Review article

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Visible-to-THz near-field nanoscopy

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Abstract

Optical microscopy has a key role in research, development and quality control across a wide range of scientific, technological and medical fields. However, diffraction limits the spatial resolution of conventional optical instruments to about half the illumination wavelength. A technique that surpasses the diffraction limit in the wide spectral range between visible and terahertz frequencies is scattering-type scanning near-field optical microscopy (s-SNOM). The basis of s-SNOM is an atomic force microscope in which the tip is illuminated with light from the visible to the terahertz spectral range. By recording the elastically tip-scattered light while scanning the sample below the tip, s-SNOM yields near-field optical images with a remarkable resolution of 10 nm, simultaneously with the standard atomic force microscopic topography image. This resolution is independent of the illumination wavelength, rendering s-SNOM a versatile nanoimaging and nanospectroscopy technique for fundamental and applied studies of materials, structures and phenomena. This Review presents an overview of the fundamental principles governing the measurement and interpretation of near-field contrasts and discusses key applications of s-SNOM. We also showcase emerging developments that enable s-SNOM to operate under various environmental conditions, including cryogenic temperatures, electric and magnetic fields, electrical currents, strain and liquid environments. All these recent developments broaden the applicability of s-SNOMs for exploring fundamental solid-state and quantum phenomena, biological matter, catalytic reactions and more.

Sections

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Introduction

Optical imaging and spectroscopy are essential for characterizing materials, structures and phenomena across biology, chemistry and physics. However, conventional far-field techniques cannot resolve features that are smaller than half of the illumination wavelength λ, a constraint imposed by the diffraction limit of light[1]. Several far-field nanoscopy techniques have been developed to circumvent the diffraction limit, such as stimulated emission depletion microscopy, photoactivated localization microscopy and stochastic optical reconstruction microscopy, allowing for routine nanoscale optical imaging[2–4]. These methods are widely used in biological imaging and offer 3D visualization, but they require fluorescent labels and imaging at visible and near-infrared (near-IR) frequencies, which may limit access to intrinsic material properties. For non-fluorescent materials in which labelling is not feasible or informative (such as hard solids), label-free nanoscale optical imaging and spectroscopy tools become essential.

Here, we review a versatile technique known as scattering-type scanning near-field optical microscopy (s-SNOM), also referred to as s-NSOM or apertureless SNOM, which enables label-free nanoscale imaging across a broad range of frequencies from visible light to sub-terahertz (sub-THz) radiation. s-SNOM relies on detecting light that is elastically scattered (Rayleigh scattering) at atomic force microscopy (AFM) tips, often utilizing nanoscale optical near-field enhancement at the apex of the tip for local optical probing (Fig. 1). Although s-SNOM is a scanning probe technique inherently limited to studying surfaces and features just below them, its capability for nanoimaging and nanospectroscopy with wavelength-independent resolution makes it highly valuable across various scientific and technological fields. It offers the advantage of label-free characterization of a wide range of optically active excitations. Specifically, s-SNOM is sensitive to mobile carrier oscillations (plasmons) at THz, IR and visible frequencies and to lattice and molecular vibrations (phonons) primarily in the THz and IR ranges. It can also probe excitons in the visible range, providing insights into electronic transitions. These capabilities enable s-SNOM to reveal detailed information about local conductivity, crystallinity, chemical composition, electronic band structure and optical properties in numerous solid-state and soft-matter samples.

The idea to circumvent the diffraction limit via SNOM dates back to Edward Hutchinson Synge, who proposed creating an optical image with subwavelength resolution by scanning a subwavelength-scale hole in an opaque screen across a sample[5]. This principle was demonstrated for microwaves in 1972 (ref. 6) and for visible light in 1984 (refs. 7,8), leading to the development of SNOM. In the 1990s, a variation of SNOM emerged, detecting light scattered at oscillating scanning probe tips[9–12], achieving a spatial resolution of $\lambda/1{,}000{,}000$ at radio-wave frequencies[13]. Despite signal demodulation at the oscillation frequency of the tip, this initially named apertureless SNOM suffered from large background scattering, which was mitigated in 2000 by combining signal demodulation at multiples of the tip oscillation frequency[14,15] with amplitude-and-phase-resolved interferometric detection of the tip-scattered light[16]. This breakthrough, combined with established AFM technology, facilitated the advancement and commercialization of s-SNOM, leading to a dynamic and expanding community applying the technique across (nano)photonics, solid-state physics, materials science, geosciences, (bio)chemistry and biology.

Numerous reviews[17–26] cover technical aspects and applications of s-SNOM. Here, we review the broad capabilities of s-SNOM and new developments, but also provide elementary clarifications, including the role of the tip in various near-field experiments and how s-SNOM material contrasts compare with that of far-field measurements. We conclude with an overview of key applications and a perspective section, in which we briefly compare s-SNOM with other techniques that utilize optical illumination of sharp scanning probe microscopy tips and have been developed in parallel.

Basic near-field probing mechanism

Near-field and background scattering

The typical near-field optical probing mechanism of s-SNOM is based on the nanoscale concentration of an illuminating field E_{in} by a metalized AFM tip. As demonstrated by numerical simulations and illustrated in Fig. 2a, p-polarized far-field illumination polarizes the tip (black dipole p_0) and yields a strongly enhanced and confined near-field spot at the very tip apex[27,28]. When the sample is approached towards the tip, the near-field spot intensifies owing to the reflection of the near field of the tip at the sample surface, which depends on the local complex-valued permittivity of the sample. It yields an additional polarization of the tip. The correspondingly induced dipole p_{nf} (Fig. 2a, red vertical arrow) radiates the field $E_{nf} \propto p_{nf}$ (of the same frequency as the incident field, as we consider elastic light scattering), which encodes the local optical properties of the sample. p_{nf} arises not solely from a single reflection of the near field of the tip at the sample surface, but rather from multiple near-field scattering events between tip and sample. Additionally, the far-field-induced dipole p_0 radiates a field $E_{bg} \propto p_0$, which represents a major contribution to background scattering and does not contain valuable information about the sample.

Isolation of near-field signals

To obtain reliable and background-free information about the local optical properties of the sample, exclusively the scattered field E_{nf} has to be measured. To suppress E_{bg}, the tip is oscillated at a frequency Ω with an amplitude A that is small compared with the illumination wavelength, and the tip-scattered field is detected at a frequency $n\Omega$ (where $n \geq 2$). We illustrate and explain this procedure in Fig. 2b. Owing to the rapid spatial decay of the near fields at the tip apex, $|E_{nf}|$ increases nonlinearly as the tip–sample distance h decreases. For this reason, the near-field scattering exhibits strong anharmonicity (Fig. 2b, middle) when the tip oscillates sinusoidally as a function of time t (Fig. 2b, top). By contrast, $|E_{bg}|$ changes approximately linearly with h and thus yields a nearly time-harmonic background scattering (Fig. 2b, bottom). Fourier analysis (FA) of $E_{bg}(t)$ and $E_{nf}(t)$ yields the Fourier coefficients $E_{bg,n}$ and $E_{nf,n}$. They decrease with increasing n, but, importantly, the decrease is faster for the background contributions, such that $E_{bg,n} \sim 0$ for $n \geq 2$. Thus, by measuring the tip-scattered field $E_{sca} = E_{bg} + E_{nf}$ at a frequency $n\Omega$ with $n \geq 2$, one obtains $E_{sca,n} = E_{bg,n} + E_{nf,n} \simeq E_n$. This method effectively isolates the near-field contribution[14–16,29–31]. It is critical to measure the field rather than the intensity, $I_{sca} \propto |E_{sca}|^2$, as intensity measurements result in a multiplicative mixing of the near-field and background contributions, preventing the isolation of pure near-field signals[16,32–34]. Furthermore, by using amplitude-resolved and phase-resolved detection (Fig. 3), one can obtain the amplitude $|E_{nf,n}|$ and phase $\mathrm{Arg}(E_{nf,n})$ of the pure nth order near-field scattering signal, which allows for the determination of the sample's local complex-valued permittivity[16,32,35–39] or the mapping of nanoscale near-field distributions[34,40–42] (see the section 'Near-field probing mechanisms').

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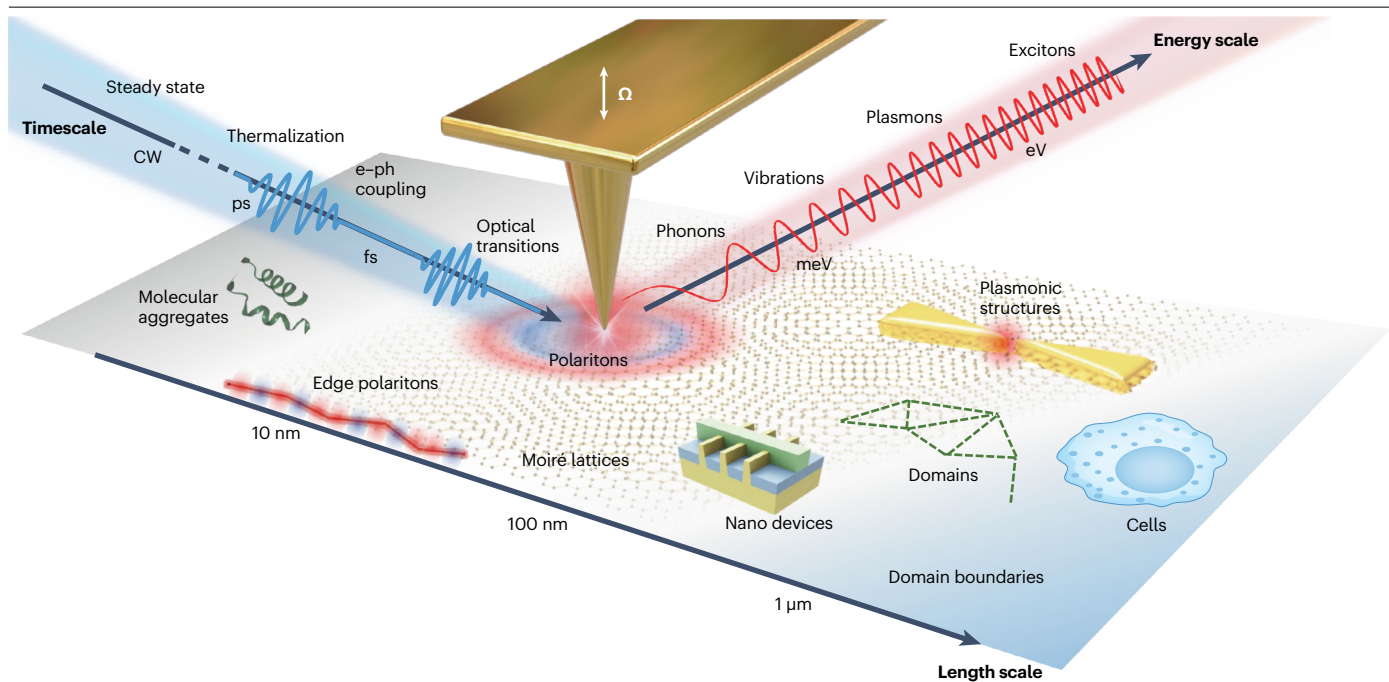
Fig. 1 | Basic concept of s-SNOM for probing material properties and phenomena throughout various length, time and energy scales. An atomic force microscopy tip oscillating at a frequency Ω is illuminated with a focused light beam. Acting as an optical antenna, the tip concentrates the incident beam into a nanoscale near-field spot (nanofocus) at the very tip apex. The nanofocus diameter is about the size of the tip apex, typically 10–50 nm, and independent of the illumination wavelength. Because of a near-field interaction between the tip and the sample, the tip-scattered light encodes valuable information about the local sample properties. Recording the tip-scattered light while raster-scanning the sample thus yields optical images of the sample surface with nanoscale spatial resolution. The type of illumination can range from monochromatic continuous wave (CW) radiation to broadband femtosecond pulses in the whole visible to sub-terahertz frequency range (corresponding to an energy range of electron volt to millielectron volt) for exploring physical, chemical and biological processes at their native energy, spatial and temporal scales. Examples include the nanoscale probing and visualization of excitonic and plasmonic responses in the visible and near-infrared (near-IR) range; phonons, plasmon polaritons, phonon polaritons and molecular vibrations in the mid-IR and far-IR range; Drude and plasmonic excitations in the IR–terahertz range. Moreover, with a probing volume of $<30^3$ nm^3 and a scanning area on the order of 100×100 μm^2, scattering-type scanning near-field optical microscopy (s-SNOM) can be employed for examining multi-length-scale phenomena and systems from nanoscopic to mesoscopic scales. These encompass polariton modes confined to sample edges, moiré superlattices, phase domains, semiconductor devices and biological molecular aggregates and cells. When combined with ultrafast time-domain spectroscopy and time-resolved pump-probe techniques, s-SNOM generates time-resolved 'movies' capturing ultrafast dynamics, for example, of hot carrier generation, metal–insulator phase percolation and transition and surface plasmon polariton propagation on picosecond-to-femtosecond scales, in addition to the steady states accessible with CW light sources. e, electron; ph, phonon.

Near-field signal detection and normalization

The tip-scattered field E_{sca} from the sample can generally be related to the incident field E_{in} through a complex-valued scattering coefficient[16,31,43,44], $\sigma_s = s_s e^{i\varphi_s}$, such that $E_{\text{sca}} = \sigma_s E_{\text{in}}$. Accordingly, the background-free demodulated scattered field can be described as $E_{\text{nf},n} \simeq E_{\text{sca},n} = \sigma_{s,n}E_{\text{in}}$, in which $\sigma_{s,n} = s_{s,n}e^{i\varphi_{s,n}}$ is the nth order Fourier coefficient of σ_s that depends on the local sample permittivity ε_s. However, in a microscope setup (see the section 'Instrumentation'), detection of the scattered field combined with signal demodulation yields the complex-valued electrical signals $S_{s,n} = FE_{\text{nf},n} = F\sigma_{s,n}E_{\text{in}}$, which are strongly influenced by several factors. These include the transmission of beam splitters, the responsivity of the detector and the precision of the beam alignment (summarized by a factor F) as well as the spectral characteristics of the light source, E_{in}. To isolate $\sigma_{s,n}$, the influence of F and E_{in} is typically eliminated by dividing the complex-valued signal $S_{s,n}$ by a complex-valued reference signal $S_{\text{ref},n} = F\sigma_{\text{ref},n}E_{\text{in}}$ from a spectrally flat reference material with a known dielectric permittivity ε_{ref} such as gold or silicon[45,46]. This division yields a relative near-field scattering coefficient, often referred to as normalized near-field signal or near-field contrast:

$$\sigma_n = s_n e^{i\varphi_n} \equiv \frac{S_{s,n}}{S_{\text{ref},n}} = \frac{\sigma_{s,n}(\varepsilon_s)}{\sigma_{\text{ref},n}(\varepsilon_{\text{ref}})}. \tag{1}$$

The relative near-field amplitude and phase signals are given by $s_n = s_{s,n}/s_{\text{ref},n}$ and $\varphi_n = \varphi_{s,n} - \varphi_{\text{ref},n}$, in which $s_{\text{ref},n}$ and $\varphi_{\text{ref},n}$ are the amplitude and phase of $\sigma_{\text{ref},n}$, respectively. Importantly, referencing is also crucial for a direct comparison of experimental and calculated near-field signals (see the section 'Modelling of near-field images and spectra').

