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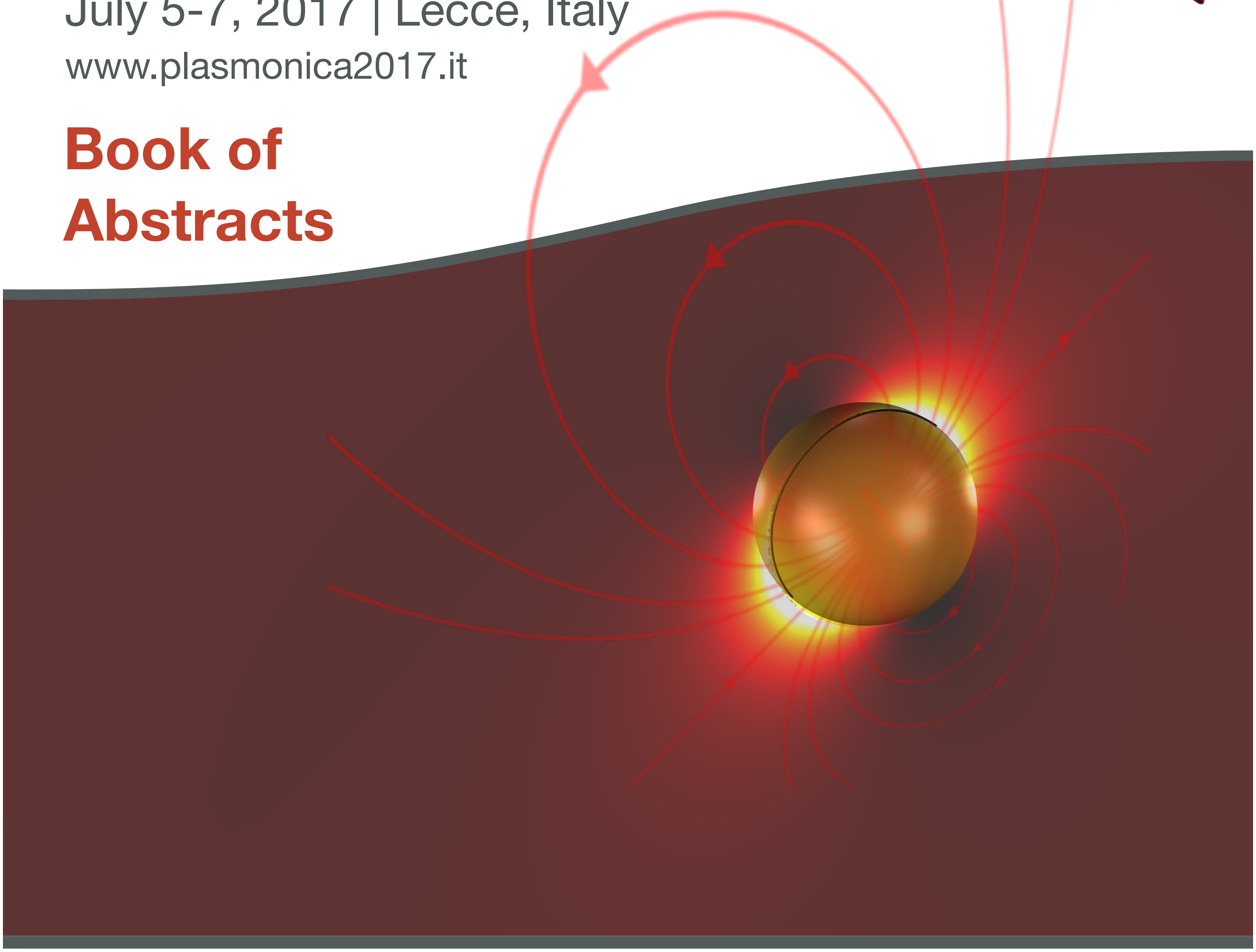
IMM Istituto per la Microelettronica e Microsistemi

PLASMONICA 2017

July 5-7, 2017 | Lecce, Italy

www.plasmonica2017.it

Book of Abstracts



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Conference mission

PLASMONICA 2017, the fifth edition of the workshop on plasmonics and its applications, is held in Lecce, Italy, on July 5-7, 2017. PLASMONICA is an annual conference intended to bring together a thriving community of people that works in plasmonics. In particular, the conference aims at attracting the interest of young researchers, PhD students and post-doctoral fellows from Italy and abroad in order to promote discussions and collaborations on challenging problems arising in the community. The conference will cover both fundamental aspects and applications, featuring several internationally renowned invited speakers, as well as oral and poster contributions.

Topics

- Active Plasmonics
- Nonlinear Plasmonics
- Quantum Plasmonics
- Spectroscopy and Nano-Imaging
- Plasmonic Nanoantennas
- Plasmonic Functional Materials and Devices
- Unconventional Materials for Plasmonics
- Plasmon-Exciton Polaritons

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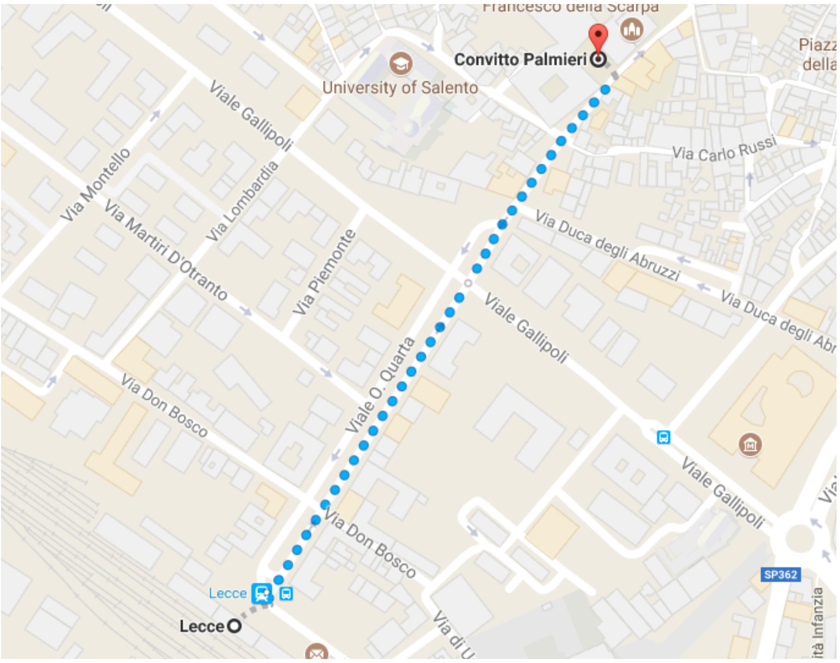
Best oral and poster awards

At the end of the conference a prize of € 500 will be offered to the Best Oral and Best Poster chosen among young scientists (students and early stage postdocs) attending PLASMONICA 2017. These awards will be offered by the Rotary Club Lecce Sud.

Conference location

The 5th International Workshop on Plasmonics, PLASMONICA 2017 is held at Convitto Palmieri in Lecce. The architectural complex represents an articulated but unitary structure, conceived and built over the centuries, and in particular during the XIX century through multiple interventions culminating in the second half of the 1800s with the placement of the highest educational institution in the city of Lecce.
The church of San Francesco della Scarpa is the original site around which the ancient convent, which today constitutes the entire structure of the Convitto Palmieri, was built and developed.

How to reach Convitto Palmieri

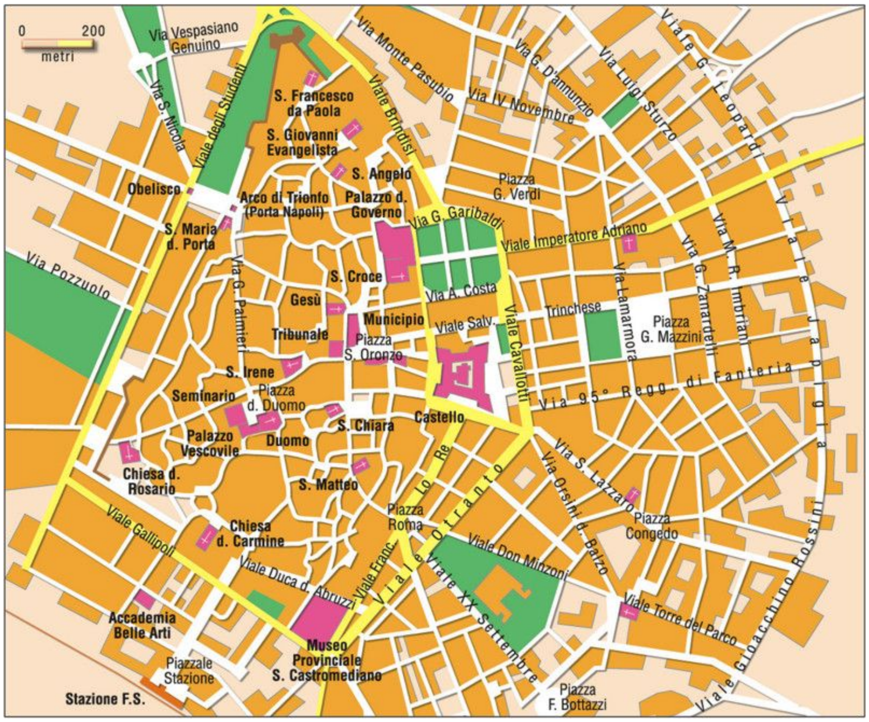


Address
Convitto Palmieri
Via Benedetto Cairoli, 15,
73100 Lecce

Lecce and the surrounding area

Lecce is a historic city in southern Italy, one of the most important cities of Apulia. Because of the rich baroque architectural monuments found in the city, it is commonly nicknamed "The Florence of the South". Lecce lies down at the heel of Italy's boot between the Adriatic and Ionian Sea in the "Salento" area. The region offers kilometers of coastal landscape, blue sea-fringed bays, dunes and white sand beaches; it holds a rich and succulent gastronomic tradition and offers a lively and dynamic cultural scenario.

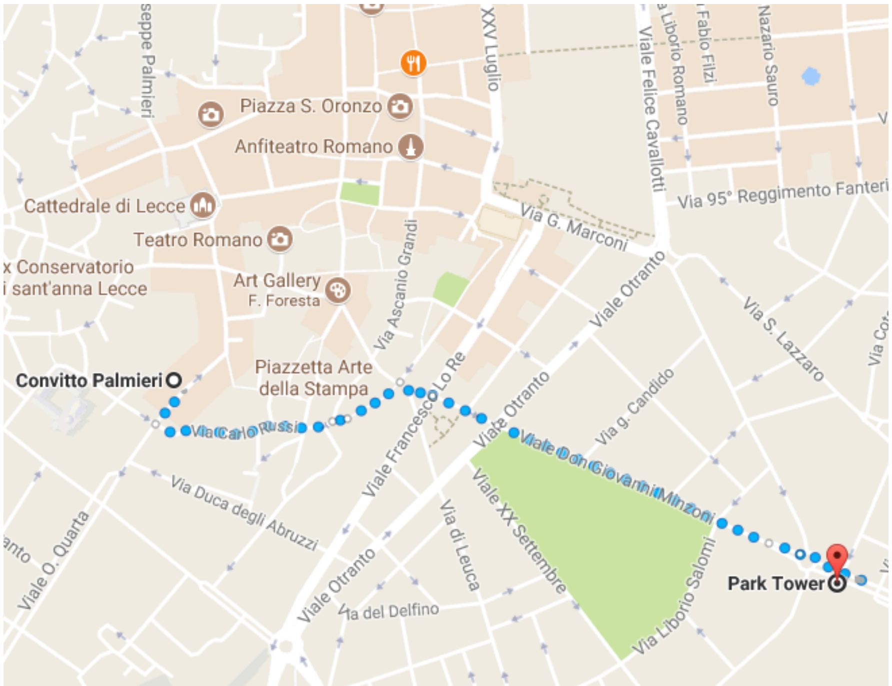
Map of Lecce



Social dinner

The social dinner will take place on Thursday July 6th at 20:30 at Torre del Parco, in Lecce, one of the most beautiful historic houses of medieval and renaissance period. Torre del Parco is located in the heart of Lecce, just 10 minutes' walk from the historic center of the city.

