Review

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Tunable electronic structure of two-dimensional transition metal chalcogenides for optoelectronic applications

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Abstract: Differing from its bulk counterparts, atomically thin two-dimensional transition metal dichalcogenides that show strong interaction with light are considered as new candidates for optoelectronic devices. Either physical or chemical strategies can be utilized to effectively tune the intrinsic electronic structures for adopting optoelectronic applications. This review will focus on the different tuning strategies that include its physics principles, in situ experimental techniques, and its application of various optoelectronic devices.

Keywords: 2D materials; electronic band; optoelectronics.

1 Introduction

Atomically thin two-dimensional (2D) transition metal dichalcogenides (TMDs) have been extensively studied in electronic, optoelectronic, and electrochemical devices because of its rich physical and chemical properties since graphene was discovered from 2004 [1]. Thanks to anisotropic layered structures, the electronic structures of 2D TMDs can be tuned by the multiple factors such as thickness thinning down, foreigner species interaction, external strain, and composition engineering or assembling heterostructures, which have been widely applied to optoelectronic devices such as electronic logic devices, photovoltaic devices, photodetection devices, nonlinear optical absorption devices, light emission devices, and so on [2]. Direct-bandgap monolayer MoS$_2$ devices with improved carrier mobility have proven the ultrasensitive responsivity of 880 AW$^{-1}$ at a wavelength of 561 nm and a response spectrum in the 400- to 680-nm range with equivalent noise level as the silicon devices [3]. A bilayer MoTe$_2$-based light-emitting diode and photodetector for silicon photonic integrated circuits were demonstrated by Bie et al. [4]. Monolayer and bilayer MoS$_2$ field-effect transistors with ionic liquid gate tuning show both holes and electrons accumulation in the ambipolar regime, thus emitting the visible light [5]. The photodetectors and emitting devices based on the 2D TMDs have been developed with large photoresponsivity, ultrahigh gain, tunable spectrum sensitivity, bandwidth, and considerable light-to-current or current-to-light conversion efficiency. At the same time with the rapid developments of large-scale preparation technology and direct patterning of specific position and geometry for the 2D films, such as chemical vapor deposition (CVD), liquid exfoliation, printing techniques, and so on, 2D TMD materials show the great potential for the optoelectronic integrated circuits, photodetection, imaging, and biomedical recording [6–11].

In this review, considering 2D MoS$_2$ as a star material, we intend to summarize the structure–optoelectronic properties relationships of 2D TMDs in Section 2. Different modulation strategies based on the distinctive crystal structure will be systematically introduced in Section 3. Finally, the development history, progress, and
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A

B

Octahedral

Trigonal prismatic

C

1T

2H

3R

D

H

K

\Gamma

A

H

E_{g'}

E_{g}

v1

v2

a

c

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2 Basic material properties

The TMD material family is rather rich owing to the combination of various transition metal elements and chalcogens and exhibits abundant charming physical properties. The material properties are strongly dependent on their chemical composition and atomic arrangement. Before reviewing the tuning of electronic structure for optoelectronics, some basic material properties related to the optoelectronics, including the crystal structure and electronic properties, are outlined in this section.

2.1 Crystal structure

Transition metal dichalcogenides can be generalized with the formula MX₂, where M denotes a transition metal from group III to group VIII and X denotes a chalcogen (S, Se, or Te). A large number of TMDs exhibit graphite-like layered structure, which can be exfoliated into 2D layers. The layered structure is composed of 2D hexagonally packed X-M-X sandwich layers – metal atoms in the middle hexagonal plane covalently bonded to chalcogen atoms located in the top and bottom hexagonal planes, stacked layer-by-layer, as shown in Figure 1A. The adjacent X-M-X sandwich layers are held together to form bulk crystal by van der Waals interactions, which is much weaker than intralayer covalent bonds. The strong intralayer and weak interlayer interactions lead to the strong anisotropy in mechanical properties, responsible for a remarkably easy mechanical exfoliation to get thin layers or monolayer (a single X-M-X sandwich layer).

