The most stable mono-layers of (111)-Pt (fcc) on Graphene: A first-principles GGA study

J Otalora-Acevedo[1,2], J A Rodríguez Martínez[1], G Moreno-Armenta[3], E Vera[2] and N Takeuchi Tan[3]
[1] Universidad Nacional de Colombia, Bogotá, Colombia.
[2] Universidad Pedagógica y Tecnológica de Colombia, Tunja, Colombia.
[3] Centro de Nanociencias y Nanotecnología, UNAM, Ensenada, B.C., México.

E-mails: jose.otalora@uptc.edu.co , jarodriguezm@unal.edu.co

Abstract. We investigate monolayers of planes (111) of Pt in the FCC structure located on graphene. The energy of formation showed that the most stable structure is $\sqrt{3} \times \sqrt{3} -$ Pt on $2 \times 2 -$ graphene. This system has a mismatch in the lattice constant of 0.45. The layers are completely flat, and its band structure shows that the new structure is metallic and the Dirac's cones are displaced 0.6eV above of the Fermi level. In this work we present the dependence of the enthalpy of formation of these structures and we calculated all structural parameters of their relaxation.

1. Introduction

Graphene is today a very important material because of its surprising physical and chemical properties. Many very interesting derivatives of graphene have been obtained as result of the deposition of nanoparticles or nanoclusters based on metals, semiconductors, magnetic atoms, and insulators. Today, graphene-metal particle nanocomposites [1] and Pt-graphene composites [2] are a reality. Graphene and graphene oxide (GO) are useful when they are doped or decorated with adsorbed atoms or with nanoparticles of Pt, Au, or Ag [3]. In this paper, we present a study of Pt-monolayer/graphene, with a new focus, because this system is very important in electrocatalysis [4-8]. Reference [9] reports that a 3D foam of graphene with Pt Ru exhibits very good electrochemical properties and also serves as a detector of hydrogen peroxide. The foregoing are reasons for the increasing importance of the Pt/graphene system. In order to contribute to this area of research, we carried out calculations of total energy, based on Density Functional Theory (DFT) of several structures of Pt-monolayer on graphene. From these results, we found that the most probable structure is $\sqrt{3}\times\sqrt{3}$–Pt/$2\times2 -$ graphene. This structure is metallic and exhibits the Dirac's cones.

2. Calculation details

We used Quantum-Espresso code (QE) [10] in order to carry out the total energy calculations. The GGA-PBE approximation [11, 12] was used. QE uses a base of plane waves (PWs) to expand the wave function, and we used 30Ry as the maximum of kinetic energy of the PWs in order to limit the size of the base. Likewise, QE expands the charge density in PWs, and the cutoff for the maximum of kinetic energy of the base was 320Ry. The convergence was 0.0001Ry. QE's relaxation process moves atoms in order to find the optimal positions that minimize the total energy and the forces acting on the atoms. This process ceased when the force was less than 0.001Ry/a.u. All calculations were

spin-polarized. Since QE works only with periodic systems, the periodicity in the direction that is perpendicular to the Pt-graphene layer was achieved by performing periodic slab calculations in which the separation between Pt-graphene bilayers was at least 12Å. In turn, this separation guarantees that the interaction between surfaces is negligible. Only one k-point was considered (Γ), because the supercells used were very large. The new approach used in this research involves the design of monolayers (111) of Pt and graphene layers. This new approach defines l_{Pt} and l_{graph} as the lengths of the sides of cells of Pt and graphene respectively, as $l_{Pt} = a_{Pt}N_{Pt}\sqrt{i}$ and $l_{graph} = a_{graph}N_{graph}\sqrt{j}$, where $a_{Pt/graph}$ are the lattice constants of 1x1 unit cells of (111) Pt and graphene, $N_{Pt/graph}$, i and j are integers. Note that $N\sqrt{i}$ is the general form of a 2D-cell. Then, we search layers such that $l_{Pt}/l_{graph} \approx$ integer or rational numbers p/q with p and q integers. Since it is impossible to get exact integers or rational numbers, a small tolerance window was selected. The tolerance chosen was 5% with respect the graphene lattice constant.

