Achieving Ultrafast Hole Transfer at the Monolayer MoS$_2$ and CH$_3$NH$_3$PbI$_3$ Perovskite Interface by Defect Engineering

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ABSTRACT: The performance of a photovoltaic device is strongly dependent on the light harvesting properties of the absorber layer as well as the charge separation at the donor/acceptor interfaces. Atomically thin two-dimensional transition metal dichalcogenides (2-D TMDCs) exhibit strong light–matter interaction, large optical conductivity, and high electron mobility; thus they can be highly promising materials for next-generation ultrathin solar cells and optoelectronics. However, the short optical absorption path inherent in such atomically thin layers limits practical applications. A heterostructure geometry comprising 2-D TMDCs (e.g., MoS$_2$) and a strongly absorbing material with long electron–hole diffusion lengths such as methylammonium lead halide perovskites (CH$_3$NH$_3$PbI$_3$) may overcome this constraint to some extent, provided the charge transfer at the heterostructure interface is not hampered by their band offsets. Herein, we demonstrate that the intrinsic band offset at the CH$_3$NH$_3$PbI$_3$/MoS$_2$ interface can be overcome by creating sulfur vacancies in MoS$_2$ using a mild plasma treatment; ultrafast hole transfer from CH$_3$NH$_3$PbI$_3$ to MoS$_2$ occurs within 320 fs with 83% efficiency following photoexcitation. Importantly, our work highlights the feasibility of applying defect-engineered 2-D TMDCs as charge-extraction layers in perovskite-based optoelectronic devices.

KEYWORDS: perovskite, S vacancies, charge transfer, two-dimensional transition metal dichalcogenides, heterojunction

Hybrid organic–inorganic methylammonium lead halide perovskite materials have attracted intense interest recently because of their alluring prospects as high-efficiency, low-cost solar cells. To date, efficiencies of such solar cells have exceeded 22%. CH$_3$NH$_3$PbI$_3$ perovskites exhibit strong solar absorption, long electron–hole diffusion lengths, and relatively low trap densities for a solution-processed system, which impart the following advantages: (1) the use of thinner layers for light harvesting, (2) efficient transfer of photoinduced charges to the heterointerface before recombination, and (3) low trapping losses. Previous reports have shown that photoinduced electrons in CH$_3$NH$_3$PbI$_3$ perovskite films were injected into TiO$_2$. Marchioro and co-workers have shown that charge separation and injection take place simultaneously within the femtosecond-to-picosecond time scale at both the CH$_3$NH$_3$PbI$_3$/TiO$_2$ and CH$_3$NH$_3$PbI$_3$/spiro-OMeTAD interfaces. Contrary to the low-cost benefit of perovskite solar cells, spiro-OMeTAD (a hole-transporting material (HTM)) is in fact more costly than gold in weight. Being organic in nature, the stability issue is another concern. Hence there are ongoing efforts to develop inorganic HTMs or to use new photovoltaic architectures that bypass the need for HTM.
MoS$_2$ films are potentially good hole-transporting layers.\textsuperscript{14−23} State-filling in MoS$_2$ occurs within 50 fs, and ultrafast charge transfer can also take place within the same time scale.\textsuperscript{24−28} Solution-processed 2H-MoS$_2$ flakes have been used as hole transport layers in P3HT:PC$_{60}$BM organic solar cells, showing better performance than PEDOT:PSS.\textsuperscript{29,30} The
selection of hole-transporting layer is based on the following principles: band alignment, atmosphere stability, transparency, and hole mobility. However, the interface physics of two-dimensional transition metal dichalcogenides (2-D TMDCs) with halide perovskites is not well understood. According to band edge analysis using ultraviolet photoelectron spectroscopy (UPS, Supplementary Figure S1), the valence band maximum (VBM) of CH$_3$NH$_3$PbI$_3$ perovskite films is at −5.79 eV, higher than the VBM of MoS$_2$ monolayer (−6.28 eV); thus a pristine MoS$_2$ monolayer and CH$_3$NH$_3$PbI$_3$ form a type I heterojunction (Figure 1a), which hampers the dissociation and transfer of photogenerated electrons and holes from CH$_3$NH$_3$PbI$_3$ to MoS$_2$. This raises the fundamental question of how to fabricate a type II interface in the 2-D MoS$_2$/CH$_3$NH$_3$PbI$_3$ heterostructure. Interestingly, we found that creating S vacancies in MoS$_2$ through mild O$_2$ plasma treatment strongly improves the hole transfer rate between CH$_3$NH$_3$PbI$_3$ and MoS$_2$. Our work underlines the importance of defect engineering in tuning the band alignment of MoS$_2$ in heterostructures.$^{31–34}$

