Carbon 115 (2017) 791–802

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Ab initio direct dynamics of transition metal atom/dimers bombardments onto graphene: Evolution of magnetic alignment

Hieu T. Nguyen-Truong [a, b], Hung M. Le [b, c, *], Yoshiyuki Kawazoe [d], Duc Nguyen-Manh [e]

[a] Theoretical Physics Research Group, Ton Duc Thang University, Ho Chi Minh City, Viet Nam
[b] Faculty of Applied Sciences, Ton Duc Thang University, Ho Chi Minh City, Viet Nam
[c] Computational Chemistry Research Group, Ton Duc Thang University, Ho Chi Minh City, Viet Nam
[d] New Industry Creation Hatchery Center, Tohoku University, Sendai, 980-8579, Japan
[e] Theory and Modeling Department, Culham Centre for Fusion Energy, United Kingdom Atomic Energy Authority, Abingdon OX14 3DB, United Kingdom

ARTICLE INFO

Article history:
Received 18 August 2016
Received in revised form
24 November 2016
Accepted 28 November 2016
Available online 11 January 2017

Keywords:
Ab initio molecular dynamics
Metal collision
Graphene
Magnetism

ABSTRACT

In this theoretical study, we perform direct *ab initio* molecular dynamic simulations for the collisions of Cr/Fe atom/dimer with the graphene surface to study the evolution of magnetic moment. During the dynamic process, the change in magnetic behavior of those systems is monitored and explained in accordance with the spin-polarized electronic structure analysis. While the magnetic moment of Fe dimer is found to remain almost unchanged (total magnetization > 6 μ_B) on the graphene surface, we find that the Cr dimer-graphene system possesses either 0 (non-magnetic) or a ferromagnetic state of ~10 μ_B. Those observations offer explanations to the switch of magnetic states during the collision dynamics.

1. Introduction

Over the past decade, graphene [1,2] has attracted a huge attention of the research community owing to its extraordinary electronic and mechanical properties, which secure promising applications in the field of nanotechnology [3–5]. It is required that a finite band-gap should be opened for the utilization of graphene in field-effect transistors [3]. This requirement can be achieved by cutting graphene into nanoribbons [6,7] or performing graphene hydrogenation [8]. In the later approach, the adsorption of atomic hydrogen on graphene was actually shown to open a substantial gap between the occupied and unoccupied electronic states [9]. An overview to the functionalization of graphene was discussed in a recent review devoted by Pykal et al. [10] Adsorption of atoms on graphene appears to be effective in controllable modification of this material [11–13]. In recent years, the adsorption of metal atoms on the graphene surface has been increasingly studied with a major focus on the magnetism aspect [14–20]. It was shown that large magnetic moments [14] and anti-ferromagnetic ordering [15] can appear in the case of 3*d* transition metal atoms adsorbed on graphene. In addition, the variance in the number of metal atoms adsorbed on graphene [18] as well as in the adsorption sites [20] can also lead to significant differences in the resultant magnetic moments. In terms of electronic structure, Khomyakov et al. [21] showed that the bonding between graphene and metal surfaces (Al, Ag, Cu, Au, and Pt) was weak but had an effect on the shift of the Fermi level. Experimentally, the interaction between graphene and different metal films was investigated using Raman spectroscopy, which revealed peak shift in the case of electron doping with the cobalt contact and hole doping with the nickel contact [22]. The doping of graphene by noble metal caused an effect on the electrochemical behavior, thus enhanced the catalytic capability of the compound [23]. By employing surface-enhanced Raman scattering technique, Lee et al. [24] concluded the interaction between Ag nanoparticles and graphene to be thickness dependant. Electronic resistance has been a critical concern in graphene-metal junction developments. In a previous experimental study, the circular transfer length method was employed to characterize the Ag, Au, Ni, Ti, and Pd contacts with graphene [25]. The resistance between graphene and the palladium surface was previously shown to

* Corresponding author. Faculty of Applied Sciences, Ton Duc Thang University, Ho Chi Minh City, Viet Nam.
E-mail addresses: nguyentruongthanhhieu@tdt.edu.vn (H.T. Nguyen-Truong), leminhhung@tdt.edu.vn (H.M. Le), kawazoe@imr.edu (Y. Kawazoe), duc.nguyen@ccfe.ac.uk (D. Nguyen-Manh).

http://dx.doi.org/10.1016/j.carbon.2016.11.078
0008-6223/

decrease with temperature decreasing [26]. In a recent effort to reduce resistance of graphene-metal contact, Guo et al. [27] demonstrated the utilization of sandwiching graphene square flakes between the graphene and metal layers, and the contact resistance was reported to be reduced by 74.3%.

Fe/Cr atom/cluster binding to graphene has been the subject of several recent works [11,28–33]. Chan and co-workers contributed an effort to study the graphene-metal systems (12 different metals in consideration) to explore the electronic structure, dipole moment, and work function [11]. For the specific case of Fe, it was found that Fe at a single vacancy site was non-magnetic, while an Fe atom residing at a double vacancy site had a higher magnetic moment [28]. Interestingly, the adsorption of Fe in the graphene trivacancy was proved to open an energy gap in graphene [31]. A dynamic study was presented by Markevich et al. [32] to explore the mechanism of Fe migration at mono-vacancy and double-vacancy sites. In general, it was shown that doping graphene with Fe should be effective to introduce magnetism in graphene [33]. Other than Fe, Cui et al. [30] suggested a possibility of attaching Co on the N atoms in the graphene plane, which should be capable of working as a counter electrode.

