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Nanoplasmonics: Concluding remarks

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The Faraday Connection

Faraday Discussions have a splendid reputation in stimulating scientific debates along the traditions set by Michael Faraday himself. The Faraday Discussion 178 on nanoplasmonics has been particularly appropriate. Nanoplasmonics is the science of harnessing the interaction of light and matter on the nanometer scale. Plasmonics is a highly interdisciplinary field bridging between physics, chemistry, modern nanotechnology and nanophotonics. Michael Faraday, firstly a chemist with original contributions in electrochemistry, paved fundamental roads in physics, establishing the basic concepts of the electromagnetic field in physics and the effect of magnetism on rays of light. He pointed out the peculiar effect metal particles have on light and the importance of the particle size. He mentioned gold as especially fitted for experiments, a tradition carried on until today.[1] As such, the spirit and scientific foundations of Michael Faraday have been ever-present at the Burlington house gathering in February 2015 (Fig. 1). Here, highlights of the presented papers and discussions are summarized with an eye on future perspectives.

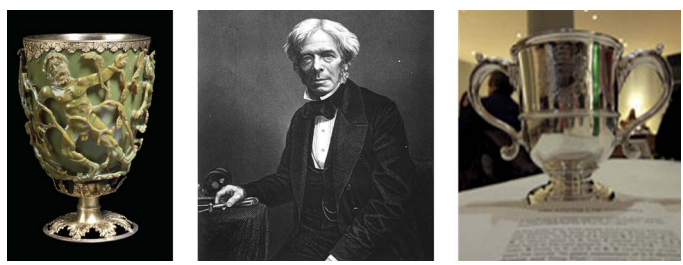

Fig. 1 Michael Faraday, amidst the 4th century Lycurgus and 18th century Loving cup. Left, the glass Roman Lycurgus cup, with distinct colours in reflection and transmission due to embedded metal plasmonic nanoparticles (© Trustees of the British Museum). Right, the silver Loving cup used at the Faraday Discussions' Dinners to toast the memory of Mr. Marlow, Angela & Tony Fish, and the Faraday Division. (Image of Michael Faraday reproduced courtesy of the Library of the Royal Society of Chemistry.)

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Introduction

In the Burlington house corridors, asking around amongst the attendees as to the perspectives of nanoplasmonics I received quite disparate first-hand answers, varying from "metal nanoparticles are good for heating and non-linear optics" to "plasmonics is dead" and "hot electrons are the future". Clearly the field has developed some history already and is moving into new directions. A more balanced reflection on where the field stands today is needed.

Primarily, nanoplasmonics stands for metallic nanoparticles and nanostructures, which allow concentrating the light to dimensions far below the wavelength of light. As such, key strengths are: strong spatial confinement of the optical light field, intimately connected to the direction and polarization of both incident and emitted light; direct control of the radiative decay (engineering of LDOS); novel building blocks for light control, such as in flat optics applications; and the ideal combination of optical and electronic properties. Mark Brongersma nicely displayed these key strengths in his Introductory lecture on nanoplasmonics (DOI: 10.1039/C5FD90020D). Driven by the potential of nanoscale light control, plasmonics has developed fiercely over the last one or two decades. Strong field enhancement, nanoscale local confinement and emission control have all been shown. Pushing towards applications, many demonstrations of nanoplasmonic circuits, plasmonic assisted photovoltaics and even plasmonic nanolasers have been presented, placing the field at the top of the research agenda. Unfortunately, the use of metals at optical frequencies is associated with appreciable losses and heating, even more as the nanostructures are often non-crystalline. Only for far sub-micron sizes and distances the losses can be neglected. Many applications have been frustrated by this loss issue. Also, plasmonics is not compatible with complementary metal–oxide–semiconductors (CMOS), which complicates upscaling and the potential combination with silicon technology.

Many questions remain to be answered. Can novel plasmonic materials overcome the losses? What are the limits to spatial confinement? What is the role of non-local effects? Which plasmonic properties last in the quantum regime? Can one actively control the plasmonic response? What is the potential of plasmonics in strong coupling? Thus, to address such questions, current nanoplasmonics is moving into new directions. In recent years, many activities have been developed on the use of electron beams in plasmonics (electron energy loss spectroscopy (EELS), photoelectron emission microscopy (PEEM), cathode luminescence (CL)); the active manipulation of plasmonic structures; the expansion of the wavelength range towards both UV and MIR; the use of plasmonics in catalysis and photochemistry; new plasmonic (2D) materials, such as graphene, MoS_2 and BN; ultrafast atto- and femtosecond plasmonics; and more fundamental quantum plasmonics.

