
B Top	3.070	2.118
C Top	3.074	2.101
A Bridge	2.729	2.027
B Bridge	3.072	2.103
C Bridge	3.068	2.163
A Hollow	2.674	2.039
B Hollow	3.074	2.101
C Hollow	2.674	2.266

We also note that doping with NH increases for all configurations the distance C-Pt as shown in the table. Therefore, the largest  $E_b$  is due to the interaction of Pt with N as we can see in the Figure 4.

Thus, we can notice that the doping with the nitrene causes an increase of the  $E_b$  then a greater stability of the Pt on the graphene.

To better understand the binding mechanisms, we studied the charge transfer phenomena by the Mulliken technique. The atom of N, which is directly related to the graphene (C1-Top configuration), gains on average  $-0.397e$  while the H, which is directly related to it, has a charge of  $0.276e$ . We see that the N behaves like an electron acceptor. The Pt has a load of  $+0.148e$  while the two carbons directly linked to it have  $-0.043e$  and  $-0.190e$ , respectively. Therefore, we see that as for Pt alone with graphene, Pt also plays here the role of electron donor. The strong attraction between NH-doped graphene and Pt-functionalized graphene can be explained by the force of attraction generated by Pt and NH radicals, which prevented Pt atom from migrating on the graphene sheet.



**Figure 4.** Optimized structures of Pt-functionalized graphene sheet with Pt atom at bridge (B), top (T) and hollow (H) and NH-doped on different position (A, B and C)

## 7. Hydrogen Adsorption on NH Doped Pt Decorated Graphene

### 7.1. $H_2$ Adsorption on NH doped Pt-decorated Graphene

As for Pt-Graphene, before studying the storage capacity we studied the most favorable site for Hydrogen adsorption.

**Table 7. Adsorption energies ( $E_{ad}$ ) of one  $H_2$  molecules in graphene functionalized with Pt atoms (Top, Bridge, Hollow) and doped with NH in three different position (A, B and C) along with their equilibrium distances between H-H atom ( $d_{H-H}$ ), Pt and C atom ( $d_{C-Pt}$ ) and Pt and H atoms ( $d_{Pt-H}$ )**

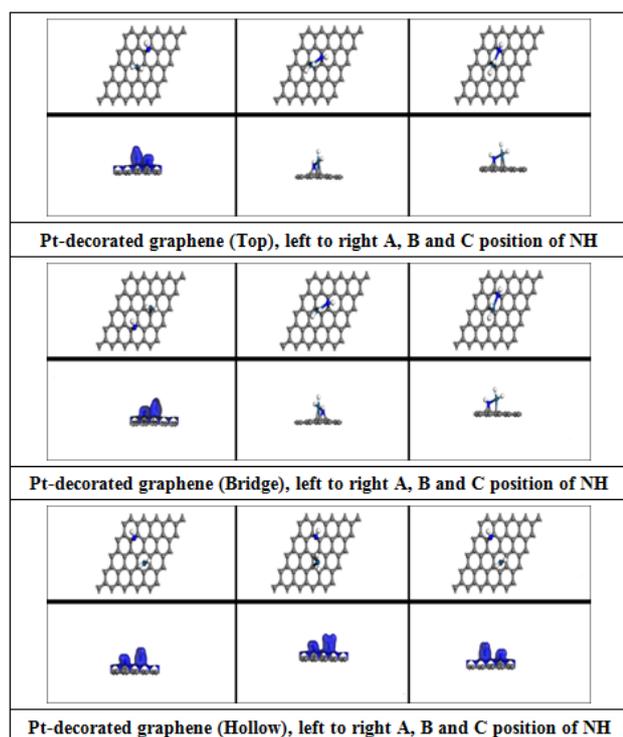
	$E_{ads}(eV)$	$d_{H-H}(\text{\AA})$	$d_{Pt-H}(\text{\AA})$	$d_{Pt-N}(\text{\AA})$
A Top	2.621	1.784	1.633	
B Top	3.389	2.002	1.542	2.118
C Top	3.261	1.541	1.545	2.132
A Bridge	2.741	1.801	1.531	
B Bridge	3.387	2.002	1.542	2.119
C Bridge	3.251	1.948	1.541	2.132
A Hollow	2.756	1.854	1.537	
B Hollow	2.543	1.870	1.534	
C Hollow	2.756	1.856	1.537	