The bulk TMDs exhibit a variety of polymorphs, which determine the unique structure and electronic properties, depending on stacking orders and metal atom coordination by the chalcogens. As illustrated in Figure 1B, within each X-M-X sandwich layer, the transition metal atom is coordinated by six chalcogens in two basic geometries: octahedral coordination or trigonal prismatic coordination, leading to different symmetries. The octahedral coordination with AbC (the letters denote different atom-arrange positions, whereas the uppercase and lowercase letters denote chalcogen and transition metal atoms, respectively) stacking sequence holds inversion symmetry for monolayer, whereas the trigonal prismatic coordination with AbA stacking sequence results in broken inversion symmetry in monolayer. There are three most commonly involved structural phases [1]: 1T (one sandwich layer per unit cell with AbC stacking order, octahedral coordination), 2H (two sandwich layers per unit cell with AbA stacking order, trigonal prismatic coordination), and 3R (three sandwich layers per unit cell with AbACaBc stacking order, trigonal prismatic coordination), as illustrated in Figure 1C. As an example, the most widely studied group VIB bulk TMDs (e.g. MoS₂, WSe₂, MoTe₂) exhibit 2H or 3R phase [2, 13–16], the group VB TMDs (e.g. TaSe₂, TaS₂) exhibit 2H or 1T phase [17–21], and all the group IVB TMDs (e.g. TiS₂, ZrS₂) are 1T phase [22–27]. It has been found that phase changes can be induced by intercalation [28–34]. For example, 2H-MoS₂ can transform to 1T phase by lithium intercalation [2, 31, 33–35]. These structural phases featured with different symmetries and stacking orders, relating to the d-electron count, primarily play important roles in affecting the electronic properties of TMDs.

2.2 Electronic properties

Most TMDs have common features in their band structures originating from d orbital on metal atoms, as demonstrated by theoretical calculations and spectroscopic experiments [1]. Different d-electron counts of transition metal elements from group III to group VIII fill the non-bonding d bands to different degrees, resulting in the
wide variety of electronic properties including insulator, semiconductor, semimetal, and superconductor [2]. In general, the partially filled group VIB TMDs, such as MoX₂ and WX₂, are semiconducting [36, 37], whereas the fully filled group VB TMDs, such as NbX₂ and TaX₂, are metallic [38, 39].

Semiconducting TMDs such as MoX₂ and WX₂ possess bandgaps in the near-infrared to the visible region, promising interesting photonics and optoelectronics applications [3, 40–52]. Their bulk materials are indirect-bandgap semiconductors with the bottom of conduction band and the top of valence band maximum located at different high symmetry points of the Brillouin zone, respectively, whereas the monolayers change to larger direct-bandgap semiconductors [53–58]. Compared to bulk TMDs, the electronic properties of 2D TMDs are considerably tuned as a result of quantum confined effect in the out-of-plane direction and the resulting reduced symmetries and alteration in hybridization between pₓ orbitals on chalcogen atoms and d orbitals on metal atoms near Γ point when thinning down thickness [55, 57, 59]. Except the indirect-to-direct bandgap transition and bandgap size enlargement, few-layer or monolayer 2D TMDs exhibit strong excitonic effects due to the weak charge carrier screening and subsequent strong Coulomb interactions caused by reducing thickness [57, 60–67].

A simplified band diagram of MoS₂, as a representative semiconducting TMD, is depicted pictorially in Figure 1D, showing the lowest conduction band c1 and the highest split valence bands v1 and v2. The indirect bandgap E′₀ for the bulk features conduction band minimum locates between Γ and K points and valence band maximum located at the Γ point, whereas the direct bandgap E₀ for the monolayer locates at K point. The valence band around K point is split as a result of spin-orbit coupling [12, 68–70]. The direct-gap transitions between the maximum of the split valence bands and the minimum of conduction band, generally called the A and B excitons, will lead to two distinct low-energy resonance peaks in optical spectrum, while the indirect-gap transition I will give rise to an even lower-energy resonance peak. The indirect-to-direct bandgap transition and strong excitonic effect in monolayer TMDs have been widely demonstrated by absorption spectra and photoluminescence [12, 59, 70–72].

3 Tuning electronic structure for optoelectronics

Transition metal dichalcogenides with tunable bandgap available are desirable for many photonic and optoelectronic applications where the direct bandgap of TMDs would allow a strong absorption and efficient production of electron–hole pairs under photoexcitation. The electronics and optoelectronics engineering of 2D TMDs have been investigated extensively by theoretical calculations and experiments. It shows that the electronic structure and associated optical properties can be well tuned by a variety of physical parameters, such as thickness [12, 40, 55, 59, 70, 71], composition [73, 74], stacked heterostructures [41, 44, 46, 50, 75–83], strain [84–92], chemical modification [93, 94], and electric field [95–100]. The progress in electronics and optoelectronics engineering and the physical mechanisms under various tuning methods will be reviewed in this section [101, 102].

