Observation of ultrafast interfacial Meitner-Auger energy transfer in a Van der Waals heterostructure

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Atomically thin layered van der Waals heterostructures feature exotic and emergent optoelectronic properties. With growing interest in these novel quantum materials, the microscopic understanding of fundamental interfacial coupling mechanisms is of capital importance. Here, using multidimensional photoemission spectroscopy, we provide a layer- and momentum-resolved view on ultrafast interlayer electron and energy transfer in a monolayer-WSe2/graphene heterostructure. Depending on the nature of the optically prepared state, we find the different dominating transfer mechanisms: while electron injection from graphene to WSe2 is observed after photoexcitation of quasi-free hot carriers in the graphene layer, we establish an interfacial Meitner-Auger energy transfer process following the excitation of excitons in WSe2. By analysing the time-energy-momentum distributions of excited-state carriers with a rate-equation model, we distinguish these two types of interfacial dynamics and identify the ultrafast conversion of excitons in WSe2 to valence band transitions in graphene. Microscopic calculations find interfacial dipole-monopole coupling underlying the Meitner-Auger energy transfer to dominate over conventional Förster- and Dexter-type interactions, in agreement with the experimental observations. The energy transfer mechanism revealed here might enable new hot-carrier-based device concepts with van der Waals heterostructures.

The unique physical properties of atomically thin two-dimensional (2D) materials1–3 and constantly improving fabrication methods4–11 have led to a great interest in novel quantum materials based on van der Waals (vdW) heterostructures12. By stacking 2D materials, vdW heterostructures inherit the properties from individual constituents, and exotic physical phenomena may emerge due to the interfacial interaction13. An emblematic example is the emergence of superconductivity in twisted bilayer graphene when stacked at the so-called “magic angle”. As another example, interlayer excitons, which are spatially separated yet Coulomb-bound electron-hole pairs in...
semiconducting transition metal dichalcogenide (TMDC) heterostructures allow exceptional control of optoelectronic properties.\textsuperscript{14} Out of the vdW heterostructure library, a basic optoelectronic building block is a monolayer (ML) semiconducting TMDC in contact with graphene.\textsuperscript{12} This hybrid structure represents a model system as it combines the strong light-matter coupling of TMDCs and the high mobility of massless Dirac carriers of graphene.\textsuperscript{12} The gapless electronic structure of graphene allows for harvesting low-energy photons, extending the spectral range covered by conventional photodetectors to the near-infrared wavelength, which is highly beneficial for photovoltaic applications.\textsuperscript{14}

Optoelectronic functionality in vdW heterostructures arises from careful design and control of optical transitions and interfacial transfer processes. Particularly, interfacial charge (ICT) and energy transfer (IET) are key processes that have triggered extensive experimental and theoretical efforts.\textsuperscript{15-20} Using time-resolved optical spectroscopies, a strong reduction of the exciton lifetime and optically active charge-interfacial charge and energy transfer processes, including those mechanisms have been discussed.\textsuperscript{15-20} Moreover, the efficiency of IET processes like Förster-type coupling (based on electronic dipole-dipole interaction) has recently been investigated theoretically, pointing out the importance of energy-momentum conservation between participating quasiparticles.\textsuperscript{15} These studies provide our current understanding of the mechanisms of interfacial interactions. However, it is still challenging to clearly distinguish and unravel the involved interlayer charge and energy transfer in vdW heterostructures based on optical spectroscopies, primarily transient absorption/reflection and terahertz spectroscopy, which are inherently sensitive to the selective spectral range and limited momentum accessible. Therefore, a momentum-resolved probe is required to monitor the dynamics directly and achieve a complete picture of interfacial charge and energy transfer processes, including those involving momentum-forbidden dark states.

