Highly mobile charge-transfer excitons in two-dimensional \( \text{WS}_{2}/\text{tetracene} \) heterostructures

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Charge-transfer (CT) excitons at heterointerfaces play a critical role in light to electricity conversion using organic and nanostructured materials. However, how CT excitons migrate at these interfaces is poorly understood. We investigate the formation and transport of CT excitons in two-dimensional \( \text{WS}_{2}/\text{tetracene} \) heterostructures. Electron and hole transfer occurs on the time scale of a few picoseconds, and emission of interlayer CT excitons with a binding energy of ~0.3 eV has been observed. Transport of the CT excitons is directly measured by transient absorption microscopy, revealing existence of delocalized and localized states. Trapping-detrapping dynamics between the delocalized and localized states leads to stretched-exponential photoluminescence decay with an average lifetime of ~2 ns. The delocalized CT excitons are remarkably mobile with a diffusion constant of ~1 cm\(^2\) s\(^{-1}\). These highly mobile CT excitons could have important implications in achieving efficient charge separation.

RESULTS AND DISCUSSION

CT excitons emission and dynamics

Figure 1 shows the construction of a heterostructure from a single-layer \( \text{WS}_{2} \) (1L-\( \text{WS}_{2} \)) and a tetracene (Tc) thin film. The optical image of the exfoliated 1L-\( \text{WS}_{2} \) flake before the Tc deposition is shown in Fig. 1A, and the reflection spectrum is shown in Fig. S1. Polycrystalline Tc thin film is deposited onto the 1L-\( \text{WS}_{2} \) flakes by physical vapor deposition, as detailed in the Supplementary Materials. A film thickness of ~20 nm is determined using atomic force microscopy (AFM) (Fig. 1B and fig. S2). The Tc molecules are likely to pack edge-on in the herringbone structure on \( \text{WS}_{2} \), as schematically shown in Fig. 1C (29).

Figure 1D compares the steady-state PL spectra from the 1L-\( \text{WS}_{2}/\text{Tc} \) heterostructure, a Tc-only region of the film, and the 1L-\( \text{WS}_{2} \) before deposition of Tc, with photoexcitation at 2.8 eV corresponding to the direct interband recombination of the A exciton (30). An additional low-energy emission peak at 1.7 eV from the heterostructure is observed in addition to the emission of the A exciton of \( \text{WS}_{2} \) and the singlet exciton of Tc. We have confirmed this low-energy emission peak in all the 1L-\( \text{WS}_{2}/\text{Tc} \) heterostructures fabricated. The intensity of the low-energy emission could vary significantly from sample to sample, probably due to the variations in morphology of different samples.

The 1L-\( \text{WS}_{2} \) and the Tc molecules form a type II heterojunction, as schematically shown in Fig. 1C. The conduction band minimum (−3.4 eV) (31) of the 1L-\( \text{WS}_{2} \) lies lower than the lowest unoccupied molecular orbital level (−2.4 eV) (32) of Tc molecules allowing electron transfer from Tc to \( \text{WS}_{2} \), whereas the valence band maximum (VBM; −5.8 eV) (31) of \( \text{WS}_{2} \) is located lower than the highest occupied molecular orbital (HOMO) level of Tc (−5.4 eV) (32), facilitating hole transport (25). However, a drawback for PL-based techniques is that only emissive species are investigated, whereas many of the CT states are nonemissive. To address this challenge, we use transient absorption microscopy (TAM) that is capable of imaging both emissive and nonemissive excitons with ~200 fs temporal resolution and ~50-nm spatial precision (28). The measurements on \( \text{WS}_{2}/\text{Tc} \) heterostructures presented here reveal highly mobile CT excitons with a diffusion constant of ~1 cm\(^2\) s\(^{-1}\), which could be an important factor in achieving efficient charge separation at 2D organic-TMD interfaces.
transfer from WS$_2$ to Tc. On the basis of the band alignment, we attribute the emission band at 1.7 eV to interlayer CT excitons where the electrons and the holes reside on the 1L-WS$_2$ and the Tc film, respectively (Fig. 1C). We have also carried out PL excitation (PLE) measurements confirming the excitation of the A exciton in WS$_2$ leads to CT exciton emission (Fig. S3). From the energy level alignment and 1.7-eV emission energy, the binding energy for the CT excitons is estimated to be ~0.3 eV, assuming that the energy levels do not change significantly at the interfaces. This binding energy is slightly larger than that of ~0.2 eV for the CT excitons in MoSe$_2$/WSe$_2$ heterostructures (19, 20), which can be explained by the lower dielectric constant of the Tc thin film (ε ~ 5) in comparison to that for MoSe$_2$ (ε ~ 15) and WSe$_2$ (4), leading to less efficient screening of the Coulomb potential.

