Project Title:

First-principles study of transition-metal atoms adsorption on MoS_2 monolayer

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1. Introduction

Over the last decades, two dimensional (2D) layer materials have attracted extensive attention from both experimentalists and theorists owing to its exceptional structure, novel electronic properties, rich physics and potential applications, especially since the discovery of graphene. MoS_2 is a typical layered transition metal dichalcogenide material formed by the stacking of weakly interacting 2D S–Mo–S layers like graphite, which shows distinct electronic, optical and catalytic properties. Many possible applications have been investigated, such as lubricants, catalysis, transistors, photo emitting devices, hydrogen storage, and Li-ion batteries. Recently, 2D MoS_2 monolayer has been fabricated by different methods, such as mechanical exfoliation, chemical exfoliation, hydrothermal synthesis and chemical vapor deposition. MoS_2 monolayer is the direct band gap of 1.9eV, which is different from the indirect band gap of 1.23eV for bulk MoS_2, which is favorable for optoelectronic applications. With its distinctive performances (due to its excellent properties), MoS_2 monolayer has been a potential candidate as the complement or substitute to graphene. In exploring the potential applications for nanoscale electronics and spintronic devices of the MoS_2 monolayer, many methods have been studied to modulate the electronic and magnetic properties of the MoS_2 monolayer, such as defect, chemical doping, elastic strain, alloy, and chemical adsorption. It is well known that TM atoms adsorption is a promising and effective method for modulating the electronic and magnetic properties of materials, and it has demonstrated great potential in many materials, such as graphene, BN monolayer, ZnO sheet, SiC nanotube, and GaN nanotube. However, the systematic research of the structures, and electronic and magnetic properties for the TM (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) atoms adsorption on the MoS_2 monolayer so far is limited.

In this work, we systematically investigated the adsorption energy, stable geometry, and magnetic and electronic properties of TM atoms adsorbed on the MoS_2 monolayer. We found the variation of the adsorption energy for the different TM atoms adsorbed on the MoS_2 monolayer maybe related to their number of *d* electrons. We also found adsorption of the different TM atoms can effectively modulate the band structures and the magnetic properties of the MoS_2 monolayer.

2. Computational methods

All the calculations are performed within the density functional theory (DFT) using projector-augmented-wave potentials implemented in Vienna *ab initio* simulation package(VASP). The exchange-correlation potential is described by the generalized gradient approximation (GGA) of the Perdew Burke–Ernzerhof (PBE) parameterization. A cutoff energy of 500eV is used for the plane-wave expansion. The Billouin Zone (BZ) is sampled by the Monkhorst–Pack (MP) scheme with 5x5x1 mesh for the structural optimizations and11x11x1 mesh for computing the band structure. For all the structures, geometry optimization was performed with the convergence thresholds of 10^{-4} eV for energy and 0.01eV/Å for Hellmann–Feynman force without any symmetry constraints.

In this work, we only consider TM atoms adsorption on the one side of the perfect MoS_2 monolayer. The adsorption system is modeled using one TM atom adsorbed on a 4x4 MoS_2 monolayer supercell, which contains 32 S atoms, 16 Mo atoms and one TM adatom. The calculated lattice constant of the MoS_2 monolayer is 3.183Å, which is consistent with the previous reports. The 4x4 supercell ensures a large distance of 12.732Å for the separation between neighboring adatoms. A vacuum layer of more than 12Å along the z-axis (perpendicular to the MoS_2 layer) is adopted to avoid the interaction between adjacent images. In our calculation, the TM adatom was first placed in three high symmetry positions on the surface of the MoS_2 monolayer (TMo, TS, and H sites) and then relaxed. The configurations of the TM atoms adsorption systems are shown in Fig. 1. The structures of TMo, TS and H are, respectively, that the TM adatoms occupy the sites above the Mo atom, S atom and the hollow site of the hexagonal ring. To check the relative stability of different adsorption configurations, we have calculated the adsorption energy (E_{ads}) using the following formula:

$$E_{ads}=E_{monolayer}+E_{atom}-E_{total} \quad (1)$$

where $E_{monolayer}$ is the total energy of the 4x4 supercell for the MoS_2 monolayer, E_{total} is the spin-polarized total energy of the optimized adsorption configurations, and E_{atom} is the spin-polarized total energy of the isolated TM atom in its ground state. More strictly speaking, the

adsorption energy should be described in terms of the chemical potential of the adatom, which is not larger than the total energy of the isolated adatom in its ground state. For simplicity, we use the total energy of the isolated adatom instead of its chemical potential in the following calculations. In order to determine the ground state of TM atom adsorbed MoS_2 monolayer, we first carried out both spin-unpolarized and spin-polarized total energy calculations including geometry optimization.

