Band Alignment Engineering in Two-Dimensional Transition Metal Dichalcogenide-Based Heterostructures for Photodetectors

Ran Liu, Fakun Wang, Lixin Liu, Xiaoyu He, Jiazhen Chen, Yuan Li,* and Tianyou Zhai*

The hybridization of two-dimensional transition metal dichalcogenides (2D TMDs) with other light-sensitive materials to fabricate the TMD-based heterostructures is an effective way to boost the overall photoelectric performance of photodetectors. In particular, the alignment of band structure at the interface of the binding materials plays a critical role in optimizing the carrier transfer path and prompting the charge separation rate, which finally lead to the simultaneous improvement of photoreponsivity and response rate and the expansion of detection range. However, the band alignment engineering topic has been barely summarized and reviewed in detail up to today. Herein, a specific review focused on the band alignment strategies and the related charge-transfer mechanism of the recently developed novel TMD heterostructures for photodetectors is provided. The band structures are classified into four categories according to the targeted function of photodetectors, including that formed by TMDs with zero-bandgap materials, narrow-bandgap semiconductors, middle-bandgap semiconductors, and wide-bandgap semiconductors. The corresponding band alignment principles and charge-transfer behaviors are summarized carefully by providing various latest research works as representative examples under each category. Herein, a key reference for applying and extending the fundamental band alignment principles in the design and fabrication of future TMD-based heterostructural photodetectors is provided.

1. Introduction

Photodetectors, which convert the incoming optical signals into electric signals, are one of the key components in many modern multifunctional technologies and devices. The application of photodetectors covers plenty of fields from the military, national economy, to people's daily lives, such as the detection of X-rays for biomedical imaging, the detection of visible light for digital camera, and the detection of infrared light for night vision and optical communications. Traditionally, various semiconductor materials such as Si, Ge, and InGaAs have been primarily used for photodetectors. For instance, Si has a low dielectric constant for fast operation and an indirect bandgap generally responds to the visible and near-infrared (NIR) light; the epitaxially grown InGaAs and HgCdTe can broaden the photodetection band to the long-wavelength-infrared (LWIR) range. These properties are highly recommended for traditional photodetectors. However, with the fast development of nanoscale and highly integrated devices, the traditional materials gradually become incapable to the increasing demand of the high light absorption coefficient, broadened specific detection range, fast response rate, as well as the superior flexibility and stability in future high-performance photodetectors.

The main physical limitations of the traditional materials lie in their limited bandgap, poor flexibility, low transparency, and ineluctable surface dangling bonds. In this regard, extensive efforts have been devoted to explore suitable materials for next-generation photodetectors in the past decades. Since the discovery of graphene by Geim et al., the family of 2D materials has drawn great attention for their favorable applications in modern electronic and optoelectronic devices. In general, 2D materials possess unique and unconventional properties such as strong light–matter interaction, tunable optical absorption, and outstanding carrier transport and thus, are expected to be one of the most potential substitute materials to compensate the limitation of traditional semiconductors.

Among the reported 2D materials, TMDs have been considered to be of great promise due to their interesting physical properties such as direct bandgap of the monolayer, tunable bandgap covering the entire visible and some of the NIR range, strong light–matter interactions, and superior mechanical flexibility. However, some unavoidable drawbacks of the single TMD materials, including poor light absorption of the monolayer, limited detection range in NIR, and serious photogain-time
(G–4) trade-off, have severely restricted their further large-scale application. Compared with the individual materials, the hybrid structures consisting of TMDs and another light-sensitive material, namely TMD-based heterostructures, exhibit a series of novel physical properties such as a broadened response wavelength, increased photoresponsivity, and the simultaneously improved response rate in photodetectors.[22,23]

Up to today, an abundance of studies regarding TMD-based heterostructures has been reported for photodetectors,[24–29] for which the most important merit with respect to the performance improvement and device behavior modulation lies in the design and construction of a high-efficiency heterojunction interface between the binding materials, namely band alignment engineering. As discussed, the carrier generation mechanism and transport behaviors of a semiconductor device are dominantly determined by its band structure,[30] and meanwhile, the influence of temperature, material preparation method, applied voltage, etc. is complex and has to be comprehensively considered in the operation of the device.[31] Thus, the deep understanding of the band construction principles as well as the fundamental charge-transfer mechanism of the TMD-based heterostructures are of great importance for the reasonable design and practical operation of future TMD photodetectors. However, to the best of our knowledge, so far, there have been no reviews specifically focused on the band alignment engineering of TMD-based heterostructures to summarize the recently reported heterostructure geometries as well as the detailed charge-transfer mechanism of photodetectors.

Herein, we provide a specific review on the band alignment engineering of the TMD-based heterostructural photodetectors. We classify the band structures of TMD heterostructures into four categories according to their targeted modulation to the function of the photodetectors and the difference of their charge-transfer mechanism, including the band structures formed by TMDs with zero-bandgap materials, TMDs with narrow-bandgap semiconductors (0.1–1.1 eV), TMDs with middle-bandgap semiconductors (1.1–3.1 eV), and TMDs with wide-bandgap semiconductors (3.1–6.2 eV). The corresponding band alignment principles and charge-transfer mechanism are summarized in detail by several representative examples of the latest research under each category. A table-of-content (TOC) schematic is shown in Figure 1, explaining the main classification of the four-type TMD-based heterostructures that is described in our Review Article. In the second section, we provide a general description of the classified band structures accordingly and further summarize the corresponding binding materials for building the heterojunctions in the recent literature. In the third section, the fundamental charge-transfer mechanism of each band structure is first explained in detail, and this is followed by providing various latest research which applies or extends the charge-transfer mechanism in real photodetectors to realize specific functions in improving the device performance, such as the responsivity, response rate, and/or the detection range as compared with single TMD materials. Finally, the general characteristics of four types of energy band structures are concluded, and outlooks are provided to shed light on the future development of this research area.

![Figure 1. Schematic illustrating the classification of 2D TMD-based heterostructures according to their aligned band structures.](image-url)

2. Types of Band Structures in 2D TMD Heterostructures

As we mentioned earlier, single materials of 2D TMDs usually show a limited detection range, poor responsivity, and/or slow response rate. For instance, the bandgap of monolayer MoS2 (=1.8 eV) limits its response to the infrared light, and meanwhile, the atomic thickness restricts its light absorption.[32] Thus, it is usually challenging for monolayer MoS2 to detect the infrared light with wavelength greater than 1100 nm with a fast response rate and high responsivity.[33] To expand their operation optical range and further enhance responsivity and response speed, various types of band structures have been designed and realized via the direct formation of heterojunctions between a 2D TMD and another binding material. As shown in Figure 2, we divide the TMD-based heterostructures into four types, including TMDs with zero-bandgap materials, TMDs with narrow-bandgap semiconductors, TMDs with middle-bandgap semiconductors, and TMDs with wide-bandgap semiconductors. An abundance of binding materials with different photoreponse ranges are also summarized for each classification in the bottom of Figure 2. When individual TMDs are excited by light, the electrons are excited from the valence band to the conduction band. Under applied bias, the electrons and holes are transferred in the reverse direction to the electrodes at two sides; in this case, the radiative recombination of electron–hole pairs is easy. Compared with the individual TMDs, TMD-based heterostructures usually generate built-in potential due to the difference in the Fermi-level arrangement of different materials and thus promote the transportation of electron–hole pairs to enhance the photogenerated current.
As shown in Figure 2, the first type of the heterostructural band structure is formed by combining TMDs with zero-bandgap materials such as graphene, carbon nanotubes, and noble metals, which usually leads to the formation of a so-called Schottky heterojunction. It is worth noting that among the zero-bandgap materials, we particularly pay our attention to graphene and noble metals and select their heterostructures with TMDs to explain the band structure configuration and the corresponding charge-transfer mechanism. As discussed, graphene is a gapless and semimetallic material, which allows its broadband light absorption over a broad bandwidth from terahertz (THz) to ultraviolet (UV) wavelength. Furthermore, due to the super high carrier mobility, graphene can possibly form heterojunctions with a variety of semiconductors to facilitate carrier transportation. When TMDs are combined with graphene, due to the difference of their work functions, a depletion region inside the semiconductor will be formed, and the resultant built-in electric field at the interface can significantly facilitate the separation of the photogenerated electron–hole pairs. Another representative example we provide for the nonbandgap binding materials is noble metal nanoparticles. When they are combined with TMDs, besides the formation of the Schottky junction similar to graphene, noble metal nanoparticles can trap light waves and produce localized surface plasmon resonance (LSPR), resulting from the interactions between the incident light and surface electrons in the conduction band. The LSPR can not only enhance the light–matter interaction of the heterostructure, but also produce an abundance of so-called “hot electrons,” which can possibly transfer to the TMD side through the Schottky barrier and accordingly enhance the photodetection performance of the device.

The second type of the energy band structure is constructed by TMDs and narrow-bandgap materials such as black phosphorus (BP), AsP, colloidal quantum dots (QDs) of lead chalcogenides (e.g., PbS, PbSe), and so on. BP exhibits a thickness-tunable bandgap that is always direct regardless of the layer number, ranging from the NIR for the monolayer to the middle-wavelength infrared (MWIR) for the bulk phase. When an n-type TMD contacts a p-type narrow-bandgap BP, a built-in electronic field is formed from the TMD to BP. Under IR illumination, the energy of the incident photon is larger than the bandgap of BP but smaller than most TMDs. The photon-induced carriers generated by BP are separated by the built-in electric field at the depletion region, the electrons move to graphene, noble metal nanoparticles can trap light waves and produce localized surface plasmon resonance (LSPR), resulting from the interactions between the incident light and surface electrons in the conduction band. The LSPR can not only enhance the light–matter interaction of the heterostructure, but also produce an abundance of so-called “hot electrons,” which can possibly transfer to the TMD side through the Schottky barrier and accordingly enhance the photodetection performance of the device.

Figure 2. Schematic showing the four-type band structures of 2D TMD-based heterostructures. Various binding materials to build the TMD heterostructures are listed in the bottom as a function of their photoresponse wavelength range.
TMDs, whereas the holes transport to the opposite side under zero bias. Another representative type of narrow-bandgap binding materials is lead chalcogenide (PbS, PbSe)\(^{[31,42]}\) and mercury chalcogenide (HgTe) QDs\(^{[43,44]}\), which are particularly attractive for performance improvement and detection of band expansion due to their strong and tunable infrared absorption, owing to the quantum confinement and relatively larger excitonic Bohr radius and low-cost solution processing. When TMDs contact narrow-bandgap QDs, the incident photons excite electron–hole pairs in the QD layer, which are then separated by the built-in electric field and transferred to a lower-energy state, similar to the carrier transport behavior of BP TMDs.

The next type of band structure alignment is related to the heterostructure building by TMDs and middle-bandgap semiconductors. Here, we define the middle bandgap as response to the visible–NIR wavelength light with a photon energy of 1.1–3.1 eV, including common TMDs, group III chalcogenides, group IV chalcogenides, perovskites, and so on.\(^{[45]}\) Through constructing this type heterostructure, the internal electronic field can also be formed across the interface, which facilitates the carrier separation similar to the above heterojunctions, leading to improved photoresponsivity and fast response rate. For instance, when an n-type TMD contacts a p-type TMD, the difference of the Fermi level results in the reconstruction of the final Fermi level, the lower side moves upward, and the higher side drops to reach a thermal equilibrium state. Under visible illumination, the energy of incident photon is larger than the bandgap of most TMDs, the photon-induced carriers generated by TMDs are separated by the similar built-in electric field at the interface region, and thus an obvious acceleration of the response speed and improvement of photoresponsivity can be realized. Similar to the TMD–TMD heterostructures, when group III chalcogenides such as GaTe, GaSe, InSe, and In\(_2\)Se\(_2\) are constructed with TMDs, typical type-II band alignments with the excellent electron–hole pair separation ability are usually formed.\(^{[46–49]}\) For group IV chalcogenides such as Sn\(_2\)S\(_2\) and SnSe\(_2\), band-to-band tunneling phenomena can be observed by applying various biases in a broken-gap heterojunction.\(^{[50,51]}\) In addition, due to the appropriate direct bandgap, large absorption coefficient, long carrier diffusion length, and high charge carrier mobility of perovskites, the heterostructures built by 2D TMDs and perovskite are found to exhibit significantly improved light absorption and carrier transport efficiency.\(^{[52–54]}\)

Finally, the wide-bandgap semiconductors (3.1–6 eV) need a larger energy of light to excite the electrons at the valence band and thus usually can only absorb UV light. The fourth type of the energy band structure is constructed by TMDs and wide-bandgap materials such as ZnS, ZnO, and so on. Among several wide-bandgap semiconductors, ZnS has a well-established material for UV photodetection due to its wide bandgap (\(\approx3.72\) eV for cubic zinc blende (ZB) and \(\approx3.77\) eV for hexagonal wurtzite (WZ)), excellent chemical and physical properties including polar surfaces, good electron mobility, decent charge transport properties, thermal stability, etc.\(^{[55]}\) In addition, ZnO has also emerged as an interesting semiconducting metal-oxide material in recent years, due to its high optical transparency, tunable electronic properties, low cost, and low toxicity.\(^{[56]}\) Taking the Mo\(_{3}\)S\(_{2}\)/ZnS heterostructure as a typical example, the Mo\(_{3}\)S\(_{2}\) and ZnS show n-type characteristics whereas the electronic affinity of ZnS is smaller than Mo\(_{3}\)S\(_{2}\), and thus ZnS has a higher Fermi level than Mo\(_{3}\)S\(_{2}\). The difference of the Fermi level induces the favorable transfer of electron flow from ZnS to Mo\(_{3}\)S\(_{2}\), and meanwhile, a unilateral depletion region formed in the ZnS side, making more electrons accumulate in the Mo\(_{3}\)S\(_{2}\) side and accordingly creating a built-in electronic field pointing from ZnS to Mo\(_{3}\)S\(_{2}\). Under UV light, both TMDs and the wide-bandgap materials such as ZnS and ZnO absorb UV light and generate electron–hole pairs which are separated by the built-in electronic field under zero bias.

