Electronic and Magnetic Properties Modulated by Adsorption of 3d Transition Metal Atoms in Monolayer and Bilayer MoS₂ Sheets

Xue-Qing Wang · Wei-Guang Chen · Zhi-Li Zhu · Yu Jia

Received: 13 October 2014/Revised: 3 March 2015/Published online: 20 March 2015
© The Chinese Society for Metals and Springer-Verlag Berlin Heidelberg 2015

Abstract The adsorption effects of 3d transitional metal (TM) adatoms on electronic and magnetic properties of monolayer and bilayer MoS₂ sheets have been investigated by using first-principle calculations based on the density functional theory. The calculated results suggest that both monolayer and bilayer MoS₂ sheets have power abilities of absorbing 3d TM atoms. The interlayer adsorption of bilayer MoS₂ is relatively more stable than the surface adsorption of monolayer MoS₂. The 3d TM adatoms and the neighboring S atoms behave a clear covalent-binding character. It was found that TM adatoms induce certain impurity states within the band gap of the pristine MoS₂ sheet which result in the systems magnetically semiconducting or half metallic. The adsorbed systems for Cr and Co on the surface of monolayer MoS₂ sheet, as well as Sc, Cr and Fe in the interlayer of bilayer MoS₂ sheet exhibit half-metallic behavior. And the other 3d TM-adsorbed systems are magnetic semiconductor except for Ni species.

KEY WORDS: Transition metals; Adsorption; Ab initio calculation

1 Introduction

Two-dimensional (2D) layered crystal materials with atomic thickness have attracted extensive attention in recent years, such as graphene due to their potential applications in future electronics. Recently, the 2D MoS₂ crystals have been synthesized experimentally by a similar

exfoliation technique as applied to graphene [1]. Notably, unlike graphene, the monolayer (with a direct gap of 1.8 eV) and bilayer MoS₂ (with an indirect gap of 1.6 eV) are semiconducting which makes them as a promising and viable alternative to graphene for nanoscale. And, the modulation on the band structures [2–4], electronic [5, 6] and magnetic [7, 8] properties of isolated monolayer and bilayer MoS₂ has been the subject for a variety of theoretical and experimental investigations. Theoretical calculations suggest that the magnetism of MoS₂ nanosheets can be induced by electric field and external strain [9], grain boundaries [10], defect and dopant [11]. Recent experiments proved the magnetism in MoS₂ nanosheets attributed to the presence of magnetic edge states [12], and in irradiated MoS₂ attributed to a combination of point defects and edge states [13].

It is now well known that TM adatoms adsorption is an effective approach to modulate the properties of graphene-like 2D materials. Perfect [14–16] and defective [17] graphenes with single TM adatom have been found to exhibit interesting magnetic behavior. However, to the best of our

Available online at <http://link.springer.com/journal/40195>

X.-Q. Wang · Z.-L. Zhu (✉) · Y. Jia
International Joint Research Laboratory for Quantum Functional
Materials of Henan, Zhengzhou University, Zhengzhou 450001,
China
e-mail: zlzhu@zzu.edu.cn

X.-Q. Wang · Z.-L. Zhu · Y. Jia
School of Physics and Engineering, Zhengzhou University,
Zhengzhou 450001, China

W.-G. Chen
Department of Physics and Electronic Science, Zhengzhou
Normal University, Zhengzhou 450044, China

knowledge, systematic studies of magnetism in MoS₂ sheet via adsorption of TM adatoms are rare. In this work, we have carried out first-principles calculations and theoretical analysis to explore the adsorption effects of TM adatoms on electronic and magnetic properties of monolayer and bilayer MoS₂.

2 Model and Methods

The geometric, electronic structure and magnetic properties were calculated using the spin-polarized density functional theory (DFT) as implemented in the plane-wave basis set VASP code [18, 19]. Projector augmented wave (PAW) potentials [20] were used to describe the core electrons, and the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) [21] was adopted for exchange and correlation. A kinetic energy cutoff 500 eV was used in all simulations. The Brillouin zone (BZ) was sampled by using $5 \times 5 \times 1$ Gamma-centered Monkhorst–Pack grid. In the structural optimization, convergence of Hellmann–Feynman forces <0.01 eV/Å per atom was achieved.

3 Results and Discussion

The top and side views of relaxed structural configurations are shown in Fig. 1. A $4 \times 4 \times 1$ supercell was constructed to simulate the TM adsorption in monolayer and bilayer MoS₂ sheets. The optimized supercell has dimensions of $12.64 \text{ Å} \times 12.64 \text{ Å} \times 20 \text{ Å}$ in the current calculations. A vacuum space more than 10 Å was included in the unit cell to eliminate the coupling between neighboring cells.

