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## Transition metal dichalcogenide magnetic atomic chains†

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Reducing the dimensions of a material to the atomic scale endows them with novel properties that are significantly different from their bulk counterparts. A family of stoichiometric transition metal dichalcogenide (TMD)  $\text{MX}_2$  ( $\text{M} = \text{Ti to Mn}$ , and  $\text{X} = \text{S to Te}$ ) atomic chains is proposed. The results reveal that the  $\text{MX}_2$  atomic chains, the smallest possible nanostructure of a TMD, are lattice-dynamically stable, as confirmed from their phonon spectra and *ab initio* molecular dynamics simulations. In contrast to their bulk and two-dimensional (2D) counterparts, the  $\text{TiX}_2$  atomic chains are nonmagnetic semiconductors, while the  $\text{VX}_2$ ,  $\text{CrX}_2$ , and  $\text{MnX}_2$  chains are unipolar magnetic, bipolar magnetic, and antiferromagnetic semiconductors, respectively. In addition, the  $\text{VX}_2$ ,  $\text{CrX}_2$ , and  $\text{MnX}_2$  chains can be converted *via* carrier doping from magnetic semiconductors to half metals with reversible spin-polarization orientation at the Fermi level. Of these chains, the  $\text{MnX}_2$  chains exhibit either ferromagnetic or antiferromagnetic half metallicity depending on the injected carrier type and concentration. The diverse and tunable electronic and magnetic properties in the  $\text{MX}_2$  chains originate, based on crystal field theory, from the occupation of the metal d orbitals and the exchange interaction between the tetrahedrally coordinated metal atoms in the atomic chain. The calculated interaction between the carbon nanotubes and the  $\text{MX}_2$  chains implies that armchair (7,7) or armchair (8,8) carbon nanotubes are appropriate sheaths for growing  $\text{MX}_2$  atomic single-chains in a confined channel. This study reveals the diverse magnetic properties of  $\text{MX}_2$  atomic single-chains and provides a promising building block for nanoscale electronic and spintronic devices.

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## 1. Introduction

Reducing the dimensionality of bulk materials has emerged as a practical route to engineer the properties of materials and create a wave of exciting research in two-dimensional (2D) materials.<sup>1</sup> One example is atomically thin 2D graphene, which exhibits intriguing physical properties.<sup>2</sup> Inspired by the discoveries of 2D atom-thin materials, atom-thin one-dimensional (1D) wires (or atomic chains), made from silicon,<sup>3</sup> carbon,<sup>4</sup> pnictogens,<sup>5</sup> chalcogens,<sup>6,7</sup> iodine,<sup>8</sup> metal chains,<sup>9,10</sup> semiconducting compounds,<sup>11,12</sup> metal oxides,<sup>13</sup> oxyhydroxides,<sup>14</sup> and molecular wires,<sup>15–17</sup> have been explored. These materials have received enormous attention for both their exotic electronic properties, such as strong quantum confinement,<sup>18,19</sup> novel edge states,<sup>20,21</sup> polarization,<sup>22,23</sup> and

their wide array of applications in nanoconnectors,<sup>10,24</sup> transistors,<sup>25</sup> optoelectronics,<sup>26</sup> catalysts,<sup>27,28</sup> and spintronics.<sup>15,29</sup>

Transition metal dichalcogenides (TMDs) are a class of layered van der Waals material with versatile electronic and magnetic properties.<sup>30</sup> In the past few years, 2D TMDs, which have different properties to those of bulk TMDs, have been widely investigated due to their unique combination of atomic thickness, direct band gap, strong spin–orbital coupling and enhanced catalytic properties.<sup>30,31</sup> Meanwhile, efforts also have been devoted to the reduction of the dimensionality of TMD materials to create atomic chains.<sup>32,33</sup> Experimentally, various ultrathin wires based on transition metal chalcogenides, such as transition metal monochalcogenides (TMM),<sup>34–38</sup> transition metal trichalcogenides (TMT),<sup>39–41</sup>  $\text{CrSbSe}_3$ ,<sup>42</sup>  $\text{Mo}_2\text{S}_5$ ,<sup>21</sup>  $\text{Mo}_5\text{S}_4$ ,<sup>43</sup>  $\text{Mo}_2\text{Se}_5$  ultrathin wires,<sup>24</sup> single-unit-cell  $\text{Cu}_9\text{S}_5$  wires,<sup>44</sup> and segmented linear chains,<sup>23</sup> have been synthesized. Fascinating physical and chemical properties, such as an anisotropic optical response,<sup>35</sup> oscillating edge states,<sup>21</sup> torsional waves,<sup>41</sup> nontrivial spin-polarization,<sup>23</sup> and high electrocatalytic activity,<sup>44</sup> have been observed. Nevertheless, stoichiometric TMD atomic chains have rarely been reported.

