A new two-dimensional TeSe₂ semiconductor: indirect to direct band-gap transitions

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ABSTRACT A novel two-dimensional (2D) TeSe₂ structure with high stability is predicted based on the first-principles calculations. As a semiconductor, the results disclose that the monolayer TeSe₂ has a wide-band gap of 2.392 eV. Interestingly, the indirect-band structure of the monolayer TeSe₂ transforms into a direct-band structure under the wide biaxial strain (0.02–0.12). The lower hole effective mass than monolayer black phosphorus portends a high carrier mobility in TeSe₂ sheet. The optical properties and phonon modes of the few-layered TeSe₂ were characterized. The few-layer TeSe₂ shows a strong optical anisotropy. Specially, the calculated results demonstrate that the multilayer TeSe₂ has a wide range of absorption wavelength. Our result reveals that TeSe₂ as a novel 2D crystal possesses great potential applications in nanoscale devices, such as high-speed ultrathin transistors, nanomechanics sensors, acousto-optic deflectors working in the UV-vis red region and optoelectronic devices.

Keywords: TeSe₂, first-principles calculations, direct band gap, phonon modes, optical absorption

INTRODUCTION

Since the isolation of graphene in 2004 [1], many new research fields emerge. One of the most important issues is the exploration of two-dimensional (2D) atomic-layer structures, including graphene and its allotrope-graphyne [2], silicene, germanene [3], phosphorene [4,5], arsenene, antimonene [6], boronphene [7] and transition metal dichalcogenides (TMDs) [8–10]. These 2D materials have unique and extraordinary properties and promising applications. Typically, graphene allows electrons to flow freely across its surfaces due to its very low carrier effective mass. Therefore, graphene is considered to be a promising candidate for high-speed field-effect transistor (FET) devices and energy storage devices [11–14]. A high-performance FET device requires a moderate band gap, a

reasonably high carrier mobility of the channel materials and excellent electrode-channel contacts [4,11–13,15,16]. However, due to the gapless intrinsic dispersion in graphene, silicene and germanene [11,12,17,18], the ability to switch current on/off in transistors is seriously reduced. Despite widespread approaches to the problem of opening a gap in different graphene nanostructures, only very small band gaps can be achieved [19–22]. However, the emergence of single-layer MoS₂ [23] has attracted substantial research interest, which exhibits superior electrical and optical properties as a semiconducting TMD. Unlike graphene, silicene and germanene, monolayer MoS₂ does not suffer from a vanishing gap [23,24], and has been used to fabricate FETs [15,25–27]. However, the band gaps of most explored 2D materials are smaller than 2.0 eV, which has greatly encumbered the development of 2D semiconductor based optoelectronic devices with response to photons with wavelengths of less than 620 nm, such as ultraviolet (UV)- and blue-light photodetectors.

In the present work, we present the theoretical discovery of a new moderate-band gap semiconductor, which is a 2D planar compound consisting of group-VI elements Te and Se, denoted as TeSe₂. According to the density functional theory (DFT) calculations, we demonstrate that TeSe₂ monolayer is kinetically stable with an indirect-band gap of 2.392 eV (calculated with the HSE06 functional). Moreover, the band gaps of multilayer TeSe₂ fall with increasing the thickness. Importantly, the indirect band structure of monolayer TeSe₂ can be converted to direct-band gap semiconductor under tensile strain, which implies that this novel 2D semiconductor can be anticipated to function as mechanical sensors and piezoelectric transistors (PETs). Furthermore, the optical properties of few-layer TeSe₂ are characterized, which present a strong anisotropy. Specially, with the polarization direction at (1.0, 0.0, 0.0), the absorption wavelength

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of five-layer TeSe_2 covers UV and all visible light regions, which denotes that it will be suitable for widely-visible light acousto-optic deflectors.