Here, we use time- and angle-resolved photoemission spectroscopy (trARPES) to investigate ultrastack interlayer carrier interactions in an epitaxially grown ML-WSe\textsubscript{2}/graphene heterostructure. Our trARPES setup combines a high-repetition rate (500 kHz) femtosecond extreme ultraviolet (XUV) source coupled to a time-of-flight momentum microscope (see Methods). It allows the measurement of the four-dimensional (4D) photoemission intensity \( R(k_{\text{in}}, k_x, k_y, \Delta \omega) \), where \( E_{\text{kin}} \) is the outgoing photoelectron kinetic energy, \( k_x, k_y \) are the in-plane momenta and \( \Delta \omega \) is the pump-probe delay, as shown in Fig. 1a, b. The probe photon energy of 21.7 eV allows accessing the entire Brillouin zone of the heterostructure and the variable pump wave-length allows us to photoexcite the heterostructure in a state-resolved manner. In the following, we present a time-, energy-, and momentum-resolved study on the excited-state dynamics in the heterostructure with two different pump photon energies: below the optical bandgap of WSe\textsubscript{2} (1.2 eV) and in resonance with its first excitonic transition (1.55 eV).

### Results

#### Interlayer quasi-free carrier transfer

First, we photoexcite the heterostructure with the pump photon energy centered at \( h\omega_{\text{pump}} = 1.2 \text{ eV} \) (pump pulse duration 200 fs FWHM), well below the optical bandgap of WSe\textsubscript{2}.\textsuperscript{29} The NIR-pump/XUV-probe experiments were performed with a pump fluence of \( F = 5 \text{ mJ/cm}^2 \) and at room temperature. Figure 2a shows energy-resolved photoemission signals along the K – K cut of the Brillouin zone, at selected time delays. The band mappings are contrast-enhanced using a multidimensional extension of the contrast limited adaptive histogram equalization (MCLAHE)\textsuperscript{30,31} for better visualization of the band structure. The momentum distributions above \( E_F \) within the first 400 fs reveal that the excited states are localized in three different types of valleys: the Dirac cones of graphene at its K points (K\textsubscript{Gr}) and the K and Q valleys of WSe\textsubscript{2} (K\textsubscript{WSe2}, Q\textsubscript{WSe2}), as shown in Fig. 2b. The Q\textsubscript{WSe2} valley localizes between the K\textsubscript{Gr} and the valley and the \( \Gamma \) point. By performing energy-momentum integration in selected regions of interest (ROIs), we extracted excited-state dynamics within these three valleys (Fig. 2f). Upon arrival of the pump pulses, the excited-state population rapidly builds up at K\textsubscript{Gr} (black curve) and decays with a time scale of ~200 fs. Strikingly, the conduction band minima (CBMs) at K\textsubscript{WSe2} (red curve) and Q\textsubscript{WSe2} valleys (green curve) are also being populated, however, with a delay of \( \Delta t = 5 \pm 9 \text{ fs} \) (see SI) compared to the rise of hot-carrier population in graphene. Since below-bandgap pump photon energy does not allow the direct photoexcitation of WSe\textsubscript{2}, the delayed electron populations in the conduction bands arise through charge transfer from graphene to WSe\textsubscript{2}. Two/multiple photon excitation can safely be ruled out (details see SI). The excited-state population of the Q\textsubscript{WSe2} valleys (Fig. 2g) could be raised via ICT from the graphene layer and the intervalley scattering from the K\textsubscript{WSe2} valleys.

