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Band structure engineering of NiS₂ monolayer by transition metal doping

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By using density functional theory calculations, we have studied the effects of V-, Cr-, Mn-, Fe- and Co-doped on the electronic and magnetic properties of the 1T-NiS₂ monolayer. The results show that pure 1T-NiS₂ monolayer is a non-magnetic semiconductor. Whereas depending on the species of transition metal atom, the substituted 1T-NiS₂ monolayer can become a magnetic semiconductor (Mn-doped), half-metal (V- and Fe-doped) and magnetic (Cr-doped) or non-magnetic (Co-doped) metal. The results indicate that the magnetism can be controlled by the doping of 3d transition metal atoms on the monolayer. In this paper, the engineering of the electric and magnetic properties of 1T-NiS₂ monolayer is revealed. It is clear that it could have a promising application in new nanoelectronic and spintronic devices.

Two-dimensional (2D) graphene, despite having significant physical and chemical properties, has a zero energy gap that limits its applications for use in electronic devices. For this reason, in recent years, new 2D materials with measurable energy gaps such as transitional metal dichalcogenides (TMDs) with the chemical formula MX₂ (M: transition metal (TM), X: chalcogen (= S, Se and Te)) have attracted a lot of attention due to the wide range of applications in optoelectronics¹, nanoelectronics², photovoltaics and photodetection³. Most 2D TMDs have two stable phases 2H (honeycomb configuration) and 1T (central honeycomb configuration). In other words, 2H and 1T phase can have trigonal prismatic and antiprismatic symmetry, respectively^{4–6}. Perhaps in some monolayers, 2H phase is more stable than 1T phase, but this rule does not correct to all monolayers. For example, MoS₂ monolayer in 2H phase is a semiconductor, however 1T phase for this monolayer is a metal. For this reason, 1T-MoS₂ monolayer used as a superior supercapacitor electrode material⁷. In addition, some monolayers were synthesized in 2H phase and others in 1T phase. As, MoS₂⁴, MoSe₂ and MoTe₂⁸ were synthesized experimentally in 2H phase and PtS₂⁹, PtSe₂¹⁰ and NiTe₂¹¹ in 1T phase. While the synthesis of 1T phase NiSe₂¹² and PtTe₂¹³ has been performed under laboratory conditions.

Though many pure 2D materials are non-magnetic semiconductors, there are many scientific methods to create magnetization in the non-magnetic 2D systems such as vacancy^{14,15}, substitutional doping^{16,17}, surface adsorptions¹⁸ and strain¹⁹. Based on previous studies, TM doping used as an effective method to create magnetization properties in TMDs. For example, Yang Baishun et al. have investigated the effects of TM atoms, alkali metals and alkaline-earth on the electronic structure and magnetic properties of 1T-ZrS₂ monolayer by using first-principle calculations²⁰. The electronic and magnetic properties of monolayer 1T-ZrSe₂ in the presence of doping have checked by Xu Zhao and Colleagues²¹. Also, X Wang et al. have studied the effects of group V and VII dopants on the electronic properties of 1T-ZrSe₂ monolayer²². Xu Zhao et al. have calculated electronic and magnetic properties of 1T-HfS₂ by doping transition-metal atoms in 2016²³. The same group, have reported the structural, electronic and magnetic properties of 3d TM atom-doped 1T-HfSe₂ monolayers in 2017²⁴ and the study of the effect of vacancy defects on pristine and Cr-doped monolayer 1T-HfS₂ conducted in 2018²⁵. Ma Xu, et al. have studied the electronic and magnetic properties of Mn-doped monolayer 1T-HfS₂²⁶. The experimental and theoretical studies of Li et al. indicated that Fe-doped on 1T-SnS₂ have high optoelectronics performance¹⁷. Y. Hao et al. have calculated Ni-doped in 1T-MoS₂ monolayer to demonstrate that TM Ni doping can boost the hydrogen evolution reaction activity of 1T-MoS₂²⁷. M Kar et al. have studied the structural properties, energetic stabilities and magnetic properties of 1T-PtSe₂ monolayer doped by different 3d, 4d and 5d TMs²⁸.

