

Roadmap on plasmonics

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Roadmap on plasmonics

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38 **Abstract**

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

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1. Foreword – Mark I. Stockman

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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 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 lattice. Plasmons are polar excitations: they are accompanied by appearance of surface charges oscillating at optical frequencies. These oscillations cause 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 simply surface plasmons (SPs). The SPPs were predicted by Ritchie to manifest themselves in scattering of fast electrons [1] and later observed [2]. The LSP's exist at the surfaces and interfaces of metal nanoparticles and are localized typically 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,

$\text{Re}\epsilon_m < 0$. The SPs are well pronounced as resonances when the losses are small enough, i.e., $\text{Im}\epsilon_m \ll -\text{Re}\epsilon_m$. This is a known property of a good plasmonic metal, valid, e.g., for silver in the most of the visible region. An important parameter of a SP resonance is its quality factor,

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

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 occur before the 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 external 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 SPs coherently accumulates over the Q optical periods. The resonant enhancement of the local fields is at the foundation of many fundamental phenomena and a multitude of 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 Sections of this Roadmap, their fundamental foundations, and 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 becomes so large in the near-infrared region that even single molecules can be detected [7], which opens up a wide area of application in chemical and biomedical studies and practices. Section 2 by Kneipp is devoted to single-molecule Raman probing.

Another well-developed application of nanoplasmonics has been optical near-field nanoscopy with 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. Section 7 of this Roadmap by Gross and Lienau considers these three nanoscopy kinds.

Another mature area of nanoplasmonics is related to waveguiding of SPPs by plasmonic metal waveguides (wires and grooves). This allows the transmission 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 Section 3 by Bozhevolnyi.

Many perspective applications of nanoplasmonics based on traditional plasmonic metals and novel plasmonic semiconductor materials are reviewed in Section 4 by Saha et al. These extend from energy conversion to sensing and detection, to plasmon-assisted magnetic memory, etc.

An important class of novel plasmonic materials – topological insulators – is the subject of Section 5 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,

1
2
3 topological) phase. This forbids electron backscattering
4 and causes high electron mobility desired for
5 plasmonics. Yet another class of the systems where
6 electron collisions are suppressed are superconductors
7 where the gap in the energy spectrum brings about
8 their vanishing resistance at zero frequencies and low
9 resistance for frequencies below the superconducting
10 gap. The superconducting plasmonic systems are
11 considered in Section 6 written by Savinov et al.

12
13 The enhanced local optical fields in plasmonic systems
14 induce many phenomena other than optical responses.
15 One class of them are the subject of thermoplasmonics
16 where heat produced by decaying plasmons is put to
17 gainful uses. One such application is in thermal
18 theranostics (diagnostics and treatment of cancer
19 tumours) [8]. An important area of thermoplasmonics
20 is enhanced heat transfer with applications to cooling
21 very large integrated circuits. The thermoplasmonics
22 and its developments are reviewed in Section 9 by
23 Boriskina.

24
25 Another class of plasmon-enhanced non-optical
26 phenomena is photo-catalysis, which is due to
27 enhanced optical fields, enhanced heat production, and
28 generation of hot carriers resulting from plasmon decay
29 [9]. This is reviewed in a Section 8 by Vadai et al.

30
31 A modern area of study is ultrafast nanoplasmonics.
32 Fundamentally, the shortest time, τ , of a response of
33 any physical system is ultimately limited by the
34 corresponding bandwidth, $\Delta\omega$, as $\tau \gtrsim \Delta\Omega^{-1}$. For
35 plasmonics, with its bandwidth spanning almost the
36 entire visible and infrared regions, this translates to τ
37 in the range of a few hundred attoseconds. There are
38 three articles in this Roadmap devoted to ultrafast
39 plasmonics. Section 7 by Gross and Lienau has already
40 been mentioned above in this Foreword.

41
42 Another, Section 13, written by van Hulst considers
43 ultrafast wide-band coherent control of nanolocalized
44 optical field. An idea that the phase modulation of an
45 ultrashort optical pulse allows one to control the
46 spatiotemporal distribution of local optical fields in
47 plasmonic nanostructures was actually introduced
48 theoretically some years ago [10, 11], and it has since
49 been significantly developed both theoretically and
50 experimentally.

51
52 Yet another Section on ultrafast (attosecond)
53 nanoplasmonics, Section 14, is written by Kling. It
54 contains a review of significant progress achieved in
55 tracking the spatiotemporal evolution of nanolocalized
56 optical fields on an attosecond time scale and a
57 nanometre spatial scale. Since the initial theoretical
58 proposal of such an attosecond/nanometre tracking
59 using a combination of photoemission electron
60 microscope with attosecond metrology [12], 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, the quantum-field
description becomes important for local optical fields
and a quantum chemistry approach is necessary for the
underlying materials. The corresponding theories are
conventionally called “quantum plasmonics”. They are
reviewed in this roadmap in Section 10 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 [13, 14]. This Roadmap has two
sections devoted to experimental studies of
fundamentals and applications of spasers.

Section 12 by Wang et al. is devoted to lasing spasers.
Such spasers were introduced as periodic plasmonic
arrays containing gain media [15]. When pumped
above threshold, a lasing spaser generates as a “flat
screen” laser producing an intense coherent beam
normal to its surface. This section describes 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, Section 11 written by Zhang and Yang reviews
the latest progress in spasers (called also plasmonic
nanolasers), which consist of a nanorod of
semiconductor gain medium at the surface of a
plasmonic metal. 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 [16-18].

Concluding Remarks

Concluding, 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 explosives' vapours [19], cancer
diagnostics and treatment [8, 20], etc. In my opinion,
the future of nanoplasmonics is in fundamental

progress with further extensions into areas of strong, ultrafast, and extremely nanolocalized fields, where theory becomes fully quantum mechanical. At the same time the existing applications will be perfected and commercialized, and new applications will be invented, among which 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 [1]. 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 subnanometer resolution. Giant SERS enhancement has been obtained for composites of nanostructures such as random aggregates or regular top down arrangement of nanoparticles with small interparticle gaps or fractal structures. 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 [2].

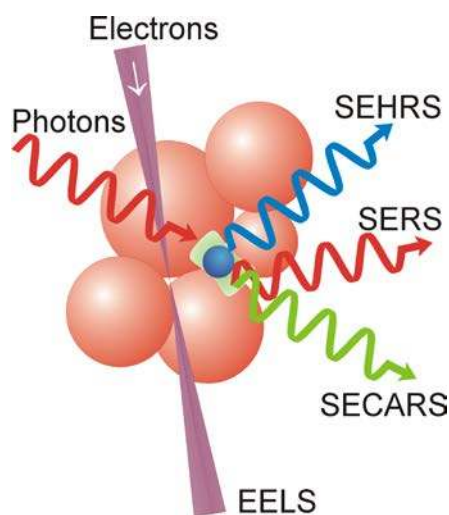


Figure 1: Linear and non-linear surface enhanced Raman scattering and electron energy loss studies on a plasmonic nanoaggregate (adapted from Chem. Sci. 6(5), 2721 (2015))

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 Raman cross sections and makes SEHRS a

regular spectroscopic tool which improves structural selectivity in sensing and imaging [3]. 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 [4]. 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 sub-nanometer spatial resolution has been reported from TERS using a scanning tunnel microscope [5]. 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. 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 [6]. Optimized plasmonic support enables pump–probe coherent Raman experiment at single molecule level and on individual nanostructures [7].

Current and Future Challenges

Important challenges might address a deeper understanding of the physics behind SERS 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 as well as mode interaction and damping is of basic interest for 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 the 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 plasmonic field enhancement on the order of 10^{12} . Interesting questions include the upper limit of SERS enhancement in the hottest spots and their dimension

1
2
3 and why molecules obviously prefer to go to the
4 hottest hot spots.

5 - For small interparticle gaps in sub-nanometer
6 dimension, “classical” plasmonic structures can exhibit
7 also quantum nature. Interestingly, composites of
8 nanoparticles with very narrow gaps seem to provide
9 the highest SERS enhancement. Therefore, in order to
10 understand plasmon enhanced Raman scattering at
11 high enhancement level, quantum effects have to be
12 incorporated and theoretical and experimental tools to
13 explore quantum effects in plasmon supported
14 spectroscopy need to be developed.

15
16 -Strong SERS signals which depend quadratically from
17 the excitation intensity can be observed at the anti
18 Stokes side [8]. Correlations between anti Stokes and
19 Stokes Raman signals have been theoretically
20 predicted [9] and recent experimental progress allows
21 to measure such correlations [10]. Extending anti
22 Stokes to Stokes correlation studies to plasmon
23 enhanced incoherent and coherent Raman effects is a
24 challenge of extreme interest.

25
26 -SERS performed in optical traps in combination with
27 sensitive measurements of mechanical forces that are
28 exerted on the SERS-active structure due to
29 momentum transfer of the emitted SERS photons [11]
30 might provide an additional observable for exploring
31 the SERS process.

32
33 -A totally different theoretical approach suggest a
34 cavity optomechanical model of SERS in which a
35 dynamic interaction takes place between molecular
36 vibration and the localized plasmon [12].

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

50
51 -Most exciting current practical applications of SERS
52 seem to occur for advanced sensing and imaging in the
53 biomedical field. SERS nanosensors inside a biological
54 object such as a living cell can provide information on
55 structures and processes from molecular perspectives.
56 Challenges include the development of multifunctional
57 sensors with optimized plasmonic nanostructures as
58 basic building blocks. Local optical fields provided by
59 these structures could enable both sensitive diagnostics
60 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 characterization the plasmonic near field at the location of the molecule.

