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Roadmap

Roadmap on plasmonics

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Abstract

Plasmonics is a rapidly developing field at the boundary of physical optics and condensed matter physics. It studies phenomena induced by and associated with surface plasmons—elementary polar excitations bound to surfaces and interfaces of good nanostructured metals. This Roadmap is written collectively by prominent researchers in the field of plasmonics. It encompasses selected aspects of nanoplasmonics. Among them are fundamental aspects, such as quantum plasmonics based on the quantum-mechanical properties of both the underlying materials and the plasmons themselves (such as their quantum generator, spaser), plasmonics in novel materials, ultrafast (attosecond) nanoplasmonics, etc. Selected applications of nanoplasmonics are also reflected in this Roadmap, in particular, plasmonic waveguiding, practical applications of plasmonics enabled by novel materials, thermo-plasmonics, plasmonic-induced photochemistry and photo-catalysis. This Roadmap is a concise but authoritative overview of modern plasmonics. It will be of interest to a wide audience of both fundamental physicists and chemists, as well as applied scientists and engineers.

Keywords: plasmonics, nanophotonics, surface plasmons, nanoplasmonics, quantum plasmonics, thermoplasmonics

(Some figures may appear in colour only in the online journal)

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[22] Guest editor of the Roadmap.

1. Foreword

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Plasmonics: introduction. This brief collective review is devoted to the place of plasmonics among sciences and its current state and future perspectives. Plasmonics studies the optical phenomena at the surfaces and interfaces of nanostructured metals with dielectrics and semiconductors. These phenomena are due to elementary excitations called surface plasmons, which are coherent collective oscillations of electrons with respect to the lattices. Plasmons are polar excitations: they are accompanied by the appearance of surface charges oscillating at optical frequencies. These oscillations cause the appearance of enhanced optical fields strongly localized at metal surfaces and interfaces.

There are two main types of surface plasmons: running surface waves called surface plasmon polaritons (SPPs) and localized, standing excitations called localized surface plasmons (LSPs) or surface plasmons (SPs). Surface plasmon polaritons were predicted by Ritchie 60 years ago to manifest themselves in the scattering of fast electrons [1], as was later observed [2]. They exist at the surfaces and interfaces of metal nanoparticles and are typically localized on the scale of the nanoparticles [3].

The existence of SPs depends entirely on the fact that the dielectric function ε_m has a negative real part, $\mathrm{Re}\varepsilon_m < 0$. The SPs are well pronounced as resonances when the losses are small enough, i.e. $\mathrm{Im}\varepsilon_m \ll -\mathrm{Re}\varepsilon_m$. This is a known property of a good plasmonic metal, valid, for example, for silver in most of the visible region. An important parameter of an SP resonance is its quality factor,

$$Q = \frac{\omega}{2\gamma} = \frac{\omega}{2\mathrm{Im}\varepsilon_m(\omega)}\frac{\partial \mathrm{Re}\,\varepsilon_m(\omega)}{\partial\omega},$$

where γ is the spectral width of the SP resonance, ω is its frequency and ε_m is the metal permittivity.

The quality factor determines how many optical periods free SP oscillations undergo before field decays. It also shows how many times the local optical field, $\mathbf{E}$, at the surface of a plasmonic nanoparticle exceeds the external field, $\mathbf{E}_0$, namely, $E/E_0 \sim Q$. A typical value of the quality factor for a good plasmonic metal, such as silver or gold in the red/near-infrared spectral region is relatively high, $Q \sim 100$, so the intensity of the local field exceeds that of the incident-wave field by four orders of magnitude, $E^2/E_0^2 \sim Q^2 \sim 10^4$.

This enhancement is of a purely resonant origin: the amplitude of the SP field is coherently accumulated over the Q optical periods. The resonant enhancement of the local fields is at the foundation of many fundamental phenomena and the multitude of the applications of plasmonics. Among these applications are surface enhanced Raman scattering (SERS) [4], sensing and detection [5], nanoscopy [6], and many others.

Roadmap and current progress in plasmonics. Here, we very briefly overview the sections of this Roadmap, their fundamental foundations and the application progress and perspectives.

Historically, the first 'killer application' of nanoplasmonics was SERS, where Raman scattering from molecules at nano-rough plasmonic-metal surfaces was enhanced by eight or more orders of magnitude. The enhancement and the contrast of SERS become so large in the near-infrared region so that even single molecules can be detected [7], which opens up a wide area of applications in chemical and biomedical studies and practices. A section by Kneipp is devoted to single-molecule Raman probing.

Another well-developed application of nanoplasmonics has been optical near-field nanoscopy with sharp pointed plasmonic probes. There are three classes of such nanoscopy: (i) aperture-probe nanoscopy where the optical energy is supplied through a metallized tapered optical fibre; (ii) apertureless nanoscopy where the source light is focused in the far-field onto the sharp tip of a plasmonic metal probe, and (iii) adiabatic nanofocusing nanoscopy where the optical excitation energy is concentrated and delivered toward the tip of a nanoplasmonic taper. A section of this Roadmap by Gross and Lienau considers these three types of nanoscopy.

Another mature area of nanoplasmonics is related to the waveguiding of SPPs by plasmonic metal waveguides (wires and grooves) [8]. This allows the transmitting of optical energy and information through conduits of nanoscopic transverse dimensions for various subfields of optical sciences and technologies, including optical information processing. This direction is reviewed in this Roadmap in a section by Bozhevolnyi.

Many prospective applications of nanoplasmonics based on traditional plasmonic metals and novel plasmonic semiconductor materials are reviewed in a section by Saha *et al.* These applications extend from energy conversion to sensing and detection, to plasmon-assisted magnetic memory, etc.

An important class of novel plasmonic materials—topological insulators—is a subject of a section by Gholipour *et al.* The topological insulators possess semimetallic surfaces which have a sense of rotation imprinted on them by the so called Berry (or topological) phase. This forbids electron backscattering and leads to the high electron mobility desired for plasmonics. Yet another class of the systems where electron collisions are suppressed are superconductors, where the gap in the energy spectrum brings about vanishing resistance at zero frequencies and low resistance for frequencies below the superconducting gap. The superconducting plasmonic systems are considered below in a section written by Savinov *et al.*

The enhanced local optical fields in plasmonic systems induce many phenomena other than optical responses. One class of them is the subject of thermoplasmonics, where heat produced by decaying plasmons is put to gainful uses. One such application is in thermal theranostics (diagnostics and treatment of cancer tumours) [9]. An important area of thermoplasmonics is enhanced heat transfer with applications

to cooling very large integrated circuits. Thermoplasmonics and its developments are reviewed in a section by Boriskina.

Another class of plasmon-enhanced non-optical phenomena is photo-catalysis, which is due to enhanced optical fields, enhanced heat production and the generation of hot carriers resulting from plasmon decay [10]. This is reviewed in a section written by Vadai *et al.*

A modern area of study is ultrafast nanoplasmonics. Fundamentally, the shortest time, τ, of a response of any physical system is ultimately limited by the corresponding bandwidth, $\Delta\omega$, as $\tau \gtrsim \Delta\Omega^{-1}$. For plasmonics, with its bandwidth spanning almost the entire visible and infrared regions, this translates to τ in the range of a few hundred attoseconds. There are three sections in this Roadmap devoted to ultrafast plasmonics. One of them by Gross and Lienau has already been mentioned above in this foreword.

Another section written by van Hulst considers ultrafast wide-band coherent control of a nanolocalized optical field. The idea that the phase modulation of an ultrashort optical pulse allows one to control spatiotemporal distribution of local optical fields in plasmonic nanostructures was originally introduced theoretically some years ago [11, 12], and it has since been significantly developed both theoretically and experimentally.

A further section on ultrafast (attosecond) nanoplasmonics is written by Kling. It contains a review of a significant progress achieved in tracking the spatiotemporal evolution of nanolocalized optical fields on an attosecond time scale and a nanometre spatial scale. Since the initial theoretical proposal of such attosecond/nanometre tracking using a combination of photoemission electron microscope with attosecond metrology [13], there has been significant theoretical and experimental progress achieved in this area, which is reviewed in the above-mentioned section by Kling.

While most of the nanoplasmonic phenomena can be understood on the basis of classical electrodynamics and the bulk dielectric response of the constituent materials, such an approach may not work for very small nanoparticles or surface formations, such as narrow nano-gaps. In such cases, quantum-field description becomes important for local optical fields and the quantum chemistry approach is necessary for the underlying materials. The corresponding theories are conventionally called 'quantum plasmonics'. They are reviewed in this Roadmap in a chapter written by Esteban and Aizpurua.

In the preceding part of this Foreword, we have discussed nanoplasmonic phenomena of many kinds: linear, nonlinear, ultrafast, plasmonically induced thermal and chemical processes, etc. One common feature of these phenomena is that experimentally they are excited by external macroscopic optical sources, typically focused laser radiation.

In contrast, there exists a nanoscopic source generating coherent SPs directly on the nanoscale. This is a spaser (surface plasmon amplification by stimulated emission of radiation), which is a nanoplasmonic counterpart of a laser [14, 15]. This Roadmap has two sections devoted to experimental studies of the fundamentals and applications of spasers.

A section written by Wang *et al* is devoted to lasing spasers. Such spasers were introduced as periodic plasmonic arrays containing gain media [16]. When pumped above the threshold, a lasing spaser generates as a 'flat screen' laser producing intense coherent beam normally to its surface. This section describes the latest developments in the field of lasing spasers based on periodic metal nanoparticle arrays and dye molecules as the gain medium. The results presented include their dynamic spectral tuning.

Finally, a section written by Zhang and Yang reviews the latest progress in spasers (also called plasmonic nanolasers), which consist of a nanorod of semiconductor gain medium at the surface of a plasmonic metals. They generate on a hybrid mode tightly localized between the semiconductor nanorod and the metal surface. Such spasers are highly efficient, able to work at room temperatures, and are tuneable [17–19].

Concluding remarks. Modern nanoplasmonics is a flourishing science, rich in ideas, fundamental achievements, and applications. Among them are: biomedical and environmental sensing [5], detection of minute amounts of vapours from explosives [20], cancer diagnostics and treatment [9, 21], etc. In my opinion, the future of nanoplasmonics is in the fundamental progress with further extensions into areas of strong, ultrafast, and extremely nanolocalized fields, where theory will need to become fully quantum mechanical to accurately predict and describe new phenomena. At the same time, the existing applications will be further improved and commercialized, and new applications will be invented, and among those ultrafast optical computing may be one of the most important.

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2. Plasmonics for Raman probing at the single molecule level and at the nanoscale

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Status. The unexpectedly high Raman scattering signal obtained from molecules in the close vicinity of nanometer scale silver and gold structures—the effect of so-called 'surface-enhanced Raman scattering (SERS)'—might be one of the most impressive effects for demonstrating the power and the potential of plasmonic approaches in optical spectroscopy [22]. Raman scattering performed in high local fields of plasmonic nanostructures allows us to detect and structurally identify single molecules and to collect vibrational information at a subnanometer resolution. Giant SERS enhancement has been obtained for composites of nanostructures, such as random aggregates or a regular top down arrangement of nanoparticles with small interparticle gaps or fractal structures [23]. During the most recent decade, electron energy loss spectroscopy (EELS) became increasingly popular for exploring plasmonic structures [24]. Figure 1 illustrates potential interactions of a plasmonic nanostructure with photons and electrons. Overall, the current experimental and theoretical insight shows that bright and dark modes, including also mode interaction and damping, are of essential importance for the SERS performance of a plasmonic nanostructure [23].

In particular, non-linear incoherent and coherent Raman processes benefit from plasmonic support since they scale with enhanced local fields to higher powers. For example, while SERS depends on local fields to the power of four, surface enhanced hyper Raman scattering (SEHRS) depends on local optical fields to the power of six. This compensates for the extremely small hyper Raman cross sections and makes SEHRS a regular spectroscopic tool which improves the structural selectivity in sensing and imaging [26]. Unique field confining properties, due to plasmonic Fano resonances along with the dependence of surface enhanced coherent anti Stokes scattering (SECARS) on the local field to the power of eight, enable coherent Raman probing at single-molecule sensitivity [27]. A combination of highly confined probed volumes produced by a metal tip apex with scanning probe capabilities is employed in tip enhanced Raman scattering (TERS). Single-molecule mapping with vibrational spectroscopic identification at a sub-nanometer spatial resolution has been reported from TERS using a scanning tunnel microscope [28]. This interesting experiment can be understood in terms of an efficient plasmonic resonance effect, due to sensitive tuning of the plasmon resonance of the nanocavity in the tunneling gap to the molecular vibronic transitions.

The first observations of surface enhanced femtosecond stimulated Raman scattering open up exciting new ways for probing ultrafast processes that might occur in plasmon-mediated interaction between molecules, surfaces and light [29]. Optimized plasmonic support enables a pump–probe coherent Raman experiment at the single molecule level and on individual nanostructures [30].

Current and future challenges. Important challenges might address the detailed quantification of the electromagnetic SERS enhancement and a deeper understanding of the chemical contribution to the SERS effect, as well as preparation of tailored and well-characterized plasmonic nanostructures. Here, we summarize a few topics, necessarily reflecting the personal view of the author.

-Information on the plasmonic spectrum, including bright and dark mode, as well as mode interaction and damping, is of a basic interest for a deeper understanding and optimizing of plasmon supported spectroscopy.

Moreover, computations show extreme changes in plasmonic near-fields within a few nanometers and less. Even sophisticated optical measurements cannot provide the spatial resolution for mapping out dramatic variations in local optical fields with sub-nanometer resolution. A challenge is to develop experimental tools for a comprehensive characterization of plasmon resonances and related local fields that also address the strong confinement of these fields.

-To our current insight, field concentration in the hottest spots of plasmonic nanostructures can result in total non-resonant SERS enhancement factors of 10^{14} with a field enhancement on the order of 10^{12}. Interesting questions include the upper limit of SERS enhancement in the hottest spots and their dimensions, as well as what drives molecules to the hottest hot spots.

-For small interparticle gaps in the sub-nanometer dimension, 'classical' plasmonic structures can also exhibit a quantum nature. Interestingly, composites of nanoparticles with very narrow gaps seem to provide the highest SERS enhancement. Therefore, in order to understand plasmon enhanced Raman scattering at a high enhancement level, quantum effects have to be incorporated, and theoretical and experimental tools to explore the quantum effects in plasmon supported spectroscopy need to be further developed (see section 10 by Aizpurua).

-Strong anti-Stokes to Stokes SERS signal ratios, which indicate deviations from the Boltzmann distribution, along with spontaneous anti-Stokes SERS, which depends quadratically on the excitation intensity, have been observed and discussed in the framework of unexpectedly high effective SERS cross sections [31]. Recently, such effects have been theoretically inferred also by a quantum mechanical description of Raman scattering from molecules in plasmonic cavities [32] and by a cavity optomechanical model of SERS [33]. In this context, it is interesting to look at the correlations between anti-Stokes and Stokes photons, as has been discussed for 'normal' Raman scattering a long time ago [34] and which has also been recently theoretically considered for Raman photons generated in a plasmonic cavity [32]. Extending experimental anti-Stokes to Stokes correlation studies to plasmon enhanced incoherent and coherent Raman effects is therefore a challenge of extreme interest.

-SERS performed in optical traps in combination with sensitive measurements of mechanical forces that are exerted on the SERS-active structure, due to the momentum transfer of the emitted SERS photons [35], might provide an additional observable for exploring the SERS process.

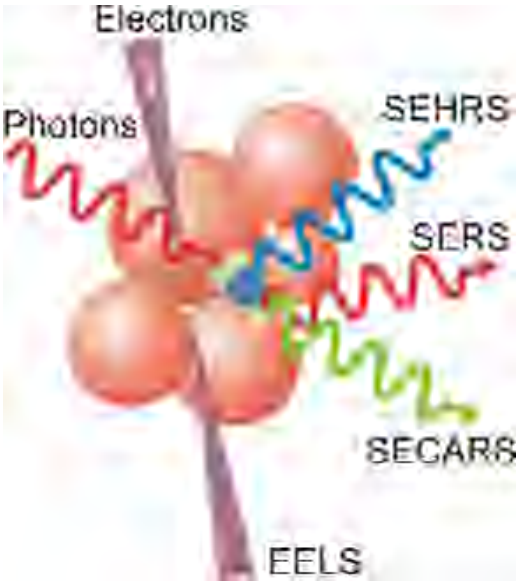

Figure 1. Linear and non-linear surface enhanced Raman scattering and electron energy loss studies on a plasmonic nanoaggregate. Reproduced from [25] with permission of The Royal Society of Chemistry.

-Since the early days of SERS, experiments suggest a second enhancement mechanism which might occur, due to so-called 'chemical or electronic effects'. Charge transfer (see also section 8 by Dionne) between the molecule and metal are considered as the most likely basic process for those 'chemical contributions'. Despite the fact that the key effect in SERS is caused by plasmonic field enhancement, the quantification and understanding of small chemical contributions to SERS on top of a well quantified plasmonic enhancement could be the basis for sensitive probes to explore surface processes, such as catalysis and spectral sensitization.

