Exciton Dynamics in MoS$_2$-Pentacene and WSe$_2$-Pentacene Heterojunctions

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ABSTRACT: We measured the exciton dynamics in van der Waals heterojunctions of transition metal dichalcogenides (TMDCs) and organic semiconductors (OSs). TMDCs and OSs are semiconducting materials with rich and highly diverse optical and electronic properties. Their heterostructures, exhibiting van der Waals bonding at their interfaces, can be utilized in the field of optoelectronics and photovoltaics. Two types of heterojunctions, MoS$_2$-pentacene and WSe$_2$-pentacene, were prepared by layer transfer of 20 nm pentacene thin films as well as MoS$_2$ and WSe$_2$ monolayer crystals onto Au surfaces. The samples were studied by means of transient absorption spectroscopy in the reflectance mode. We found that A-exciton decay by hole transfer from MoS$_2$ to pentacene occurs with a characteristic time of 21 ± 3 ps. This is slow compared to previously reported hole transfer times of 6.7 ps in MoS$_2$-pentacene junctions formed by vapor deposition of pentacene molecules onto MoS$_2$ on SiO$_2$. The B-exciton decay in WSe$_2$ shows faster hole transfer rates for WSe$_2$-pentacene heterojunctions, with a characteristic time of 7 ± 1 ps. The A-exciton in WSe$_2$ also decays faster due to the presence of a pentacene overlayer; however, fitting the decay traces did not allow for the unambiguous assignment of the associated decay time. Our work provides important insights into excitonic dynamics in the growing field of TMDC-OS heterojunctions.

KEYWORDS: transition metal dichalcogenides, organic semiconductors, pentacene, exciton dynamics, transient reflection spectroscopy, MoS$_2$, WSe$_2$

1. INTRODUCTION

The study of van der Waals heterojunctions based on transition metal dichalcogenides (TMDCs) and organic semiconductor (OS) thin films has been ongoing for several years; however, there are still many fascinating avenues for researchers to explore. The TMDCs themselves exhibit fascinating physical phenomena such as exceptionally large exciton binding energies, spin-valley locking, and the exciton Hall effect. TMDCs and organic semiconductors are highly dissimilar nonconventional semiconductors that share the characteristic of interlayer bonding via van der Waals interactions. Forming heterojunctions of these materials offers interesting opportunities for combining diverse (opto-)electronic properties. An important step for the technological development of such structures has been taken recently, in the demonstration by some of us of devices fabricated by layer transfer of TMCDs as well as organic semiconductor thin films. A strong advantage of this approach is that the organic semiconductors can be grown on a suitable substrate for obtaining high quality crystalline layers, avoiding molecular disorder that occurs upon direct deposition on TMCD substrates.

The wide variety of devices that have been constructed in the field so far include light emitting diodes, tunneling transistors, and photovoltaic cells. Arguably, one of the most promising applications out of these possibilities is photovoltaics, and the present work is carried out in its context, focusing on exciton dynamics at TMDC/OS interfaces. Some of the aforementioned heterojunctions have been studied previously in various combinations and conditions by similar ultrafast pump probe spectroscopic techniques. Most of these previous studies focused on 2D TMDCs grown on quartz and SiO$_2$/Si wafers, which were then...
covered by an OS layer directly deposited onto the TMDC monolayers. TMDCs such as MoS$_2$ and WSe$_2$ monolayers have attracted a lot of attention as promising 2D semiconductors and have been studied thoroughly.$^{17–20}$ Here, we examine high quality monolayers of MoS$_2$ and WSe$_2$ prepared by a dedicated chemical vapor deposition (CVD) technique and transferred to a UV ozone treated Au substrate.$^{21–23}$ Homogeneous pentacene films, 20 nm in thickness, were also transferred to the samples after uniform controlled growth on poly(acrylic acid) (PAA) substrate films.$^9$