**RESULTS AND DISCUSSION**

**Ultrafast Hole Transfer from CH$_3$NH$_3$PbI$_3$ Perovskite to a Vacancy-Engineered MoS$_2$ Monolayer.** In order to verify the occurrence of ultrafast charge transfer at the MoS$_2$/perovskite interface, transient absorption spectroscopy (TAS) was performed to compare the dynamics at the MoS$_2$/CH$_3$NH$_3$PbI$_3$ and vacancy-engineered MoS$_2$/CH$_3$NH$_3$PbI$_3$ heterojunctions. Briefly, the “pump−probe” technique is based on using a pump pulse to first excite the carriers at the MoS$_2$/CH$_3$NH$_3$PbI$_3$ interface and then using a time-delayed probe pulse to interrogate the occupancy of these carriers at the valence or conduction bands by monitoring the absorption changes. Here, we monitor the photobleaching peaks (or +ΔT/T peaks from a reduction in absorption) of the direct gap transition from the valence band maximum to the conduction band minimum (CBM) of CH$_3$NH$_3$PbI$_3$, which give rise to a photobleaching peak located at ~1.63 eV (or ~760 nm).$^{35}$ Spatially resolved (or micro-area) transient absorption measurements were performed on the heterojunction and its nearby region with only CH$_3$NH$_3$PbI$_3$ (i.e., as the control without MoS$_2$). The MoS$_2$/CH$_3$NH$_3$PbI$_3$ heterostructure was prepared by spin-coating a ~30 nm thickness CH$_3$NH$_3$PbI$_3$ layer on the MoS$_2$ monolayer flake (Figure 1b and Supplementary S2). MoS$_2$ monolayers were mechanically exfoliated from bulk crystal and transferred onto clear quartz treated by a mild O$_2$ plasma process. Figure 1c shows the microscope image of a ~100 μm MoS$_2$ monolayer on a SiO$_2$/Si substrate. The AFM image indicates the thickness of monolayer MoS$_2$ is ~0.72 nm (Figure 1d), which is closed to the interlayer distance of ~0.65 nm.$^{36}$ A very strong photoluminescence (PL) peak of MoS$_2$ at ~1.85 eV is detected upon optical excitation at 2.33 eV with a power of 0.1 mW, which is characteristic of the typical MoS$_2$ A-exciton resonances, and the strong PL of CH$_3$NH$_3$PbI$_3$ films is at ~1.63 eV (Figure 1e). Figure 2a shows the buildup of the normalized photobleaching signature from
the 1.63 eV peak for both the CH3NH3PbI3 control (without MoS2) and the pristine MoS2/CH3NH3PbI3 heterostructure, following ~1.72 eV (or ~720 nm) pump excitation to selectively excite CH3NH3PbI3 only. This rise of the photo-bleaching transients reflects the state-filling at the perovskite band edges. A delayed rise time is indicative of charge extraction of the carriers prior to them relaxing to the band edges. However, the near invariance of the rise times signifies the absence of any such charge transfer, which is consistent with a type I band alignment between pristine MoS2 and CH3NH3PbI3 (Figure 2b). The rise time for both the CH3NH3PbI3 control sample and the pristine MoS2/CH3NH3PbI3 heterostructure are 