Three high symmetry adsorption sites were considered for monolayer MoS₂ sheet, namely the top site of Mo atom (T_{Mo}) and S atom (T_{S}), and the hollow site of hexagonal ring (H), respectively. The adsorption geometry was obtained from the positions of atoms after relaxation. And, the site with the highest adsorption energy was considered as the favorable site. In this work, the adsorption energy (E_{a}) is defined as

$$E_{\text{a}} = E_{(\text{TM}+\text{MoS}_2)} - E_{\text{MoS}_2} - E_{\text{TM}}, \quad (1)$$

where $E_{(\text{TM}+\text{MoS}_2)}$ is the spin-polarized total energy for the optimized equilibrium configuration for the system of MoS₂ sheet absorbing with TM adatom, E_{MoS_2} is the total energy of the isolated MoS₂ sheet, and E_{TM} is the spin-polarized total energy of the corresponding adsorption adatom in its ground state.

Adsorption energies and structural parameters for the three sites considered for monolayer MoS₂ sheet are summarized in Table 1. It is found that all $3d$ TM atoms binding to the T_{Mo} sites are energetically more favorable than the other two adsorption sites. And the T_{S} sites have the highest total energy among the three adsorption sites. It is easy to understand that the smallest adsorption energy for T_{S} site is because there is only one nearest neighbor S atom for adsorbed TM adatoms. It was found that the adsorption energy at the most favorable surface adsorption site of T_{Mo} for Sc, Ti, V, Fe, Co, Ni atoms is larger than 2 eV, which indicate that the monolayer MoS₂ sheet has a power ability of adsorbing these TM atoms. However, it is only about 0.6 eV for Cr and Mn atoms which suggest that both of them are easy to diffuse in the surface of monolayer MoS₂ sheet.

In this study, we were particularly interested in the magnetic behavior of MoS₂ sheets via adsorption of TM adatoms. As shown in Table 1, all systems of MoS₂ sheet

Fig. 1 **a** Top view of three different adsorption sites of monolayer and bilayer MoS₂ sheets with the $4 \times 4 \times 1$ supercell; **b** side view of the supercell of monolayer MoS₂ sheet; **c** side view of the supercell of bilayer MoS₂ sheet

Table 1 Adsorption energy and structural properties for the top site of Mo atom (T_{Mo}), the top site of S atom (T_{S}), and the hollow site of hexagonal ring (H) investigated for 3d TM atoms adsorption in monolayer of MoS₂ sheet in this work

Atom	Site	E (eV)	Bond length (Å)	Height (Å)	M (μ_{B})
Sc	T_{Mo}	−2.18	2.43 (3)	1.61	0.88
	T_{S}	−1.17	2.42 (1)	2.42	1.19
	H	−1.68	2.29 (3)	1.39	0.59
Ti	T_{Mo}	−2.53	2.10 (3)	1.05	1.81
	T_{S}	−1.30	2.23 (1)	2.23	2.17
	H	−1.59	2.15 (3)	1.13	1.49
V	T_{Mo}	−2.27	2.41 (3)	1.31	2.78
	T_{S}	−1.02	2.14 (1)	2.14	3.23
	H	−1.25	2.09 (3)	1.03	2.57
Cr	T_{Mo}	−0.62	2.18 (3)	1.19	4.00
	T_{S}	−0.12	2.07 (1)	2.07	6.00
	H	−0.38	2.06 (3)	0.97	4.00
Mn	T_{Mo}	−0.61	2.14 (3)	1.12	3.00
	T_{S}	−0.11	2.03 (1)	2.03	5.00
	H	−0.47	2.06 (3)	0.96	3.00
Fe	T_{Mo}	−2.01	2.12 (3)	1.04	2.01
	T_{S}	−0.61	1.98 (1)	1.98	3.11
	H	−1.48	2.05 (3)	0.94	1.99
Co	T_{Mo}	−2.72	2.09 (3)	1.03	1.00
	T_{S}	−1.12	1.97 (1)	1.97	1.32
	H	−2.14	2.06 (3)	0.92	0.99
Ni	T_{Mo}	−3.29	2.10 (3)	1.11	0.00
	T_{S}	−1.76	1.96 (1)	1.96	0.00
	H	−2.74	2.09 (3)	1.02	0.00

