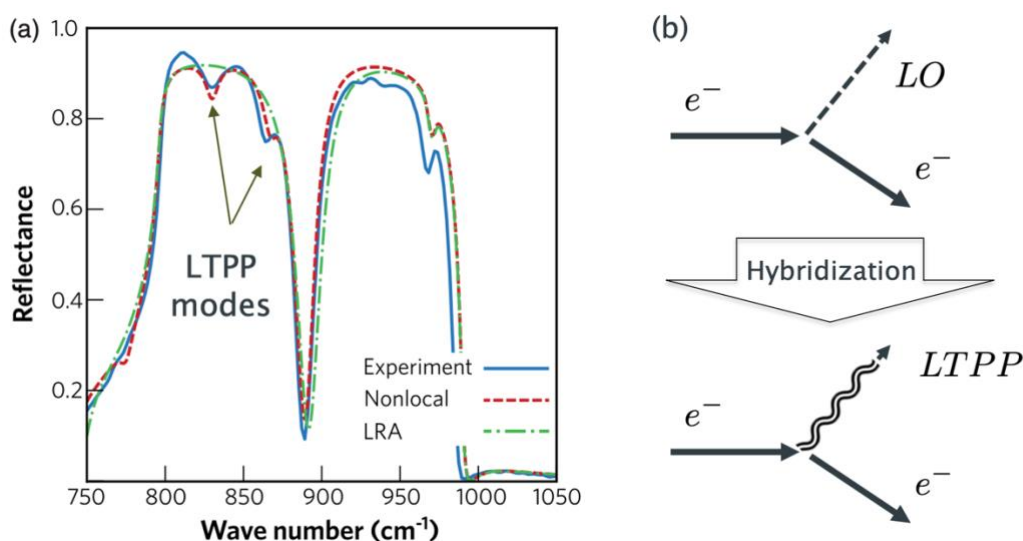


# Nanophotonics and Optoelectronics with surface phonon polaritons

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Surface phonon polaritons, electromagnetic modes supported at the interface of polar materials have opened new avenues for mid-infrared nanophotonics and optoelectronics, thanks to their extremely sub-wavelength confinement and long lifetimes<sup>1</sup>. Given the lack of adequate materials with bandgap in the mid-infrared region, electrical excitation of phonon polaritons has until now been performed either thermally, leading to narrowband directional thermal emitters<sup>2</sup>, or using quantum cascade structures<sup>3</sup>. Notwithstanding their merits, the former approach has intrinsically limited efficiency and cannot lead to lasing, while the latter presents the usual complexity and cost constraints of standard quantum cascade lasers. An important dissipation channel in polar materials is the emission of longitudinal optical phonons via the Fröhlich interaction, which accounts for a large part of Ohmic losses. Due to their longitudinal nature these phonons do not couple with light. Transverse optical phonons couple with light instead, and they can hybridize with photons to create phonon polaritons.



**Fig. 1** In panel (a) we show the reflectance of a nanometric dielectric multilayer. The experimental data shows resonances which are not correctly described by a local response theory (LRA) ignoring the phonon dispersion. Our nonlocal theory from Ref.<sup>4</sup> correctly reproduces the resonances and identifies them as LTPP modes. In panel (b) we sketch the concept of LTPP emission, in which the Fröhlich interaction in polar semiconductors is dressed by the photonic field, leading to the resonant electrical emission of LTPPs.

We discovered that longitudinal and transverse optical phonons, which are perfectly decoupled at small wavevectors, can become coupled when the large-wavevector dispersion of the phonons is taken into account. Our nonlocal theory predicted the existence of novel quasiparticles with a hybrid longitudinal and transverse nature, which we named longitudinal-transverse phonon polaritons (LTPP). We initially experimentally observed them in polytypes of silicon carbide (SiC) characterized by elongated unit cells which fold longitudinal phonons back into the light-line<sup>5</sup>. We then demonstrated that LTPP are a ubiquitous feature of polar nanostructures when the crystal features are small enough to couple photons to large wavevector phonon modes<sup>4</sup> (see Fig. 1(a)). The LTPPs can thus be electrically excited thanks to their longitudinal component, while emitting mid-infrared light in the far-field thanks to their transverse one, as schematized in Fig. 1(b).

I will conclude this talk showing some recent theoretical results describing the LTPP-mediated electrical emission of mid-infrared radiation from polar dielectrics. Our results demonstrate that this emission channel has the features to empower a novel generation of efficient and ubiquitous mid-infrared optoelectronic devices.

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# Anisotropic Polaritons in Heterostructures made of Rotated Thin Layers and Dielectric Spacers

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Polaritons in strongly anisotropic media have recently emerged as a promising tool for controlling light at the nanoscale. Among them, understanding phonon polaritons (PhPs) in biaxial van der Waals crystals [1] arise as one of the cornerstones for future communication and sensing devices at the mesoscopic regime. In this sense, twisted heterostructures made of biaxial slabs offer singular properties, such as confinement [2], canalization, ultralow losses and topological transitions [3], among others. However, a general theoretical model that describes the light propagation in these systems is still needed. Moreover, light propagation in systems made of the stacking of biaxial slabs and dielectric media [4] remain exempt of a general theoretical model. Here [5], a complete general derivation of a model for such a system is performed, considering three rotated biaxial slabs separated by dielectric media, as well as a quantitative characterization of the coupling of the electromagnetic modes of the anisotropic materials. An extension to simpler systems made of anisotropic materials and a comparison with their analytical models is also detailed in this paper, showing a perfect agreement with previous models [4,6]. All calculations are compared with full-wave electromagnetic simulations. This work lays the foundations for future experiments in the field of twistoptics, allowing for a theoretical prediction and justification of the behavior of electromagnetic modes in heterostructures made of twisted biaxial slabs measured by near-field techniques.

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# Quasinormal mode theory of Purcell factors and chiral radiation from nanophotonic resonators near an exceptional point

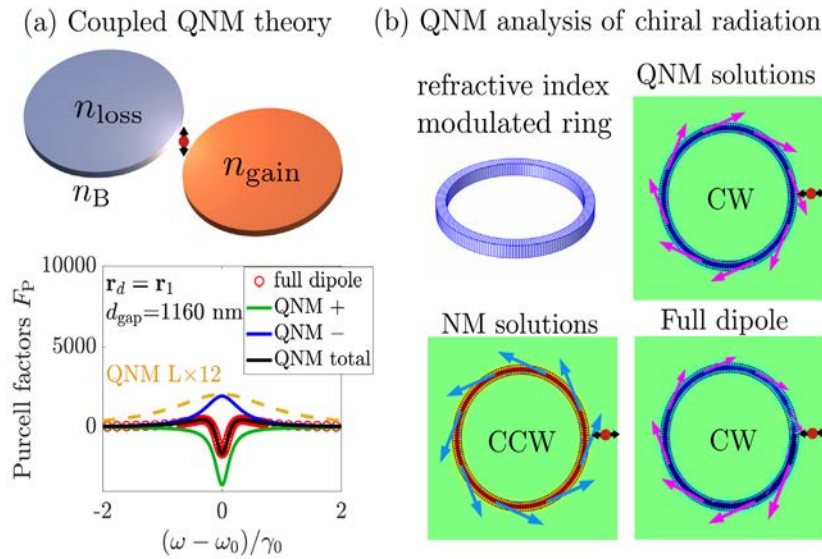
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Non-Hermitian optical physics has been intensively investigated recently, exploring aspects of parity-time symmetry and exceptional points (EPs). One general design consists of two resonators or coupled modes, e.g., one with material loss and the other with gain. Coupled normal mode (NM) theory predicts that a perfect EP can occur when the loss and gain is balanced. However, describing open cavities with NM theory is ambiguous, where the loss is usually added phenomenologically, which motivates one to develop a more quantitative non-Hermitian theory for the cavity modes. Here we use quasinormal modes (QNMs) to study coupled cavity resonators, and describe the new physics that emerges in these systems. We show how one can use just the bare QNMs of the individual resonators to have a quantitatively accurate theory of the emerging hybrid modes, using coupled QNM theory. We also show how the criteria for finding EPs is generalized. Furthermore, we show a drastic breakdown of the widely used classical Purcell formula for coupled gain-loss media [1] and show how this is fixed [2]. A second way to achieve EP-like phenomena is through a modulated refractive index in a single whispering gallery mode resonator, as demonstrated experimentally in [3], where they also reported chiral emission for linear dipole emitters and explained this in terms of a decoupling of the eigenmodes to a “missing dimension”. We show how our QNM theory can successfully explain the chiral radiation close to an EP in terms of only the underlying two QNMs [4], and we show how the chirality can be controlled in terms of dipole position and frequency.



**Fig. 1** (a) Schematic of a coupled loss-gain resonator and computed classical Purcell factors for a dipole placed in the gap. ‘QNM +/-’ are the two hybrid modes obtained from coupled QNM theory. Their separate contribution (green/blue curves) and total contribution (black curve) are shown, which agree very well with the full numerical dipole results (red circles). For comparison, ‘QNM L’ shows the case with the bare lossy cavity only, which is multiplied by 12 for clarity (orange curve). (b) Schematic of a refractive index modulated ring and the chiral radiation of a linear (polarized) dipole from QNM/NM solutions and full numerical dipole calculations. The QNM solutions recover the full dipole results, while the NM solutions fail.

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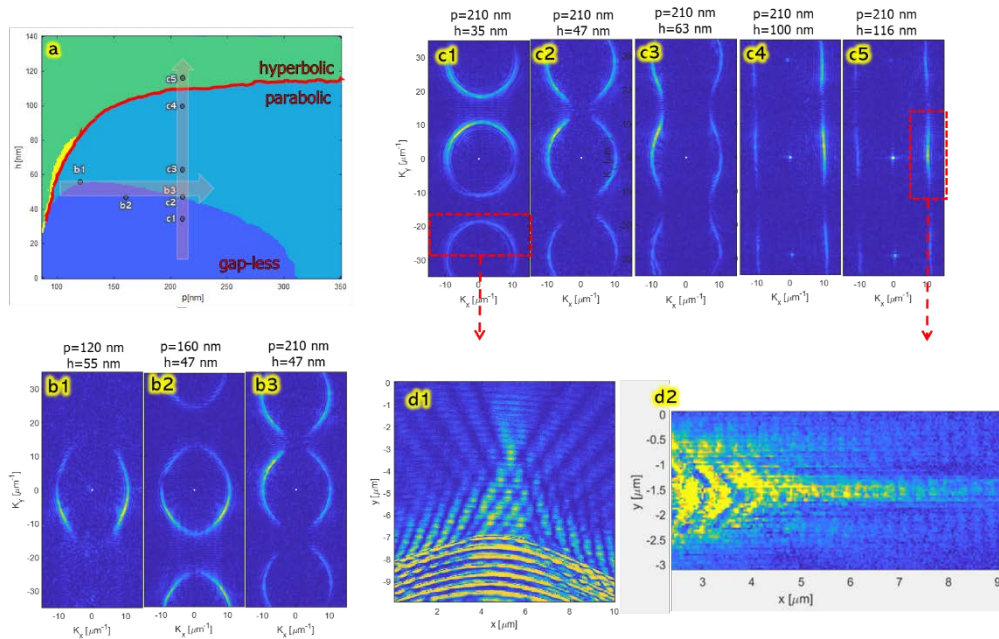
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# Topological transitions and surface umklapp scattering in periodically-modulated metasurfaces beyond the effective medium

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Metamaterials and metasurfaces are at the pinnacle of wave propagation engineering, with their design been mainly focused on deep-subwavelength periodicities, practically forming an effective medium. Such an approach overlooks important structural degrees-of-freedom, e.g. the interplay between modulation amplitude and periodicity, which determine the properties of waves, guided in the meta-structure. Metasurfaces (MSs) – the interfaces between two materials structured in the subwavelength scale[1] – have been widely investigated in recent years for their ability to manipulate light for various applications. Additionally, they play an important role in surface wave engineering, attaining unidirectional and spin-selective coupling, as well as surface wave-guidance at low frequencies. Interestingly, the surface wave properties can be strongly influenced even by simple periodic structuring of the interface, exhibiting tunable propagation characteristics. In this respect, one-dimensional modulation was shown to produce hyperbolic metasurfaces (HMSs), wherein the modulation amplitude tuned the spatial dispersion anisotropy from elliptic to hyperbolic [2-4], giving rise to a topological transition predicted by effective medium theory. Here, we show control and manipulation of surface waves achieved by periodically modulated interface that go beyond the effective medium. We reveal dispersion regimes and topological transitions unattainable in effective media and utilize phase-resolved near-field microscopy to observe geometry-dependent transitions in the surface-wave transport as well as unique phenomenon of backward focusing – mediated by umklapp scattering. Our findings offer a comprehensive approach for engineering surface and guided waves in artificial periodic systems and can be implemented to produce novel kinds of photonic circuitry and electromagnetic modes with intricate and unique dispersion features.



**Fig. 1** control over surface wave diffraction. (a) a “phase diagram” comprising different surface-propagation regimes depending on the periodicity and depth of the structuring. (b-c) Fourier plane extraction from phase-resolved near-field measurements of the E-field under different structuring. (b) varying depth (c) varying periodicity. (d) near-field measurement of anomalous focusing based on the band marked by the red boxes. (1) Umklapp-mediated and (2) hyperbolic focusing.

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# Quantitative modelling and engineering of photoluminescence from light-emitting metasurfaces via absorption calculations

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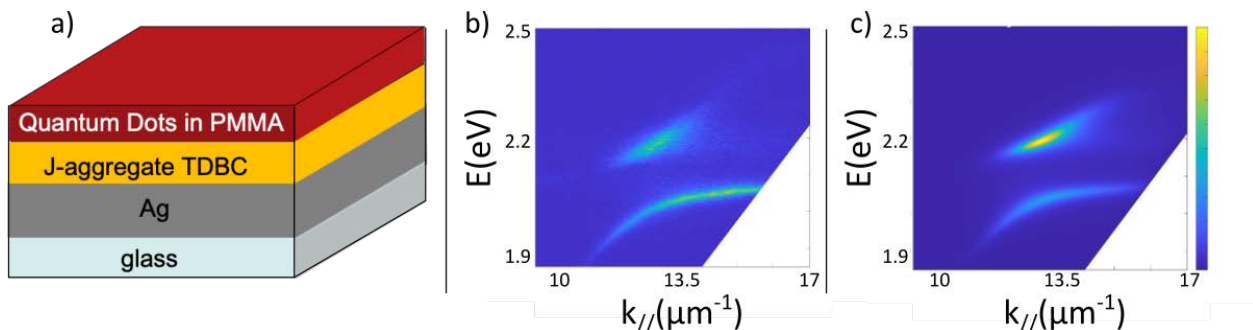
Light-emitting metasurfaces are ultrathin devices consisting of a nanostructured surface covered with dense ensemble of emitters. The interaction between emitters and the metasurface allows for a precise control of the emission properties. In the standard model, the emitters are considered as a collection of electric dipoles randomly oriented inside the structure, whose contribution can be added incoherently. Their emission spectrum is a Stokes-shifted counterpart of their absorption spectrum. The emission spectrum of the whole structure is then described as resulting from the modification of the fluorophore photoluminescence via radiative decay rate enhancement and extraction efficiency of the device [1]. However, this approach does not account for modifications of the spectrum influenced by temperature and pumping conditions and cannot predict the intensity of the emitted signal.

In this presentation, we first present a procedure to model emission by light-emitting metasurfaces using a generalized Kirchhoff's law formalism. We show that the power  $dP_e^{(l)}(\mathbf{u}, \omega)$  emitted by a metasurface in a direction  $\mathbf{u}$  at a frequency  $\omega$  can be expressed as [2]:

$$dP_e(\mathbf{u}, \omega) = d\Omega \iiint \alpha_{abs}(-\mathbf{u}, \mathbf{r}', \omega) \frac{\omega^2}{8\pi^3 c^2} \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega - \mu(\mathbf{r}')}{k_B T(\mathbf{r}')}\right) - 1} d^3\mathbf{r}' ;$$

This expression shows a product of the local absorptivity rate  $\alpha_{abs}$  by a Planckian exponential contribution depending on the temperature  $T$  and the photon chemical potential  $\mu$ .  $\alpha_{abs}$  encompasses the angular and polarization dependance of the structure. Therefore, the directivity of the system as well as its polarization features can be designed by engineering its local absorptivity, whereas the Planckian exponential explains spectral modifications between absorption and emission.

