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Imaging of Pure Spin-Valley Diffusion Current in WS₂/WSe₂ Heterostructures

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Abstract:

Transition metal dichalcogenide (TMDC) materials are promising for spintronic and valleytronic applications because valley-polarized excitations can be generated and manipulated with circularly polarized photons, and the valley and spin degrees of freedom are locked by strong spin-orbital interactions. Here we demonstrate efficient generation of pure and locked spin-valley diffusion current in WS_2/WSe_2 heterostructures without any driving electric field. We image the propagation of valley current in real time and space using pump-probe spectroscopy. The valley current in the heterostructures can live for over 20 μs and propagate over 20 μm ; both the lifetime and the diffusion length can be controlled through electrostatic gating. The high efficiency and electric-field-free generation of locked spin-valley current in TMDC heterostructures holds promise for applications in spin and valley devices.

Main Text:

Transition metal dichalcogenides (TMDCs) offer a promising platform for applications in spintronics and valleytronics owing to their unique electronic structure and strong spin-orbital interactions (*1-13*). At the K and K' points of the Brillouin zone in TMDCs, two degenerate but inequivalent valleys are present, which can be used to encode binary information. In addition, spin-orbital coupling leads to locked spin and valley degrees of freedom in TMDC monolayers. The locked spin-valley polarization of charge carriers can exhibit a very long lifetime because intervalley scattering requires a large momentum change and a flip of the spin simultaneously and is therefore a rare event (*14-18*).

An outstanding challenge in spintronics/valleytronics is to efficiently generate, transport, and detect pure spin/valley current, which will be crucial not only for understanding novel spin-valley physics, but also for potential applications in charge-current-free devices with low power consumption (*19, 20*). In traditional spintronic systems, a transverse spin current is generated through the spin Hall effect in materials with a large spin Hall angle, such as tantalum and tungsten (*21-23*). Similarly, a transverse valley current has also been realized through the valley Hall effect in TMDC materials, but with low efficiency caused by a small valley Hall angle (*13*). In both cases a strong driving electric field is necessary, resulting in a dominant and unavoidable longitudinal electric current.

Here we exploit TMDC heterostructures for efficient optical generation of pure valley diffusion current without an external electric field, which is also accompanied by a pure spin diffusion current thanks to the spin-valley locking in TMDCs.

Figure 1, A and B show an optical microscopy image and a side-view illustration of a representative heterostructure device, respectively. A WSe₂/WS₂ heterostructure (black dashed line in Fig. 1A) is encapsulated in two hexagonal boron nitride (hBN) flakes, with the ~40 nm thick bottom hBN also serving as the gate dielectric. A few-layer graphene (FLG) back gate is used to tune the carrier concentration in the WSe₂/WS₂ heterostructure, and two FLG source and drain contacts (yellow dashed lines in Fig. 1A) are symmetrically placed on two sides of the heterostructure. All of the two-dimensional materials were first mechanically exfoliated from bulk crystals and then stacked together by a dry transfer method using a polyethylene terephthalate (PET) stamp (24). The whole stack was then transferred onto a 90 nm SiO₂/Si substrate.

We first characterize the gate-dependent optical transitions in the heterostructure using reflection spectroscopy. The results are summarized in Fig. 1C for carrier concentration ranging from $-5 \times 10^{12} \text{ /cm}^2$ (hole-doping) to $5 \times 10^{12} \text{ /cm}^2$ (electron-doping). Two prominent resonance features appear around 1.72 eV and 2.05 eV, corresponding to the A exciton energy in the WSe₂ and WS₂ monolayers, respectively. However, the WSe₂ and WS₂ resonances exhibit distinctively different gate-dependences. Resonances from WSe₂ vary dramatically on the hole-doping side, showing both a decrease in the exciton response and an emergence of the trion

response, consistent with the behavior of hole-doped monolayer WSe₂ (25, 26). Meanwhile, the WS₂ resonance only shows a slight redshift. The behavior on the electron-doping side is the opposite: there is only a slight redshift in the WSe₂ resonance, but the WS₂ exciton and trion transitions vary dramatically. This peculiar gate-dependence can be understood from the type II band alignment (27-29) between WSe₂ and WS₂ (Fig. 1D): the conduction and valence bands in WS₂ are lower than the corresponding bands in WSe₂. Consequently, electrostatically induced electrons and holes will only stay in the WS₂ and WSe₂ layer, respectively.

We then generate spin-valley current in the hole-doped heterostructures using local circularly polarized laser excitation (Fig. 2, A-D). The mechanism exploits the selective coupling of valley excitons to photon helicity, the ultrafast interlayer charge transfer process, and the ultralong valley hole lifetime in WS₂/WSe₂ heterostructures. First, left-handed circularly polarized photons at 1.80 eV selectively excite K-valley excitons in WSe₂. The excited electrons transfer to the conduction band of WS₂ within the first ~ 100 fs (28, 29), turning off the exciton valley depolarization channel (Maialle-Silva-Sham mechanism) (30) and creating excess valley-polarized holes in the WSe₂ K valley (Figure 2A) (18). Afterwards, electrons in WS₂ recombine with holes in WSe₂ within ~ 100 ns. As will be shown later, the recombination with K-valley and K'-valley holes in WSe₂ have almost equal probability (Fig. 2B), which leads to an excess of K-valley holes and a deficiency of K'-valley holes in WSe₂ with an ultralong lifetime of many μ s (Fig. 2C). The local imbalance of valley-polarized

holes excited by a focused laser light can drive a pure spin-valley diffusion current (with zero net charge current) through diffusion in the heterostructure (Fig. 2D).

