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Symmetrical metallic and magnetic edge states of nanoribbon from semiconductive monolayer PtS_2

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ABSTRACT

Transition metal dichalcogenides (TMD) MoS_2 or graphene could be designed to metallic nanoribbons, which always have only one edge show metallic properties due to symmetric protection. In present work, a nanoribbon with two parallel metallic and magnetic edges was designed from a noble TMD PtS_2 by employing first-principles calculations based on density functional theory (DFT). Edge energy, bonding charge density, band structure, density of states (DOS) and simulated scanning tunneling microscopy (STM) of four possible edge states of monolayer semiconductive PtS_2 were systematically studied. Detailed calculations show that only Pt-terminated edge state among four edge states was relatively stable, metallic and magnetic. Those metallic and magnetic properties mainly contributed from 5*d* orbits of Pt atoms located at edges. What's more, two of those central symmetric edges coexist in one zigzag nanoribbon, which providing two atomic metallic wires thus may have promising application for the realization of quantum effects, such as Aharanov–Bohm effect and atomic power transmission lines in single nanoribbon.

1. Introduction

Conventional one-dimensional (1D) metallic wires have been widely studied during the last twenty years using semiconductor heterostructures with a length scale of micro meter [1]. Up to date, the growth of atomic one-dimensional metallic wire still remains somewhat challenging, instead scientists have been trying to find metallic edges by tailoring two-dimensional (2D) semiconductive materials [2,3]. Such edge states would then be a realization of 1D transporting channels as metallic wires. Besides graphene [4], monolayer TMDs have also received much attention due to their excellent physical properties of both fundamental significance and potential applications in electronics, optoelectronics, spintronics and catalysis [3–13]. Recently, in a monolayer MoS_2 nanoflake, localized metallic states, i.e., 1D metallic channels at the edges have been realized, which may provide a platform for the studies on quantum phenomena like Aharanov–Bohm effect, persistent currents and weak localization in atomic scale [12,14]. Controlled bottom-up fabrication of $MoSe_2$ nanoribbons have demonstrated that the self-passivation morphological phase transition of the Mo-terminated edges show metallic properties [15,16]. However, the atomic structural symmetry of both monolayer MoS_2 and $MoSe_2$ are trigonal (2H phase) which determines the zigzag-edge nanoribbons of those 2D materials should have two different edges (one is Mo-terminated and the other is S-terminated) [3]. The Mo-terminated edge is metallic and magnetic while the S-terminated is not. Such a nanoribbon from MoS_2, $MoSe_2$ or graphene only has one metallic channel.

Is it possible to have two channels in one nanoribbon? Herein we address the question whether a more flexible metallic edge states of nanoribbons could be realized by tailoring another type of monolayer materials, such as Nobel TMD PtS_2. Nobel TMDs (10 group) are not our familiar 2D TMDs (6 group) [17]. They show extraordinary electronic and electrocatalysis properties [18–21], attracting much attention recently. Structurally, the space group of the stable structure of PtS_2 is $P\bar{3}m1$ with Pt in octahedral coordination, while 2H-MoS_2 is $P\bar{6}m2$ where Mo site is in a trigonal prism coordination [22]. For the possible edges of monolayer PtS_2, there are four types of edge states, i.e., Pt–S, S–Pt, S–S and armchair edges, as shown in Fig. 1. However, up to date, the edge states of the noble TMD PtS_2 are still unknown and designing two parallel metallic edges of nanoribbon is expected to be realized.

In this work, we employ first-principles calculations within DFT to explore systematically all possible edge states of monolayer

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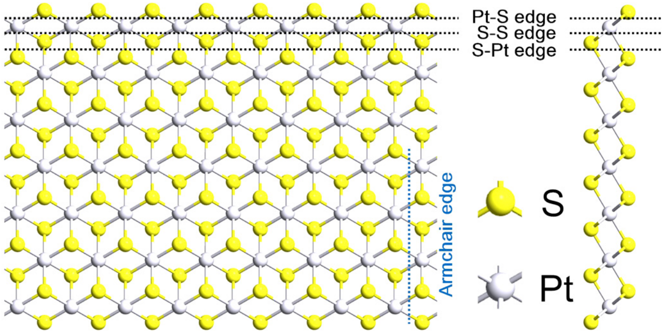


Fig. 1. Schematic drawing show on how to cut three zigzag- and one armchair-edge from monolayer PtS_2 nanoribbon, which then named as Pt–S, S–S, S–Pt and armchair nanoribbons respectively. The left and right panels were drawn from top- and side-view.

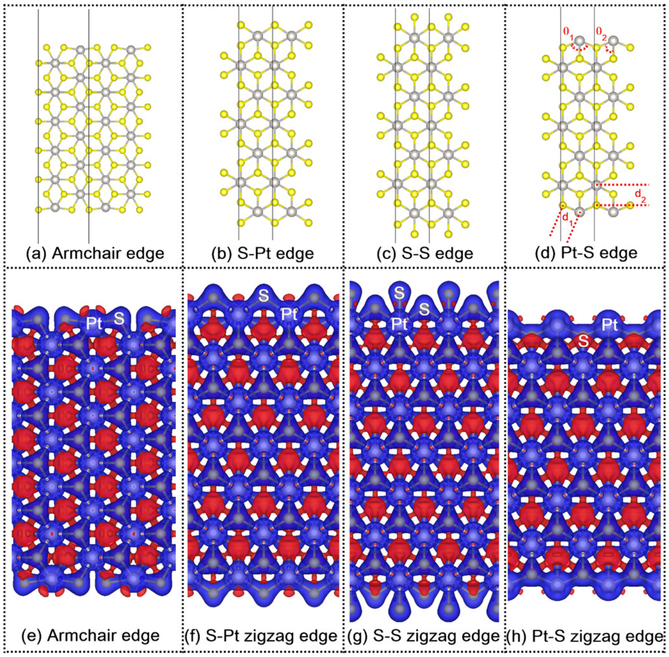
PtS_2. It is found that Pt-terminated zigzag-edge nanoribbon was the only one among the four possible types edges showing metallic and magnetic electronic structure properties. Detailed calculations show that those properties come from 5*d* orbit of Pt atoms located at two symmetric edges of the nanoribbon. Besides the symmetric edges, what intriguing were the bands crossing and near the Fermi level also show closely central symmetry. This kind of two symmetric channels of nanoribbon may be promising quantum devices for realization of atomic power transition lines.