COMPUTATIONAL METHOD

All calculations were carried out by utilizing the DFT and using the density functional perturbation theory (DFPT) [28]. General gradient approximation (GGA) was used with the Perdew–Burke–Ernzerhof (PBE) functional to describe the exchange–correlation potential [29] to calculate electronic properties. Local density approximation (LDA) [30] was used to calculate phonon and optical properties. Ultrasoft pseudopotentials were used to calculate electronic properties, and norm-conserving pseudopotentials were used to calculate phonon and optical properties. All structural models were entirely relaxed until the ionic Hellmann–Feynman forces were smaller than $0.01 \text{ eV } \text{\AA}^{-1}$ and the energy tolerances were less than $5 \times 10^{-6} \text{ eV/atom}$. The tolerances of ionic displacement and stress were $5 \times 10^{-4} \text{ \AA}$ and 0.02 GPa , respectively. A vacuum of $15 \text{ \AA}$ between these few-layer structures was adopted using $10 \times 13 \times 4$ Monkhorst–Pack K-points, and the plane-wave cutoff energy of 550 eV . Moreover, in the calculations of strain affecting electronic structure, HSE06 functional [31] was employed to compare the result with that of PBE functional. To describe the interlayer van der Waals interactions of the multilayer TeSe_2 during the calculations of structural optimization and properties, we used the PBE functional with Grimme dispersion correction [32], and LDA functional with OBS dispersion correction [33], respectively.

RESULTS AND DISCUSSION

Naturally, bulk Te and Se have many allotropes (Table S1 in the supplementary material), and their structures are stable under ambient conditions. The bond lengths of Te–Te and Se–Se are around $2.8\text{--}3.1 \text{ \AA}$ and $2.4 \text{ \AA}$ within the chains or rings, but the distance of adjacent rings or chains is larger than $3.1 \text{ \AA}$. Thus, the adjacent atomic chains and rings are held by significant van der Waals interactions. Previously, selenene and tellurene have been predicted using theoretical calculations [34–36], which have been confirmed in a high thermal stability with a direct-band gap (considering spin-orbital coupling). It is encouraging that larger-area monolayer tellurene and multilayer tellurene have been synthesized by a substrate-free solution process, and their potential applications as highly air-stable, and high-performance FETs have been proved [37]. The atomic configuration of monolayer tellurene is depicted in Fig. 1a. Our design of TeSe_2

monolayer was initially inspired by the previously study. Monolayer TeSe_2 is isoelectronic to monolayer tellurene in the valance electron, and can be considered as formed by replacing the Te atoms with Se atoms. The optimized structure of our designed TeSe_2 monolayer is presented in Fig. 1b. One unit cell of TeSe_2 monolayer consists of two Se atoms and one Te atom, with the optimized lattice constants of $a = 5.08 \text{ \AA}$ and $b = 3.86 \text{ \AA}$. Similar to tellurene monolayer, the surface of TeSe_2 monolayer is wrinkling with incised serration viewing from the side. We also found that Te atoms always are in the same plane, but Se atoms are situated alternately in an upper and a lower plane. The thickness of the tellurene layer is $2.16 \text{ \AA}$ and that of TeSe_2 layer is $2.969 \text{ \AA}$ (Fig. 1c, d).

To determine whether the TeSe_2 monolayer has perfect stable structure, phonon spectra and cohesive energies of monolayer and few-layer TeSe_2 were characterized. The optimized lattice parameter and the interlayer distance (d) of few-layer TeSe_2 are listed in Table 1. Firstly the stability of few-layer TeSe_2 was evaluated. The cohesive energy of monolayer TeSe_2 (2.81 eV/atom) is higher than tellurene [35,36] (2.56 eV/atom) by 0.25 eV/atom . This result demonstrates that it would be energetically more favorable to obtain 2D TeSe_2 from tellurene. It should be noticed that the formation of TeSe_2 may require a higher temperature than tellurene. The similar cohesive energy computed provides clear evidence that the structure of TeSe_2 are bonded by relatively strong covalent bonds. As shown in Fig. 1e, the calculated electron density difference demonstrates that strong covalent bonds exist between theses adjacent Te and Se atoms. Moreover, the cohesive energies computed for few-layer increase with increasing the number of layers. The reason for that is the weak interlayer interaction with significant Van der Waals character. Therefore, the interlayer interactions of multilayer TeSe_2 with two to five layers are shown in Fig. S1.

