1. Introduction

Optoelectronic devices, transforming light to information or energy, are the basic elements of the modern information-processing system. The photoelectric processing includes series of comprehensive physical phenomena: light absorption, carrier excitation, hot-carrier relaxation, charge transfer, recombination, and so on. These processes may happen at the same time or be followed by others. Observing the photoelectric phenomena is an essential strategy to investigate the inherent properties of materials. Based on these photoelectric effects, many applications have arisen, such as solar cells, photodetectors, light-emitting devices, and so forth. For these applications, the traditional semiconductor materials, such as Si, Ge, and GaAs have dominated for more than fifty years. However, slow photoresponse and high dark current are also attained at room temperature. The junctions based on 2D materials are expected to constitute the ultimate functional elements of nanoscale electronic and optoelectronic applications.

Van der Waals heterostructures based on 2D layered materials have received wide attention for their multiple applications in optoelectronic devices, such as solar cells, light-emitting devices, and photodiodes. In this work, high-performance photovoltaic photodetectors based on MoTe2/MoS2 vertical heterojunctions are demonstrated by exfoliating-restacking approach. The fundamental electric properties and band structures of the junction are revealed and analyzed. It is shown that this kind of photodetectors can operate under zero bias with high on/off ratio (>10^5) and ultralow dark current (~3 pA). Moreover, a fast response time of 60 μs and high photoresponsivity of 46 mA W^-1 are also attained at room temperature. The junctions based on 2D materials are expected to constitute the ultimate functional elements of nanoscale electronic and optoelectronic applications.

First, layered materials restrict carriers to move only in two directions, simplifying the study model for exploring carrier transport at the nanoscale. Furthermore, thickness-dependent band structures of abundant 2D materials display infinite possibilities to fabricate heterostructures with various bandgap combination. More importantly, the van der Waals heterostructures (vdWHs) based on 2D materials can be assembled by any kinds of materials without considering their lattice mismatch, which is an obstacle in 3D crystalline heterostructure fabrication. 2D vdWHs are usually fabricated by the exfoliating–restacking approach, which is a little complicated but exists no restrictions in fabricating heterostructures with any kinds of materials in atomic scale. Some researchers tried to synthesize lateral heterostructures by chemical vapor deposition and have made great progresses. Numerous novel phenomenon and properties of 2D vdWHs, such as negative differential conductance, ultrastable transport, interlayer excitons, ballistic transport, high photoresponse and high external quantum efficiency up to 12%, have been discovered in recent years. Based on different band structure alignments, all heterostructures are classified into three types: straddling gap (type I), staggered (type II), and broken gap (type III). Hereinto, type II heterostructures are superior candidates for optoelectronic devices. They have outstanding performance compared with those devices fabricated by homogeneous 2D materials. Du and co-workers have reported that WSe2/MoS2 p–n diodes show rapid photoresponse and high external quantum efficiency up to 12%, and Kim et al. fabricated the same atomically thin p–n junctions, showing gate-tunable photovoltaic response. The optoelectronic properties of vdWHs are also found to be configuration-dependent. These type II band alignment heterostructures show promising potentials in photodetectors and solar cells. However, the carrier transport and light–matter reactions in vdWHs are demonstrated not exactly the same as the processes in bulk heterostructures. More efforts should be made to investigate the underlying mechanisms of the light-induced microscopic process.

Here, we fabricated type II heterostructures based on MoS2 and MoTe2 because of their stable, outstanding electrical and optical performances. The heterostructures exhibit obvious rectification characteristic. The designed heterostructures shows ultra-sensitive bias-dependent photoresponse without gate modulation. Due to the strong interlayer built-in field, the
dark current is extremely low (pA) in this structure and light induced switching on/off ratio is larger than $10^5$ at zero bias. Importantly, the photosresponse of this device is very fast ($60 \mu s$ rise and $25 \mu s$ decay). Additionally, the unique photogenerated carrier transport in atomic heterostructures has been discussed in detail.