Transient absorption/reflection spectroscopy (TAS/TRS) is a well-known technique to study ultrafast processes of exciton formation and dissociation in various materials.$^{12,24,25}$ Even though the performance of photovoltaic devices is based on many different aspects, one of these is the temporal difference between exciton decay and charge separation on the junction interface. Recently, relatively long lasting (≥5 ns) charge-separated states at MoS$_2$/pentacene interfaces have been reported.$^{15}$ In this work, pentacene was directly grown on the surface of MoS$_2$, while MoS$_2$ was deposited on the substrate by a CVD method similar to ours. Here, we focus on the ultrafast exciton dynamics in van der Waals heterojunctions of WSe$_2$ and MoS$_2$ monolayer crystals covered by a 20 nm transferred thin film of pentacene. This allows us to investigate to which extent molecular (dis)order at the MoS$_2$/pentacene interface affects exciton dissociation rates. Charge transfer dynamics at WSe$_2$/pentacene interfaces have not been studied previously.

2. RESULTS AND DISCUSSION

Here, the obtained TRS results are presented in the following manner. First, we discuss the pentacene reflection spectra. Next, TRS results of MoS$_2$ and MoS$_2$-pentacene heterojunctions are presented, with analysis and conclusions. Lastly, the ultrafast spectroscopic analysis of the results of WSe$_2$ and WSe$_2$-pentacene composites are presented and discussed.

Figure 1 shows the structural arrangement of pentacene molecules on MoS$_2$. We expect highly oriented vertically transferred to gold. The sample is photoexcited at 515 nm, and the transient reflectivity spectra are recorded. $\Delta OD_R$ is calculated as $-\log(I_{R,exc}/I_{R,noexc})$ where $I_{R,exc}$ and $I_{R,noexc}$ are the reflected light intensity with and without excitation, respectively. The temporal resolution of the experiment is 80 fs. The spectra are dominated by a strong ground state bleach feature, attributed to the depopulation of the ground state by the pump pulse. This feature is centered at 688 nm and corresponds to the lowest energy singlet exciton in pentacene. Two weaker bleach signals are recognizable at 635 and 597 nm. The spectrum recorded at a pump–probe delay time of 0.53 ps can be found in the inset of Figure 2b. These results are in good agreement with previously published works on (transient) optical absorption spectroscopy of (poly)crystalline pentacene.$^{25–27}$ The separation between the 688 nm (1.80 eV) and 635 nm (1.95 eV) peaks can be attributed to the Davydov splitting due to the presence of two inequivalent pentacene molecules in the unit cell$^27$

Figure 2b shows the kinetic trace extracted at the main bleach feature of the pentacene film (integrated signal intensity from 675 to 695 nm). The data show that the ground state bleach is long-lived and hardly evolves within 1 ns after excitation. Note that ultrafast (sub 150 fs) fission of singlet excitons into two triplet excitons, which is known to be an efficient process in pentacene,$^{23,26}$ is not detectable on the comparatively long time scales probed in our measurements.

2.2. Molybdenum Disulfide (MoS$_2$). Figure 2c,d shows transient reflection spectra for uncovered MoS$_2$ single crystals on Au (Figure 2c), as well as MoS$_2$ monolayer crystals on Au that are covered by a 20 nm continuous film of pentacene (Figure 2d). There are two main ground state bleach peaks observed for the MoS$_2$ single crystals, centered at 615 nm and at 662 nm. These values represent the B- and A-excitons of MoS$_2$, respectively. The decay processes that these excitons undergo in similar samples (i.e., MoS$_2$ monolayers on amorphous SiO$_2$, quartz and sapphire) have been thoroughly studied previously.$^{30,38–30}$ For pentacene-covered MoS$_2$ (see Figure 2d and Figure 3), two partially overlapping ground state bleach features appear at about 670 nm, which are attributed to the MoS$_2$ A-exciton and the closely located pentacene bleach peak at 688 nm.

Figure 3 shows the transient reflection spectra of three different samples: the MoS$_2$ monolayer in blue, pentacene in green, and the MoS$_2$ crystal covered with the pentacene thin film in orange. These spectra were captured 0.53 ps after photoexcitation. As was discussed earlier, pentacene has three main bleach peaks, and MoS$_2$ has two, while the intense pentacene ground state bleach at 688 nm is located very close to the MoS$_2$ A-exciton peak. In the MoS$_2$-pentacene data, one can observe a composite feature that results from the superposition of the two individual peaks.

