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Vanadium sulfide nanoribbons: Electronic and magnetic properties

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ABSTRACT

We report the structural, electronic and magnetic properties of zigzag-type 2H-VS_2 nanoribbons based on the first-principles calculations. Our results suggest that the zigzag-type 2H-VS_2 nanoribbons are intrinsic ferromagnetic or ferrimagnetic materials dependent on their edge structures. The S-terminated VS_2 nanoribbons with or without hydrogen saturation at the edges are ferromagnetic, whereas V-terminated VS_2 nanoribbons are ferrimagnetic at their ground states. The average magnetic moment per V atom of VS_2 nanoribbons increases monotonously with their width, but still smaller than that of perfect VS_2 monolayer. These results imply the great potential of VS_2 nanoribbons in spintronics application.

1. Introduction

Developing spintronics with two-dimensional monolayer materials have attracted much research attention recently to meet the need of miniaturization of devices and massive information storage [1–7]. Much effort has been devoted to graphene and graphene-like materials, such as BN and ZnO monolayer. Although these materials are usually nonmagnetic, intensive studies have predicted that graphene, BN, or ZnO monolayer may possess magnetic properties via various physical or chemical methods [8–13]. For instance, the graphene nanoribbon (NR) with zigzag-type edges may be tuned into half metal by applying external electric field or chemically modified with different functional groups at both edges [8,9]. Introducing native defect, doping, or creating interface with substrate may also induce various magnetic properties in graphene, BN, ZnO, $MoTe_2$, $MoSe_2$, and WS_2 monolayer [10–16].

As a member of layered transition–metal dichalcogenide compounds, VS_2 has attracted increasing research attention since the first discovery in 1970s for its novel properties and promising applications in spintronics and energy storage [17–24]. There are two possible phases of VS_2 crystal, i.e. 1T- and 2H-phase, where 1T-phase has been observed experimentally with various interesting properties, such as coexistence of the charge density wave state and Mott transition [20–24]. In VS_2 compound, one layer of metal V is sandwiched between two layers of S, and the triple layers stack together through weak Van der Waals interaction. Thus, the graphene-like VS_2 monolayer may be realized by exfoliating VS_2 crystal. Recently, less than five VS_2 triple layers have been synthesized by intercalation compound precursor of $VS_2.NH_3$ into VS_2 ultrathin nanosheet [6]. Interestingly, the theoretical simulation has predicted that 2H-VS_2 monolayer is magnetic metal, suitable for spintronics applications [25].

In this Letter, we report the electronic and magnetic properties of 2H-VS_2 NRs based on the first-principles calculations. Both V and S-terminated zigzag-type VS_2 NRs are considered. Our results suggested that zigzag-type VS_2 NRs are intrinsic ferromagnetic or ferrimagnetic materials dependent on their edge structures. These results open a new door to design VS_2 monolayer based spintronic devices.

2. Materials and methods

All calculations are performed using the Vienna *ab initio* Simulation (VASP) package [26,27]. The frozen-core all-electron projector augmented wave (PAW) method was used to describe electron–ion interaction during the calculation, with the generalized gradient approximation with the PW91 functional for exchange-correlation energy [28–30]. A kinetic-energy cutoff of 400 eV is chosen for the plane wave expansion of the electronic wave function. To simulate one-dimensional VS_2 NRs with infinite length, a tetragonal supercell was used with two adjacent NRs separated by a vacuum region of at least 13 Å. A K-point mesh of $1 \times 1 \times 8$ grid was employed for geometry optimization, and $1 \times 1 \times 18$ grid for static electronic structure calculations. The axial lattice constant and atomic positions are fully relaxed until the force on each atom was less than 0.02 eV/Å, and the convergence criteria for energy 10^{-5} eV.

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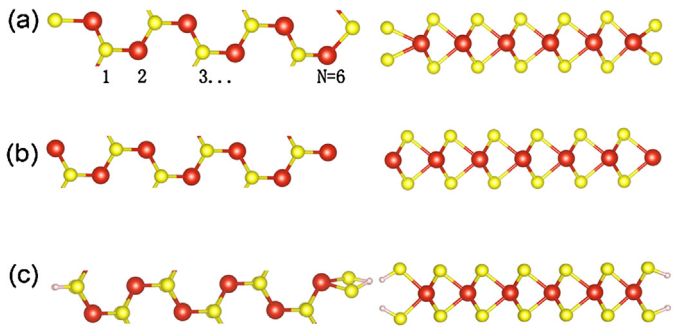

Fig. 1. The optimized structure of zigzag-type VS_2 NR terminated with (a) S, (b) V, or (c) hydrogenated S is illustrated. The red, yellow and small white balls represent V, S, and H atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this Letter.)

3. Results

Fig. 1 shows the optimized structures of three examples of 2H-VS_2 zigzag-type NRs terminated with V, S, or hydrogenated S atoms, namely VS_2-V, VS_2-S, and VS_2-H NRs, respectively. The width of ribbon is chosen as $N = 6$, where N indicates the number of zigzag-type atomic lines along the ribbon's direction, as shown in Fig. 1(a). The optimized lattice constant along the ribbon's direction is about 3.19 Å, which is in good agreement with that of previous work [6]. The V–S bond lengths in VS_2 NRs vary remarkably depending on the position of atoms due to the reconstruction of their edge. For example, the V–S bond lengths within the VS_2-S NR ($N = 6$) range from 2.36 to 2.38 Å, whereas range from 2.25 to 2.35 Å on the edge. For VS_2-V NR ($N = 6$), the V–S bond lengths range from 2.16 to 2.44 Å on the edge. The difference of V–S bond lengths for VS_2-V and VS_2-N NRs mainly originates from the number of dangling bonds at their edges. For instance, the edged V atom in the VS_2-V NR has two dangling bonds, whereas the edged S atom in the VS_2-S NRs has one dangling bond when cutting from VS_2 monolayer. The optimized S–H bond length of VS_2-H NR ($N = 6$) is about 1.36 Å. Also, the widths of zigzag-type VS_2 NRs depend on their edge structure for same N. The optimized widths of VS_2-V, VS_2-S, and VS_2-H NRs ($N = 6$) are 15.65, 16.87 and 18.68 Å, respectively.