In the second part of the presentation, we apply our procedure to model the photoluminescence features of complex systems consisting of ensembles J-aggregated dyes (TDBC) deposited on metallic substrates [3]. We will highlight an important aspect of light-emitting metasurfaces engineering: far from material resonances, the absorptivity is extremely low - however, light emission can still occur provided that the Planckian factor takes significant values. Therefore, a quantitative and reliable modelling of emission also require accurate permittivity models in the low energy tail of the absorption spectrum. In an example involving various types of emitters (quantum dots and dye molecules, see Fig. 1), we will show that Brendel-Bormann models of permittivity overcome limitations faced when using Lorentzian models. Our work paves the way towards a reliable engineering procedure to design ultrathin light sources with on-demand properties, such as controlled directivity, polarization state and emission spectrum.



**Fig. 1 a)** Schematic of the system under study: a layer of quantum dots (QDs) embedded in PMMA are deposited on a layer of J-aggregate dye (TDBC molecules) and on silver. The system is excited at 445 nm and the emitted light is collected in a spectrometer. **b)** Photoluminescence map obtained experimentally. **c)** Photoluminescence map obtained by numerical simulations based on our local Kirchhoff's approach used with Brendel-Bormann's models of permittivities.

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# Nanophotonics controlling free-electron-light-matter interactions

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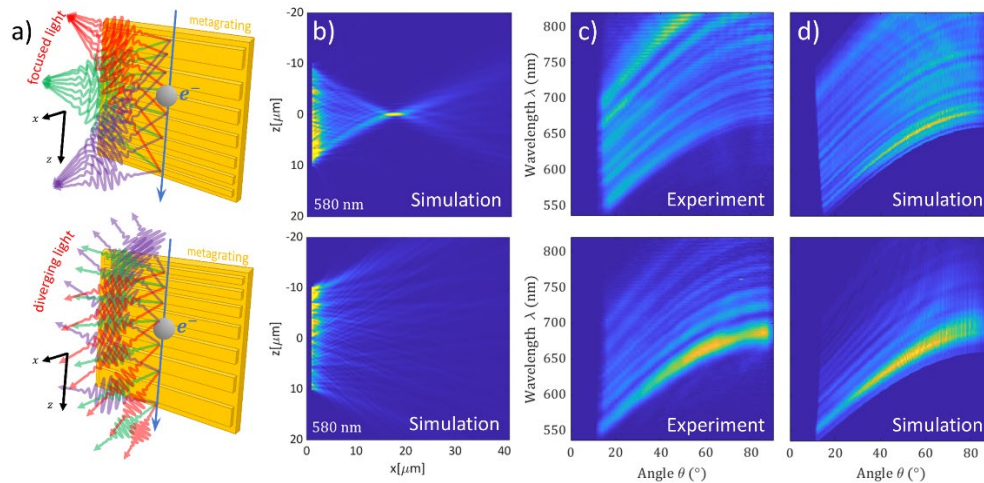
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The time-varying evanescent electric field of a free electron can couple to a broad spectral range of electromagnetic modes in a material, rendering a unique interplay between free electrons and light at the nanoscale [1]. In this work, we apply nanophotonics to manipulate free electron radiation mechanisms, and – vice versa – design optical near fields that permit a quantum-coherent modulation of the electron wave function.

Smith Purcell (SP) radiation is a broadband phenomenon occurring upon coherent excitation of periodically-arranged emitters by a grazing free electron, with the excitation phase-lag giving rise to discrete diffraction orders in the far field [2]. By designing nano-gratings with a non-linear chirp [3], we show – for the first time in experiment – that the wavefront of SP radiation can be shaped to induce lensing effects of focusing and defocusing near the grating surface (Fig. 1a, b). The corresponding cylindrical emission wavefronts are observed in the far field using in-situ hyperspectral angle-resolved light detection in a scanning electron microscope (SEM) at 30 keV incident electron energy. Our data (Fig. 1c) are found in good agreement with the results of analytical theory as well as a hybrid-simulation approach (Fig. 1c), combining full-wave numerical near-field calculations with a ray-tracing model of our light collection setup. To further exemplify the wide-ranging functionalities that can be embedded with electron-driven light sources, we design a metasurface composed of split-ring-resonator (SRR) meta-atoms, permitting simultaneous SP focusing and tunable polarization control via spatially-selective SRR mode excitation.



**Fig. 1** a) Metagratings of 20  $\mu\text{m}$  length with opposing chirp along the electron beam axis were patterned into a 40 nm thin gold film on a silicon substrate. b) Full-wave numerical simulations of the near field induced upon 30 keV free-electron excitation, revealing focusing (top) or defocusing (bottom) near the grating surface at a design operational wavelength of 580 nm. c) Simulated and d) measured hyperspectral angle-resolved far field emission patterns, featuring multiple characteristic curved emission bands.

Free electrons not only provide a unique source of electromagnetic excitation. Under external stimulation, their interaction with optical fields also permits a quantum-coherent manipulation of the electron wave function itself [4]. To this end, phase-matching is required between the optical field and the incident electron wave packet – a condition that can be only fulfilled in the presence of matter [5]. In particular, sub-relativistic electrons, as routinely provided by SEM, can undergo strong interactions with tightly-confined near fields at the nanoscale [6]. Here, we tailor the mode profile of a layered metasurface to enhance electron-light-matter coupling over short interaction ranges, permitting us to observe the quantum-coherent energy modulation of 6 keV-electrons in our new quantum scanning electron microscope (QSEM). Our work merges the worlds of nanophotonics and free-electron-light-matter interactions, rendering a prosperous platform for both fundamental research and advanced technological applications.

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# 2D chemical mapping of light driven reactions by plasmonic nanostructures

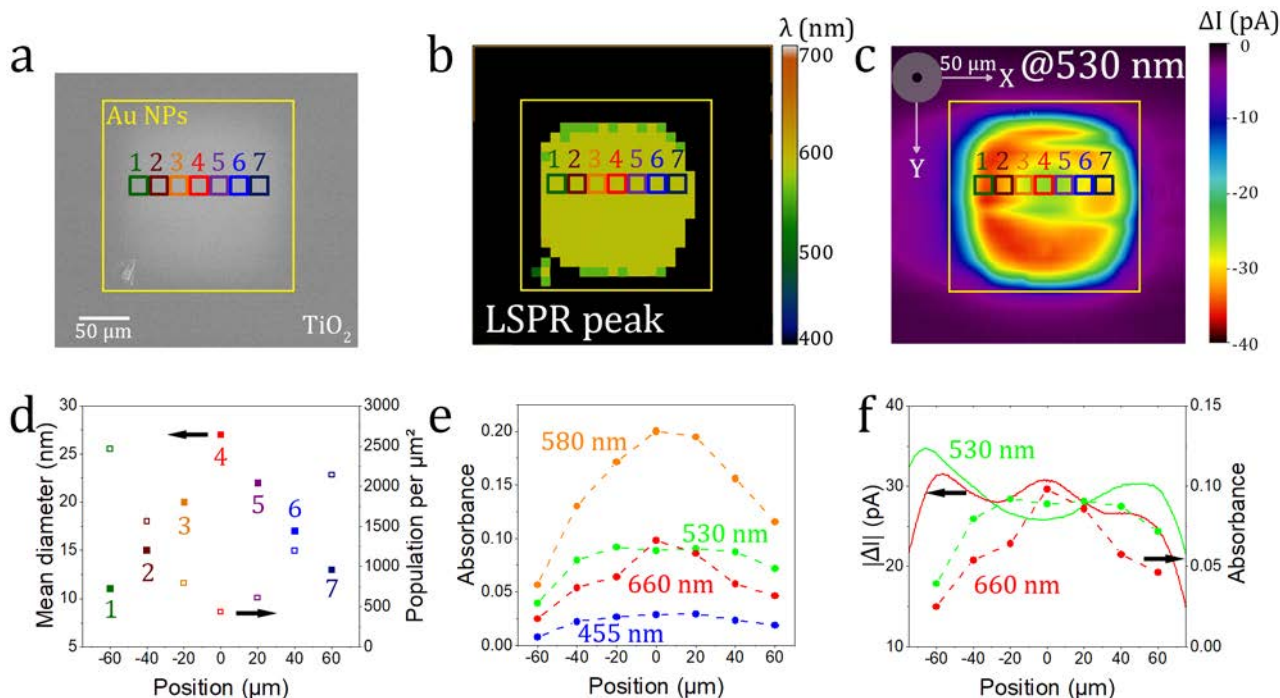
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Upon light illumination, surface plasmons (SPs) produce very intense electric fields localized in nanoscale volumes. SPs decay by generating non-thermal (hot) electron-hole pairs having enough energy to drive chemical reactions. Plasmonic photocatalysis received soaring interest due to the possibility of using plasmonic effects to enhance reactions rates or activate non-trivial reaction pathways [1].

Herein, we present an original methodology to investigate locally the photoactivity of plasmon nanostructures by scanning probe microscopy (SPM) techniques. As presented in Fig.1, we investigate the material morphology (a,d), optical properties (b,e) and photochemical activity (c) thanks to SEM, scanning spectrophotometer microscopy (SSM) and scanning photoelectrochemical microscopy (SPECM), respectively. The collected data unravel structure-activity relationships at the origin of the plasmonic activity. For instance, the localized surface plasmon resonance (LSPR) peak shift observed in Fig.1.b is directly related to the morphology disparity (Fig.1.d). Moreover, the optical properties corresponded well with the observed photoactivity (Fig.1.f).



**Fig. 1.** Investigation of the Au NPs on TiO<sub>2</sub>/ITO substrate morphology, optically and photochemically wise. (a) SEM image of the Au NPs on TiO<sub>2</sub>/ITO substrate. (b) SSM map presenting the LSPR peak position at the different positions. (c) Photoactivity map of the Au NPs, with the probe depicted to scale on (c), at 530 nm at 4.7 μW. (d) Mean diameter (left axis, filled squares) and population density (right axis, empty squares) of the different positions from (a). (e) Absorbance from the line across the center of the square at 455 (blue), 530 (green), 580 (orange) and 660 (red) nm. (f) Photoactivity (left axis, solid lines) and absorbance (right axis, dashed lines with filled circles) at the same line position for 530 (green) and 660 (red) nm. SPECM measurement conditions:  $r_T = 5 \mu\text{m}$ ,  $RG = 5$ ,  $Z = 20 \mu\text{m}$ ,  $v_{scan} = 20 \mu\text{m/s}$  in 1 mM  $\text{Fc}(\text{MeOH})_2$  and 0.1 M KCl.

The presented results are set up on a reference model including Au nanoparticles deposited on a semiconductor/charge collector substrate formed by a TiO<sub>2</sub>/ITO substrate, which is already well-referenced in the literature [3]. Ultimately, we aim to shed light on plasmonic material properties and their impact on the photochemistry thanks to correlation between the plasmonic system (e.g. size, shape, composition, interface and embedding media) and its activity at the nanoscale.

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# Hot Electron Extraction Enabled by Single-Crystal Metal Films and Nanostructures

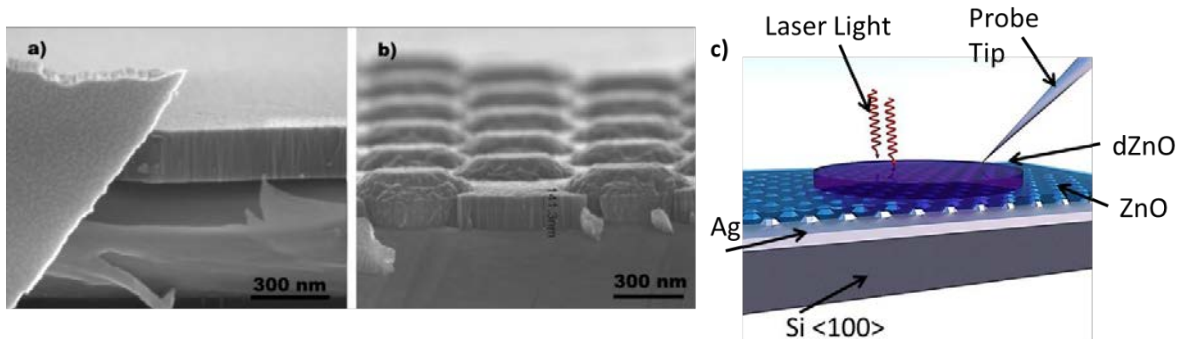
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Surface plasmons concentrate the extended three-dimensional fields of propagating electromagnetic waves to nanometer-scale structures, where their enhanced and confined local fields can drive new physical and chemical phenomena. Plasmon-mediated hot carrier generation is particularly interesting and can provide a means for direct energy harvesting, photocatalytic chemistry, and the development of new optical sensor technologies. However, identifying and optimizing the factors that lead to efficient hot electron extraction have remained a challenge and have limited the utility of surface plasmon-based devices for these applications. Here, we describe the requirements for efficient hot electron extraction in smooth and nanostructured Ag/ZnO plasmonic photovoltaic devices. Device efficiency is found to be highly correlated with material quality and the electronic character of the interfaces.

Our findings have driven the development of a new scalable and environmentally friendly electroless deposition method for single-crystal epitaxial noble metals films and nanostructures [1]. The method produces smooth, low-loss, single-crystal noble metal films ideal for subtractive patterning of nanostructures through ion beam milling, and high definition, sub-wavelength single-crystal nanostructured arrays through lithographic patterning. We describe the nucleation and growth of these metal films and nanostructures in the absence and presence of anionic shape-control agents and examine the role of specific anions in determining the resulting film and nanostructure morphologies via scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) [2]. These effects have been exploited to yield large area patterned, and shape-controlled nanoarrays of single-crystal metal nanostructures, yielding plasmonic metasurfaces with tailored local fields that can be tuned to exploit local field enhancements. These approaches offer new and cost-effective routes to achieve crystalline, shape-controlled surface nanostructure for nanophotonic and nanodevice applications.



**Fig. 1.** ZnO deposited on single-crystal a) planar and b) nanostructured silver to form plasmonic photovoltaic structures. c) device structure for free space-coupled hot electron extraction measurements.

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# NFO16 Template

## TERS study of phonon localization in low-angle twisted bilayer graphene and other two-dimensional Systes

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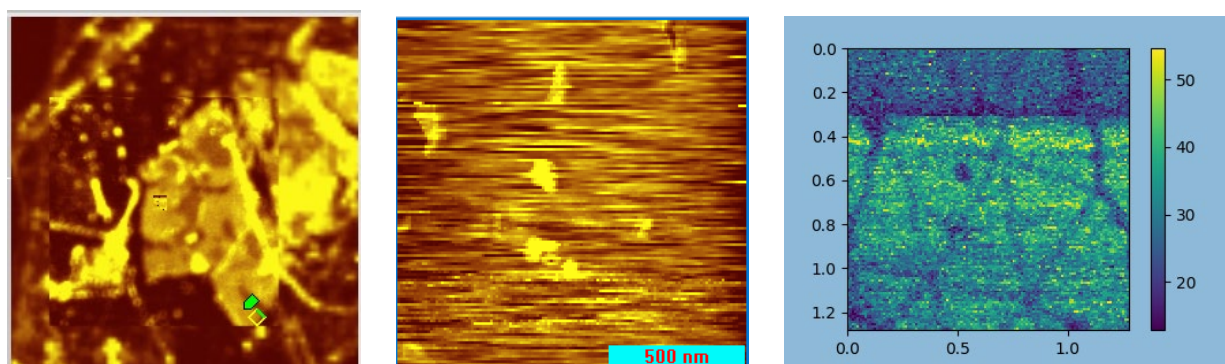
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This talk reports hyperspectral tip-enhanced Raman spectral (TERS [1]) imaging of the crystal superlattice in reconstructed (low-angle) twisted bilayer graphene and other local effects in two-dimensional systems [2]. Gate-induced homojunctions are formed and imaged in graphene and MoS<sub>2</sub> [3]. For small twist angles, twisted bilayer graphene undergoes a self-organized lattice reconstruction, leading to the formation of a periodically repeated domain, which can be observed in TERS experiments (see Fig.1) [4,5]. The resulting superlattice modulates the vibrational and electronic structures within the material, leading to changes in the behaviour of electron–phonon coupling [6]. The results are rationalized by an atomistic model that enables evaluation of the local density of the electronic and vibrational states of the superlattice. Our observations highlight the relevance of solitons and topological points for the vibrational and electronic properties of the structures, particularly for small twist angles, and they represent a step towards understanding the relevance of electron-phonon interaction in these systems, relevant in context of twistronics. Technical details about samples preparation and characterization are also discussed [7,8].