How to reach Torre del Parco



Address
Torre del Parco
V.le Torre del Parco, 1,
73100 Lecce

Scientific programme

Wednesday, 5th July

14:20 - 14:30		**OPENING**
14:30 - 16:15		**[S1] Novel Plasmonic Materials, Structures and Devices** *Chairman: Michele Ortolani*
Keynote	14:30 - 15:00	**Laura Na Liu** *Dynamic nanoplasmonics*
T01	15:00 - 15:15	**Marianna Casavola** *Nanocrystals and ordered superstructures with tunable plasmonic properties in the Near-Infrared*
T02	15:15 - 15:30	**Leonetta Baldassarre** *Mid-Infrared plasmonic platform based on Ge-on Si: waveguiding and molecular sensing with germanium nano-structures*
T03	15:30 - 15:45	**Mauricio Pilo-Pais** *Zig-Zag chains of metallic nanoparticles self-assembled using DNA-templates*
T04	15:45 - 16:00	**Arrigo Calzolari** *Beyond noble metals: plasmonic properties of alternative materials*
T05	16:00 - 16:15	**Simona Scarano** *Functional poly(dimethylsiloxane)–gold nanoparticles composite nanomaterials: an in situ synthesis approach*
16:15 - 16.45		**COFFEE BREAK**
16:45 - 19:00		**[S2] Magneto-Plasmonics and Exotic Phenomena** *Chairman: Giuseppe Strangi*
Keynote	16:45 - 17:15	**Antonio García-Martín** *Resonant magneto-optically active structures: external control and enhancement*
T06	17:15 - 17:45	**Cesar de Julian Fernandez** *Nanostructure, magnetic and hyperthermia properties of Fe oxide @ Gold magneto-plasmonic heterostructures*
T07	17:45 - 18:00	**Filippo Capolino** *Plasmonic nanoprobe enabling photoinduced magnetic and chiral force microscopy*
T08	18:00 - 18:15	**Alessandro Belardini** *Extrinsic chirality in self-assembled GaAs nanowires partially covered by gold studied by different optical techniques*
T09	18:15 - 18.30	**Francesco Pineider** *Plasmon-enhanced magneto-optical detection of single-molecule magnets*
T10	18:30 - 18:45	**Maria Grazia Donato** *Optical trapping of plasmonic particles and hybrid systems*

Thursday, 6th July

09:00 - 10:30		**[S3A] Linear and Nonlinear Light-Matter Interactions in Plasmonics** *Chairman: Francesco De Angelis*
Keynote	09:00 - 09:30	**Jaime Gomez Rivas** *Plasmonic surfaces for solid state lighting, strong light-matter coupling and polariton lasing*
T11	09:30 - 09:45	**Radoslaw Jurga** *Towards the limits of nonlocal plasmonic models in the strong coupling regime*
T12	09:45 - 10:00	**Michele Celebrano** *Evidence for cascaded third harmonic generation in non-centrosymmetric gold nanoantennas*
T13	10:00 - 10:15	**Francesco Todisco** *Plexcitonic coupling evolution by dynamic molecular aggregation*
T14	10:15 - 10:30	**Vincenzo Giannini** *Plasmonics with topological insulator nanoparticles*
10:30 - 11.00		**COFFEE BREAK**
11:00 - 12:30		**[S3B] Linear and Nonlinear Light-Matter Interactions in Plasmonics** *Chairman: Paolo Biagioni*
T15	11:00 - 11:15	**Riccardo Sapienza** *Nanoscale photonic networks to trap and control light*
T16	11:15 - 11:30	**Emmanuel Cottancin** *Fano transparency in rounded nanocube dimers Induced by gap plasmon coupling*
T17	11.30 - 11:45	**Filipa Rodrigues Prudêncio** *Asymmetric Cherenkov emission in a topological plasmonic waveguide*
T18	11:45 - 12:00	**Gwénaëlle Lamri** *Active control of the photoluminescence emitted by quantum dots using metallic nanoparticles and photochromic molecules*
T19	12:00 - 12:15	**Francesco Pastorelli** *Printed organic smart devices characterized by nonlinear optical microscopy*
T20	12:15 - 12:30	**Roberto Gaspari** *Intermediate band semiconductor nanocrystals as a general class of plasmonic-like materials with zero free carriers*
12:30 - 14.30		**LUNCH**

Thursday, 6th July

14:30 - 16:15		**[S4] Quantum and Tunneling Plasmonics** *Chairman: Antonio De Luca*
Keynote	14:30 - 15:00	**Javier Aizpurua** *Driving plasmonics to the atomic scale*
T21	15:00 - 15:15	**Emanuele Coccia** *Dissipation and dephasing for molecules close to plasmonic nanoparticles: an ab initio approach*
T22	15:15 - 15:30	**Nikolai Schmitt** *3D Simulations of spatial dispersive metals with a Finite Element Time Domain method*
T23	15:30 - 15:45	**Dean Kos** *Plasmonic rulers track the smallest graphene oxygen tank*
T24	15:45 - 16:00	**Shuiyan Cao** *A microsource of light from an electrically excited plasmonic lens*
T25	16:00 - 16:15	**Vanessa Knittel** *Optical control of plasmonic devices for single-electron nanotunneling*
16:15 - 16.30		**COFFEE BREAK**
16:30 - 18:00		**Poster Session**
18:00 - 19:00		**Round Table**
20:00 - 23:00		**Social Dinner**

Friday, 7th July

09:00 - 10:30		**[S5A] Plasmon-based Imaging and Ultrafast Dynamics** *Chairman: Giovanni Mattei*
Keynote	09:00 - 09:30	**Niek Van Hulst** *Tracking femtosecond dynamics at the nanoscale*
T26	09:30 - 09:45	**Chiara Novara** *Microfluidic SERS chips for the selective detection of miRNAs in biological matrixes*
T27	09:45 - 10:00	**Patrick O'Keeffe** *Ultrafast transient optical properties of silver nanoclusters*
T28	10:00 - 10:15	**Vito Mocella** *Enhanced fluorescence emission and Raman scattering using bound states in the continuum of a photonic crystal membrane*
T29	10:15 - 10:30	**Matteo Ardini** *Plasmonic silver-alkyne nanoclusters as putative intracellular SERS-active probes*
10:30 - 11.00		**COFFEE BREAK**
11:00 - 12:30		**[S5B] Plasmon-based Imaging and Ultrafast Dynamics** *Chairman: Milena De Giorgi*
T30	11:00 - 11:15	**Francesca Intonti** *Deep-subwavelength hyper spectral imaging and tuning of individual disorder modes*
T31	11:15 - 11:30	**Valeria Giliberti** *Near-field Infrared spectroscopy of Bacteriorhodopsin hydration state in single purple membrane*
T32	11.30 - 11:45	**Giovanni Pellegrini** *Local field enhancement: comparing self-similar and dimer nanoantennas*
T33	11:45 - 12:00	**Roberto Tricarico** *Material-independent modes for electromagnetic scattering from nanoparticles*
T34	12:00 - 12:15	**Luca De Stefano** *Silica-gold nano devices for biomedical applications*
T35	12:15 - 12:30	**Gabriele C. Messina** *Efficient injection of hot electrons in water through plasmonic nanoelectrodes*
12:30 - 14.30		**LUNCH**

Friday, 7th July

14:30 - 16:15		**[S6] Optical Antennas for Sensing and Biodetection** *Chairman: Vittorianna Tasco*
Keynote	14:30 - 15:00	**Stefan Maier** *Hybrid nanostructures for sub-wavelength imaging, nonlinear optics, and chemistry*
T36	15:00 - 15:15	**Nicola Palombo Blascetta** *Tilted dipolar plasmonic antenna for super resolution imaging on LH2 light harvesting complexes*
T37	15:15 - 15:30	**Fulvio Ratto** *Bio-inspired strategies to target the tumor microenvironment with gold nanorods*
T38	15:30 - 15:45	**Benjamin Demirdjian** *Following with a high sensitivity the adsorption of gases on nanoparticles by indirect nanoplasmonic sensing*
T39	15:45 - 16:00	**Attilio Zilli** *Quantitative measurement of the optical cross-sections and optical sizing of individual nano-objects*
T40	16:00 - 16:15	**Ionut Gabriel Balasa** *Plasmonic arrays of nanostructures for biosensing: extended vs localized plasmons*
16:15 - 16.30		**BEST ORAL AND POSTER AWARDS** **CLOSING REMARKS**

Posters

P01	Baratto Camilla	*Plasmonic enhanced chemical sensing with SnO2 nanowires*
P02	Barelli Matteo	*Self-organised flexible plasmonic arrays*
P03	Biagioni Paolo	*n-type Ge-on-Si epilayers for mid-IR plasmonics with active doping above 10^20 cm^–3*
P04	Brasili Francesco	*Tuning the optical properties of hybrid bio-plasmonic colloids*
P05	Caligiuri Vincenzo	*Resonant gain singularities in hyperbolic metamaterials*
P06	Calvani Paolo	*Infrared detection of plasmon-polaritons in the two-dimensional electron system at the LAO/STO interface*
P07	Capocefalo Angela	*Thermophilic rearrangement of bio-plasmonic aggregates: morphological and plasmonic related evidences*
P08	Catone Daniele	*Plasmonic effects and localized melting in self-assembled dye-stabilized gold nanoparticle systems*
P09	Chiadò Alessandro	*Optimization of plasmonic metal-elastomer nanostructures for Surface Enhanced Raman Scattering*
P10	Ciano Chiara	*Nano-infrared photo-expansion spectroscopy of phonon-polaritons in few-layer h-BN*
P11	Colombelli Adriano	*2D and 3D plasmonic nanostructures prepared by physical methods: modeling and functional characterization*
P12	Condorelli Marcello	*Silver nanoplatelets : a promising dual SPR-SERS substrate for plasmonic sensing*
P13	Cuscunà Massimo	*Nanoscale study of the Tarnishing process in silver nanoparticles*
P14	Dardano Principia	*Numerical analysis and characterization of photothermal effects in colloidal plasmonic nanoparticles*
P15	De Stefano Luca	*Inverse identification of the optical properties of hybrid spherical nanoparticles*
P16	Esposito Marco	*Origin of the chiral plasmonic behaviour in helix based "composite" metamaterials by FIBID*
P17	Ferraro Antonio	*Narrow and broad band terahertz filters*
P18	Fregoni Jacopo	*Azobenzene photoisomerization in the strong coupling regime*
P19	Garoli Denis	*Nanoporous aluminum for UV plasmonic enhanced spectroscopy*
P20	Gazzola Enrico	*Design and optimization of a plasmonic grating to enhance silicon photodetectors performances in the Near-Infrared*
P21	Giannone Giulia	*Plasmonic dimers analysis within Density Functional Tight Binding method*
P22	Gintoli Michele	*Development of a multiphoton-multicolor and super-resolution STED microscope for in vivo experiments*
P23	Grande Marco	*Hybrid metal-dielectric nano-pillar array structures*
P24	Huang Jian-An	*Investigation of cell membrane dynamics by 3D nanoplasmonic electrodes*

