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# Density functional theory study on adsorption of Pt nanoparticle on graphene

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## ARTICLE INFO

### Article history:

Received 25 September 2012

Received in revised form

10 December 2012

Accepted 20 December 2012

Available online 26 January 2013

### Keywords:

CO

Pt nanoparticle

Adsorption

Density functional theory

## ABSTRACT

The mechanism of CO oxidation was catalyzed by Pt nanoparticles on graphene through first-principle density functional theory (DFT) calculations. The simulation results show that the lowest-energy Pt<sub>7</sub> nanoparticle carries slightly negative charges which enhance the O<sub>2</sub> binding energy compared to the corresponding graphene surfaces. We placed the Pt nanoparticle on different adsorption sites, and the Pt<sub>7</sub> nanoparticle was found to preferentially adsorb on Bond (B) site. To gain insight into the high-catalytic activity of the Pt nanoparticles, the interaction between the adsorbate and substrate was also analyzed by detailed electronic analysis such as activation barrier, adsorption energy and Mulliken charge analysis.

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## 1. Introduction

The chemical reaction mechanisms for various molecules deposited on a graphene surface have been widely investigated in order to design a novel and more efficient catalyst, both in experiment [1,2] and in theory [3–6]. In experiment, Ayman and colleagues studied the adsorption of CO on the Pt cluster surface by temperature programmed desorption (TPD), ultraviolet photo electron spectroscopy, and X-ray photo electron spectroscopy [7]. Mu et al. investigated the decomposition of CO molecules on the surface of a Pt–Ni bimetallic catalyst using TPD and measured the X-ray absorption near-edge structure (XANES) spectra [8]. In a theoretical study, Kim and Jhi [9] employed the force-matching method to fit

Gibbs free energy with experimental data, and control the binding of Pt nanoparticles to graphene and the molecular adsorption on Pt by introducing defects on graphene. The results show that the strong binding of Pt nanoparticles on defective graphene could enhance the CO poisoning and stability. Zhou et al. [10] applied density functional theory (DFT) calculation to investigate the adsorption, dissociation, and diffusion mechanisms of the CO molecule, and the CO oxidation catalyzed by Pt cluster on the defective graphene surface. In our previous study [11], we studied the adsorption and dissociation of CO using DFT calculation. The calculated results show that the CO oxidation on the Au nanoparticle surface occurs via LH and ER pathways. In addition, Okazaki-Maeda et al. [12] employed density functional theory to find

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<http://dx.doi.org/10.1016/j.ijhydene.2012.12.116>

**Table 1** – Parameters of tight-binding potential for Pt metal.

A (eV)	$\xi$ (eV)	$p$	$q$	$r_0$ (Å)
0.655	2.666	10.142	3.788	2.555

different stable adsorption sites of different size Pt nanoparticles on a graphene surface, as well as providing more detailed information about the adsorption of Pt/graphene. To better understand the platinum catalysis, in the present paper, we first employ DFT to study the effect of deposition site on both the O–O and C–O bond lengths and the adsorption energy. Furthermore, the dissociation of the O<sub>2</sub> molecule on the most favorable graphene surface adsorption site is also investigated.