2. Results and Discussion

We prepared the 2D vdWHSs by mechanical exfoliation and targeted transferring technique (see more details in the Experimental Section). The optical image of the MoTe$_2$ and MoS$_2$ heterostructure device is shown in Figure 1a. The thicknesses of MoTe$_2$ and MoS$_2$ are confirmed by atomic force microscope (AFM), as shown in Figure 1b. From the green and blue line scan profiles, the thickness of MoS$_2$ is estimated to be 7 nm (about 10 layers) and MoTe$_2$ to be 3.3 nm (about 4 layers), respectively. 3D schematic view of the MoTe$_2$ and MoS$_2$ heterostructure device is exhibited in Figure 1c. Because MoTe$_2$ has a smaller bandgap, we put it on the top of MoS$_2$ based on the consideration of better light absorption. High work function metal Pd was deposited on the ambipolar MoTe$_2$ to make holes transport easily, which is an efficient way to engineer MoTe$_2$ as p-type.$^{[32]}$ On the MoS$_2$ side, Cr/Au was employed to ensure a good semiconductor–metal contact. Figure 1d shows the Raman spectra of multilayer MoTe$_2$ and MoS$_2$ nanoflakes as well as the overlapped heterostructures. Two peaks appear at 384.98 and 407.48 cm$^{-1}$ in Raman spectra of MoS$_2$ (the navy line), representing in-plane vibration mode (E$_{12g}$) and out-of-plane vibration mode (A$_{1g}$), respectively.$^{[33]}$ The red line represents the data for MoTe$_2$, in which three peaks are observed at 171.85 cm$^{-1}$ (out-of-plane mode A$_{1g}$), 234.85 (in-plane mode E$_{12g}$), and 291.23 cm$^{-1}$ (bulk in-active phonon mode B$_{2g}$).$^{[34]}$ All these peaks are appeared in Raman spectrum of the overlapped heterostructure region (black line), evidencing good formation of a van der Waals heterostructure.

The bandgap diagrams of MoTe$_2$ and MoS$_2$ (i) before contact and (ii) after contact are displayed in Figure 2a. The bottom of conduction band and the top of valence band of MoTe$_2$ (MoS$_2$) are approximately $-3.8$ eV ($-4.2$ eV) and $-4.8$ eV ($-5.4$ eV). So the offsets of conduction band and valence band, fixed values once the heterostructure formed, are about 0.4 and 0.6 eV, respectively. Thus, a type II (staggered) heterostructure is formed and an equilibrium is reached, which means a state that diffusion current and drift current are equal and flows opposite. The electrical measurements schematic of the MoTe$_2$/MoS$_2$ heterostructure device is shown in Figure 2b. Current–voltage (I–V) characteristic is shown in Figure 2c, indicating a rectification property and the inset exhibits it on a logarithmic scale. The I$_{sd}$ and V$_{sd}$ represent source–drain current and voltage, respectively. The rectification factor RF ($RF = |I_{forward}|/|I_{reverse}|$) is about 80 at $|V_{sd}| = 1$ V. Although our devices showed better reification behavior than most heterojunctions that have been reported,$^{[24,35]}$ the voltage–current relationship still does not perfectly fit the ideal I–V curves for p–n

![Figure 1. Device structure and basic properties of MoTe$_2$/MoS$_2$ heterostructures. a) Optical image of the MoTe$_2$/MoS$_2$ heterostructure device, scale bar 5 µm. b) The thicknesses of MoTe$_2$ and MoS$_2$ nanoflakes measured by AFM. c) Schematic diagram of the MoTe$_2$/MoS$_2$ van der Waals heterostructure. d) Raman spectra of the multilayer MoS$_2$, MoTe$_2$, and their overlapped heterostructures.](image-url)
junctitions. To find the inner reason for this, brief sketches of the carrier transport at forward bias and reverse bias are depicted in Figure 2d,e. When a forward bias is applied, which is opposite to the built-in electrical field, the junction no longer maintains in an equilibrium state 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. On the contrary, if a negative voltage is applied to the MoTe$_2$ with respect to the MoS$_2$, the potential barrier will increase. The increased built-in field accelerates the transport speed of minority carriers, generating small drift current. This is a common question in junctions based on 2D materials. The possible related factors are as follows: surface effect, generation current in barrier zone, high-level injection, and series resistance effect. Of all these possible reasons, generation current in barrier zone may take the most of responsibilities in this case. In the condition of thermal equilibrium, the rate of carrier generation equals to recombination by recombination centers in space charge region. When applied a reverse bias, the strengthened built-in field repels electron–hole pairs apart too quick to recombine, causing a net generation rate. For junctions based on 2D materials, the width of space charge region is exactly the thickness of the junction because the required depletion width is larger than the thickness of 2D vdWHs. Consequently, the reverse bias strengthened the electrical field rather than broaden the space charge region. This process makes the electron–hole pairs separate more quickly than that in bulk materials and the generation rate is much higher than recombination rate, resulting in an extra reverse current.

We performed time-resolved photoswitching experiments at different biases to investigate a best working condition of MoS$_2$/MoTe$_2$ photodetectors as shown in Figure 3a–c, respectively. All the measurements were under the illumination of 637 nm laser with light power of 5.46 µW and chopping frequency of 0.5 Hz.