We note that for Top and Bridge configuration we are seeing an increase in  $E_{ad}$  except for A Top and Bridge as shown in the Table 7. However, for Hollow configuration, doping with NH decreases  $E_{ad}$ . We see, as shown in

Figure 5, that the covalent bond between Pt and N tends to increase  $E_{ad}$ . Similarly, we note that the distance Pt-H increases in general for the three configurations as shown in table. We also note that the distance C-Pt tends to be reduced. The shortening of the  $d_{C-Pt}$  distance implied an increasing of the average binding energy of  $H_2$  molecules on NH-Pt-G which varied between 3.389eV—2.543eV. All these results show that NH created a fundamental defect that enhanced the binding of Pt on graphene, and that is crucial for the reversible adsorption and desorption processes.

We notice that the most suitable configuration for  $H_2$  storage is the B-Top configuration.

As these results show, the adsorption energy of  $H_2$  on NH-doped Pt-functionalized graphene was increased ( $E_{ad} = -3.389\text{eV}$ ) compared to the case of Pt-functionalized graphene. This result shows the strong influence of the NH-doping on the adsorption of  $H_2$ . This is in a good agreement on what is reported in the literature [14,25]. Also Seenithurai.S et al. have reported this energy decrease when using Li-decorated double vacancy graphene [49], which means that the presence of the nitrene radical enhanced the binding of Pt atoms on graphene and prevented their migration. This result is promising for achieving reversible adsorption /desorption of hydrogen in this system.



**Figure 5.** Optimized structures and electron density of Pt-functionalized graphene sheet with Pt atom at bridge (B), top (T) and hollow (H) and NH-doped on different position (A, B and C) with one  $H_2$  molecule

## 7.2. Hydrogen Adsorption on Top-B NH Doped Pt-decorated Graphene

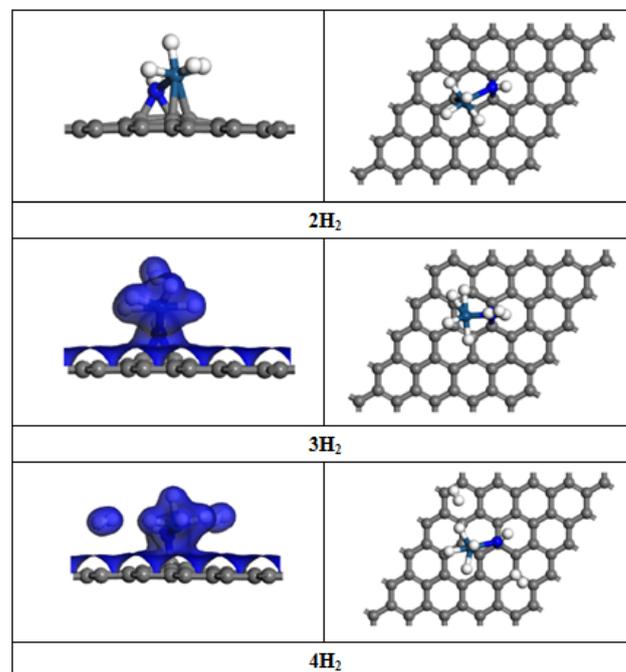
We then studied the successive addition of  $H_2$  molecules on B-Top-Pt-functionalized graphene. Figure 6 shows, respectively, the optimized structures for  $nH_2$  addition on NH-doped Pt-functionalized graphene (B Top NH-Pt-G).