260 ± 50 and 260 ± 40 fs, respectively (Figure 2a and Supplementary S3) after deconvolving the instrument response function. In contrast, the photo-bleaching signatures for the vacancy-engineered MoS2/CH3NH3PbI3 heterostructures (Figure 2c) show a delayed rise as compared to the CH3NH3PbI3-only film, which is indicative of charge transfer to MoS2 in the former. When the photoinduced holes in CH3NH3PbI3 are transferred into the vacancy-engineered MoS2 monolayer, the band edge state-filling in perovskite becomes slower. The observed dynamical behavior (of longer PB rise time) in the vacancy-engineered MoS2/CH3NH3PbI3 is analogous to that in a previous report, although the detailed mechanisms of the hole transfer in these cases are different. This would be consistent with a type II energy alignment at the vacancy-engineered MoS2/CH3NH3PbI3 heterostructure (Figure 2d). Similarly, the rise times of the CH3NH3PbI3 control and the vacancy-engineered MoS2/CH3NH3PbI3 heterostructures were fitted to be 265 ± 40 and 580 ± 50 fs after deconvoluting the instrument response function (red circles with the fitted red solid line in Figure 2c and Supplementary S3). Using a simple phenomenological model given by (1), where and are the hot hole cooling rates of CH3NH3PbI3 in CH3NH3PbI3-only films and the vacancy-engineered MoS2/CH3NH3PbI3 heterostructure, respectively, and is the hole transfer rate from CH3NH3PbI3 to vacancy-engineered MoS2 (see Supplementary S4 for details), we can estimate the hole transfer time from CH3NH3PbI3 to vacancy-engineered MoS2 in the heterostructure using 1/. Accordingly, is estimated to be ~490 ± 50 fs (see Supplementary S4 for details). The hole transfer efficiency can be determined using the equation (2), where is the chemical potential of constituent i referenced to elemental solid or gas with chemical potential . The are the number of S atoms, extrinsic defects O, and the number of electrons transferred from the host to the reservoirs in forming the defect MoS2. The calculated results show that the defect formation energy, ( ), of the S vacancy ( ) is 1.33 and 2.73 eV under S-poor and S-rich conditions, which is smaller than those of other intrinsic defects, i.e., Mo vacancy ( ), Antisite (S), and Antisite and Antisite (S, 4.5 and 8.7 eV) (Supplementary S6, Table S1); therefore S vacancies are the main defect in monolayer MoS2. The projected density of states (pDOS) of monolayer MoS2 with a defect level is shown in Figure 3c. The defect level of Vs is mainly dominated by the S atom, indicating that an acceptor energy level is introduced in the band gap. Thus, the defect results in p-type doping in monolayer MoS2. The lowering of the Fermi level to the VBM increases the work function of the MoS2 monolayer, which contributes to the breakdown of band offset at the MoS2/CH3NH3PbI3 interface.