3. Results

Many structures were calculated. Table 1 shows a summary of results, and Figure 1 shows the structures as a model of spheres. The formation energy, E_f (structure), is used to compare the relative stability of structures containing different quantity of atoms, and is calculated as:

$$E_f(\text{structure}) = n_{Pt}E_{Pt}^{FCC-vol} + n_C E_C^{graphite} - E_{slab}^{DFT} \quad (1)$$

Where n is the number of Pt/C atoms in the considered structure, $E_{Pt/C}^{Fcc/graphite}$ is the energy of one atom of Pt/C in the $FCC/graphite$ unit cell, and E_{Slab}^{DFT} is the energy of the slab calculated by QE. $E_{Pt}^{FCC-vol} = -86.6289$Ry and $E_C^{graphite} = -11.3985$Ry.

Table 1. Detail of structures Pt/graphene proposed.

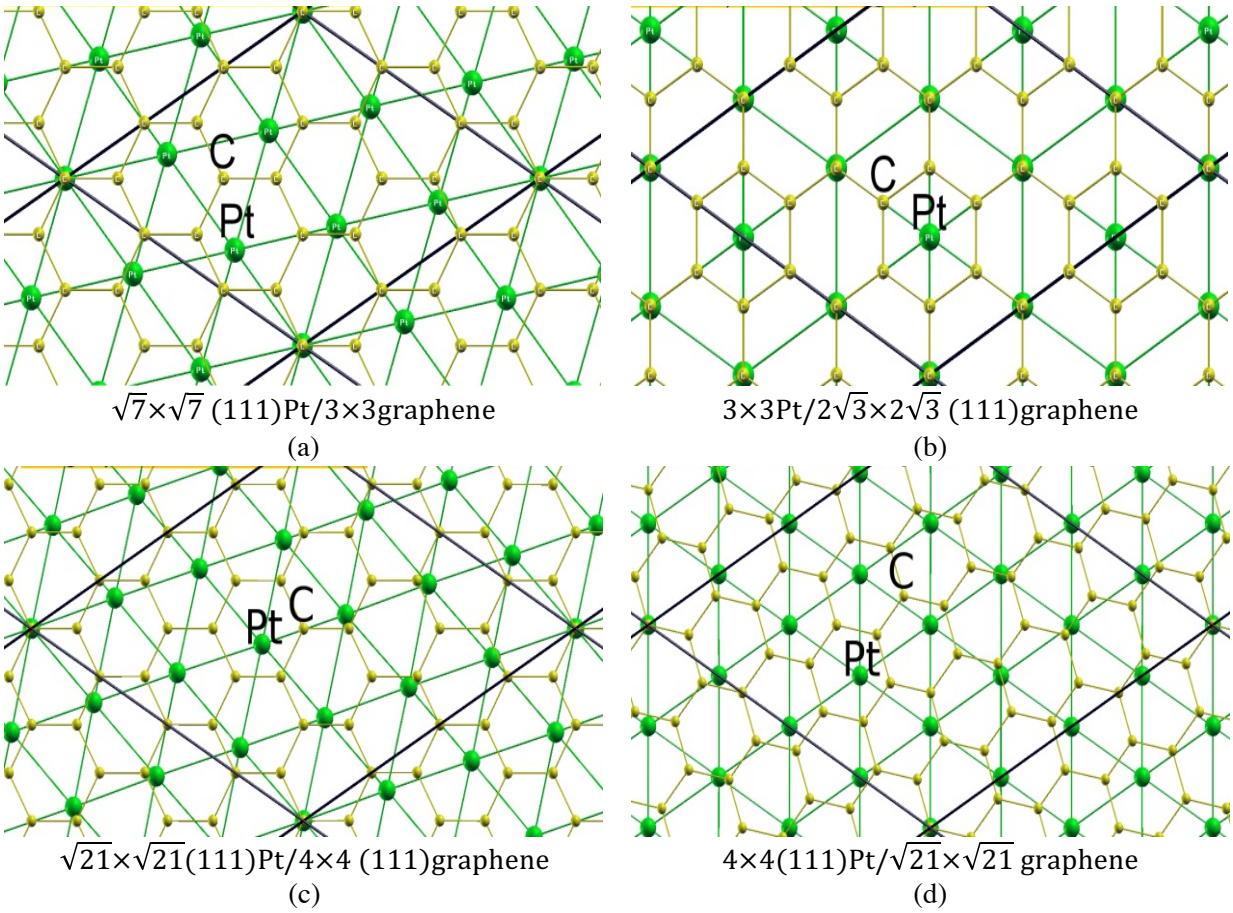
Structure		Atoms in unit cell		Mismatch %	Formation energy (eV) per atom
		Pt	C		
$\sqrt{3}\times\sqrt{3}Pt/2\times2$graphene	Structure #3	3	8	-0.450	0.3534
	Structures #1, #2, #4, #5				0.3704
	Structure #4				0.3849
$\sqrt{7}\times\sqrt{7}Pt/3\times3$ graphene	Structures #1, #2, #5, #8, #9	7	18	1.377	0.3873
	Structures #3, #6, #7				0.3874
$3\times3Pt/2\sqrt{3}\times2\sqrt{3}$graphene	Structure #3	9	24	-0.450	0.3746
	Structure #1				0.3747
$\sqrt{13}\times\sqrt{13}Pt/4\times4$graphene	Structure #1	13	32	3.615	0.4384
$4\times4Pt/\sqrt{21}\times\sqrt{21}$graphene	Structure #6	16	42	0.337	0.3751
	Structures #7, #3				0.3752
	Structure #2				0.3755
	Structure #4				0.3762