-The most exciting current practical applications of SERS seem to occur for advanced sensing and imaging in the biomedical field. SERS nanosensors inside a biological object, such as a living cell, can provide information on the structures and processes from molecular perspectives. Challenges include the development of multifunctional sensors with optimized plasmonic nanostructures as basic building blocks. Local optical fields provided by these structures could enable both sensitive diagnostics and efficient therapeutic tools based on SERS in combination with plasmon supported improved light-based therapies.

Advances in science and technology to meet challenges. Linear and non-linear SERS signals collected from single molecules open up direct ways for sensitive characterizing the plasmonic near field at the location of the molecule. The complementary use of photons and electrons enables us to access a new level of information by combining the high energy selectivity of laser radiation with the atomic scale spatial resolution of electron microscopy. This will allow us to probe the complete plasmon resonance spectrum including bright and dark modes and to generate maps of local fields and hot spots at subnanometer resolution, as well as to determine local field intensities as a function of photon energy.

New capabilities to characterize plasmonic properties are of particular interest for structures where quantum effects start to play a role, such as metal nanostructures with small gaps. Sophisticated SERS studies show a decrease of the enhancement for dimers with gaps in the subnanometer range, in contrast to the behavior of 'classical' plasmonic dimers, which show an increases of SERS enhancement with decreasing gap widths [36]. EELS studies show that silver dimers with atomic scale gaps can exhibit a regime, in which charge transfer plasmon modes, as a hallmark of a quantum nature, and 'classical' bright and dark dipolar plasmon modes, can exist simultaneously [37]. This critical range determines the limit in plasmonic SERS enhancement.

Advances in nanotechnology will enable the controlled preparation of tailored nanostructures that can generate field localization at the plasmonic limit.

Improved models and computations, also including quantum effects, will allow us to theoretically describe such plasmonic structures and plasmon enhanced effects.

Concluding remarks. SERS, and also in particular its extension to multiphoton excitation and to coherent non-linear Raman effects, as well as its combination with scanning probe techniques, provides exciting spectroscopic capabilities: (i) structural sensitivity and selectivity of vibrational spectroscopy, (ii) methodological advantages of multiphoton and coherent spectroscopy, (iii) single molecule sensitivity and subnanoscale resolution, which is inherent to plasmon supported spectroscopy, due to dramatic field concentration. Vice versa, linear and non-linear single molecule Raman spectroscopy is a powerful tool to probe the plasmonic nearfield. As a model process, a deeper understanding of controlling the plasmon supported Raman effects can deliver important insights for the optimization of other photon-driven processes performed in enhanced local fields (see also section 4 by Shalaev).

3. Plasmonic waveguides and circuits

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Status. Surface plasmon polaritons, often shortened to surface plasmons (SPs), represent electromagnetic (EM) excitations coupled to surface collective oscillations of free electrons in metal, thus forming two-dimensional (2D) bound waves propagating along metal–dielectric interfaces and exponentially decaying into neighboring media [38]. The topology of the metal surface determines the characteristics of the propagating SP modes that, although featuring limited propagation lengths, due to inevitable EM absorption in metals, can be localized far beyond the diffraction limit in the cross section perpendicular to the propagation direction. Recognition of this unique feature of SP-based waveguides, implying the possibility of combining the compactness of an electronic circuit with the bandwidth of a photonic network, has attracted enormous attention to the field of SP-based nanophotonics [39]. Many different SP-based waveguide configurations (figure 2), each offering specific advantages and suffering from particular limitations, have been developed over a decade of intensive research in an attempt to optimise the tradeoff between the mode confinement and propagation loss (stronger confinement causes larger loss) found in all plasmonic waveguides [38]. Another unique feature of SP waveguides is related to the possibility of the SP propagation control with electrical currents conducted by the same metal circuitry that supports the propagating SP modes, a feature that can advantageously be exploited to drastically decrease energy consumption in active components [40]. The inherent problem of propagation loss in plasmonic waveguides with extreme SP confinement can be circumvented by judiciously designed couplers interfacing plasmonic and low-loss photonic (i.e. all-dielectric) waveguides [41]. Finally, besides the unprecedented compactness of SP-based circuitry and its seamless integration with electrical wiring, extreme SP mode confinement opens a way to very efficient coupling of quantum emitters (QEs) to SP modes, as well as boosting up the QE emission rates via the Purcell effect [42]. Overall, the current status in SP-based nanophotonics indicates clear perspectives to the realization of complex ultrafast, compact and green (i.e. with low power consumption) plasmonic circuitry for diverse applications, including quantum optics.

Current and future challenges. Most important challenges in the field of SP-based nanophotonics are associated with the aforementioned loss-confinement tradeoff materializing in very short propagation lengths of strongly confined SP modes. This feature, along with the fact that all material effects (thermo-, electro- and magneto-optical, as well as nonlinear optical effects) are inherently weak, implies that the challenge of realizing efficient, low-loss and compact active SP-based components is enormous. For the same reason, it is very difficult to design an entire plasmonic circuit that would efficiently integrate several (passive and active) components into a single chip [43]. Another challenge is related to the fact that the widely used noble metals, gold and silver, although exhibiting superior plasmonic characteristics, especially with respect to energy dissipation, are not compatible with CMOS (complementary metal-oxide semi-conductor) technology, i.e. are not allowed for use in semiconductor foundries with technological processes being extremely well developed (in terms of node definition and large-scale production) for the needs of the computer industry. Additionally, the softness of noble metals and their low melting points preclude the usage of conventional plasmonic components in many real-life applications. These material challenges have stimulated intensive search for alternative plasmonic materials that would, at least partially, alleviate the problems associated with the usage of noble metals [44].

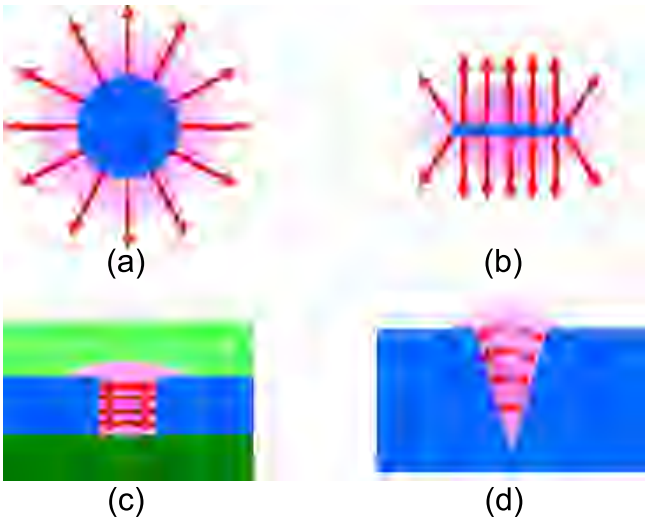

Figure 2. Main configurations of plasmonic waveguides, whose modes can be confined far beyond the diffraction limit (with blue colour marking metal, green—dielectric, pink—mode intensity distributions, and red arrows indicate the electric field direction): (a) nanowire with a radially polarized mode, (b) nm-thin metal stripe with a short-range SP mode, (c) slot with a gap SP mode, and (d) V-groove with a channel SP mode. Reproduced from [38]. Note that nm-sized wires and metal stripes can be supported by low-index dielectric substrates without significant changes in the corresponding mode properties.

Advances in science and technology to meet challenges. Recent advances in fundamental science dealing with light–matter interactions at the nanoscale and in technological aspects of nanofabrication, material processing and optical characterization suggest several strategies for tackling the challenges listed above. One direction can be in developing stand-alone plasmonic components, which would take full advantage of unique features found in plasmonics while being also coupled to low-loss photonic waveguides, so as to ease their integration into photonic chips. Thus, recently compact (10 μm-long) all-plasmonic Mach–Zehnder modulators (figure 3) that operate at 70 GHz and feature energy consumption of 25 fJ per bit have been experimentally demonstrated [45], outperforming state-of-the-art silicon

Figure 3. Colorized SEM image of the main part of the Mach–Zehnder modulators, showing a silicon (blue) ridge waveguides supported by SiO_2 (grey) sublayer of a SOI substrate and gold (yellow) circuitry. The latter includes contact pads (1–3) with a gold island contacted through a suspended bridge. Note that gold electrodes also serve as walls of 90-nm-wide slot waveguides. Reprinted by permission from Macmillan Publishers Ltd: Nature Photonics [45], Copyright (2015).

modulators in terms of footprint, speed and energy consumption. These excellent characteristics stem from the very strong SP mode field confinement in slot waveguides (figure 2(c)) that serve as the two arms of a Mach–Zehnder interferometer (figure 3), resulting in an excellent field overlap between the gap SP modes and applied electrical signals and also causing considerable slow-down effects. Overall, this breakthrough achievement became possible due to developments in the efficient coupling of plasmonic slot waveguides with dielectric silicon-on-insulator (SOI) waveguides and in producing highly nonlinear polymers that can feature (after poling at elevated temperatures) the linear electro-optic coefficients larger than those of the best crystalline materials [46]. It is to be noted that the modulators operate at telecom wavelengths within at least a bandwidth of 100 nm, promising the modulation bandwidth of $\sim$1.1 THz, and that the SOI technology used for fabrication of the dielectric waveguides in the reported modulators is, in principle, CMOS compatible. It should be emphasized that a complete CMOS compatibility requires the usage of something other than noble metals, and the intensive search for alternative plasmonic materials has been conducted during the last five years [44]. Thus, transition metals, titanium and zirconium, nitrides have recently been proposed as refractory, i.e. capable of sustaining high-temperature and high durability, plasmonic materials that exhibit good optical properties, while also offering CMOS compatibility (see 'Novel Plasmonic Materials' in this Roadmap).

Concluding remarks. Theoretical and experimental studies of plasmonic waveguides capable of confining SP guided modes far beyond the diffraction limit [38] and the development of SP-based passive (splitters, waveguide-ring resonators, Bragg gratings and directional couplers) and active (modulators, switches, logic gates, single-photon sources, lasers and detectors) components [39] have already demonstrated the superior performance and unique characteristics of plasmonic devices [45], revealing the enormous potential of SP-based nanophotonics [47]. The key features of plasmonic waveguides are strong local field enhancement (several orders of magnitude) and concentration of light energy into nm-sized volumes, which also open up new, exciting avenues in sensing, detection, imaging and manipulation techniques at the nanoscale, as well as in the fields of quantum optics and opto-mechanics. The successful exploration following these important research directions, including the realization of various plasmonic devices and circuits exploiting their unique features and benefits, hinges on further technological and theoretical progress. Nanofabrication techniques securing sub-nm precision in dimensions and, especially, gaps in metal-dielectric-metal structures have to be developed further, bringing them closer to the realm of industrial-scale production. Importantly, the control of surface roughness has to be reinforced as the impact of surface roughness on strongly localized SPP modes in plasmonic nanostructures is significant, causing additional (both scattering and absorption) losses and reducing practically achievable local field enhancements. The latter is of crucial importance for quantum plasmonics, which is expected to provide enormous Purcell factors, resulting in ultrafast single-photon sources (see section 10 in this Roadmap). Here, major progress in our theoretical knowledge is required to develop an adequate description of electromagnetic fields in and around sub-nm-sized gaps and edges with both tunneling and nonlocal (linear and nonlinear) effects being taken into account. Finally, all of these developments should be carried out in conjunction with research into new materials, including better plasmonic metals, dielectrics with stronger material effects, as well as more robust and efficient single-photon sources and detectors.

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4. Practical applications of plasmonics enabled by new materials

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Status. The large wave-vectors of surface plasmons enable the confinement of electromagnetic fields into dimensions much smaller than the diffraction limit. The strong field-confinement and fast speeds lead to applications in optical signal processing in communications (see for example [48] and references therein), plasmon-enhanced sensing of chemicals [49, 50], and particle trapping using plasmonic nano-tweezers for applications in quantum optics and bio-science [51, 52]. The scattering and absorption of light and the associated ohmic heating in plasmonic nanostructures have found use in various applications such as photothermal therapy [53] and energy harvesting [54, 55]. To support the development of practical plasmonic systems, the exploration of novel plasmonic materials has received significant attention over the last decade. The focus of such research is to establish material platforms that overcome the limitations of traditional plasmonic materials (see review [56] and references therein). Figure 4 serves as an illustration of this trend. The following sections describe the state of the art for plasmonic applications across major fields.

Ultra-compact, high-speed interconnects and modulators for communications. The high field-confinement in plasmonic waveguides enables the design of interconnects with dimensions much smaller than the diffraction limit, which operate at optical bandwidth. The enhanced light–matter interaction in metal-insulator-metal slots enable the design of modulators that can operate an order of magnitude faster than their electronic counterparts and with a reduced footprint than their optical counterparts. Most of the research on plasmonic waveguides has centred on gold and silver, due to their low ohmic loss, wide availability, and ease of deposition, but they are not CMOS-compatible. Despite this, the benefits of nanoscale light guiding and control has continually fuelled the exploration of plasmonic waveguides and modulators. These efforts have resulted in devices that match or even exceed the performance of photonic interconnects/modulators [57, 58].

Photothermal therapy and photocatalysis. Hot-carriers are photoexcited charge carriers with energies larger than those that are thermally excited at ambient temperatures. In their transient high-energy state, photoexcited hot-electrons can catalyse chemical reactions by exciting vibrational transitions in molecules adsorbed onto the metal surface. This effect is known as photocatalysis [59, 60]. The decay of hot-carriers within specially designed nanostructures can heat the surrounding environment significantly. This effect is used in plasmon induced photothermal therapy, where plasmonic nanoparticles are injected into tumours, and then are excited with photons, killing the tumour cells through resonant heating (see for example [53, 61] and references therein). Noble metals have been frequently utilized in pioneering studies, due to well-understood nanoparticle synthesis and high-quality plasmon resonances located in the visible range.

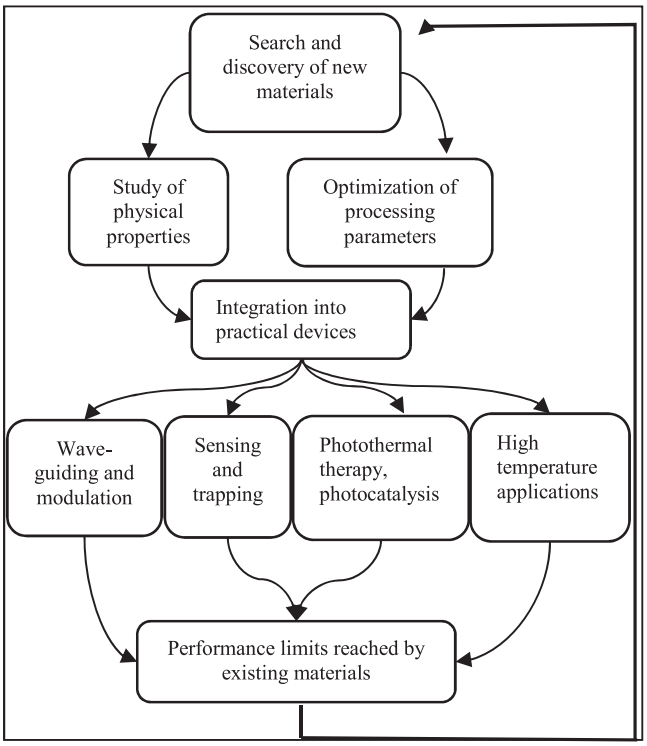

Figure 4. New plasmonic materials: from discovery to application.

Refractory plasmonics. Several plasmonic applications involve operation at elevated temperatures. For data storage applications, heat-assisted magnetic recording (HAMR) employs plasmonic nanoantennas to achieve sub-diffraction focusing of light into a magnetic medium. The absorption of light by the magnetic medium results in localized heating of the medium, thereby reducing the coercivity of nanomagnets for a short duration of time, enabling re-writable data storage (see references in [61]). For energy harvesting, thermophotovoltaic (TPV) systems rely on engineered spectral emission from an intentionally heated body, causing it to emit light in a spectral range that can be readily absorbed by a silicon solar cell, boosting the absorption efficiency [62]. Metamaterial designs have been shown to achieve broad absorption in the visible and near infrared regions, which shows that there is strong potential in employing metamaterial based absorbers using refractory plasmonic materials to further this goal [61].

Current and future challenges. Integrating plasmonic modulators with on-chip photonic circuitry requires the integration of plasmonic interconnects and modulators with electronic circuits on a CMOS platform. The large coupling and

Table 1. Plasmonic materials for various applications.

Applications	Desired properties	Materials
Interconnects [48, 56, 57]	Low optical losses	TiN, ZrN
	CMOS compatibility	Cu, Al
	Cheap	
Ultrafast switching [57, 62, 63]	Ultrafast carrier response	AGO, GZO
	Electrical tunability	Graphene
	Optical tunability	
Photothermal therapy [53, 59]	Chemical inertness	Au and TiN nanoparticles
	High field-enhancement	
	Resonance in the biological transparency regime	
Photocatalysis [59–61]	Chemical inertness	TiN nanostructures
	High field enhancement	
Energy harvesting [55, 59, 61, 62]	Light concentration and trapping	TiN
	Broadband absorption	Ag nanostructures
High-temperature applications [59, 61]	High thermal stability	TiN, ZrN
	High field-enhancement	

propagation losses of passive plasmonic components have been a major deterrent against the integration of plasmonic components in practical photonic circuits. Another big challenge is the CMOS incompatibility of noble materials. Cheap, CMOS-compatible, low-loss plasmonic materials in the form of transition metal nitrides have been investigated. However, nitride films are typically grown in a high-ambient temperature to achieve sufficient optical quality, which is a challenge to their back-end implementation in CMOS foundries [57].

