

Gate-tunable hot electron extraction in a two-dimensional semiconductor heterojunction

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ABSTRACT

Hot carrier solar cells (HCSCs), harvesting excess energy of the hot carriers generated by above-band-gap photoexcitation, is crucial for pushing the solar cell efficiency beyond the Shockley–Queisser limit, which is challenging to realize mainly due to fast hot-carrier cooling. By performing transient reflectance spectroscopy in a MoSe₂/hBN/WS₂ junction, we demonstrate the gate-tunable harvest of hot electrons from MoSe₂ to WS₂. By spectrally distinguishing hot-electron extraction from lattice temperature increase, we find that electrostatically doped electrons in MoSe₂ can boost hot-electron extraction density (n_{ET}) by factor up to several tens. Such enhancement arises from interaction between hot excitons and doped electrons, which converts the excess energy of hot excitons to excitations of the Fermi sea and hence generates hot electrons. Moreover, n_{ET} can be further enhanced by reducing the conduction band offset with external electric field. Our results provide in-depth insights into design of HCSCs with electrostatic strategies.

TEXT

When a semiconductor absorbs photons with energy above its band gap, hot carriers with excess kinetic energy are generated. One solution of harvesting such energy, termed as hot carrier solar cells (HCSCs)¹, is to extract hot carriers to the higher-energy band of energy selective contacts (ESCs) before cooling, as illustrated in Figure 1c. The perfect HCSCs can increase the efficiency up to 66%², about twice the Shockley–Queisser (SQ) limit^{2,3}. However, this approach is extremely challenging⁴, since most of the excess energy is quickly lost to the lattice by optical phonon emission typically within several picoseconds (ps). Although efforts have been devoted to slowing down the phonon-assisted cooling process, such as exploiting hot-phonon bottleneck effect^{5,6} and trapping hot carriers in higher-energy side valleys⁷, no HCSCs beyond the SQ limit have been realized yet.

Two-dimensional (2D) materials act as a promising platform for the hot-electron extraction owing to the strong carrier-carrier scattering, which can compete with the electron-phonon scattering due to the reduced screening effect⁶. In addition, 2D heterostructures can be fabricated by choosing plentiful types of material and possess the high electrical-tunability⁸, which could offer abundant opportunities in optimizing the efficiency of hot-electron extraction. For example, graphene can efficiently convert absorbed photon energy to hot carriers⁹, which can be extracted to the higher-energy band of adjacent semiconductor^{10,11}. However, zero band gap of graphene is not favored for photovoltaic applications, since most of hot carriers will relax to the Dirac point

within several ps⁹. In this regard, semiconductor transition metal dichalcogenides (TMD) with band gap of $\sim$ eV and strong light-matter interaction^{12–14} are better candidates for HCSCs. Ultrafast dynamics studies^{8,15,16} have revealed fast interface charge transfer within 100 femtoseconds (fs) in TMD heterostructures, in which photoexcited carriers transfer to the lower-energy band in the other layer and all excess energy is lost. The extraction of hot carriers in TMD to a nearby higher-energy band¹⁷ still remains a challenge, which is vital for realizing HCSCs.

In this study, we fabricate a dual-gated MoSe₂/hBN/WS₂ heterostructure wherein MoSe₂ and WS₂ play the roles of the photoabsorber and the ESC of HCSCs, respectively, and perform transient reflectance (TR) spectroscopy. We demonstrate highly tunable hot-electron extraction dynamics from the conduction band of MoSe₂ to the higher-energy conduction band of WS₂. Specifically, we develop a rigorous method of extracting n_{ET} from the TR spectrum, as well as photoinduced increment of lattice temperature. Upon electron doping MoSe₂, n_{ET} shows a giant enhancement with a factor of several tens that arises from efficient scatterings between hot excitons and doped electrons, and scales linearly within a wide range of applied electric field. Our results highlight the exciton-electron interaction as a novel strategy for harvesting the excess energy of hot carriers in TMD materials.

