

Journal of Materials Chemistry C

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**Dihalogen Edge-Modification: An Effective Approach to Realize
the Half-Metallicity and Metallicity in Zigzag Silicon Carbon
Nanoribbons**

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Abstract

By means of first-principles computations, we have systematically investigated the electronic and magnetic properties of the zSiCNR with not only homogeneous but also heterogeneous diatomic edge-modification by employing halogen atoms, where one edge is saturated by double halogen F/Cl atoms, and the other is terminated by single or double F/Cl/H atoms, respectively. The computed results reveal that this kind of edge-modification by dihalogen atoms can break the magnetic degeneracy of the pristine zSiCNR, and the intriguing electronic and magnetic behaviors invoking not only the antiferromagnetic (AFM) metallicity but also the AFM half-metallicity and ferromagnetic (FM) half-metallicity can be achieved, where the decorated atoms to the C-edge of zSiCNR can play an important role in affecting the electronic and magnetic properties of the modified zSiCNR systems, and the heterogeneous asymmetric edge-modification by the halogen/hydrogen pair with great electronegative difference can more effectively strengthen robustness of half-metallicity. Additionally, employing strong electron-withdrawing halogen atom to perform a diatomic edge-modification can also significantly lower the edge formation energy of the modified zSiCNR systems, endowing them with higher structural stability. Obviously, diatomic edge-modification with halogen atoms can be an effective strategy to modulate the electronic and magnetic behaviors of zSiCNRs, which can be of benefit to promoting excellent SiC-based nanomaterials in the application of spintronics and multifunctional nanodevices.

Keywords: first-principles computations, silicon carbon nanoribbons, edge modification, halogen F/Cl atoms, electronic and magnetic properties

1. Introduction

Since the successful realization of single-layer graphene, considerable interest has been focused on not only the graphene itself but also graphene-based materials, in view of the potential application in the next generation of electronic devices.¹⁻¹⁵ One of the most charming superstars in the carbon-based family is one-dimensional (1D) graphene nanoribbons (GNRs),^{5,6} which can be synthesized in experiment via cutting the graphene.¹⁻³ The reduction of dimension endows GNRs with the different electronic and magnetic properties from graphene, such as, the GNRs terminated by H atoms have a nonzero band gap,^{5,6} where the zigzag and armchair GNRs (zGNRs and aGNRs) are antiferromagnetic and nonmagnetic, respectively.^{5,6} Many investigations have been performed on functionalizing GNRs for applications in spintronics and multifunctional nanodevices by proposing different strategies, for instance, applying an electric field,⁶ (non)covalent surface-modification,⁷⁻⁹ and foreign-atom substitution.^{10,11}

Among others, motivated by the case that an intriguing half-metallic behavior can be observed in zGNRs by applying a strong transverse electric field to induce the electrostatic-potential difference between both edges,⁶ the edge modification with electron-donating or –withdrawing groups/atoms, seemingly like the application of an electric field, has been becoming a popular strategy to modulate the electronic and magnetic behaviors of zGNRs.¹³⁻¹⁵ For instance, it is revealed that the half-metallicity can be achieved in the edge-modified zGNRs with the electron donor/acceptor pair (CH₃/NO₂),¹³ in which a certain spin-polarized band is elevated to cross the Fermi level. Similarly, the half-metallic characteristic can be also obtained in the zGNRs with the edge modification by the donor/acceptor pairs OH/SO₂ and OH/NO₂,¹⁴ while the metallicity can be produced rather than the half-metallicity when decorating the both edges of zGNR with the OH/CN pair. Further, when the electron-donating OH group is reserved, and the electron-withdrawing groups (involving SO₂, NO₂ and CN) are substituted by the corresponding hybrid group plus a H atom (SO₂+H, NO₂+H and CN+H, respectively), the half-metallic behavior can be also realized in all of the edge-modified zGNRs systems.¹⁴ Moreover, it is revealed that employing isolated

SO₂ group at one edge can result in the underlying half-metallicity in zGNRs, almost independent of the type of functional group modifying the other edge, such as, the sampled F, H or OH group/atom, even with a bare edge.¹⁴ Clearly, the edge modification by various electron-donating or withdrawing groups/atoms can effectively engineer the band gap of GNRs, especially achieving the intriguing half-metallicity, promoting the applications in multifunctional and spintronic nanodevices.

As the structural analogue of GNRs, the inorganic SiC nanoribbons (SiCNRs) have been capturing the researchers' considerable attention.^{16-18,27-43} It is worth mentioning that SiC has long been the leading material for the application in harsh environments (e.g. high temperature, pressure or power),¹⁹⁻²² in view of the large mechanical strength, high thermal conductivity, as well as excellent oxidation and corrosion resistances.²³⁻²⁶ Experimentally, several synthetic routes have been developed to realize SiCNRs with different polymorphs.²⁷⁻³⁰ For example, via a catalyst-free route under relatively low growth temperature, wurtzite-type SiC (2H-SiC) nanoribbons with tens to hundreds of microns in length, a few microns in width and tens of nanometers in thickness have been synthesized.²⁷ The SiC (3C-SiC) nanoribbons have been realized by means of a lithium assisted synthetic route or the thermal evaporation approach.^{28,29} Additionally, the fabrication of carbon-rich SiC nanoribbons has been reported by Salama *et al.*³⁰ in a single crystal 4H-SiC wafer with the nanosecond pulsed laser direct-write and doping (LDWD) technique, which are proposed as transistor-resistor interconnects for nanodevices and photonic band-gap arrays in the microstrip circuits.

Besides, considerable theoretical endeavors have been also focused on the one-dimensional inorganic SiCNRs.³¹⁻⁴⁶ For instance, it is predicted that the armchair SiCNRs (aSiCNRs) are the nonmagnetic semiconductor with the band gap exhibiting a three-family behavior as a function of the ribbon width,^{17,31} and zigzag SiCNRs (zSiCNRs) are magnetic metal or semiconductor depending on the ribbon width.^{17,32} However, a recent high-level DFT work³³ revealed that the ground state of zSiCNRs should be the degenerate ferromagnetic (FM) and antiferromagnetic (AFM)

configurations, where the corresponding metallic and half-metallic behaviors can be observed, respectively. At present, many strategies have been proposed to tune the electronic and magnetic properties of SiC nanoribbons for promoting the SiC-based nanomaterials in the application of multifunctional nanodevices.³⁴⁻⁴⁶ For example, very recently, Guan *et al.* proposed a simple and effective approach, through hydrogenating the corresponding pristine zSiCNRs step by step starting from the active edge of ribbon, to engineer the electronic and magnetic behaviors of SiC nanoribbons, where the transition of the semiconductor – metal – half-metal and the conversion of the nonmagnetism – magnetism can be achieved in the hydrogenated zSiCNR by means of manipulating the hydrogenation patterns and ratios.³⁴ Also, Guan *et al.* reported that introducing the SW defect can reduce the band gap of aSiCNRs regardless of the defect orientation, while zSiCNRs with SW defects can exhibit degenerate FM and AFM states, where metallic or half-metallic behavior can be observed.³⁵ Additionally, it is revealed that the vacancy defects, selective edge reconstruction, adatoms, and substitutions *etc.* can also engineer the band gaps and magnetism of zigzag or armchair SiCNRs,³⁶⁻⁴⁰ where the intriguing half-metallic, metallic and semiconducting behaviors can be achieved. Moreover, applying a suitable electric field can induce a metal behavior in zSiCNRs and aSiCNRs,⁴¹ where magnetization of zSiCNRs can be also manipulated.¹⁸ Besides, like the case of GNRs,¹³⁻¹⁵ the edge modification has been employed as an effective approach to modulate the electronic and magnetic properties of the zSiCNR.^{33,42-44} For instance, Ding *et al.* have reported that the unilateral/bilateral modification, with the different electron-acceptor (e.g. CN and NO₂) and electron-donor (e.g. CH₃, OH and NH₂) groups, can break the energy degeneracy of FM and AFM states in the pristine zSiCNR, where the intriguing AFM half-metallicity, AFM metallicity and FM metallicity can be realized.⁴² The asymmetric hydrogen-termination can break the magnetic degeneracy and favor the FM state for zSiCNRs: the configurations with bare Si edge and H-terminated C edge present the half-metallicity, while those with H-saturated Si/C edge and H-terminated C/Si edge become quasi-half-metal.³³ Further, the electronic and magnetic properties for the edge hydrogenated zSiCNRs can be

also modulated by controlling the hydrogen content of environment and the temperature, as well as the ribbon width,⁴³ in which two type of stable zSiCNR systems with H-saturated Si edge and H-saturated/terminated C edge can exhibit a transition of the semiconductor to half-metallicity, along with the increase of ribbon width.

Obviously, some progress has been made on investigations on SiCNRs. In this work, we intend to understand how the diatomic edge-modification by halogen atom (e.g. F and Cl) will affect the electronic and magnetic properties of zSiCNRs, and whether this approach can conquer the bottleneck that owing to the magnetic degeneracy, the FM metallicity and AFM half-metallicity in pristine zSiCNRs are vulnerable to even small disturbances, somewhat preventing the practical application in multifunctional nanodevices. It is worth mentioning that the dihalogen edge-modification can usually exhibit the different effect from the parallel dihydrogen edge-decoration, for example, the inorganic zBNNR (considered as the analogue of zSiCNR) with two-fluorine terminated B edge and one-fluorine terminated N edge can exhibit the intriguing half-metallic behavior,⁴⁷ while the counterpart terminated by the H atoms is metallic characteristic.⁴⁸ Moreover, employing the halogen atom to decorate the ribbon edge can significantly enhance structural stability, since the strong electron-withdrawing capability is advantageous for strengthening the related chemical bonds, as reflected by the edge-fluorinated zBNNRs reported.⁴⁷ Therefore, it is highly anticipated that this kind of diatomic edge-halogenation can be an effective strategy to break the magnetic degeneracy, promoting the application in electronic nanodevices.