These observations support the following picture of the underlying processes with a below-bandgap excitation: light is absorbed by graphene and populates unoccupied states at \( E_p = E_F + h\omega_{\text{pump}}/2 \), leaving holes at \( E_p = E_F - h\omega_{\text{pump}}/2 \) (Dirac energy in a p-doped system or \( E_p < 0 \) for an n-doped system). The energy position of the Dirac point in our heterostructure is estimated to be \( -0.1 \text{ eV} \) below the Fermi level, obtained from the conical crossing\textsuperscript{32,33} (see SI). The photo-
to excited carriers quickly reach a quasi-thermalized states in -10 fs and could further increase their energy via intraband electron-electron scattering and interband Auger recombination in few tens of femtoseconds. Once electrons gained a sufficient amount of energy to overcome the energy barrier, they scatter to WSe$_2$ via a phonon-assisted tunneling process, filling the single-particle CBMs at WSe$_2$ and QWSe$_2$. This ICT mechanism is called interlayer hot-carrier injection, and is schematically illustrated in Fig. 2g. The excited electrons in WSe$_2$ may subsequently scatter back to graphene and relax down towards the Fermi energy ($E_F$). Based on the observed carrier dynamics, we performed microscopic calculations of the phonon-assisted interlayer tunneling process, allowing us to estimate the electronic wavefunction overlap between the involved conduction bands of WSe$_2$ and graphene to be ~4% (see SI for details).

**Interlayer energy transfer**

Next, we select a pump photon energy of $\hbar\omega_{pump} = 1.55$ eV (pump pulse duration: 35 fs FWHM, pump fluence: $F = 1.7$ mJ/cm$^2$), near-resonant to the A-exciton transition of WSe$_2$. In this case, the pump photon energy allows both the WSe$_2$ and the graphene layer to be simultaneously photoexcited. One striking observation is that the energy-momentum distribution of hot carriers in graphene. As shown in the early-time 2D differential spectrum $\Delta t = 0$, the valence bands of WSe$_2$ and graphene are filled with quasi-free electrons that have tunneled from the graphene layer. Therefore, this -100 meV energy difference is a direct photoemission signature of exciton formation, when near-resonantly pumping using 1.55 eV photons: the bound electron-hole (e-h) pair reduces the quasi-free particle bandgap by the exciton binding energy. In addition to this excitonic feature, we also observe a transient shift of WSe$_2$ valence bands. In Fig. 3d, EDCs at $K_{\text{WSe}_2}$ are shown at $\Delta t = 0$ fs (red) and $\Delta t = -200$ fs (black), in which the two top valence bands, VB1 and VB2, are fitted using Gaussian lineshape functions (see SI). The peak position of VB1 shifts towards the conduction band within the first 100 fs, transiently shrinking the electronic bandgap. This is due to the arrival of ICT-induced charge carriers from the graphene layer. With near-resonantly pumping the A-exciton, the occurrence of ICT and injection of quasi-free carriers from graphene to WSe$_2$ is expected, similar to the case of below-bandgap excitation. This could lead to dynamical screening effect and the observed bandgap renormalization, as reported in highly-excited or doped ML TMDC materials. As the magnitude of such a transient bandgap renormalization has been shown to scale with the excited charge carrier density, we utilize the VB shift in the following as a measure of the ICT transferred carriers dynamics from graphene layer.