Herein, we reported a family of stable 1D stoichiometric TMDs  $\text{MX}_2$  ( $\text{M} = \text{Ti to Mn}$ , and  $\text{X} = \text{S to Te}$ ) atomic chains *via* the use of first-principles calculations. Stable  $\text{MX}_2$  atomic chains

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consist of a metal backbone, which is tetrahedral coordinated with a chalcogen exterior cap. The computed formation energies of these  $\text{MX}_2$  chains are on the same order as those of their 2D counterparts. With the exception of the  $\text{TiX}_2$  chain, the 1D  $\text{MX}_2$  chains are either ferromagnetic (FM) or antiferromagnetic (AFM) semiconductors, depending on the occupation of metal d orbital. Meanwhile, a transition from a magnetic semiconductor to a half-metal with a tunable magnetic ground state and coupling strength can be achieved *via* electron or hole doping. The  $\text{VTe}_2$  chain has a large magnetic anisotropic energy (MAE) of 3.78 meV per metal and strong inter-chain FM coupling. Finally, the  $\text{MX}_2$  chains may possibly be realized experimentally by growing them as armchair (7,7) or armchair (8,8) carbon nanotubes (CNT). The semiconducting character of TMD atomic chains together with their tunable magnetic and electronic properties make them promising building blocks for use in optoelectronics and spintronics.

## 2. Results and discussion

As illustrated in Fig. 1a, different configurations of 1D  $\text{MX}_2$  ( $M$  = transition metal atoms from Sc to Ni;  $X$  = S, Se, or Te) atomic chains, including the armchair (A-type), zigzag (Z-type), planar quadrilateral (Q-type), tetrahedral (T-type), and cage-like (C-type)<sup>45</sup> atomic arrangements, were investigated to determine the most stable structures. The calculated energy differences

between different configurations vary from 0.04 to 2.62 eV per metal atom, as summarized in Table S1 (see ESI†). According to the calculated energies,  $\text{TiX}_2$ ,  $\text{VX}_2$ ,  $\text{CrX}_2$ ,  $\text{MnS}_2$ ,  $\text{MnSe}_2$ ,  $\text{FeS}_2$ , and  $\text{FeSe}_2$  chains prefer T-type configurations, while  $\text{MnTe}_2$ ,  $\text{FeTe}_2$ ,  $\text{ScX}_2$ ,  $\text{CoX}_2$ , and  $\text{NiX}_2$  chains prefer Z-type configurations. Here, only the most energy favourable configurations were considered to explore their stability. Note that the tetrahedral coordination geometry widely exists in binary compounds (*e.g.* the zinc blende crystals) and the repeat units have been observed in metal chalcogenide molecules and clusters.<sup>46–50</sup>

The optimized lattice constants range from 5.13 to 6.72 Å and from 3.19 to 4.09 Å for T-type and Z-type  $\text{MX}_2$  atomic chains, respectively (Table S2†). The variation of the atomic radius is consistent with the calculated lattice constants. The lattice stability of the 1D  $\text{MX}_2$  atomic chains was further investigated through phonon dispersion spectra calculations and *ab initio* molecular dynamics simulations (AIMD). From Fig. S1† we can see that  $\text{TiX}_2$ ,  $\text{VX}_2$ ,  $\text{CrS}_2$ ,  $\text{MnX}_2$ , and  $\text{NiTe}_2$  atomic chains are lattice-dynamically stable as they lack an imaginary vibrational mode. In addition, AIMD simulations were performed at a temperature of 300 K for 5 ps to check the thermodynamical stability of the  $\text{MX}_2$  chains. A supercell containing five repeat units was used. From Fig. S2† we can see that only the T-type atomic chains,  $\text{TiX}_2$ ,  $\text{VX}_2$ ,  $\text{CrX}_2$ , and  $\text{MnX}_2$ , can retain their 1D lattice structures at 300 K without significant distortion and that the maximum fluctuation of the total energy is 0.06 eV per atom. This implies that their structures are thermodynamically stable at room temperature. The atomic coordinates of these nine stable chains are summarized in Table S3†.

The thermal stability of the  $\text{MX}_2$  atomic chains can be understood using the M–X bond strength and formation energy. As summarized in Table 1, Bader charge analysis indicates that about 0.88 to 1.93 electrons are moved from the metal onto the chalcogens.<sup>51</sup> These values are larger than those in TMM chains,<sup>52</sup> resulting in smaller bond lengths between the metal and chalcogen,<sup>53</sup> and thus stronger bonding in the  $\text{MX}_2$  chains. In addition, the average formation energies per metal atom of the  $\text{MX}_2$  chains, defined as  $E_f = (E_{\text{NW}}(\text{M}_2\text{X}_4) - 2E(\text{M}) - 4E(\text{X}))/6$ , were also calculated.  $E_{\text{NW}}(\text{MX}_2)$ ,  $E(\text{M})$ , and  $E(\text{X})$  represent the total energies of the atomic chain and the metal atoms

