Manipulation of The Magnetic Properties of Janus WSSe Monolayer By The Adsorption of Transition Metal Atoms

Kai Chen  
Xiamen University

Weiqing Tang  
Xiamen University

Mingming Fu  
Nanchang University

Xu Li  
Xiamen University

Congming Ke  
Xiamen University

Yaping Wu  
Xiamen University

Zhiming Wu (zmwu@xmu.edu.cn)  
Xiamen University  https://orcid.org/0000-0002-9642-6449

Junyong Kang  
Xiamen University

Keywords: Magnetic anisotropy, First-principles calculations, Janus TMDC, Surface adsorption

DOI: https://doi.org/10.21203/rs.3.rs-377207/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License. Read Full License
Abstract

Two-dimensional Janus materials have great potential for the applications in spintronic devices due to their particular structures and novel characteristics. However, they are usually non-magnetic in nature. Here, different transition metals (TMs: Co, Fe, Mn, Cr, and V) adsorbed WS\textsubscript{Se} frameworks are constructed, and their structures and magnetic properties are comprehensively investigated by first-principles calculations. The results show that the top of W atom is the most stable absorption site for all the TM atoms, and all the systems exhibit magnetism. Moreover, their magnetic properties significantly depend on the adsorbed elements and the adsorbent chalcogens. A maximal total magnetic moment of 6 \( \mu \text{B} \) is obtained in the Cr-adsorbed system. The induced magnetism from S-surface-adsorption is always stronger than that for the Se-surface-adsorption due to its larger electrostatic potential. Interestingly, the easy magnetization axis in the Fe-adsorbed system switches from the in-plane to the out-of-plane when the adsorption surface changes from Se to S surface. The mechanism is analyzed in detail by Fe-3d orbital-decomposed density of states. This work provides a guidance for the modification of magnetism in low-dimensional systems.

Introduction

Spintronics is an emerging technology exploiting the spin degree of freedom and holds great promise for next-generational devices with high speed and low power consumption [1-4]. Since the discovery of mechanically exfoliated graphene in 2004, there sets off a research boom on spin-electronic devices based on two-dimensional (2D) materials, especially on 2D graphene owing to its long spin diffusion length and coherent time [5-7]. However, graphene possesses zero band gap, limiting its development in optoelectronic devices [5]. Recently, transition metal dichalcogenides (TMDCs) are considered as promising candidates for optoelectronic applications due to the rich variety of materials and the tunable bandgap [8-11]. They generally exhibit a sandwich structure with the form of X-M-X (MX\textsubscript{2}, where M and X represent transition metal and chalcogen element, respectively), such as WS\textsubscript{2} and WSe\textsubscript{2}, whose upper and lower layers have the same element. Interestingly, a new type of TMDCs, namely Janus structure of X-M-Y (X and Y represent different chalcogen elements, respectively) [12-14], shows many new features owing to the particular structures, such as strong Rashba spin-orbit coupling (SOC) effect [15, 16], large valley splitting [17, 18], strong piezoelectric effect [19], and so on. For example, Yao et al reported that the Rashba coefficient of single-layer WSeTe is up to 0.92 eVÅ [15], which is even higher than that in traditional semiconductor heterojunctions of InGaAs/InAlAs[20] and LaAlO\textsubscript{3}/SrTiO\textsubscript{3} [21]. Zhou et al predicted that a large valley splitting of about 410 meV could be produced in Janus WS\textsubscript{Se} monolayer by the coupling with a MnO substrate [17].

Despite of the above-mentioned excellent properties, Janus TMDCs are intrinsically non-magnetic, which hinders its further application in spin-electronic devices. Up to now, the design and manipulation of low-dimensional magnetic materials is a major challenge. The previous research have introduced magnetism in conventional TMDCs through various approaches including the adsorption or doping of transition
metal (TM) atom [22-25], the introduction of defects, chirality and edge structure [26-29], etc. Although it is predicted that the substitution of 3d-TM atoms can induce magnetism and modify the band structures in Janus MoSSe monolayer [30], such method is experimentally difficult to implement. In comparison, the surface atom adsorption is an effective and convenient way to tailor the physical properties of 2D materials. However, how the adsorbed atoms modify the electronic structure and physical properties of Janus TMDCs is rarely reported. The mechanism of magnetic regulation in Janus TMDCs remains unclear.