To understand the role of the oxygen defect, if any, in facilitating the charge transfer, we also calculated monolayer MoS2 doped with O atoms, since the latter are present in the plasma environment. In the monolayer MoS2 supercell, we consider two doping cases, one based on the substitutional doping of an O atom by O (O) and the other based on the adsorption of an O atom on the sulfur site (Oads). The results show that although the band gap decreases as the
concentration increases, the VBM hardly shifts. There is only a 0.05 eV downward shift of the VBM in the case of Os doping and a 0.1 eV shift for the Oads doping case (Supplementary S6, Figure S6). Therefore, the introduction of O atoms into monolayer MoS2 does not influence the VBM and Fermi level.

Figure 3d shows the projected band structure of Os-doped monolayer MoS2 with a band gap of 1.65 eV. The red circles represent the O component, where the size of the circle means the weight of O2p states. It is found that the O2p states are far below the VBM, which further confirms that O states do not contribute to the electron transition near the Fermi level and VBM. Therefore, our theoretical results suggest that S vacancies in the MoS2 monolayer are the origin of the shifts in Fermi level following the plasma treatment, which leads to an improved band alignment at the interface, facilitating ultrafast hole transfer.

Scanning Kelvin probe microscopy (SKPM) was used to measure the work function of pristine and a vacancy-engineered MoS2 monolayer. The concentration of S vacancies can be increased by raising the plasma power and reaction time. Consequently, the work function is increased due to the lowering of the Fermi level. Figure 4a shows that the work function of vacancy-engineered MoS2 can be engineered between 4.7 and 5.3 eV by varying the concentration of the S vacancies, which is consistent with our first-principles calculation results. It is worth pointing out that AFM studies show that the topography of the MoS2 monolayer is almost indistinguishable before and after mild plasma treatment (Supplementary Figure S7). The photoluminescence feature peak of monolayer MoS2 is at ~1.85 eV, which is characteristic of A-exciton resonances. The PL intensity of the MoS2 monolayer gradually decreases with increasing plasma treatment power (Figure 4b) and eventually became completely quenched. The peak intensity of A-exciton and B-exciton transitions at ~1.9 and 2.05 eV decreases drastically (Figure 4c). We suggest that increasing the plasma power leads to the increasing concentration of S vacancies and other types of dislocations in the MoS2 monolayer, which leads to a decrease in the exciton absorption intensity. Meanwhile, the nonradiative rate of electron–hole recombination increases, resulting in the gradual PL quenching of the vacancy-engineered MoS2 monolayer. The Raman in-plane E2g mode and out-of-plane A1g mode of an exfoliated MoS2 monolayer are at 386.7 and 405.1 cm−1 (Figure 4d), respectively. The creation of S vacancies in the MoS2 lattice results in the softening of the out-of-plane A1g vibration mode and stiffening of the in-plane E2g mode; thus the A1g peak red-shifts and the E2g peak blue-shifts. Significant disorders are generated in the lattice, leading to the increase in FWHM of the A1g and E2g peaks.

Tuning of Ultrafast Hole Transfer Rate. To further validate our hole transfer model, we also photoexcite the vacancy-engineered MoS2/CH3NH3PbI3 at a higher energy of 2.48 eV, where a longer charge transfer time is expected due to holes cascading/transferring from deeper valence states. A detailed comparison of the photobleaching transients at the 1.63 eV photobleach peak following 2.48 eV excitation with a fluence of 6 μJ cm−2 for both the vacancy-engineered MoS2/CH3NH3PbI3 and CH3NH3PbI3-only film was carried out (Figure 5a and Supplementary S8). Although in this case, both
the vacancy-engineered MoS$_2$ and CH$_3$NH$_3$PbI$_3$ can be excited, the photobleach signature is mainly from the perovskite, as the transient absorption signals from the vacancy-engineered MoS$_2$ alone are below the detection limit of our setup (blue circles in Figure 5a). By deconvoluting the instrument response function, the rise time of the 1.63 eV photobleach transient in the CH$_3$NH$_3$PbI$_3$ sample and vacancy-engineered MoS$_2$/CH$_3$NH$_3$PbI$_3$ heterostructures are estimated to be 270 ± 40 and 450 ± 50 fs, respectively (Figure 5a). The charge transfer time and efficiency are estimated to be ∼675 ± 50 fs and ∼40%, respectively. Indeed, photoexcitation at 2.48 eV results in a delayed transfer as expected. These transient absorption measurements unambiguously validate the ultrafast hole transfer from CH$_3$NH$_3$PbI$_3$ to the vacancy-engineered MoS$_2$ monolayer.