The NiS₂ monolayer can be considered as an excellent candidate for use in semiconductor devices similar to other monolayers^{29,30}, but the absence of magnetism limits its applications in spintronic devices. Thus, by substituting atoms, we want to engineer the electronic and magnetic properties of the 1T-NiS₂ monolayer. Despite

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Figure 1. (a) Top and (b) side views of atomic structure for the doped $3 \times 3 \times 1$ 1T-NiS₂ monolayer. Ni, S and TM atoms are represented by green, yellow and purple balls, respectively. The unit cell is denoted by the red frame.

all the studies on TMDs, the doping of the NiS₂ monolayer have not reported yet. In this work, we figure out the effect of 3d TM, V-, Cr-, Mn-, Fe- and Co-doping on the structural, electronic and magnetic properties of 1T-NiS₂ monolayer by using density functional theory (DFT)-based calculations. Our results show that V, Cr, Mn and Fe substitutions create magnetic pattern in 1T-NiS₂ monolayer. The rest of the paper is as follow: we introduce the computational methods in “Computational methods” and we present the results in “Results and discussion”. The last section will be devoted to conclusion.

Computational methods

We used DFT-based calculations to find the electrical and magnetic properties at 1T-NiS₂ monolayer. The generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) form was used to represent the exchange–correlation functional of electrons. In all simulations, the kinetic energy of cutoff plane-waves is equal to 400 Ry. During structural optimization, the forces on each atom are smaller than 0.05 eV/Å under the periodic boundary condition. The Brillouin zone was sampled using a $4 \times 4 \times 1$ Monkhorst–Pack k-point mesh for the $3 \times 3 \times 1$ 1T-NiS₂ supercell³¹. The 1T-NiS₂ monolayer is including 27 atoms (containing 9 Ni and 18 S atoms), in which a Ni atom is substituted by a Mn, Fe or Co atom in doping situation. The difference between valence electrons of substituted atoms induces new electrical and magnetic properties in the monolayer. The valence electrons for S, V, Cr, Mn, Fe, Co and Ni are $4s^2 3p^4$, $4s^2 3d^3$, $4s^1 3d^5$, $4s^2 3d^5$, $4s^2 3d^6$, $4s^2 3d^7$ and $4s^2 3d^8$, respectively.

Results and discussion

Electronic properties of pure 1T-NiS₂ monolayer. The NiS₂ monolayer has 1T and 2H phases and we checked both phases for stability. The results of this study showed that the total energy of 1T phase is 5.273 eV more than 2H phase, so 1T phase is more stable. In addition, 1T phase is a semiconductor, while 2H phase is a metal. Therefore, 1T phase of the NiS₂ monolayer is considered to be doped by TM atoms. Because the band structure engineering is efficiently accessible in semiconductors. Also, to investigate the effects of substitution doping, we first study the structural, electronic and magnetic properties of the pure 1T-NiS₂ monolayer. The pure 1T-NiS₂ monolayer belongs to the hexagonal family with space group $p\bar{3}m1$. Figure 1 shows the top view (a) and side view (b) of a $3 \times 3 \times 1$ supercell for doped 1T-NiS₂ monolayer in which Ni atoms are in contact with six S atoms. Our calculations show that the lattice constant of the unit cell and the bond lengths between the Ni atom and the nearest S atoms are $a = 3.35$ Å and $d_{\text{Ni-S}} = 2.26$ Å, respectively, which is in agreement with the theoretical results reported recently³². Figure 2a,b shows the total density of state (TDOS) and the band structure of the pure 1T-NiS₂ monolayer. It is clear that the monolayer is a non-magnetic semiconductor due to symmetric spin-up and spin-down DOSs. The valence band maximum is located at G k-point while the conduction band minimum is placed along G-M. The partial density of states (PDOSs) and band structure on d orbitals of Ni atoms and p orbitals of S atoms are shown in Fig. 2c–f. d orbitals of Ni atoms are split into two twofold degenerated $1e_g$ (d_{xy} and $d_{x^2-y^2}$) and $2e_g$ (d_{xz} and d_{yz}) and a single, a_1 (d_{z^2}) states due to crystal field. a_1 state has a more efficient contribution in the valence band, especially in the energy range of -1 to -2.5 eV than other d orbitals, but the same orbital has the lowest contribution in the conduction band. The conduction band originates mainly from $2e_g$ states in the energy range of 0.5 to 1.75 eV. Thus, the $1e_g$ state constitute the valence band maximum and the