We perform spatial-temporal imaging of the spin-valley current in the WS₂/WSe₂ heterostructure by tracking the valley polarized holes in the device using space- and time-resolved circular dichroism spectroscopy. An elliptically shaped pump beam at 1.80 eV efficiently generates spin/valley polarized holes in the heterostructure, and a second elliptically shaped probe beam at 1.70 eV probes their evolution in space and time by varying both the spatial separation and the temporal delay between the pump and probe pulses (24). Figure 2E displays the profile of the elliptically shaped pump and probe beams at the sample, each with a half width of $\sim 1.5 \mu\text{m}$. The temporal delay Δt between the pump and probe pulses is electronically generated by a data acquisition card with 12.5 ns resolution, whereas the spatial separation Δx between the pump and probe pulses along the width direction is controlled with $\sim 0.2 \mu\text{m}$ resolution by tuning the angle of a mirror (24). The circular dichroic reflection contrast of the probe pulse directly measures the valley-polarized hole density in the heterostructure at a specific probe position and time (18). All experiments are carried out at 10 Kelvin.

Figure 2F shows the measured evolution of the valley-polarized hole density in real space and real time for the hole-doped WS₂/WSe₂ heterostructure at an initial electrostatic hole doping $p_0 = 1 \times 10^{12} / \text{cm}^2$. The horizontal and vertical axes represent the temporal and spatial separation between the pump and probe pulses, respectively; the color represents the amplitude of the circular dichroism signal on a

logarithmic scale. The signal at the origin (corresponding to spatially and temporally overlapped pump and probe pulses) is normalized to 1. At zero time delay, the valley-polarized hole population is localized at the origin with a distribution matching the pump profile (half-width of $\sim 1.5 \mu\text{m}$), and the circular dichroism signal is negligible at a pump-probe separations larger than $3 \mu\text{m}$. At finite delay time, valley-polarized holes start to diffuse out of the excitation region, generating a pure spin-valley diffusion current. This leads to a strong decrease in signal close to the origin, but an increase in signal in the region with large pump-probe spatial separation. In particular, a finite signal emerges at $\Delta x > 3 \mu\text{m}$, where no valley polarization is present from the direct pump excitation. As can be seen in Figure 2F, the valley current can readily propagate to a distance over $8 \mu\text{m}$ within a time period of 800 ns.

We can compare the measured spatial-temporal image of the valley polarized hole density to diffusion theory and extract important dynamic transport parameters. The spatial-temporal evolution of the one-dimensional valley-polarized hole density $\Delta p_v(x, t)$ is described by a simple diffusion-decay model (24):

$$\Delta p_v(x, t) = \frac{\Delta p_0}{\sqrt{\pi(\sigma_0^2 + 4Dt)}} e^{-\frac{x^2}{\sigma_0^2 + 4Dt}} e^{-\frac{t}{\tau}} \quad (1)$$

where Δp_0 is the total number of pump-induced spin-valley polarized holes, σ_0 is the half width of the pump beam, D is the hole diffusion constant, and τ is the lifetime of valley polarized holes (limited by a finite inter-valley scattering time). The pump-probe signal $S(\Delta x, \Delta t)$ can be calculated by convolving $\Delta p_v(x, \Delta t)$ with the probe beam intensity $T(x)$ at a given pump-probe separation Δx (24). Figure 2G

shows the simulated pump-probe signal with a hole diffusion constant of $D = 0.2 \text{ cm}^2/\text{s}$ and a valley lifetime of $\tau = 20 \text{ }\mu\text{s}$. The excellent agreement between the experimental and theoretical results confirms the diffusion-dominated dynamics of valley polarized holes. Figure 2H shows several horizontal line cuts of Figure 2F over a longer time scale (different curves are shifted vertically and successively by 40% of the major tick separation for visual clarity. See Fig. S2 for vertical line cuts). We observe that the whole region within $\Delta x = 8 \text{ }\mu\text{m}$ becomes homogeneous after $2 \text{ }\mu\text{s}$ owing to the diffusive valley current and exhibits an overall slow decay afterwards. This dynamic is well-captured by the diffusion-decay model in Eq. 1 (solid curves in Figure 2H). The valley lifetime of $\tau = 20 \text{ }\mu\text{s}$ extracted here is more than one order of magnitude longer than the earlier reported values (14-18). From the valley hole diffusion constant and valley polarization lifetime, we obtain a valley diffusion length of $l = \sqrt{D\tau} = 20 \text{ }\mu\text{m}$. In addition, the optical generation can produce a very high valley current density, reaching $2 \times 10^7 \text{ A/m}^2$ in the $\sim 1 \text{ nm}$ thick heterostructure at a valley-polarized hole density of $10^{12}/\text{cm}^2$ (24).