We monitor the CT exciton emission with a photoexcitation energy below the Tc bandgap at 2.1 eV exciting only WS$_2$ to eliminate the background emission from Tc at energy similar to the CT excitons. As shown in Fig. 2A, the emission from the interlayer CT excitons is broad, indicative of a distribution in CT exciton energy levels. The CT excitons exhibit overall much longer PL lifetime than the singlet exciton of the Tc film (~100 ps) and the A exciton of WS$_2$ (~500 ps), as expected from the spatial indirect nature of the CT excitons (Fig. 2B). We have carried out excitation intensity–dependent measurements that show negligible variations in dynamics with fluences ranging from 1.25 to 125 μJ cm$^{-2}$ (Fig. S4), indicating that exciton-exciton annihilation processes do not play an important role here. The PL decay of the CT excitons is not a single exponential but only can be fitted with a stretched-exponential function

$$I(t) = I_0 e^{-(t/\tau)^\beta}$$  \hspace{1cm} (1)$$

where $\tau = 0.97 \pm 0.01$ ns and $\beta = 0.48 \pm 0.01$ is the stretching exponent (33). The need for a stretched-exponential fit is due to a superposition of many exponentials with different decay time constants $\tau_j$ (33, 34) that probably arises from multiple configurations of the CT excitons. The dispersion of the decay time constant is described by $\beta$ ($0 < \beta < 1$), where the smaller the $\beta$ value, the broader the distribution of $\tau_j$. The average exciton lifetime ($\langle \tau \rangle$) is given as $\langle \tau \rangle \Gamma(\frac{1}{\beta}) = 2.1$ ns, where $\Gamma$ represents Gamma function (34). More discussion on different CT exciton states will be presented in the later part of the manuscript.

**Hole transfer from WS$_2$ to Tc**

We excite the 1L-WS$_2$/Tc heterostructure with a pump photon energy of 2.1 eV that is below the absorption edge of Tc (Fig. S1) to selectively investigate hole transfer from WS$_2$ to Tc. The dynamics of the same 1L-WS$_2$ flake is probed at the A exciton bleach (2.0 eV) before and after Tc deposition (Fig. 2C). On the time scale of a few picoseconds, the dynamics become faster after the deposition of Tc, which can be explained by the additional hole-transfer pathway from WS$_2$ to Tc in the heterostructure. The dynamics before Tc deposition can be fitted with a biexponential decay function (Fig. 2C), and hole transfer is competing with the fast decay component on the picosecond time scale. We can extract the hole-transfer rate by subtracting the fast decay rate before Tc deposition from that of after Tc deposition and obtain a hole-transfer time constant of 3.2 ± 0.5 ps. This hole-transfer time is consistent with recent measurements at pentacene/MoS$_2$ interfaces (15).

To investigate driving force for dissociating the A exciton in WS$_2$, we perform measurements on WS$_2$/Tc heterostructures constructed with different thickness ranging from 1 layer to 7 layers (7L-WS$_2$) (Fig. S5). The interlayer CT exciton emission disappears as the thickness of the WS$_2$ increases to two layers or thicker (Fig. 2A). There is also no obvious difference in the WS$_2$ transient absorption dynamics after Tc deposition (Fig. 2D for 2L-WS$_2$ and Fig. S6 for 4L-WS$_2$, 5L-WS$_2$, and 7L-WS$_2$), implying that hole transfer does not occur, which explains the absence of the CT exciton in these heterostructures. This thickness dependence confirms that the below-bandgap emission is from CT excitons and not from defects or other origins.

In order for hole transfer to occur, the offset between the VBM of WS$_2$ and the HOMO of the Tc molecules that provides the driving force...
A exciton dissociation has to be greater or similar to the A exciton binding energy of ~0.4 eV (36). This requirement is satisfied in 1L-WS₂/Tc heterostructures. However, as thickness increases to 2L-WS₂, the VBM energy level increases (31), and energy offset decreases to ~0.2 eV. The fact that hole transfer is not observed in the heterostructures constructed with 2L-WS₂ or thicker indicates that the energy offset between the VBM of WS₂ and the HOMO of Tc is not large enough to drive the dissociation of the A exciton in WS₂, and hence, the CT excitons do not form.

