Strain Engineering on the Electronic and Optical Properties of WS\textsubscript{Se} Bilayer

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Abstract

Controllable optical properties are important for optoelectronic applications. Based on the unique properties and potential applications of two-dimensional Janus WS\textsubscript{Se}, we systematically investigate the strain-modulated electronic and optical properties of WS\textsubscript{Se} bilayer through the first-principle calculations. The preferred stacking configurations and chalcogen orders are determined by the binding energies. The bandgap of all the stable structures are found sensitive to the external stress and could be tailored from semiconductor to metallicity under appropriate compressive strains. Atomic orbital projected energy bands reveal a positive correlation between the degeneracy and the structural symmetry, which explains the bandgap evolutions. Dipole transition preference is tuned by the biaxial strain. A controllable transformation between anisotropic and isotropic optical properties is achieved under an around $-6\%$ critical strain. The strain controllable electronic and optical properties of the WS\textsubscript{Se} bilayer may open up an important path for exploring next-generation optoelectronic applications.

Keywords: WS\textsubscript{Se} bilayer, Biaxial strain, Optical anisotropy, The first-principle calculations

Introduction

Two-dimensional (2D) materials with their novel properties have been showing great application prospect in next-generation electronic devices. As a promising candidate, 2D-layered transition metal dichalcogenides (TMDCs) with tunable bandgap were widely studied over the past decade and were intensively exploited as tunneling field-effect transistors [1], light-emitting diodes, photodetectors [2, 3], sensors [4], and so on.

Beyond the highly symmetrical MX\textsubscript{2} ($M = Mo, W; X = S, Se, Te$) configuration, new Janus structural TMDCs, with the chemical formula of MXY ($M = Mo, W; X \neq Y = S, Se, Te$) have attracted increasing interest due to their distinctive optical and electronic properties. The monolayer MXY is constructed by two different chalcogen atom layers marked as A, A’ and one transition-metal atom layer B to form an ABA' atomic stacking. Compared with that of MX\textsubscript{2}, MXY possesses an asymmetry-ordered configuration with the breaking of mirror symmetry, which leads to a vertical dipole and enhanced Rashba spin-orbit coupling [5]. Geometric and electronic structures of Janus WS\textsubscript{Se} have already been reported and proved to have plenty of distinguishing features different from both WS\textsubscript{2} and WSe\textsubscript{2}. For instance, the hydrogen evolution reaction catalytic activity of WS\textsubscript{Se} was found superior to that of current TMD-based catalysts [6]. The WS\textsubscript{Se} field-effect transistors also have achieved better performance in electron mobilities and $I_{ON}/I_{OFF}$ ratio than that of conventional TMD monolayers [7]. Despite the exciting characters of the intrinsic monolayer, Janus TMDCs with bilayer and multilayer thickness and various stacking structures may possess profound physical connotations considering the asymmetry of the MXY configuration. For example, the Se-Se-S-ordered WS\textsubscript{Se} bilayer was predicted to improve the efficiency of photoelectric conversion efficiency for solar cell applications [8].

Based on the unique Janus TMDC materials, realizing an accurate control of their electronic and optical properties is vital to meeting the multiple needs of device design. Electric field [9, 10], strain [11, 12], surface decoration [13, 14], and magnetic doping [15–17] have...
been proven as effective means to modulate the electronic and optical behaviors of 2D TMDCs. Among these methods, strain engineering is reversible with the controllable process, while without generating additional lattice defects and damage in the materials. Besides, strain engineering will alter the structural symmetry, which may give rise to the polarized characteristics of 2D materials and endow them with great prospects in future applications. As has been reported, the strained WSe$_2$ monolayers show obvious variation in electronic band structure [18–22] and demonstrate unique advantages in the applications of photoactive devices [23], valleytronics [18, 24], photodetectors [25], and anode material for Li-ion battery [26]. Nevertheless, strain engineering on the electronic and optical properties, such as band evolution and optical anisotropy of 2D Janus WSSe bilayer has not yet been reported so far.

In this work, we perform an investigation on the strain modulation of the electronic and optical properties of WSSe bilayer through the first-principle density function calculations. The investigation is initiated with the determination of the most favorable stacking order of the bilayer. Strain-dependent band structures of the three stable configurations are calculated. The bandgaps of WSSe bilayers are tailored and the atomic orbital contribution is revealed to understand the related mechanism. Optical anisotropy is also modulated by tuning the dielectric properties through the applied strain. A controllable transformation between anisotropic and isotropic optical properties is demonstrated.