Additionally, electron energy loss spectroscopy (EELS) became increasingly popular for exploring plasmonic structures [13]. 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, to generate maps of local fields and hot spots at subnanometer resolution, 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 [14]. 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 [15]. This critical range determines the limit in plasmonic SERS enhancement.

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

Quantum effects require new theoretical approaches (see also Section 10 by Aizpurua). A quantum corrected model that incorporates quantum-mechanical effects within a classical electrodynamic framework has been suggested for addressing quantum effects in realistic plasmonic structures [16]. Recently, also a fully quantum mechanical model of inelastic nonresonant Raman scattering from a molecule placed in a lossy plasmonic cavity has been implemented [17].

Concluding Remarks

SERS, in particular also its extension to multiphoton excitation and 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 and controlling of plasmon supported Raman effects can deliver important insight for the optimization of other photon-driven processes performed in enhanced local fields (see also Section 4 by Shalaev).

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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 [1]. Topology of the metal surface determines characteristics of propagating SP modes that, although featuring limited propagation length 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 [2]. Many different SP-based waveguide configurations (Fig. 1), each offering specific advantages and suffering from particular limitations, have been developed over a decade of intensive research in the attempt of alleviating the tradeoff between the mode confinement and propagation loss (stronger confinement causes larger loss) found in all plasmonic waveguides [1]. 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 [3]. 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 [4]. Finally, besides 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 [5]. 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

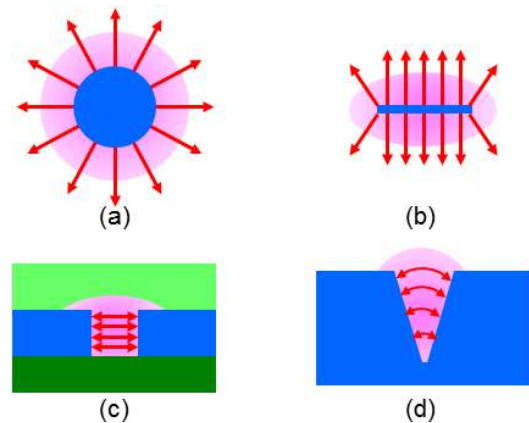


Figure 1. Main configurations of plasmonic waveguides, whose modes can be confined far beyond the diffraction limit (with blue colour marking metal, green – dielectric, pink – mode intensity distributions, and red arrows indicate the electric field direction): (a) nanowire with a radially polarized mode, (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 [1]. Note that nm-sized wires and metal stripes can be supported by low-index dielectric substrates without significant changes in the corresponding mode properties.

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 [6]. 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 semiconductor) 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 needs of computer industry. Additionally, 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 [7].

Advances in Science and Technology to Meet Challenges

Recent advances in fundamental science dealing with light-matter interactions at nanoscale and in technological aspects of nanofabrication, material processing and optical characterization suggest several

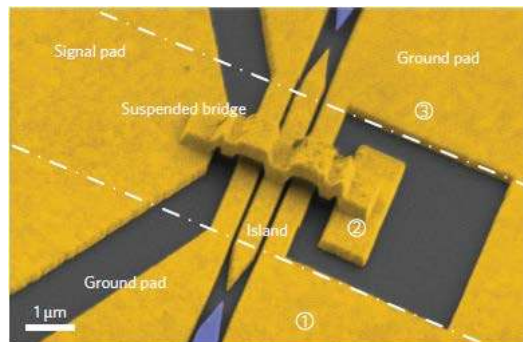


Figure 2. Colorized SEM image of the main part of the Mach-Zehnder modulators, showing a silicon (blue) ridge waveguides supported by SiO₂ (grey) sublayer of a SOI substrate and gold (yellow) circuitry. The latter includes contact pads (1-3) with a gold island contacted through a suspended bridge. Note that gold electrodes serve also as walls of 90-nm-wide slot waveguides. Reprinted by permission from Macmillan Publishers Ltd: Nature Photonics [8], copyright (2015).

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 (Fig. 2) that operate at 70 GHz and feature energy consumption of 25 fJ per bit have been experimentally demonstrated [8], outperforming state-of-the-art silicon modulators in terms of footprint, speed and energy consumption. These excellent characteristics stem from the very strong SP mode field confinement in slot waveguides [Fig. 1(c)] that serve as two arms of a Mach-Zehnder interferometer (Fig. 2), resulting in an excellent field overlap between the gap SP modes and applied electrical signals and causing also considerable slow-down effects. Overall, this breakthrough achievement became possible due to developments in 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 [9]. 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 ~ 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 other than noble metals, and the intensive search for alternative plasmonic materials has been conducted during the last 5 years [7]. Thus transition metal, 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 Section 4).

Concluding Remarks

Theoretical and experimental studies of plasmonic waveguides capable of confining SP guided modes far beyond the diffraction limit [1] 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 [2] have already demonstrated superior performance and unique characteristics of plasmonic devices [8], revealing enormous potential of SP-based nanophotonics [10]. The key features of plasmonic waveguides—strong local field enhancement (several orders of magnitude) and concentration of light energy into nm-sized volumes—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 that is expected to provide enormous Purcell factors resulting in ultrafast single-photon sources (see Section 10). Here, major progress in our theoretical knowledge is required to develop 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 these developments should be coherently intervened 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

Surface plasmons are collective oscillations of free electrons that can be excited when light waves are incident on a metal-dielectric interface. The large momentum of surface plasmons enables electric field confinement into dimensions much smaller than the diffraction limit. The strong field confinement leads to plasmonics applications in optical signal processing and communications (see for example [1] and references therein), in plasmon-enhanced sensing of gases and chemicals, and in particle trapping using plasmonic nano-tweezers for applications in quantum optics and bioscience [2] [3]. The scattering and absorption of light and the associated Ohmic heating in plasmonic nanostructures has found use in various applications such as photothermal therapy [4] and energy harvesting [5], [6], to name just a few. 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 [7] and references therein). Figure 1 serves as an illustration of this trend.

Plasmonics for communications: Historically, most of the research on plasmonic waveguides has been centered around gold and silver, which are the best metals in terms of loss, but are not CMOS compatible. Despite this, the potential of nanoscale light guiding has continued the exploration of plasmonic waveguides and modulators. These efforts have resulted in closing the performance gap between photonic and nanophotonic interconnects [8]. In addition to this, they have enabled the design of plasmonic modulators operating at optical bandwidths that have a smaller on-chip footprint compared to their photonic counterparts [1], [8].

On-chip sensing: The high field-enhancement and mode-confinement in plasmonic structures make the devices very sensitive to changes in the local refractive index. This feature has led to the design of surface plasmon resonance based systems that enable real-time monitoring of biochemical reactions, and label-free sensing applications. Plasmonics based sensors have been successfully demonstrated for chemical and gas sensing [9]. Furthermore, waveguide based sensors have been used to detect biological components such

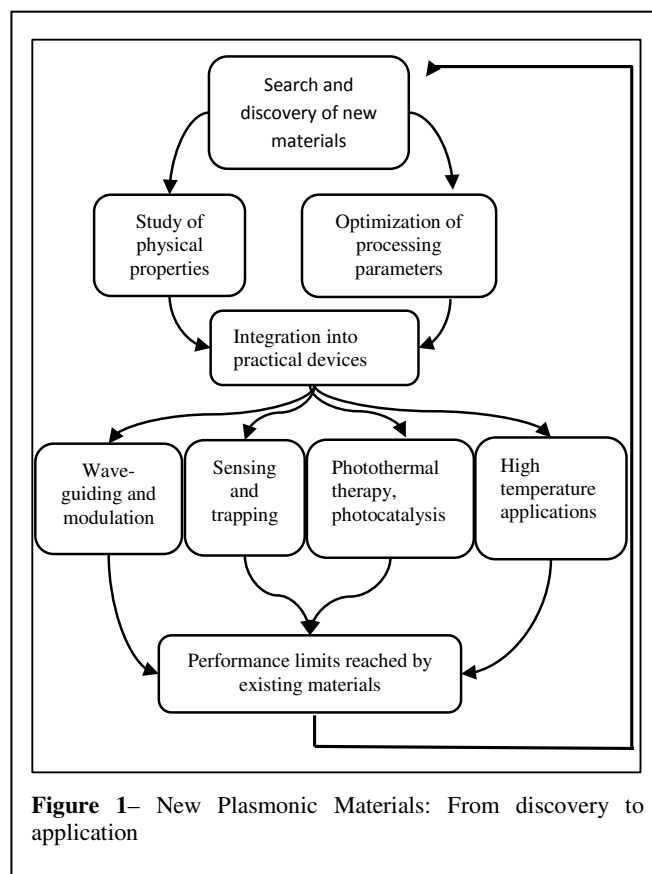


Figure 1– New Plasmonic Materials: From discovery to application

as cells and proteins [10]. Integrated optical planar long-range surface plasmon polariton (LRSPP) waveguides, in particular, are very efficient in this regard because a long optical interaction length can be engineered within the sensing region. In addition to this, they have the added advantage of in-plane coupling, ease of fabrication, and the potential for integration in planar, chip-based sensing platforms.

Photothermal therapy and photocatalysis: Resonant nanostructures of plasmonic materials enable a variety of applications through local field enhancement and heat generation at the nanoscale. 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. Particularly interesting implementations have been demonstrated in plasmon induced photothermal therapy (see for example [4], [11] and references therein) and photocatalysis [12], [13].

