Hot carrier extraction from 2D semiconductor photoelectrodes

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Hot carrier-based energy conversion systems could double the efficiency of conventional solar energy technology or drive photochemical reactions that would not be possible using fully thermalized, “cool” carriers, but current strategies require expensive multijunction architectures. Using an unprecedented combination of photoelectrochemical and in situ transient absorption spectroscopy measurements, we demonstrate ultrafast (<50 fs) hot exciton and free carrier extraction under applied bias in a proof-of-concept photoelectrochemical solar cell made from earth-abundant and potentially inexpensive monolayer (ML) MoS2. Our approach facilitates ultrathin 7 Å charge transport distances over 1 cm2 areas by intimately coupling ML-MoS2 to an electron-selective solid contact and a hole-selective electrolyte contact. Our theoretical investigations of the spatial distribution of exciton states suggest greater electronic coupling between hot exciton states located on peripheral S atoms and neighboring contacts likely facilitates ultrafast charge transfer. Our work delineates future two-dimensional (2D) semiconductor design strategies for practical implementation in ultrathin photovoltaic and solar fuel applications.

2D materials | solar energy conversion | hot carrier | transient absorption spectroscopy | photoelectrochemistry

All semiconductors absorb photon energies greater than their bandgap, temporarily creating hot carriers with excess energy. In a conventional solar cell material like Si, 40% of the absorbed solar energy is lost as heat because hot carriers rapidly cool in <100 fs (1). This ultrafast hot-carrier cooling process prevents current solar cell technology from reaching theoretical efficiency limits (2).

A long-standing challenge in the field is to develop materials and selective charge-extraction contacts that efficiently collect hot carriers before they cool (3). The first experimental demonstration of hot-carrier extraction involved the transfer of photogenerated hot carriers from a bulk InP crystal to p-nitrobenzonitrile molecules in an electrochemical cell (4). Unfortunately, a significant fraction of hot electrons thermalized in the InP bulk. Recent efforts in solid-state photovoltaics have focused on enhancing hot-carrier populations in the semiconductor absorber and using charge-energy-selective contacts to preferentially extract hot electron and hole populations [e.g., In0.78Ga0.22As0.81P0.19 quantum well surrounded by thick In0.5Ga0.5As0.49P0.50 barriers contacted by n- and p-doped InP contact layers (5)]. Unfortunately, such multilayer structures require expensive materials and growth methods, especially for the critical charge-selective contacts.

Nanostructured materials possess unique photophysical and structural properties that could make hot-carrier-based energy conversion systems both efficient and inexpensive, but this remains a formidable challenge (6). For example, while hot-carrier extraction in graphene optoelectronics is possible (7), graphene-based photovoltaics exhibit low quantum efficiency and small photovoltages (8, 9). Plasmonic metal nanostructure solar energy conversion systems suffer from low power conversion efficiency due to fast hot-carrier cooling (10). While hot-carrier extraction at model interfaces made of solution-processed organic–inorganic lead halide perovskite (11) and lead chalcogenide nanocrystals (12) has been demonstrated, electrical measurements of hot-carrier effects in a working solar energy conversion system are scant. Indeed, recent ultrafast X-ray measurements of lead halide perovskites highlight the need for concurrent electrical measurements because interpretation and quantification of hot electron and hole temperatures can be difficult using optical measurements alone (13).

In this work, we investigate the intriguing possibility of using inexpensive, earth-abundant, and potentially scalable (14) transition metal dichalcogenides (TMDs) such as monolayer (ML) MoS2 for hot-carrier extraction using a proof-of-concept photoelectrochemical solar cell. The bulk MoS2 is an ideal candidate due to its large fraction of sunlight, but this remains a formidable challenge. ML TMDs are exciting absorber materials because high-energy photons generate hot excitons that are 0.98 eV above the optical band gap, often called C-excitons.