Before examining the electronic properties of TeSe_2 , we need to answer the question that whether the monolayer TeSe_2 is in a kinetic stability or not. To verify the kinetic property, phonon dispersion calculations were implemented by using the DFPT [28]. The absence of soft modes in the phonon spectrum is a criterion of structural stability [38]. Distinctly, as depicted in Fig. 2a, no soft phonon modes were observed in the computed phonon dispersion spectrum, indicating that monolayer TeSe_2 is kinetically stable. These multilayer models were optimized by DFT calculations with Grimme van der Waals correction [32], and Fig. S3 depicts the optimized five-layer TeSe_2 configurations.

We then investigated the variation of electronic struc-

Figure 1 Two-dimensional structures of tellurene and TeSe_2 , the rectangular box in green color denotes unit cell. (a) Top view and (c) side view of monolayer tellurene; (b) top view and (d) side view of monolayer TeSe_2 . (e) Top view of electron density difference ($2 \times 2 \times 1$ cell); (f) Brillouin zone path of TeSe_2 unit cell.

Table 1 Lattice constants a , b , cohesive energies, d (interlayer distance) and in-plane covalent bond lengths of the few-layer TeSe_2 , calculated using the PBE functional with Grimme van der Waals correction

Number of layers	Lattice parameters (Å)		d (Å)	Bond length (Å)		Cohesive energy (eV/atom)
	a	b		Te-Se	Te-Te	
Monolayer-tellurene	5.49	4.17	—	3.02 (Te-Te)	2.75	2.56
1	5.08	3.86	—	2.823	2.345	2.81
2	5.27	3.87	4.075	2.834	2.361	2.89
3	5.32	3.88	4.092	2.835	2.368	2.93
4	5.36	3.88	4.002	2.834	2.376	2.95
5	5.37	3.89	4.040	2.837	2.370	2.96

tures upon increasing the number of layers, as shown in Fig. S2 and Fig. 2b. The band gaps of the few-layer TeSe_2 reduce from 1.699 eV to 0.538 eV with increasing the number of layers from one to five. Zhang [6] gave an interpretation of the intrinsic mechanism of this phenomenon for multilayer arsenene and antimonene. The main factor affecting the electronic structure transition is the second-order effects from the wrinkled parallels and interlayer interactions. Like arsenene and antimonene, the

layered TeSe_2 shows wrinkled parallels due to Se atoms situated alternately in an upper and a lower plane, resulting in second-order Jahn-Teller distortions [39]. As shown in Fig. S1, the interlayer interactions calculated for multilayer TeSe_2 with two to five layers are in the range of 65–110 meV/atom and increase with an increase in layer thickness. Thus, the dependence of the interlayer interaction on the layer thickness most likely plays an important role in the transition of moderate- to narrow-

Figure 2 (a) Phonon dispersion relations of monolayer TeSe₂ using DFPT calculation. (b) Band structure of monolayer TeSe₂ based on the DFT calculations with PBE functional (blue solid line) and HSE06 functional (red dash line). The Fermi level is assigned as 0 eV.

band gap in few-layered TeSe₂ systems. However, the DFT calculations for monolayered TeSe₂ were performed using not only the PBE functional [29,40], but also HSE06 [31] functional. According to the computed results from HSE06 functional, the monolayer TeSe₂ shows a large band gap of 2.134 eV along *M-X-Γ* path and 2.392 eV along *M-X-D* (*E-D-X*) path. This difference denotes that TeSe₂ presents anisotropy of electronic property. Moreover, the effective mass of hole according to the valence bands of TeSe₂ monolayer is also calculated using $m^* = \hbar^2 / (\partial^2 E / \partial k^2)$. The effective masses at the Γ point along Γ -X and Γ -Y direction were computed to be $m^{*\Gamma-X}_h = 0.077m_0$ and $m^{*\Gamma-Y}_h = 0.13m_0$ (m_0 is the free electron mass). These values are smaller than black phosphorus monolayer ($m^{*\Gamma-X}_h = 0.15m_0$, $m^{*\Gamma-Y}_h = 6.35m_0$) [4]. The smaller effective carrier masses, the higher mobility appears. This outstanding property with a moderate band gap should render TeSe₂ monolayer suitable for future applications in high-speed ultrathin transistors.