The high-quality plasmon resonances of noble metal plasmonic nanoparticles make them useful for research in photocatalysis. However, challenges like their high costs, poor chemical stability, poor thermal stability, and their incompatibility with CMOS fabrication technology hinder the large-scale implementation of photocatalytic devices employing these metals.

Plasmonic applications, such as HAMR and TPV, involve operation at high temperatures. However, at such elevated temperatures, nanostructures of noble metals inevitably undergo structural deformations [61]. As a result, plasmonic responses dramatically degrade at elevated temperatures, making it preferable to construct these structures with a material that can sustain such high temperatures.

Furthermore, few investigations have been reported on the optical properties of plasmonic materials at elevated temperatures. At high temperatures, various physical processes, such as increasing electron-phonon interactions, changes in the carrier densities, crystallinity and grain boundary movements, are expected to greatly affect the optical properties of the materials being used. These temperature-induced changes must be incorporated into numerical models to accurately describe their behaviour, making it critical to study the optical response of both noble and refractory materials at elevated temperatures.

Advances in science and technology to meet challenges. Several groups of materials exist which can address each of the challenges outlined in the previous section.

Transition metal nitrides, such as titanium nitride (TiN) and zirconium nitride (ZrN), have optical properties close to that of noble metals. Studies involving their use in applications, such as plasmonic interconnects, optical sensing, particle trapping, TPV and HAMR, show very promising results [56, 57, 61]. Transparent conducting oxides, such as indium tin oxide (ITO), aluminium-doped zinc oxide (AZO) and gallium-doped zinc oxide (GZO), are CMOS compatible, tunable and are suitable for use in modulation applications [57].

The added flexibility in design and fabrication offered by newly developed CMOS-compatible plasmonic materials adds another degree of freedom for the design of active components for integrated plasmonics. The material properties of TMNs, such as their epsilon-near-zero (ENZ) crossovers and their carrier concentrations, can be altered by controlling the growth environment, enabling customizable optical properties based on application. TiN as a CMOS-compatible material for on-chip LRSPP interconnects was recently demonstrated [57]. For a TiN-based plasmonic modulator, transparent conducting oxides such as ITO, AZO and GZO can serve as an ideal active component. Recent investigations into the high nonlinear modulation of the refractive index of doped oxides in the epsilon-near-zero region [63] have opened a path towards the design of on-chip ultrafast optical modulators. Moreover, compact, CMOS integrated modulators involving 2D materials such as graphene have been explored and have the potential to outperform existing silicon photonic modulators in terms of speed, size and energy consumption per bit [58].

For use in photothermal therapy, nanoparticles must be biocompatible, of sizes that can be efficiently absorbed and released by cells and should act as efficient absorbers in the biological transparency window to achieve efficient heating with lower concentration. TiN nanoparticles possess all these properties [61]. TiN nanoparticles also have a native oxide layer on their surface that can be used to functionalize them with biological molecules for easier uptake by cells. These properties make TiN a viable candidate for use in the

photothermal treatment of cancer. In addition to their gold like optical properties, the thermal and chemical stability, corrosion resistance and CMOS compatibility make transition metal nitrides a practical alternative to noble metals for applications in photocatalysis.

TiN and ZrN have nearly three times higher melting points than gold and silver, making them promising candidates to realize plasmonic components for high-temperature applications such as TPV and HAMR [61].

Table 1 provides a summary of the desired material properties different areas research need, and suitable plasmonic materials that cater to these demands.

Conclusion. The past decade has witnessed a series of consistent technological developments in the realm of plasmonics. Noble metal plasmonics has played a key role in exploring different aspects of plasmonic technology and the design of proof-of-concept devices. But practical, industry scale applications of such technology call for the establishment of a wide material-base with materials that are cheap, robust, durable, tunable and have good optical properties. With continued exploration of new materials and a deeper understanding of the underlying physics in their interaction with light, we expect to see a significant impact of new plasmonic materials across multiple disciplines.

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5. Chalcogenide plasmonics: Topological insulators and phase-change media

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Status. Almost from its inception, the field of plasmonics has recognized and sought solutions to the assorted (in some cases application-dependent) technological drawbacks of reliance upon noble metals, including optical losses, low-melting-points, cost and CMOS-incompatibility. The quest for alternative material platforms now encompasses conductive oxides, nitrides, superconductors, graphene and other 2D materials, to name but a few (see sections 4 and 6).

Chalcogenides—compounds containing at least one of the 'chalcogen' (periodic table group 16)—elements sulphur, selenium or tellurium—are perhaps best known as 'phase-change media'. Alloys such as Ge:Sb:Te (GST) have properties that are widely compositionally controllable, and they can be switched in non-volatile fashion by external (optical or electronic) stimuli between physical states with markedly different refractive indices, conductivities, etc. Such materials underpin optical data storage technologies (i.e. rewritable CDs/DVDs), and have played a significant recent role in (nano)photonics and photonic metamaterials research as 'active media', delivering a variety of tuneable, reconfigurable, and nonlinear optical functionalities through hybridisation with noble metal plasmonic structures. With the recent demonstration that sputtered thin-film GST can itself be plasmonic at optical frequencies [64], indeed that phase switching may reversibly (de)activate plasmonic characteristics, it is apparent that chalcogenide phase-change media have more to offer in the field of active plasmonics.

Indeed, many chalcogenide alloys are so-called topological insulators (TIs)—semiconductors with topologically protected metallic surface states arising through strong spin–orbit interactions. After first being predicted in the late 1980s [65], the emergence of topological surface states within semiconductor bandgaps (figure 5) was confirmed only relatively recently via angle-resolved photoemission spectroscopy (PES), and is now typically verified by magneto-transport measurements. The presence of Drude-like conducting surface carriers makes TIs extremely attractive for plasmonics, because: (i) the surface states are inherently immune to scattering from disorder and defects, which may reduce optical losses; (ii) their optical properties may be controlled again compositionally and dynamically via external electric, magnetic or optical excitations [66]; (iii) the optoelectronic response can be highly sensitive to the polarization state of incident light, via the spin-momentum locking effect [67], potentially enabling hybridization of spintronic and plasmonic devices. Recent demonstrations of TI metamaterials with THz to UV spectral dispersions engineered through artificial structuring [68, 69], and experiments showing electrical and magnetic control of mid-IR to THz plasmonic response [66], clearly illustrate the future potential of TIs for broadband and reconfigurable plasmonics.

Current and future challenges. From a fundamental perspective, many intriguing aspects of TI materials are yet to be understood, and will necessitate development of new theoretical frameworks and advanced experimental techniques. For instance, the recent development of spin-, time- and angle-resolved PES has recently enabled the identification of a new surface resonance which is distinct from topological surface states [70]. There is also a need to extend the library of TI material systems beyond conventional chalcogenide TI crystals, for example, to include more rare-earth compounds [71]. From a practical standpoint, the surface layer in TIs is extremely thin (of order 1–2 nm) so its contribution to the overall optical response is relatively small, particularly at optical frequencies. Harnessing the unique properties of topological surface states therefore necessitates production of high-quality thin crystalline films, providing reduced bulk contributions, over large areas with very high compositional uniformity.

Phase-change active plasmonic devices present similar challenges around compositional control and thin-film deposition quality, with the added practical complication in typical hybrid architectures—wherein the chalcogenide is in direct contact with (or extremely close proximity to) noble metal plasmonic components—that inter-diffusion of metal and chalcogenide elements under repeated cycling between phase states steadily degrades performance. The problem may be mitigated by passivation layers, but these inevitably compromise optical (e.g. reflection/transmission) switching contrast by distancing the active medium from the near-field of the plasmonic structure. Alternative device configurations are thus required.

Advances in science and technology to meet challenges. At near-IR wavelengths, GST is a broadly transparent dielectric with a (compositionally-dependent) refractive index >2 (higher in the crystalline phase). As such, it can serve as a material platform for all-dielectric (as opposed to plasmonic) metamaterials, with non-volatile, laser-induced phase transitions enabling resonance switching in nanostructured metasurfaces [72] and reversible greyscale direct-(re)writing of arbitrary flat-optical metadevices in unstructured thin films [73]. Dramatically different behaviour is observed in the UV–vis spectral range. Here, the amorphous-to-crystalline transition produces a change in the sign of the real part of GST's relative permittivity ε, from positive to negative (figure 6): it becomes a plasmonic, and for certain wavelengths an 'epsilon-near-zero' (ENZ), medium [64].

High quality single crystal TIs can readily be grown from molten alloys and the optical frequency plasmonic properties of $Bi_{1.5}Sb_{0.5}Te_{1.8}Se_{1.2}$ have been demonstrated through the realization of metasurface structures, with resonances between 350 and 550 nm, on the cleaved face of such a monocrystal [68]. High-end fabrication techniques, such as

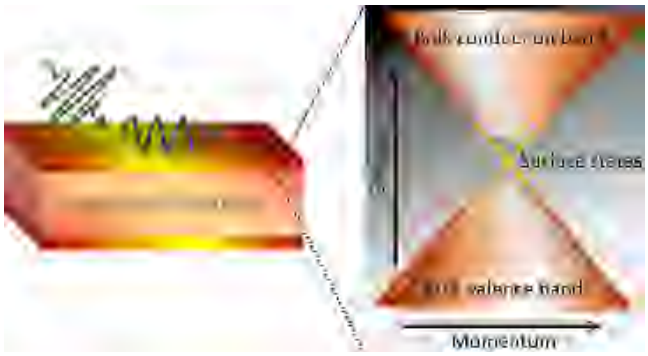

Figure 5. Light incident on a TI generates surface plasmons by coupling to topological surface states, which arise in the bulk bandgap due to strong spin-orbit coupling as depicted in the simplified schematic band structure to the right.

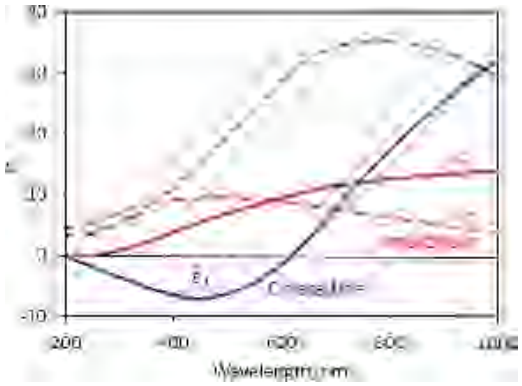

Figure 6. Ellipsometrically measured spectral dispersion of the real (ε_1) and imaginary (ε_2) parts of the relative permittivity of a 500 nm GST film in its amorphous (red lines) and crystalline (blue) phases, showing a negative value of ε_1 in the UV-visible range between zero-crossings at ∼200 and ∼600 nm.

molecular beam epitaxy, are now being employed for the growth of high-quality TI thin films and can provide exceptional control over a variety of growth and compositional parameters. A broad search is now required to identify alloy compositions providing low-loss TI plasmonic and ENZ characteristics in application-specific wavebands, together ideally with fast, high-contrast switching responses to low-energy optical and/or electronic excitations. This 'materials discovery' challenge is not dissimilar to that presently faced in relation to phase-change data storage and memristor research, and must be accompanied, for photonic and electro-optic applications, by the evolution of scalable materials processing (including nanostructuring) techniques that preserve the highest levels of optical quality and uniformity. New optical polarimetry techniques may also be developed to screen the topological character and properties of TI materials, as an alternative to angle-resolved PES and magneto-transport measurements.

Concluding remarks. As phase-change media, chalcogenides have a substantial and long-established applications footprint in optical and electronic data storage technologies. We envision that the rapidly progressing understanding of the fundamental physics of TI plasmonic chalcogenides, together with the ongoing development of specialized growth, characterization, and device fabrication technologies, will lead to the establishment of a uniquely flexible CMOS-compatible platform, with compositionally tuneable as well as optically/electronically switchable properties, for active plasmonic, electro-optic and nanostructured photonic metadevices.

6. Superconductor plasmonics

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Introduction. Superconductivity is a fascinating phenomenon common to many materials at temperatures below 100 K [74]. The key important properties of superconductors are the ability to conduct currents with virtually no loss at low frequencies, perfect diamagnetism and the Josephson effect. In the past, the extremely low resistivity of superconductors, as well as the excellent nonlinear properties of Josephson junctions, have been used extensively in high-performance superconducting microwave devices. Over the last decade, superconductors have found applications in the growing field of terahertz/sub-terahertz plasmonics and in the related field of metamaterials [75]. Indeed, the combination of low-loss, strong nonlinearity and sensitivity to a wide range of external stimuli, such as temperature, light and magnetic field, could make superconductors the material of choice for plasmonics at terahertz/sub-terahertz frequencies (around 0.1–1 THz), a traditionally under-explored part of the electromagnetic spectrum, which has been steadily gaining prominence over the last two decades.

Central to plasmonics of superconductors is the diamagnetism. The free energy of a superconductor is minimized when no magnetic field exists in its bulk. Consequently, in response to an applied magnetic field, screening currents will be set up inside a superconductor to force the field out. The applied field will only penetrate a thin surface layer of a superconductor, with thickness of about $\lambda_L \sim 100$ nm, the London penetration depth. At low frequencies, the diamagnetic response contributes $\Delta\varepsilon_r = -(\lambda_0/2\pi \cdot \lambda_L)^2$ to the dielectric constant of a superconductor, where λ_0 is the free-space wavelength of the applied electromagnetic signal. It follows that in the terahertz/sub-THz range, with $\lambda_0 \sim 0.3$–30 mm, the real part of superconductor dielectric constant will be negative and in the range 10^5–10^9. The corresponding imaginary part of the dielectric constant can be of comparable size near the critical temperature, but decays to zero as temperature is lowered. This makes superconductors the most plasmonic solid materials available in nature. An added feature of plasmonics in superconductors is the ability to turn off the plasmonic response simply by heating the superconductor above its critical temperature. This allows us to experimentally distinguish the phenomena that arise solely as a consequence of plasmonic response.

Status. Having established the nature and magnitude of plasmonic response in superconductors, we now discuss the status of superconducting plasmonics in several different contexts.

Extraordinary optical transmission. Extraordinary optical transmission (EOT) refers to an increase in the transmission of light through films of perforated plasmonic materials as a result of excitation of localized or propagating surface plasmon modes [76]. Being a hallmark of plasmonics, extraordinary transmission was one of the first effects studied during the early development of superconducting plasmonics, with two groups reporting EOT in thin films of high-temperature superconductor yttrium-barium-copper-oxide in 2010 [77, 78] (see figures 7(a) and (b)). Subsequent studies demonstrated EOT in other common superconductors, such as niobium-nitride [75].

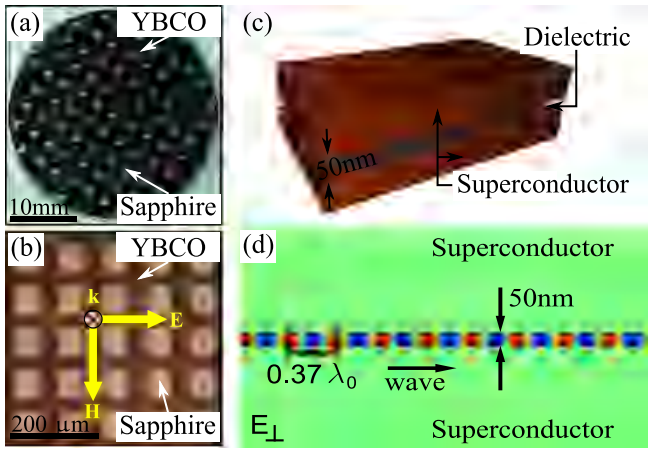

Figure 7. THz/sub-THz plasmonics using superconductors. (a), (b) Sub-wavelength hole arrays in yttrium-barium-copper-oxide film used to study extraordinary optical transmission in the terahertz/sub-THz range. (a) Reprinted from [76], with the permission of AIP Publishing. (b) Reproduced from permission from [77]. Yellow arrows in (b) denote the orientation of the electric (E) and magnetic (H) fields of the incident light, as well as the wavevector (k). (c) Schematic of the superconductor-insulator-superconductor (SIS) waveguide. (d) The simulation of the SIS waveguide performance (vertical scale is stretched). (c), (d) Reproduced from [78]. © IOP Publishing Ltd. All rights reserved. The colour map shows the longitudinal electric field ($\boldsymbol{E}_\perp$). The light is guided despite being confined to 50 nm laterally, which is 6000 times smaller than its free-space wavelength (λ_0).

Sub-micron scale plasmonic waveguides. Large negative real part and vanishingly small imaginary part of superconductor dielectric constant, at THz/sub-THz frequencies, in principle allows to trap and guide electromagnetic energy at substantially sub-wavelength length scales. However, the strong mismatch between the free-space dielectric constant and that of a superconductor, means that in case of guided surface plasmon modes, most of the electromagnetic energy will be in free-space, and, as a result, will not be localized to a significant degree. As demonstrated by Tsiatmas *et al* [78], strong localization of guided terahertz waves can be achieved in a thin dielectric layer sandwiched between the two superconducting layers (see figures 7(c) and (d)). The ratio between free-space wavelength and lateral confinement in such waveguides can be as large as 1:6000 whilst maintaining the propagation length of order 100 free-space wavelengths [79].

