



# Study of interaction between transition metal atoms and bigraphene monovacancy by means of quantum chemistry



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## ABSTRACT

First-row transition metal atoms adsorption on bigraphene monovacancy was studied within the framework of DFT in periodic boundary conditions. Electronic and magnetic properties of composites were analyzed and their potential utilization in spintronics was discussed. Barriers of metal atoms migration from bigraphene surface to the interlayer space through the vacancy were estimated in order to consider both thermodynamic and kinetic aspects of composites experimental preparation. Formation of metal atoms inner-sorbed on bigraphene was found to demand harsh synthesis conditions; whereas outer-sorbed composites demonstrate significantly higher degree of spin polarization which makes them perspective for usage in spintronic devices.

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## 1. Introduction

A large number of theoretical and experimental studies are concerned with graphene and its electronic properties [1,2]. This material is of a great interest due to its unique properties provided by the presence of Dirac cones [3–5].

Electronic and magnetic structure of graphene can be changed significantly by its doping. This effect is also known as Kondo effect and may be implemented in spintronics [6–9]. Rather big transition metal atoms can be adsorbed on the graphene as adatoms and replace one or two carbon atoms [10–12].

The knowledge about the interaction between transition metal and  $sp^2$  carbon atom is essential for understanding carbon nanotubes growing mechanism [13], fuel cell properties [14], and possibility of magnetic ordering in carbon-based materials by doping with magnetic metals, for instance, Fe [15].

Sorption of transition metals, namely, 3d-metals (Sc–Zn), Au, Pt, was investigated experimentally [11,16] and theoretically [10–12,17–20]. All metals were found to prefer the adsorption on graphene vacancies. Strong covalent bonding between transition metal atom and carbon 2D structure makes these structures more stable than others.

Binding energy of transition metal with mono- or bivacancy lies in the range of 2–8 eV [10,17–20]. In contrast with Cu, Zn, Pt and Au, metals from Sc to Ni are likely to adsorb rather on bivacancy than monovacancy [10].

All the abovementioned structures [10] may be divided into four groups according to their magnetic properties: both mono- and bivacancy are non-magnetic (Sc, Ti, Ni, Zn, Pt); monovacancy is magnetic ( $\mu_{Cu} = 1.5 \mu_B$ ,  $\mu_{Au} = 1 \mu_B$ ) while bivacancy is not; opposite case of non-magnetic monovacancy and magnetic bivacancy ( $\mu_{Fe} = 3.2 \mu_B$ ); both mono- ( $\mu_V = 1 \mu_B$ ,  $\mu_{Cr} = 2 \mu_B$ ,  $\mu_{Mn} = 3 \mu_B$ ,  $\mu_{Co} = 1 \mu_B$ ) and bivacancy ( $\mu_V = 3 \mu_B$ ,  $\mu_{Cr} = 2 \mu_B$ ,  $\mu_{Mn} = 3 \mu_B$ ,  $\mu_{Co} = 1.5 \mu_B$ ) are magnetic.

Composites containing Fe, Mn, V show much bigger values of magnetic moment and, hence, are the most interesting for spintronics applications. Low mobility of vacancies along with adsorbed TM atoms is one more advantage of these materials due to the high migration barriers [10,16,20].

Method proposed [10] for experimental preparation of described composites involves irradiation by the focused electron beam in order to reach the atomic precision of defect creation which is followed by the high temperature coprecipitation of metal atoms.

This method was implemented for Fe, Co, Mo, Pt and In atoms [21,22]. All methods of defect creation and doping of graphene with a precise spatial control are quite difficult and have some

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constraints, but they are very important in graphene properties control.

Recent studies showed that vacancies in graphene may be created with a spatial precision of  $10 \times 10 \text{ nm}^2$  by the electron beam irradiation with accelerating voltage of 80 kV [23,24]. Enhanced chemical activity of these vacancies gives a possibility of the surface adatom capture.

Similar studies were also performed for bigraphene containing a monovacancy and adsorbed metal atom (Au, Mn, Mo) [25–27]. Doping of bigraphene epitaxially grown on 4H-SiC (0001) by Mo was investigated by both experimental and theoretical techniques. Molybdenum atoms were found to replace  $\alpha$ -carbon atoms and occupy the interlayer space [25]. Local magnetic moment of Mo atom is equal to  $1.81 \mu_B$  in this case. Composites of Mn and Au atoms adsorbed on the monovacancy and carbon atom in bigraphene have been simulated [26,27]. Charge transfer of 1.6 e to the defect-free graphene layer was observed in the case of Au doping. Local magnetic moment of Mn ( $1.76 \mu_B$ ) and high spin polarization of composite suggests the possibility of electron separation by the spin.

The present study is aimed to reveal the features of transition metals sorption on the bigraphene monovacancy by means of quantum chemistry. Metal atom migration from surface to the interlayer space through the monovacancy is also discussed.