3.1 Quantum confinement by thickness thinning down

The thickness-dependent band structures of TMDs, due to the resulting quantum confinement effect of thinning thickness, greatly affect the optical properties and optoelectronic performance. Benefiting from the easily mechanical cleavage [7] and bottom-up growth by CVD [103–107] or metal–organic chemical vapor deposition [15, 108, 109], atomic thin layers can be achieved to provide opportunities for studying thickness-dependent physical properties in experiments. As first reported by Splendiani et al. [59] in 2010, a strong photoluminescence, which is absent in bulk, emerges in the monolayer MoS₂, indicating an indirect-to-direct bandgap transition in this d-electron material. Through characterization by absorption, photoluminescence, and photoconductivity spectroscopy, Mak et al. [12] traced the thickness-dependent electronic properties and the resulting optical properties of MoS₂ from one to six layers (Figure 2C). It shows that the indirect bandgap increases with decreasing thickness and changes into direct bandgap at the monolayer, whereas the direct excitonic transition energy almost keeps unchanged. In addition, the monolayer MoS₂ exhibits a considerable increase in luminescence quantum efficiency compared with bulk, as a result of the strong excitonic effect due to reducing thickness. The observation of thickness-dependent band structure and resulting optical properties evolution shows possibility of tuning electronic properties for optoelectronic applications by thinning thickness [3, 40, 42, 48, 110, 111].

Band structure calculations through the first principles show qualitative agreement with experimental researches. The thickness-dependent band structure of various TMDs has been studied by lots of theoretical works including ab initio calculations [36, 55, 58, 59, 112]. As an example
Figure 2: Quantum confinement with tuning thickness.  
(A) Band structures of bulk MoS$_2$, its monolayer, and few layers calculated at the DFT/PBE level. The horizontal dashed lines indicate the Fermi level. The arrows indicate the fundamental bandgap (direct or indirect) for a given system. The top of valence band (blue/dark gray) and bottom of conduction band (green/light gray) are highlighted. Reproduced with permission from Kuc et al. [55]. Copyright 2011 American Physical Society.  
(B) ARPES spectra of monolayer, bilayer, trilayer, and 8 ML MoSe$_2$ thin films along the G–K direction. White and green dotted lines indicate the energy positions of the apices of valence bands at the G and K points, respectively, with energy values written in the same colors. Reproduced with permission from Zhang et al. [70]. Copyright 2014 Springer Nature Limited.  
(C) Left: PL spectra for monolayer and bilayer MoS$_2$ samples in the photon energy range from 1.3 to 2.2 eV. Inset of left: PL QY of thin layers for $N=1–6$. Middle: Normalized PL spectra by the intensity of peak $A$ of thin layers of MoS$_2$ for $N=1–6$. Feature $I$ for $N=4–6$ is magnified, and the spectra are displaced for clarity. Right: Bandgap energy of thin layers of MoS$_2$, inferred from the energy of the PL feature $I$ for $N=2–6$ and from the energy of the PL peak $A$ for $N=1$. The dashed line represents the (indirect) bandgap energy of bulk MoS$_2$. Reproduced with permission from Mak et al. [12]. Copyright 2010 the American Physical Society.  
(D) Left: Schematic 3D view of single-layer transistor with hexagonal structure MoS$_2$ nanosheet, 50-nm-thick Al$_2$O$_3$ dielectric and ITO top-gate under monochromatic light. Middle: The schematic band diagrams of ITO (gate)/Al$_2$O$_3$ (dielectric)/single-layer (1 L), double-layer (2 L), and triple-layer (3 L) MoS$_2$ (n-channel) under the light ($E_{\text{light}}=h\nu$) illustrate the photoelectric effects for bandgap measurements. Right: Respective photocurrent dynamics of single-layer MoS$_2$-based top-gate transistors under monochromatic red and green lights. Reproduced with permission from Lee et al. [40]. Copyright 2012 American Chemical Society.
shown in Figure 2A, the valence band maximum of MoS$_2$ shifts from $\Gamma$ to K point when the thickness is thinned to monolayer, resulting in indirect-to-direct bandgap transition [55]. The unusual thickness-dependent band structure of TMDs is attributed to quantum confinement effect and the characters of $d$-electron orbitals that comprise the conduction and valence bands [59, 70, 71]. Theoretical calculations for MoS$_2$ [59] show that conduction band states at the K point are mainly composed of localized $d$ orbitals on Mo atoms, located in the middle of the S-Mo-S sandwich layers and having relatively weak interlayer coupling. However, states near the $\Gamma$ point originate from combination of $d$ orbitals on Mo atoms and antibonding $p_z$ orbitals on S atoms, having strong interlayer coupling and being more sensitive to thickness. Therefore, as thickness decreases, the conduction band states near K point are almost unchanged, while the conduction bands and valence bands near the $\Gamma$ point are changed considerably [113]. The direct observation of the thickness-dependent electronic band structure evolution is achieved by angle-resolved photoemission spectroscopy (ARPES) measurements on mechanically exfoliated and CVD-grown MoS$_2$ and molecular beam epitaxy-grown MoSe$_2$ thin films [70, 71]. The significant step-by-step evolution of the valence band (Figure 2B) provides direct evidence of the valence band maximum shifts from $\Gamma$ to K point (indirect-to-direct bandgap transition), when the thickness is thinned to monolayer [70]. A lot of TMDs including MoX$_2$ and WX$_2$ are expected to possess a similar indirect-to-direct bandgap transition with decreasing thickness to monolayer, covering the bandgap energy range of ~1 to 2 eV [12, 40, 55, 70, 71, 114–116].