High-temperature plasmonics: Several plasmonic applications involve operation at elevated temperatures. For instance, heat-assisted magnetic recording (HAMR) employs efficient local field enhancement via plasmonic antennas to reduce the coercivity of nanomagnets for a short duration of time to write data. This idea was demonstrated in an experiment in which a gold nanoantenna was used to locally heat a 70-nm track [see references in [11]]. Thermophotovoltaic (TPV) systems rely on engineered spectral emission from a body intentionally heated up

1
2
3 to temperatures exceeding 1000°C [14]. The
4 technology was demonstrated with one-dimensional
5 photonic crystal emitters based on silicon/silicon-
6 dioxide layers integrated with a carbon nanotube
7 broadband absorber [see references in [11]]. Broad
8 absorption in the visible and near infrared regions have
9 been recently demonstrated utilizing a metamaterial
10 design consisting of patterned rectangular rings, which
11 shows that there is strong potential in employing
12 metamaterial based absorbers using refractory
13 plasmonic materials to further this goal [11].

14 15 16 **Current and Future Challenges**

17 Integrating plasmonic modulators with on-chip
18 photonic circuitry requires the integration of plasmonic
19 interconnects. A majority of demonstrations of
20 plasmonic interconnects involve the use of noble
21 metals such as gold and silver which are not CMOS
22 compatible. So a big challenge in this field has been to
23 come up with CMOS compatible, low-loss plasmonic
24 materials [8].

25
26 For optical sensing and trapping applications, gold is
27 the most abundantly used material. Materials that have
28 good optical performances at different ranges in the
29 optical spectrum than gold, would enable the sensing
30 of a wider array of analytes, and thereby, broaden the
31 horizons of optical and plasmonics-enhanced sensing.
32 The difficulty here is to find materials which, in
33 addition to having good optical properties, are
34 biocompatible, CMOS-compatible, and tunable.

35
36 Because of their high-quality plasmon resonances,
37 plasmonic nanoparticles made of noble metals have
38 been extensively used in research involving
39 photocatalysis. However, challenges like their high
40 costs, poor chemical stability, poor thermal stability,
41 and their incompatibility with CMOS fabrication
42 technology hinder the large-scale implementation of
43 photocatalytic devices employing these metals.

44
45 Plasmonic applications such as HAMR and TPV
46 involve operation at high temperatures. However, at
47 such elevated temperatures, nanostructures of noble
48 metals inevitably undergo structural deformations [11].
49 As a result, plasmonic responses dramatically degrade
50 at elevated temperatures, making it preferable to
51 construct these structures with a material that can
52 sustain such high temperatures.

53 54 55 **Advances in Science and Technology to Meet** 56 **Challenges**

57
58 Several groups of materials exist which can address
59 each of the challenges outlined in the previous section.
60 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 [7], [8], [11]. 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 waveguiding and modulation
applications[8]. These materials have received
significant attention from the plasmonic community at
large over the past decade.

TiN as a CMOS-compatible material for on-chip
LRSP interconnects has already been demonstrated
[see references in [8]]. 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 [15] have opened a path
towards the design of on-chip ultrafast optical
modulators.

In the field of sensing, transition metal nitrides are a
promising group of materials for lab-on-a-chip devices.
TiN is biocompatible, chemically inert and durable,
and is currently used in dentistry, in surgical tools and
as a protective coating in bone-implants. Transparent
conducting oxides such as AZO and GZO have very
low loss in the telecommunications range. Integrated
with plasmonic sensors, plasmonic waveguide based
particle manipulation can propagate innovations in
fields like nanoparticle surface characterization and
drug discovery. For example, switchable TiN based
plasmonic waveguides, using doped oxides such as
AZO as active components, can be utilized for the
design of optofluidic modulators to control analyte
transport and mixing in optofluidic chips.

To be suitable for use in photothermal therapy,
nanoparticles have to be biocompatible, of sizes that
can be efficiently absorbed and released by cells, and
should act as efficient absorbers in the biological
transparency window in order to achieve efficient
heating with lower concentration. TiN nanoparticles
possess all these properties [11]. In addition to this,
the 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 [11]. A key point to note here is that at elevated temperatures, various physical processes (increasing electron-phonon interactions, changes in the carrier densities, crystallinity and grain boundary movements, etc.) are expected to greatly affect the optical properties of the materials being used. These temperature-induced changes must be incorporated into numerical models in order to accurately describe their behaviour at elevated temperatures, making it critical to study the optical response of both noble and refractory materials at elevated temperatures.

Conclusion

The past decade has witnessed a series of consistent technological developments in the realm of plasmonics - integrating novel plasmonic materials with tailorable optical properties and ultrafast optical response. We expect to see a significant impact of new plasmonic materials in the realms of optical communications, on-chip sensing and trapping, photocatalysis, photothermal therapy and energy harvesting.

Acknowledgement

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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 [1], 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 [2], the emergence of topological surface states within semiconductor bandgaps (Fig. 1) 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,

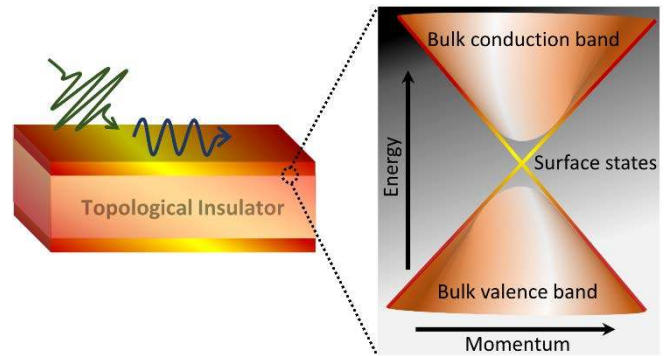


Figure 1 – Light incident on a TI generates surface plasmons by coupling to topological surface states, which arise in the bulk bandgap due to strong spin-orbit coupling as depicted in the simplified schematic band structure to the right.

magnetic or optical excitations [3]; (iii) the optoelectronic response can be highly sensitive to the polarization state of incident light, via the spin-momentum locking effect [4], potentially enabling hybridization of spintronic and plasmonic devices. Recent demonstrations of TI metamaterials with THz to UV spectral dispersions engineered through artificial structuring [5, 6], and experiments showing electrical and magnetic control of mid-IR to THz plasmonic response [3], 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 [7]. 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 [8]. 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

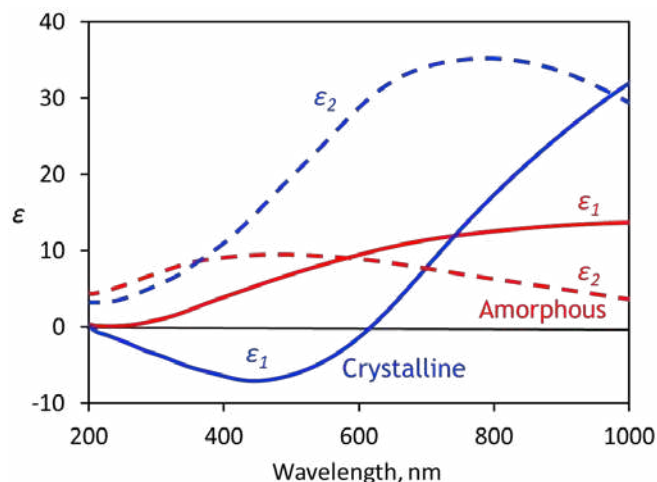


Figure 2 – Ellipsometrically measured spectral dispersion of the real (ϵ_1) and imaginary (ϵ_2) parts of the relative permittivity of a 500 nm GST film in its amorphous (red lines) and crystalline (blue lines) phases, showing a negative value of ϵ_1 in the UV-visible range between zero-crossings at ~ 200 and ~ 600 nm.

– 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 [9] and reversible greyscale direct-(re)writing of arbitrary flat-optical metadevices in unstructured thin films [10]. 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 (Fig. 2): it becomes a TI plasmonic, and for certain wavelengths an 'epsilon-near-zero' (ENZ), medium [1].

High quality single crystal TIs can readily be grown from molten alloys and the optical frequency plasmonic properties of $\text{Bi}_{1.5}\text{Sb}_{0.5}\text{Te}_{1.8}\text{Se}_{1.2}$ (BSTS) have been demonstrated through the realization of metasurface structures, with resonances between 350 and 550 nm, on the cleaved face of such a monocrystal [5]. High-end fabrication techniques such as 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 (inc. 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.

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6. Superconductor plasmonics – Vassili

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Status

Introduction: Superconductivity is a fascinating phenomenon common to many materials at temperatures below 100K [1]. 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 [2]. 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 0.1-1THz), 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 $\lambda_L \sim 100\text{nm}$, the London penetration depth. At low frequencies the diamagnetic response contributes $\Delta\epsilon_r = -(\lambda_0/2\pi\lambda_L)^2$ to the dielectric constant of a superconductor, where λ_0 is the free-space wavelength of the applied electromagnetic signal. It follows, that in terahertz/sub-THz range, with $\lambda_0 \sim 0.3\text{-}30\text{mm}$, the real part of superconductor dielectric constant will be negative and in the range $10^5\text{-}10^9$. 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 experimentally distinguishing the phenomena that arise solely as a consequence of plasmonic response.

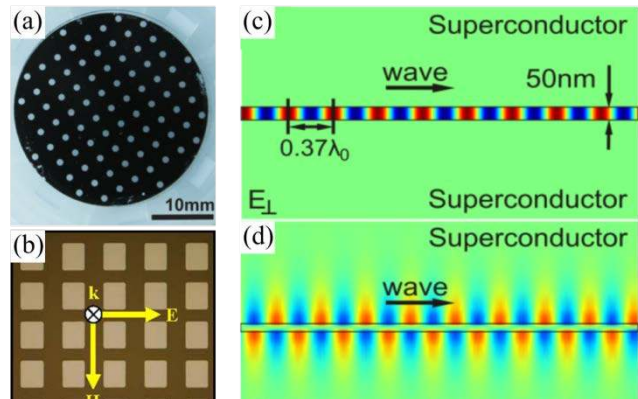


Figure 1: THz/sub-THz plasmonics using superconductors. (a,b) Sub-wavelength hole arrays in Yttrium-Barium-Copper-Oxide film used to study Extraordinary Optical Transmission in terahertz/sub-THz range [3] [4]. (c,d) Superconductor-insulator-superconductor waveguide (simulation) [5]. The light is guided without any significant loss for several times its free-space wavelength λ_0 , despite being confined to 50nm laterally ($\sim\lambda_0/6000$).