As shown in Figure 3a, under reverse bias voltages, the dark current increases with bias from $-0.1$ to $-5$ V but the photocurrent increases nonsignificantly, trending to a saturation state. However, at the equilibrium state (shown in Figure 3b), the photocurrent on/off ratio is up to 10$^3$. When applied a forward bias, photocurrent becomes complex as shown in Figure 3c. At 0 V $<$V$_{sd}$ $<$ 0.2 V, the device exhibits fast and positive photoreponse but deteriorates with the V$_{sd}$. The light-induced current on/off ratio ranges from 10$^2$ to 10. When the V$_{sd}$ increases to 0.3–0.4 V, the light-induced current turns negative compared to dark current, leading to a drop of total current. Continuously increasing the bias higher than 0.5 V, the photosresponse turns positive effect again but shows a small on/off ratio and slow response. Figure 3d displays the output characteristic curves under dark and 637 nm illumination. In logarithmic coordinates, it is clearly shown that photocurrent is smaller than dark current at bias between 0.25 and 0.5 V, which is in accordance with time-resolved negative photoreponse in Figure 3c. From the inset, we can perceive that the open-circuit voltage (V$_{oc}$) and short-circuit current (I$_{sc}$) are 0.51 V and 1.09 µA, separately. These two fundamental factors are essential to assess the performances of photovoltaic solar cells and they are both larger than those previously reported in lateral or vertical heterojunctions. Moreover, the current under illumination does not show a rectification characteristic any more, which means the photocurrent under reverse bias is comparable to that under forward bias. In other words, the p–n junction is under the saturated light absorption state and V$_{oc}$ can be considered as the difference between Fermi levels of MoTe$_2$ and MoS$_2$. For a more intuitive understanding, the cross-section diagram of the heterojunction and its corresponding bandgap structure are depicted in Figure 3e. As discussed above, the width of space depletion region (W) can be considered as the total thickness of the overlapped region. The built-in field direction is from n-type MoS$_2$ to p-type MoTe$_2$. Figure 3f reveals the light-induced carrier...
transport in the p–n junction under different biases. Under the illumination of 637 nm laser, a wavelength that both MoTe2 and MoS2 can absorb, electron–hole pairs are generated in the junction and swept by built-in field, forming a reversed photocurrent $I_L$. Under short-circuit state ($V_{sd} = 0$ V), current flowed in the p–n junction is only made of light-induced current $I_L$, which is equal to $I_{sc}$. Under this circumstance, the photocurrent on/off ratio is up to $10^5$ and the dark current is extremely low (3 pA). To our best knowledge, other vdWHs photodetectors cannot achieve comparable performance even applied a bias or tuned by gate. Comparing many factors of similar photodetectors, the appropriate thickness may contribute to this merit. Photodetectors based on monolayer 2D semiconductor are unable to withstand high on-current whereas large dark current may emerge when using the too thick materials. The accurate value of the thickness depends on the depletion width of the junction. The measurement or calculation of the width is still inconvenient because it is sensitive to charge density, especially in 2D semiconductors. When a negative bias is applied, the external field and built-in field are in the same direction, under a combined action of which minorities in p and n regions flow to the other side. In that case, the total current is the sum of photocurrent and dark reversed current. It is recognized that the photoinduced field is in the opposite direction to the built-in field. When applied a forward bias which is smaller than the open-circuit voltage (0.51 V), the effect of total electrical field is equal to a small reversed bias and creates a reversed current. When $V_{sd}$ is increased larger than 0.51 V, photocurrent does not flow reversely anymore because the built-in field is covered by forward bias. We can conclude that the p–n junction is a self-powered photodetector and it can operate with high performances at zero bias and without gate tuning. Moreover, we can change its operating mode by applying a small bias.

Systematically studies of the photoelectric performances of MoTe2/MoS2 photodetectors are shown in Figure 4. The response time is one of the most significant parameters for photodetectors. In Figure 4a, our device shows 60 µs rising edge ($\tau_r$) and 25 µs fall edge ($\tau_f$), which is better than most of the reported devices. Comparing many factors of similar photodetectors, the appropriate thickness may contribute to this merit. Photodetectors based on monolayer 2D semiconductor are unable to withstand high on-current whereas large dark current may emerge when using the too thick materials. The accurate value of the thickness depends on the depletion width of the junction. The measurement or calculation of the width is still inconvenient because it is sensitive to charge density, especially in 2D semiconductors. When a negative bias is applied, the external field and built-in field are in the same direction, under a combined action of which minorities in p and n regions flow to the other side. In that case, the total current is the sum of photocurrent and dark reversed current. It is recognized that the photoinduced field is in the opposite direction to the built-in field. When applied a forward bias which is smaller than the open-circuit voltage (0.51 V), the effect of total electrical field is equal to a small reversed bias and creates a reversed current. When $V_{sd}$ is increased larger than 0.51 V, photocurrent does not flow reversely anymore because the built-in field is covered by forward bias. We can conclude that the p–n junction is a self-powered photodetector and it can operate with high performances at zero bias and without gate tuning. Moreover, we can change its operating mode by applying a small bias.

