Ultrafast multi-terahertz nano-spectroscopy with sub-cycle temporal resolution

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Phase-locked ultrashort pulses in the rich terahertz spectral range1–18 have provided key insights into phenomena as diverse as quantum confinement7, first-order phase transitions6,12, high-temperature superconductivity13 and carrier transport in nanomaterials6,13–15. Ultrabroadband electro-optic sampling of few-cycle field transients1 can even reveal novel dynamics that occur faster than a single oscillation cycle of light6,8,10. However, conventional terahertz spectroscopy is intrinsically restricted to ensemble measurements by the diffraction limit. As a result, it measures dielectric functions averaged over the size, structure, orientation and density of nanoparticles, nanocrystals or nanodomains. Here, we extend ultrabroadband time-resolved terahertz spectroscopy to the sub-nanoparticle scale (10 nm) by combining sub-cycle, field-resolved detection (10 fs) with scattering-type near-field scanning optical microscopy (s-NSOM)16–26. We trace the time-dependent dielectric function at the surface of a single photoexcited InAs nanowire in all three spatial dimensions and reveal the ultrafast (<50 fs) formation of a local carrier depletion layer.

Combining time-resolved terahertz spectroscopy with nanometre spatial resolution promises exciting possibilities for studying ultrafast dynamics in single nanoparticles. Few-terahertz (0.1–10 THz, far-infrared) to multi-terahertz (10–100 THz, mid-infrared) frequencies are home to many low-energy elementary excitations in condensed matter1–3, including collective lattice, charge and spin excitations. One valuable feature of terahertz spectroscopy is electro-optic sampling (EOS), which measures the oscillating electric field of light1–4. It provides the absolute phase and amplitude information of a broadband polarization response with time resolution faster than a single optical oscillation cycle3,4,10. However, although some nanoscale information can be inferred1, the spatial resolution of far-field terahertz spectroscopy is intrinsically limited to the scale of the probing wavelength (λ ≈ 3–300 μm).

Ultrafast terahertz spectroscopy beyond the diffraction limit has been a longstanding goal. It has been demonstrated that coupling terahertz pulses to sharp metallic tips encodes subwavelength spatial information onto the scattered fields4–6,8–28, which have been detected either by intensity-resolving measurements in the multi-terahertz range19–28 or EOS in the few-terahertz window16–18. None of these studies, however, has probed photoinduced dynamics in single particles with nanometre lateral dimensions. Conversely, time-integrated intensity detection has been used to measure multi-terahertz pulses scattered from photoexcited graphene26 with a temporal resolution of 200 fs, limited by the duration of the terahertz-probe pulse. Following a different scheme, ultrafast charging dynamics in single nanoparticles have recently been measured electronically on the 1 nm scale using terahertz scanning tunnelling microscopy (THz-STM)15, where local currents are induced by few-terahertz field transients.

Here, we use EOS of multi-terahertz pulses to directly trace the scattered electric near field with a 10 fs gate pulse, revealing the dynamics of the dielectric function at a nanowire surface with 10 nm spatial resolution. Our experiment marks the first field-resolved pump–probe spectroscopy on the nanoscale and introduces sub-nanoparticle spatial resolution to sub-cycle multi-terahertz studies. We apply our new technique to InAs nanowires, a prototypical sample for conventional terahertz spectroscopy6,13–14. Nanowires based on III–V semiconductors have been shown to operate as efficient terahertz sources13, active elements in one-dimensional field-effect transistors22 or nanoscale infrared lasers28–30. Such nanodevices rely on a detailed knowledge of femtosecond carrier dynamics and surface charge distributions. Field-resolved terahertz nanoscopy of InAs nanowires allows us to directly resolve these ultrafast local effects for the first time and sets the stage for future sub-cycle near-field experiments in a wide range of nanosystems.

Our set-up is based on state-of-the-art, ultrastable, Er-fibre laser technology30, which was used to generate the pump, probe and electro-optic gate pulses (see Methods), as summarized in Fig. 1a. The transient dielectric response of an InAs nanowire was probed with phase-stable, 2.5-cycle multi-terahertz pulses (Fig. 1b,c) following photoionization of free carriers by near-infrared pump pulses. The terahertz pulses were focused onto the apex of a metallic atomic force microscope (AFM) tip, where they were strongly confined in the optical near field. Nanoscale information was retrieved from the scattered pulses when the evanescent field extending from the tip apex was modified by the sample. To isolate the near-field response from background scattering, the tip was operated in tapping mode and the scattered electric-field waveform E(t) or the scattered intensity I was measured. For detection of the third demodulation order of the tapping frequency18–21,23–26. The field transient E(t) was mapped out by EOS and I was detected using a time-integrating mercury cadmium telluride (MCT) photodiode, which was also used to perform standard Fourier transform infrared (FTIR) spectroscopy26.