Significance

Solar cell materials absorb a large fraction of sunlight, but most of the solar energy is not converted to electricity. Instead, most of the absorbed solar energy is lost as heat. Here, we show that ultrathin 2D materials can extract the excess solar energy before it is lost as heat.
with >100 ps lifetimes (16). These long and tunable (17) lifetimes exceed ultrafast photocurrent response in optoelectronic devices (18), which suggests that hot carriers could be contributing to current in the device. Optical signatures of hot-carrier transfer from MoS$_2$ to graphene (16) and gold (19) also suggest that hot-carrier transfer could outpace cooling, but electrical signatures of hot-carrier transfer have remained elusive. Electrical measurements of solid-state ML TMD devices typically require edge-on contacts for charge extraction, meaning charge carriers travel micron-long distances to the charge-collecting interfaces. The long transport distances promote cooling and recombination, which likely explains why hot carrier-induced currents have not been reported in any 2D TMD-based solar energy conversion device. The advantage of employing TMD absorbers in a photoelectrochemical cell is that photogenerated charge carriers need only travel across three atoms (0.7 nm) to reach the electron-selective indium tin oxide (ITO) substrate and hole-collecting redox electrolyte (Fig. 1 A). The long lifetime of C-excitons combined with short charge-transfer distances and intimate charge carrier-selective contacts thus raises the exciting possibility of extracting hot carriers in the model ML-MoS$_2$|I$_2$|I$_3$|Pt solar cell.

Using an unprecedented combination of photoelectrochemical and in situ time-resolved spectroscopic techniques, here we show that hot-carrier extraction outcompetes exciton formation and relaxation in a working photoelectrochemical cell. We demonstrate that hot carriers can be extracted to generate photocurrent before cooling to the band-edge and develop a picture of the photocurrent generation mechanism in ML-MoS$_2$ photoelectrodes.

Results and Discussion

Optical and Photoelectrochemical Characterization of the ML-MoS$_2$ Photoelectrode. Here, we test our hypothesis that one should be able to preferentially extract hot carriers from the C-exciton manifold in ML-MoS$_2$ using the electron- and hole-selective contacts in a photoelectrochemical cell because the three

![Fig. 1. Optoelectronic properties of the monolayer MoS$_2$ photoelectrochemical cell. (A) Cartoon illustration of the three-electrode photoelectrochemical cell. The solid blue and rainbow arrows indicate pump and probe pulses for TA measurements. Pt counter and Ag/AgI reference electrodes are omitted for clarity. (B) Absorbance spectra in 0.025 V increments from 0.0 V to 0.55 V. (C) EQE spectra vs. applied potential from 0.35 V to 0.55 V. EQE($\lambda$) = $qi / I_0(\lambda)$, where $q$ is the electronic charge (in units of C), $i$ is the photocurrent (in units of A), and $I_0$ is the monochromatic light power (in units of s$^{-1}$). (D) Monochromatic i-E measurements for resonant A-, B-, and C-exciton excitation (i.e., 650 nm, 605 nm, and 432 nm, respectively).](https://doi.org/10.1073/pnas.2220333120)
atom-thick transport distance minimizes the electron and hole transport times relative to the cooling times. Photoluminescence (PL), Raman spectroscopy, and absorbance spectroscopy confirmed that the chemical vapor deposition (CVD) growth method produced ML-MoS$_2$ (*SI Appendix*, Fig. S1). To probe the hot-carrier generation, recombination, and extraction processes, we constructed a transparent photoelectrochemical cell that enables in situ ultrafast spectroscopy measurements to measure relative exciton populations after photo-excitation (Fig. 1A). The ML-MoS$_2$-coated ITO electrode serves as the working electrode in a three-electrode microfluidic electrochemical cell containing 1 M sodium iodide (NaI) electrolyte. Fig. 1A schematically shows that under illumination and applied positive potentials, photogenerated holes move to the semiconductive/liquid interface and oxidize I$^- $ to I$_2$, while photogenerated electrons transfer to the ITO substrate, generating net anodic current flow through the cell.