Electron versus energy transfer from Tc to WS₂

Next, we use a pump photon energy of 3.1 eV to investigate electron and energy transfer dynamics from Tc to WS₂. Under this condition, excitons are generated in both WS₂ and Tc. Because the singlet exciton emission of Tc overlaps with absorption spectrum of WS₂ (fig. S1), Förster-type resonance energy transfer from Tc to WS₂ is also possible. Dynamics probed at the A exciton resonance (2.0 eV) in WS₂ before and after Tc deposition are shown in Fig. 3 (A and B) for the 1L-WS₂/Tc and 2L-WS₂/Tc heterostructures, respectively. Note that measurements on Tc-only regions under the same experimental conditions show no detectable transient absorption signal when probing at 2.0 eV. Dynamics probed at the A exciton resonance become slower in the 1L-WS₂/Tc heterostructure than in the control 1L-WS₂ (Fig. 3A), which is the opposite from when only 1L-WS₂ is excited (Fig. 2C). The slower decay in the heterostructure could be due to either energy transfer or electron transfer from Tc to WS₂. We follow the procedure of Rowland et al. (37) to subtract the dynamics of the control 1L-WS₂ from that of the 1L-WS₂/Tc heterostructure (Fig. 3C), and a rise time of 2.1 ± 0.2 ps is obtained, which might contain contributions from both electron and energy transfer.

To separate the contribution from energy transfer, we examine dynamics in heterostructures constructed with 2L-WS₂ (Fig. 3B) and thicker (fig. S7). In these heterostructures, type I instead of type II heterojunctions are formed because hole transfer from WS₂ is blocked, and only exciton energy transfer is possible (schematically shown in Fig. 3D). After the deposition of Tc, the dynamics probed at the A exciton resonance become slower in these heterostructures when the Tc molecules are excited because of energy transfer. By subtracting the dynamics of the control 2L-WS₂ from that of the 2L-WS₂/Tc heterostructure, we obtain a rise time constant of 44 ± 5 ps corresponding to energy transfer from Tc to 2L-WS₂ (Fig. 3C). Energy transfer rates have been measured as a function of the thickness of WS₂, ranging from 2L to 7L, as plotted in Fig. 3E. Energy transfer rate decreases as the thickness of WS₂ increases, which is consistent with the recent reports on energy transfer between quantum dots and MoS₂ (38–40). This thickness dependence arises from the decreased electric field strength of the top layer WS₂ as thickness increases due to enhanced dielectric screening (38, 39).
We fit the WS₂ thickness-dependent energy transfer rate by using the electromagnetic model developed by Raja et al. (39), as described in the Supplementary Notes, and by adopting 16.2 and 6.4 for the real and imaginary parts of dielectric constant for WS₂ (41), respectively. Using this model, a time constant of 37 ps is extrapolated for energy transfer from Tc to 1L-WS₂. Because this energy transfer time is more than one order of magnitude slower than the rise time of 2.1 ± 0.2 ps, we conclude that electron transfer instead of energy transfer dominates the dynamics in the 1L-WS₂/Tc heterostructure. The electron transfer time can be obtained by subtracting the energy transfer contribution from the rise time, \( \frac{1}{\tau_{\text{ET}}} = 2.2 \text{ ps} \). Transient absorption dynamics of the 1L-WS₂/Tc heterostructure probed at the A exciton resonance show an additional slow decay with a characteristic time >1 ns (limited by the time window of the measurements), as shown in Fig. 3A, which is attributed to the recombination of the interlayer CT excitons.

**Transport of the delocalized and localized CT excitons**

A possible mechanism leading to the stretched-exponential behavior of the CT exciton PL decay as shown in Fig. 2B is trapping and detrapping dynamics between delocalized and localized states (33). This mechanism known as multiple trapping–detrapping has successfully explained the stretched-exponential PL decay observed in porous silicon (42). In WS₂/tetracene heterostructure, because CT exciton binding energy \( E_B \) is inversely proportional to the e-h distance, delocalized CT excitons with large e-h distance have smaller \( E_B \) and higher energy. When the e-h distance is reduced, the more localized CT excitons with lower energies can serve as traps (43). There could be certain sites to accommodate the lower-energy and more localized states where emission is more likely to occur (25). PL dynamics of the CT excitons are controlled by the competition between the diffusion to these sites and the detrapping of the exciton from these sites (42). The density and spatial distribution of the low-energy sites determine the dispersion of CT exciton lifetime and hence the value of \( \beta \) in Eq. 1 (42).