Figure 2. (a) TDOS and (b) band structure of 1T-NiS₂ monolayer. (c,d) show the PDOS and band structure of the monolayer on d orbitals of Ni atoms, respectively. (e,f) denote to the contribution of p orbitals of S atoms on the DOS and band structure of the monolayer, respectively. The positive (negative) amounts of DOSs denote to spin-up (spin-down) states. The vertical dashed line represents the Fermi level which is set to zero.

$2e_g$ state the conduction band minimum (see Fig. 2c,d). It is also clear that p_z orbital of S atoms has a significant contribution on the valence and conduction band in comparison with the p_x and p_y orbitals. the valence band maximum consists of the p_x and p_y orbitals and the conduction band minimum consists of the p_z orbital (see

	a (Å)	d _{TM-S} (Å)	μ_{tot} (μ_B)	μ_{TM} (μ_B)	μ_{Ni} (μ_B)	μ_S (μ_B)	ΔE (meV)
Ni ₈ ScS ₁₈	9.984	2.558	0	0	0	0	0
Ni ₈ TiS ₁₈	9.981	2.438	0	0	0	0	0
Ni ₈ VS ₁₈	9.982	2.361	1.056	1.029	0.042	− 0.057	− 62.73
Ni ₈ CrS ₁₈	9.972	2.320	2.651	2.639	0.045	− 0.087	− 661.49
Ni ₈ MnS ₁₈	9.973	2.285	2.921	2.913	0.015	− 0.052	− 1027.81
Ni ₈ FeS ₁₈	9.961	2.258	1.735	1.726	− 0.019	− 0.002	− 247.68
Ni ₈ CoS ₁₈	9.987	2.254	0	0	0	0	0
Ni ₈ CuS ₁₈	10.061	2.353	0	0	0	0	0
Ni ₈ ZnS ₁₈	9.990	2.497	0	0	0	0	0

Table 1. The lattice constants (a), the bond length between doped TM and the nearest S atoms (d_{TM-S}), the total magnetic moments (μ_{tot}), the magnetic moments for the dopant (μ_{TM}) and its nearest neighbor Ni (μ_{Ni}) and S (μ_S) atoms and the energy difference between the spin-polarized and non-spin-polarized states (ΔE).

Fig. 2e,f). By considering the PDOSs, it reveals that the valence band maximum is consisted of p orbitals of S atoms, while the conduction band minimum is mainly made by the hybridization of d orbitals of Ni and p orbitals of S atoms. The exchange–correlation functional is an important term for investigation of band structure and band gap of 2D materials, so we have considered local density approximation (LDA), GGA, Heyd–Scuse–ria–Ernzerhof (HSE06) methods to investigate the band structure and band gap of 1T-NiS₂ monolayer which is shown in Fig. S1 and S2 of the supplementary. The results show that the monolayer is an in-direct semiconductor regardless of the chosen method and the valence band maximum and the conduction band minimum location are approximately conserved. The obtained band gap by LDA and GGA is equal to 0.73 eV and 0.54 eV, respectively while it is 1.08 eV by HSE06. As it was predictable, the screened hybrid functional, HSE06, modified the band gap amount of the monolayer but it increases the cost of calculations. In many 2D materials studies, such as TM-doped in MoSe₂³³, HfS₂^{26,34} and ZrS₂²⁰ monolayers, DFT calculations with GGA functional had been used and acceptable results had obtained, so we have reported the results calculated by GGA method for TM-doped monolayers. The spin–orbit coupling (SOC) has a considerable effect on the electronic structures such as band gap in semiconductor TMDs monolayers^{35,36}. Therefore, we have investigated both GGA and GGA + SOC methods in the calculation of the band structure of 1T-NiS₂ monolayer (see Fig. S1).