3. Band Alignment Strategies and Mechanism in Photodetectors

3.1. Band Alignment in TMDs and Zero-Bandgap Materials

The typical charge-transfer mechanism in a photodetector built on TMD–graphene heterostructures is shown in Figure 3. As shown in Figure 3a, when graphene contacts an n-type semiconductor material, due to the difference of work function, a depletion region called Schottky junction often forms at the semimetal/semiconductor interface, which separates a large yield of photoinduced electron–hole pairs in TMDs and transports them rapidly in the graphene layer, resulting in the significant enhancement of the photoelectric efficiency.\(^{[57]}\) As shown in Figure 3b, when a forward bias is applied, the built-in electric field decreases and the Schottky barrier becomes lower, which facilitate charge transfer across the barrier. When a reverse bias is applied (Figure 3c), the barrier increases and restrains the transfer of the electrons from Mo\(_{3}\)S\(_{2}\) to graphene; in contrast, minority carriers drift through the depletion region.\(^{[58]}\) Under illumination, both TMDs and graphene absorb incident light and generate electron–hole pairs.\(^{[57]}\) Due to the internal potential, photoinduced holes flow to graphene whereas electrons are trapped as a local gate under zero bias (Figure 3d). When the applied bias is forward, the internal potential decreases and electrons transport to graphene across the low barrier (Figure 3e). When the applied bias is reverse, the internal potential increases and holes transport to graphene whereas electrons are blocked by the high barrier. (Figure 3f).

3.1.1. TMDs with Graphene

To date, integrating graphene with TMDs, such as Mo\(_{3}\)S\(_{2}\)\(^{[58–61]}\), W\(_{3}\)S\(_{2}\)\(^{[62,63]}\), WSe\(_{2}\)\(^{[64]}\), and MoTe\(_{2}\)\(^{[57,65,66]}\) which possess moderate bandgaps and strong light–matter interaction compared with graphene, has been extensively investigated. High-performance photodetectors based on graphene/TMD van der Waals (vdW) heterostructures have the typical Schottky barrier, which makes a great contribution to the photoexcited carrier separation due to the presence of the built-in electric field.\(^{[14,67]}\) Among these, the graphene/Mo\(_{3}\)S\(_{2}\) heterostructure is one of the most favorable choices to fabricate electronic/optoelectronic devices with both aesthetic value and design flexibility. For instance, the high specific detectivity of \(1.8 \times 10^{10}\) Jones has been obtained from the photodetector based on few-layer Mo\(_{3}\)S\(_{2}\)/glassy–graphene heterostructure under 532 nm light illumination.\(^{[59]}\) In addition, W\(_{3}\)S\(_{2}\)
and WSe$_2$, with similar properties as MoS$_2$, have also been used to construct high-performance heterojunctions with graphene.

MoTe$_2$ has a bandgap of 1.0 eV in its bulk form, smaller than most TMDs, and thus is a good candidate for NIR photodetectors. With this consideration, Flöry reported a vertical heterostructure with a small carrier transit path length in MoTe$_2$ and a tunable Schottky barrier in MoTe$_2$/graphene, in which MoTe$_2$ acted as the light-absorbing layer (Figure 4a). Similar to a previous article reported by Yu et al., the difference in the work function of Au and graphene in the Au–MoTe$_2$–graphene structure leads to a built-in potential in the device (Figure 4b). The energy bands drop to MoTe$_2$ after contact and produces an internal electric field that points from MoTe$_2$ to graphene. Under light illumination, the electron–hole pairs generated in MoTe$_2$ will be separated by the built-in electric field at the MoTe$_2$/graphene interface. In particular, holes moved to the graphene, whereas electrons trapped in MoTe$_2$ acted as a local gate, which attracts more holes in graphene to reduce the resistance. As shown in Figure 4c, the device with a 45 nm-thick MoTe$_2$ generated a considerable photocurrent of 2 μA for 150 μW input power at zero-applied voltage, demonstrating the efficient separation of photoexcited electron–hole pairs in the built-in electronic field. By changing the thickness of MoTe$_2$ and increasing the applied bias, a record-high bandwidth of 50 GHz can be measured. Moreover, the waveguide design of this device reaches a high responsivity of 0.2 A W$^{-1}$ at 1300 nm.

The band alignment in TMD heterostructures not only depends on their intrinsic properties, but also can be modulated by gate voltage, source–drain voltage, and so on, which can be used to improve the photoelectric performance. For instance, an asymmetrical Schottky barrier at the Au–MoS$_2$ and MoS$_2$–graphene interface results in a rectification ratio over $2 \times 10^4$ in the Au–MoS$_2$–graphene heterojunction, which can be further tuned by external gating. In another example, Kang et al. fabricated a device based on a hybrid vdW heterostructure of ReS$_2$ and graphene using the stacking method. ReS$_2$ is a new reported 2D TMD material, attracting much attention for its layer-dependent direct bandgap and thus an anisotropic crystal structure of 1T phase. There is no significant difference in work function between graphene and ReS$_2$, and thus different carrier transport characteristics are shown with the gate voltage modulation. For $V_C < V_{Dirac}$, the holes inject into graphene and the Fermi level of graphene moves down, a Schottky barrier is generated. Under illumination, electron–hole pairs are excited in the ReS$_2$ layers and separated by the built-in potential. The holes move toward graphene whereas electrons trapped by the Schottky barrier act as a local gate for the photogating effect. In contrast, for $V_C > V_{Dirac}$, the photogenerated electrons move to graphene whereas the holes act as a local gate. Benefiting from the fast charge transport at the interface and high carrier mobility in graphene, an ultrahigh photoresponsivity of $7 \times 10^4$ A W$^{-1}$, as well as a fast response time less than 30 ms, were achieved.

However, it is worth noting that among these devices there is an unwanted photocurrent depression around zero-bias voltage. Some researchers have made efforts to induce asymmetric tunneling between photocarriers and dark carriers through the h-BN layer. Jeong et al. observed better current rectification and a much higher current flow in the graphene/h-BN/monolayer MoS$_2$ diode than the graphene/monolayer MoS$_2$ diodes. Vu et al. demonstrated a highly sensitive photodetector with a MoS$_2$/h-BN/graphene heterostructure. The authors find that the large electron barrier of 2.7 eV at the graphene/h-BN interface suppresses the dark current and results in a ultrahigh detectivity of $2.6 \times 10^{13}$ Jones. Furthermore, to reveal the mechanism of the loss of zero-bias photocurrent, Li et al. fabricated MoS$_2$/graphene photodiode and MoS$_2$/h-BN/graphene photodiode using transfer approach. The photoluminescence (PL) spectra and photoelectronic characteristics of the related heterostructures have been studied to indicate the interlayer
The small band bending in MoS$_2$ leads to the depression of photocurrent near zero bias, which is because the photogenerated holes diffused to graphene are consumed by the strong interlayer coupling with the photogenerated electrons in MoS$_2$ and hence cannot contribute to the photocurrent. Therefore, an ultrathin layer of h-BN was introduced into the heterostructure to prevent the electron transport between layers whereas the photogenerated holes in MoS$_2$ can tunnel through the ultrathin h-BN film with the help of the internal electric field.\cite{58} As a result, the photocurrent of the self-powered tunneling photodiode based on the MoS$_2$/h-BN/graphene heterostructure is increased by over three orders of magnitude, demonstrating an ultrahigh experimental specific detectivity of $6.7 \times 10^{10}$ Jones. In addition, Pak et al. reported vDW heterostructure phototransistors constructed using monolayer MoS$_2$ with graphene as a gate electrode and inserted 2D h-BN as a dielectric layer, which provides a near-ideal interface with MoS$_2$ enabling low-voltage operation.\cite{60}

Figure 4. Photodetectors based on TMD–graphene heterostructures. a) A schematic illustration of a vertical MoTe$_2$–graphene heterostructure photodetector coupled to a silicon waveguide buried in SiO$_2$ claddings. b) The corresponding band diagrams of the MoTe$_2$–graphene heterostructure under negative bias (upper) and positive bias (lower), respectively. c) I–V curves with and without light for three different wavelengths. Reproduced with permission.\cite{65} Copyright 2020, Springer Nature. d) Schematic showing the preparation of graphene–WS$_2$–graphene heterojunction by the in situ CVD growth method. e) Optical image and f) PL map of the graphene–WS$_2$–graphene junction. g) Time-resolved photorepons of the device under illumination of different wavelengths. h) Close-up look of a single ON/OFF switch of the device under 550 nm illumination. Reproduced with permission.\cite{76} Copyright 2019, American Chemical Society. i) Schematic showing h-BN/MoTe$_2$/graphene/SnS$_2$/h-BN device configuration. j) Band diagram and photoexcited carrier transport of the heterostructures. k) Temporal photocurrent response under various wavelengths from the UV region to NIR. Inset: Temporal photocurrent response under 1550 nm wavelength. Reproduced with permission.\cite{78} Copyright 2018, Wiley-VCH.
In addition to heterojunctions combining graphene with 2D TMDs, researchers often design multistage carrier transport channels to further improve carrier separation efficiency. The graphene–TMD–graphene sandwich structures for high-performance photodetectors have been demonstrated as a typical example. For instance, a recent research reported the use of indium adatoms to cover graphene–WS$_2$–graphene junctions to obtain a ultrahigh gain of $6.3 \times 10^5$ electrons per photon and an ultrafast response time of 45–60 μs. As shown in Figure 4d, a graphene sheet is transferred onto a sapphire substrate, followed by another chemical vapor deposition (CVD) system to grow WS$_2$ in the channel region. Figure 4e,f shows the optical image and PL image of the In/graphene–WS$_2$–graphene junction, respectively. Such devices are constructed by graphene and TMD, in which graphene serves as a transparent electrode and TMDs act as the photoactive layer, respectively. For metal electrodes, the Fermi level is pinned down below the conduction band minimum of WS$_2$, resulting a barrier height of hundreds of meV. Compared with the metal contact, graphene has been considered as a suitable choice to decrease the barrier height. Figure 4g shows clear ON/OFF switch behavior of this device for 550 and 700 nm incident light. A fast response time of 47 μs is obtained for 550 nm light (Figure 4h). In addition, Zhang et al. fabricated NIR photodetectors based on the graphene/MoTe$_2$/graphene vertical vdW heterostructure via a site-controllable layer-by-layer transfer method. For this device, the Schottky barrier height of $G_{up}$/MoTe$_2$ and $G_{bottom}$/MoTe$_2$ had a remarkable influence on photocurrent generation and transportation, which can be modulated by back-gate voltage. The large-scale graphene/WS$_2$/graphene vertical-stacked cross-bar phototransistor device was also fabricated to reveal the layer-dependent photocconductivity of 1L WS$_2$ and 2LWS$_2$.