P25	Kalinic Boris	*Dexter-like energy transfer between metal quantum clusters and Er3+ ions in silica*
P26	Lebeault Marie-Ange	*Plasmonic spectroscopy of silver based bimetallic clusters under reactive atmosphere*
P27	Maccaferri Nicolò	*Grating-coupled hyperbolic metamaterials*
P28	Magnozzi Michele	*Temperature-dependent plasmonic properties of self-assembled Au NPs arrays*
P29	Magnozzi Michele	*Ultrafast laser-induced nanoparticle melting*
P30	Manera Maria Grazia	*Plasmon-enhanced fluorescent molecules: towards single-molecule imaging sensing*
P31	Nabil Mahi	*Angular plasmon response of metal monomers and dimers nanoparticles*
P32	Novara Chiara	*Microfluidic growth of Ag nanoparticles onto porous silicon/PDMS surface for reliable SERS detection*
P33	Ortolani Michele	*Mid-Infrared scanning nanoantennas for near-field photoexpansion microscopy*
P34	Paladini Alessandra	*Transient absorption as a time-resolved measurement of temperature in 2D gold nanoparticle arrays*
P35	Palermo Giovanna	*Gain assisted thermo-plasmonic effects in gold nanoparticles solutions*
P36	Pellarin Michel	*Development of spatial modulation spectroscopy of single nano-objects in liquid environments for biosensing applications*
P37	Pezzolla Maria	*Density Functional Theory investigation of electron over-rich silicon clusters*
P38	Primiceri Elisabetta	*Tunable plasmonic nanostructures arrays: a template mediated low cost approach*
P39	Ricciardi Loredana	*Plasmonics enables nanotheranostic systems: synthesis, photophysics and cancer phototherapy*
P40	Servidio Alessandro	*Increasing Organic Solar Cells (OSCs) efficiency through plasmonic anisotropic gold nanoparticles incorporated in the hole transport layer*
P41	Toschi Francesco	*Excitation of coherent vibrations of nanoparticles of different shapes*
P42	Triolo Claudia	*Plasmon vortices around isolated nanoholes cratered on a gold film: polarization dependent coupling of SPPs and excitation beam*
P43	Triolo Claudia	*Spin-orbit interactions of light in the near field of metal nanoparticles*
P44	Zucchiatti Paolo	*Collective enhanced IR-SR absorption microscopy for conformational studies of protein of biomedical interest*

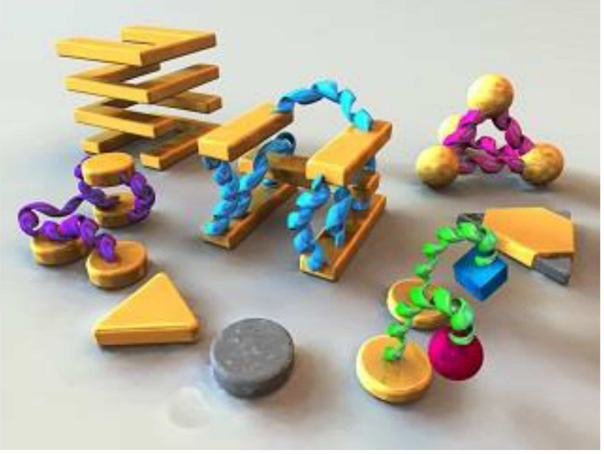
Dynamic nanoplasmonics

Laura Na Liu
Kirchhoff-Institut für Physik, Universität Heidelberg

The key component of nanoplasmonics is metals. When metal nanoparticles are placed in close proximity, the possibilities for shaping and controlling near-field and far-field optical properties increase enormously. Near-field coupling between metal nanoparticles is extremely sensitive to nanometer conformational changes. Such strong dependence on conformation provides unique opportunities in manipulating optical response on the nanoscale. Simultaneously, it also raises significant challenges in realization of dynamic plasmonic systems, which can exhibit immediate conformational changes upon a regulated physical or chemical control input.

Also importantly, plasmonic nanostructures can serve as an efficient far-field to near-field transformer, converting optical radiation into strong localized electromagnetic fields. This unprecedented ability enables probing local dynamic changes on the nanoscale that are extremely crucial in nanocatalysis and phase transitions of nanomaterials, where many unanswered questions abound.

In this talk, I would like to present a new generation of dynamic nanoplasmonic building blocks for biology, chemistry, and materials science. These plasmonic building blocks either can exhibit dynamic structural changes themselves or can be integrated with functional materials, where dynamic events take place. I will utilize both bottom-up and top-down nanotechniques to advance the perspective of plasmonics towards synthetic plasmonic machinery as well as on-chip dynamic plasmonic devices with both tailored optical response and dynamic functionality. Such plasmonic systems will allow for unprecedented resolution when optically disseminating dynamic behavior and multidisciplinary experiments that were not possible to be performed before.



Resonant magneto-optically active structures: external control and enhancement

Antonio García-Martín

IMM-Instituto de Microelectrónica de Madrid (CNM-CSIC), Isaac Newton 8, PTM, E-28760 Tres Cantos, Madrid, Spain
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The control of light propagation in the visible and near-infrared domain using resonant systems such as plasmonic excitations or optical nanoantennas has been a matter of intense research during the last decades. The possibility to create and manipulate nanostructured materials encouraged the exploration of new strategies to control the electromagnetic properties without the need to modify the physical structure, i.e. by means of an external agent. A possible approach is combining magnetic responsive materials (magneto-opticaly active) and resonant materials (e.g. metals exhibiting plasmonic modes), where it is feasible to control the optical properties with magnetic fields in connection to the excitation of plasmonic resonances [1] (magnetoplasmonics).

These nanostructures can involve localized resonances or nano-antenna modes, or extended resonances such as surface plasmon polaritons SPP in thin continuous or perforated films.

Here I will review the fundamental aspects behind magneto-optically active resonant nanostructures and then show that they can be employed in a wide variety of systems and ranges of the electromagnetic spectrum.

I will specifically show that these structures:
(i) can be used to modulate the propagation wavevector of SPPs [2], which allows the development of label free sensors with enhanced capabilities [3-5]
(ii) give rise to enhanced values of the magneto-optical response in isolated or interacting entities as well as perforated films, either metallic or dielectric, but always in connection with a strong localization of the electromagnetic field [6-8]
(iii) can be used to actively control thermal emission and the radiative heat transfer between objects in the near and far field [9-10]

References

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[4] M.G. Manera, et al., Biosens. Bioelectron. 58, 114 (2014)
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[6] N. de Sousa et al., Phys. Rev. B 89, 205419 (2014)
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Plasmonic surfaces for solid state lighting, strong light-matter coupling and polariton lasing

Jaime Gomez Rivas
Dutch Institute for Fundamental Energy Research and Eindhoven University of Technology

Surfaces containing resonant structures which are precisely positioned enable the control of electromagnetic waves over extended areas. In this presentation, I will discuss nanostructured surfaces that are resonant at optical and THz frequencies. These structures are formed by conducting materials supporting localized surface plasmon polaritons (LSPPs). Near- and far-electromagnetic field coupling of LSPPs across the surface enables the control of the distribution of the field enhancement, the losses of the system and the strength of interaction with the surrounding. Resonant surfaces can enhance the electromagnetic field over large areas, enabling applications in solid state lighting, and eventually leading to strong light-matter coupling, exciton-polariton condensation and polariton lasing.

Driving plasmonics to the atomic scale

Javier Aizpurua
Center for Materials Physics in San Sebastian (CSIC-UPV/EHU) and Donostia International Physics Center DIPC,
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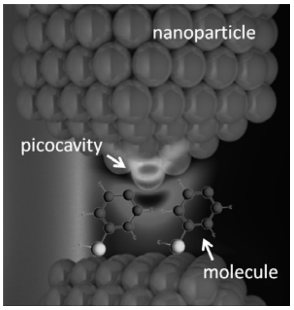
Plasmonic nanocavities are formed at the junction of two metallic interfaces and provide a great opportunity to explore atomic-scale morphologies and complex photochemical processes by optically monitoring the excitation of their intense surface plasmonic modes. In recent years, optical spectroscopy of these cavities has proven to be extremely sensitive to atomic-scale features that determine the chemistry and the optoelectronics in the gaps. Quantum theoretical approaches can be exploited to address the optics of metallic nanogaps when the separation distances are taken to the extreme, reaching Ångstrom-scale dimensions. In this regime, classical theories fail to address the fine details of the optical response, and more sophisticated quantum theories are needed [1-2]. Several examples of how atomic features determine the optical response in plasmon-enhanced spectroscopy, and how they can set the performance of active control strategies in optoelectronic devices will be provided [3].

The extreme subnanometric localization of light allows to understand ultraresolution in molecular vibrational spectroscopy, as recently achieved in intramolecule-resolved Surface-Enhanced Raman Spectroscopy [4]. The small effective volumes associated to these new type of optical 'picocavities' are of particular interest in quantum nanooptics, as they provide particularly large values of the coupling strength of the photons in the cavity with excitons of an emitter, or with mechanical vibrations of a molecule located in the cavity [5-6]. This opportunity of large coupling can be exploited in molecular optomechanics of single molecules.

Figure 1: Subnanometric optical cavity, "picocavity", formed in a plasmonic nanogap by an atomic protrusion, with a molecule in the proximity of the induced inhomogeneous local field, where strong optomechanical dynamics is induced.



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[5] M.K. Schmidt, et al., ACS Nano **10**, 6291–6298 (2016).
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Tracking femtosecond dynamics at the nanoscale

Niek F. van Hulst

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ICREA – Institució Catalana de Recerca i Estudis Avançats, Barcelona
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I'll present the advances of pulse control and ultrafast coherent excitation of both plasmonic nanoantennas and individual molecular systems. Essential concepts from coherent control of ultrashort broadband laser pulses are combined with nanoscale diffraction limited detection and imaging of single photon emitters; that is, the central area of this research is where "ultrafast meets ultrasmall".

First, I'll discuss the critical role of dedicated pulse shaping and phase control, which is crucial to realize free of spatiotemporal coupling Fourier limited pulses inside a high numerical aperture microscope at the diffraction limited spot. Next we apply this scheme to plasmonic antennas, exploiting broadband two-photon excitation, to determine amplitude and phase of plasmonic resonances, to achieve ultrafast switching of nanoscale hotspots, and multicolor second harmonic detection for imaging applications.

Subsequently, phase-shaped pulses can equally be used to address single molecules and control the electronic state population to retrieve single molecule vibrational dynamics response. Single molecule detection generally relies on detection of fluorescence; here I'll enter into some innovative alternatives: optical antennas to enhance quantum efficiency; transient absorption on singles; detection of stimulated emission.

Finally, imaging nanoscale light transport requires local excitation and detection far beyond the diffraction limit. I'll address the use of nanoholes and scanning resonant antenna probes to confine the light field and couple effectively to single emitters on the nanoscale. The plasmonic antenna acts as a nanocavity with relative strong coupling (~100GHz), speeding up the radiative decay to picosecond time scale and allowing > GHz single photon emission.

I will conclude with an outlook of the challenges ahead and the perspectives of addressing coupled networks in real nano-space and on femtosecond timescale.

Hybrid nanostructures for sub-wavelength imaging, nonlinear optics, and chemistry

Stefan A Maier[1]
Department of Physics, Imperial College London, London SW7 2AZ, UK

We demonstrate how controlled emission of hot electrons in plasmonic nanoantennas leads to highly localized nanochemistry. This scheme is utilized for the assembly of hybrid metallic nanoantennas consisting both of top-down fabricated elements, and nanosized colloids. The second part of the talk will show new results for dielectric and hybrid metallic/dielectric antennas, based on Si, Ge and GaP, for highly enhanced harmonic generation and surface-enhanced sensing.

Plasmonic nanoantennas with nanoscale gaps act as efficient transducers of electromagnetic energy from the far to the near field at optical frequencies, creating hot spots of field energy utilized extensively in surface-enhanced spectroscopy and sensing. Using a super-resolution localization scheme, we demonstrate direct imaging of these electromagnetic hot spots via single-molecule emission events, paying careful attention to coupling between molecular emission and antenna modes, in order to determine the true position of the single emitters [1]. We then introduce the notion of "reactivity hot spots" — nanosized regions in plasmonic antennas where hot electrons generated via plasmon decay are emitted. We demonstrate that control over this emission process can lead to highly localized surface chemistry [2], allowing the positioning of colloidal nanospheres around bow tie antennas with high accuracy (Figure 1). A combination of experimental imaging of these reactivity hot spots and ab initio theory will be used to elucidate this process.

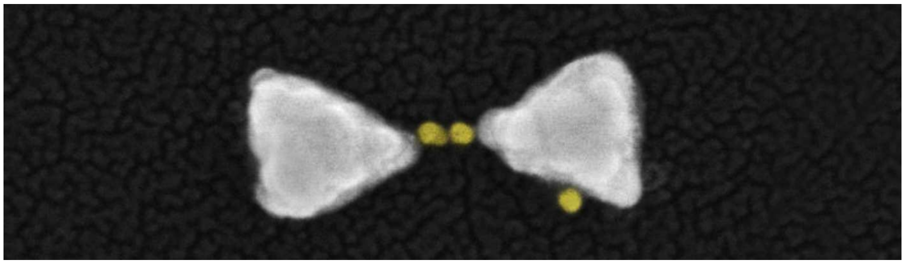

Figure 1: Gold nanospheres arranged in the gap of a silver bow tie antenna via localized hot electron emission [2]. SEM image false-coloured to distinguish between the two materials. The diameter of the gold spheres is 15 nm.