To validate the mechanism proposed, we image the transport of CT excitons directly with TAM by mapping population in both the spatial and temporal domains (28). The pump beam is held at a fixed position, whereas the probe beam is scanned relative to the pump with a pair of galvanometer scanners to obtain the exciton distribution at a given pump-probe delay time (more details in Materials and Methods and fig. S8). The pump-induced change in probe reflectance \( \Delta R = R_{\text{pump}} - R_{\text{off}} \) is collected. The pump energy is 3.1 eV exciting both WS₂ and Tc, and the probe energy is 2.0 eV probing WS₂. At zero delay time, the TAM results reflect the initial population created by the pump beam, and at later delay time, the TAM images directly visualize how excitons transport out of the initial volume. We have also carried out exciton transport experiments on a control 1L-WS₂ flake.

In 1D, the initial population \( n(x,0) \) follows Gaussian distribution as created by a Gaussian pump beam of 3.1 eV at position \( x_0 \) with a variance of \( \sigma^2_0 \) and is given by \( n(x,0) = N \exp \left[ -\frac{(x-x_0)^2}{2\sigma^2_0} \right] \). Population as a function of space and time can be described by a differential equation that includes both the diffusion out of the initial volume and population decay, which is given by

\[
\frac{\partial n(x,t)}{\partial t} = D \frac{\partial^2 n(x,t)}{\partial x^2} - \frac{n(x,t)}{\tau}
\]
where $D$ is the exciton diffusion constant and $\tau$ is the exciton lifetime. Solution to Eq. 2 dictates that exciton distribution at any later delay time $(t)$ is also Gaussian and can be described as $n(x, t) = N \exp \left[-\frac{(x-x_0)^2}{2\sigma^2_0}\right]$ with a variance of $\sigma^2_0$. The solution also gives the diffusion constant $D$ as

$$D = \frac{\sigma^2_t - \sigma^2_0}{2t}$$

Using this analysis, the population of the A excitons in the control 1L-WS$_2$ flake is fitted to Gaussian functions at different delay times, and the diffusion constant is determined to be $1.7 \pm 0.1 \text{ cm}^2 \text{ s}^{-1}$ (Fig. 4, A and B).

For the 1L-WS$_2$/Tc heterostructure, population profiles at different delay times have been taken along the line indicated in Fig. 4C with a pump fluence of $4.4 \mu \text{ J cm}^{-2}$. Sums of at least two Gaussian functions are required to fit the population profile at a given pump-probe delay time (Fig. 4D and fig. S9), as given by $n(x, t) = N_1 \exp \left[-\frac{(x-x_0)^2}{2\sigma^2_1}\right] + N_2 \exp \left[-\frac{(x-x_0)^2}{2\sigma^2_2}\right]$, implying that there are at least two populations migrating with different diffusion constants. The extracted $\sigma^2_1$ and $\sigma^2_2$ are plotted as a function of pump-probe delay time in Fig. 4E. Very rapid diffusion is observed before 100 ps, possibly due to the transport of the free electrons in the 1L-WS$_2$ dissociated from the hot CT exciton states created by the 3.1-eV pump that has 1.4-eV excess energy ($I$).

We focus on time scales > 100 ps where the intralayer A excitons in the 1L-WS$_2$ have mostly decayed (Fig. 3A). The long-lived transient absorption signal in the heterostructures reflects the CT exciton population because the formation of CT excitons leaves the electronic states occupied in WS$_2$ and results in the long-lived bleaching of A exciton transition. A diffusion constant $D_1 = 1.0 \pm 0.1 \text{ cm}^2 \text{ s}^{-1}$ is obtained in the heterostructure for delay time > 100 ps by fitting the time dependence of $\sigma^2_1$, corresponding to the fast-moving population with $N_1 = 0.4$. The diffusion constant for the slow moving population ($N_2 = 0.6$) is more than one order of magnitude slower, $D_2 = 0.04 \pm 0.01 \text{ cm}^2 \text{ s}^{-1}$.