In this work, we construct different TMs (Co, Fe, Mn, Cr, and V) adsorbed WSSe frameworks, and comprehensively study their structures and magnetic properties by using first-principles calculations, especially their magnetic anisotropy energies (MAEs) at different adsorption surfaces. Their stable structures are identified by the calculated total energies, and their magnetic properties are analyzed by the total density of states (DOS) and differential charge densities. It is found that the magnetic moment and easy magnetization axis significantly depend on the adsorbed elements and the adsorbent chalcogens. In the case of Fe adsorption, the easy magnetization axis of the system can be switched from in-plane (Se side) to out-of-plane direction (S side). The physical mechanism of magnetic anisotropy is further analyzed by Fe-3d orbital-decomposed DOS.

**Calculation Details**

All calculations are performed using the Vienna ab initio software package (VASP) based on density functional theory with spin-polarized periodic [31]. The generalized gradient approximation (GGA) with the Perdew-Burke-Emzerhof (PBE) description is adopted for the exchange-correlation potential [32,33]. In order to rule out the interaction between TM atoms, a 4×4×1 supercell is selected. A 15 Å vacuum layer is used to eliminate the interlayer interaction and the periodic image. The interlayer vdW interaction is described by using the DFT-D2 method [34]. All structures are fully relaxed until the force and the total energy reach the convergence criterion, where the convergence values are set to $10^{-6}$ eV and 0.01 eV, respectively. The Brillouin zone is sampled with $7\times7\times1$ and $11\times11\times1$ dense mesh by using Gamma-centered Monkhorst-Pack grid in structural optimization and self-consistent calculation, respectively. The cutoff energy of the plane wave expansion is optimized to 500 eV, which ensures the convergence of the system. The MAE is calculated by taking the difference between the total energies as the magnetization oriented along the in-plane [100] and out-of-plane [001] directions: $\text{MAE} = E_{\text{in}} - E_{\text{out}}$. SOC is considered in the calculations [35,36].

**Results And Discussion**

To simulate the adsorption of TM atoms on Janus WSSe monolayer, we first construct a monolayer WSSe supercell consisting of 48 atoms, as shown in the Figure 1(a). Pristine Janus WSSe monolayer possesses a spatial $C_{3v}$ symmetry and exhibits the sandwich structure with one layer of S atoms, one layer of W atoms, and one layer of Se atoms. The monolayer thickness is calculated to be 3.35 Å. The planar projection shows an ideal hexagonal honeycomb structure with a lattice constant of 3.24 Å. The
bond lengths of W-S (d_{W-S}) and W-Se (d_{W-Se}) are 2.42 Å and 2.54 Å, respectively, and the bond angle θ_{S-W-}
Se is 81.76°, which are consistent with the previous reports [37]. Figure 1(b) shows the planar average electrostatic potential energy of the monolayer WSSe, where Z₀ is the thickness of the unit cell, Z is a coordinate variable, and Z/Z₀ means the relative position in the unit cell. As expected, the broken mirror symmetry along the Z direction results in the different potential energies on the S and Se surfaces, and the S surface has the larger electrostatic potential. Meanwhile, we also calculated the spin-resolved DOS of Janus WSSe monolayer. As shown in Figure 1(c), the DOS for the spin-up and spin-down channels are symmetrically distributed, indicating that the ground state is non-magnetic. It can also be seen that the band gap of Janus WSSe monolayer is about 1.7 eV, which is between that of WS₂ [38] and WSe₂ [39].