The particular InAs nanowire investigated is shown in the AFM topography image in Fig. 1d. Near-field intensity maps of the nanowire (Fig. 1e) were measured as a function of the relative arrival time (tpp) between the near-infrared pump and terahertz probe at the sample. Upon photoexcitation, scattering from the central axis of the nanowire surface is strongly enhanced (tpp ≈ +50 fs). This increased scattering is short-lived. At tpp ≈ +150 fs the nanowire has dimmed significantly in the near-field image. In Supplementary Discussion 1 we show differential images, which act as maps of the photoinduced carrier density. Line scans over a
metal test sample are shown in Fig. 1f, demonstrating 10 nm edge resolution.

Pump–probe intensity scans \( (I_3(t_{pp})) \) were taken at specific positions on the nanowire, as identified in Fig. 1d. The dynamics are found to be highly dependent on tip position. In the centre of the nanowire (Position 1) the evolution of \( I_3(t_{pp}) \) is characterized by a large peak at \( t_{pp} = +50 \) fs, followed by a decay with two distinct time constants. The first decay occurs over ~100 fs, close to the time resolution of the pump–probe intensity measurements (~60 fs). In contrast, at the extremities of the nanowire the peak height is reduced (Positions 2 and 3). No pump–probe dynamics are present on the diamond substrate (Reference position).

To investigate the origin of the observed intensity dynamics we extend time-resolved multi-terahertz spectroscopy to the sub-nanoparticle scale. The initial 100 fs decay of \( I_3(t_{pp}) \) is of particular interest, as it is faster than typical carrier recombination or trapping times in semiconductors. Using EOS, we show that it is possible to ascertain the local dielectric function over timescales shorter than an oscillation cycle of the probe pulse. An ultrashort gate pulse samples the instantaneous terahertz electric field, and an entire effective waveform is recorded with sub-cycle temporal resolution (~60 fs time resolution) by scanning the terahertz-gate delay \( t_{EOS} \) while keeping the pump-gate delay \( t_{pp} \) fixed (Supplementary Discussion 2).

To perform such two-time measurements on a single nanowire, the complete near-field terahertz waveform must be recorded at the third harmonic of the tip tapping frequency. High sensitivity is a prerequisite, as this signal corresponds to only 50 photons per terahertz pulse. Using optimized EOS in GaSe, we detected electric field transients from a 10-nm-wide area on the surface of the nanowire with a noise floor of less than one coherent photon per pulse, as shown in Fig. 2b (black curves). We can even resolve changes to the transients triggered by sample photoexcitation. For \( t_{pg} > 0 \) fs, a phase shift emerges in the latter half of the transient and the pulse rings for multiple oscillation cycles, indicating a pump-induced
In Fig. 3e, and the carrier densities $N > +50f s$ for low (50 nm) and high (130 nm) tapping amplitudes accompanied by a redshift for $\tilde{E}_3 \sim 16t$ and scattering time $t=+50fs$ that allows us to resolve the plasma frequency of free carriers in the nanowire. Thus, $f_0$ directly tracks the local carrier density following photoexcitation. The resonance position is plotted as a function of $t_{pp}$ in Fig. 3e, and the carrier densities extracted from the point-dipole model are shown in Fig. 3f. The two distinct time constants observed in the intensity dynamics also appear in the dynamics of $f_0$ and $N_c$. At early times, both quantities drop rapidly, with time constants significantly faster than the resolution-limited decay observed in the intensity measurements. In fact, the time constant of the decay of $f_0$ extracted directly from the electro-optic spectra reaches $40 \pm 10$ fs. Alternatively, the same behaviour can be characterized by FTIR spectroscopy, with reduced time resolution ($>60$ fs, Supplementary Discussion 5).

The near-field confinement that enables 10 nm lateral resolution in our measurements also applies to the field extending vertically from the tip apex into the sample. Interestingly, the tapping amplitude can be used to tune the effective decay length in free space of the scattered evanescent near field sampled at the third demodulation order, as shown in Fig. 4a. Equivalently, the tapping amplitude controls the probing depth into the sample when the tip is approached.

We exploit this dependence to develop a new technique—femtosecond tomography—that allows us to resolve depth-dependent dynamics and identify the source of the 40 fs decay. Figure 4b shows the effect of the tapping amplitude on the resonance frequency 300 fs after photoexcitation. For tapping amplitudes below 70 nm, $f_0$ exhibits a distinct redshift, implying a reduced carrier density at shallower probing depths (depletion layer). Surprisingly, the pump–probe intensities at $t_{pp}=+50$ fs coincide for all tapping amplitudes (Fig. 4c), indicating that the carrier distribution is homogeneous immediately following photoexcitation. For a comprehensive picture, we directly traced the evolution of $f_0$ for low (50 nm) and high (130 nm) tapping amplitudes (Fig. 4d). The data confirm that the fast initial decay of $f_0$ corresponds to the formation of the depletion layer. For sufficiently small tapping amplitudes (50 nm) a built-in surface field accelerates photoinduced carriers out of our probing volume (estimated thickness of $\sim 10$ nm). After 200 fs the depletion layer is fully formed, leading to a $\sim 10\%$ difference in average carrier density between the probing volumes for low and high tapping amplitudes. The carrier densities subsequently decay on approximately the same timescale for low and high tapping amplitudes (2 ps) due to carrier trapping into defect states. Measurements of surface depletion layer formation at the end of the nanowire (Position 3, Fig. 1d) are shown in Supplementary Discussion 7, as is an estimate of the surface field.