To assess which excitonic transitions contribute to current flow in the ML-MoS$_2$ photoelectrode, we simultaneously measured optical absorbance and photocurrent signals under working photoelectrochemical conditions. Fig. 1B shows absorbance spectra of ML-MoS$_2$ as a function of the applied potential ($E$, referenced to the Ag/AgI electrode). All spectra feature three peaks corresponding to the band-edge A (1.90 eV) and B (2.01 eV) excitons, and the higher-energy C-exciton (2.98 eV). The A- and B-exciton peak intensities increase and blue shift with increasing positive potential, in agreement with the literature, while the high-energy C-exciton increases slightly with positive bias and does not shift with potential. The origin of this potential-dependent absorption behavior can be explained as follows. Two distinct optical transitions contribute to the absorption feature in the A-exciton region. The neutral A-exciton absorbance dominates at positive potentials. At more negative potentials, the negatively charged trion absorbs strongly, resulting in a shoulder feature at 1.85 eV. The A-exciton absorption feature increases in intensity and narrows in width as the potential moves from negative to positive values because oscillator strength transfers from the trion to the neutral exciton (20). This sharpening effect has also been observed by Carroll et al. (21) and Sie et al. (22). The observed potential-dependent absorbance changes (Fig. 1B) have important consequences for interpreting the relative populations of excitons gleaned from ultrafast TA measurements, as will be discussed below.

Photocurrent measurements performed concurrently with the absorbance measurements revealed at which potentials the different excitons dissociate and contribute to current flow in the cell. Fig. 1C shows potential dependent external quantum efficiency (EQE) spectra, where $\text{EQE} = ilqI_0$ and $i$ is the photocurrent, $q$ is the elementary charge, and $I_0$ is the light power. At positive bias (e.g., $E > 0.5 \text{ V}$), the EQE spectrum mimics the absorbance spectrum (solid purple line in Fig. 1C), indicating that the applied potential generates a sufficiently strong interfacial electric field to effectively dissociate all the three excitonic species. Close examination of the potential-dependent spectra reveals subtle differences between the photocurrent onset potential ($E_{\text{on}}$) for the A-, B-, and C-excitons that could be further distinguished in monochromatic $i$-$E$ curve measurements (Fig. 1D). Interestingly, photocurrent generation onsets first (i.e., less positive potentials) for the C-exciton and the slope of the C-exciton $i$-$E$ curve is significantly steeper than that of the A/B-excitons. Note, we observed no photocurrent upon illuminating the ITO substrate under these illumination conditions (*SI Appendix*, Fig. S2A). The photovoltage, defined as $E_{\text{on}} - E^0_c$ (T, 1), where $E^0_c$ (T, 1) is the formal potential of the iodide/iodine couple (0.63 V vs. Ag/AgI), is largest for C-exciton illumination. The lower $E_{\text{on}}$ value means that, under conditions of equivalent interfacial electric field strength, photo-excited C-excitons require less driving force to dissociate and contribute to current flow in the cell compared to the lower-energy A/B-excitons (23). Since we did not observe photocurrent upon directly exciting the A/B-excitons at the same applied potential as that of the C-exciton (specifically $E = 0.35 \text{ V}$ in Fig. 1D), our monochromatic $i$-$E$ data strongly suggest that C-excitons are extracted before they cool to the band-edge and form low-energy A/B-excitons.

**Nature of Excitonic States and Their Implication for Charge Transfer.** Why is C-exciton extraction more efficient than low-energy A/B-exciton extraction in an ML-MoS$_2$ photoelectrode? To shed light on this critical question, we turned to a theoretical treatment of the spatial distribution of the A/B- vs. C-excitons in ML-MoS$_2$.

The goal of this theoretical investigation is to qualitatively compare the magnitude of electronic coupling between the different exciton states in the charge donor (MoS$_2$) and the electron/hole acceptors (ITO substrate/iodide anions), which ultimately allows us to rationalize why charge transfer from the C-exciton is more efficient than that of A/B-excitons.

We first analyzed the excitonic wavefunctions obtained by solving the Bethe–Salpeter equation (BSE) for unsupported ML-MoS$_2$ in vacuum (*Methods*). This approach accounts for excitonic effects by explicitly treating electron–hole correlation. Fig. 2, *Center* shows the resulting Eigen spectrum of pristine ML-MoS$_2$, where the bound eigenstates arising from a BSE calculation are linear combinations of independent-particle states at different points in quasi-momentum (k-) space. The purple lines are the lowest energy excitonic states around the K point. The lowest energy transition is the A-exciton ($E^0_A$) and optical bandgap of MoS$_2$, while the higher energy states are the A-exciton “hydrogenic series,” consistent with the literature (24, 25). The green lines represent the levels in the band nesting region between K and $\Gamma$, where the lowest energy transition is the C-exciton $E^0_C$. The B-exciton states do not appear in Fig. 2, *Center* because our calculations do not include spin-orbit coupling effects.