Plasmonics in Josephson junctions. An important device related to superconductor-insulator-superconductor waveguide is the Josephson junction [80]. Josephson junctions are created by separating two superconductors by insulating layer thin enough (up to few nm) for superconducting charge carriers to tunnel through it coherently. Dynamics of Josephson junctions are highly nonlinear and can be both classical and quantum-mechanical depending on exact fabrication conditions and the operating temperature (∼1–100 mK for quantum-mechanical effects). In the linear regime, the effects of tunneling superconducting charge carriers contribute an effective inductance to the equations of motion. This is known as Josephson inductance [75]. Together, the Josephson inductance and the diamagnetism-related inductance allow for the propagation of plasma waves inside the junctions, known as Josephson plasma waves [80]. Josephson junctions offer a rich variety of effects including THs/sub-THz wave generation, sensing, modulation, etc. The research into Josephson junctions goes back several decades, but is now experiencing a revival, aided by the interest in their applications in terahertz technology, quantum computing and quantum metamaterials [75, 80].

Plasmonic superconducting metamaterials. Superconductor plasmonics is central to the miniaturization of superconducting resonators in the microwave-THz range [75]. Consequently, there is a strong link and cross-fertilization between the fields of superconducting plasmonics and superconducting metamaterials.

Historically, there has been a lack of materials and devices with desired properties in the terahertz/sub-terahertz range (so-called 'terahertz gap'). Metamaterials, the man-made composites created by patterning on the scale smaller than the free-space wavelength of the electromagnetic excitation, have over the last decade been shown to provide numerous solutions to close the terahertz-gap [81]. Amongst them, superconducting metamaterials have been particularly important in delivering low-loss terahertz-range metamaterial devices for filtering, modulation, detection and nonlinear switching of terahertz radiation [75, 81, 82] (see figure 8).

Current and future challenges. Whilst superb performance can be achieved using superconductors as plasmonics waveguides and metamaterials, the gains are offset by the need to cool superconductors to low temperatures. Great advances have been made in increasing the transition temperatures of superconductors close to and even above 100 K [74], however the new high-temperature superconductors are generally harder to produce and harder to structure, thus their applications remain limited.

Fabrication precision required for terahertz metamaterials is usually quite low, with typical smallest feature size in the region of 10 μm. Even if one targets quality factors of order

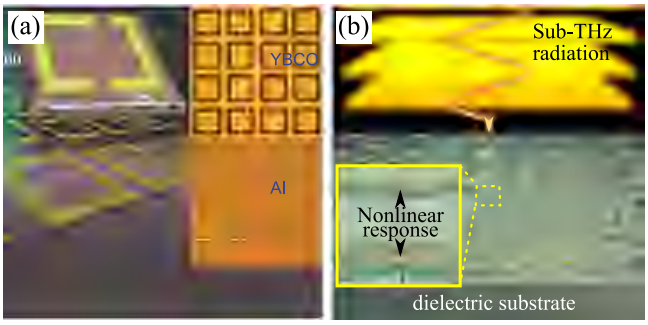

Figure 8. High-quality and nonlinear THz/sub-THz superconducting metamaterials. (a) Yttrium-barium-copper-oxide (YBCO) metamaterial with record high-quality response in THz range (dimensions in microns). [83] John Wiley & Sons. The inset shows the microscope pictures of the YBCO metamaterial, and non-superconducting aluminium (Al) metamaterial manufactured for the reference. (b) Niobium metamaterial with record-strong nonlinearity in the sub-THz range [84]. The constrictions in the split ring resonators (see inset) are primarily responsible for the nonlinear response.

$Q \sim 100$, the required fabrication precision is around 100 nm, which is quite tolerable for modern lithography and etching techniques. However, in the case of nonlinear superconducting metamaterials [83, 84], and even more so, in the case of devices that rely on Josephson effect [75, 80], the required fabrication precision can be 1–10 nm. The search for new and improved fabrication methods thus remains and important driver for nonlinear and quantum superconducting plasmonics.

Advances in science and technology to meet challenges. Discovery of high-temperature superconductivity in 1986, and the rapid rise in transition temperatures that followed it, has been an extremely important advance in the applied superconductivity [74]. However, the increase in critical temperatures has since stalled at around 130–160 K. The current advances that drive the applications of superconductors generally, and superconductor plasmonics in particular, are the continued improvements in conventional cryostat technology, as well as developments in solid-state optical cooling.

Concluding remarks. In conclusion, superconductors are great plasmonic materials for the terahertz/sub-terahertz range, offering low loss, extremely high kinetic inductance as well as a rich variety of nonlinear effects. Their future applications will depend on the continued development of compact cryostats, as well as discovery of new high-temperature superconductors well-suited for nano-fabrication.

7. Plasmonic nanoscopy

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University of Oldenburg

Status. Optical spectroscopy provides a wealth of information about the optical and electronic properties of nanoscale materials. It gives access to a variety of elementary optical excitations (excitons, spins, phonons, plasmons, magnons, etc.) in a broad spectral range, from the terahertz to the x-ray regime, probes polarization anisotropies and reveals nonlinear optical properties with unprecedented resolution. The use of ultrafast laser excitation gives insight into the quantum dynamics of optical excitations on femto- and even attosecond time scales and probes, for instance, the energy and spin relaxation or charge migration and transfer processes. Thus, optical spectroscopy is undoubtedly a most important tool to unravel structure-function relations in technologically relevant nanomaterials, such as semiconductor quantum dots, metallic, magnetic, hybrid or biological nanoparticles, solar cells, (photo-)catalysts or nanoscale batteries. An important restriction of optical spectroscopy is its spatial resolution, inherently diffraction-limited to approximately half a wavelength of the illumination light. For visible light, this is a few hundreds of nanometers, much larger than the typical geometric size of most nanoparticles. As such, diffraction-limited optical techniques usually cannot look into a single nanostructure and cannot resolve the wavefunctions of their elementary excitations. Super-resolution techniques can overcome the diffraction limit but usually do not provide spectroscopic information as they probe specific fluorophores rather than the embedding nanostructure itself. Thus, spectroscopic techniques providing nanometric spatial resolution are urgently needed to advance our understanding of the structure-function relation of nanomaterials. This holds in particular for time-resolved nanoscopy, offering nanometer spatial and femtosecond temporal resolution and thus the ability to trace the quantum dynamics of (coherent) charge- and energy-transport phenomena in space and time.

Current and future challenges. Metals, more precisely metal/dielectric interfaces, have very favorable properties for implementing ultrahigh resolution nanoscopy. They support surface plasmon polariton (SPP) excitations, mixed modes of charge oscillations in the metal and the re-emitted electric field that can transport optical excitations in the form of evanescent, surface-bound waves over distances of up to millimeters. In addition, surface plasmons can be localized to dimensions given by the geometric size of a metallic object or, more precisely, by the spatial extent of their localized electronic wavefunctions. This enables, in principle, light localization even down to atomic dimensions [86]. Hence, a smart combination of both properties, plasmon propagation and localization, may be used for generating a confined light source that is optimally suited for plasmonic nanoscopy (figure 9).

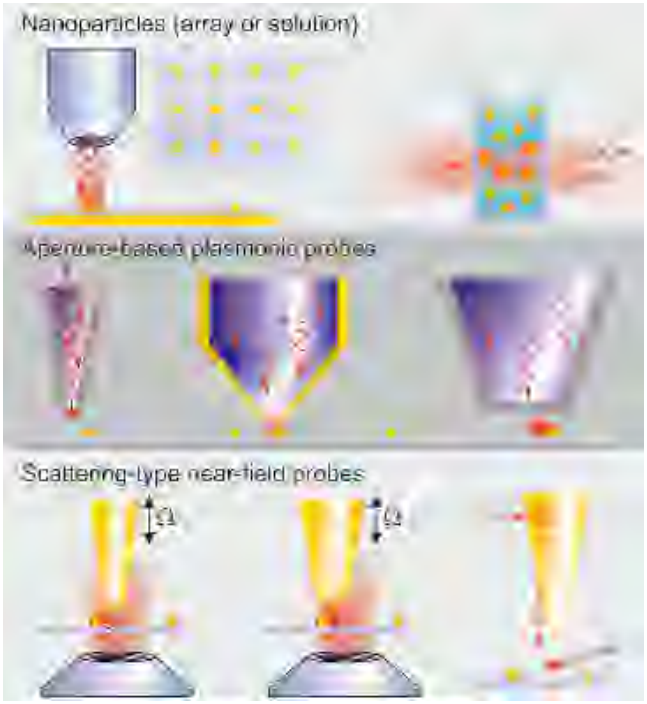

Figure 9. Schematic overview of plasmon-based approaches to light localization and nanoscopy.

This concept has been explored ever since the early days of near-field spectroscopy, when Pohl, Lewis, Betzig and others confined light by transmitting it through tiny apertures at the apex of a metal-coated fiber probe [87]. For aperture diameters below 50 nm the transmission coefficients are exceedingly low. A more favorable approach localizes far-field light by focusing it to the apex of a small conical metal taper, making use of local field enhancement to confine light to a size of roughly the radius of curvature of the tip. This scattering-type scanning near-field optical microscopy (s-SNOM) [28] is now implemented in different, commercially available instruments and is used, in particular in the infrared and terahertz region, for optical imaging of surface-bound electromagnetic fields with $\sim$10 nm resolution. Localization of light in the gap between tip apex and surface can further improve the resolution to below 1 nm, e.g. when detecting Raman sidebands [88]. It is challenging, however, to probe the weak optical near-fields that are resonantly scattered from the taper apex. Typically, these fields are superimposed on a large background of propagating fields and complex modulation and heterodyning techniques are needed to access the local optical near-field. This often puts constraints on the use of s-SNOM for broadband spectroscopy and makes the quantitative interpretation of the image contrast difficult. Consequently, serious effort has been put in the design of efficient near-field probes that can optimize the localized near-field intensity, reduce the scattering background and overcome the need for modulation techniques. Among the most interesting concepts are tip-on-aperture designs [89], metal particles attached to dielectric tapers [90] or the use of gold nanoflakes [91] as scanning probes. All these antennas display spectrally rather sharp resonances and hence are mostly

suited for light localization in a limited spectral region, hampering, again, applications in broadband spectroscopy. A powerful, highly efficient and broadband antenna design is the campanile probe [92]. It uses a metal-dielectric-metal cantilever waveguide to efficiently guide light to the apex and has been used for spectroscopic imaging of quantum wires, photonic crystals or two-dimensional semiconductor layers with a spatial resolution down to 40 nm. So far, the fabrication of all those antennas is quite demanding and they are conceptually much more difficult than, for example, a scanning tunneling microscopy tip for which the image contrast is basically just defined by its last atom.

Advances in science and technology to meet challenges. In principle, Maxwell's equations provide elegant solutions to the challenging problem of creating a point-like, isolated and spectrally broadband light source. A favorable geometry is a sharply pointed conical metallic taper [93, 94]. Such a taper supports rotationally symmetric, evanescent SPP modes with different angular momenta m. When exciting these modes at a finite distance from the taper apex, for example, by focusing far-field light to a grating coupler on the taper shaft (figure 10), the launched SPP wavepacket can propagate towards the taper apex. All higher order modes with $|m| \geqslant 1$ will radiate off the taper at a finite distance from the apex. The lowest order, monopolar $m = 0$ mode, however, is a bound mode even for vanishingly small taper radii. Hence, the far field light that is coupled to this mode is nanofocused to a localized spot with a field distribution of a point-dipole oriented along the taper axis. The spot size is solely given by the apex diameter, which can be as small as 10 nm [95]. Plasmonic nanofocusing is rather wavelength independent and may be realized in a broad spectral range from the visible to the infrared, provided that absorptive or reflective losses during SPP propagation are low and that the taper surface is sufficiently smooth to prevent SPP scattering into the far field. This has been achieved, for example, by using chemically etched, single crystalline gold tapers in the wavelength range between 700 nm and 2000 nm [96]. Effectively, such conical gold tapers form a broadband, almost dispersion-free plasmonic superlens that can localize light to dimension of one hundredth of the wavelength or even below. Scattering spectra from a single gold nanorod with 40 nm length and 10 nm diameter illustrate their plasmonic focusing power. These spectra are recorded by scanning a conical taper, illuminated at the grating with a coherent white-light source, across the surface. The light that is scattered from the apex is collected and detected with a CCD spectrometer. Spectra taken at the rim of the nanoparticle clearly reveal strong light absorption at the longitudinal SPP resonance of the nanorod. The signal vanishes completely when moving the tip a few nanometers away from the rod. The large amplitude of the absorption dip is the signature of essentially background free light localization to the taper apex. Such spectra are recorded

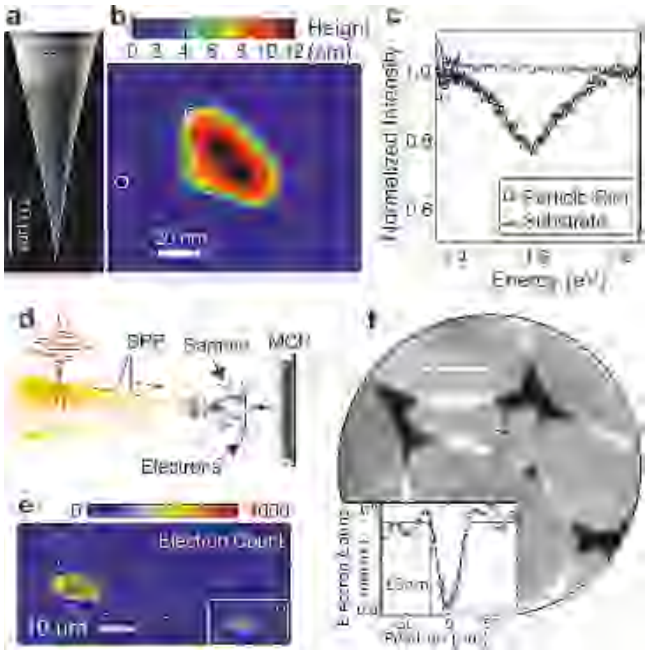

Figure 10. Plasmonic nanofocusing spectroscopy. (a) A gold nanotaper with grating coupler yields, (b) a topological image of a single gold nanorod and (c) optical spectra with nanometer resolution. (d), (e) Upon grating illumination electrons are emitted from the apex for (f) ultrafast electron microscopy.

within only a few milliseconds for every position on the sample and provide a detailed map of the local optical density of states of the nanorod or, more precisely, the coupled tip-nanorod system, in a broad spectral range.

When using ultrashort, few cycle light pulses for grating illumination, a temporal resolution of the localized light of 10–20 fs is reached, sufficient to probe, for example, the rapidly decaying dynamics of localized SPP hot spots in transient four wave mixing experiments [97]. Importantly, plasmonic nanofocusing of ultrashort pulses gives rise to high local electric strengths at the taper that can reach or even surpass the atomic field strength. This enables for instance multiphoton photoemission from the very apex of the tip and creates a bright, nanometer-sized and ultrafast electron source with pulse duration in the 10 fs range [98]. This source can immediately be employed for high-resolution point-projection electron microscopy, as illustrated with an image of a lacey carbon grid. Plasmonic nanofocusing facilitates short emitter −sample distances and hence prevents temporal dispersion of the electron pulse, making this concept interesting for application in femtosecond electron microscopy.

Concluding remarks. Plasmonic nanofocusing on conical metal tapers has the potential to generate bright and isolated light and electron spots with diameters of less than 10 nm and pulse duration of 10 fs or even below. The conceptual simplicity of these sources makes them highly interesting for

future applications in (ultrafast) nanospectroscopy and electron microscopy. Research is needed to transfer the concept to metals other than gold, to expand the wavelength range accessible by plasmonic nanofocusing and to implement reliable and cost-efficient tip fabrication methods.

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8. Controlling photochemistry with plasmonic nanoparticles

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Status. Photocatalysis plays an increasingly important role in our everyday lives, from water purification to air filtration, surgical instrument sterilization and self-cleaning windows. Traditional semiconducting photocatalysts, as well as metal complexes and clusters, have already proven to be invaluable in processes such as water splitting for hydrogen production and conversion of organic pollutants into H_2O and hydrocarbons. However, these traditional photocatalysts generally suffer from low efficiency, due to their limited optical absorption and their short electron-hole pair recombination times. Plasmonic particles have recently emerged as promising complements to traditional photocatalysts, either on their own or as co-catalysts [98]. Plasmonic nanoparticles possess a number of useful features for photocatalysis, including local heat generation, (figure 11(a)), optical near-field enhancement (figure 11(b)), and efficient hot carrier generation (figure 11(c)) [99], which can be exploited to control and enhance photocatalytic reactions [100]. For example, the strong electromagnetic fields at the surface of nanoparticles can enhance photopolymerization, photoisomerization and enantioselective reactions, based on the locally-enhanced photon flux. Similarly, localized heating associated with plasmonic near-fields can increase reaction rates and potentially enable spatially-dependent product formation, due to nanoscale reaction-rate variations. Finally, hot carriers generated upon plasmon decay are known to activate bond formation and/or dissociation; these hot carriers have already been used to induce chemical reactions including hydrogen dissociation on gold nanoparticles and the conversion of aldehydes to esters, which, notably, are prohibitively challenging with conventional photocatalysts. Measurements on both ensembles of plasmonic photocatalysts and single particles have revealed redox activity that is highly dependent on the excitation wavelength and polarization state, as well as the particle's shape, size, surface chemistry and interfacial barrier with semiconductor or molecular sensitizers.