Besides the homogeneous edge modification of dihalogens, the related heterogeneous edge modification is also considered in this work, namely, one edge saturated by halogen atoms and the other saturated/terminated by H atoms, considering that the great electronegative difference between halogen and hydrogen atoms can result in an evident electrostatic-potential difference between the two edges of the zSiCNR. Particularly, the dihalogen edge-modification can convert the original sp^2 to sp^3 hybridization for the edge Si/C atoms, and further cause the consecutive

double bonds along the ribbon width, like the case of edge-saturated zGNR by H atoms.¹⁵ This unique arrangement mode of π -bonding is highly expected to be able to more effectively modulate the electronic and magnetic behaviors of zSiCNR, compared with the usual pristine configuration.

Here, we have carried out systematic first-principles computations to investigate the structures, electronic and magnetic properties of the diatomic edge-modified zSiCNR by the halogen atoms (F and Cl) with strong electron-withdrawing ability, where both homogeneous and heterogeneous modes are involved. Our computed results reveal that this type of halogenated edge-modification can be an effective strategy to break the magnetic degeneracy of the pristine zSiCNRs, where the intriguing FM half-metallicity, AFM half-metallicity and AFM metallicity can be realized in the modified zSiCNRs, accompanied by the significantly enhanced edge stability. These fascinating findings can provide some valuable insights for promoting the practical applications of excellent SiC-based nanomaterials in the spintronics and multifunctional nanodevices.

2. Computational Methods

The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof exchange-correlation functional was employed to perform all the density-functional theory (DFT) computations, as implemented in the Vienna *ab initio* simulation package (VASP),^{49,50} where the projector augmented wave (PAW)^{51,52} pseudo-potentials were used to model the electron-ion interactions with a 450 eV cutoff for the plane-wave basis set. Considering that there may exist weak interactions between the modified atoms, a semiempirical van der Waals (vdW) correction to account for the dispersion interactions was adopted.⁵³ Moreover, the vacuum regions along the nonperiodic directions were wider than 15 Å in order to avoid interactions between the adjacent images in the repeated supercells. $1 \times 1 \times 11$ Monkhorst-Pack grid k -points were utilized for the geometric optimization, and the convergence threshold was set as 10^{-4} eV in energy and 10^{-3} eV/Å in force, respectively. To further investigate the electronic property, 21 k -points were used to sample the 1D Brillouin

zone on the basis of the fully relaxed structures. Note that, to better confirm the ground state of the studied dihalogen-edge-modified zSiCNRs systems, we have performed a computational test, where different antiferromagnetic states have been considered, besides the corresponding nonmagnetic and ferromagnetic states. It can be revealed that in all the antiferromagnetic configurations, the one with the same spin orientation for each edge yet opposite between two edges is lowest-lying in energy, and thus only this type of the antiferromagnetic arrangement is considered in this work, as discussed detailedly in Electronic Supplementary Information (ESI).

3. Results and Discussions

Following the convention, the different widths of zSiCNRs can be named as N_z -zSiCNR, where the N_z represents the number of parallel zigzag lines across the ribbon width (W_z), as illustrated in Figure 1. In this study, we take the pristine 8-zSiCNR terminated by the H atom as a prototype system (Figure 1), and investigate the effect of diatomic edge modification by employing halogen atoms (F and Cl) on the electronic and magnetic properties of zSiCNRs, where the homogeneous and heterogeneous edge modifications are considered. The former means one edge of zSiCNR modified with two halogen atoms and the other with one or two same halogen atoms, while the latter corresponds to two halogen atom saturating one edge and the other with one or two hydrogen atoms. For the convenience, all of the studied 8-zSiCNR systems with the dihalogen edge-modification can be defined as nX -zSiCNR- mX' ($X/X' = \text{F, Cl or H}$; $n, m = 1 \text{ or } 2$), where $X(X')$ and $n(m)$ stand for the atoms modifying the Si(C) edge and the number of the $X(X')$ atom, respectively.

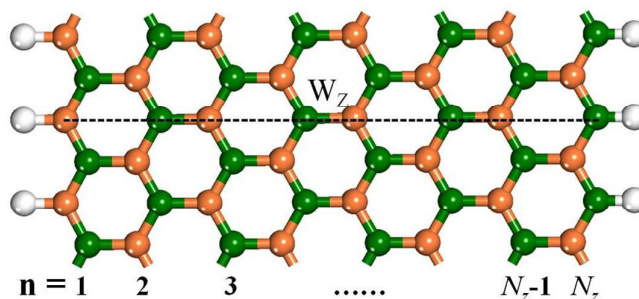


Figure 1. Geometric structure of the pristine zigzag SiCNR, where the jungle green, jacinth and grey balls represent C, Si and H atoms, respectively.

Initially, we investigated the electronic and magnetic properties of pristine 8-zSiCNR terminated by H atom. To determine the ground state, we performed both spin-polarized and spin-unpolarized computations, where the ferromagnetic (FM), antiferromagnetic (AFM) and nonmagnetic (NM) states are taken into account. It is revealed that the unpaired spin distribution mainly concentrates on the edge Si and C atoms (Figure 2), but their orientations are parallel and antiparallel between the Si and C edges for the FM and AFM states, respectively, where both of states are energetically degenerate with energy difference between them within 1.0 meV, yet much lower (*ca.* 68 meV) than the corresponding NM state, indicating that the generate FM and AFM configurations are the ground state. Our computed results also show that the metallicity and half-metallicity can be observed in the FM and AFM states of the pristine zSiCNR, respectively. Note that all of our present computed results on the pristine zSiCNR are well consistent with a recent high-level DFT work on the basis of screened hybrid density functional of Heyd-Scuseria-Ernzerhof (HSE).³³

Subsequently, the total density of states (TDOS) and local density of states (LDOS) of the pristine 8-zSiCNR have been plotted to explore the origination of the metallic and half-metallic properties. As illustrated in Figure 2, we can find that the metallicity in the FM configuration can be dominated by both of states across the Fermi level, in which spin-up and spin-down states mainly originate from the edge C and Si atoms, respectively (Figure 2a). Comparatively, the half-metallicity in the AFM configuration can be decided by the case that the spin-down states originating from the edge C and Si atoms cross the Fermi level, while the other spin channel does not (Figure 2b).

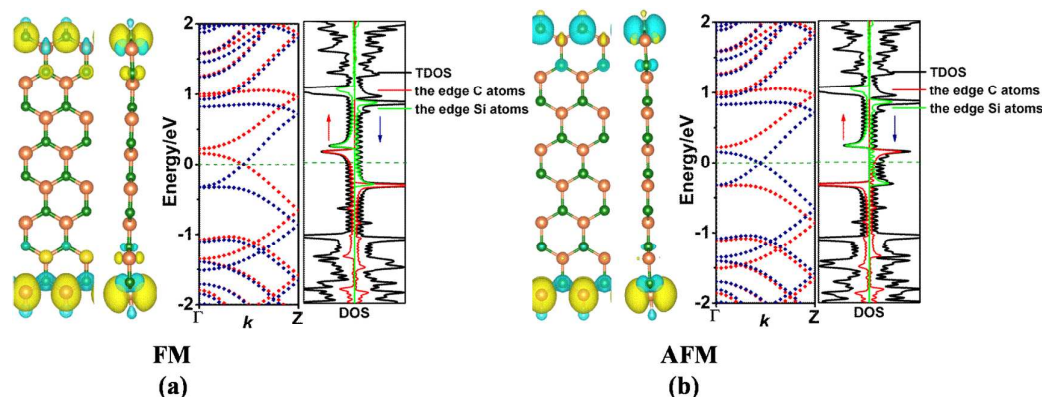


Figure 2. The spin charge densities, electronic band structures, and according DOSs of the pristine 8-zSiCNR at the (a) FM and (b) AFM state, where the red and blue lines denote the spin-up (\uparrow) and spin-down (\downarrow) channels, respectively. The Fermi-level is set as zero and indicated by the green dotted line.

3.1 Homogeneous diatomic edge modification

In this section, we performed a detailed investigation on the effect of the homogeneous edge modification by dihalogen atoms on the magnetic and electronic properties of the pristine zSiCNR by sampling strong electron-withdrawing F and Cl atoms, where two halogen atoms decorating one edge, while the other edge is modified by one or two same halogen atoms. As illustrated in Figures 3 and 4, it can be found that the Si/C edge saturated by the two F/Cl atoms can exhibit the out-of-plane structural deformation due to the steric effect between the adjacent dihalogen atoms, while the planar configuration can be still maintained when employing the one F/Cl atom to terminate the Si/C edge of zSiCNR.

Initially, we mainly focused on the nX -zSiCNR- mX' ($X = X' = \text{F or Cl}$; $n = m = 2$) systems with the homogeneous symmetric edge-modification by the same dihalogen atoms decorating both of edges (Table 1 and Figure 3). For the purpose of comparison, the parallel zSiCNR system with the Si and C edges saturated by double H atoms (namely, 2H-zSiCNR-2H) was also studied in this work. It is found that the edge modification by double H atoms can break the magnetic degeneracy of FM and AFM states in pristine zSiCNR, leading to an AFM half-metallic behavior (Figure 3a), which is similar to the previous report.⁴³

Comparatively, when employing the halogen F atom to replace the H atom, this

kind of homogeneous diatomic edge-modification with strong electron-withdrawing characteristic can also break the magnetic degeneracy of zSiCNR, but result in an AFM metallic behavior in 2F-zSiCNR-2F (Table 1). Specifically, we can find that the double F atoms saturating the Si/C edge of zSiCNR can eliminate the magnetism of the edge Si and C atoms, and the unpaired spin distribution mainly concentrates on their respective neighboring C and Si atoms in both the edge zigzag chains, where the spin orientation between them is antiparallel, presenting the AFM ground state in 2F-zSiCNR-2F (Figure 3b). The computed DOSs results reveal that both spin states crossing the Fermi level lead to the metallic behavior, where the energy levels in spin-up/down channel mainly originate from the inner C/Si atoms in two edge zigzag chains as well as the decorated F atoms at the Si/C edge, respectively (Figure 3b). Besides, the inner Si atoms adjacent to edge C atoms are also involved in spin-up state to make a contribution to the metallicity in 2F-zSiCNR-2F.