## 2. Simulation model

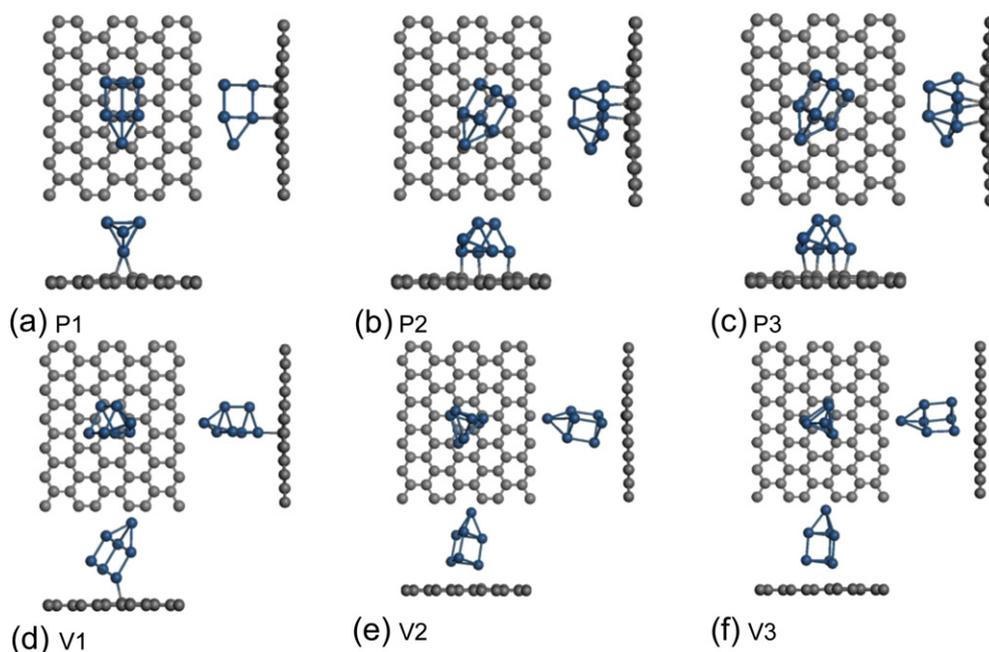
To obtain the lowest-energy structures of Pt nanoparticles (global minimum structures), the basin-hopping (BH) [13] stochastic method was first carried out by using tight-binding potential [14]. The interaction between two Pt atoms depends not only on the distance between them, but also on their local environment. The algorithm for computing this potential is relatively simple compared to other many body potentials. This model commences by summing the band energy, which is characterized by the second moment of the *d*-band density of state (DOS), and a pairwise potential energy of the Born–Mayer type. The interatomic energy of atom *i* is thus expressed as follows:

$$E_i = - \left\{ \sum_j \xi^2 \exp \left[ -2q \left( \frac{r_{ij}}{r_0} - 1 \right) \right] \right\}^{1/2} + \sum_j A \exp \left[ -q \left( \frac{r_{ij}}{r_0} - 1 \right) \right] \quad (1)$$

where  $\xi$  is an effective hopping integral,  $r_{ij}$  is the distance between atom *i* and *j*, and  $r_0$  is the first-neighbor distance. The parameters *A*, *p*, *q*, and  $\xi$  for bulk Pd material are listed in Table 1.

The one hundred lowest-energy structures for nanoparticles with the same Pt atom number, obtained by BH method with tight-binding potential, were further optimized by the Dmol [3] package [15] with density functional theory (DFT) simulation in order to determine more accurate Pt nanoparticles and Pt/graphene structures. All calculations employed the generalized gradient approximation (GGA) [16] by Perdew and Wang parameterization (PW91) [17] correction and DFT semi-core pseudo-potential (DSPP) calculations with double numerical basis sets plus polarization functional (DNP). Spin-polarization was considered in our calculation. The Brillouin zone was sampled with the Monkhorst-Pack grid [18]. The calculations were carried out by using the (3 × 3 × 1) Monkhorst-Pack mesh *k*-points for bulk and surface calculations. A 450 eV cutoff energy, which allows convergence to 1 × 10<sup>−5</sup> eV in total energy, was used.