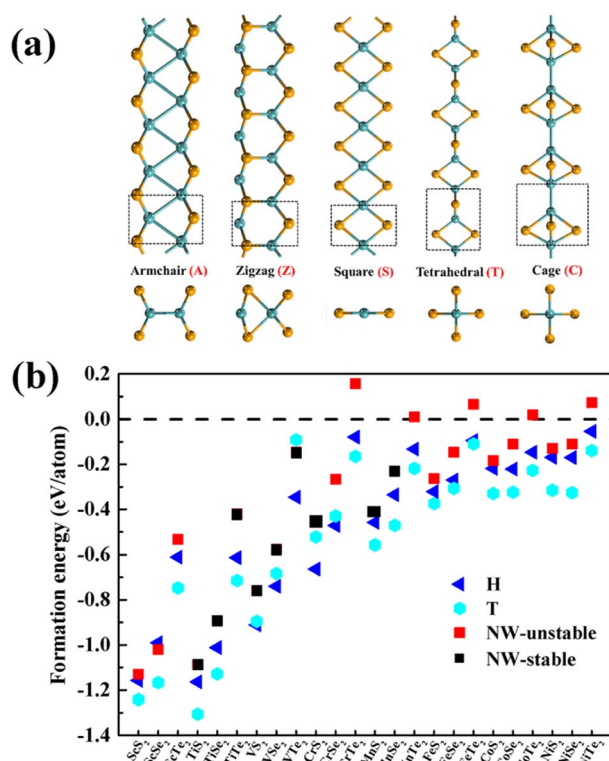


Fig. 1 (a) Five 1D  $\text{MX}_2$  configurations with armchair, zigzag, planar quadrilateral, tetrahedral, and cage-like atomic arrangements. Black rectangles represent the repeated unit cells. (b) The formation energies of H-phase and T-phase TMD monolayers and TMD atomic chains (NW denotes nanowire).

Table 1 The distance between metals ( $D$ , Å), M–X bond lengths ( $B$ , Å), charge on the metal ( $C$ , e), local magnetic moment of the central metal ion ( $M$ ,  $\mu_B$ ), ground state (GS, SC denotes semiconductor), energy gap ( $E_g$ , eV), and gap type (D and In represent direct and indirect band gap) of the TMD chains

Chains	$D$	$B$	$C$	$M$	GS	$E_g$
$\text{TiS}_2$	3.09	2.29	1.93	0.0	NM-SC	2.39 (D)
$\text{TiSe}_2$	3.19	2.41	1.78	0.0	NM-SC	1.96 (D)
$\text{TiTe}_2$	3.36	2.64	1.56	0.0	NM-SC	1.31 (D)
$\text{VS}_2$	2.86	2.21	1.18	0.9	FM-SC	1.34 (D)
$\text{VSe}_2$	2.95	2.35	1.37	1.0	FM-SC	0.67 (D)
$\text{VTe}_2$	3.09	2.56	1.08	1.2	FM-SC	1.26 (D)
$\text{CrS}_2$	2.66	2.15	1.23	2.0	FM-SC	1.32 (In)
$\text{MnS}_2$	2.62	2.11	1.04	1.2	AFM-SC	1.64 (In)
$\text{MnSe}_2$	2.71	2.25	0.88	1.3	AFM-SC	1.07 (D)



calculated from their most stable bulk or molecular phases. The calculated values of  $E_f$  for the  $\text{MX}_2$  atomic chains are negative, with the exception of the  $\text{MTe}_2$  atomic chains, implying that the synthesis of  $\text{MX}_2$  atomic chains from their bulk precursors is exothermic. The calculated  $E_f$  increases monotonically with the atomic number of the metals or X, varying from S to Te. The formation energies of nine stable T-type  $\text{MX}_2$  chains are comparable with those of their 2D  $\text{MX}_2$  counterparts and previously-synthesized 1D TMM and TMT wires (Fig. 1b and Tables S2 and S4†).<sup>53</sup> In particular, nine stable T-type  $\text{MX}_2$  chains have more negative formation energies than an experimentally synthesized T-phase  $\text{CrTe}_2$  nanosheet<sup>54</sup> and single-chain NWs made from  $\text{W}_6\text{Te}_6$ ,  $\text{VTe}_3$  and  $\text{NbTe}_3$  (Fig. 1b),<sup>38,39,53</sup> implying that the creation of T-type  $\text{MX}_2$  atomic chains is experimentally feasible.