**Fig. 1** (left) optical image of a twist bilayer graphene sample, with the green pointed showing the location where AFM and TERS were acquired; (meddle) AFM-based topography of the sample at the location shown in the left panel; (right) TERS based image of the 2D band intensity, at the location shown in the left panel [4].

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# THz-Light Canalization by Phonon Polaritons in 2D van der Waals Materials

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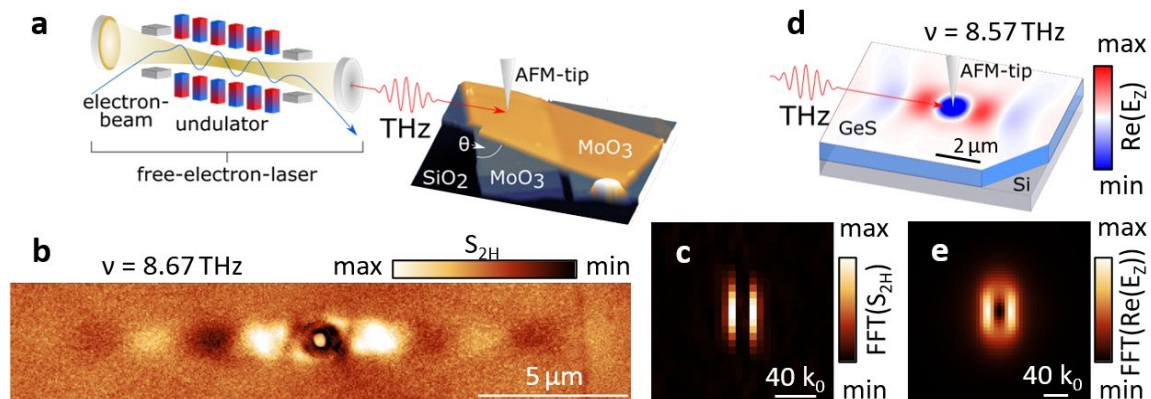
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Terahertz (THz) electromagnetic radiation is key to optically accessing collective excitations such as magnons (spins), plasmons (electrons), and phonons (atomic vibrations) bridging between optical and solid-state physics. In particular, confining THz light at nanometer length scales is desirable for the local probing of such excitations in low dimensional systems, thus inherently circumventing the large spatial distribution and low spectral power density of far-field THz optics. For that purpose, hyperbolic phonon polaritons (PhP) in anisotropic, 2D van der Waals (vdW) materials present a promising platform for THz nanooptics [1], as they not only allow strong confinement of THz radiation but, furthermore, also for energy transport directed along specific crystallographic axes without the need of topographical structuring. However, the lateral spread due to the hyperbolic shape of these polaritons entails undesirable losses. To that end, the demonstration of diffraction-less propagating “canalized” PhPs in vertically stacked and twisted  $\alpha$ -MoO<sub>3</sub>-flakes (so called “twisted bilayer (TBL) MoO<sub>3</sub>”) in early 2020 introduced a major breakthrough in polariton physics [2-5]. Spectrally, the canalization regime of TBL-MoO<sub>3</sub>-polaritons is determined by the hyperbolic optical material response  $\tilde{\epsilon}(v)$  as well as by the specific twist angle  $\theta$ , and so far has been studied exclusively at MIR wavelengths. In this talk we explore canalized polaritons in TBL-MoO<sub>3</sub> at THz wavelengths, where recently hyperbolic PhP have been demonstrated [6] and where long wavelengths make strong confinement even more desirable. Subsequently, we contrast the intriguing THz PhP channeling properties predicted in the 2D vdW material GeS based on the flattening of the elliptical iso-frequency-curve.

In particular, we experimentally study the spectral response of PhPs in TBL  $\alpha$ -MoO<sub>3</sub> between  $\nu = 8.28$  and 9.38 THz. For this purpose, the free-electron laser FELBE (HZDR, Germany) is combined as the tunable narrow-band light source with scattering scanning near-field optical microscopy (s-SNOM) (Fig. 1a). For a twist angle of  $\theta = 50^\circ$ , we find canalized PhPs at  $\nu = 8.67$  THz (Fig. 1b,c) with a 6.8  $\mu\text{m}$  wavelength, a propagation length of 7  $\mu\text{m}$ , a quality factor of 6.5, and a confinement perpendicular to the propagation direction of 1  $\mu\text{m}$ . These results are directly compared with single flake PhP and the elliptical response of orthogonally  $\theta = 90^\circ$  twisted TBLs. Moreover, as an alternative material for THz light canalization, we introduce  $\alpha$ -germanium(II) sulfide ( $\alpha$ -GeS) in this talk, a novel highly anisotropic 2D vdW semiconductor that suggests natural PhP canalization even within a single slab (Fig. 1d) [7,8] due to the unique interaction of a phonon in out-of-plane direction with the PhP and the substrate. The resulting shape of the PhPs in k-space around 8.57 THz (Fig. 1e) resembles the one found for canalization in TBL  $\alpha$ -MoO<sub>3</sub>.



**Fig. 1** a) Schematic of the experimental setup using the free electron laser for THz near-field excitation in s-SNOM on the TBL  $\alpha$ -MoO<sub>3</sub> (twist angle  $\theta = 50^\circ$ ); b) canalized polariton propagation observed at  $\nu = 8.67$  THz; c) Fast-Fourier-transform (FFT) of the near-field image in (b) featuring two parallel lines corresponding to the PhP’s directive propagation; d) outline for measurements on a single GeS-flake mounted on a silicon substrate, showing the full-wave simulated real-space field distribution of the single-  $\alpha$ -GeS-flake polaritons at  $\nu = 8.57$  THz [8]; e) FFT of the field distribution in (d) featuring two strong straight lines closely resembling the canalized response in (c).

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# Imaging the Bandgap Shifting in $W_xMo_{1-x}S_2$ by Near-Field Broadband Transmittance Microscopy

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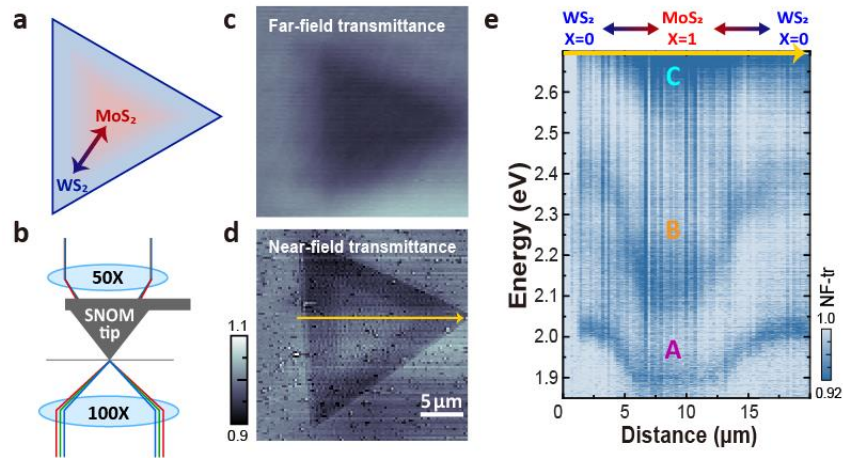
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Two-dimensional (2D) transition metal dichalcogenide (TMD) alloys allow tunable bandgap, which enable a broad range in optoelectronics applications. The  $W_xMo_{1-x}S_2$  alloy was synthesized by gradually changing temperature in one-pot CVD growth, [1] which exhibits spatially-varied bandgaps shift as a function of constitutional atoms ( $x/1-x$ ) from the pure  $MoS_2$  at the center to the  $WS_2$  at the edge. Typically, Photoluminescence (PL) spectroscopy is utilized to characterize the A exciton of single-layer TMDs since they exhibit direct bandgap. However, in the cases of multilayers or highly-defective TMDs, the PL emission are quenched due to the non-radiative exciton recombination. Here, we introduce home-built broadband near-field transmittance (NF-tr) microscopy to overcome the problems of PL detection. [2] Collimated white light was focused into the apertured tip by a 50 $\times$  objective lens (N.A. 0.5). The transmittance light was collected by a 100 $\times$  objective lens (N.A. 0.9) and then coupled into a spectrometer. Absorption spectrum mapping of alloy TMD flake can be recorded in the energy range from 1.8 to 2.7 eV, which contains all A, B, and C exciton bands and has never been realized for TMDs up to now.



**Figure (a)** The schematic of the  $W_xMo_{1-x}S_2$  sample. **(b)** The optical setup for NF-tr measurement. **(c)** The far-field transmittance image of  $W_xMo_{1-x}S_2$  and **(d)** the NF-tr image of  $W_xMo_{1-x}S_2$  at 520 nm (2.38 eV). **(e)** Energy-location diagram along the yellow line in (d).

The far-field (FF) and the near-field (NF) transmittance images at 520 nm are shown in fig. c and d. The far-field image is blurred due to the chromatic aberration of the optical system. Oppositely, the NF image shows sub-diffraction-limited and aberration-free contrast in transmittance. The energy-location diagram (fig. e) presents the location-dependent band shift of the A and B excitons. However, both the shift of the A and B excitons are not a linear function of  $x$ , so the bowing factor is introduced as a prominent indication of the bending curvature relative to  $x$ . In summary, our NF- transmittance technique provides an aberration-free and sub-diffraction-limited imaging and spectroscopy tool to reveal the spatial variance of alloy TMDs. This technology can make a very useful tool for investigating the various layered structures in the era of “stacking materials” in quest of novel quantum devices.

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# Probing vibrational strong coupling with tip-enhanced near-field spectroscopy

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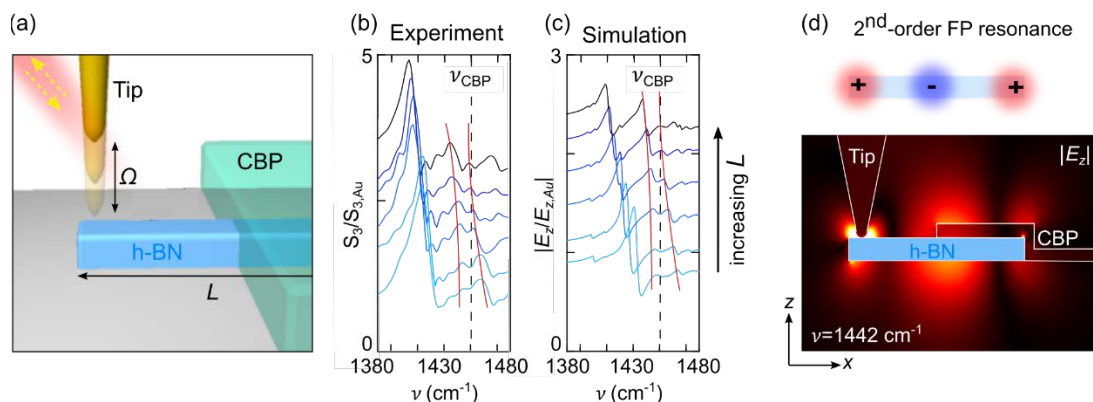
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Vibrational strong coupling (VSC) occurs when the coherent energy exchange between infrared cavity photons and molecular vibrations exceeds the decay rates of both, the cavity mode and the molecular vibration [1]. In this strong light–matter interaction regime, new hybrid states – polaritons – are formed exhibiting interesting possibilities for ultra-sensitive vibrational spectroscopy and for modifying chemical reactions [2,3]. Typically, VSC is achieved by filling microcavities with a high concentration of organic molecules limiting access to quantum phenomena that can occur for a single or a few number of molecules. Phonon–polariton (PhP) nanoresonators could be ideal candidates to achieve VSC at the nanoscale, due to their small mode volumes and large quality factors [4]. Although VSC employing arrays of PhP resonators has been reported before [5], the study of VSC with individual PhP resonators is challenged by their extremely small extinction cross sections, which makes difficult to use conventional far-field optical techniques to probe VSC on single resonators.



**Fig. 1** (a) Sketch of the system. The blue rod represents the h-BN nanoresonator of length  $L$ . The green rectangular structure represents the CBP layer covering half of the h-BN nanoresonator. The elongated conical structure at the top-left part of the blue rod represents the non-resonant tip being illuminated with a broadband infrared laser. The height of the tip oscillates with frequency  $\Omega$ . (b) Experimental nano-FTIR amplitude spectra, obtained for different nanoresonator lengths  $L$ . (c) Theoretical calculation of the near-field amplitude below the tip for different  $L$ . Red lines are guide to the eye and mark peak positions. The dashed vertical line marks the CBP molecular vibration frequency at  $1450\text{ cm}^{-1}$ . In the theoretical calculations the tip is simulated as a point-dipole. (d) Numerical simulation of  $|E_z|$  around an h-BN nanorod, whose right half is covered by a CBP layer. 1 nm above the left nanorod extremity a tip of 25 nm apex radius is placed. Tip and nanorod are illuminated with a plane wave of  $\nu = 1442\text{ cm}^{-1}$  at an angle of  $60^\circ$  relative to the tip axis.

In this work, we experimentally and theoretically address the use of tip-enhanced near-field spectroscopy to probe and map the hybrid polaritonic modes of single hexagonal boron nitride (h-BN) nanoresonators coupled to molecular vibrations. We achieve this by covering half of the h-BN nanoresonator with CBP (4,4'-bis(N-carbazolyl)-1,1'-biphenyl; organic semiconductor) molecules having a well-defined molecular vibration at  $\nu_{\text{CBP}} = 1450\text{ cm}^{-1}$  [see Fig. 1(a)]. In addition, at the region between  $\nu = 1400\text{--}1500\text{ cm}^{-1}$ , the h-BN nanoresonator supports phonon polaritons exhibiting Fabry–Perot (FP) resonances [see Figs. 1(b)–1(c)] and thus, by varying the nanoresonators length, we can tune the 2<sup>nd</sup>-order FP resonance [see Fig. 1(d)] with respect to  $\nu_{\text{CBP}}$ . We probe the nanoresonator–molecule coupled system with a non-resonant tip and minimize the potential influence of the tip by probing only the part of the nanoresonator not covered with CBP molecules. Our results can constitute an avenue for near-field imaging of strongly coupled systems that are not accessible by far-field spectroscopy.