The bond length (Å) presents the distance between the TM adatom and nearest sulfur atoms; the height (Å) is the perpendicular interval from the TM adatom to the surface plane of MoS₂ layer; M represents the local magnetic moments of TM adatom

absorbing with TM adatoms except for Ni are magnetic. In addition, the magnetic moments are associated with the adsorption sites. It shows that the atoms adsorbed on T_{S} sites are with the largest magnetic moments among the studied three adsorption sites. Furthermore, the Cr and Mn adatoms have the same moment value as that of free atoms. The adatoms on T_{Mo} and H sites exhibit near magnetic moments but both smaller than that of isolated adatoms. The magnetic moments of all TM adatoms at the most favorable adsorption site of T_{Mo} in monolayer MoS₂ sheet are 0.88, 1.81, 2.78, 4.00, 3.00, 2.01, 1.00 μ_{B} ($1 \mu_{\text{B}} = 9.27 \times 10^{-24}$ J/T), respectively.

For the TM-adsorbed MoS₂ sheets, electrons may be transferred from the TM adatoms to MoS₂ sheets which results the reduced magnetic moments in comparison with free atoms. In order to give a direct insight into the charge transfer, the charge density difference $\Delta\rho$ was calculated and analyzed

$$\Delta\rho = \rho[\text{MoS}_2 + \text{TM}] - \rho[\text{MoS}_2] - \rho[\text{TM}], \quad (2)$$

where $\rho[\text{MoS}_2 + \text{TM}]$ is the charge density of the whole system, $\rho[\text{MoS}_2]$ and $\rho[\text{TM}]$ are the charge densities of noninteracting bare MoS₂ and separated TM adatom. All charge densities were calculated in the same supercell. Figure 2 shows the optimized stable configurations and their corresponding difference in charge density for 3d TM adsorption in monolayer MoS₂ sheet. It is clearly seen that the charge densities are reduced at the center of TM adatoms, while additional charges appear between TM adatom and its neighboring S atoms along the bonding direction. The charge transfer from the TM atom to the MoS₂ monolayer will result in the reductions in unpaired electrons of the adatoms and thus depress their magnetic moment compared to that of free TM atom. On the other hand, the results indicate that TM adatom and the neighboring S atoms behave a clear covalent-binding character. The differences in the electro-negativity between S atoms and 3d TM adatoms Sc, Ti, V, Cr, Mn, Fe, Co and Ni are 1.22, 1.04, 0.95, 0.92, 1.03, 0.75, 0.70, 0.67, respectively [22], which are also less than the critical value 1.7 of ionic bond [23]. The difference of bonding atom number of the adatom of the MoS₂ monolayer as well as the variety of bond length will result in the charge transfer variations for different adsorption sites. So, the magnetic moment of the TM adatom is depended on the adsorption site.

To give a further insight of the electronic structure and magnetic properties of TM absorbed monolayer of MoS₂ sheet, the spin-polarized total states (DOS) were calculated and analyzed. As shown in Fig. 3, it is obvious that the adsorption of TM atoms induces certain impurity state within the band gap of the pristine MoS₂ sheet in all adsorption systems. Moreover, it is shown that impurity states around the Fermi level are formed from majority-spin electronic states for Sc, Ti and V adsorption systems, but from minority-spin electronic states for Cr, Mn, Fe, Co and Ni atoms. It is interesting that the Cr and Co adsorption systems present half-metallic behavior with a portion of impurity states formed from minority-spin electrons just across the Fermi level, resulting in the full spin polarization at the Fermi level.

Recently, the doping effects on the magnetic properties of monolayer MoS₂ were studied using first-principles calculations [24–27]. In particular, Cheng *et al.* [24] indicated that (Mo, X)S₂ ($X = \text{Mn, Fe, Co, and Zn}$) are the promising system of 2D diluted magnetic semiconductor. Similarly, Ramasubramaniam [25] also assumed that the Mn-doped monolayer MoS₂ may be an atomically thin dilute magnetic semiconductor. It is noticed that the substitution with certain magnetic impurities in MoS₂ may result in the thin dilute magnetic semiconductor. However, the adsorption in MoS₂ sheet induces the half-metallic behavior for some certain TM species.

Fig. 2 Top view of the charge density of T_{Mo} site adsorption of Sc **a**, Ti **b**, V **c**, Cr **d**, Mn **e**, Fe **f**, Co **g**, Ni **h** in monolayer MoS_2 , the isosurface value is $0.004 \text{ e}/\text{\AA}^3$

Fig. 3 DOS of the 3d TM atoms adsorbed on the surface of monolayer MoS_2 at the most favorable T_{Mo} site

In order to better understand the magnetic and electronic properties of MoS_2 sheets with adsorption of TM adatoms, we also examined the AB-stacked bilayer MoS_2 with TM adatoms on its surface or in its interlayer. It is found that the surface adsorption of TM atoms for bilayer MoS_2 is similar to that of monolayer MoS_2 . However, the interlayer

adsorption of TM atoms results in some interesting physics which are different with monolayer adsorption.