In the second part of the talk, we will present new results on dielectric and hybrid dielectric/metallic nanoantennas, focusing on highly enhanced harmonic generation and surface-enhanced spectroscopy under low-loss conditions. As an example, GaP nanopillars allow to utilize the advantages of dielectric antennas in terms of low loss and high field confinement throughout the visible regime [3]. We will further show new, unpublished results on hybrid Si/plasmonic antennas, as highly efficient nanoscale sources of third harmonic radiation.

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Nanocrystals and Ordered Superstructures with Tunable Plasmonic Properties in the Near-Infrared

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Nanocrystals of metal chalcogenides such as $Cu_{2-x}X$ (with X= S, Se, Te) have recently emerged as a new class of *nonmetallic* plasmonic nanomaterials showing tunable localized surface plasmon resonance (LSPR) at near infrared wavelengths. These nanocrystals have a great potential in many fields, such as biomedical imaging with high tissue penetration depth, photothermal cancer therapy, sensing, communication technologies, energy conversion and storage. Nevertheless, the actual exploitation in devices is still limited by the insufficient knowledge of important features, such as the origin of the LSPR and its straightforward correlation both with the atoms displacement within the nanocrystalline structure, and with the band structure of the nanocrystals.

In our work we synthesized nanocrystals of CuS and Ti_2S via colloidal routes, allowing for nanocrystals with narrow size dispersion and controlled anisotropic geometries (nanodiscs and nanorods) to be developed. Due to their peculiar crystallographic structure with a strong 2D character, these nanocrystals are characterized by a high concentration of charge carriers and a metallic-*like* behaviour. In order to better understand the physical origin of the LSPR of this type of material, and the interplay between plasmons and band gap, we developed a model based on the band structure rather than from the Drude model, to better describe the anisotropic contribution of the dielectric constant in the *in plane* and *out of plane* directions. The model developed well matched with the experimental data obtained for nanocrystals with different geometric parameters.

Furthermore, we optimized a method to fabricate thin films of plasmonic nanocrystals easily transferrable to different substrates. By changing a few parameters it was possible to induce the assembly of disc-shaped nanocrystals either on a layer via a *side-by-side* arrangement, or by forming stacks with a *face-to-face* orientation. Notably, these two configurations show a remarkable shift of the LSPR, in agreement with the coupling of the *in plane* and *out of plane* plasmonic modes, respectively. This method shows that assembling the nanocrystals with different orientation configurations can be used as a method to further tune the LSPR in a wider range by controlling interparticle plasmonic coupling.

Mid-Infrared plasmonic platform based on Ge-on Si: waveguiding and molecular sensing with germanium nano-structures

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The quest for novel plasmonic materials has been a lively area of research over the last few years [1]. In the mid-infrared (mid-IR) spectral region, localized plasmon resonances in nano-particles and nano-antennas hold promise for enhanced IR spectroscopies, with key applications in biology, medicine, and security. Our approach is based on the use of plasmonic elements made of germanium integrated on silicon wafers, exploiting silicon foundry-compatible growth and nanofabrication processes. We aim at developing individual building blocks for sensing platforms in the mid-IR, in particular plasmonic antennas and waveguides, with the perspective of future integration with detectors. This perspective is extremely appealing considering that we are developing an all group-IV platform, that will enable a low-cost integration of plasmonic sensing devices into the existing silicon technology.

n-type germanium (n-Ge), doped in the 10^{19}-10^{20} cm^{-3} range, is grown on silicon wafers by low energy plasma enhanced chemical vapor deposition. We demonstrate that the unscreened plasma frequency can be tuned up to 3000 cm^{-1} (3.33 μm), by complementing the in-situ doping process with laser and flash lamp annealing. The Ge thin films are characterized using reflectance spectroscopy and by analysis using a multilayer Drude modelling and the Kramers-Kronig approach, the optical constants are calculated. The average electron scattering rate is found to be dominated by scattering with optical phonons and charged impurities and to increase almost linearly with frequency [2]. We investigate, by continuous-wave FTIR reflection/transmission spectroscopy, arrays of n-doped germanium nanoantennas and arrays of plasmonic slits, demonstrating the occurrence of localized plasmonic resonances in the mid-IR and we exploit them for molecular sensing [3].

Intrinsic germanium is, on the other hand, transparent in the mid-IR region and it can be used for guiding through simple Ge-on-Si strip waveguides. The main difficulty related to this emerging integrated photonics technology is to couple light from an external mid-IR laser source into the Ge waveguide, and not into Si substrate. In this work, we have fabricated pure Ge waveguides on Si wafers starting from Ge- on-Si films grown by chemical vapour deposition. We introduce photothermal expansion spectroscopy as a scanning local sensing tool of the out-coupled power at the waveguide end. In-coupling efficiencies of a few-percent and transmission losses down to 2 dB/cm are demonstrated.

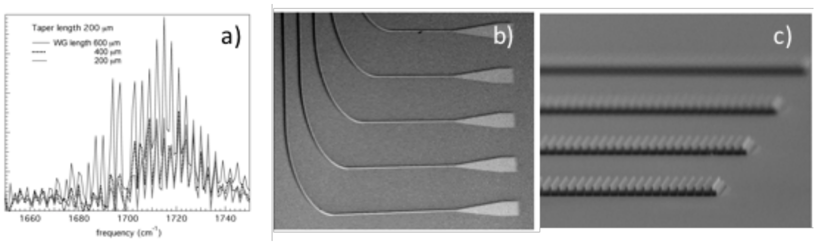

Figure 1: a) The intensity spectra of the radiation coupled at the end of three waveguides of different length. The presence of interference fringes indicates that the radiation travels several times along the waveguides and is reflected by the open end and by the grating coupler. The in-coupling efficiency spectrum of the grating is measured with the photo-thermal near-field probe while the QCL wavelength is tuned across the range shown in the plot. SEM images of b) bent waveguides with taper and c) grating couplers.

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Zig-Zag chains of metallic nanoparticles self-assembled using DNA-templates

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Metallic nanoparticles (NPs) chains arranged in a Zig-Zag configuration have been shown to sustain plasmonic topological edge states [1-3]. Such states can be selectively activated by switching the incident polarization. Here, we demonstrate the use of the DNA-origami technique to self-assemble Zig-Zag chains of gold NPs, and explore the resulting plasmon states and NP coupling efficiency as a function of the NP size (10 nm - 30 nm), spacing, and angles. In addition, our pre-programmable approach permits the placement of fluorophores, which can be used as probes of the polarization-dependent hot spots. The design flexibility of DNA to assemble plasmonic NP chains is an ideal approach to study topological edge states and to integrate them with other nanocomponents for optical applications.

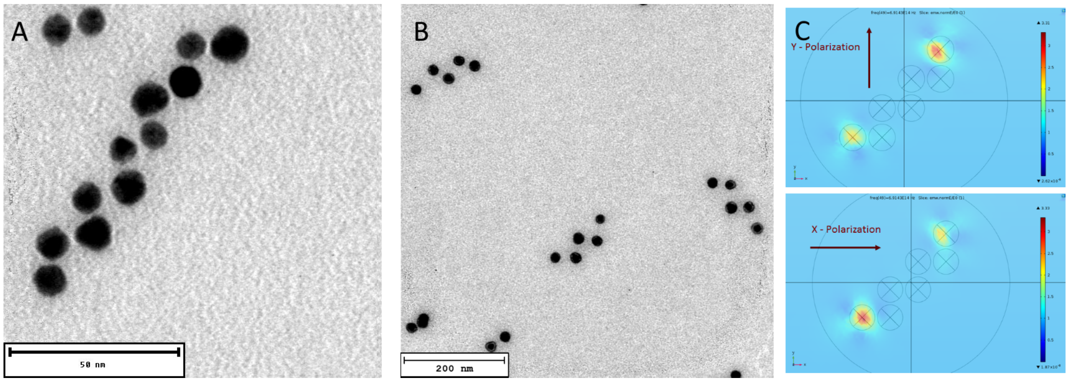

Figure 1: TEM images of **a)** 10 nm and **b)** 20 nm gold NPs arranged on a Zig-Zag conformation using different DNA origami templates schemes. **c)** Numerical simulations showing 20 nm AuNPs Zig-Zag chains displaying polarization-dependent active hot-spots.

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Beyond noble metals: plasmonic properties of alternative materials

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An ideal plasmonic material should have tunable plasma frequency, low energy loss, high chemical, mechanical and thermal stability, low cost and high integrability with existing CMOS technology. Obviously, gathering together all these properties in a single material is not trivial, and depending on the specific application specific features are preferred. For example, because of their plasmonic response in the visible range, the high chemical stability, and biocompatibility, noble metals (especially Au and Ag) are considered the plasmonic materials *per excellence*, and have been largely used for biological sensing, waveguiding, energy transfer processes, light-harvesting. However, the high negative permittivity and high energy losses prevent their use as hyperbolic metamaterials in the visible range; moreover, the chemical softness and the low melting points make noble metals unsuitable for applications in high temperature and strong light illumination regimes, such as thermophotovoltaic, photothermoelectric, and heat-assisted magnetic recording systems. Thus, while the tunability of the plasma frequency of noble metals can be partially improved by changing the geometry, the size and the intermetallic composition of the samples, other properties related to the thermal and mechanical stability or to the growth conditions impose to find alternative materials. Here, by using fully first principles approaches based on (TD)DFT, we present the optoelectronic and plasmonic properties of two different class of materials proposed as alternative to noble metals, namely transparent conducting oxides (TCOs) and refractory ceramics.

First, we present an ab initio investigation of the optical and plasmonic properties of metal-doped ZnO systems (MZO) [1], as a prototype of plasmonic TCOs [2]. We investigate how doping and defects (e.g. oxygen and zinc vacancies) affect the optical and plasmonic properties of MZOs [3]. We study the origin of plasmonic activity in MZO transparent conducting oxides and we provide a microscopic insight on the formation of surface-plasmon polaritons at the Al:ZnO/ZnO interfaces in terms of characteristic lengths that can be measured by experiments. These systems present tunable plasmonic activity in the near-IR range and in particular at wavelength relevant for telecommunications (1,5 μm), in agreement with the experimental results [4].

Then, we present the plasmonic properties of refractory binary compounds MX [5], where M is a group IV and V transition metal (Ti, V, Zr, Nb, Hf, Ta) and X is C or N. Such transition-metal nitrides (e.g. TiN, VN, ZrN, NbN) and carbides (e.g. TiC, VC, ZrC, NbC) have optical and plasmonic properties (e.g. color, electron density, plasmon frequency) very similar to gold and has been exploited for the realization of waveguides, broadband absorbers, local heaters, and hyperbolic metamaterials [6]. Moreover, being refractory these compounds have an extraordinary mechanical stability over a large range of temperatures (~ 2000◦C) and pressures (~3.5 Mbar), well above the melting point of standard noble metals (~ 800◦C). The microscopic origin of plasmonic excitations in the different range of the electromagnetic spectrum are analyzed in terms of the fundamental collective and/or radiative excitations of MX electronic structure. In particular, from the simulation of energy loss spectra at different momentum transfer we derivate the plasmon dispersion relations that are directly accessible by experimental EELS measurements. Further, the comparison between simulated dispersion curves and ideal free-electron model allows us to investigate the origin of the dissipative behavior of the material, which is an unavoidable prerequisite for any realistic application. We further demonstrate the retention of optical proper ties against the applied pressure and we prove a universal scaling law that relates the bulk modulus and the plasmonic properties of TiN. Finally, we present the analysis of the surface-plasmon polaritons of TiN when interfaced with dielectric materials as proposed for the realization of hyperbolic metamaterials and waveguides.