We note that in the literature near-field amplitude and phase signals (or spectra) are referred to as normalized near-field amplitude and phase signals, simply near-field amplitude and phase signals (or spectra) or sometimes as near-field amplitude and phase contrasts

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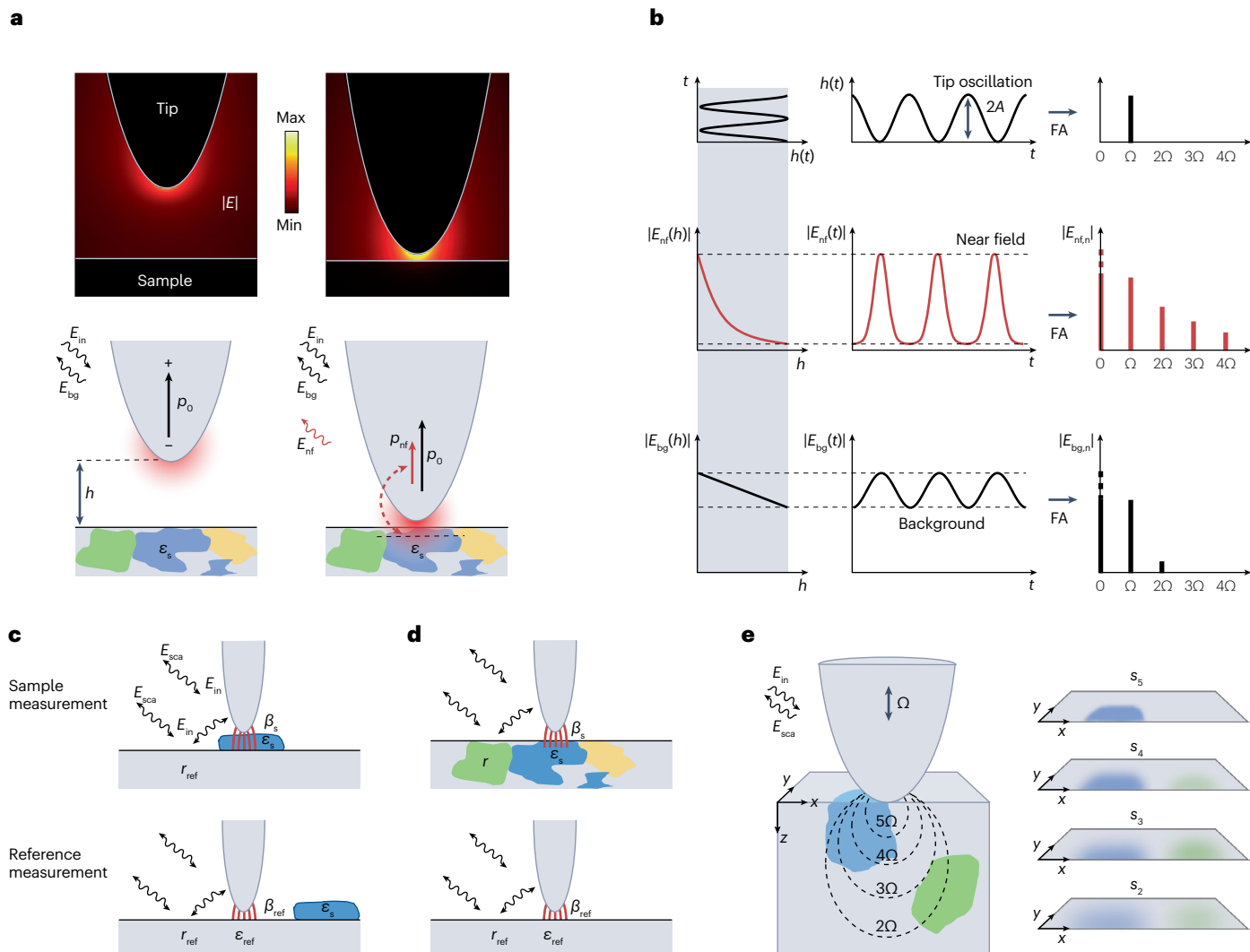
Fig. 2 | Basic near-field probing mechanism of scattering-type scanning near-field optical microscopy. a, Numerical simulation (top), showing the electric field enhancement and confinement at the apex of a metal tip illuminated with p-polarized light. Illustration of the near-field scattering process (bottom). p_0 represents the dipole induced by the incident field, E_{in}, whereas p_{nf} represents the dipole induced by the tip's near field reflected at the sample surface. E_{bg} and E_{nf} represent the fields radiated by p_0 and p_{nf}, referred as to background and near-field scattering, respectively. ε_s is the local permittivity of the sample and Ω the tip oscillation frequency. **b**, Tip height h as a function of time t and Fourier analysis (FA) of $h(t)$ (top). $|E_{nf}|$ as a function of h and t, as well as FA of

$E_{nf}(t)$ (middle). $|E_{bg}|$ as a function of h and t, as well as FA of $E_{bg}(t)$ (bottom). **c**, Illustration of near-field signal normalization for the case in which far-field reflections in sample (top) and reference (bottom) measurements cancel out. β_s and β_{ref} indicate near-field reflections. r_{ref} indicates the far-field reflection at the substrate serving as reference. **d**, Illustration of near-field signal normalization for the case in which far-field reflections in sample (r, top) and reference (r_{ref}, bottom) measurements do not cancel out. **e**, Illustration of the sample volumes probed by demodulating the tip-scattered field at $n\Omega$ (left). The illustrative near-field amplitude images s_n (right) schematically depict the improved lateral resolution and reduced probing depth as the signal demodulation order n increases.

(or spectroscopic near-field contrasts). The term near-field amplitude or phase contrast, however, is used in various other contexts, such as to relate the near-field signal of the sample to that of another sample area. These contrasts can arise either from variations in the permittivity of the sample or from differences in the local electromagnetic (EM) fields above the sample surface.

In this Review, we use the following terminology:
- Near-field signals for both non-normalized near-field signals and near-field signals normalized to a reference.
- Near-field spectra for near-field spectra normalized to a reference.

- Near-field material contrasts for contrasts observed in images or spectra arising from spatial or spectral variations of material properties, respectively.

Consequences of far-field reflection at the sample surface
Up to this point, we have not considered the influence of far-field reflections at the sample surface (Fig. 2c,d). When these reflections are not negligible, the field illuminating the tip is given by $(1 + cr)E_{in}$, in which r is the far-field reflection coefficient of the sample and c is an unknown weighting factor[31,47–49]. Consequently, the scattered field

becomes $E_{sca} = (1+cr)^2\sigma_s E_{in}$, leading to the normalized near-field signal:

$$\sigma_n = \frac{(1+cr)^2}{(1+cr_{ref})^2}\frac{\sigma_{s,n}}{\sigma_{ref,n}} \tag{2}$$

in which r_{ref} is the far-field reflection coefficient for the reference measurement. Equation (2) shows that normalized near-field signals, even after signal demodulation, may contain both near-field and far-field contributions. This mixture can lead to misinterpretation of results, depending on the sample, but may be made
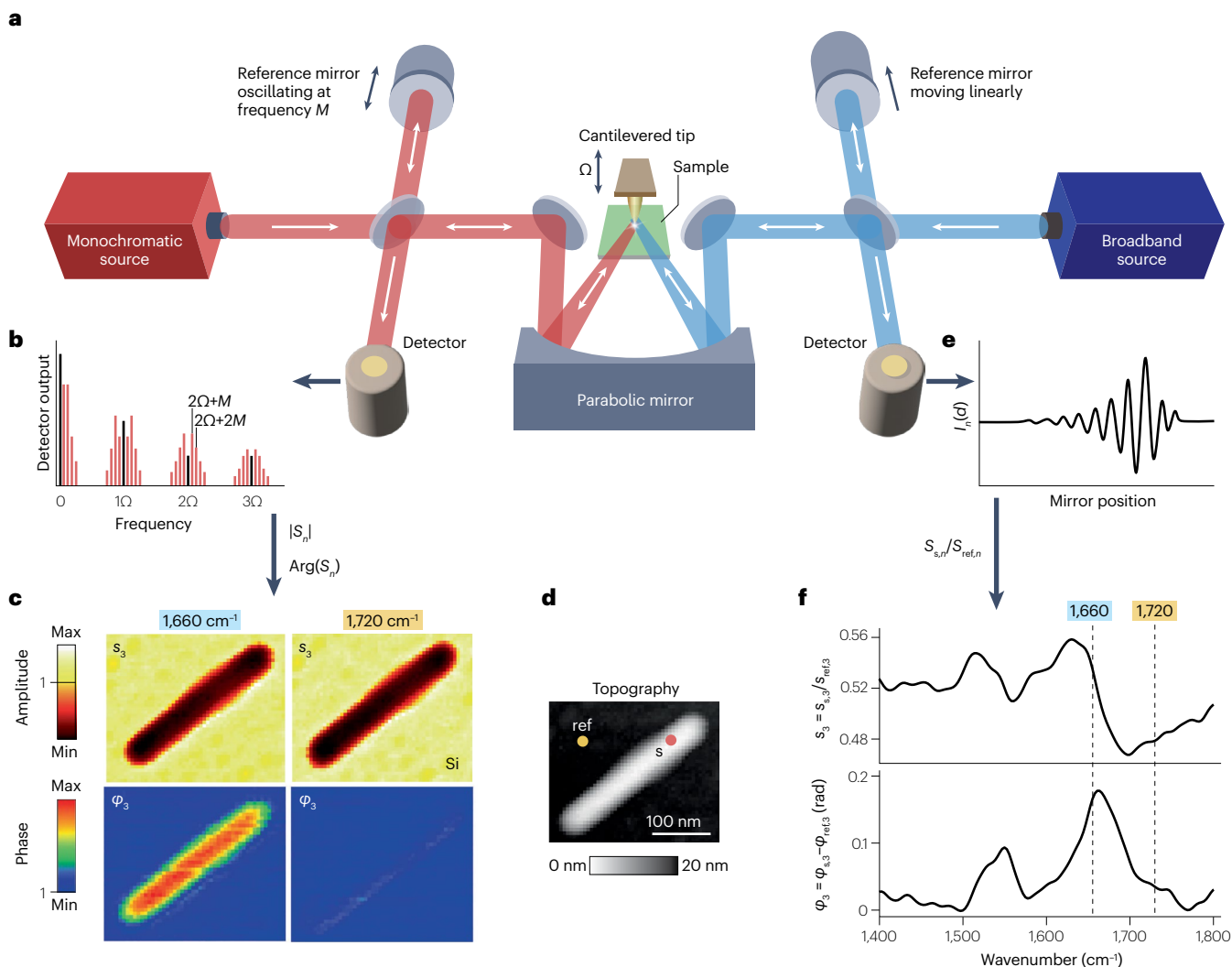
Fig. 3 | Modern dual-path scattering-type scanning near-field optical microscopy setup. a, Configuration including a monochromatic imaging and a broadband nanoscale Fourier transform infrared (nano-FTIR) spectroscopy module. A parabolic mirror is used for focusing incident light either from the left or the right side onto the atomic force microscopy (AFM) tip oscillating at frequency Ω. The parabolic mirror is also used for collecting the tip-scattered light. On the left is the pseudo-heterodyne interferometric detection module, which can operate with various light sources ranging from gas lasers to optical parametric amplifiers. The Michelson-type interferometer uses a reference mirror oscillating at a frequency M to phase-modulate the reference beam. Detectors are chosen according to the illumination wavelength and used to record the interference between the tip-scattered light and the reference beam. On the right is the Fourier transform spectroscopy module, which can operate with various light sources ranging from broadband laser continua to synchrotron radiation. It is based on a Michelson-type interferometer, in which the reference mirror is linearly translated to be able to record interferograms of the tip-scattered light. In contrast to standard Fourier transform spectroscopy, the sample is located inside one interferometer arm, yielding amplitude and phase spectra when the interferograms are Fourier-transformed. **b**, Schematic of time-domain Fourier analysis of the detector output for the case of a monochromatic source. Amplitude and phase signals, $|S_n|$ and $Arg(S_n)$, are calculated in the simplest case from the two signal intensities at $n\Omega + M$ and $n\Omega + 2M$ (ref. 32). **c**, Near-field amplitude and phase images of a tobacco mosaic virus (TMV) at 1,660 cm^{-1} and 1,720 cm^{-1}, normalized to the Si substrate. **d**, AFM topography image of the virus. **e**, To obtain background-free spectra when using a broadband source, the detector signal I is demodulated at $n\Omega$ and recorded as a function of the position d of the reference mirror, yielding asymmetric interferograms $I_n(d)$. Fourier transformation of these interferograms and normalization to a reference measurement yield amplitude and phase spectra, $s_n(\omega)$ and $\varphi_n(\omega)$ (refs. 37,44,112,114). **f**, Nano-FTIR amplitude and phase spectra of the TMV, showing the typical amide I and II bands of the protein forming the TMV capsid. The spectra were recorded at the position marked by the red dot in the AFM topography image shown in panel **d** and normalized to the reference spectrum at the position marked by the yellow dot. Panel **b** adapted with permission from ref. 32, AIP. Panels **c**, **d** and **f** adapted from ref. 191, CC BY 4.0.

negligible[47,50] or resolved, for example, by changing the sample orientation[47].

There are two typical scenarios. In the first (Fig. 2c), near-field and far-field contributions are not mixed because the far-field reflection coefficients for the sample and reference measurements are the same. This occurs, for example, when a small object is studied on a substrate serving as the reference. Here, far-field reflections at the position of the object mainly occur at the substrate, such that $r = r_{ref}$, leaving a pure near-field signal as far-field contributions cancel out in equation (2). For more complex samples, similar conditions may be achieved by adjusting the sample orientation[47]. In the second scenario (Fig. 2d), a heterogeneous sample is studied and the reference measurement is performed on a homogeneous material. In this case, the far-field contributions in equation (2) do not cancel out and mix with the near-field signals. This issue can be addressed by analysing the ratio of background-free near-field signals, σ_n/σ_{n-1}, in which far-field reflection terms cancel out[47,51,52], although this reduces the signal-to-noise ratio and near-field contrast. Future developments may offer solutions, such as utilizing multiple near-field signal harmonics[53].

Near-field material contrast of low-permittivity materials

For samples with small positive permittivity, such as polymers or biological matter, σ_n is approximately proportional to β_s, where $\beta_s = (\varepsilon_s - 1)/(\varepsilon_s + 1)$ is the quasi-electrostatic local near-field reflection coefficient of the sample. Accordingly, near-field amplitude and phase signals are given approximately by $s_n \propto |\beta_s|$ and $\varphi_n \propto \mathrm{Arg}[\beta_s]$ (refs. 43,44,46). Interestingly, one also finds the approximate relations $|\beta_s| \propto |r_s|$ and $\mathrm{Arg}[\beta_s] \propto A_s$, in which $|r_s|^2 = R_s$ is the reflectance and A_s the absorbance in far-field absorption spectroscopy of macroscopic samples. For this reason, s_n and φ_n can be related to the local reflectance and absorbance of the sample. A precise quantitative assessment of s-SNOM signals, however, requires careful modelling[43,54]. Furthermore, for materials with negative permittivity values, the above relationships no longer apply. In such cases, accurate modelling becomes essential for even a qualitative understanding of near-field material contrasts[31,45]. For further details, see the sections 'Near-field spectroscopic material response' and 'Modelling of near-field images and spectra'. We note that determining a precise validity range for the above considerations will require future systematic studies.