To correctly measure exciton transport, it is important to account for exciton-exciton annihilation processes. Because the exciton density at the center of the spot is higher than at the edge, exciton-exciton annihilation could lead to artificially broadening of $\sigma$. We have carried out pump intensity-dependent dynamics and transport measurements to rule out the interference from exciton-exciton annihilation. Transient absorption dynamics measured at pump fluences from 2.2 to 20.6 $\mu \text{ J cm}^{-2}$ exhibit essentially the same decay (fig. S10). TAM measurements at two higher pump fluences of 10.0 and 20.6 $\mu \text{ J cm}^{-2}$ show a similar bipopulation diffusion behavior (figs. S11 and S12). These measurements yield almost identical diffusion constants as those measured at 4.4 $\mu \text{ J cm}^{-2}$,
the 1L-WS2/Tc heterostructures is that charge transfer processes occur very rapidly, with time constants of ~2 and ~3 ps, respectively. TAM measurements of exciton transport at these 2D interfaces reveal coexistence of delocalized and localized CT excitons, with diffusion constants of ~1 cm$^2$ s$^{-1}$ and ~0.04 cm$^2$ s$^{-1}$, respectively. The trapping-detrapping dynamics of the delocalized and localized states leads to stretched-exponential PL decay. The high mobility of the delocalized CT excitons could be the key factor to overcome large CT exciton binding energy in achieving efficient charge separation.

**MATERIALS AND METHODS**

**Sample preparations**
WS$_2$ flakes of different thicknesses were obtained by mechanically exfoliating bulk WS$_2$ onto Si/SiO$_2$ substrates. WS$_2$ flakes from one to seven layers have been exfoliated and integrated with Tc thin film to fabricate the heterostructures. The number of WS$_2$ layers was identified by PL microscopy (Supplementary Notes). Tetracene thin film was deposited onto WS$_2$ flakes by the physical vapor deposition method (Supplementary Notes). The Tc film thickness of ~20 nm was measured by AFM.

**Steady-state and time-resolved PL**
Steady-state and time-resolved PL measurements have been performed by a home-built confocal micro-PL setup. A picosecond-pulsed diode laser (LDH-P-C-450B, PicoQuant) with and excitation energy of 2.8 eV (full width at half maximum, 50 ps) was used to excite the sample, which was focused by a 50× objective. The PL emission was collected with a monochromator (Andor Technology), and detected by a thermoelectric-cooled charge-coupled device (Andor Technology). Time-resolved PL was measured using a single-photon avalanche diode (PDM series, PicoQuant) and a single-photon counting module (PicoQuant). The time resolution of the time-resolved PL setup is ~100 ps. Measurements with excitation energy of 2.1 eV were carried out with an optical parametric amplifier (OPA; TOPAS-Twins, Light Conversion Ltd.) pumped by a high-repetition rate amplifier (400 KHz, PHAROS, Light Conversion Ltd.).

**Transient absorption dynamics**
Two independent OPAs (TOPAS-Twins, Light Conversion Ltd.) pumped by the output of a high-repetition rate amplifier (400 KHz, PHAROS, Light Conversion Ltd.) provided the pump and probe beams. One OPA provided the pump, and the other supplied the probe. An acousto-optic modulator (R23080-1, Gooch and Housego) was used to modulate the pump beam at 100 kHz. A mechanical translation stage (DDS600-E, Thorlabs) was used to delay the probe with respect to the pump. Both the pump and probe beams were spatially filtered before being focused onto the sample by a 40× objective (NA, 0.60) objective (CFI Apo TIRF, Nikon Inc.) The probe beam was collected by the same objective and was detected by an avalanche photodiode (APD) (C5331-04, Hamamatsu). The change in the probe reflectance (AR) induced by the pump was detected by a lock-in amplifier.

**Transient absorption microscopy**
A Ti:sapphire oscillator (Coherent Mira 900) pumped by a Verdi diode laser (Coherent Verdi V18) was used as the light source (output at 1.6 eV, 80-MHz repetition rate). Seventy percent of the pulse energy was fed into the optical parametric oscillator (Coherent Mira OPO) to generate probe light at 2.0 eV, whereas the remaining 30% was
doubled to 3.1 eV and served as the pump beam. The repetition rate of both beams was reduced to 2.5 MHz using two clock-synchronized double oscillators (CFI Apo TIRF, Nikon Inc.) was used to focus the laser beams onto the sample, and the reflection light was collected by the same objective and detected by an APD (CP331-04, Hamamatsu). A galvanometer scanner (GV8012, Thorlabs) was used to scan the probe beam relative to the pump beam in space to obtain the exciton diffusion profiles. A schematic of the TAM setup is presented in fig. S8.

SUPPLEMENTARY MATERIALS

Supplemental material for this article is available at http://advances.sciencemag.org/cgi/content/full/4/1/eaao3104/DC1

REFERENCES AND NOTES


Acknowledgments
Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 6 July 2017
Accepted 1 December 2017
Published 12 January 2018
10.1126/sciadv.aao3104

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DOI: 10.1126/sciadv.aao3104