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Electronic and magnetic properties of transition-metal atoms absorbed on Stone–Wales defected graphene sheet: A theory study

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ABSTRACT

The adsorption of transition metal (TM) atoms on graphene monolayer with Stone–Wales (SW) defects was investigated using the first-principles density functional theory (DFT). The binding energy, geometry, charge transfer, band structure, density of states, and magnetic properties were calculated and analyzed. It was found that the presence of SW defect enhanced the interaction between TM adatoms and graphene and had a strong impact on the corresponding band structure. The partial density of states (PDOS) analysis suggested a strong hybridization of TM-3d orbital and C-2p orbital. These results indicated that the properties of graphene could be strongly modified by introducing Stone–Wales defect and adsorbed 3d transition-metal adatoms.

1. Introduction

Graphene consists of a two-dimensional carbon sheet in which the sp^2 hybridized carbon atoms are arranged on a hexagonal lattice, resembling a honeycomb network. Since its discovery in 2004 [1,2], it has attracted enormous attention due to its special physical properties, such as Dirac-type quasiparticles, giant mobility of charge carriers, and anomalous quantum Hall effect [3,4], showing various potential applications in the fields of light emitting diodes, gas sensors, spintronics and photovoltaic devices [5–8]. Nevertheless, the properties of graphene will be affected by its microscopic inner defects including Stone–Wales (SW) defects [9–14], vacancies [11], inverse Stone–Wales defects [15], adatoms, and 5–8 pair defects [16]. SW defect, for instance, is a typical topological defect in graphene and carbon nanotube, consisting of two pairs of pentagon–heptagon rings. The effects of SW defects in graphene and CNTs on their electronic and magnetic structures have been theoretically investigated in recent years [17–25]. Slanina et al. [24] studied the interaction between adatoms and SW defects in fullerene by first-principles simulation. Li Chen and co-workers [25] investigated the magnetism of graphene with SW defects, with or without absorbed hydrogen.

In another aspect, carbon-based materials decorated by transition-metal nowadays are of great interest and of which many interesting properties have been observed and investigated [26–33]. Moreover, combining the two hotspots aforementioned, some theoretical studies were performed on the atomic and molecular adsorption in graphene and CNTs with SW defects [22–35]. Their researches suggested that the physical and chemical parameters during adsorption process were extremely affected in the presence of SW defects. Yang et al. studied chromium-chain-embedded graphene and CNTs with a line defect by density functional theory (DFT), showing that the Cr-chain-embed defect acted as a quasi-one-dimensional half-metallic wire with a local spin band gap [36]. Krasheninnikov et al. studied transition metal (TM) atoms (Sc–Zn, Pt, and Au) embedded in defect graphene sheet, which exhibited interesting magnetic behavior [32]. Although several researches have been performed on the combination effects of defect and adatom for carbon-based materials, the current developments are still insufficient and unsatisfactory. Therefore, more investigations should be developed in this aspect.

In this paper, we present a detailed study on the combination effects of SW defects and a series of transition metal adatoms (Sc, Ti, V and Cr), on graphene sheet. Meanwhile, the corresponding results were compared with that of perfect graphene (PG) on which the TM adatoms were adsorbed at the interstitial site of a hexagon carbon ring.

2. Computational method

All calculations were implemented with the DMol^3 package [37] within the framework of DFT. A hardness conserving DFT semicore pseudopotential (DSPP) was used [38]. The electron exchange

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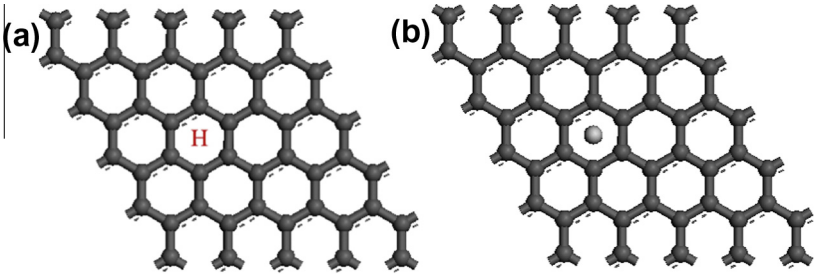

Fig. 1. (a) Optimized geometries of perfect graphene and (b) Sc absorbing on the hollow site.

correlation effects were incorporated using the generalized gradient approximation (GGA) with the Perdew, Burke and Ernzerhof (PBE) functional. The GGA description, in contrast to the local-density approximation (LDA) which tends to overbid neighboring atoms, can correct this error and improve the precision of total energy, atomization energy, and energy barrier. The double numerical plus polarization (DNP) basis set [39] was employed in order to obtain relatively accurate results of interaction energy between TM adatoms and graphene. Meanwhile, all the atoms in the unit cell were fully relaxed without any constraint.