Table 1. The relative energies of different magnetic couplings to the ground state, the edge formation energy, the electronic property and the band gap in minority channel of the ground state for the zSiCNRs with homogeneous edge-modification. The NM, FM and AFM here represent the nonmagnetic, ferromagnetic and antiferromagnetic spin couplings, respectively.

System	$\Delta E(\text{meV})$			Edge formation energy($\text{eV}/\text{\AA}$)	Electronic property	Gap in minority channel (eV)
	NM	FM	AFM			
2H-zSiCNR-2H	146.2	2.7	0.0	0.148	half-metallicity	0.62
2F-zSiCNR-2F	232.4	1.3	0.0	-1.688	metallicity	-
2Cl-zSiCNR-2Cl	164.5	1.1	0.0	-0.439	metallicity	-
2H-zSiCNR-1H	231.3	0.0	1.9	0.168	half-metallicity	2.57
1H-zSiCNR-2H	64.3	0.0	4.7	0.191	half-metallicity	2.29
2F-zSiCNR-1F	195.7	0.0	4.8	-1.330	half-metallicity	2.48
1F-zSiCNR-2F	24.0	-	0.0	-0.958	metallicity	-
2Cl-zSiCNR-1Cl	172.3	0.0	6.8	-0.361	half-metallicity	2.34
1Cl-zSiCNR-2Cl	31.8	1.5	0.0	-0.086	metallicity	-

Further, the similar case can be also produced in the homogeneous diatomic edge-modified zSiCNR by the halogen Cl atom with the different electronegativity,

where the magnetic degeneracy of pristine zSiCNR can be destroyed and the AFM metallic behavior can be observed in 2Cl-zSiCNR-2Cl (Table 1 and Figure 3c). The computed DOSs results show that the metallicity can be dominated by the energy levels in spin-up/down channel across the Fermi level, mainly originating from the inner C/Si atoms in two edge zigzag chains as well as the decorated Cl atoms at the Si/C edge, respectively (Figure 3c).

Obviously, the homogeneous symmetric diatomic-edge-modification, by employing the double halogen atoms (F and Cl) with the strong electron-withdrawing ability to saturate the edge Si/C atoms, can break the magnetic degeneracy of the pristine zSiCNR, where the sole AFM metallic behavior can be achieved.

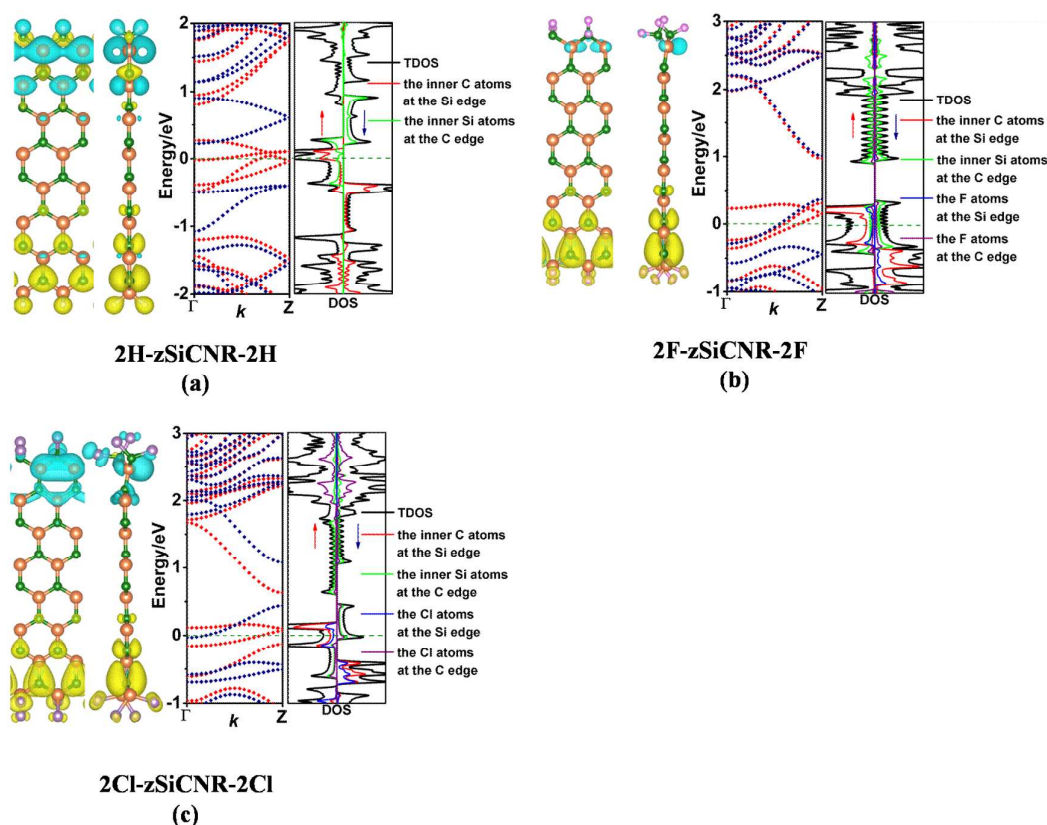


Figure 3. The spin charge densities, electronic band structures, and according DOSs of three systems with the homogeneous symmetric edge-modification, namely, (a) 2H-zSiCNR-2H, (b) 2F-zSiCNR-2F and (c) 2Cl-zSiCNR-2Cl. The red and blue dotted lines denote the spin-up (\uparrow) and spin-down (\downarrow) channels, respectively. The Fermi-level is set as zero and indicated by the green dotted line.

Subsequently, we go to investigate the homogeneous asymmetric edge-modification by the halogen atom for zSiCNR, namely nX -zSiCNR- mX' ($X = X' = F$ or Cl ; $n, m = 1$ or 2 ($n \neq m$)), in which one edge is modified with the double halogen atoms, while the other is decorated by the same single halogen atom. For the purpose of comparison, both the correlative zSiCNR systems with the asymmetric hydrogen-termination, i.e., 2H-zSiCNR-1H and 1H-zSiCNR-2H, are also considered (Figures 4a and 4b). Our computed results reveal that the asymmetric edge modification with H atom can break the magnetic degeneracy of pristine zSiCNR, and both of systems uniformly exhibit an intriguing FM half-metallic behavior (Table 1, Figures 4a and 4b), which is consistent with the previous study.⁴³

In contrast, employing the strong electron-withdrawing F atom to perform the homogeneous asymmetric edge-modification can also break the magnetic degeneracy of zSiCNR, but both the studied systems, 2F-zSiCNR-1F and 1F-zSiCNR-2F, can present different electronic and magnetic behaviors, where the former is the FM half-metallicity, while the latter is the AFM metallicity (Table 1, Figures 4c and 4d). Similar case can be also observed in the homogeneous asymmetric edge-modified zSiCNR systems by the Cl atom with the different electronegativity, that is, the magnetic degeneracy of zSiCNR can be still destroyed, as well as the parallel systems 2Cl-zSiCNR-1Cl and 1Cl-zSiCNR-2Cl can display the FM half-metallic and AFM metallic behaviors (Table 1, Figures 4e and 4f), respectively. Clearly, employing the double halogen atoms saturating the Si edge and the same single halogen atom terminating the C edge can achieve the FM half-metallicity in the modified zSiCNRs, while an AFM metallic behavior can be observed in zSiCNRs with a reverse mode of edge modification, namely, using the single/double halogen atom(s) decorating the corresponding Si/C edge, respectively.

Further, we plot the corresponding DOSs pictures (Figure 4) of these systems with homogeneous asymmetric edge-modification to shed light on the half-metallicity and metallicity. It can be found that the spin-up states crossing Fermi level, dominating the half-metallic behavior in both 2F-zSiCNR-1F and 2Cl-zSiCNR-1Cl, mainly originate from the neighboring C atoms to the saturated edge Si atoms as well as the

edge C atoms and the decorated halogen F/Cl atoms (Figures 4c and 4e). Moreover, the origination for both of spin states across Fermi level, determining the metallic characteristic in two systems 1F-zSiCNR-2F and 1Cl-zSiCNR-2Cl, shares the adjacent Si atoms to the saturated edge C atoms as well as the F/Cl atoms decorating the C edge (Figures 4d and 4f). Besides, the edge Si atoms and the F atoms modifying the Si edge in spin-down state of 1F-zSiCNR-2F and the edge Si atoms in spin-up channel for 1Cl-zSiCNR-2Cl can also make a contribution to the metallicity in the respective system (Figures 4d and 4f).

Obviously, employing halogen F/Cl atoms to perform homogeneous symmetric/asymmetric diatomic-edge-modification is an effective strategy to break the magnetic degeneracy of the pristine zSiCNR, in which the sole intriguing FM half-metallic or AFM metallic behavior can be achieved.