To study the mechanism(s) of exciton decay in the kinetic traces and to provide quantitative comparison of the various samples, we fitted the data with a triple exponential decay function as shown below:

$$\Delta OD_R = A_1 \times \exp\left(-\frac{t}{t_1}\right) + A_2 \times \exp\left(-\frac{t}{t_2}\right) + A_3 \times \exp\left(-\frac{t}{t_3}\right)$$

(1)
The results of this fitting can be seen in Figure 4a, corresponding to the kinetic trace of the A-exciton of MoS$_2$. The fast decay component of the A-exciton in uncovered MoS$_2$ crystals was fitted to be $1.0 \pm 0.5$ ps. This component is usually attributed to fast trapping processes of excitons at intrinsic defect sites such as atomic S- and S$_2$-vacancies, and/or to exciton cooling effects. The second component of $28.3 \pm 9.4$ ps represents the nonradiative decay of exciton–phonon pairs. The slow component of $1.9 \pm 0.3$ ns is usually associated with the lifetime of free charges and their radiative recombination. The fractional weight of each decay component is presented in Table 1 next to the values of the decay times.

For the MoS$_2$-pentacene heterojunction results, we follow a similar fitting method applied by Homan et al., in which decay components that are not affected by the presence of pentacene are fixed, such as ultrafast defect-assisted decay and the slow decay components. The new intermediate component, with a decay time of $21 \pm 3$ ps, then is associated with the hole transfer from pentacene to the MoS$_2$ crystal (see ref 15 for schematic diagrams illustrating the corresponding decay processes). This new component accounts for 34% of the fit, to be compared to the previous intermediate fraction of 26%. We were not able to detect any new component associated with slow recombination processes of transferred holes with excess electrons in MoS$_2$ on the scale of a few nanoseconds, which most probably fall outside our time window of 2 ns used in the experiments. The exciton decay characteristics of MoS$_2$ crystals covered by the pentacene thin film are found to be quite similar to those of uncovered MoS$_2$. Notably, the time scale for exciton dissociation at the MoS$_2$-pentacene interface of $21 \pm 3$ ps is slow compared to the previously reported hole transfer time of 6.7 ps for pentacene grown on MoS$_2$ on SiO$_2$/Si. The decay process of the B-exciton, which is presented in Figure 4b, is similarly not significantly affected by the presence of the pentacene film: All the fitted decay components (see Figure 2. (a) Two-dimensional transient reflection spectra of a 20 nm pentacene film on a gold substrate. Here and further the background subtraction (described in Supporting Information 2) is applied to this type of result. (b) A kinetic trace of the main feature at 675–695 nm from the averaged spectra in (a); inset represents the spectrum at 0.53 ps delay time. (c, d) Two-dimensional transient reflection spectra of (c) MoS$_2$ monolayer crystals transferred to a gold substrate and (d) similar MoS$_2$ monolayer crystals on gold covered by a pentacene thin film. Figure 3. Transient reflection spectra of a MoS$_2$ monolayer, a MoS$_2$-pentacene junction, and a pentacene thin film (all on Au substrates) probed at 0.53 ps.)
Supporting Information) are very similar and agree within the error bar for both the MoS$_2$ and MoS$_2$-pentacene samples in our measurements. Figure 4b shows the data without fitted time traces, and the overlapping data sets clearly show the same type of behavior for both systems.