Table 2 lists the summary of results of interlayer adsorption in bilayer MoS_2 for the optimized structures. There are two typical interlayer adsorption sites for bilayer MoS_2 . They are labeled as B_{Mo} (bottom of the Mo atoms of the first-layer MoS_2), and H_{in} (between the center of two S–Mo–S hexagon rings of the upper and lower MoS_2 layers). The position of the bottom of the first-layer S atoms is the same as B_{Mo} according to the system symmetry. The B_{Mo} (directly on bottom of the first-layer Mo atoms) is the most favorable interlayer adsorption site for bilayer MoS_2 . It can be seen that the adsorption energy is larger than that of T_{Mo} site for monolayer MoS_2 which indicates that the interlayer absorption position is relatively more stable than the surface absorption site for MoS_2 sheet. On the other hand, the optimized interlayer spaces of bilayer MoS_2 after adsorbing TM adatoms are 4.18, 3.87, 3.90, 3.51, 3.47, 3.42, 3.42, 3.44, 3.48 Å for Sc, Ti, V, Cr, Mn, Fe, Co and Ni, respectively, which are larger than the reported value of 3.135 Å [28]. The local magnetic moments of the

Table 2 Adsorption energy and structural properties of TM adatoms adsorbed in the interlayer of bilayer MoS_2 sheet at the favorable adsorption site B_{Mo}

Atom	E (eV)	Bond length (Å)	Height (Å)	M (μ_B)
Sc	−3.37	2.48 (3)/2.49 (1)	1.69/2.49	0.73
Ti	−3.84	2.37 (3)/2.36 (1)	1.51/2.36	1.62
V	−3.35	2.26 (3)/2.25 (1)	1.65/2.25	2.52
Cr	−1.91	2.22 (3)/2.25 (1)	1.26/2.25	4.01
Mn	−1.76	2.19 (3)/2.26 (1)	1.21/2.26	3.00
Fe	−3.07	2.18 (3)/2.23 (1)	1.19/2.23	2.00
Co	−3.87	2.15 (3)/2.29 (1)	1.15/2.29	0.83
Ni	−4.17	2.19 (3)/2.26 (1)	1.22/2.26	0.00

Fig. 4 Spin-polarized total DOS of the 3d TM atoms adsorbed in the interlayer of bilayer MoS₂ sheet for the most stable configuration

interlayer with TM adatoms Sc, Ti, V, Cr, Mn, Fe, Co and Ni are 0.88, 1.81, 2.78, 4.00, 3.00, 2.01, 1.00 μ_B , respectively, which are near with the values of monolayer with adatoms.

The spin-polarized total DOS of the 3d TM atoms adsorbed in the interlayer of bilayer MoS₂ are presented in Fig. 4. It is shown that the Sc and Fe interlayer adsorption systems present half-metallic behavior, and these two species adsorption in monolayer MoS₂ are with magnetic semiconductor characters. Zhong *et al.* [29] also suggested that Fe-adsorbed system changes from semiconductor in monolayer MoS₂ to half metal for interlayer adsorption in bilayer MoS₂. It is noticed that the Co-adsorbed system exhibits semiconducting behavior in bilayer instead of half metal in monolayer MoS₂. However, the Cr-adsorbed system keeps the constant half-metallic property in both monolayer and bilayer MoS₂ adsorptions.

4 Conclusions

The electronic and magnetic properties and binding characters of TM atoms adsorbed on monolayer and bilayer

MoS₂ sheets were studied, and it was found that the adsorptions on T_{Mo} and B_{Mo} sites give the minimum energy for 3d TM atoms in monolayer and bilayer MoS₂ sheets. The interlayer adsorption is relatively more stable than the surface adsorption for MoS₂ sheet. All the studied systems of MoS₂ sheet absorbing with 3d TM adatoms are magnetic except for Ni species. Meanwhile, the Sc- and Fe-adsorbed systems change from semiconductor in monolayer MoS₂ to half metal in bilayer MoS₂. The Cr-adsorbed system keeps the constant half-metallic property in both monolayer and bilayer MoS₂ adsorptions, while the Co-adsorbed system exhibits semiconducting behavior in bilayer MoS₂ instead of half-metal in monolayer MoS₂.

Acknowledgments This work was financially supported by the National Basic Research Program of China (No. 2012CB921300).

