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Subcycle contact-free nanoscopy of ultrafast interlayer transport in atomically thin heterostructures

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Tunnelling is one of the most fundamental manifestations of quantum mechanics. The recent advent of lightwave-driven scanning tunnelling microscopy has revolutionized ultrafast nanoscience by directly resolving electron tunnelling in electrically conducting samples on the relevant ultrashort length and time scales. Here, we introduce a complementary approach based on terahertz near-field microscopy to perform ultrafast nano-videography of tunnelling processes even in insulators. The central idea is to probe the evolution of the local polarizability of electron-hole pairs with evanescent terahertz fields, which we detect with subcycle temporal resolution. In a concept proof, we resolve femtosecond interlayer transport in van der Waals heterobilayers and reveal pronounced variations of the local formation and annihilation of interlayer excitons on deeply subwavelength, nanometre scales. Such contact-free nanoscopy of tunnelling-induced dynamics should be universally applicable to conducting and non-conducting samples and reveal how ultrafast transport processes shape functionalities in a wide range of condensed matter systems.

Ultrafast scanning tunnelling microscopy^{1–10} (STM) has turned a long-standing dream into reality: femtosecond snapshot imaging on the atomic scale is now possible^{2,4,8}. By biasing the tip-sample junction of an STM with the oscillating carrier field of light, one can reach a time resolution faster than a cycle of light, and access the motion of a single molecule^{2,8}. Yet, the concept requires electrically conducting samples and the electrical current in the STM junction may perturb intrinsic tunnelling processes within the sample. Tunnelling microscopy on insulators has recently become accessible with a new tip-tapping AC STM concept¹¹, but it does not provide ultrafast temporal resolution. Often, the best of both worlds – access to insulating samples and sensitivity to tunnelling with time resolution faster than an oscillation cycle of light – is required.

Atomically thin heterostructures of van der Waals monolayers represent a prototypical example in which the optoelectronic properties sensitively depend on ultrafast electron tunnelling. For example, interlayer hopping is at the heart of superconducting¹² and Mott^{13,14} transitions, ultrafast photodetectors¹⁵ and nanoscale magnetoresistance devices^{16,17}. In transition metal dichalcogenide (TMDC) heterobilayers¹⁸, type-II band alignment enables electron tunnelling^{19–21}, which is crucial for atomically thin p–n junctions²², solar cells²³, and the formation of interlayer excitons^{19,24}. These spatially separated, bound electron-hole (e – h) pairs hold great promise for high-temperature condensation and future information technologies²¹. A microscopic understanding of interlayer charge transfer and recombination in van der Waals (vdW) heterostructures calls for non-invasive nanoscopy of ultrafast tunnelling processes.

Running an external current through the layered structure risks altering the intrinsic ultrafast interlayer dynamics. Meanwhile, diffraction-limited optical probes average over the nanoscale inhomogeneities of strain, doping, or dielectric disorder²⁵. Conversely, near-field microscopy has accessed the ultrafast linear^{26–28} and nonlinear²⁹ optical responses of vdW systems with spatial resolution many orders of magnitude below the diffraction limit. In this way, intersubband transitions in few-layer TMDCs³⁰ and the impact of domain boundaries or moiré superlattices on surface polariton propagation have been revealed³¹. However, spatiotemporal studies of the unique out-of-plane tunnelling and decay dynamics in vdW heterostructures have thus far remained out of reach.

Here, we use ultrafast scattering-type scanning near-field optical microscopy^{29,32,33} (s-SNOM) at terahertz (THz) frequencies^{27,34–43} as a non-invasive, subcycle, and contact-free probe of charge transfer dynamics in WSe₂/WS₂ heterostructures on insulating substrates. Our approach builds on a critical change of the polarizability of e – h pairs during interlayer tunnelling, as explained by *ab initio* density functional theory and confirmed by THz emission directly linked to the ultrafast charge separation. We track the subcycle polarizability with THz near fields confined to the tip apex to map the nanoscale build-up and decay of interlayer e – h pair populations.