We now consider the comparative ease of extracting electrons from the photo-excited C-exciton in contrast to A/B-excitons from a classic Marcus-type charge transfer (26, 27) pathway comparing the relative magnitude of the electronic coupling associated with electron (hole) transfer from the C- vs. A/B-excitons in MoS$_2$ to ITO (iodide). Marcus-type arguments have been previously employed to analyze charge transfer characteristics between TMDs and quantum dots or molecular species (28). When the rate of electron (hole) transfer to the ITO substrate (iodide) is in the small electronic coupling regime, then the rate of charge transfer is proportional to $|V|^2$, the absolute value of the electronic coupling that connects the donor and acceptor states. The A- and C-excitons, formed from states in different regions of the band structure, have different spatial distributions within the MoS$_2$ layer. Fig. 2, *Top* illustrates that A-excitons are localized on interior Mo atoms, whereas C-excitons have significant electron density on the peripheral S atoms, consistent with the atomic orbital composition of these k-space regions in previous DFT calculations (29–31). Since $V$ decays exponentially with the distance between the donor and acceptor, one would expect that the C-excitons’ closer approach to the ITO/aqueous interfaces results in a faster charge transfer rate. To make this a quantitative Marcus-type analysis, one would additionally require the construction of charge localized states, the calculation of their energies and couplings, the calculation of exciton/charge phonon coupling, and its modulation by the disorder of the solution. Methods for these calculations are still under development (32–36) and, therefore, beyond the scope of this
study. Nevertheless, our results and calculations provide unique insight into the origin of distinct photocurrent efficiencies for the A/B- and C-excitons in an ML-MoS2 photoelectrode. Furthermore, since the hole density of the C-exciton is localized on the interior Mo atoms and less electronically coupled to the iodide acceptors, one might hypothesize that the redox mechanism is a sequential electron transfer to ITO preceding hole transfer to the iodide acceptors. Therefore, it is possible to hypothesize that the redox mechanism is a sequential electron transfer to ITO preceding hole transfer to the iodide acceptors, and that the redox mechanism is a sequential electron transfer to ITO preceding hole transfer to the iodide acceptors.

Exciton Population Dynamics via Ultrafast Transient Absorption (TA) Spectroscopy. We leveraged ultrafast pump-probe TA spectroscopy to assess the feasibility and elucidate the mechanism of hot-carrier extraction in ML-MoS2 photoelectrodes. In situ TA spectroscopy allowed us to measure relative changes in exciton populations under working photoelectrochemical conditions. In this experiment, we employ a transform-limited, <50 fs, 3.1 eV pump pulse corresponding to the high energy side of the C-exciton to generate a distribution of excited states, including hot free carriers in continuum states of ML-MoS2. Experiments were performed with a pump fluence of 75 µJ/cm², where the exciton bleach intensities are linear with pump fluence (SI Appendix, Fig. S3), in agreement with the literature (16). A white light continuum probe pulse spanning 3.1 eV to 1.65 eV was used to measure the absorbance changes of the sample as a function of pump-probe delay time (Methods). A potential-dependent anodic current flows through the cell upon photoexcitation of the sample with the pump pulse (SI Appendix, Fig. S4), further confirming that the TA experiment reports on exciton populations under working photoelectrochemical conditions. Fig. 3A shows TA spectra at τ = 1 ps as a function of applied potential. Control experiments with bare ITO electrodes do not produce TA bleach signals (SI Appendix, Fig. S2B). The τ = 1 ps condition yields spectra whose excitonic features are not dominated by the influence of hot electrons or free carriers and, therefore, this delay time provides a clear picture of the relative changes in exciton population vs. applied potential (37). The TA signal is given by

$$\Delta A(\tau) = A_{\text{pumped}}(\tau) - A_{\text{unpumped}},$$

where $$A_{\text{pumped}}(\tau)$$ and $$A_{\text{unpumped}}$$ represent the absorbance values of the pumped and unpumped samples, respectively. Fig. 3A shows bleach features (negative $$\Delta A(\tau)$$) at the exciton peak energies due to exciton formation and some positive $$\Delta A(\tau)$$ features due to pump-induced lineshape narrowing and excited state absorption. The fact that we observe bleach signals from all exciton states indicates that free electrons and holes in unbound states relax into A, B, and C-exciton populations, in agreement with the literature (38). However, C-excitons do not decay into A/B-exciton states, as will be discussed in further detail below. Unlike bulk semiconductors, $$A_{\text{unpumped}}$$ changes significantly with applied potential (Fig. 1B) for ML-MoS2 and must be considered when interpreting relative exciton populations from in situ TA data.