In summary, we have combined ultrabroadband field-resolved detection of multi-terahertz pulses with scattering-type near-field scanning optical microscopy (s-NSOM) to enable single-nanoparticle terahertz spectroscopy with simultaneous 10 nm spatial resolution and sub-cycle, 10 fs temporal resolution. Our novel system has been applied to probe the photoinduced dynamics in single InAs nanowires, where we have also developed femtosecond tomography to observe ultrafast depletion layer formation. Multi-terahertz spectroscopy of single nanoparticles with both sub-cycle time resolution and three-dimensional local field sensitivity opens up a new world for terahertz spectroscopy far below the diffraction limit ($\lambda^3/10^9$). Nanoscale experiments completely free of effective medium theories can now be envisioned for virtually any physical, chemical and biological process appropriate for time-resolved spectroscopy in the multi-terahertz range.
Femtosecond tomography. a, Amplitude spectra (in arbitrary units (a.u.)) of terahertz electric-field waveforms measured in the centre of the nanowire (Position 1, Fig. 1d) as a function of pump–gate delay ($t_{pg}$). b, Theoretical scattered amplitudes simulated with the point-dipole model and a dielectric function given by the Drude model. See Supplementary Discussion 3 for simulation details. c, Absolute phases of scattered waveforms measured by EoS. A phase shift of ~2.5 rad is observed at the resonance. d, Theoretical phases extracted from the point-dipole model. Blue points in a–d mark the dip frequencies $f_0$ in a, and blue curves serve as guides to the eye. e, Resonance frequency $f_{re}$ extracted from a as a function of $t_{pg}$ plotted on a semi-logarithmic scale. A crossover between fast (40 fs) and slow (~4 ps) dynamics occurs at $t_{pg} = +200$ fs, pointing towards two distinct physical mechanisms in the temporal evolution of the carrier density. Error bars are estimated based on the spectral resolution and the widths of the minima. f, Carrier density $N_c$ extracted from the simulations in b and d plotted on a semi-logarithmic scale. The corresponding scattering rates are shown in Supplementary Discussion 4. As in $f_0(t_{pg})$, a crossover is observed between two different time constants (20 fs and 2 ps) at $t_{pg} = +200$ fs. Red dashed lines in e and f are exponential decays included as guides for the eye. Pump fluence, 1.1 mJ cm$^{-2}$; tapping amplitude, 130 nm.

Figure 3 | Sub-cycle spectral dynamics. a, Amplitude spectra (in arbitrary units (a.u.)) of terahertz electric-field waveforms measured in the centre of the nanowire (Position 1, Fig. 1d) as a function of pump–gate delay ($t_{pg}$). b, Theoretical scattered amplitudes simulated with the point-dipole model and a dielectric function given by the Drude model. See Supplementary Discussion 3 for simulation details. c, Absolute phases of scattered waveforms measured by EoS. A phase shift of ~2.5 rad is observed at the resonance. d, Theoretical phases extracted from the point-dipole model. Blue points in a–d mark the dip frequencies $f_0$ in a, and blue curves serve as guides to the eye. e, Resonance frequency $f_{re}$ extracted from a as a function of $t_{pg}$ plotted on a semi-logarithmic scale. A crossover between fast (40 fs) and slow (~4 ps) dynamics occurs at $t_{pg} = +200$ fs, pointing towards two distinct physical mechanisms in the temporal evolution of the carrier density. Error bars are estimated based on the spectral resolution and the widths of the minima. f, Carrier density $N_c$ extracted from the simulations in b and d plotted on a semi-logarithmic scale. The corresponding scattering rates are shown in Supplementary Discussion 4. As in $f_0(t_{pg})$, a crossover is observed between two different time constants (20 fs and 2 ps) at $t_{pg} = +200$ fs. Red dashed lines in e and f are exponential decays included as guides for the eye. Pump fluence, 1.1 mJ cm$^{-2}$; tapping amplitude, 130 nm.

