Tunneling Photocurrent Assisted by Interlayer Excitons in Staggered van der Waals Hetero-Bilayers

Dinh Hoa Luong, Hyun Seok Lee,* Guru Prakash Neupane, Shrawan Roy, Ganesh Ghimire, Jin Hee Lee, Quoc An Vu, and Young Hee Lee*

Vertically stacked van der Waals (vdW) heterostructures have been suggested as a robust platform for studying interfacial phenomena and related electric/photovoltaic transport for numerous optoelectronic devices. While the interlayer Coulomb interaction mediated by the vdW coupling has been extensively studied for carrier recombination processes in a diode transport, its correlation with the interlayer tunneling transport has not been elucidated. Here, a contrast is reported between tunneling and drift photocurrents tailored by the interlayer coupling strength in MoSe2/MoS2 hetero-bilayers (HBs). The interfacial coupling modulated by thermal annealing is identified by the interlayer phonon coupling in Raman spectra and the emerging interlayer exciton peak in photoluminescence spectra. In strongly coupled HBs, positive photocurrents are observed owing to the inelastic band-to-band tunneling assisted by interlayer excitons that prevail over exciton recombinations. By contrast, weakly coupled HBs exhibit a negative photovoltaic diode behavior, manifested as a drift current without interlayer excitonic emissions. This study sheds light on tailoring the tunneling transport for numerous optoelectronic HB devices.

Heterostructure platforms for conventional III–V semiconductors have been considered as a promising alternative to silicon for high-performance electronic and optoelectronic devices.1 However, it is difficult to fabricate heterojunctions, owing to the lattice mismatch between the two constituent materials and interfacial dangling bonds, which affects the crystal growth and modulates the physical properties of the grown heterostructures.1,2 Meanwhile, van der Waals (vdW) heterostructures, fabricated via direct growth3 and using an artificial transfer method based on mechanical exfoliation,4–8 could alleviate the above issues owing to the relatively weak vdW interaction between adjacent layers and the lack of dangling bonds in the layers. The vdW heterostructures have been extensively considered for p–n diodes9,10 photodetectors,9,10 photovoltaics10 light-emitting diodes (LEDs),6,11 and tunneling devices.12,13 Staggered vdW hetero-bilayers (HBs), obtained by vertical stacking of two different monolayer transition metal dichalcogenides (TMDs), have been found to exhibit exceptional performances at the atomic scale.4,5,8,10,11

In these vdW junction platforms, the unique features arising from vdW gaps are the interlayer exciton and the interlayer tunneling. The staggered band of HBs enables an ultrafast layer-to-layer hopping of photoexcited carriers; thus, the carriers are spatially separated into individual layers via hot-carrier relaxations.18 The Coulomb interaction between electrons and holes in opposite layers, which can be tuned by modulating the vdW gap,15–21 is sufficiently strong for inducing excitons owing to the reduced dielectric screening of HBs. This results in tightly bound interlayer excitons18,20,22–24 that have been considered promising for a Bose–Einstein condensation.21,22

Another crucial application for utilizing vdW interfaces is tunneling devices based on vdW materials, including band-to-band tunneling (BTBT) field-effect transistors11,12,15 and Esaki diodes.12,25 These devices have been spotlighted as promising building blocks for potential ultradense and low-power electronics. In contrast to bulk vdW junctions, however, the BTBT-mediated carrier transport mechanism is likely to be different in vdW HB structures, owing to interlayer excitonic interactions. Nevertheless, interlayer excitonic effects related to the BTBT-mediated carrier transport have rarely been studied in atomically thin bilayer heterostructures, whereas the Langevin recombination in rectifying carrier transport processes has been extensively investigated in HB diodes.5 Moreover, understanding such excitonic effects associated with the BTBT carrier transport is a key for manipulating optoelectronic processes in light-harvesting devices and LEDs, which have not been considered in bulk devices.