Current standing: 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 the increase in transmission of light through films of perforated plasmonic materials as a result of excitation of localized or propagating surface plasmon modes. 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 the high-temperature superconductor Yttrium-Barium-Copper-Oxide in 2010 [3] [4] (see Fig. 1a,b). Subsequent studies demonstrated EOT in other common superconductors such as Niobium-Nitride [2].

Sub-micron scale plasmonic waveguides

A large negative real part and a vanishingly small imaginary part of the superconductor dielectric constant, at THz/sub-THz frequencies, in principle allows one 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 the 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. [5], strong localization of guided terahertz waves can be achieved in a thin dielectric layer sandwiched between the two superconducting layers (see Fig. 1c,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 [5].

Plasmonics in Josephson junctions

An important device related to the superconductor-insulator-superconductor waveguide is the Josephson junction [6]. Josephson junctions are created by separating two superconductors by an insulating layer thin enough (up to few nm) for superconducting charge carriers to tunnel through it coherently. The dynamics of Josephson junctions are highly nonlinear and can be both classical and quantum-mechanical depending on the exact fabrication conditions and the operating temperature ($\sim 1\text{-}100\text{mK}$ 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 [2]. Together, the Josephson inductance and the diamagnetism-related inductance, allow for propagation of plasma waves inside the junctions, known as Josephson plasma waves [6]. Josephson junctions offer a rich variety of effects including THz/sub-THz wave generation, sensing, modulation etc. 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 [2] [6].

Plasmonic superconducting metamaterials

Superconductor plasmonics is central to miniaturization of superconducting resonators in the microwave-THz range [2]. 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 [7]. 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 [2] [7] (see Fig. 2). Furthermore, applications of superconducting plasmonic metamaterials are now beginning to be explored in the optical part of the spectrum [8].

Current and Future Challenges

Whilst superb performance can be achieved using superconductors as plasmonic waveguides and metamaterials, the gains are offset by the need to cool superconductors to low temperatures. Great advances

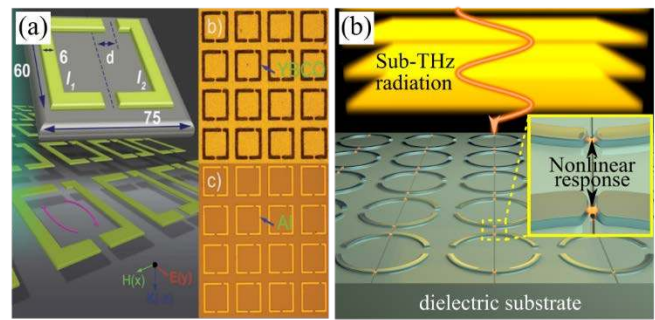


Figure 2: High-Quality and nonlinear THz/sub-THz superconducting metamaterials. (a) Yttrium-Barium-Copper-Oxide metamaterial with record high-quality response in THz range [10]. (b) Niobium metamaterial with record-strong nonlinearity in the sub-THz range [9].

have been made in increasing the transition temperatures of superconductors close to and even above 100K [1], 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 a typical smallest feature size in the region of $10\mu\text{m}$. Even if one targets quality factors of order $Q\sim 100$, the required fabrication precision is around 100nm, which is quite tolerable for modern lithography and etching techniques. However, in the case of nonlinear superconducting metamaterials [9], and even more so, in the case of devices that rely on the Josephson effect [2] [6], the required fabrication precision can be 1-10nm. The search for new and improved fabrication methods thus remains an important driver for nonlinear and quantum superconducting plasmonics.

Advances in Science and Technology to Meet Challenges

Discovery of high-temperature superconductivity (HTS) in 1986, and the rapid rise in transition temperatures that followed it, has been an extremely important advance in applied superconductivity [1]. However, the increase in critical temperatures has since stalled at around 130-160K. 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 fabrication.

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7. Plasmonic nanoscopy – Petra Groß and Christoph Lienau

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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, 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, e.g., 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

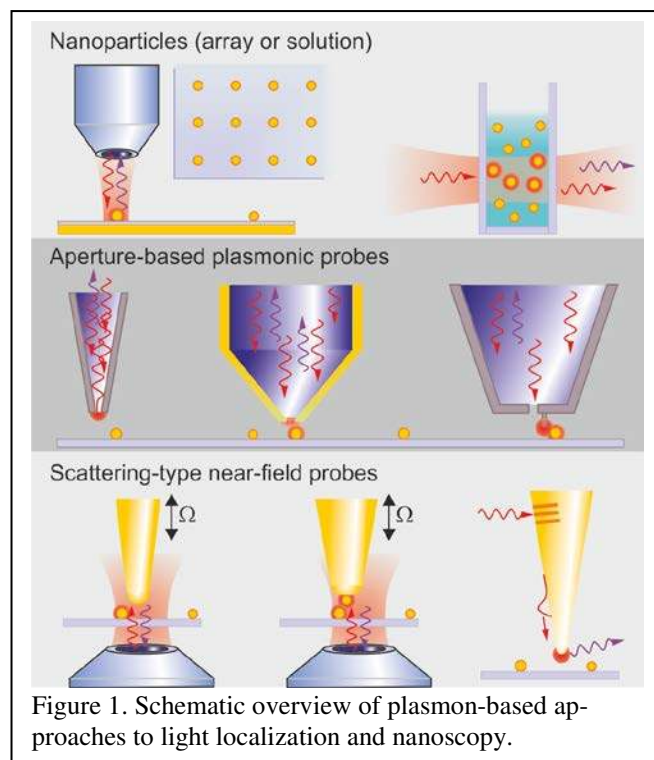


Figure 1. Schematic overview of plasmon-based approaches to light localization and nanoscopy.

enables, in principle, light localization even down to atomic dimensions¹. 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 1). 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 probe². 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)³ 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 ~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 sidebands⁴. 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 efforts have been put in the design of efficient near-field probes that can optimize the localized near-field inten-

sity, reduce the scattering background and overcome the need for modulation techniques. Among the most interesting concepts are tip-on-aperture designs⁵, metal particles attached to dielectric tapers⁶ or the use of gold nanoflakes⁷ 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 probe⁸. 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^{9,10}. 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 2), the launched SPP wavepacket can propagate towards the taper apex. All higher order modes with $|m| \geq 1$ 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 nm¹¹. 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, e.g., by using chemically etched, single crystalline gold tapers in the wavelength range between 700 nm and 2000 nm¹². 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 scan-

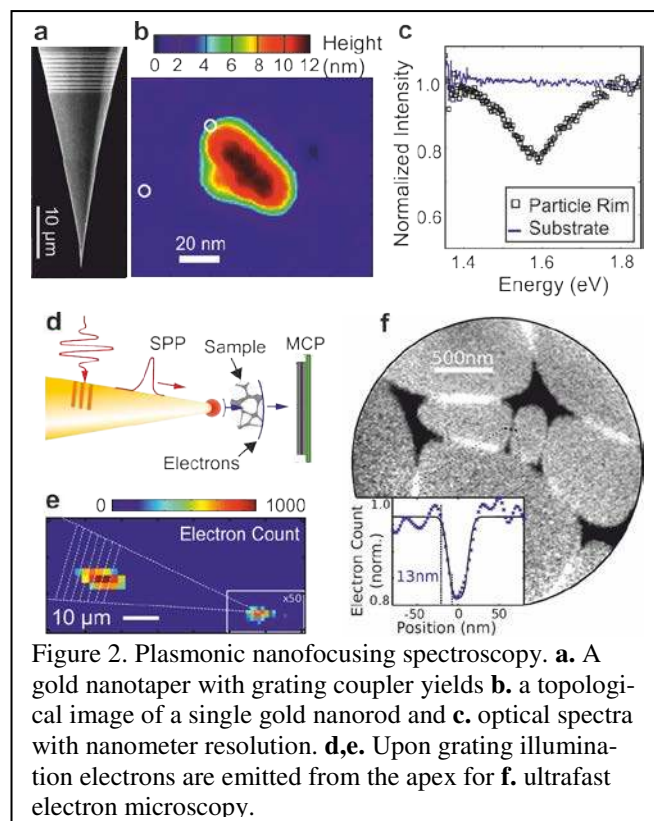


Figure 2. Plasmonic nanofocusing spectroscopy. **a.** A gold nanotaper with grating coupler yields **b.** a topological image of a single gold nanorod and **c.** optical spectra with nanometer resolution. **d,e.** Upon grating illumination electrons are emitted from the apex for **f.** ultrafast electron microscopy.

ning 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 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 experiments¹³. 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 range¹⁴. 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 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 [1]. Plasmonic nanoparticles possess a number of useful features for photocatalysis, including optical near-field enhancement (Figure 1a), local heat generation (Figure 1b), and efficient hot carrier generation (Figure 1c) [2], which can be exploited to control and enhance photocatalytic reactions [3]. 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

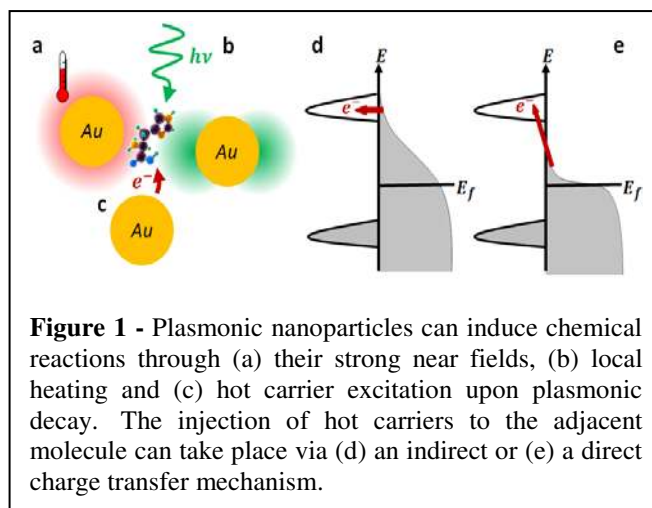


Figure 1 - Plasmonic nanoparticles can induce chemical reactions through (a) their strong near fields, (b) local heating and (c) hot carrier excitation upon plasmonic decay. The injection of hot carriers to the adjacent molecule can take place via (d) an indirect or (e) a direct charge transfer mechanism.