Results

Subcycle non-invasive polarization nanoscopy of ultrafast charge separation. The experimental principle is sketched in Fig. 1a. Femtosecond light pulses (centre wavelength, 515 nm; pulse duration, 140 fs) photo-generate e – h pairs by interband transitions within each of the monolayers of a WSe₂/WS₂ heterostructure prepared by mechanical exfoliation and all-dry viscoelastic stamping (see Methods). Type-II band alignment (Fig. 1a, inset) then allows electrons and holes to separate into the WS₂ and the WSe₂ layer, respectively, by interlayer tunnelling. To record this ultrafast process on the nanoscale, we probe the polarizability of the e – h pairs with the near field of a single-cycle THz pulse coupled to the nanoscale tip of an s-SNOM (Fig. 1a, red arrows). Qualitatively, e – h pairs that are quantum confined into a single monolayer should screen external fields less efficiently than pairs delocalized over two monolayers. Such a difference in polarizability may leave a measurable fingerprint in the scattered THz field E^{scat} , which we detect by electro-optic sampling^{33,38,43} (see Methods).

The probe frequency is chosen to remain below all relevant electronic resonances, such that the polarization of the e – h pairs can follow the external field quasi-instantaneously. For background suppression, we demodulate the electric fields E_n at the n^{th} harmonic of the tip tapping frequency. Excellent sensitivity is required because of the extremely sub-wavelength dimensions of the light-matter interaction region. Its volume, set by the tip radius of curvature (<20 nm) and the thickness of the heterostructure (~1 nm), is smaller than the diffraction limit of THz radiation by more than 12 orders of magnitude. To observe clear nanoscopic pump-probe signals, we pioneer a new combination of ultrafast nanoscopy with a high-power, ultrastable Yb:YAG thin-disc laser source operating at high repetition rates (see Methods and Supplementary Section 1).

In Fig. 1b, a representative scattered waveform E_1^{scat} (black) recorded on the equilibrium WSe₂/WS₂ heterostructure is depicted together with the maximum differential change ΔE_1^{scat} (blue) induced by the visible pump pulse. Interestingly, ΔE_1^{scat} displays a phase shift of 90° with respect to E_1^{scat} , whereas the overall temporal shape of the electric field is mostly preserved. The same holds true for ΔE_1^{scat} obtained on a WSe₂ monolayer (orange). Thus, the relative photo-induced amplitude and phase ($\Delta E_1^{\text{scat}}/E_1^{\text{scat}}$) exhibit no distinct signatures within our spectral range (Fig. 1c). This is expected, as even low-energy electronic quantum transitions such as Lyman-like $1s$ - $2p$ resonances of excitons lie more than an order of magnitude above our probing frequency¹⁹. Remarkably, the pump-induced signal from the heterobilayer is substantially larger than twice the monolayer response. We will show below that this observation is well explained by the dramatic increase of the non-resonant subcycle polarization of e - h pairs⁴⁴ upon tunnelling into different monolayers.

To illuminate the ultrafast photo-carrier dynamics, we trace the peak of the photo-induced waveform, $\Delta \hat{E}_1^{\text{scat}}$, which yields the spectrally integrated response as a function of the pump delay time t_p . Interestingly, there are significant differences in the ultrafast charge carrier dynamics in monolayer and heterostructure areas (Fig. 1d,e). The pump-probe traces of the monolayers exhibit a rapid onset within the response time of our setup (see Methods and Supplementary Section 1) as unbound e - h pairs are injected and intralayer excitons are expected to form⁴⁵. The subsequent decay of $\Delta \hat{E}_1^{\text{scat}}$ within ~ 2 ps is consistent with spatially averaged lifetimes determined in far-field experiments¹⁹. In contrast, the heterostructure behaves profoundly differently: the magnitude of $\Delta \hat{E}_1^{\text{scat}}$ is increased by up to a factor of 8 and the decay is drastically slowed down to ~ 100 ps (Fig. 1e, inset), indicating the formation of long-lived interlayer excitons. Moreover, the maximum of the pump-probe trace is significantly delayed (vertical dashed lines). These signatures reflect the interlayer tunnelling and subsequent recombination of highly polarizable, spatially separated e - h pairs, as we demonstrate next.