The magnetic configurations of four 1D  $\text{MX}_2$  chains, including nonmagnetic (NM), FM, and AFM orderings, were considered when determining the magnetic ground state (Fig. S3†). As summarized in Table S5,† the  $\text{TiX}_2$  chains have NM ground states, while the  $\text{MnS}_2$  and  $\text{MnSe}_2$  chains have AFM-1 ground states where the FM-AFM energy differences are equal to 540 and 709 meV per metal atom at the HSE06 level, respectively. In contrast, the  $\text{VS}_2$ ,  $\text{VSe}_2$ ,  $\text{VTe}_2$ , and  $\text{CrS}_2$  chains have FM ground states with energy differences ranging from 62 to 426 meV per metal atom. The plotted spin charge density profiles in Fig. S4† reveal that the spin polarization is predominantly distributed on the central metal atom. As shown in Table 1, the local magnetic moments at the metal atom are 0.9 ( $\text{VS}_2$ ), 1.0 ( $\text{VSe}_2$ ), 1.2 ( $\text{VTe}_2$ ), 2.0 ( $\text{CrS}_2$ ), 1.2 ( $\text{MnS}_2$ ), and 1.3 ( $\text{MnSe}_2$ )  $\mu_B$ , respectively.

From Fig. 2 and S5† we can see that all  $\text{MX}_2$  chains are either direct or indirect band gap semiconductors where the values of the band gap range from 0.67 to 2.39 eV, as summarized in Table 1.  $\text{TiX}_2$  chains are NM semiconductors with a direct band

gap ranging from 1.31 to 2.39 eV. The  $\text{MnS}_2$  chain is an AFM indirect band gap semiconductor, while  $\text{MnSe}_2$  is an AFM direct band gap semiconductor. The  $\text{VX}_2$  and  $\text{CrX}_2$  chains are unipolar magnetic semiconductors (UMS) and bipolar magnetic semiconductors (BMS).<sup>55</sup>

The projected density of states (PDOS) and the partial charge density of the valence band maximum (VBM) and conduction band minimum (CBM) were plotted to reveal the contributions of the metal and chalcogen atoms (Fig. 2 and S6†). The orbital energy levels and distributions indicate that the VBM and CBM of the  $\text{TiX}_2$  chains consist of chalcogen and Ti orbitals, respectively, while the orbitals of both the chalcogens and the Cr atoms contribute to the VBM and CBM of the  $\text{CrS}_2$  chain. Conversely, the CBM of the  $\text{VX}_2$  chains are generated, with the exception of the  $\text{VTe}_2$  chain which is formed from Te orbitals, from the orbitals of the chalcogens. The  $\text{MnX}_2$  chains consist of orbitals from both the Mn and chalcogen atoms. Meanwhile, the VBM states of the  $\text{VX}_2$  and  $\text{MnX}_2$  chains receive contributions from both the metal and chalcogen orbitals.

According to crystal field theory, the metal ions in  $\text{MX}_2$  chains are tetrahedrally coordinated, and the five d orbitals will split into degenerate  $e_g$  ( $d_{x^2-y^2}$ ,  $d_{z^2}$ ) and  $t_{2g}$  ( $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$ ) orbitals, as illustrated in Fig. 3a. Note that Ti, V, Cr, and Mn atoms in the  $\text{MX}_2$  chains have a +4 oxidation state with their 3d electron

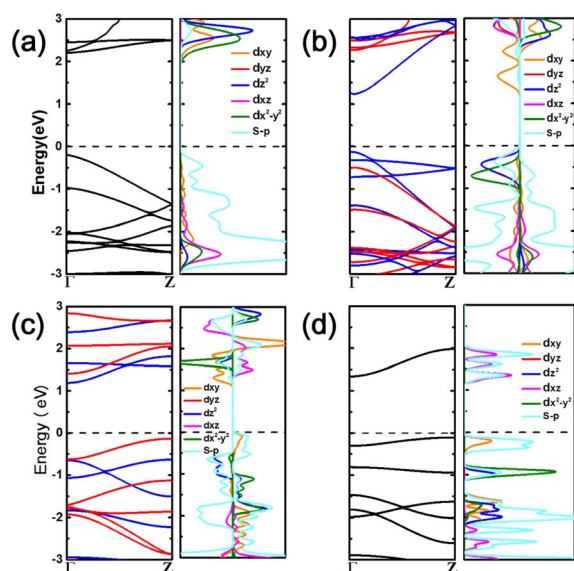


Fig. 2 Electronic structures of (a)  $\text{TiS}_2$ , (b)  $\text{VS}_2$ , (c)  $\text{CrS}_2$ , and (d)  $\text{MnS}_2$  atomic chains, respectively. The spin up and down states are indicated in red and blue colors in the band structure.