Electronic and magnetic properties of 3d TM-doped 1T-NiS₂ monolayer. For the doped systems, one Ni atom is substituted by one TM (TM = 3d group) atom in a 3 × 3 × 1 supercell. The calculated lattice constants (a), bond length between TM dopant and its first nearest neighbor S atom (d_{TM-S}), total magnetic moments (μ_{tot}), magnetic moments for the TM (μ_{TM}) and its nearest neighbor Ni (μ_{Ni}) and S (μ_S) atoms and finally the energy difference between the spin-polarized and non-spin-polarized states (ΔE) of 1T-NiS₂ monolayer are listed in Table 1. As can be seen in Table 1, the calculated total magnetic moments of V-, Cr-, Mn- and Fe-doped monolayers are 1.056 μ_B , 2.651 μ_B , 2.921 μ_B and 1.735 μ_B , respectively. But the total magnetic moments of other TM-doped (Sc, Ti, Co, Cu, and Zn) 1T-NiS₂ monolayers are zero. Therefore, these systems are non-magnetic and don't create any magnetization in the monolayer. In Ref.²¹, similar results reported for doped ZrSe₂ monolayer. In addition, the non-magnetic behavior of the monolayers has been demonstrated by Sc and Ti doping in ZrS₂²⁰, HfS₂²³ and HfSe₂²⁴. Whereas, for V-, Cr-, Mn- and Fe-doped monolayer, the magnetic moment mainly locates on the V, Cr, Mn and Fe atoms (more details are given later). As is obvious from the obtained values in Table 1, for V-doped, the V atom has local magnetic moment and total magnetic moment 1.029 μ_B and 1.056 μ_B , respectively. But, a very small amount of magnetic moment distributes on its surrounding atoms. For V-doped, each of its six nearest neighbor Ni and S atoms show a magnetic moment 0.042 μ_B and − 0.057 μ_B , respectively. On the other hand, for Cr-, Mn- and Fe-doped monolayers, Cr, Mn and Fe atoms have local magnetic moments 2.639 μ_B , 2.913 μ_B and 1.726 μ_B and total magnetic moment 2.651 μ_B , 2.921 μ_B and 1.735 μ_B , respectively. In Cr-, Mn- and Fe-doped, like V-doped, surrounding atoms have a very small amount of magnetic moment. According to obtained results, coupling between TM atoms (V, Cr, Mn and Fe) and S atoms is anti-ferromagnetic like coupling between Ni atoms and Fe atoms in Fe-doped monolayer, while coupling between Ni atoms with V, Cr and Mn atoms for V-, Cr- and Mn-doped monolayers is ferromagnetic. Also, the obtained results in Table 1 show that the bond lengths between TM and S atoms are reduced from Sc to Co by the reduction of atomic radius from Sc to Co and then this value increases for Cu and Zn with increasing atomic radius for Cu and Zn. In addition, the bond length of Co-S in the Ni₈CoS₁₈ system is shorter than other doped systems, which suggesting the stronger covalent interaction. In following, we calculate the energy differences between the spin-polarized and non-spin-polarized, i.e., $\Delta E = E_{\text{sp}} - E_{\text{nsp}}$ for TM-doped 1T-NiS₂ monolayers. We can see that the V-, Ti-, Mn- and Fe-doped 1T-NiS₂ monolayers display the negative energy differences ΔE , indicating the spin-polarized state is more stable than the non-spin-polarized state. By comparing the energy differences, it is observed that Mn-doped than V-, Cr- and Fe-doped has higher energy differences and spin-polarized pattern, while the energy differences between the spin-polarized and non-spin-polarized for other TM-doped monolayers is zero. So we illustrated the details of obtained results for Mn- and Fe-doped as a magnetic semiconductor and a half-metal and Co-doped monolayer as a representative of a non-magnetic system in the main text. To find a comprehensive view, the band structure, DOS, spin density and local magnetic moments of V- and Cr-doped 1T-NiS₂ monolayers are given in Fig. S3, S5 and S6, respectively, of the supplementary.