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 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 1d), 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 1e) 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 [4]. 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 [5]. 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 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 [6]. 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 [7]. 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 TiO₂ nanorods was monitored by the signal of the fluorescent product [8]. 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 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. 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. Incorporating state-of-the-art ultrafast pump-probe spectroscopy into these experiments will present an

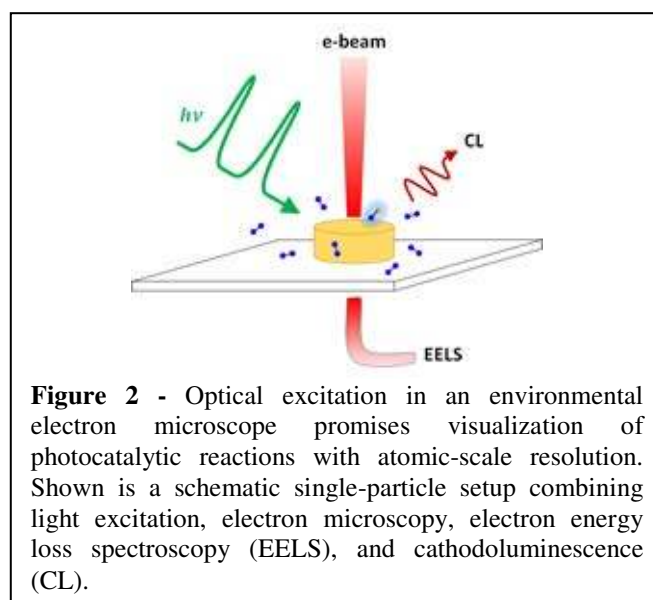


Figure 2 - Optical excitation in an environmental electron microscope promises visualization of photocatalytic reactions with atomic-scale resolution. Shown is a schematic single-particle setup combining light excitation, electron microscopy, electron energy loss spectroscopy (EELS), and cathodoluminescence (CL).

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 [9]. 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 [10]. 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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3 Conversion” Energy Frontier Research Center under
4 grant DE-SC0001293.
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9. Thermoplasmonics: turning material losses into performance gain – Svetlana V. Boriskina

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Status

Traditionally, dissipative losses in plasmonic materials have been treated as an unavoidable nuisance [1,2], 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 [3] (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 [4] (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 [5] (see Sections 4, 5 and 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 [6–9]. This opened up new application areas for plasmonics beyond traditional sensing, spectroscopy, and metamaterials development. These areas include: solar and thermal energy harvesting [10,11], solar treatment of water and waste [12,13], nanofabrication [14], nano-manipulation [15] and cancer therapy [16].

Other emerging applications – including plasmonically enhanced heat transfer through radiative channels [6,9], thermophotovoltaics [11] and heat-assisted magnetic recording [17] – 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 [9] and Section 4).

The unique localized nature of plasmonic heating makes the thermoplasmonic technology very attractive for precise nanofabrication (Fig. 1a), 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 [14]. Targeted photo-thermal ablation of cancer cells (Fig. 1b) utilizes localized plasmonic heating to avoid damage to nearby healthy tissue [16]. Localized

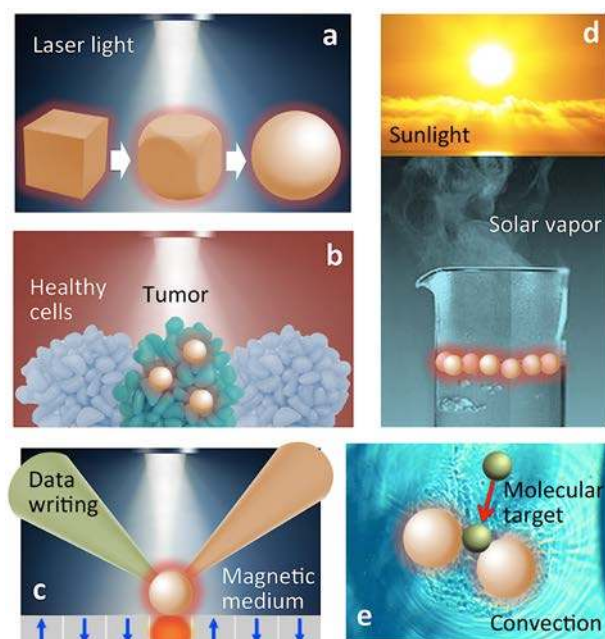


Figure 1 – Light and heat localization underlies the use of thermoplasmonics for (a) nanofabrication, (b) cancer treatment, (c) heat-assisted magnetic recording, (d) solar water treatment, and (e) nanomanipulation.

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 [17] (Fig. 1c). It promises to increase the data storage density above 10 Tb/in². Ancient solar still technology is undergoing a surprising revival spurred by the possibility to dramatically increase the efficiency of the solar vapor generation by the interfacial heat localization between water and air [12,13]. Plasmonics offers a mechanism to achieve such localization, yielding efficiency increase from 30 to 90% in recent experiments (Fig. 1d). 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 [15] (Fig. 1e).

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 [9,11]. 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 thermophotovoltaics [9,11]. Both applications require high absorptance of high-energy photons and suppressed emittance of low-energy photons (Fig. 2a). Nanoparticle-filled thermal fluids can provide excellent selective filters for hybrid photovoltaic and solar-thermal energy conversion platforms (Fig. 2b) [10]. 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 provided by the surface plasmon mode fields (Fig. 2c) [6,9]. 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, non-toxicity and biocompatibility of plasmonic materials plays 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 [5] pave the way to the development of high-temperature selective absorbers and emitters [11]. Successful attempts to replace rare noble metals with more abundant and cheap materials such as aluminum and carbon hold promise for the cost reduction of thermoplasmonic technologies [13]. 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 [18]. 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 [6], thermoelectrics, and nanothermometry among others. 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 [19]. In turn, large temperature gradients induced by the plasmonic photo-thermal converters call for the development of new approaches to achieve local nanoscale temperature readout, such as nanothermometry [20].

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 [21].

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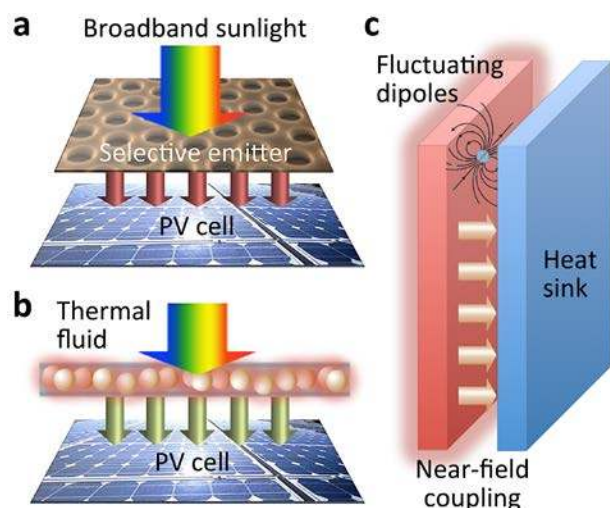


Figure 2 – (a) Spectral conversion of broadband solar radiation by a plasmonic selective absorber/emitter for thermophotovoltaic applications, (b) Spectrally-selective nanoparticle-filled thermal fluids harvest the parts of the solar spectrum not suitable for efficient PV conversion, (c) Near-field radiation can be enhanced by orders of magnitude via plasmonic near-field coupling.

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10. Quantum plasmonics – Ruben Esteban^{1,2} and

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Status

The optical properties of surface plasmons have been very successfully described during the 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 nearby¹. 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 Plasmonics², as schematically depicted in Fig. 1.