Before discussing changes in the relative exciton populations, we first examine the exciton formation and depletion processes in the ML-MoS2 photoelectrode. Fig. 3B shows A- and C-exciton TA decay dynamics at 0.5 V and 0.0 V, corresponding to conditions of significant anodic photocurrent and no photocurrent, respectively. The B-exciton behavior closely follows that of the A-exciton (SI Appendix, Fig. S5) and is omitted from Fig. 3B for visual clarity. The temporal behavior of the C-exciton and the band-edge A/B-excitons display three key differences (Fig. 3B and SI Appendix, Figs. S5 and S6 and Table S1). First, the C-exciton bleach intensity reaches a maximum value almost instantaneously (i.e., τ = 0 ps), indicating that C-excitons form on a faster timescale than our instrument response (<50 fs), which aligns with previous work (38) and is expected since the pump pulse is tuned to the high energy side of the C-exciton spectrum. The C-exciton bleach signal increases at ~400 fs because in our TA experiments, the pump pulse and probe pulse overlap at the sample to produce the third-order signal. The instrument response function of this pump-probe overlap is approximately 100 fs full-width-half-maximum. The pump energy is also nearly resonant with the C-exciton, which is why the early rise time occurs for the C-excitons and not for the A-excitons. The A-exciton bleach signal that appears upon pumping ML-MoS2 at 3.1 eV has been attributed to band-gap renormalization, a process by which underlying electronic states that belonged to the C-exciton in the unexcited material now belong to the A-exciton in the excited material (39). The A-exciton bleach reaches a maximum value at longer times (τ = 200 fs, SI Appendix, Table S1). During this time, we observe no decay of the C-exciton bleach, indicating that C-excitons do not cool to A-excitons on the 200 fs timescale, if C-excitons decayed to A-excitons over this timescale, one would expect to observe a fast C-exciton decay component commensurate with the A-exciton rise time. We also observed that the A/B-exciton bleach signals decay slower under conditions of charge...
extracted (SI Appendix, Table S1), suggesting that photo-excited C-excitons do not cool to form band-edge A/B-excitons that then dissociate and inject into the ITO electrode. Instead, after C-exciton formation, the fast component for C-exciton decay occurs within the first tens of picoseconds (SI Appendix, Table S1), consistent with intervalley relaxation mechanisms (16, 17). Third, the C-exciton bleach magnitude at $\tau = 0$ ps is greater (i.e., more negative) at 0.0 V than +0.5 V, but the opposite trend occurs for the A-exciton. This third observation is critical for interpreting how the exciton populations change as a function of applied potential and will be discussed below.

We now exploit steady-state absorbance and ultrafast TA measurements to disentangle the relative exciton population changes. Recalling the TA signal, $\Delta A(\tau) = A_{\text{pump}}(\tau) - A_{\text{unpumped}}$, and recognizing that steady-state absorbance measurements represent $A_{\text{unpumped}}$, we extract relative changes in the exciton populations from $A_{\text{pumped}}$ where a larger magnitude indicates more exciton population. Fig. 3 C and D compares steady-state absorbance and TA bleach intensities of the A- and C-excitons as a function of applied potential. For the A-exciton (Fig. 3C), the TA and steady-state data closely follow one another, suggesting that the increase in $\Delta A(\tau)$ can be attributed to $A_{\text{unpumped}}$ instead of $A_{\text{pumped}}$. In contrast to the A-exciton, $A_{\text{unpumped}}$ for the C-exciton slightly increases with $+E$ (Fig. 1B), but $\Delta A(\tau)$ significantly decreases for the C-exciton (Fig. 3D), suggesting that fewer C-excitons contribute to the TA signal under these conditions.