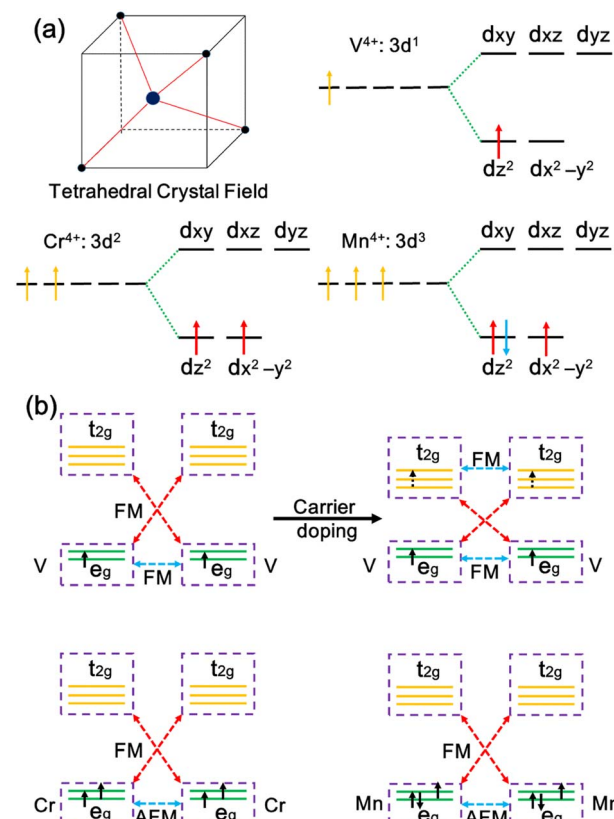


Fig. 3 (a) The tetrahedral crystal field and the 3d electron configurations of  $\text{V}^{4+}$ ,  $\text{Cr}^{4+}$  and  $\text{Mn}^{4+}$  ions. (b) Schematic representation of the 3d orbitals and magnetic exchange interactions. The blue and red dotted lines represent direct exchange and superexchange interactions, respectively.





configurations being  $3d^0$ ,  $3d^1$ ,  $3d^2$ , and  $3d^3$ , respectively. The  $e_g$  orbitals are occupied with one, two, and three electrons, generating one, two, and one unpaired 3d electrons. Thus, 1, 2, and  $1 \mu_B$  magnetic moments are located on the metals in the  $VX_2$ ,  $CrX_2$ , and  $MnX_2$  chains, respectively.

The magnetic ground state in the  $MX_2$  chains relies on the occupation of the metal d orbital and can be interpreted by exchange interactions between the metal ions. In the  $MX_2$  chains, the metal–ligand–metal bonding angle varies from  $74.5^\circ$  to  $85.0^\circ$ , close to  $90^\circ$ , leading to the coexistence of superexchange and direct exchange interactions between the metal ions.<sup>56</sup> As illustrated in Fig. 3b, the lower energy  $e_g$  orbitals are half-filled while the higher energy  $t_{2g}$  orbitals of the Cr ion are empty. As a result, the direct exchange interaction between the half-filled orbitals is AFM, and the virtual hopping between the half-filled  $e_g$  and empty  $t_{2g}$  orbitals *via* a superexchange interaction is FM according to the Goodenough–Kanamori–Anderson (GKA) rules.<sup>57,58</sup> Given that the FM superexchange interaction between the half-filled  $e_g$  orbitals and empty  $t_{2g}$  orbitals is generally stronger than AFM direct exchange in a tetrahedral crystal, FM coupling is induced overall in the  $CrS_2$  chain.<sup>59</sup> As for the  $VX_2$  chains, in addition to the FM coupling driven by superexchange interactions, direct exchange, *i.e.*, real hopping between partially occupied  $e_g$  orbitals, is also FM.<sup>60,61</sup> Therefore, FM coupling is induced in the  $VX_2$  chains. However, the direct exchange interactions in the  $MnX_2$  chains are enhanced because the  $e_g$  orbitals are more than half-filled and there is a decreased distance between the metal ions. Thus, the AFM coupling between the  $e_g$  orbitals dominates over the FM virtual hopping, resulting in an AFM ground state.

As the exchange interaction between the metal ions is related to the occupation of the metal d orbitals, the magnetic coupling strength and magnetic ground state of the  $MX_2$  chains may be tuned by controlling the number of occupied electrons in the metal d orbitals. Next, the electronic structures and magnetic coupling tunability of  $MX_2$  chains with carrier doping were investigated. A carrier concentration of up to  $9.3 \times 10^{13} \text{ cm}^{-2}$  (0.03 carriers per atom) was used, a level which is experimentally reachable.<sup>62</sup> As illustrated in Fig. 4a and S7,<sup>†</sup> the  $VX_2$ ,  $CrS_2$ , and  $MnS_2$  chains retain their ground state magnetic order following carrier doping. However, an AFM to FM transition is observed in the  $MnSe_2$  chain when doping with 0.02 or 0.03 holes per atom. In addition, the energy differences in the  $VX_2$  chains increase monotonically with the total electron concentration, as illustrated in Fig. 4a and S7,<sup>†</sup> which can be explained by the aforementioned exchange interaction mechanism. Taking the  $VS_2$  chain as an example, the doped electrons partially occupy the empty  $t_{2g}$  orbitals, as depicted in Fig. 2b. Compared with a pristine  $VS_2$  chain, the extra FM exchange interactions between the  $t_{2g}$  orbitals arising from the doped electrons enlarge the energy differences between the FM and AFM states in the  $VS_2$  chain.<sup>64</sup> Meanwhile, the gap between the  $e_g$  and  $t_{2g}$  levels narrows when the  $VS_2$  chain is doped with electrons, as illustrated in Fig. 4b, which further enhances the virtual hopping between the  $e_g$  and  $t_{2g}$  orbitals.<sup>56</sup> On the contrary, after hole injection, fewer electrons occupying the  $e_g$  orbitals weakens the strength of the FM coupling induced by