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 Nozieres. 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 models³ as well as time-dependent density functional theory (TDDFT) methods⁴. The latter allows for a proper quantization of electrons (and atoms) which captures important aspects in plasmonics such as (i) quantum size effects⁵, (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

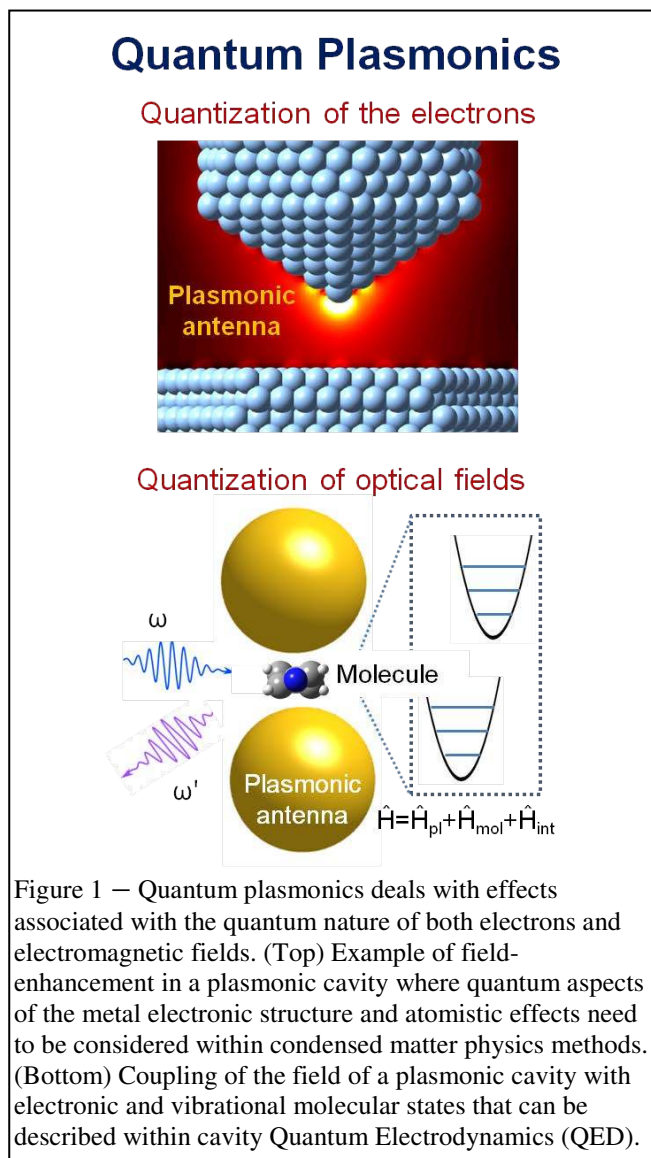


Figure 1 – Quantum plasmonics deals with effects associated with the quantum nature of both electrons and electromagnetic fields. (Top) Example of field-enhancement in a plasmonic cavity where quantum aspects of the metal electronic structure and atomistic effects need to be considered within condensed 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).

nanoantennas and their coupling with other systems such as molecules or semiconductor structures.

A second important aspect of plasmonics concerns the quantization of the electromagnetic field associated with plasmon resonances⁶ and its coupling with excitonic and vibrational states of molecular adsorbates, 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 very strong coherent interaction with emitters, and thus to very fast energy transfer, which can be beneficial for generation of non-classical states of light as well as for other applications in quantum information^{7,8}. 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

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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 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 techniques⁹. 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.

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Furthermore, the coupling of plasmonic excitations with molecular species^{10,11} and semiconductor structures opens new possibilities regarding the interaction of photons with excitons, engineering of vibrational states of molecules, or the decay of plasmons into ‘hot’ electrons and holes¹² for photodetection, energy harvesting, and induced-reactivity¹³, 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.

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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 performance¹⁴, 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^{15,16}.

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 demands¹⁷ 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 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^{12,13}.

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 emission¹⁸. 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 in electrons, photons, and vibrations in plasmonic systems will not only allow a deeper understanding of light-matter interactions at subnanometric and atomic scale 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 – Xiang Zhang and Sui Yang, University of California Berkeley

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 a promising solution 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 [1]. In 2009, the subwavelength plasmon lasers have been experimentally demonstrated and implemented, opening up new avenues to optoelectronic devices and photonic circuits [2-4].

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 [5]. Such Purcell enhancement preferentially increase the utilization of spontaneous emission into the lasing mode and therefore can significantly reduce the threshold and increase operation speed of a lasing device. Secondly, the small mode volume in the plasmon laser cause spatial mode redistribution with large mode spacing. As a result, the lasing outputs are subject to efficient mode manipulation and selection for limited gain, leading 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 [6]. 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

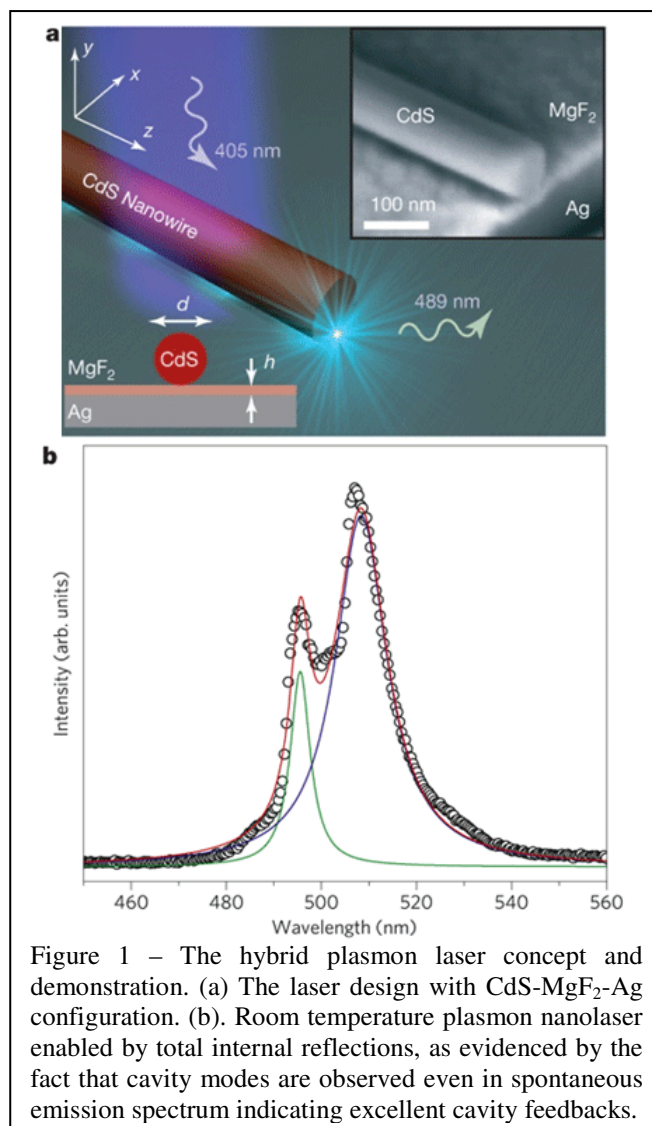


Figure 1 – The hybrid plasmon laser concept and demonstration. (a) The laser design with CdS-MgF₂-Ag configuration. (b). Room temperature plasmon nanolaser enabled by total internal reflections, as evidenced by the fact that cavity modes are observed even in spontaneous emission spectrum indicating excellent cavity feedbacks.

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, the collision of electrons leads to the intrinsic Ohmic loss of the plasmon cavity. In light of that, a ‘hybrid plasmon’ approach has been proposed which couples dielectric waveguiding with plasmonics [2]. The key to this design is the high permittivity contrast at the gain/dielectric/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 1a). 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 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 [7]. The feedback mechanism is extremely effective, as shown by the well-pronounced cavity modes in the spontaneous emission spectrum below the threshold (Figure 1b). Such 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 2a). The metal and semiconductor strips forming networking plasmon laser cavities which simultaneously serve as out-coupling waveguides and electrical contacts [8]. 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 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 [9] (Figure 2b). The exceptional plasmon nanolaser sensor envisages the potential of actively excited surface plasmons for 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

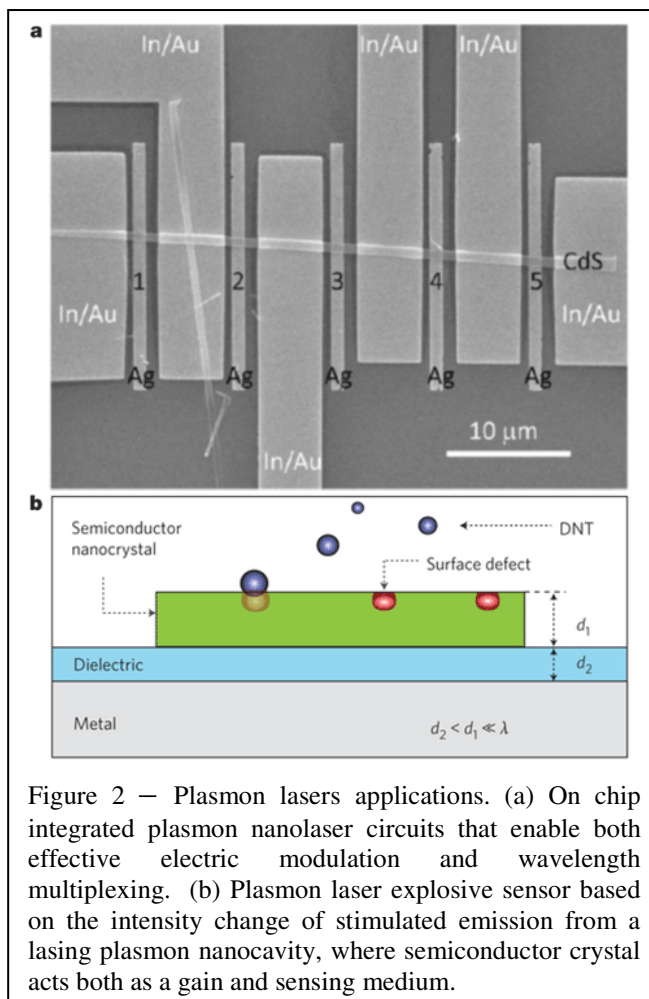


Figure 2 – Plasmon lasers applications. (a) On chip integrated plasmon nanolaser circuits that enable both effective electric modulation and wavelength multiplexing. (b) Plasmon laser explosive sensor based on the intensity change of stimulated emission from a lasing plasmon nanocavity, where semiconductor crystal acts both as a gain and sensing medium.

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 (MBE) can fabricate plasmon nanolaser

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3 epitaxially [10], optimizing both optical and electrical
4 contact constraints. The successful integration of such
5 technique into microelectronics may lead to the first
6 electric driven plasmon laser. Moreover, the advances
7 of fundamental sciences lead to the discovery of a
8 number of new materials. For example, the metallic
9 Nitrides exhibit losses even surpassing silver whose
10 metal loss is currently considered lowest at optical
11 frequency. Two dimensional (2D) materials such as
12 graphene can be used as electric contact for its high
13 carrier mobility. 2D semiconductors or perovskites can
14 be used as gain materials in plasmon lasers for their
15 superior emission properties. These emerging materials
16 may lead to the exploration of fundamental polariton
17 physics and light-matter interactions in plasmon lasers
18 at the nanoscale.