We note that local sample absorption typically yields a positive phase contrast relative to a non-absorbing reference[43,44,46]. However, thin non-absorbing films on highly reflective substrates may exhibit a negative phase contrast relative to the substrate[36,47,55,56], with initial studies[57] indicating that this effect arises from larger radiation losses or dissipation when the tip is located directly on the substrate. Although further studies are needed for a more precise understanding, this effect may be corrected through spectroscopic data analysis[57,58].

Effects of demodulation order and tip oscillation amplitude

Background suppression largely depends on the oscillation amplitude A of the tip, the harmonic n and the illumination wavelength. With increasing demodulation order n and/or decreasing tip oscillation amplitude A, the background suppression improves. For example, at visible to IR wavelengths, when the amplitude A exceeds 40 nm, background-free measurements typically require $n \geq 3$. The absence of background can be verified by measuring $|S_{s,n}|$ and $|S_{ref,n}|$ as a function of tip–sample distance h and confirming that these signals rapidly and monotonically decay to the noise floor within distances comparable to the tip radius[16,59,60]. Interestingly, near-field material contrasts[15,16,37,61,62]

and spatial resolution[15,30,61,63–67] increase with increasing n, the later effect sometimes referred to as effective or virtual tip sharpening[15,68]. For near-field transparent samples, in which subsurface near-field imaging with a probing depth up to a few tip radii is possible[51,59,69–73], the probing depth decreases as n or A increases[30,64,74,75] (Fig. 2e). This effect can be applied for reconstructing the vertical sample composition and for developing near-field optical nanotomography of the sample volume below the sample surface[30,74,76–78]. By contrast, the signal-to-noise (S/N) ratio decreases. For typical tip oscillation amplitudes (midpoint to maximum) between 30 nm and 100 nm, background-free imaging with a sufficiently large S/N ratio can be typically achieved for $n = 3$ and 4.

Substrate-enhanced near-field probing

For thin layers and small objects, the near-field amplitude signals, and thus the S/N ratio, can be enhanced by up to an order of magnitude by placing them on highly reflective substrates, such as Si or Au, instead of on low-refractive-index substrates such as CaF_2. This improvement can be explained by increased tip illumination and scattering via the substrate, along with enhancement of the near fields beneath the tip apex owing to stronger tip–substrate near-field interaction[48,49,73,79,80]. By exploiting polariton-resonant tip–substrate near-field interaction (see the section 'Near-field spectroscopic material response'), an additional signal enhancement can be achieved[48,49,79].

Instrumentation

Basic setup

s-SNOM is typically based on a tapping mode AFM, in which a cantilevered tip is oscillated perpendicular to the sample surface at the resonance frequency Ω of the cantilever. A parabolic mirror is typically used for both illumination of the tip and collection of the radiation elastically scattered at the tip (Fig. 3a, middle). For imaging, the sample is scanned beneath the laterally stationary tip, ensuring that the tip remains precisely aligned with the focus of the incident beam.

At visible-to-mid-IR frequencies, standard metal-coated AFM tips with a length of 10–20 μm and a tip apex radius of 20–50 nm are typically used. Although these tips are not optimized for their near-field probing performance, they often provide a sufficiently large S/N ratio and a spatial resolution on the order of the tip radius. However, particularly at THz frequencies, where wavelengths are much longer than the tip lengths, the lightning-rod or antenna effect of standard AFM tips is considerably weaker than at IR frequencies. For this reason, longer tips[81–83] or larger tip apex radii[68,81,84,85] are beneficial, as they yield larger THz near-field signals. It has also been demonstrated that the engineering of geometric antenna resonances can further enhance THz and IR near-field signals[68,83,86].

s-SNOM employing monochromatic illumination

s-SNOM is mostly used for nanoimaging with monochromatic light sources. In this case, amplitude-resolved and phase-resolved detection of the tip-scattered radiation is performed with a Michelson-type interferometer combined with higher-harmonic signal demodulation. To this end, the tip-scattered radiation is interfered at the detector with a reference beam reflected at a planar reference mirror (Fig. 3a, left). Complete background suppression requires the reference beam to be either frequency-shifted (heterodyning interferometry)[16,34], phase-modulated[32], phase-shifted[87,88] or amplitude-modulated[89]. Both amplitude and phase modulation of the reference beam yield near-field amplitude and phase signals within milliseconds and can be implemented in the whole visible to sub-THz spectral ranges. Typically, phase

modulation of the reference beam and higher-harmonic sideband demodulation are employed (Fig. 3b), a technique known as pseudo-heterodyne detection[32]. Amplitude and phase images are obtained by recording $|S_n|$ and $\text{Arg}(S_n)$ while the sample is scanned (Fig. 3c), simultaneously with an AFM topography image (Fig. 3d). The spatial resolution is determined by the size of the near-field spot at the tip apex, which is on the scale of the apex radius.

In the visible-to-near-IR spectral range, the radiation from diode or Ti:Sapphire lasers is often used for tip illumination, whereas quantum cascade lasers (QCLs) are the major light source in the mid-IR spectral range. At THz frequencies, tunable gas lasers can be used[90,91], but they are expensive and bulky. The emergence of THz-QCLs and self-detection schemes could be a promising compact alternative[92,93]. Even electronically generated and detected sub-THz radiation can be employed for imaging with 50 nm spatial resolution[62,94]. The narrowband radiation from free-electron lasers can be used as well. As it can be tuned from IR to THz frequencies, it enables s-SNOM applications in the far-infrared spectral range[95–97]. Tunable optical parametric oscillators (OPOs) with linewidth down to a few wavenumbers are emerging sources for s-SNOM imaging from near-IR to mid-IR frequencies[50,98,99]. Pseudo-monochromatic imaging can also be achieved by combining broadband sources with grating monochromators[100–102].

By repeatedly imaging the sample at various frequencies with a tunable monochromatic source, local spectroscopic information can be extracted from the set of s-SNOM images. This has been demonstrated at THz (refs. 96,103–106), IR[38,46,50,107] and visible frequencies[108]. An alternative and emerging method for obtaining local spectroscopic information is to sweep the frequency of a QCL[109] or narrow-band OPO[110] while keeping the sample position fixed.

s-SNOM employing broadband illumination
s-SNOM can also be operated with broadband light sources. In its earliest implementation, the tip was illuminated with broadband mid-IR radiation generated by difference-frequency generation and the tip-scattered field was recorded using dual-comb spectroscopy combined with higher-harmonic signal demodulation[111]. To date, the most common implementation uses a Michelson-type interferometer, operated as an asymmetric Fourier transform (FT) spectrometer[37,44,112–116] (Fig. 3a, right, and Fig. 3e). In this setup, the tip and sample are placed in one arm of the interferometer, similar to configurations used with monochromatic illumination. Unlike conventional FT spectroscopy, this arrangement enables the acquisition of both amplitude and phase spectra (Fig. 3f). Combined with higher-harmonic signal demodulation, it thus provides background suppression equivalent to pseudo-heterodyne detection with monochromatic light. However, the lower power of broadband sources often reduces the S/N ratio, requiring signal demodulation at lower harmonics where background suppression is less effective. Originally demonstrated with IR illumination and standard detectors, the technique was termed nanoscale Fourier transform infrared (nano-FTIR) spectroscopy[114], although it can be also implemented with visible, far-IR[19] and THz radiation[117].

Nano-FTIR spectroscopy typically employs broadband IR laser[37,44,112,113] or synchrotron radiation[19,21,39,117–119]. In the case of the latter, the technique is often referred to as synchrotron IR nanospectroscopy. Furthermore, argon arc[86,120] or laser-driven[121] plasma sources can be used. The latter may offer a rather compact and economical solution for ultra-broadband spectroscopy, although they significantly lag behind synchrotron radiation in terms of spectral power density and brilliance[122].

Acquisition times for nano-FTIR spectra can range from several seconds to many minutes. Consequently, spectra are often recorded only at specific sample positions. However, hyperspectral nanoimaging can be achieved by recording nano-FTIR spectra at each pixel of a 2D array across the sample surface[123]. From the resulting hyperspectral data cubes, local spectra or monochromatic images can be extracted. As hyperspectral nanoimaging is slow, sparse sampling techniques are increasingly used to reduce acquisition times[124–128].

s-SNOM can be also combined with time-domain spectroscopy[129]. In this technique, single-cycle or few-cycle IR or THz pulses are used for tip illumination. The waveforms of the tip-scattered pulses are measured as a function of time by coherent electro-optic or photo-conductive sampling[130]. Subsequent higher-harmonic signal demodulation allows for background-free amplitude-resolved and phase-resolved near-field spectroscopy[71,78,81,131] and hyperspectral nanoimaging[132,133].
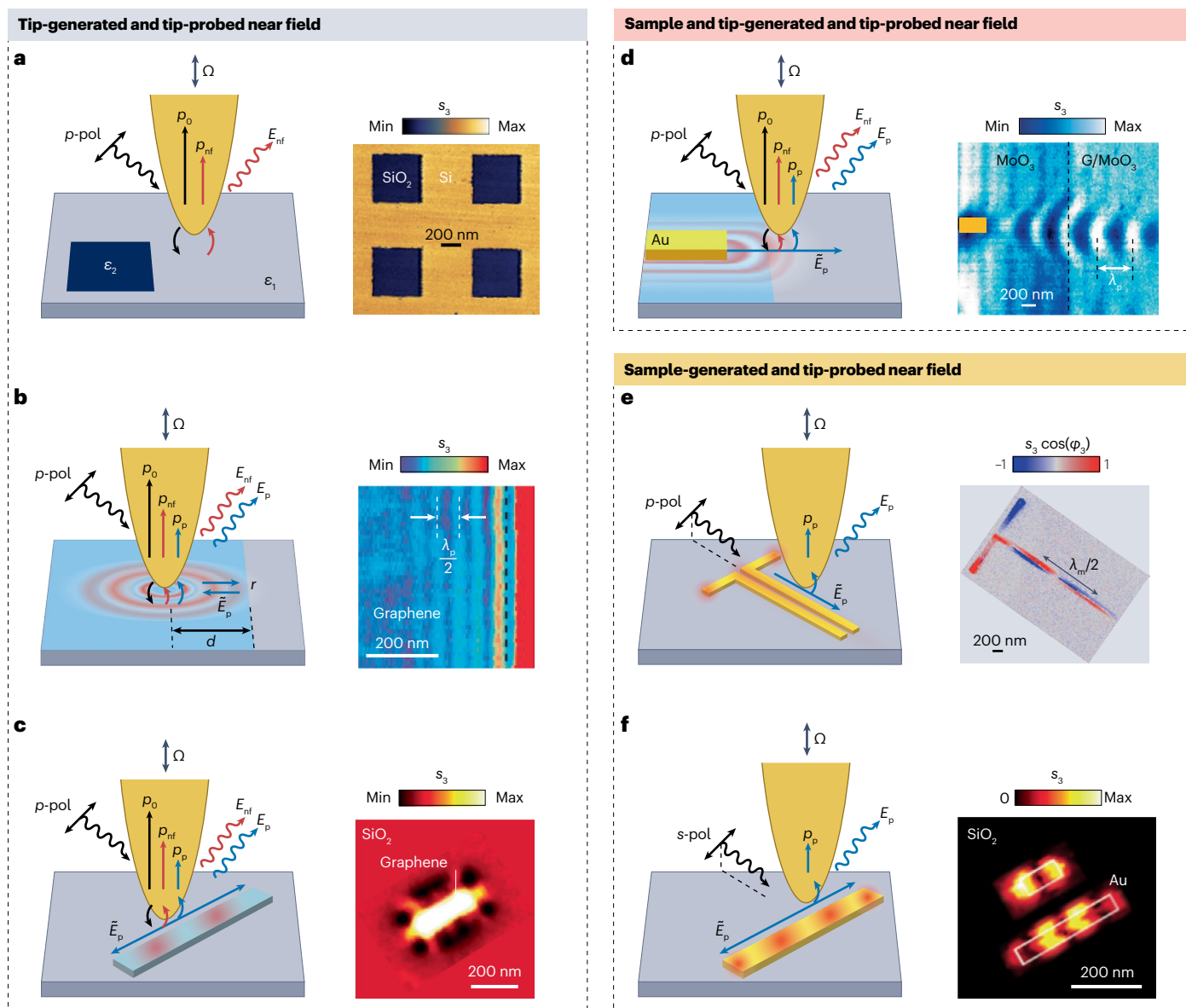
Near-field probing mechanisms
The electrodynamics of the tip-sample near-field interaction is multi-faceted, but two primary roles of the tip can be discerned (Fig. 4). The enhanced electric near field at the apex, typically of a metal tip, can be harnessed for probing material properties and eventually for launching and detecting EM modes (Fig. 4a–c). In other experiments, the tip is employed for scattering the EM modes that are predominantly excited by the sample itself, for example, by plasmonic antennas (Fig. 4d–f).

Near-field probing of material properties
Figure 4a illustrates the most basic s-SNOM experiment, with the underlying near-field probing mechanism detailed in Fig. 2a. In the case of monochromatic tip illumination, amplitude and phase images reveal spatial variations of the permittivity of the sample ε. As a simple example, we show in Fig. 4a a mid-IR near-field amplitude image of SiO_2 patches on an Si surface[134]. The SiO_2 patches appear as dark squares with smaller near-field amplitude than the brighter Si substrate, primarily because SiO_2 has a smaller permittivity than Si at the imaging frequency. By performing amplitude-resolved and phase-resolved spectroscopy using broadband sources or tunable lasers, the local dielectric function, $\varepsilon(\omega)$, can be determined through theoretical modelling or reconstruction. Having determined $\varepsilon(\omega)$, various sample properties can be derived, such as chemical composition and structure, crystal properties and mobile carrier concentration, as discussed later.