Two scenarios could explain why C-excitons contribute less to the TA signal with $+E$. First, bound C-excitons could dissociate, producing photocurrent in the external circuit via the Marcus-type scheme introduced above. This scenario requires that photocurrent generation occurs faster than TA signal generation. The second possibility is that a portion of the hot, free electrons (charge carriers that have not cooled to the band-edge A/B-exciton states) created by the pump pulse in the continuum levels of the conductor band do not cool to form C-excitons. Instead, hot electrons inject directly into the ITO electrode before C-exciton formation and generate photocurrent. Scheme 1 schematically shows the hot-carrier process in the ML-MoS$_2$ photoelectrochemical cell. Exciting ML-MoS$_2$ with 3.1 eV light generates hot, free carriers in continuum states. This photon energy also generates C-excitons. Under 0.00 V bias, photo-excited free carriers cool to A/B/C-excitons. No carrier extraction occurs. Under 0.35 V bias, ultrafast carrier extraction occurs from only the high-energy free carriers/C-exciton populations. Under 0.50 V bias, ultrafast extraction from the high-energy free carriers/C-exciton population occurs in addition to some extraction from the band-edge A/B-exciton states, likely at longer times. On the ultrafast timescales of our TA experiments, we observe extraction of free carriers.
before C-exciton formation occurs and C-excitons do not cool to the band-edge states. These are hot-carrier extraction processes because the free carriers/C-excitons transfer to the ITO substrate before they cool to the band-edge. This mechanism of hot electron injection offers exciting opportunities to achieve solar energy conversion efficiencies beyond the detailed balance limit.

Theoretically, the latter mechanism of hot electron injection into the ITO is compatible with a scenario where bound C-excitons and continuum unbound carriers interconvert through isoenergetic scattering processes. Our calculations indicate that the binding energy of C-excitons is on the order of that of the A-exciton, making them degenerate with unbound continuum states elsewhere in the Brillouin zone; an observation consistent with previous calculations (23, 40). Since these bound and unbound species are degenerate, one may imagine highly efficient intra- and inter-band scattering, known to occur on timescales of tens to hundreds of femtoseconds (41), that would establish a dynamic equilibrium between C-excitons and free carriers. These unbound species could then be extracted as hot carriers by a moderate applied field or subsequently relax to the band-edge, where they may only contribute to the current at sufficiently high applied fields. In contrast, A-excitons (and their hydrogenic series) are necessarily mid-gap, and so cannot be degenerate with unbound carriers. This means that to extract an electron or hole from these species, one will always incur the additional cost of overcoming their binding energy, presumably explaining the additional driving force (more positive potential) required for A/B-exciton photocurrent generation in Fig. 1 D, Inset. Currently, ab initio methods are being developed to calculate the scattering matrix elements that would make an in-depth analysis of such an argument possible, albeit primarily on charge-neutral systems (42, 43).

While our theoretical treatment is presently useful in delineating the possibilities of how hot-carrier extraction can occur in ML-MoS₂, we emphasize that these calculations are only valid for unsupported MoS₂ in vacuum. Indeed, it is challenging to treat the full system accurately within the BSE, since one must include the role of the ITO substrate and electrolyte screening, the finite carrier population (as a function of potential), phonon coupling, and excitonic band-dispersion (in the nesting region in particular) into an already-costly computation. The aforementioned factors are in fact major areas of current research (20, 44, 45) and the results presented in this paper strongly motivate their continued study. Beyond the fundamental challenge of an affordable, unified electronic structure of this material, a full theoretical treatment will need to address the statistical, electrochemical aspects of the device, meaning this is only the first step in the construction of a predictive multiscale model of photoelectrochemical activity in ultrathin TMDs.