Figure 1a shows a dual-gated device schematic. MoSe₂ and WS₂ monolayers are separated by a thin hBN layer ($\sim$ 1 nm), and grounded via a graphite electrode; top and

bottom gate voltages (V_t and V_b) are applied. See device fabrication and characterization in the Supporting Information (SI), as well as Figure S1 and S2. As shown in Figure 1b, the heterostructure has an intrinsic type-I band alignment^{18,19}, where the band gap of MoSe₂ is fully encompassed within that of WS₂. This is verified by the doping dependence of steady reflectance contrast (RC) spectrum (Figure 1d). Upon both electron and hole doping, the A-exciton resonance of MoSe₂ (A_M) is suppressed and the Fermi polarons²⁰⁻²⁴ (A_M^- and A_M^+) form, but little changes for the A-exciton resonance of WS₂ (A_W). The intrinsic conduction and valence band offsets (Δ_C and Δ_V) are respectively determined to be about 170 meV and 250 meV (Figure S3), consistent with previous studies^{18,19}. Doping is modulated by $V_D = V_t + 1.15V_b$, where the coefficient of 1.15 mainly counts for different thicknesses of top and bottom hBN dielectrics; for a given V_D , the band offsets are modulated by $V_E = V_t - 1.15V_b$ (see the SI for details). Unless otherwise specified, all optical measurements are performed at a sample temperature of 10 K.

To explore the hot-electron extraction, we perform TR spectroscopy with the scheme illustrated in Figure 1b. Analogous to the principle of HCSCs (Figure 1c), MoSe₂ works as a photoabsorber with tunable electron doping density n_e ; WS₂ works as a broadband ESC with tunable band offset Δ_C . A pump pulse with photon energy about 1.746 eV is to generate hot excitons in MoSe₂ without exciting WS₂ (Figure 1e); a broadband pulse is to probe optical resonances of WS₂ and thus monitor hot-electron transfer from

MoSe₂ to WS₂; the time delay (τ) between pump and probe pulses is varied (see the SI for details of the ultrafast setup). Hot-hole transfer is not favored, due to the much larger Δ_V . To be noted, WS₂ is kept electrostatically neutral for all ultrafast measurements.

Let's first take a glance at TR spectra of optical resonances of WS₂ with MoSe₂ electron doped. Figure 2a shows the contour plot of the TR spectrum at varying τ , from which several spectral linecuts are extracted (Figure 2b). The TR signal $\Delta R/R$ is defined as $(R_{\text{on}} - R_{\text{off}})/R_{\text{off}}$, where R_{on} and R_{off} are the reflected probe spectra with and without pump, respectively. The TR spectrum shows appearance of negative Fermi polaron resonance (A_W^-) of WS₂ around 2.03 eV after several ps, evidencing transferred hot electrons in WS₂. For the more pronounced TR feature around A_W resonance (~ 2.06 eV), it shows a complicated temporal evolution: at $\tau = 0.8$ ps, the spectral weight of $\Delta R/R < 0$ is much larger than that of $\Delta R/R > 0$; from 0.8 to 10 ps, the spectral weights of $\Delta R/R < 0$ and $\Delta R/R > 0$ gradually become comparable; after 10 ps, the spectral profile slightly changes. In the following, we will focus on A_W resonance for its large signal-to-noise ratio.

This complicated evolution indicates multiple effects following the optical excitation, and here we consider three effects—transferred hot electrons, lattice temperature increment, and enhanced surrounding screening, the last of which likely arises from mobile photoexcited carriers in MoSe₂. We identify the TR spectral profiles of A_W resonance induced by these effects independently, based on the steady RC spectrum

modulated by: electrostatically doping WS₂ that corresponds to the electron-transfer TR profile (Figure S4); increasing sample temperature that corresponds to the temperature-increase TR profile (Figure S5); electrostatically doping MoSe₂ that corresponds to the screening TR profile (Figure S6). As shown in Figure S7, we can see that the temperature-increase and screening TR profiles are almost the same, which are different from the electron-transfer TR profile. We expect that temperature increase has a larger contribution to the TR signal than that of the screening, because photoexcited excitons in MoSe₂ are dipole-like neutral quasiparticles that should have weak remote screening effect on the hBN-separated WS₂. See the SI for more discussion about the three effects.

We use the two TR profiles of electron transfer and temperature increase as the bases to fit the experimental TR spectrum, referred as the two-profile analysis, which can give n_{ET} and lattice temperature increment ΔT^* . Figure 2c and d show the TR spectra at $\tau = 1.2$ and 40 ps, respectively, in spite of distinct shapes, both of which can be well fit by the two-profile analysis. We extract n_{ET} and ΔT^* as a function of τ shown in Figure 2e and f, respectively, except initial delays (≤ 0.4 ps) that suffer from contaminating effects of coherent light-matter interaction (see fittings at other time delays in Figure S8). The n_{ET} and ΔT^* dynamics are further fit by a two-exponential function (dashed) that gives the rise and decay time constants. n_{ET} shows a rise time constant of 2.6 ps and a decay time constant of 138 ps. The rise dynamics of n_{ET} is

the convolution of the electronic thermalization (e.g., via exciton-electron scatterings) that generate hot electrons and the hot-electron tunneling from MoSe₂ to WS₂. Here, we attribute the rise dynamics of n_{ET} to the electronic thermalization in MoSe₂, as a result of faster hot-electron tunneling (<1 ps, see more discussion later); the decay dynamics of n_{ET} is attributed to the electron back-transfer from WS₂ to MoSe₂, driven by the conduction band offset, which is consistent with another ultrafast study of hBN-separated TMD heterostructures²⁵. The magnitude of ΔT^* is also in line with previous reports^{26,27}.