Interferometry of propagating EM modes excited by the near field of the tip
When thin layers or nanowires can support strongly confined propagating EM waves, the momentum of the concentrated near field at the tip apex may be large enough to efficiently excite them. These waves (Fig. 4b, red circles) include IR and THz plasmon polaritons in graphene[135,136], carbon nanotubes[137], semiconductor nanowires[138] and platelets[106]. Furthermore, the near field of the tip can excite IR and THz phonon polaritons in h-BN flakes[139,140], BN nanotubes[141], SiC layers[142], dielectric-loaded quartz[143] and MoO_3 flakes[96,144,145]. At visible and near-IR frequencies, exciton polaritons[146] and dielectric waveguide modes[146,147] in transition metal dichalcogenide layers can be launched, as well as surface plasmon polaritons (SPPs) on thin gold layers[148,149]. On extended homogeneous surfaces or nanowires, as well as on edges[150–152], the waves propagate away from the tip without manifesting visually in the near-field images. However, when these EM waves reflect back at discontinuities, such as edges[135,136], defects[153], grain boundaries[154,155] or

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Fig. 4 | Comparison of near-field probing mechanisms. a, Near-infrared near-field material contrast between Si (larger permittivity (ε_1)) and SiO$_2$ (smaller permittivity (ε_2)) at 6,452 cm^{-1}. s_3 is the near-field amplitude. **b**, The near field at the tip apex can additionally excite propagating electromagnetic (EM) waves on the sample. When these waves are reflected at sample discontinuities, they are scattered by the tip and imaged. The example shows an infrared s-SNOM image of graphene plasmon polaritons at 943 cm^{-1}, manifesting as periodic fringes parallel to the graphene edge. **c**, If the sample is nanostructured, it can act as a resonator structure for the tip-launched waves. The example shows an infrared s-SNOM image of a rectangular graphene plasmon polariton nanoresonator at 884 cm^{-1}, where the interference of multiple Fabry–Perot modes yields a complex near-field pattern. **d**, Propagating EM waves can be launched at discontinuities or antenna structures on the surface of the sample. The waves are scattered by the tip, allowing to map their wavefronts. The example image at 893 cm^{-1} shows how phonon polaritons on MoO$_3$ (left, launched by au Au antenna) experience negative refraction when they enter the region where the MoO$_3$ is covered by graphene (right). **e**, Applying s-polarized illumination and appropriate sample orientation allows for efficient excitation

of EM modes on the sample, whereas the optical excitation of the tip is minimized. The example image shows the antisymmetric propagating mode of a two-wire IR transmission line coupled to a dipole antenna. It was obtained by recording the real part of the p-polarized tip-scattered light at 1,020 cm^{-1}. **f**, Near-field probing of antenna and nanoresonator modes, with a configuration similar to that in panel **c**, but using an s-polarized illuminating field. The example shows a near-field amplitude image of the first-order and third-order dipolar resonance of Au nanorods at 10,616 cm^{-1}. p_0, p_{nf} and p_p are the dipoles induced, respectively, by the incident field, by the tip's near field reflected at the sample surface and by the electric field generated by the back-reflected EM waves. E_{nf} and E_p indicate the light radiated by the dipoles p_{nf} and p_p, respectively. The light scattered by p_0 is not indicated, as it is not measured. $\tilde{E}_p$ indicates EM surface waves and λ_p their wavelength. Panel **a** adapted with permission from ref. 134, Elsevier. Panel **b** adapted from ref. 158, Springer Nature Limited. Panel **c** adapted from ref. 150, Springer Nature Limited. Panel **d** adapted with permission from ref. 171, AAAS. Panel **e** adapted with permission from ref. 180, American Chemical Society. Panel **f** adapted with permission from ref. 183, American Chemical Society.

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domain walls[156,157], their electric field $\widetilde{E}_p$ induces an additional polarization (represented by the dipole p_p) in the tip, yielding a scattered field E_p depicted by a blue sine wave. The interference between the radiated fields E_{nf} and $E_p \propto p_p \propto \widetilde{E}_p$ subsequently yields interference fringes in both the near-field amplitude s_n and phase φ_n images. The fringe spacing corresponds to $\lambda_p/2$, in which $\lambda_p = 2\pi/k_p$ is the wavelength of the propagating EM wave. Figure 4b shows as an example the interference fringes of IR plasmon polaritons on high-quality graphene[158]. By measuring the periodicity and decay of the fringes, the dispersion and losses can be determined. Furthermore, various material properties of the sample can be accessed, including isotropic and anisotropic permittivities[147,159], local optical conductivity[154], strain[160] and anisotropic electron masses[106]. However, as the tip simultaneously launches and detects the propagating waves, this method does not allow for the direct mapping of the wavefront evolution. For instance, it is not possible to image how the waves propagate across an interface or undergo focusing. This problem can be circumvented when the tip scatters the field of a wave that is launched by structures on the sample rather than by the tip (Fig. 4d).

Interferometry of localized EM modes excited by the near field of the tip

When the thin layers discussed in the previous section are nanostructured, they can act as resonant cavities for tip-launched waves $\widetilde{E}_p$ (Fig. 4c). The near-field amplitude s_n and phase φ_n images thus exhibit patterns that can be associated with plasmonic[135,150,151,157] or phononic[161–165] cavity modes. Intriguingly, unlike far-field measurements, s-SNOM can probe not only bright but also dark modes, owing to local mode excitation by the strongly confined near fields at the tip apex. However, the near-field images often do not directly reveal the intrinsic mode profiles. This is because a complex near-field pattern is mapped, which is caused by the interference of the fields E_{nf} and $E_p \propto \widetilde{E}_p$ scattered by the dipoles p_{nf} and p_p (refs. 150,155). Furthermore, p_p may be induced not by the near field of a single cavity mode but by the near field arising from the interference of spatially and spectrally overlapping cavity modes[150]. Reliable mode identification thus requires a careful analysis of the near-field patterns, for example, by comparing them with simulated mode profiles of the cavities under study. Figure 4c shows, as an example, the mid-IR near-field amplitude image of a rectangular graphene cavity. The destructive and constructive interference of the various Fabry–Perot plasmon modes with the near fields below the tip apex yields dark and bright spots relative to the bare SiO₂ substrate, as a consequence of destructive and constructive mode interferences, respectively[150].

Interferometry of propagating EM modes excited by near fields of the sample

EM waves can be also excited at the edges of the layers supporting them[148,149,158,166], as well as by the strongly enhanced near fields generated at the edges of metal layers[167–169] or by antennas[166,170,171] located on the sample. As these near fields can assume much lower momenta than the ones generated at the tip apex of radius a, EM waves with wavelength much larger than a can be efficiently launched[168,172]. Figure 4d illustrates the launching of an EM wave by a gold nanorod when p-polarized illumination is used. The wave of field $\widetilde{E}_p$ propagates away from the launcher and polarizes the tip, represented by the dipole p_p. This polarization is additional to the one induced in the tip by the tip–sample near-field interaction, represented by the dipole p_{nf}. Analogue to the situation in Fig. 4b, interference of the fields $E_{nf} \propto p_{nf}$

and $E_p \propto p_p$ occurs. However, the interference fringe spacing is now λ_p as long as λ_p is much smaller than the photon wavelength. More importantly, the near-field amplitude s_n and phase φ_n images reveal the wavefronts and their evolution, which cannot be accomplished when the tip launches the EM wave. This method was applied to visualize the concave wavefronts of a diverging phonon polariton beam on an h-BN metasurface[170] and on in-plane anisotropic MoO₃ flakes[173]. Even the wavefronts of hyperbolic shear phonon polaritons on low-symmetry CdWO₄ crystals could be mapped[174], as well as the negative refraction and focusing of a diverging in-plane anisotropic phonon polariton beam crossing the straight interface between bare and graphene-covered MoO₃ (ref. 171) (Fig. 4d).

We note that in such experiments the tip can launch EM waves as well. In many cases, the reflection of these waves from the launcher can be neglected and thus does not disturb the wavefront patterns. However, when the tip-launched EM waves reflect efficiently at the launcher or other sample discontinuities back to the tip (Fig. 4b), the additional interference yields fringes with spacing $\lambda_p/2$ and needs to be considered[158,166]. In some cases, the interference fringes due to tip-launched polaritons might be removed by Fourier filtering the near-field images[175].
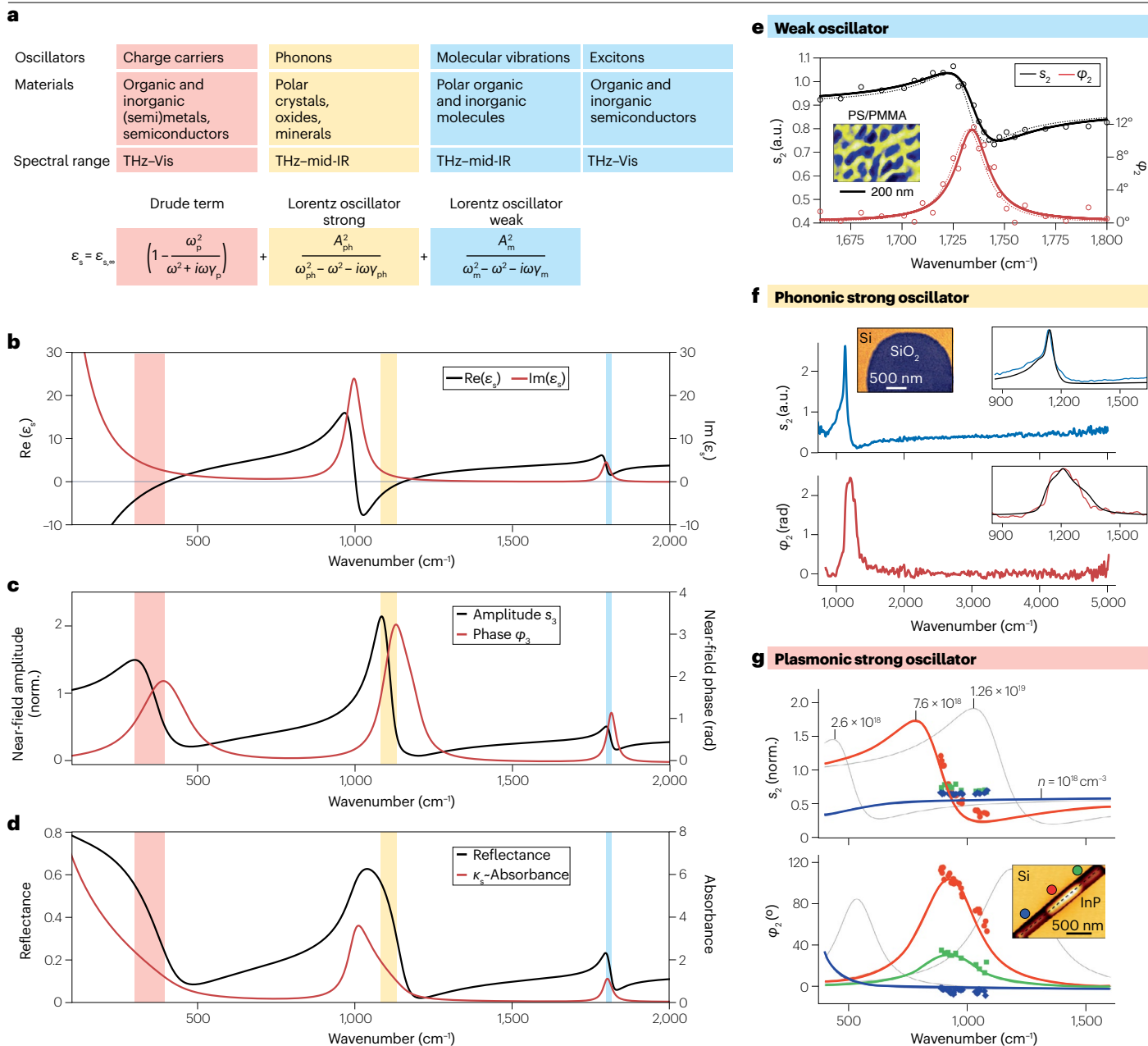
Mapping the near-field distribution of propagating EM modes

s-polarized far-field illumination can efficiently excite propagating EM modes on the sample, for example, on a metal two-wire transmission line (TL) coupled to a dipole antenna, whereas the direct excitation of the tip is minimized[176–179] (Fig. 4e). Thus, it is essentially the propagating mode that polarizes the tip, as illustrated by the dipole p_p. Recording the p-polarized tip-scattered field $E_p \propto p_p$ thus yields images of the spatial distribution of the vertical near-field component E_z of the mode, in contrast to the case illustrated in Fig. 4d, in which the interference between $E_p \propto p_p$ and $E_{nf} \propto p_{nf}$ is mapped. The tip can be illuminated from the side, as shown in the schematic, or from below through a transparent substrate, as in the example experiment, showing a near-field image of a mid-IR mode propagating along the TL. By plotting the real part of the near-field signal, $s_n\cos(\varphi_n)$, one can see the periodically changing polarity of the field along the TL. It reveals not only the wavelength of the mode but also that the antisymmetric TL mode is excited, as recognized by the opposite polarity of the field on the two wires[180]. This imaging modality was also applied for visualizing the compression of an IR mode propagating along a tapered TL[176], near-IR plasmons on tapered gold stripes[177] and slot waveguides[179,181] and optical skyrmion lattices formed by SPPs[182]. Employing side illumination, it was possible to map the refraction of antenna-launched IR graphene plasmons passing through a prism-shaped graphene bilayer[178].

Mapping the near-field distribution of resonator EM modes

s-polarized illumination can also be applied for near-field imaging of antenna and nanoresonator modes[41,42] (Fig. 4f). The far-field excited localized modes polarize the tip and induce the dipole p_p and subsequent far-field scattering $E_p \propto p_p$. Owing to the elongation of the tip, out-of-plane near-field components are scattered more efficiently than in-plane near-field components and thus are typically mapped when the p-polarized tip-scattered field is recorded. This technique offers the advantage of efficiently exciting resonator modes while minimizing the near-field coupling between the tip and the antenna. Furthermore, the images yield the spatial distribution of the vertical near-field component E_z of the mode, as in the configuration shown in Fig. 4e, in contrast to Fig. 4c, in which the interference between $E_p \propto p_p$ and $E_{nf} \propto p_{nf}$ is

a

Oscillators	Charge carriers	Phonons	Molecular vibrations	Excitons
Materials	Organic and inorganic (semi)metals, semiconductors	Polar crystals, oxides, minerals	Polar organic and inorganic molecules	Organic and inorganic semiconductors
Spectral range	THz–Vis	THz–mid-IR	THz–mid-IR	THz–Vis

Drude term	Lorentz oscillator strong	Lorentz oscillator weak

$$\varepsilon_s = \varepsilon_{s,\infty} \left(1 - \frac{\omega_p^2}{\omega^2 + i\omega\gamma_p}\right) + \frac{A_{ph}^2}{\omega_{ph}^2 - \omega^2 - i\omega\gamma_{ph}} + \frac{A_m^2}{\omega_m^2 - \omega^2 - i\omega\gamma_m}$$

b

Re(ε_s) / Im(ε_s) — Re(ε_s), Im(ε_s)
Wavenumber (cm^{-1})

c

Near-field amplitude (norm.) / Near-field phase (rad) — Amplitude s_3, Phase φ_3
Wavenumber (cm^{-1})

d

Reflectance / Absorbance — Reflectance, κ_s~Absorbance
Wavenumber (cm^{-1})

e Weak oscillator

s_2 (a.u.) / φ_2 — s_2, φ_2
PS/PMMA
200 nm
Wavenumber (cm^{-1})

f Phononic strong oscillator

Si
SiO$_2$
500 nm
s_2 (a.u.)
φ_2 (rad)
Wavenumber (cm^{-1})

g Plasmonic strong oscillator

2.6×10^{18} 7.6×10^{18} 1.26×10^{19}
s_2 (norm.)
$n = 10^{18}$ cm^{-3}
φ_2 (°)
Si
InP
500 nm
Wavenumber (cm^{-1})

mapped. As an example, Fig. 4f shows a near-field amplitude image of gold nanorods acting as antennas for visible light. It reveals the strong out-of-plane near fields, indicating the first-order and third-order dipolar antenna (nanoresonator) mode[183]. Applications of this imaging modality include the identification of resonator modes[41,42,183–185]. When the *s*-polarized tip-scattered field is measured, the nanoscale hot spots in narrow nanoantenna gaps can be mapped[186–188]. However, the interpretation of the near-field images may be more complicated, as the near-field signal generally does not reveal an individual near-field component[189].