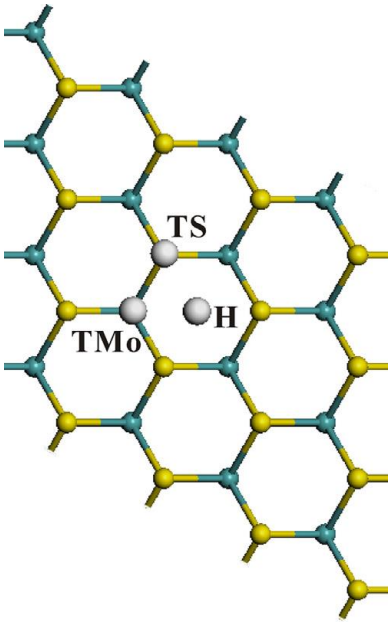

Fig. 1. Schematic view of three sites of a TM atom adsorbed on the MoS_2 monolayer: TS, TMo and H stand for the sites above the S atom, Mo atom, and the center of the hexagonal ring of the MoS_2 monolayer, respectively. The yellow, green and white balls represent S, Mo and TM atoms, respectively. (For interpretation of the references to color in this figure legend.)

Table1 Calculated adsorption energies (E_{ads}) of the TM atoms adsorbed on the MoS_2 monolayer at the most stable adsorption sites, the total magnetic moments (μ_{total}) of the system, the magnetic moments of the adatom (μ_{adatom}) and the free atom (μ_{atom}), the magnetic moments in the parentheses based on Hund's rule, amounts of charge transferred (CT) from the TM atom to the MoS_2 monolayer.

Atom	Site	E_{ads} (eV)	μ_{total} (μ_B)	μ_{adatom} (μ_B)	μ_{atom} (μ_B)	CT (e)
Sc	H	2.444	1	0.223	1 (1)	1.461
Ti	H	2.678	0	0	4 (2)	1.248
V	TMo	2.597	4.990	2.988	5 (3)	0.958
Cr	TMo	1.207	5.996	4.136	6 (6)	0.695
Mn	H	1.221	2.994	3.019	5 (5)	0.831
Fe	TMo	2.303	1.998	2.111	4 (4)	0.613
Co	TMo	2.764	0.993	0.960	3 (3)	0.467
Ni	TMo	3.514	0	0	2 (2)	0.385
Cu	TMo	1.307	0.989	0.125	1 (1)	0.389
Zn	TMo	0.037	0	0	0 (0)	0.065

3. Results and discussion

Table1 shows the adsorption energies of the TM atoms adsorbed on a MoS_2 monolayer at the most stable adsorption sites. It can be seen that the TMo site is the most favorable surface adsorption site for the V, Cr, Fe, Co, Ni, Cu and Zn atoms, while the Sc, Ti and Mn atoms prefer to adsorb on the H site. All the TM atoms do not favor the TS site. The adsorption energies show that all TM atoms can be chemically adsorbed on the MoS_2 monolayer even at room temperature except for the Zn atom. Fig. 2 shows the comparison of the $d_{TM\text{-}S}$ ($d_{TM\text{-}Mo}$) and the sum of the covalent radii $r_{TM}+r_{Mo}$ ($r_{TM}+r_{Mo}$) along the 3d TM series, the $d_{TM\text{-}S}$ ($d_{TM\text{-}Mo}$) is the distance of the TM adatom and the nearest S (Mo) at the most stable configurations. The results suggest that the TM–S bond length is very close to the sum of the covalent radii for Sc to Cu adsorbed configurations; even the maximum difference for Cr was only 9%. These features indicate that the interaction of adatoms (Sc to Cu) with the nearest S atoms can be easily qualified as a covalent interaction, and such TM atoms are considered to be chemisorbed. At the same time, we also find the TM–Mo bond lengths for the Fe, Co and Ni adsorbed configurations are close to the sum of covalent radii, while the TM–Mo bond lengths for the Cr, Mn and Zn adsorbed configurations are far away from the sum of the covalent radii. So the adsorption energy for the Cr, Mn and Zn atoms should be smaller. The Zn–S (Mo) bond length is larger the sum of the covalent radii by more than 50%. Thus the Zn adatom is very weakly bonded to the S (Mo) atom and is considered as physical adsorption, which also shows that it is difficult to realize the isolate Zn atom adsorbed on the MoS_2 monolayer experimentally because the atom would tend to diffuse and aggregate into metallic clusters. The variation of the adsorption energies with different TM atoms may be related to their d electrons as shown in Fig. 3. The Sc, Ti and V with a small number of d electrons form strong bond with the adsorption energies of 2.444, 2.678 and 2.597eV, respectively. The adsorption energies of Cr and Mn with the half-filled d electrons show minima between two maxima. Ni with 8 d electrons has the largest adsorption energy. While the adsorption energies of Cu and Zn with full filled d electron are small, the adsorption energy of Zn is only 0.037eV. The