Steady-state and ultrafast spectro-electrochemical experiments support an ultrafast, hot-carrier extraction mechanism in an ML-MoS₂ photoelectrochemical cell. We employed theoretical treatments to construct a photophysical model of photocurrent generation and hot-carrier extraction. In our working model, the extraction of hot carriers following high-energy photo-excitation can be accomplished before the formation of excitonic species, leading to the high photocurrent yields in our proof-of-concept photoelectrochemical solar cell architecture. Calculation of excitonic states suggested two possible mechanisms: one arising from a classic Marcus picture of charge transfer that implies that the delocalized orbital composition for high-energy C-excitons may facilitate efficient and ultrafast carrier extraction within the photoelectrochemical cell, and the other invoking a rapid equilibrium between bound C-excitons and isoenergetic free carriers that can be extracted more easily than their bound counterparts. Importantly, our experimental results present a grand challenge to the existing theory and motivate the continued improvement of many-body theories in 2D materials and their heterostructures.

The mechanisms we suggest delineate the development of 2D semiconductors for practical implementation in ultrathin photovoltaic and solar fuel applications. A lightweight ML 2D semiconductor photovoltaic device can achieve 70 kW/kg of specific power (46). Hot-carrier effects could improve the cell photovoltage if suitable energy-selective contacts could be interfaced with the 2D semiconductor such that the hot electron and hole populations could be maintained in the external circuit after the ultrafast charge extraction process (5, 47). Our work also highlights opportunities to develop large-area solid-state systems that intimately couple the ultrathin semiconductor to energy-selective contacts without short-circuiting the device. Engineering novel 2D semiconductor/substrate architectures could also maximize light absorption in these thin semiconductors (48).
photocatalysis and solar fuel research, we envision Janus-type 2D semiconductor absorbers where a reductive cocatalyst for H₂ production or CO₂ reduction is attached to one layer of S atoms and an oxidative cocatalyst is positioned on the opposing S layer; the redox potentials of the cocatalysts can be tuned relative to the excited state electron and hole levels in the 2D semiconductor. There are rich opportunities to study how the energy level alignment between redox species in the liquid electrolyte and hot electron/hole states of ML-MoS₂ affect hot-carrier extraction rates and yields.

Materials and Methods

Sample Characterization. ML-MoS₂ films (1 cm × 1 cm, 6Carbon Technology, Shenzhen, China) were synthesized via CVD on sapphire substrates and mechanically transferred to ITO-coated glass slides using a polymethyl methacrylate stamp and stored in nitrogen-purged glovebox until use. Raman and PL microspectroscopy experiments confirmed that the commercial samples were ML-MoS₂ (SI Appendix, Fig. S1). The PL and Raman spectra were measured on an inverted Olympus IX73 optical microscope by directing an Ondax 532 nm laser excitation source through a 100× N.A. = 0.95 air objective (Olympus PlanFL N100X) onto the sample. Both signals were collected in a backscatter geometry, filtered by the Ondax 532 nm Hg Tzan system to remove the fundamental excitation light, passed through a Horiba iHR 550 spectrometer, and then detected by a Synapse charge-coupled device detector. Spatially resolved in situ UV-Vis measurements were performed using the procedures described in our previous publications (49). The sample was excited via monochromatic light from a Horiba OBB Tunable PowerArc illuminator. A 20× microscope objective collected the light transmitted through the sample and a Photometrics Prime 95B back illuminated complementary metal-oxide-semiconductor camera acquired wide-field images of the sample at different monochromatic excitation wavelengths. Absorbance spectra were calculated from the hyperspectral imaging data by spatially selecting the light transmitted through the sample (I) and the ITO substrate (I₀), where A(x) = −log₁₀(I₀/I(x)). SI Appendix, Fig. S7 shows a representative image of the sample as well as λ₁ and λ₂ regions used for absorbance spectra calculations. Note, absorbance data were acquired at the film edge to obtain I₀ measurements. TA data were acquired in the film interior where the sample morphology is >90% pure ML-MoS₂ (49).

Electrochemical Flow Cell Construction. MoS₂-coated ITO substrates were constructed into three-electrode microfluidic flow cells as described in our previous publications (49). Briefly, inlet and outlet ports for electrolyte flow through the cell were achieved by drilling holes in the ITO substrate and inserting Teflon tubing into the holes. Two pieces of approximately 50 µm-thick polytetrafluoroethylene spacers were placed between the ITO substrate and a glass coverlip (Thermo Scientific), which formed a microfluidic channel. An electrode chamber containing an Ag/AgCl reference electrode and Pt counter electrode was attached to the outlet port. All components were attached/sealed with Locite epoxy. Electrolyte solution (1 M NaI, Fisher Scientific) was pulled through the cell at a constant rate of 0.5 mL/h using a Kent Scientific syringe pump.