To capture these new developments, Faraday Discussion 178 focused on 5 themes:

- Plasmonic and new plasmonic materials.
- Surface plasmon enhanced spectroscopies.
- Quantum plasmonics, gain and spasers.
- Applications in nanophotonics.

- Sensing, imaging and chemistry applications of plasmonics.

Here, let's revisit and discuss particular highlights of the various themed sessions.

New materials

Clearly the major problem in nanoplasmonics is related to the material limitations, specifically the losses of gold and silver. The first day of the discussions was largely devoted to the quest for alternative superior materials. Vladimir Shalaev presented a new class of materials: transition metal nitrides (TiN, ZrN, HfN, TaN, AlN) as refractory optical materials, exhibiting promising plasmonic dispersion properties in the IR-Vis regime, along with high temperature durability (DOI: 10.1039/C4FD00208C). The dispersion of TiN is comparable to that of Au, yet TiN possesses superior hardness, a higher melting point, and CMOS compatibility and biocompatibility, all of which are important for applications. The novel material graphene is receiving great interest in the plasmonics community: graphene causes extreme localization of the optical field, together with fields increased over many orders of magnitude. Moreover, graphene, with a single Dirac point in the band-diagram, allows steep and broadband tuning through doping, *i.e.* a promising tunable plasmonic material. Inspired by the concept of atomically thin 2-dimensional materials, F. Javier García de Abajo presented 1–3 atom-thin gold nanodisks providing completely tunable optical absorption and potential for strong-coupling to quantum emitters (DOI: 10.1039/C4FD00216D). During the discussion, he extended the concept to graphene triangles, spanning 2 to 10 aromatic carbon hexagons, and "doped" with up to 6 charge carriers, showing the graphene plasmon tunability for absorption through the IR-Vis regime with a figure of merit better than those of Au and TiN. Interestingly, at the smallest scale of just 2 or 3 hexagons, such nanoscale graphene factually represents basic organic aromatic molecules such as anthracene, and the theory presented for plasmonic graphene also describes the optical properties of these charged molecules. Based on the intuitive graphene picture, García de Abajo coined the term "molecular plasmons", bridging the condensed-matter and molecular-physics schools, which generated an interesting debate. The concept for another new material was presented by Evgenii Narimanov by combining metamaterials and a photonic crystal in a so-called photonic hypercrystal, for which the plasmonic dispersion follows band gap zones, resulting in large wave-vectors and yet low losses (DOI: 10.1039/C4FD00207E). Viktor Podolskiy presented gold nanorods forming nonlocal plasmonic metamaterials for strong radiation coupling (DOI: 10.1039/C4FD00186A). Nader Engheta presented the concept of EMNZ (ε and μ near-zero) materials, with both relative permeability and permittivity near zero, which offer exceptional properties in light–matter interaction (DOI: 10.1039/C4FD00205A). With both ε and μ approaching zero, the curl of both electric and magnetic field approaches zero; that is, the light becomes static and the electric and magnetic fields decouple. Engheta showed the peculiar electromagnetic behaviour of optical circuit end-points filled with an EMNZ medium. EMNZ materials might actually exist at the Dirac point of artificial materials, topological insulators or in stacked layers.