The next typical example for the further application of such TMD–graphene-type band alignment is the so-called p–g–n heterostructure device. Li et al. constructed a 2D h-BN/p-MoTe$_2$/graphene/n-SnS$_2$/h-BN p–g–n junction to obtain a specific detectivity up to $\approx 10^{10}$ Jones in the UV–NIR range (Figure 4i), which used h-BN to screen charged impurities from the substrate surface and the environment contamination. As shown in Figure 4j, when the energy of photons is larger than MoTe$_2$, or SnS$_2$, the photoactive layer will absorb photons to generate electron–hole pairs. The electrons will transport to SnS$_2$ as the opposite direction of the built-in electric field and holes transport to MoTe$_2$. When the energy of photons is smaller than the bandgap of MoTe$_2$ of 1 eV, graphene is the only light-absorption layer, and the generated electrons move to SnS$_2$ whereas holes move to the opposite side. As shown in Figure 4k, broadband detection from the visible to middle infrared (MIR) wavelength has been acquired.

Another p–g–n structure formed by sandwiching graphene into MoS$_2$ and WS$_2$ has been presented by the transfer method to suppress the dark current in the device and extend photoreponse range to the short-wavelength-infrared range at room temperature. There were two Schottky barriers and a strong built-in electric field to ensure the separation of photogenerated electrons and holes. Different from the vertical stack structure, the authors also indicated lateral structure. Deng et al. presented a phototransistor composed of lateral the MoS$_2$/graphene/MoS$_2$ heterostructure by the common CVD technique, which exhibited broadband photoreponse from the visible to infrared range (532–1600 nm). Two Schottky barriers formed between graphene and MoS$_2$, which could effectively separate the photo-excited carriers generated at graphene or MoS$_2$ region. To sum up, the formation of heterojunctions between TMDs and graphene is an effective way to expand the photoreponse range of the resultant photodetectors and meanwhile realize the effective separation of carriers due to the presence of the Schottky barrier and photogating effect. Under the built-in electric field, carrier transport will be accelerated to decrease recombination probability and thus enhance the photoreponse.

3.1.2. TMDs with Noble Metals

To overcome the limitation of poor light absorption and low photoresponsivity of single TMDs, a considerable plasmon resonance enhancement of photocurrent in few-layer MoS$_2$ phototransistors has been demonstrated utilizing Au/Ag nanoparticles or nanowires. The authors indicated lateral structure. Deng et al. presented a phototransistor composed of lateral the MoS$_2$/graphene/MoS$_2$ heterostructure by the common CVD technique, which exhibited broadband photoreponse from the visible to infrared range (532–1600 nm). Two Schottky barriers formed between graphene and MoS$_2$, which could effectively separate the photo-excited carriers generated at graphene or MoS$_2$ region. To sum up, the formation of heterojunctions between TMDs and graphene is an effective way to expand the photoreponse range of the resultant photodetectors and meanwhile realize the effective separation of carriers due to the presence of the Schottky barrier and photogating effect. Under the built-in electric field, carrier transport will be accelerated to decrease recombination probability and thus enhance the photoreponse.

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In another typical example, Li et al. reported the development of plasmon photodetectors based on Au@MoS$_2$ heterostructures and perfectly realized the intimate and direct interfacing of Au and MoS$_2$ (Figure 5d). The photoresponsivity with a number of 22.3 A W$^{-1}$ was higher than the most significant value of similar grating free photodetectors reported in the past. For the Au@MoS$_2$ structure, which encapsulated an Au nanoparticle core by a CVD-grown multilayer MoS$_2$ shell, the redistributed and enhanced electromagnetic field increased light absorption and thus improved electron–hole pair generation efficiency in contrast to Si–MoS$_2$ (Figure 5e). By applying a gate voltage larger than the threshold voltage, the Schottky barrier at the Au/MoS$_2$ interface slopes downward, which increases the efficiency of photocarrier extraction, leading to increased photoreponse. Figure 5f shows the comparison of ON/OFF photocurrent with and without light and noted that after combining with
Au@MoS$_2$, the photodiodes exhibit a much smaller dark-state current and a larger photocurrent compared with the Si conductor.\(^\text{[84]}\) Moreover, a photodetector based on gap-mode structures sandwiched MoS$_2$ between metal nanoparticles and metal substrates.\(^\text{[85]}\) The photocurrent responsivity increased by 880% under incident light of 532 nm by the gap-mode plasmon. In summary, the LSPR effect, which was usually used to enhance the light–matter interaction of 2D materials by the electromagnetic field, is an efficient way to improve the charge-transfer efficiency across the Schottky barrier between TMDs and noble metals and thus finally increase the optoelectronic performance of the photodetectors.

### 3.2. Band Alignment in TMDs and Narrow-Bandgap Semiconductors

The second type of the energy band structure is constructed by TMDs and narrow-bandgap semiconductors such as BP, black arsenic phosphorus (AsP), PbS QDs, and PbSe QDs to broaden the response range.\(^\text{[85]}\) Here we will discuss the typical charge transport behavior in a TMD-narrow-bandgap material photodetector. As shown in Figure 6a, as the Fermi level of MoS$_2$ is higher than that of BP,\(^\text{[86]}\) when n-type MoS$_2$ contacts p-type narrow-bandgap material (BP), the electrons move from MoS$_2$ to BP, resulting in an equilibrium of the Fermi level. The majority carries depletion across the interface of MoS$_2$ and BP, leading to the formation of a built-in electric field, which points from MoS$_2$ to BP.\(^\text{[86]}\) Under forward bias, the MoS$_2$ contacts the metal electron, an opposite electronic field is induced and the depletion region is narrowed, the majority carriers in MoS$_2$ overcome the barrier to cross the junction, whereas holes are blocked when the forward bias is small, which will induce an increased photocurrent (Figure 6b). Under negative bias, the majority carrier depletion region becomes wider, the barrier increases and blocks the majority carriers, and the built-in potential becomes larger than zero-bias state (Figure 6c). Although minority carriers are extracted to the other side of the junction, the low concentration of minority carriers results in the current being much lower than in forward bias, generating the current-rectifying characteristics. Under IR illumination, the energy of the incident photon is larger than the bandgap of BP whereas smaller than most TMDs.\(^\text{[87]}\) When the junction is under zero bias, the photon-induced carriers generated by BP are separated by the built-in potential at the overlapped region, the electrons move to MoS$_2$, whereas the holes transport to the opposite side (Figure 6d). Under forward bias, the electrons induced by the incident light and injected by the source electrode diffuse to BP and then to the drain electrode (Figure 6e). Under negative bias, the electrons generated by the applied bias and light-induced e–h pairs move from BP to MoS$_2$ (Figure 6f). An obvious decrease in response time attributed to the built-in potential is indicated by a certain number of studies.\(^\text{[87,88]}\)
3.2.1. TMDs with BP

Due to the small bandgap and high mobility of few-layer BP, it has promising possibilities for broadband and sensitive photodetection. The detection of long-wavelength light corresponding to low-energy photons generally requires suitable narrow-bandgap semiconductors to absorb photons. Functions based on TMDs and narrow-bandgap materials provide with an effective method to extend the detection range and decrease noise current. Deng et al. reported a BP–MoS$_2$ vdW heterojunction p–n diode for the first time, the 2D p–n diodes exhibited strong gate-tunable current-rectifying I–V characteristics, and showed a three-magnitude higher photoresponsivity of 418 mA W$^{-1}$ than the reported BP phototransistor. Furthermore, several studies have demonstrated that BP combined with TMD such as MoS$_2$, WSe$_2$, MoTe$_2$ and ReS$_2$ can effectively construct a range of functional vdW heterojunctions.

Based on the anisotropic optoelectronic properties of BP, Bullock et al. significantly improved the performance of BP/MoS$_2$ heterostructure photodiodes for the detection of MWIR light at room temperature. As shown in Figure 7a,b, a thin n-type MoS$_2$ layer serves as an electron-selective contact and a Au pad serves as a MWIR back reflector in this device. The asymmetric contact of BP with MoS$_2$ and Au electrode is shown in Figure 7c, which makes electrons move from BP to MoS$_2$ while blocking the flow of holes from BP to MoS$_2$ to separate the electron–hole pairs. The transmission electron microscopy (TEM) images of the completed device and the BP/MoS$_2$ and BP/Au interfaces are shown in Figure 7d–f. The ultrafast rise and fall times were 3.7 and 4.6 µs under $\lambda=2.7$ µm light at zero bias (Figure 7g,h), which indicates a fast carrier transport characteristic for this device. In addition, room-temperature ultrahigh specific detectivities (D$^*$) of $1.1 \times 10^{9}$ Jones in the MWIR band were achieved.

Furthermore, Ye et al. demonstrated a photodetector with visible-to-NIR detection ability based on the few-layer BP/MoS$_2$ heterojunction with a photoresponse time of 15 µs. Another work about the BP/WSe$_2$ vertical heterostructure demonstrated a broadband photodetector with the photogate layer of BP as well as a carrier channel of WSe$_2$. Under visible illumination, both BP and WSe$_2$ absorb photons and generate electron–hole pairs at the contact region. Then the built-in potential of the junction separates the photoinduced electron–hole pairs, resulting in the photocurrent enhancement. Different from visible illumination, the BP layer is the only photoactive layer under infrared illumination. The electron–hole pairs are generated in BP and then separated by the built-in potential and produces photocurrent by $V_{ds}$. Another vdW p–n junction diode based on BP and WS$_2$ was also designed with an atomically sharp interface functionality. By tuning the gate voltage and the thickness of WS$_2$, the modulation of rectification of $2.6 \times 10^{4}$ was reached. Recently, Zheng et al. developed a new way to enhance the photoresponsivity of a p–n diode using surface acoustic waves (SAWs). In this case, SAWs promote the separation of photo-generated carriers and thus greatly increase the photocurrent, obtaining a measured photocurrent $10^{3}$ times higher for the device with SAWs than without SAWs.

AsP is an alloy of BP with As atoms in the forms of As$_n$P$_{1-x}$, various As atoms’ ratios enable a tunable bandgap ranging from 0.3 to 0.15 eV. This bandgap range indicates that AsP may absorb light with a wavelength of 8.5 µm. Through constructing AsP field effect transistors (FETs) and AsP/MoS$_2$, researchers measured the properties and indicated that the noise figure of the AsP/MoS$_2$ heterostructure was improved significantly compared with that of AsP FET, which is attributed to the energy band modulation of 2D vdW heterojunctions. The p-type AsP and n-type MoS$_2$ can build a typical p–n junction, which was indicated by rectification curves. The energy barrier formed at the AsP/MoS$_2$ interface depresses the random transport of the photogenerated carriers, which remarkably suppresses the dark current. Furthermore, this AsP/MoS$_2$ photodetector shows long-wavelength IR response as well as a specific detectivity higher than $4.9 \times 10^{7}$ Jones in the 3–5 µm range.
Different from the conventional p–n junctions, recently, Wu et al. reported a novel pp\textsuperscript{+} MoS\textsubscript{2}/AsP vdW heterophotodiode consisting of thick MoS\textsubscript{2} flakes with weak p-type conduction and thick AsP flakes.\textsuperscript{[87]} Figure 7i, j shows the schematic of device structure and atomic force microscopy (AFM) image with the thickness of MoS\textsubscript{2}/AsP. As AsP is a typical p-type 2D semiconductor with a narrow bandgap of 0.15–0.3 eV, the thin MoS\textsubscript{2}/AsP p–n photodiode comprises bilateral depletion regions (Figure 7k).\textsuperscript{[98]} Under IR illumination, the photogenerated electrons in AsP can easily transfer and cross the small conduction band barrier at the interface; thus, a negative short-circuit current and clear ON/OFF switch are shown in Figure 7.

![Photodetectors based on TMDs and narrow-bandgap BP or AsP. a) Schematic of the MoS\textsubscript{2}–BP device configuration. b) Optical micrograph of a completed device. c) Simulated energy band diagram of the device under equilibrium. d) Cross-sectional TEM image of the complete photodiode. e,f) High-resolution cross-sectional TEM image showing the BP/MoS\textsubscript{2} interface (e) and the BP/Au interface (f). g) Photocurrent measured from BP/MoS\textsubscript{2} photodiode under a modulated illumination source ($\lambda = 2.7 \mu m$). h) Rise and fall time under 2.7 \mu m illumination. Reproduced with permission.\textsuperscript{[93]} Copyright 2018, Springer Nature. i) Schematic of the fabricated MoS\textsubscript{2}/AsP device. j) Line scan profile of the heterostructure from the AFM image shown in the inset. Scale bar is 5 \mu m. k) MoS\textsubscript{2}/AsP p–n heterodiode and m) MoS\textsubscript{2}/AsP pp\textsuperscript{+} heterodiode under IR laser illumination at zero bias. l) IR photovoltaic response of the MoS\textsubscript{2}/AsP p–n heterodiode. n) Time-resolved photoresponse of the MoS\textsubscript{2}/AsP diode at $V_{ds} = 0$ V. Reproduced with permission.\textsuperscript{[93]} Copyright 2019, Springer Nature.