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# Molecular optomechanics to address the Raman signal from organic molecules in complex plasmonic nanocavities

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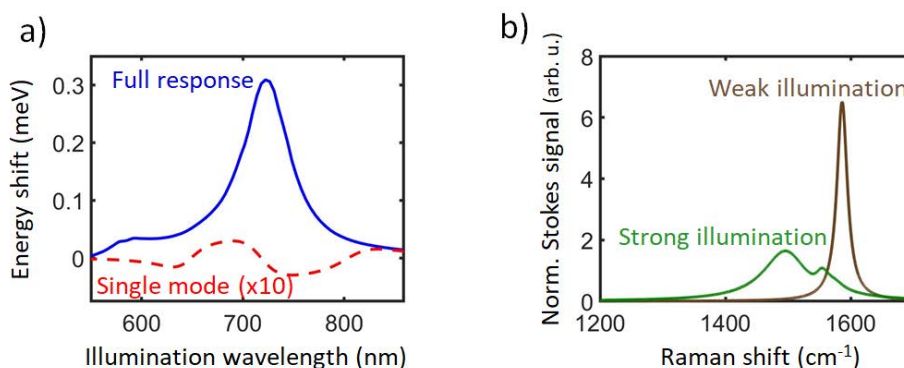
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Surface-Enhanced Raman Scattering (SERS) exploits the strong interaction between molecules and plasmonic resonances in metallic nanostructures to enable the characterization of vibrational modes of very small amounts of molecules, as desired for sensing applications. An often-used classical description of SERS describes the strong enhancement of the Raman lines in the emission spectrum, but it assumes that the properties of the molecular vibrations are fixed. On the other hand, a recent quantum description of SERS based on molecular optomechanics [1,2] shows how, for very intense lasers, the width and the frequency of the Raman lines can change, corresponding to a significant modification of the effective losses and of the energy of the molecular vibrations, respectively. These changes are accompanied by a strongly non-linear dependence of the emitted signal on the intensity of the laser illuminating the system [3,4].

The molecular optomechanics approach often considers a single plasmonic mode. Here, we use a continuum-field model [5] to show the importance of including the full plasmonic response in the description of the optomechanical interaction under strong laser illumination in configurations where a molecule couples efficiently with higher order plasmonic modes [6], as in extreme  $\sim 1$ nm-thin plasmonic nanogaps. Higher order plasmonic modes do not only modify the strength of the Raman signal, but they can also change the general spectral trends, leading, for example, to an increase instead of a decrease of the Raman spectral width. The effect of the plasmonic modes is particularly evident in determining the vibrational energy, increasing the vibrational energy shift by up to two orders of magnitude, as compared with the single-mode results (Fig. 1a)

We further consider the case where multiple molecules are placed in the plasmonic nanocavity. In this case, we find that in order to capture accurately the optomechanical interaction it is important to consider both the higher-order plasmonic modes as well as the formation of collective vibrational modes [7]. Different collective modes experience different vibrational linewidths and frequency shifts, so that, under strong illumination, more peaks can appear in the spectra: one narrower and less shifted, and another broader and more shifted (Fig 1.b). The results of the calculations are consistent with experimental results [8] that show a saturation of the intensity of the narrow Raman peak. Thus, our results show that new intriguing effects can appear in SERS for large laser intensity, as described in the molecular optomechanics framework.



**Fig. 1** a) Change of the vibrational energy of a molecule placed at the gap of a plasmonic nanocavity. The illumination intensity is  $1\text{ W } \mu\text{m}^{-2}$ . The results obtained with a single-mode approximation (red line) are much smaller than those obtained when considering the full plasmonic response (blue line). (b) Raman spectra for 100 molecules placed at the nanocavity gap with weak (brown line) or strong (green line) laser illumination. For strong illumination, a strong change of the vibrational lineshape is observed due to the emergence of a broad and strongly shifted peak associated with a bright vibrational mode.

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# Atomically-resolved luminescence mapping of Lamb shift, Stark and Purcell effects from a single chromophore-picocavity junction

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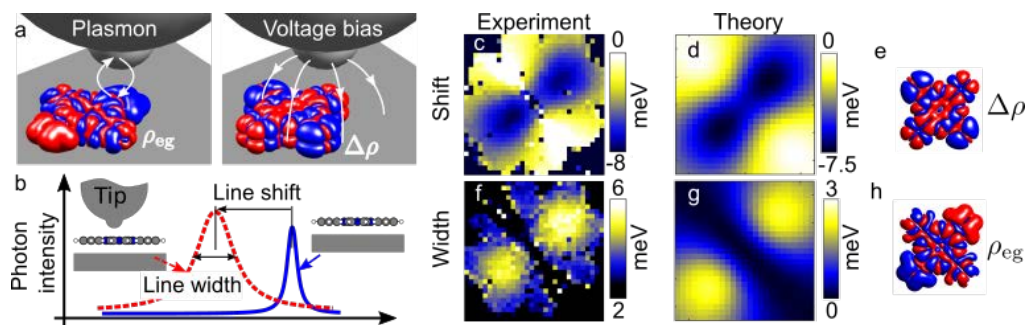
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Fundamental studies of the optical properties of single molecular emitters have led to the development of super-resolution optical microscopy techniques which go beyond the fundamental diffraction limit of optical resolution. Despite their success, exploited for example in bioimaging, the resolution of these microscopy techniques is still limited to scales larger than the size of individual organic molecules. This limitation has been lifted using the atomically sharp tip of a scanning tunnelling microscope (STM) [1] covered by noble metal, which can squeeze optical electromagnetic fields into plasmons localized on the atomic scale and conversely collect photons from within individual molecules with atomic-scale lateral resolution.

Here we present a correlated theoretical and experimental study of the optical properties of an individual free-base phthalocyanine molecule excited electrically by the tip of a STM [2,3]. We theoretically and experimentally show that the variation of the spectral position and width of the electroluminescence emission line of the molecular exciton (recorded as a function of the lateral and vertical position of the tip, see Fig.1) can be linked with the tip-position-dependent plasmonic Purcell effect, Lamb shift, and DC Stark effect induced by the static voltage applied across the tip-substrate gap. We demonstrate that the Stark shift is responsible for the observed variations of the luminescence spectral line energy as a function of the tip position, yielding  $\sim 10$  meV contrast as the tip position is varied. We computationally show that this Stark shift dominates over the dynamical effect associated to the plasmonic Lamb shift. This allows us to interpret the tip-position-dependent spectral line shift map as an image of the difference between the excited- and ground-state electron densities of the molecule (the difference electron density,  $\Delta\rho$ ). On the other hand, by analyzing the broadening of the spectra, we are able to map the plasmon-induced lifetime shortening of the exciton (reaching  $\sim$ ps lifetimes) with atomic-scale resolution, thus revealing a purely optical image of the molecule unperturbed by the artefacts emerging from the excitation of the molecule by the tunneling current. Our theory then allows us to interpret the tip-position-dependent map of the excitonic line-width variation as an image of the transition electron density,  $\rho_{eg}$ , representing the oscillating dipole associated with the electronic excitation in the molecule. These results constitute the foundation for the development of correlated optical and transport atomically resolved microscopies, but also shed light on the microscopic electrodynamic and electrostatic interactions of molecular excitons in plasmonic *picocavities* [4].



**Fig. 1** Mapping the excited-state properties of an organic molecule in a STM. (a) The atomically sharp noble-metal STM tip concentrates plasmonic electric fields to sub-molecular scales in plasmonic gaps. At the same time, DC voltage bias between the tip and the substrate creates a strong static electric field in the tip-substrate gap. These static and induced dynamical (plasmonic) fields act on the sample molecule and cause shifts and broadening of photon emission spectra of molecular excitons dependent on the position of the tip, as schematically shown in (b). (c-h) In the far field, the photon spectra are analysed and used to perform mapping of these line shifts (c,d) and line widths (f,g) that can be interpreted as images of the (e) molecular difference electron density  $\Delta\rho$ , and (h) transition electron density  $\rho_{eg}$ , respectively.

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# Single-millisecond SERS measurement of DNA oligonucleotides with single-base resolution using gold nanoparticle dimers under Brownian motion

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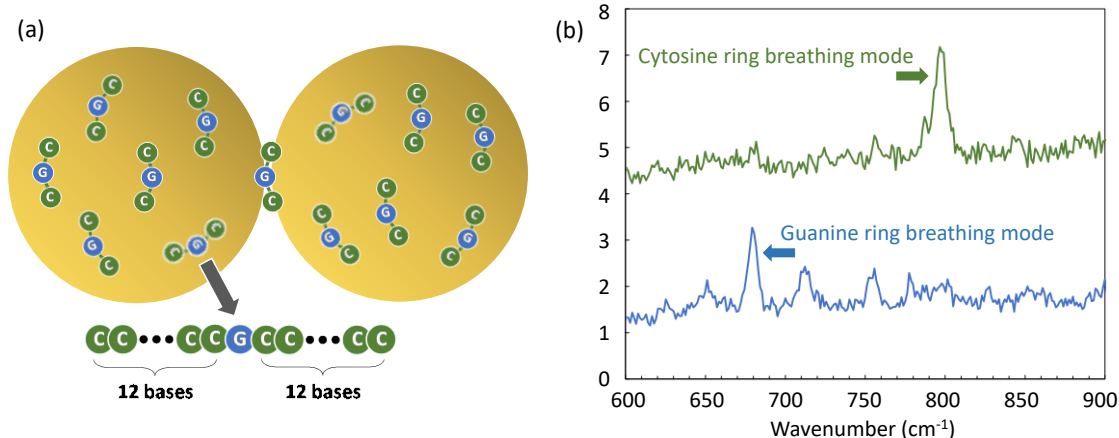
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Nanopore technologies allow for developing single-molecule DNA sequencing, in which single-stranded DNA molecules passing through a nanoscale ion channel are observed by detecting current blocking signals. Currently, nanopore ionic current detection enables discrimination of four nucleotide bases (adenine, thymine, cytosine, and guanine) included in a DNA strand, but it is much more challenging to identify chemically modified bases for epigenetic sequencing and twenty amino acids for protein sequencing. Optical DNA sequencing based on surface-enhanced Raman scattering (SERS) is promising as an alternative method for spectroscopic identification of bases. SERS utilizes extremely high field enhancement in a sub-nanometer volume (hot spot) of metal nanostructures to provide single-base spatial resolution and sensitivity. In this study, we develop a method to spontaneously form Au nanoparticle (AuNP) dimers, which sandwiches a single DNA oligonucleotide within a gap of less than 1 nm. SERS measurement of single AuNP dimers in aqueous suspension demonstrates single-base resolution obtained within a 10-ms measurement period.

AuNP dimers sandwiching oligonucleotides are formed in aqueous suspension by using colloidal AuNPs with a diameter of 50 nm and oligonucleotides containing guanine (G) and cytosine (C) bases with a sequence of CCCCCCCCCCGCCCCCCCCCCC (12C-1G-12C; 25 mers length) as shown in Fig. 1(a). The adsorption of oligonucleotides on AuNP surface and the formation of AuNP dimer was promoted by protonation of oligonucleotides, addition of salt, and incubation at elevated temperature. The conditions are carefully examined and optimized for enhancing the dimerization efficiency and for maximizing the probability to find the oligonucleotide in the dimer gap, which should be minimized to obtain pronounced SERS activity and single-base resolution.

We performed micro-Raman measurements for the AuNP dimers under Brownian motion in aqueous suspension. The dimer suspension was diluted such that single dimer spectroscopy could be conducted. Although the dwell time of dimer in the observation volume is approximately 10 ms, the effective measurement time should be less than 10 ms due to the rotational diffusion of dimers. Figure 1(b) shows Raman spectra obtained from two different single dimers. The lower spectrum exhibits a characteristic peak only from guanine while the upper one only from cytosine. According to the principle of bianalyte SERS technique, we demonstrated single-base resolution: Because we observed nucleotides containing guanine and cytosine, the SERS signal should also include both peaks even in a single nucleotide observation. The fact that we obtained SERS spectra only from guanine is evidence that the hot spot is localized in a single-base volume.



**Fig. 1** (a) AuNP dimer sandwiching oligonucleotide of 12C-1G-12C. (b) Bianalyte (binucleotide) SERS spectra obtained from two different single AuNP dimers under Brownian motion.

# Dynamic Single-Molecule SERS Fluctuations in an Aqueous Environment

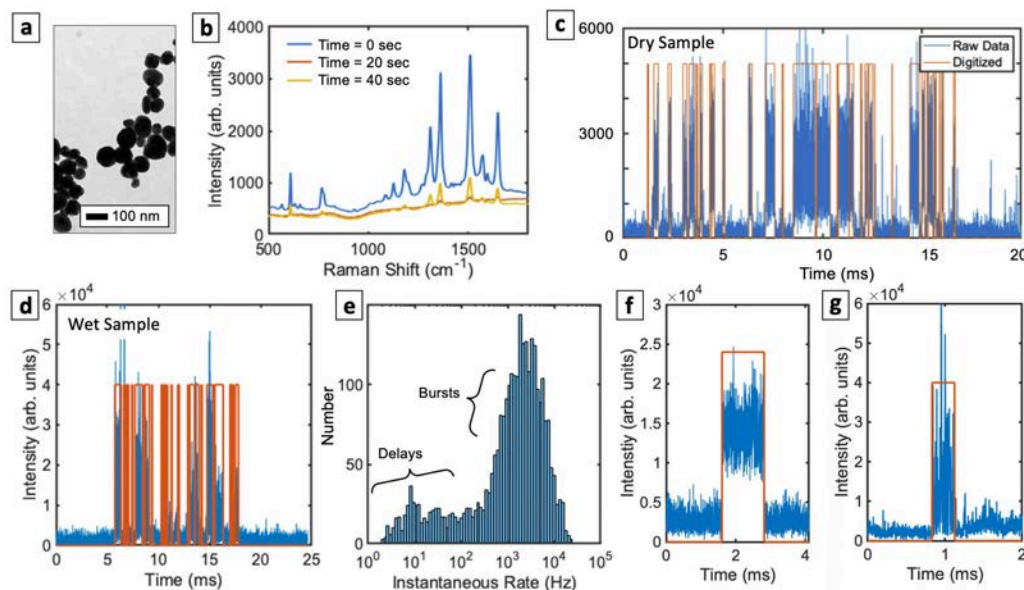
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Surface enhanced Raman spectroscopy (SERS) is a well-known and highly-studied effect that effectively represents both the challenges and opportunities inherent to nanophotonics and nanotechnology [1]. This is due to the extremely localized nature of the SERS effect, where intense atomic-scale plasmonic “hotspots” can increase Raman scattering by orders of magnitude, generating signals from single molecules [2]. These localized SERS signals also can show significant fluctuations, both in intensity and spectral features. This is considered a hallmark of few to single molecule events, and interpreted as being due to the dynamic nature of light-matter interaction at the atomic scale. Recent experiments have even shown these SERS intensity fluctuations (SIFs) to occur over an extremely wide range of timescales, from seconds to micro-seconds [3]. While many mechanisms have been proposed for these fluctuations, such as molecular diffusion or transient plasmonic hotspot generation, the underlying source of these fluctuations are likely to be a complex interplay of different effects. For example, SERS experiments done with fully coated, but dry, nanoparticles would have less movement of the probe molecule but may still have transient hotspot generation due to the mobility of metallic atoms. Alternatively, experiments done with low concentrations of a molecular probe in liquid might tend to see fluctuations caused by freely-diffusing molecules that visit and become trapped within a static hotspot. In Figure 1 we compare high-speed SIFs in both dry and wet environments.



**Fig. 1** Demonstration of SIFs in both a wet and a dry environment with R6G molecules. (a) TEM image of Ag nanoparticle clusters. (b) After incubating with R6G and dried, the SERS spectrum fluctuated in time. (c) These fluctuations occur on extremely fast timescales and can be digitized and analyzed. (d) Wet Ag clusters immersed in a 50 nM solution also fluctuated. (e) Analyzing these fluctuations in time shows distinct regions of delays on the ~Hz timescale and high-speed SIF activity on the >kHz scale. (f) While both wet and dry samples fluctuated on similar timescales, the dry samples tended to have more uniform on-off behavior whereas (g) the wet samples tended to show noisier SIFs after digitizing. Over dozens of samples and tens of thousands of SIFs, the coefficient of variation (Standard Deviation / Mean) during a SIF was higher for wet samples (0.82) versus dry (0.65) samples.