Mind the gap: the ultimate limit of Ångstrom-gap plasmonics

Many nanoplasmonic structures can provide field enhancement, yet gap-nano-antennas composed by two metal particles separated by a narrow dielectric gap are particularly effective. The nanogaps underlie the spectacular enhancements observed in SERS. Classically, when the gap size approaches zero, one expects arbitrarily large charge densities at the opposite sides of a plasmonic gap, leading to extremely intense fields and strongly red-shifted resonances. Obviously the classical divergence in the gap cannot be correct as it disregards nonlocal and quantum effects. The classical local model fails to describe the smooth transition of the electron density at the interfaces, the strong nonlocal interactions, and the tunnelling regime metal nanoparticles. The proper understanding of such Ångstrom-gaps has been an important topic during this Faraday Discussion. Javier Aizpurua presented an overview of the aspects of the classical local regime, the nonlocal regime and the quantum regime of interaction (DOI: 10.1039/C4FD00196F). He presented his classical effective model, the Quantum Corrected Model (QCM), which correctly describes the main features of optical transport in plasmonic nanogaps, showing a non-local regime below the 2 nm gap and the onset of tunnelling below a threshold gap size of about 4 Ångstrom. Jeremy Baumberg, one of the first to identify the quantum regime in plasmonic gaps, presented his experimental work on plasmon resonance spectroscopy on sub-nm plasmonic gaps, coupling gold nanoparticles to a gold surface (DOI: 10.1039/C4FD00195H). The localised field of the coupled mode appeared extremely sensitive to morphological fluctuations and changes in the dielectric properties of the gap. Clear differences were observed in the spectral positions and intensity of the plasmonic modes on a variety of ultrathin molecular spacers such as cucurbiturils (both filled and empty) and graphene. Gap size, shape and facets, all matter, together with the effective "conductivity" of the molecule in the gap. Ångstrom sensitivity is highly promising for surface plasmon enhanced spectroscopies towards the single molecule limit. In an alternative approach to reach the Ångstrom regime in plasmonic gaps, Sang-Hyun Oh presented the use of atomic layer deposition (ALD) to grow controlled spacers with Ångstrom accuracy (DOI: 10.1039/C4FD00233D). He presented high-density metallic nanogap arrays for ultra-sensitive detection of thin films and biomolecules. Using ALD with Al_2O_3, the gaps could be varied up to 10 nm in order to tune the plasmonic spectra for dedicated SERS applications. Also, Masayuki Futamata presented a wide range of spectra using both nanogaps of silver dimers and silver nanoparticle-surface junctions (DOI: 10.1039/C4FD00188E). The critical role of the molecular junctions was nicely resolved in attenuated total reflection and SERS spectra, again a promising way to monitor molecular conformation. A radically different approach was put forward by Riccardo Sapienza with a plasmonic network consisting of a large cluster of nanoparticles with a multitude of nanogaps, fabricated with designed fractal topology (DOI: 10.1039/C4FD00187G). By changing the percolation of the network, the effects of both long-range interactions and local fields on the fluctuations in the local mode density were studied through the lifetime variation of embedded fluorophores. Local properties in the percolating plasmonic networks appeared to dominate the fluorescence variation.

Strong coupling and quantum plasmonics

Nanoplasmonic structures provide strongly enhanced and confined local fields, which establish ideal conditions to induce strong light-matter coupling in molecular materials. Sufficiently high concentrations of molecular materials in such strongly confined fields will form hybrid light–matter states: polaritonic states with a Rabi splitting which can range from over 100 meV up to almost 1 eV. Thomas Ebbesen presented strong plasmon induced light–matter coupling for various types of molecules (DOI: 10.1039/C4FD00197D). Remarkably, the static absorption of the red-shift polariton state did not lead to generation emission, nor to transient absorption of the same state. The excitation spectra appear very different from the static absorption of the coupled systems, the understanding of which needs further studies. Similarly striving for strong coupling, Sergey Bozhevolnyi presented a theoretical model of the relaxation dynamics of a quantum emitter resonantly coupled to a coherent state of localized surface plasmon (DOI: 10.1039/C4FD00165F). The model predicted relaxation dynamics with non-exponential decay and intriguing transient behaviour on the picosecond timescale. David Zueco went a step further in exploiting strong light–matter coupling for non-linear quantum optics (DOI: 10.1039/C4FD00206G). He calculated the propagation properties of multiple photons in 1-dimensional plasmonic waveguides coupled to multiple qubits, showing that the inter-qubit distance enhances the non-linear response in very strong coupling conditions and that inelastic processes are robust against the number of qubits.

Applications in nanoprobing, nanosensing, nanoruling and nanoimaging

The strong spatial confinement and local enhancement of optical fields in nanoplasmonic structures is bringing forward a wide variety of applications, largely in chemistry and biology. At Faraday Discussion 178 a variety of such applications was presented and discussed. The strong local fields are particularly advantageous for non-linear interactions with quadratic or even cubic response on the enhancement. Alessandro Belardini presented a second harmonic generation on self-assembled gold nanowires (DOI: 10.1039/C4FD00200H). By tilting and exciting the wires with circularly polarized pulsed light, he addressed the optical chiral response of the nanowire surface. Very much in the spirit of the early experiments by Michael Faraday himself, at FD178 Michael Flatté presented the electrical control of Faraday polarization rotation at a liquid/liquid interface using nanoparticles (DOI: 10.1039/C4FD00210E). Specifically, a monolayer of charged magnetic (yttrium iron garnet) nanoparticles was positioned at an electrified liquid/liquid interface, where the polarization fields of neighbouring nanoparticles enhance the Faraday rotation. Electrical control of the nanoparticle adsorption–desorption at the interface then provided electro-variable Faraday rotation.