Near-field spectroscopic material response

In this section, we describe in more detail the near-field material contrast discussed in Figs. 2a and 4a. The reflection of the near field of the tip at the sample and the associated scattering of the dipole p_{nf} are highly sensitive to the complex-valued local dielectric function $\varepsilon_s(\omega)$ of the sample. Recording the tip-scattered field thus allows us to probe various material excitations (Fig. 5a), including collective mobile charge carrier oscillations (plasmons), lattice (phonons) and molecular vibrations and electron–hole pairing (excitons). Plasmons can occur in metallic and semiconducting materials within a wide spectral region, ranging from sub-THz to visible frequencies, and can be often well described by the Drude term. Phonons can be found in polar crystals in the mid-IR to THz spectral range and can be well described by Lorentz oscillators with large oscillator strength. Molecular vibrations and excitons are adequately accounted for by Lorentz oscillators with weaker oscillator strengths. To demonstrate how these distinct contributions manifest

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in spectroscopic s-SNOM data, we constructed an artificial dielectric function using the Drude–Lorentz model, which incorporates both the Drude terms and Lorentz oscillators described earlier (Fig. 5b).

In Fig. 5c, we present the calculated near-field amplitude and phase spectra, $s_3(\omega)$ and $\varphi_3(\omega)$, of a corresponding semi-infinite isotropic bulk sample. To appreciate similarities and differences compared with typical far-field spectra, we show in Fig. 5d the calculated normal incidence far-field reflectance spectrum, $R_s(\omega)$, of the semi-infinite bulk sample and the absorption coefficient $\kappa_s(\omega)$, which is the imaginary part of the complex-valued refractive index $\tilde{n}_s = n_s + i\kappa_s = \sqrt{\varepsilon_s}$. We show κ_s, because the absorbance $A_s \propto \kappa_s d$ scales linearly with κ_s but diverges for semi-infinite samples of infinite thickness d.

Weak oscillator samples

For weak oscillators (Fig. 5c,d, blue-shaded area), $s_3(\omega)$ compares qualitatively well to Re$[\varepsilon_s(\omega)]$ and $R_s(\omega)$, whereas $\varphi_3(\omega)$ resembles Im$[\varepsilon_s(\omega)]$ and $\kappa_s(\omega)$ (refs. 38,43,69,74,113,190). For this reason, near-field phase spectra of molecular vibrations can be compared with far-field absorbance spectra from databases for chemical identification, without the need for modelling[44,54,191,192]. As an example, we show in Fig. 5e s-SNOM amplitude and phase spectra taken for a nanoscale region of PMMA of a PMMA-PS block copolymer sample[38]. The experimental s-SNOM amplitude and phase spectra (open circles) and their fit by a Lorentzian oscillator (solid lines) agree well with $n_s(\omega)$ and $\kappa_s(\omega)$ obtained from ellipsometry (dashed lines). Owing to the near-field interaction between tip and sample, however, small deviations between near-field and far-field spectra exist[43,54,74]. For example, for thin layers, the height and spectral position of amplitude and phase peaks depend on the layer thickness and the dielectric function of the substrate[51,54,70,193], which necessitates the modelling of s-SNOM spectra (see the next section) when an accurate quantitative analysis of the local oscillator resonances is required. We note that $a_n = \text{Im}[\sigma_n]$, referred to as nano-FTIR absorption, has been introduced as an alternative for comparing near-field with far-field spectra[44,190], since the peak positions in nano-FTIR absorption spectra of samples thicker than the near-field probing depth correspond to those in far-field absorbance spectra obtained by transmission FTIR spectroscopy.
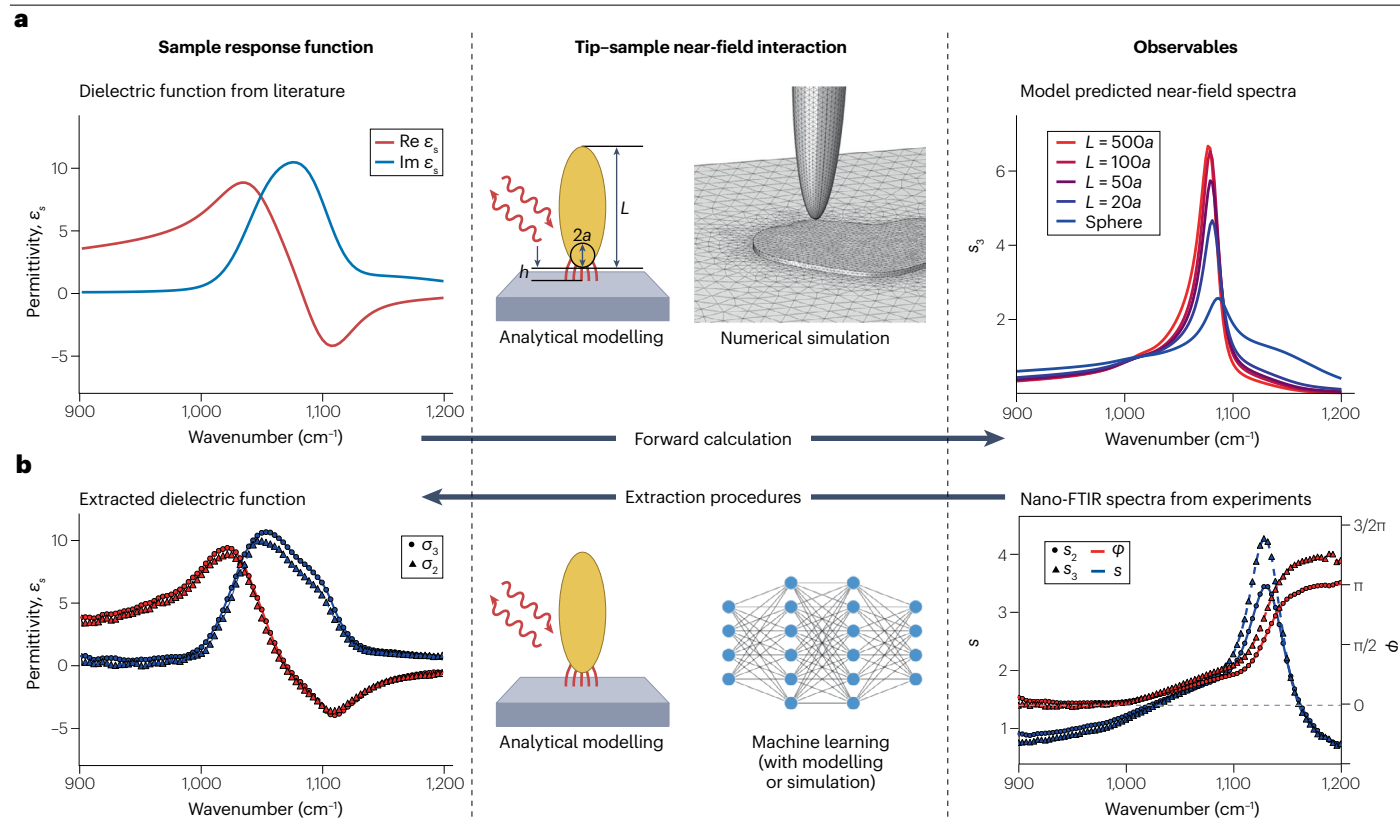
Strong oscillator samples

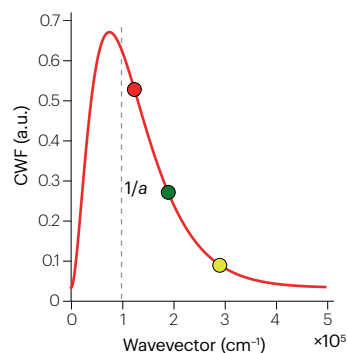In stark contrast to weak oscillators, we find a significantly different behaviour of near-field spectra when strong Lorentz oscillators or Drude materials are probed, or more generally, when Re$[\varepsilon_s(\omega)]$ assumes negative values (Fig. 5b, yellow-shaded and red-shaded areas). The peaks observed in the $s_3(\omega)$ and $\varphi_3(\omega)$ spectra are significantly blue-shifted compared with those of Re$[\varepsilon_s(\omega)]$ and Im$[\varepsilon_s(\omega)]$. Moreover, the near-field spectra do not match far-field spectra, where regions with Re$[\varepsilon_s(\omega)] < 0$ give rise to broad spectral reflection and absorption features known as Reststrahlen bands. Remarkably, the near-field amplitude signals can exceed that of a gold sample, such that $s_3(\omega) > 1$. This intriguing phenomenon can be explained by the near-field reflection coefficient (that is, Fresnel reflection coefficient at momenta much larger than that of the free-space photon), which in the electrostatic limit is given by $\beta_s = (\varepsilon_s - 1)/(\varepsilon_s + 1)$ (ref. 45). The divergence of β_s near $\varepsilon_s = -1$ yields an exceptionally strong reflection of the tip's near field at the sample surface and subsequently a strong near-field interaction and scattering. The physical origin of this divergence can be attributed to a resonant near-field excitation of localized SPPs in the Drude material[35,78,90,194–196] and localized surface phonon polaritons (SPhPs) in the strong Lorentz oscillator sample[37,39,45,104,197,198]. Importantly, the near fields at the tip apex may excite propagating SPPs and SPhPs when $\varepsilon_s < -1$, leading to polariton interference fringes near sample edges[142,143,168,172,199] (Fig. 4b,c). Although the appearance of these fringes provides valuable information about the polaritons, they may disturb the pure material contrast and need to be considered when the local dielectric function is to be determined.
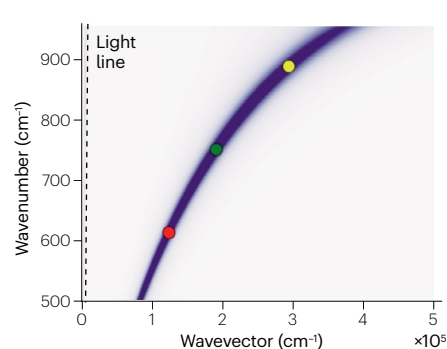
Phononic strong oscillator samples

In Fig. 5f, we show the measured nano-FTIR spectrum of SiO$_2$, a typical example of a sample in which an SPhP-resonant near-field interaction leads to exceptionally strong and narrow peaks in both near-field amplitude and phase spectra[39]. We also observe a significant blue shift of the amplitude peak (1,130 cm^{-1}) relative to the transverse optical phonon of SiO$_2$ (1,074 cm^{-1}), analogue to the calculated near-field spectrum of the artificial strong phonon oscillator in Fig. 5b–d. Generally, the spectrally sharp and strong phonon polariton peak allows for highly sensitive characterization of the local chemical composition of polar crystals. Examples include the identification of calcite and phosphate bands in biominerals and human teeth[200], as well as of minerals in meteorites and cometary dust grains[201]. Structural properties can be mapped as well, as the optical phonon frequencies are highly sensitive to the crystal lattice parameters and thus to polytypes[202], crystal quality and
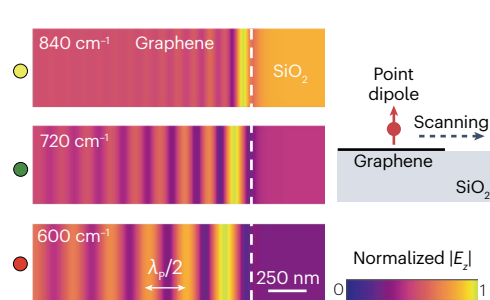
a

Sample response function

Dielectric function from literature

Tip–sample near-field interaction

Analytical modelling   Numerical simulation

Observables

Model predicted near-field spectra

Forward calculation

b

Extracted dielectric function

Extraction procedures

Analytical modelling   Machine learning (with modelling or simulation)

Nano-FTIR spectra from experiments

c **Coupling weight function**

d **Plasmon dispersion**

e **Simulated real-space images**

defects[153,203] and strain[204,205]. In the presence of mobile charge carriers in doped semiconductors or heterostructures, carrier–phonon coupling can modify the spectral position and width of the SPhP-resonant near-field interaction, allowing for sensitive local measurements of low carrier concentrations[156,197,202,206,207].

Plasmonic strong oscillator samples

Figure 5g illustrates an example of an SPP-resonant near-field interaction, showing both calculated (lines) and measured (symbols) near-field amplitude and phase spectra of an InP nanowire[35]. The bright and dark areas in the near-field amplitude image correspond to doped and undoped regions. The peaks in the amplitude and phase spectra of the doped area (red) stem from the SPP-resonant near-field interaction.

Their position strongly depends on the mobile carrier concentration n. Generally, via modelling of the near-field spectra (see the next section), n can be quantified with nanoscale spatial resolution not only in semiconductor nanowires but also in doped wafers, organic semiconductors and nanoelectronic devices[78,90,121,196,208].

Remarks

The interpretation of polariton resonances in near-field spectra of strong oscillators requires a careful analysis by modelling, as a direct comparison with far-field spectra from databases is typically not possible. Furthermore, the description of the near-field optical material contrasts given in this section and in Fig. 5 is valid for isotropic bulk materials and, generally, cannot be directly applied to anisotropic

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materials. For example, the tip-induced SPP and SPhP resonances are not observed on uniaxial materials with optical axis perpendicular to the surface, where the amplitude peak occurs near the transverse optical frequency[140,144]. This finding may be explained by the fact that the polaritons in such materials are volume polaritons rather than surface polaritons.

Modelling of near-field images and spectra

Permittivity determination is well established in far-field optics using techniques such as ellipsometry and FTIR spectroscopy, but it remains challenging in s-SNOM and nano-FTIR spectroscopy. Efforts to model near-field interactions in s-SNOM have been ongoing since the early 2000s[10,15,16,45], following the original dipole model of apertureless SNOM[9]. The complex tip–sample near-field interaction and irregular probe and sample geometries make it difficult to establish an accurate mathematical relationship between the local permittivity of the sample, ε_s, and experimentally measured near-field signals σ_n (equation (1)). Consequently, simplifications and approximations are necessary for simulating s-SNOM and nano-FTIR data using known or assumed sample dielectric functions. The role of approximations becomes increasingly pertinent when attempting to reconstruct the dielectric function from near-field data – a notably challenging task that is still in rather early stages of development.

Modelling of material contrasts

In a rudimentary analytical approach, the AFM tip is modelled as a point dipole located inside the tip apex. The near-field interaction between this dipole and a semi-infinite sample can be described using the quasistatic approximation[10,15,16], which yields an effective dipole polarizability $\alpha_{eff}(\varepsilon_s, h)$ that depends on the permittivity ε_s of the region of interest of the sample and the tip–sample distance h. When far-field reflections at the sample surface are negligible, the scattering coefficient (see the section 'Near-field signal detection and normalization') can be expressed as $\sigma_s \propto \alpha_{eff}(\varepsilon_s, h)$. By considering a sinusoidal tip oscillation, $h = h(t)$, one obtains $\alpha_{eff}(\varepsilon_s, t)$, whose Fourier decomposition yields the Fourier coefficients $\alpha_{eff,n}(\varepsilon_s)$. By normalizing these Fourier coefficients to those of a reference sample, one obtains $\sigma_n = \alpha_{eff,n}(\varepsilon_s)/\alpha_{eff,n}(\varepsilon_{ref})$. This ratio allows for a direct comparison with normalized experimental near-field signals (equation (1)). Later, this point dipole model (PDM) was expanded by fully retarded calculations for layered samples[48]. Although the PDM omits the elongated tip shank,

whose length is often comparable to or larger than the wavelength of visible or IR illumination, it can qualitatively describe the experimentally observed near-field material contrasts for all three types of sample excitations[10,45,46,194,196] described in Fig. 5. The PDM, however, fails to quantitatively describe material contrasts when polariton-resonant tip–sample near-field interactions occur[45], such as the ones described in Fig. 5f,g. For example, the model does not correctly describe the position, width and magnitude of the spectral peaks[31]. For improved quantitative modelling, more sophisticated models beyond the PDM were thus developed, such as the finite-dipole model (FDM) for bulk samples[31]. The FDM phenomenologically approximates the tip by a spheroid with several point charges placed along its major axis, yielding a more accurate expression of the effective tip polarizability. This model agrees well with experimental material contrasts and is widely used. Several extensions of the FDM were made for layered samples[70,74,209]. We note that the dipole models are inherently simple but involve various parameters that are often insufficiently described in the literature. To facilitate the use of these models, clarify their parameters and ensure consistency, a Python package with a detailed discussion of these parameters has been developed[210]. More rigorous, although complicated, approaches to modelling near-field contrasts can be achieved through theoretical and numerical calculations that treat the tip as an elongated spheroid[198,211] or cone[30,61,68,212,213] (Fig. 6a, middle).