Current and future challenges. While plasmonic nanoparticles are promising next generation photocatalysts, decoupling and distinguishing the various mechanisms by which plasmons induce chemical reactions at the nanoparticle surface presents a significant current challenge.

Specifically, several important questions persist: (1) to what extent do local electromagnetic fields, local heating and hot-carrier generation each contribute to certain reactions; (2) can one mechanism be promoted over another by controlling the particle composition, illumination conditions or other reaction conditions; (3) how do the nanoscale materials properties, including the composition, crystallinity and surface

Figure 11. Plasmonic nanoparticles can induce chemical reactions through (a) local heating, (b) strong near fields interactions and (c) hot carrier excitation upon plasmonic decay. The injection of hot carriers to the adjacent molecule can take place via (d) an indirect or (e) a direct charge transfer mechanism.

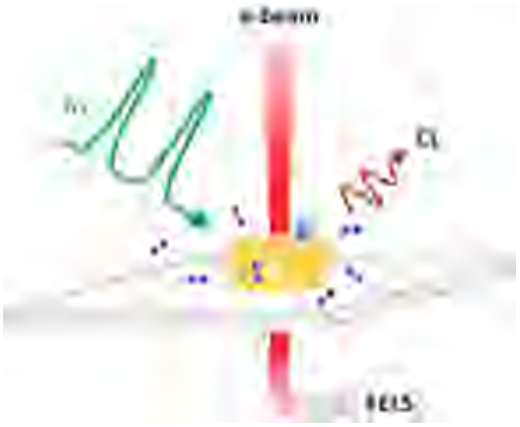

Figure 12. Optical excitation in an environmental electron microscope promises visualization of photocatalytic reactions with atomic-scale resolution. Shown is a schematic single-particle setup combining light excitation, electron microscopy, electron energy loss spectroscopy (EELS) and cathodoluminescence (CL).

construction, direct the chemistry; and (4) can plasmons be utilized to elicit selective chemical reaction pathways?

In the case of hot carrier injection, it is still unclear by what mechanism electrons are injected into unoccupied molecular orbitals. According to the indirect transfer process (figure 11(d)), the non-equilibrium electron energy distribution in the plasmonic particle transfers an excited electron into the orbital of a nearby molecule with similar energy. It has been recently argued, however, that a direct electron transfer (figure 11(e)) from a lower energy state in the metal to a higher energy orbital in the molecule is dominant in nanoparticle-adsorbate systems, without major modification of the metal's energy distribution [99, 101]. While these interesting findings are the result of extensive theoretical research, the experimental study of hot carrier generation in nanoparticles has received much less attention. It is thus desirable to extend current experimental capabilities and to demonstrate how both hot electrons and holes can be utilized in photocatalytic reactions. Such work will not only improve the efficiency of plasmonic photocatalysts, but will also have tremendous impact on other related applications, including photon upconversion and photovoltaics.

In the context of plasmon catalyst design, it is well known that the shape and size of nanoparticles, along with the material properties themselves, determine the plasmonic resonances and the accompanying decay paths [102]. Designing new plasmonic materials with precisely tuned photonic and electronic densities of states can expand the plasmonic toolbox for next generation photocatalysis with high product selectivity. For example, bimetallic nanoparticles may offer a highly controllable platform for photocatalysis, with one metal playing the role of the active catalyst for the reaction, while the other amplifies the plasmonic field and takes the role of the antenna. Alternately, plasmons in highly-doped semiconductors or hybrid semiconductor-metal particles may provide both tunable optical properties and controlled charge separation and charge transfer into selective molecular orbitals. It will also be crucial to carefully consider the particle geometry, and in particular, its surface. Many common photocatalysts have dimensions of less than 10 nm, and often only contain tens to hundreds of atoms. It has already been shown that quantum effects, such as the energy discretization in these small particles, modify their plasmonic response [103]. How their surface faceting affects plasmonic energies is still unclear. Both effects could have a strong influence on the efficiency of plasmon mediated photocatalysis.

Advances in science and technology to meet challenges. The current research frontier lies in *in situ* single-particle studies of plasmon dynamics. Such measurements offer advantages over those done in an ensemble, where nanoparticle heterogeneity conceals many important structure-dependent catalytic properties. Using advanced optical microscopies, photocatalytic reactions taking place on a single nanoparticle can be monitored with a resolution of tens of nanometers. One example is the pioneering study of the oxidation of ascorbic acid on a single gold nanoparticle [104]. In this work, dark field microscopy was used to image the nanoparticles while single particle surface plasmon spectra was acquired over time, allowing for determination of the reaction rate. In another super-resolution study, a redox reaction catalyzed by TiO_2 nanorods was monitored by the signal of the fluorescent product [105]. With this technique, it was possible to visualize the spatial distribution of the reaction with a sub-particle resolution of 30 nm.

In order to study structure-function correlation at increasingly smaller length scales, electron microscopy will prove to be invaluable. Recently, the remarkable capabilities of combined transmission electron microscopy (TEM) and electron spectroscopy were shown through studies of hydrogen intercalation dynamics in a single Pd nanoparticle [106]. When coupled with external optical illumination, this technique holds great promise for studying photocatalytic reactions with unprecedented resolution. New TEM systems are being designed with cathodoluminescence capabilities, promising an atomic-level view into both radiative and non-radiative decay pathways in plasmonic particles (figure 12). Incorporating state-of-the-art ultrafast pump-probe spectroscopy into these experiments will present an expansive set of tools for real time, high resolution analysis of reaction dynamics

Advances in scanning probe microscopies offer yet another high resolution toolkit for understanding plasmon-mediated chemistry at the nano- and pico-scale. For example, by spectrally matching the plasmon resonance of the STM tip to the molecular vibronic transition, Raman spectral mapping of isolated molecules was performed with sub-nanometer resolution, revealing structural and conformational information at a single molecule level [28]. In another study, a new approach for quantifying the number of molecules in small gaps was proposed based on the shift in the junctions plasmonic resonance and their conductivity [107]. Finally, a very recent study using atomic force microscopy offers opportunities for enantioselective chemical reactions mediated by plasmonic optical forces.

Concluding remarks. Far from simply amplifying photophysical and photochemical processes, small plasmonic nanoparticles promise new control of light-mediated reactions. These particles support a number of coexisting relaxation mechanisms for both photons and excited electrons, with distinct spatial, spectral and temporal signatures. While the contribution of individual mechanisms within plasmonic systems is still not fully understood, cutting edge theoretical tools and advanced microscopies and spectroscopies are helping to unravel carrier dynamics and their impact on catalysis. In the foreseeable future, researchers will be able to probe and control plasmon photocatalysis with sub-nanometer-scale spatial resolution and ultrafast temporal resolution, accelerating the synthesis of crucial chemical and biological products.

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9. Thermoplasmonics: turning material losses into performance gain

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Status. Traditionally, dissipative losses in plasmonic materials have been treated as an unavoidable nuisance [3, 108], and a lot of effort has been channeled towards their reduction or compensation. This effort fueled the emergence of several new directions in plasmonics research. One direction yielded increased use of hybrid photonic −plasmonic architectures [109] (see sections 3 and 11). Hybrid structures offer high spectral selectivity unattainable in purely plasmonic elements, albeit at the price of increased footprint, which impedes their use for metamaterial design. Another direction is in harvesting loss by utilizing hot carriers generated from nonradiative plasmon decay [59] (see sections 4 and 8). While highly promising, this mechanism makes use of a very short-lived (sub-picosecond-scale) window of opportunity before the hot carriers thermalize with the crystal lattice. Finally, new plasmonic materials have been discovered and synthesized to address the issue of material losses [110] (see sections 4–6).

Recently, a new paradigm emerged, in using excellent photo-thermal conversion efficiency of plasmonic materials and exploring new avenues of research based on harvesting and using generated heat [111–115]. This opened up new application areas for plasmonics beyond traditional sensing, spectroscopy, and metamaterials development. These areas include: solar and thermal energy harvesting [62], solar treatment of water and waste [116, 117], nanofabrication [118], nano-manipulation [119] and cancer therapy [120].

Other emerging applications—including plasmonically enhanced heat transfer through radiative channels [111, 114], thermophotovoltaics [62] and heat-assisted magnetic recording [121]—make use of the thermal activation of surface plasmon modes. Thermal pumping of plasmonic devices enables conversion of heat into partially-coherent thermal radiation with controllable spectral bandwidth and polarization properties (see [114] and section 4).

The unique localized nature of plasmonic heating makes the thermoplasmonic technology very attractive for precise nanofabrication (figure 13(a)), enabling heat-induced modification of individual nanoscale features as well as nano-welding that does not damage the underlying substrate or other parts of the plasmonic chip [118]. Targeted photo-thermal ablation of cancer cells (figure 13(b)) utilizes localized plasmonic heating to avoid damage to nearby healthy tissue [120]. Localized nanoscale heating already revolutionized data storage technology by helping to break the so-called 'magnetic recording trilemma' via increase of the individual grain temperature for data writing without affecting the surrounding grains [121] (figure 13(c)). It promises to increase the data storage density above 10 Tb/in^2. Ancient solar still technology is undergoing a surprising revival spurred by the possibility to dramatically

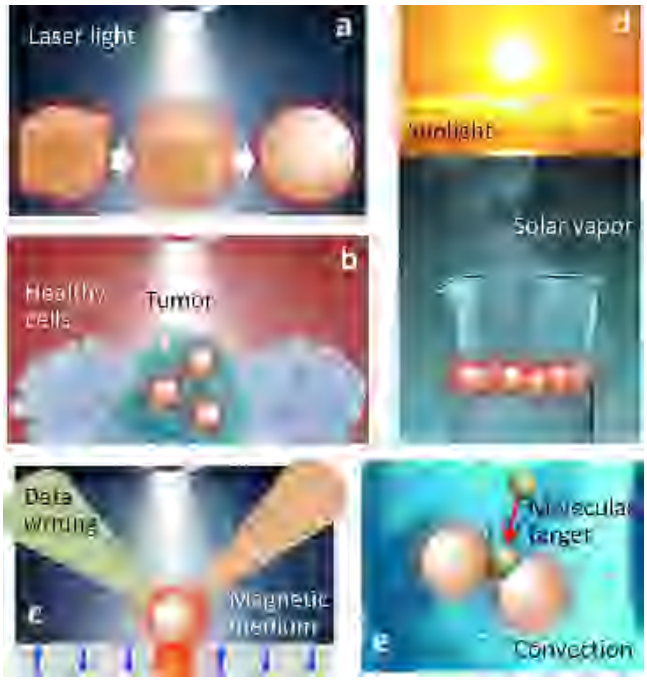

Figure 13. Light and heat localization underlies the use of thermoplasmonics for (a) nanofabrication, (b) cancer treatment, (c) heat-assisted magnetic recording, (d) solar water treatment, and (e) nanomanipulation.

increase the efficiency of the solar vapor generation by the interfacial heat localization between water and air [116, 117]. Plasmonics offers a mechanism to achieve such localization, yielding efficiency increase from 30 to 90% in recent experiments (figure 13(d)). Targeted heat transfer from plasmonic antennas to surrounding liquids also offers exciting opportunities for nano-manipulation and sensing of dilute molecular targets through thermally-induced local fluid convection [119] (figure 13(e)).

Superior spectral selectivity and strong near-field enhancement of plasmonic nanoantennas and surfaces makes them attractive candidates for solar and thermal energy harvesting as well as radiative cooling technologies. Unlike signal-processing or sensing, energy conversion processes typically require tailored spectral absorption characteristics of devices across a very broad spectral range, covering both visible and infrared spectral bands [62, 114]. Plasmonics offers tremendous opportunities for size, shape-, and coupling-driven spectral shaping and tuning of material absorptance. Successful plasmonic solutions to achieving spectral selectivity include nanostructured solar-thermal receivers as well as selective thermal emitters for thermo-photovoltaics [62, 114]. Both applications require high absorptance of high-energy photons and suppressed emittance of low-energy photons (figure 14(a)). Nanoparticle-filled thermal fluids can provide excellent selective filters for hybrid photovoltaic and solar-thermal energy conversion platforms (figure 14(b)). Finally, efficiency of plasmonically-enhanced thermal emitters can be dramatically elevated in the near-field coupling regime by making use of orders-of-magnitude increase of the local density of photon states

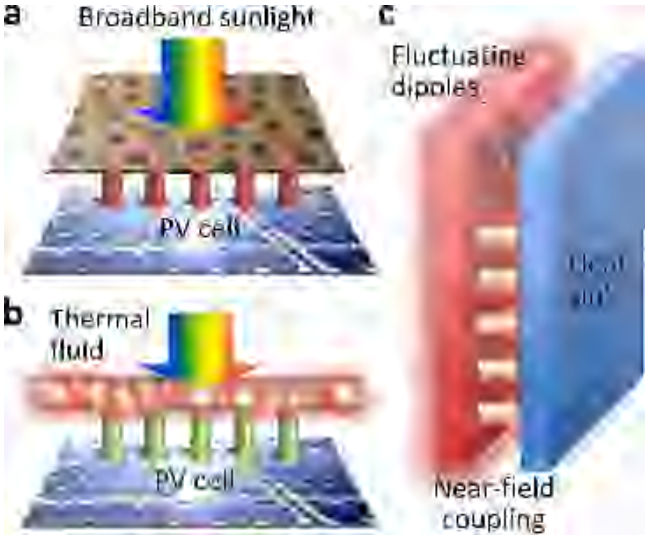

Figure 14. (a) Spectral conversion of broadband solar radiation by a plasmonic selective absorber/emitter for thermophotovoltaic applications. (b) Spectrally-selective nanoparticle-filled thermal fluids harvest the parts of the solar spectrum not suitable for efficient PV conversion. (c) Near-field radiation can be enhanced by orders of magnitude via plasmonic near-field coupling.

provided by the surface plasmon mode fields (figure 14(c)) [111, 114]. This paves the way for non-contact radiative cooling technologies and can boost both the efficiency and the power output of thermophotovoltaic and thermoradiative cells.

Current and future challenges. The biggest challenges to successful adoption of thermoplasmonics for energy applications are material costs, high-temperature stability and recyclability. Renewable-energy related installations typically require large capital investments, where material cost and abundance become extremely important. For health-related applications, the non-toxicity and bio-compatibility of plasmonic materials play an important role. Optical properties of many plasmonic materials have only been measured at near-room temperatures, necessitating further studies and data collection. Dissipative losses still need to be addressed, as they limit spectral bandwidth of absorption bands, as well as the near-field enhancement effects. Finally, practical realization of sub-micron gaps between near-field-coupled thermal emitters and heat sinks is extremely technologically challenging, calling for the development of new precise techniques for nanoscale fabrication and mechanical alignment.

Advances in science and technology to meet challenges. Recent advances in synthesis and characterization of new refractory plasmonic materials, including metals, metal alloys, oxides and nitrides [110], pave the way to the development of high-temperature selective absorbers and emitters [62]. Successful attempts to replace rare noble metals with more abundant and cheap materials, such as aluminum and carbon [115, 117], as well as strategies for material recycling via centrifugation or magnetization [122], hold promise for cost reduction of thermoplasmonic technologies. Near-field heat transfer across planar nanoscale gaps has also been recently achieved in the laboratory settings, bringing closer the era of near-field enhanced on-chip heat management [123]. Incorporation of phase-change materials into thermoplasmonic device designs can add switching, modulation and tunability functionalities.

Advances in thermoplasmonics have also spurred research and development in related fields. These include material phonon spectroscopy, thermal and thermally-enhanced photocatalysis and thermoelectrics among others [111]. Nanoscale plasmonic heaters help to overcome the diffraction limit in creating confined hot spots necessary to map the photon mean free path distributions for characterization of thermoelectric materials [115]. In turn, large temperature gradients induced by the plasmonic photothermal converters call for the development of new approaches to achieve a local nanoscale temperature readout, such as nanothermometry [114, 124].

Concluding remarks. High opto-thermal conversion efficiency provided by plasmonic materials opens the door to many unconventional applications in renewable energy and heat management. Despite many initial successes, the most impactful thermoplasmonic technologies will likely be only those that exploit unique properties of surface plasmons, such as spectral and spatial localization of light and heat not achievable with other materials. However, for large scale energy-harvesting installations, plasmonic solutions may ultimately prove too costly unless used with powerful optical concentrators and/or enable material recycling, and they may be replaced by cheap abundant materials, such as carbons and polymers [125].

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10. Quantum plasmonics

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Status. The optical properties of surface plasmons have been very successfully described during recent years within classical approaches that consider the dynamics of valence electrons in a metal as a collective harmonic oscillation of the electron charge density, whose behavior can be encoded into a classical polarizability. The electromagnetic fields associated with this collective motion are then obtained within the framework of Maxwell's equations. This description assumes a classical behavior of both electrons and electromagnetic fields to address the near-field and far-field properties of metallic nanoconstructs acting as effective optical nanoantennas.

