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Subject: Plasmonics and Metamaterials

Title: Unrelenting Plasmons

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Standfirst: *World-wide research efforts on plasmonics and metamaterials have been growing exponentially over the last 10 years. Will this course hold true over the next decade?*

Following a brief historic introduction to plasmons, their useful properties and early applications, we highlight some of the key advances in the field over the last decade. Along the way we offer future outlook on new directions of the field, such as the use of 2D materials and strong coupling phenomena, which will shape it over the next 10 years.

For centuries, metals were only employed in optical applications as mirrors and gratings. New vistas opened up in the late 70's and early 80's with the discovery of surface enhanced Raman scattering and the use of surface plasmon (SP) resonances for sensing. However, it was not until the 90's, with the appearance of accurate and reliable nanofabrication techniques, that plasmonics blossomed. Initially, the attention focused on the exploitation of surface plasmons (collective electronic oscillations at the surface of metals) for sensing, sub-wavelength waveguiding and extraordinary optical transmission [1]. Since then, the scientific and technological interest on SPs has expanded. Correspondingly, as illustrated in Figure 1, the number of publications in the field has increased in a steady exponential fashion for more than two decades. In the following, we argue that momentum on plasmonics research will continue in the future.

In a simplified picture, there are four distinctive characteristics that make surface plasmons so attractive: their ability to concentrate light beyond the diffraction limit, their capability to modify the local density of photonic states, their ultrafast response, and their environmental sensitivity and flexibility in design. The main factor limiting the efficacy of these SP attributes is the high optical absorption inherent to metals. Therefore, the quest for minimizing dissipative damping has been a crucial driving force for plasmonics.

Beyond Noble Metals and graphene

The endeavour of refining plasmonic performance has been accompanied by the pursuit for materials outperforming noble metals at specific optical functionalities. Different proposals, such as aluminium, metallic alloys and heavily doped semiconductors, have advanced our understanding and broaden the catalogue of available plasmonic platforms. However, noble metals may still have more to offer. Recently, it has been shown that their plasmonic characteristic can be largely improved using standard surface science fabrication protocols [2]. This finding may require revisiting previous experimental results and theoretical predictions to re-asses the performance of noble metal architectures.

The advent of graphene has unveiled a new class of materials, characterized by their atomic thickness, which is very promising for THz and Mid-IR applications. Doped graphene supports SPs in these frequency ranges, featuring out-of-plane decay lengths and in-plane wavelengths that are 3 orders of magnitude smaller than free space radiation. This fact, together with their large electrical tunability, makes graphene plasmons excellent candidates for resonators and sensors. Despite the inherent absorptive character of graphene, there are reasons for being optimistic about the prospects of reducing damping in graphene-based plasmonics. For instance, the encapsulation of graphene within BN films has enlarged SP propagation lengths by one order of magnitude [3]. Moreover, graphene is not the only member of the set of 2D plasmonic materials. Apart from BN, which supports hyperbolic modes, the interest in other media, such as semiconducting MoS_2 or black phosphorus, has been mounting over the last year or so. We envisage that atomic-thick plasmonic materials will be a very active and fruitful research area over the next 10 years.

Sensing

The efficiency of SP-based phenomena in metallic platforms has been pushed to unprecedented limits for different applications. For example, through the implementation of plasmonic tips designed at the sub-nanometric scale, spectroscopic techniques are approaching the level of chemical recognition and spatial resolution required to identify single molecules [4]. It is likely that the combination of advances in nano-metrology and a deeper understanding of Raman enhancement mechanisms will establish single molecule spectroscopy as a widespread tool relatively shortly. Similarly, the large field enhancement and acute environmental sensitivity of SPs are being exploited in prototypes for micro-fluidic sensors. These are versatile and label-free instruments able to detect extremely low sample volumes and concentrations. Furthermore, SPs are key ingredients for optical nano-tweezers. These take advantage the complex force fields that originate from plasmonic light confinement to trap and manipulate accurately individual nano-objects in real-time. This SP-assisted miniaturization of equipment (spectroscopes, biosensors or tweezers, among many others) has made possible lab-on-a-chip devices integrating all the functionalities of a conventional laboratory, a technology which is currently close to industrial production.