In our work, a transition metal adatom was placed on the surface of a graphene monolayer in a $4 \times 4 \times 1$ supercell with a vacuum of 15 Å along the z axis. The Monkhorst–Pack K-point sampling scheme was employed with a $4 \times 4 \times 1$ grid for the Brillouin zone integration. The maximum root-mean-square convergent tolerance was less than 2×10^{-5} Ha and the force on each atom should be less than 0.004 Ha/Å in all cases.

On the other hand, the total energy of an isolated TM atom was approximated by placing a single atom in a cubic supercell with a side length of 13 Å and only the Gamma point was used to generate the K-point mesh in this case. Then the binding energy of the adatom–graphene system E_b can be obtained as:

$$E_b = E_t(AG) - E(A) - E_t(G),$$

where $E(A)$, $E_t(G)$ and $E_t(AG)$ stand for the total energies of an isolated TM atom, a graphene monolayer and the optimized adatom–graphene system respectively.

3. Results and discussion

3.1. TM adatoms adsorption on the perfect graphene

Before analyzing the atomic adsorption on a defected graphene system, we first considered a perfect graphene monolayer without any defect. It has been reported that the hollow site is the most stable adsorption site in this case [32,41]. Therefore, Sc, Ti, V and Cr were introduced to the center of a hexagon carbon ring within the monolayer. The optimized structures of perfect graphene and Sc absorbing on the hollow site were shown in Fig. 1. The corresponding results, as shown in Table 1, were consistent with previous researches. Chan and co-workers, for instance, studied adsorption of 12 different kinds of metal atoms on the graphene [30]. According to our simulations, Ti adatom has the largest adsorption energy of −2.220 eV. However, the distance between V adatom and its nearest-neighbor carbon atom was found to be the shortest. The previous investigations suggested that the large binding energy resulted from the contribution of the 3d-orbital of these TM adatoms. For comparison, we will later discuss the SW defect how to affect the interaction between adatoms and graphene.

Table 1
Distance between adatom and nearest-neighbor carbon atom (d_{AC}) and corresponding binding energy (E_b) for various transition metal atoms on perfect graphene (PG).

	Sc/PG	Ti/PG	V/PG	Cr/PG
E_b (eV)	−0.792	−2.220	−1.127	−0.334
d_{AC} (Å)	2.415	2.331	2.245	2.537

3.2. TM adatoms adsorption on the graphene with SW defects

The SW defect was built by rotating a C–C bond in the hexagonal network by 90° to convert four hexagonal rings into two pentagons and two heptagons. It was found in our work that the rotated C–C bond and contiguous ones were more or less stretched or compressed. Particularly, the length of the rotated C–C bond considerably decreased from 1.42 Å to 1.34 Å. Moreover, the defect atoms moved out of plane in the opposite direction to lower the energy by allowing the compressed C–C bonds to expand in its vicinity and the result was well consistent with the investigation by Qin and co-workers [40]. The adsorption of various TM adatoms (Sc, Ti, V and Cr) on such defected graphene was then systematically investigated. Fig. 2(a) exhibites the optimized structure of SW-defected graphene with an adatom of Sc. Considering the symmetry of SW defect, we introduced Sc adatom at three different hollow sites, namely, the centers of carbon heptagon (H1), pentagon (H2) and hexagon (H3). The corresponding binding energy in each case was obtained after optimization, showing that H1 site was energetically more favorable. Besides, the band structure of SW-defected graphene without adsorbed atom was analyzed as shown in Fig. 2(b). The value of the band gap was 0.726 eV which was larger than that of perfect garphene in our previous calculations, indicating that a band gap was induced in the presence of SW defects. Our calculation results were in agreement with the investigation by Azadi and co-workers [41].

Table 2 exhibits a series of parameters which detailedly describe the adatom–graphene adsorption, including the distance between the adatom and its nearest-neighbor carbon atom, binding energy, magnetic moment, and Mulliken charge. We found that Ti was the most energetically favorable adatom with a binding energy of −2.771 eV. In general, the binding energy of different TM adatoms on the SW-defected graphene varied from −0.997 eV to −2.771 eV, in contrast to the values using PG substrate within the range from −0.334 eV to −2.220 eV, showing that the interaction between adatoms and graphene was enhanced in the presence of SW defects. We also made a comparison of the distance between adatom and the nearest-neighbor carbon, namely d_{AC} in Tables 1 and 2, on both perfect and defected graphene substrate. As for the same kind of transition metal, the adatom was found closer to the nearest-neighbor carbon atom in case of SW-defected graphene due to the stronger interaction.

To deeply understand the mechanism, charge transfer between the adatom and graphene was studied by Mulliken population analysis during the adsorption process. Take, for instance, the case