Reconstruction of sample properties by inversion of normalized near-field signals

Several of the s-SNOM models can be inverted and have been applied to determine the local sample properties from s-SNOM and nano-FTIR data. The accuracy and consistency of the reconstructions can be tested with well-known sample materials. To this end, the permittivity results obtained from the inversion of normalized near-field amplitude and phase data, $s_n(\omega)$ and $\varphi_n(\omega)$, for different signal demodulation orders n or tip-oscillation amplitudes (Fig. 3) should be consistent and should match literature data. Reconstruction of the dielectric function of thin layers of the well-known polymer PMMA[43,74] and SiO_2 (ref. 198) were successfully demonstrated with the FDM[74] and the lightning-rod model (LRM)[198,211], respectively. The LRM rigorously accounts for the electromagnetic interaction between the tip and the sample and can accommodate arbitrary tip geometries, diverse sample configurations and electrodynamic effects. The LRM was later applied to measure mid-IR

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in-plane and out-of-plane permittivities of the van der Waals material 2H-WSe$_2$ (ref. 214). The reconstruction of the permittivity of complex multilayer materials has been achieved using the FDM for layered samples, for example, of topological insulators at THz (refs. 78,105) and mid-IR frequencies[76]. In the latter study, the reconstructed permittivity revealed an intersubband transition within the massive 2D electron gas, whereas an additional broadband absorption background potentially indicated the presence of a topological surface state. By contrast, these models have not been extensively verified with well-known materials in terms of their capability to fit experimental near-field data at several n simultaneously.

Modelling and reconstruction example

We now discuss an example of modelling s-SNOM material contrasts[198]. The left panel of Fig. 6a depicts the mid-IR permittivity of SiO$_2$. The IR-active phonon leads to the typical Lorentzian line shape. Using this permittivity, near-field amplitude and phase spectra of thin SiO$_2$ layers were calculated using the LRM[198] (middle panel). The right panel of Fig. 6a shows the third harmonic near-field amplitude spectra, $s_3(\omega)$ of a 300 nm-thick SiO$_2$ film on an Si substrate for different tip lengths. The results show that the spectral peak position and height of the near-field phonon polariton resonance are sensitive to the tip length, likely due to the lightning-rod effect. For comparison, the right panel of Fig. 6b shows the experimentally measured second and third harmonic near-field amplitude and phase spectra, $s_n(\omega)$ and $\varphi_n(\omega)$, of a 300 nm SiO$_2$ film on Si substrate, showing good agreement with the lightning-rod model calculations.

The left panel of Fig. 6b shows the dielectric function of SiO$_2$ as reconstructed from the experimental s-SNOM via the LRM. In this optimization problem, a continuous path $\varepsilon_s(\omega)$ in the complex ε space is systematically varied, such that the near-field signal calculated from $\varepsilon_s(\omega)$ matches the experimental complex-valued nano-FTIR spectra $\sigma_n(\omega)$ the best. Additional numerical techniques can be applied to enhance the robustness of the inversion and ensure the uniqueness and smoothness of $\varepsilon_s(\omega)$ (ref. 198). The results shown in the left panel of Fig. 6b are the best estimation of the sample permittivity. It matches well the permittivity obtained from far-field ellipsometry measurements (Fig. 6a, left).

Modelling and simulation of images resulting from tip-launched polaritons

Modelling does not only allow for describing s-SNOM material contrasts but also provides basic insights into the various other probing mechanisms described in Fig. 4. For instance, it is well established that the momentum distribution of the near-field interaction within the PDM follows a coupling weight function of q^2e^{-2qz} (Fig. 6c), in which q is the in-plane momentum and $z = a + h(t)$ the distance between the dipole and the sample surface[48,107,209]. Although the tip height h and, consequently, the weight function vary over time, the dominant momenta in the near-field interaction, where the weight function peaks, are around $1/a$, with a being the tip radius. These momenta are sufficiently large to match those of ultra-confined polaritons, as illustrated in Fig. 6d, in which we show an example dispersion for mid-IR graphene plasmons. This explains why the near fields at the tip apex can effectively launch ultra-confined polaritons in 2D materials[28,107,135,136] (Fig. 4b–d). The experimental near-field images of these modes can be thus well reproduced by modelling the tip as a point-dipole source or finite dipole and plotting the near field of the dipole as a function of position[150,154,155] (Fig. 6e). Beyond the verification of experimental polariton images, fitting of the experimental data allows for extracting

polariton properties and related material properties on complex samples[103,144,213], such as conductivity variations around graphene grain boundaries[154]. Furthermore, it is possible to identify and disentangle individual plasmonic and phononic eigenmodes from the complex interference patterns observed in s-SNOM images of graphene (Fig. 4c) and h-BN nanoresonators[150,161].

Advanced numerical simulations

Despite significant advancements, the analytical modelling of material contrasts continues to be encumbered by certain limitations. For instance, analytical models typically require the sample to be flat and homogeneous, a condition that frequently deviates from experimental reality. By contrast, full numerical simulations offer a viable platform for examining the intricate interplay between light, finite-size probes and laterally heterogeneous samples[61,213,215,216] (Fig. 6a, middle). Moreover, it has been shown that simulating the actual tip geometry based on scanning electron micrographs, even incorporating the cantilever, is computationally feasible[217].

Although numerical simulations can accurately account for tip and sample geometries, they are computationally intensive and therefore are difficult to use for backward extraction of the sample properties using experimental data. A predominantly data-driven approach utilizing machine learning has recently been demonstrated as another feasible backward extraction method[218–220] (Fig. 6b, middle). In this approach, a neural network can link sample permittivity with near-field data from experimental or simulated data sets. With the increasing availability of near-field instruments, a large amount of data is generated daily. Applying advanced machine learning and other AI techniques to big data has the potential to unveil valuable insights and uncover complex physics.

s-SNOM with distinct sample environments

s-SNOM exhibits great versatility in its ability to operate in a broad range of environmental conditions (Fig. 7).

Elevated temperatures

s-SNOM-based nanoimaging and spectroscopy can be performed at elevated temperatures up to 400 K (refs. 131,221–226), via either a heating stage or laser illumination (Fig. 7a). This enables, for example, studies of phase transitions, as demonstrated in Fig. 7b, in which nanoscale-resolved IR imaging reveals the coexistence of metallic (white) and insulating (blue) stripes in a vanadium dioxide microbeam at ~345 K (ref. 223). Similar reversible phase transitions in VO$_2$ thin films can be triggered by increasing the incident light power to 10–20 mW using a pulsed IR laser, heating the entire illuminated region[224]. Laser heating has also been employed to induce irreversible changes of sample properties, which can be conveniently probed through consecutive s-SNOM imaging. Figure 7c shows that local heating through enhanced optical near fields below the tip apex can be utilized for nanolithography of proteins. The top image shows the heat-induced local topography change in a silk film, which is accompanied by an increased local IR absorption (bottom image), revealing a conformational change of the silk protein[227].

Cryogenic temperatures

Cryogenic s-SNOM (cryo-SNOM) is an essential tool for studying materials at low temperatures, offering unique insights into phenomena that are not accessible at ambient conditions (Fig. 7d). Typically, cryo-SNOM systems incorporate a sample-scanning AFM coupled to a motorized focusing mirror housed in a high vacuum, or preferably, ultra-high

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vacuum chamber equipped with anti-vibration stages[169]. They operate using either continuous flow[169] or closed-cycle cryo-systems[228], reaching sample temperatures below 20 K (refs. [169,228–232]). Recent advancements in cryo-SNOM have led to the development of various types of tabletop systems and expanded their application to large-scale beamline facilities such as tunable free-electron lasers[231]. Conducting nano-imaging and nano-spectroscopy at cryogenic temperatures has facilitated the study of quantum phase transitions in correlated electron materials[229,233], 2D electron gases at oxide interfaces[228] and the reduced damping of polaritons at low temperatures[169,234,235].

For example, Fig. 7e shows the nanotextured phase separation in a V_2O_3 thin film that is revealed during the metal-to-insulator transition at 169 K (ref. [226]). The bi-directional 'tweed' texture of the metallic (red areas) and insulating (blue areas) states demonstrates a substrate-strain-induced symmetry breaking of V_2O_3 thin films during the transition. Figure 7f shows that at cryogenic temperature down to 60 K, the propagation distance of plasmon polaritons in graphene is greatly extended compared with room temperature, exceeding 10 μm, or 50 plasmonic wavelengths[169].

Future developments in cryo-SNOM may include minimizing cryogen usage in ultra-high vacuum environments while managing sample vibration, surface icing and optimizing tip control for best AFM performance. Additionally, improving the S/N ratio of interferometric measurements without excessive laser heating will require innovative solutions for detection optics. For instance, employing a parabolic mirror with a high numerical aperture in combination with an in-chamber reference arm can effectively mitigate the noises generated in the different paths of the asymmetric interferometer by mechanical vibrations owing to the cryogen flow.

Ultrafast optical excitation

s-SNOM experiments can also be performed in an ultrafast pump–probe scheme, combining high spatial, temporal and energy resolution[78,195]. As illustrated in Fig. 7g, a fs-pump pulse (blue sine wave) is focused onto the tip and photoexcites the sample in the vicinity of the tip. Subsequently, a fs-probe pulse (red sine wave) is focused onto the tip with a controlled time delay relative to the pump pulse. Detecting the tip-scattered probe pulse by either nano-FTIR spectroscopy[195,236–238] or electrooptic sampling[78,239] combined with higher-harmonic signal demodulation as a function of the time delay t_{pp} between the probe and pump pulses allows for ultrafast time-resolved near-field measurements of the transiently altered local sample properties. So far, mostly visible-to-near-IR pulses have been used for pumping, whereas probing has been typically performed with IR[78,195,223,236,237,240] and THz (refs. [241–243]) pulses, and in few cases with visible[244] pulses. The technique has been applied for studying photoinduced metal–insulator phase transitions[236,240,245,246], ultrafast carrier dynamics in semiconductors and graphene[78,195,239,247,248] and for the ultrafast control of plasmon and phonon polariton propagation[244,249–252]. In these studies, the pump pulses mostly triggered electronic interband and intraband transitions or heating.

For instance, the ultrafast dynamics of a photoexcited InAs semiconductor nanowire was investigated using 1.56 μm pump and ~10 μm probe pulses[78]. Figure 7h shows the IR near-field images at a delay time of −2 ps (before excitation) and +50 fs (after excitation). The increased near-field signal at +50 fs stems from the increased carrier density after photoexcitation. Analysing the transient near-field spectra as a function of the time delay revealed the ultrafast carrier dynamics, including the ultrafast formation of a depletion layer. In another example[249],

near-IR pulses were used to generate transient electron–hole pairs in a thin WSe_2 flake, and nano-FTIR spectroscopy was employed to visualize the resulting hyperbolic polariton rays travelling inside the crystal along conical trajectories (Fig. 7i). The transient polaritons manifest as circular features in the near-field image at $t_{pp} = +2$ ps after pumping due to the excessive exciton pairs induced by the pump excitation. In the future, IR/THz pumping and visible/IR probing could be promising variations for optical doping at the technologically important low photon energy range[253].

Electric and magnetic fields

s-SNOM can also address field or current switching (Fig. 7j). Electric switching can be induced through predeposited electrodes on the sample surface, by applying either an electric field or current. For example, it was observed that the plasmon wavelength in graphene depends on the direction of the applied electric current. This phenomenon is related to the nonlinear electrodynamics of Dirac electrons in graphene and is known as the 'Fizeau drag'[254,255] (Fig. 7k). It was also shown that electric currents can induce an insulator–metal phase transition in the $4d$ transition metal oxide Ca_2RuO_4, as can be recognized by clear phase boundaries between metallic and insulating states[256].

The recent introduction of s-SNOM operating under high magnetic fields (also known as m-SNOM), reaching up to 7 T, has the potential to map nanoscale phenomena associated with the breaking of time-reversal symmetry. Still in its early stages, the m-SNOM setup integrates a strong magnet, often a superconducting one, with a cryogenic system to ensure a stable temperature and magnetic field environment[232,257]. Owing to the small bore size of the superconducting magnet, the system usually requires a miniaturized AFM and compact optics to accommodate everything within a limited space[257].
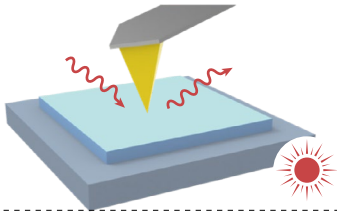
The development of m-SNOM opens up exciting possibilities for exploring correlated electron systems and low-dimensional materials under magnetic excitations. One promising application is nanoscale Landau level spectroscopy, in which the presence of Landau levels modifies the optical conductivity, revealing the magneto-optical properties of the material at the nanoscale. At IR frequencies, this provides valuable insights into controlling polaritonic excitations and allows for uncovering many-body physics related to Landau level excitations in graphene[257] (Fig. 7l). In the THz frequency range, magneto-nanoscopy could be used for investigating magnetic excitations, charge order dynamics and quasiparticle energy gaps in phase-separated microcrystals, in which the energy scale aligns with low-energy photons. One preliminary example demonstrates the potential of THz s-SNOM operating at ultra-low temperatures and magnetic fields up to 5 T were used to detect magnetic field-induced electromagnetic responses in superconductors and Weyl semimetals[232].