Optical antennas

For many purposes, the excitation of SPs by an external light source is a requisite. Due to their large momentum mismatch, this cannot be done in a straightforward manner. One option is nano-antennas [5] which are arrangements of nanoparticles designed to carry out this task. They operate with visible and IR light in a similar way as conventional antennas do with radio and telecom waves. By means of the strong field amplification and small modal volume of SPs, nano-antennas can improve the radiative properties of light emitters (like fluorophores or dye molecules). Such plasmonic-enhanced microscopic light sources are expected to have a strong impact on areas such as super-resolution imaging or solid-state lightning [6]. Large distributions of nano-antennas can also act as macroscopic light receivers. This ability is appealing for solar energy conversion, as SPs can boost solar-cell absorption efficiency [7]. However, the high costs of plasmonic materials are currently hindering their wide-spread implementation in photovoltaic technology. Moreover, nano-antennas can function as frequency-selective, non-fading light reflectors too. This makes them excellent candidates for the next generation of colour printing technology pixels [8]. The development of polarization-dependent, three-dimensional and stereoscopic microprints based on these plasmonic pixels will also have great repercussion in sectors including lithography, holography or anti-counterfeiting.

Nanolasers

Plasmonic nanostructures can be tailored not only to increase the near-to-far-field coupling of light and microscopic emitters (like nano-antennas do) but alternatively to decrease it. This way, they can be used in optical nano-cavities, in which the small modal volume of SPs can be used to enhance light-matter interactions. Perhaps one of the most interesting applications of SP-cavities occurs when they are filled with optically active media to yield nano-lasers [9]. These can be open systems, composed of single or periodic arrays of metallodielectric nanostructures, designed to amplify SP-assisted stimulated emission. The reduced dimensions and ultrafast operation speed of nano-lasers represent an important advance towards the on-chip integration of optical and electronic technologies. The plasmonic nano-laser development is not without hurdles and even some controversies, and the challenge towards real-world applications will require much attention in the next few years. One of the main goals over the next decade will be realizing efficient and practical nano-laser devices operating under electrical, instead of optical, pumping.

Enhanced non-linear optics

Macroscopic optical nonlinearities are extensively used in standard photonics technology. They originate from small anharmonicities in the electromagnetic response of matter, which makes them inherently weak and, crucially, super-linearly dependent on the amplitude of the electric excitation. Hence plasmonic field enhancement represents an exceptional means to boost nonlinear effects at the sub-wavelength scale. Proof-of-concept experiments implementing this idea have recently shown orders-of-magnitude amplification of frequency conversion, switching, and modulation of optical signals [10]. Moreover, SP-amplified optical nonlinearities also provide a feedback mechanism for plasmonic signals themselves. Thus, optical gain can be used to compensate for plasmon decay, giving rise to self-sustained or soliton-like SPs. In this context, plasmonics in ultra-smooth metal surfaces offers novel strategies to miniaturize the current (inherently bulky) nonlinear optics technology.

Exploiting dissipation and hot-electrons

The dissipation experienced by conduction electrons undergoing plasmon oscillations was initially thought to be detrimental for nano-optics. However, in some contexts the previous hindrance has been converted into a potential benefit. At extremely short (few femtosecond) time scales, SP decay generates hot electrons (and holes), which occupy short-lifetime states above the Fermi energy. The quasi-bound character of these plasmon-induced carriers serves as an efficient channel for optical-to-electrical energy transduction [11]. Recent experiments demonstrate that hot carrier generation in plasmonic nanostructures can yield efficient photodetectors and photocatalysts. At much longer time scales, thermalization takes place and SP absorption gives rise to nanometric-sized heat sources and sinks. This allows the creation of temperature gradients at the nano-scale, a prospect with is under investigation for magnetic recording and bioimaging. Furthermore, thermoplasmonic prototypes are currently undergoing clinical trials for medical therapy (cancer treatment) applications [12].

Hand-in-hand with metamaterials

Despite being initially established as an independent research area, metamaterials science has evolved hand in hand with plasmonics for the last decade. Figure 1 shows that after an initial surge in metamaterials literature, prior to maturity, the exponential evolution of the number of papers per year in both fields run parallel in time. SP modes and antennae arrays acquired a pivotal role in metamaterials as the quest for demonstrating effects like negative index at frequencies approaching the visible regime took place. This pushed the field into the challenge of SP damping too, which found solution in particular cases through loss compensation and optical gain [13].

