Ultrafast Photocurrent Response and High Detectivity in Two-Dimensional MoSe₂-based Heterojunctions


ABSTRACT: Two-dimensional (2D) transition metal dichalcogenide (TMDC) materials have garnered great attention on account of their novel properties and potential to advance modern technology. Recent studies have demonstrated that TMDCs can be utilized to create high-performing heterostructures with combined functionality of the individual layers and new phenomena at these interfaces. Here, we report an ultrafast photoresponse within MoSe₂-based heterostructures in which heavily p-doped WSe₂ and MoS₂ flakes share an undoped MoSe₂ channel, allowing us to directly compare the optoelectronic properties of MoSe₂-based heterojunctions with different 2D materials. Strong photocurrent signals have been observed in both MoSe₂−WSe₂ and MoSe₂−MoS₂ heterojunctions with a photoresponse time constant of ∼16 μs, surmounting previous MoSe₂-based devices by three orders of magnitude. Further studies have shown that the fast response is independent of the integrated 2D materials (WSe₂ or MoS₂) but is likely attributed to the high carrier mobility of 260 cm² V⁻¹ s⁻¹ in the undoped MoSe₂ channel as well as the greatly reduced Schottky barriers and near absence of interface states at MoSe₂−WSe₂/MoS₂ heterojunctions, which lead to reduced carrier transit time and thus short photocurrent response time. Lastly, a high detectivity on the order of ∼10¹⁴ Jones has been achieved in MoSe₂-based heterojunctions, which supersedes current industry standards. These fundamental studies not only shed light on photocurrent generation mechanisms in MoSe₂-based heterojunctions but also open up new avenues for engineering future high-performance 2D optoelectronic devices.

KEYWORDS: heterojunction, 2D Materials, MoSe₂, TMDCs, photocurrent

INTRODUCTION

Two-dimensional (2D) van der Waals (vdW) materials have received considerable attention due to their novel electrical, optical, and mechanical properties as well as the ease of heterostructure fabrication of lattice mismatched materials without strain.¹ In particular, transition metal dichalcogenides (TMDCs) have established themselves as an attractive class of 2D materials as they typically feature sizeable band gaps, strong light–matter interactions, and broad spectral responses.² These characteristics naturally facilitate the incorporation of TMDCs into electronic and optoelectronic devices, such as field-effect transistors (FETs),³−⁵ photodetectors,⁶ photovoltaic cells,⁷,⁸ and many other applications.⁹ While some device improvements are achieved through the use of different TMDC channels,¹⁰−¹² other works suggest that 2D heterostructures will also enhance device performance.¹³−¹⁶ Therefore, substantial efforts have been expended in understanding the underlying mechanisms within TMDC heterostructures¹⁷−²² and their commercial synthesis.²³−²⁶ For example, it has been shown that heterostructures consisting of different atomically thin materials like black phosphorus, graphene, and TMDCs can result in devices with improved optoelectronic properties, such as increased mobility and reduced response times while foregoing thermal stability in the former examples.¹⁴,²⁷−²⁹ Moreover, heterostructures formed between heavily doped TMDCs and undoped TMDCs display similar enhancements whilst further reducing Schottky barrier heights, resulting in low-resistance ohmic contacts.³⁰ Such improvements are imperative to attain high-performance optoelectronic devices which allow for the ultrafast movement of information, a highly sought after property of commercial and academic endeavors alike.³¹

Recently, MoSe₂-based devices have become more prominent as their weakly bound excitons result in intrinsically faster response times.³² MoSe₂ holds properties indicative of its value in optoelectronic applications, such as a sizable direct band gap of ∼1.6 eV,⁴,³³ high optical absorption,¹ and carrier mobility reaching 100 cm² V⁻¹ s⁻¹.³⁵ Despite three-dimensional MoSe₂-based heterostructures featuring exceedingly fast response...
times,36 response times of 2D MoSe2-based devices are on the scale of milliseconds,35,37−39 which are significantly slower than those of commercial semiconductors.40 Therefore, it is important to investigate MoSe2-based heterostructures with inherited unique properties from MoSe2 plus the fast photoresponse.

In this work, we report the ultrafast photoresponse in MoSe2−WSe2 and MoSe2−MoS2 heterojunctions, where heavily p-doped MoS2 and WSe2 flakes are bridged by an undoped MoSe2 channel. The fast rise and decay time constants (as low as ∼16 μs) have been achieved in both MoSe2−WSe2 and MoSe2−MoS2 heterojunctions. Further studies have shown that the fast photoresponse likely results from the high carrier mobility (260 cm2 V−1 s−1) as well as negligible Schottky barriers and near absence of interface states at MoSe2−WSe2/MoS2 heterojunctions, which are expected to reduce the carrier transit time and thus the photoresponse time. Moreover, a detectivity of ∼1014 Jones has been observed in MoSe2−WSe2/MoS2 heterojunctions, which are higher than commercial Si- and InGaAs-based photodetectors. Our experimental results offer a way to build ultrafast 2D heterojunctions, opening a door for engineering future high-performance 2D optoelectronics.