Figure 7. Photodetectors based on TMDs and narrow-bandgap BP or AsP. a) Schematic of the MoS\textsubscript{2}–BP device configuration. b) Optical micrograph of a completed device. c) Simulated energy band diagram of the device under equilibrium. d) Cross-sectional TEM image of the complete photodiode. e,f) High-resolution cross-sectional TEM image showing the BP/MoS\textsubscript{2} interface (e) and the BP/Au interface (f). g) Photocurrent measured from BP/MoS\textsubscript{2} photodiode under a modulated illumination source ($\lambda = 2.7 \mu m$). h) Rise and fall time under 2.7 \mu m illumination. Reproduced with permission.\textsuperscript{[93]} Copyright 2018, Springer Nature. i) Schematic of the fabricated MoS\textsubscript{2}/AsP device. j) Line scan profile of the heterostructure from the AFM image shown in the inset. Scale bar is 5 \mu m. k) MoS\textsubscript{2}/AsP p–n heterodiode and m) MoS\textsubscript{2}/AsP pp\textsuperscript{+} heterodiode under IR laser illumination at zero bias. l) IR photovoltaic response of the MoS\textsubscript{2}/AsP p–n heterodiode. n) Time-resolved photoresponse of the MoS\textsubscript{2}/AsP diode at $V_{ds} = 0$ V. Reproduced with permission.\textsuperscript{[93]} Copyright 2019, Springer Nature.

![Photodetectors based on TMDs and narrow-bandgap BP or AsP. a) Schematic of the MoS\textsubscript{2}–BP device configuration. b) Optical micrograph of a completed device. c) Simulated energy band diagram of the device under equilibrium. d) Cross-sectional TEM image of the complete photodiode. e,f) High-resolution cross-sectional TEM image showing the BP/MoS\textsubscript{2} interface (e) and the BP/Au interface (f). g) Photocurrent measured from BP/MoS\textsubscript{2} photodiode under a modulated illumination source ($\lambda = 2.7 \mu m$). h) Rise and fall time under 2.7 \mu m illumination. Reproduced with permission.\textsuperscript{[93]} Copyright 2018, Springer Nature. i) Schematic of the fabricated MoS\textsubscript{2}/AsP device. j) Line scan profile of the heterostructure from the AFM image shown in the inset. Scale bar is 5 \mu m. k) MoS\textsubscript{2}/AsP p–n heterodiode and m) MoS\textsubscript{2}/AsP pp\textsuperscript{+} heterodiode under IR laser illumination at zero bias. l) IR photovoltaic response of the MoS\textsubscript{2}/AsP p–n heterodiode. n) Time-resolved photoresponse of the MoS\textsubscript{2}/AsP diode at $V_{ds} = 0$ V. Reproduced with permission.\textsuperscript{[93]} Copyright 2019, Springer Nature.

![Photodetectors based on TMDs and narrow-bandgap BP or AsP. a) Schematic of the MoS\textsubscript{2}–BP device configuration. b) Optical micrograph of a completed device. c) Simulated energy band diagram of the device under equilibrium. d) Cross-sectional TEM image of the complete photodiode. e,f) High-resolution cross-sectional TEM image showing the BP/MoS\textsubscript{2} interface (e) and the BP/Au interface (f). g) Photocurrent measured from BP/MoS\textsubscript{2} photodiode under a modulated illumination source ($\lambda = 2.7 \mu m$). h) Rise and fall time under 2.7 \mu m illumination. Reproduced with permission.\textsuperscript{[93]} Copyright 2018, Springer Nature. i) Schematic of the fabricated MoS\textsubscript{2}/AsP device. j) Line scan profile of the heterostructure from the AFM image shown in the inset. Scale bar is 5 \mu m. k) MoS\textsubscript{2}/AsP p–n heterodiode and m) MoS\textsubscript{2}/AsP pp\textsuperscript{+} heterodiode under IR laser illumination at zero bias. l) IR photovoltaic response of the MoS\textsubscript{2}/AsP p–n heterodiode. n) Time-resolved photoresponse of the MoS\textsubscript{2}/AsP diode at $V_{ds} = 0$ V. Reproduced with permission.\textsuperscript{[93]} Copyright 2019, Springer Nature.
Figure 7l. Figure 7m further shows a unilateral depletion region of the heterostructure. As AsP has a higher Fermi level than MoS\textsubscript{2}, the holes in MoS\textsubscript{2} move toward AsP and accumulate in the AsP side in the MoS\textsubscript{2}/AsP \( \mu^+ \) heterodiode. Under the built-in electric field with direction pointing toward the MoS\textsubscript{2} side, the electrons primarily move to the AsP side and are collected by the drain electrode, and the recombination of the photogenerated electron–hole pairs is significantly suppressed. Thus, the MoS\textsubscript{2}/AsP heterodiode exhibits a high external quantum efficiency (EQE) of 71% and a fast response time of 9 \( \mu \)s (Figure 7n)\textsuperscript{[87]}. 

Recently, Xie et al. constructed a MoTe\textsubscript{2}/BP heterostructure by consecutively stacking the flakes of h-BN, BP, and MoTe\textsubscript{2} on the SiO\textsubscript{2}/Si substrate\textsuperscript{[95]}. As the Fermi level of MoTe\textsubscript{2} can be tuned from the valence band edge to the conduction band edge, while the Fermi level of BP moves slightly under different \( V_{gs} \), the device can be tuned from the p–n junction to p–p junction by gate modulation. When \( V_{gs} \) is of forward value, MoTe\textsubscript{2} exhibits an n-type behavior, and thus, the heterostructure acts as a typical p–n diode, with the built-in electrical field pointing from MoTe\textsubscript{2} to BP\textsuperscript{[95]}. In addition, a novel vdW photodiode based on BP and n-type PdSe\textsubscript{2} heterojunction was reported. The device shows broadband photoresponse ranging from visible to infrared wavelength and a high rectification and photoreponsibility can be tuned by gate voltage\textsuperscript{[99]}. Similar to the gate voltage modulation of the Fermi level of MoTe\textsubscript{2}, for \( V_{bg} < 0 \) V, the holes are injected into BP and PdSe\textsubscript{2} layers, making the Fermi level tuned to the valence band and increasing the potential barrier at the BP/PdSe\textsubscript{2} interface, which increases the rectifying current. In contrast, the electrons are injected into BP and PdSe\textsubscript{2} layers, causing the Fermi level to move away from the valence band when \( V_{bg} > 0 \). The transition of the interlayer charge carriers between the maximum valence band of BP and the minimum conduction band of PdSe\textsubscript{2} has been demonstrated. Such a limited interlayer bandgap (less than 0.5 eV) shows an expected broadband detection range up to 2000 nm\textsuperscript{[99]}. Recently, Cao et al. reported the photoelectric properties of a vertically integrated vdW heterojunction made from the multilayer-exfoliated n-type Re\textsubscript{2}S\textsubscript{2} and p-type BP; the heterojunction diode exhibits a high responsivity of 4120 A W\textsuperscript{−1} to UV illumination (\( \lambda = 365 \) nm)\textsuperscript{[100]}. In summary, BP possesses a tunable direct narrow bandgap, has an expected response wavelength up to NIR (\( \sim 1500 \) nm), which can significantly broaden the detection range when building junctions with TMD materials, and provides an efficient way to suppress the dark current and improve optoelectronic properties of photodetectors.

3.2.2. TMDs with QDs

To improve the optical absorption property of TMDs, colloidal QDs of lead chalcogenides (e.g., PbS, PbSe, and PbTe) are considered to be prospective candidates to combine with 2D TMD materials. Kufer et al. reported a hybrid 0D–2D phototransistor based on p-type PbS QDs and n-type MoS\textsubscript{2}\textsuperscript{[106]}. The size-tunable light absorption of PbS QDs and the high in-plane carrier mobility in the MoS\textsubscript{2} layer make low dark current possible. In the following studies, the hybridization of 2D TMDs with QDs has been demonstrated to be an ideal platform for low dark current and highly sensitive photodetection. For instance, field-effect phototransistors based on monolayer WS\textsubscript{2} and PbS QDs heterojunction were demonstrated to show high responsivity (up to \( \sim 14 \) A W\textsuperscript{−1}), wide electric bandwidth (\( \sim 396 \) Hz), and excellent stability\textsuperscript{[109]}. 

Recently, Chen et al. demonstrated interfacial electron transfer in core-only PbS–MoS\textsubscript{2} and core/shell PbS/CdS–MoS\textsubscript{2} hybrids (Figure 8)\textsuperscript{[102]}. As shown in Figure 8a–c, the size of the QDs and the number of MoS\textsubscript{2} layers are changed to alter the bandgap and furthermore tune the charge-transfer rate of the heterojunction. Layer-dependent electron transfer between core/shell PbS/CdS QDs and layered MoS\textsubscript{2} via energy bandgap engineering indicated that five-layer MoS\textsubscript{2} provides an effective charge-transfer method for 2D MoS\textsubscript{2} with QD hybrid devices\textsuperscript{[102]}. Hu et al. combined light-sensitive PbS QDs with 2D WSe\textsubscript{2} to develop hybrid PbS/WSe\textsubscript{2} phototransistors with a responsivity of up to \( \sim 2 \times 10^{-3} \) A W\textsuperscript{−1} and a specific detectivity over 10\textsuperscript{11} Jones in both ON and OFF state\textsuperscript{[103]}. For this structure, PbS QDs can efficiently absorb the incident illumination whereas the WSe\textsubscript{2} layer serves as a transport path for photogenerated carriers. The photogating effect is considered to be the main reason for the observed performance enhancement of the hybrid structure compared with the individual materials.

Interestingly, a novel concept involving consecutive type-II junctions based on hybrid MoS\textsubscript{2}/PbS phototransistors was reported very recently\textsuperscript{[108]}. Apart from the n–n junction formed at the interface of MoS\textsubscript{2}/PbS QDs, the additional built-in potential was created by sequentially using n-type TBAI and p-type EDT ligands to the PbS layers, creating p–n junctions in PbS QD photovoltaics. The effects of the two built-in electric fields along the same direction across the depletion region are clearly found to enhance the separation of photogenerated carriers; as a result, the responsivity and photoresponse times reach \( \sim 5.4 \times 10^{7} \) A W\textsuperscript{−1} and 950 \( \mu \)s, respectively\textsuperscript{[108]}. 

Two color-band (visible broadband and tunable short-wave infrared) photodetectors were constructed by integrating PbS QDs with MoS\textsubscript{2} nanosheets synthesized using a facile and in situ approach\textsuperscript{[104]}. The solution-based fabrication of hybrids is compatible with flexible platforms, making it attractive for various applications. When the PbS/MoS\textsubscript{2} hybrids are illuminated, the photogenerated electrons in PbS can be easily transferred to the conduction band of MoS\textsubscript{2}, whereas holes move in the opposite direction. The enhanced photoresponse of the detector with applied bias is corroborated by the efficient collection of photocarriers at the electrodes in the presence of an electric field, resulting in enhanced photocurrent\textsuperscript{[104]}. Özdemir et al. studied the performance of two kinds of TMD materials, WS\textsubscript{2} and MoS\textsubscript{2}, as carrier transport layers and demonstrated that WS\textsubscript{2}-based hybrid photodetectors outperform those of MoS\textsubscript{2} due to a more adequate band alignment that favors carrier transfer from the QDs\textsuperscript{[105]}. 

