Supporting Information

Dielectric Environment-Robust Ultrafast Charge Transfer Between Two Atomic Layers

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S1. Experiment details

Sample fabrication. Monolayers of WS_2 and WSe_2 were mechanically exfoliated onto gel-films and SiO_2 (or SiO_2/Si) substrates from bulk crystals (hq graphene). Both monolayers were confirmed by their PL spectra and optical contrast. We fabricated WSe_2/WS_2 heterostructures by dry pick-up and stacking methods.[1-2] The samples were annealed for 2 hours at 250 °C in high vacuum before measurements. Gated samples were prepared on SiO_2/Si substrate with pre-patterned electrodes and the back-gate voltage was supplied by Keithley 2614b.

Steady-state Optical measurements. The reflectance contrast was measured with a tungsten halogen source (SL201L Thorlabs) by normalizing the reflected spectra from the sample on substrate to that from the bare substrate. The reflected light was collected and analyzed by EMCCD (Princeton Instruments). Photoluminescence spectra was obtained by the same set-up with a 532 nm laser excitation.

Transient reflectance measurements. For time-resolved reflectance measurements, the fundamental beam produced by Yb:KGW laser (Pharos, Light Conversion Ltd) was divided into several light beams. One was introduced to a noncollinear optical parametric amplifier to generate a certain wavelength as pump beam (< 35 fs). The other was focused onto a YAG crystal to generate a continuum white light as probe beam. Both beams were combined and focused by a microscope with a 70 X reflective objective to spots size < 1 μm. (mFemto-TR100, time-tech spectra) The delay time between pump and probe was controlled by a high-resolution motorized delay stage (Newport). The reflected probe light was collected by EMCCD (Princeton Instruments) with the pump beam filtered and the transient reflectance signal was calculated by normalizing the probe spectra from pumped ones to that from unpumped ones. We avoid using transmissive optics along the optical pass and carefully compressed the pump pulse and characterized the pulse duration by FROG. The pump-probe cross-correlation function was performed on a WS_2 monolayer sample under exactly same experiment setup which yields a full-width-at-half-maximum (FWHM) of the convolution of two pulses of < 60 fs (IRF). Therefore, through convolution fitting with a single exponential function, we can accurately extract an ET lifetime > 15 fs (~ IRF/4), as can be justified by the fitting error. Therefore, the ET lifetimes we reported in manuscript are not limited by limited time resolution. Low-temperature measurements were conducted in a microscope cryostat (MicrostatN Oxford Instruments) with sample in high vacuum.

S2. Comparison between photoexcited TR spectrum and electron doping induced reflectance change