We calculated the sequential hydrogen adsorption energies and these along with the various equilibrium parameters: adsorption energy ( $E_{ad}$ ), the distance between Pt atom and the nearest C atoms ( $d_{C-Pt}$ ) are summarized in Table 8.

**Table 8.** Adsorption energies ( $E_{ad}$ ) of  $H_2$  molecules in graphene functionalized with Pt atoms (Top) and doped with NH (B position) along with their equilibrium distances between H-H atom ( $d_{H-H}$ ), Pt and C atom ( $d_{C-Pt}$ ) and Pt and H atoms ( $d_{Pt-H}$ )

	$E_{ads}$ (eV)	$d_{H-H}$ (Å)	$d_{Pt-H}$ (Å)
2	3.389	2.002	1.542
4	2.254	1.963	1.534
6	1.534	0.982	1.552

We then analyzed the successive addition of  $H_2$  molecules and found that the interaction strength was achieved after adsorbing three  $H_2$  molecules because the four  $H_2$  molecule was quite far from a Pt atom at 2.949Å. As Table 5 also shows the adsorption energy of  $H_2$  molecules decreased as we increased their concentration on the NH-doped Pt-functionalized graphene. We observed that the distances of the three  $H_2$  molecules to the Pt atom were respectively, 1.542Å, 1.534Å, 1.552Å. If we added one additional  $H_2$  molecule, after relaxation the result shows that this molecule was located at a distance of 3.726Å, and the analysis of the electron density (Cf Figure 6) show that there is no interaction between this  $H_2$  and the NH-doped Pt-functionalized graphene.



**Figure 6.** Optimized structures and electron density of Pt-functionalized graphene sheet with Pt atom at top (T) and NH-doped (A position) with two to four  $H_2$  molecules

## 8. Conclusion

In summary, to pursue the search for material for storage of hydrogen for mobile applications, we used first-principles calculations based on density functional

theory (DFT) to study the interaction of H<sub>2</sub> with free Pt, Pt-decorated graphene complex and NH- Pt-decorated graphene. We predicted that the molecular configuration of PtH<sub>2</sub> is more stable than the atomic configuration. We predicted also, that free Pt atoms could bind four H<sub>2</sub> molecules in the binding energy interval (1.753– 3.560 eV) in the molecular configuration. Furthermore, our study of the interaction between Pt atoms and graphene demonstrated that the interaction between the Pt and the graphene is more stable when the Pt is in a bridge site with a binding energy equal to 2.611eV. However, for hydrogen storage, the interaction between Pt and H<sub>2</sub> is more stable when the Pt is in a Top site with an adsorption energy of 3.049eV. We note also that, when the Pt is adsorbed to the graphene their adsorption energy with H<sub>2</sub> decrease. Moreover, we show that our complex Pt-decorated graphene on the Top site can absorb three H<sub>2</sub> in the energy window of 3.049–1.731eV in the atomic form. We also predicted that the successive addition of H<sub>2</sub> molecules on Pt-decorated graphene induced the desorption of nH<sub>2</sub>–Pt complex from the graphene sheet when the number of H<sub>2</sub> molecules was higher than three H<sub>2</sub>. The most crucial part of our work is measuring the effect of nitrene radical on the H<sub>2</sub> adsorption of Pt-functionalized graphene. We demonstrated that the doping of Pt-decorated graphene by nitrene lead to a more stable interaction between Pt and the graphene because it has increase their binding energy. We also demonstrated that the most suitable site is at the top of graphene with a binding energy of 3.074eV. Likewise, for hydrogen storage, the interaction between Pt and H<sub>2</sub> is more stable when the Pt is in a Top site with an adsorption energy of 3.389eV. We also note that, the addition of NH increase the adsorption of H<sub>2</sub> on the Pt. Finally, we predict that the NH doped Pt-decorated graphene cannot adsorb like Pt-decorated graphene up to three H<sub>2</sub> molecule, with adsorption energy between 1.534-3.389eV. Our results also predict Pt-functionalized NH-doped graphene is a good configuration for potential hydrogen storage.

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