The top, side and front views of the Pt/graphene structures are shown in panels (a–f) of Fig. 1, respectively. Fig. 1 presents the 3-dimensional diagrams of Pt/graphene structures in the present study, namely a Pt nanoparticle with a diameter of 0.83 nm. The number of atoms in the Pt/graphene system totaled 82 atoms. The lateral cell has dimensions of *a* = 12.8 Å, *b* = 14.5 Å and *c* = 28.5 Å, which includes a large vacuum region to guarantee no interactions between the two slabs of



**Fig. 1** – Stable configurations for the Pt<sub>n</sub> nanoparticle adsorption on graphene. Parallel and vertical adsorption of two type of Pt/graphene configuration, P1 (a), P2 (b), P3 (c), V1 (d), V2 (e), and V3 (f). Blue and gray circles indicate Pt and C atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Table 2 – Calculation results for the Pt<sub>7</sub> nanoparticle and Pt/graphene structure with parallel and vertical types. The definitions of  $E_{\text{coh}}$ ,  $E_{\text{ads}}$ , and  $E_{\text{int}}$  are shown in the text.**

	$E_{\text{coh}}$ (eV/atom)		$d_{\text{Pt-Pt}}$ (Å)	
Pt <sub>7</sub>	3.22		2.499–2.695	
	$E_{\text{ads}}$ (eV)	$E_{\text{int}}$ (eV)	$d_{\text{Pt-Pt}}$ (Å)	$d_{\text{Pt-C}}$ (Å)
P1	–2.133	25.044	2.539–2.641	2.241–2.255
P2	–2.077	24.988	2.576–2.741	2.220–2.271
P3	–1.990	24.901	2.576–2.768	2.219–2.243
V1	–1.009	23.920	2.564–2.668	2.241
V2	–0.998	23.909	2.547–2.703	2.428
V3	–0.947	23.858	2.556–2.688	2.420

graphene in z directions. All atoms were fully relaxed during the calculations. In this study, adsorption energies are calculated according to the following equation:

$$E_{\text{ads}} = (n \times E[\text{Pt}] + E[\text{C}]) - E[\text{Pt}_n/\text{C}] \quad (2)$$

where  $E[\text{Pt}_n/\text{C}]$ ,  $E[\text{Pt}]$ , and  $E[\text{C}]$  are total energies of the Pt<sub>n</sub>/graphene system, the Pt, and the graphene. The interfacial interaction energy,  $E_{\text{int}}$  is defined as follows:

$$E_{\text{int}} = (E[\text{Pt}_n] + E[\text{C}]) - E[\text{Pt}_n/\text{C}] \quad (3)$$

where  $E[\text{Pt}_n]$  is the total energy of the Pt<sub>n</sub>/graphene system. Due to the adsorption process,  $E_{\text{int}}$  contains the deformation energies of the Pt/graphene configuration. In addition, the cohesive energy,  $E_{\text{coh}}$  is

$$E_{\text{coh}} = E[\text{Pt}] - E[\text{Pt}_n]/n \quad (4)$$

### 3. Results and discussion

First of all, in order to confirm the accuracy of the computational approaches used in this work, the lattice constant of bulk Pt and the distance of Pt–Pt bond are computed as 4.018 Å and within 2.841 Å, respectively, both of which are consistent with experimental values of 3.92 Å and 2.772 Å. The calculated cohesive energy of 5.62 eV in our calculation is close to the

experimental value of 5.84 eV [19]. Except for bulk Pt, the dimer gives a well-defined local minimum energy state with a bond length of 2.376 Å, and the cohesive energy of 3.2 eV. The dimers are also in agreement with available experimental data.