Here, we report the generation of an extraordinary tunneling photocurrent assisted by interlayer excitons in strongly coupled MoSe2/MoS2 vdW HB devices. The vdW coupling strength for interlayer excitons is modulated by thermal annealing: (i) the...
pristine HB device, denoted as a weak-interface device and (ii) the annealed HB device, denoted as a strong-interface device (Figure 1a). We observe a conversion of a conventional photovoltaic behavior without interlayer excitonic emissions into a tunneling photocurrent with interlayer excitonic emissions via thermal annealing.

A MoSe2/MoS2 HB was artificially fabricated by stacking MoSe2 onto MoS2 monolayers, where each monolayer was prepared by mechanical exfoliation from bulk flakes. Figure 1a shows an optical micrograph of the fabricated HB (D1) and illustrates the concept of the vdW interface modulation of HBs. We constructed two types of interfaces: (i) weak interfaces before annealing (D1-weak) and (ii) strong interfaces after annealing (D1-strong) in a single HB. The former is a simply as-prepared HB, and while no polymer residues were left at the interface during the transfer process, some ambient gases and unexpected speckles were trapped at the interface, forming a weak interface. The latter is a postannealed HB, for which bubbles were removed (see the Experimental Section and Figure S1, Supporting Information), establishing a strongly coupled vdW interface. It has been demonstrated previously that annealing induces strong vdW interfaces.

To characterize the interfaces, we performed Raman and photoluminescence (PL) spectroscopies for two conditions (D1-weak and D1-strong, respectively) of the same device. Figure 1b shows the Raman spectra of the individual MoS2 and MoSe2 as well as that of their HB. Changes in the peak positions of A1g (∼238 cm⁻¹, out-of-plane mode) and E2g (∼285 cm⁻¹, in-plane mode) for MoSe2 as well as those of A1g (∼403 cm⁻¹) and E2g (∼384 cm⁻¹) for MoS2, induced by annealing, were negligible. The slight downshift of the A1g peak in MoS2 after annealing was attributed to the n-doping effect by the desorbed ambient gases. Individual layers maintained their respective intrinsic properties after annealing.

Meanwhile, the E2g peak of MoS2 in the HB exhibited a prominent redshift (∼1.5 cm⁻¹) relative to that of the individual MoS2 layer after annealing. This was ascribed to the thermal...
lattice mismatch between two layers in the stacked configuration.\textsuperscript{[28]} The A\textsubscript{1g} peak in the HB was also redshifted by $\approx 0.8$ cm$^{-1}$ relative to that of the individual MoSe\textsubscript{2} layer, indicating a charge transfer from the MoSe\textsubscript{2} layer to the MoS\textsubscript{2} layer in the strong-interface HB. The reduced A\textsubscript{1g} intensity in the HB was attributed to the suppression of the out-of-plane phonon mode caused by the stacking of the top MoSe\textsubscript{2} layer. More importantly, the B\textsubscript{2g} peak ($\approx 351$ cm$^{-1}$, out-of-plane mode), which is only emerged in native MoSe\textsubscript{2} bilayers and in bulk, is only observed in the D\textsubscript{1}-strong HB owing to the enhanced interlayer interaction at the interface, whereas this mode was not detected in the D\textsubscript{1}-weak HB. The emergence of the B\textsubscript{2g} peak is congruent with the reduction of interlayer distance after annealing that was revealed by atomic force microscopy measurements (Figure S1, Supporting Information).

Figure 1c shows the PL spectra of the individual MoS\textsubscript{2} and MoSe\textsubscript{2} layers (bottom) as well as of the HB (top). In the individual layers (bottom), the A exciton peaks of pristine MoSe\textsubscript{2} ($\approx 1.59$ eV) and MoS\textsubscript{2} ($\approx 1.85$ eV) were prominently redshifted after annealing, while any other additional peaks, such as potential defect-related peaks, were not observed,\textsuperscript{[30]} congruent with the Raman spectra results. The peak quenching and red-shifting of the individual annealed layers were ascribed to a rich multie exciton contribution by reduced native surface adsorbates, such as oxygen, during annealing in the Ar/H\textsubscript{2} gas flow.\textsuperscript{[31]} Such annealing effects were much more prominent in the HB (top). After annealing, the MoS\textsubscript{2} peak in the HB was redshifted in comparison with that of the corresponding individual layer, indicating an additional charge transfer from MoSe\textsubscript{2} to MoS\textsubscript{2} (increased trion contribution).