With the two-profile analysis, we explore hot-electron extraction dynamics with varying electron doping in MoSe₂, as shown in Figure 3a. The maxima of n_{ET} dynamics, denoted as $n_{ET,m}$, are shown in Figure 3b. Upon MoSe₂ electron doped, $n_{ET,m}$ gets vastly enhanced by a factor up to ~ 30 , with an onset behavior. Moreover, the rise dynamics also shows an onset behavior, which suddenly slows down at low n_e and then becomes faster with further increasing n_e (Figure 3c). The largest $n_{ET,m}$ corresponds to the hot-electron extraction efficiency about 5%, defined as $n_{ET,m}/n_{ex}$, where n_{ex} is the initial photoexcited hot exciton density in MoSe₂. The corresponding ΔT^* dynamics is shown in Figure S9.

To gain more insights about doping-enhanced hot-electron extraction, we study ultrafast dynamics of A_M resonance of MoSe₂ with varying electron doping in MoSe₂. Surprisingly, the rise timescale (empty circles) of A_M resonance shows onset doping

behavior similar to that of n_{ET} , as shown in Figure 3c and Figure S10. Upon electron doping MoSe₂, both rise timescales of A_M and n_{ET} increase up to about 6 ps; as electron doping further increases, both timescales decrease to about 1 ps. The rise dynamics of A_M resonance reflects the electronic thermalization in MoSe₂, during which hot excitons interact with the Fermi sea and thus hot electrons are generated. Since the dynamics of n_{ET} is the temporal convolution of the electronic thermalization and the hot-electron tunneling, the similarity of the rise timescales evidences that, the rise dynamics of n_{ET} can be mainly attributed to the electronic thermalization, and the hot-electron tunneling itself should be much faster (<1 ps that corresponds to the shortest rise timescale of n_{ET} dynamics at $V_D=6.45$ V). Similar fast hot-electron tunneling has been observed in WS₂/graphene heterostructures^{10,28}. Hence, we propose a doping-assisted mechanism illustrated in Figure 3e,f: Through the scatterings between excitons and electrons in MoSe₂, the excess energy of hot excitons is converted to the excitations of the Fermi sea, which generate hot electrons with enough kinetic energy that can transfer to the higher-energy conduction band of WS₂; higher electron doping leads to more frequent scatterings (i.e., faster electronic thermalization), which generate more hot electrons and lead to faster rise dynamics of n_{ET} . Once the electronic quasi-equilibrium is achieved with the formation of Fermi polaron, no more hot electrons get generated and the hot-electron extraction terminates. For neutral MoSe₂ (Figure 3d), the scatterings among excitons can also generate hot electrons that can transfer to WS₂,

likely via Auger recombination—the recombination of one exciton leads to the ionization of the other exciton. It should be noted that, it is hard to extract hot-electron transfer from the A_M dynamics of MoSe₂, since which involves multiple other effects, such as interaction between photo-excited excitons and doped electrons, electron-hole recombination, and temperature change.

We further explore the power dependence of hot-electron extraction with electron doped and neutral MoSe₂, as shown in Figure 4a and b, respectively. For doped MoSe₂, when the pump fluence increases, n_{ET} shows overall increase and faster rise dynamics. In Figure 4c, $n_{ET,m}$ exhibits a sublinear power dependence that gives enhanced hot-electron extraction efficiency for a lower pump fluence (Figure 4d). This is a favored character for photovoltaic applications under weak illumination intensity, such as sunlight, in contrast to the hot-phonon bottle neck effect that requires high illumination intensity^{5,6}. Moreover, for neutral MoSe₂, $n_{ET,m}$ shows a linear-like power dependence with the extrapolation deviating from the origin (Figure 4c), which gives increased hot-electron extraction efficiency for a higher pump fluence (Figure 4d). See Figure S11 for the corresponding ΔT^* dynamics.