The controllability of band structure with tuning thickness paves the way for new optoelectronics. The electronic band structures of TMDs described earlier directly influence their optical properties. A variety of photodetectors based on thickness-modulated TMDs have been demonstrated. Lee et al. [40] have realized photodetection of different wavelengths using MoS$_2$ layers with different thickness. As shown in Figure 2D, devices with single- and double-layer MoS$_2$, exhibiting significant energy bandgaps of 1.82 and 1.65 eV, respectively, are demonstrated effective for green light detection, whereas devices made of triple-layer MoS$_2$ with a bandgap of 1.35 eV are effective for red light detection. Yin et al. [110] have fabricated a single-layer MoS$_2$ phototransistor showing good photoresponsibility.

### 3.2 Defect engineering

Previous studies have shown 2D material–fabricated electronic devices could emit photons out of the materials, detect incident photons, or control the properties of incident light [117]. Photoluminescence transition of bulk to monolayer MoS$_2$ is directly related to their different electronic structures [43, 59]. Briefly speaking, photoluminescence consists of photoexcitation (i.e., photons that excite electrons to a higher energy level), relaxation processes, and emitting electromagnetic radiation, whose emitting intensity is proportional to the decrease in the concentration of defects. The defects of 2D materials are experimentally revealed: (1) point defects including foreigner dopants, vacancies, and ad adsorbed atoms; (2) line defects such as grain boundaries, edges, and so on. Hong et al. [118] have experimentally revealed monolayer MoS$_2$ of physical vapor deposition often showed antisite defects with one Mo atom replacing one or two S atoms (Mo$_x$ or Mo$_{x,2}$). However, mechanical-exfoliated and chemical vapor–deposited MoS$_2$ samples are dominantly shown with S vacancies with one (V$_s$) or two (V$_{s,2}$) S atoms absent [118, 119]. The researchers exceptionally found that antisite defects (Mo$_x$ or Mo$_{x,2}$) reduced the mobility of monolayer MoS$_2$ by three times than by the presence of vacancies (V$_s$ or V$_{s,2}$), whereas the phonon-limited mobility of holes carried by the intrinsic valence band is much more sensitive. The measured carrier mobilities of monolayer MoS$_2$ are mostly controlled by the primary type of defects, regardless of carrier density and contact resistance.

Influence of defects could not only change electronic structure and charge-carrier mobility of TMDs but also create midgap states in the bandgap and introduce the in-gap defect levels, which can significantly modify and improve the performance of optoelectronic properties [120]. As shown in Figure 3G, defect engineering and strong oxygen bonding on the defect sites of monolayer MoS$_2$ could tune the photoluminescence intensity up to at least thousands of times. The physical-adsorbed O$_2$/H$_2$O molecules at defect sites induced heavy p-type doping and switched the trions recombination to exciton recombination process. The reduced nonradioactive recombination from excitons at defect sites could guarantee the enhancement of photoluminescence intensity under the vacuum (Figure 3A). The strong bonding energy of 2.395 eV for an oxygen molecule adsorbed on an S vacancy of MoS$_2$ was used to controllably introduce defects and oxygen bonding in MoS$_2$ by oxygen plasma, resulting in a controllable manipulation of photoluminescence [120].