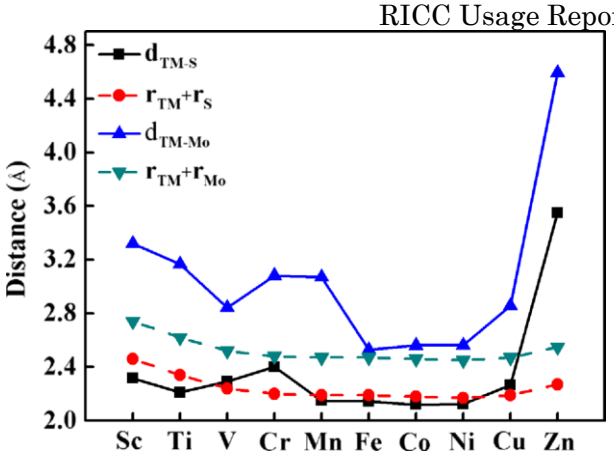

Fig. 2. Calculated TM adatom and the nearest S (Mo) atom distances (d_{TM-S}, d_{TM-Mo}) corresponding to the most adsorption configurations. The dashed line represents the sum of r_{TM} and r_S (r_{Mo}) for TM atom and S (Mo) atom.

overall variation trend of the adsorption energies for different TM atoms with the number of d electron is consistent with the analysis of the bond length of TM–S (Mo), which is similar to the results for TM atoms adsorbed graphene, Ge nanowire and SiC nanotube.

Magnetic properties of TM adatom and the system are important aspects to study the TM atom adsorbed MoS_2 monolayer. The magnetism of the TM atom adsorbed MoS_2 monolayer should originate from the adsorbed TM atoms, because the ground state of pure MoS_2 monolayer is nonmagnetic. In Table1, we show the local magnetic moments of the TM adatoms, the whole system and the free TM atoms at the most stable adsorption configurations. From the results, we can see that no magnetism is observed for the Ti, Ni and Zn adsorbed systems. The local magnetic moments of Sc, V, Cr, Mn, Fe, Co and Cu are 0.223, 2.988, 4.136, 3.019, 2.111, 0.960 and 0.125μ_B, respectively, which are smaller than those of the free TM atoms, and the local magnetic moments of V, Cr, Mn, Fe, and Co are reduced about 2μ_B. To explore the origin of the reduction of the magnetic moments for the TM adatoms, we have calculated the charge transfer between the TM adatom and the MoS_2 monolayer using Bader charge analysis, as listed in Table1. From the results, it can be seen that there are obvious electrons transfer from the TM atom to the MoS_2 monolayer, which will induce the reduction of magnetic moment for the TM adatom. At the same time, we find that the number of the electron transferred reduces gradually from the Sc to Zn except Cr, which is related with the Pauling electronegativity of the TM adatom. The contour of the charge density difference for the TM atoms adsorbed system except for Zn. The charge density difference is obtained as the following formula:

$$\Delta\rho = \rho_{total} - \rho_{monolayer} - \rho_{addatom} \quad (2)$$

where the ρ_{total}, $\rho_{monolayer}$ and ρ_{adatom} are the charge density of the whole adsorbed system, the MoS_2 monolayer and the TM adatom, respectively. Fig. 4 shows the obvious electron transfer between the TM adatom and the MoS_2 monolayer. So the interactions between TM