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Functional poly(dimethylsiloxane)–gold nanoparticles composite nanomaterials: an in situ synthesis approach

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Poly(dimethylsiloxane) (PDMS) is one of the most widely used polymer materials for fabricating microfluidic chips due to its transparency, outstanding elasticity, good thermal and oxidative stability, ease to be fabricated and sealed with various materials. In spite of these advantages, PDMS is not a ''faultless'' material: in fact, its surface inertness greatly limits the use of PDMS in on-chip bioassays based on immobilized biomolecules. To resolve this problem and expand the applications of PDMS microfluidic chips, chemical modification layers, sol-gel and nano- or microparticles have been introduced to PDMS microchannels.

Recently, nanocomposites consisting of metal nanoparticle doped polymer matrices, especially free-standing nanoparticles– polymer films, have attracted enormous interest in both the science and technology fields, due to their potential applications in optical devices, nanoelectromechanical systems (NEMs) and biosensors[1,2]. The integration of plasmonic nanomaterials with flexible matrices, thus combining optical responses and mechanical flexibility, could allow active control of the interparticle distance under stretching and mechanical stress thus resulting in optical tunability and providing a tunable platform for enhanced spectroscopy. Moreover, using AuNPs as optothermal transduction elements allows focused localization of heating, which can be employed to selectively ablate cancerous tissue or kinetically drive local chemical processes. By exploiting specific metal nanoparticles properties with the bio-compatible nature of polymers, cell adhesion and patterning, bio-electrochemical sensing, and antimicrobial functionalities can be demonstrated, leading to advanced bio-functional materials. Finally, being metal nanoparticles held firmly within the PDMS while still being chemically accessible to substances soluble in PDMS, they can be used for water purification applications [3].

In this work, a method for in situ synthesis of Au nanoparticles in free standing PDMS is proposed , on the basis of reductive properties of the cross-linking agent of PDMS. The proposed method is an environmentally safe synthesis method circumventing the need of using pre-formed nanoparticles and without requiring any additional reducing/stabilizing agents. The region where the resulting gold nanoparticles distribute (in the matrix or on the surface of the polymer) and the size of the nanoparticles, as well as the colour of the free-standing films, can be simply controlled by adjusting the ratio of curing agent and the PDMS monomer. Morphological, optical and functional characterization in controlled liquid or gaseous ambient of the realized nanocomposite materials are proposed. Metal PDMS nanocomposite showed to be a functional transducer for monitoring biomolecules interactions at the metal/dielectric interface thus demonstrating that they can be easily introduced to PDMS microfluidic chips the application of DNA sensors, immunoassays and other biochemical analysis on microchips.

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Nanostructure, magnetic and hyperthermia properties of Fe oxide @ Gold magneto-plasmonic heterostructures

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Magnetic - plasmonic heterostructures combine noble metals like Au and Ag with magnetic metallic or oxides moieties in a single nanostructure. These structures join simultaneously the optical absorption and all the opportunities provided by the plasmon resonance with all the chances offered by the magnetic counterpart. For these reasons, many potential applications, in particular in the biomedical field, are possible, like combined magnetic and photo thermal therapy, or dual magnetic (MRI) and optical probe for cell imaging and drug delivery are now of great interest.

Au@ Fe oxide heterostructures are largely investigated in biomedical applications due the excellent biocompatibility of both moieties. However the complex intertwining of the structural, compositional, electronic and magnetic features of the different moieties determine the final magnetic, plasmonic and magneto-optical properties [1-4]. Recently synergy enhanced hyperthermia effects have been observed when simultaneously plasmonic and magnetic excitations are combined [5,6]. On the other hand there is a wide debate on the structure/composition and optical and magnetic properties of these heterostructures. On one side, magnetic component appears to be composed by different oxides like magnetite, maghemite and wustite with different properties. On the other hand interface effects can leads to charge transfer and spin frustration phenomena.

In this study we investigate the properties of different Au@ Fe oxide nanostructures with core@shell and heterodimeric morphology prepared by thermal decomposition using different precursors to modify the Fe-oxide properties. Depending on the precursor and the morphology, the magnetic moiety appears composed mainly by magnetite but also by the antiferromagnetic wustite. Morphological and magnetic characterizations performed in samples aged in the air and in samples transferred to water show that the magnetic properties can change due to the manipulation or by the chemical functionalization. The magnetic hyperthermia properties of these multifunctional nanostructures will be presented to show their potential application in this cancer therapy. Plasmonic features are determined by the morphology of the heterostructures.

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Plasmonic nanoprobe enabling photoinduced magnetic and chiral force microscopy

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Interrogating optical magnetism and chirality of matter at nanoscale is of significant importance in modern optics, biology, chemistry and material science [1, 2]. However, magnetism and chirality are typically weakly-coupled material properties which are not hard to reveal by conventional optics based on the interaction of matter with the electric field component of light. Here we present a novel methodology into the microscopy of optical magnetism and chirality of materials by implementing specially designed plasmonic or dielectric nanoprobes under particular structured light illumination into a photoinduced force microscopy (PiFM) system [3]. The illuminated nanoprobe actively responds to material magnetism and chirality, and exhibit measurable photoinduced force between probe and sample to retrieve the critical properties with nanoscale resolution.

First, we investigate optical magnetism by designing magnetic nanoprobes in PiFM system. Several nano structures, such as plasmonic circular cluster of nanospheres or pillars, dielectric spheres, and plasmonic split-ring antennas, are designed to support magnetic resonance at visible frequencies [4]. We propose structured light illumination as the sharply focused azimuthally polarized beam (APB), which has a strong longitudinal magnetic field and vanishing electric field to exclusively excite the magnetic nanoprobes while shielding the electric field [5]. The PiFM characterized intensity distribution of a sharply focused APB, schematic of photoinduced magnetic force measurement, and proposed magnetic nanoprobes are shown in Fig. 1.

Next, we propose the microscopy technique for enantio-specific detection of chirar samples based on a similar principle. In this system we measure the photoinduced force between an *achiral* plasmonic probe and a *chiral* sample when the probe-sample system is illuminated by right and left circularly polarized beams separately (RCP and LCP). We calculate the photoinduced force versus material chirality in a special example shown on Fig. 1 (d). The result emphasizes that there is no force difference between two cases of RCP and LCP incidences for chirality parameter $\kappa = 0$. However, as we increase the chirality parameter κ of the sample, the difference between induced forces on the tip for two cases of RCP and LCP illiminations becomes more pronounced. It clearly demonstrates that by measuring differential photoinduced force we can differentiate between chiral enantiomers.

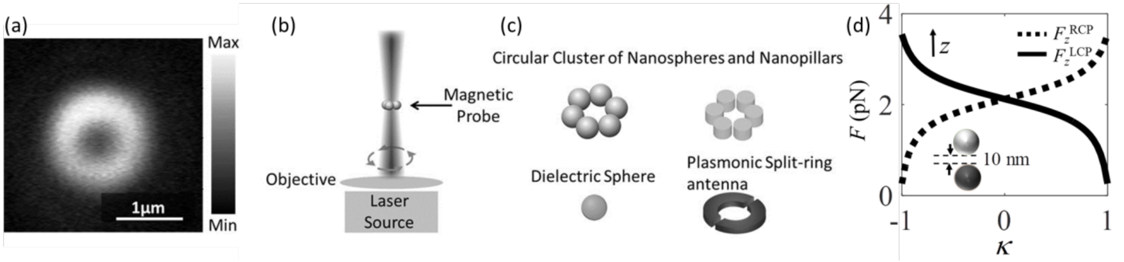

Figure 1: (a) A PiFM measured sharply focused APB. (b) Schematic of magnetic probe in sharply focused APB to detect photoinduced magnetic force. (c) Proposed nanostructures for magnetic probes. (d) Distinctive photoinduced force exerted on the achiral nanotip by a chiral sample under CP incidence.

In summary we explore special nanoprobes for a PiFM system illuminated by structured light that is responsive to optical magnetism and chirality of matter at nanoscale, and it exhibits enantiospecific measurable photoinduced force to investigate these properties with nanoscale resolution.

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Extrinsic chirality in self-assembled GaAs nanowires partially covered by gold studied by different optical techniques

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Hybridized nanostructures composed by metals and dielectrics, semiconductors or organics offer new opportunities achieving new functionalities in nonlinear optics, plasmonics, sensing [1]. III-V semiconductor vertical NWs have good waveguiding properties for energies above the bandgap owing to high refractive indices, and they can support a number of discrete photonic modes. The coupling of light to guided modes is essential for photonic applications. In particular GaAs-AlGaAs-GaAs core-shell-supershell nanowires (NWs) fabricated by self-catalyzed growth on Si substrates were partially covered with gold, thus producing a symmetry breaking in the sample geometry that induces an extrinsic chiral response [2]. This will be of particular interest for circular dichroism applications in biological molecules recognition. Here we use the photo-acoustic (PA) technique with circular polarised light [3-4] to put into evidence the different absorption for circular polarizations of opposite headedness when the light impinges on such structures under a proper oblique angle, see Fig.1.

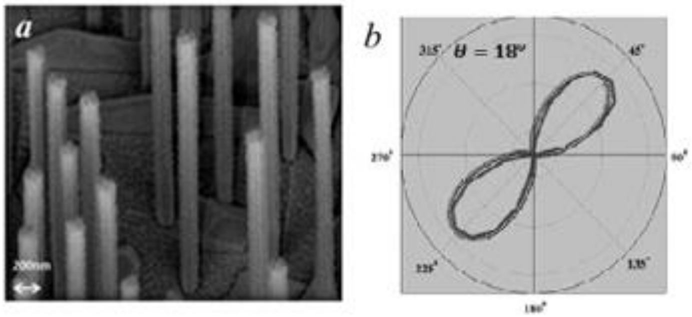

Figure 1: (a) Realized sample; (b) PA signal as a function of polarization ellipticity; chiral response on asymmetric coated sample together with numerical fit.

Experiment with second harmonic generation (SHG) and photoluminescence were carried out and also reported.

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Plasmon-enhanced magneto-optical detection of single-molecule magnets

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Magnetoplasmonics, the interaction of surface plasmons with magnetism, can provide exciting prospects in non-reciprocal nanophotonics, optically-controlled nanomagnetism and highly-efficient chemical sensing.[1,2] To gain these functionalities, one typically combines plasmonic and ferromagnetic films, alternatively – localized plasmon nanoantennas and ferromagnetic nanostructures.[3,4] Here we investigate the so far unexplored combination of molecular magnets with plasmonic nanostructures to reveal how the magneto-optical response of the former is modified in such hybrids. In order to accurately interpret the magneto-optical response of the molecular-plasmonic hybrid structure, the magnetoplasmonic behavior of the gold nanodisks was modelled and taken into account.[5,6] We found that such contribution is far from being negligible, and it is mandatory to understand the optical and magneto-optical processes taking place in the hybrid nanostructure. Leveraging on the strong overlap of the nanoantenna and the molecular resonance of a thin film (~2 nm) of the single-molecule magnet TbPc2, we demonstrate a significantly boosted magneto-optical signal from the molecular layer, indicating the possibility of sub-monolayer magnetic circular dichroism detection, which is currently only available in the soft x-rays regime at large synchrotron facilities.[7,8]

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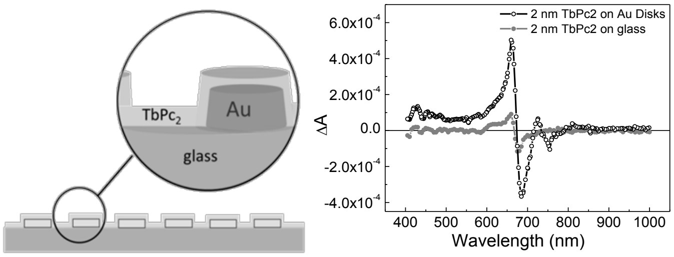

Figure 1: Left, scheme of the molecular-plasmonic hybrid. Right, magneto-optical signal from the TbPc2 single-molecule magnet with and without plasmonic amplification.

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Optical trapping of plasmonic particles and hybrid systems

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Optical trapping and manipulation of metal nanoparticles has acquired increasing interest in recent years. Size and shape affect the plasmonic properties of metal nanoparticles, and, thus, their trapping behaviour. Spherical [1, 2], non-spherical [3-7] and aggregated [8,9] plasmonic particles have been trapped. The challenge in optical trapping of metal nanoparticles is to enhance gradient forces while maintaining acceptably low scattering forces.

