Interaction of Transition Metal Atoms with Bigraphene Monovacancy: Theoretical Study

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Graphene and graphene-based materials are of a great interest due to their unique properties provided by the presence of Dirac cones [1]. 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 [2]. Rather big transition metal atoms can be adsorbed on the graphene as adatoms and replace one or two carbon atoms [3]. A number of experimental [4] and theoretical [3, 5] studies reveal the preferable sorption of 3d-metals on the vacancies in graphene. Strong covalent bonding of transition metal atom with carbon 2D structure makes these structures more stable than others.

This work is aimed to investigate the sorption of transition metal (TM) atoms on bigraphene monovacancy by means of quantum chemistry, and to shed the light on the migration of TM from surface to the interlayer space.

All calculations were performed within density functional theory (DFT) using plane wave basis set and PBE-GGA exchange-correlation functional with Grimme correction of dispersion interaction. In order to determine transition state and potential barriers of TM migration in bigraphene interlayer space, nudged elastic band method (NEB) was implemented.

According to our calculations, the most energetically favorable location of monovacancy is on top of the second-layer carbon atom (*top* configuration). However, metal atom deposition may lead to formation of so-called *hexagon* structure (vacancy on top of the hollow site in the second layer). Keeping this in mind, we then considered both types of complexes.

Then, adsorption sites of TM atoms (TM=Cr, Fe, Mn, Ti, and V) on the monovacancy both on the outer surface and in the interlayer space was studied. Latter ones were found to be more favorable for all considered metals (see Table 1) which can be attributed to the larger degree of coordinational saturation. Bonding with carbon atoms lead to the positive charge on metal atom and, then, to the higher polarization and binding energy increase. All TM atoms tend to be localized rather in *hexagon*-type vacancies than in the *top* ones. Only the composites of bigraphene with Cr, Mn and V were found to be interesting for spintronics applications due to the magnetic moments in these systems. It's worthnoting that the magnetic moment presence does not depend on the vacancy type or the adsorption site of metal (see Table 2).

References

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Table 1. Binding energies of TM with bigraphene monovancy depending on TM, vacancy type and the adsorption site

Type of Me	Interlayer space		Outer surface	
	hexagon	*top*	*hexagon*	*top*
Ti	-3.25	-2.90	-2.55	-2.14
V	-2.70	-2.33	-1.75	-1.52
Cr	-2.79	-2.45	-1.72	-1.62
Mn	-2.92	-2.73	-2.13	-1.93
Fe	-3.20	-2.99	-2.24	-1.92

Table 2. Magnetic moment of TM adsorbed on bigraphene monovancy depending on TM, vacancy type and the adsorption site

Type of Me	Interlayer space		Outer surface	
	hexagon	*top*	*hexagon*	*top*
Ti	0.00	0.00	0.00	2.00
V	0.94	0.57	1.00	3.00
Cr	2.00	1.91	2.00	2.00
Mn	1.72	2.32	3.00	3.00
Fe	0.00	0.00	0.00	0.00

Next, the migration of TM atom from the outer surface to the interlayer space and vice versa was simulated to estimate kinetic factors affecting the formation of the composites. Potential energy barriers of these migration paths are summarized in Table 3. It can be clearly seen that all the barriers are higher than 2.5 eV. The analysis of DOS in magnetic composite with the lowest barrier of migration shows (namely, Mn/bigraphene) reveals high degree of spin polarization in this system which makes this system interesting for utilization in spintronics devices.

Table 3. Potential barriers of TM migration from the outer surface of bigraphene to the interlayer space

Vacancy type	Type of Me	Potential barrier of migration, eV	
		to the interlayer space	to the outer surface
hexagon	Ti	5.88	6.59
	V	4.39	5.29
	Cr	3.69	4.76
	Mn	3.01	3.78
	Fe	2.63	3.60
top	Ti	6.93	7.67
	V	6.66	7.51
	Cr	3.73	4.55
	Mn	2.91	3.70
	Fe	2.55	3.61

Thus, according to our results, all composites are energetically stable. Bigraphene with Cr, Mn and V atoms adsorbed possess magnetic properties, in contrast to Ti and Fe. Bigraphene/Mn composites demonstrate high degree of spin polarization which allows suggesting them as promising materials for spintronics.