Polarizabilities of intra- and interlayer electron-hole pairs. We first show that e - h pairs located in mono- and bilayers exhibit dramatically different responses to a quasi-static, dominantly out-of-plane THz electric field (Fig. 2a). Our *ab initio* density functional theory directly provides the band structures and the underlying wavefunctions, including spin-orbit coupling (see Methods and Supplementary

Section 2). For both the unbiased WS₂ monolayer (Fig. 2b, left) and the unbiased WSe₂/WS₂ heterobilayer (Fig. 2c, left), the orbital structure of the relevant valence and conduction band states (which host photo-induced holes and electrons, respectively) is localized around the transition metal atoms. An out-of-plane electric field redistributes the photo-induced charge density differently in the two cases: while the charge redistribution in the monolayer is almost mirror-symmetric along the out-of-plane direction (Fig. 2b, right), the heterobilayer exhibits a clear asymmetry and the charge is deflected even beyond the chalcogen atoms in WSe₂ (Fig. 2c, right). By evaluating the quadratic component of the field-induced energy shift, we determine the out-of-plane polarizabilities $\alpha_{\perp}$ of the $e-h$ pairs (Fig. 2d, Supplementary Section 2). Electrons confined into a single monolayer are only weakly susceptible to out-of-plane electric fields⁴⁶, whereas the finite extension of the wavefunction in heterostructures drastically increases the deflection of wave packets by an external stimulus by up to one order of magnitude.

Our experimental sensitivity to in-plane components of the THz near field is smaller than to its out-of-plane counterpart by more than two orders of magnitude (Supplementary Section 3). Yet, the in-plane polarizability of monolayer materials has been reported to exceed typical values of the out-of-plane polarizability by one to two orders of magnitude (see Supplementary Section 4), at least partially compensating for the relative insensitivity to in-plane fields. Nonetheless, the in-plane polarizability $\alpha_{\parallel}$ is larger for interlayer $e-h$ pairs than for intralayer pairs by approximately the same factor as for out-of-plane polarizabilities $\alpha_{\perp}$. To illustrate this fact, we compute two-dimensional, atom-like⁴⁷ excitonic wavefunctions with established dielectric screening and exciton Bohr radii¹⁹ and compare the effect of an in-plane electric field on intralayer (Fig. 2e) and interlayer excitons (Fig. 2f). Spatial separation into different monolayers weakens the Coulomb attraction between electron and hole, increasing $\alpha_{\parallel}$ by one order of magnitude, as also confirmed by recent experiments resolving the mid-infrared dielectric functions¹⁹ (Fig. 2g, Supplementary Section 5). Thus, irrespective of the probe field direction, the tunnelling process transforming photoexcited intralayer $e-h$ pairs into interlayer species can be followed by resolving the dramatic change in polarizability during the charge transfer process. Moreover, the ratios between the experimental values for $\Delta\hat{E}_1^{\text{scat}}$ recorded on the monolayers and the heterostructure in Fig. 1e are reproduced well by the theoretically predicted polarizabilities (Fig. 2d,g).

Clocking interlayer tunnelling by THz emission nanoscopy. To put our concept to a final test, we compare the delayed onset of the pump-probe signal from the heterostructure with the tunnelling dynamics independently measured by laser THz emission nanoscopy^{38,41,43} (LTEN). Interlayer tunnelling should generate a time-dependent out-of-plane current of density $j_z(t)$ that produces coherent THz emission²⁰, providing direct access to the ultrafast charge transfer dynamics. This emission is scattered into the far field for electro-optic detection^{38,43} (Fig. 3a). The ultimately thin sample requires us to push this technique to record sensitivity. After sufficient averaging (more than one hour), a clean THz waveform E_1^{em} consisting of an asymmetric single cycle with a period of ~ 1 ps emerges from a photoexcited WSe₂/WS₂ heterobilayer (Fig. 3b, blue). The field polarity and hence the direction of the out-of-plane current $j_z(t)$ flip when the stacking order of the monolayers is inverted (Fig. 3b, purple). Since no emission signatures are obtained from the substrate or the monolayer regions (Fig. 3b, grey), we unambiguously identify interlayer charge transfer as the origin of the detected waveforms.