Here, we will discuss the optical trapping and manipulation of plasmonic particles, hybrid core-shell and silica-gold systems [10-12]. The scaling of optical trapping forces with the particle dimensionality and the hybrid structure geometrical parameters will be shown. These results agree with calculations of optical trapping forces based on electromagnetic scattering theory in the T-matrix approach. Furthermore, the pushing of plasmonic particles by means of optical forces has been exploited to pattern a standard glass substrate or even to metallize non-planar objects, such as spherical particles or even small tips. The application of optical force pushing to high resolution spectroscopy of molecular species (SERS) will be discussed.

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Towards the Limits of Nonlocal Plasmonic Models in the Strong Coupling Regime

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The fluorescence of an optical emitter can be strongly enhanced in the proximity of a plasmonic nanoantenna [1]. However below an emitter-metal separation of a few nanometres, the nonlocal response of the plasmonic structure becomes important and has to be taken into account. In this work we compare numerically the traditional local model to the Hydrodynamic Model (HDM) [2] and the Generalized Nonlocal Optical Response (GNOR) model [3] for an emitter near gold and silver nanostructures.

The effects of nonlocality on plasmonic fluorescence enhancement have already been studied for geometries such as single nanospheres or nanoshells [4]. Firstly, we extend this analysis to the case of an emitter between a dimer of gold nanospheres with 30 nm radii. The plasmon resonance is blueshifted with the HDM and the GNOR models. With the GNOR model the total decay rate becomes broader and smaller. Similarily, the quantum yield and the fluorescence enhancement are lower. For a dipole oriented along the dimer with a gap of 1 nm, the maximum value reached by the quantum yield with the GNOR model is 2.5 times lower than with the local model, leading to a fluorescence enhancement 7.4 smaller.

Secondly, we compare the nonlocal models in the strong coupling regime near different metal nanostructures. Fig. 1 shows the case of a quantum emitter between a dimer of silver cones.

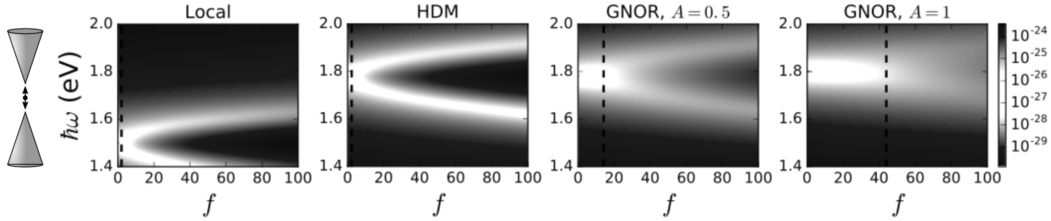

Figure 1: Dipole spectrum of an emitter between a dimer of silver cones with semi-aperture $\pi/12$, height 20 nm and gap 4 nm. The dashed vertical line is the estimated oscillator strength threshold for the onset of Rabi splitting.

Rabi splitting can occur when the oscillator strength f of the dipole is high enough, above some threshold f_{th} [5, 6]. This threshold increases from the local model to the HDM and to the GNOR model. This is directly attributed to nonlocality through the broadening and damping of the total decay rate.

In the case of gold nanostructures, Rabi splitting does not occur with the HDM and the GNOR model. This is in contrast to experimental results [7] and points to the limits of these models. Further study of nonlocal effects on strong coupling at small gaps will require models that can take into account the quantum behavior of electrons such as an accurate description of the electron density and quantum tunneling.

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Evidence for cascaded third harmonic generation in non-centrosymmetric gold nanoantennas

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The optimization of nonlinear optical processes at the nanoscale is a key challenge in state-of-the-art nanoscience, given their potential key role in the development of building blocks for quantum-optical networks as well as in molecular sensing. In this context, plasmon-enhanced nonlinear effects are gaining ground thanks to the development of innovative nanoantenna designs and hybrid nanostructures [1-2]. Due to the relatively low nonlinear conversion efficiencies achievable in plasmonic nanoantennas, a widely accepted approach consists in treating different order phenomena such as, for instance, third harmonic generation (THG) and second harmonic generation (SHG), as independent from each other [3-4]. In this work, we demonstrate that this paradigm dramatically fails in non-centrosymmetric plasmonic nanoantennas [5], where we find evidence for the presence of a SHG-mediated cascaded effect in THG [6] (see figure 1). This mechanism is enabled by the commensurate conversion efficiencies, $\eta_{SHG} \cong \eta_{THG} \sim 10^{-8}$ achieved for both the SHG and THG process in this nanostructure. We have disentangled this mechanism from pure $\chi^{(3)}$-mediated THG thanks to its unique nonlinear emission fingerprint that can be addressed through the analysis of its polarization state. The possibility of tuning the coupling efficiency between nonlinear processes in plasmonic nanoantennas represents a crucial step toward the realization of nanoscale photon conversion and manipulation at room temperature, which opens new possibilities in quantum optics and in nonlinear optical sensing.

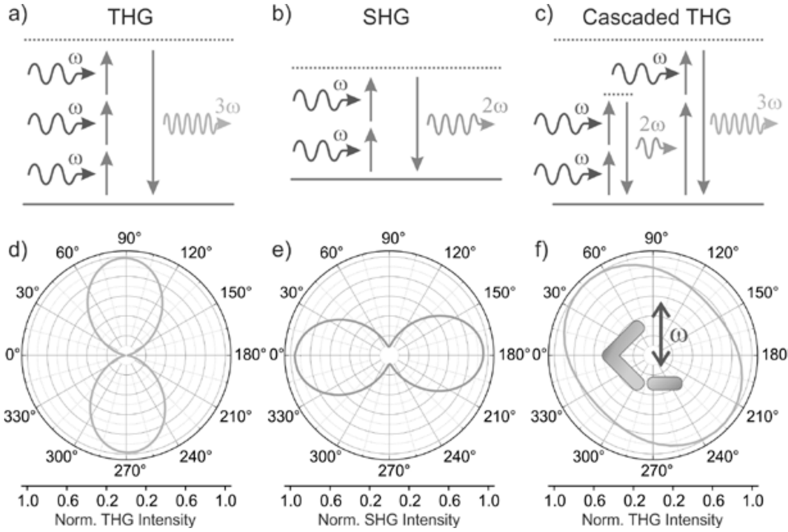

Figure 1: (a-c) Conversion schemes of the (a) THG, (b) SHG and (c) cascaded THG processes that can be mediated by the nanoantenna. (d-f) Simulated emission polar plot for (d) purely $\chi^{(3)}$-mediated THG, (e) $\chi^{(2)}$-mediated SHG, and (f) purely cascaded THG. A sketch of the nanoantenna with the polarization direction of the excitation laser are also shown in panel (f).

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Plexcitonic Coupling Evolution by Dynamic Molecular Aggregation

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The coupling of localized plasmonic and excitonic modes is an extremely powerful strategy to mould metal nanoparticles and nanoemitters properties. Such coupled modes are characterized by a hybrid wavefunction with an effective mixture of light and matter components (often called plexcitons) that offers unique possibilities to dress plasmons with excitonic nonlinearities. Strong coupling between excitons and plasmons has been extensively studied in gold[1], silver[2] and aluminium[3] nanostructures, either with individual or array of nanoparticles. The control of such a regime, however, has been only demonstrated with the use of photochromic molecules[4] or polarization sensitive nanostructures[1], simply resulting in a switchable splitting, and leaving a fully controllable coupling regime still unexplored.

In this work, by integrating plasmonic nanostructure arrays in a microfluidic device, we show the real time build-up of plasmon-exciton strong coupling, from the uncoupled modes to the ultrastrong coupling regime. By injecting a dilute solution of a near-infrared cyanine dye, we clearly observe the transition from a crossing to an anticrossing behaviour in the plasmon-exciton extinction dispersion, and an increase of the Rabi splitting due to the progressive deposition of injected molecules on the metallic nanostructure surface. In particular, for sufficiently long interaction times, the Rabi splitting increases up to the 35% of the exciton energy, thus entering the regime of ultrastrong coupling. Our results can open the way towards a full active control of the Rabi splitting in plasmonic systems, spanning from the strong to the ultrastrong regime.

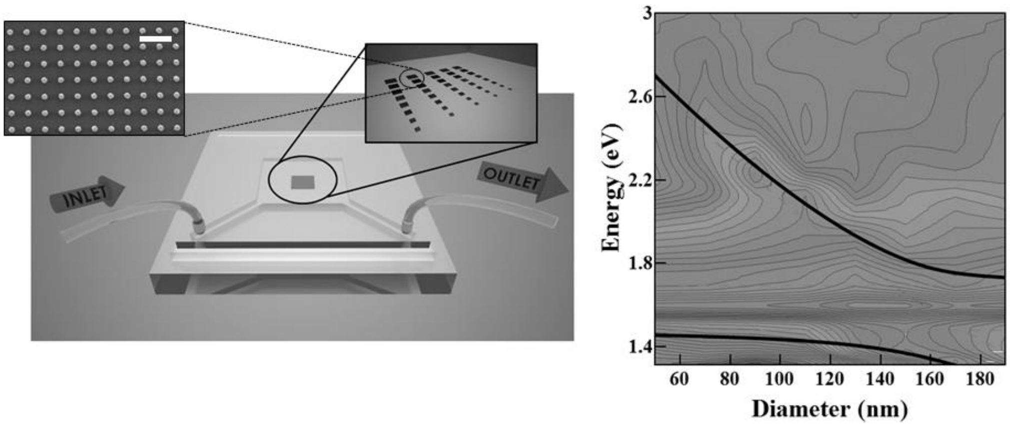

Figure 1: (Left) Sketch of the plasmonic nanoparticle arrays integrated in the microfluidic device for the controlled injection of a dilute interacting dye solution. Scale bar in the SEM image is 1 μm. (Right) Extinction dispersion for the system under strong coupling, showing an anticrossing as a function of the nanodisks diameter. Black lines are fitting of the peaks position with a full Hopfield Hamiltonian.

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Plasmonics with topological insulator nanoparticles

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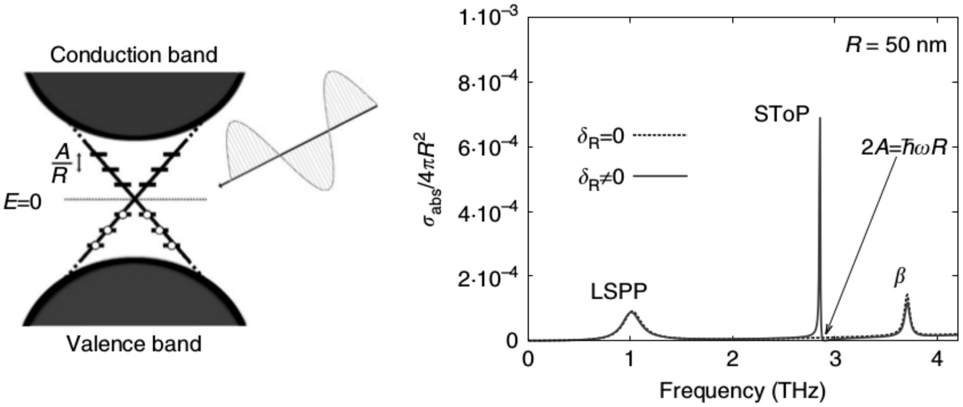
A key feature of topological insulators is the presence of surface states immune to disorder and impurities due to topological protection. These states modify the optical properties of topological insulators compared to their ordinary counterparts.
We show that topological insulators nanoparticles sustain a new kind of excitation when interacting with light. This is a topological localized surface plasmon polariton obtained perturbing the nanoparticle surface electron state with light.

Quantum phenomena are usually restricted to the nanoscale (atoms, molecules), low temperatures (superfluids, superconductors) or both. Here we demonstrate a phenomenon which may pave the way for quantum behaviour to be observed at the mesoscale and room temperature.
The key role is played by topological insulators materials that have surface states protected by time-reversal symmetry. Such states are delocalised over the surface and are immune to its imperfections in contrast to ordinary insulators. For topological insulators the effects of these surface states will be more strongly pronounced in the case of nanoparticles.