We note that two additional peaks at $\approx 1.34$ eV (defined as X\textsubscript{1}) and $\approx 1.5$ eV (originating from the band renormalization, as discussed below) were prominent in the D\textsubscript{1}-strong HB. The location of X\textsubscript{1} as an interlayer exciton ranges from $\approx 1.3$ to $\approx 1.38$ eV for MoSe\textsubscript{2}/WSe\textsubscript{2} HBs,\textsuperscript{[4,22,24]} whereas the peak at $\approx 1.34$ eV has been rarely reported for MoSe\textsubscript{2}/MoS\textsubscript{2} HBs.\textsuperscript{[16]} We excluded damage-related emission of host materials as a possible cause of X\textsubscript{1} because our annealing condition was mild compared with other annealing conditions ($\approx 500$ °C)$\textsuperscript{[26]}$ and epitaxial synthesis conditions of heterostructures ($\approx 650$ °C).\textsuperscript{[3]} Moreover, X\textsubscript{1} emerged consistently in the overall HB region, particularly in the strong-interface HB, although the peak intensity fluctuated owing to the inhomogeneity of the interface (Figure S2, Supporting Information). Therefore, we attributed X\textsubscript{1} to the interlayer excitons and provide a more detailed discussion below.

To investigate the photocurrent characteristics that depend on the vdW interfacial coupling, we prepared two different HB devices: (i) the pristine HB with a weak interface (D\textsubscript{2}-weak) and (ii) the postannealed HB with a strong interface (D\textsubscript{3}-strong), respectively, as discussed in Figure 1. For the D\textsubscript{3}-strong device, the electrode was deposited on the patterned source (S) and drain (D) after annealing as shown in Figure 2a. Thus, the same conditions were maintained for the metal–semiconductor contacts in the D\textsubscript{2}-weak and D\textsubscript{3}-strong devices. Figure 2b schematically shows the MoSe\textsubscript{2}/MoS\textsubscript{2} device with electrodes under light illumination (top), together with the staggered band alignment (bottom).\textsuperscript{[16]} A focused laser beam, with the beam diameter under $\approx 1$ μm, was illuminated exclusively onto the HB region except the metal/TMD contact regions. Figure 2c shows the drain current ($I\textsubscript{D}$) as a function of the drain bias ($V\textsubscript{D}$), for the D\textsubscript{2}-weak device. The photocurrent exhibits nonlinearity regardless of the laser power ($P\textsubscript{ex}$), which is typical for a rectifying photodiode. The short circuit current ($I\textsubscript{SC}$) at $V\textsubscript{OC} = 0$ V increased in the reverse direction as $P\textsubscript{ex}$ increased. In an open circuit state ($I\textsubscript{S} = 0$ A), as photocarriers increase, accumulated photocarriers in each band reduce the built-in potential, resulting in a positive open circuit voltage ($V\textsubscript{OC}$) in proportion to $P\textsubscript{ex}$. This is consistent with a typical photovoltaic behavior in various HB p–n diodes.\textsuperscript{[5,10]}

However, in the D\textsubscript{3}-strong device, the photocurrent linearly depended on the drain bias, and $I\textsubscript{SC}$ increased in the forward direction with increasing $P\textsubscript{ex}$. This was ascribed to the BTBT between the layers via a vdW interfacial gap. At an open circuit state, the tunnelled photocarriers in each band increase the band offset, contributing to the negative open circuit voltage. Notably, this has rarely been observed in type-II HBs (Figure S3, Supporting Information), while the tunneling photocurrent has been reported for graphene/TMD/graphene\textsuperscript{[9]} and a type-III broken band such as vdW Esaki diodes.\textsuperscript{[12]} This behavior of the tunneling photocurrent for the D\textsubscript{3}-strong device was reliably confirmed using another D\textsubscript{1}-strong device (Figure S4, Supporting Information). We attributed this unusual photocurrent behavior in the strong-interface HB to the interlayer exciton-assisted BTBT tunneling effect. The details are discussed below.

