Chiral vectors-tunable electronic property of MoS₂ nanotubes

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Abstract

It has been demonstrated that the mechanical and electronic properties of materials change significantly when the external dimension are confined to the nanoscale. Consequently, one-dimensional (1D) transition-metal dichalcogenide (TMDC) nanotubes (NTs), obtained from scrolling two-dimensional (2D) TMDC, have attracted much attentions because of their intriguing properties wherein the chirality of NTs plays a key role in affecting the electronic properties. Taking into the amount of speculations on the mechanism and the increasing needs for better device design and performance control, understanding the effect of chirality on the electronic properties is timely and relevant. Here, MoS₂ NTs are comprehensively studied by first-principles calculations. The results show that the armchair ($6 \leq ch \leq 14$) exhibits the indirect-band-gap and zigzag ($10 \leq ch \leq 20$) with direct-band-gap. Moreover, the carrier mobility is enhanced with the decrease of radial length, in accord with the smaller effective mass of hole and electron for both types NTs. Finally, the formation energy showed that the smaller the radial diameters is, the harder the NTs is to form. Moreover, the similarity of lattice parameters and formation energy implies a potential possibility of transition between two types of NTs with low index chiral vectors, such as ANT(6,6)/ZNT(10,0).

Keywords: MoS₂ nanotubes; Chiral vectors; Formation Energy; First principles

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calculations.

1. Introduction

Analogous to carbon nanotubes (NTs), one-dimensional (1D) transition-metal dichalcogenide (TMDC) nanotubes, such as MoS₂ [1-3] and WS₂ NTs [4], have attracted much attentions and prompted numerous studies because of their potential for a wide range of technological applications and also because they are of fundamental scientific importance [2]. Their intriguing properties, such as, high mobility, organic-like flexibility, large on/off ratio, excellent lubrication, and ultra-strength [5,6], render them applicable for many fields, relating to: field effect transistors [7], lubricants[8,9], optoelectronic[10,11] and luminescent devices[12], and electrochemical hydrogen storage [13]. MoS₂ NT, which consists of a middle-Mo layer sandwiched between two S layers (space group *P63/mmc*) [14], could be classified as armchair NTs (ANTs) and zigzag NTs (ZNTs) based on their chiral vectors [Fig.1 (a)]. The definition $\vec{Ch} = m \bullet \vec{e}_1 + n \bullet \vec{e}_2$ is adopted for signifying two types of NTs: ANTs ($m=n=Ch$) and ZNTs ($m=Ch, n=0$). Fig.1(b) and (c) show the ANT (6,6) and ZNT (10,0) structures, by wrapping a MoS₂ monolayer along Armchair and Zigzag chiral vector [Fig.1(a)], respectively. The R_o , R , R_i and d_a (d_z) denote the outer, middle, inner radial diameters and axial length of ANTs (ZNTs) unit cell. The counterpart of monolayer MoS₂ unit cell with length of da and dz is indicated by shadow area in Fig.1 (b) and (c), wherein the da_0 and dz_0 is initially axial length of unit cell for ANTs and ZNTs, respectively. Moreover, it is easy to gain the relationship between dz/da in primitive unit cell of monolayer: $dz_0/da_0 = \sqrt{3}$. Hereafter, the

chirality of NTs in present paper, ANTs ($m=n=Ch$) and ZNTs ($m=Ch, n=0$), were defined as A (Ch) [$Ch=6-14$], and Z(Ch) [$Ch=10-20$], respectively.

Fig. 1. (Color online) The atomic structures of MoS₂: (a) monolayer, the chiral vectors ($\vec{Ch}$) could be defined as $\vec{Ch} = m \cdot \vec{e}_1 + n \cdot \vec{e}_2$, (b) ANT(6,6) and (c) ZNT (10,0), and corresponding side view (d), (e) and (f). The axial and radial lengths of MoS₂ as a function of $\vec{Ch}$ are shown in (g) and (h), respectively. The da_0 and dz_0 with values of 3.165 and 5.482 Å, are lattice lengths of monolayer MoS₂ and denoted by dot lines in (g). In order to compare with each other, the axial length of ZNTs is divided by $\sqrt{3}$ (labeled as dz').