From the LTEN temporal waveform, the local tunnelling current $j_z(t)$ can be reconstructed: we parameterize $j_z(t)$ with an effective time constant τ_{tunnel} and numerically propagate the emitted THz transient from the tip apex to the electro-optic detector using finite element method simulations⁴⁸ (see Methods, Supplementary Section 6 and 7, and Supplementary Movies 1 and 2). Our experimental emission waveforms are well reproduced for $\tau_{\text{tunnel}} = 200$ fs (Fig. 3b, red) – a value that is compatible with previous experimental results^{19,20,49} and coincides with the response time of our setup. Most importantly, the temporal build-up of the density of spatially separated $e-h$ pairs (Fig. 3c, red curve) perfectly matches with the onset of the pump-probe signal from the heterostructure (Fig. 1e, red broken line, see also Supplementary Section 8). These observations validate our polarization nanoscopy as an ultrafast contact-free probe of tunnelling $e-h$ pairs that works by monitoring the population of the interlayer species.

Contact-free subcycle nanovideography. While LTEN can quantify interlayer tunnelling on the nanoscale, it is insensitive to the dynamics following the tunnelling process and is limited by the low number of photons spontaneously emitted by the accelerated $e-h$ pairs. Conversely, the signal-to-noise ratio of polarization nanoscopy can be scaled by the incident coherent probe field. Our setup enables a

polarization signal up to 25 times larger than the THz emission field, reducing the data acquisition time by almost three orders of magnitude and facilitating nanoscale images even if only ~ 10 -100 charge carriers per laser pulse give rise to the detected signals. Most importantly, THz probing is independent of interband optical selection rules. Owing to the weak spatial overlap of electron and hole wavefunctions, interlayer excitons are optically dark in interband absorption¹⁹. Even photoluminescence (PL) from interlayer excitons is typically so weak that micro-PL measurements cannot be directly traced to a local density distribution of interlayer $e-h$ pairs. Our new polarization nanoscopy not only directly probes local $e-h$ pair densities, but also adds the essential benefits of nanometre spatial resolution and ultrafast temporal resolution, far outperforming micro-PL.

To illustrate how this new approach reveals previously elusive ultrafast and spatially inhomogeneous dynamics of optically dark $e-h$ pairs, we record femtosecond snapshots of a representative sample region for different delay times t_p after photoexcitation. At each point in space, we analyse the peak of the pump-induced change to the electric field $\Delta \hat{E}_1^{\text{scat}}$ as a function of t_p and fit the respective trace with a mono-exponential decay of the form $\Delta E_1^{\text{max}} \cdot e^{-t/\tau}$ (Fig. 4a inset and Supplementary Movie 3). The amplitude ΔE_1^{max} and the decay constant τ are measures of the local density and the lifetime of all interlayer $e-h$ pairs (i.e. including optically dark pairs), respectively. Figures 4a and 4b show the first nanoscale measurement of these quantities as colour-coded maps on the three-dimensional topography of the heterostructure. Subtle variations in ΔE_1^{max} (Fig. 4a) indicate that the formation of interlayer $e-h$ pairs may be modulated by previously undetected nanoscale differences in charge transfer efficiency. The lifetime τ (Fig. 4b) of the spatially separated $e-h$ pairs varies by as much as a factor of three within the investigated area. Local regions of extended lifetimes seem to correlate with high photo-induced pair densities (Supplementary Section 9). Conversely, negligible densities and short lifetimes are observed at topographic irregularities, which we attribute to spatial separation of the heterostructure into its constituent monolayers. Remarkably, we observe significant differences in $e-h$ pair lifetimes between topographically similar flat regions (Fig. 4a, inset).

Figure 4c displays close-up images of the flat regions indicated in Fig. 4b with spatial resolution better than 50 nm (Supplementary Section 10). Intriguingly, while the magnitude of $\Delta \hat{E}_1^{\text{scat}}$ (lower

panels) varies slowly within these regions, it appears immune to few-nanometre-tall topographic folds (top panels). We therefore conclude that the heterostructure remains intact on the nanoscale, with the interlayer exciton likely robust to the subtle changes to the local dielectric environment. Hence, we propose that the larger area of extended lifetime shown in Figure 4b (blue square) could arise from an advantageous local atomic registry, through twist angle¹⁹ or strain⁵⁰. Such hitherto inaccessible local information is essential for the optimization of vdW heterostructures and foreshadows the power of using ultrafast THz s-SNOM as a contact-free probe of tunnelling.