### 3.3 Chemical composition modification

Ternary TMD alloys composed of two MX$_2$ compounds with controllable concentrations show composition-dependent
band structure, providing an effective strategy for tuning optical properties [66, 74, 121–127]. As mentioned earlier, the electronic properties of TMDs range from insulating, semiconducting, to metallic, due to the $d$-electron counts related to chemical compositions of TMDs. A necessary bandgap for optoelectronic applications requires at least one of the alloyed material is semiconducting. Thus, alloys are investigated either between metals and semiconductors, or semiconductors to semiconductors. For successfully alloying different materials, lattice match and bond distance are crucial [124]. Figure 4A shows how these TMDs meet the requirements by plotting theoretical bandgap differences with lattice mismatch [124]. The shaded area in the upper left corner corresponds to the largest difference in bandgaps (metal–semiconductor alloys), while the smallest lattice mismatch, potentially indicating the most suitable compound pairs for bandgap-tunable alloying. In this metal–semiconductor–type alloys, the represented metal is $VX_2$, whereas the represented semiconductor is $MoX_2$ or $WX_2$. The shaded area in the lower left corner corresponds to the semiconductor–semiconductor alloys with small lattice mismatch and moderate bandgap variation with concentration. The represented semiconductor–semiconductor–type alloys are $Mo–W$ dichalcogenides. In general, alloying TMDs within the same transition metal group or different chalcogenides are expected because they have the same lattice symmetry, as well as only small lattice mismatches. Figure 4B shows the calculated bandgaps for two representative types of TMD alloys ($Mo_{1-x}W_xS_2$ represents alloys of the same transition metal group, and $MoSe_{23–x}S_{2x}$ represents alloys of different chalcogenides) at different concentrations [124]. It shows significant modulation of bandgaps by composition concentrations, expected to be observed in optical absorption or emission experiments.

Two-dimensional TMD alloys can be obtained by mechanical exfoliation of bulk alloys [122] and synthesis through physical vapor deposition [129, 130] or CVD
[74, 131, 132], stimulating experimental exploration of bandgap engineering by chemical composition control. It is characterized by the combination of Raman and photoluminescence spectrum that 2D TMD alloys show tunable optical properties modified by the composition of alloys [66, 74, 122, 126, 127, 129, 131]. Figure 4C
It has been reported that intercalation of alkali metal ions (Li⁺, Na⁺, K⁺) into 2D-layered TMDs induces structural phase change and alters electronic properties, which result in modified optical properties [29–31, 33, 134, 135]. A commonly studied example is the 2H-to-1T phase transition in Li-intercalated 2D-layered MoS₂, which consequently results in alteration of electronic band structure. It is predicted by calculations that the 2H phase of the original 2D MoS₂ is semiconducting with a sizeable bandgap, whereas the 1T phase of Li-intercalated MoS₂ is metallic with overlapped conduction and valence bands (see schematic in Figure 5B) [31]. This consequently affects many optical properties and opens up new opportunities for optoelectronics. Xiong et al. [31] observe that without bandgap in 1T phase the light transmission in ultrathin MoS₂ layers after Li intercalation is substantially enhanced due to the light absorption reduction (Figure 5C). Wang et al. [134] report large modulation of photoluminescence of liquid phase-exfoliated MoS₂ nanoflakes by electrochemical controlled ion intercalation, showing significant application prospect in bio-optical sensors, as well as optical modulators or switches (Figure 5D). The observed modulation of photoluminescence is attributed to the lattice expansion, as well as the transition from originally semiconducting 2H into metallic 1T crystal phase after ion intercalation. In addition, they successfully achieved plasmon resonances of 2D MoS₂ nanoflakes in the visible and near-UV regimes by the electrochemical intercalating Li⁺ ions into 2D MoS₂ nanoflakes, providing a great application potential for future plasmonic biosensing and optical systems (Figure 5E) [135]. The emergence of plasmon resonances is ascribed to the formation of semimetallic states controlled by doping level of intercalated Li⁺. The phase change induced by alkali metal intercalation may be attributed to the d-electron count alteration as a result of charge transfer from s orbital of the alkali metal to the d orbital of the transition metal.

Phase change from 1T to 2H has been observed in TaS₂ after Li intercalation [137]. Except alkali metals,
molecular intercalation in 2D MoS<sub>2</sub> also induces phase transition from semiconducting 2H to metallic 1T phase [34]. Local phase transition has been proposed to achieve 2H–1T hybrid structures [138]. The influence of intercalation on optical properties is not limited to 2D TMDs. Many nontransition metal chalcogenides are demonstrated to show evident modulated optical properties after intercalation. Bi<sub>2</sub>Se<sub>3</sub> nanoplates intercalated by zero-valent Cu atoms have been studied to show dramatic enhancement of optical transmission, due to the increase in the effective bandgap caused by the increased free electron density introduced via intercalation of Cu atoms [139]. Organic molecules–intercalated Bi<sub>2</sub>Se<sub>3</sub> nanoribbon has been reported to show a wide tunability of the photonic and plasmonic properties of the host material [140, 141]. In short, the ability to modify the electronic structures and optical properties of 2D TMDs by intercalation provides a new effective control manner for future tunable optoelectronics and attracts a new round of attention.