MoS₂ NTs are obstinately semiconducting unlike to that of carbon NTs and the MoS₂ nanoribbons (NRs): a) carbon NTs could be either metallic or semiconducting depending on their chirality and diameter; and b). MoS₂ NRs could interestingly exhibit either ferromagnetic and metallic behavior (zigzag NRs), irrespective of the ribbon width and thickness, or nonmagnetic and semiconducting properties (Armchair NRs) [15]. Consequently, much efforts expended to date to tune the band gap have mainly focused on two techniques. One is mechanical way via applying tensile, compressive, and shear strain. For instance, W. Li *et al* [1] performed density functional theory (DFT) calculations to study the effect of mechanical strain on the electronic and transport properties of MoS₂ NTs and showed that strain could significantly modulate the band gap and carrier effective mass of MoS₂ NTs. The other alternative is to import chemical dopants and defects. For example, M. Remskar *et al* measured the metallic behavior and blue shift in optical absorbance of MoS₂ NTs with a high defect concentration [16]. As much less investigation for TMDC NTs with comparison to their carbon counterparts, the properties of TMDC NTs could be further widely explored and technologically utilized for electronics devices. Therefore, a comprehensive understanding of formation energy and electronic property for simple TMDC-NTs is fundamental and relevant.

2. Computational details

The calculations are based on density functional theory (DFT) and are performed using the Vienna *Ab-initio* Simulation Package (VASP) with Projector Augmented Wave (PAW) potential [17]. Plane waves with kinetic energy cutoff of 500 eV are

used to expand the wave function of valence electrons ($3s^2p^4$ for S and $4p^65s^14d^1$ for Mo) [18]. The generalized gradient approximation of Perdew-Buker-Ernzerhof (GGA-PBE) is adopted for exchange-correlation functional [19]. Brillouin zone sampling is performed with Monkhorst-Pack (MP) special k-points meshes [20]. A grid of $1 \times 1 \times 7$ is adopted for geometrical relaxation and increased to $1 \times 1 \times 50$ for more accurate electronic properties [21, 22]. Meanwhile, a group of $24 \times 24 \times 5$ ($24 \times 24 \times 1$) is used for structure optimization and electronic properties of bulk materials (monolayer) for comparison [23]. A vacuum layer larger than 15 Å was added to avoid the interaction between the adjacent images. All atoms are allowed to relax until the calculated Hellman-Feynman force on each atom was less than 0.03 eV/Å [24, 25]. All of MoS₂ NTs were considered as one-dimensional systems, and just k-points along axial direction (Γ to Z), comprising of 30 k points, are calculated for band structures. The partial (band decomposed) charge density are adopted to describe the distributions of charge density for the lowest Unoccupied Molecular Orbital (LUMO) sited on Conductance Band (CB) and Highest Occupied Molecular Orbital (HOMO) localized on Valance Band (VB). Two steps are taken to obtain the band decomposed charge density. Firstly, the k-vector (that is, band number) corresponding to the LUMO in CB or HOMO in VB, is established based on the band structure. Secondly, the partial charge density is evaluated for the exactly specified k-vectors corresponding to HOMO and LUMO, respectively.

The carrier mobility is described by effective mass. Based on the band structures of representative NTs cases, the effective mass (m^*) of carrier (electrons and holes) in

MoS₂ NTs, e.g. that of electrons (m_e^*) at the conduction band minimum (CBM) and that of holes (m_h^*) at the valence band maximum (VBM), could be differentiated from the curves passed through the CBM and the VBM base on the following formula [26,27]

$$\frac{1}{m_\alpha^*} = \left(\frac{h}{2\pi} \right)^{-2} \times \frac{\partial^2 E(k)}{\partial k^2} \quad (1)$$

where $E(k)$ and k correspond to energy and reciprocal lattice vector along axial direction of the nanotube, and h is *planck* constant.