Unfortunately, the calculated results indicate that monolayer and multilayer TeSe₂ are in an awkward position of poorly efficient light emission due to indirect band gaps. However, the previous reports [6,41,42] en-

lighten that a relatively small strain should significantly affect the band structures. Herein we discuss the band structure behavior of TeSe₂ monolayer under biaxial strain. Computations were implemented using unit cell as illustrated in Fig. 3a. The lattice constants a and b are varied with the strain value from -0.12 to 0.12 in step of 0.02 . The band gaps were calculated by both GGA-PBE and HSE06 functionals, and they give the same trend. Moreover, the strain energies (E_s) at each strain step were also calculated, which is energy difference between strained and equilibrium systems. These results are shown in Fig. 3b. Like graphene [41], within the enforced tensile and compressive strain range, the strain energy increases monotonously as strain increases, demonstrating the deformation of TeSe₂ monolayer is elastic.

Unsurprisingly, the band gap of TeSe₂ presents tunable band gap under strain. In the circumstance of tensile strain, the band gap decreases with increasing the tensile strain, and it decreases with increasing compressive strain. These changes of band gap are different from graphene under tensile and compressive strain [41]. At $\epsilon=0.12$, the band gap is 1.38 eV (GGA-PBE) and 1.77 eV (HSE06) smaller than that in equilibrium state. Significantly, the decreasing of band gap almost exhibits linearity in the strain range from -0.12 to -0.02 (from 0.02 to 0.12). The calculated slopes using GGA-PBE and HSE06 are 12.237 and 9.769 (-14.936 and -16.965 eV under tensile strain range), respectively. Fig. 3c presents the changes in the valence-band top and the conduction-band bottom based on HSE06 functional. For $\epsilon=-0.12\sim 0$, the indirect band gap character of TeSe₂ is still maintained, and it shows tunable band gap under strain. Encouragingly, TeSe₂ monolayer presents an intriguing indirect-to-direct band gap transition at $\epsilon=0.02$ to 0.12 . The direct band structure of the strained TeSe₂ monolayer has a distinct advantage for its applications in optoelectronic devices, as electronic excitation is now feasible with lower photons energies. Moreover, the tensile strain has more effects on the values of band gap than the compressive strain. We believe that the tunable band gap of TeSe₂ under biaxial strain promises its applications in future nanomechanics, such as mechanical sensors and PETs.

The optimized geometry of TeSe₂ shows a monoclinic structure, which consists one Te and two Se atoms in the unit cell. Monolayer TeSe₂ has a $P12_1/M1$ ($P2_1/M$) symmetry, which has a rotation axis, inversion center and mirror plane, respectively. Using the DFPT calculations with 514.5 nm laser excitation, the Raman spectra of few-layer TeSe₂ were computed as illustrated in Fig. 4a and

Figure 3 (a) Schematic representation of TeSe₂ monolayer under biaxial strain (including tensile and compressive strain). (b) Variation of strain energy and band gap of TeSe₂ monolayer under biaxial strain. The band gaps were calculated using both GGA-PBE (magenta circles) and HSE06 (cyan triangles) functional. (c) Changes in the valence-band top and the conduction-band bottom with increasing biaxial strain from -0.12 to 0.12, based on HSE06 functional. The Fermi level is assigned as 0 eV. The magenta lines denote direct band gap, and gray lines denote indirect band gap.

Figure 4 (a) Raman scattering and IR spectra computed for monolayer TeSe₂ using the DFPT calculations with 514.5 nm laser excitation. (b) The lattice heat capacity (green scatter) and debye temperature (red line) calculated for monolayer TeSe₂.