### 3.5 Strain engineering

Strain engineering has both theoretically and experimentally proved to be an effective approach to continuously tune the bandgap of TMDs, which subsequently modulates the electronic, optical, and photonic properties of TMDs [84–91, 142–144]. The ability to continuously tune
the band structure of a TMD is most desirable for optic and photoelectronic applications, motivating a vast array of theoretical works that study the strain effect on band structure. Applying strain on a crystal will cause lattice stretching or compressing in different directions, resulting in the change of lattice constant. This causes the change of overlapping and hybridization of electron orbital and can be responsible for the modified electronic and optical properties. In order to study the influence of mechanical strains on the monolayer group VIB TMDs MoX₂ and WX₂, Johari and Shenoy [84] performed first-principles density functional theory based calculations and revealed that both tensile and shear strain continuously reduce the bandgap, whereas tensile strain decreases the bandgap more rapidly (Figure 6A). Specially, they found that application of biaxial tensile strain causes a direct-to-indirect bandgap and semiconductor-to-metal transition of the monolayer TMDs. Another theoretical work by Yun et al. [85] found, for the monolayer of MoX₂ and WX₂, the tensile strain reduces the bandgap, whereas the compressive strain enhances bandgap. For those beyond group VIB TMDs, density functional theory calculations suggest different strain effects. For example, the bandgap of group IVB TMDs (TiX₂, ZrX₂, HfX₂) is predicted to increase with the tensile strain. All these calculations suggest a reversible and flexible manner to engineer the electronic and optic properties of TMDs.

In experiments, mechanical strain can be applied through bending of samples on flexible substrates or via lattice mismatch between substrates and epitaxy layers. Using a cantilever device to apply a uniaxial tensile strain, it has been observed that the A and B resonance peaks in both absorption and photoluminescence spectrum, corresponding to direct bandgap transitions, show a similar red-shift rate with increasing the tensile strain in both monolayer and bilayer MoS₂ (Figure 6B) [87], whereas the I peak related to the indirect bandgap transition in bilayer MoS₂ has a larger red-shift rate. This experimental result indicates applying a uniaxial tensile strain can continuously reduce the bandgap of atomic thin MoS₂ layer, which agrees well with the first-principles calculations. On the contrary, through a piezoelectric substrate, the compressive strain was applied to trilayer MoS₂, and it has been demonstrated to increase the bandgap, manifested as both the photoluminescence peak and Raman modes are blue-shifted [88, 146].

The effective strain tunability of the electronic structure of TMDs promises a wide range of applications in optoelectronics. Applying local tensile strain, TMDs can exhibit spatially varying bandgap [86], and subsequent confinement potentials for photoinduced excitons can be generated to trap excitons for quantum optics, photodetection, and photovoltaics because of the exciton funnel effect that excitons will move to lower bandgap regions induced by locally applied tensile strain before recombining. This funnel effect has been utilized to design a photovoltaic device by introducing inhomogeneous elastic strain [165]. An “artificial atom” made of a nanoindented
MoS$_2$ monolayer (Figure 6C) has been proposed and predicted to be able to absorb a broad range of the solar spectrum along the elastic strain gradient and concentrate photoexcited charge carriers. Introducing compressive strain, photoresponsibility is controllably modulated by the piezo-phototronic effect in a flexible MoS$_2$/WSe$_2$ van der Waals photodiode, leading to excellent strain-tunable photodetection performance [52]. Benefiting from the various manners of applying mechanical strains and the richness of TMDs, the development of novel optoelectronics is on the way.