In addition to the excited-state dynamics in WSe$_2$, important insight can be drawn from the energy-momentum distribution of hot carriers in graphene. As shown in the early-time 2D differential spectrum $\Delta t = 0$ fs (Fig. 3c), obtained by subtracting the spectrum at the negative time, hot carriers distribute in a broad energy range. The momentum-integrated spectrum along the linearly dispersing band in Fig. 3e clearly features the energy distribution of net electron gain (positive; red area) and loss (negative; blue area) following near-resonant photoexcitation. Remarkably, besides the modification of the distribution function near the Fermi level, we notice a strong negative peak at $E-E_F = -1.5$ eV. As noted earlier, for direct photoexcitation in graphene the photoexcited carriers are expected to be spread ±0.77 eV ($\hbar\omega_{pump}/2$) around the Dirac point and quickly relax back to the Fermi level. Thus, this simple excitation mechanism cannot explain this peculiar feature in the valence band spectrum. The electron-electron scattering and Auger recombination could lead to a transient broadening of the momentum-space carrier distribution, but without any preferential energy localization. Hole transfer can also be ruled out, as the top valence band of WSe$_2$ lies at $E-E_F = -1.0$ eV. It would require a multi-phonon absorption to populate the hole-states localized deeply in the valence band, taking the typical phonon energy of ~0.17 eV in graphene, a process of very low probability. However, the energy difference of deep-lying valence holes ($E-E_F = -1.8$ eV) and states near $E_F (E-E_F = -0.2$ eV) in graphene well matches the energy of the A-exciton in WSe$_2$ ($E_{A} = -1.6$ eV). Combined with the fast depletion of exciton population shown in Fig. 4a (black curve) extracted from the
excited state of WSe$_2$ (ROI$_1$ in Fig. 3c), this brings about the following scenario for the excitation of these carriers: annihilation of excitons in WSe$_2$ drives the intraband excitation of deep-lying valence electrons in graphene into empty hole states below the Dirac point. In more detail, this exciton energy transfer process, which we term Meitner-Auger energy transfer\cite{51}, considers recombination of excitons in WSe$_2$ with center-of-mass (COM) momentum $Q$ and exciton energy $E_x$. The photoexcitation prepares the required hot hole vacancy below $E_F$ in graphene, thus enabling the intraband excitation. The photo-generated hole density plays an important role in the MA-type IET process (see the discussion of pump fluence dependence in SI). Besides the observation of the deep-lying hot holes, we also identify a substantial suppression of hole-like spectral weight (Meitner-Auger type IET-induced hot electrons) below the Fermi level with near-resonant excitation, supporting the occurrence of intraband transition in the graphene layer (details see SI, section Meitner-Auger type IET-induced hot electrons near the Fermi level). The momentum of the valence electron-hole pair $k_{eh}$ is determined by the Fermi velocity of the graphene bands and the transition energy $E_{Gr}$. This required momentum is provided by the optically pumped excitons which gain finite COM momenta during the population formation process via phonon-mediated dephasing and intravalley thermalization\cite{51-54} (see the discussion in SI). The highly efficient IET of the excitons and intraband electron-hole pairs is thus possible under the conservation of energy and momentum, i.e., $E_x - E_{Gr}$ and $Q = k_{Gr}$. In a similar trARPES study of a ML WS$_2$/graphene heterostructure, dominating interfacial charge transfer has been observed\cite{17}. Compared with our study, the different charge transfer rates could be raised from the different band structure alignment near the interface and the density of defect sites\cite{26}. While the additional exciton energy transfer was not excluded, its relative efficiency might be reduced due to the larger COM momentum required at the larger A-exciton energy of WS$_2$ and the energy level alignment of these specific samples.

In order to gain information on the time scales of the energy and charge transfer processes, next we analyze the dynamics of excited-state populations extracted from the ROIs shown in Fig. 3c, including the excited-state carriers in WSe$_2$ (ROI$_1$), VBI shifting (ROI$_2$), hot electrons in graphene (ROI$_3$) and IET-driven deep valence band holes (ROI$_4$). The time trace of hot carriers in the CBM of WSe$_2$ (black curve in Fig. 4a) contains two types of quasiparticles dynamics: the photo-generated excitons $N_x$ and the IET-induced quasi-free electrons $N_{Gr}$. The decay of excitons excite the valence band electrons in graphene via IET with a transfer time of $\tau_{\text{IET}}$ (Fig. 4f). On the other hand, the arrival of ICT-induced electrons transiently shifts the VBs of WSe$_2$.