However, fabrication and synthesis techniques have evolved, producing progressively sophisticated nanostructures and devices with control up to atomic dimensions, often involving interactions at the single emitter level with molecules nearby [28]. These situations emphasize the importance of considering the quantum nature of the *electrons* building the plasmonic response as well as that of the *electromagnetic fields* associated with the charge density oscillations. These two aspects of quantization set the basis of the field of quantum plasmonics [126], as schematically depicted in figure 15.

The study of the quantum nature of electrons in a metal and their collective optical response has a long tradition in condensed matter physics, since the pioneering works of Bohm, Pines and Nozières. The consideration of surfaces necessary in nanophotonics adds an additional degree of complexity that requires specific methods of solid state physics to properly address the complex quantum interactions and dynamics of the electrons and nearby excitations. In this context, the surface response of the electron gas has been treated within different quantum approaches, including semiclassical hydrodynamical models [127] as well as time-dependent density functional theory (TDDFT) methods [128]. The latter allows for a proper quantization of electrons (and atoms) which captures important aspects in plasmonics, such as (i) quantum size effects [103], (ii) dynamical screening of the electron gas, (iii) atomistic effects, (iv) spill-out of the electrons beyond the surface edges and (v) the possibility of tunneling at optical frequencies. The consideration of all these quantum effects provides crucial insights into the fundamental limits of localization and field enhancement in plasmonics, as well as the correct establishment of optoelectronic properties in metallic nanoantennas and their coupling with other systems, such as molecules or semiconductor structures.

The second important aspect of plasmonics concerns the quantization of the electromagnetic field associated with

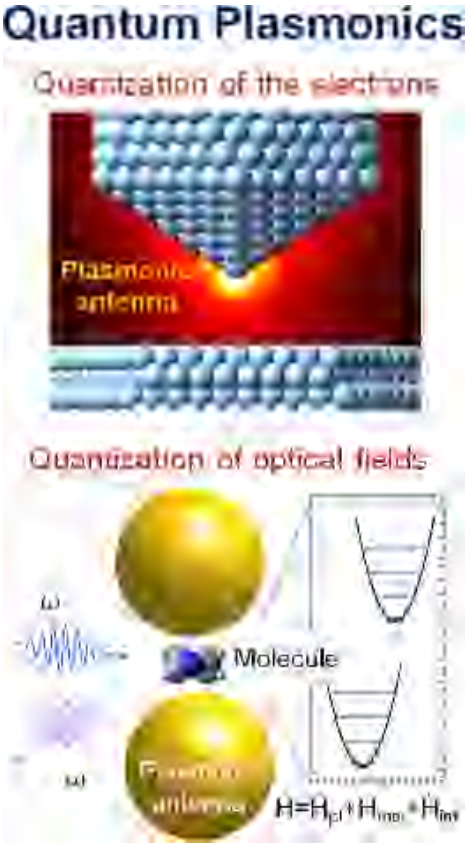

Figure 15. Quantum plasmonics deals with effects associated with the quantum nature of both electrons and electromagnetic fields. (Top) Example of field-enhancement in a plasmonic cavity where quantum aspects of the metal electronic structure and atomistic effects need to be considered within condensed matter physics methods. (Bottom) Coupling of the field of a plasmonic cavity with electronic and vibrational molecular states that can be described within cavity quantum electrodynamics (QED).

plasmon resonances [42] and its coupling with excitonic and vibrational states of molecular adsorbates [85], following the scheme of second quantization according to the prescriptions of cavity quantum electrodynamics (QED). Notably, the huge field localization achievable in nanoplasmonic structures leads to a very strong coherent interaction with emitters, and thus to very fast energy transfer, which can be beneficial for the generation of non-classical states of light as well as for other applications in quantum information [129, 130]. An accurate description of the dynamics of quantum states of plasmonic nanoantennas and molecular emitters is thus a prerequisite for full characterization and control of light −matter interaction at the (sub)nanometric scale.

Current and future challenges. Quantum plasmonics is a lively and rapidly evolving subfield of plasmonics whose importance has just started to emerge. Much work is underway to exploit the standard metals to confine plasmonic energy to the nanometer and subnanometric scale with a high degree of control. The study of the interplay between *electronic transport and optical properties* in

plasmonic nanocavities requires progressively sophisticated experimental conditions, as well as quantum models based on condensed matter theory techniques [131]. Optoelectronic switches at fast frequencies with femtojoule operation per cycle, optical rectification in nanodevices, electrical active control of nonlinear optical responses, ultrafast electronic processes in metallic surfaces, or photoinduced current in tunneling junctions could benefit enormously from atomic scale control of the gap configurations.

Furthermore, the coupling of plasmonic excitations with molecular species [132, 133] and semiconductor structures opens new possibilities regarding the interaction of photons with excitons [134], engineering of vibrational states of molecules, or the decay of plasmons into 'hot' electrons and holes [135] for photodetection, energy harvesting, and induced-reactivity [136], where complex dynamical processes involve different time scales, coupling strengths and decays of one type of excitation into another. Quantum descriptions that account for partial aspects of these interactions usually focus on one aspect of the interaction (simplified electronic and molecular states, semiclassical descriptions,…) and often lack a complete picture of the quantum dynamics involved. In this regard, a molecule located in a plasmonic nanocavity is a canonical system to test quantum interactions where the complex chemical structure of the molecule and its interaction with the metal surface, the presence of other molecular species, the possibilities to induce special forms of reactivity, or the activation of complex optomechanical interactions are challenges that need to be verified experimentally, and addressed within unified quantum descriptions.

The emergence of *new materials* with interesting plasmonic properties is another focus of attention of the plasmonic community. A good quantum description of the optical and infrared response of two-dimensional (2D) materials has turned out to be crucial to understand complex behaviors of the electron gas for atomic-scale confinement. Materials such as graphene or boron nitride push the limits of confinement to extreme subwavelength dimensions for long wavelength performance [137], providing a suitable platform for active control of the optical response in nanodevices, as well as new possibilities for plasmon detection at the nanoscale, demonstrating the potential of 2D materials as practical technological platforms in nanophotonics.

Quantum information (QI) technology is another field where plasmonics could make an impact. It is important to understand under which conditions plasmonic structures can act as interconnects for nonclassical states of light, thus serving as building blocks of QI platforms over other alternatives such as dielectric resonators, or superconducting materials. While plasmonic structures show the advantage of allowing very fast processes in ultrasmall volumes, thus providing very strong coupling strengths, they also suffer from large losses, a big challenge for typical quantum applications. Interesting nonlinear effects derived from the quantized dynamics of plasmonic interactions can also emerge in fluorescence and vibrational spectroscopy [138, 139].

Theoretical descriptions of quantum plasmonics typically put the emphasis either on the condensed-matter description of the electronic structure of metals, interfaces and molecules, an approach severely limited by the size of the computationally feasible systems, or on QED treatments that consider simplified models of plasmons and molecules. To consider these two approaches together, implementing more realistic descriptions of the plasmonic response and of the complex excitonic and vibronic structure of molecular states, and to develop semiclassical models of the optical response to diminish the computational demands [140] are among the current challenges of theoretical descriptions within quantum nanooptics.

Advances in science and technology to meet challenges. Surface physics fabrication methods, as well as synthetic chemistry techniques, are constantly introducing new capabilities for highly-reproducible atomic-scale control of plasmonic structures and exquisite molecular deposition in their proximity. Such advances are important steps towards many practical quantum plasmonics applications in spectroscopy, sensing and optoelectronics. Engineering strong coupling between plasmons and vibrational states of molecules, and further progress in the understanding and control of hot carriers dynamics is beneficial to advance towards optical control of chemical reactions at the nanoscale, an important long-term objective in the field of plasmon-assisted photochemistry [135, 136].

Much of the optical testing in plasmonic structures has been performed in configurations where the response and interactions are fixed at fabrication and where only the classical linear response is exploited. In contrast, a reliable integration of electrical contacts with nanometer-gap plasmonic antennas would allow to exploit the full potential of quantum plasmonics for active opto-electronic devices, nonlinear optics and light emission [141]. For quantum information applications, it would be of interest to create and analyze complex networks involving the coupling of several emitters via plasmonic excitations, to explore and engineer quantum properties of non-classical states of light in practical nanoenvironments.

The use of plasmonic nanoconstructs as reliable platforms in quantum nanophotonics will require extending proof-of-principle results obtained in the labs to more practical environments where these applications take place. The emergence of admixtures of new materials, such as 2D Van der Waals layers, organic molecules, topological insulators or conductive oxides, might be key to meet these requirements.

Concluding remarks. Experimental and theoretical developments devoted to improve our understanding and control of quantum effects involving electrons, photons and vibrations in plasmonic systems will not only allow a deeper understanding of light−matter interactions at the subnanometric and atomic scales

but should also impact a wide range of technologies and applications, opening exciting possibilities in photochemistry, nanoscopy, molecular spectroscopy, optomechanics and quantum information.

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11. Plasmon lasers: coherent light source at the single molecular scale

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Status. Laser, light amplification by stimulated emission of radiation, is a powerful light source with broad applications spanning all physical sciences and engineering. Since its invention in 1960, laser science has seen tremendous development from basic centimetre-scale ruby lasers to smaller semiconductor lasers. However, the diffraction limit of light imposes a fundamental barrier on the miniaturization of laser dimensions for integrated photonics for information processing and communications. Surface plasmon polaritons (SPPs), allowing the compact storage of optical energy in electron oscillations at the interfaces of metals and dielectrics, have emerged as promising solutions to overcome such a barrier. The idea is to amplify light coupled SPPs for stimulated emission of radiation, named 'spaser' for localized plasmon, or more generally 'plasmon laser', which offers confinement of light enabling its physical size and mode volume way below the diffraction limit [142]. In 2009, the subwavelength plasmon lasers have been experimentally demonstrated and implemented, opening up new avenues to optoelectronic devices and photonic circuits [143–145].

In contrast to conventional semiconductor lasers, new features of plasmon lasers are evident from their deep subwavelength mode sizes. Firstly, the strong optical confinement in a plasmon laser drastically modifies the laser action by enhancing spontaneous emission, which is known as the Purcell effect, which scales inversely with the cavity mode volume [146]. Such Purcell enhancement preferentially increases the utilization of spontaneous emission into the lasing mode and therefore can significantly reduce the threshold and increase the operation speed of a lasing device. Secondly, the small mode volume in the plasmon laser causes spatial mode redistribution with large mode spacing. As a result, the lasing outputs are subject to efficient mode manipulation and selection for limited gain, leaing to effective single mode operation. Thirdly, the lifetime of SPPs due to electron collisions are on the order of 10–100 femtoseconds. Therefore, plasmon lasers can be potentially modulated at frequencies in the terahertz range [147]. With the unprecedented ability to generate coherent electromagnetic radiation, plasmon lasers have aroused the exploration of exceptionally broad scientific and technological laser innovations at the single molecular scale.

Current and future challenges. The recent advances in the field of plasmon laser have made a number of important fundamental and applied breakthroughs. However, it comes with a trade-off, as the collision of electrons leads to the intrinsic Ohmic loss of a plasmon cavity. In light of that, a 'hybrid plasmon' approach has been proposed which couples dielectric waveguiding with plasmonics [143]. The key to this design is the high permittivity contrast at the gain/dielectric/

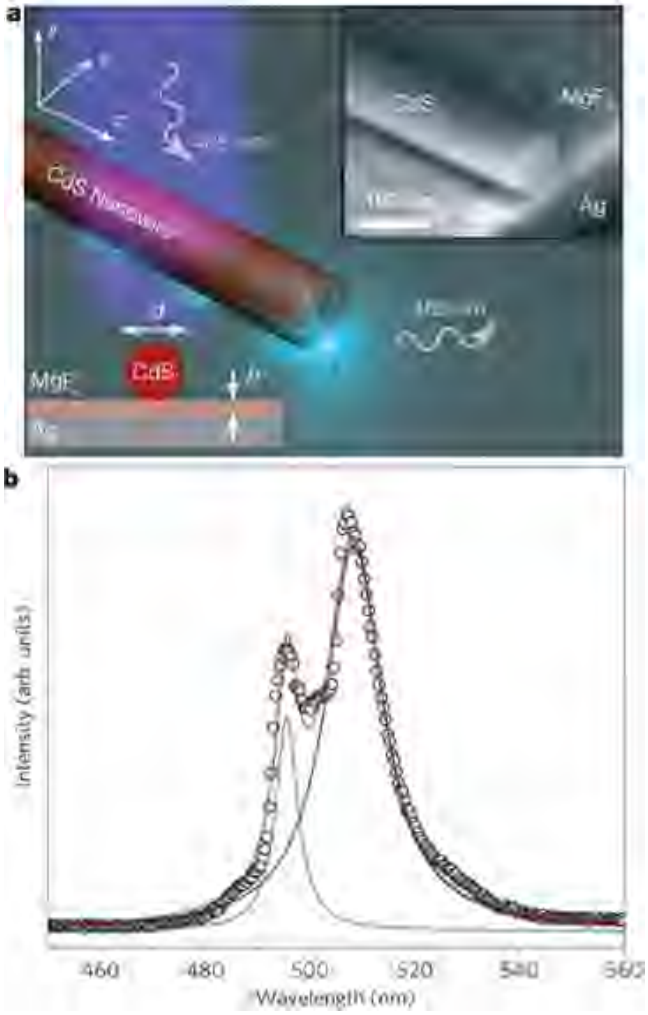

Figure 16. The hybrid plasmon laser concept and demonstration. (a) The laser design with CdS-MgF_2-Ag configuration. (b) Room temperature plasmon nanolaser enabled by total internal reflections, as evidenced by the fact that cavity modes are observed even in spontaneous emission spectrum indicating excellent cavity feedbacks. Experimental data are well fitted (red curve) by convolution of two calculated cavity modes (green: 495.5 nm; blue: 508.4 nm).

metal interfaces, allowing for strong mode confinement (a few nanometers) while maintaining significant modal overlap with the gain material to provide optical amplification and thus lasing action.

The first demonstration of such laser consists of a semiconductor nanowire sitting atop of a metallic surface, separated by a nanometre-scale insulating gap (figure 16(a)). The coupling between the plasmonic and waveguide modes across the gap enables energy storage in the thin layer of low index dielectric regions. Therefore, the hybrid plasmon laser not only realizes deep subwavelength optical confinement but also enables the feedback of electromagnetic energy stored in the dielectric region significantly reducing the Ohmic losses.

Upon an increase in temperature, the plasmon lasers yet experience dramatically increased losses and reduced gains. Room-temperature operation of plasmon lasers would be very challenging. By designing the plasmonic cavity of higher quality factor, sustained plasmonic lasing action at room

temperature becomes possible. For example, a total internal reflection of SPPs feedback enables a room-temperature plasmon laser due to the mitigated both metal and cavity losses [148]. The feedback mechanism is extremely effective, as shown by the well-pronounced cavity modes in the spontaneous emission spectrum below the threshold (figure 16(b)). The room temperature plasmon lasers enable new possibilities in practical applications such as single-molecule sensing, data storage and optical communications.

Plasmon lasers can play a key role in the scaling down of integrated photonics for optical communications. The effective integration of photonic and electronic functionality, however, brings a fundamental challenge for the ultracompact optoelectronic circuitry. A promising solution is to design a multiplexed plasmon nanolaser interconnects (figure 17(a)). The metal and semiconductor strips forming networking plasmon laser cavities, which simultaneously serve as out-coupling waveguides and electrical contacts [149]. Such on-chip integrated plasmon laser circuits allow more than 70% directional emission coupling with dramatically enhanced radiation efficiency.

Due to the amplification of the surface plasmons, plasmon nanolasers can provide an unprecedented ability in sensing with ultrahigh sensitivities down to a single molecule level. In a label free fashion, an ultrasensitive explosives sensor in a lasing plasmon nanocavity has been achieved recently with a sub-part-per-billion detection sensitivity, the lowest reported to date for plasmonic sensors [150] (figure 17(b)). The exceptional plasmon nanolaser sensor envisages the potential of actively excited surface plasmons for a number of important applications ranging from security screening, defense to chemical diagnostics.

Despite the remarkable progress in plasmon lasers research and a host of promising applications, the challenges still remain in such novel devices. Electrical injection under ambient conditions would be one of the major challenges in the field, which is essential for on-chip integration with electrical data input. Although we have shown that the plasmon laser can be coupled to waveguide, the development of on-chip electrically driven SPP sources will be need for truly integrated systems without external driving fields. At this point, the potential for useful emission enhancements in plasmon lasers have not been extensively explored. For example, the Purcell enhancement in current experiments are largely constrained due to the multiple loss channels, e.g. ohmic loss from metals and scattering losses from surface roughness and defect. The limited Purcell enhancement will fundamentally restrict the modulation speed (bandwidth) and efficiency (threshold) a lasing device. In addition, many realistic applications would require a cheap and scalable fabrication method in order to fulfil the potential of plasmon lasers.