References

- [1] K.S. Novoselov, D. Jiang, F. Schedin, T.J. Booth, V.V. Khotkevich, S.V. Morozov, A.K. Geim, *Proc. Natl. Acad. Sci. USA* **102**, 10451 (2005)
- [2] T. Cheiwchanchamnangij, W.R.L. Lambrecht, *Phys. Rev. B* **85**, 205302 (2012)
- [3] Y. Zhou, P. Yang, H. Zu, F. Gao, X. Zu, *Phys. Chem. Chem. Phys.* **15**, 10385 (2013)
- [4] Y. Ma, Y. Dai, M. Guo, C. Niu, Y. Zhu, B. Huang, *ACS Nano* **6**, 1695 (2012)
- [5] H. Wang, L. Yu, Y.H. Lee, Y. Shi, A. Hsu, M.L. Chin, L.J. Li, M. Dubey, J. Kong, T. Palacios, *Nano Lett.* **12**, 4674 (2012)
- [6] H. Qiu, L.J. Pan, Z.N. Yao, J.J. Li, Y. Shi, X.R. Wang, *Appl. Phys. Lett.* **100**, 123104 (2012)
- [7] Y. Li, Z. Zhou, S. Zhang, Z. Chen, *J. Am. Chem. Soc.* **130**, 16739 (2008)
- [8] C. Ataca, H. Sahin, E. Akturk, S. Ciraci, *J. Phys. Chem. C* **115**, 3934 (2011)
- [9] L. Kou, C. Tang, Y. Zhang, T. Heine, C. Chen, T. Frauenheim, *J. Phys. Chem. Lett.* **3**, 2934 (2012)
- [10] Z. Zhang, X. Zou, V.H. Crespi, B.I. Yakobson, *ACS Nano* **7**, 10475 (2013)
- [11] R. Shidpour, *Nanoscale* **2**, 1429 (2010)
- [12] S. Mathew, K. Gopinadhan, T.K. Chan, X.J. Yu, D. Zhan, L. Cao, A. Rusydi, M.B.H. Breese, S. Dhar, Z.X. Shen, T. Venkatesan, J.T.L. Thong, *Appl. Phys. Lett.* **101**, 102103 (2012)
- [13] S. Tongay, S.S. Varnoosfaderani, B.R. Appleton, J. Wu, A.F. Hebard, *Appl. Phys. Lett.* **101**, 123105 (2012)
- [14] K.T. Chan, J.B. Neaton, M.L. Cohen, *Phys. Rev. B* **77**, 235430 (2008)
- [15] H. Sevincli, M. Topsakal, E. Durgun, S. Ciraci, *Phys. Rev. B* **77**, 195434 (2008)
- [16] A.V. Krasheninnikov, P.O. Lehtinen, A.S. Foster, P. Pyykkö, R.M. Nieminen, *Phys. Rev. Lett.* **102**, 126807 (2009)
- [17] B. Uchoa, T.G. Rappoport, A.H. Castro Neto, *Phys. Rev. Lett.* **106**, 016801 (2011)
- [18] G. Kresse, J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996)
- [19] G. Kresse, J. Hafner, *Phys. Rev. B* **48**, 13115 (1993)
- [20] P.E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994)
- [21] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996)

- [22] R.E. Dickerson, H.B. Gray, G.P. Haight (eds.), *Chemical Principles*, 3rd edn. (Benjamin Cummings Publishing Co., Inc., Menlo Park, 1979)
- [23] P. Atkins, L. Jones, *Chemistry: Molecules, Matter and Change*, 3rd edn. (WH Freeman and Company, New York, 1997)
- [24] Y.C. Cheng, Z.Y. Zhu, W.B. Mi, Z.B. Guo, U. Schwingenschlögl, Phys. Rev. B **87**, 100401 (2013)
- [25] A. Ramasubramaniam, Rev. B **87**, 195201 (2013)
- [26] R. Mishra, W. Zhou, S.J. Pennycook, S.T. Pantelides, J.C. Idrobo, Phys. Rev. B **88**, 144409 (2013)
- [27] A.N. Andriotis, M. Menon, Phys. Rev. B **90**, 125304 (2014)
- [28] T. Böker, R. Severin, A. Müller, C. Janowitz, R. Manzke, D. Voß, P. Krüger, A. Mazur, J. Pollmann, Phys. Rev. B **64**, 235305 (2001)
- [29] Z.Y. Huang, G.L. Hao, C.Y. He, H. Yang, L. Xue, X. Qi, X.Y. Peng, J.X. Zhong, J. Appl. Phys. **114**, 083706 (2013)