2. Method

First-principles calculations were based on DFT implemented in the Vienna Ab initio Simulation Package (VASP) [23–25] with projector-augmented wave (PAW) potential [26]. The generalized gradient approximation (GGA) with the exchange-correlation functional of Perdew–Burke–Ernzerhof (PBE) [27] was employed. Convergence tests indicated that 365 eV was a sufficient cutoff (higher than $1.3*$default value) for PAW potential to achieve high precision in all the zigzag and armchair nanoribbons supercells calculations. The global break condition for the electronic self-consistency is chosen as 10^{-5} eV per supercell. Due to the ferromagnetic nature of Pt and Mo, all related calculations were performed using spin-polarized approximation unless otherwise noted. All atoms on edges and on center partial of the nanoribbons are fully optimized for calculations until the residual forces were less than 0.01 eV/Å by using conjugate gradient (CG) algorithm. STM images were simulated in constant-current mode at different bias voltages by using Tersoff–Hamann approximation, which illustrates that the tunneling current is proportional to the local density of states (LDOS) of the sample [28]. The crystal structure and charge density are plotted by VESTA [29].

3. Result and discussion

Let's begin with the calculation of electronic structure of monolayer PtS_2. It is a semiconductor with indirect bandgap of 1.60 eV from experimental data [30]. Our DFT calculation indicates an indirect bandgap of 1.81 eV, which well consistent with previous simulation work of 1.80 eV [20]. For the structure of nanoribbons of PtS_2, there are three possible zigzag nanoribbon edges could be cut from PtS_2, while for cutting armchair nanoribbon, we have only one option. To avoid the interaction between the two edges, the minimum width of nanoribbon used in the calculations was sufficiently large as 18.11 Å (Pt–S edge supercell).



(a) Armchair edge (b) S-Pt edge (c) S-S edge (d) Pt-S edge
(e) Armchair edge (f) S-Pt zigzag edge (g) S-S zigzag edge (h) Pt-S zigzag edge

Fig. 2. (a–d) are relaxed armchair, S–Pt, S–S and Pt–S edge nanoribbon supercells, respectively. The isosurfaces of 0.008 eV^{-3} level are drawn in (e–h) corresponding to (a–d), where the red zones represent accumulation of electron while the blue ones loss of electron. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The stability of PtS_2 nanoribbons are quite important since it determine whether the nanostructure with such edges could be realized experimentally. The stabilities of nanoribbons were determined by the stabilities of the edges. We tailor four types of edges as Pt–S, S–Pt, S–S and armchair edge from PtS_2 nanoribbons, as shown in Fig. 1. Then four nanoribbon supercells named as Pt–S, S–Pt, S–S and armchair nanoribbons were built for later first principles electronic structure calculations. The edge at one side is central symmetrical to the opposite side. In order to determine the stabilities of the edges, we first relax all the atoms in the four supercells. During the relaxation, Pt and S atoms along all the four kinds of edge supercells are slightly contracting, while the position of center atoms remain unchanged, as shown in Fig. 2 (a–d). Take Pt–S edge nanoribbon supercell, for example, shown in Fig. 2 (d), outermost of two of three Pt–S bonding (d_1) along edge relaxed to be shorter, from 2.40 Å to 2.22 Å, while one Pt–S bonding (d_2) from 2.40 Å to 2.41 Å, which resulting in two angle of S–Pt–S to be larger, θ_1 from 96° to 107° and θ_2 from 84° to 93° separately. The central atoms of the nanoribbon remain unchanged. When we employ an enlarged supercell to the same relaxation, we get the similar structure of nanoribbon. The relaxation reveals that the zigzag and armchair nanoribbons of PtS_2 are mechanically stable because atoms along edges didn't obviously move during relaxing, not to mention phase transformation.

In order to quantitatively determine the stability of the types of nanoribbons, the so-named edge energy was defined as follows. The edge energy σ of PtS_2 here could be calculated by: $\sigma = (E - N_{Pt} * \mu_{Pt} - N_S * \mu_S)/(N * 2L)$, where E, N and L represent the total energy, the number of atoms and the length of the edges of supercell respectively. While μ_{Pt} and μ_S are the chemical potentials of Pt and S respectively. They satisfy the formula of $E_{PtS_2} = \mu_{Pt} + 2 * \mu_S$, where E_{PtS_2} is the total energy of single crystal cell of monolayer PtS_2 with three atoms. In order to obtain the relative edge energy of supercells with different stoichiometry, we vary the chemical potential of S atom. For the edge energy related to stability, those with the lowest curve are most stable. The edge energies of all the possible nanoribbons were summarized in Fig. 3. Present results demonstrate that the most stable PtS_2 edge are Pt–S for $\mu_S < -5.8$ eV, armchair edge for $-5.8 < \mu_S < -3.2$ eV and S–S edge for $\mu_S > -5.8$ eV. This can be understood by simply relating high S chemical potential to S-rich stable edges, and the low

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