In addition, researchers keep exploring multiple ways to construct high-performance infrared photodetectors with fast photoresponse, low noise, as well as broadband spectrum coverage. Kufer et al. implement interface engineering using an appropriate buffer layer between MoS\textsubscript{2} sheets and colloidal QDs to maintain the field-effect transistor characteristics of the MoS\textsubscript{2} channel and thereby improve phototransistor performance\textsuperscript{[106]}. The wide-bandgap semiconductor TiO\textsubscript{2} was
applied to form a p–n junction with PbS, which suppresses the high density of localized states. Compared with the MoS$\text{\textsubscript{2}}$/PbS devices, such device structures demonstrated an improvement in ON/OFF ratio by more than two orders of magnitude and fast response times of less than 12 ms.\[106\]

As shown in Figure 8d,e, HgTe QDs formed a type-II band alignment with TiO$_2$/MoS$_2$ which has been determined by ultra-violet photoelectron spectroscopy (UPS) measurement.\[107\] Similarly, TiO$_2$ plays a role as a protective layer of the MoS$_2$ channel and as an n-type electron-acceptor medium facilitating the charge transfer to the MoS$_2$ channel as mentioned earlier. In the effect of the built-in electric field, the photogenerated electrons are moved into the MoS$_2$ channel across the thin TiO$_2$ layer whereas the holes remain trapped in the QD layer (Figure 8f). Meanwhile, the noise current is significantly suppressed. Attributed to the high mobility of MoS$_2$ and the short channel length, the transit time that electrons took to transfer to the drain is much shorter than the trapping lifetime in the QDs when applying the source–drain bias. Thus, multiple electrons are recirculated in the MoS$_2$ channel, resulting in a significant photoconductive gain. Moreover, the detection range of this hybrid 2D–0D photodetector based on MoS$_2$ and HgTe QDs can extend to 2 µm at room temperature with an ultrahigh specific detectivity of 10$^{12}$ Jones.\[107\]

Furthermore, Wen et al. exploited a gapless heterostructure with factitious S vacancies, created by annealing the saturated MoS$_2$, and connected S dangling bonds of nonlayered PbS to the bonding sites of MoS$_2$ via strong orbital hybridization.\[108\] There is a blocking barrier for the carrier flow in the vdW interaction. The gapless heterostructure has no vdW gap, leading to higher efficiencies of charge injection due to the lack of the additional tunnel barrier. Considering the fast transport of electron–hole pairs, fast rise and decay time of about 47 and 49 μs were achieved, respectively. Also, the gapless heterostructure exhibits ultrahigh responsivity and photogain (G) exceeding 10$^5$, and the specific detectivity is beyond 10$^{14}$ Jones.\[108\]

Except for QDs, there are some other narrow-bandgap materials that can also construct heterostructures with 2D TMDs to expand the detection range obviously. Theoretical calculations predict that group X TMDs (e.g., Ni, Pd, Pt) are promising narrow-bandgap semiconductors in the bulk phase (≤0.25 eV) and meanwhile with high room-temperature mobility.\[109\] For instance, an air-stable photodetector based on PdSe$_2$ FETs and PdSe$_2$–MoS$_2$ heterostructures operating at room temperature and at LWIR (up to 10.6 μm) was demonstrated.\[109\] In addition, as a narrow-bandgap (≤0.3 eV) semiconductor, p-type-layered Sb$_2$Te$_3$ has drawn considerable attention due to structural stability and high carrier mobility (200 cm$^2$ V$^{-1}$ s$^{-1}$).\[111\] Liu et al.
have successfully achieved vertically stacked Sb$_2$Te$_3$/MoS$_2$ vdW p–n heterostructures though the CVD approach. Upon light illumination, the p–n diode shows obvious photovoltaic behaviors with the highest photon-to-electron conversion efficiency up to 4.5%.[111] In summary, narrow-bandgap materials show excellent light absorption in the IR region, which has been difficult for high-mobility TMDs. Therefore, TMD-narrow-bandgap semiconductor photodetectors indicate broadband detection and obviously enhanced photoresponsivity in the IR region.

### 3.3. Band Alignment in TMDs and Middle-Bandgap Semiconductors

In this section we will discuss the band alignment strategies in heterostructures built by TMDs and the middle-bandgap materials and the corresponding charge transport behaviors. Figure 9 shows a typical example for the band structure of a MoS$_2$/MoTe$_2$ heterojunction. The Fermi levels of MoTe$_2$ and MoS$_2$ are −4.3 eV and −5.1 eV, respectively.[112] When an n-type MoS$_2$ contact a p-type MoTe$_2$, the electrons transfer from MoS$_2$ to MoTe$_2$ due to the difference of the Fermi level of MoS$_2$ and MoTe$_2$; as a result, the Fermi level moves to the valence band of MoS$_2$ and conduction band of MoTe$_2$ to reach the thermal equilibrium conditions (Figure 9a).[113] As shown in Figure 9b, when the applied bias is forward, which opposes the direction of the built-in electric field, the equilibrium state breaks and the potential barrier becomes lower so that carriers can easily overcome. Therefore, majority carriers in both sides flow to the other side driven by the concentration gradient, causing a large diffusion current in the p–n junction. In contrast, a negative voltage applied to the MoTe$_2$ will lead to the increase in potential barrier (Figure 9c). The increased built-in electric field accelerates the carriers transport speed of minority carriers, which generate small drift current.[112]

Under visible illumination, the energy of incident photons is larger than the bandgap of most TMDs. The photon-induced carriers generated by TMDs are separated by the built-in potential at the interface region, and the electrons move to MoS$_2$ whereas holes transport to the opposite side when zero bias is applied (Figure 9d). Under forward bias, the electrons are excited by incident light and injected by the source electrode as the majority carriers in MoS$_2$ shift to MoTe$_2$ and then to the metal electrode (Figure 9e). Under reverse bias, the electrons generated by the applied bias and light-induced electron–hole pairs move from MoTe$_2$ to MoS$_2$ with the help of the built-in electric field (Figure 9f). With such a manner, the obvious decrease of response time due to the presence of the built-in electric field has been demonstrated by a certain number of researches.[114]

#### 3.3.1. TMDs with TMDs

The heterostructures built by two kinds of 2D TMD materials (MX$_2$, M = Mo, W; X = S, Se, Te) have attracted tremendous attention.[115] TMDs such as MoX$_2$ and WX$_2$ crystals have similar lattice constants, which is very conducive for the construction of atomic thin 2D lateral heterostructures.[116] The WS$_2$–MoS$_2$ and MoS$_2$–WS$_2$ heterostructures have been successfully synthesized using the CVD growth technique.[117,118] Ye et al. successfully synthesized lateral bilayer WS$_2$–MoS$_2$ heterostructures via a two-step CVD method.[117] Kelvin probe force microscopy (KPFM) measurement shows a potential difference of 100.78 mV with a depletion width of 1.1 μm of this device, implying the existence of the built-in potential inside the WS$_2$–MoS$_2$ heterostructure. Wu et al. reported the photovoltaic light sensors based on monolayer MoS$_2$–WS$_2$ in-plane heterostructures that were created through a one-step synthesis strategy.[118] The lateral structure shows a type-II band structure in which electrons move from the WS$_2$ side to MoS$_2$ region, due to the higher potential of WS$_2$ compared with that of MoS$_2$.

Interestingly, n–n junction can be formed at the MoS$_2$/WS$_2$ interface, for which electrons are the majority carriers in both materials; the schematics of photodetectors and optical image

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**Figure 9.** The energy band structure of MoS$_2$–MoTe$_2$ standing for the heterostructures of TMDs and middle-bandgap semiconductors. a–c) The band diagrams under zero bias (a), forward bias (b), and reverse bias (c) in the dark. d–f) The band diagrams under zero bias (d), forward bias (e), and reverse bias (f) under illumination.
of this heterostructure are shown in Figure 10a,b.\textsuperscript{119} For this structure, the formation of a built-in potential was revealed by KPFM measurement in the dark and under illumination. A higher-surface potential difference suggests that the electrons tend to move away from WS\textsubscript{2} to MoS\textsubscript{2} under illumination. Figure 10c shows the distinct response and high responsivity of photodetectors under 532 nm wavelength. It is worth noting that the response under 1030 nm is attributed to the interlayer coupling effect as both individual WS\textsubscript{2} and MoS\textsubscript{2} cannot absorb light of 1030 nm. Interlayer coupling reduces the energy interval and thus makes the response wavelength of heterostructures longer than the individual components.\textsuperscript{119} Moreover, surface plasmon resonance is applied to enhance light absorption by integrating periodical Au nanoparticle patterns with MoS\textsubscript{2}/ WS\textsubscript{2} heterostructures. As a result, an impressive $\approx 25$ times enhancement on the responsivity of 1030 nm light was achieved.

To further improve the photoelectric performance using the fast charge transfer across the band structure of such TMD–TMD heterostructures, Huang et al. reported a method to engineer the light–matter interactions in few-layer MoS\textsubscript{2} and WSe\textsubscript{2} via an asymmetric Fabry–Perot cavity.\textsuperscript{120} Fabry–Perot interference originates from multiple internal reflections between two parallel reflecting interfaces. The optical resonance absorption can be excited under the constructive resonant
condition, which is generally realized by optimizing the spacer thickness. The cavity is based on the hybrid integration of TMD/h-BN/Au/SiO₂ heterostructures realized through layer-by-layer stacking. By modulating the thickness of the underlying h-BN, the maximum enhancement of Raman and absorption intensity from individual MoS₂ and WSe₂ on the h-BN/Au substrate can be achieved, which results from constructive resonant absorption induced by Fabry–Perot cavity. These results show a promising approach to achieve enhanced light absorption in few-layer TMD vdW heterostructures, which can be exploited to boost the performance of photodetector and photovoltaic devices.

Similar to the earlier band construction strategy, very recently, Lee et al. fabricated an array of self-assembled WSe₂/MoS₂ heterostructures through facile solution-based directional precipitation. The realized WSe₂/MoS₂-based p–n heterojunction shows not only high rectification (ideality factor: 1.18) but also promising optoelectrical properties with a high responsivity of 5.39 A W⁻¹ and response speed of 16 μs. Apart from WSe₂ and WSe₅, other TMDs such as MoTe₂ have also been used to construct heterostructures with MoS₂. Yin et al. proposed a device composed of vertical MoTe₂/MoS₂ transistors, where the lateral MoTe₂ parts act as channels and the vdW heterostructures underneath the electrodes form vertical transport paths. Based on the asymmetric carrier injection, dynamic control of the conducting polarity in field-effect transistors at the mercy of bias voltage was achieved. High-performance photovoltaic photodetectors based on MoTe₂/MoS₂ vertical heterojunctions were demonstrated by an exfoliating approach. When a forward bias is applied, the potential barrier becomes lower, causing a large diffusion current in the p–n junction. On the contrary, if the voltage applied to MoTe₂ is negative, the increased built-in electric field accelerates the transport speed of minority carriers. Ding et al. further synthesized the atomically thin, vertically stacked 2H-MoTe₂/MoS₂ heterostructures using the single-step CVD method and a magnet-assisted secondary precursor delivery tool. The photoelectrical measurements exhibit a high responsivity with an EQE at 4.71 A W⁻¹ and 532% at 1100 nm, whereas 4.67 A W⁻¹ and 1935% at 300 nm, one-to-two orders of magnitude higher than other reported exfoliated MoTe₂ heterostructure devices so far.

As shown in Figure 10d, a few-layer group-6 WSe₂ with group-7 ReS₂ has been used through the vertical-stacking method to show a 0.7 eV near-direct type-II bandgap at the heterointerface. The optical images of the heterojunction constructed by different numbers of layer are shown in Figure 10e. It should be noted that for optical generation across the heterointerface, compared with the 0.68 eV indirect bandgap, the 0.7 eV near-direct bandgap transition will not require phonon assisted momentum conservation. Hence, this near-direct electronic structure can facilitate photo absorption and lead to significant enhancement in photogeneration. Meanwhile, Figure 10f shows the interlayer coupling effect for an IR response and the presence of built-in potential resulting in the ultrafast response time. Similarly, a gate-tunable transition between positive photoconductance (PPC) and negative photoconductance (NPC) based on the ReS₂/h-BN/MoS₂ vdW heterostructure phototransistor has been revealed. In addition, highly efficient NIR photodetection based on ReS₂ with gate-controllable staggered bandgap alignment was demonstrated. More recently, infrared photodetection enabled by interlayer excitons generated between WS₂/HfS₂ has been reported, which provides a promising technology to realize room-temperature infrared photodetectors.