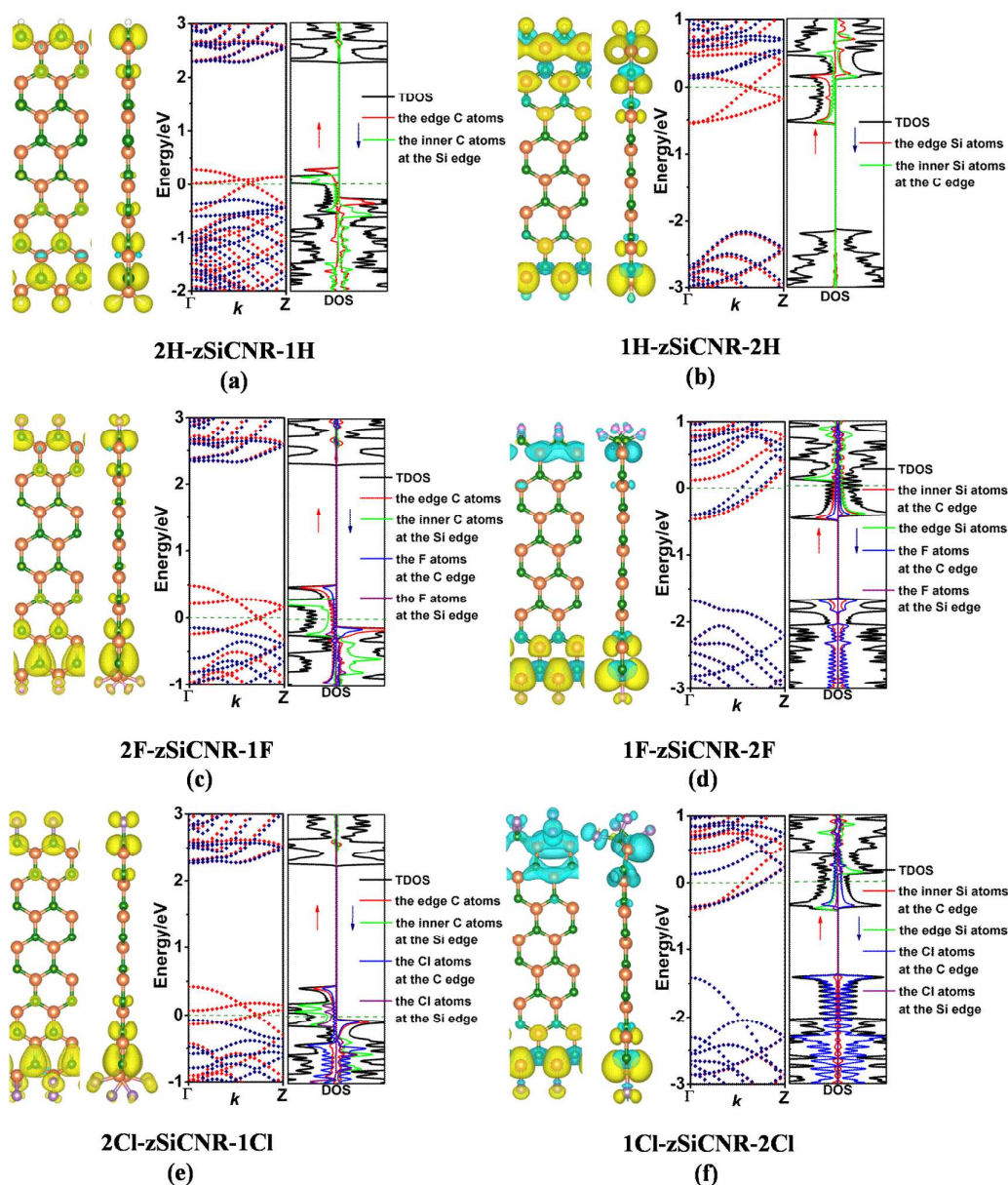


Figure 4. The spin charge densities, electronic band structures, and according DOSs of six structures with the homogeneous asymmetric edge-modification, namely, (a) 2H-zSiCNR-1H, (b) 1H-zSiCNR-2H, (c) 2F-zSiCNR-1F, (d) 1F-zSiCNR-2F, (e) 2Cl-zSiCNR-1Cl and (f) 1Cl-zSiCNR-2Cl. The red and blue dotted lines denote the spin-up (\uparrow) and spin-down (\downarrow) channels, respectively. The Fermi-level is set as zero and indicated by the green dotted line.

3.2 Heterogeneous diatomic edge modification

Based on the findings above, we understand that the homogeneous diatomic edge-modification by employing only halogen atoms can effectively break the magnetic degeneracy of the pristine zSiCNR and realize the sole FM half-metallicity and AFM metallicity. In this section, we intend to further investigate how the

heterogeneous diatomic edge-modification by combining halogen and hydrogen atoms will affect the electronic and magnetic properties of the zSiCNR, where one edge is saturated by two halogen F/Cl atoms, and the other is terminated by one or two H atoms, respectively. It is highly expected that this kind of heterogeneous diatomic edge-halogenation can also effectively engineer the band structure of zSiCNR, and even cause the intriguing electronic and magnetic behaviors different from the corresponding homogeneous edge-modified ones, considering that the great electronegative difference between the halogen and hydrogen atoms can formally result in an evident electrostatic-potential difference between the two edges of zSiCNR.

Table 2. The relative energies of different magnetic couplings to the ground state, the edge formation energy, the electronic property and the band gap in minority channel of the ground state for the zSiCNRs with the heterogeneous edge-modification. NM, FM and AFM here represent the nonmagnetic, ferromagnetic and antiferromagnetic spin couplings, respectively.

System	$\Delta E(\text{meV})$			Edge formation energy($\text{eV}/\text{\AA}$)	Electronic property	Gap in minority channel (eV)
	NM	FM	AFM			
2F-zSiCNR-2H	224.9	1.0	0.0	-1.178	half-metallicity	0.75
2H-zSiCNR-2F	301.6	-	0.0	-0.388	metallicity	-
2Cl-zSiCNR-2H	226.1	1.1	0.0	-0.439	half-metallicity	0.81
2H-zSiCNR-2Cl	152.1	1.0	0.0	0.149	metallicity	-
2F-zSiCNR-1H	226.1	0.0	1.2	-1.130	half-metallicity	2.71
1H-zSiCNR-2F	42.8	-	0.0	-0.353	metallicity	-
2Cl-zSiCNR-1H	232.8	0.0	3.2	-0.393	half-metallicity	2.68
1H-zSiCNR-2Cl	38.3	1.0	0.0	0.158	metallicity	-

All the geometrical structures of studied zSiCNRs systems with the heterogeneous diatomic edge-modification are shown in Figures 5 and 6. It can be found that similar to the case of homogenous diatomic edge-modification, the edge deformation of out-of-plane distortion in the heterogeneous diatomic edge-modification can be only observed at the Si/C edge saturated by the double F/Cl atoms, and the Si/C edge in other case can still exhibit the planar configuration.

Specifically, we first focus on employing double F and double H atoms to make a heterogeneous diatomic edge-modification on the 8-zSiCNR (Figures 5a and 5b), where the Si and C edges are saturated by two F(H) atoms and the corresponding two H(F) atoms, respectively (named as 2F-zSiCNR-2H and 2H-zSiCNR-2F). Our computed results reveal that the heterogeneous diatomic edge-modification by the 2F/2H pair can effectively break the magnetic degeneracy of zSiCNRs, where both 2F-zSiCNR-2H and 2H-zSiCNR-2F can uniformly display the AFM ground state (Table 2, Figures 5a and 5b), like the correlative homogeneous diatomic edge-modified systems 2F-zSiCNR-2F and 2H-zSiCNR-2H. However, the distinct electronic properties can be observed in 2F-zSiCNR-2H and 2H-zSiCNR-2F (Table 2, Figures 5a and 5b), where the former exhibits the similar half-metallic behavior to 2H-zSiCNR-2H (Figure 3a), while the latter with reverse modified mode presents the metallic characteristic, like 2F-zSiCNR-2F (Figure 3b).

Intriguingly, the similar situation can be also observed in the heterogeneous diatomic edge-modified zSiCNRs systems with the combination of double Cl and double H atoms, that is, both the studied systems 2Cl-zSiCNR-2H and 2H-zSiCNR-2Cl can exhibit the corresponding half-metallic and metallic behaviors in their AFM ground states (Table 2, Figures 5c and 5d), which are similar to the case of two related homogeneous diatomic edge-modified systems, namely, the half-metallicity in 2H-zSiCNR-2H (Figure 3a) and the metallicity in 2Cl-zSiCNR-2Cl (Figure 3c), respectively.

Obviously, the heterogeneous diatomic edge-modification by combining double halogen (F/Cl) and double H atoms can break the magnetic degeneracy of zSiCNR, where the sole AFM half-metallic and AFM metallic behaviors can be realized. By making a comparison, we can find that when the same double atoms are employed to decorate the C edge of zSiCNR in the heterogeneous and homogeneous edge-modification, the same electronic characteristic can be observed, regardless of the case of the Si edge, indicating that the atom modifying the C edge can have a crucial impact on the electronic properties of zSiCNR systems with the diatomic edge-modification. Moreover, we can also find that the gaps in minority channel for

half-metallic 2F-zSiCNR-2H (0.75 eV) and 2Cl-zSiCNR-2H (0.81 eV) systems are larger than that of the correlative 2H-zSiCNR-2H (0.62 eV) with homogeneous diatomic edge-modification (Table 2), suggesting that the heterogeneous diatomic edge-modification can be an effective approach to realize more robust half-metallic characteristic in the SiC-based nanomaterials, which is advantageous for promoting the practical application in the spintronics. This case can be further reflected by the following discussions on the heterogeneous asymmetric edge-modification.