To induce magnetism in Janus WSSe, five different kinds of 3d-TM atoms (Co, Fe, Mn, Cr, and V) were adopted to adsorb on the surface of monolayer WSSe. On account of the structural symmetry, three possible adsorption sites are considered for atom adsorption on either the S or Se layer. As shown in Figure 2, the three cases are on the top of W atom (labeled as T_{WS} or T_{WSe}), on the hollow of hexagonal ring (labeled as H_{S} or H_{Se}), and on the top of S (Se) atom (labeled as T_{S} or T_{Se}). The total energies for these configurations are calculated to determine the most stable adsorption site. The results are shown in Table 1. It is clearly seen that when the TM atom is located on T_{WS} or T_{WSe}, the system has the lowest energy, indicating that the top of W atom is the most stable adsorption site. Hence, all the following calculations of electronic structures and magnetic properties are based on this configuration. Table 2 lists the calculated results including the bond length (d_{W-S}, d_{W-Se}, and d_{TM-S(Se)}), the height difference (∆h) between the upper layer S(Se) atom and the TM atom, the total magnetic moment M_{T}, the local magnetic moment M_{L} of TM atom, and MAE. Obviously, the structure parameters of d_{W-S} and d_{W-Se} are different from that of the primitive Janus WSSe. For the case that the TM atoms are adsorbed on the S-side of WSSe, the d_{W-S} is elongated by comparing with that in primitive Janus WSSe (2.41 Å), whereas the d_{W-Se} is almost kept same (2.54 Å). Similarly, this behavior occurs in the case that TM atoms are adsorbed on the Se-side, where the d_{W-Se} is also expanded. This is because that the covalent interaction between the TM atoms and the neighboring S(Se) atoms weakens the coupling between W and S(Se), and then leads to the extension of the W-S(Se) bond. In addition, the d_{TM-S(Se)} and the ∆h for the different adsorption surface are distinct. They exhibit the smaller value for the S adsorbing surface, which is owing to the stronger electronegativity for the S atom, as revealed in Figure 1(b).

In the following, we focus on the magnetic behavior of Janus WSSe after the adsorption of TM atoms. As shown in Table 2, the distinguished magnetism for the different configurations is observed. A maximal M_{T} of 6 μB is obtained in Cr-adsorbed system. Interestingly, different adsorption surfaces do not cause an obvious difference in the M_{T}, albeit there is a relatively big difference in the M_{L}. The calculated M_{L} are 0.92, 1.83, 2.73, 4.80, and 2.90 μB on the S surface, and 0.93, 1.88, 2.78, 4.86, and 2.98 μB on the Se surface for Co, Fe, Mn, Cr, and V adatoms, respectively. Notably, the M_{L} on the S surface is always smaller than that on the Se surface for each kind of TM adatom, indicating the stronger induced magnetism in Janus WSSe for the case of S adsorbing surface.
To gain insight into the magnetic properties of the different systems, the spin-resolved total DOS is calculated with the results shown in Figure 3. The positive and negative values denote the majority and minority spin channels, respectively, and the Fermi level is set to be zero. The majority and minority spin states in all the systems exhibit asymmetric characterization, confirming the existence of the magnetism. Compared with the DOS of pure Janus WSSe shown in Figure 1(c), some new impurity states appear in the bandgap in all the systems. These impurity states are mainly attributed to the TM-3d states, a small amount of hybridization of the first nearest S-3p or Se-3p states, and the second nearest W-5d states [22]. Due to the localization of TM-3d orbitals, the impurity states show a narrow energy range. Notably, in the case of Co, Fe, and Mn adsorptions, the induced impurity states around Fermi level only distribute in the minority spin channel, demonstrating a 100% spin polarization. Whereas for the other two cases, there are only the majority spin states in the band gap. In addition, due to the influence of the internal electrostatic potential for the different adsorption surfaces, the energy level and intensity of impurity states are slightly different. These results suggest that the magnetic properties strongly depend on the adsorbed element and the adsorbent chalcogen layer.