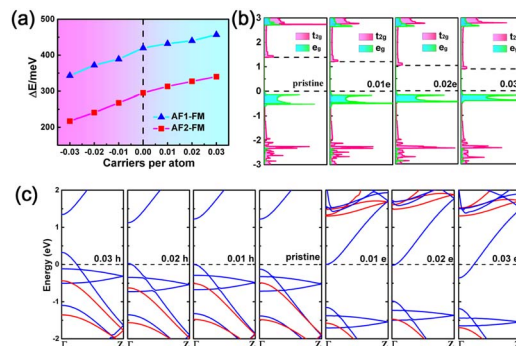


Fig. 4 (a) Energy differences between the AFM and FM configurations of the  $VS_2$  chain following carrier injection. The injection of electrons and holes is represented by positive and negative carrier concentration values, respectively. (b) The projected density of states of a  $VS_2$  chain with different levels of electron injection. The edges of the  $e_g$  and  $t_{2g}$  orbitals are shown with dashed lines, and the edge of the  $e_g$  orbitals is set as zero. (c) Band structures of a  $VS_2$  chain with levels of carrier injection.

superexchange and direct exchange, and thus the energy difference between the AFM and FM states is decreased. As for the  $CrS_2$  and  $MnX_2$  chains, the decrease in occupied electrons shrinks the AFM exchange interaction due to there being no  $e_g$  orbitals less than half-filled.

Fig. 4c and S8 to S10<sup>†</sup> show the band structures of the  $MX_2$  chains doped with electrons or holes. Transitions from semiconductor to metal are observed in the carrier-doped  $MX_2$  chains. The  $VX_2$ ,  $CrS_2$ , and  $MnX_2$  chains are transformed into half metals (HM) following carrier injection. The  $VX_2$  chains can be converted from UMS to FM HM *via* carrier injection. In particular, hole (electron) doping in  $CrS_2$  and  $MnS_2$  chains would lead to the transition from a BMS and AFM semiconductor to a FM HM and AFM HM with reversible spin-polarization orientation, respectively. However, the  $MnSe_2$  chain can be switched from an AFM semiconductor to an AFM HM with electron doping or doping with no more than 0.01 hole per atom. Meanwhile, a FM HM can be induced in a  $MnSe_2$  chain by doping with 0.02 or more holes per atom. The results demonstrate the potential that  $MX_2$  chains hold for use in electronically controlled spintronics applications.

It has been accepted that no long-range magnetic ordering can exist in infinite strictly 1D isotropic systems above 0 K.<sup>63</sup> However, thermal fluctuation is possibly blocked by strong inter-chain coupling and large magnetic anisotropic energy (MAE) and thus, long-range magnetic order could be stabilized.<sup>15,17,29,64</sup> For example, Pt substrate supported 1D Co atomic chains present long-range magnetic coupling below 15 K due to a large MAE of 2.0 meV per Co atom.<sup>29</sup> Our results indicate the easy axes (EA) of the  $MX_2$  chains are parallel to the axial direction, except in the  $CrS_2$  and  $MnS_2$  chains where they are perpendicular to the axial direction (Table S6<sup>†</sup>). The calculated MAE values vary from 0.019 to 3.78 meV per metal. Among them, the MAE value of the  $VTe_2$  chain reaches 3.78 meV per metal, which is larger than those of Co atomic chains<sup>29</sup> and Fe-benzenetetramine coordination polymers.<sup>65</sup> Furthermore, the



inter-chain interactions of the  $\text{MX}_2$  chains were also studied. As illustrated in Fig. S11,<sup>†</sup>  $\text{MX}_2$  bundles are arranged in AA-, AB-, AC-, and AD-stacking configurations to determine the most energy favorable configuration. The total energies per metal of these bundles are summarized in Table S7.<sup>†</sup> AD-stacked  $\text{MX}_2$  bundles are energetically preferred, with inter-chain coupling energies varying from  $-166$  to  $-318$  meV per metal atom and inter-chain distances ranging from  $3.59$  to  $4.12$  Å. The inter-chain coupling of  $\text{VS}_2$ ,  $\text{VSe}_2$ , and  $\text{CrS}_2$  chains are AFM with energy differences of  $-0.3$ ,  $-20.6$ , and  $-14.4$  meV per metal, respectively. Meanwhile, the  $\text{VTe}_2$  chains are FM coupled with an FM-AFM energy difference of  $27.3$  meV per metal atom. This difference is distinctly larger than those of the  $\text{MnH}_3$ ,<sup>15</sup>  $\text{V}(\text{Bz})$ , and  $\text{Mn}(\text{Bz})$  bundles,<sup>64</sup> indicating the feasibility of maintaining their FM order at nonzero temperatures.