Electrochemical Measurements. All electrochemical measurements were made using an ivium Compactstat Potentiostat in a 3-electrode configuration. We assigned anodic photocurrent due to iodide oxidation at the working electrode (the MoS₂/ITO electrode) to positive current. The open circuit potential of the MoS₂/ITM cell was 0.27 V vs. Ag/AgCl. For a typical potential-dependent absorbance measurement, the working electrode was held at a fixed potential vs. the Ag/AgCl reference electrode while in situ absorbance spectra were acquired.

The potential was stepped from 0.00 V to 0.55 V vs. Ag/AgCl in steps of 0.025 V. Likewise, photocurrent spectra were acquired by applying a fixed potential to the working electrode and measuring the resulting current as a function of monochromatic illumination wavelength using a Horiba OBB Tunable PowerArc illuminator. The light source was scanned from 750 nm to 375 nm in 1 nm steps. The current and monochromator output were synced in time using a data acquisition card (DATAQ Instruments). Monochromatic current-voltage curves were measured from 0.00 V to 0.55 V vs. Ag/AgCl while monochromatic light resonant with the A₅⁺, B₂, or C-C excitons (650 nm, 605 nm, and 432 nm, respectively) illuminated the sample. In this case, the light source was chopped at 10 Hz and the current output from the potentiostat was connected to the input channel of a Stanford Research Systems SR830 lock-in amplifier. The lock-in signal was converted from arbitrary units to units of amperes via a proportionality constant, as discussed in our previous work (49). We calculated the EOE according to EOE = i/dg₀, where i is the photocurrent in units of C/s, g is the elementary charge in units of C, and d₀ is the incident laser power measured at the cover glass in units of photons s⁻¹. Control experiments were done on bare ITO without MoS₂ to test for photocurrent of the ITO; no measurable ITO photocurrent was detected.

TA Measurements. TA measurements were performed with a home-built, femtosecond, pump-probe spectrometer. The schematic layout of the spectrometer is shown in SI Appendix, Fig. S8. Compressed light from a Ti:sapphire regenerative amplifier (Wyvern 1000, KM Laboratories) produced sub-50 fs pulses centered at 790 nm carrying 3.3 mJ of energy per pulse at a repetition rate of 1 kHz. Front reflections of a beam splitter and wedge CdF₂ plate were used to lower the light intensity before splitting the light with a half-wave plate (λ/2) and polarizer. A fraction of the light was sent through a delay stage controlled by a Newport motion controller stage (model number XMS50-S) to control timing and then directed onto a 1-mm beta barium borate (BBO) crystal to frequency double the light by second harmonic generation to 395 nm. The 395 nm light served as the pump pulse in TA measurements. A neutral density filter was used to adjust the pump fluence. The probe pulse was created by taking the remaining portion of the split light and focusing it down in a 2-mm quartz cuvette filled with 18 Ω water, creating a white-light continuum spanning 400 nm to 800 nm. The pump and probe pulses were focused down to a spot size of approximately 30 µm full width half max and overlapped at the sample in a noncollinear beam geometry. The probe light transmitted through the sample was collected, collimated, and focused into a spectrometer (HRS550, Horiba) with a 200-mm slit opening, equipped with a 100 line/mm grating (450 blaze), and detected by a single-line 2048 element array detector (OctoPlus, Teledyne e2v). The spectral and temporal resolution of the setup was 0.6 nm and ~50 fs, respectively. The pump pulse was modulated by an optical chopper (Thorlabs) triggered by the pump laser and set to operate at half the repetition rate of the laser (500 Hz). The spectrally resolved “pumped” and “unpumped” signals are acquired and used to calculate the AA spectrum. A pump fluence of 75 µJ/cm² is used throughout this investigation. Control experiments were done on bare ITO without MoS₂, to test for TA signal of the ITO; no measurable ITO TA signal was detected (SI Appendix, Fig. S2).

Data, Materials, and Software Availability. Raw data and analysis code files have been deposited in Dryad (https://doi.org/10.5061/dryad.dwwpzn2x)(50).

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