Discussion

In conclusion, we have exploited the transient polarizability of electron-hole pairs for non-invasive THz nanoscopy of ultrafast interlayer transport in atomically thin heterostructures. Our experiments not only make use of the versatile portfolio of ultrafast THz near-field microscopy, including LTEN and s-SNOM, but also conceptually bridge the gap to lightwave-driven STM. In contrast to ultrafast STM, though, our approach offers spatiotemporal access to tunnelling processes without driving external currents – a concept that should readily lend itself to the observation of tunnelling in insulating, conducting, or superconducting systems on subcycle time scales. Already, we have demonstrated that the interlayer tunnelling processes that govern phase transitions, energy harvesting and light-emission in atomically thin heterostructures are now accessible *in situ* on the relevant length and time scales. Looking forward, this may also facilitate the visualization of photo-carrier trapping in moiré potentials.

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Figure 1 | Probing interlayer transfer of photo-carriers by their polarizability. **a**, Schematic of ultrafast optical-pump/THz-probe s-SNOM experiments. The photo-generated $e-h$ pairs (blue and red spheres) are interrogated by a THz probe pulse E_{THz} as a function of the pump-probe delay time t_p . The dominantly out-of-plane polarized THz fields beneath the tip apex (red arrows, see Supplementary Section 3 for distributions of the electric field) locally displace the $e-h$ pairs, such that their polarizability is encoded in the scattered fields E^{scat} . Inset: Schematic of the type-II band alignment of the heterostructure and the tunnelling of charge carriers through the van der Waals gap. **b**, Steady-state (E_1^{scat} , black) and pump-induced (ΔE_1^{scat}) THz waveforms scattered off a WSe₂/WS₂ heterostructure (HS, blue; $t_p = 1.25$ ps) and a WSe₂ monolayer (ML, orange; $t_p = 0.55$ ps). **c**, Relative photo-induced change to amplitude ($\Delta \tilde{E}_1^{\text{scat}} / \tilde{E}_1^{\text{scat}}$, top panel) and phase spectra ($\Delta \phi_1 - \phi_1$, lower panel) recorded on the heterostructure and the WSe₂ monolayer. **d**, Atomic force microscopy image of a typical region featuring a WS₂ monolayer (green, left) and heterostructure area (blue, right). **e**, Pump-induced changes of the peak electric field $\Delta \hat{E}_1^{\text{scat}}$ for both monolayers (orange, green) and the heterostructure (blue) as a function of the pump delay time t_p . The density of tunnelled $e-h$ pairs, corresponding to the build-up of the dipole moment (red, compare to Fig. 3c), matches the temporal evolution of $\Delta \hat{E}_1^{\text{scat}}$ of the HS. Inset: Additional data plotted for a larger range of delay times t_p recorded at the marked positions in **d**.

Figure 2 | Out-of-plane and in-plane polarizability of intralayer and interlayer electron-hole pairs.

a, Sketch of the electric-field-induced displacement of intra- and interlayer $e-h$ pairs highlighting the larger susceptibility of interlayer excitons to out-of-plane electric fields. **b**, Charge density $\rho(E_{\text{THz}} = 0) = e \cdot (|\Psi_{\text{VB}}|^2 - |\Psi_{\text{CB}}|^2)$ of the relevant valence (VB) and conduction band (CB) at the K point of a WS₂ monolayer calculated by density functional theory in units of the elementary charge e (left side). Photo-induced mobile holes (electrons) contributing to the polarizability are located in the valence (conduction) band and hence are labelled as positive (negative) charge density. On the right side, the redistribution of charge density $\Delta\rho = \rho(E_{\text{THz}} = 1 \text{ V/nm}) - \rho(E_{\text{THz}} = 0)$ upon application of a quasi-static out-of-plane electric field E_{THz} is visualized. For clarity, these data were calculated neglecting spin-orbit coupling (see Supplementary Section 2). **c**, Charge density at the K point (left) and redistribution of charge density (right) as in **b** of a lattice commensurate WSe₂/WS₂ heterostructure. The band extrema of the valence and conduction bands relevant for interlayer $e-h$ pairs are localized in the top and bottom layer, respectively. **d**, Out-of-plane polarizabilities $\alpha_{\perp}$ of the intra- and interlayer $e-h$ pairs in the monolayer and heterostructure (with atomic relaxation) in **c** normalized to $\alpha_{\perp}$ of WSe₂/WS₂ (Supplementary Section 2). **e, f**, Modulus of the wavefunction $|\Psi(r)|$ of intralayer (**e**) and interlayer (**f**) 1s A excitons for $E_{\text{THz}} = 0$ (left panels) and for an in-plane field $E_{\text{THz}} = 0.3 \text{ V/nm}$ (right panels) obtained by analytically solving the two-dimensional hydrogen model⁴⁷ with literature values¹⁹ (see Supplementary Section 5). **g**, In-plane polarizabilities $\alpha_{\parallel}$ of the intra- and interlayer $e-h$ pairs in monolayers and heterostructure calculated with the model in **e, f**. For comparison, $\alpha_{\parallel}$ extracted from the dielectric function in ref. ¹⁹ is also plotted (spheres). In each case, $\alpha_{\parallel}$ is normalized to the respective $\alpha_{\parallel}$ of WSe₂/WS₂.