The power dependence of the hot-electron extraction efficiency can be understood in terms of the aforementioned mechanism (Figure 3). As the pump fluence increases, the amount of the excess energy to be dissipated increases. However, for a given electron-doping density, the dissipation capacity of the Fermi sea is limited by the scattering rate

between hot excitons and electrons. As the excess energy exceeds the capacity of the Fermi sea, other dissipation channels such as the electron-phonon scatterings become more involved, which will lead to a reduced hot-electron extraction efficiency at high pump fluence. In contrast, for neutral MoSe₂, hot electrons arise from Auger recombination of excitons, in which increasing initial exciton density leads to more efficient generation of hot electrons.

Lastly, for shedding light on the impact of the conduction band offset, we explore the electric field dependence of the hot-electron extraction with doped and neutral MoSe₂, as shown in Figure 5a and b, respectively. For both doped and neutral MoSe₂, as V_E increases and thus Δ_C decreases, n_{ET} shows overall increase and slower decay dynamics. This can be understood as follows. Reducing Δ_C gives rise to more hot electrons that have enough kinetic energy to transfer to WS₂, and less driving force for the electron transfer from WS₂ back to MoSe₂. Worthy to note, the electron transfer back to MoSe₂ will only slightly modify the decay dynamics of A_M , instead of leading to any rise, owing to other overwhelming processes in MoSe₂, such as the recombination of electron-hole pairs. Moreover, as shown in Figure 5c,d, the maximum of n_{ET} shows linear dependence within a wide range of V_E , indicated by dashed lines. This is distinct from the Fowler-Nordheim tunneling for the devices with thick hBN barrier²⁹⁻³² wherein the tunneling current is highly nonlinear with the bias voltage²⁹, which means that, in this work, hot electrons in MoSe₂ directly tunnel to WS₂, without

travelling to the bands of the inset hBN. See Figure S12 for the corresponding ΔT^* dynamics.

In this work, we demonstrate gate-tunable hot-electron extraction, as well as a rigorous method of obtaining both transferred electron density and lattice temperature increment, which demonstrate a doping-assisted mechanism in harvesting excess energy of hot carriers in TMD materials. Although the current hot-electron extraction efficiency is only a few percent, it can be further enhanced by reducing the thickness of inset hBN (e.g., the tunneling probability of 1L hBN is about one order larger than that of 3L hBN³³), using a multilayer MoSe₂ with indirect band gap^{12,13,34} that can reduce radiative recombination losses, and aligning the crystal orientation of both TMDs layers for minimizing momentum mismatch.