### 3.6 Heterostructure constructing

Forming heterostructures of materials is a common strategy to modify the electronic band structures of the materials [147]. The heterostructures composed of different 2D TMDs stacked along the out-of-plane direction (vertical heterostructure) or in-plane direction (lateral structure) [148] can exhibit significant different electronic and optical properties compared with each component material, having great potential for atomically thin optoelectronic and photovoltaic applications [75, 149–152]. For a heterostructure, many aspects, such as the stacking order, lattice mismatch, component layers, and so on, can affect its electronic structure. For example, it is theoretically found that heterobilayers composed of particularly stacked different monolayer TMDs exhibit a direct bandgap, where electrons and holes are physically separated and localized in different layers (Figure 7A) [153]. The predicted direct bandgaps of the heterobilayer TMDs ranging from 0.79 to 1.15 eV are much smaller than the direct bandgaps of monolayer WS$_2$ (2.1 eV) and MoS$_2$ (1.8 eV), which extends the optical applications in the infrared range. Additionally, the band offset calculations show both the conduction band minimum and valence band maximum of WX$_2$ are higher than those of MoX$_2$ due to the higher energy of the 5d orbital of W than that of the 4d orbital of Mo (Figure 7B) [76]. As a result, MoX$_2$/WX$_2$ heterostructures will form a type II band alignment with the conduction band minimum and valence band maximum located in MoX$_2$ and WX$_2$, separately. A type II band-aligned heterostructure, in which free electrons and holes prefer to spontaneously stay at separate positions (Figure 7B), is suitable for optoelectronics and light harvesting. Accordingly, TMD heterostructures enable bandgap engineering, which could further offer more flexible choices for the construction of novel high-performance optoelectronic devices.

Experimentally, TMD heterostructures are widely available through sequential transfer or various growth methods [149]. Stimulated by the graphene stacked on h-BN showing ultrahigh mobility, concerted efforts are expected to explore the modified physical properties of heterostructures formed by different 2D layers. In case of TMDs, high-quality heterostructures have been demonstrated not only to improve electrical transport properties, but also to enhance the optoelectronic performance [41, 44, 46, 50, 78, 80, 81, 154]. Researchers observed significant photoluminescence quenching and gate-tunable efficient photocurrent generation in a vertical heterostructure with the n-type monolayer MoS$_2$, transferred onto the top of a p-type monolayer WSe$_2$ (Figure 7C) [46]. The observed
Figure 7: Optoelectronics of 2D TMD heterostructures.
(A) Left: Bilayer formed by overlapping WSe$_2$ on WS$_2$ with stacking type B denoted as bilayer (WS$_2$, WSe$_2$, B) and bilayer formed by placing WSe$_2$ on MoS$_2$ with stacking type A denoted as bilayer (MoS$_2$, WSe$_2$, A). In stacking type B, the transition metal atoms are on top of the chalcogen atoms. In stacking type A, the chalcogen atoms are on top of each other. The dotted lines indicate the alignment of atoms between layers, and the arrows correspond to the distance dS-Se between chalcogen atoms of different layers. Right: Type 2 family band structure showing the direct bandgap of bilayer (WS$_2$, WSe$_2$, B), bilayer (WSe$_2$, MoS$_2$, A), and the infinite number of layers case: Crystal (WS$_2$, WSe$_2$, A). The red line indicates the top of the valence band. Reproduced with permission from Terrones et al. [153]. Copyright 2013 Springer Nature Limited. (B) Left: Calculated band alignment for MX$_2$ monolayers. Solid lines are obtained by PBE, and dashed lines are obtained by HSE06. The dotted lines indicate the water reduction (H$^+$/H$_2$) and oxidation (H$_2$O/O$_2$) potentials. The vacuum level is taken as zero reference. Middle and right: Charge densities of VBM (middle) and CBM (right) states for monolayer WX$_2$-MoX$_2$ lateral heterostructures with common X. Reproduced with permission from Kang et al. [76]. Copyright 2013 American Institute of Physics. (C): (i) Bottom left: Schematic diagram of a van der Waals–stacked MoS$_2$/WSe$_2$ heterojunction device with lateral metal contacts. Top: Enlarged crystal structure, with purple, red, yellow, and green spheres representing Mo, S, W, and Se atoms, respectively. Bottom right: Optical image of the fabricated device, where D1 and D2 (S1 and S2) indicate the metal contacts for WSe$_2$ (MoS$_2$). Scale bar, 3 μm. (ii) Schematic illustrations of exciton dissociation (top) and interlayer recombination (bottom) processes. Top: Horizontal and vertical arrows represent charge transfer and intralayer recombination processes, respectively. Bottom: Red and blue arrows indicate Shockley–Read–Hall (SRH) and Langevin recombination processes, respectively. (iii) Photoresponse characteristics at various gate voltages under white-light illumination. Inset: Color plot of photocurrent as a function of voltages $V_{ds}$ (x axis) and $V_g$ (y axis). The dashed line represents the profile of short-circuit current density $J_{sc}$ at $V_{ds} = 0$ V. (iv) Top: Photocurrent map of the device presented in (i) for $V_{ds} = 0$ V and 532-nm laser excitation. The junction area and metal electrodes are indicated by dashed and solid lines, respectively. Scale bar, 3 μm. Bottom: Photoluminescence spectra measured from the isolated monolayers (blue curve for MoS$_2$; red curve for WSe$_2$) and the stacked junction region (brown curve). (v) Photoluminescence spatial maps for emission at 1.66 eV (top) and 1.88 eV (bottom), corresponding to direct gap transitions of monolayer WSe$_2$ and MoS$_2$, respectively. The junction area is indicated by dashed lines. Scale bars, 3 μm. Reproduced with permission from Lee et al. [46]. Copyright 2014 Macmillan Publishers Limited.
gate-tunable photovoltaic response originates from spontaneous dissociation of photogenerated excitons into free electrons and holes in different layers and subsequent tunneling-assisted interlayer recombination driven by large band offsets in a heterostructure with type II band alignment. The charge transfer processes in photoexcited MoS2/WS2 heterostructures have been proved to be ultrafast through photoluminescence mapping and femtosecond pump–probe spectroscopy [78]. It is found that hole transfers from the MoS2 layer to the WS2 layer within 50 fs after optical excitation.