In addition to heterojunctions of different materials, mono-/multilayer MoS₂ can also build multiheterojunction structures. Recently, Kim et al. fabricated a photodetector based on mono-/multilayer MoS₂ heterojunction, which demonstrated a high responsivity of 2.67 × 10⁴ A W⁻¹ at 520 nm wavelength and 1.65 × 10⁴ A W⁻¹ at 1064 nm wavelength, respectively. Figure 10g shows the schematic of the nanobridge multiheterojunction. Figure 10h shows the AFM image of the mono-/multilayer heterojunction that has a 3–5 nm height difference. Due to the built-in electric field in the carrier depletion region, under illumination, the photogenerated holes go to the multilayer MoS₂ region, whereas the photogenerated electrons in the multilayer MoS₂ are trapped at the interface; meanwhile, the photogenerated electrons in the monolayer MoS₂ stay in the same region away from the interface. As a result, electrons and holes flow in multi- or monolayer bridges; thus, the possibility of recombination decreased significantly and an ultrafast response speed can be obtained (Figure 10i). In summary, to utilize the extraordinary physical properties of TMDs, the construction of vdW heterostructures can be realized via stacking different 2D materials or the multiple-step CVD method. These heterostructures usually show a type-II energy band structure due to similar bandgap and the difference of work function, which induced built-in electrical field to promote electron–hole separation. Thus, a significantly enhanced photoresponse and decreased response time can be generally observed.

3.3.2. TMDs with III–VI/IV–VI Chalcogenides

The III–VI chalcogenides and IV–VI chalcogenides are also promising candidates for photoelectric applications. Atomically thin GaTe-MoS₂ p–n heterojunctions coupled by vdW interaction has been demonstrated for a fast response time less than 10 ms. Different from the transfer method, a two-step CVD technology was applied to fabricate 2D GaSe/MoS₂ heterostructures with a large lattice mismatch. By modulating the Ar flow and growth time, both vertically stacked vdW heterostructures and lateral heterostructures can be obtained, which tend to grow under low Ar flow and high Ar flow, respectively. Similarly, Zhou et al. reported the synthesis of p-GaSe/n-MoS₂ heterostructures via vdW epitaxial growth, Figure 11a shows the schematic of device structure. A type-II energy band structure based on a p–n junction is formed based on the p-doping of GaSe and n-doping of MoS₂. A typical carrier transportation behavior of p–n junction has been observed. In other words, a built-in electric field pointing from MoS₂ to GaSe separates the electron–hole pairs effectively and pushes electrons to move to MoS₂ whereas holes to transfer to GaSe. As shown in Figure 11b,c, the response times of rise and fall in GaSe/MoS₂ are sped up for more than three orders of magnitude, resulting from the built-in potential, which are ≈60 and ≈15 s for the individual MoS₂ device whereas 80 and 20 ms for the heterojunction device. Tan et al. further reported that the rise time of the...
and n-SnS vdW heterostructure on the heterostructure exhibits high responsivity of $3.5 \times 10^4$ A W$^{-1}$ reached at 500 nm.

To further make better use of the third type of band structure, Lv et al. fabricated a photodetector range from UV to visible wavelength, which was made of a p-GaSe/n-WSe$_2$ heterojunction, sandwiched by top and bottom graphene electrodes. Under zero bias, the photogenerated electron–hole pairs move to opposite directions across the junction into the graphene electrodes by the built-in electric field in the heterojunction. The device exhibits an overall high performance, including high rectification ratio ($\approx 10^5$), high responsivity ($\approx 149$ A W$^{-1}$ at 410 nm), and fast response speed (a rise and fall time of 37 and 43 $\mu$s). Furthermore, Islam et al. reported a GaSe/MoS$_2$ heterostructure stacked with a few-layer graphene contacts with low contact resistance to reach an ultralow noise of $10^{-14}$ W Hz$^{-1/2}$. Zou et al. reported the controlled growth of vertically stacked 2H- In$_2$Se$_3$/MoS$_2$ vdW heterostructures through a typical two-step CVD method. Both the conduction band minimum and the valence band maximum of In$_2$Se$_3$ are lower than those of MoS$_2$, leading to a type-II band alignment between the two components. Under 532 nm light, electron–hole pairs will be generated in both In$_2$Se$_3$ and MoS$_2$. It is well known that electrons tend to transfer to a lower-energy state; thus, the carriers transport behavior is similar to that described in Figure 9.

On the other hand, novel self-driven photodetectors based on a graphene/InSe/MoS$_2$ heterostructure exhibits high photoresponsivity (110 mA W$^{-1}$), and fast photoresponse (less than 1 ms) has been reported. Zhou et al. constructed SnSe$_2$/MoS$_2$-based vdW heterostructures using MoS$_2$ as the template, which show efficient interlayer charge transfer due to the strong coupling. In addition, p-WSe$_2$ and n-SnS$_2$ have been calculated to be broken band alignments with the conduction band of SnS$_2$, a little lower than the valence band of WSe$_2$. Furthermore, monolayer SnS$_2$ has shown a high electron mobility of $\approx 50$ cm$^2$ V$^{-1}$ s$^{-1}$ and a high responsivity of 722 A W$^{-1}$. As shown in Figure 11d, Zhou et al. further constructed a highly sensitive WSe$_2$/SnS$_2$ photodiode on the h-BN thin film by exfoliating each material and stacking them layer by layer. At reverse bias, the measured current is ultralow because of the depletion of WSe$_2$ and the electron accumulation in SnS$_2$, resulting in nearly no charge flow through the heterostructure. However under light illumination, large amounts of photoinduced electron–hole pairs generated in WSe$_2$ and SnS$_2$ sides. Figure 11e shows the process of tunneling transport and highly efficient separation of photoinduced charge carrier. Figure 11f shows the time-dependent photoresponse curves under 550 nm with the power density of 3.77 mW cm$^{-2}$, suggesting good stability and fast response time. With a similar manner, Xue et al. reported a high-photoresponsivity photodetector based on a WSe$_2$/SnSe$_2$ heterostructure, by applying a proper bias, and a change of band structure from the near-broken state to broken-gap band alignment resulted. In addition, a multifunctional device based on a SnSe$_2$/MoTe$_2$ vdW heterostructure has been constructed. In the dark, most of the light leads to interband transitions of carriers. Thus, the electrons in SnSe$_2$ near the conduction band barely pass through the junction. The laser illumination causes both interband and...
intraband transitions. A large number of electrons in SnSe$_2$ near the unoccupied states above the conduction band easily pass through the barrier by Fowler–Nordheim (FN) tunneling.$^{[160]}$

3.3.3. TMDs with Perovskites

Due to the various outstanding characteristics such as the appropriate direct bandgap, large absorption coefficient, long carrier diffusion length, and high charge carrier mobility, inorganic perovskites and organic–inorganic hybrid perovskites have recently drawn great research interest in various fields.$^{[137–149]}$ Here, we also reviewed the band alignment and charge transfer in TMD perovskite-based heterostructure photodetectors considering their unique merits for the improvement of device performance. Photodetectors based on the hybridization of perovskite with CNTs,$^{[141]}$ graphene, and$^{[142]}$ zinc oxide (ZnO),$^{[143]}$ have been previously reported. Cheng et al. initially reported perovskite 2D crystal heterojunction devices by the vapor-phase intercalation of lead iodide (PbI$_2$)$^{[144]}$ After that, a series of researches presented interesting phenomena of heterojunctions based on perovskites and 2D TMDs materials. The heterostructures of perovskites with TMDs are of great interest due to their unique band structure alignment and interesting charge-transfer behaviors.$^{[145]}$ Lu et al. presented a 2D photodetector based on a hybrid bilayer of WS$_2$/CH$_3$NH$_3$PbI$_3$, which shows high performance using laser healing and perovskite coating.$^{[146]}$ Ma et al. fabricated and characterized a photoco conductor made of heterostructures of the CH$_3$NH$_3$PbI$_3$ perovskite film and monolayer WS$_2$.$^{[147]}$ The PL of the perovskite in the heterojunction was quenched, which was considered to result from the interfacial charge transfer with WS$_2$.

Yang et al. further fabricated an ultrathin perovskite/TMD vertical semiconductor heterostructure through the controlled vapor-phase growth of few-nanometer-thick perovskite layers.$^{[148]}$ Figure 12a shows the back-gate photodetector device based on the perovskite/WS$_2$ heterostructure. Interestingly, a band structure modulation has been proved by theoretical calculation of the band structure offsets. The conduction band minimum and the valence band maximum positions will be changed upward by decreasing the thickness of the (CH$_3$NH$_3$)$_{3–n}$PbI$_{3n+1}$ layer. As a result, the heterostructure shows type-II band alignments for $n < 9$ whereas type-I band alignments for $n \geq 9$ (Figure 12b). Figure 12c further shows responsivity under different laser power densities. The heterostructures composed of thinner perovskites have higher responsivity and faster photoresponse speed.$^{[148]}$

To further reveal the charge generation and transport mechanism in heterostructures of perovskite and 2D TMDs, Bai et al. built two types of heterojunctions, respectively, with vertical and planar structures based on MoS$_2$/CH$_3$NH$_3$PbI$_3$ through the wetting transfer method and UV exposure-nested etching technology.$^{[145]}$ Under illumination, electron–hole pairs are generated in the perovskite film, and electrons are transferred to MoS$_2$ film, attributed to the built-in electric field formed at the interface of MoS$_2$/CH$_3$NH$_3$PbI$_3$ heterojunction. Compared with the planar-type photodetector, the vertical-type photodetector based on the MoS$_2$/CH$_3$NH$_3$PbI$_3$ hybrid junction demonstrates better

![Figure 12. Photodetectors based on heterostructures of TMDs and perovskites. a) Schematic illustration of the three-terminal back-gate device based on perovskite/WS$_2$ heterostructures. b) Calculated band structures and band alignments of the heterostructures. c) Photoresponsivity as a function of illumination power intensities of the heterostructure photodetector. Reproduced with permission.$^{[148]}$ Copyright 2019, American Chemical Society. d) Schematic model of a photodetector device based on MoS$_2$ and perovskite QDs. e) The schematic of the channel current transport mechanism and energy band diagram of the phototransistor under OFF state and ON state. f) Photoresponsivity and specific detectivity with an inset shows the EQE as a function of illumination power. Reproduced under the terms of the Creative Commons CC-BY license.$^{[144]}$ Copyright 2019, The Authors, published by Wiley-VCH.](image-url)
responsivity, higher ON/OFF ratio, and faster response speed.\textsuperscript{[145]} In addition, conductive and photoconductive AFM (C-AFM and PC-AFM) were also used to study the mechanisms of photocurrent generation and transport across the heterointerface.\textsuperscript{[149,150]} Li et al. used C-AFM and PC-AFM to measure the dark current and photocurrent of WS\textsubscript{2}/CH\textsubscript{3}NH\textsubscript{2}PbI\textsubscript{3} heterostructures.\textsuperscript{[149]} Density functional theory (DFT) calculations indicate a type-II band alignment of WS\textsubscript{2}/CH\textsubscript{3}NH\textsubscript{2}PbI\textsubscript{3} heterostructures.\textsuperscript{[53]} Compared with the MAPbI\textsubscript{3}-only photodetectors, the device of WS\textsubscript{2}/CH\textsubscript{3}NH\textsubscript{2}PbI\textsubscript{3} shows higher responsivity and faster response speed, which proves that atomically thin TMD monolayers play a role in promoting charge separation. Thus, the combination of perovskites and 2D TMD materials provides a platform to study light–matter interactions and charge-transfer mechanisms in optoelectronic devices.\textsuperscript{[149]}

0D perovskite QDs with a superior absorption coefficient, large spectral coverage, tenability bandgaps, and low-cost solution processing were also considered as ideal sensitizers to combine with 2D TMDs for improving their photoresponse.\textsuperscript{[151–154]} All-inorganic CsPbI\textsubscript{3}–Br\textsubscript{3} QDs were primarily used to construct the 0D–2D mixed-dimensional heterostructure with monolayer MoS\textsubscript{2}. Figure 12d shows the schematic diagram of the device.\textsuperscript{[54]} For this device, increasing photoresponsivity has been found by increasing gate voltage under illumination, which could be attributed to the modulation of gate voltage on energy band structure. As shown in Figure 12c, in the OFF state, $V_{g} < V_{th}$, the increased Schottky barrier blocks the thermionic and tunneling current, so the dark current is obviously suppressed. However in the ON state, the barrier height decreases and the thermionic and tunneling current as well as the channel current gradually increase.\textsuperscript{[54]} Compared with the OFF state, the synergistic effect of the photogating effect and the Schottky barriers modulation enhance the channel current and produce an ultrahigh photoresponsivity on ON state. As shown in Figure 12f, the PQDs/MoS\textsubscript{2} mixed-dimensional phototransistor yields a very high EQE value, exceeding 10\% at a $V_{G}$ of 60 V, which is several orders of magnitude higher than those of the previously reported ones.\textsuperscript{[54]}

Another research also designed typical type-I and type-II band alignments in 0D–2D vdW heterostructures of perovskite QDs and MoS\textsubscript{2}. Wu et al. synthesized CH\textsubscript{3}NH\textsubscript{2}PbBr\textsubscript{3} QDs and CsPbI\textsubscript{3}–Br\textsubscript{3} QDs to construct type-I and type-II energy band alignments with monolayer MoS\textsubscript{2}, respectively. Upon illumination, photoexcited electrons can effectively transfer from QDs to ML-MoS\textsubscript{2}, whereas the generated holes remain in the QDs, resulting in reduced recombination and a quenched PL intensity in QDs.\textsuperscript{[140]} However in type-I vdW heterostructures, electrons (holes) transfer from the QDs to MoS\textsubscript{2} in the same direction. Moreover, researchers have made a series of comparisons and shown that the designed device with the type-II band structure performs much better than the device with type-I band structure, with a photogain larger than 10\textsuperscript{3} and $D_{\text{h}}$ of 1.95 $\times$ 10\textsuperscript{12} Jones. Because of the existence of surface defects in 0D colloidal QDs, capping ligands are used to provide sufficient surface passivation and reduce surface defects for stability.\textsuperscript{[140]} In consideration of charge carrier transport property between individual QDs and interfacial charge transfer in vdW heterostructures, Wu et al. conducted the 1-octane/ethanol acetate mixed-solvent treatment to realize solution-processed surface ligand density engineering.\textsuperscript{[155]} As a result, the charge injection efficiency is effectively improved.