The photo-generated valley diffusion current can be modulated significantly through electrostatic gating. Figure 3, A and C, show the spatial-temporal mapping of the valley-polarized hole density with the initial hole doping at ~ 0 and $2.8 \times 10^{12}/\text{cm}^2$, respectively. We found that the valley-polarized hole density decays over time but maintains the same spatial profile for near-zero initial doping (Figure 3A). This indicates that at the low-doping limit valley-polarized holes are largely localized, and there is no valley current. In contrast, the valley diffusion current flow becomes quite

large for the highly hole-doped heterostructure at $2.8 \times 10^{12}/\text{cm}^2$ (Figure 3C), leading to a peak spin-valley diffusion current density of $1.2 \times 10^8 \text{ A/m}^2$ at a valley-polarized hole density of $10^{12}/\text{cm}^2$ (24).

Figures 3, B and D, show theoretical modeling of the valley hole diffusion at $p_0 = 0$ and $2.8 \times 10^{12}/\text{cm}^2$, respectively. The extracted diffusion constants are summarized in Figure 3E. From the diffusion constant, we can directly obtain the density-dependent hole mobility using the Einstein relation for a Fermi liquid at 10 Kelvin (24). The holes are almost completely localized at a doping level close to the charge neutrality point. Therefore both the diffusion constant and the mobility are negligibly small. At larger carrier concentrations, the hole diffusion constant and mobility both increase significantly, reaching $D = 1.2 \text{ cm}^2/\text{s}$ and $\mu = 160 \text{ cm}^2/(\text{V} \cdot \text{s})$ at $p_0 = 2.8 \times 10^{12}/\text{cm}^2$. The localization of holes at low carrier density signifies a mobility edge in TMDC materials, which may be related to Anderson localization from potential fluctuations (31). We note that traditional low-temperature transport measurements at such low carrier concentration are quite challenging or almost impossible because of an exponentially large contact resistance. Here the spatially and temporally resolved optical imaging provides a contact-free approach to measure the intrinsic charge transport in TMDCs, and it can be a powerful and general tool for characterizing the transport behavior of two-dimensional systems at low carrier concentrations.

Like the hole diffusion constant, the valley-polarized hole lifetime also depends strongly on the electrostatic gating. Interestingly, the valley-polarized hole population

$(\Delta p_v \equiv \Delta p_K - \Delta p_{K'})$ can exhibit very different behavior compared to the total excess hole population ($\Delta p_{tot} \equiv \Delta p_K + \Delta p_{K'}$). Here Δp_K and $\Delta p_{K'}$ are photo-generated excess hole densities in the K and K' valleys of WSe₂, respectively. The different dynamic behavior of Δp_{tot} and Δp_v can be probed from the sum and difference responses of left- and right-circularly polarized probe light, respectively (18). Figure 4A shows the population decay of the total excess holes in the heterostructure at $\Delta x = 0$ for different initial carrier concentrations, with the decay constants summarized in Fig. 4B (blue triangles). The decay lifetime of Δp_{tot} ranges from 20 to 500 ns and becomes shorter at both larger electron and hole doping of the heterostructures. In contrast, the valley-polarized hole lifetime (red circles in Fig. 4B) is the same as the total hole population lifetime for charge neutral and electron-doped heterostructures, but decouples and becomes much longer for hole-doped cases.

The unusual dynamics of doping-dependent valley lifetime arises from the unique interlayer electron-hole recombination process in the heterostructure, as illustrated in Fig. 4, C and D (24). For electron-doped or charge neutral heterostructures (Figure 4C), all of the holes in WSe₂ are pump-generated “excess holes”. Therefore, when Δp_{tot} decays to zero owing to interlayer electron-hole recombination, no holes -- and certainly no valley-polarized holes -- remain in the WSe₂. In these cases, the valley lifetime is limited by the total excess hole lifetime. The scenario is completely different for hole-doped heterostructures (Fig. 4D). If the original hole density is much larger than the photon-generated one, excess electrons in WS₂ will recombine with holes from both valleys of WSe₂ with almost equal probability (24).

Consequently, the valley-polarized hole density Δp_v decouples from the net excess hole population Δp_{tot} and persists long after the latter one decays to zero, enabling the generation of pure spin-valley diffusion current.

The generation efficiency of pure spin-valley diffusion current in our heterostructure-based device can be very high owing to the near-perfect conversion from optical excitation to pure valley diffusion current (24). Intriguingly, because of the lack of any associated charge current in our device, the pure spin-valley diffusion current density scales linearly with the optical excitation power, as opposed to the square-root scaling with power for electrically generated current. Therefore the power-efficiency of heterostructure devices can be favorable for generating large spin- and valley-current. Along with the ultralong spin-valley lifetimes and diffusion lengths, TDMC heterostructures provide exciting opportunities to realize future spintronic and valleytronic devices.