In Table 1, column 2, different structures correspond to different relative positions of the graphene layer with respect to the layer of *Pt*, which were obtained by relative displacement. Therefore, *C* atoms

are placed at different positions on top the unit cell of (111)-Pt layer. The structure with the smallest formation energy is $\sqrt{3}\times\sqrt{3}\mathrm{Pt}\ /2\times 2\mathrm{graphene}$ structure #3 (Pt atoms at two different bridge points of the graphene), which is shown in Figure 2(a). The mismatch is calculated as:

$$\mathrm{mismatch} = \frac{\mathrm{l_{Pt-cel}}\times \mathrm{a}^{\mathrm{attice}}_{(111)\mathrm{Pt}}}{\mathrm{l_{graphene}}\times\ \mathrm{a}^{\mathrm{lattice}}_{\mathrm{grahene}}} - 1 \qquad (2)$$

With: $a^{lattice}_{graphene} = 2.4595\text{Å}$, $a^{lattice}_{(111)Pt} = 2.8272\text{Å}$, and l is the length of the cell of *Pt* or *graphene* of column 1.



$\sqrt{7}\times\sqrt{7}\ (111)\mathrm{Pt}/3\times 3\mathrm{graphene}$ (a)

$3\times 3\mathrm{Pt}/2\sqrt{3}\times 2\sqrt{3}\ (111)\mathrm{graphene}$ (b)

$\sqrt{21}\times\sqrt{21}(111)\mathrm{Pt}/4\times 4\ (111)\mathrm{graphene}$ (c)

$4\times 4(111)\mathrm{Pt}/\sqrt{21}\times\sqrt{21}\ \mathrm{graphene}$ (d)

Figure 1. Top view of the structures (111) Pt /graphene, mentioned in Table 1.

Figure 2(b) shows that both layers are completely flat. No deformation is induced in the graphene or Pt layers. The separation between the layers is about 4.14Å, and it seems that the interaction in the vertical direction is weak. However, the electronic bands show that the influence of the Pt atoms on the graphene is sufficient to produce an alteration in the bands with respect to bands of the isolated graphene. Figure 2(c) shows the bands of this structure. This structure exhibits no magnetic moment. Although the semi-metallic behavior of graphene is lost, the Dirac's cones have moved toward the conduction band by about 0.6eV. This feature is emphasized in Figure 2(c) with a red circle that highlights the cones. Other derivative structures are obtained by means of relative displacements between the layers.