Motivated by experimentally observed torsional waves in single-chain nanowires,<sup>41</sup> here we used the  $\text{TiS}_2$  atomic chain as a prototype to investigate the atomic and electronic structures of a twisted single chain with a variable rotation angle. Twisted nanowires with  $15^\circ$ ,  $30^\circ$ ,  $45^\circ$ ,  $60^\circ$ ,  $75^\circ$ , and  $90^\circ$  rotation angles are displayed in Fig. S12.<sup>†</sup> First, we calculated the variation of the rotation energy, *i.e.*,  $E_{\text{NW}}(\theta) - E_{\text{NW}}(\theta = 0)$  as a function of the rotation angle. The results demonstrate that the total energy of the twisted  $\text{TiS}_2$  nanowire increases monotonically with the rotation angle, and that there is a high energy barrier of  $1.4$  eV per metal atom between the square and tetrahedral configurations (Fig. S13<sup>†</sup>). Further, from the calculated band structures of the twisted nanowires (Fig. S14<sup>†</sup>), we can see that the direct band gap decreases from  $1.40$  ( $\theta = 0$ ) to  $0.06$  eV ( $\theta = 60^\circ$ ) and then increases into an indirect band gap of  $0.15$  eV ( $\theta = 75^\circ$  and  $90^\circ$ ), implying that the electronic structure of these nanowires is dependent on the rotation angle.

Experimentally, the  $\text{MX}_2$  chains may be synthesized in ultra-narrow carbon nanotubes (CNTs), analogous with previously reported TMC chains.<sup>36,38–41</sup> Here, the suitable diameters of a CNT sheath in which to grow  $\text{MX}_2$  chains were evaluated by plotting the variation of the binding energy  $E_b$  against the diameter of the CNT. The binding energy is defined as  $E_b = E_{\text{NW@CNT}} - E_{\text{NW}} - E_{\text{CNT}}$ , where  $E_{\text{NW}}$ ,  $E_{\text{CNT}}$ , and  $E_{\text{NW@CNT}}$  are the total energies of the atomic chain, CNT, and their joint system, respectively. The lattice mismatch between the atomic chain and CNT is less than  $5.5\%$  (Table S8<sup>†</sup>). The calculated  $E_b$  decreases at first and then increases as the diameter is augmented. This behavior is attributed to the competition between the attraction and repulsion interactions between the chain and CNT (Fig. 5a and S15<sup>†</sup>). It is clear that insertion of the  $\text{MX}_2$  chains inside (7,7) or (8,8) CNTs leads to the lowest  $E_b$  values, ranging from  $-0.792$  to  $-0.698$  eV per metal, which are on the same order of magnitude as that of  $\text{NbSe}_3$  inside a CNT.<sup>41</sup> Therefore, we believe (7,7) and (8,8) CNTs may be suitable for growing  $\text{MX}_2$  chains inside them. As presented in Fig. S16,<sup>†</sup> the equilibrium separation  $d$  between the chains and CNTs range from  $3.06$  to  $3.74$  Å, and about  $0.02$  to  $0.17$  electrons per metal are transferred from the CNT to the chain, as shown in Fig. S17.<sup>†</sup> A smaller binding energy and larger separation between the chain and CNT than in the case of  $\text{NbSe}_3$  suggest that the interaction between the  $\text{MX}_2$  chains and CNT is only

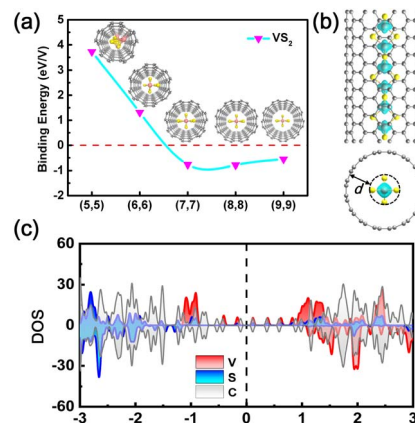


Fig. 5 (a) The evolution of binding energy with diameter of CNT. The inset shows front views of a single-chain nanowire embedded in a CNT. (b) Spin charge density distribution in the joint system with an isovalue of  $1.5 \times 10^{-2} \text{ e bohr}^{-3}$ . (c) Projected density of states of a  $\text{VS}_2$  single-chain encapsulated inside a CNT.

a van der Waals interaction.<sup>41</sup> Both spin charge density profiles and PDOS analysis indicate that the electronic and magnetic properties of the  $\text{TiX}_2$  and  $\text{VX}_2$  chains are preserved inside the (7,7) and (8,8) CNTs, while a transition from a semiconductor to a HM is observed in the  $\text{CrS}_2$ ,  $\text{MnS}_2$ , and  $\text{MnSe}_2$  chains (Fig. 5b and c, S18, and S19<sup>†</sup>).