Two qualities are adopted to compare the energy among the two types of NTs. One is formation energy per formula unit (ΔE_f) of NTs, which is used for comparison among the NTs, could be expressed as follows:

$$\nabla E_f = [E_{total} - N * (\mu_{Mo} + 2 * \mu_S)] / N \quad (2)$$

where E_{total} is the total energy of NTs, N is the number of MoS₂ unit, μ_{Mo} and μ_S is chemical potential Mo and S, respectively. And the corresponding formation energy (ΔH) of MoS₂ in bulk materials satisfies the relationship

$$\nabla H_{bulk} = \mu_{MoS_2} - (\mu_{Mo} + 2 * \mu_S) \quad (3)$$

The other one is zero-temperature surface energy per unit length (da or dz), which could be considered as the energy of rolling a plane MoS₂ sheet, was calculated using

$$E_{surface} \equiv (E_{total} - N \times E_{unit}(MoS_2)) / d \quad (4)$$

In which E_{total} is the total free energy of NT cell, $E_{unit}(MoS_2)$ is the free energy of primitive cell of monolayer MoS₂, and N is the number of MoS₂ formula unit in a cell, d , denotes da or dz , is the length of a cell.

3. Results and Discussions

Fig.1(g) and (h) show the lattice length (axial and radial length) evolution as a function of Ch for the ANTs and ZNTs. It is worth noting that the axial lengths of ZNTs is divided by $\sqrt{3}$ in order to compare with those of ANTs. From the Fig.1(g), one can see that compared with that of mono-layers MoS_2 (3.165 Å) the axial length of ANTs is getting longer, that means ANTs are stretched, while it is getting shorter for ZNTs, which means ZNTs are compressing. Both strains decrease with Ch increasing, indicating the tendency of transition from ANTs and ZNTs to monolayer. Moreover, the radial lengths of MoS_2 NTs monotonously increase with Ch increasing. However, the variation of ANTs is steeper than those of ZNTs [Fig.1(h)]. The analogous radial lengths between ANTs and ZNTs, such as close radial length between A6 and Z10, trigger one hypothesis that whether the heterojunction composed of two types of TMDC-NTs could be formed by controlling the selection of template and thermodynamical conditions. It looks accessible based on their similar radial lengths at equilibrium state.

For further studying the electronic property of TMDC-NTs, the general variations of band-gap for ANTs and ZNTs are firstly shown in Fig. 2(a). Compared to the monolayer MoS_2 with value of 1.738 eV (direct band-gap), the evolution of energy band-gap spectra in ANTs or ZNTs can be considered as MoS_2 transition from one-dimensional tubes to two-dimensional monolayer, that is to say, the monolayer MoS_2 could be regarded as a nanotube with infinite diameters [28]. In general, the energy band-gap is open for both ANTs and ZNTs. When the Ch decreases to 6 (10)

for ANTs (ZNTs), however, the band gap is almost a zero-gap semiconductor with value of 0.017 eV (0.015 eV). The extremely small band gap is further corroborated in the band

Fig.2. (a) The variation of energy band gap of MoS₂ NTs with respect to chiral vector (Ch). The energy band gap of monolayer MoS₂ and bulk MoS₂ is 1.738 eV (direct) and 1.034 eV (indirect), respectively; (b) Band structure for A6, A10, A14, Z10, Z15, and Z20; (c) the effective mass (**unit**: m_e) of carriers (hole and electron) in MoS₂ A6, A10 and Z10, Z15; (d) decomposition of projected density of states for A10 and Z15, the Fermi level (E_F) is aligned to zero and indicated by vertical line.