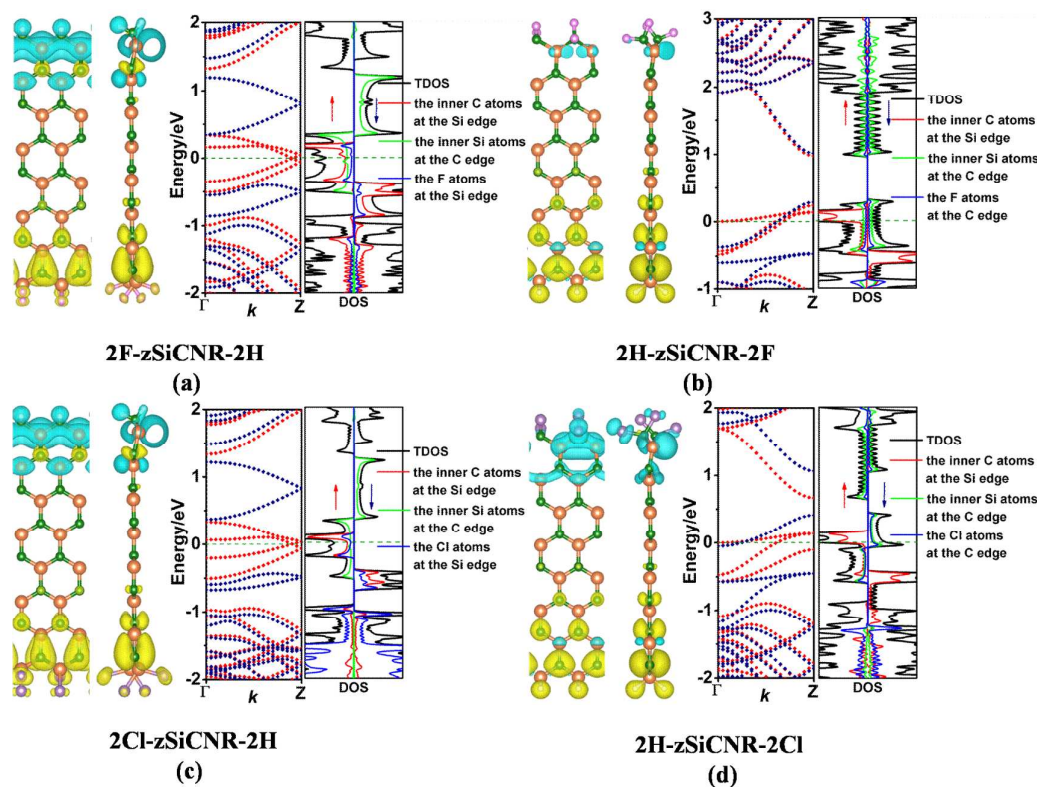


Figure 5. The spin charge densities, electronic band structures, and according DOSs of four systems with the heterogeneous symmetric edge-modification: (a) 2F-zSiCNR-2H, (b) 2Cl-zSiCNR-2H, (c) 2H-zSiCNR-2F and (d) 2H-zSiCNR-2Cl. The red and blue dotted lines denote the spin-up (\uparrow) and spin-down (\downarrow) channels, respectively. The Fermi-level is set as zero and indicated by the green dotted line.

To explore the origination of the half-metallicity and metallicity in these heterogeneous diatomic edge-modified zSiCNRs systems, we plot the corresponding DOSs pictures, as illustrated in Figure 5. It can be revealed that the half-metallic

behavior in 2F-zSiCNR-2H and 2Cl-zSiCNR-2H is uniformly attributed to the inner C/Si atoms in the same zigzag chain with the corresponding Si/C edge saturated by two halogen/hydrogen atoms and the decorated halogen atoms (Figures 5a and 5c). Comparatively, in the metallic 2H-zSiCNR-2F and 2H-zSiCNR-2Cl, both the energy levels across the Fermi level mainly originate from the inner C atoms bonding to the saturated Si edge in spin-up channel, and the inner Si atoms bonding to the saturated C edge as well as the modified halogen atoms in spin-down channel, respectively (Figures 5b and 5d).

Besides the heterogeneous mode by double halogen plus double hydrogen atoms, we further investigated the effect of heterogeneous asymmetric edge-modification by double halogen atoms partnering single H atom on the electronic and magnetic properties of zSiCNR, where one edge is saturated by two halogen F/Cl atoms and the other terminated by one H atom (Figure 6). Our computed results reveal that compared with the uniform AFM ground state of the heterogeneous edge-modified systems with double atoms decorating both of edges, different magnetic ground states can be observed in the correlative 2F/2Cl-zSiCNR-1H and 1H-zSiCNR-2F/2Cl systems with the heterogeneous asymmetric edge-modification (Table 2). Specifically, when double halogen atoms and single H atom decorate the Si and C edges of zSiCNR, respectively, the FM ground state can be found in the 2F/2Cl-zSiCNR-1H series, where the intriguing half-metallic behavior can be dominated by the inner C atoms at the saturated Si edge and the decorated halogen atoms, as well as the edge C atoms (Figures 6a and 6c). Moreover, we can find that similar to the case of heterogeneous pattern by double halogen plus double H atoms modifying both of edges (2F/2Cl-zSiCNR-2H), the heterogeneous asymmetric edge-modification can also bring a larger band gap in minority channel of the half-metallic 2F-zSiCNR-1H (2.71 eV) and 2Cl-zSiCNR-1H (2.68 eV) than the correlative homogeneous edge-modified 2F-zSiCNR-1F (2.48 eV), 2Cl-zSiCNR-1Cl (2.34 eV) and 2H-zSiCNR-1H (2.57 eV), respectively (Table 2). This can further demonstrate that the heterogeneous diatomic edge-modification can be an effective strategy to strengthen robustness of half-metallicity in the SiC-based nanomaterials.

Comparatively, when the corresponding reverse asymmetric modes are performed, namely, moving double halogen F/Cl atoms to modify the C edge and single H atom to the Si edge, respectively, the electronic and magnetic behaviors can be converted from the FM half-metallicity in 2F/2Cl-zSiCNR-1H to the AFM metallicity in 1H-zSiCNR-2F/2Cl (Table 2, Figures 6b and 6d), where the energy states crossing the Fermi level in both spin states can uniformly originate from the inner Si atoms at the saturated C edge and the modified halogen atoms, as well as the edge Si atoms (Figures 6b and 6d). Moreover, by making a comparison, we can observe that when using the same single/double atoms to modify the C edge of zSiCNR in the heterogeneous and homogeneous asymmetric edge-modification, the same electronic behavior can be also achieved, independent of the case of the Si edge, which can further reflect that the atom modifying the C edge can play a crucial role in dominating the electronic behavior of zSiCNR systems with the diatomic edge-modification (Tables 1 and 2).

Undoubtedly, like the homogeneous diatomic edge-modification by only halogen atoms, employing the combination of halogen F/Cl and H atoms with great electronegative difference to perform a heterogeneous diatomic edge-modification can be an effective strategy to break the magnetic degeneracy of zSiCNR, where more abundant electronic and magnetic behaviors invoking not only the AFM metallicity but also the AFM half-metallicity and FM half-metallicity can be observed. Particularly, this kind of heterogeneous asymmetric edge-modification can more effectively strengthen robustness of the half-metallicity, which is of benefit to promoting the application of excellent SiC-based nanomaterials in the spintronics. Additionally, by comparing the homogeneous and heterogeneous edge-modified systems, it can be found that the decorated atoms to the C-edge of zSiCNR can play an important role in affecting the electronic behavior of the modified systems.

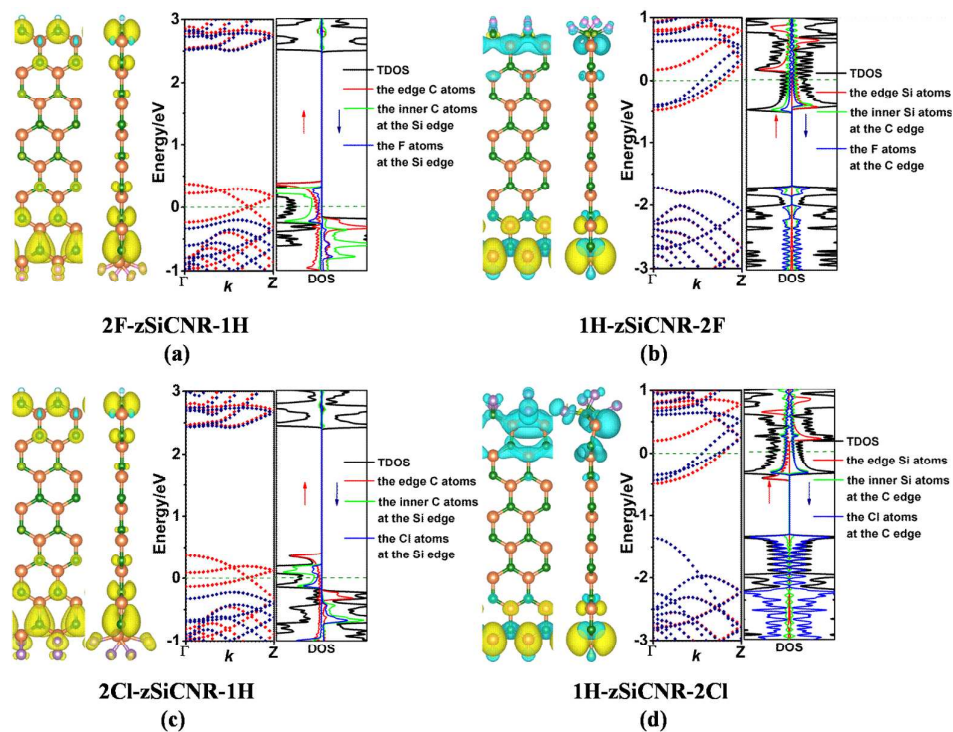


Figure 6. The spin charge densities, electronic band structures, and according DOSs of four systems with the heterogeneous asymmetric edge-modification: (a) 2F-zSiCNR-1H, (b) 2Cl-zSiCNR-1H, (c) 1H-zSiCNR-2F and (d) 1H-zSiCNR-2Cl. The red and blue dotted lines denote the spin-up (\uparrow) and spin-down (\downarrow) channels, respectively. The Fermi-level is set as zero and indicated by the green dotted line.