#### 3.1. Adsorption of Pt nanoparticle on graphene

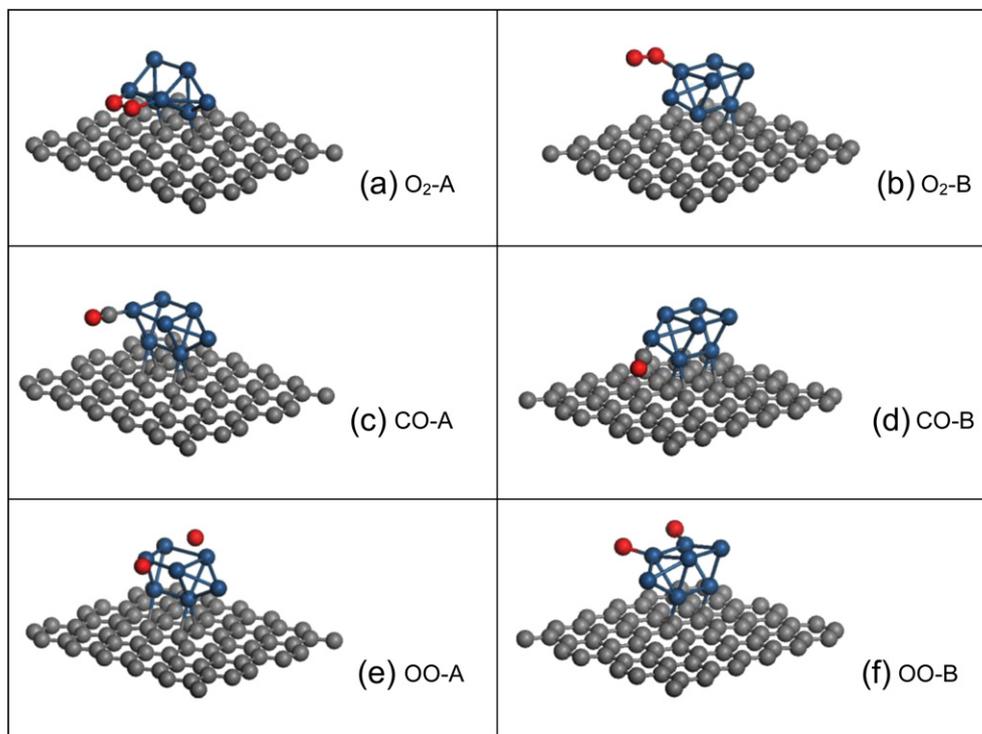
To understand the adsorption properties of Pt on the graphene surface, Pt nanoparticles of different types are placed at various sites on the graphene, as shown in Fig. 1(a–f). Those Pt adsorption sites are both parallel and vertical types. Generally, the adsorptions on graphene occur at top, hollow site or bridge sites. We employed a computation method to find the most stable adsorption site according to random angle and random distance, and found about one hundred structures. Furthermore, all structures are optimized by first-principle calculation. P1 is the most stable site, where two Pt atoms of a Pt<sub>7</sub> nanoparticle bind to graphene, and at the lowest-energy configuration. The calculation results for the Pt<sub>7</sub> nanoparticle and Pt/graphene structure with parallel and vertical types are shown in Table 2.

#### 3.2. O<sub>2</sub>, CO, and O–O molecule adsorption on Pt nanoparticle

Because a molecule adsorbing on a Pt/graphene system is more complex, determining whether or not the O<sub>2</sub>, CO, or O atom adsorbing on the Pt nanoparticle is nucleophilic or electrophilic is our first step in clarifying the adsorption mechanism. We found three configurations in the adsorption of molecules and Pt nanoparticles, termed Pt/O<sub>2</sub>, Pt/CO, and Pt/OO, shown in Table 3 along with their interfacial interaction energies. Table 3 presents calculation results of Mulliken charge,  $E_{\text{int}}$ ,  $d_{\text{O-O}}$ , and  $d_{\text{Pt-O}}$  for the O<sub>2</sub> molecule adsorbed on the Pt nanoparticles. The Mulliken charges of the pure O atoms are –0.05 and –0.05, respectively. The charges enhance to –0.155 ~ –0.242 after adsorbing on the Pt nanoparticle in our former calculations, with the Pt charges having very little enhancement in Pt/O<sub>2</sub>, Pt/CO, and Pt/OO types. From the analysis of Mulliken charge, we know the O<sub>2</sub> and O atoms are

**Table 3 – Calculation results of Mulliken charge,  $E_{\text{int}}$ ,  $d_{\text{O-O}}$ ,  $d_{\text{C-O}}$ , and  $d_{\text{Pt-O}}$  ( $d_{\text{adsorbate}}$ ) for Pt/graphene/O<sub>2</sub>, Pt/O<sub>2</sub> system, Pt/graphene/CO, Pt/CO system, Pt/graphene/CO and Pt/OO system.**