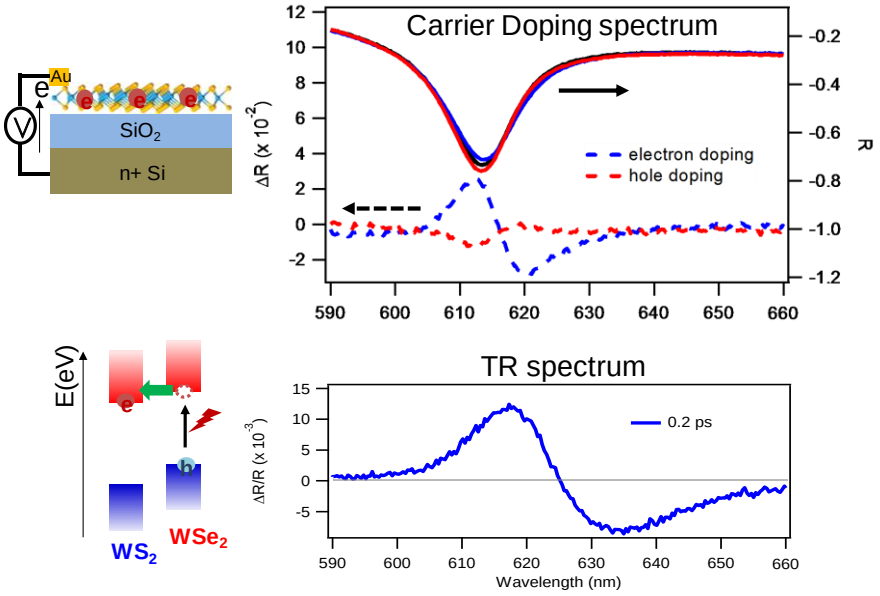

Figure S1. Carrier doping induced reflectance change in WS_2 (top panel) and transient reflectance (bottom panel) on WSe_2/WS_2 heterostructure. The samples were fabricated on SiO_2/Si substrate for applying gating voltage. The agreement between TR spectrum of WSe_2/WS_2 heterostructure and reflectance change of WS_2 under electron doping confirms electron transfer from WSe_2 to WS_2 under WSe_2 excitation. Note the samples here are all on SiO_2 (100nm)/Si substrate for applying back gating therefore the TR spectrum looks different from that on transparent SiO_2, as shown in main text. This doesn't affect the comparison here.

S3. Color plot of TR spectra of WSe_2/WS_2 vdW heterostructures capped with BN and Mica layers

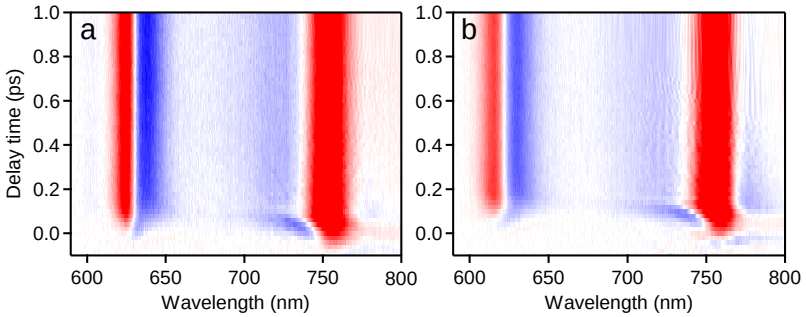

Figure S2. Color plot of TR spectra of WSe_2/WS_2 vdW heterostructures capped with (a) BN and (b) Mica layers. Note the samples here are on SiO_2 (100nm)/Si substrate.

S4. Detailed properties of solvents and dielectrics in this study

Table S1. Properties of different solvents and dielectrics

Solvent	ε_{op}	ε_{st}	τ_s (ps)[a]	λ (meV)[b]	E_b (meV)[c]
vacuum	1	1		< 1[d]	306
Toluene	2.3	2.4	1.1	51	259
Chloroform	2.1	4.8	2.3	556	202
Pentanol	2.0	13.9	87	886	107
Isopropanol	1.9	19.9	18	983	79
Ethanol	1.9	24.3	10	1023	66
Methanol	1.8	33.6	2.3	1102	47
Water	1.8	80.4	0.2	1131	17
Formamide	2.1	101.0	0.8	962	13
BN		5			195
Mica		8			150

[a] Solvent relaxation time is mostly taken from reference[3] and cross-checked with references.[4-5] We take 1/e characteristic time $\tau_{1/e}$ as solvent relaxation time and the initial time constant τ_0 is shorter than $\tau_{1/e}$ in a few solvents but still much slower than ET time in vdW heterostructure.

[b] Solvent reorganization energy was estimated by $\lambda = \lambda_s/2 = \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0}\frac{1}{R}\left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_{st}}\right)$, where $\frac{1}{2}$ considers only half of space filled with solvent, R is half of the monolayer thickness (0.7 nm)

[c] The estimate of E_b is shown in details in S6.

[d] The reorganization energy of TMD is expected to be very small considering partial compensation of electron-hole pair and their orbital nature.[6]

S5. ET in WS_2/WSe_2 on SiO_2 substrate in different solvents

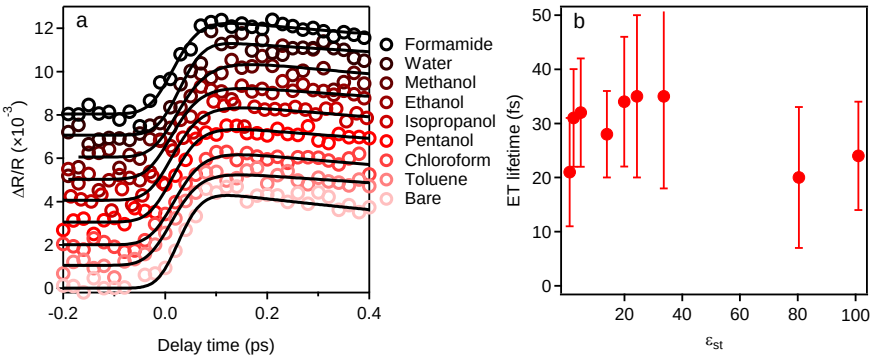

Figure S3. (a) TR kinetics of WS_2/WSe_2 heterostructure (WS_2 on top) immersed in different solvents. ε_{st} increases from bottom to top: bare, toluene, chloroform, pentanol, isopropanol, ethanol, methanol, water, formamide. Solid lines are fits to the kinetics. (b) Interfacial ET time in solvents with different ε_{st}, showing no dependence on ε_{st}.