3.3 Half-metallic N_z -2F-zSiCNR-2H and N_z -2F-zSiCNR-1H/1F systems with the different width ($N_z=6, 8, 10, 12$ and 16)

It is well known that the half-metallicity in the low-dimensional nanostructures has aroused researchers' extensive attention,^{7, 13, 14, 57, 58} due to the promising application in spintronics. In this work, the intriguing half-metallic behavior can be observed in the homogeneous edge-modified 2F/2Cl-zSiCNR-1F/1Cl, as well as the heterogeneous 2F/2Cl-zSiCNR-1H and 2F/2Cl-zSiCNR-2H systems with the double halogen atoms uniformly saturating the Si edge (Tables 1~2 and Figures 4~6), where the magnetic coupling of ground state can be modulated by changing the decorated mode of the C edge: one halogen/hydrogen atom terminating the sp^2 -hybridized C edge can cause a FM behavior in the half-metallic 2F/2Cl-zSiCNR-1F/1Cl and 2F/2Cl-zSiCNR-1H, while an AFM coupling can be observed in 2F/2Cl-zSiCNR-2H with half-metallicity when double H atoms saturating the sp^3 -hybridized C edge.

Motivated by these fascinating findings, we naturally intend to investigate whether the half-metallic characteristic with controllable magnetic coupling can be maintained in the correlative modified zSiCNRs, when widening the ribbon width. For convenience, the studied systems can be denoted as N_z - nX -zSiCNR- mX , where N_z means the different ribbon width. In this section, we take the fluorinated structures, involving N_z -2F-zSiCNR-1F, N_z -2F-zSiCNR-1H and N_z -2F-zSiCNR-2H, as representatives to investigate the effect of the ribbon width on their electronic and magnetic properties by sampling $N_z=6, 8, 10, 12$ and 16 , considering that the fluorinated decoration can bring same electronic and magnetic behaviors as the corresponding chlorinated one, yet the former can endow these edge-decorated systems with larger edge formation energy (Table 3), which has been discussed in detailed in the next section.

Table 3. The relative energies of different magnetic couplings to the ground state, the edge formation energy, the electronic property and the band gap in minority channel of the ground state for some edge-fluorinated zSiCNRs with various widths ($N_z = 6, 10, 12$ and 16). NM, FM and AFM here represent the nonmagnetic, ferromagnetic and antiferromagnetic spin couplings, respectively.

System	$\Delta E(\text{meV})$			Edge formation energy($\text{eV}/\text{\AA}$)	Electronic property	Gap in minority channel (eV)
	NM	FM	AFM			
6-2F-zSiCNR-1F	188.4	0.0	1.2	-1.333	half-metallicity	2.52
10-2F-zSiCNR-1F	201.6	0.0	1.9	-1.333	half-metallicity	2.48
12-2F-zSiCNR-1F	196.3	0.0	1.9	-1.331	half-metallicity	2.46
16-2F-zSiCNR-1F	192.4	0.0	1.0	-1.332	half-metallicity	2.43
6-2F-zSiCNR-1H	217.6	0.0	1.6	-1.132	half-metallicity	2.78
10-2F-zSiCNR-1H	235.4	0.0	1.2	-1.132	half-metallicity	2.68
12-2F-zSiCNR-1H	232.4	0.0	1.3	-1.130	half-metallicity	2.64
16-2F-zSiCNR-1H	233.4	0.0	1.4	-1.330	half-metallicity	2.60
6-2F-zSiCNR-2H	192.9	10.9	0.0	-1.188	half-metallicity	0.78
10-2F-zSiCNR-2H	238.1	1.1	0.0	-1.179	half-metallicity	0.78
12-2F-zSiCNR-2H	247.2	1.0	0.0	-1.181	half-metallicity	0.76
16-2F-zSiCNR-2H	257.7	1.0	0.0	-1.181	half-metallicity	0.77

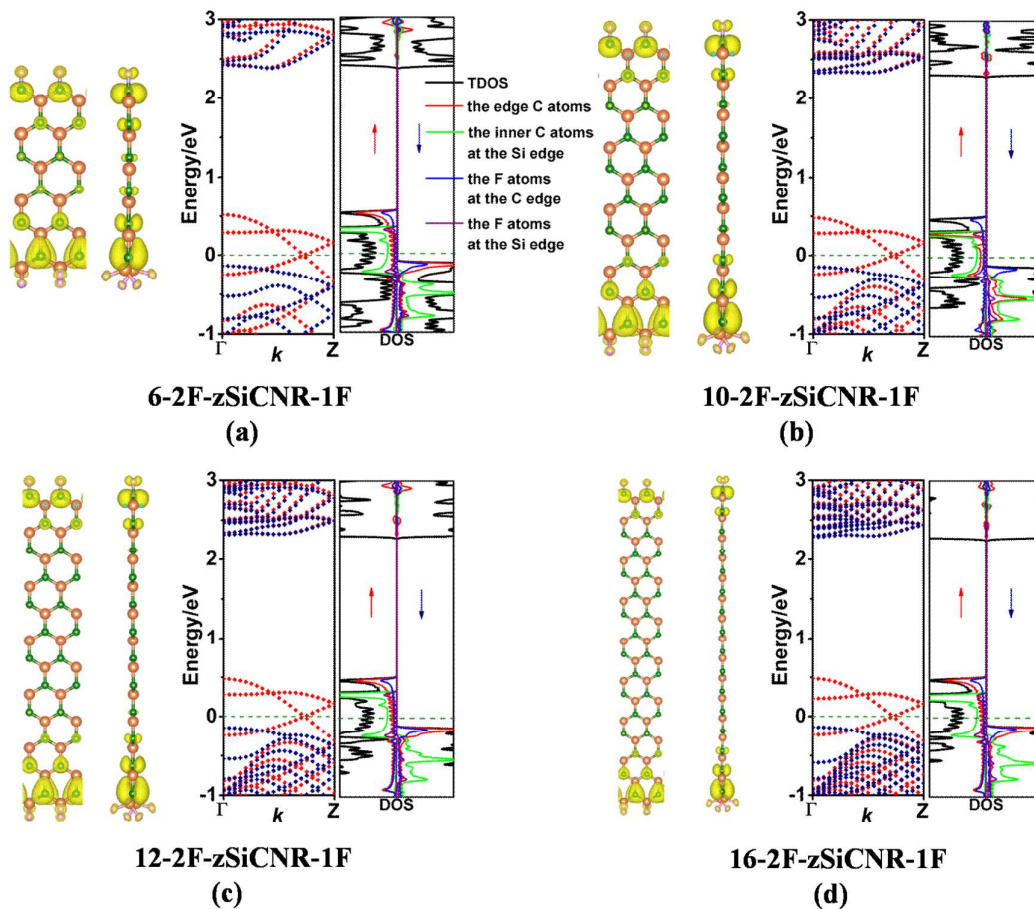


Figure 7. The spin charge densities, electronic band structures, and according DOSs of N_z -2F-zSiCNR-1F with $N_z=6, 10, 12$ and 16 , namely, (a) 6-2F-zSiCNR-1F, (b) 10-2F-zSiCNR-1F, (c) 12-2F-zSiCNR-1F and (d) 16-2F-zSiCNR-1F. The red and blue dotted lines denote the spin-up (\uparrow) and spin-down (\downarrow) channels, respectively. The Fermi-level is set as zero and indicated by the green dotted line.

Our computed results reveal that similar to the corresponding case with $N_z = 8$, all of these studied structures with different ribbon width can uniformly exhibit the out-of-plane structural deformation at the only Si edge saturated by dihalogen atoms, due to the steric effect (Figures 7 and 8).

Initially, we investigate the electronic and magnetic properties of the N_z -2F-zSiCNR-1F series ($N_z=6, 8, 10, 12$ and 16) with homogeneous asymmetric edge-modification. As illustrated in Table 3 and Figure 7a, we can find that when the ribbon width N_z is narrowed from 8 to 6, the robust FM half-metallic behavior can be

sustained, where the gap in minority channel can be as large as 2.52 eV in 6-2F-zSiCNR-1F. Conversely, as widening the width N_z to 10 and 12, even 16, a robust FM half-metallic characteristic can be also maintained, where the gaps in minority channel are also considerably large in the range of 2.43~2.48 eV (Table 3 and Figures 7b~7d).

