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Special Collection: Optical Nanoprobe Spectroscopy and Imaging

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The power of optical spectroscopy and microscopy for minimally invasive characterization of materials is well established across many disciplines. However, in general, its spatial resolution is inherently limited by the diffraction of light. To circumvent this limitation, it was proposed already a century ago to make use of the evanescent character of the near-field of light.[1] Following the conceptual realizations by Ash and Nicholls,[2] Pohl *et al.*[3] demonstrated ∼25 nm spatial resolution in the visible using tapered optical fiber tips manipulated by atomic force microscopy. Here, the evanescent wave penetrating a subwavelength aperture is brought in close proximity to a sample to harvest the spatially highly confined near-field interaction. The derived techniques termed near-field scanning optical microscopy (NSOM) or scanning near-field optical microscopy (SNOM) and associated theories established the principles of sub-diffraction spatial resolution optical imaging.

While NSOM or SNOM provides for a promising approach to optical nano-imaging, the limitations soon became apparent. Relying on a tapered optical fiber with a sub-diffraction sized aperture, waveguide cutoff, low throughput, dispersion, and transparency limit practical sensitivity to visible spectroscopy in linear optics and photoluminescence imaging. The extension into the infrared, or implementation of Raman, nonlinear, and coherent spectroscopies, proved very difficult.

It was soon recognized that instead of aperture confinement with an optical fiber, near-field localization of light with just a metallic scanning probe tip is also possible.[4,5] This alternative approach equally provides for near-field imaging, yet with several superior attributes of improved sensitivity, higher spatial resolution, and broader wavelength range. This led to the terminology of *apertureless* or *scattering* SNOM (*a*-SNOM or *s*-SNOM)—with *s*-SNOM now the more widely adopted term with tip-induced scattering of the near-field into detectable far-field radiation reflecting the contrast mechanism.

Significantly, *s*-SNOM readily allowed, e.g., for the extension into the mid-infrared[6] by combining modulation techniques and spectroscopic imaging[7] using interferometric detection with full phase and amplitude information (nano-FTIR and nano-ellipsometry).[8] In parallel development, the local field-enhancement of the metallic tip provided the much-needed boost in sensitivity to allow for tip-enhanced Raman scattering (TERS)[9,10] and opened the development into the nonlinear-optical regime[11] with nanometer spatial resolution. Related, yet not near-field techniques, photo-induced force microscopy (PiFM) or photo-thermal AFM (IR-AFM)[12] relies on the exquisitely sensitive AFM opto-mechanical sensing of a thermal sample expansion and provides for IR absorption spectroscopy with nanometer spatial resolution.

Initially, field-enhancement as in TERS and scattering as in *s*-SNOM were thought to be rather independent contrast mechanisms of the different modalities of near-field nano-imaging. Later, it was recognized that the localized plasmon and optical antenna coupled light–matter interactions in the tip–sample junction are the common underlying mechanism.[13,14] This led to a generalization based on a unified description of the role of the tip as a nano-antenna or -cavity[13,15,16] mediating the coupled tip–sample induced near-field polarization. Applicable in principle to any optical process, this then led to a proliferation of the field of nano-probe imaging over the past two decades. Implementing a series of new spectroscopic methods, rapidly maturing from proof-of-concept to analytical, material, and quantum science applications, solved outstanding problems by spatial, spectral, and temporal nano-imaging.

Beyond achieving merely super-resolution imaging across the full electromagnetic spectrum from the UV to MHz,[17] and with in

principle and optical modality, optical nano-probe imaging is not merely an extension of far-field microscopy to higher spatial resolution. Key attributes are improved sensitivity and contrast based on the enhancement of light–matter interaction in the near-field (Purcell effect) and extension of selection rules compared to far-field spectroscopy.[18] With the near-field providing momentum states at IR frequencies comparable to far-field x-ray radiation, this opened plasmon, exciton, and phonon polariton nano-imaging and -control[19,20] otherwise not possible by far-field excitation.[21,22] Further, previously inaccessible fundamental phenomena, from the elusive thermal near-field, which surrounds every object at finite temperature,[23] to radiative heat-transfer in the near-field on atomic scales,[24] can now be probed.

Combining ultrafast and nonlinear optics and spectroscopy with nano-probe imaging has become one of the recent frontiers in the field. Simultaneous nanometer spatial and femtosecond temporal resolution is achieved from probing few-fs coherent dynamics on the nanoscale,[25] to pump-probe nano-imaging with far from equilibrium excitation[26,27] turning ultrafast movies of coupled quantum dynamics in materials. Similarly, the long-envisioned dream of atomic resolution imaging, with ultrafast THz-STM[28,29] and with intramolecular Raman,[30] became reality, yet the understanding of the contrast mechanism is still in its infancy.

The field of nano-optical imaging science is still rapidly expanding with both new techniques and new application areas. One growth area is the extension from room temperature imaging under ambient conditions to vacuum and cryogenic temperatures down to a few kelvin to image a wide range of quantum phenomena in, e.g., 2D materials[31] and complex oxides.[32] Likewise, extension to variable pressure, in liquid, and *in situ* conditions permits nanoscale probing of chemical and biological processes.

A particularly interesting development is that the field initially was much concerned about the perturbation and convolution of the tip in the imaging process—issues which have since been resolved through the selectivity of the detection process, understanding the role of the tip in the light–matter interaction, and well-founded modeling, with the goal of the tip to only minimally perturb the material response to be studied. This concept, however, has recently experienced an interesting development in the opposite direction. Here, by purposefully perturbing the material response with the tip itself, new spectroscopic insights can be gained through active control of the tip–sample response. For example, in inducing tip-induced strain, strong laser field perturbation or modification of local electromagnetic density of states and Purcell enhancement competing processes in complex materials can be accessed.[33,34] Most notably, the extreme case of tip-enhanced strong coupling (TESC), where the tip nano-localized optical field forms a nano-cavity with the sample,[35] results in the formation of quantum hybrid light matter states that allow for quantum-enhanced imaging, quantum sensing, and with single quantum state control even at room temperature.

Other exciting new directions are the expansion toward multimodal imaging in combination with electron and x-ray techniques. Further, to overcome long image acquisition times inherent to raster-scanning probe microscopy in general, the implementation of new computational imaging with prior knowledge, machine learning, and compressed sensing algorithms are being explored. New laser light sources with more controlled light fields, from super-continuum to synchrotron sources, new detectors, and detection schemes with extended spectral sensitivity are having great impact.

This editorial provides an overview of state-of-the-art contributions to optical nano-imaging and -spectroscopy. The field of IR nano-polaritonics is represented and continues to attract much attention with advances in surface phonon polariton (SPhP)[36,37] and hyperbolic phonon polariton (HPhP) nano-imaging.[38,39] In the extension to low-temperature IR, *s*-SNOM has been achieved using Akiyama probes.[40] Innovation in detection schemes with benefits for ultrafast *s*-SNOM imaging has been demonstrated.[41] Beyond near-field imaging, surface plasmon interferometry in photoemission electron microscopy has been advanced,[42] nonlinear-optical super-resolution achieved in the infrared,[43] and with single quantum dot spectroscopy, the sensitivity in PiFM improved.[44] This collection of works shows the many facets of the field as it continues to diversify with new methods and new applications.

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