Generally, the wet environment showed extremely high-speed fluctuations during a single SIF event, whereas a dried and more stable molecule-hotspot environment showed SIF events with less overall variation. Both environments still displayed strong SIF behavior over several orders of magnitude of time-scales, with the dry particles on average having slightly longer events. These results provide some new insight into the underlying mechanisms of high-speed SERS fluctuations, and may prompt further studies and applications of SERS in a variety of environments and for various metal-molecule systems.

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# Exosome detection using a double resonant nanoantenna device in the mid-infrared range

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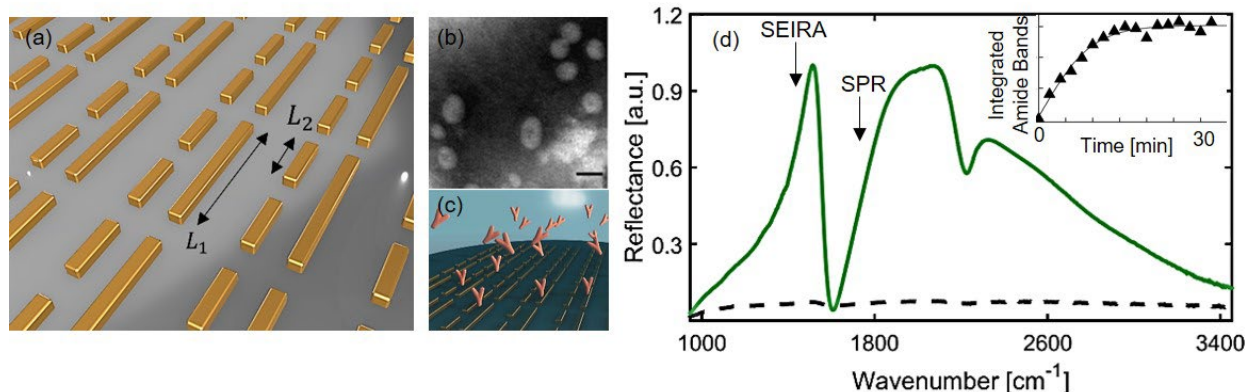
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Infrared (IR) spectroscopy finds application in the field of biomedical sensing as it can provide label-free information on the molecular composition of a biological sample, targeting even subtle variations or differences. The limits of IR-based diagnostics are related to the relatively large amount of pure molecule solution required to obtain a spectrum and to the strong IR absorption of the aqueous component required to maintain biomolecules in their physiological state. The development of plasmonic near-field approaches, such as antenna-enhanced IR spectroscopy, have allowed to overcome both issues by reducing the required sample volume for sensing, ideally limited to the intense plasmonic hotspots that form on the nanoantenna surface, where target molecules can be attached [1].

In the present work, we realized a microfluidic device based on a gold nanoantenna array with a double resonance in the mid-IR wavelength range, around 4  $\mu\text{m}$  and 6  $\mu\text{m}$  respectively, for the detection of exosomes released by human cell cultures (Fig.1a). These extracellular bodies are lipid bilayer-enclosed structures with nanometer size carrying biological matter (i.e. proteins, nucleic acids...) (Fig.1b). Since they are involved in the intercellular communication process, they can be exploited as pathology biomarkers of the parent cells in a so-called “liquid biopsy” [2]. Despite this potential, the difficulty to gain information on the very small amount of molecules that forms the cargo hampers their application for clinical diagnostic. The mid-IR device has been designed to detect exosomes through the vibrational absorption of their protein content. Indeed, the nanoantenna array displays a first resonance at 1600  $\text{cm}^{-1}$  that is suitable for surface enhanced IR absorption (SEIRA) spectroscopy of the amide bands of proteins [3]. At the same time, the sharp reflectivity drop around 1750  $\text{cm}^{-1}$  produced by the interaction of the second resonance with the first is strongly sensitive to changes in the refractive index at the interface between the metal antenna and the sample (Fig.1d). The reflectivity drop is thus employed as a surface plasmon resonance (SPR) for mass-sensing [4], allowing to monitor the presence of non-proteic material on the nanoantenna surface not specifically attached to the antibody functionalization layer. We performed micro-FTIR measurements of 100  $\mu\text{m}$  x 100  $\mu\text{m}$  arrays in reflection mode during sample solution flow, collecting simultaneously the two sensorgrams (inset of Fig. 1d). First, we demonstrated the monolayer sensitivity of our device by following the attachment of exosome-specific antibodies on the functionalized antenna surface (Fig.1c). We then started to acquire systematic data from exosomes released by human cell cultures.



**Fig.1** (a) Schematic view of the plasmonic device. (b) Representative TEM image of exosomes (scale bar: 200 nm). (c) Sketch of the surface functionalization with antibodies. (d) IR reflectance spectra of the nanoantenna array with incident polarization parallel (green line) and perpendicular (dashed gray line) to the long axis of the nanoantennas. The inset shows an example of the SEIRA signal sensorgram in the case of antibody solution.

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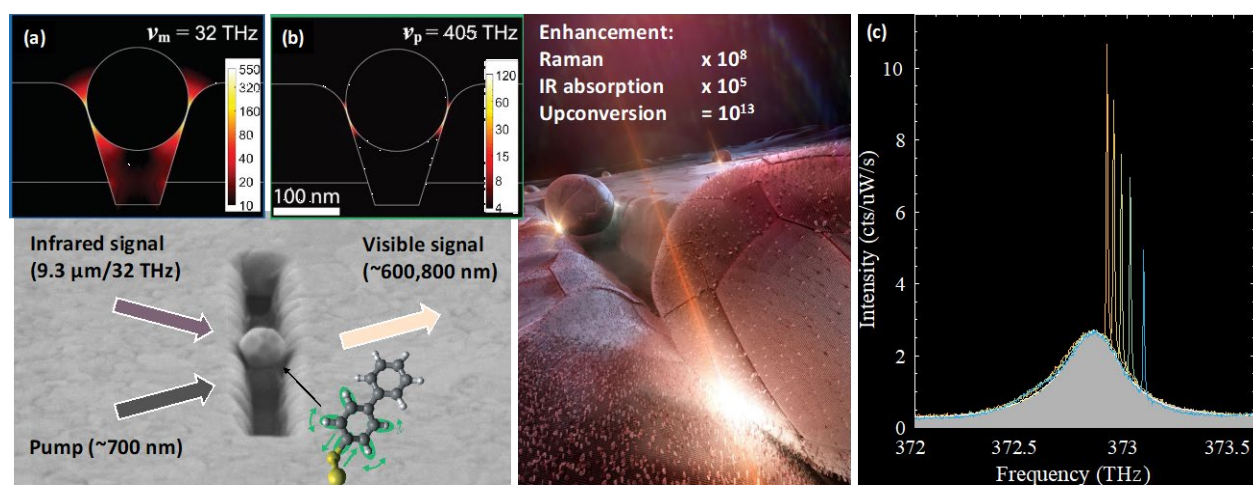
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# Mid-IR to Visible Optomechanical Transduction with Molecules in a Nanocavity

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The internal vibrational modes of molecules embedded in plasmonic nanogap can be used as ultrahigh frequency (1 – 50 THz) mechanical oscillators and constitute a new form of optomechanical nanocavities [1]. I will first briefly review recent experiments evidencing quantum correlations that are generated between light and collective molecular vibrations in the process of spontaneous off-resonant Raman scattering [2-5], in the absence of any cavity. Then, I will introduce our work on plasmonic gap modes [6,7] and show that coupling molecular vibrations to properly designed dual-resonant plasmonic cavities [8] allows for the observation of coherent optomechanical transduction between mid-infrared (~32 THz) and visible (~450 THz) electromagnetic fields [9].



**Fig. 1** Coherent frequency conversion with a molecular optomechanical cavity. (a,b) Simulated field enhancement factors for mid-IR and visible illumination. The lower panel shows an SEM picture of the nanoparticle-in-groove cavity, while the right panel is an artistic rendering of the device. Estimated enhancement factors result in 13 orders of magnitude improvement in per-molecule upconversion efficiency. (c) Example of high-resolution Raman spectrum (Stokes sideband, laser at 405 THz) with the upconverted signal (colored lines) riding on the spontaneous emission line (grey shade) as the mid-IR laser frequency is tuned around 32.4 THz (or 1080  $\text{cm}^{-1}$ ).

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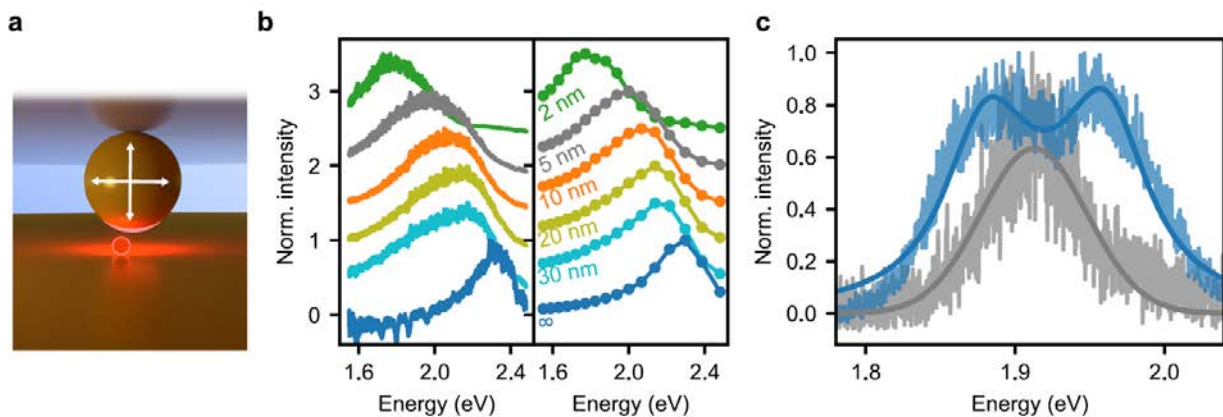
# Using a novel scanning probe technique to strongly couple a single quantum dot to a tunable plasmonic nanogap antenna at room-temperature

**Michael A. Becker<sup>1</sup>, Hsuan-Wei Liu<sup>1</sup>, Korenobu Matsuzaki<sup>1</sup>, Randhir Kumar<sup>1</sup>, Stephan Götzinger<sup>2,1</sup> and Vahid Sandoghdar<sup>1,2</sup>**

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Scanning probe techniques are indispensable methods for optical investigations of structures smaller than the diffraction limit. Moreover, techniques like scanning near-field optical microscopy and atomic force microscopy can be used to probe near-field light-matter interactions and measure electrical and thermal conductance. All these methods use a sharp tip that is operated in close proximity to the sample surface.

Here, we report on a novel, simple, and versatile tip-less scanning technique (*PROscan*) capable of performing high-precision optical near-field measurements [1]. We demonstrate its scanning capabilities and remarkable stability even in the absence of any feedback stabilization mechanism. Moreover, we utilize the *PROscan* method to create an open and tunable nanogap antenna (Fig. 1.a), where the gap distance can be controlled, allowing one to tune the plasmon resonance and to modify the fluorescence of single emitters with sub-nanometer resolution (Fig. 1.b). Locating single quantum dots at the hotspot of the nanogap antenna and tuning its resonance to the exciton transition, we observe a clear transition from the weak to the strong light-matter coupling regime, evidenced by a vacuum Rabi splitting in the fluorescence signal as shown in Fig. 1c [2]. Furthermore, by scanning the plasmon resonance we observe a characteristic anti-crossing behavior.



**Fig. 1.** **a** Schematic of the open and tunable nanogap antenna. **b**, *Left*: Measured plasmon resonance for different nanogap sizes. *Right*: Simulated scattering cross section of a nanogap antenna for six different gap sizes. **c**, Photoluminescence spectra of uncoupled (grey) quantum dot and of the same quantum dot coupled to a nanogap antenna (blue), exhibiting a vacuum Rabi splitting.

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# Holography, nanothermometry, and quantum correlations in extreme near fields probed with high-energy electrons

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We use time-resolved cathodoluminescence spectroscopy using 30-keV electrons to reveal the emission statistics of optical emitters, use holography to reveal the phase distribution of plasmonic scattering wavefronts, demonstrate nanothermometry, and let the electrons climb quantum ladders creating superpositions states in extreme near fields shaping electron wavepackets in space and time.

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# Inelastic in-line holography in an ultrafast electron microscope

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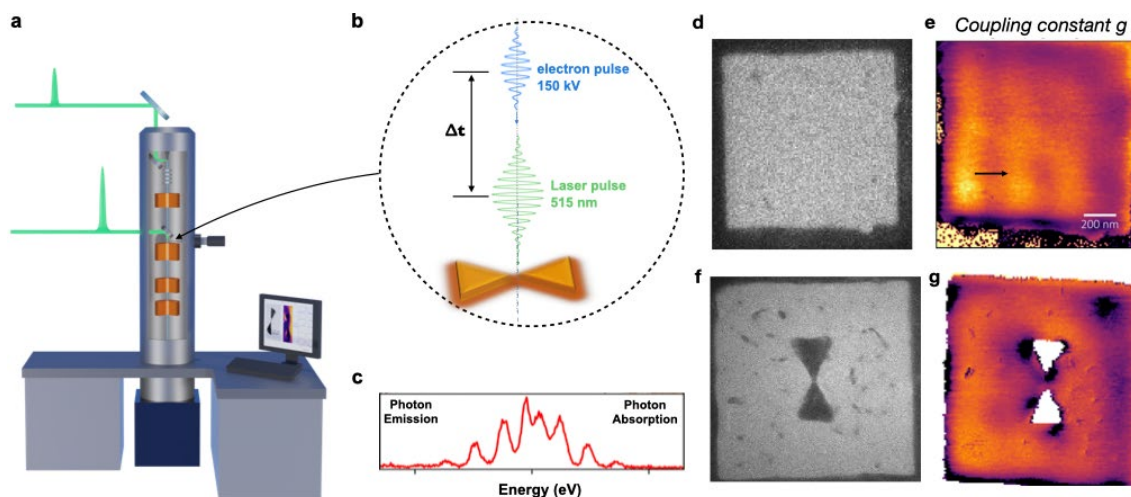
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Ultrafast Transmission Electron Microscopes (UTEM) combining the femtosecond temporal resolution of ultrafast optical spectroscopies and the nanometer scale spatial resolution of electron microscopy have opened up many new possibilities to investigate light-matter at unique spatio-temporal scales [1]. In particular, Photon-Induced Near-field Electron Microscopy (PINEM) has recently aroused great interest due to its ability to efficiently probe nano-optical excitations.

PINEM works on a so-called pump-probe scheme: A first laser pulse (pump) excites the optical nearfield around a nanostructure which is then probed by a subsequent electron (probe) pulse (see fig. a and b). During its transit in the optical near-field, the travelling electron can emit or absorb photons, thus leading to a modification of its energy (see fig. c). This inelastic interaction yields a characteristic electron energy spectrum composed by a series of peaks reflecting the discrete nature of the photon exchange. The magnitude of these peaks being directly related to the strength of the optical near-field, the analysis of the electron energy spectrum allows to map the optical near-field at the nanometer scale. However, conventional PINEM experiments yield an uncomplete picture of the nano-optical excitation as the phase of the electromagnetic field is not measured. The situation is different when the investigated optical excitation (e.g a plasmon mode) is excited simultaneously with a secondary scattered wave that acts as a reference signal. The interference between the two electromagnetic fields then imprints the phase of the plasmon mode in the electron/near-field coupling constant extracted from the PINEM signal [2]. These holographic PINEM experiments are the inelastic analog of the in-line holography technique proposed by D. Gabor in the late 1940s.

We have performed scanning electron energy-loss/gain spectroscopy experiments on our high-brightness UTEM to investigate the optical near-field excited on gold bowtie antennas. These nanostructures have been fabricated by focused ion beam milling of a 40 nm thick gold film evaporated on a 50 nm thick  $\text{Si}_3\text{N}_4$  membrane. As shown on fig. f, each nano-antenna is sculpted in a square aperture. At each position of the electron beam, an electron energy spectrum is acquired. As shown in figure e and g, this 3D dataset yields a complete map of the electron-field coupling constant  $g$ . In addition, we observe clear modulations of the PINEM signal around the nano-antenna. The latter are signatures of the interference between the plasmonic near-field and the wave scattered by the membrane edge and therefore indicate the realization of the above-mentioned holographic scheme.