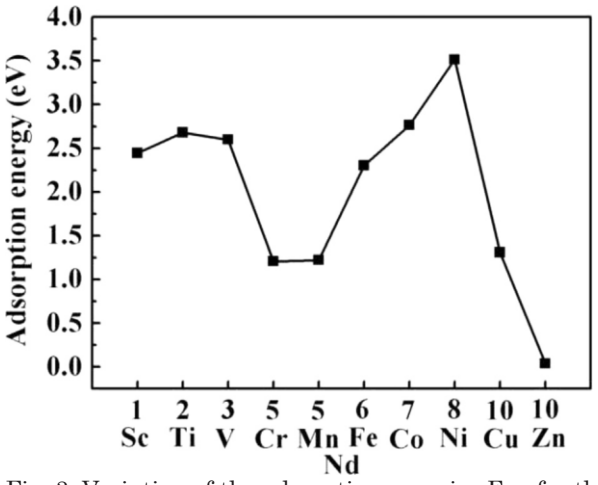

Fig. 3. Variation of the adsorption energies E_{ads} for the most stable configuration of the TM atoms with respect to the number of d electrons N_d of the 10 TM elements.

adatoms and the MoS_2 monolayer also exhibit partially ionic property. To further illuminate the reason of the reduction of magnetic moment, the projected density of states (PDOS) of the TM adatoms show that the Ti, Ni and Zn adatoms are nonmagnetic. The magnetic moment of the TM adatom is mainly contributed from the 3d electron orbital except Cr and Cu, especially the magnetic moment of Cu adatom mainly arises from the 4s electron orbital, which may be because there is only one electron on the 4s state for the ground state Cr and Cu atoms. The electrons transfer from 4s into 3d states for the TM adatoms can be observed, which will result in the reduction of unpaired electrons and thus induce the decrease of the magnetic moment of the TM adatoms, as in the case of the TM adatoms adsorbed on the grapheme or BN sheet. The spin density contour of the magnetic system can be seen that the magnetic moment is mainly contributed by the TM adatom. We also find the nearest and the second nearest S and Mo atoms have opposite spin density with the Mn, Fe and Co atoms, respectively. So the total magnetic moment of the system is smaller than the local magnetic moments of the adatom as shown in Table1. It can be seen that the magnetic moment is mainly contributed by the s orbital of the Cu adatom.

4. Conclusions

In summary, we systematically investigated the adsorption energy, stable geometry, and magnetic and electronic properties of transition metal (TM) (from Sc to Zn) atoms adsorbed on

the MoS_2 monolayer by first principle calculations. All the TM atoms are chemically adsorbed on the MoS_2 monolayer except for the Zn atom. The results show that the most stable adsorption sites are the TMo site, while the Sc, Ti and Mn atoms prefer the H site. The adsorption energies vary obviously with different TM atoms, which maybe related to their number of d electrons. By comparison of the bond length of TM–S (Mo) and the sum of the covalent radii $r_{TM}+r_S$ ($r_{TM}+r_{Mo}$) as well as the analysis of the electron transfer between the TM adatom and the MoS_2 monolayer, we found the bond character of TM atom and the MoS_2 monolayer exhibits mainly covalent property, which also shows a partially ionic property. The adsorption of Sc, V, Cr, Mn, Fe, Co and Cu produces magnetism for the TM atom adsorbed MoS_2 monolayer, while the Ti, Ni and Cu adsorbed MoS_2 monolayer is nonmagnetic. The total magnetic moments are contributed by the TM adatom. The local magnetic moment of the TM adatom is smaller than the free TM atom, which originates from the electron transfer from the TM adatom to the MoS_2 monolayer and the redistribution of the electron for TM atom 4s and 4d states. The narrow gap direct or indirect semiconductor and semimetal or narrow gap director indirect semiconductor for different spin channels can be obtained in different TM atom adsorbed MoS_2 monolayer. These results can have potential application in spintronics.