An amazing property of the piezotronic and piezo-phototronic effect has been reported in single-crystalline 1D CsPbBr\textsubscript{3} nanowires, which is crucial for wearable electronics, human–machine interfaces, etc.\textsuperscript{[156]} Xu et al. applied the mechanically exfoliated 2D WS\textsubscript{2} nanoflakes and single-crystalline 1D CsPbBr\textsubscript{3} nanowires to construct WS\textsubscript{2}/CsPbBr\textsubscript{3} vdW planar photodetectors.\textsuperscript{[157]} The vdW photodetector was fabricated on the flexible PEN substrate, which was applied to tensile and compressive stress, respectively. When tensile strain was applied, negative polarization charges were induced at the vdW interface, both energy bands of these two materials are reversely bent. As a result, the interfacial carrier transfer is improved due to the weakened interfacial carrier transfer barrier. However, when compressive strain was applied, the photocurrent was highly reduced.\textsuperscript{[157]}

Apart from the lead-bearing perovskite, 2D Ruddlesden–Popper perovskites with great environmental friendliness have drawn more attention.\textsuperscript{[158–160]} Fang et al. reported photodetectors based on few-layer n-type MoS\textsubscript{2} and p-type lead-free 2D perovskite (PEA)\textsubscript{2}SnI\textsubscript{4} heterostructures.\textsuperscript{[92]} The heterojunction device has a photodetection range over the visible and NIR wavelength band with a tunable response peak. In a word, such low-dimensional perovskite materials (2D, 1D, and 0D) have shown excellent photoelectric properties, which can be combined with TMD materials to obtain amazing photoelectric detection performance.

### 3.4. Band Alignment in TMDs and Wide-Bandgap Semiconductors

The fourth type of the energy band structure is constructed by TMDs and wide-bandgap materials, such as ZnS, ZnO, $\beta$-Ga\textsubscript{2}O\textsubscript{3}, GaN, TiO\textsubscript{2}, and so on, all of which have a wide bandgap greater than 3.1 eV.\textsuperscript{[161–164]} Here we will first discuss the carrier transportation mechanism of these types of heterostructure photodetectors using MoS\textsubscript{2}–ZnS as a typical example. As discussed, MoS\textsubscript{2} and ZnS show n-type characteristics but the electronic affinity of ZnS is smaller than MoS\textsubscript{2}, and thus ZnS has a higher Fermi level than MoS\textsubscript{2}.\textsuperscript{[165]} The difference of the Fermi level induces a diffusion of electron flow from ZnS to MoS\textsubscript{2}. A unilateral depletion region forms in the ZnS side and makes more electrons accumulate in the MoS\textsubscript{2} side, in which a built-in electric field pointing from ZnS to MoS\textsubscript{2} is formed at the interface (Figure 13a). When a forward bias is applied, the electrons are injected to ZnS and further move to MoS\textsubscript{2} due to the concentration gradient. However, the holes are blocked by the large valance band offset under a smaller bias (Figure 13b).\textsuperscript{[165]}

When a reverse bias is applied, the unilateral depletion region becomes wider and the built-in potential is enhanced. The electrons transfer across the barrier and move from MoS\textsubscript{2} to ZnS, whereas holes transfer to the opposite direction (Figure 13c). Under UV light, the wide-bandgap materials such as ZnS absorb the UV light and generate electron–hole pairs, which are separated by the built-in electric field under zero bias (Figure 13d). For both forward bias and reverse bias condition, an obvious increase of free carriers in the channel is acquired by the light excited (Figure 13e,f).
ZnS is a well-established material for UV photodetection with a wide bandgap of 3.77 eV. To further broaden the photodetection range of TMDs, efforts have been made to combine the UV-sensitive ZnS and vis–IR-sensitive TMDs. For instance, a broadband photodetector based on ZnS/MoS₂ hybrids has been fabricated using a two-step hydrothermal method (Figure 14a). A schematic of charge-transfer mechanism is shown in Figure 14b. The responsivity of 4.5 mA/W for IR, 9.4 mA/W for UV light, and 17.85 mA/W for visible light were reached, respectively. Figure 14c shows that the fabricated photodetector is more sensitive to visible light than UV and IR range, attributed to the efficient photon absorption in the visible band of MoS₂. In addition, ZnO is a wide-bandgap oxide semiconductor with an energy bandgap of ~3.3 eV. A subsequent study based on the 2D WSe₂ and 1D ZnO p–n heterojunction photodetector indicated piezotronic effect on interfacial charge modulation, which were fabricated by the transfer method on a flexible substrate of polyethylene terephthalate. A clear switching behavior during illumination is turned to dark is shown in Figure 14f. Furthermore, by increasing the tensile strain from 0 to 0.87% at zero bias, obvious photocurrent enhancement was observed and a relatively high photoresponsivity (394 mA/W) was achieved.

As shown in Figure 14g, Lee et al. constructed a mix-dimensional vdW heterojunction photodiode by stacking the 2D WSe₂ nanosheet (p-type) onto 1D ZnO nanowire (n-type). For this diode, WSe₂ was the only photosorber for which the wavelength is greater than 400 nm. A p–n junction is formed at the interface of ZnO–WSe₂, and a built-in electric field pointing from ZnO to WSe₂ was established by the difference of work function. Under illumination, the photogenerated electron–hole pairs in the WSe₂ are dissociated by the built-in electric field, and the electrons move to ZnO whereas holes transport to WSe₂, both of which contribute to the enhancement of photocurrent.

Figure 14h shows the photocurrent dynamic curve at a constant reverse bias of −5 V under visible (620 nm) and NIR (950 nm) illumination at 1 Hz.

Note that the high-gain photodetectors result from long carrier lifetime often at a cost of response speed due to the inherent G–t trade-off. Interestingly, a very recent research reported by Guo et al. showed a novel junction field-effect transistor combining n-type ZnO belt with the p-type WSe₂ nanosheet to break the G–t trade-off. In this structure, p-type WSe₂ serves as a top gate to tune the carrier transport and depletion region in the channel material. When Vgs > 0.7 V, the electrons flow from ZnO into WSe₂, and the depletion region in ZnO becomes narrower, resulting in a high Id. When a smaller Vtg is applied, the depletion region becomes wider to decrease the photocurrent. A high responsivity of 4.83 × 10⁴ A/W with a gain of ~10⁴ and a fast response time of ~10 μs was reached at the same state in this device. In addition, the photodetectors based on 1D/1D heterostructures of ZnO/WS₂ core/shell nanowires were also reported with fast responsivity and UV–vis–NIR broadband photodetection. In short, such wide-bandgap materials can be used to expand the detection range of TMD-based photodetectors, which are expected to be applied in the detection of UV light, through the formation of the built-in electric field in the heterostructure to facilitate carrier separation.

4. Summary and Outlook

In summary, the energy band structure of hybrid materials plays a critical role in the generation and transport of photocarriers in optoelectronic devices. In this article, we have reviewed the most recent state-of-the-art researches on the band alignment engineering of 2D TMD-based heterostructures for advanced photodetectors (Table 1). The studies on the building strategies...
and charge-transfer mechanism of the band structures reveal the fundamental photoelectric conversion process and further provide theoretical support for the performance improvement of the device as well as the future practical development of novel photodetectors. In this section, we will summarize the critical advantages and limitations of the current energy band construction strategies and prospect the future development direction.

For heterostructures of TMDs and zero-bandgap materials, a typical Schottky barrier will form due to the difference of work function. In this type of band structure, charges are generated by incident light and separated by the built-in potential. The applied bias is used to modulate the barrier height to suppress dark current and achieve photocurrent enhancement. As a typical example, it has been proved that graphene can broaden the detection range in the graphene–TMD heterostructure photodetectors. For TMD narrow-bandgap semiconductor heterostructures, the binding materials such as BP and AsP exhibit significant light absorption in the infrared region and usually sever as the light function.

Figure 14. Photodetectors based on heterostructures of TMDs and wide-bandgap materials. a) Schematic illustrating a ZnS–MoS$_2$ heterojunction photodetector. b) SEM image of the ZnS–MoS$_2$ heterostructure. c) Temporal response of ZnS–MoS$_2$ toward UV, visible, and IR, respectively. Reproduced with permission.[165] Copyright 2017, Wiley-VCH. d) Schematic diagram of a WSe$_2$–ZnO photodetector on a flexible substrate. e) Optical image of the flexible photodetector under tensile strain. Inset: an individual flexible photodetector. f) Time-resolved photoresponse of the WSe$_2$–ZnO photodetector under different strains. Reproduced with permission.[166] Copyright 2019, Elsevier Ltd. g) Schematic illustration of a ZnO–WSe$_2$ heterojunction photodiode. h) Temporal photocurrent characteristics under periodic red (620 nm) and NIR (950 nm) illumination. i) Original image made from an overhead projector film and corresponding image acquired with a blue (470 nm) illumination. Reproduced with permission.[167] Copyright 2017, Wiley-VCH.
active layer to extend the response range of the photodetectors. Moreover, other narrow-bandgap QDs (e.g., PbS, PbSe) are also very suitable for band structure modulation due to their size-tunable semiconductor properties. The third type of the band structure we summarized is built by TMDs and middle-bandgap semiconductors such as TMDs, III–VI, and IV–III chalcogenides and the new-rising perovskite materials. Very interestingly, a series of p–n, n–n, p–p junctions have been fabricated with this type of band alignment with the purpose of decreasing the response time and meanwhile broadening the detection range. Finally, wide-bandgap semiconductors such as ZnS and ZnO are also considered as promising candidates to combine with TMDs, enabling their potential application in the detection of high-energy UV light. Particularly, it is worth mentioning that ZnO is easy to be prepared in nanowire or nanobelt geometries, showing good stability and flexibility, which further enables their advanced applications in future flexible and imaging devices.