■ EXPERIMENTAL SECTION

**Device Fabrication.** MoSe2, heavily p-doped WSe2 (Nb0.005W0.995Se2), heavily p-doped WSe2 (Nb0.005Mo0.995Se2), and hBN flakes were mechanically exfoliated from bulk crystals and transferred via a dry transfer method to a silicon substrate with 280 nm of thermally grown SiO2. The thickness of each material was identified by noncontact mode atomic force microscopy (Park-System XE-70). Electron beam lithography and subsequent deposition of Au/Ti were used to form metal electrodes for the heavily p-doped TMDCs.

**Electrical and Optoelectronic Characterization.** All experiments were performed in a Janis ST-500 microscopy cryostat in a high vacuum environment (∼10−6 Torr). Current signals were collected via a DL instrument 1211 current preamplifier. Scanning photocurrent measurements were executed using an Olympus BX51WI microscope. A linearly polarized continuous wave laser beam (NKT Photonics SuperK Supercontinuum Laser) was expanded and focused with a 40x objective (N.A. = 0.6) into a diffraction-limited spot (∼1 μm) and scanned over the device by a piezo-controlled mirror with nanometer-scale spatial resolution.

■ RESULTS AND DISCUSSION

Figure 1a depicts a schematic diagram of the MoSe2 heterostructure that consists of an undoped MoSe2 channel with two asymmetric contacts of heavily p-doped WSe2 and MoS2 flakes, respectively, which are connected to Au/Ti electrodes. MoSe2 has been selected as a channel material, while other TMDCs with distinct band gaps serve as a basis for the choice of contact materials. This not only sheds light on the photocurrent generation mechanisms in TMDC-based heterojunctions but also provides a way to fabricate fast MoSe2 phototransistors. The device is fabricated on top of a thin flake of hBN to provide a clean substrate and thus to avoid charge traps and surface bonds present on SiO2.41 An optical image of a typical device is presented in Figure 1b, where different materials are outlined with the following color scheme: Au contacts (yellow), hBN (purple), WSe2 (green), MoSe2 (blue), and MoS2 (pink). As shown in Figure S1, the MoS2 and WSe2 flakes were ∼23 nm and ∼16 nm thick, respectively, while the MoSe2 channel and hBN were ∼7 nm and ∼15 nm, respectively. These materials were mechanically exfoliated and transferred.
from bulk crystals, and their thickness was found via atomic force microscopy (AFM). The undoped MoSe2 and the heavily p-doped TMDC heterojunctions were formed via a dry transfer method. Electron beam lithography and deposition of 50/5 nm Au/Ti were subsequently conducted to form the metal electrodes. A dielectric stack made of 280 nm SiO2 and a 15 nm hBN flake facilitates the application of a back-gate voltage to the device. The electrical and optoelectronic properties of this device were investigated under high vacuum (≈10−6 Torr) and at a low temperature (80 K) using a Janis ST-500 microscopy cryostat. Figure 1c shows a p-type behavior of the device, which is due to the two heavily p-doped contacts (WSe2 and MoS2) that only allow the MoSe2 channel to be turned on under a negative gate voltage. The field-effect hole mobilities are extrapolated as ~260 cm2 V−1 s−1 at 80 K and ~70 cm2 V−1 s−1 at room temperature, respectively, which is higher than previous reports of MoSe2 devices.35,42−44 Specifically, the expression used to calculate mobility is

$$\mu_{\text{FET}} = \frac{1}{C_{bg}} \times \frac{L}{W} \times \frac{d\sigma}{dV_{bg}}$$

where $C_{bg}$ is the back-gate capacitance of the 280 nm thick SiO2 in series with a ~15 nm hBN flake. L and W are the length and average width of the channel, respectively, and the derivative is the extrapolated slope of the linear portion of the transfer curve. Figure 1d displays linear and symmetric output characteristics of the MoSe2 heterostructure when a wide range of back-gate voltages were applied at 80 K, indicating ohmic behaviors of the device. This suggests that the 2D/2D contacts allow low contact resistance, and the resistances between heavily p-doped TMDCs and external metal electrodes are negligible due to the tunneling effect through an extremely narrow (on the order of nm) depletion region, leading to high hole mobility of our device.45,54,45