Strain

s-SNOM can be also applied for the mapping of strain and strain-induced physical and chemical properties, either ex situ (Fig. 7m) or in situ[52,153,160,204,205,258]. The strain field can be applied through epitaxial strain[226], nanoindentation[204,205] or dynamically tuned using piezo strain stages[52]. For example, strain was created in an SiC crystal by nanoindentation before s-SNOM imaging. By using an IR wavelength near the optical phonon frequencies of SiC, it was possible to highlight compressive and tensile strain (bright and dark areas) due to strain-induced spectral phonon shifts[204] (Fig. 7n). Compressive and tensile strain can be also applied while the sample is imaged, for example, by bending or stretching the sample employing piezoelectric actuators. The latter

a Elevated temperature

b VO$_2$

Max — s_n — Min

T = 345 K

1 µm

c Silk

21 — h (nm) — −6

10 — φ_3 — −15

1,631 cm^{-1}
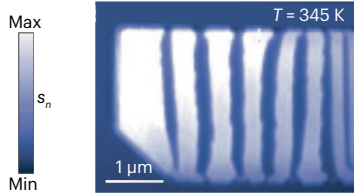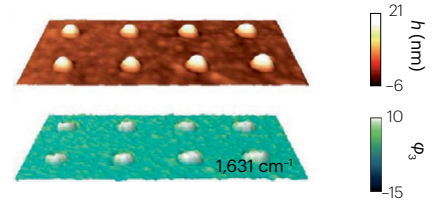
d Cryogenic temperature

e V$_2$O$_3$

Max — s_3 — Min

T = 169 K

1 µm

f Graphene

Au

T = 60 K

Max — s_3 — Min

1 µm

g Optical excitation

Probe

Pump

t_{pp}

h InAs

Max — s_3 — Min

t_{pp} = −2 ps

InAs

Diamond

t_{pp} = 50 fs

500 nm

i WSe$_2$

t_{pp} = −8 ps

1 µm

t_{pp} = −2 ps

Max — φ_2 — Min
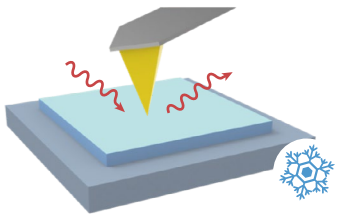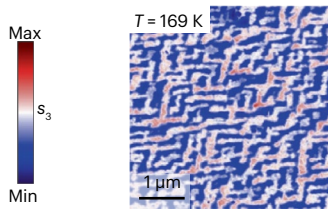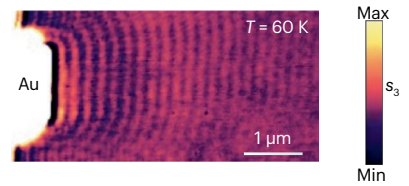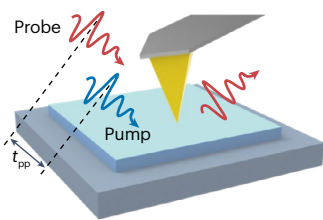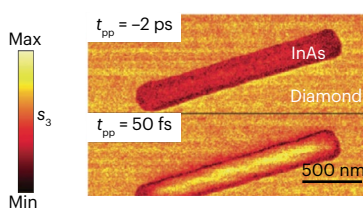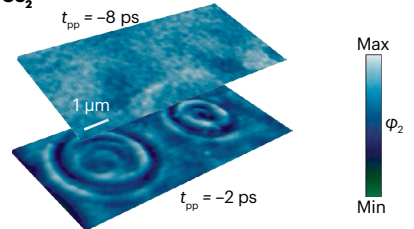
j Electric or magnetic field, current
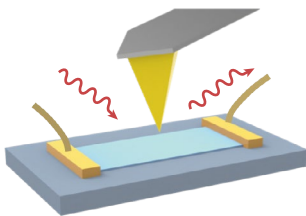
k Graphene
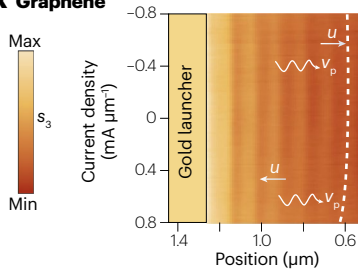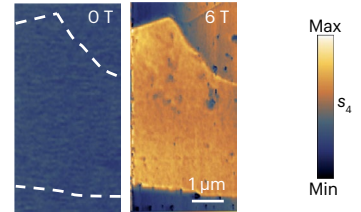
Max — s_3 — Min

Gold launcher

u

v_p

u

v_p

Current density (mA µm^{-1})

−0.8 −0.4 0 0.4 0.8

Position (µm)

1.4 1.0 0.6

l Graphene

0 T

6 T

Max — s_4 — Min

1 µm

m Strain

n SiC

Max — s_2 — Min

1 µm

o Ca$_3$(Ti$_{0.1}$Ru$_{0.9}$)$_2$O$_7$

1% compressive

Unstrained

1% tensile

Strain

Max — s_3/s_2 — Min

10 µm

p Liquid

Immersion in liquid

Membrane-capped cell

q Living cancer cells

Max — s_2 — Min

3 µm

r Biomembranes

Max — φ_3 — Min

1 µm

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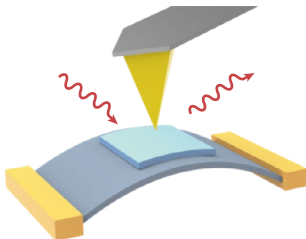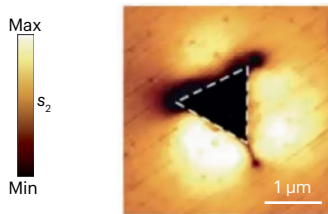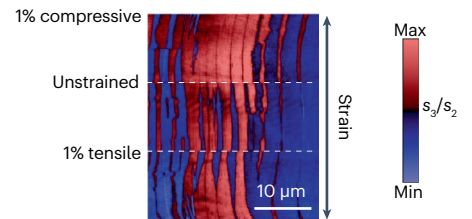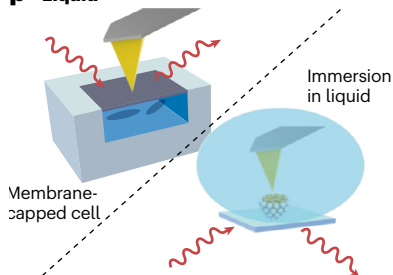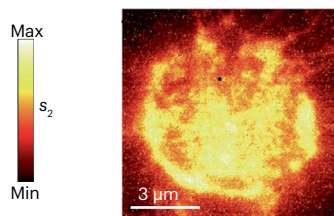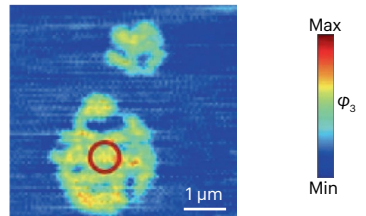
Fig. 7 | Scattering-type scanning near-field optical microscopy setup with distinct sample environments. a, Schematic illustration of a setup for measurements at elevated temperatures. **b**, Infrared (926 cm⁻¹) image of a VO₂ microcrystal at 345 K, showing metallic (white) and insulating (blue) domains. **c**, Heating through the near fields at the tip apex. The topography of a silk layer with heat-induced protrusions (top) is shown together with an infrared (1,631 cm⁻¹) phase image showing stronger infrared absorption at the protrusions. **d**, Schematic illustration of a setup for measurements at cryogenic temperatures. **e**, Infrared (920 cm⁻¹) amplitude image of a V₂O₃ film at 169 K, showing metallic (red) and insulating (blue) domains. **f**, Infrared (886 cm⁻¹) amplitude image of long-lived plasmons on back-gated graphene at 60 K. **g**, Schematic illustration of a setup for ultrafast pump–probe nano-spectroscopy. t_{pp}, time delay between pump and probe pulses. **h**, Infrared (2,000 cm⁻¹) amplitude images of an InAs nanowire recorded for different pump–probe delay times. At t_{pp} = +50 fs, the nanowire appears brighter due to pump-induced mobile charge carriers. **i**, Time-resolved infrared (910 cm⁻¹) near-field phase images of a WSe₂ slab on top of a metal disk. At t_{pp} = +2 ps, circular fringes reveal pump-induced hyperbolic Rydberg polaritons in WSe₂. **j**, Schematic illustration of a setup for measurements with electric and magnetic fields. **k**, Infrared amplitude (890 cm⁻¹) signal of graphene as a function of position relative to gold launcher and current density, showing that the plasmon wavelength (horizontal fringe periodicity) varies with current density, as indicated by the white dotted line ('Fizeau drag'). The arrows labelled v_p indicate

the direction of plasmon propagation, the arrows labelled u the direction of the electron flow. **l**, Infrared (900 cm⁻¹) amplitude images of graphene (outlined by dashed lines) at 0 T and 7 T, revealing enhanced optical conductivity at 7 T owing to Landau level transitions. **m**, Schematic illustration of a setup for measuring while strain is applied. **n**, Infrared (937 cm⁻¹) amplitude image of a nanoindent in an SiC crystal, revealing areas of tensile (dark) and compressive (bright) strain. **o**, Infrared (~1,000 cm⁻¹) amplitude signal of a $Ca_{n+1}Ru_nO_{3n+1}$ single crystal, showing the evolution of metallic (red) and insulating (blue) domains as strain is applied (vertical axis). **p**, Schematic illustration of a setup for measuring in liquid environments. **q**, Broadband infrared amplitude image of a living A549 cancer cell in water underneath a 10-nm SiN membrane. **r**, Infrared (1,660 cm⁻¹) phase image of a native biomembrane (fragments of archaeon *Halobacterium salinarum*) immersed in a bulk aqueous solution. Panel **b** adapted from ref. 223, Springer Nature Limited. Panel **c** adapted from ref. 227, Springer Nature Limited. Panel **e** adapted from ref. 226, Springer Nature Limited. Panel **f** adapted from ref. 169, Springer Nature Limited. Panel **h** adapted from ref. 78, Springer Nature. Panel **i** adapted with permission from ref. 249, AAAS. Panel **k** adapted from ref. 254, Springer Nature Limited. Panel **l** adapted from ref. 257, Springer Nature Limited. Panel **n** adapted from ref. 204, Springer Nature Limited. Panel **o** adapted from ref. 52, Springer Nature Limited. Panel **q** adapted with permission from ref. 51, Springer Nature Limited. Panel **r** adapted with permission from ref. 55, American Chemical Society.

method was applied to image the strain-induced anisotropic nucleation and growth of coexisting insulating (blue) and metallic (red) domains in single crystals of the bilayer ruthenate $Ca_3(Ti_xRu_{1-x})_2O_7$ across its first-order Mott transition at $T \approx 95$ K (ref. 52) (Fig. 7o). Future experiments might include the use of stretchable or bendable substrates to induce even larger strain for thin-film studies.

Liquid and gaseous environments

For the study of biological samples or bio-chemical and electro-chemical reactions, it is often required that the sample is immersed in a liquid. To address this need, two different approaches have been developed (Fig. 7p). In the first approach, s-SNOM imaging of a wet sample is achieved by covering the biological object — a wet Tabaco mosaic virus in the first implementation — with graphene and scanning the graphene-covered object[259]. This method offers the advantage that neither the tip nor the IR beam needs to be immersed in the liquid, thus avoiding tip contamination and IR absorption by the liquid. The idea was further developed, leading to membrane-capped liquid cells (Fig. 7p) that allow for IR spectroscopic studies of biomolecules in water or buffer solution[260,261], electrochemical processes in electrolytes[262,263] and even larger objects including living cells[51,102,264] (Fig. 7q) with nanoscale spatial resolution. In the second approach, both the sample and the tip are immersed in the liquid, analogous to typical AFM operation in liquids. To avoid IR absorption by the liquid, the tip is illuminated from below through an IR-transparent substrate[55,265,266] (Fig. 7p). The technique has been applied for chemical identification and structural analysis of biomembrane fragments of the archaeon *H. salinarum* (purple membrane)[55] (Fig. 7r), catalase nanocrystals and biomimetic peptoid sheets[265] as well as for studying the influence of water on the dispersion of phonon polaritons on hexagonal boron nitride[266]. When the sample has to be studied in inert gases, the whole s-SNOM setup can be placed into environmental chambers, including gloveboxes[133,267,268].

Applications

Several review articles discuss s-SNOM and nano-FTIR applications in soft matter and solid-state materials[18,24], energy materials[269],

corrosion[270] and biological sciences[23,271,272]. Here, we organize the applications into three categories: the mapping of material properties, the characterization of structures and devices and the study of phenomena.

Mapping of local material properties

s-SNOM and nano-FTIR have been widely applied for the nanoscale mapping of the chemical composition of polymers[38,46,73,123,192,273–276], biological matter such as proteins[36,89,191,227,261,277,278] and phospholipids[279,280], biominerals[200,281,282] and inorganic crystals[45,201,231,283]. Furthermore, structural properties can be mapped, which allows for distinguishing crystallinity and crystal orientation[95,202,203,274,284,285], strain[160,204,205,233,258] or the secondary structure of proteins and other macromolecules[190,191,277,278,286,287]. For materials such as semiconductors[35,78,94,133,194–196], Mott insulators[221,225], topological insulators[76,105] and perovskites[236,268,288–292], one of the major applications is the discrimination between weakly insulating and highly conducting domains, as well as the quantitative mapping of the mobile carrier concentration and mobility.

For example, in block copolymer samples, the phase-separated components can be distinguished and identified based on their molecular vibrational fingerprint[273] (Fig. 8a). In Li_xFePO_4 microcrystals, which are used in electrode materials for Li-ion batteries, IR s-SNOM images provide direct evidence of coexisting $LiFePO_4$ and $FePO_4$ phases[293] (Fig. 8b). This image highlights the remarkable potential of s-SNOM for characterizing electrochemical materials and interfaces. Furthermore, the secondary structure of proteins can be mapped at the level of single aggregates and fibres[191] (Fig. 8c), which is crucial for studying protein aggregation and amyloid fibrils related to neurodegenerative diseases.