There are several possible explanations for the different exciton dynamics in our MoS$_2$-pentacene samples fabricated by layer transfer as compared to the observations of Homan et al.\textsuperscript{15} The pentacene layers grown by physical vapor deposition on water-soluble poly(acrylic acid) are highly crystalline, as has been confirmed by X-ray diffraction measurements performed on similar samples both before and after layer transfer.\textsuperscript{6} Consequently, the MoS$_2$-pentacene interface features pentacene molecules that are “standing up” as they would on the

Table 1. Fit Parameters for Decay Traces of A-Excitons in Composite MoS$_2$ and MoS$_2$-Pentacene Samples

| Sample                        | $t_1$ [ps] (A1) | $t_2$ [ps] (A2) | $t_3$ [ps] (A3) | $t_4$ [ps] (A4) |
|-------------------------------|-----------------|-----------------|-----------------|-----------------|
| MoS$_2$ single crystal        | 1.0 ± 0.5 (19%) | 28 ± 9 (27%)    | 1900 ± 265 (54%) |                 |
| MoS$_2$-pentacene heterojunction | 1.0 (18%)      | 21 ± 3 (34%)   | 1900 (48%)      |                 |

“Bold values are fixed during the fit for the heterojunction.

Figure 5. Transient reflection spectra of (a) WSe$_2$ monolayer crystals transferred to a gold substrate and (b) WSe$_2$ monolayer crystals covered by a pentacene thin film on the same substrate. A pentacene bleach peak appears at 688 nm in (b). (c) Transient reflection spectra of WSe$_2$ monolayer, WSe$_2$-pentacene junction and pentacene thin film, all on gold substrates, probed at 0.53 ps. (d) Normalized decay traces of B-excitons in a WSe$_2$ monolayer compared to a WSe$_2$-pentacene junction probed at 618 nm, both on gold substrates.
growth substrate. In contrast, disordered MoS$_2$-pentacene interfaces formed by physical vapor deposition of pentacene on MoS$_2$ are expected to exhibit molecules that are more randomly oriented, including molecules that are lying flat on the substrate. Several experimental studies indeed have shown that molecular monolayers of pentacene deposited onto MoS$_2$ comprise molecules that adopt such an orientation on the surface. Since exciton dissociation by hole transfer relies on the electronic coupling between the $\pi$- and $\pi^*$-orbitals of pentacene and the MoS$_2$ bands, the increased overlap of the electronic wave functions for molecules that are lying flat on MoS$_2$ would indeed give rise to faster exciton decay.

In addition, the substrates on which the MoS$_2$-pentacene layers reside may play a role. Our MoS$_2$-pentacene heterojunctions were transferred onto gold substrates, while in the work of Homan et al. quartz substrates were used. For MoS$_2$ gold interfaces, Fermi level pinning has been observed by us previously. According to a recent publication, the bandgap of MoS$_2$ and WSe$_2$ is also somewhat affected by the substrate: The band gap of MoS$_2$ is decreased by 0.21 eV and that of WSe$_2$ by 0.16 eV when the monolayers are located on Au substrates. These effects might lead to a different alignment of MoS$_2$ and pentacene energy levels as compared to MoS$_2$-pentacene heterojunctions on insulating quartz substrates. Huang et al. reported that the presence of a gold substrate modifies the charge distribution in MoS$_2$. All of the above could affect the hole transfer rates at the MoS$_2$/pentacene interface. We would like to stress, however, that in our experiments we used UV/ozone-treated Au substrates exhibiting a thin surface oxide, which decreases the aforementioned effects of gold on the TMDC monolayers significantly. For a strongly coupled Au/MoS$_2$ system, photoexcited states in MoS$_2$ could decay via interactions with the gold substrate, which then could affect the exciton decay behavior in samples both with and without pentacene. Since the exciton decay dynamics observed for our Au/MoS$_2$ samples are quite similar to the findings of Homan et al., who studied MoS$_2$ on SiO$_2$, this mechanism most probably does not play a major role in our experiments, and it can be concluded that the coupling between Au and MoS$_2$ is rather weak.