The understanding of magnetic properties in the graphene-metal system is necessary to fabricate graphene-based electronic and spintronic devices. In fact, the magnetic behavior of graphene at nanoscale is difficult to determine experimentally [17]. Studies based on density-function theory calculations (DFT) [34,35], on the other hand, provided an atomic-level understanding of the metal atoms-graphene interactions. Moreover, investigating the dynamic process helps to understand the relationship between the metal atoms-graphene interactions and the rise of magnetism given by the coordination interactions. In this study, we perform *ab initio* direct molecular dynamic (MD) simulations of metal atom/dimer bombarding the graphene surface. In particular, a Cr adatom and Cr_2, Fe_2 dimers are set to strike the graphene surface with relatively high velocity in comparison with thermal translation. During the process, we focus on the evolution of magnetic alignment of those systems, which is deliberately examined and explained in accordance with the spin-polarized electronic structures.

2. Computational experimental set-ups and details

The objective of this study is to investigate the progress of magnetization change when a single transition metal atom (M) or M_2 dimer is set to collide with the graphene monolayer. This goal can be attained by performing classical MD on a direct *ab initio* force field with three primary steps:

(i) Setting up a configuration of periodic graphene equilibrated with thermal fluctuation at 300 K.
(ii) Executing direct *ab initio* dynamics for the graphene-metal system.
(iii) Selecting representative configurations from the trajectories to perform highly-qualitative self-consistent calculations.

In the following sub-sections, we will present how computational experiments are set up and what information is to be obtained for the later discussions.

2.1. Setting up a thermally equilibrated configuration

Initially, a graphene monolayer consisting of 50 C atoms in a (5×5) supercell and a metal atom/dimer at 9 Å apart from the graphene layer are allowed to fluctuate around the equilibrium positions for 10,000 steps with a fixed step size of 5 Rydberg time units (Rtu). In real time unit, the whole integration period accounts for 2.4 ps. Upon the consideration of a (5×5) supercell, the *a* lattice parameter is 12.34 Å, while the *c* lattice parameter is chosen as 24.34 Å. Both of these parameters ensure a good vacuum assumption for the metal atom/dimer in the periodic system.

We then conduct Car-Parrinello molecular dynamics [36] (CPMD) for this early stage for the graphene-metal system with a cut-off energy of 35 Rydberg and the Martin-Troullier norm-conserving pseudo-potentials [37] are employed for the participating atoms (C, Fe, Cr). In order to make our systems experimentally realistic, the temperature is thermostated at 300 K. After accomplishing the CPMD process, we obtain a graphene layer and M atom/dimer with well randomized configurations. It should be noted that the CPMD process would not produce an alternation to the distance between metal atom/dimer and graphene. In other words, the centers of mass of metal atom/dimer and graphene are preserved during the CPMD process.

When a metal dimer is set to strike a graphene surface, there are many different interacting configurations that M_2 can interact with graphene. Therefore, in the metal dimer investigations, we consider

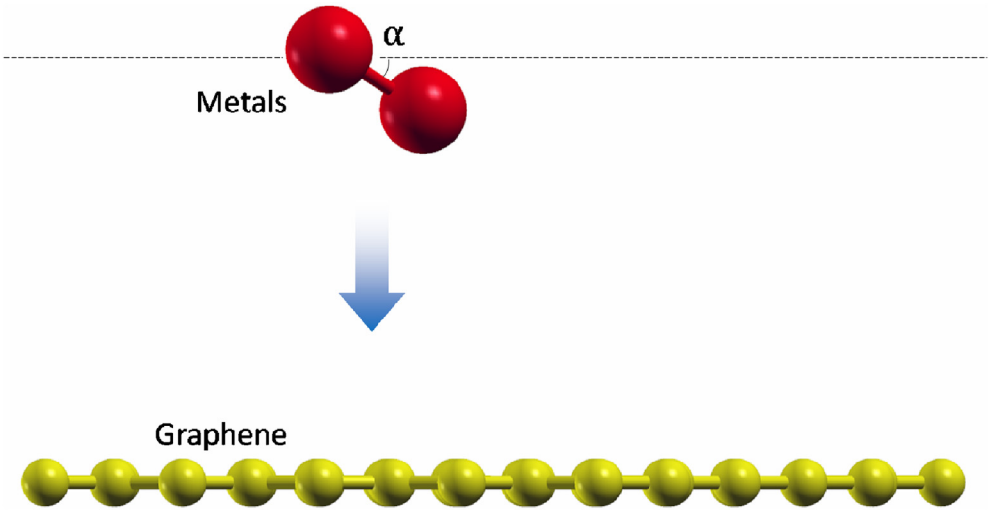

Fig. 1. Definition of the aligning angle (α) made between the vector connecting two metal atoms and the approximated graphene surface. (A colour version of this figure can be viewed online.)