The charge transfer rate is determined by the expression $1/\tau_{CT} = cN_h$, where $c$ (cm$^3$/s) is the hole-capture coefficient and $N_h$ is the concentration of S vacancies in the vacancy-engineered MoS$_2$ monolayer. Thus, the hole transfer rate between vacancy-engineered MoS$_2$ and CH$_3$NH$_3$PbI$_3$ can be tuned by adjusting the concentration of S vacancies in the MoS$_2$ monolayer via increasing the treatment time of mild plasma. A pump beam at 1.72 eV with a fluence of 7.2 µJ cm$^{-2}$ is used to selectively photoexcite CH$_3$NH$_3$PbI$_3$ only. Using the same instrument response function for time convolution, the rise time of photobleaching transients at 1.63 eV in a heterostructure consisting of vacancy-engineered MoS$_2$ with more treatment time (VM 5) and CH$_3$NH$_3$PbI$_3$ is estimated to be 1.56 ± 0.06 ps (Figure 5b). Accordingly, the charge transfer time is significantly improved to ∼320 ± 50 fs, and the hole transfer efficiency is increased to ∼83%. The hole transfer efficiency at the vacancy-engineered MoS$_2$ monolayer/CH$_3$NH$_3$PbI$_3$ interface is comparable with that of the reported hole injection efficiency from CH$_3$NH$_3$PbI$_3$ to spiro-OMeTAD (90 nm thickness), which occurs within picoseconds following photoexcitation. This suggests that the vacancy-engineered MoS$_2$ monolayer is an excellent hole-transporting material and a promising alternative to spiro-OMeTAD in terms of its ultrathin, chemically and thermally stable, and highly efficient photovoltaic architecture. It should be noted that the hole transfer efficiency is 40%, 54%, and 83% with the increasing S vacancy concentration in the vacancy-engineered MoS$_2$ monolayer (VM 3, VM 4, VM 5), while the hole transfer times are 675 ± 50, 490 ± 50, and 320 ± 50 fs, respectively, as shown in Figure 5c. Thus, our results suggest that the hole transfer efficiency increases with the increasing population of S vacancies in the vacancy-engineered MoS$_2$ monolayer.

CONCLUSION

Our charge transfer dynamics studies reveal that holes can be efficiently transferred at the heterointerface of a vacancy-engineered MoS$_2$ monolayer and CH$_3$NH$_3$PbI$_3$, but not at the
interface comprising pristine monolayer MoS2. The formation of S vacancies in the MoS2 monolayer p-dopes the material and facilitates ultrafast hole transfer from CH3NH3PbI3 to MoS2. A viable strategy to tune the hole transfer dynamics is based on controlling the population of S vacancies, where a higher population leads to higher charge transfer efficiency. Vacancy-engineered MoS2/CH3NH3PbI3 heterostructures exhibit ultrafast hole transfer dynamics within the hundreds of femtoseconds time scale, suggesting that the vacancy-engineered MoS2 monolayer and CH3NH3PbI3 can be incorporated as an ultrathin hole extraction layer and active layer in optoelectronic devices.56 Recent developments in the large-scale preparation of MoS2 by CVD will allow the integration of a vacancy-engineered MoS2 monolayer as a cost-effective ultrathin hole transport layer in large-area perovskite solar cells.51,57–60

The poor stability of lead halide perovskite solar cells in air has so far hampered sustained operation under normal conditions,61 thus addressing the long-term stability is critical for future developments. The perovskite photoactive layer can be protected by using stable inorganic hole transport layers (CuSCN, CuI, NiOx and Ni3MgO4).62–65 Using partially oxidized 2H-phase MoS2 nanosheets (MoO3−MoS2) as hole-transporting material, long-term performance and stability have been achieved in organic solar cells (MoO3−MoS2/P3HT:PC61BM/Al).29 Therefore, it is possible that a MoS2 monolayer, besides serving as a hole transport layer, can also act as an excellent protective layer to protect the perovskite from moisture and air.

METHODS

CH3NH3I Synthesis. CH3NH3I was synthesized by using a reported method.66 Briefly, 3.04 mL of methylamine (40% in methanol, TCI) was added in 50 mL of ethanol under Ar gas, and the solution was stirred for 30 min at 0 °C. Then, 2 mL of hydroiodic acid (55 wt % in water, Sigma-Aldrich) was added. The mixed solutions were further stirred for 2 h. The white raw product methylammonium iodide (CH3NH3I) was obtained by rotary evaporation at 50 °C, washed three times with diethyl ether, and then finally recrystallized from a mixed solvent of diethyl ether and ethanol. The white solid was dried under vacuum for 24 h and stored in a glovebox.