Characterization of structures and devices

Imaging and characterizing nanoscale structures are crucial for understanding their composition and function, optimizing their performance and advancing new technologies. s-SNOM and nano-FTIR have been applied to study the chemical composition and structural properties of various samples, including individual viruses[36,191,294],

Materials

Semiconductors

Low-dimensional materials

Biomaterials and energy materials

Polymers

Oxides

Topological systems

Structures

(Opto)electronic devices

Nanostructures

Photonic components

Biological structures

Phenomena

Light–matter interactions

Phase transitions

(Bio)chemical phenomena
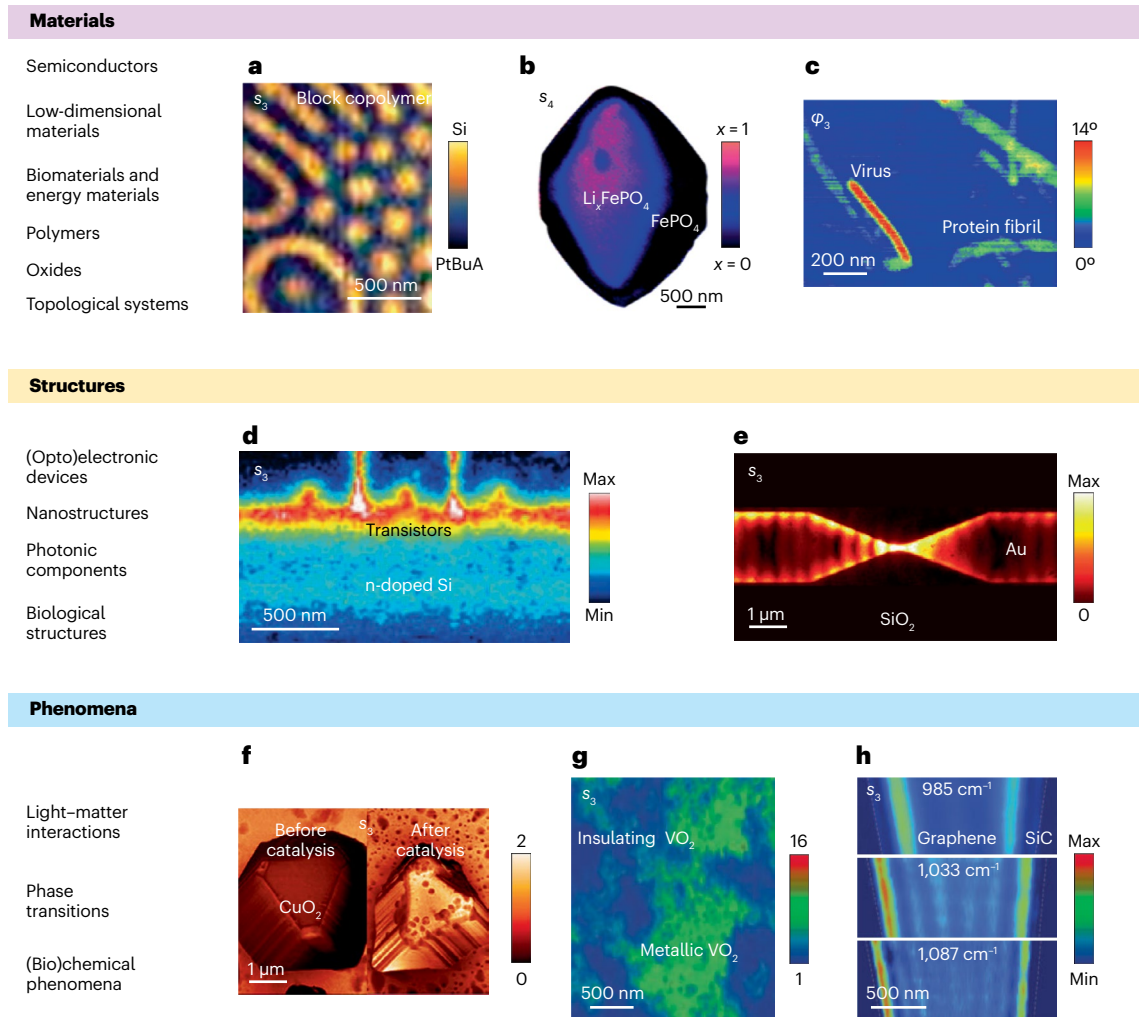
Fig. 8 | Overview of s-SNOM applications. a, Infrared (1,728 cm^{-1}) amplitude image of a block copolymer, visualizing absorption based on the vibrations of the carbonyl bond in the PtBuA block. **b**, Infrared (1,042 cm^{-1}) amplitude image of phase distribution of lithiated Li$_x$FePO$_4$ (LFP) and delithiated FePO$_4$ (FP), showing an outer FP-rich region and an inner LFP-core. **c**, Infrared (1,660 cm^{-1}) phase image distinguishing a virus (dominantly α-helical protein structure) from insulin fibrils (dominantly β-sheet protein structure). **d**, Terahertz (84.7 cm^{-1}) amplitude image of a polished cut through a multiple-transistor device structure, revealing materials and carrier concentration. **e**, Near-infrared (7,017.5 cm^{-1}) amplitude image of surface plasmon polaritons (SPPs) on a tapered metal stripe, showing SPP focusing and interference of forward propagating (from left to right) and back-reflected SPPs. **f**, Infrared (905 cm^{-1}) amplitude image of CuO$_2$ nanocrystals before and after the electrochemical reduction of CO$_2$. **g**, Infrared (930 cm^{-1}) amplitude image revealing the spatially inhomogeneous insulator-to-metal transition of VO$_2$ at 343 K. **h**, Infrared amplitude images of plasmon polaritons on graphene, which manifest as fringes parallel to the graphene edges. Panel **a** adapted with permission from ref. 273, American Chemical Society. Panel **b** adapted with permission from ref. 293, American Chemical Society. Panel **c** adapted from ref. 191, CC BY 4.0. Panel **d** adapted with permission from ref. 90, American Chemical Society. Panel **e** adapted with permission from ref. 177, American Chemical Society. Panel **f** adapted with permission from ref. 376, American Chemical Society. Panel **g** adapted with permission from ref. 221, AAAS. Panel **h** adapted from ref. 135, Springer Nature Limited.
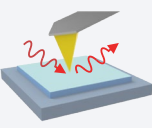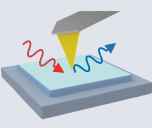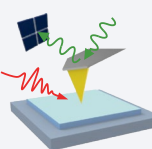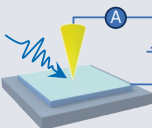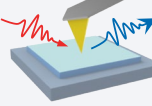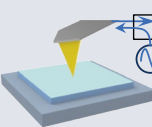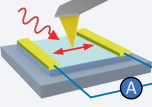
fibrils and fibres[190,191,277,295], membranes[55,89,123,265], cells[51,296–298], bones[281], teeth[102] and core–shell polymer[299] and metal-organic framework[56] particles. Furthermore, semiconductor nanowires[35,138,208], 2D electron gases at interfaces[206,207,228,300] and moiré superlattices in twisted 2D materials[156,157,301] have been explored, often in terms of their local conductivity and optical excitations. Electronic and optoelectronic building blocks and devices can be characterized as well, such as transistors[90,196] or static random-access memory samples[94,133], graphene-based IR and THz photodetectors[302–304] and solar cells[305].

For instance, the THz image of the cross-section of an industrial transistor device (Fig. 8d) allows for distinguishing the different materials and, more importantly, to measure the local carrier concentration[90].

Moreover, the function of the studied structure or device can be tested and verified. In this regard, s-SNOM has been widely used for visualizing the localization, guiding or focusing of electromagnetic fields with nanophotonic elements[306], including linear plasmonic and phononic waveguides[177,307], dielectric[308], plasmonic[41,91,150,183,186,188,189] and phononic resonators[161,163,164,185], polaritonic crystals[157,309–312], twisted

Table 1 | Comparison of light-assisted scanning probe microscopy techniques

Technique	Basis and resolution	Illumination	Measured quantity	Accessible properties and effects	Environmental conditions	Samples
s-SNOM	AFM 10–100 nm	CW fs to ps pulses Vis to sub-THz	Amplitude and phase of elastically tip-scattered light	Complex-valued dielectric function and related materials properties such as chemical composition, structure and conductivity as well as near-field distributions of EM modes	Air Vacuum Liquid Gas Low-T to RT	Insulators Conductors Bulk Thin layers
TERS[23,365–368]/TEPL[367]	AFM, STM 1–100 nm	CW fs to ps pulses UV to near-IR	Intensity of inelastically tip-scattered light (Raman, PL)	TERS: molecule and lattice vibrations, yielding information, for example, on chemical composition and structural properties TEPL: electronic transitions, yielding information on bandgaps, binding energies, carrier recombination, radiative emission rates	Air Vacuum Liquid Gas Low-T to RT	Insulators Conductors Thin layers, often on Au substrate
AFM-IR[365,369]/PiFM[370]	AFM 10–100 nm	ps to ms pulses Vis to IR	Cantilever response due to sample expansion (AFM-IR) or optical forces (PiFM)	AFM-IR: absorption, yielding information on chemical composition and structure PiFM: dielectric properties, yielding chemical composition and structural properties, as well as near-field distributions of EM modes	Air Liquid Gas RT	Insulators Conductors Bulk Thin layers
THz-STM[22]	STM <1 nm	Subcycle THz pulses	Tunnel currents induced by strong THz near fields	Transient occupation of density of states and related ultrafast dynamics	Air Vacuum Low-T to RT	Thin layers on conducting substrate
LTEN[371,372]	AFM 10–100 nm	fs pulses Vis and THz	Amplitude and phase of optically induced THz emission scattered by the tip	Mobile carrier properties	Air Vacuum RT	Insulators Conductors Bulk Thin layers
MIM[373]	AFM 10–100 nm	Microwaves	Amplitude and phase of reflected microwaves	Complex-valued dielectric function and related materials properties such as microwave conductivity	Air Vacuum Liquid Gas Low-T to RT	Insulators Conductors Bulk Thin layers
PCN[374,375]	AFM 10–100 nm	CW UV to THz	Photocurrent-induced near fields at tip apex	Optoelectronic, thermoelectric and thermal properties	Air Vacuum Low-T to RT	Conductors

AFM-IR, atomic force microcopy-based infrared spectroscopy; CW, continuous wave; EM, electromagnetic; IR, infrared; LTEN, laser THz emission nanoscopy; MIM, microwave impedance spectroscopy; PCN, near-field photocurrent nanoscopy; PiFM, photo-induced force microscopy; PL, photoluminescence; RT, room temperature; s-SNOM, scattering-type scanning near-field optical microscopy; TEPL, tip-enhanced photoluminescence spectroscopy; TERS, tip-enhanced Raman scattering spectroscopy; THz, terahertz; THz-STM, THz-scanning tunnelling microscopy; UV, ultraviolet; Vis, visible.

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polaritonic slabs[313,314] and polaritonic metasurfaces[170,315]. For example, the s-SNOM image of a metal waveguide structure (Fig. 8e) could verify the efficient compression (focusing) of near-IR plasmon polaritons propagating through a tapered waveguide section[177]. The specific probing mechanisms related to mapping localized and propagating electromagnetic fields are illustrated in Fig. 5b–f.

Exploring phenomena

s-SNOM and nano-FTIR offer nanoscale spatial resolution and high chemical sensitivity for exploring chemical and biological phenomena, all while being largely non-invasive. For example, heterogeneous catalytic and enzymatic processes can be studied on individual nanoparticles[56,316,317] (Fig. 8f). Further applications include the local characterization of corrosion and material degradation[318–320], electrochemical processes[262,263,321], growth of water layers[322], hydrogen storage in magnesium[101], (bio)mineralization[323], as well as protein folding and aggregation[227,261,277]. Phase transitions in different material classes such as ferroelectrics[231], correlated oxides[52,229,233,245,256,324,325] and transition metal dichalcogenides[326] are another widely studied phenomenon, particularly the Mott metal–insulator transition in VO_2 (refs. 221–223,225,240) and V_2O_3 (ref. 226) (Fig. 8g). Furthermore, the photoexcitation of charge carriers, as well as carrier accumulation at defects and grain boundaries, for example, in photovoltaic materials and battery materials, can be studied[78,154,195,197,288,305]. The nanoscale concentrated near fields at the tip apex also allow for circumventing the momentum mismatch between free-space light and ultra-confined hybrid light–matter quasiparticles, such as plasmons, phonons and exciton polaritons, and thus for mapping their propagation or localization on nanostructured surfaces[106,135,136,140,144,150,152,173]. For example, Fig. 8h shows an image of graphene plasmon interference fringes near the graphene edges, from which the plasmon dispersion can be measured[135] (see also Fig. 5b).

Perspectives

Advances in instrumentation, light sources, scanning methods, environmental control and artificial intelligence are set to enhance s-SNOM applications across various fields.

Future developments at synchrotrons[19,21,39,118,119] and free electron lasers[95,96,253] together with tip engineering[82,83,86,327,328] could enable routine nano-FTIR spectroscopy at far-IR[19] and THz frequencies[117]. Monochromatic THz imaging could benefit from QCLs and self-detection schemes[92,93]. Tunable tabletop laser sources such as narrow-band OPO systems[98] could improve the S/N ratio of nanospectroscopy based on sweeping the laser frequency[109,110]. Implementations of ultrafast lasers and field-detecting approaches, such as electrooptic sampling, could be applied for space–time mapping of electromagnetic wave propagation in low-dimensional or photonic systems with ultra-short, subcycle time resolution[78,329] and for near-field imaging and spectroscopy approaching atomic length scales[330]. Non-classical light with time-correlated photon pairs[331,332] may be used for studying quantum phenomena at the single quasiparticle level.

The combination of s-SNOM with traditional scanning probe microscopy techniques, such as force–distance spectroscopy[333], magnetic force microscopy[233] and Kelvin probe force microscopy[288,334], will significantly advance multi-messenger nanoscopy[233,335]. This integration enables the simultaneous and comprehensive analysis of optical, mechanical, transport and magnetic properties. We particularly anticipate benefits from combining s-SNOM with other light-assisted scanning probe microscopy techniques (Table 1). Notably, a fruitful combination has emerged with photocurrent nanoscopy and laser THz

emission nanoscopy, both of which are largely developed from s-SNOM instrumentation and utilize higher-harmonic signal demodulation. Owing to their close connection with s-SNOM, these two methods are described in detail in the Supplementary information.

The use of different tip-modulation schemes (such as peak force AFM)[336], better usage of low-repetition rate[236,337,338] and high-intensity ultrafast lasers may enable the nanoscale probing of nonlinear dynamics or photoinduced phase transitions[223,240]. Retrieving valuable information from hyperspectral data[123,133] with a low S/N ratio might be improved by the integration of compressed sensing[124–128] and advanced machine-learning methods[219] to enhance data analysis[339] and/or to accelerate data acquisition speed. Advances in modelling and calibration methods[340], in combination with advanced machine learning, may also push forward the idea of near-field optical nanotomography[74,76–78], that is, the measurement of the local sample permittivity in multilayer samples or more complex 3D sample geometries as a function of both lateral and vertical position.

We anticipate an increasing role of s-SNOM in probing corrosion and material degradation[318–320,341], electrochemical processes[262,263], artificial synaptic devices[342] and battery materials[293]. This includes nanoscale studies of the discharge behaviour in conversion batteries, decomposition pathways of electrolytes[321], formation of interphases[343], as well as physicochemical interplay at electrode/electrolyte interfaces[293,344,345]. Advances in wet cell sample fabrication[260–262] could facilitate the routine in situ nanoscopy of various aqueous biological materials, including living cells[51], tissues and catalytic materials[346]. Mapping the secondary structure of proteins[190,191,261,278] might benefit the understanding of the molecular-level development of Alzheimer, Parkinson and other neuro-degenerative diseases. The capability of s-SNOM to quantitatively analyse polymer nanocomposite materials and particles could benefit polymer synthesis[24,273,299,347] and help the identification of microplastics and nanoplastics[348].

We envision the further exploration of new quantum phases utilizing cryogenic s-SNOM at ultralow temperatures via the application of electric[254,255] or magnetic[257] fields. In this regard, THz or multi-THz photons are especially suitable for probing low-energy excitations (in the order of 1–10 meV) at cryogenic temperatures[232,349], including correlation gaps, carrier densities or quasiparticle dispersions in topological semimetals[350], low-dimensional material systems[329,351,352] or superconductors[353–355]. By integrating simultaneous near-field photocurrent mapping, new and innovative measurement techniques can be developed to advance the study of quantum phase transitions under extreme conditions.

We finally anticipate a growing role of s-SNOM in exploring fundamental aspects of nanoscale strong light–matter coupling involving plasmons, phonons, excitons and molecular vibrations[146,356–364]. Different application scenarios can be distinguished, depending on sample and illumination geometries: in one, s-SNOM minimally invasively probes the intrinsic light–matter coupling of the sample[146,358,359,361]; in another one, the probing tip actively engages in the coupling process[356,357,363], enabling the controlled tuning of the coupling strength by adjusting, for example, the distance between the tip and the sample.

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Author contributions

Y.A. proposed the initial idea and structure of this Review. R.H. completed the main text, with contributions and figures from Y.A., M.L. and X.C., and input from D.N.B. All authors contributed to the selection of key references used in this Review.

Competing interests

R.H. is a co-founder of Neaspec, now part of attocube systems, a company producing scattering-type scanning near-field optical microscope systems, such as the one described in this Review. The remaining authors declare no competing interests.

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