To elucidate the correlation between the tunneling photocurrent and interlayer excitons in the D\textsubscript{3}-strong device, exciton complexes were analyzed further. Figure 3a shows the normalized PL spectra at $P\textsubscript{ex} = 1$ μW for the D\textsubscript{3}-strong device and their Lorentzian deconvolution. We denote the respective A exciton peaks of MoS\textsubscript{2} and MoSe\textsubscript{2} for the individual layers by A\textsubscript{S} and A\textsubscript{Se}, while those appearing in the HB spectrum are referred to as A\textsubscript{S}′ and A\textsubscript{Se}′. In addition, the B exciton peaks of MoS\textsubscript{2} for the individual layer and the HB are referred to as B\textsubscript{S} and B\textsubscript{S}′, respectively. In the HB region (bottom), X\textsubscript{1} is clearly visible at $\approx 1.34$ eV, consistent with that of the D\textsubscript{1}-strong HB (Figure 1c). Moreover, in the Raman spectra of this D\textsubscript{3}-strong device, the emergence of the B\textsubscript{2g} peak and the prominent reduction in the A\textsubscript{1g} peak for MoS\textsubscript{2} were also consistently observed (Figure S5, Supporting Information), similar to the D\textsubscript{1}-strong HB (Figure 1b). Interestingly, an additional broad peak (X\textsubscript{2}) at $\approx 1.5$ eV emerged near A\textsubscript{Se}′, which was not observed in the weak-interface HB (Figure 1c, top) and individual MoSe\textsubscript{2} layer.

To identify the origin of X\textsubscript{1} and X\textsubscript{2} peaks, we show the predicted band alignment of the MoSe\textsubscript{2}/MoS\textsubscript{2} HB in terms of the exciton transition energies, band renormalization,\textsuperscript{[12]} the binding energies of intralayer and interlayer excitons,\textsuperscript{[18,20,24,33]} and the valence band offsets\textsuperscript{[3,34]} (Figure 3b,c). In what follows, we assume that the binding energy ($E_{\text{B}}$) of interlayer excitons for the MoSe\textsubscript{2}/MoS\textsubscript{2} HB is similar to that of MoSe\textsubscript{2}/WSe\textsubscript{2} ($\approx 0.2$ eV).\textsuperscript{[24]} MoS\textsubscript{2}/WSe\textsubscript{2} ($\approx 0.28$ eV),\textsuperscript{[20]} and MoS\textsubscript{2}/WSe\textsubscript{2} ($\approx 0.36$ eV)\textsuperscript{[28]} HBs, because the dielectric constants and intralayer binding energies of monolayer TMDs are comparable.\textsuperscript{[20,33,35]} The predicted transition energy of interlayer excitons, in the 1.24–1.43 eV range, agrees well with our observed X\textsubscript{1} (1.34 eV). Therefore, we refer to X\textsubscript{1} as an interlayer exciton of MoSe\textsubscript{2}/MoS\textsubscript{2} HBs. Notably, the peak positions of X\textsubscript{1} for the D\textsubscript{1}-strong and D\textsubscript{3}-strong devices are similar, although the stacking orientation of these HBs are random. The weak dependence of the emergence of X\textsubscript{1} on
the orientation agrees well with observations for other HBs, although the peak position and intensity fluctuate, because the interlayer exciton transition does not prominently depend on the momentum mismatch between two layers, which is compensated by hot-carrier relaxations. The emergence of $X_2$ was attributed here to indirect excitons owing to the indirect band transition between the $K$ point of MoS$_2$ and the $\Gamma$ point of the HB in the Brillouin zone (also see Figure S6, Supporting Information). We posit that the band structure of the HB is renormalized owing to the vdW interaction, as typically predicted by theoretical band structure calculations. In HBs, while the valance band at the $K$ point is similar to individual layers owing to a weak interlayer hybridization, that at the $\Gamma$ point is strongly hybridized, resulting in the upsplitting of the $\Gamma$ point of the valence band. This band renormalization activates an indirect band transition between the $K$ and $\Gamma$ points, as shown in Figure 3c, which is similar to the case of MoSe$_2$/WSe$_2$ HBs and MoSe$_2$ homo-bilayers. The rotation angle between MoSe$_2$ and MoS$_2$ presumably alters the renormalized band structure. Nevertheless, we attributed the obvious contrast of the $X_2$ emergence between the weak- and strong-interface HBs to the vdW coupling effect because the orientation dependence of the band structure renormalization effect was predicted to be negligible in MoSe$_2$/MoS$_2$ HBs.