Advances in science and technology to meet challenges. The development of a variety of scientific and technological innovations could bring new capabilities that may directly address the challenges in the field of plasmon laser. In particular, the major hurdle in pursuing an electric driven plasmon laser lies in the poor transport properties between the electric contact and semiconductor gain materials, causing significant losses at the interface. With selective-area growth controlled at the atomic scale, molecular beam epitaxy can fabricate a plasmon nanolaser epitaxially [151], optimizing both the optical and electrical contact constraints. The successful integration of such a technique into microelectronics may lead to the first electic driven plasmon laser. Moreover, the advances of fundamental sciences lead to the discovery of a number of new materials. For example, the metallic nitrides exhibit losses even surpassing silver, whose metal loss is currently considered lowest at optical frequency. Two dimensional (2D) materials, such as graphene, can be used as an electric contact for its high carrier mobility. 2D semiconductors or perovskites can be used as gain materials in plasmon lasers for their superior emission properties. These emerging materials may lead to the exploration of fundamental polariton physics and light–matter interactions in plasmon lasers at the nanoscale.

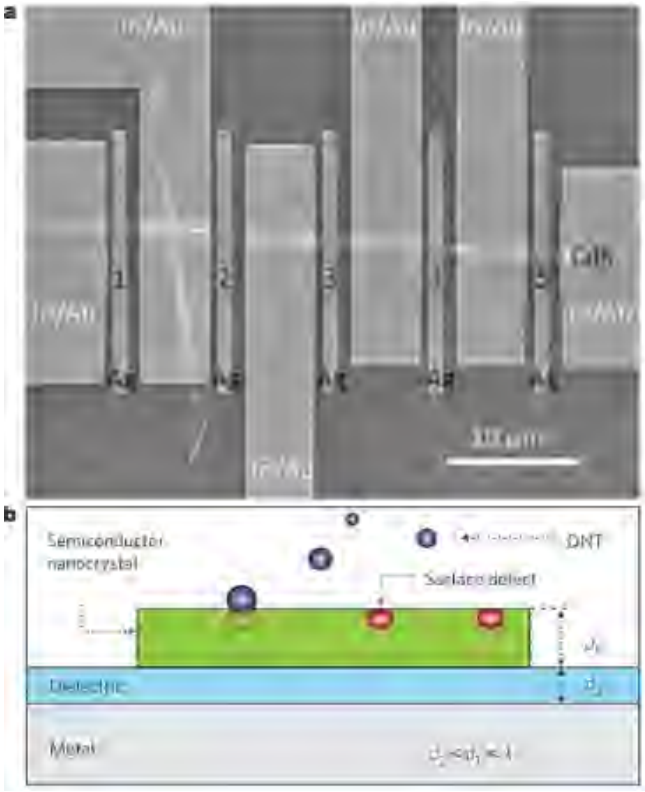

Figure 17. Plasmon lasers applications. (a) On chip integrated plasmon nanolaser circuits that enable both effective electric modulation and wavelength multiplexing. (b) Plasmon laser explosive sensor based on the intensity change of stimulated emission from a lasing plasmon nanocavity, where semiconductor crystal acts both as a gain and sensing medium.

The creation of single crystal nanostructures by chemical assembly have many potential uses in self-assembled electronics. Recent advances in nanochemistry suggest that such assemblies may also lead to photonic structures at large scale. These advances suggest that the assembly of materials (metals and semiconductors, etc.) with three-dimensional

control over particle position and orientation will soon be feasible. Such scalable and single-crystalline growth methods present important opportunities to new design of plasmon lasers, as well as assembling ultracompact laser arrays on-chip.

Concluding remarks. Plasmon laser, or spaser, presents the unique capability to generate strong localized optical-frequency fields below diffraction limit, opening up new possibilities in the field of both nanophotonics and optoelectronics. With rapid advances in device fabrication and integration techniques, growing knowledge and understanding of light–matter interactions at the fundamental level, we anticipate that plasmon lasers will continue to stretch the boundaries on both the scientific and technological fronts.

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12. Nanoarray lasing spasers

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Status. Nanoscale coherent light sources are important for miniaturized photonic devices and for interrogating physical-chemical processes at the nanoscale. Plasmon-based lasers or spasers (surface plasmon amplification by stimulated emission of radiation) can overcome diffraction effects in photonic lasers by exploiting either localized surface plasmons (LSP) around nanoparticles (NPs) or surface plasmon polaritons (SPP) on a metal film to achieve amplification in the sub-wavelength vicinity of the metal surface [143, 152]. Gain materials typically used to be organic dyes for the former and inorganic nanostructures for the latter. However, single-particle spasers face challenges in synthesis and reproducibility [152] and single nanowire-dielectric-metal nanolasers suffer from random emission directions and require low temperature operation [143] (see section 11).

Plasmonic lasers based on arrays of nanostructures for nanocavities have garnered attention recently, since the constructive interference between individual units can suppress radiative loss, and the array organization can achieve directional emission. Such a system—a nanoarray lasing spaser—was first proposed theoretically based on split ring resonators as the building units, where the coherent current excitations among rings facilitated spatially and temporally coherent radiation [153]. A simpler design unit, based on cylindrical NP, was first realized in experiment [154], closely followed by work on circular holes [155].

Periodic plasmonic NP arrays with sub-wavelength NP spacing can be generated over cm^2 areas using multi-scale nanofabrication (figure 18(a)) [156]. Such NP arrays in a homogeneous dielectric environment support lattice plasmons that show sub-wavelength localized field enhancement around the NPs with high quality factors ($Q > 200$) [157, 158]. Because of the in-phase oscillation of the NPs in the array, the local field around each NP is enhanced by two orders of magnitude compared to that of an isolated NP at resonance. The organic dye IR-140 is a convenient gain material for these array parameters because its emission bandwidth can readily overlap the lattice plasmon mode. To achieve an index-matching condition and highest Q for the nanocavity, the dye was dissolved in dimethyl sulfoxide (DMSO, $n = 1.48$) and later sandwiched between NP arrays on fused silica ($n = 1.46$) and a glass coverslip (figure 18(b)). By pumping IR-140-DMSO covering the NP arrays using an 800 nm fs-pulsed laser, we found that a single-mode lasing peak emerged at $\lambda = 855$ nm, the same wavelength as the band-edge lattice plasmon resonance (figure 18(c)) [154, 158].

Compared to plasmon lasers based on a single unit for the cavity structure, nanocavity array lasers are advantageous because they can achieve: (1) single-mode emission with narrow linewidths (<0.5 nm); (2) controlled directionality of nanolasing emission normal to the surface; (3) room-temperature operation; (4) tunable lasing wavelengths by changing NP spacing and dielectric environment; and (5) nanoscale localized fields over large areas ($\sim cm^2$). Moreover, such architectures can be easily scaled and manufactured.

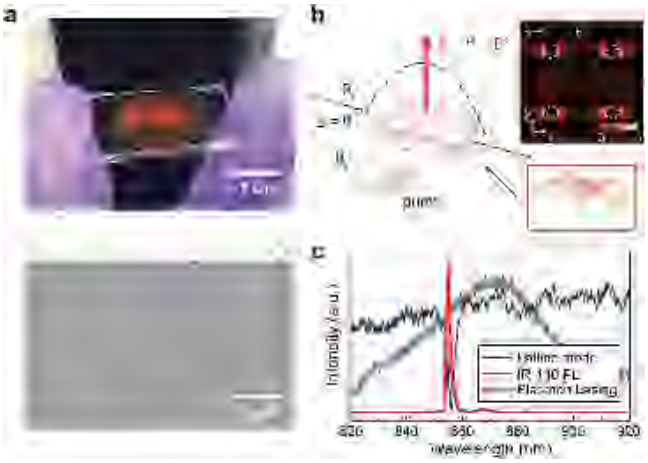

Figure 18. Plasmonic nanocavity array laser. (a) Photograph and SEM image of fabricated gold NP arrays with diameter $d = 120$ nm and spacing $p = 600$ nm. (b) Scheme of nanocavity array laser. Upper inset shows that the electric field is nanolocalized at the vicinity of NPs at resonance. (c) Lasing (red curve) observed at lattice plasmon band-edge resonance where the IR-140 photoluminescence in DMSO (blue curve) overlapped with the lattice plasmon resonance (black curve).

Current and future challenges. We performed some of the first semi-quantum modelling of plasmon nanolasers by combining rate equations and Maxwell's equations [154, 158]. However, one challenge in understanding this open cavity architecture is how to relate the cavity quality to the Purcell effect, which influences the build-up of lasing action [159] and is the current standard in determining how ultrafast dynamics of gain are modified. In the simplified expression of Purcell factor F,

$$F = \frac{3}{4\pi^2}\left(\frac{Q}{V}\right)\left(\frac{\lambda}{2n}\right)^3.$$

Q depends on the linewidth of the resonance peak, and mode volume V defines extent of electromagnetic field confinement. However, this definition of V neglects the leaky nature of common photonic and plasmonic cavity modes, where the field diverges exponentially at large distances outside of the cavity [160].

Additionally, this semi-quantum model cannot describe oblique incidence or scattering related to the dispersive properties of lattice plasmons, where the propagating modes at non-zero wavevectors can contribute to amplified emission that is not surface-normal (amplified spontaneous emission (ASE)). For example, at high dye concentrations or pump power, ASE can surpass even the lasing signal. Also, molecular interactions between dyes can affect lasing action by damping and dephasing effects, which cannot be described in the current model.

General considerations to integrate nanolasers with on-chip applications include: (1) device efficiency with output power in ∼mW scale; (2) electrical pumping for opto-electronic interconnects; and (3) high modulation speed for information processing. Applications such as sensing require tunability of nanolasing to manipulate the light source in real-time, which is not possible in solid-state cavity designs (inorganic semiconductor nanowire or organic dye in a solid matrix). Moreover, for metal NP arrays, an index-matching environment is required to achieve high-quality lattice plasmons. This condition restricts the choice of gain media that can couple to plasmonic nanocavity arrays.

Furthermore, for on-chip multiplexing, multiple optical frequencies are needed to increase the storage capability and facilitate optical processing. However, nanoarray lasing spasers based on a single periodicity exhibit only a robust, single-mode lasing line. Access to multiple lattice plasmon resonances could potentially result in multiple, uncoupled lasing modes. Plasmonic superlattices—finite-arrays of NPs grouped into microscale patches—can support multiple superlattice plasmon resonances with controlled mode number and spectral location by varying patch spacing [161]. Such an architecture could potentially lead to engineered light–matter interactions at multiple cavity modes simultaneously [162]. Also, the number of NPs in a finite array could assist in determining the spatial and temporal coherence of nanolasing based on this nanocavity array architecture.

Advances in science and technology to meet challenges. Recent advances in nanoarray lasing spasers include real-time and tunable lasing emission, characteristics that cannot be realized in conventional solid-state lasers without changing the cavity structure. By incorporating liquid gain with 2D gold NP arrays, we demonstrated the first dynamically tunable nanolaser (figure 19(a)) [158]. Liquid gain makes the integration of large-area arrays (∼cm^2) of gold NPs with microfluidic channels possible (figure 19(b)); hence, different refractive solvents can shift the lattice plasmon resonance and result in on-demand tuning of the nanoscale lasing signal.

Figures 19(c) and (d) show that the lasing emission from nanocavity arrays can be switched between two wavelengths or continuously shifted by alternating plugs of liquid dye in the microfluidic channel. This nanolasing system produces superior emission characteristics and device stability compared to solid systems because the liquid gain can be continuously refreshed to avoid photo-oxidation and photo-bleaching of the dye. Additionally, the wavelength and switching speed of the lasing can be controlled by adjusting the composition and flow rate of the liquid dye.

Metal NPs on a mirror film are another platform that can be integrated with microfluidics, and advantages are that the index-matching requirement of plasmonic NP arrays is lifted and the nanolasing emission can occur in a single direction [163]. Compared with bi-directional lasing from NP arrays [154, 158] and nanohole arrays [155], where half of the energy is dissipated into an opposite direction, the metal film beneath the NPs functioned similar to an end mirror in conventional lasers. Moreover, this architecture enables ready incorporation of different gain media, such as quantum emitters and semiconductor materials that can result in new classes of plasmon nanolasers.

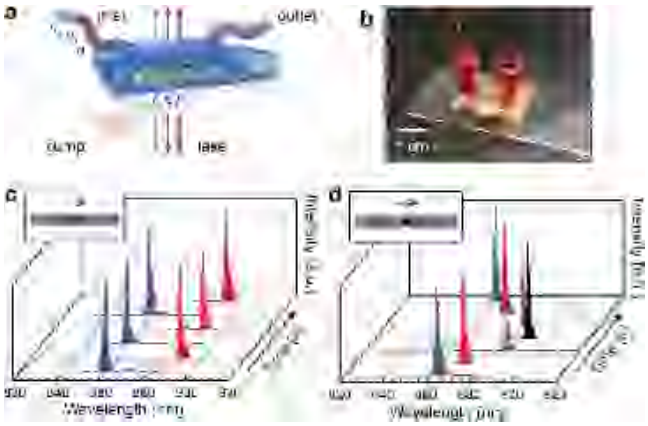

Figure 19. Real-time tunable lasing emissions from gold NP arrays. (a) Scheme of dynamic nanolaser. (b) Optical micrograph of device. (c) Real-time switching between two lasing wavelengths and (d) four lasing wavelengths.

Recent progress on theoretical modeling of lasing action in plasmonic NP arrays includes incorporating the Purcell factor and ASE at off-normal angles. After a separate electrodynamics calculation, the Purcell factor was included in the lasing modelling, which is essential in describing the spatial dependence of decay rate [159]. By integrating the electronic properties of dye molecules in commercialized finite-difference time-domain software, we can study emission in directions that are off-normal to the sample surface, which is critical for understanding competing ASE processes and lasing action. In the future, we can also modify the rate-equation description of dye-molecule photophysics to a Liouville equation description [164] so that damping and dephasing effects in the time evolution of the four-level dye system can be considered.

Concluding remarks. Nanoarray lasing spasers offer an attractive way to suppress the radiative loss intrinsic to metal NPs and to control the directionality of nanolasing. The production of nano-coherent light sources over wafer-scale areas offers prospects for enhancing light–matter interactions on the nanoscale, real-time monitoring of nonlinear optical processes, and functioning as coherent nanoscale sources for lab-on-a-chip applications. The present research on nanoarray lasing spasers opens a wide range of possibilities for future work on new cavity architectures and unusual types of gain materials.

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13. Ultrafast broad-band control of resonant optical nanoantennas and nanoparticles

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Status. Optical antennas offer unprecedented possibilities to control and enhance the interaction of light on the nanoscale: excitation and emission can be controlled by near-field coupling to a properly designed antenna mode. The use of optical antennas to improve single molecule detection, to brighten single-photon sources and to achieve true nanometric resolution microscopy is well established [165, 166], see also section 7. Combining the nanoscale with ultrafast approaches has been a rapidly developing challenge in the most recent decade [93, 152, 167]. Advanced control of ultra-short broadband laser pulses and nanoscale detection and imaging are now being exploited to coherently excite and control plasmonic nanoantennas, transmission lines and a variety of individual quantum systems (molecules, quantum dots, diamond NV centres, etc.) [168, 169], see also section 14.

Conventionally coherent control concepts have been mainly applied to ensembles of systems, particularly atoms and molecules. Here, we aim to manipulate light−matter interactions at the nanoscale, and thus focus on ultrafast coherent control of nonlinear optical processes in individual nanoparticles. In this context, here we address both coherent and incoherent nanoparticles (NPs), figure 20. Coherent NPs present an intrinsic response, an amplitude or phase response, which can be frequency resolved by the laser field. Resonant plasmonic nanoantennas constitute the main example of such coherent NPs, with the resonance determined by size, shape, metal, etc. In contrast, incoherent NPs are non-resonant or broad band, such as dielectric nonlinear NPs and semiconductor quantum dots (QDs). Incoherent NPs are very useful as their nonlinear interaction mainly depends on the laser itself, making these ideal NPs to test the performance of coherent control on the nanoscale. Especially towards the realization of Fourier limited pulses in-side a high numerical aperture (NA) microscope in a diffraction limited spot, free of spatio-temporal coupling, non-resonant second harmonic NPs have proven beneficial [170]. In contrast, coherent NPs can be manipulated by ultrafast coherent control schemes [171]. Combined with precise nanofabrication of tailored NPs and suitable resonances, novel applications in nanophotonics can be developed, such as multiphoton imaging of NPs as shown here [172].

Current and future challenges. A major challenge in ultrafast excitation of single NPs is the combination of diffraction limited excitation/detection using high NA objectives with ultra-broad band lasers, figure 20. Dispersion and spatio-temporal coupling need to be controlled such that the Fourier limit is obtained inside the diffraction limited focus. Typically, a 4f-pulse shaper is used, on one hand to compensate for the dispersion in the imaging system and on the other hand to actually exert phase control to manipulate the NPs in the sample. The dispersion in high NA objectives is easily several 1000 fs^2, which is much stronger than the actual required range for phase control. As such, proper compensation is critical to subtle phase control experiments.