### 2.3 Tungsten Diselenide (WSe$_2$)

The second part of our work is dedicated to tungsten diselenide (WSe$_2$) monolayer crystals compared to WSe$_2$-pentacene heterojunctions. The pentacene layer is nominally the same as in the case of MoS$_2$: a 20 nm thick continuous film. The WSe$_2$ and pentacene layers again have been transferred onto a gold substrate. Our TRS measurements of WSe$_2$ single crystals, shown in Figure 5a, show a bleach peak at 610 nm for the B-exciton and a positive signal near the expected wavelength of the A-exciton above 730 nm. The peak position of the B-exciton is in agreement with previous publications. The positive signal might be related to a photoinduced absorption feature of an excited state. In addition, excitonic features could sometimes produce positive signals instead of bleaching due to broadening of the absorption spectra after excitation by the pump pulse. The positive signal appears at the border of the studied spectral window, and hence its temporal evolution cannot be traced accurately. Figure 5b shows TRS data for the WSe$_2$-pentacene junction. Besides the just discussed features of WSe$_2$, one can easily recognize a bleach peak of pentacene at 688 nm.

Figure 5c shows the TRS spectra of a WSe$_2$ monolayer (orange) and a WSe$_2$-pentacene heterojunction (green), as well as a pentacene thin film (all on Au substrates). The spectra are recorded at 0.53 ps after excitation of the system by the pump pulse. The B-exciton peak is experiencing a slight blue shift in the presence of pentacene, to 615 nm from 621 nm for the WSe$_2$-only sample. The observed shift might be related to a reduction of the exciton binding energy due to screening effects, as has been predicted for WSe$_2$ encapsulated by hexagonal boron nitride.

The most interesting region of the measured TRS data is associated with the B-excitons of WSe$_2$ as was mentioned earlier. In this section, we repeat the same procedure of fitting an exponential decay function described above to WSe$_2$-pentacene samples for the two different samples. The exciton behavior in monolayer crystals of WSe$_2$ is not as well studied as is the case for MoS$_2$. A number of previous works focused attention on A- and C-excitons in few layer and bulk WSe$_2$ mostly studying the ultrafast component <1 ps. He et al. provide some information on lifetimes of excitons in WSe$_2$ monolayers. For the uncovered WSe$_2$ monolayer, the decay traces of the B-excitons in our TRS measurements are well described by just two exponential components (see Figure 5d). Using a two exponential fit is not a unique way of studying the decay dynamics in TMDC monolayers and has been already implemented previously in work on MoSe$_2$ monolayers.

We do not detect a sub-picosecond decay component corresponding to ultrafast carrier trapping associated with defects in the single crystal, as found for MoS$_2$. Previously, we reported that similarly prepared monolayers of WSe$_2$ on metallic substrates feature vacuum level alignment according to the Schottky–Mott limit, unlike MoS$_2$ layers for which Fermi level pinning is observed. This different energy level alignment points to a considerably lower defect density in WSe$_2$ as compared to MoS$_2$, consistent with the absence of ultrafast defect-assisted trapping. The obtained values for $t_1$ and $t_2$ are 12 ± 1 ps and 624 ± 112 ps. The latter component corresponds to one-quarter of the weight in the biexponential fit. The decay traces of the WSe$_2$-pentacene heterojunction require an extra component with $t_1$ equal to 7 ± 1 ps to obtain a good fit, which we attribute to hole transfer from pentacene to WSe$_2$. In the WSe$_2$-pentacene case, $t_2$ (12 ps) is kept fixed; keeping both $t_2$ and $t_1$ or only $t_1$ fixed did not provide any reasonable fitting results. It should be noted, however, that similar values for $t_1$ as well as the weights of the slow decay component are found in the case of the heterojunction and uncovered WSe$_2$ case.

In addition, the decay of A-excitons in WSe$_2$ was measured with a silicon detector using spectral filters only, by means of lock-in detection resulting in better S/N in the data while losing some spectral resolution. The filter used to obtain the data is a PB700-40, i.e., with a 40 nm range centered at 700 nm (Supporting Information 1). Using this filter is suitable for

| WSe$_2$ single crystal | WSe$_2$-pentacene heterojunction |
|------------------------|----------------------------------|
| $t_1$ [ps] (A1) h* transfer | $12 \pm 1$ (75%) $7 \pm 1$ (39%) |
| $t_2$ [ps] (A2) exciton–phonon scattering | $12 \pm 1$ (75%) $7 \pm 1$ (39%) |
| $t_3$ [ps] (A3) radiative recombination and e$^–$ trapping | $624 \pm 112$ (25%) $705 \pm 95$ (20%) |