While interlayer excitons have been intensively studied in various HB systems, the correlation between intra-layer exciton complexes and interlayer excitons has rarely been reported. To investigate this correlation, the $P_{ex}$-dependent PL spectra were obtained and deconvoluted using a Lorentzian function (Figures S7 and S8, Supporting Information). Figure 4a (top) shows the peak positions as a function of $P_{ex}$ for the strongly coupled HB, where $E_p$ denotes the positions of exciton peaks. With increasing $P_{ex}$, the peak positions for the HB ($A'_S$, $A'_Se$, and $X_2$) and individual layers ($A_S$) were redshifted. Conversely, the $A_{Se}$ peak shift for MoSe$_2$ was negligibly small and $X_1$ was clearly blueshifted. These peak shifts are summarized at the bottom of Figure 4a, where $\Delta E_p$ corresponds to the change in $E_p$ with $P_{ex}$ and is obtained by subtracting the peak position of $E_0$ for $P_{ex} = 1 \mu W$. The detailed peak changes are as follows: (i) The values of $\Delta E_p$ for both $A_S$ and $A'_S$ reach $\sim 30$ meV, congruent with the MoS$_2$ trion binding energy. (ii) For $A_{Se}$ (MoSe$_2$ peak in the individual layer), $\Delta E_{p} \approx 0$ meV at various $P_{ex}$ because the trion formation is negligible in the individual MoSe$_2$ layers (lightly n-doped). (iii) For $A'_Se$ (MoSe$_2$ peak in the HB), however, the hole injection from the MoS$_2$ layer to the MoSe$_2$ layer allows...
Figure 3. Identifying exciton complexes. a) PL spectra for MoS$_2$, MoSe$_2$, and the HB, for the D3-strong device at $P_{ex} = 1 \mu W$, and their Lorentzian deconvolutions. $A_S$ and $A_{se}$ are the A exciton peaks of MoSe$_2$ and MoS$_2$ for the individual layers; $A'_S$ and $A'_{se}$ are those of MoSe$_2$ and MoS$_2$ for the HB; $B_S$ and $B'_{se}$ are the B exciton peaks of MoS$_2$ for the individual layer and the HB, respectively. b) Predicted band alignment based on observed exciton transition energies, reported band offset and binding energies, and predicted band renormalization effect. c) $X_1$ for spatially separated interlayer excitons and $X_2$ for indirect excitons generated from the K−Γ indirect transition in the Brillouin zone.