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Author contributions: C.J. and J.K. contributed equally to this work. F.W. and C.J. conceived the research. C.J., J.K. and E.R. carried out optical measurements. C.J., F.W. and E.R. performed theoretical analysis. J.K., C.J., M.I.B.U., H.K., M.J.S., A.S. and A.Z. fabricated van der Waals heterostructures. H.C., Y.S. and S.T. grew WSe₂ and WS₂ crystals. K.W. and T.T. grew hBN crystals. All authors discussed the results and wrote the manuscript.

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Data availability: Experimental data files are available from the Open Science Framework at <https://osf.io/8jpgg/>.

Supplementary Materials

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Materials and Methods

Supplementary Text

Fig. S1-S4

References (32-33)

Figures:

Figure 1. Gate-dependent optical transitions in WSe₂/WS₂ heterostructure. (A and B) Optical microscope image (A) and side-view illustration (B) of the heterostructure device. Black and yellow dashed lines in (A) mark the heterostructure region and few-layer graphene source/drain electrodes, respectively. (C) Doping-dependent reflection contrast of the WSe₂/WS₂ heterostructure. Horizontal and vertical axes represent photon energy and carrier concentration, respectively. Color scale corresponds to reflection contrast. Black dashed line labels charge neutrality. The two prominent resonances around 1.72 eV and 2.05 eV correspond to the A exciton energy in the WSe₂ and WS₂ monolayers, respectively, which exhibit distinctively different doping dependence owing to the type II band alignment of the heterostructure. (D) Type II band alignment of the WSe₂ and WS₂ interface. The conduction band minimum and the valence band maximum reside in WS₂ and WSe₂, respectively. Electrostatically-doped electrons stay only in WS₂ for the n-doping case (left panel) whereas holes stay only in WSe₂ for p-doping case (right panel).

Figure 2. Pure spin-valley diffusion current in hole-doped WSe₂/WS₂ heterostructure. (A)-(D), Experimental scheme for valley current generation in hole-doped WSe₂/WS₂ heterostructures. The black dashed line represents the Fermi level before optical excitation. (A) Excitons in the K valley of WSe₂ are selectively excited by circularly polarized pump light and efficiently converted into excess holes within ~100 fs through the ultrafast interlayer charge transfer process. (B) Electrons in WS₂ recombine with K-valley and K'-valley holes in WSe₂ with almost equal probability, resulting in an excess of K-valley holes and a deficiency of K'-valley holes in WSe₂. (C) This valley polarized hole population persist for tens of microseconds. (D) Local excitation of such valley-polarized holes can drive a pure

valley diffusion current (with zero net charge current) through diffusion in the heterostructure. This pure valley diffusion current will be uni-directional if excited at one edge of the device. **(E)-(H)** Spatial-temporal imaging of the pure spin-valley current. **(E)** Elliptically shaped pump and probe beam profiles each with $\sim 1.5 \text{ }\mu\text{m}$ half width. The long axis of the elliptical light ($>50 \text{ }\mu\text{m}$) is much longer than the sample width ($\sim 10 \text{ }\mu\text{m}$). Therefore, the illumination is nearly homogeneous along the long axis direction. **(F)** The spatial-temporal evolution of spin-valley polarized holes in the heterostructure with an initial hole doping $p_0 = 1 \times 10^{12} \text{ /cm}^2$. The horizontal and vertical axes represent the temporal and spatial separation between the pump and probe pulses, respectively. The color represents the amplitude of the circular dichroism signal on a logarithmic scale, which is proportional to the valley-polarized hole density. The fast decrease in signal at small Δx and increase in signal at large Δx signifies the propagation of valley diffusion current, which can be well captured by simulation from a diffusion-decay model **(G)** see text. **(H)** Horizontal cuts from **(F)** (symbols) and fits from the diffusion-decay model (solid curves) over a longer time scale. The whole region within $\Delta x = 8 \text{ }\mu\text{m}$ becomes homogeneous after $2 \text{ }\mu\text{s}$ owing to the diffusive valley current, and shows an overall slow decay afterwards.

Figure 3. Strong modulation of spin-valley current with electrostatic gating. (**A** and **C**) Spatial-temporal imaging of spin-valley current at initial hole concentration of near-zero (**A**) and $2.8 \times 10^{12}/\text{cm}^2$ (**C**). (**B** and **D**) Corresponding simulation results from the diffusion-decay model. The valley-polarized holes have negligible diffusion near the charge neutral point (**A** and **B**). In contrast, holes diffuse efficiently at large hole doping (**C** and **D**) creating a large spin-valley current density up to $1.2 \times 10^8 \text{A}/\text{m}^2$ at an optical excitation density of $10^{12}/\text{cm}^2$. (**E**) Extracted hole diffusion constant (red triangle) and mobility (blue triangle) show a strong dependence on the initial hole concentration.