System	Pt/graphene/O <sub>2</sub>	Pt/O <sub>2</sub>	Pt/graphene/CO	Pt/CO	Pt/graphene/O	Pt/OO
Mulliken charge						
Pt (1)	–0.116	–0.108	–0.104	–0.102	–0.108	–0.104
Pt (2)	0.033	0.087	0.062	0.086	0.068	0.106
Pt (3)	–0.095	–0.042	–0.179	–0.12	0.221	0.266
Pt (4)	–0.048	–0.03	–0.043	–0.061	–0.064	–0.048
Pt (5)	0.037	0.077	0.069	0.098	0.268	0.306
Pt (6)	0.245	0.267	0.039	0.072	0.231	0.266
Pt (7)	0.203	0.228	–0.209	–0.195	0.248	0.283
O (8)	–0.242	–0.239	0.398	0.397	–0.538	–0.533
O/C (9)	–0.242	–0.239	–0.174	–0.175	–0.556	–0.543
$E_{\text{int}}$ (eV)	–0.044	–0.103	–0.048	–0.104	–0.095	–0.148
$d_{\text{ad}}$ (Å)	1.433		1.168		4.028	
$d_{\text{Pt-ad}}$ (Å)	1.976		1.837		1.79	



**Fig. 2 – Stable configurations for the O<sub>2</sub>, CO, and O atoms adsorbing on two types of Pt<sub>7</sub>/graphene configurations: O<sub>2</sub>-A (a), O<sub>2</sub>-B (b), CO-A (c), CO-B (d), OO-A (e), and OO-B (f). Red, blue and gray beads indicate O, Pt and C atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)**

electrophilic, and the Pt nanoparticles are nucleophilic, but the charge transfers of CO are not clear. In a normal case, the C atom is jointed on the Pt nanoparticle during the adsorption process of CO on Pt nanoparticle, but when the O end adsorbs on the Pt, repulsion occurs, and the interaction direction is the opposite. A comparison of O and O<sub>2</sub> adsorption on Pt nanoparticle shows the interfacial interaction energies in O atoms are larger than O<sub>2</sub>; this illustrates that it is easier for the O atoms to adsorb on the Pt nanoparticle, an outcome in agreement with experimental results.

### 3.3. O<sub>2</sub>, CO, and O–O molecule adsorption on graphene-based Pt substrates

The Pt/graphene/molecule system with two types (A and B) are shown in Fig. 2(a–f) and the most stable configurations are analyzed. Table 3 lists the Mulliken charge, interfacial interaction energies,  $d_{O-O}$ ,  $d_{C-O}$ , and  $d_{Pt-OO}$  of A type structures for O<sub>2</sub>, CO molecule, and O atom adsorption at various adsorption sites. As can be seen from the table, adding graphene to the Pt/molecule system results in an increase in  $E_{int}$ . This illustrates that the graphene causes a desorption and dissociation effect on the adsorbate.

## 4. Conclusions

In summary, the ground-state Pt nanoparticle is obtained by basin-hopping method and the adsorption properties of

certain molecules on graphene are investigated by DFT calculation. Analysis of the adsorption energy of the Pt nanoparticle adsorbed on three different surfaces on the graphene shows that the bridge site is the most stable. In addition, we also found the most stable adsorption sites for O<sub>2</sub>, CO, and O atoms on the Pt nanoparticle, which indicates a nucleophilic Pt and electrophilic O<sub>2</sub> and O atoms. Finally, the structures of Pt/graphene/molecule systems were also investigated, with results showing that the graphene causes desorption and dissociation in the adsorbate.

## Acknowledgments

The authors would like to thank the (1) National Science Council of Taiwan, under Grant No. NSC101-2628-E-110-003-MY3 and NSC99-2911-I-110-512, (2) National Center for High-performance Computing, Taiwan, for supporting this study. (3) National Center for Theoretical Sciences, Taiwan.

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