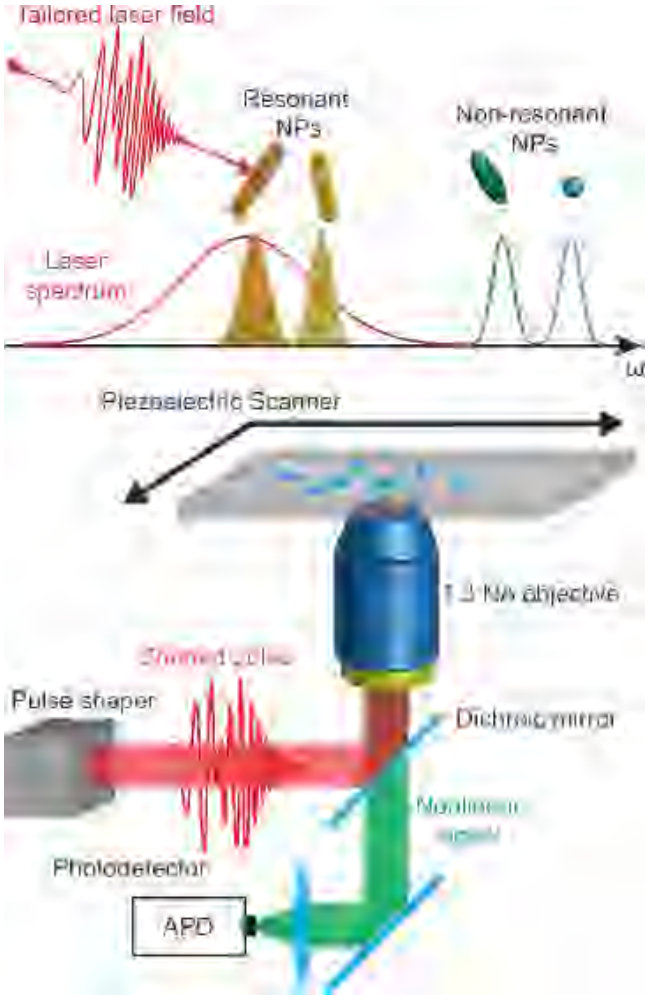

Figure 20. (Top) A broadband ultrashort laser pulse interacts with nanoparticles (NPs). By fabricating nanostructures in resonance with the laser spectrum, tailored laser fields can actively control light-matter interactions in resonant NPs. (Bottom) The phase-shaped laser beam excites a NP in a diffraction-limited spot. The non-linear signal of the NP is collected by a high-NA objective and detected on a photon counting avalanche photodiode (APD).

Advances in science and technology to meet challenges. The spectral non-linear response of plasmonic nanoantennas is intimately connected to their local surface plasmon resonances. As such different nanoantennas produce different second harmonic (SH) spectra. Moreover, the pulse shaping capability provides a direct degree of freedom to create customized SH spectra on the nanoscale [173]. Combining these two features, using different nanoantennas characterized by detuned resonances and precise phase shaping, it is possible to obtain contrast in the SH between nanoantennas, and thus produce different colors in their SH spectra, which can be applied in multicolour SH imaging, as

alternative to conventional imaging based on fluorescent labels.

To illustrate the potential of such non-linear multicolour NP imaging, figure 21 shows a sample of gold nano-rods of length varying between 90 nm and 130 nm. In order to have the smallest nanoantennas, in resonance with the laser field, the rods were fabricated in resonance with the lowest $\lambda_{\text{eff}}/2$ mode. As shown in the SEM images of figure 21(a), in the same array, columns of 100 nm alternated with columns of 120 nm and 130 nm long NPs. The 100 nm NPs are resonant with the blue side of the broad-band Ti:S laser spectrum and the resonance shifted to the red for longer nanoantennas. The array was imaged with two different APDs simultaneously. With a dichroic mirror and additional spectral filters, the blue part of the SH light ($\lambda < 400$ nm) was sent to one APD and the red part to the other ($400 < \lambda < 420$ nm). The false colour image of figure 21(b) was obtained, with good contrast between the 100 nm nanoantenna and the 120 nm and 130 nm, due to the difference in plasmon resonance. The 100 nm NPs appear blue to violet in the image, while the 120 and 130 nm NPs are purple to red.

Next, we turn to a real closed loop phase optimization experiment, where the coherent response of an individual NP is actively manipulated to reach the desired outcome; specifically optimizing the two-photon excited photon luminescence (TPPL) of single QDs. The dots are characterized by broadband absorption in two-photon excitation, thus non-resonant NPs. Figure 22(a) shows a distribution of QDs, all with anti-bunched photon emission (figure 22(c)), i.e. single photon emitters. Using a novel optimization algorithm controlling the spectral phase [174], the luminescence of the QDs is optimized and enhanced up to 6 times (figure 22(d)). The optimization found by the algorithm is targeted for generating a Fourier limited pulse in the diffraction limited focus.

Concluding remarks. Clearly, pulse shaping applied to the excitation of nanoantennas can optimize the non-linear response and provides new contrast routes to discriminate the nanoantennas in imaging and sensing applications.

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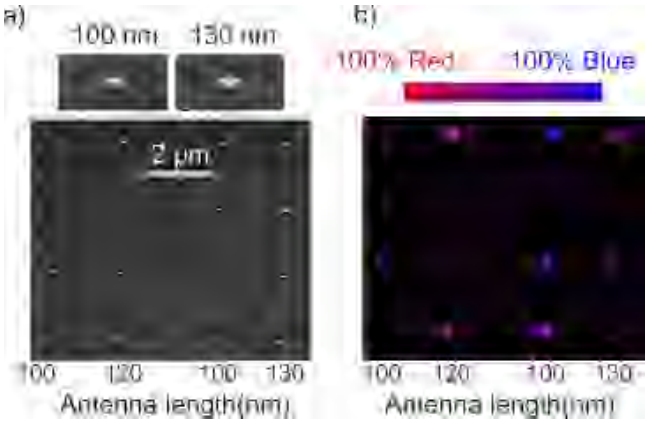

Figure 21. Spectrally selective SH imaging. (a) SEM images of an array of Au nanoantennas of different lengths and zoom-in on individual 100 nm and 130 nm nanoantennas. (b) Two-colour SH image of the same array, showing contrast between different NPs, with longer nanoantennas more red. The blue ($\lambda < 400$ nm) and red ($400 < \lambda < 420$ nm) side of the SH-spectrum are pseudo-coloured blue and red. Reprinted from [172], with the permission of AIP Publishing.

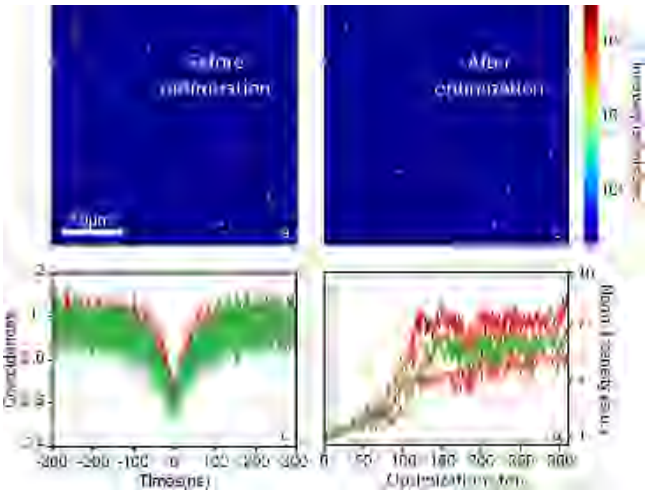

Figure 22. (a), (b) TPPL image of single QDs before and after control optimization. (c) Photon correlation as a function of inter-photon time for the indicated QDs, showing anti-bunching at zero-time. (d) Optimization traces taken on different QDs. In 100–300 steps, the TPPL is enhanced between four and six times compared to initial conditions. Reproduced from [174]. CC BY NC-ND 4.0.

14. Attosecond tracing of plasmonic fields

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Status. The interaction of intense tailored fields with nanomaterials opens a new perspective for ultrafast light-driven (plasmonic) nano-electronics [175]. Ultrashort laser fields can be applied to drive and monitor attosecond controlled electric currents in dielectrics [176], attosecond photoemission from metals [177], and are key to the realization of ultrafast dielectric electronics [175]. When such fields are applied to nanostructured materials, enhanced and well-controlled near-fields can be excited, permitting tailoring them on nanometer spatial and attosecond temporal scales [178].

For probing such ultrafast dynamics, conventional time-resolved methods, such as frequency-resolved optical gating techniques, cannot easily be applied since they do not offer the required spatial resolution and often the temporal resolution is not sufficient. For processes that occur within fractions of a laser cycle, such as the metallization of dielectrics [175], attosecond resolution is essential. Extending attosecond metrology towards probing nanometer-scale near-fields can provide a suitable method, and was considered by a body of theoretical work (for an overview, see e.g. [179]).

Attosecond tracing of plasmonic fields offers insight into details of the formation and decay of plasmons. The field-free dephasing time of nanolocalized plasmons is typically in the lower femtosecond domain across the plasmonic spectrum, with the fastest dynamics given by the inverse bandwidth of plasmons reaching into the attosecond domain. Stockman *et al* [180] introduced the concept of nanoplasmonic streaking to study plasmonic excitations in real-time. The scheme of the proposed experiment is depicted in figure 23. A near-infrared pulse excites localized and propagating plasmons on a metal nanostructure. The enhanced fields are probed via photoemission using a time-delayed attosecond extreme-ultraviolet (XUV) pulse. The momenta of released electrons are measured with a time-of-flight photoemission electron microscope (PEEM) providing nanometer spatial resolution. Depending on the relative time delay between the two pulses, the measured change in momenta bears a fingerprint of the plasmonic surface near-fields at the time of the electrons' release (the approach has also been termed ATTO-PEEM). It should be stressed that nanostructures have evanescent, spatially varying near-fields, which renders attosecond nanoplasmonic streaking different from conventional attosecond streaking. Different regimes can be identified, which may be separated by an adiabaticity parameter $\delta = T_{esc}/T_0$, where T_{esc} is the escape time of an electron from the near-field and T_0 is the laser period [181, 182].

For large adiabaticities ($\delta > 1$), an electron is ponderomotively accelerated in the near-field and the method becomes sensitive to the surface field if additional acceleration by the driving laser field is negligible. For very small

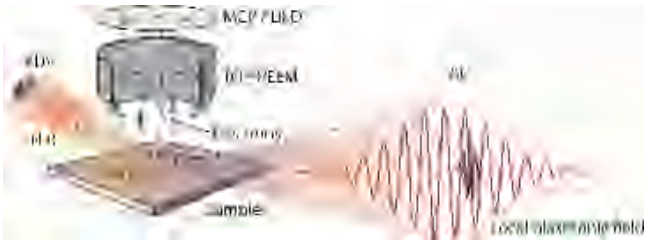

Figure 23. Principle of attosecond nanoplasmonic microscopy (ATTO-PEEM). A near-infrared (NIR) pulse induces plasmonic oscillations which are probed by a time-delayed attosecond extreme-ultraviolet (XUV) pulse. The emitted electrons are measured with a photoemission electron microscope, where their time-of-flight and position are detected by a microchannel plate (MCP)/delay-line detector (DLD). An attosecond streaking trace for each image point is recorded by a delay sweep between the pump and probe pulses and facilitates the extraction of the local plasmonic field. Reproduced with permission from [185], © 2014 WILEY-VCH Verlag GmbH & Co. KGaA.

adiabaticities ($\delta < 0.05$), the electron is instantaneously accelerated and the measured streaking trace directly proportional to the surface field. This regime works well for plasmonic hot-spots with very high field enhancement, and was already discussed in the pioneering work by Stockman *et al* [180]. For all other adiabaticity parameters, the situation is more complex, and extraction of the near-fields requires extensive simulations. Therefore, generally, some a-priori knowledge about the nanostructure geometry and near-field distributions and their evanescent decay is required to implement attosecond nanoplasmonic streaking.

While attosecond streaking from nanostructures was analysed in a body of theoretical work, an experimental implementation even without the spatial imaging of the photoemitted electrons, proved challenging. The linear XUV-induced photoemission process typically probes a much larger area than the nanoscale region of interest, and the streaking trace can be distorted, because electrons emitted from different regions are streaked by different local fields.

Despite these challenges, a recent milestone has been reached with the implementation of streaking spectroscopy of nanoscale near-fields [181]. By combining attosecond streaking measurements with a thorough analysis of the near-field spatial distribution and photoelectron trajectories, the near-fields surrounding a gold nanotaper could be retrieved with attosecond precision (see figure 24).

Current and future challenges. Using attosecond metrology, we can learn how collective excitations are formed and how their phase coherence is lost. Not only are the experiments challenging, also an accurate modelling of the creation and decay of plasmons in nanostructures creates a challenge to theory. The experiments by Förg *et al* [181] were an important feasibility test, but did not yet report on attosecond-resolved measurements of nanoplasmonic fields, which are currently pursued in several laboratories around the globe. Combining the described nanoplasmonic streaking technique with ultrahigh, nanometer spatial resolution is highly desirable for measurements of propagating plasmonic

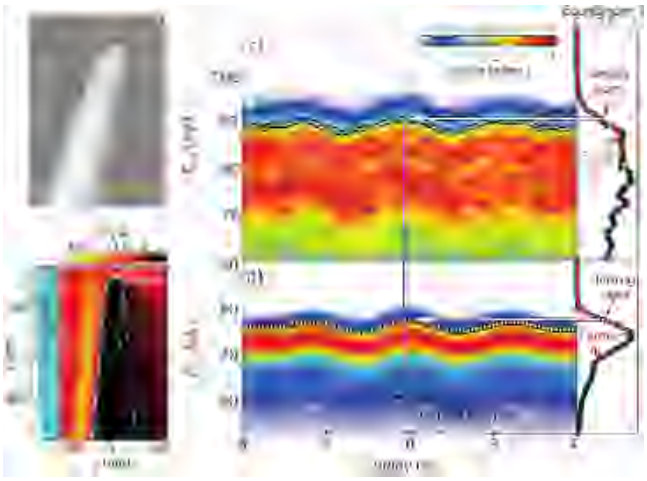

Figure 24. (a) SEM image of nanotaper sample. (b) Normalised field strength of the field component parallel to the nanotaper axis, calculated using an FDTD method. The blue line shows the region of the sample illuminated by the XUV, and the spatial profile of the XUV focus is shown on the left. (c) Streaking measurement from the nanotaper sample. The energy shift of the streaking trace versus the time delay between the XUV and NIR pulses, shown by the white data points, was extracted by fitting a Fermi function (red) to the cut-off. (d) Reference streaking measurement in neon gas. The neon streaking trace is shifted in time by $\Delta t = (250 \pm 50)$ as relative to the nanotaper trace, similar to what is expected from the FDTD and classical trajectory simulations for the near-field on the incident side of the nanotaper. Reproduced with permission from [186], © 2017 IOP Publishing Ltd.

fields on surface-assembled nanostructures. While imaging nanostructures with sub-micrometer resolution has been successfully realized with attosecond light pulses [183] and presents an important milestone, the theoretical development is currently ahead of an experimental implementation of the ATTO-PEEM approach. A challenge arises from a limited emission current that can be tolerated while achieving good spatial resolution, which results in incompatibility with low-repetition rate (kHz) attosecond light sources. Furthermore, chromatic aberrations can limit the resolution with broadband XUV pulses. Finally, the presence of the exciting laser field might result in photoemission from hot spots, limiting the resolution by additional charge interaction.

Advances in science and technology to meet challenges. Most of the challenges for the implementation of ATTO-PEEM can be overcome with developments towards hundreds of kilo- and megahertz repetition rate attosecond laser systems [183]. Such laser systems are becoming feasible thanks to a paradigm shift in laser technology, where optical parametric amplification based systems replace commonly used Ti: sapphire laser systems and can be more easily scaled to higher average powers. Intense developments of such laser systems are pursued in several laboratories. Furthermore, the European Light Infrastructure—Attosecond Light Pulse Source (ELI-ALPS) in Szeged, Hungary, is planning to implement a 500 W power OPCPA laser system, providing 100 kHz attosecond light pulses for user operations, including ATTO-PEEM experiments. With additionally improved experimental setups and samples of high quality (e.g. clean metal samples with low surface roughness and accordingly lower number of undesired hot spots), the full potential of ATTO-PEEM can be unlocked. A very high repetition rate might also provide the head room for energy selective imaging to reduce chromatic aberrations in the microscope.

The light-field control of electron motion in nanostructures is an important part of the development of lightwave (nano)electronics. Future studies may not only employ advanced attosecond imaging techniques such as ATTO-PEEM, but also employ light fields synthesized from continua spanning over several octaves [184], which offer full control over collective electron motion on the nanoscale.

Concluding remarks. It has been a decade since the proposal for attosecond-resolved measurements of nanoplasmonic fields. Experimental work is currently rapidly catching up with theory, and several groups are working towards the implementation ATTO-PEEM and related methods. With the demonstration of nanoscale near-field streaking by Förg *et al* [181], the door is now open towards the first realization of attosecond measurements of plasmonic fields and their multi-dimensional imaging. The realization of attosecond metrology on the nanoscale will give unprecedented, novel insight into the collective electron dynamics for dielectric, semiconductor and metal nanostructures. It will enable the exploration of not only the fastest dynamics in plasmonics, but can also provide avenues for the characterization and utilization of nonlinear plasmonics.

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