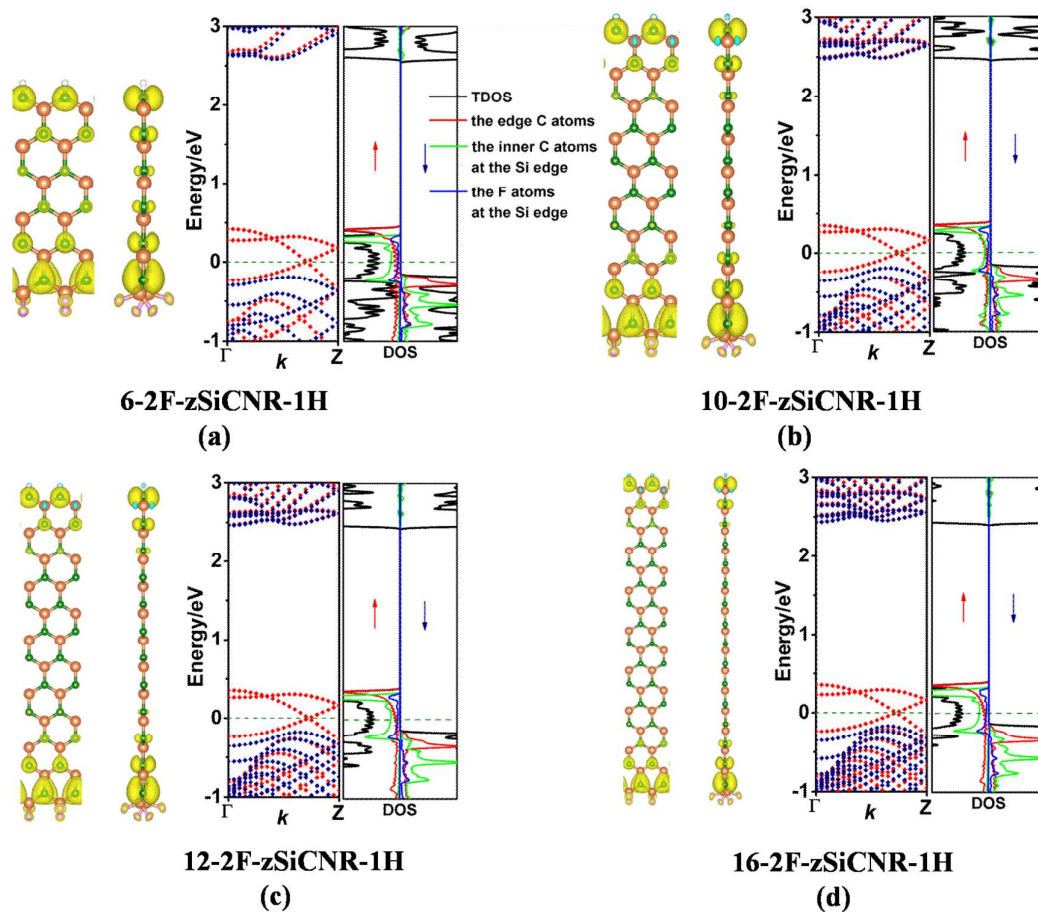


Figure 8. The spin charge densities, electronic band structures, and according DOSs of N_z -2F-zSiCNR-1H with $N_z = 6, 10, 12$ and 16 , namely, (a) 6-2F-zSiCNR-1H, (b) 10-2F-zSiCNR-1H, (c) 12-2F-zSiCNR-1H and (d) 16-2F-zSiCNR-1H. The red and blue dotted lines denote the spin-up (\uparrow) and spin-down (\downarrow) channels, respectively. The Fermi-level is set at zero and indicated by the green dotted line.

Similar to the homogeneous asymmetric N_z -2F-zSiCNR-1F series, the robust half-metallicity with FM magnetic couplings can be also maintained in N_z -2F-zSiCNR-1H ($N_z = 6, 8, 10, 12$ and 16) systems with heterogeneous asymmetric

edge-modification (Table 3 and Figure 8), which can be considered as the accordingly obtained structures by employing the H atom substituting the F atom decorating the C edge. However, it can be found that these heterogeneous asymmetrically edge-modified N_z -2F-zSiCNR-1H structures can exhibit much larger gap in minority channel in the range of 2.60~2.78 eV than the parallel the homogeneous ones (2.43~2.52 eV) (Table 3), which can further support that the heterogeneous asymmetric edge-modification can bring more robust half-metallicity, independent of ribbon width.

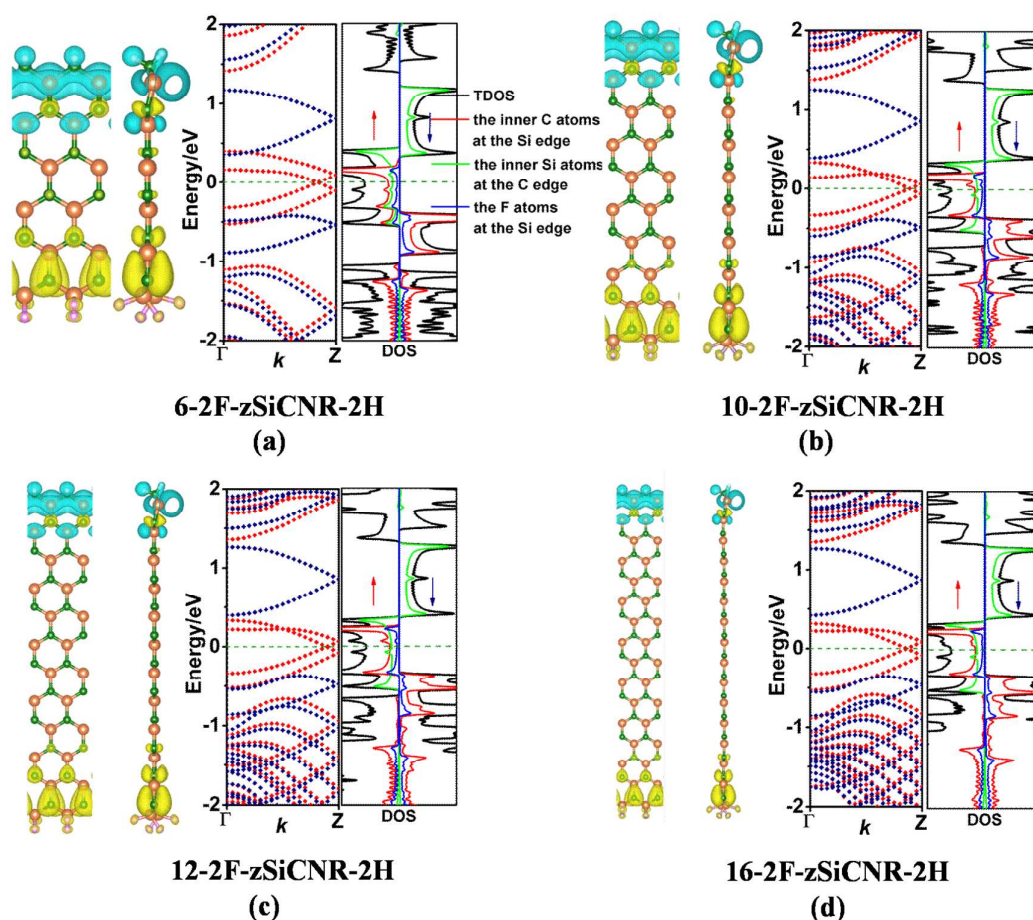


Figure 9. The spin charge densities, electronic band structures, and according DOSs of N_z -2F-zSiCNR-2H with $N_z = 6, 10, 12$ and 16 , namely, (a) 6-2F-zSiCNR-2H, (b) 10-2F-zSiCNR-2H, (c) 12-2F-zSiCNR-2H and (d) 16-2F-zSiCNR-2H with the saturated Si/C edge by two F/H atoms. The red and blue dotted lines denote the spin-up (\uparrow) and spin-down (\downarrow) channels, respectively. The Fermi-level is set as zero and indicated by the green dotted line.

Additionally, the similar continuity of half-metallicity can be also observed in the different widths of N_z -2F-zSiCNR-2H ($N_z = 6, 8, 10, 12$ and 16) series with heterogeneous edge-modification by 2F/2H pair, but the AFM instead of FM magnetic couplings correspond to their ground states (Table 3 and Figure 9), and their gaps in minority channel (0.75~0.78 eV) are smaller than the corresponding ones of homogeneous/heterogeneous asymmetric N_z -2F-zSiCNR-1F (2.43~2.52 eV) and N_z -2F-zSiCNR-1H (2.60~2.78 eV) series.

Further, the computed DOSs results reveal that the spin-up state crossing the Fermi level can share the similar DOS origination to the corresponding case with $N_z = 8$ for each fluorinated series (Figures 7~9), which can be responsible for the uniform half-metallic behaviors in the N_z -2F-zSiCNR-1F, N_z -2F-zSiCNR-1H and N_z -2F-zSiCNR-2H ($N_z = 6, 8, 10, 12$ and 16) series.

Clearly, regardless of the ribbon width, a robust half-metallicity can be achieved and maintained in the modified zSiCNR systems with dihalogen decorating Si edge, where not only AFM but also FM magnetic couplings can be achieved by tuning the decorated mode of the C edge. This is advantageous for promoting the SiC-based nanomaterials in the application of spintronics.