**Computational Method**

All theoretical calculations are based on the density functional theory (DFT) with the generalized gradient approximation (GGA). The accurate projector-augmented wave (PAW) method, as implemented in the Vienna *Ab-initio* Simulation Package (VASP) [27–29] code is used. A slab model with a 1 × 1 unit cell is constructed, and a 20 Å vacuum layer along the z direction is used to minimize artificial interactions between neighboring slabs. The valence electron configurations of W, S, and Se atoms adopted are $5p^65d^46s^2$, $2s^23p^4$, and $4s^24p^4$, respectively. The GGA [30] with Perdew-Burke-Ernzerhof (PBE) [31] parameterization is employed as the exchange-correlation functional. Electron wave functions are expanded in plane waves with an energy cutoff of 400 eV. The Brillouin zone is sampled with a $19 \times 19 \times 1$ Monkhorst-Pack grid of $k$ points. The DFT-D2

![Fig. 1 Top and side views of the atomic configuration of WSSe bilayer. The purple balls represent the W atoms, and the yellow and green balls represent the S and Se atoms, respectively](image-url)
dispersion correction method is included in the structural relaxation and electronic structure calculations to correctly describe the effect of van der Waals integrations. All atomic degrees of freedom, including lattice constants, are fully relaxed with self-consistent convergence criteria of $0.01 \text{ eV/Å}$ and $10^{-6} \text{ eV}$ for the atomic forces and total energy, respectively.

**Results and Discussion**

The Janus WSSe monolayer has a hexagonal lattice, where the unit cell consists of a middle W atom in its planar honeycomb lattice that bonded three-coordinately with the surface S and Se atoms. The optimized lattice constant of WSSe is 3.23 Å with the W-S and W-Se bond lengths of 2.42 and 2.53 Å, respectively, which are aligned with the previous reported values [32]. According to the structural symmetry, five different stacking configurations of WSSe bilayer are taken into account, which is marked as AA, AA', AB, AB', and A'B, respectively. For each stacking, three different orders of chalcogen layers: S-Se-S-Se, Se-S-S-Se, and S-Se-Se-S are considered. All equilibrium geometric configurations of the WSSe bilayer are depicted in Fig. 1. Each configuration is fully relaxed respectively to optimize the interlayer spacing.

In order to determine the structural stability of the WSSe bilayer quantitatively, the binding energies $E_b$ of all above geometric configurations are calculated from the relation:

$$E_b = 2E_{\text{WSSe}} - E_{\text{bilayer}},$$

where $E_{\text{bilayer}}$ and $E_{\text{WSSe}}$ are the total energies of WSSe bilayer and monolayer, respectively.

![Fig. 2 Binding energies of all the equilibrium geometric configurations of WSSe bilayer](image)

![Fig. 3 Band structures of $I_1$, $I_2$, and $I_3$, respectively, where the bandgaps are denoted by the blue arrows](image)
As shown in Fig. 2, for all the stacking structures, chal-
cogen layers with the order of S-Se-Se-S possess the lar-
gest binding energy, while the reversed order Se-S-S-Se
has the smallest binding energy. In addition, it is visual-
ized that AA', AA', and AB are the most stable stacking
configurations of S-Se-Se-S, S-Se-S-Se, and Se-S-S-Se
orders, with the binding energies of 0.322, 0.304, and
0.281 eV, respectively. This indicates that the Janus
WSSe bilayer prefers to form a bilaterally symmetrical
AA' stacking with the S-Se-Se-S chalcogen order, which
is different from the MoSSe/WSSe heterostructure of
AB stacking [33].

Considering the most stable stacking structures men-
tioned above for each chalcogen order, both the elec-
tronic and optical properties are profoundly investigated.
For convenience, the AA' stacking with S-Se-Se-Se struc-
ture, the AB stacking with Se-S-S-Se structure, and the
AA' stacking with S-Se-Se-S structure are named as I_1,
I_2, and I_3, respectively, in the following discussion.

Band structures of the Janus WSSe bilayers I_1, I_2, and
I_3 are calculated, as shown in Fig. 3. All the three config-
urations exhibit a fundamental indirect bandgap struc-
ture, which is similar to that of the pure bilayer WS_2
and WSe_2. The valence band maximums (VBM) are all
locating at Γ point, while the conduction band minimum
(CBM) locating at K point for I_1, and situating between
K and Γ points for both I_2 and I_3. The indirect bandgap
of I_3 is calculated to be roughly 1.3 eV, slightly larger
than that of I_1 and I_2 whose bandgaps are approximately
1.0 eV. Despite that the bandgaps are underestimated
without the screened hybrid HSE06 functional, the band
structure distributions have no significant change, and
thus, the underestimation will not substantially influence
the evolution tendency of the electronic properties
under the strain modulation.