To further reveal the origin of magnetism in different systems, the differential charge densities are calculated. As shown in Figure 4, there are strong negative differential charge densities around TM atoms and the nearest neighboring chalcogen atoms. While in the middle of the TM-S(Se) bond, significant charge accumulations are observed. This means that the TM atoms and the chalcogen atoms are combined by covalent bonds. It is worth noting that the charge accumulation between TM-S bonds is more evident than that between TM-Se bonds, which indicates the stronger covalent interaction and the shorter bond length. Meanwhile, a small number of charges are accumulated between the TM atom and the lower W atom due to the internal electric field along the z direction. The charge accumulations in the case of Cr and V adsorption are smaller than that in the other cases, which is consistent with the relatively long bond length shown in Table 2. The transfer of charges between the TM atoms and the WSSe layer leads to the decrease of the unpaired electrons in TM atoms, which reduces the magnetic moment of the TM atom on the one hand, and induces the magnetism of the WSSe on the other hand.

The magnetic anisotropy for different systems is investigated as well. The calculated results are shown in Table 2. Positive and negative MAE indicate the vertical and parallel easy magnetization axis of the system, respectively. The Cr- and V- adsorbed systems have the negative MAE, while the Mn- and Co-adsorbed systems show positive MAE, demonstrating that their easy magnetization axis are in-plane and out-of-plane, respectively. Different adsorption surfaces cause slight changes in MAE, but do not give rise to the changes in their easy magnetization axis. Interestingly, the characteristics in the Fe-adsorbed system is completely different. Its easy magnetization axis switches from the in-plane (MAE: -0.95 meV) to the out-of-plane (MAE: 2.66 meV) when the adsorbing surface changes from Se to S.

To better understand the mechanism of the changed MAE in Fe-adsorbed system, we calculated the Fe-3d orbital-decomposed DOS with the results shown in Figure 5. According to the second-order perturbation theory [23, 40-42], the MAE arising from the SOC can be approximately formulated as:
\[
MAE = E_{||} - E_{\perp} \approx \xi^2 \sum_{\mu, \sigma} \frac{\mu^{\downarrow}(\|) |L_z| \sigma^{\downarrow}(\perp) - \mu^{\uparrow}(\|) |L_x| \sigma^{\uparrow}(\perp)}{E_{\mu} - E_{\sigma}},
\]

where \( \sigma^{\downarrow}(\|), \mu^{\downarrow}(\perp) \) and \( E_{\sigma}, E_{\mu} \) denote the eigenstates and eigenvalues of the occupied (unoccupied) states with spin state (\( \downarrow \) or \( \uparrow \)), respectively; \( \xi \) represents the strength of SOC; \( L_z \) and \( L_x \) stand for the angular momenta operators. The SOC is regarded as the perturbative term in the Hamiltonian, and the MAE is expressed as the energy difference between the occupied states and the unoccupied states through the coupling of angular momenta \( L_z \) and \( L_x \). In general, MAE is determined by non-zero elements in \( L_z \) and \( L_x \) matrices near the Fermi level. As for the same spin states (\( \downarrow \downarrow \) or \( \uparrow \uparrow \)), when the occupied and unoccupied states have the same magnetic quantum number \( m \), they make a positive contribution to the MAE under the action of the operator \( L_z \); whereas when they have different \( m \), a negative contribution to the MAE is made through the action of the operator \( L_x \). As for the different spin states(\( \downarrow \uparrow \) or \( \uparrow \downarrow \)), the contribution is just the opposite. The non-zero matrix elements include \( <xz|L_z|yz> = 1, <xy|L_x|^2-y^2> = 2, <z^2|L_x|xz, yz> = 1, <xy|L_x|xz, yz> = 1 \).

In our case, as shown in Figure 5(a) and (b), only the minority spin states appear near the Fermi level, so it determines the MAE. According to ligand-field theory, the \( C_{3v} \) symmetry makes the degenerated Fe-3d orbitals splitted into three kinds of states: single state \( a \) \( (dz^2, |m| = 0) \), degenerated states \( e_1 \) \( (dyz, dxz, |m| = 1) \) and \( e_2 \) \( (dxy, dx^2-y^2, |m| = 2) \). As shown in Figure 5(c-g), when Fe is adsorbed on the S surface, the DOS mainly includes the \( dxz, dyz, dxy \) and \( dx^2-y^2 \) minority spin states, and a significant positive contribution to MAE comes from the spin-conservation term \( <xz|L_z|yz> = 1 \) and \( <xy|L_x|^2-y^2> = 2 \), whereas the relatively weak negative contribution is from the spin-conservation term \( <xy|L_x|xz, yz> = 1 \). As a result, a positive MAE of 2.66 meV is achieved. As for the case of Fe adsorbed on Se surface, the \( dxz \) and \( dyz \) minority spin states dramatically reduces, and as the result, the MAE reduces to -0.95 meV owing to the significant decrease of the positive contribution term \( <xz|L_z|yz> \).