S6. Calculation of exciton binding energy in different dielectrics and solvents

We consider the potential of exciton in 2D material between substrate and different dielectric environment is strongly dependent on a new variable $\frac{\varepsilon_r-\varepsilon'}{\varepsilon_r+\varepsilon'}$,which describe the effect of dielectric field to exciton. ε' is dielectric field's relative dielectric constant and ε_r is the dielectric constant of TMDs.

we consider the potential experienced by an electron at (ρ, z) due to the presence of a hole at (0, z0) as:[7]

$$V(\rho)=-\frac{e^2}{4\pi\varepsilon_0\varepsilon_r}\{\frac{1}{\sqrt{(z-z_0)^2+\rho^2}}+\frac{\varepsilon_r-\varepsilon'}{\varepsilon_r+\varepsilon'}[\sum_{n=0}^{\infty}\frac{(\frac{\varepsilon_r-\varepsilon'}{\varepsilon_r+\varepsilon'})^{2n}}{\sqrt{(z-z_0-2a+2nc)^2+\rho^2}}$$

$$+\sum_{n=0}^{\infty}\frac{(\frac{\varepsilon_r-\varepsilon'}{\varepsilon_r+\varepsilon'})^{2n}}{\sqrt{(z-z_0+2b+2nc)^2+\rho^2}}]+2(\frac{\varepsilon_r-\varepsilon'}{\varepsilon_r+\varepsilon'})^2\sum_{n=0}^{\infty}\frac{(\frac{\varepsilon_r-\varepsilon'}{\varepsilon_r+\varepsilon'})^{2n}}{\sqrt{(z-z_0+2c+2nc)^2+\rho^2}}\}$$

Since the monolayer we built is 2×10^{-7} m size square on x-y plane and 0.72 nm in height, we make original point at the center of monolayer. a = - 0.36 nm, b = 0.36 nm, is the z coordinate of the lower and upper surface, c=b-a is the thickness of monolayer. $\rho=(x^2+y^2)^{1/2}$ is the distance of electron and hole on x-y plane. We assume z_0=z which means hole and electron are at the same position on z axis. Potential compose of second-order polynomial expansion of independent variable, whose expansion coefficient is the sum of z-direction space finite element contribution. For our model, absolute value of a and b is equal, so we can simply consider $\varepsilon'=\frac{\varepsilon_{substrate}+\varepsilon_{environment}}{2}$. We use COMSOL Multiphysics calculate Schrödinger equation of WSe_2 monolayer on SiO_2 under different dielectric environment.

$$[-\frac{\hbar^2}{2m_u^*}\nabla^2+V(\rho)]\phi=\lambda\phi$$

the effective mass of the excitonic quasi particle m_u^* can be obtained from $\frac{1}{m_u^*}=\frac{1}{m_e^*}+\frac{1}{m_h^*}$. The calculated binding energies are shown in Table 1.

S7. ET rate in different solvents assuming nonadiabatic charge transfer process

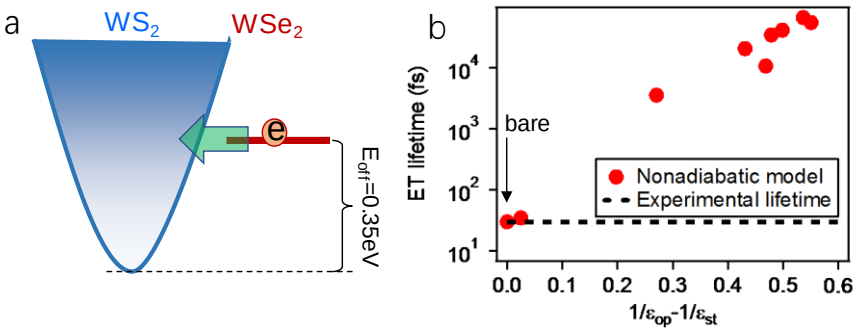

Figure S4. (a) Schematic showing the electron transfer from the conduction band edge in WSe_2 to continuum accepting states in conduction band of WS_2. The quasi-particle band offset is about 0.35 eV. (b) Calculated ET lifetime for different solvents assuming nonadiabatic Marcus ET model involving solvent reorganization. The lifetime of bare sample has been scaled to match the experimental lifetime (~ 30 fs).