**Fig. 3 | Photoemission signatures of exciton formation and interfacial interactions.** a With near-resonant A-exciton pump (1.55 eV), carriers within both the WSe$_2$ and the graphene layer are photoexcited (time integration of 100 fs). The energy of the excited states carriers at $K_{WSe2}$ is 0.63 eV, shown in the EDC (left panel figure). b With below-bandgap excitation (1.2 eV), the local CBM of $K_{WSe2}$ is filled with ICT-induced electrons and centered at 0.73 eV. c Differential energy-momentum cut with 1.55 eV pump at time zero, obtained by subtracting the negative time delay spectrum. d The normalized EDC of $K_{WSe2}$ (momentum integration of 0.2 Å$^{-1}$) at $\Delta t = 200$ fs (black) and $\Delta t = 0$ fs (red). The VBs are fitted with two Gaussian functions (dashed curves) and the positions of VBI are indicated by the dash lines. e The momentum-integrated spectrum of graphene Dirac bands (between the dashed yellow lines in e) shows the electron gain (positive, red area) and loss (negative, blue area) following photoexcitation. The intensity is normalized to the total electron count C obtained from negative time delay spectrum. Apart from the carriers accumulation near the $E_F$, the hole population forms another prominent peak around $E-E_F = 1.8$ eV, indicated between the dash lines. The EDC of graphene with 1.2 eV pump (green) is also shown as a comparison.
and \( \tau \)valence bands of WSe\(_2\) (Fig. 4h). The complete dynamics across the interface can be described as a function of COM momentum \( Q \) with different photo-induced hole vacancy at \( E = \mu_{Gr}^\text{ef} \). d) Calculated Förster coupling rate as a function of \( Q \) with varied interlayer distance of \( d \). Sketch of the underlying carrier dynamics: e) Meitner-Auger IET with creation of intraband electron-hole pairs in graphene by absorbing the exciton energy. f) Förster-type energy transfer with the generation of interband electron-hole pairs in graphene. g) Dexter-type energy transfer with electrons and holes injection to graphene simultaneously. h) ICT-induced hot electron injection into WSe\(_2\) and transient energy shift of its valence band.

**Discussion**

To elucidate the interfacial coupling mechanism at play in our experiment, in particular the observed ultrafast energy transfer rate, we perform microscopic calculations of three types of IET mechanisms: Meitner-Auger, Förster, and Dexter energy transfer. The interlayer MA process is described by the dipole-monopole energy transfer from excitons to valence band excitation, schematically shown in Fig. 4e. The photoexcited holes in graphene quickly relax and distribute below \( E_f \) near a transient chemical potential \( \mu_{Gr}^\text{ef} \). This allows an MA-type transition from the deep hole band to the hole vacancy by absorbing the exciton energy. The microscopic calculations suggest transfer rate is plotted as a function of \( Q \) in Fig. 4c with different transient chemical potentials for the hole distributions \( \mu_{Gr}^\text{ef} \). When the hole vacancy is located around \( \mu_{Gr}^\text{ef} = -0.3 \text{ eV} \), the maximum transfer rate reaches \( \Gamma_{\text{IET}} \approx 2.4 \text{ meV} \), corresponding to a \( \tau_{\text{IET}} \approx 270 \text{ fs} \) transfer time. The MA-type IET process could describe the observed energy-momentum distribution of intraband transition of valence electrons in a reasonable quantitative agreement with the extracted transfer rate. As the transient chemical potential is subject to the doping level of graphene, we also calculate the MA-type IET with n-doped graphene by artificially increasing the Fermi energy. The IET-induced intraband transition in the valence bands is suppressed with decreased photon-generated hole vacancies. However, the intrinsically doped electrons above the Dirac point enable the MA-type IET in the conduction bands (details see SI).