Figure 4. Doping-dependent lifetime of total excess hole and valley-polarized hole population. (A) Decay dynamics of the total excess hole density at different initial carrier concentrations. The decay lifetime is the longest near charge neutrality and decreases with both electron (positive carrier concentration) and hole doping (negative carrier concentration). (B) Comparison between valley-polarized hole lifetime (red circles) and total excess hole lifetime (blue triangles). The valley lifetime is limited by the total population lifetime in charge neutral and electron-doped heterostructures; in hole-doped heterostructures the valley lifetime can be orders of magnitude longer than the total excess hole lifetime. (C) For electron-doped or charge neutral heterostructures, interlayer electron-hole recombination directly reduces the valley polarized hole density. Dark and light blue colors represent the electrostatically-injected electrons and photo-generated electrons, respectively. (D) If the initial hole doping density (dark red) is much larger than the photo-generated one (light red), electrons in WS₂ (blue) will recombine with holes at K and K' valleys of WSe₂ with almost equal probability, reducing only the total excess hole population but not the valley-polarized hole density.

A **B** **C** **D**

A **B** **C** **D** **E**

Supplementary Materials for

Imaging of Pure Spin-Valley Diffusion Current in WS₂/WSe₂ Heterostructures

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Materials and Methods

Heterostructure preparation

WSe₂/WS₂ heterostructures were prepared by dry transfer method with polyethylene terephthalate (PET) stamp (31). Monolayer WSe₂, monolayer WS₂, few-layer graphene, and thin-layer hBN flakes were first exfoliated onto silicon substrate with a 90 nm SiO₂ layer. We used a PET stamp to pick up the top hBN flake, monolayer WS₂, monolayer WSe₂, few-layer graphene source/drain electrode, and bottom hBN flake in sequence. The PET stamp with the above heterostructure stack was then stamped onto a few-layer graphene flake as the back gate. Polymer and samples were heated to 60 °C for the pick-up and to 130 °C for the stamp process. Finally, we dissolved the PET in dichloromethane for 12 hours at room temperature.

Generation of optical pump probe pulses with controlled time delay and spatial separation

To generate optical pump probe pulses, we first generate two synchronized electronic pulses using two electronic pulse generators (HP 8082A and HP 214B). Both pulse generators are triggered by the digital output of a data acquisition card, and therefore the period and delay of the two triggering signals can be directly controlled with computer. The output electronic pulses have ~ 20 nanosecond pulse duration, which are then converted to optical pulses by two RF-coupled laser diode modules, with center wavelength of diode laser at 690 nm (pump) and 730 nm (probe), respectively. The spatial separation between pump and probe light is achieved by changing the angle of the pump beam using a mirror in its beam path before combining with the probe beam.

Supplementary Text

Experimental setup

Figure S1 illustrates the experimental configuration for spatially and temporally resolved pump-probe spectroscopy. A polarizer (P) and quarter-wave plate (QWP) are used to generate the pump beam with left circular polarization, while the probe light can be switched between left- and right-circular polarization through an additional half-wave plate (HWP). Without the cylindrical lens, both pump and probe beams are tightly focused on the sample plane. A cylindrical lens with 10 cm focal length further converts the pump and probe beams into narrow elliptical shapes on the sample, as shown by Figure 2E in the text.

Diffusion-decay model for spatial and temporal evolution of spin-valley polarized holes

According to Boltzmann's transport equation the spin-valley current $I_v(x, t)$ can be expressed as the sum of two components:

$$I_v(x, t) = -q \left[D \frac{\partial \Delta p_v(x, t)}{\partial x} - \mu \Delta p_v(x, t) E(x, t) \right], \quad (S1)$$

where $\Delta p_v(x, t)$ is the one-dimensional density of spin-valley polarized holes, defined as the total number of spin-valley polarized holes per unit length along the x direction; μ is the hole mobility, D is the hole diffusion constant, E is the electric field, and q is the elementary charge. The first and second components on the right hand side come from diffusion and drift contribution, respectively.

In our device, no external in-plane electric field is present. Furthermore, the pure spin-valley density $\Delta p_v(x, t)$ does not have associated charge density and therefore does not generate any

electric field. We therefore have $E(x, t) = 0$, and the current is completely originating from the gradient of spin-valley density.

The continuity equation reads

$$\frac{\partial \Delta p_v(x, t)}{\partial t} = -\frac{1}{q} \frac{\partial I_v(x, t)}{\partial x} - \frac{\Delta p_v(x, t)}{\tau}. \quad (\text{S2})$$

The second term on the right hand side describes the decay of spin-valley polarization from relaxation processes, with decay lifetime τ . Combining Eq. S1 and S2 gives the master equation governing the evolution of $\Delta p_v(x, t)$:

$$\frac{\partial \Delta p_v(x, t)}{\partial t} = D \frac{\partial^2 \Delta p_v(x, t)}{\partial^2 x} - \frac{\Delta p_v(x, t)}{\tau}. \quad (\text{S3})$$

A general solution to Eq. S3 is given by

$$\Delta p_v(x, t) = \frac{\Delta p_0}{\sqrt{\pi \sigma^2(t)}} e^{-\frac{x^2}{\sigma^2(t)}} e^{-\frac{t}{\tau}}. \quad (\text{S4})$$

Here $\sigma(t) = \sqrt{(\sigma_0^2 + 4Dt)}$ is the half width of the spin-valley polarized hole distribution defined by where the density drops to $1/e$ of the center value, with $\sigma_0 \approx 1.5\mu\text{m}$ from the profile of pump beam.