*Bold values are fixed during the fit for the heterojunction.*
detecting the temporal evolution of the A-exciton signal because even though it covers a rather large portion of the spectrum, there is no (ultra)fast decay of other excited states, e.g., of pentacene, which could negatively impact the data, such that the information that we obtain derives from the A-excitons. In the case of the WSe$_2$ pentacene heterojunction, the presence of pentacene again resulted in overall faster decay of the WSe$_2$ A-exciton. It was however not possible to assign individual decay components unambiguously to known processes because fixing the decay components did not provide reasonable fits. We believe that our results on TMDC-OS heterojunctions will help to stimulate future research and technical advancements in the area.

4. METHODS AND MATERIALS

MoS$_2$ and WSe$_2$ monolayer single crystals were grown on thermally oxidized silicon substrates (Siltronix, oxide thickness 300 nm, roughness <0.2 nm RMS) by a modified CVD growth method in which a Knudsen-type effusion cell is used for the delivery of sulfur and selenium precursors.\(^{21,23}\)

For heterostructure fabrication, the as-grown TMDs were transferred onto a suitable gold substrate. We have employed a poly(methyl methacrylate) (PMMA) assisted transfer protocol for the transfer.\(^{21}\) A PMMA layer of 200 nm (950 kDa, Allresist GmbH, AR-P 679.04) was spin coated onto the SiO$_2$/Si substrate with CVD grown TMD crystals. Then the substrate was kept floating on top of a bath of KOH solution (85%, Carl Roth) to etch away the SiO$_2$ layer and release the TMD crystals supported by PMMA followed by washing several times with ultrapure water (18.2 MΩcm, Membrapure) to remove any residual KOH. Then the PMMA supported monolayer TMD was placed on the target substrate and baked at 90 °C for 10 min, followed by immersion in acetone for 2 h to remove the PMMA support, followed by rinsing with isopropyl alcohol.

A 50 nm thick poly(acrylic acid) (PAA) layer was spin coated on a borosilicate glass substrate as water-soluble sacrificial layer. Then, 20 nm thick pentacene was evaporated on PAA with a deposition rate of 0.1 Å s$^{-1}$, while the substrate was held at room temperature. After the pentacene deposition, the highly ordered organic nanosheet was delaminated by dissolving the PAA layer by side injection of water from a reservoir.\(^{5}\) The floating nanosheet was transferred to a DI beaker to ease the transfer onto the target substrate. In parallel, the target substrate with transferred MoS$_2$ was immersed into acetone for 2 h to remove the PMMA supporting layer prior to nanosheet transfer. Then, the floating nanosheet was picked up by the target substrate and carefully dried under ambient conditions.

The process of transient absorption/reflectivity spectroscopy was conducted by a dedicated system at the research institute ELI-ALPS (Szeged, Hungary). The setup consists of a high speed (2000 spectra/s) fiber optic spectrometer and a laser driving the experiments. The laser system is a few-optical cycle ytterbium fiber chirped-pulse amplifier system that generates 30 fs pulses, with a 100 μJ pulse energy, at a repetition rate of 100 kHz centered at 1030 nm. The schematic layout, a more detailed description, and validation experiment of the custom-built transient absorption/reflection spectrometer are described in Supporting Information 1. The generated laser pulse is split into a 80/20 ratio where 80% of the

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**Table 3. Fit Parameters for Decay Traces of A-Excitons in WSe$_2$/WSe$_2$-Pentacene Samples**

|                  | $t_1$ [ps] (A1) | $t_2$ [ps] (A2) | $t_3$ [ps] (A3) | $t_4$ [ps] (A4) |
|------------------|----------------|----------------|----------------|----------------|
| WSe$_2$ single crystal | 8.1 ± 0.9 (56%) | 32.2 ± 5.6 (24%) | 401.4 ± 34.8 (20%) | 125.1 ± 11.3 (17%) |
| WSe$_2$-pentacene heterojunction | 6.6 ± 1.3 (54%) | 17.3 ± 4.9 (29%) | | |