Another IET mechanism is Förster energy transfer (Fig. 4f). The energy of the exciton excites an interband transition from valence bands to above Dirac point via the dipole-dipole coupling. In contrast to the MA-type IET process, the interband excitation via Förster-type energy transfer populates the conduction bands of graphene above the Fermi level, independent of the photon-
induced hot carriers distribution. The coupling strength is explicitly evaluated (for derivation, see SI) and determined by the momentum \( \mathbf{Q} \) and interlayer distance \( d \). The strong exciton oscillator strength and intrinsic in-plane exciton dipole moment in many 2D materials favor the Förster-type IET\(^{46} \). However, the calculated transfer rate is only 0.08 meV (a transfer time of ~8.1 ps), even assuming a tightly stacked heterostructure with interlayer distance of \( d = 0 \) nm (Fig. 4d). Our calculations reveal that the IET process preferably excites an intraband rather than an interband transition. The experimentally observed energy-momentum distribution of excited-state hot holes supports this conclusion. To further distinguish the MA- and Förster-type IET, we calculate the transfer rates of these two mechanisms as a function of layer distance, and identify the distinct layer distance dependence (details see SI). In addition, we also performed calculations of Dexter-type IET (Fig. 4g), in which the electron and hole components of excitons in WSe\(_2\) scatter to the graphene layer simultaneously. However, due to the small wavefunction overlap and the finite momentum distance between \( k_{\text{WSe}_2} \) and \( k_{\text{Gr}} \), we found a very weak Dexter-type interlayer coupling strength, more than three orders of magnitude smaller compared to the other two mechanisms (see SI). Compared with Förster- and Dexter-type IET, the calculated transfer time of MA-type energy coupling is in closest tune to our experimental results. We can thus identify the MA-type conversion of excitons in WSe\(_2\) to intraband excitations in graphene as the dominant IET mechanism.

In this work, we provide a detailed microscopic picture of interfacial charge and energy transfer processes in photoexcited ML-WSe\(_2\)/graphene heterostructures. Optical excitation of electrons in graphene leads to interlayer charge transfer of quasi-free electrons from the graphene layer to the K and Q valleys of the semiconductor which in turn transfers the hole component to the two conduction bands on a time scale of ~50 fs (Fig. 4d). The interlayer dipole-monopole interaction leading to annihilation of an exciton in WSe\(_2\) and non-vertical intraband excitations in graphene. The momentum of the electron-hole pair in graphene originates from the finite center of mass momentum of the hot excitons in WSe\(_2\). The interfacial Förster-Auger mechanism is found to dominate the energy transfer process over established mechanisms like Förster- and Dexter-type transfer. This mechanism results in transient hole distributions as low as 2 eV below the Dirac points. These observations enrich the physical toolbox for designing van der Waals heterostructures and might be utilized in hot-carrier photovoltaic device concepts to harness the ultrafast and efficient carrier transfer processes at interfaces\(^{2} \).

**Methods**

**Time- and angle-resolved photoemission spectroscopy**

We used a 500 kHz tabletop femtosecond optical parametric chirped pulse amplification (OPCPA) laser system operating at a center wavelength of 800 nm and delivering average power up to 15 W. The high harmonic generation is produced in a vacuum chamber by tight focusing (10 μm) the second harmonic (400 nm) of the OPCPA fundamental on a thin and dense argon gas jet. We select the photons with a time constant of ~70 fs. This previously unidentifiable process is governed by interlayer dipole-monopole interactions leading to annihilation of an exciton in WSe\(_2\) and non-vertical intraband excitations in graphene. The momentum of the electron-hole pair in graphene originates from the finite center of mass momentum of the hot excitons in WSe\(_2\). The interfacial Förster-Auger mechanism is found to dominate the energy transfer process over established mechanisms like Förster- and Dexter-type transfer. This mechanism results in transient hole distributions as low as 2 eV below the Dirac points. These observations enrich the physical toolbox for designing van der Waals heterostructures and might be utilized in hot-carrier photovoltaic device concepts to harness the ultrafast and efficient carrier transfer processes at interfaces\(^{2} \).
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Author contributions
S.D., S.B., T.P., M.D., J.M., A.N., and L.R. performed the trARPES measurement. S.D. analyzed the data and wrote the first draft of the manuscript. R.E., L.R., and M.W. were responsible for developing all the experimental infrastructures. M.S. and D.C. performed the microscopic calculation with the guidance of A.K. R.P.X. and developed the 4D data processing code. P.R. and H.N. provided the epitaxially grown hetero-structure, with support from U.S. and H.T. A.M., A.S., and M.S. conducted Raman and photoluminescence measurements, with guidance from M.J. and P.M. J.D.Z. and A.C. prepared the exfoliated ML sample with the hBN substrate provided by K.W. and T.T. All authors contributed to the final version of the manuscript.

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