Figure 3 | Clocking ultrafast interlayer tunnelling using THz emission nanoscopy. **a**, Interlayer transfer of electron-hole ($e-h$) pairs (blue and red spheres) in a WSe₂/WS₂ heterostructure causes an out-of-plane current $j_z(t)$, which emits a characteristic THz transient. **b**, THz electric fields outcoupled by a sharp metallic tip and electro-optically sampled in the far field, E_1^{em} , as a function of the delay time. WSe₂/WS₂ heterostructure: blue symbols; WS₂/WSe₂ heterostructure: purple symbols; WS₂ monolayer: grey symbols; dashed lines: guides to the eye; red line: simulated waveform based on the current density depicted in **c**, accounting for the tip transfer function and electro-optic detector response. The trailing oscillations at $t = 3$ ps are caused by reflection at the end of the cantilever (see Supplementary Section 6 and 7, Supplementary Movies 1 and 2). Inset: amplitude spectra $\tilde{E}^{\text{em}}$. **c**, Out-of-plane current density j_z (black) originating from interlayer charge transfer for a characteristic tunnelling time $\tau_{\text{tunnel}} = 200$ fs. The tunnelled $e-h$ pairs (red) are obtained by numerical integration of the current density $j_z(t)$.

Figure 4 | Resolving nanoscale inhomogeneities of tunnelling efficiency and electron-hole pair lifetimes by ultrafast contact-free nanoscopy. **a,b**, Magnitude of the pump-induced changes in scattered electric field ΔE_1^{max} (**a**) and characteristic lifetime τ (**b**) of the photo-generated carriers colour-coded onto the topography of a representative region of the WSe₂/WS₂ heterostructure (recorded by atomic force microscopy). The two-dimensional maps were obtained by evaluating a series of s-SNOM snapshot images and fitting a mono-exponential decay to the temporal evolution of $\Delta \hat{E}_1^{\text{scat}}$ at each pixel (for details see main text). For two representative, flat areas indicated by the arrows, the experimental data (symbols) and fits (solid lines) are shown in the inset in **a**. **c**, Atomic force microscopy maps of the flat areas (see coloured frames in **b**, corner for orientation) and $\Delta \hat{E}_1^{\text{scat}}$ scans for different delay times. The characteristic length scale of the modulation in $\Delta \hat{E}_1^{\text{scat}}$ (~ 400 nm) is significantly larger than both the spatial resolution of our s-SNOM setup (~ 50 nm) and the topographic features in the top panel. For further details see Supplementary Section 10. Scale bar: 400 nm.

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Author contributions

M.P. and F.M. fabricated the samples. M.P., F.M., T.S., M.Z., F.Sa., F.Sc., S.M., M.A.H., J.L.B., T.L.C., and R.H. conducted the experiments. P.E.F.J., M.G. and J.F. performed the density functional theory calculations, F.M. performed the finite element simulations, and J.F, T.L.C. and R.H. supervised the study. M.P., F.M., and R.H. wrote the manuscript with input from all authors.

Competing interests

The authors declare no competing interests.