Figure 4 | Femtosecond tomography. a, Decay distance (1/e) of scattered intensity as a function of tapping amplitude (TA) extracted from retraction scans over a gold reference sample. The grey dashed line is a linear fit. We estimate the probing depth into the nanowire to be the free-space decay length divided by the index of refraction of InAs. Error bars correspond to 95% confidence intervals. b, Resonance frequency $f_0$ as a function of TA at $t_{pg} = +300$ fs (Position 1, Fig. 1d), reflecting changes to the carrier density as a function of probing depth. Grey dashed lines are guides to the eye. c, Pump-probe dynamics of the scattered intensity (in arbitrary units (a.u.)) showing a strong dependence on TA. Scans are normalized to the unpumped baseline at $t_{pg} = -5$ ps to account for changes to scattering efficiency with TA. d, Resonance frequencies extracted from measured FTIR spectra as a function of time after photoexcitation for TA = 130 nm (black points) and TA = 50 nm (red points) plotted on a semi-logarithmic graph. The resonance frequency is reduced for low TA when a depletion layer is present. Grey dashed lines are exponential guides to the eye. Error bars in b and d are estimated as in Fig. 3e. Pump fluence, 0.75 mJ cm$^{-2}$. Similar $f_0$ dynamics are shown in Supplementary Discussion 6 for pump fluences of 0.5 mJ cm$^{-2}$ and 1.0 mJ cm$^{-2}$.
Materials and methods

InAs nanowires. Self-assembled indium arsenide (InAs, Fc ≈ 0.35 eV) nanowires were grown bottom-up on InAs (111)B substrates by chemical beam epitaxy (CBE) in a Riber Compact-21 system using gold particles as a growth catalyst. Tri-methyl-indium (TMIn) and tertiary-butyl-arson (TBA) were used as metal–organic chemical precursors, and di-tertiary-butyl-selenide (DTBSe) served as a selenium source for n-type doping. A 0.5-mm-thick Au film was first deposited on the InAs substrate by thermal evaporation. The wafer was then transferred to the CBE system and annealed at 520 °C under TBA flow to remove the surface oxide and generate the Au nanoparticles by thermal dewetting. The InAs segment was grown for 90 min at a temperature of 430 ± 10 °C, with metal–organic line pressures of 0.3 and 1.0 torr for TMIn and TBA, respectively. The DTBSe line pressure was fixed at 0.1 torr to achieve n-type doping with a doping level of Nc ≈ 4 × 10^{15} cm⁻³. The nanowires were then mechanically transferred to a diamond substrate.

Ultrafast near-field nanoscopy set up. The laser system used for ultrafast near-field microscopy was based on four separate erbium-doped fibre (Er fibre) amplifiers seeded by a common oscillator (Fig. 1a), resulting in four mutually coherent pulse trains operating at repetition rates of 20–40 MHz with pulse energies of 9–15 nJ (TOPTICA Photonics AG). The pulses from each amplifier were spectrally shaped by nonlinear fibres: amplifier 1, which was used to pump the sample, operated at 40 MHz and produced 22 fs-long (full width at half maximum, FWHM) near-infrared pulses centred at 192 THz after spectral shaping. The multi-terahertz probe pulses were generated by critically phase-matched, non-collinear difference frequency generation (DFG) of the pulses from amplifier 2 (centre frequency, 153 THz; pulse energy, 1.5 nJ; pulse length, 30 fs) and amplifier 3 (centre frequency, 192 THz; pulse energy, 2.0 nJ; pulse length, 30 fs) of the same Er fibre (GaSe) crystal. By adjusting the phase-matching condition in GaSe we could spectrally tune the multi-terahertz pulses to cover the frequency range from 15 THz to 60 THz with a pulse length of 60 fs and a pulse energy of 30 pJ. Sub-cycle detection of terahertz waveforms was achieved via EOS. The terahertz pulses were focused by a GaSe crystal (thickness, 180 μm) which was then transferred to the CBE system and annealed at 520 °C under TBA flow to remove the surface oxide and generate the Au nanoparticles by thermal dewetting. The InAs segment was grown for 90 min at a temperature of 430 ± 10 °C, with metal–organic line pressures of 0.3 and 1.0 torr for TMIn and TBA, respectively. The DTBSe line pressure was fixed at 0.1 torr to achieve n-type doping with a doping level of Nc ≈ 4 × 10^{15} cm⁻³. The nanowires were then mechanically transferred to a diamond substrate.

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Author contributions

M.E., T.L.C. and R.H. conceived the study and built the experimental set-up. M.E., T.L.C., M.A.H. and R.H. carried out the experiment and analyzed the data. M.A.H., T.L.C. and M.E. performed simulations. D.E. and L.S. grew the InAs nanowires. L.V. and M.S.V. designed, fabricated and characterized the nanowire samples. T.L.C., M.E., M.A.H. and R.H. wrote the manuscript. All authors contributed to the discussions.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to R.H.

Competing financial interests

The authors declare no competing financial interests.