Fabricating devices larger than a handful of unit cells thick has been a constant challenge hampering metamaterials technology. Again, this disadvantage has been spun into an advantage. Recently, structures based on single metamaterial layers, i.e. 2D metamaterials or metasurfaces [14], have been proposed. These are much thinner than the operating wavelength, which makes them easier to fabricate and much less sensitive to absorption losses. By increasing the complexity of the internal composition and the collective coupling of meta-atoms, metasurfaces yield efficiencies comparable to bulk metamaterials. Moreover, by combining metals with 2D materials such as graphene, electrically and/or optically tunable metasurfaces can be realized. Paradigmatic functionalities, such as negative refraction [15] and cloaking [16], have been accomplished through metasurfaces. This anticipates the key part that they will play in photonics technology, for example, by providing tunable planar transfer functions for superlenses, reflectarrays or beam steerers and shapers.

Strong coupling

By shrinking their modal volume, the interaction between SPs and an ensemble of quantum emitters (quantum dots and organic molecules) can be pushed into the so-called collective strong coupling regime. This phenomenon takes place when light and matter states exchange energy faster than their respective decay channels, giving rise to new quasi-particles, usually termed plasmon-exciton-polaritons. The properties of these hybrid states can be adjusted through their light and matter content, which means a new, and qualitatively different, degree of light manipulation. Plasmon-exciton-polaritons can potentially undergo bosonic condensation at room temperature and low threshold lasing. A different research route consists in taking advantage of the phenomenon of collective strong coupling to take chemistry and materials science into new directions, i.e., modifying chemical and material properties through vacuum fluctuations [17]. We envisage that plasmonic cavities will find applications as catalysts, inhibitors of chemical reactions, and enhancers of energy and charge transport, prospects that are now attracting much fundamental research.

Strong coupling of plasmons and quantum emitters can also appear at the single emitter level, as has been demonstrated experimentally very recently [18]. In this regime, the hybrid nature of quantum light sources is expected to have a strong impact in the optical properties of the compound system. As illustrated in Figure 2, contrary to semiconductor microcavities, the large coupling strengths attainable in metallic nano-cavities make them robust to thermal fluctuations. Therefore, emitter-plasmon devices represent an auspicious basis for nonlinear nanophotonic components at the single photon level, able to operate at room temperature.

Quantum plasmonics

From a theoretical perspective, current plasmonics often far transcends the realm of classical electromagnetics. Among the latest generation of nano-optical devices, some are designed to support SP modes localized within sub-nanometric dimensions, and others are devised to operate at the level of a few plasmon quanta. The need for theoretical tools able to describe all these systems has pushed plasmonics into the domains of condensed matter physics and macroscopic quantum electrodynamics. The interplay with these two fields has led to significant advances in our understanding of plasmonic phenomena. However, crucial aspects, such as establishing the actual limits that the interacting character of conduction electrons poses to plasmonic field enhancement, or the robustness of quantum coherence and correlations achievable in SP platforms, yet need to be addressed.

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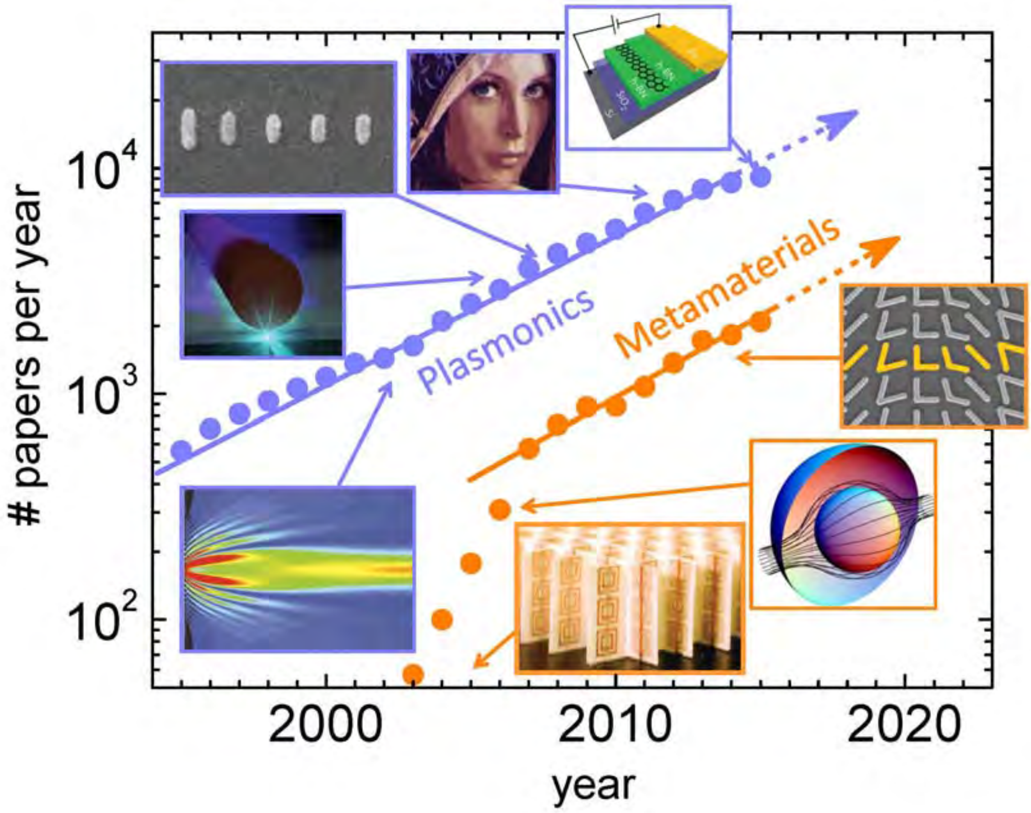