Fig. S4. For multilayer TeSe₂, the dispersion was corrected with OBS scheme [33]. The previous calculated phonon dispersion relation (Fig. 2a) presents that, TeSe₂ monolayer totally has 9 phonon modes, 3 of which are Raman-active: 2 Ag modes and 1 Bg mode; 3 of IR-active (infrared radiation (IR)): 1 Au mode and 2 Bu modes. The calculated frequency values and the corresponding 9

phonon modes are listed in Table S2. For multilayer TeSe₂, the calculated total phonon modes from 2 to 5 layers are 18, 27, 36 and 45, respectively. Based on the phonon calculations, we also implemented the thermodynamic calculations as depicted in Fig. S5, and the calculated lattice heat capacity (C_v) of monolayer TeSe₂ in unit cell and debye temperature (Θ_D) are shown in Fig. 4b.

We find that the lattice heat behavior approaches Du-long–Petit limit at high temperature. The calculated debye temperature shows substantial and linear variation with temperature. The value of Θ_D at room temperature (300 K) for TeSe₂ in the present calculations is 950.

Besides Raman scattering, we further investigated polarized optical absorption of few-layer TeSe₂ with polarization direction at (1.0, 0.0, 0.0), (0.0, 1.0, 0.0) and (0.0, 0.0, 1.0), respectively. In brief, the absorption probability can be given by the absorption coefficient. Herein, we discuss the range of absorption wavelength when the absorptivity greater than 10^5 cm^{-1} as depicted in Fig. S6. The absorptivity of the few-layer TeSe₂ increases with increasing number of layers, as well as the range of absorption wavelength. With the polarization direction at (1.0, 0.0, 0.0), the absorption wavelength of five-layer TeSe₂ covers UV and all visible light regions. Moreover, the absorption visible light region decreases with decreasing the number of layer, until it vanishes in UV region for monolayer TeSe₂. Comparing with the other two polarization directions ((.0, 1.0, 0.0) and (0.0, 0.0, 1.0)), glaring anisotropy of optical absorption is observed in few-layer TeSe₂. All these results indicate that the new material, 2D TeSe₂ will be suitable for widely-visible and UV-light acousto-optic deflectors.

CONCLUSION

In summary, we reported 2D semiconducting TeSe₂ nanosheets with thermal stability for the first time. Phonon dispersion calculation demonstrates that this novel 2D sheet possesses very kinetic stability. The cohesive energy of monolayer TeSe₂ (2.81 eV/atom) is 0.25 eV/atom higher than that of the tellurene (2.56 eV/atom), which demonstrates that the formation of TeSe₂ requires a higher temperature than that of tellurene. Calculated results indicate that the monolayer TeSe₂ is indirect semiconductor with wide-band gap of 2.392 eV (using HSE06 functional). A sudden transition from indirect-band gap to direct-band gap is observed when a little biaxial strain ($\epsilon=0.02$) imposed to monolayer TeSe₂, and it still retains direct-band gap even if the biaxial strain is up to 0.12. Absorption spectra computed for few-layer TeSe₂ show a strong anisotropy. Moreover, we find a conspicuous thickness dependence of the absorptivity and absorption wavelength range in TeSe₂. Particularly, with the polarization direction at (1.0, 0.0, 0.0), the absorption wavelength of five-layer TeSe₂ covers UV and all visible light regions. All these results indicate that the new material will be suitable for some devices, such as high-speed ultrathin transistors, mechanical sensors, PETs, UV- and

blue-light emitting diodes and widely-visible light acousto-optic deflectors.

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Conflict of interest The authors declare they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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新型二维半导体TeSe₂: 间接带隙到直接带隙的转变

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摘要 本文基于第一性原理计算预测了一种新颖的二维稳定结构TeSe₂, 结果显示单层TeSe₂是一种半导体材料, 其带隙值为2.392 eV. 有趣的是单层TeSe₂的间接能带在宽范围的双向负应变(0.02~0.12)作用下转变为直接能带. 比单层黑磷烯更小的有效空穴电子质量预示了TeSe₂具有更高的载流子迁移速率. 此外, 对不同厚度TeSe₂的声子模及光学性质也进行了计算, 结果显示不同厚度的TeSe₂具有较强的光学各向异性, 尤其是多层TeSe₂具有更宽的吸收波长. 这些结果表明, TeSe₂作为一种新颖的二维结构在纳米器件领域具有巨大的应用潜力, 如高速超薄晶体管, 纳米力学传感器, 紫外-可见红光区声光偏振器及光电子器件等.