FIGURES

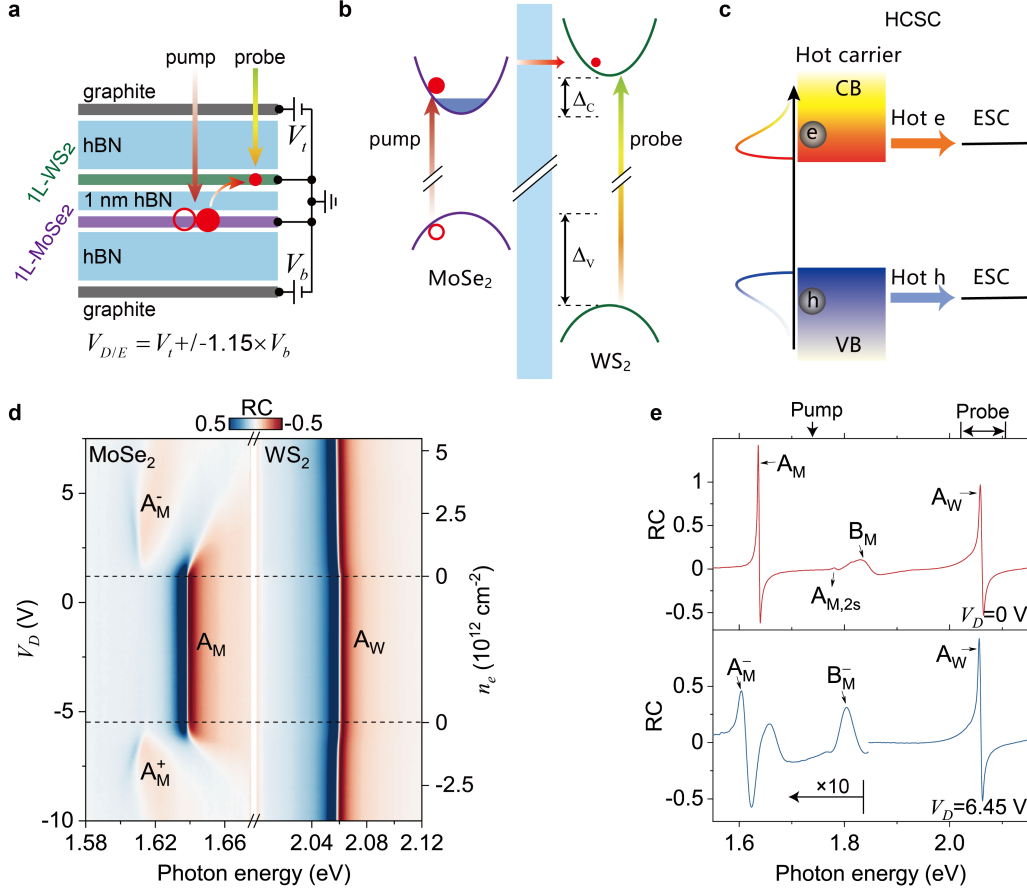


Figure 1. Schematics of the device, hot carrier photovoltaics, and pump-probe scheme. (a) Schematic of a dual-gated $\text{WS}_2/\text{hBN}/\text{MoSe}_2$ heterostructure. WS_2 and MoSe_2 monolayers are grounded; top and bottom gate voltages (V_t and V_b) are applied. (b) For the pump-probe scheme, only MoSe_2 is optically excited, and optical resonances of WS_2 are probed for monitoring hot-electron extraction dynamics, with varying doping and band offsets. (c) The concept of HCSCs. Photoexcited hot electrons and holes are collected by the electron ESC (above the conduction band minimum) and the hole ESC (below the valence band maximum), respectively. (d) Contour plot of the doping dependence of steady RC spectrum with $V_E = 0$ V. (e) Two RC spectra with neutral and electron doped MoSe_2 , extracted from (d). A_M , A_M^- , B_M , B_M^- represent A-exciton, A-exciton-derived Fermi polaron, B-exciton, and B-exciton-derived Fermi polaron resonances of MoSe_2 , respectively. Similar label conventions are applied to reflectance resonances of WS_2 .

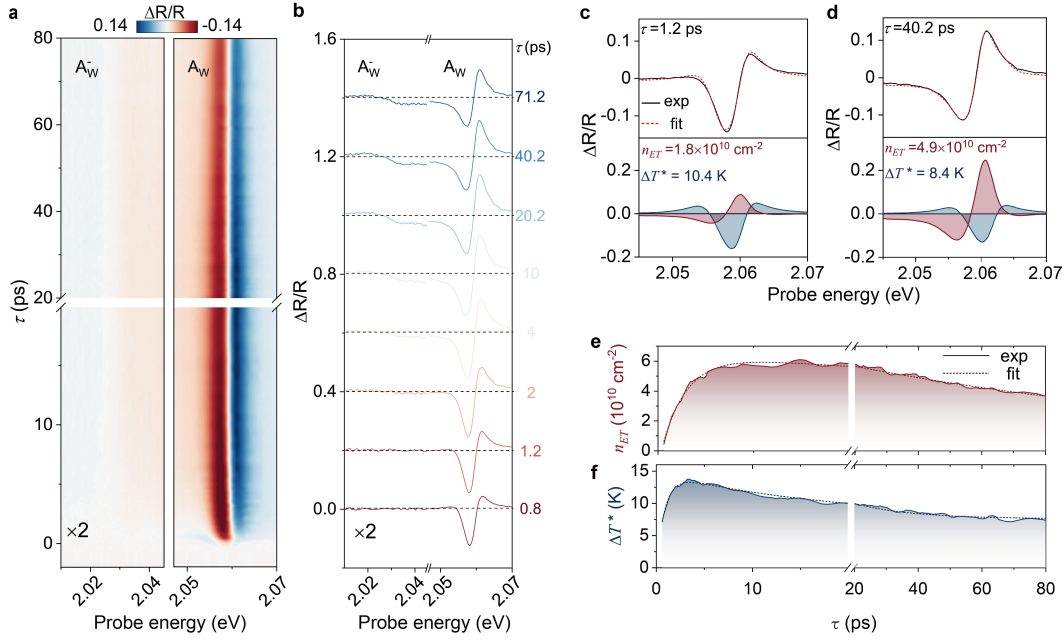


Figure 2. The hot-electron extraction and lattice temperature increase distinguished in transient reflectance spectra. (a) Contour plot of transient reflectance (TR) spectrum as a function of pump-probe delay τ with probe energy covering A_W and A_W^- resonances of WS_2 . With $V_D = 2.6$ V and $V_E = 0$ V, n_e in $MoSe_2$ and Δ_C are about $1.3 \times 10^{12} \text{ cm}^{-2}$ and 120 meV, respectively. The pump fluence of $63 \mu\text{J}/\text{cm}^2$ generates an initial exciton density n_{ex} about $2.5 \times 10^{12} \text{ cm}^{-2}$, which is determined by multilayer interference calculation (see the SI). (b) Spectral linecuts at various τ , extracted from (a). The curves are vertically displaced for clarity, with dashed lines denoting $\Delta R/R=0$. (c, d) The two-profile analysis of the TR spectra at $\tau=1.2$ and 40.2 ps. The upper panel shows the experimental data and fitting; the lower panel shows the two TR profiles used in the fitting, revealing n_{ET} and ΔT^* . (e, f) The dynamics of n_{ET} and ΔT^* , fitted with a two-exponential function (dashed).