Here we study the interaction of such nanoparticles with light. We report a previously unknown light-matter mode that was not revealed in earlier studies, which focused on bulk samples and thin films of topological insulators. In the nanoparticles the topologically protected surface states efficiently couple phonons and light giving rise to the topological particle polariton mode. In addition, the surface states can act as a screening layer which suppresses absorption inside the particle. These effects may be useful in the areas of plasmonics, cavity electrodynamics and quantum information.



Surface Dirac cone in a topological nanoparticles consisting of discrete levels symmetrically placed with respect to the Dirac point. An electron in a surface state couples to other states under the influence of light producing a time-dependent surface charge density. (b) Light interaction with a topological nanoparticle. The absorption cross-section of a bare nanoparticle (dashed line) is dictated by the dielectric function of the material. It is modified when electrons occupy delocalized topological surface states (solid line). The resultant spectrum contains an additional surface topological polariton (SToP) mode and a zero in absorption (marked with an arrow).

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Nanoscale photonic networks to trap and control light

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When two light emitters in vacuum are more than a wavelength apart, their optical coupling is practically zero and no energy can be transferred between them [1]. This limits progress in optical transistors and computing at the single photon level, and those optical technologies based on collective optical synchronisation such as lasing.

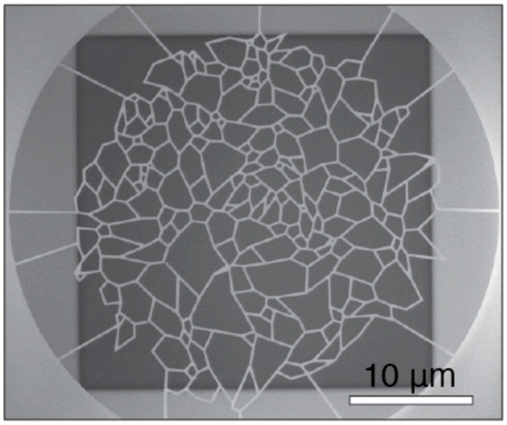

Figure 1: Suspended random photonic network

I will show that a disordered nanophotonic network, composed of connected sub-wavelength waveguides [2], is an ideal scattering geometry to route photons, promote coupling between embedded emitters and enhance stimulated emission [3,4,5]. I will discuss how the optical properties can be designed from its topological correlations, ranging from order to disorder, as measured by the degree of hyperuniformity [6]. The network controls single-photon emitters, as indicated by momentum spectroscopy experiments, as well as (random) lasing action when many emitters are coupled.

Random lasing is especially interesting as it can be dynamically controlled via adaptive pumping of the network modes, and can form the basis of very sensitive sensors for living tissue integration.

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Fano Transparency in Rounded Nanocube Dimers Induced by Gap Plasmon Coupling

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Pairs of interacting metallic nanoparticles (NPs) form plasmonic nano-antennas (NA) the optical response of which is strongly correlated to the electrostatic coupling between them. For instance, the plasmon resonance induced by an exciting field polarized along the interparticle axis will be progressively redshifted as the NPs are brought closer together. This is due to the increasing interaction of each NP with the scattered near field of the other. Gold or silver nanocube dimers constitute model systems from this point of view because the facing sides of both cubes form a coupling region of controlled geometry similar to a planar capacitor.

Thanks to the Spatial Modulation Spectroscopy (SMS) technique, a depletion signal was systematically observed in the longitudinal excitation band of individual dimers in both visible (silver cubes of 50 nm) and infrared (gold cubes of 160 nm) ranges. A recent modification of the setup has made it possible to show that this transparency window is associated with a scattering signal dip correlated to an increase of the absorption.

These observations have been interpreted as the possible excitation of gap cavity modes confined within the Fabry–Perot cavity delimited by facing cube surfaces in which standing waves associated with quantified wavelength of propagation can be excited [1]. Destructive interference in the strong coupling regime between one of these highly localized modes and the highly radiating longitudinal dipolar plasmon of the dimer is responsible for the opening of a spectral window of anomalous transparency for the exciting light (red curve in the figure). This dispersion signal appears as an anti-resonance as in the case of coupled electric oscillators due to capacitive effects. It can also be compared to the Fano effect in atomic spectroscopy and more generally reflects the coupling between a localized excitation mode and a quasi-continuum. This is the case of the gap plasmon mode and the broad scattering band of dipolar character.

This study has made it possible to interpret not only the spectral position but also the depth of the induced transparency window in the extinction spectrum through the crucial dependence of the coupling strength on the rounding of the edges and corners of the nanocubes.

This induced transparency window demonstrates a spectral quality factor far better than that of the main dipolar resonance which makes such systems prime candidates for ultrasensitive sensors in future experiments in environmental plasmonics.

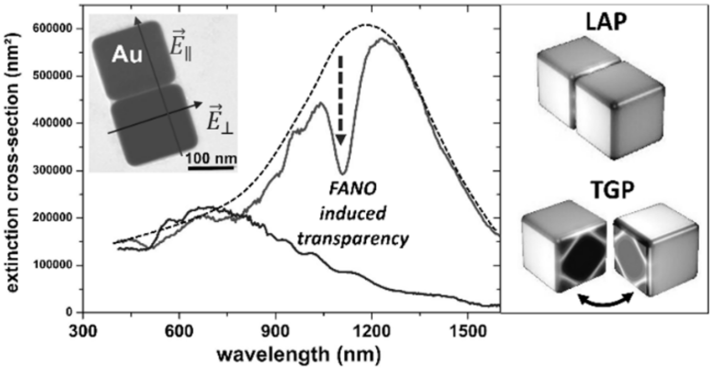

Figure 1: experimental extinction cross-section of a single gold nanocube dimer

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Asymmetric Cherenkov Emission in a Topological Plasmonic Waveguide

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The use of topological methods in photonics opened up a myriad of novel photonic platforms with fascinating properties [1-3]. Remarkably, nonreciprocal photonic systems are characterized by a topological index [1,2], the Chern number, which depends on the *global* properties of the band structure. Interestingly, in Ref. [2] it was demonstrated that the ideas of topological photonics can be extended to a wide family of electromagnetic continua with no intrinsic periodicity.

It is natural to wonder what are the consequences of topologically protected edge sates in the context of the radiation emitted by a moving charged particle: the Cherenkov effect. The Cherenkov phenomenon has important applications in particle detection, nanoscale light sources, or biomedicine [4]. Here, we consider that a linear array of charges flies with a constant velocity $\mathbf{v} = v\hat{\mathbf{x}}$ in a vacuum at a distance d from a plasmonic waveguide formed by a topologically nontrivial magnetized plasma with plasma frequency ω_p, cyclotron frequency ω_0 and collision frequency ω_c. Our analysis shows that the main radiation channels of the Cherenkov problem are the edge states (plasmons) supported by the plasmonic waveguide. The plasmon resonance $\omega_\pm \equiv \left(\mp\omega_0 + \sqrt{2\omega_p^2 + \omega_0^2}\right)/2$ depends on the direction of the wave propagation $\pm x$. Thus, the radiation channels for a moving charge are separated in the spectral (frequency) domain, and it is expected that moving charges with $v > 0$ ($v < 0$) emit predominantly light with frequency ω_+ (ω_-). To illustrate the ideas, we show in Fig. 1a and 1b a snapshot of the magnetic field emitted by a beam of moving charges with $v = 0.7c$ and $v = -0.7c$, respectively. As seen, the emitted wave is an edge mode. Figure 1c shows the spectral density of emitted light $g(\omega)$ (in arbitrary units). Clearly, the emission spectra is highly asymmetric being peaked near $\omega_\pm$ (vertical gridlines in Fig. 1c) depending on the sign of the electrons velocity. At the conference, we will present a detailed account of our research on this topic and further highlight the role of topologically protected edge states in the asymmetric Cherenkov radiation.

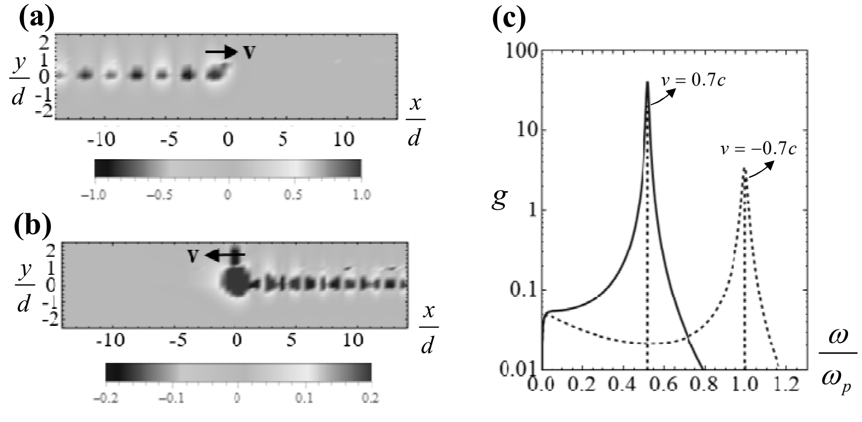

Figure 1: **(a)-(b)** Snapshot (at t=0) of the magnetic field emitted by a linear array of charges moving at a distance d from a magnetized plasma with $\omega_0 = 0.5\omega_p$, $\omega_c = 0.002\omega_p$ and $d = 2c/\omega_p$. **(a)** $v = 0.7c$. **(b)** $v = -0.7c$. **(c)** Spectral density of light g (in arbitrary units) as a function of the normalized frequency ω/ω_p.

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Active control of the photoluminescence emitted by quantum dots using metallic nanoparticles and photochromic molecules

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Metallic nanoparticles (MNP) may sustain Localized Surface Plasmon (LSP) resonances and the coupling between MNP and quantum dots (QD) is known to lead either to the enhancement or to the quenching of the QD photoluminescence [1]. The distance between QD and MNP is one of the switch parameters between both regimes. The goal of this study is to control the coupling distance (different from the physical distance) between QD and MNP by changing the refractive index of the surrounding medium using photochromic molecules (PM). These molecules are optical switches, which move from a transparent state to a colored one by absorbing UV light.

The main drawback concerns the spectral overlap and the lifetime of each optical phenomenon (Fig.1), since the photochromic molecules can couple to LSP to induce strong coupling [2] or couple to QDs to quench the photoluminescence [3]. In this study, we measured photoluminescence spectra, images and lifetimes of QDs deposited on a glass substrate, with or without the presence of MNPs and PM.

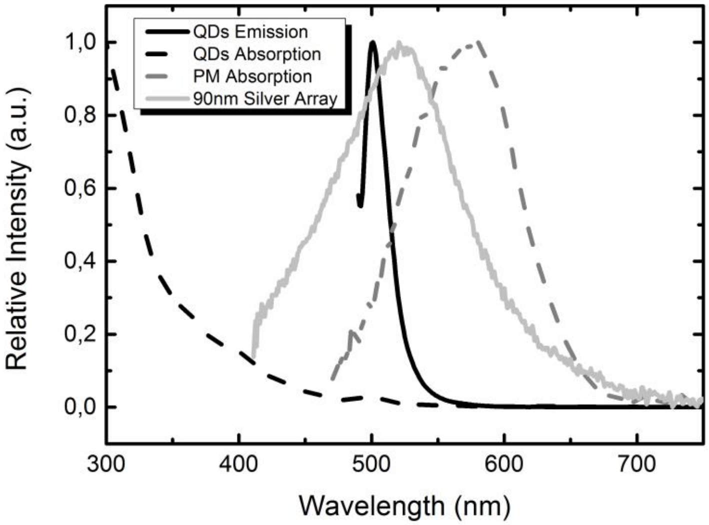

Figure 1: Spectrum of the QDs emission (black line), the QDs absorption (black dotted line), the PM absorption (gray dotted line) and the plasmon resonance of 90 nm silver array (gray line).