Figure 3. Band structures of (a) Mn-doped, (b) Fe-doped and (c) Co-doped 1T-NiS₂ monolayer. The blue and red lines represent the spin-up and spin-down, respectively. Fermi level is located in zero energy.

Finally, to understand the stability of the desired monolayers, the binding energy is calculated by $E_b = [E_{\text{Ni8TMS18}} - E_{\text{TM}} - 8E_{\text{Ni}} - 18E_{\text{S}}]/27$. The binding energy of the pure monolayer is equal to -4.176 eV/atom. On the other hand, the binding energy for V-, Cr-, Mn-, Fe- and Co-doped monolayers is -4.237 , -4.149 , -4.147 , -4.178 and -4.178 eV/atom, respectively. According to the calculated values, the binding energy of the V-, Fe- and Co-doped are less than pure, Cr- and Mn-doped monolayers. So, V-, Fe- and Co-doped monolayers are considered as the most stable states. In fact, the structure is more inclined to absorb V, Fe and Co atoms.

In order to study the effect of doping on electronic and magnetic properties, we calculate the band structures 1T-NiS₂ monolayer in the presence TM atoms and the results are shown in Fig. 3. Depending on the species of TM atoms, the substituted 1T-NiS₂ monolayer can be a semiconductor, half-metal or metal. Figure 3a shows that in the Mn-doped monolayer, the spin-up and spin-down channels are asymmetric. So, this system is a magnetic semiconductor. In fact, the presence of Mn atom in the monolayer causes spin separation and changes the band-gaps. On the other word, when the Ni atom is replaced by Mn atom, the bands dispersion is changed in both majority spin and minority spin bands and the spin-splitting has occurred. Similarly, Mn-doped HfS₂³⁴, HfSe₂²⁴ and ZrSe₂³⁷ monolayers are magnetic semiconductor. In the case of Fe-doped (V-doped), as shown in Fig. 3b (see Fig. S3 (a)), several spin-down (spin-up) branches cross the Fermi level, while the spin-up (spin-down) band structures remain semiconductor. Therefore, this system is a half-metal, like Fe-doped in SnS₂ monolayer³⁸ (V-doped in HfSe₂ monolayer²⁴). Half-metal systems are generally the source of quite spin-polarized electrons which are promising for development of high performance spintronic devices. However, from Fig. 3c (Fig. S3 (b)), we can see that in the Co-doped (Cr-doped) case, the symmetric (asymmetric) spin-up and spin-down channels pass through the Fermi level, showing a non-magnetic (magnetic) metallic behavior, which is similar to the behavior of Co-doped HfSe₂ monolayer²⁴ (Cr-doped HfS₂²³ and HfSe₂²⁴ monolayers). On the other hand, we know that the valence electrons of Co atoms are in $3d^7 4s^2$ configuration. So p-type doping is created in Co-doped monolayer because the substituted Co atom has one electron less than Ni. Due to the presence of massive TM atoms in the monolayers, the effect of SOC should be noticed. The band structure of TM-doped monolayers with SOC are given in Fig. S4 of the supplementary. It shows that the amount of band gap is slightly reduced with SOC calculations.

The TDOSs and PDOSs onto p orbitals of S, d orbitals of substituted TM and Ni atoms are displayed in Fig. 4. Figure 4a–c displays TDOS for spin-up and spin-down of Mn-, Fe- and Co-doped monolayers. Also, $1e_g$, $2e_g$ and a_1 states of TM atoms (Mn, Fe, Co and Ni) and p_x , p_y and p_z orbitals of chalcogen atoms (S) are drawn separately in Fig. 4d–l. The energy and splitting of these states vary significantly depending on the kind of doped TM atoms. TDOS and PDOS for V- and Cr-doped monolayers are showed in Fig. S5 of the supplementary. In the case of Mn-doped, the asymmetric TDOS is occurred for spin-up and spin-down surrounding the Fermi level. So, as we mentioned earlier this system is a magnetic semiconductor with total magnetic moment of $2.921 \mu_B$ (see Table 1). For Fe-doped 1T-NiS₂ monolayer, in the spin-down channel, the doping states pass through the Fermi level showing a metallicity, which are derived mostly from the p_x and p_y orbitals of S atom with significant contribution of $1e_g$ and $2e_g$ states of Fe atom. Whereas, the spin-up channel remains semiconductor, which are derived mostly of p_x and p_y orbitals of S atoms in the valence band maximum and also the significant