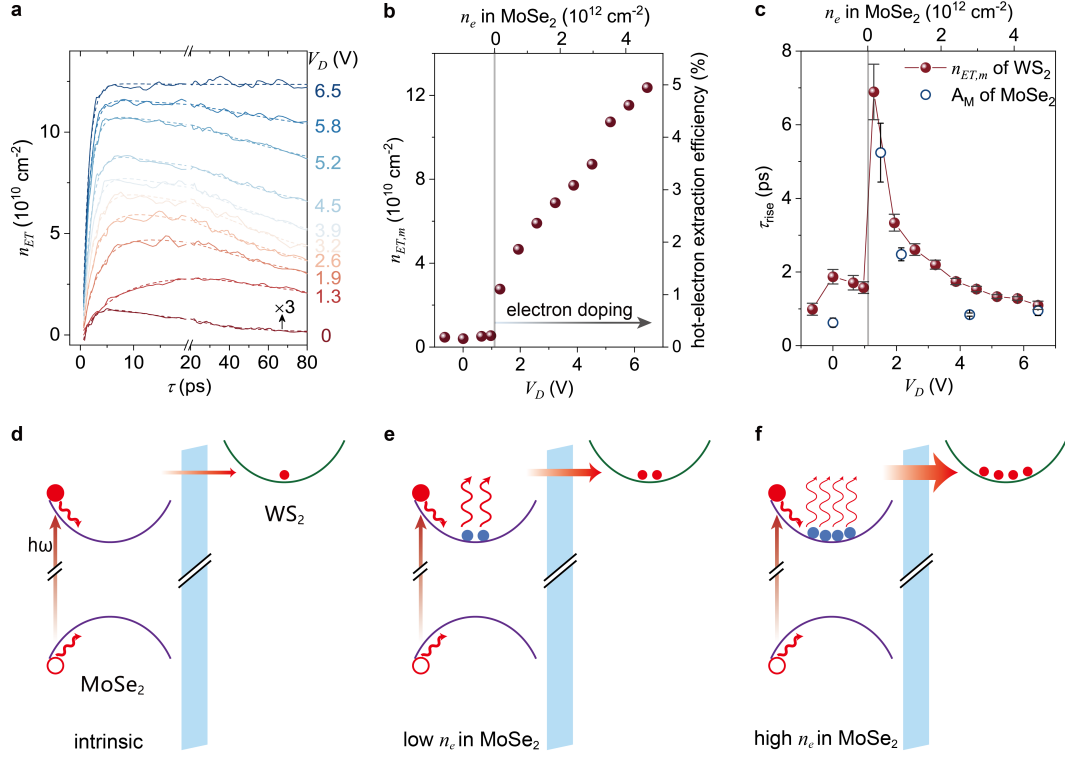


Figure 3. Enhanced hot-electron extraction upon electron doping MoSe₂. (a) The n_{ET} dynamics with n_e varying from 0 to $4.6 \times 10^{12} \text{ cm}^{-2}$ in MoSe₂, corresponding to V_D varying from 0 V to 6.45 V. The initial n_{ex} is about $2.5 \times 10^{12} \text{ cm}^{-2}$, corresponding to pump fluence about $63 \mu\text{J}/\text{cm}^2$. V_E is kept at 0 V. The dynamics is fitted with a two-exponential function (dashed). (b) The maximum of hot-electron extraction density $n_{ET,m}$ and the corresponding hot-electron extraction efficiency as a function of V_D . The vertical gray line indicates the initial of electron doping. (c) The doping-dependent rise time constant of n_{ET} as a function of V_D , compared with the rise time constant of A_M resonance (Figure S10). (d-f) The schematic of hot-electron extraction mechanism for neutral and doped MoSe₂. The scatterings between hot excitons and doped electrons (e,f) can generate hot electrons more efficiently than the scatterings among excitons (d). See main text for detailed discussion.