MoS2/CH3NH3PbI3 Heterostructure Preparation. MoS2 monolayer flakes were mechanically exfoliated from bulk crystal onto PDMS films and then transferred onto various substrates such as clear quartz, flat Au film, and Si/SiO2 (300 nm) substrates. The MoS2 monolayer was treated by a reactive ion etching system (VITA-MINI) to generate S vacancies (Supplementary S9). The 6.4 wt % solutions of PbI2 and CH3NH3I were added. The mixed solutions were stirred for 30 min at 30 °C, filtered by a 740 nm long-pass filter and a 775 nm band-pass filter, and then treated by mild O2 plasma. The samples, which were kept under vacuum for 1 h to remove the residual DMF solvent. MoS2/CH3NH3PbI3 heterostructures were stored in a glovebox before measurements.

Spatially Resolved (or Micro-area) Transient Absorption Spectroscopy. Spatially resolved transient absorption spectroscopy was performed in transmission mode driven by a femtosecond laser system seeded by a mode-locked Ti-sapphire oscillator (Coherent Vitesse, 80 MHz). The system output beam at 800 nm was generated using a 4-f étendue (NA 0.7). The pump beam passing through the sample was filtered by a 775 ± 23 nm band-pass filter and a 740 nm long-pass filter, while the transmitted probe beam was detected by a photodiode and a lock-in amplifier after modulating the pump beam with a 83 Hz chopper.

Scanning Kelvin Probe Microscopy Measurement. SKPM was measured using a Park Systems XE-100 AFM. The exfoliated MoS2 monolayer was first transferred onto flat Au substrates prepared by the procedures described in the literature67 and then treated by mild O2 plasma. The cantilevers with Au-coated tips used for the measurements were purchased from Mikromasch. The topographic and surface potential (SP) measurements were obtained using a dual-pass tapping mode with a cantilever resonant frequency of approximately 160 kHz. In the SKPM measurement, the Fermi levels are aligned between the electrically connected sample surface and the Au tip. The work function (WF) difference between the sample and tip will generate a field that will be nullified by the voltage applied from the SKPM system identified as the surface potential. The SP is defined as

\[ SP = WF_{tip} - WF_{sample} \]

where WFtip and WFsample are the WFs of the conductive tip and the sample, respectively. In this study, the probe tip has been calibrated with highly ordered pyrolytic graphite (HOPG) (WFHOPG = 4.6 eV) in order to convert the SP to the absolute work function of the sample as follows:

\[ WF_{sample} = 4.6 + SP_{HOPG} - SP_{sample} \]

HRTEM Measurement. TEM imaging was carried out in an image aberration-corrected TEM (FEI Titan 80-300 operating at 60 kV), and a charge-coupled device camera (2*2 k, GatanUltraScan 1000) is used for image recording with an exposure time of 0.5 s. The third-order spherical aberration was set in the range 0.2–1 nm, and the TEM images were recorded slightly underfocused.

UV–Vis Absorption, PL, and Raman Measurement. UV–vis absorption data of pristine and vacancy-engineered MoS2 monolayers were obtained by a CACR 20 UV–visible–NIR spectrophotometer. The PL and Raman signals were recorded by a Witec Alpha 300R Plus confocal Raman microscope upon 532 nm laser excitation with 0.1 mW.

ASSOCIATED CONTENT

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.6b02845.

Determination of band alignment in a MoS2/CH3NH3PbI3 heterostructure; thickness measurement of CH3NH3PbI3 perovskite films; system response deconvolution; charge transfer modeling; triangular vacancy clusters and defect agglomerations; calculation method; topography images of MoS2 monolayer before and after O2 plasma treatment on MoS2 monolayer (PDF).

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Author Contributions

T.C.S., and K.P.L. performed data analysis. All authors discussed the results and wrote the manuscript.

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Notes
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