Next, we explore the optoelectronic properties of the MoSe2 heterostructure using spatially resolved scanning photocurrent measurements. The positions of the photocurrent signals ($I_{PC} = I_{\text{white}} − I_{\text{dark}}$) were precisely located by the correlation of the reflection image of the device with its optical image, as depicted by Figure 1e, where the red/blue color represents positive/negative photocurrent. As seen in the aforementioned figure, remarkable photocurrent signals are found at both MoSe2−WSe2 and MoSe2−MoS2 heterojunctions. To further investigate the contrasting characteristics of these heterojunctions, the wavelength-dependent photocurrent measurements were conducted with a focused beam. Here, the device was explored under the drain-source bias of −30 mV and zero bias for MoSe2−WSe2 and MoSe2−MoS2 heterojunctions, respectively. Figure 1f shows a photocurrent peak at ~1.59 eV detected in both heterojunctions, which is likely related to the A exciton energy of few-layer MoSe2.45 This observation indicates that the photocurrent signals mainly result from the optical absorption of the MoSe2 channel under 780 nm illumination. Moreover, a photocurrent peak is observed at ~1.68 eV in the MoSe2−WSe2 heterojunction, which is close to the A exciton energy of WSe2.23,27 This suggests that the p-doped WSe2 flake also contributes to the photocurrent generation at the heterojunctions. Interestingly, a maximum photocurrent signal is found at both heterojunctions for wavelengths with energies surrounding ~1.84 eV, which may be attributed to the B exciton energy of the MoSe2 channel.45,46 We also know that the A exciton energy of few-layer MoS2 occurs in this region of the spectrum (1.8−1.9 eV).50,51 Indeed, the photocurrent intensity of the MoSe2−MoS2 heterojunction is higher than that of the MoSe2−WSe2 heterojunction under 674 nm illumination, suggesting that the contribution from the optical absorption of the p-doped MoS2 flake cannot be neglected. Our experimental results indicate that both the undoped MoSe2 and p-doped MoS2/WSe2 flakes contribute to the photocurrent generations in these heterojunctions.

To further elucidate the photoresponse generation mechanisms of MoSe2-based heterojunctions, bias-dependent scanning photocurrent measurements were performed by sweeping the drain-source bias voltages from −30 to 30 mV. The resulting photocurrent mappings of the device are depicted in...
Figure 3. (a) Diagram depicting the experimental setup used to measure time-dependent photocurrent signals. (b) Photocurrent responses as a function of time under 650 nm illumination. The photocurrent signals were collected for the (c) MoSe$_2$–MoS$_2$ junction under zero bias and the (d) MoSe$_2$–WSe$_2$ junction with $V_{ds} = -30$ mV, respectively.

Figure 4. Photocurrent signals as a function of drain-source bias under a zero gate voltage for various values of laser power ($\lambda = 650$ nm) on (a) MoSe$_2$–WSe$_2$ and (b) MoSe$_2$–MoS$_2$ junctions, respectively. Power dependence of photocurrent responses on (c) MoSe$_2$–WSe$_2$ and (d) MoSe$_2$–MoS$_2$ junctions, respectively.
Figure 2a, while quantitative measurements of photocurrent are extracted along the black dotted line and plotted spatially in Figure 2b. Under zero bias, photocurrent responses are primarily observed at the MoSe₂–MoS₂ junction, where electron-hole pairs (EHPs) are separated by a band offset between the heavily p-doped MoS₂ and undoped MoSe₂ flakes, leading to a current from MoSe₂ to MoS₂. The relatively weak photocurrent response at the MoSe₂–WSe₂ junction is likely attributed to a smaller band offset between the MoSe₂ and WSe₂, suggesting that the p-doping level in the WSe₂ is slightly lower than that in the MoS₂ flake. When the bias is increased to 30 mV, the band offset at the MoSe₂–MoS₂ junction increases, and consequently, the photocurrent intensity is enhanced. On the other hand, when the device is under a negative bias voltage of −30 mV, negative photocurrent signals begin to appear at the MoSe₂–WSe₂ heterojunction, which may result from the increase in the band offset between the undoped MoSe₂ and p-doped WSe₂ flakes. Here, the photoexcited holes can flow from MoSe₂ to WSe₂ and thus generate negative photocurrent responses at this heterojunction. These behaviors are depicted in Figure 2c and Figure S2.