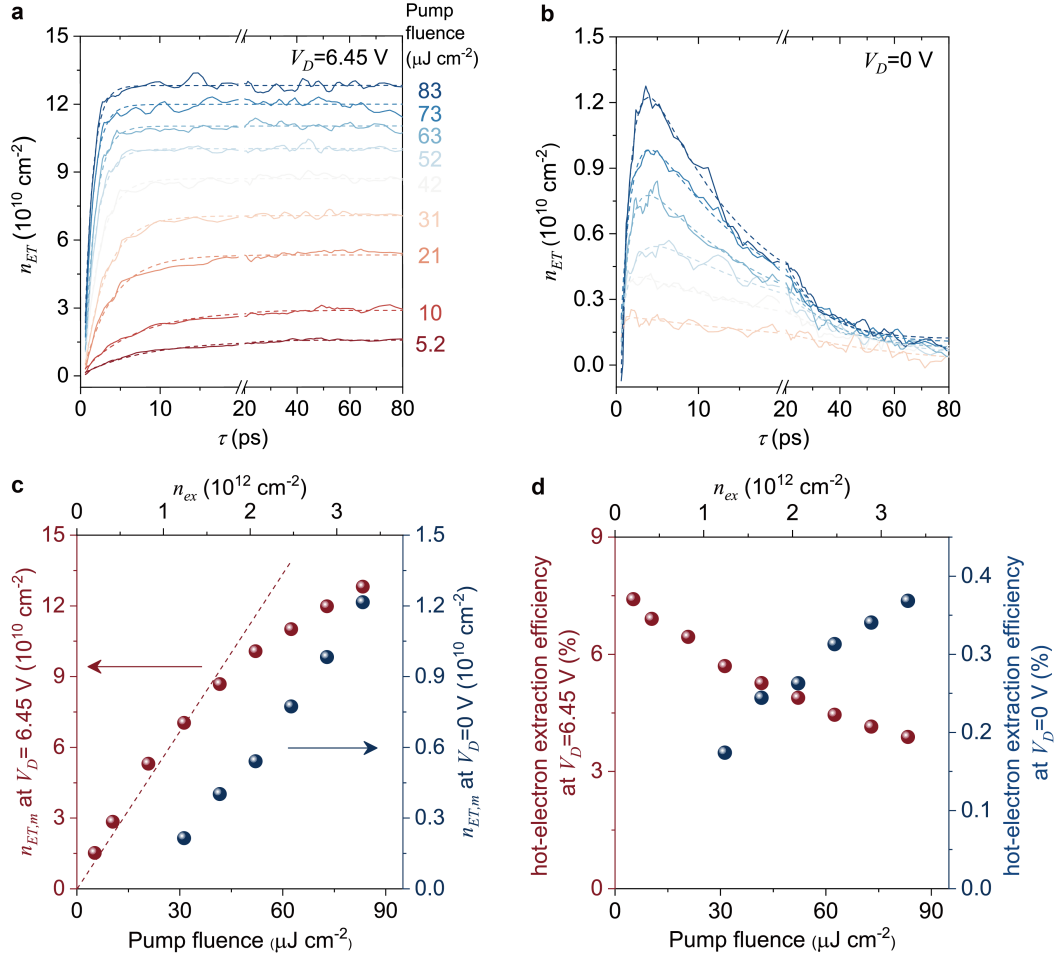


Figure 4. The power dependence of hot-electron extraction with electron doped and neutral MoSe₂. (a, b) The n_{ET} dynamics with pump fluence varying from 5.2 to 83 $\mu\text{J cm}^{-2}$, corresponding to n_{ex} from about 0.2 to $3.3 \times 10^{12} \text{ cm}^{-2}$. V_D is set to 6.45 V and 0 V, corresponding to electron doped MoSe₂ with n_e about $4.6 \times 10^{12} \text{ cm}^{-2}$ and neutral MoSe₂, respectively. V_E is kept at 0 V. The dynamics is fitted with a two-exponential function (dashed). (c, d) The power dependence of $n_{ET,m}$ (c) and hot-electron extraction efficiency (d) for the two doping scenarios. The straight dashed line is to highlight sub-linear behavior.