To explore the electronic properties of VS_2 NRs, we calculated the total density of states (DOS) and partial DOS of V's 3d orbital and S's 2p orbital, as illustrated in Fig. 2. Three examples of zigzag-type VS_2 NRs are magnetic metals, independent of the chemical characteristic of their edges. The V's 3d orbital and S's 2p orbitals contribute significantly to the total DOS in the displayed energy windows of $[-6.0, 6.0]$ eV around the Fermi energy level, suggesting the strong hybridization of V's d orbital and S's p orbital. It is also evident that the magnetism of VS_2 NRs is mainly contributed by the V atoms, whereas S atoms only have a little contribution to the total magnetic moment.

In Fig. 3, we plotted the profiles of spin charge density distribution of three VS_2 NRs with $N = 6$. The spin charge density mainly distributes on V atoms, consistent with the calculated DOS. However, VS_2 NRs present an edge-dependent magnetic property. For VS_2-S and VS_2-H NRs, the ground state is ferromagnetic. The V atoms at the center region of NRs play an important role to the total magnetism, where the V atoms at the edge have a little contribution to the total magnetism. This behavior is different from that of zigzag graphene NR, where the edged carbon atoms have the largest contribution to the total magnetism [8]. The VS_2-V NR is ferrimagnetic at its ground state, as shown in Fig. 3(b). The total energies of its ferromagnetic, antiferromagnetic, and nonmagnetic states are higher than those of its ferromagnetic state of about 5.2, 12.0, and 254.3 meV per supercell. The V atoms neighbor to the edged V atoms are coupled in antiferromagnetic order with other V atoms. Different from those in VS_2-S and VS_2-H NRs, the edged V atoms in VS_2-V NR have the largest contribution to the total magnetism. Both H and S atoms have negligible contribution to the magnetism.

At last, the effect of ribbons' widths on their magnetic properties has been investigated. As shown in Fig. 4, the spin charge density distribution profiles of VS_2-S, VS_2-V, and VS_2-H NRs with various widths are plotted. Clearly, the magnetic orders of VS_2 NRs are not sensitive to their widths. For instance, the VS_2-S and VS_2-H NRs with $N = 4$ and 10 are ferromagnetic at their ground states, and have similar spin charge density distributions as the ribbon with $N = 6$. The V atoms at the center regions have the major contribution, whereas the edge ones have minor contribution to the total magnetism. The VS_2-V NRs with various widths ($N = 4, 5, 7, 8, 10$) are ferrimagnetic at their ground states and present the same magnetic order, i.e. the V atoms neighbor to the edged one are coupled with other V atoms in antiferromagnetic order. The edged V atoms present the largest contribution to the total magnetism of VS_2-V NRs. Note here we mainly studied the magnetic properties of zigzag-type VS_2 NRs with V, S or H termination. Test calculations were also performed on the zigzag-type VS_2 NRs with both V and S edge (VS_2-S-V), as well as the armchair-type VS_2 NRs. As shown in Fig. 5, the zigzag-type VS_2-S-V NR is ferrimagnetic at its ground state with similar spin charge distribution as that of zigzag-type VS_2-V NR at V edge. The armchair-type VS_2 NR is ferromagnetic at its ground state and spin charge density mainly locates on the V atoms within the ribbon.

In Fig. 6, we plotted the average magnetic moment of V atom for VS_2 NRs with different edge structures and widths. The average magnetic moment of V atom is defined as the total magnetic moment of VS_2 NR divided by the number of V atoms. For

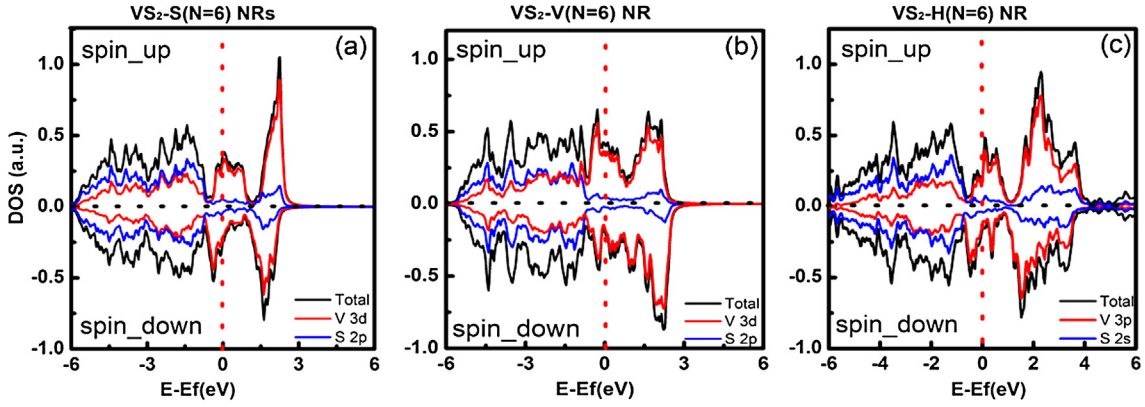

Fig. 2. The total DOS and partial DOS of V's 3d orbital and S's 2p orbital are plotted for (a) VS_2-S, (b) VS_2-V, and (c) VS_2-H NRs ($N = 6$), respectively.