Figure 4. (a–c) show TDOS of Mn-, Fe- and Co-doped 1T-NiS₂ monolayers, respectively. (d–f) denote to the projection of the monolayer DOS on d orbitals of doped atoms, while (g–i) refer to the projection of the monolayer DOS on d orbitals of Ni atoms and (j–l) represent the contribution of p orbitals of S atoms on the DOS of Mn-, Fe-, Co-doped monolayers, respectively. The vertical dashed line represents the Fermi level which is set to zero.

Figure 5. Schematic energy level diagram of TM-doped NiS₂ monolayer.

contribution of $2e_g$ state of Fe atom and p_z orbitals of S atoms are observed in the conduction band minimum. As a result, Fe-doped monolayer with $\mu_{\text{tot}} = 1.735 \mu_B$ (see Table 1) is a half-metal. Thus, Fe-doped monolayer can be used in spintronic material operating as a spin valve or can be an active component in 2D magnetic tunnel junctions. Finally, Co-doped in 1T-NiS₂ monolayer display a metallic behavior for both spin-up and spin-down bands that crossing the Fermi level. In addition, the spin-up and spin-down channels are symmetric, indicating the Co-doped 1T-NiS₂ monolayer is a non-magnetic metal, hence as shown in Table 1, Ni₈CoS₁₈ system has no magnetic moment. In fact, in this system, p orbitals of S and d orbitals of Co atoms are mainly responsible for the metallicity of the Co-doped 1T-NiS₂ monolayer. To understand the magnetic moment according to PDOS of the monolayers, it is observed that both spin-up and spin-down, degenerated $1e_g$ and $2e_g$ and single a_1 states of d orbital are below the Fermi level and hence fully occupied in Co-doped monolayer (see Fig. 4f). Therefore, its magnetic moment becomes zero. In Mn- and Fe-doped monolayers, it is clear that only spin-up single a_1 state is located below the Fermi level, so it is occupied. But spin-down single a_1 state is located at top of the Fermi level which is empty. For this reason, they have non-zero magnetic moments. According to the Fig. 4f, it is obvious that no exchange splitting exists in the d orbitals of Co atom, while the exchange splitting is happened for d orbitals of Mn and Fe atoms (see Fig. 4d,e). A schematic graph of the spin states of TM-d orbitals is represented in Fig. 5. The states of Co atom are degenerated and there is no spin separation. For Mn and Fe atoms, the spin separation is quite noticeable. On the other hand, the degeneration of spin-down $1e_g$ and $2e_g$ states of Fe atom at zero energy (see Fig. 4e) makes a half-metal Fe-doped monolayer.