The pump-probe signal $(\Delta x, \Delta t)$ can be calculated by convolving $\Delta p_v(x, \Delta t)$ with the probe beam intensity $T(x)$ at a given pump-probe separation Δx :

$$T(x, \Delta x) = \frac{T_0}{\sqrt{\pi \sigma_0^2}} e^{-\frac{(x-\Delta x)^2}{\sigma_0^2}},$$

$$S(\Delta x, \Delta t) = \int dx \Delta p_v(x, \Delta t) \cdot T(x, \Delta x),$$

For example, the half width of the spin-valley polarized hole distribution and the probe beam are both $\sigma_0 \approx 1.5\mu\text{m}$ at time zero, therefore their overlap will be small if the center separation Δx is greater than $2\sigma_0 = 3\mu\text{m}$, giving negligible pump-probe signal.

Time evolution of the valley current spatial profile

Figure S2 shows the vertical line cuts of Figure 2F, from which we can directly see the evolution of the spatial profile of the pump-probe signal at different time delays (symbols). The fitting from the diffusion-decay model is also given (lines). The signal clearly diffuses out over time, becoming almost homogeneous after a few microseconds.

Relation between diffusion constant and mobility

The relationship between the diffusion constant and the mobility, often referred to as the Einstein relation, can be derived by considering an equilibrium case where the drift and diffusion currents cancel:

$$j_p = qp\mu_p E - qD_p \frac{dp}{dx} = 0. \quad (\text{S5})$$

Here p is the hole density, μ_p is the hole mobility, E is the magnitude of the applied electric field (in x -direction for simplicity), D_p is the hole diffusion constant, and q is the elemental charge. Using the chain rule, we can express the hole density gradient as

$$\frac{dp}{dx} = \frac{dp}{dU} \frac{dU}{dx} = -qE \frac{dp}{dU}, \quad (\text{S6})$$

where $U = -qEx$ is the potential energy from the electric field.

For a two-dimensional semiconductor at thermal equilibrium, the hole density is related to energy through Fermi-Dirac distribution:

$$p = \frac{2m^*k_B T}{\pi \hbar^2} \ln \left(1 + \exp \left(\frac{\varepsilon_v - \varepsilon_F}{k_B T} \right) \right), \quad (\text{S7})$$

where m^* is the effective mass of the holes, k_B is Boltzmann's constant, T is the temperature, $\hbar$ is the reduced Planck's constant, and ε_F is the Fermi energy (independent of position at thermal equilibrium). $\varepsilon_v(x) = -U(x)$ is the energy of valence band maximum, which is defined as energy zero when the external potential U vanishes.

Combining Eq. S6 and S7, the Einstein relation can be generally derived as

$$\frac{D_p}{\mu_p} = -\frac{p}{q} \left(\frac{dp}{dU} \right)^{-1} = \frac{k_B T}{q} \frac{(1 + \eta) \ln(1 + \eta)}{\eta}, \quad (\text{S8})$$

where $\eta = \exp \left(\frac{\varepsilon_v - \varepsilon_F}{k_B T} \right)$ can be determined from hole density through Eq. S7. Therefore, the ratio between the diffusion constant and the mobility generally depends on the carrier concentration, as shown by the blue curve in Figure S2. At low carrier concentration $\eta \ll 1$ (non-degenerate case), Eq. S7 reduces to the classical Boltzmann distribution, and Eq. S8 becomes $D_p/\mu_p = k_B T/q$, the Einstein relation for classical particles (yellow line in Figure S2). On the other hand, at $\eta \gg 1$ (highly-degenerate case), the ratio D_p/μ_p will increase significantly with higher carrier concentration, see red curve in Figure S3.

Interlayer electron-hole recombination model

The interlayer electron-hole recombination model describes the non-radiative recombination process between photon-generated electrons in WS₂ and holes in WSe₂. Define the excess hole density in the K and K' valleys of WSe₂ to be Δp_K and $\Delta p_{K'}$, the excess electron density in WS₂ to be Δn , and the original electrostatically-injected hole density in WSe₂ and electron density in WS₂ to be p_0 ($p_0/2$ in each valley) and n_0 , respectively. All the densities are assumed uniform in space to focus on the effect of relaxation process. The dynamics of Δp_K and $\Delta p_{K'}$ is described by the following coupled differential equations:

$$\begin{aligned} \frac{d\Delta p_K}{dt} &= -a(n_0 + \Delta n)(\Delta p_K + p_0/2) - b(\Delta p_K - \Delta p_{K'}) \\ \frac{d\Delta p_{K'}}{dt} &= -a(n_0 + \Delta n)(\Delta p_{K'} + p_0/2) - b(\Delta p_{K'} - \Delta p_K) \\ \frac{d\Delta n}{dt} &= -a(n_0 + \Delta n)(\Delta p_K + \Delta p_{K'} + p_0). \end{aligned} \quad (\text{S9})$$

The first term on the right hand side of each equation corresponds to the interlayer recombination between electrons in WS₂ and holes in WSe₂, which is proportional to both the total electron density in WS₂ and the hole density in each valley of WSe₂. The second term on the right-hand side describes intervalley scattering between two valleys in WSe₂. a and b are two constant coefficients describing the rate of interlayer electron-hole recombination and intervalley scattering processes, respectively. We have $\Delta n \equiv (\Delta p_K + \Delta p_{K'})$ from conservation of total charge.