Methods

Sample fabrication and characterization. The TMDC monolayers were fabricated via mechanical exfoliation⁵¹. A thin flake of the material was exfoliated with Nitto tape (Nitto Denko, SPV 224P) from the bulk single crystal (bought at HQgraphene.com) and placed on a viscoelastic poly-dimethyl-siloxane (PDMS) film. By gently lifting the tape, a single monolayer of the TMDC was left on the PDMS film. The monolayer was pre-characterised under an optical microscope before being stamped onto a silicon wafer covered with 300 nm of thermal oxide using a micro-positioning stage. This procedure was repeated to produce heterobilayers. The prepared heterostructures were annealed in high vacuum at 150° Celsius for 2 hours to remove trapped adsorbates and to ensure good contact between the monolayers.

Ultrafast optical-pump/THz-probe near-field microscopy. The THz near-field microscopy experiments (Supplementary Fig. 1) are based on a high average-power, low-noise Yb:YAG thin-disc oscillator, which combines pulse energies of up to 3.75 μJ with a repetition rate of 24 MHz. These specifications yield the required sensitivity for retrieving the minute electric near fields of the emitted waveforms (LTEN) or for resolving the subtle changes to the scattered fields caused by the photo-induced polarizability (s-SNOM). The THz probe pulses are directly generated by optical rectification of 200-fs-long pulses centred at a wavelength of 1030 nm in a 2-mm-thick gallium phosphide (GaP) crystal. Sample photoexcitation is provided by the second harmonic (centre wavelength: 515 nm; pulse duration: 140 fs) of the oscillator output generated using a β -barium borate crystal (thickness: 1.2 mm). By modulating the pump beam using an acousto-optic modulator, background-free detection of the pump-induced change is achieved by serial lock-in detection. The THz and pump pulses are focused onto the tip of a commercial scattering-type scanning near-field optical microscope (NeaSNOM, Neaspec GmbH) using a parabolic mirror with high numerical aperture. Subsequently, the residual pump radiation is separated from the scattered THz waveforms with a germanium wafer. The THz electric field is detected via electro-optic sampling^{33,36} in a second GaP crystal with a thickness of 4 mm. The demodulated scattered field E_n is determined by analysing the harmonic of order n of the tip tapping frequency using a lock-in amplifier^{32,33,38,48,52}.

Based on the specifications described above, spectral components of the scattered electric fields can reliably be resolved up to a frequency of ~ 2.5 THz. Consequently, we determine a response time of ~ 400 fs for our experimental setup. This value coincides with the quasi-instantaneous onset of the pump-probe response of the monolayers in Fig. 1e.

Field polarity of the emitted waveforms. The polarity of the LTEN waveforms was calibrated to the underlying current using the photo-Dember effect on an indium arsenide (InAs) reference sample, where highly mobile electrons diffuse into the bulk material faster than the holes. This creates a net transient current $j_z(t)$ towards the surface^{20,38}, to which we assign a positive peak electric field. Since the transfer of electrons in the WSe₂/WS₂ heterostructure (Fig. 3a, purple arrow) corresponds to a current along the same out-of-plane direction as for InAs, the waveform (Fig. 3b, blue) has the same positive field polarity. Conversely, we find a negative peak electric field emitted from the WS₂/WSe₂ structure (Fig. 3b, purple), which confirms that the current is reversed in this case.

Finite element method simulation. The electromagnetic fields generated by the interlayer tunnelling current were calculated numerically using a commercial finite element method software (COMSOL Multiphysics, including the radiofrequency (RF) package). A spherical simulation volume with a diameter of 1.2 mm was chosen to accommodate the long wavelengths in the THz spectral range. In addition to these macroscopic dimensions, the nanoscale confinement of the electric field at the tip apex requires fine resolution, which renders realistic simulations of THz nanoscopy computationally demanding. Yet, a high-performance computer with 196 GB of RAM allows us to choose a fine mesh with up to one million individual elements. The exact geometry of tip and sample system is discussed in detail in Supplementary Section 6. The interlayer tunnelling current is modelled by a point-dipole source, which is placed 1 nm above the sample surface, at the centre of the simulation volume. For a range of frequencies up to 3 THz (in steps of 0.1 THz), we then calculate the electromagnetic fields emerging from this source. Comparing the emitted far fields in the presence of the tip $E_z^{\text{far,tip}}$ with the ones emitted by the bare dipole $E_z^{\text{far,bare}}$, the entire scattering response of the tip can be captured in a complex-valued transfer function $\Omega^{\text{transfer}} = E_z^{\text{far,tip}} / E_z^{\text{far,bare}}$ (see Supplementary Fig. 6c).