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interlayer recombination by vertical. This leads to recombination time (fall time) is faster than photocurrent collection time (rise time). In general, the rapid photoresponse suggests the intrinsic response of the p–n junction. Most van der Waals p–n junctions exhibit nonideal performances, such as slow photoresponse or small RF, which are always due to the existence of Schottky barrier. The real-time photocurrent mapping technique is an effective approach to identify the dominant part of the vdWHs photodetectors. A focused laser beam with an extremely small diameter scans the sample with a uniform speed. When the laser spot irradiated on a part of the heterostructure, photocurrent is generated and recorded by oscilloscope. As shown in Figure 4b, photocurrent mapping of the junction was performed under 637 nm illumination ($V_{sd} = 0$ V) and the laser beam was focused on the device with a spot diameter of $\approx 2 \mu$m. Compared to the optical image of this junction, the highlight part, which means strong photoresponsivity, is exactly the place where MoS$_2$ and MoTe$_2$ overlapped. The phenomena were observed when $V_{sd} < 0$ V as well. It is a clear indication that the p–n junction is well formed by MoS$_2$ and MoTe$_2$ and light-induced carrier spontaneous separation occurs at the junction. To sum up, we can conclude that the photocurrent is generated in the space charge region when $V_{sd} \leq 0$ V, from where we can confirm that a good quality of vertical p–n junctions was constructed by stacking MoS$_2$ and MoTe$_2$ vdWHs. But when it comes to 1 V (or a bias higher than 0.51 eV), as shown in Figure S1a (Supporting Information), the response area is changed. Only a small region between MoS$_2$ and its electrode shows response to the illumination of 637 nm. The photocurrent is completely generated from the contact. And the corresponding dynamic response characteristic is showed in Figure S1b (Supporting Information). The response time is about 130 $\mu$s, much larger than the rise time at $V_{sd} \leq 0$ V.

The dependence of photocurrent and photoresponsivity with power of incident 637 nm laser is displayed in Figure 4c. Photocurrent $I_{ph}$ is calculated by the equation: $I_{ph} = I_{illum} - I_{dark}$ and photoresponsivity is defined as $R = I_{ph}/P$, in which $P$ is the irradiated laser power on the junction. The relationship between photocurrent and laser power obeys a power law $I_{ph} = P^\alpha$, where $\alpha$ is calculated by exponential fitting to be 0.701. The nonunity value reflects that traps play a role in electron–hole generation and recombination processes in the p–n junctions.\[42\] The responsivity of a photodetector is defined as $R = I_{ph}/P = P^{1-\alpha}$. So, it decreases with the power of incident illumination increasing. The responsivity of the p–n junction is calculated to be 43.6 mA W$^{-1}$ under the illumination of 637 nm laser with intensity of 2.43 nW, detectivity ($D^*$), as the figure of merit of a detector, is defined by the equation, $D^* = R S^{1/2}/(2eI_{dark})^{1/2}$, where $R$ is the responsivity, $S$ is the active area of detector, $e$ is the electron charge, and $I_{dark}$ is the dark current. This device achieved the detectivity of $1.06 \times 10^8$ Jones under the illumination of 637 nm laser with intensity of 2.43 nW at $V_{sd} = 0$ V. Figure 4d shows the spectral photoresponse from 500 to 1550 nm wavelength under the light of wavelength from 550 to 1550 nm ($V_{sd} = 0$ V, $P = 100 \mu$W).
to the photocurrent. The device shows a cutoff wavelength detecting near 1500 nm. The photothermaloelectric effect can be excluded for its no wavelength selectivity.

The comparisons of figure-of-merit with the related photodetectors are displayed in Table 1, which the open-circuit voltage, short-circuit current, response time, and responsivity are included. For fairly comparing, the material thickness, wavelength of illumination, and gate voltage are also listed. It is obvious that the devices we fabricated exhibit fast response and considerable responsivity in an energy-efficient way.