The spin-valley polarized hole density $\Delta p_v \equiv (\Delta p_K - \Delta p_{K'})$ and the total excess hole density $\Delta p_{tot} \equiv (\Delta p_K + \Delta p_{K'})$ can be directly solved from Eq. S9. They show distinctively different behavior depending on the initial carrier concentration. First, we consider an electron-doped

heterostructure. As discussed in the text, only WS₂ is electron-doped on the n-doping side, and therefore $p_0 = 0$. Eq. S9 can be simplified as

$$\begin{aligned}\frac{d\Delta p_{tot}}{dt} &= -a(\Delta p_{tot} + n_0)\Delta p_{tot} \\ \frac{d\Delta p_v}{dt} &= -a(\Delta p_{tot} + n_0)\Delta p_v - 2b\Delta p_v.\end{aligned}\quad (S10)$$

In the limit of large initial carrier density ($n_0 \gg \Delta p_{tot}$), the solution simply reads

$$\begin{aligned}\Delta p_{tot}(t) &= \Delta p_{tot}(0)e^{-an_0t} \\ \Delta p_v(t) &= \Delta p_v(0)e^{-an_0t}e^{-2bt}.\end{aligned}$$

The total excess hole density Δp_{tot} shows an exponential decay, with shorter lifetime at larger carrier concentration n_0 due to the faster interlayer electron-hole recombination. The spin/valley polarized hole density Δp_v decay together with Δp_{tot} , with additional factor e^{-2bt} from intervalley scattering process. As a result, although the decay from intervalley scattering e^{-2bt} can be very slow in reality, the spin/valley lifetime will be still limited by total lifetime of excess carriers.

On the other hand, we have $n_0 = 0$ when the heterostructure is hole-doped. Eq. S9 becomes

$$\begin{aligned}\frac{d\Delta p_{tot}}{dt} &= -a(\Delta p_{tot} + p_0)\Delta p_{tot} \\ \frac{d\Delta p_v}{dt} &= -a\Delta p_{tot}\Delta p_v - 2b\Delta p_v\end{aligned}\quad (S11)$$

In the limit of $p_0 \gg \Delta p_{tot}$, the solution is

$$\begin{aligned}\Delta p_{tot}(t) &= \Delta p_{tot}(0)e^{-ap_0t} \\ \Delta p_v(t) &= \Delta p_v(0)e^{-2bt}.\end{aligned}$$

The dynamics of Δp_{tot} is symmetric between the p-doping side and the n-doping side, exhibiting a decrease of lifetime with increasing carrier concentration. In contrast, the spin/valley lifetime in hole-doped heterostructure is only limited by intervalley scattering processes but not total excess carrier decay. Actually, a faster decay of total excess carriers can be desirable in this situation because it facilitates efficient conversion from the mixed charge-spin/valley excitation into pure spin/valley polarization.

Near-perfect conversion from optical excitation to valley polarization

As illustrated in Figure 2, A-C, the conversion from photon-excited excitons to pure spin-valley polarization takes two steps: First, the ultrafast interlayer charge transfer process splits excitons into electrons and holes at separate layers; then the interlayer electron-hole recombination process creates pure valley imbalance.

The time scale of the charge transfer process (~ 100 fs) is significantly shorter than any intervalley scattering process, and therefore the degradation of valley polarization is negligible during the first step. This has also been experimentally demonstrated previously (18).

The interlayer electron-hole recombination model predicts that the degradation of valley polarization can also be negligible during the interlayer electron-hole recombination process, with sufficient initial electrostatic hole doping in WSe₂. To confirm this, we investigate the decay dynamics of the total excess hole and valley-polarized hole, with homogeneous pumping condition to eliminate the complication from spatial diffusion (Figure S4). The total excess hole density decays with a lifetime of ~ 50 ns, within which the valley polarized hole density almost maintains a constant value. Therefore, the overall conversion efficiency from exciton to pure

valley polarization can be nearly perfect. This also confirms that electrons in WS₂ recombine with holes from both valleys of WSe₂ with almost equal probability.