Figure 4. Excitation laser power-dependent exciton complexes. a) $E_p$ peak positions for exciton complexes in the D3-strong device (top). Summary of each peak shift (bottom). $\Delta E_p = E_p - E_0$ and the peak position of $E_0$ for $P_{ex} = 1 \mu W$. b) Schematic of a complex intralayer and interlayer excitons depending on the excitation light intensity. The dashed circles are the Bohr circles for excitons.
for positive trion formation. Consequently, the resulting $\Delta E_P$ for $A'_\text{Se}$ reaches $-25$ meV, consistent with the trion binding energy of MoSe$_2$.[42] (iv) The value of $\Delta E_P$ for $X_1$ reaches $-20$ meV, possibly attributed to the negative trion formation for $X_1$ because of the similar $P_{ex}$ dependence of intralayer excitons ($A_S$ and $A'_S$). (v) The $X_1$ peak is blueshifted in proportion to $P_{ex}$, and $\Delta E_P$ for $X_1$ reaches $40$ meV. This was attributed to the plasma screening effect of the interlayer excitons, while a blueshift of the interlayer excitons peak in the MoSe$_2$/WSe$_2$ HBs was ascribed to the conduction band splitting in the MoSe$_2$ layer[22] (Note 1, Supporting Information). Moreover, the blueshift of $X_1$ was again confirmed in the D1-strong device (Figure S9, Supporting Information).

Figure 4b schematically summarizes the possible exciton complexes and the Bohr circle (dashed circle) of intralayer (left) and interlayer (right) excitons, depending on the excitation light power. As the optical density increases, negative and positive trions for intralayer excitons are formed owing to the increased exciton density and interlayer charge transfer (Figure 4b, left). However, for the long-lived (>1.8 ns) interlayer excitons,[22] a probability of Coulomb interaction screening from photocarriers is much prominent than the short-lived (<500 fs) intralayer excitons.[43] The increasing amount of charge in each layer screens the Coulomb interaction of $X_1$, thus increasing the Bohr radius (Figure 4b, right). Because the Bohr radius is inversely proportional to the exciton binding energy,[33] $X_1$ is blueshifted as $P_{ex}$ increases (Figure 4a).

Figure 5a shows comparative $I_{SC}$ curves as a function of $P_{ex2}$ for the D2-weak and D3-strong HBs, obtained from Figure 2c,d. For the D2-weak HB, $I_{SC}$ increases with $P_{ex2}$ in the reverse direction owing to the normally observed charge drift in diodes. Conversely, in the D3-strong HB, $I_{SC}$ increases in the forward direction owing to the direct BTBT. Figure 5b,c illustrates possible photocurrent generation processes for both cases. For the weak-interface HB, the charge hopping of photoexcited hot carriers between individual layers results in complex intralayer excitons such as charge-transfer-induced trions in each layer,[44] while interlayer excitonic emission is not prominent[5,15,18] (Figure 5b-i). Moreover, such a weak interlayer Coulomb interaction allows for drift currents arising from the built-in potential in the staggered band offset, resulting in negative $I_{SC}$ (Figure 5b-ii), as normally observed in HB diodes.[5,10]

By contrast, in the strong-interface HB, the interlayer Coulomb interaction between the layers allows not only for the appearance of intralayer exciton complexes but also for the appearance of interlayer excitons (Figure 5c-i), where a life time of interlayer excitons is longer owing to the spatial separation.[5,22] While interlayer excitons are partially recombined via $X_1$ emission, others can generate inelastic BTBT and flow through the external circuit, resulting in the tunneling photocurrent with a positive $I_{SC}$ curve (Figure 5c-ii). Figure 5d depicts such a tunneling process in detail. In type-III band structures with a broken gap, BTBT is possible, because Fermi levels are allowed in each band. On the other hand, such levels are not