**Fig. 1** a) ultrafast Transmission Electron Microscope b) close-up of the electron-light interaction on a gold bowtie. c) Electron energy spectrum showing the sidebands associated with photon absorption/emission by the fast particle. TEM image of a square aperture (d) and corresponding map of the electron-light coupling constant extracted from the electron spectra. f) and g): corresponding data for a gold bowtie.

Numerical simulations based on the Green Dyadic Method accurately reproduce the experimental results and allow us to extract the characteristics of the electric field excited around the nano-objects from the holographic data. These results open promising perspectives for the characterization of optical nano-excitations with unprecedented spatio-temporal resolution.

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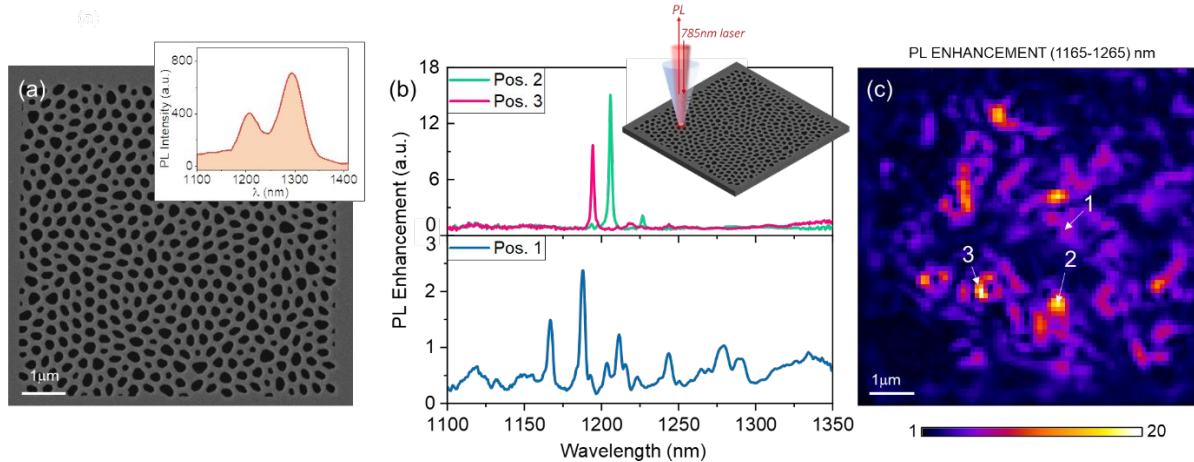
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# Near-field optical study of Hyperuniform Disordered photonic structures

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In the last few years, disordered dielectric materials with structural correlations, which fill the gap between random structures and perfectly ordered photonic crystals, have generated an ever-growing interest. A special class of these materials are the Hyperuniform Disordered (HuD) photonic systems [1]. HuD systems have recently been shown to display unconventional optical behavior such as transparency in thick optical media and large isotropic photonic band gaps (PBG) comparable in width to band gaps found in photonic crystals [2], as well as Anderson localization of light. Within this framework, a complete characterization of luminescent HuD structures in the optical range is still missing. Here, we tackle this challenge by designing and nanofabricating the first ever *optically active* hyperuniform structures (SEM image in Fig. 1a) with embedded quantum dots emitting at telecom wavelengths (as shown in the inset of Fig. 1a) [3]. This breakthrough in the field, which we linked to the very first optical *near-field hyper-spectral-imaging* of HuD systems, led to several innovative and unexpected results on the peculiarities of HuD modes. The investigated system is a HuD dielectric structure on a GaAs slab architecture, with air holes following a specific hyperuniform pattern; we employ a Near-field Scanning Optical Microscope in illumination-collection configuration (sketch of Fig. 1b), which allows us to have a direct measurement of the local density of states (LDOS) of the system. In Fig. 1b are reported three typical PL enhancement spectra acquired in three different tip positions, obtained by dividing the recorded spectrum by the PL spectrum of the QDs, that are embedded in the middle of the membrane and act as optically active medium. Many sharp resonances are clearly visible. Doing this procedure for every position of the probe it is possible to reconstruct the near-field spatial distribution of the PL enhancement over a broad range of wavelengths (1165-1265 nm), which reflects the distribution of the electric field intensity: this collective map, reported in Fig. 1c, shows a high spatial density of modes that exhibit a very high PL enhancement (of the order of 20) and Q factors one order of magnitude larger in respect to disordered systems (like it is shown in the upper panel of Fig. 1b). The positions (1, 2 and 3) where the spectra of Fig. 1b were acquired are indicated also in the map of Fig. 1c. The hyper-spectral method allows also to map the spatial distribution of each mode singularly. This optical characterization allowed to record a large plethora of interesting properties of the photonic modes in HuD systems, from the Q factor to the localization length, and to link them to specific light transport regimes. We experimentally demonstrate, after careful support provided by numerical simulations, that these resonances are intrinsically reproducible and resilient against fabrication induced disorder and local perturbation. For these reasons, and thanks to special features combining the advantages of both ordered and disordered structures, they are eligible as relevant candidates for a large plethora of quantum electrodynamics applications yet to be explored.



**Fig. 1** a) SEM image of the HuD sample; the inset shows the PL emission spectrum of the QDs. (b) Sketch of the near-field illumination-collection geometry, along with three typical PL enhancement spectra acquired in three tip positions. (c) Near-field PL enhancement map filtered around a broad wavelength interval, showing a high density of modes with a maximum PL enhancement of 20. The white numbers indicate the acquiring positions of the spectra shown in (b).

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# Invited: Nanophotonics-Enabled Mid-Infrared Microspectrometers For Chemical Identification and Related Topics

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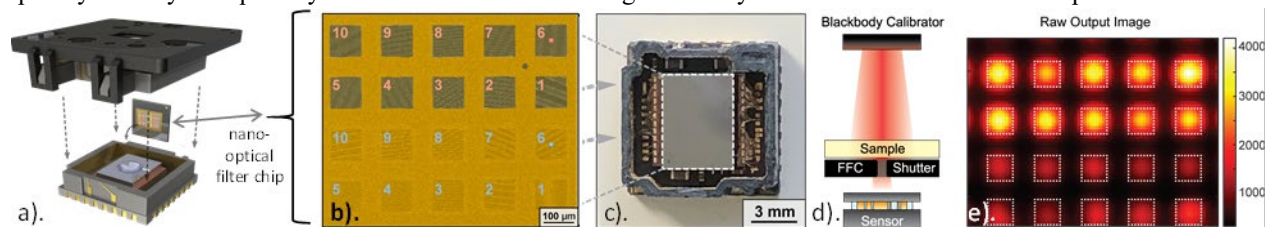
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The identification of chemicals from their mid-infrared spectra has applications that include the industrial production of chemicals, food production, pharmaceutical manufacturing, and environmental monitoring. This is generally done using laboratory benchtop tools, such as the Fourier transform infrared spectrometer. Although such systems offer high performance, alternative platforms offering reduced size, weight, and cost can enable a host of new applications, e.g. in consumer personal electronics. In this presentation, we will describe our recent work [1] on a compact microspectrometer platform for chemical identification. If time permits, we may describe a selection from our related work on other topics in nanophotonics from 2021-2022, e.g. microspectrometers [2,3], photodetectors and LEDs based on 2D materials [4], metasurface holograms [5], metasurface lasers [6,7], and optical nanotweezers [8].

Our recent microspectrometer platform [1] comprises a nanophotonic filter chip integrated with a miniature thermal camera (Fig. 1a). The nanophotonic chip is silicon with a thin gold coating. It contains twenty spectral filters (each  $100 \times 100 \mu\text{m}^2$ ) that span the wavelength range 6-14  $\mu\text{m}$ . The filters are divided into two categories: bandstop filters (arrays of gold rings, Fig. 1b-upper) and bandpass filters (arrays of coaxial apertures, Fig. 1b-lower). A photograph of a prototype IR microspectrometer is provided as Fig. 1c. Experiments are performed by placing the material to be studied ("sample") between the IR blackbody source and the IR microspectrometer (Fig. 1d). A typical raw (i.e. unprocessed) sensor output is shown as Fig. 1e. The twenty spots of high intensity (Fig. 1e) correspond to the twenty spectral filters (Fig. 1b). One may regard these as the representation of the IR absorption spectrum of the material, divided into twenty spectral channels. Provided that the material has absorption features within the wavelength range of the filter set (6-14  $\mu\text{m}$ ), the resultant sensor output (i.e. Fig. 1e) exhibits a distinctive pattern. We have demonstrated that this platform can be used with a machine learning (ML) algorithm. After this is trained, it can quickly identify and quantify unknown chemicals with high accuracy from the measured sensor output.



**Fig. 1** a). Schematic of integration of nanophotonic filter chip onto thermal camera (FLIR Lepton). b). False-color scanning electron microscope (SEM) image of nano-optical filter chip. c). Photo of completed microspectrometer. d). Schematic of experimental set-up. e). Raw data from microspectrometer.

To evaluate the performance of our IR microspectrometer, we perform experiments in two steps. First, the ML algorithm is trained on data recorded by the IR microspectrometer while it is subjected to different chemicals at a variety of concentrations. Second, the system is subjected to unknown chemicals. The sensor output (e.g. Fig. 1e) is provided to the ML algorithm, which then predicts what chemical is present. High accuracy identification of four liquid chemicals, concentration quantification of ethyl lactate in cyclohexane down to subpercentage levels, and the classification of food and drug samples is demonstrated.

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# Order Structure Recognition by Schubert Polynomials Generated by Optical Near-Field Statistics via Nanometer-Scale Photochromism

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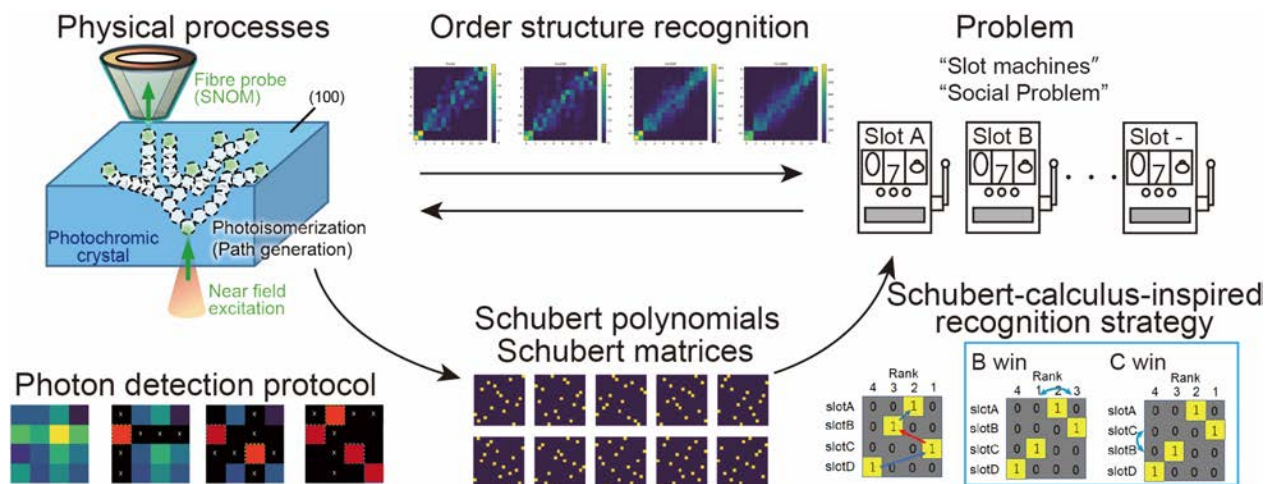
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Light-matter interactions, especially optical near-field interactions, are important in the realization of natural intelligent devices, which solve problems by mapping them to complex physical processes. The quantum nature of single photons has been reported to solve decision-making problems [1,2]. We focused on the nanometer-scale photon transfer paths generated by the chain of nano-photochromism due to the near-field photoexcitation on photochromic crystals [3]. In this study, we demonstrate a strategy to recognize the order structure in the system under study via utilizing nanometer-scale photon transfer paths generated in photochromic crystals combined with a single photon detection protocol [4].

The photochromic crystal used in this study consists of diarylethene molecules, which become colored or decolorized by photoisomerization even in the crystalline state. When near-field photoexcitation is applied to the surface of the crystal, a nanoscale photoisomerized structure is formed from the surface to inside the crystal due to a complex local photoisomerization chain formed by the combination of photoisomerization and crystal distortion.

The photoisomerized structures generate the two-dimensional probability map of photons transferring from the exit positions of the branched photoisomerization pathway to the rear-side sample surface. We extracted the order structure from the two-dimensional probability map of the transferring photons via a photon detection protocol [3]. The obtained order structures are matrices that show one-to-one correspondence with the Schubert polynomials and are called Schubert matrices [4]. The series of Schubert matrices has both fluctuation and order, which corresponds to permutations for a statistical system such as a group of slot machines.

We demonstrated recognition of the order structure in a problem without direct probability estimation by a Schubert-calculus-inspired strategy to map the nano-optical isomerization structure to an ordering problem (such as solving an order in a set of slot machines). In this strategy, we reorder the rows or columns of the entire matrix series according to the results of playing the slot machines corresponding to the elements that form the singular structure in the matrix. The order structure recognition can be used for any ordered structures in optimization and decision-making problems even when the problem systems include environmental fluctuations based on physical structures. The nano-photochromism encompasses both classical and quantum phenomena, so it can be applied to complex problems such as social problems where quantum computing is expected to be applied.



**Fig. 1** Order structure recognition by Schubert polynomials generated by optical near-field statistics generated by nanometer-scale photoisomerized structures via a photon detection protocol and a Schubert-calculus-inspired recognition strategy.

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# Seeing the Forces: Single Avalanching Upconverting Nanoparticles as Ultrasensitive Local Force Transducers

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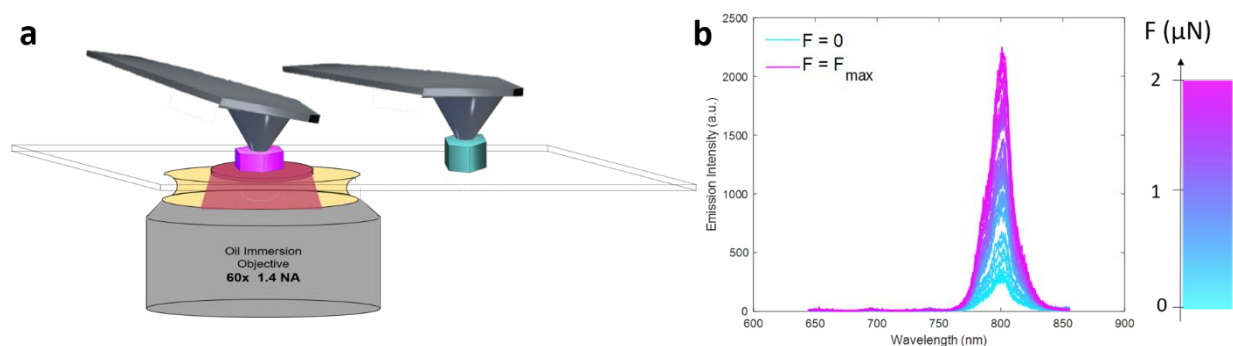
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It has lately been shown that ensembles of lanthanide-doped upconverting nanoparticles (UCNPs) exhibit changes in their emission spectra due to applied forces in the nano-Newton regime and beyond [1-3]. Avalanching UCNPs (ANPs) [4], possessing steeply nonlinear optical responses, are ideally suited for sensing minute changes in their environments, as small perturbations are expected to usher large changes in signal. Because ANPs absorb and emit tissue-penetrating near-infrared (NIR) light, they are uniquely positioned for sensing within biological cells and fluids. In order to characterize and understand the response of these ANPs to local stress and hence determine their functionality as mechano-sensors, it is important to study their mechano-opto-physics on a *single particle level*. Utilizing a custom designed combined AFM and inverted optical microscope system (Fig. 1a), we correlate sub-nano-Newton-range applied forces and observable changes in hyperspectral optical signals for isolated single ANPs, demonstrating their attractiveness as physiologically-relevant local force sensors.