Very recently, a new type of platinum-based single-metal-atom chain (SMAC) has been fabricated in a controlled manner *via* a chemical vapor co-deposition method.<sup>66</sup> However, the synthesized Pt-based SMAC differs from our proposed  $\text{MX}_2$  wires in terms of atomic arrangement, band structure, and magnetic properties. Firstly, although the metal ions in the T-type  $\text{MX}_2$  chains and Pt-SMAC are both bonded with four chalcogen atoms, the metals in the  $\text{MX}_2$  and Pt-SMAC structures have tetrahedral and square coordination symmetries, respectively. Secondly, the band structure calculations indicate that the  $\text{MX}_2$  wires are semiconductors while a metallic behavior is observed in Pt-SMAC. Lastly, Pt-SMAC is intrinsically non-magnetic while the majority of the  $\text{MX}_2$  wires are magnetic.

### 3. Conclusions

In conclusion, we have proposed a family of 1D stoichiometric transition metal dichalcogenide (TMD) atomic chains featuring magnetic properties and band gaps. Different from their bulk and 2D counterparts, the  $\text{TiX}_2$ ,  $\text{VX}_2$ ,  $\text{CrX}_2$ , and  $\text{MnX}_2$  chains are nonmagnetic semiconductors, unipolar magnetic semiconductors, bipolar magnetic semiconductors, and antiferromagnetic (AFM) semiconductors, respectively. In particular, the  $\text{VX}_2$ ,  $\text{CrX}_2$ , and  $\text{MnX}_2$  chains can be converted by carrier injection from ferromagnetic (FM) or AFM semiconductors to half metals (HMs) with tunable spin-polarization orientation at the Fermi level. The diverse and tunable electronic and magnetic properties in the  $\text{MX}_2$  chains rely on the occupation of metal d orbitals and the exchange interaction between the tetrahedrally coordinated metal atoms. Of these  $\text{MX}_2$  chains,  $\text{VTe}_2$



possesses the largest magnetic anisotropic energy (MAE) of 3.78 meV per metal and the inter-chain coupling is FM, revealing the potential to maintain FM ordering at nonzero temperatures. The calculated interaction between carbon nanotubes (CNTs) and the MX<sub>2</sub> chains reveals that armchair (7,7) or armchair (8,8) carbon nanotubes are appropriate sheaths for growing MX<sub>2</sub> atomic chains. In addition, both the magnetic and electronic properties of the TiX<sub>2</sub> and VX<sub>2</sub> chains were maintained inside the CNTs, while a conversion from a semiconductor to a HM is observed in the CrS<sub>2</sub>, MnS<sub>2</sub>, and MnSe<sub>2</sub> chains. The diverse and tunable electronic and magnetic properties of the MX<sub>2</sub> atomic single-chains make them a promising building block in the field of electronics and spintronics.

## 4. Methods

First-principles calculations were performed based on density functional theory as implemented in the Vienna *Ab Initio* Simulation Package (VASP).<sup>67,68</sup> The projector augmented wave (PAW) method was used,<sup>69,70</sup> and the generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) parametrization was adopted to deal with exchange–correlation functional.<sup>71</sup> The cut-off energy was set to 500 eV. A vacuum space larger than 15 Å was used to eliminate interactions between the adjacent periodic images of the NWs. Brillouin zone integration was performed using a  $1 \times 1 \times 18$   $\Gamma$ -centered grid. The energy and forces convergence criteria were set to  $10^{-6}$  eV and  $10^{-3}$  eV Å<sup>-1</sup>. A DFT-D3 method was adopted to include a van der Waals dispersion correction for the joint systems.<sup>72</sup> For accurate calculations of the electronic properties, a well-performed hybrid HSE06 functional was employed.<sup>73</sup> Unless stated otherwise, band structures, DOS, charge densities, and magnetic properties were obtained using the HSE06 functional. Spin–orbital coupling calculations were not considered during the structural relaxation but were then added into the MAE calculations by including the interaction between the electron-spin and the orbital angular momentum in the Hamiltonian. To investigate the thermodynamic stability of the designed NWs at the PBE level, the phonon calculations were performed using the PHONOPY code with a finite difference method,<sup>74</sup> and *Ab Initio* Molecular Dynamics (AIMD) simulations were simulated in the NVT ensemble using a Nosé Hoover thermostat at 300 K for 5 ps with a time step of 1 fs.

## Conflicts of interest

There are no conflicts to declare.

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