structure [Fig.2 (b)], which also reveals that MoS₂ ANTs are indirect-gap semiconductors while ZNTs are direct-gap semiconductors. Detailed examination of band structures of A6, A10 and A14, the open gap is composed of one valley in conduction bands, nearly at $\pi/3$ proximal to Z point in the wave vector space, and two peaks in valence bands, shifting towards Z point and decaying the states slightly with the increasing of *Ch*. Meanwhile, the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) for ZNTs always possess the Γ point. The difference in the band structure of two types also modify the carrier mobility. The effective mass (unit: m_e) of A6 hole (-0.78) is smaller than that (-1.62) of A10, as well, that (-3.30) of Z10 are also smaller than that (-10.07) of Z15. Conversely, the electron of ANTs and ZNTs varies slightly with the *Ch* increasing. The results indicate that the NTs with lower chiral vectors occupy the relatively higher carrier mobility. To shed more light on the contribution from the atomistic orbitals, the projected density of states (PDOSs) decomposed to atoms near the Fermi level for A10 and Z15 NTs are shown in Fig.2(d). For A10, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are both primarily from Mo-*dxy* and Mo-*dz²*, yet secondly from S-*py*, S-*px* and Mo-*dx²* for HOMO, as well, Mo-*dx²* for LUMO. In contrast, for Z15, the HOMO are mainly composed of Mo-*dx²*, Mo-*dz²* and Mo-*dxy*, with a weak distribution from S-*py* and S-*px*, meanwhile, the LUMO of

Mo- dx_y and Mo- dz^2 , with Mo- dz^2 , which could be attributed to the different atomistic symmetry of two types NTs [2, 29, 30].

Fig.3 **Partial** (band-decomposed) charge density for HOMO and LUMO: (a) A6, (b) A10 and (c) Z10, (d) Z15, respectively. The isosurface of electron density is set to $0.001 \text{ e}/\text{\AA}^3$ for all nanotubes for comparison.

For seeing vividly the charge distribution of HOMO and LUMO, those of A6, A10 and Z10, Z15 are deliberately chosen for examples (Fig.3). It is found that the HOMO for both ANTs and ZNTs is located on outer-S and middle Mo atoms, meanwhile, the LUMO mainly sites on middle Mo atoms. The difference of HOMO between ANTs and ZNTs is that the HOMO of ANTs covers the bonds between Mo and outer-S atoms, and HOMO of ZNTs is **independently** located on Mo and outer-S. Moreover, the LUMO of both types of NTs all exhibits the crossed-lobes fashion. These results could further **confirm** the analysis of PDOS.

Fig.4 a). Surface energy($E_{surface}$) of MoS₂ NTs as a function of Ch ; b). The formation energies (ΔE_f in eV/f.u.) of MoS₂ NTs as a function of Ch , the corresponding value for monolayer MoS₂ is also plotted as horizontal dash line for comparison.

Based on above analysis, it could be concluded that the electronic properties are strongly depended on the chirality of NTs. For better manipulating the NTs, it is necessary to investigate the energy related to the formation, such the surface energy ($E_{surface}$) and formation energy (ΔE_f in eV/f.u.). The surface energy could be

considered as the energy of rolling a plane MoS₂ sheet, as shown in Fig. 4(a). The surface energy monotonically decreases with the Ch increasing, indicating that the smaller radial diameter is, the harder it forms. The conclusion is further confirmed by the formation energy [Fig. 4(b)], wherein the energy for ANTs and ZNTs gradually approaches to that of monolayer. It should be noted that the curves of formation energy for ZNTs and ANTs also have cross-area, indicating that they are stable as each other. However, it could be inferred from the formation energy that the ANTs are more stable than ZNTs for larger radial diameters, in contrast, ZNTs are more stable for smaller radial diameters. This is different from the MoS₂ nanoribbons, where the formation energy of zigzag MoS₂ nanoribbons are always lower than those of the armchair MoS₂ [31]. The similarity of surface energy and formation energy between two types NTs further validates the possibility of transition between ANTs and ZNTs, such as A6 and Z10.

4. Conclusions

In summary, we have calculated the electronic property and formation energy of MoS₂ NTs using the first-principles calculations. The results show that the electronic property is strongly dependent on the chirality of NTs, wherein the ANTs possess the indirect-band gap and ZNTs with direct-band gap. The carrier mobility is enhanced when the radial length is decreased. Moreover, the smaller the radial diameters is, the harder the NTs is to form. The similarity of length and formation energy between two types of NTs implies the potential transition between the ANTs and ZNTs, which may be applicable for designing future electronics based TMDC-NTs heterojunctions such

as MoS₂ A6/ MoS₂ Z10.

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Graphical Abstract