### Table 1. Comparisons of the figure of merits of photodetectors on related materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness [nm]</th>
<th>( \Lambda ) [nm]</th>
<th>( V_{oc} ) [V], ( I_{sc} ) [A]</th>
<th>( r ) [ms]</th>
<th>( R ) [mA W(^{-1})]</th>
<th>( V_{g} ) [V]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoTe(_2)/MoS(_2)</td>
<td>3.3/7</td>
<td>637</td>
<td>0.51, 1.09( \mu )</td>
<td>0.06</td>
<td>46</td>
<td>0</td>
<td>This work</td>
</tr>
<tr>
<td>MoTe(_2)</td>
<td>3.4</td>
<td>1060</td>
<td>–</td>
<td>1.4</td>
<td>16.4</td>
<td>0</td>
<td>[30]</td>
</tr>
<tr>
<td>MoS(_2)</td>
<td>0.8</td>
<td>550</td>
<td>–</td>
<td>50</td>
<td>7.5</td>
<td>50</td>
<td>[28]</td>
</tr>
<tr>
<td>MoTe(_2)/MoS(_2)</td>
<td>1.5/3.8</td>
<td>473</td>
<td>0.17, 0.6( \mu )</td>
<td>385</td>
<td>64</td>
<td>80</td>
<td>[24]</td>
</tr>
<tr>
<td>WSe(_2) p–n</td>
<td>0.8</td>
<td>–</td>
<td>0.8, 5( \mu )</td>
<td>–</td>
<td>16</td>
<td>40, –40</td>
<td>[40]</td>
</tr>
<tr>
<td>WSe(_2) p–n</td>
<td>0.8</td>
<td>640</td>
<td>0.7, 0.4( \mu )</td>
<td>10</td>
<td>0.24</td>
<td>–50</td>
<td>[37]</td>
</tr>
<tr>
<td>WSe(_2)/MoS(_2)</td>
<td>1.6/0.8</td>
<td>514</td>
<td>0.27, 0.22( \mu )</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>[38]</td>
</tr>
</tbody>
</table>

3. Conclusion

In conclusion, we have fabricated MoTe\(_2\)/MoS\(_2\) heterostructures stacked by van der Waals force. This heterostructure exhibited good rectification characteristic like p–n junction. The photoresponse under different biases was measured and the corresponding light-induced charge transport was discussed. As a self-powered photodetector, our vertical 2D p–n junctions can achieve fast response and broad detection wavelength range. Furthermore, we can change its operating mode by applying a small bias. These outstanding properties indicate that 2D van der Waals junctions possess promising applications in photodetection, on-chip logic circuits, and related applications.

4. Experimental Section

**Device Fabrication:** The heterostructure devices were fabricated by exfoliation and restacking techniques. MoS\(_2\) (supplied by SPI) nanosheets were exfoliated by Scotch tape and transferred to 285 nm SiO\(_2\)/Si substrates after the substrates were cleaned by acetone, isopropanol alcohol, and deionized water and then treated by oxygen plasma. The MoTe\(_2\) (supplied by HQ Graphene) flakes were exfoliated by polydimethylsiloxane and transferred onto desired MoS\(_2\) by dry transfer method. This procedure completes the assembly of MoTe\(_2\)/MoS\(_2\) flakes. The electrodes were patterned by electron beam lithography. Then, 10 nm Pd and 50 nm Au (Pd/Au) were deposited on MoTe\(_2\) and 10 nm Cr and 50 nm Au (Cr/Au) on MoS\(_2\) by thermal evaporation. After lift-off process, the devices were annealed at 200 °C for 2 h in argon atmosphere to remove the residual organics and make better contact between semiconductor and metal.

**Electrical and Photoelectrical Measurement:** The morphology structures were characterized by optical microscope and AFM equipment. The Raman spectra were performed by Lab Ram HR800 from HORIBA with a 532 nm excitation laser. All the electrical measurements of the MoTe\(_2\)/MoS\(_2\) heterostructure devices were performed by Agilent B2912A. The data of respond time were acquired from a high-speed Tektronix MDO3014 oscilloscope. The photoelectrical properties were measured under 637 nm laser beam with a diameter about 100 \( \mu \)m to ensure a uniform power intensity on the device. The area of the p–n junction is about 20 \( \mu \)m\(^2\). All the data is acquired from one device except data in Figure 4c,d is supplemented by a similar device.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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### Conflict of Interest

The authors declare no conflict of interest.

### Keywords

2D materials, photodetectors, van der Waals heterostructures

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