interfaced, due to the Fermi level of MoS$_2$ being pinned to that of the gold substrate.\(^{20}\) In the case of WSe$_2$-pentacene heterojunctions, the A- and B-excitons showed different decay schemes. The B-exciton signal of the WSe$_2$ monolayer was fitted with a two-exponential decay function, with 12 and 624 ps components. In the presence of pentacene, the best fit was obtained by adding a fast 7 ps component associated with hole transfer, while keeping the 12 ps component fixed and changing the slow component to 705 ps. The A exciton decay was best described by fitting of a three-exponential decay function. The presence of pentacene again resulted in overall faster decay of the WSe$_2$ A-exciton. It was however not possible to assign individual decay components unambiguously to known processes because fixing the decay components did not provide reasonable fits. We believe that our results on TMDC-OS heterojunctions will help to stimulate future research and technical advancements in the area.

3. CONCLUSION

We studied exciton dynamics in van der Waals heterojunctions of MoS$_2$-pentacene and WSe$_2$-pentacene. We have found that in the case of MoS$_2$-pentacene heterojunctions the presence of the pentacene film has a moderate influence on the decay kinetics of A- and B-excitons. The A exciton was mostly affected by the presence of the pentacene film, exhibiting a 21 ± 3 ps decay component associated with hole transfer from MoS$_2$ to pentacene. Our results are noticeably different compared to a previous report on a similar structure, i.e., pentacene grown on MoS$_2$ on SiO$_2$, showing a faster hole transfer on the time scale of 6.7 ps. Several factors contribute to this, in particular, the different molecular orientations in transferred versus vapor deposited pentacene films, and the utilization of a different substrate (gold in this work versus SiO$_2$ substrate). The exciton dynamics could be affected by a different energy level alignment at the MoS$_2$-pentacene interface, due to the Fermi level of MoS$_2$ being pinned to that of the gold substrate.\(^{20}\) In the case of WSe$_2$-pentacene heterojunctions, the A- and B-excitons showed different decay schemes. The B-exciton signal of the WSe$_2$ monolayer was fitted with a two-exponential decay function, with 12 and 624 ps components. In the presence of pentacene, the best fit was obtained by adding a fast 7 ps component associated with hole transfer, while keeping the 12 ps component fixed and changing the slow component to 705 ps. The A exciton decay was best described by fitting of a three-exponential decay function. The presence of pentacene again resulted in overall faster decay of the WSe$_2$ A-exciton. It was however not possible to assign individual decay components unambiguously to known processes because fixing the decay components did not provide reasonable fits. We believe that our results on TMDC-OS heterojunctions will help to stimulate future research and technical advancements in the area.

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beam is used for the pump beam generation, and the remaining 20% generates the probe beam. The pump beam is frequency doubled on a Type-I BBO crystal (Eksma optics, 2 mm) resulting in a 515 nm center wavelength pulse. The pump-beam was focused on the sample surface with an excitation fluence of 0.7 mJ cm$^{-2}$. The probe beam was focused on the sample surface into a 60 μm × 50 μm spot with a 10 μJ cm$^{-2}$ fluence ensuring that the probe beam focus was smaller than the pump beam focus for optimal signal levels.

The obtained data were processed by a specially tuned Python script for background subtraction (Supporting Information 2). Spectral regions between the bleach peaks were adopted as reference points according to which background was subtracted appropriately. An example of the raw versus processed data, as well as the code, can be found in Supporting Information 2. The transient reflection spectra in images 3 and 6 were not additionally processed. Decay kinetic traces were obtained by direct averaging over a specified wavelength window without additional processing. The process of fitting the three-exponential decay function to study the exciton decay constants was compiled in a Python script utilizing the sklearn library including a least-squares error method.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.2c06144.

Experimental details of transient absorption/reflection spectroscopy, transient reflection spectra of mechanically exfoliated MoS$_2$, validation of the setup, a description of Python scripts for data processing, and fits of decay traces of B-excitons in MoS$_2$ and MoS$_2$-pentacene samples (PDF)

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