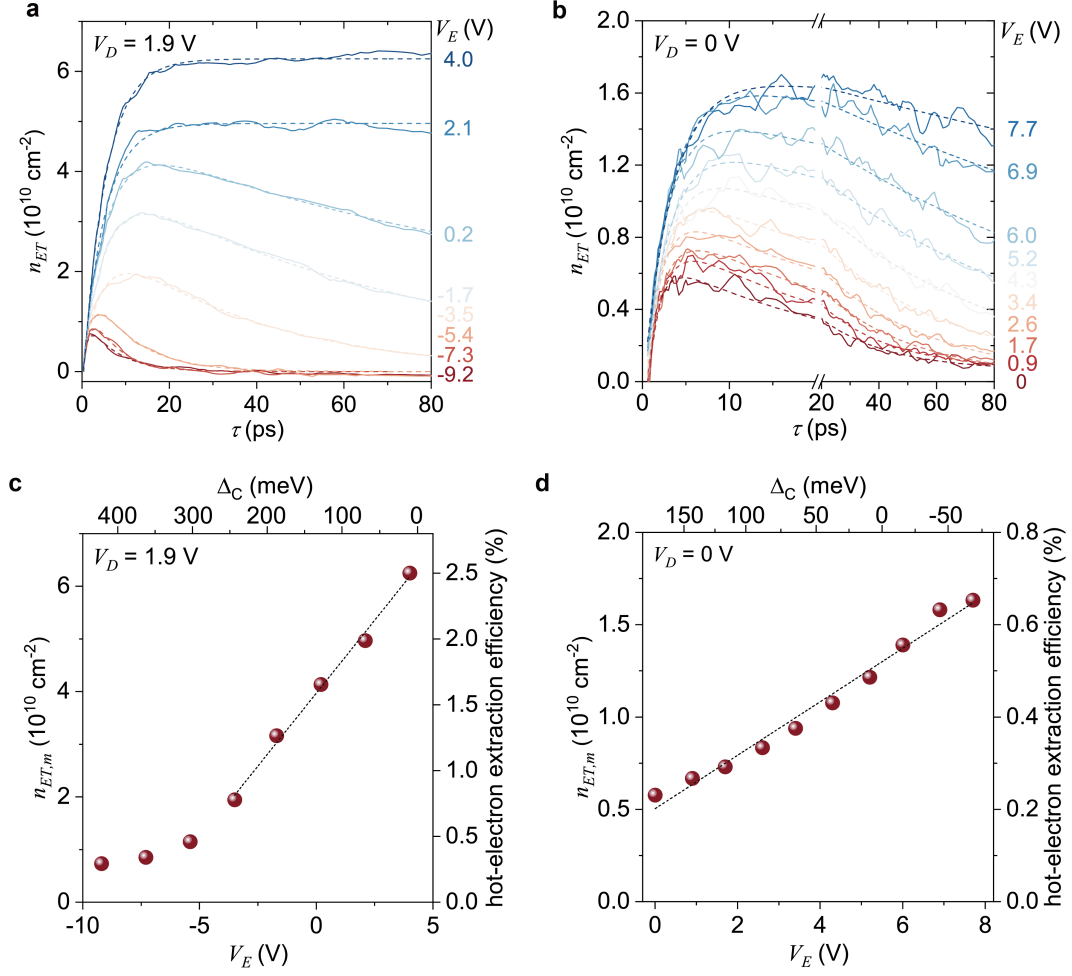


Figure 5. The electric field dependence of hot-electron extraction with electron doped and neutral MoSe₂. (a, b) The n_{ET} dynamics with varying V_E . V_D is set to 1.9 V and 0 V, corresponding to electron doped MoSe₂ with n_e about $0.7 \times 10^{12} \text{ cm}^{-2}$ (a) and neutral MoSe₂ (b), respectively. The dynamics is fitted with a two-exponential function. (c, d) The electric field dependences of $n_{ET,m}$ and the corresponding hot-electron extraction efficiency for the two doping scenarios. Dashed lines are eye-guidance to the linear behavior.

ASSOCIATED CONTENT

Supporting Information

Device fabrication and characterization, the steady RC spectroscopy, the transient reflectance spectroscopy, electrostatic calculation of n_e and Δ_C , estimation of initial n_{ex} , identifying the TR profiles of the A_W resonance induced by various effects, the two-profile analysis of the TR spectrum, ΔT^* dynamics with varying doping in MoSe₂, the TR spectrum around the A_M resonance upon electron doping MoSe₂, the pump-fluence dependence of ΔT^* dynamics, the electric-field dependence of ΔT^* dynamics, and discussion of hot-electron extraction at ambient condition

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Author contributions: Y.T. designed the scientific objectives; Y.T., D.W. and S.Z. supervised the project; C.X. built up the ultrafast setup and performed TR spectroscopy under Y.T.'s supervision, with assistance from X.X.; C.X. and Y.T. analyzed the data; Chen Xu and J.Z. fabricated the devices, with assistance from Z.S., W.S. and W.L.; K.W. and T.T. grew the hBN crystals; Y.T. and C.X. wrote the manuscript with the input from all the authors. C.X. and Chen Xu contributed equally to this work.

Competing interests

The authors declare no competing interests.

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