The temporal response of the device was subsequently explored using an ON/OFF light modulation accomplished by the addition of an optical chopper to the laser path, as shown in Figure 3a. The photocurrent signals can be plotted versus time (Figure 3b), where the rise and decay time constants of the signals are extracted with a single exponential fitting function. Under zero bias, where the MoSe₂–MoS₂ heterojunction features sizable photocurrent signals, the rise and decay time constants are ∼18 μs and ∼16 μs (Figure 3c), respectively, which are three orders of magnitude faster than previous 2D MoSe₂-based phototransistors.4,10,38,39,52 and is comparable with other 2D TMDC phototransistors.29,58 Interestingly, the rise and decay time constants for the MoSe₂–WSe₂ heterojunction under −30 mV bias are ∼17 μs (Figure 3d), which are similar to those of the MoSe₂–MoS₂ heterojunction. The ultrafast photoresponse in MoSe₂-based heterojunctions is likely attributed to their unique 2D/2D heterostructures, where the near absence of interface states at the MoSe₂–WSe₂ and MoSe₂–MoS₂ van der Waals heterojunctions can significantly reduce charge trapping compared to conventional metal–2D semiconductor junctions, where interface states are almost ubiquitous. (More details are present in the Supporting Information.) In addition, the high mobility of 260 cm² V⁻¹ s⁻¹ in the MoSe₂ channel on the hBN substrate and the greatly lowered Schottky barriers at the heterojunction contacts are expected to reduce transit time and thus shorten photoresponse time. Furthermore, the photoexcited carriers can be easily collected by the external metal electrodes through the tunneling effect due to the narrow depletion region between heavily doped TMDCs and metal electrodes.

The performance of the MoSe₂ heterostructure device was subsequently assessed when the device is in the OFF state with a negligible dark current of ∼10⁻¹⁰ A. Figure 4a,b shows the photocurrent signals of the MoSe₂-based heterojunctions with various laser powers when the drain-source bias voltages are swept from −300 to 300 mV. The photocurrent signals of the MoSe₂–WSe₂ junction are negligible for zero and positive bias voltages, while exponentially increasing as the bias changes from zero to approximately −50 mV. As the negative bias further increases beyond −50 mV, the photocurrent signals at the MoSe₂–WSe₂ junction increase at a much slower rate. On the other hand, the MoSe₂–MoS₂ junction features substantial photocurrent signals even under zero bias, which slowly increase with an increasing positive bias voltage. As the bias changes from zero to negative, the photocurrent signals drop rapidly and nearly diminish at −50 mV. The photocurrent intensity shows a linear dependence on laser power with maximum photoresponsivities of ∼140¹⁻¹ and ∼60 mA W⁻¹ for MoSe₂–WSe₂ and MoSe₂–MoS₂ junctions (Figure 4c,d), respectively, suggesting that photocurrent generation is directly proportional to absorption of incident photons.59 Furthermore, the MoSe₂-based heterojunctions demonstrate a high specific detectivity on the order of ∼10¹⁴ Jones, a value better than state-of-the-art devices frequently used for photodetection.60

CONCLUSIONS

In conclusion, we report MoSe₂-based heterostructures with a fast photoresponse of as low as ∼16 μs, which is three orders of magnitudes faster than previously reported values for MoSe₂-based devices. Moreover, detectivity on the order of ∼10¹⁴ Jones has been achieved in our MoSe₂-based heterojunctions, greater than current industry standards. Further studies have shown that the ultrafast photoresponse is not dependent on the integrated TMDC materials (either heavily p-doped WSe₂ or MoS₂) in MoSe₂-based heterojunctions, but it is likely attributed to the high hole mobility (260 cm² V⁻¹ s⁻¹) and negligible contact resistance at 2D/2D interfaces,30 which are expected to foster carrier transit time and thus shorten the photocurrent response times. These results suggest that ultrafast performance can be attained within MoSe₂-based heterojunctions, providing a way to build future ultrafast 2D optoelectronics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c12155.

Thickness of different materials, energy levels of different materials, and mechanisms for a fast photocurrent response

AUTHOR INFORMATION

Corresponding Author

Ya-Qiong Xu — Department of Physics and Astronomy and Department of Electrical Engineering and Computer Science, Vanderbilt University, Nashville, Tennessee 37235, United States of America; orcid.org/0000-0003-1423-7458; Email: yaqiong.xu@vanderbilt.edu

Authors

Christian D. Ornelas — Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235, United States of America

Arthur Bowman — Department of Physics and Astronomy, Wayne State University, Detroit, Michigan 48201, United States of America

Thayer S. Walmsley — Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235, United States of America

Tianjiao Wang — Department of Electrical Engineering and Computer Science, Vanderbilt University, Nashville, Tennessee 37235, United States

https://dx.doi.org/10.1021/acsami.0c12155
ACS Appl. Mater. Interfaces 2020, 12, 46476–46482
46480
REFERENCES