As correct evidence of the charge transfers between the doped atoms and 1T-NiS₂ monolayer, we plot the spin density ($\rho_{\uparrow} - \rho_{\downarrow}$) for Mn- and Fe-doped systems in Fig. 6a,b. Also, the spin density for V- and Cr-doped monolayers are showed in Fig. S6a,b of the supplementary. $\rho_{\uparrow}$ and $\rho_{\downarrow}$ show the charge density of spin-up and spin down states, respectively. From the magnetic moment of the TM and its nearest neighbor Ni/S, as listed in Table 1, we found that the significant contribution of the total magnetic moment comes from the TM atom. These results are in agreement with the spin density as shown in Fig. 6. In the case of the Mn-doped monolayer (Fig. 6a), the positive magnetic moment of the Mn atom induces the negative (positive) magnetic moments on the first nearest-neighbor S (Ni) atoms (see Table 1). In addition, Fig. 6a shows that the Mn atom induces magnetic moments only on the first nearest-neighbor S atoms and this amount is greater than the induced positive magnetic moments on the first nearest-neighbor Ni atoms. On the other hand, the S atoms are easier to be magnetized rather than Ni atoms in Mn-doped monolayer. So, coupling between Mn atom and S (Ni) atoms is anti-ferromagnetic (ferromagnetic), like V- and Cr-doped monolayers (see Fig. S6a,b). Unlike V-, Cr- and Mn-doped monolayers, in the Fe-doped monolayer, the positive magnetic moment of the Fe atom induces the negative magnetic moments on the first nearest-neighbor S and Ni atoms. According to Fig. 6b, it is easier for Ni atoms to be magnetized rather than S atoms in Fe-doped monolayer. Thus, Fe and S/Ni atoms are coupled anti-ferromagnetically. The alignments of local magnetic moments (μ_{TM} and μ_S) for Mn- and Fe-doped monolayers are shown in Fig. 6c,d. Also, the alignments of local magnetic moments for V- and Cr-doped monolayers are displayed in Fig. S6c,d. In the V-, Cr- and Mn-doped monolayers, the magnetic moment of the V-, Cr- and Mn atoms and the first nearest-neighbor Ni (S) atoms are parallel (anti-parallel). For example, as shown in Table 1, Ni₈MnS₁₈ system provided

Figure 6. The spin density ($\rho_{\uparrow}-\rho_{\downarrow}$) (first row) and the local magnetic moment (second row) plots for Mn-doped (a,c) and Fe-doped (b,d) 1T-NiS₂ monolayers. The red (blue) isosurfaces represent positive (negative) spin densities of 0.02 e Å⁻³. Also, the blue and red arrows in local magnetic moments are drawn to indicate the orientation of spin polarization of the TM (Mn, Fe and Ni) and chalcogen (S) atoms.

a positive magnetic moment for Mn and Ni atoms, while it provided negative magnetic moment for S atoms which is clearly displayed in Fig. 6a,c. Whereas, the conditions for Fe-doped monolayer is completely different. In the Fe-doped monolayer, the magnetic moment of the Fe atom with the first nearest-neighbor Ni and S atoms are anti-parallel i.e., Ni₈FeS₁₈ system provided a positive magnetic moment for Fe atom, while provided negative magnetic moments for Ni and S atoms. It seems that in general the strong exchange interaction in Mn-doped monolayer causes the relatively small spin orientation of Ni atoms by Mn atom. While for Fe-doped monolayer, due to the weak exchange interaction, the equal orientation of the spins of the Ni atoms by Fe atom is not possible.

Conclusions

In summary, we have investigated the effect of 3d transition metal, V-, Cr-, Mn-, Fe- and Co-doping on the structural, electronic and magnetic properties of 1T-NiS₂ monolayer by using density functional theory calculations. The results show that pure 1T-NiS₂ monolayer is a non-magnetic semiconductor. Whereas, depending on the species of substituted transition metal atom, this monolayer can be a magnetic semiconductor (Mn-doped), half-metal (V- and Fe-doped) and magnetic (Cr-doped) or non-magnetic (Co-doped) metal. The doped monolayers can be used in nanoelectronics and spintronics devices due to their controllable features. Moreover, the V-, Cr-, Mn- and Fe-doped induce total magnetic moments of 1.056 μ_B , 2.651 μ_B , 2.921 μ_B and 1.735 μ_B , respectively, while Co atom does not induce any magnetic moment. These results indicate that the magnetism can be controlled by doping of 3d transition metal atoms. We hope that our result can be useful in the field of new 2D magnetic materials.

Received: 21 December 2020; Accepted: 22 February 2021

Published online: 11 March 2021

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Author contributions

H.R.S. and H.K. developed the theoretical formalism, performed the analytic calculations and performed the numerical simulations. S.I.V. contributed to the design and implementation of the research, to the analysis of the results. H.K. and M.O. wrote the main manuscript text. All authors discussed the results and contributed to the final manuscript. H.R.S. supervised the project.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1038/s41598-021-84967-3>.

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