The strong field enhancements at nanoplasmonic particles and surfaces, obviously imply a highly modified photonic density of states: radiative and non-radiative rates are changed, and even energy transfer rates can be affected. Particularly the fluorescence lifetime is the observable of choice to expose any rate

changes. David Richards presented an interesting study using fluorescence lifetime changes, as a function of the distance to a metal surface, as a "nanoruler" to measure out-of-plane distances inside a biological cell; a kind of axial nanotomography exploiting the nanoscale range of the plasmonic interaction (DOI: 10.1039/C4FD00198B). Also using fluorescence lifetime imaging, Yu Chen showed the co-localisation and coupling of gold nanorods with fluorescent protein labels; moreover, by two photon luminescence the nanorods could individually be mapped (DOI: 10.1039/C4FD00199K). The intra-cellular movement of the nanorods was readily applied to monitor endocytosis. Whether the plasmonic mode density also affects the energy transfer rate is a topic of discussion. In practise, the influence depends mainly on the relative sizes of the plasmonic field extent and the molecular distance: a field gradient along the molecular spacing is required. Mikhail Noginov addressed the topic of Förster energy transfer by measuring lifetime changes of donor–acceptor pairs in the vicinity of metallic surfaces (DOI: 10.1039/C4FD00184B). Surprisingly, he concluded that the enhancement of spontaneous emission rates is accompanied by quite strong inhibition of the Förster energy transfer. The localized nanoplasmonic fields and field gradients have been shown to generate local forces on nanoparticles and are interesting as nano-optical tweezers. Olivier Martin presented a visionary picture to use optical forces in nanoplasmonic systems as drivers to control the different manufacturing steps in a nanofactory (DOI: 10.1039/C4FD00224E).

Hot electrons

Nanoplasmonic structures have definite promise in solar energy conversion applications. Firstly, plasmonic antennas are efficient in capturing light and have been explored for the improvement of semiconductor-based solar energy devices. Secondly, surface plasmons excited in Au nanoparticles decay into hot electrons with energies between the vacuum level and the work function of the metal, and the hot electrons and holes can be exploited directly, with the added advantage of their tunability over the solar spectrum. In this context, Martin Moskovits presented a plasmonic photocatalytic device: a 2D gold nanoparticle array combined with a thin electrolytic liquid junction supporting a redox couple (DOI: 10.1039/C4FD00185K). The device produced about 10^{23} hot electrons per cm^2 per second, resulting in photocurrent densities in excess of 40 $\mu A\ cm^{-2}$.

Ultrafast plasmonics

Finally it should be mentioned that ultrafast spectroscopy plays an increasing role in nanoplasmonics research. Femtosecond pulses allow coherent control of the spatio-temporal dynamics of electromagnetic excitations in nanoplasmonic structures and hybrid nanostructures. Control of the nanoscale field localization has potential applications for novel laser structures, the exploitation of optical non-linearities, in biochemistry, *etc.* No experimental work on ultrafast plasmonics was presented at FD178, yet Ortwin Hess presented a theoretical study of the spatio-temporal femtosecond dynamics of coherent amplification and lasing in a planar gain-enhanced nanoplasmonic structure, showing that a sub-wavelength localised vortex in the mode density can provide a stopped-light

feedback allowing cavity-free surface-plasmon polariton nanolasing (DOI: 10.1039/C4FD00181H).

The collective set of papers presented at the Faraday Discussion reflects the wide range of advances in the field of nanoplasmonics in recent years. The field is gradually coming off age and, particularly, the growing diversity of the applications should be noted. From the fundamental point of view, it is shown again and again that, even at the nanometer scale and PHz frequencies, Maxwell's equations hold pretty well. It is mainly through the continuous advances in nanofabrication and new materials that Maxwell's equations unveil previously unimagined surprises. With a growing community active in nanoplasmonics, it can be anticipated that significant advances in the control of the nanoscale light–matter interaction will be achieved in the very near future. Surely Michael Faraday would have enjoyed participating in the inspiring discussion.

References

1 M. Faraday, *Philos. Trans. R. Soc. London*, 1857, **147**, 145–181.