Figure 1: Number of papers published per year in the fields of plasmonics (blue circles) and metamaterials (orange circles) between 1995 and 2015 (data taken from ISI Web of Knowledge, 2016). Solid lines are a guide for the eye illustrating the exponential growth experienced by the volume of the literature on both areas. Dotted lines are speculative projections of this trend into the near future. The insets sketch some of the most relevant milestones in the evolution of both research fields. From left to right: SP-assisted beaming [1], nano-lasing [9], optical antennas [5], color printing [8], and graphene plasmons [3] (Plasmonics), and negative refraction [15], cloaking [16] and metasurfaces [14] (Metamaterials).

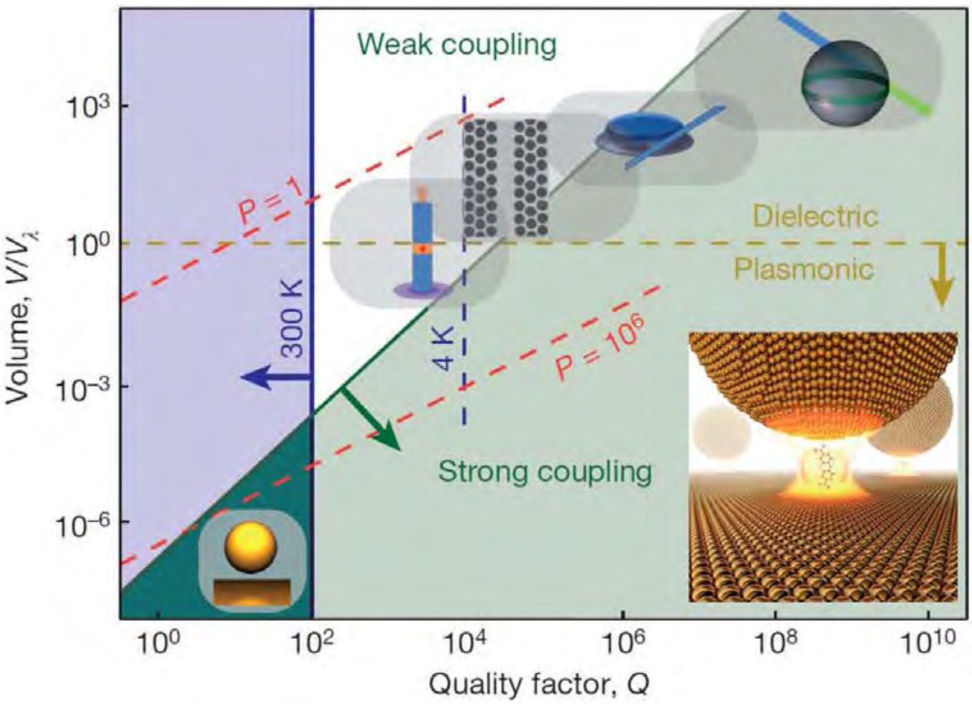

Figure 2: Modal volume versus quality factor for different photonic cavities. Contrary to their semiconductor counterparts, plasmonic nano-cavities can provide strong-coupling (green shaded area) at room temperature (blue shaded area). Inset: illustration of a particle-on-mirror plasmonic cavity strongly coupled to a single molecule placed within its (sub-)nanometric gap [18].