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**Figure 5.** Photocurrent generation mechanism. a) Short circuit current ($I_{SC}$) as a function of $P_{ex2}$ for the D2-weak and D3-strong HB devices obtained from Figure 2c,d. Schematic of photocurrent generation processes under light illumination for the b) weak and c) strong interfaces. Photocarriers generated in the HB flow to the source (S) and drain (D) electrodes, resulting in photocurrents through the external circuit. d) Interlayer exciton-induced quasi-Fermi levels ($E_F$) for different bands, and the inelastic band-to-band tunneling process.
allowed in type-II staggered band structures (Figure S3, Supporting Information). However, as shown in Figure 5d, under the light illumination, the generated interlayer excitons in the type-II HBs allow for a transient quasi-Fermi level ($E_F$) within each valence and conduction band. Therefore, the electrons in the interlayer exciton states of MoS$_2$ tunnel to the unoccupied valance band states of MoSe$_2$ via inelastic tunneling.[45] As the optical density increases, while the Coulomb interaction of electrode metals of Cr/Au (10/50 nm) were deposited using the e-beam/dry transfer technique.[7] The PMMA layer was removed by acetone and sequentially, the lithography method. The PMMA e-beam masks for the electrodes were patterned on the MoSe$_2$/MoS$_2$ heterostructure flakes. Sequentially, the monolayer MoSe$_2$/MoS$_2$ hetero-bilayers were annealed in an Ar/H$_2$ environment (0.3 Torr, 100 sccm of Ar, and 5 sccm of H$_2$) at 350 °C for 2 h in vacuum) using a dry transfer technique.[7] The PMMA layer was transferred onto the top of the MoS$_2$ monolayer on SiO$_2$ (300 nm)/Si wafers (annealed at 200 °C for 2 h in vacuum) using a dry transfer technique.[7] The PMMA layer was removed by acetone and then rinsed with isopropyl alcohol. In this process, the vdW interface between MoSe$_2$ and MoS$_2$ was not in contact with other materials to prevent interface contaminations. For the annealed samples, the monolayer MoSe$_2$/MoS$_2$ hetero-bilayers were annealed in an Ar/H$_2$ environment (0.3 Torr, 100 sccm of Ar, and 5 sccm of H$_2$) at 350 °C for 6 h, to enhance the van der Waals interaction between the monolayers. The electrodes were fabricated using an electron beam (e-beam) lithography method. The PMMA e-beam masks for the electrodes were patterned on the MoSe$_2$/MoS$_2$ heterostructure flakes. Sequentially, the electrode metals of Cr/Au (10/50 nm) were deposited using the e-beam/thermal evaporation methods, and the liftoff was conducted in acetone.

Optical Characterization: PL and Raman spectra were measured under ambient conditions using a lab-made confocal microscope equipped with an argon laser (514 nm wavelength) and objective lens (numerical aperture of 0.9). The PL and Raman signals were recorded using a spectrometer and a cooled charge-coupled device camera.

Opto-electronic Characterization: The photocurrent characteristics were measured using an electrical characterization system (Keithley 2636A, Keithley Instruments) and a lab-made microscope equipped with a diode laser (532 nm wavelength) and objective lens (numerical aperture of 0.6) in a vacuum chamber at room temperature.[46]

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.

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Experimental Section

Sample Preparation: The MoS$_2$ and MoSe$_2$ monolayers were mechanically exfoliated from bulk materials (SPI Corp. and 2D semiconductors Corp.) onto SiO$_2$ (300 nm)/Si wafers and polymethyl methacrylate (PMMA) and polyvinyl alcohol coated SiO$_2$ (300 nm)/Si wafers, respectively. Both monolayers were identified by optical contrast and were confirmed by performing Raman spectroscopy and photoluminescence measurements. The MoSe$_2$ monolayer on the PMMA layer was transferred onto the top of the MoS$_2$ monolayer on SiO$_2$ (300 nm)/Si wafers (annealed at 200 °C for 2 h in vacuum) using a dry transfer technique.[7] The PMMA layer was removed by acetone and then rinsed with isopropyl alcohol. In this process, the vdW interface between MoSe$_2$ and MoS$_2$ was not in contact with other materials to prevent interface contaminations. For the annealed samples, the monolayer MoSe$_2$/MoS$_2$ hetero-bilayers were annealed in an Ar/H$_2$ environment (0.3 Torr, 100 sccm of Ar, and 5 sccm of H$_2$) at 350 °C for 6 h, to enhance the van der Waals interaction between the monolayers. The electrodes were fabricated using an electron beam (e-beam) lithography method. The PMMA e-beam masks for the electrodes were patterned on the MoSe$_2$/MoS$_2$ heterostructure flakes. Sequentially, the electrode metals of Cr/Au (10/50 nm) were deposited using the e-beam/thermal evaporation methods, and the liftoff was conducted in acetone.

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