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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

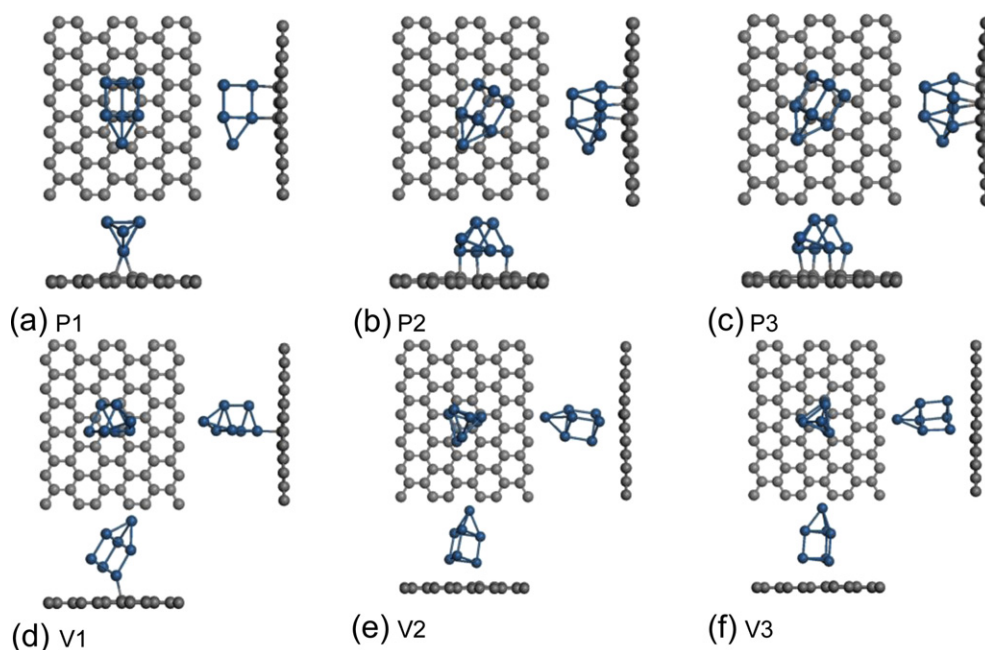
To obtain the lowest-energy structures of Pt nanoparticles (global minimum structures), the basin-hopping (BH) [13] stochastic method was first carried out by using tight-binding potential [14]. The interaction between two Pt atoms depends not only on the distance between them, but also on their local 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.)

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