**Conclusion**

In this work, we systematically studied the structures and the magnetic properties of different TM-atom adsorbed WSSe frameworks by the first-principles calculations. The pristine Janus WSSe monolayer shows the different potential energies on S and Se surfaces due to the broken mirror symmetry along the Z direction. Meanwhile, it is non-magnetic in nature. The adsorbed configurations have the lowest energy when TM atom adsors on \( T_{WS} \) or \( T_{WSe} \) indicating the most stable adsorption site. All the adsorbed systems exhibit magnetism. Their magnetism strongly depends on the adsorbed elements and the adsorbent chalcogens. The maximal \( M_T \) of 6 \( \mu_B \) is obtained in the Cr-adsorbed system. Different adsorption surfaces do not cause an obvious difference in \( M_T \), however, there was a relatively big difference in \( M_L \). The \( M_L \) for the S surface adsorption is always smaller than that for the Se surface adsorption due to the stronger electrostatic potential, revealing the stronger induced magnetism. The differential charge densities reveal that the magnetism of the system is attributed to the covalent interaction and the charge transfer between TM atoms and WSSe. In addition, different adsorption
surfaces do not result in the changes of the easy magnetization axis in Cr-, V-, Mn-, and Co- adsorbed systems. However, as for the Fe-adsorbed system, the easy magnetization axis switches from the in-plane to the out-of-plane when the adsorption surface changes from Se to S surface. It is found that the strong coupling between the minority states $d_{xy}$, $d_{x^2-y^2}$ and $d_{xz}$, $d_{yz}$ on the S surface contribute to the positive MAE, while the dramatically reduced $d_{xz}$ and $d_{yz}$ minority spin states on the Se surface leads to the negative MAE. This work provides a new perspective for adjusting the magnetic properties in two-dimensional systems.

**Declarations**

**Acknowledgement**

This work was supported by the National Natural Science Foundations of China (Grants No. 61974123, 61774128, 61874092, 11604275, 61704040, and 61804129), the Natural Science Foundation of Fujian Province of China (Grants No. 2018I0017), Science and Technology Key Projects of Xiamen (Grant No 3502ZCQ20191001), and the Fundamental Research Funds for the Central Universities (Grant Nos. 20720190055 and 20720190058).