## 2. Computational methods

Quantum chemical modeling was performed by generalized gradient approximation (GGA) of density functional theory (DFT) [28,29], plane wave basis set and PAW formalism [30,31] using VASP code [32–34]. Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional with the dispersion correction of Grimme [35] was used for taking into account van der Waals interactions.

Transition state and energy barriers of transition metal atom migration from the surface to the interlayer space through the monovacancy were found by using nudged elastic band (NEB) method [36].

Hexagonal unit cell of bigraphene ( $a = b = 2.45 \text{ \AA}$ ,  $c = 3.33 \text{ \AA}$ ) was optimized as a first step. Then, bigraphene supercell containing  $5 \times 5 \times 1$  unit cells and a single monovacancy was simulated. Two different positions of vacancy were considered (Fig. 1): the first is placed directly above the carbon atom in adjacent layer (*top*), and the second one is on top of the middle of the hexagon (*hex*).

The Monkhorst–Pack [37]  $k$ -point Brillouin sampling was used during the optimization. The  $k$ -point grid contained  $12 \times 12 \times 1$  points in the case of unit cell, and  $3 \times 3 \times 1$  points for supercell, respectively.

To avoid artificial interactions between adjacent bigraphene images in periodic boundary conditions, a vacuum interval along the normal direction to the carbon planes was fixed as 20 Å. Energy

cutoff was specified as 400 eV. Maximum acting forces being equal to 0.01 eV/Å were used as a stopping criterion for geometry optimization.

## 3. Results and discussion

### 3.1. Stability and properties of TM/bigraphene composites

The *top* vacancy was found to be more energetically favorable than the *hex* one. Formation energy of this vacancy is equal to 7.70 eV and its magnetic moment is  $1.2 \mu_B$ , while the formation energy of *hex* monovacancy is equal to 7.81 eV, and corresponding magnetic moment is  $0.9 \mu_B$ .

Probabilities of vacancy formation were estimated according to the Gibbs distribution:

$$P_i = \frac{e^{-\frac{E_{V_i}}{k_B T}}}{\sum_{i=1}^2 e^{-\frac{E_{V_i}}{k_B T}}}, \quad (1)$$

where  $E_{V_i}$  is the formation energy of *top* or *hex* vacancy, correspondingly.

Low mobility of monovacancies in graphene at normal conditions (migration barrier is equal to  $\sim 1.17 \text{ eV}$  [38]) allows to suppose that bigraphene vacancies will be formed according to their thermodynamic stability (see Table 1). It can be clearly seen that *top* vacancy is dominating in wide temperature range. However, formation of *hex* structure still may occur when TM atoms are deposited on bigraphene. Keeping this in mind, we then considered both types of composites.

Sorption of 3d transition metals, namely, Cr, Fe, Mn, Ti and V, was studied for structures with transition metal atoms adsorbed on the bigraphene surface (hereafter  $\text{TM}_{\text{out}}$ ), and also for those intercalated into the interlayer space (hereafter  $\text{TM}_{\text{in}}$ ). Transition metal atoms were adsorbed on monovacancy in both cases. For the sake of comparison binding energy of metal atoms with bigraphene was calculated as:

$$E = E_{\text{total}} - E_{\text{defect}} - E_{\text{Me}}/n, \quad (2)$$

where  $E_{\text{total}}$  is total energy of hybrid system,  $E_{\text{defect}}$  is energy of bigraphene supercell containing monovacancy,  $E_{\text{Me}}$  is unit cell energy of corresponding metal, and  $n$  is number of metal atoms in unit cell (for the most stable modification).

For better understanding of binding features, total energies of hybrid structure were also reduced to the most stable one for each type of metal.

According to our results (see Table 2), all metals tend to locate in the interlayer space which can be attributed to higher degree of coordinational saturation in this case comparing with adsorption on the surface.

Formation of additional bonds with carbon atoms leads to increase of TM atom positive charge. This, in turn, results in higher

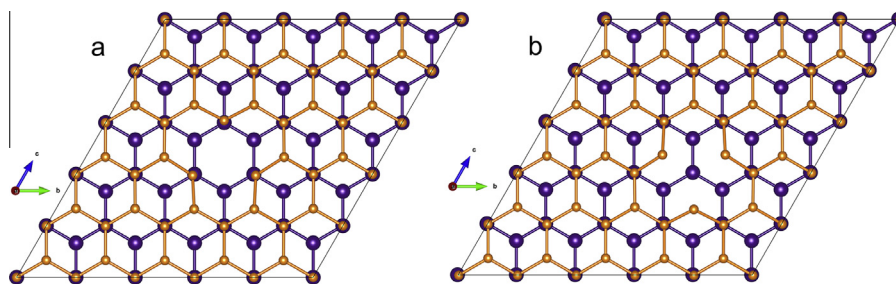


Fig. 1. (a) *hex* and (b) *top* type of bigraphene monovacancy. First- and second-layer carbon atoms are denoted as orange and purple balls, correspondingly. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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