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21 The creation of single crystal nanostructures by
22 chemical assembly have many potential uses in self-
23 assembled electronics. Recent advances in
24 nanochemistry suggest that such assemblies may also
25 lead to photonic structures at large scale. These
26 advances suggest that assembly of materials (metals
27 and semiconductors, etc.) with three-dimensional
28 control over particle position and orientation will soon
29 be feasible. Such scalable and single-crystalline growth
30 methods present important opportunities to new design
31 of plasmon lasers as well as assembling ultracompact
32 laser arrays on-chip.

33 34 35 **Concluding Remarks**

36 Plasmon laser or Spaser presents the unique capability
37 to generate strong localized optical-frequency fields
38 below diffraction limit, opening up new possibilities in
39 the field of both nanophotonics and optoelectronics.
40 With rapid advances in device fabrication and
41 integration techniques, growing knowledge and
42 understanding of light-matter interactions at the
43 fundamental level, we anticipate that plasmon lasers will
44 continue to stretch the bounds in both scientific and
45 technological fronts.
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49 **Acknowledgments** – This work was supported by the
50 Office of Naval Research (ONR) MURI program
51 under Grant No. N00014-13-1-0649.
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55 56 **References**

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12. Nanoarray lasing spasers – Danqing Wang, Weijia Wang, Teri W. Odom Northwestern University

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.^{1,2} Gain materials typically used have been organic dyes for the former and inorganic nanostructures for the latter. However, single-particle spasers face challenges in synthesis and reproducibility¹ (see Section 11: *The spaser as a nanoscale quantum generator and ultrafast amplifier*), and single nanowire-dielectric-metal nanolasers suffer from random emission directions and require low temperature operation² (see Section 11: *Plasmonic Nanolaser Using Epitaxially Grown Silver Film*).

Plasmonic lasers based on arrays of nanostructures for nanocavities have garnered attention recently since 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.³ A simpler design unit, based on cylindrical NP, was first realized in experiment,⁴ closely followed by work on circular holes.⁵

Periodic plasmonic NP arrays with sub-wavelength NP spacing can be generated over cm² areas using multi-scale nanofabrication (Fig. 1a).⁶ 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 ($Q > 200$).^{7,8} 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 (Fig. 1b). By pumping IR-140-DMSO covering the NP arrays using an 800-nm fs-pulsed laser, we found that a single-mode

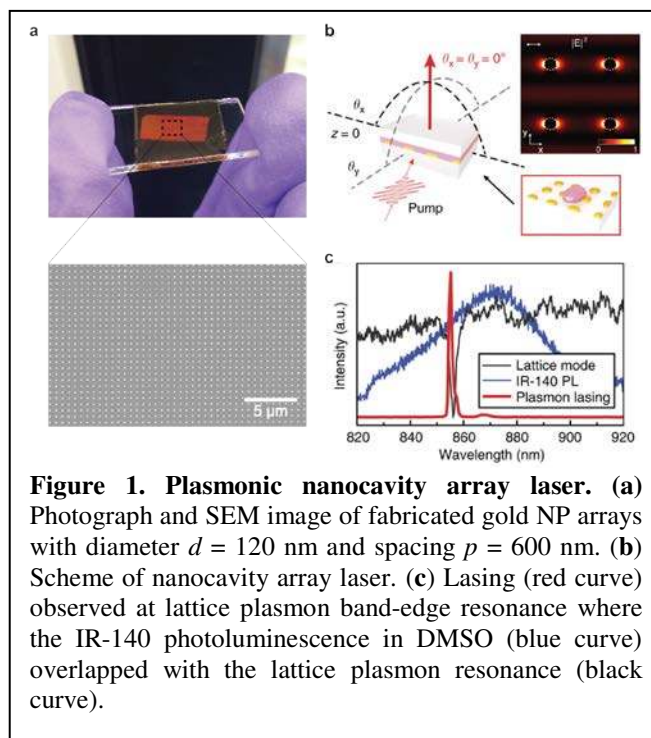


Figure 1. Plasmonic nanocavity array laser. (a) Photograph and SEM image of fabricated gold NP arrays with diameter $d = 120$ nm and spacing $p = 600$ nm. (b) Scheme of nanocavity array laser. (c) Lasing (red curve) observed at lattice plasmon band-edge resonance where the IR-140 photoluminescence in DMSO (blue curve) overlapped with the lattice plasmon resonance (black curve).

lasing peak emerged at $\lambda = 855$ nm, the same wavelength as the band-edge lattice plasmon resonance (Fig. 1c).^{4,8}

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 cm²). Moreover, such architectures can be easily scaled and manufactured.

Current and Future Challenges

We performed some of the first semi-quantum modelling of plasmon nanolasers by combining rate equations and Maxwell's equations.^{4,8} 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 action⁹ 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.¹⁰

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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 \sim 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.¹¹ Such an architecture could potentially lead to engineered light-matter interactions at multiple cavity modes simultaneously. Also, the number of NPs in a finite array could assist in determining 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 (Fig. 2a).⁸ Liquid gain makes possible integration of large-area arrays (\sim cm²) of gold NPs with microfluidic channels (Fig. 2b); hence, different refractive solvents can shift the lattice plasmon resonance and result in on-demand tuning of the nanoscale lasing signal.

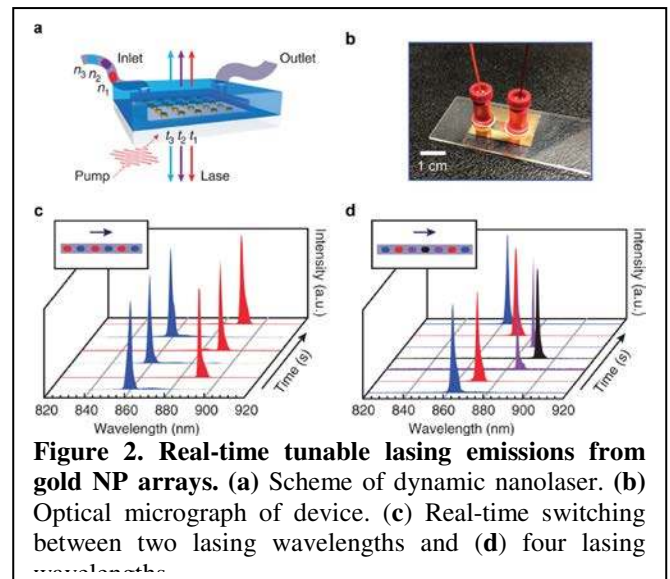


Figure 2. Real-time tunable lasing emissions from gold NP arrays. (a) Scheme of dynamic nanolaser. (b) Optical micrograph of device. (c) Real-time switching between two lasing wavelengths and (d) four lasing wavelengths.

Figures 2c-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.¹² Compared with bi-directional lasing from NP arrays^{4,8} and nanohole arrays,⁵ 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.

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.⁹ 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

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3 photophysics to a Liouville equation description¹³ so
4 that damping and dephasing effects in the time
5 evolution of the four-level dye system can be
6 considered.
7

8 **Concluding Remarks**

9 Nanoarray lasing spasers offer an attractive way to
10 suppress the radiative loss intrinsic to metal NPs and to
11 control the directionality of nanolasing. The production
12 of nano-coherent light sources over wafer-scale areas
13 offers prospects for enhancing light-matter interactions
14 on the nanoscale, real-time monitoring of nonlinear
15 optical processes, and functioning as coherent
16 nanoscale sources for lab-on-a-chip applications. The
17 present research on nanoarray lasing spasers opens a
18 wide range of possibilities for future work on new
19 cavity architectures and unusual types of gain
20 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 [1,2], see also Section [Lienau]. Combining the nanoscale with ultrafast approaches has been a rapidly developing challenge in the recent decade [4-6]. 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) [7, 8], see also Section [Kling].

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 1. 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 inside a high numerical aperture (NA) microscope in a diffraction limited spot, free of spatio-temporal coupling, non-resonant second harmonic NPs have proven beneficial [10]. In contrast coherent NPs can be manipulated by ultrafast coherent control schemes [11]. Combined with precise nanofabrication of tailored NPs and suitable resonances, novel