**References**

1. Das R, Kalappattil V, Phan M-H, Srikanth H (2021) Magnetic anomalies associated with domain wall freezing and coupled electron hopping in magnetite nanorods. J. Magn. Magn. Mater. 522: 167564
2. Datta S, Das B (1990) Electronic analog of the electro-optic modulator. Appl. Phys. Lett. 56(7):665-667
3. Manzeli S, Ovchinnikov D, Pasquier D, Yazyev O V, Kis A (2017) 2D transition metal dichalcogenides. Nat. Rev. Mater. 2(8):17033
4. Xu R, Zou X, Liu B, Cheng H-M (2018) Computational design and property predictions for two-dimensional nanostructures. Materials Today 21(4):391-418
5. Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V, Firsov A A (2004) Electric field effect in atomically thin carbon films. Science 306(5696):666-669
6. Mas-Balleste R, Gomez-Navarro C, Gomez-Herrero J, Zamora F (2011) 2D materials: to graphene and beyond. Nanoscale 3(1):20-30
7. Xu M, Liang T, Shi M, Chen H (2013) Graphene-like two-dimensional materials. Chem. Rev. 113(5):3766-98
8. Kerelsky A, Nipane A, Edelberg D, Wang D, Zhou X, Motmaendadgar A, Gao H, Xie S, Kang K, Park J, Teherani J, Pasupathy A (2017) Absence of a Band Gap at the Interface of a Metal and Highly Doped Monolayer MoS$_2$. Nano Lett. 17(10):5962-5968
9. Lin Y C, Dumcenco D O, Huang Y S, Suenaga K (2014) Atomic mechanism of the semiconducting-to-metallic phase transition in single-layered MoS$_2$. Nat. Nanotechnol. 9(5):391-396
10. Lu C P, Li G, Mao J, Wang L M, Andrei E Y (2014) Bandgap, mid-gap states, and gating effects in MoS$_2$. Nano Lett. 14:4628-33
11. Mak K F, Lee C, Hone J, Shan J, Tony F H (2010) Atomically Thin MoS$_2$: A New Direct-Gap Semiconductor. Phys. Rev. Lett. 105(13):136805
12. Wei Y, Xu X, Wang S, Li W, Jiang Y (2019) Second harmonic generation in Janus MoSSe a monolayer and stacked bulk with vertical asymmetry. Phys. Chem. Chem. Phys. 21(37):21022-21029
13. Lu A Y, Zhu H, Xiao J, Chuu C P, Han Y, Chiu M H, Cheng C C, Yang C W, Wei K H, Yang Y, Wang Y, Sokaras D, Nordlund D, Yang P, Muller D A, Chou M Y, Zhang X, Li L J (2017) Janus monolayers of transition metal dichalcogenides. Nat. Nanotechnol. 12(8):744-749
14. Zhang C, Nie Y, Sanvito S, Du A (2019) First-Principles Prediction of a Room-Temperature Ferromagnetic Janus VSSe Monolayer with Piezoelectricity, Ferroelasticity, and Large Valley Polarization. Nano Lett. 19(2):1366-1370
15. Hu T, Jia F, Zhao G, Wu J, Stroppa A, Ren W (2018) Intrinsic and anisotropic Rashba spin splitting in Janus transition-metal dichalcogenide monolayers. Phys. Rev. B 97(23):235404
16. Yao Q F, Cai J, Tong W Y, Gong S J, Wang J Q, Wan X G, Duan C G, Chu J H (2017) Manipulation of the large Rashba spin splitting in polar two-dimensional transition-metal dichalcogenides. Phys. Rev. B 95(16):8
17. Zhou W, Yang Z, Li A, Long M, Ouyang F (2020) Spin and valley splittings in Janus monolayer WS$_2$ on a MnO(111) surface: Large effective Zeeman field and opening of a helical gap. Phys. Rev. B 101(4):045113
18. Zhao X W, Qiu B, Hu G C, Yue W W, Ren J F, Yuan X B (2019) Transition-metal doping/adsorption induced valley polarization in Janus WS$_2$: First-principles calculations. Appl. Surf. Sci. 490:172-177
19. Dong L, Lou J, Shenoy V B (2017) Large In-Plane and Vertical Piezoelectricity in Janus Transition Metal Dichalcogenides. ACS Nano 11(8):8242-8248
20. Nitta J, Akazaki T, Takayanagi H, Enoki T (1997) Gate Control of Spin-Orbit Interaction in an Inverted In$_{0.53}$Ga$_{0.47}$As/In$_{0.52}$Al$_{0.48}$As Heterostructure. Phys. Rev. Lett. 78(7):1335-1338
21. Fête A, Gariglio S, Caviglia A D, Triscone J M, Gabay M (2012) Rashba induced magnetoconductance oscillations in the LaAlO$_3$-SrTiO$_3$ heterostructure. Phys. Rev. B 86(20):201105