Besides the heterostructures composed of two different TMDs, there are a lot of heterostructures formed by TMDs with other 2D materials, showing tunable optoelectronic properties [49]. The first to mention is the TMDs/graphene heterostructures [41, 44] because their distinct properties could be utilized to realize novel functionalities. The high mobility of graphene means fast response rate, whereas the large direct bandgap of TMDs results in strong electronic properties [49]. The first to mention is the TMDs/graphene heterostructures, including TMD bilayers, with well-defined electronic and optical properties modification and stay compatible with optoelectronic devices, through tuning strategies such as thinning thickness down, chemical composition modification, and heterostructure constructing. Foreigner species intercalation has been identified as an effective modulation method, but still is challenged with ordering stability of intercalated atoms. Strain engineering is proved to be an effective approach to continuously tune the bandgap of TMDs but is challenged with how to quantitatively apply strain in devices. At the same time, there are much more fruitful tuning freedoms for 2D TMDs or the whole family of 2D materials, whose electronic structures and optical properties can be coupled with magnetic properties, biological compatibility, surface plasmonic structures, piezoelectricity/ferroelectricity, electrochemical activities, and so on, for designing the multifunctional device application [157–164]. On the other hand, considering the preparation methods, we can expect the combination of diverse tuning methods or large-scale preparation with retaining precise modulated properties [165]; thus, we can implement the tunable optoelectronic devices not only in the fundamental research but also for the industrial-level application [166]. With the rapid development of controlled synthesis and physical and chemical approaches, the multifunctional magnetic and mechanical response, thermal transport devices [167], and electrochemical storage and conversion devices [168, 169] will be continuously springing up [170–179].

4 Conclusions and outlook

We have summarized several strategies on the electronic structures modulation of 2D TMDs, including thinning thickness down, defect engineering, chemical composition modification, foreigner species intercalation, strain engineering, and heterostructure construction, to tune its optical absorption, charge carrier’s mobility, and band structure alignments, thus adapting for the different optoelectronic devices. As the great development of nanofabrication techniques, it is more convenient to realize electronic and optical properties modification and stay compatible with optoelectronic devices, through tuning strategies such as thinning thickness down, chemical composition modification, and heterostructure constructing. Foreigner species intercalation has been identified as an effective modulation method, but still is challenged with ordering stability of intercalated atoms. Strain engineering is proved to be an effective approach to continuously tune the bandgap of TMDs but is challenged with how to quantitatively apply strain in devices. At the same time, there are much more fruitful tuning freedoms for 2D TMDs or the whole family of 2D materials, whose electronic structures and optical properties can be coupled with magnetic properties, biological compatibility, surface plasmonic structures, piezoelectricity/ferroelectricity, electrochemical activities, and so on, for designing the multifunctional device application [157–164]. On the other hand, considering the preparation methods, we can expect the combination of diverse tuning methods or large-scale preparation with retaining precise modulated properties [165]; thus, we can implement the tunable optoelectronic devices not only in the fundamental research but also for the industrial-level application [166]. With the rapid development of controlled synthesis and physical and chemical approaches, the multifunctional magnetic and mechanical response, thermal transport devices [167], and electrochemical storage and conversion devices [168, 169] will be continuously springing up [170–179].

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