By optimizing ANP lanthanide concentration, core and shell sizes, particle geometry, and host material, we design ANPs with record-breaking mechano-sensitivity and unprecedented stress-dependent responses. While the decrease in inter-ionic distance and the change in crystal field with applied pressure usually leads to a decrease in UCNP optical signal intensity, newly designed ANPs exhibit optical *signal enhancement* (Fig. 1b) when subjected to forces as low as *pico-Newtons*. The signal enhancement persists for a large range of applied force, from pico-Newtons to micro-Newtons, in a predictable fashion, over many cycles, for the same particle. Optimally-engineered ANPs - with their NIR wavelength operating regime, high single particle brightness, substantial mechano-sensitivity, and unique mechano-response - emerge as highly promising candidates for non-invasive ultra-sensitive force-sensing.



**Fig. 1.** a) Sub-nano-Newton force is applied to a single ANP with an AFM tip while excited with NIR light from below. b) Force-dependent emission spectra, attained for a single ANP while excited at 1064 nm.

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# Imaging life at high temperature enabled by plasmonic heating

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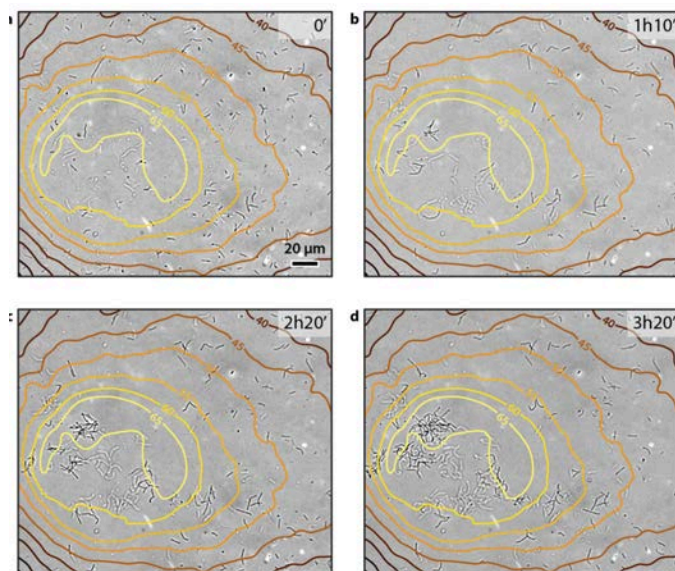
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At the bottom of the ocean, close to black smokers, microorganisms can thrive at temperatures higher than 100°C. Understanding how life can sustain such harsh conditions is of utmost interest for the fundamental understanding of how Nature copes with high temperatures, and for the development of biological applications at high temperature. However, it remains very hard to observe thermophilic micro-organisms living in vitro, because it would require heating a microscope stage at 100°C or more. As a result, most microscopy observations of thermophilic micro-organisms today are conducted using electronic microscopy, that is on dead samples, a rather frustrating condition for biologists.

In this contribution, we show how plasmonic heating can successfully activate thermophilic bacteria using a conventional microscope, without complex apparatus [1]. Thermophilic bacteria are cultured on a glass coverslip covered with gold nanoparticles, which are illuminated at their plasmonic resonance wavelength within the field of view of the microscope at the required temperature (Fig. 1). The temperature distribution is imaged using cross-grating phase microscopy [2,3]. This work paves the way for the easy study of thermophiles and a better understanding of their metabolism and interaction.



**Fig. 1** Wide field intensity images of the growth of *G. stearotherophilus* bacteria upon laser heating at different time, (a)  $t=0$  min, (b) 1 h 10 min, (c) 2 h 20 min, (d) 3 h 20 min, extracted from a 200 min long movie, superimposed with the associated temperature map. The laser was switched on at time  $t = 0$ . Isotherms have been added to the intensity images.

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# Strong coupling of semiconductor nanocrystals with plasmonic resonators at ambient conditions

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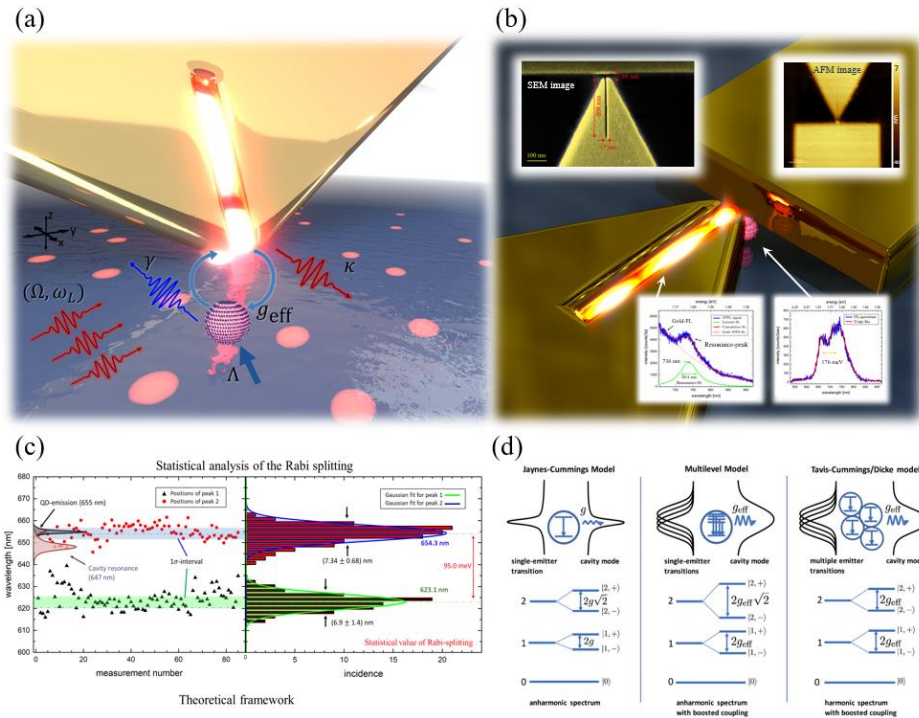
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Strong coupling and the resultant mixing of light and matter states is an important asset for quantum technologies. We have successively improved our previously demonstrated deterministic room temperature strong coupling of a mesoscopic colloidal quantum dot (Fig. 1a) to a plasmonic nanoresonator [1] and substantiated the results of enormous Rabi splitting up to 110 meV in extensive statistical analysis (Fig. 1c). Furthermore, we developed the scanning experiment into an on-chip platform which provides a stable and continuous strongly coupled system (Fig. 1b). For this purpose, we use ultraprecise He-ion beam milling to fabricate high-quality plasmonic slit resonators from single-crystalline gold microplatelets in combination with dielectrophoresis to position single quantum dots close to the slit opening. These novel nanostructures provide additional degrees of freedom as well as the opportunity to apply electric fields to induce tunability.

We also have recently established a comprehensive theoretical framework for extending the Jaynes-Cummings model to a multilevel coupling model [2]. Based on the broadband nature of the interaction and the full control of the coupling, our platform paves the way towards ultrafast coherent manipulation of light-matter interaction in any 0D, 1D or 2D quantum system at ambient conditions.



**Fig. 1** (a) Artistic illustration of a plasmonic nanoresonator (PNR) probe interacting with colloidal semiconductor QDs embedded in a polymer film. (b) On-chip strong-coupling device. SEM- and AFM images illustrate the geometry as well as a proof of successful attraction of single QDs to the PNR via dielectrophoresis. In addition, two photoluminescence spectra characterize the PNR's plasmonic resonance as well as a clear Rabi-splitting obtained for a coupled system. (c) Compilation of several measurements and statistical strong coupling mean values. (d) Visual summary of the theoretical light-matter interaction models.

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# Tunable nano-plasmonic photodetectors

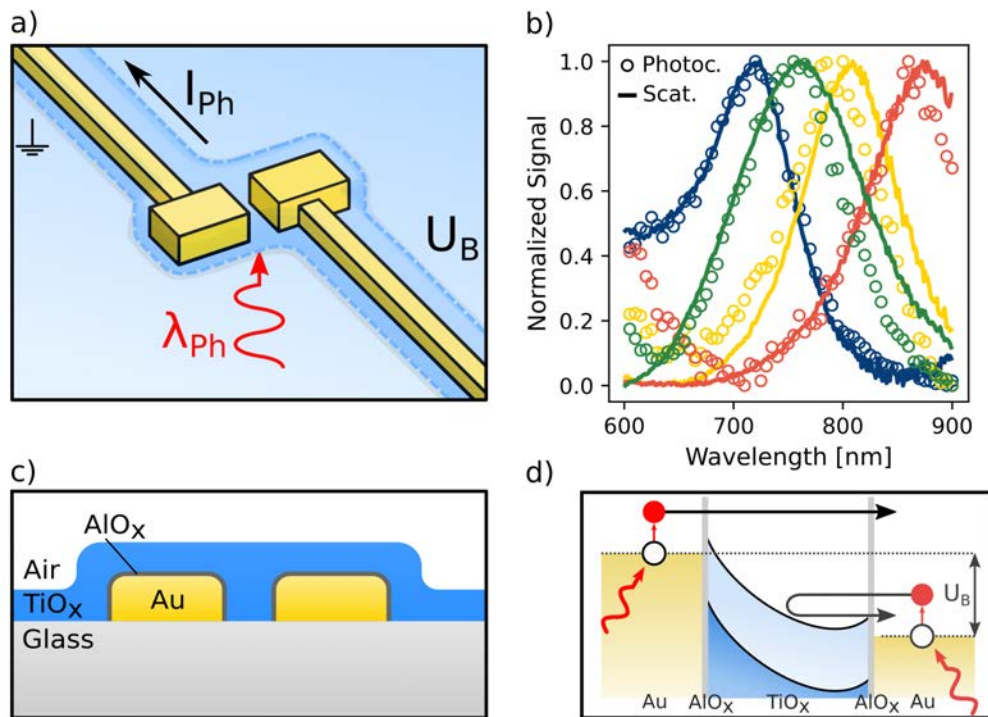
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The internal photoeffect has been widely used to detect photons with a broadband response in the visible and infrared regime. By using plasmonic nanostructures, wavelength selectivity can be introduced to these detectors via geometry-dependent resonances [1]. Also, additional functionality, like electronic responsivity switching and polarization-sensitive detection have been realized [2,3]. However, previous devices consisted of large arrays of nanostructures to achieve reasonable photocurrents.

Here we show that this concept can be scaled down to a single antenna level, resulting in detector dimensions well below the resonance wavelength of the device. Our design consists of a single electrically-connected plasmonic nanoantenna covered with a wide-bandgap semiconductor allowing photodetection in the VIS/NIR (Fig. 1). We demonstrate electrical switching of the resonance wavelength as well as polarization detection. Our results hold promise for the realization of ultra-small photodetectors with advanced functionality controllable by the antenna design.



**Fig. 1** (a) Schematic drawing of our photodetector consisting of a plasmonic nanoantenna (gold) covered with TiO<sub>2</sub> (blue). (b) Geometry dependent scattering and photocurrent of four different nanoantenna-detectors. (c) Cross section and (d) energy-diagram of the nanoantenna photodetector.

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# Engineering polariton launchers for nanophotonic chips

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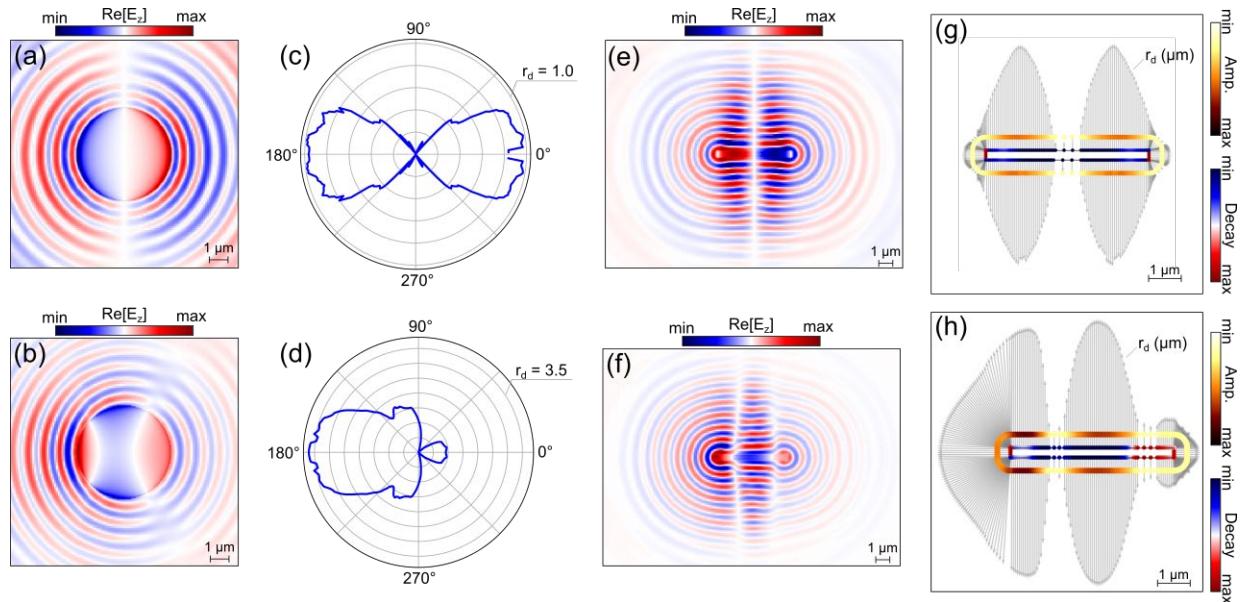
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Two-dimensional (2D) crystals have been considered fundamental building blocks for several applications, from optical modulators to biosensors. The reason for such success originates in their ability to confine light in the form of polaritons, which are quasi-particles that result from the coupling of light and collective excitations in matter. However, coupling polaritons to 2D crystals is challenging, as their momentum may be dozens of times larger than the photon momentum. On the other hand, studies have shown that metallic antennas can be ideal for the coupling, as they are excellent light concentrators and can be easily patterned on top of crystals.

Despite the vast literature on plasmonic antennas as polariton launchers [1-3], the basic rules which govern their launching properties are still unspecified. Here, we combine concepts of radiofrequency (RF) antennas and polariton modeling to deliver insights on the directional launching properties of plasmonic antennas.

Using Finite-Difference Time-Domain calculations, we simulated hyperbolic phonon polaritons (HPhP) in hexagonal Boron Nitride (hBN) launched by gold antennas (Fig. 1a,b,e,f). The waves were modeled as evanescent waves for a collection of directions outwards the antenna edges. By classifying the region surrounding the antenna into Fresnel and Fraunhofer zones, we were able to select the directions that optimized the model accuracy. Furthermore, the classification indicates the type of radiation pattern representation for illustrating the antenna properties (Fig. 1c,d,g,h).

Our results show that the antenna geometry, the resonance order, and the illumination setup are crucial for defining the polariton pattern. For instance, we may design the antenna dimensions to control the local polariton decay. By changing the dimensions of the edges, polaritons can propagate as circular or plane-waves. Moreover, asymmetric near-field distribution on the antennas may lead to highly directive launching (Fig. 1d,h). Because the incidence angle of the source and the antenna dimensions strongly influence the antenna polarization, we may tune the directivity by simply changing these parameters. We envision that our insights will be substantial for planning and designing antennas for near-field experiments on 2D crystals and future photonic chips.



**Fig. 1** Simulated near-field patterns on top of disks (a,b) and rod (e,f) antennas for normal (a,e) and oblique incidence (b,f). Polar representation of the polariton detectable distance,  $r_d$  ( $\mu\text{m}$ ), for disks under normal (c) and oblique (d) incidence. Representation of launching properties of a rod for normal (g) and oblique (h) incidence. “Amp.” and “Decay” represent the model-extracted launching amplitude and geometric spreading decay factor, respectively.