22. Xie L Y, Zhang J M (2016) Electronic structures and magnetic properties of the transition-metal atoms (Mn, Fe, Co and Ni) doped WS$_2$: A first-principles study. Superlattice. Microst. 98:148-157
23. Song Y X, Tong W Y, Shen Y H, Gong S J, Tang Z, Duan C G (2017) First-principles study of enhanced magnetic anisotropies in transition-metal atoms doped WS$_2$ monolayer. J. Phys. Condens. Matt. 29(47):475803
24. Zhao X, Dai X, Xia C, Wang T (2015) Structural defects in pristine and Mn-doped monolayer WS$_2$: A first-principles study. Superlattice. Microst. 85:339-347
25. Li L, Qin R, Li H, Yu L, Lu J (2011) Functionalized Graphene for High-Performance Two-Dimensional Spintronics Devices. ACS Nano 5(4):2601-2610
26. Du A, Sanvito S (2012) First-Principles Prediction of Metal-Free Magnetism and Intrinsic Half-Metallicity in Graphitic Carbon Nitride. Phys. Rev. Lett. 108(19):197207
27. Cai L, He J, Liu Q, Yao T, Chen L, Yan W, Hu F, Jiang Y, Zhao Y, Hu T, Sun Z, Wei S (2015) Vacancy-Induced Ferromagnetism of MoS$_2$ Nanosheets. J. Am. Chem. Soc. 137(7):2622-2627
28. Son Y W, Cohen M L, Louie S G (2006) Energy Gaps in Graphene Nanoribbons. Phys. Rev. Lett. 97(21):216803
29. Lee H, Son Y W, Park N, Han S W, Yu J J (2005) Magnetic ordering at the edges of graphitic fragments: Magnetic tail interactions between the edge-localized states. Phys. Rev. B 72(14):174431
30. Guan S-S, Ke S-S, Yu F-F, Deng H-X, Guo Y, Lü H-F (2019) Controlling magnetism of monolayer Janus MoSSe by embedding transition-metal atoms. Appl. Surf. Sci. 496: 143692
31. Kresse G, Furthmüller J, Hafner J (1994) Theory of the crystal structures of selenium and tellurium: The effect of generalized-gradient corrections to the local-density approximation. Phys. Rev. B 50(18):13181-13185
32. Kim Y S, Hummer K, Kresse G (2009) Accurate band structures and effective masses for InP, InAs, and InSb using hybrid functionals. Phys. Rev. B 80(3):1132-1136
33. Perdew J P, Burke K, Ernzerhof M (1997) Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 77(18):3865-3868
34. Grimme S (2004) Accurate description of van der Waals complexes by density functional theory including empirical corrections. Journal of Computational Chemistry 25:1463-1473
35. Xie Q, Lin W, Yang B, Shu X, Chen S, Liu L, Yu X, Breese M B H, Zhou T, Yang M, Zhang Z, Wang S, Yang H, Chai J, Han X, Chen J (2019) Giant Enhancements of Perpendicular Magnetic Anisotropy and Spin-Orbit Torque by a MoS$_2$ Layer. Adv Mater 31(21):1900776
36. Hasan M Z, Kane C L (2010) Colloquium: Topological insulators. Rev. Mod. Phys. 82(4):3045-3067
37. Er D, Ye H, Frey N C, Kumar H, Lou J, Shenoy V B (2018) Prediction of Enhanced Catalytic Activity for Hydrogen Evolution Reaction in Janus Transition Metal Dichalcogenides. Nano Lett. 18(6):3943-3949
38. Wang Q, Wu P, Cao G, Huang M (2013) First-principles study of the structural and electronic properties of MoS$_2$–WS$_2$ and MoS$_2$–MoTe$_2$ monolayer heterostructures. J. Phys. D: Appl. Phys. 46(50):505308
39. Kang J, Tongay S, Zhou J, Li J, Wu J (2013) Band offsets and heterostructures of two-dimensional semiconductors. Appl. Phys. Lett. 102(1):666
40. Wang D, Wu R, Freeman A J (1993) First-principles theory of surface magnetocrystalline anisotropy and the diatomic-pair model. Phys. Rev. B 47(22):14932-14947
41. Dieny B, Chshiev M (2017) Perpendicular magnetic anisotropy at transition metal/oxide interfaces and applications. Rev. Mod. Phys. 89(2):025008
42. Cong W T, Tang Z, Zhao X G, Chu J H (2015) Enhanced magnetic anisotropies of single transition-metal adatoms on a defective MoS$_2$ monolayer. Sci. Rep. 5:9361
Tables