3.4 The edge formation energies of the nX -zSiCNR- mX' ($X/X' = F, Cl$ and H ; $n, m = 1$ or 2).

In this study, for all the diatomic edge-modified SiCNRs systems nX -zSiCNR- mX' ($X/X' = F, Cl$ and H ; $n, m = 1$ or 2), their edge formation energies per unit length of the edge (briefly named as the edge energy, E_{edge}) are evaluated by using the following formula,

$$E_{edge} = \frac{1}{2L} \left[E_T(nX - zSiCNR - mX') - n_{zSiC} E_{SiC} - (nE_{X_2} + mE_{X'_2})/2 \right]$$

where $E_T(nX$ -zSiCNR- mX') is the total energy of nX -zSiCNR- mX' system, E_{SiC} is the energy of one SiC pair in the optimized infinite SiC sheet, and n_{zSiC} is the number of SiC pairs in the modified zSiCNR. $E_{X_2}(E_{X'_2})$ is the energy of the isolated halogen/hydrogen molecule $X_2(X'_2)$, $n(m)$ is the total number of $X(X')$ atoms bonding

to the Si/C edge, and the factor of 2 in the last term accounts for the case that each $X_2(X_2')$ molecule can contribute two $X(X')$ atoms. Moreover, L is the length of an edge (the length of the unit cell), and the factor of 2 in front of L accounts for the fact that a zSiCNR has two edges. It is this edge energy that is usually used to determine the stability of structures with different edges.^{43,54-56} For example, the stability of the armchair edge over the zigzag edge for GNRs can be demonstrated by the case that the computed edge energies (*ca.* 0.06 ~ 0.10 eV per edge atom) for the armchair GNRs with different widths are totally lower than those (0.20 ~ 0.29 eV) of the zigzag GNRs.⁵⁶

All the computed edge formation energies of the studied $2X$ -zSiCNR- $2X'$ systems with the double atoms saturating both the edges, as well as $2X$ -zSiCNR- X' and X -zSiCNR- $2X'$ systems with the asymmetric modification, have been listed in Tables 1~2. For the purpose of comparison, three parallel H-passivated zSiCNR systems involving 2H-zSiCNR-2H, 2H-zSiCNR-1H and 1H-zSiCNR-2H were taken as references, where the calculated edge energies E_{edge} are 0.148, 0.168 and 0.191 eV/Å, respectively (Table 1). Clearly, the gradual increase of E_{edge} reflects a decreasing trend of the stability of these three diatomic-modified zSiCNRs with H atoms, which is consistent with the result reported previously by Lou.⁴³ Moreover, it is worth mentioning that these edge-modified zSiCNR systems with double H atoms, 2H-zSiCNR-2H, 2H-zSiCNR-1H and 1H-zSiCNR-2H, can exhibit much higher edge stability than the extensively studied 1H-zSiCNR-1H, with the single H atom terminating the Si/C edge, as a popular model.⁴³

Our computed results reveal that when employing the dihalogen atoms to substitute dihydrogen atoms modifying the Si/C edge of zSiCNR, the computed edge formation energies are -1.688 and -0.439 eV/Å for the obtained 2F-zSiCNR-2F and 2Cl-zSiCNR-2Cl systems, respectively, where the former is superior to the latter, yet both of which are much lower than that of the parallel 2H-zSiCNR-2H (0.148 eV/Å) (Table 1). Note that the negative edge energy means these halogenated structures can be formed spontaneously. Clearly, this kind of homogeneous symmetric diatomic edge-modification by the halogen F/Cl atoms can more significantly enhance the edge

stability of zSiCNR, where using the F atom can be more effectively than the Cl atom.

Similarly, the negative edge formation energies can be also observed in 2F/2Cl-zSiCNR-1F/1Cl (-1.330/-0.361 eV/Å) and 1F/1Cl-zSiCNR-2F/2Cl (-0.958/-0.086 eV/Å) systems with the homogeneous asymmetric edge-modification (Table 1), which are more favorable in energy than ones of the parallel asymmetric hydrogenated systems 2H-zSiCNR-1H (0.168 eV/Å) and 1H-zSiCNR-2H (0.191 eV/Å), and the edge-fluorinated structures are also more stable than the corresponding chlorinated counterparts. Moreover, the asymmetric edge-modified 2F/2Cl-zSiCNR-1F/1Cl (-1.330/-0.361 eV/Å) can exhibit the lower edge energies than the corresponding 1F/1Cl-zSiCNR-2F/2Cl (-0.958/-0.086 eV/Å) with the reverse modified mode, indicating that when performing the asymmetric edge-modification, using the dihalogen atoms to modify the Si-edge rather than the C-edge can more effectively improve the edge stability of zSiCNR.

Subsequently, we have computed the edge formation energies of zSiCNRs with the heterogeneous diatomic edge modification. It is revealed that the edge formation energies of 2F/2Cl-zSiCNR-2H and 2F/2Cl-zSiCNR-1H, as well as their corresponding reverse modified systems 2H-zSiCNR-2F/2Cl and 1H-zSiCNR-2F/2Cl are -1.178/-0.439, -1.130/-0.393, -0.388/0.149 and -0.353/0.158 eV/Å, respectively (Table 2). We can find that except for the 2H/1H-zSiCNR-2Cl (0.149/0.158 eV/Å) with the double/single H atoms and double Cl atoms modifying the corresponding Si and C edges, the rest of these heterogeneous edge-modified SiCNRs systems can uniformly exhibit the negative edge energies, much lower than ones of the parallel hydrogenated counterparts 2H-zSiCNR-2H (0.148), 2H-zSiCNR-1H (0.168) and 1H-zSiCNR-2H (0.191 eV/Å), respectively. Additionally, similar to the case of the homogeneous diatomic edge-modification, the heterogeneous edge-modified zSiCNRs systems with the double F atoms plus double/single H atoms can also exhibit the lower edge energies than the corresponding those with the Cl partnering H atoms; and the dihalogen atoms to modify the Si-edge can be also more advantageous to enhance the edge stability of zSiCNR with heterogeneous edge-modification.

Moreover, the edge formation energies have been also evaluated for three typical

series of N_z -2F-zSiCNR-1F, N_z -2F-zSiCNR-1H, and N_z -2F-zSiCNR-2H systems with the different widths ($N_z=6, 8, 10, 12$ and 16), as shown in Table 3. We can find that the edge energies for all the series are negative, and they are almost same for each series, namely, about -1.33 , -1.13 , and -1.18 eV/Å for N_z -2F-zSiCNR-1F, N_z -2F-zSiCNR-1H and N_z -2F-zSiCNR-2H, respectively. This indicates that these edge-fluorinated zSiCNR structures can be formed spontaneously independent of ribbon width.

Obviously, the homogeneous/heterogeneous symmetric/asymmetric diatomic edge-modification by the strong electron-withdrawing halogen atoms can be an effective strategy to significantly enhance the edge stability of zSiCNR by lowering substantially the corresponding edge formation energies, where employing the F atom is more favorable in energy than the Cl atom, and the double halogen atoms saturating the Si-edge can be more effective.

4. Conclusions

On the basis of first-principles DFT computations, we have performed a detailed investigation on the structures, electronic and magnetic properties of the homogeneous/heterogeneous diatomic edge-modified zSiCNR with double halogen F/Cl atoms decorating one edge and single/double halogen F/Cl or H atoms decorating the other, respectively. The following intriguing findings can be achieved:

(1) When the only halogen F/Cl atoms with strong electron-withdrawing ability are employed to modify the Si and C edges of 8-zSiCNR, this kind of homogeneous diatomic edge-modification can lift the magnetic degeneracy of the pristine zSiCNRs, where the sole AFM metallicity can be observed in the symmetrically decorated zSiCNRs with double halogen F/Cl atoms saturating both the edges, and FM half-metallicity and AFM metallicity can be achieved in the asymmetrically modified zSiCNRs with double halogen F/Cl atoms saturating one edge and the same single halogen F/Cl atom terminating the other, respectively.

(2) When applying the combination of halogen and hydrogen atoms with great electronegative difference to perform the heterogeneous diatomic edge-modification

for the pristine 8-zSiCNR, the broken energy degeneracy of FM and AFM states also occurs, where the sole AFM half-metallicity and AFM metallicity can be found in the heterogeneous edge-decorated zSiCNRs with double halogen F/Cl plus double H atoms, and the FM half-metallicity and AFM metallicity can be realized in the asymmetric edge-modified zSiCNRs with double halogen F/Cl atoms partnering single H atom, respectively. By comparing the homogeneous and heterogeneous edge-modified systems, it can be observed that the decorated atoms to the C-edge of zSiCNR can play an important role in affecting not only their electronic but also magnetic behaviors.

(3) Independent of ribbon width, the robust AFM or FM half-metallic behavior can be maintained in the sampled edge-fluorinated zSiCNR systems with double F atoms saturating Si edge and single H/F atom or double H atoms terminating C edge, where the heterogeneous asymmetric edge-modification can more effectively strengthen robustness of the half-metallicity, which is of benefit to promoting the SiC-based nanomaterials in the application of spintronics.

(4) For the all the studied zSiCNR systems, the only Si/C edge saturated by double F/Cl atoms can exhibit the out-of-plane structural deformation due to the steric effect, and the planar configuration can be still maintained at the Si/C edge in other cases. Employing strong electron-withdrawing halogen atom (especially F atom) to perform diatomic edge-modification can be advantageous to significantly improve the edge stabilities of the modified zSiCNR systems.

Undoubtedly, the diatomic edge-modification with halogen F/Cl atoms can be an effective strategy to break the magnetic degeneracy of the pristine zSiCNRs, and achieve the sole FM half-metallicity, AFM half-metallicity and AFM metallicity, which can endow the excellent SiC-based nanomaterials with the great potential for the application in spintronics and multifunctional nanodevices.

Acknowledgements. This work was supported in China by NSFC (21103065, 21373099 and 21173097), National Basic Research Program of China (973 Program) (2012CB932800), and the Ministry of Education of China (20110061120024 and

20130061110020). We acknowledge the High Performance Computing Center (HPCC) of Jilin University for supercomputer time.

Electronic Supplementary Information (ESI) Available: A computational test on the determination of the ground state by considering different antiferromagnetic configurations of the sampled 2F-zSiCNR-1F system (Table S1 and Figure S1).

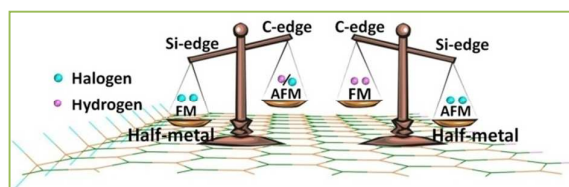
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TOC



The dihalogen edge-modification can effectively break the magnetic degeneracy of the pristine zSiCNRs, and significantly enhance edge stability.