Strain engineering is a promising method for manipu-
lating the structural symmetry and the interlayer inter-
action, which could give rise to plenteous charming
phenomena. To study the electronic structures of WSSe
bilayers modulated by the applied strain, the energy
bands are analyzed, as illustrated in Fig. 4a–r. When a
compressive strain ranging from −6 to −2% is applied, the original VBM at Γ point changed to K point for I₁ and I₃ configurations, while shows little variety for I₂. The original CBM at K point shifts to the position between Γ and K points for all the three structures. Once the tensile strain in the region of 2%~6% is employed, the VBM remains at Γ point while the CBM is all locating at the K point.

Figure 5 summarizes the strain-dependent bandgap for the three structures. It is apparent at a glance that the responses of the bandgap to compressive strain and tensile strain are not only with unequal responsivity but also with different gradients as the applied strain increases. The bandgap is less sensitive to compressive strain, while dramatically decreases with the enhanced tensile strains. As the compressive strain increases, the CBM of both I₁ and I₃ is uplifted to higher energy, whereas that of I₂ is downshifted to lower energy, resulting in a slight decrease for I₂ and increase for I₁ and I₃ in the indirect bandgaps. In the presence of the tensile strain, the CBM...
enormously decreases while the VBM rises gently. The indirect bandgap thus exhibits a conspicuous diminishment and decreases sharply when the tensile strain reaches 6%. Compared with that of the strained Janus WSSe monolayer [34], the bandgaps of I₁ and I₃ show generally similar evolution with both compressive and tensile strain modulations, while the bandgap of I₂ behaves oppositely under the compressive strains.

In order to gain an insight into the electronic structure of WSSe bilayer in the presence of the strains, the atomic orbital projected energy band is studied, as seen in Fig. 6. Owing to its center inversion symmetry (Fig. 1l), the orbitals of the upper and lower layers for I₃ are energy degenerate, which make identical contributions to the band structure. On the contrary, because of the structure inversion asymmetry of I₁ and I₂, the orbitals of the upper and lower layers are splitted. The above results suggest that there is a positive correlation between the degeneracy and the structural symmetry. Owing to the center inversion symmetry of I₂ stacking, the orbitals of the upper and lower layers for I₂ are energy degenerate, which make identical contributions to the band structure regardless of the varying strains. As depicted in Fig. 6g–i, both the CBM and VBM equally derived from the two WSSe layers. On the contrary, because of the structural inversion asymmetry of I₁ and I₂, the orbitals of the two layers are splitted, as shown in Fig. 6a–c and Fig. 6d–f. The original I₁ structure exhibits a typical type-II heterostructure, with the CBM and VBM contributed from the lower and upper WSSe Janus layers, respectively. The band alignment does not vary under either the compressive or tensile strains (Fig. 6a–c). As for the I₂ stacking without and with a compressive strain, the CBM comes from both the two layers, and the VBM originates from the upper layer (Fig. 6d, e). The I₂ heterostructure changes to a type-II band alignment under the tensile strain (Fig. 6f), which indicates a promising prospect for developing high-performance optoelectric conversion and energy storage devices [35].

To further explore the spin-orbit coupling (SOC) effect in the strain engineering in the WSSe bilayer, the band structures with the consideration of SOC are
further calculated without and with the strains of −4% and 4%, as shown in Fig. 7. It is found that, for all the three configurations, the band structures including the momentum positions of VBM and CBM, the bandgaps, and band distributions show similar evolution tendency with the varying strains. This suggests that the strain modulation regularity still remains, and the SOC effect does not obviously influence the main conclusions.

With the aim to modulate the optical properties of the WSSe bilayer, the response of the dielectric function under external varying strain is studied. Figure 8 displays the complex dielectric function $\varepsilon_{xx}$ ($\varepsilon_{yy}$) and $\varepsilon_{zz}$ of WSSe bilayer versus the applied strain. $\varepsilon_{xx}$ ($\varepsilon_{yy}$) is found to shift to lower energies with the increasing tensile strain, and on the contrary, shift to the higher energy region while a compressive strain is applied. Compared with the unstrained WSSe bilayer with the dipole transition of 0.79, 1.18, and 1.15 eV, respectively for $I_1$, $I_2$, and $I_3$ structures, the strain modulation is able to obtain a wide-range transition energy from 0.24 to 1.47 eV in near-infrared and mid-infrared area, which could be offering extensive possibilities for assorted detectors, for instance, infrared detector and pyroelectric detector.