Table 1. The total energy for different configurations.

| TM    | S side (eV) | Se side (eV) |
|-------|-------------|--------------|
|       | $T_{WS}$   | $H_{S}$      | $T_{S}$ | $T_{WS}$ | $T_{Se}$ | $H_{Se}$ |
| Co    | -375.365   | -375.134     | -373.631 | -374.820 | -373.484 | -373.477 |
| Fe    | -376.865   | -376.584     | -374.894 | -376.386 | -374.373 | -375.394 |
| Mn    | -376.816   | -376.635     | -376.276 | -376.269 | -375.028 | -376.252 |
| Cr    | -377.387   | -377.177     | -376.909 | -377.089 | -376.797 | -373.477 |
| V     | -376.623   | -376.155     | -375.459 | -376.007 | -375.275 | -375.894 |

Table 2. The calculated results including the bond length ($d_{W-S}$, $d_{W-Se}$, and $d_{TM-S(Se)}$), the height difference ($\Delta h$), the total magnetic moment $M_T$, the local magnetic moment $M_L$ of TM adatom, and MAE.

| TM    | side | $d_{W-S}$ (Å) | $d_{W-Se}$ (Å) | $d_{TM-S(Se)}$ (Å) | $\Delta h$ (Å) | $M_L$ (μB) | $M_T$ (μB) | MAE (meV) |
|-------|------|---------------|----------------|--------------------|----------------|-------------|------------|-----------|
| Co    | S    | 2.51          | 2.52           | 2.12               | 1.24           | 0.92        | 1.00       | 0.79      |
|       | Se   | 2.41          | 2.66           | 2.22               | 1.37           | 0.93        | 1.00       | 2.68      |
| Fe    | S    | 2.51          | 2.53           | 2.16               | 1.21           | 1.83        | 2.00       | 2.66      |
|       | Se   | 2.42          | 2.67           | 2.24               | 1.36           | 1.88        | 2.00       | -0.95     |
| Mn    | S    | 2.47          | 2.54           | 2.21               | 1.36           | 2.73        | 3.00       | 3.88      |
|       | Se   | 2.43          | 2.61           | 2.31               | 1.45           | 2.78        | 3.00       | 3.33      |
| Cr    | S    | 2.47          | 2.54           | 2.41               | 1.82           | 4.80        | 6.00       | -2.72     |
|       | Se   | 2.42          | 2.57           | 2.60               | 1.91           | 4.86        | 6.00       | -0.57     |
| V     | S    | 2.50          | 2.53           | 2.31               | 1.70           | 2.90        | 5.00       | -4.19     |
|       | Se   | 2.42          | 2.62           | 2.42               | 1.84           | 2.98        | 5.00       | -2.76     |

Figures
Figure 1

(a) Top view and side views of Janus WSSe monolayer. (b) The average in-plane electrostatic potential distribution of WSSe monolayer. (c) Total DOS of primitive Janus WSSe monolayer.
Figure 2

Top view and side views of different configurations. (a, d) TM atom locates on the top of W atom; (b, e) TM atom locates on the hollow site; (c, f) TM atom locates on the top of S(Se) atom.
Figure 3

Spin-polarized total DOS of the different TM atom adsorbed WSSe monolayer. (a, b) Co; (c, d) Fe; (e, f) Mn; (g, h) Cr; (i, j) V.

Figure 4

Differential charge densities of different TM atom adsorbed systems. (a) Co; (b) Fe; (c) Mn; (d) Cr; (e)V.
Figure 5

DOS of Fe-adsorbed system with different adsorption surface, (a) on the S adsorption surface; (b) on the Se adsorption surface. (c-g) The 3d-orbital decomposed DOS of Fe atom adsorbed on the S surface. (h-l) The 3d-orbital decomposed DOS of Fe atom adsorbed on the Se surface.