With the summarization and understanding of the band alignment strategies and the related charge-transfer mechanism as shown in Table 2, we further prospect the potential directions for the design and construction of new 2D TMD-based heterostructures for next-generation photodetectors. First, nowadays, an abundance of heterojunctions is mainly constructed by the polymer-based mechanical transfer method, difficult to avoid interface contamination; as a result, the charge transport at the interface will be severely restrained. To solve this issue, the development of in situ or single-step fabrication techniques as well as the further surface and interface clean approach are required to optimize the photocarrier generation and separation efficiency. Second, we have noted that the light absorption based on atomically thin TMD materials is limited. The combination of TMDs with noble metal nanoparticles and colloid QDs can significantly improve their light–matter interactions and thus increase the optical absorption. However, the inevitable interface contamination issues are still remaining. With this regard, the in situ growth of curved TMD layers on these nanostructures holds great potential for providing a super-sharp interface. However, the studies under this topic are very limited and may require significant exploration. Third, the spintronic and valleytronic properties of TMDs are unique and have recently drawn great attention. Although the photo-induced charge generation and transfer behaviors of TMD-based heterostructures have been

Table 1. Summarization of photodetector performance of TMD heterostructures built by different band-alignment strategies.

| Type                        | Heterostructures | Wavelength | Responsivity [A W⁻¹] | D [Jones] | Rise/decay time | EQE [%] | Ref. |
|-----------------------------|------------------|------------|----------------------|----------|-----------------|---------|------|
| TMDs with zero-bandgap materials | WSe₂/Gr         | Vis–NIR    | 2056                 | –        | –               | –       | [64] |
|                             | MoTe₂/Gr        | Vis–infrared | 970.82 (1064 nm)  | 1.55 × 10⁻¹² | 78/– ms     | –       | [57] |
|                             | Res₂/Gr         | –          | 7 × 10⁻¹³           | 1.9 × 10⁻¹⁴ | <30/– ms   | 1.7 × 10⁻⁵ | [70] |
|                             | WS₂/Gr          | –          | 6.4                 | –        | 10/20 ms      | –       | [62] |
|                             | Gr/h-BN/MoS₂   | 532 nm     | 0.36                | 6.7 × 10⁻¹⁰ | –             | >80     | [58] |
| h-BN/MoS₂/Gr/SnSe₂/h-BN     | 405–1550 nm     | 2600       | 10⁻¹⁵               | 17.6/72.3 ms | –       | [78] |
|                             | Gr/MoTe₂/Gr     | Vis–NIR    | 205                 | –        | 24/46 μs      | ≈12.9   | [66] |
|                             | MoSe₂/Gr/WSe₂  | Vis–SWIR   | 10⁻⁶ (vis)          | 10⁻¹² (NIR) | 53.6/30 μs | –       | [79] |
|                             | MoS₂/Gr/MoS₂   | 532–1600 nm | –                | >10⁻¹³ (vis) | 10⁻⁵ (NIR) | –       | [80] |
|                             | In/Gr/WSe₂/Gr | 490–940 nm | 2.6 × 10⁻¹³         | 2.2 × 10⁻¹² | 40/65 μs   | –       | [76] |
|                             | Au@MoS₂        | 600–750 nm | 22.3                | –        | <20/– ms      | –       | [84] |
|                             | 1L-MoS₂/Ag NW   | –          | 59.60               | 4.51 × 10⁻¹⁰ | –       | –       | [83] |
| TMDs with narrow-bandgap semiconductors | MoS₂/BP        | –          | 0.0015 (1550 nm)  | 2.13 × 10⁻⁹ | 0.015/– s  | –       | [112] |
|                             | BP/WSe₂        | Vis–infrared | ≈10⁻⁴ (vis) | 10⁻⁴⁴ (vis) | 10⁻¹⁵ (infrared) | –       | [94] |
|                             | MoS₂/BP        | 1.3–4.5 μm | –                   | 1.1 × 10⁻¹⁰ | 3.7/4 μs    | 35      | [93] |
|                             | AsP/MoS₂       | 2.2–8.2 μm | 4.9 × 10⁻⁵         | 0.54/0.52 ms | –       | [90] |
|                             | BP/ReS₂        | UV         | 4120 (365 nm)       | –        | –               | 71      | [96] |
|                             | MoS₂/PbS       | 400–1500 nm | 6 × 10⁻¹⁰          | –        | 0.33/– ms      | –       | [100] |
|                             | WSe₂/PbS       | 540–1400 nm | 14                 | –        | 153/226 μs    | –       | [101] |
|                             | MoS₂/PbS       | 700–850 nm | 2 × 10⁻¹⁴          | 7 × 10⁻¹³ | 7 ms/0.48 s   | –       | [103] |
|                             | MoS₂/PbS       | –          | 5.4 × 10⁻⁴         | 10⁻¹¹    | 950/– μs      | –       | [88] |
|                             | PbS/MoS₂       | 400–1600 nm | 0.6                | 10⁻⁴      | –               | –       | [104] |
|                             | PbS/TMD        | 2 μm       | 1400               | 10⁻¹²    | 0.03/– s      | –       | [105] |
|                             | MoS₂/HgTe      | 2 μm       | 10⁻⁶               | 10⁻¹⁴    | –               | –       | [107] |
|                             | PdSe₂/MoS₂     | LWIR       | 42.1 (10.6 μm)     | 8.21 × 10⁻⁶ | 74.5/93.1 ms | –       | [110] |
|                             | Sb₂Te₃/MoS₂    | –          | 330                | 10⁻⁵     | 360/– μs      | –       | [111] |
widely studied, their fundamental spintronic and valleytronic properties regarding the special interface band alignment have been barely probed for the heterostructures. The studies on the valleytronics as well as the valleytronic devices may be an interesting and promising research topic in the future. Fourth, the in situ study of the atomic structure of TMD heterostructures using some advanced technologies such as in situ high-resolution TEM is important and very interesting in understanding the band alignment principles and the related charge-transfer mechanism. Finally, it is worth mentioning that the current studies of 2D TMD-based heterostructures are mostly focused on the understanding of band alignment principles and interface charge-transfer mechanism of single transistors or diodes, the development of large-scale growth, and array fabrication technologies for integrated devices, and chip-based application is difficult and has very little exploration. Thus, the fundamental application of the band alignment strategies and the related photogeneration principles to the massive integrated devices are greatly essential to realize the practical development of TMD-based heterostructures.

Table 1. Continued.

| Type                        | Heterostructures       | Wavelength      | Responsivity [A W⁻¹] | D [Jones]       | Rise/decay time | EQE [%] | Ref. |
|-----------------------------|------------------------|-----------------|----------------------|----------------|-----------------|--------|-----|
| TMDs with middle-bandgap    |                        |                 |                      |                |                 |        |     |
| semiconductors              |                        |                 |                      |                |                 |        |     |
| MoS₂/WS₃                   | 457–671 nm             | 6.72 × 10⁻³     | 3.09 × 10⁻¹³         | 39/47 ms       | –               |        | [117]|
| MoS₂/WSe₂                  | 350–650 nm             | 4.36 × 10⁻³     | 4.36 × 10⁻¹³         | ≈4/– ms        | –               |        | [118]|
| WSe₂/MoS₂                  | 580–840 nm             | 0.285           | –                    | –              | 7.50            |        | [120]|
| WSe₂/MoSe₂                 | –                      | 5.39 (405 nm)   | –                    | 16/– ms        | –               |        | [122]|
| MoTe₂/MoS₂                 | –                      | 46              | –                    | 0.06/– ms      | –               |        | [113]|
| MoTe₂/MoSe₂                | UV–vis–IR              | 4.71 (1100 nm)  | –                    | –              | –               |        | [112]|
| MoTe₂/MoSe₂                | –                      | 1.39 × 10⁻⁴     | 1.42 × 10⁻¹²         | 0.98/1.1 ms    | –               |        | [114]|
| MoS₂                       | Vis–NIR                | 2.67 × 10⁻³     | –                    | 1.5/2.5 ms     | –               |        | [127]|
| PtS₂/PtSe₂                 | 405–2200 nm            | 0.188           | –                    | 66/75 ms       | 1.2             |        | [171]|
| Gr/MoS₂/WS₂                | 400–1550 nm            | 6.6 × 10⁻⁷      | –                    | 7/– ms         | –               |        | [172]|
| ReS₂/ReSe₂                 | –                      | 6.78 × 10⁻⁶ (405 nm), 1.58 × 10⁻¹ (1310 nm) | – | 4/12 ms | – | [125]|
| GaTe/MoS₂                  | –                      | 1.365           | –                    | <10/– ms       | 266             | [46]   |     |
| GaSe/MoSe₂                 | 400–800 nm             | 0.03            | –                    | –              | –               |        | [128]|
| GaSe/MoS₂                  | 550–800 nm             | –               | –                    | 80/20 ms       | –               |        | [129]|
| GaSe/WS₂                   | UV–vis                | ≈149            | –                    | 37/43 µs       | –               |        | [130]|
| Gr/InSe/MoS₂               | –                      | 0.11 (332 nm)   | 1.08 × 10⁻¹²         | <1/– ms        | 25.65           |        | [173]|
| β-In₃Se₂/MoS₂              | Vis–NIR                | 4.47            | 1.07 × 10⁻⁷          | 51/159 ms      | –               |        | [49]  |
| SnSe₂/MoS₂                 | –                      | 9.1 × 10⁻⁶      | –                    | –              | –               |        | [132]|
| WSe₂/Se₂                  | Vis–infrared           | 588 (532 nm)    | 80 (1550 nm)         | 4.4 × 10⁻¹⁰ (532 nm) | 1.4 × 10⁻¹⁰ (1550 nm) | – | [51]  |
| WSe₂/CH₃NH₃PbI₃           | –                      | ≈950            | –                    | 22/37 ms       | –               |        | [147]|
| WSe₂/CH₃NH₃PbI₃           | –                      | 17              | ≈10¹²               | 2.7/7.5 ms     | –               |        | [147]|
| WSe₂/CH₃NH₃PbI₃           | –                      | 110             | 2.2 × 10¹¹           | 2.5 × 10⁰      | –               |        | [146]|
| MoS₂/CH₃NH₃PbI₃           | –                      | 68.11           | –                    | 205/206 ms     | –               |        | [145]|
| WS₂/CH₃NH₃PbI₃            | –                      | 0.0767          | 3.4 × 10⁹            | 13.5/8.7 ms    | –               |        | [149]|
| CH₃NH₃PbI₃/CdS            | –                      | 0.43            | 2.3 × 10¹¹           | 3.2/9.6 ms     | –               |        | [150]|
| (CH₃NH₃)₃PbI₃/CdS/WS₂      | 600–800 nm             | 1117.4          | –                    | 64/– µs        | –               |        | [148]|
| CsPbI₃Br₃/MoS₂            | –                      | 7.7 × 10⁻⁶      | 5.6 × 10⁻¹¹          | –              | 10²             |        | [54]  |
| CsI₃Br₃/MoS₂              | –                      | 1.13 × 10⁵      | –                    | 0.42/0.19 ms   | –               |        | [155]|
| (PEA)₂SnI₃/MoS₂           | –                      | 5.5 × 10⁻⁶      | 1.95 × 10⁻¹²         | –              | –               |        | [140]|
| WS₂/CsPbI₃Br₃             | –                      | 57.2            | 1.36 × 10¹⁴          | 2/– ms         | 157             |        | [157]|
| (PEA)₂SnI₃/MoS₂           | –                      | 1100            | 8.09 × 10⁵           | 34/38 ms       | 38.2            |        | [52]  |
| TMDs with wide-bandgap     |                        |                 |                      |                |                 |        |     |
| semiconductors              |                        |                 |                      |                |                 |        |     |
| ZnS/MoS₂                   | UV–vis–IR              | 9.4 × 10⁻⁶ (UV) | –                    | 22/– s         | 0.4 × 10⁻²      | [165] |
| ZnO/WSe₂                   | –                      | 0.117–0.394     | –                    | –              | –               | [166] |
| ZnO/WS₂                    | –                      | 2.25            | –                    | 21/95 ms       | 5.2             | [169] |     |
Table 2. Summarization of advantages and disadvantages of various types of heterostructures.

| Types of heterostructures | Advantages                                                                 | Disadvantages                                                                 |
|----------------------------|---------------------------------------------------------------------------|-------------------------------------------------------------------------------|
| TMDs and zero-bandgap materials | 1) Enhanced optical absorption;                                            | 1) The adjustability through electric field is limited;                        |
|                             | 2) Prompted carrier separation by the built-in potential;                  | 2) Spectrum detection range is dominated by TMD;                              |
|                             | 3) Tunable Schottky barrier height.                                        | 3) Light absorption efficiency of the zero-bandgap materials is relatively low.|
| TMDs and narrow-bandgap semiconductors | 1) Improved responsivity due to the enhanced optical absorption;          | 1) The intrinsic photocconductivity is poor and the response speed is slow;   |
|                             | 2) Prompted carrier separation by the built-in potential;                  | 2) Large dark current resulted from the relatively high conductivity of narrow-bandgap materials. |
|                             | 3) Expand detection range up to NIR and MIR.                              |                                                                               |
| TMDs and middle-bandgap semiconductors | 1) Accelerated carrier transportation;                                     | 1) The charge transitions between layers are mostly indirect transitions with weak response to infrared; |
|                             | 2) Low dark current and fast response rate;                               | 2) Low EQE due to the limited internal gain.                                   |
|                             | 3) Expanded detection range due to the interlayer exciton transition.      |                                                                               |
| TMDs and wide-bandgap semiconductors | 1) Enhanced carrier separation due to the built-in potential;            | 1) Low responsivity due to large barriers to carrier transmission;             |
|                             | 2) Expanded detection range down to UV;                                   | 2) Limited detection range.                                                   |
|                             | 3) Low dark current due to large contact barrier between bands.           |                                                                               |

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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