We modeled ET process from WSe_2 conduction band to WS_2 conduction band using conventional nonadiabatic Marcus ET model where a single donating state weakly coupled to a continuum accepting states. This model has been extensively applied to describe ET from a molecule or a quantum dot to semiconductor film:[8-9]

$$k_{ET} = \frac{2\pi}{\hbar}\int_{-\infty}^{\infty} dE\rho(E)\left|H_{DA}(E)\right|^2 \frac{1}{\sqrt{4\pi\lambda k_b T}}\exp\left(-\frac{(\lambda+\Delta G_0+E)^2}{4\lambda k_b T}\right)$$

where $\rho(E)$ is the density of continuum accepting states and can be usually described by a $\sqrt{E}$ dependence; $\left|H_{DA}(E)\right|$ is the electronic coupling which can be assumed to be energy-independent in a small energy range; λ is the reorganization energy including TMDs materials and solvents, the former one is very small (< 1 meV, see Table S1) and we estimated the latter one using simple dielectric continuum model (as shown in Table S1); ΔG_0 is the maximum driving force which is the conduction band offset, which is partially cancelled by intralayer energy binding energy in initial state ($\Delta G_0 = -E_{off} + E_B$). Here we neglect the binding energy in final state (interlayer exciton binding state) since it would be much smaller than the binding energy in initial state[7] and recent experiment even suggests hot charge transfer state with even smaller binding energy[10]. Therefore, the ET rate can be simplified to

$$k_{ET} \propto \int_0^{\infty} dE\sqrt{\frac{E}{\lambda}}\exp\left(-\frac{(\lambda-E_{off}+E_b+E)^2}{4\lambda k_b T}\right)$$

with E_{off} = 350 meV, λ and E_b estimated in table S1. We can estimate the relative ET rate in different solvents and the ET rates are shown in Figure S4b as a function of $1/\varepsilon_{op} - 1/\varepsilon_{st}$ (i.e. reorganization energy). The calculated ET lifetime varies

dramatically in different solvents, contradicting with experimental results.

S8. TR spectra of WSe_2/WS_2 at different temperatures

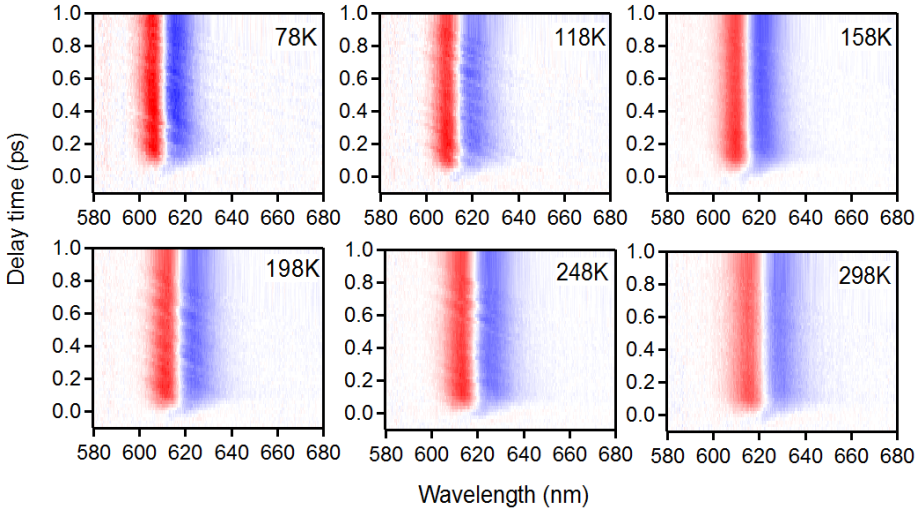

Figure S5. Color plot of TR spectra of WSe_2/WS_2 heterostructure at different temperatures.

References

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