The main peaks in the imaginary part of the dielectric function labeled as $P_1$ and $P_2$ in Fig. 8a, c, and e could be assigned to the principal interband transitions. This is achieved by fitting the peak energies in Fig. 8 with that of the interband transitions in Fig. 4. When a strain ranging from −6 to 6% is applied, the peak energies of $P_1$ and $P_2$ peaks are found to take place in the energy range of 1.3–3.0 eV, which exhibit great enhanced response in a wide spectrum from ultraviolet, visible to the near-infrared area. The widely distributed peaks should be suitable for the design of multiband metamaterial emitters with promising photoelectric applications.
Controllable anisotropy of WSSe bilayer through the strain engineering is further investigated. Compared with that of $\varepsilon_{xx}$ ($\varepsilon_{yy}$), $\varepsilon_{zz}$ exhibits insignificant variation regardless of the tensile or compressive strain. This manifest the fact that the imaginary part of the dielectric function possesses different response properties with the increased strain. Without the strain, the $\varepsilon_{xx}$ ($\varepsilon_{yy}$) and $\varepsilon_{zz}$ are anisotropy with $E[\varepsilon]$ transformation preference for all the $I_1$, $I_3$, and $I_4$ structures. For either $I_1$ or $I_3$, while a compressive strain is applied, the anisotropy of dipole transition is firstly enhanced and then weakened and that with the tensile strain is always enhanced. Nevertheless, the anisotropy of $I_2$ is enhanced with the increasing tensile strain and becomes weakened once a compressive strain is introduced. An isotropy of dipole transition occurs when the compressive strain continues to increase to $6\%$ $\sim$ $4\%$, where both $E[I\varepsilon]$ and $E[I\varepsilon]$ possess equal transformation preference. Thus, the WSSe bilayer with a suitable strain modulation will be leading to a transition from optical anisotropy to isotropy. Since the excitonic effect usually plays an important role in the optical absorption [36, 37], the dielectric function determined dipole transition preference may be explored for the potential optoelectronic applications with an electroluminescence process.

As has been demonstrated that some typical TMDC monolayers with 2H phase have the same hexagonal lattices and similar characters in their monolayer band structures [5, 33, 38, 39]. Therefore, the Janus monolayer and bilayer derived from these TMDC materials, such as MXY ($M = Mo$ or $W$, $X/Y = S$, $Se$, or $Te$, and $X \neq Y$), would be expected to possess similar band structures [8, 32] and thus the similar electronic and optical properties, as well as evolution tendency with strain modulation. Therefore, the main calculation results will have certain universality in 2H-TMDC Janus materials. Going through the previous reports, the mechanical properties of out-of-plane bended MoS$_2$ thin films have been revealed [40], the electronic and optical properties of TMDC compounds have been studied [22], and the energy gaps of monolayer and Janus heterobilayer TMDCs have been demonstrated to control the electric field [41]. Comparing with these works, we provide a series of innovative results in strain-modulated electronic and optical properties of 2D Janus WSSe bilayer, which enriches the physical connotation of the Janus materials and provides a promising control strategy towards the application of next-generation electronic and optoelectronic nanodevices.

**Conclusion**

In summary, the strain dependence of electronic and optical properties of the WSSe bilayer is systematically studied. By comparing the binding energies of different stackings, the most favorable configuration of the WSSe bilayer is determined. The WSSe bilayer preserves an indirect bandgap structure, which is sensitive to the external stress. The bandgap of all the stable structures can be tailored from the semiconductor to metallicity under to obtain a wide-range spectrum in near-infrared and mid-infrared area. Atomic orbital projected energy bands reveal a positive correlation between the degeneracy and the structural symmetry, which explains the bandgap evolutions. Dipole transition preference is investigated from the dielectric properties and tuned by the biaxial strain. Under around $6\%$ $\sim$ $4\%$ critical strain, a controllable transformation between anisotropic and isotropic optical properties is realized. The strain-modulated electronic and optical behaviors of Janus WSSe bilayer possess a wide application prospect in next-generation electronic and optoelectronic nanodevices.

**Abbreviations**

2D: Two-dimensional; CBM: Conduction band minimum; DFT: Density functional theory; SOC: Spin-orbit coupling; TMDCs: Transition metal dichalcogenides; VBM: Valance band maximum

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Not applicable

**Authors’ Contributions**

JG drafted the manuscript, and CK helped to guide the calculations. JG, CK, YW, and JK took part in the data analysis. Dr. YW and Prof. JK participated in the conception of the project, improved the manuscript, and coordinated between all the participants. All authors discussed the results and the implications of this manuscript. The authors read and approved the final manuscript.

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**Availability of Data and Materials**

All data generated or analyzed during this study are included in this published article.

**Competing Interests**

The authors declare that they have no competing interests.

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