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# Harnessing electron beams to unveil quantum effects in nanoplasmonics

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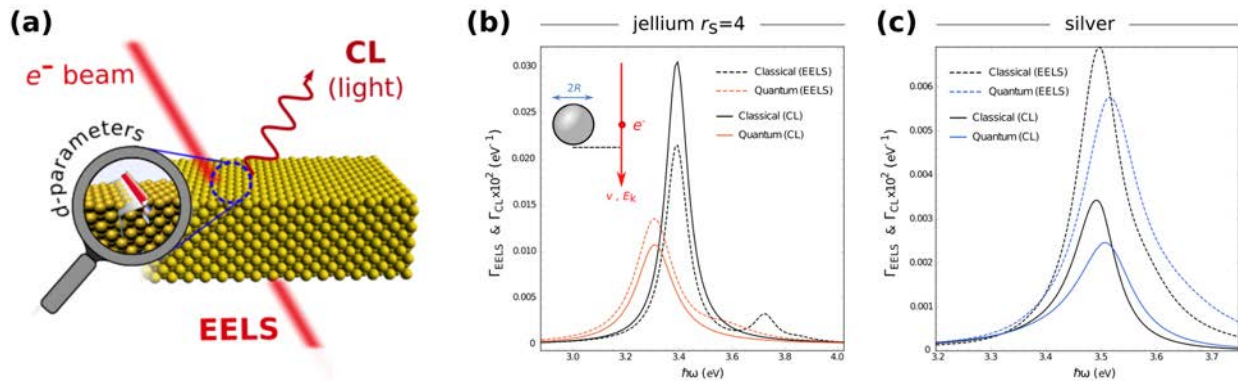
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Nonlocal (i.e.,  $q$ -dependent) response and quantum-mechanical effects are ubiquitous in truly nanometer-scale plasmonic structures—now well within reach of state-of-the-art nanofabrication techniques—wherein the intrinsically quantum-mechanical nature of the plasmon-supporting electron gas manifests itself through nonclassical signatures in the observed optical response [1–4]. Typically, the impact of quantum nonlocal effects becomes important when the characteristic size of the system falls below  $\sim 10$ – $20$  nm or when the optical response is governed by extremely subwavelength near-fields (i.e., involving field-components with large wavevectors). However, fully quantum mechanical treatment of the metal’s electrodynamic response [e.g., through time-dependent density-functional theory (TDDFT)] is severely constrained to few-atom clusters or extremely small systems which are, invariably, much smaller than the typical nanoplasmonic systems of interest in nearly all experiments. As such, common strategies typically rely on simplified quantum-informed models that seek to capture the dominant quantum effects to leading-order [1,2,4]. Among these, the so-called Feibelman  $d$ -parameter formalism [2] for nanoscale electrostatics has been shown to enable the simultaneous incorporation of nonclassical effects including electron spill-out/spill-in, nonlocality, and surface-assisted Landau damping [2–5]. Crucially, the  $d$ -parameter approach has the advantage of being practical to implement, scalable, and has an amenable computational cost (and even allows analytical treatments in highly symmetric systems). At its heart, it relies on the introduction of two surface-response functions,  $d_{\perp}(\omega)$  and  $d_{\parallel}(\omega)$ , that encode the quantum-mechanical response of the underlying electron gas [2–4]. Naturally, that hinges upon our ability to compute the  $d$ -parameters based on a suitable theoretical description, which, in practice, can be challenging (particularly in beyond-jellium TDDFT, as it is required for Au and Ag).

Here, we show that electron-beam spectroscopies can be harnessed to infer such quantum surface-response functions directly from experimental measurements of electron energy-loss and/or cathodoluminescence spectra, whereby quantum nonlocal effects imprint nonclassical spectral shifts ( $\sim \text{Re } d_{\perp, \parallel}$ ) and nonlocal broadening ( $\sim \text{Im } d_{\perp, \parallel}$ ) in the measured spectra [5]. Specifically, we present a quantum-corrected theory of electron energy-loss spectroscopy (EELS) and cathodoluminescence (CL) based on the  $d$ -parameter formalism and macroscopic quantum electrodynamics. Our results establish a brand-new, concrete scheme for interrogating the complex optical response of plasmonic nanostructures with free-electrons, from which one can retrieve the quantum surface-response [i.e.,  $d_{\perp}$  and  $d_{\parallel}$ ] by capitalizing on the free-electron’s ability to generate near-fields which can be tuned by controlling the electron’s kinetic energy [5]. Such a quantitative knowledge of the material response is paramount not only from a fundamental point-of-view but also as a key ingredient for modeling and designing the next-generation of nanophotonic devices with truly nanometric dimensions.



**Fig. 1** (a) Conceptual approach for probing the quantum surface-response of metals using free-electrons. (b)–(c) Classical and quantum (i.e., via the  $d$ -parameters) EELS and CL spectra of a metal nanosphere [(b) jellium metal with Wigner–Seitz radius  $r_s=4$ ; (c) silver], showing nonclassical spectral shifting and nonlocal broadening. The nanosphere diameter is  $D = 10$  nm, the probing electron’s kinetic energy is  $E_k = 20$  keV, and the impact parameter is  $b = 10$  nm (measured relative to the nanoparticle’s center).

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# Unidirectional DNA-origami based ultracompact optical antennas for single molecule emission

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Optical antennas have been widely used for manipulating light-matter interactions at the nanoscale in order to control the emission intensity, lifetime and directivity of single molecules [1], [2]. In particular, increasing the directionality of single emitters takes on crucial significance, for example in the context of future integrated optical circuits or quantum communication and computing schemes, which hold potential for lower energy consumption and higher efficiency using states that can be controlled up to the fundamental quantum limit [3], [4]. To date most efforts were focused on designs adapted from the Yagi-Uda antenna that can reach high directionality with a significant number of elements spanned over approximately a wavelength [5]. Despite this tremendous proof of concept, further development of these antennas is hindered by the challenges involved in the fabrication and positioning of the single emitters and metallic elements that limits the coupling control and performance that can be achieved.

In this contribution, we report on the realization of ultra-compact directional antennas for single photon emitters by means of DNA self-assembly. Adapting the design proposed by Pakizeh et al. [6], we used the DNA origami technique [7] to place two gold nanorods in a side-to-side (or end-fire) arrangement with an overall footprint an order of magnitude smaller than the optical Yagi-Uda antenna. By coupling a single fluorescent molecule to one of the nanorods, unidirectional emission is registered red-shifted from the bonding mode [8], when the nanorods are driven close to the antiphase mode.

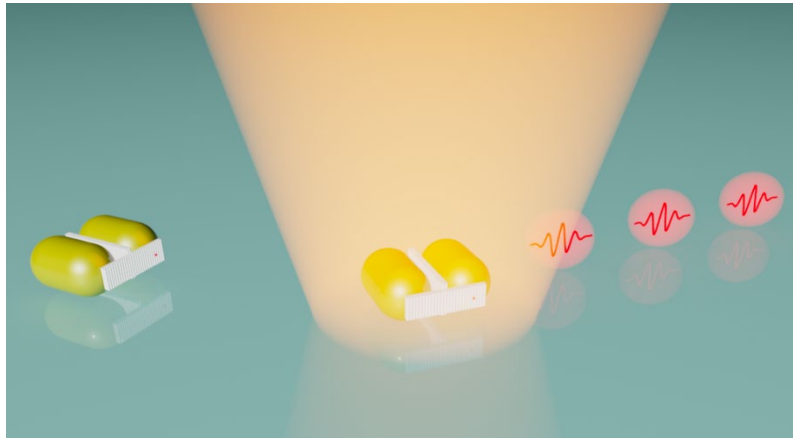


Fig. 1: Sketch of an ultracompact antenna showing unidirectional emission

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# Conformational Dynamics of Single Proteins – Exciting Opportunities with Plasmonic Optical Tweezers

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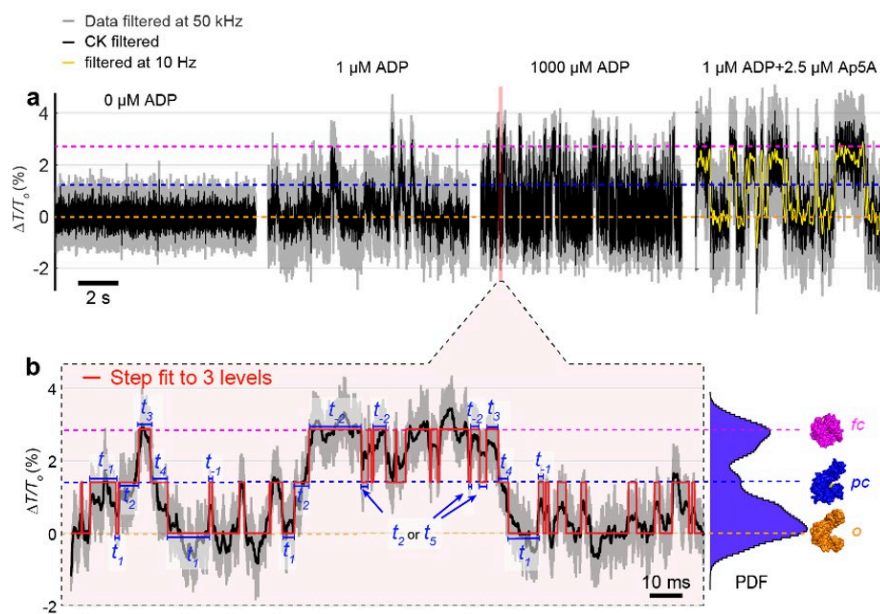
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This talk will present an update of our ongoing efforts to assess the potential of nanoplasmonic optical tweezers for interrogating the conformational dynamics of single unmodified proteins in aqueous solution. Specifically, we employ double nanohole (DNH) structures to trap single enzyme proteins [1,2] for minutes to hours. Concurrently, we monitor changes in transmission through the DNH upon exposure of the trapped protein to substrate, product, or inhibitor molecules. We show that experiments with trapped enzymes that are known to undergo significant conformational changes during their catalytic cycle, exhibit multiple, well-defined transmission levels.[3] Increasing concentration of substrate molecules increases the frequency of transitions between these transmission levels in a dose-dependent manner, while the presence of different inhibitors reduces the frequency of transitions by favoring certain transmission levels (Fig. 1). Step-fitting the transmission recordings makes it possible to follow the rate of transition between all levels, revealing individual enzymatic cycles, single molecule turnover frequencies, as well as heretofore unknown enzymatic sub-cycles during catalysis.[3] The talk will conclude with an outlook of applying this approach to additional unmodified enzymes, motor proteins, and transporters as well as a discussion of its current limitations and possible improvements.



**Fig. 1** Monitoring changes in normalized transmission through a double nanohole (DNH) with a single trapped adenylate kinase (AdK) enzyme in response to increasing concentrations of the enzyme substrate ADP as well as the presence of the inhibitor Ap5A.[3] The magnified area shaded in pink shows a step-fit to three transmission levels and reveals the lifetime of each level as well as the turnover frequency of the enzyme on a single molecule level. Considering the polarizability [4] of various conformations of AdK, combined with previous observations that AdK populates predominantly its open conformation in the absence of substrate (0 μM ADP) and that AdK must cycle through the closed conformation during catalysis, made it possible to assign the lowest transmission level to AdK's open (o) conformation, the intermediate transmission level to its partially closed (pc) conformation and the highest transmission level to its fully closed (fc) conformation.

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# Near- and far-field properties of few element mid-infrared subwavelength antennas

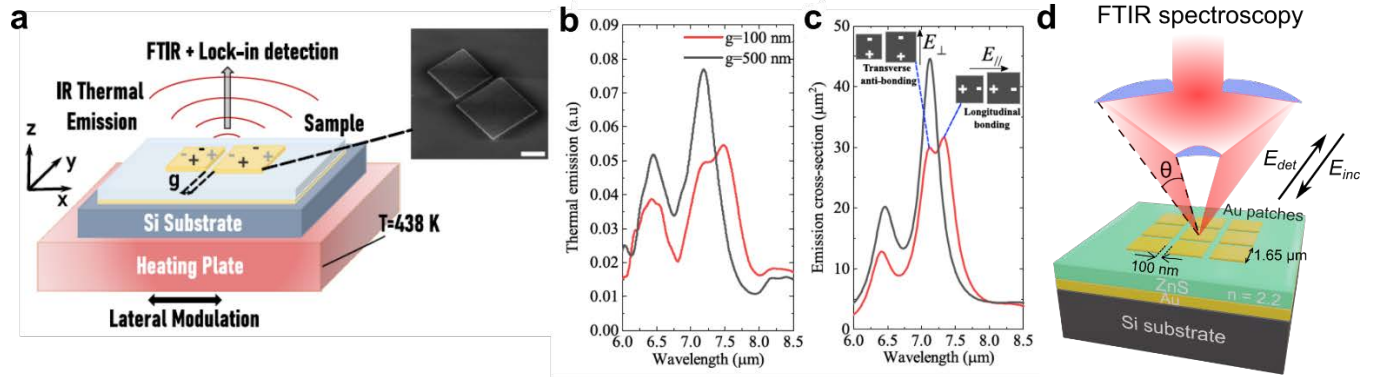
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Tailoring the mid-infrared (mid-IR) optical and thermal radiative properties of individual antennas is of paramount importance for various pertinent applications, such as, radiative cooling, photo-detection, and solar cell design. Nevertheless, the electromagnetic radiation emitted by a single mid-IR subwavelength antenna is extremely weak, and in practice, most studies are limited to periodic arrays, in which the resultant diffraction orders preclude the measurement of the response of a single antenna. In this study, we push the limits of various highly sensitive IR microscopy techniques in order to probe the electromagnetic radiation of antennas made of a single or a few elements, and to understand the fundamental interactions between them.



**Fig. 1** (a) Schematic illustration of the MIM pair and the IR-SMS technique. Inset: SEM image of the sample, the scale bar is 1  $\mu\text{m}$ . (b) Measured thermal emission spectra of the MIM pair for different gaps  $g$ . (c) FDTD calculations of emission cross-sections corresponding to the measurements. The inset shows a sketch of the dimer geometry showing two of the hybrid modes of the MIM pair, for electric field polarizations parallel and perpendicular to the dimer axis. The positive (+) and negative (-) signs indicate the surface charge distribution [2]. (d) Schematic illustration of the 3x3 element antenna geometry and the angle-resolved microscope reflectivity setup.

Using infrared spatial modulation spectroscopy (IR-SMS) [1] we have studied the coupling effects between an asymmetric pair of thermally excited metal-insulator-metal (MIM) antennas [2]. The geometry of the experiment is sketched in Fig. 1(a). It is found that for tiny gaps ( $g \leq 100$  nm) the two gold patches of the MIM antennas form a dimer pair and a splitting starts to form in the resonance peak between 7 and 8  $\mu\text{m}$  of the pair's thermal emission spectrum (Fig. 1(b), red curve). The obtained splitting is a direct result of the simultaneous excitation of the hybrid bonding and anti-bonding modes of the dimer [3], shown in the inset of Fig. 1(c). This striking result shows that various coupled modes of a single nano-antenna can be simultaneously excited by thermal fluctuations, an essentially incoherent process arising from fluctuating thermal currents.

Next, we investigate the electromagnetic radiation of a more complex two-dimensional 3x3 element antenna structure made up of 9 patch MIM antennas in near-field interaction (Fig. 1 (d)). Through angle-resolved microscope reflectivity measurements, it is found that in contrast to a single patch MIM antenna, the 3x3 element antenna structure exhibits an angularly dependent optical response. The non-symmetrical optical properties exhibited by the geometrically symmetric 3x3 antenna structure is a direct consequence of the near-field interaction among its elements, which we probe via a scattering type scanning near-field optical microscope [4].

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