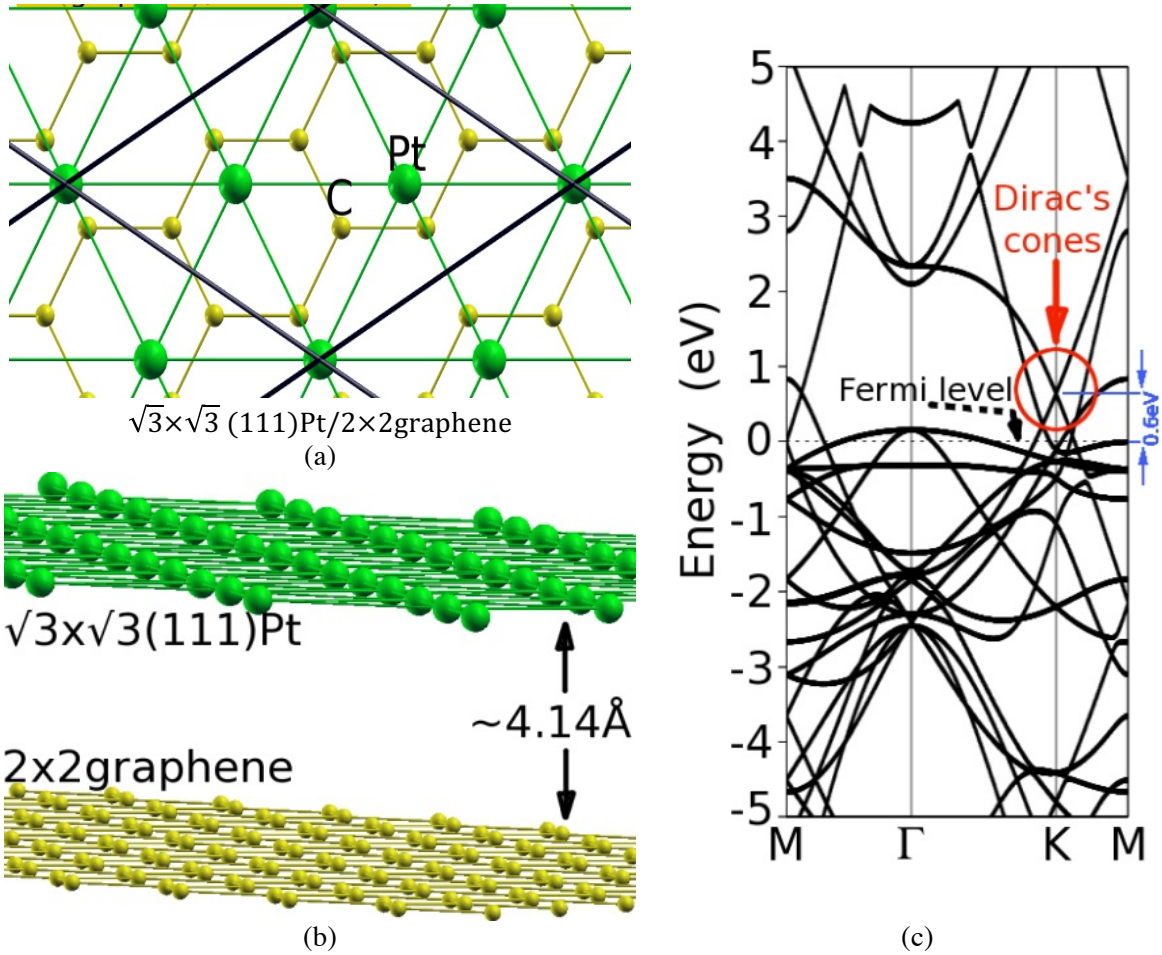


Figure 2. (a) $\sqrt{3}\times\sqrt{3}-$ Pt/ $2\times2-$ graphene. Black lines show the limits of the unit cell of the structure. As can be seen, this lattice constant contains two graphene lattice constants and $\sqrt{3}$ times the lattice constant of the surface (111) of Pt in the FCC structure. Additionally, it can be seen that the Pt atoms are situated at the two bridge points over the graphene. (b) Lateral view of the structure. (c) The band structure of the stable structure. The Dirac's cones are highlighted with a red circle.

4. Summary and conclusions

We presented calculations of total energy of systems composed of one monolayer of (111) of Pt in the FCC structure located on graphene. The structure with the smallest formation energy is $\sqrt{3}\times\sqrt{3}-$ Pt/ $2\times2-$ graphene, the separation between the layers is about 4.14Å, and the layers are flat. On the other hand, the bands show that it exhibits metallic behavior, its magnetic moment is zero, and the Dirac's cones are located 0.6 eV above the Fermi level.

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