For the emission field distributions, we superimpose the calculated frequency-domain field distributions according to the spectral weight set by the ultrafast temporal evolution of the interlayer tunnelling current in Fig. 1e and Fig. 3c. Here, we additionally account for the detector response of the electro-optic sampling (see Supplementary Section 7). By systematically evolving the phase of the complex-valued electric field for each frequency component individually, we obtain a time-domain movie of the emission process (see Supplementary Movies 1 and 2).

Numerical modelling of the interlayer current. We adapted a three-state model²⁰, in which two main processes are expected to determine the interlayer current: (i) intralayer relaxation and (ii) interlayer transfer. Following the non-resonant photoexcitation (2.4 eV), hot intralayer $e-h$ pairs most efficiently tunnel at the points of intersection of intra- and interlayer exciton dispersion relations, due to energy and momentum conservation¹⁹. This is accounted for by an additional delay at the rate $1/\tau_{\text{relax}}$ before the carriers can tunnel into the adjacent layer at a rate $1/\tau_{\text{tunnel}}$ and thereby contribute to the net interlayer current $j_z(t)$. The current can then be written as $j_z(t) = (\tau_{\text{tunnel}} - \tau_{\text{relax}})^{-1} \left[\exp\left(-\frac{t}{\tau_{\text{tunnel}}}\right) - \exp\left(-\frac{t}{\tau_{\text{relax}}}\right) \right]$. We found the best agreement with our experimental data by assuming $\tau_{\text{tunnel}} \approx \tau_{\text{relax}}$. In this case, both processes happen on similar time scales and cannot be distinguished in this experiment. This leads to a current of the form $j_z(t) = \frac{t}{\tau_{\text{tunnel}}^2} \exp\left(-\frac{t}{\tau_{\text{tunnel}}}\right)$, with a characteristic duration of $\sim 2\tau_{\text{tunnel}}$ (see Fig. 1e). Additionally, the current is convoluted with a Gaussian with a full width at half maximum of 140 fs to include the finite duration of the pump pulse. Finally, we use Maxwell's equations to calculate the emitted waveform based on $j_z(t)$, where we additionally account for the tip and detector transfer functions (for further details see Supplementary Section 7).

Ab initio DFT calculations. The electronic structures of monolayers WS₂, WSe₂ and their heterostructure were obtained via the full-potential linearized augmented plane-wave method as implemented in the Wien2k package⁵³. The Perdew-Burke-Ernzerhof⁵⁴ exchange-correlation functional was considered and, for the heterostructure, van der Waals interactions were accounted for using the D3 correction⁵⁵. The wavefunctions are expanded in atomic spheres with orbital quantum numbers up to 10

and the plane-wave cut-off multiplied with the smallest atomic radii is set to 8. Spin-orbit coupling was included fully relativistically for core electrons, while valence electrons were treated within a second-variational procedure with the scalar-relativistic wavefunctions calculated in an energy window up to 5 Ry. Self-consistency was achieved using a Monkhorst-Pack k-grid of $15 \times 15 \times 1$ with convergence criteria of $10^{-6} e$ for the charge and 10^{-6} Ry for the energy. To account for the lattice mismatch in the heterostructure, WS_2 and WSe_2 layers are strained by 1.81 % and -1.74 %, respectively. The optimized interlayer distance with spin-orbit coupling is 3.6389 Å, consistent with recent calculations⁵⁶. The strained lattice parameters were taken from ref. ⁵⁷ and a vacuum space of 20 Å was considered. The out-of-plane electric field was modelled with a zig-zag potential added to exchange-correlation functional⁵⁸ with 40 Fourier coefficients. For additional details, see Supplementary Section 2.

Data availability. The data sets generated during and/or analysed during the current study are available from the corresponding authors upon reasonable request.

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a **c** **b**

a **b** **c**