Evaluation of spin-valley current density in TMDC heterostructure

The near-perfect charge-spin/valley conversion enables ultra-efficient generation of spin/valley current. For example, assume the pump beam with a half width of $\sigma_0 = 1.5\mu\text{m}$ and length of $10\mu\text{m}$ is hitting at one edge of the device to selectively generate spin-valley current along one direction. The amplitude of generated spin-valley current density is directly given by Eq. S1 and S4 as

$$I_v(x, t) = -qD \frac{\partial \Delta p_v(x, t)}{\partial x} = qD \frac{\Delta p_0}{\sqrt{\pi \sigma^2(t)}} \frac{2x}{\sigma^2(t)} e^{-\frac{x^2}{\sigma^2(t)}} e^{-\frac{t}{\tau}}.$$

The peak spin-valley current I_v^M is given by

$$I_v^M = I_v\left(\frac{\sigma_0}{\sqrt{2}}, 0\right) = \frac{2e^{-\frac{1}{2}} qD \Delta p_0}{\sqrt{2\pi} \sigma_0^2}.$$

With valley-polarized hole density of $10^{12}/\text{cm}^2$, the total pump generated valley polarized hole population is $\Delta p_0 = 1.5 \times 10^5$. We thereby obtain a peak spin-valley current of $I_v^M = 1.2 \mu\text{A}$ and $0.2 \mu\text{A}$ at initial electrostatic hole concentration of $p_0 = 2.8 \times 10^{12}/\text{cm}^2$ and $1 \times 10^{12}/\text{cm}^2$, respectively, which corresponds to spin-valley current density of $j_v^M = 1.2 \times 10^8 \text{ A/m}^2$ and $2 \times 10^7 \text{ A/m}^2$ by assuming an effective thickness of 1nm for the heterostructure.

Estimation of the upper limit of spin-valley current density

The achievable spin-valley current in the heterostructure device is determined by both the density of valley polarized holes and their diffusion constant or mobility. The mobility mainly depends on sample quality and device fabrication technique. In our heterostructure, we observed a mobility around $100 \text{ cm}^2/(\text{V} \cdot \text{s})$. However, WSe₂ hole mobility as high as $4000 \text{ cm}^2/(\text{V} \cdot \text{s})$ has been reported in other experimental studies, presumably due to even better sample quality (32).

On the other hand, the valley polarized hole density may be limited by several factors:

Firstly, from our interlayer recombination model, the valley polarized hole density should be smaller than the initial electrostatic hole doping in WSe₂. Experimentally the latter is limited to $\sim 10^{13}/\text{cm}^2$ due to the breakdown electric field of the gate dielectric.

A more intrinsic limitation is the band alignment of the heterostructure due to the charge transfer. The conduction band offset in a WSe₂/WS₂ heterostructure is predicted to be $\sim 300 \text{ meV}$ (26). With a simple geometrical capacitance model (assuming a dielectric constant of 10 and thickness of 1nm for the capacitor), the band alignment shift of 300 meV corresponds to at a transferred charge density of $2 \times 10^{13}/\text{cm}^2$.

Combing the above considerations, we would expect the upper limit of the peak spin-valley current density to be in the order $\sim 10^{10} \text{ A/m}^2$ by using a valley polarized hole density of $10^{13}/\text{cm}^2$ and mobility of $4000 \text{ cm}^2/(\text{V} \cdot \text{s})$.

Efficient generation of spin-valley current in TMDC heterostructure

In addition to the outstanding spin-valley current density, the heterostructure device can also have favorable power consumption owing to the lack of charge current. For example, with continuous light excitation, the spin-valley current at equilibrium can be directly obtained from:

$$I_v = \frac{\Delta Q}{\Delta t} = \frac{q \Delta p_0}{\Delta t}.$$

where q is elemental charge, Δp_0 is the injected spin-valley-polarized hole population during the time of Δt . The energy consumed for the generation is simply from the light absorbed, $W_{HT} = \Delta p_0 E_0$, where $E_0 \approx 1.8\text{eV}$ is the energy of each photon in the pump beam. We can thereby obtain directly the relation between power consumption P_{HT} and generated spin-valley current I_v :

$$P_{HT} = \frac{W_{HT}}{\Delta t} = I_v \times 1.8 \text{ V}.$$

On the other hand, to generate spin/valley current I_v in spin/valley Hall effect scheme, the power consumption P_{VH} is directly given by

$$P_{VH} = I_c^2 R = \left(\frac{I_v}{\theta_{VH}} \right)^2 R,$$

where I_c is the longitudinal charge current, and is related to the transverse spin-valley current by $I_v/I_c = \theta_{VH}$.

Comparing the power consumption in the two cases, the scaling law between power consumption and spin-valley current amplitude is fundamentally different. The lack of charge current in our heterostructure-based device enables high power efficiency especially at large current amplitude.

Fig. S1.

Figure S1. Experimental configuration of spatially and temporally resolved pump probe spectroscopy.

Fig. S2.

Figure S2. Spatial profile of the pump probe signal at different time delay (symbols) and fitting from the diffusion-decay model (lines).

Fig. S3.

Figure S3. Einstein relation (D/μ) for holes in WSe₂ as a function of hole concentration for the exact, degenerate, and nondegenerate cases at temperature of 10K.

Fig. S4.

Figure S4. Decay dynamics of total excess hole and valley polarized hole density without spatial diffusion by using pump beam size much greater than the sample. Valley polarized hole density almost maintains constant value during the interlayer electron-hole recombination process.