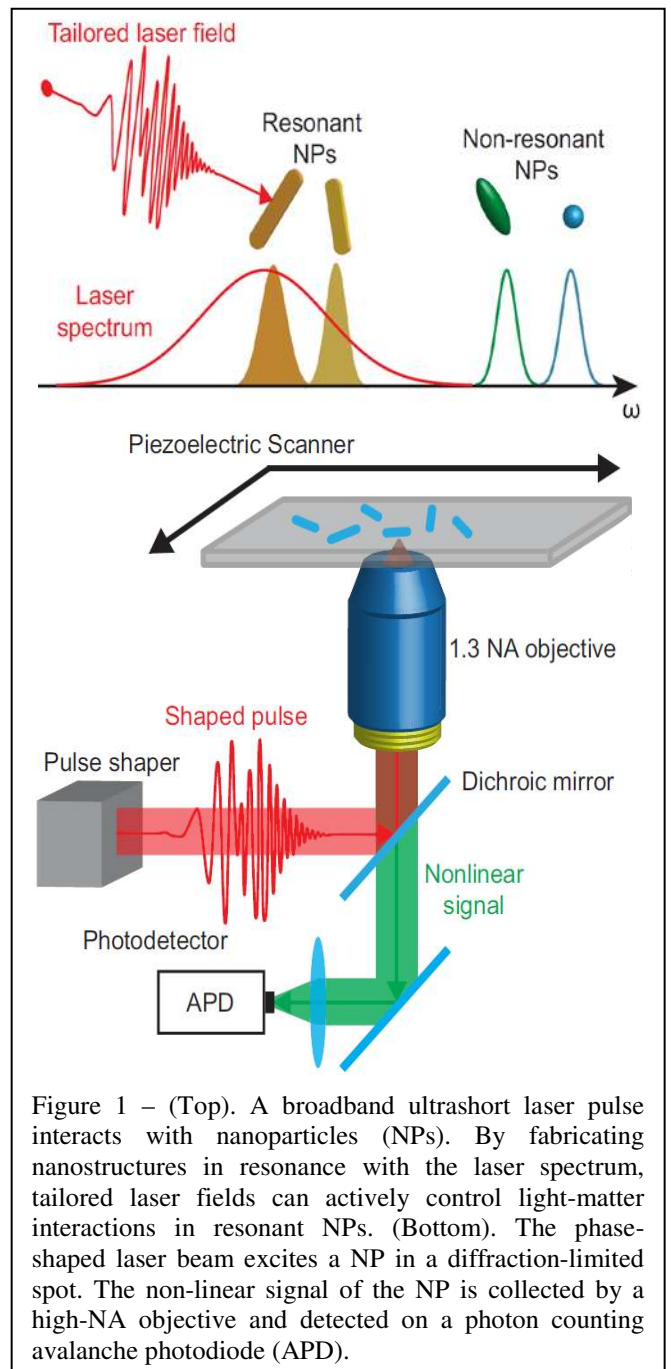


Figure 1 – (Top). A broadband ultrashort laser pulse interacts with nanoparticles (NPs). By fabricating nanostructures in resonance with the laser spectrum, tailored laser fields can actively control light-matter interactions in resonant NPs. (Bottom). The phase-shaped laser beam excites a NP in a diffraction-limited spot. The non-linear signal of the NP is collected by a high-NA objective and detected on a photon counting avalanche photodiode (APD).

applications in nanophotonics can be developed, such as multiphoton imaging of NPs as shown here [12].

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 1. 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

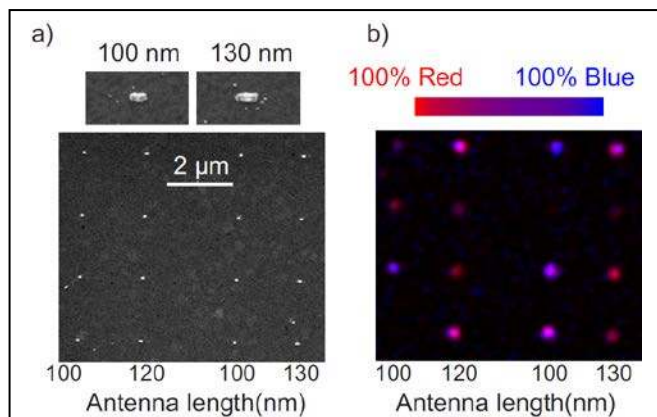


Figure 2 – Spectrally selective SH imaging. a) SEM images of an array of Au nanoantennas of different lengths and zoom-in on individual 100 nm and 130 nm nanoantennas. b) Two-colour SH image of the same array, showing contrast between different NPs, with longer nanoantennas more red. The blue ($\lambda < 400$ nm) and red ($400 < \lambda < 420$ nm) side of the SH-spectrum are pseudo-coloured blue and red [12].

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.

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 [13]. 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 2 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 2a, in the same array, columns of 100 nm alternated with columns of 120 nm and 130nm 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

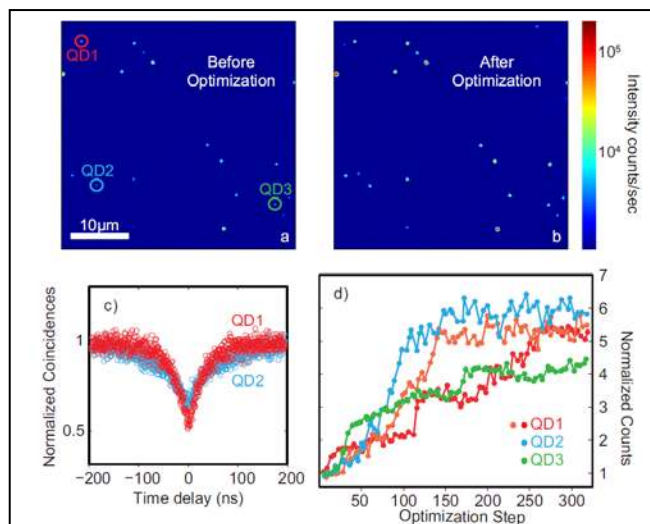


Figure 3 – a, b) TPPL image of single QDs before and after control optimization. c) Photon correlation as a function of inter-photon time for the indicated QDs, showing anti-bunching at zero-time d) Optimization traces taken on different QDs. In 100-300 steps the TPPL is enhanced between 4 and 6 times compared to initial conditions [14].

image of figure 2b 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 130nm 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 3a shows a distribution of QDs, all with anti-bunched photon emission (figure 3c), i.e. single photon emitters. Using a novel optimization algorithm controlling the spectral phase [14], the luminescence of the QDs is optimized and enhanced up to 6 times (figure 3d). The optimization found by the algorithm is targeted to 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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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 [1]. Ultrashort laser fields can be applied to drive and monitor attosecond controlled electric currents in dielectrics [2] and attosecond photoemission from metals [3] and are key to the realization of ultrafast dielectric electronics [1]. 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 time scales [4].

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 [1], attosecond resolution is essential. Extending attosecond metrology towards probing nanometer-scale near-fields can provide a solution and was considered by a body of theoretical work (for an overview see e.g. [5]).

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.* [6] introduced the concept of nanoplasmonic streaking to study plasmonic excitations in real-time. The scheme of the proposed experiment is depicted in Fig. 1. 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

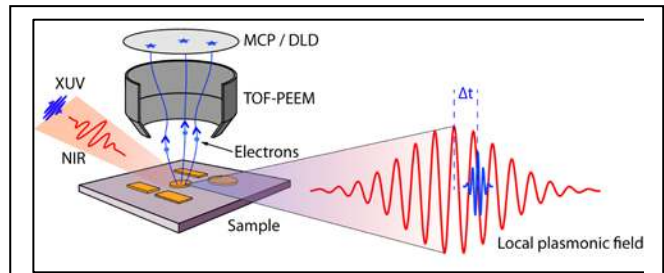


Figure 1 – Principle of attosecond nanoplasmonic microscopy (ATTO-PEEM). A near-infrared (NIR) pulse induces plasmonic oscillations which are probed by a time-delayed attosecond extreme-ultraviolet (XUV) pulse. The emitted electrons are measured with a photoemission electron microscope, where their time-of-flight 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.

parameter $\delta = T_{\text{esc}} / T_0$, where T_{esc} is the escape time of an electron from the near-field and T_0 is the laser period [7, 8].

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 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.* [6]. 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 [7]. By combining attosecond streaking measurements with a thorough analysis of the near-field spatial distribution

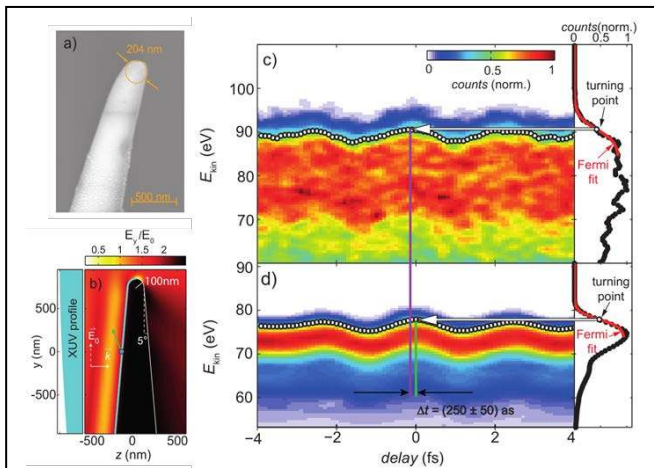


Figure 1 – (a) SEM image of nanotaper sample. (b) Normalised field strength of the field component parallel to the nanotaper axis, calculated using an FDTD method. The blue line shows the region of the sample illuminated by the XUV, and the spatial profile of the XUV focus is shown on the left. (c) Streaking 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.

and photoelectron trajectories, the near-fields surrounding a gold nanotaper could be retrieved with attosecond precision (see Fig. 2).

Current and Future Challenges

Using attosecond metrology, we can learn how collective excitations are formed and how their phase coherence is lost. Not only the experiments, also an accurate modelling of the creation and decay of plasmons in nanostructures creates a challenge to theory. The experiments by Förg *et al.* [7] 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 fields on surface-assembled nanostructures and the successful implementation of the ATTO-PEEM. While imaging nanostructures with sub-micrometer resolution has been successfully realized with attosecond light pulses and presents an important milestone, the theoretical

development is currently ahead of an experimental implementation of the ATTO-PEEM. 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 the ATTO-PEEM can be overcome with developments towards hundreds of kilo- and megahertz repetition rate attosecond laser systems [9]. 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, and furthermore the European Light Infrastructure – Attosecond Light Pulse Source (ELI-ALPS) in Szeged, Hungary, is planning to host a 500 W power OPCPA laser system providing 100-kHz attosecond light pulses for user operations, including ATTO-PEEM type 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 true potential of ATTO-PEEM can be unlocked. The high repetition rate might also provide the head room for energy selective imaging to reduce chromatic aberrations.

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 the ATTO-PEEM, but also employ light fields synthesized from continua spanning over several octaves [10], 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.* [7], 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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