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Printed organic smart devices characterized by nonlinear optical microscopy

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In this study, we demonstrate that nonlinear optical microscopy is a promising technique to characterize organic printed electronics. Using ultrashort laser pulses we stimulate two-photon absorption in a roll coated polymer semiconductor and map the resulting two-photon induced photoluminescence (TPPL) and second harmonic response. First, we show that the different nonlinear optical signals can be used to discriminate between the polymer semiconductor material and embedded metal nanoparticles which constitute the electrode in a real device. Next we demonstrate that the TPPL quenches when applying a current between source and drain; this decrease can be used to determine the electrical characteristic of the device [1]. Finally, we show that the TPPL increases with higher temperature in the 20 - 120 °C range, closely following the supported current characteristics of the semiconductor. With this technique, we can recognize different nanomaterials and we propose that the TPPL is a good indicator to map and monitor the charge carrier density and the molecular packing of the printed polymer material. Importantly, simple calculations based on the signal levels, suggest that this technique can be extended to the real time mapping of the polymer semiconductor film, even during the printing process, in which the high printing speed poses the need for equally high acquisition rates.

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Intermediate band semiconductor nanocrystals as a general class of plasmonic-like materials with zero free carriers

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Localized surface plasmon resonances (LSPRs) of metal nanoparticles (NPs) are commonly used for several applications including sensing, energy harvesting and cancer therapy [1]. LSPR in NPs are usually understood in terms of collective excitations of free carriers. Plasmonics in semiconductors are therefore generally limited to doped or degenerate semiconductors, which display metal-like properties [2]. Pure semiconductors, with no free carriers in their ground state are usually not considered suitable for applications in the field of plasmonics. It has however been recently demonstrated that undoped iron-based chalcopyrites NPs display a large light absorption in the visible range [3, 4]. The origin of this absorption is however controversial. In this talk I will discuss the mechanism of light absorption by iron-based chalcopyrites NCs, using a model which combines the classical Mie theory with ab-initio computed chalcopyrites dielectric functions. It will be shown that iron determines the presence of an empty intermediate band (IB), occurring between the valence and conduction band of chalcopyrites. This IB is responsible for the fulfillment of the Froehlich condition of light absorption in the visible range, i.e. IB semiconductors resonances can be understood within the same mathematical framework of metal LSPR. Furthermore, I will present a model for the relaxation of the electrons excited into the IB by optical pumping and compare it with the results obtained by transient spectroscopy pump-probe experiments. This represents a first attempt to quantitatively model the excellent photothermal efficiency of chalcopyrites NPs, which have been recently proved to be cytotoxic and thereby suitable for possible uses in photothermal therapy.

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Dissipation and dephasing for molecules close to plasmonic nanoparticles: an ab initio approach

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Quantum decoherence is a fascinating property of matter occurring when a given system interacts with an external environment [1]. The theory of open systems is successful in describing decoherence in terms of loss of information of the system, for instance, as dissipation and dephasing. Here, we have exploited a computational protocol based on the real-time propagation of the time-dependent electronic wave function, expanded in configuration-interaction eigenstates of the molecular target [2]. Computational results in Ref. [2] have confirmed the enhancement in the optical properties of the LiCN molecule induced by plasmonic effects, due to the presence of a metal nanoparticle. The molecule is treated at full quantum level, and the electron dynamics is influenced by the mutual polarization between molecule and nanoparticle.

Dissipation and dephasing effects are introduced in the framework of the stochastic Schrödinger equation (SSE) [3], which has been seen to be fully equivalent to the master equation approach for the reduced density matrix [4]. We have implemented three different interaction channels with the environment (i. e., the metal nanoparticle): relaxation to the ground state by means of spontaneous emission, nonradiative relaxation through internal conversion and pure dephasing of the wave function. The propagation of the SSE has then been performed by using a quantum jump algorithm [5] or a continuous stochastic propagator [6].

We have applied this ab inition approach to the study of the evolution of the electronic and optical properties of the LiCN molecule close to a metal nanoparticle, under the influence of an electromagnetic field, as a function of the distance between the molecule and the nanoparticle [7]. Moreover, the interplay among the different channels has been investigated.

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3D Simulations of Spatial Dispersive Metals with a Finite Element Time Domain Method

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We present recent advances in the development of a Finite Element Time Domain (Discontinuous Galerkin) solver for computational nanophotonics, focusing on metallic nano structures irradiated by laser pulses. Metallic nano structures of sizes between 2 nm and 25 nm are well known to show spatial dispersion which is modeled by a nonlocal dispersion model for the electron gas [1, 2]. We briefly review and classify the dispersion model used in this work and then step to the numerical modeling of the resulting linear hydrodynamic equations when coupled to the 3D Maxwell's equations in time-domain.

The considered 3D finite element time domain method combines the advantage of high order polynomial solutions on very flexible unstructured tetrahedral meshes and a broad band frequency solution due to short pulses [3].

We assess the performance of the numerical method on multiple setups. Among them, we considered a spherical dimer system. Such systems are well known for high field enhancements in the gap and are well suited for single molecule detection [4]. Our numerical simulations investigate the influence of spatial dispersion on the scattering cross-section of spherical dimers with a diameter of 20 nm and 2 nm gap size. Figure 1 compares the scattering cross-section for an incident polarization of the electric field along the dimer.

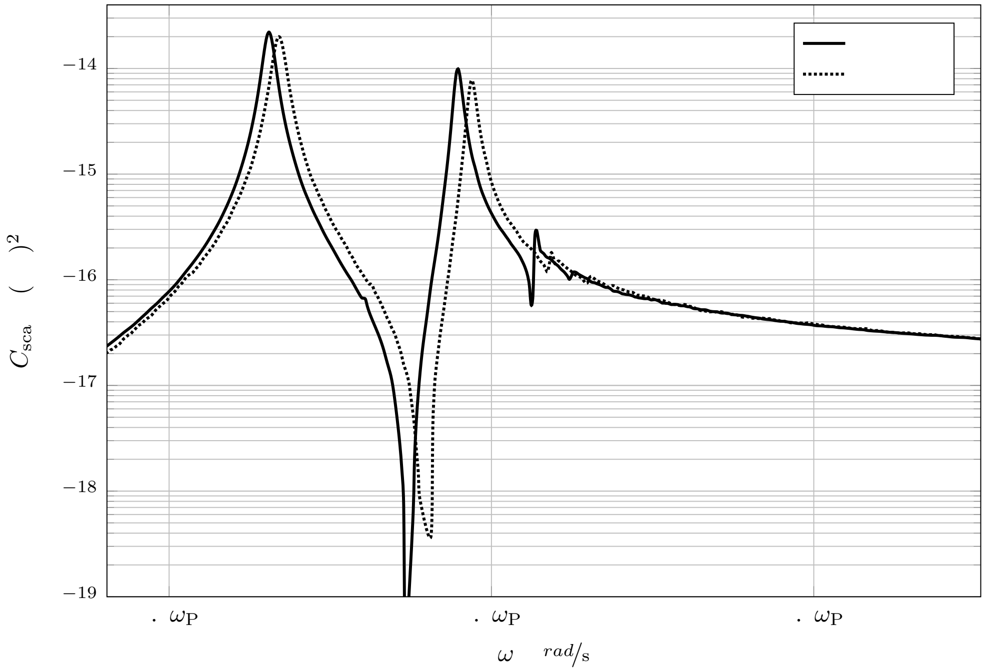

Figure 1: Scattering cross-section of the sphere dimer for an incident wave: $\mathbf{k} = k_0\mathbf{e}_z$ and $\mathbf{E} = E_x\mathbf{e}_x$

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Plasmonic rulers track the smallest graphene oxygen tank

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The industrial process for production of aluminium suffers from extremely high energy requirements and temperatures exceeding 2000°C [1]. Here we present a device able to perform full redox cycling of Al at room temperature while forming O_2 gas reversibly from a nanoscale Al_2O_3 layer, through a flexible graphene top electrode (Fig. 1a). We use plasmonics to observe this process dynamically.

Au nanoparticles (NPs) are embedded between a graphene sheet and a 12nm Al_2O_3 film. The resulting nanoparticle-on-mirror (NPoM) geometry tracks the Al_2O_3 electrochemical dynamics, exploiting the high field confinement between the Au NP and the bottom Au electrode. Applying a voltage, we observe formation and subsequent expansion of nano-reservoirs encapsulating O_2 gas underneath the graphene layer. The process is reversible and inverting the potential readily resets the device to its original state, reincorporating O_2 into the oxide film. The strong blue-shift (~ 50nm) of the plasmonic coupled mode of the NP atop the Al_2O_3 layer reveals in real time the O_2 reservoir expansion to hundreds of nm in height and several μm in diameter (Fig. 1b). We demonstrate the presence of the thin newly formed Al layer through reflectivity measurements, thereby confirming reversible reduction of Al_2O_3 into Al and O_2 gas. Such reservoirs prove to be stable over long periods (several months), with deflation observed only upon application of a reset voltage.[2]

Our system represents an extremely sensitive plasmonic ruler to provide real time access to electrochemical reaction dynamics in nano-reservoirs. We show a powerful method to trap and store gas at the nanoscale, enabling extremely low-power reactions, novel actuation, and opening new frontiers to technological applications requiring a restricted and enclosed nano-environment.

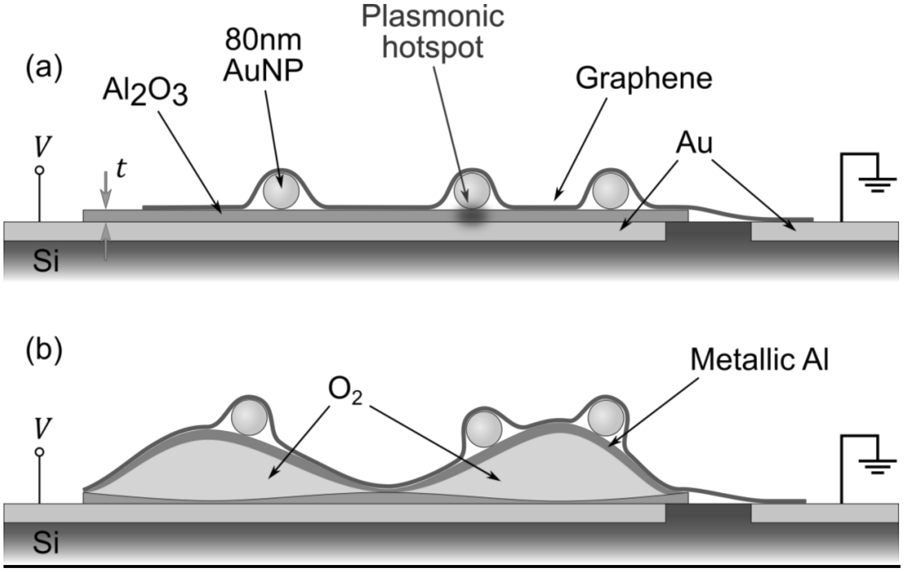

Figure 1: Device structure (a) before and (b) after applying voltage. The Al_2O_3 layer reduces into a metallic Al film and O_2 gas within a graphene coated reservoir.

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A microsource of light from an electrically excited plasmonic lens

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Plasmonic micro- and nanostructures may be used to locally convert electron current into light beams or surface plasmons and are thus expected to play a key role in integrating nanophotonics into electronic devices. Such structures are also used in all kinds of optical microcomponents and plasmonic circuits. Some of these structures, such as optical nanoantennas, plasmonic crystals or plasmonic lenses, have already been the subject of numerous studies in which they are excited by a laser beam or by near-field coupling to a fluorescent molecule[1-3]. However, their excitation by electrical current, in particular by inelastic tunneling, has been rarely studied. A characteristic of inelastic tunneling is that it is extremely local and broadband in frequency, which requires adapting the design of the excited plasmonic structures that are often designed to operate at a given frequency. Thus, it is essential to be able to accurately measure the spectral response of these plasmonic structures under local electrical excitation. To this end, we have developed an experimental setup that combines a scanning tunneling microscope (STM), an optical microscope and an optical imaging spectrometer. The tunneling current is used to electrically excite surface plasmons on a gold microstructure under the STM tip. The scattering and leakage radiation of the excited surface plasmons are collected by the optical microscope and an image of this light emission in the Fourier space is projected on the entrance slit of the spectrometer which disperses light onto a cooled CCD camera. The spectral response of the plasmonic structure and the energy-wavevector dispersion of its modes are thus measured. Experimental results show that the spectral response of the plasmonic lens may be tuned by varying the slit period and the number of slits that make up the lens. We show that this technique may be used to optimize the design of plasmonic lenses for integrated electric microsources of radially polarized light beams.

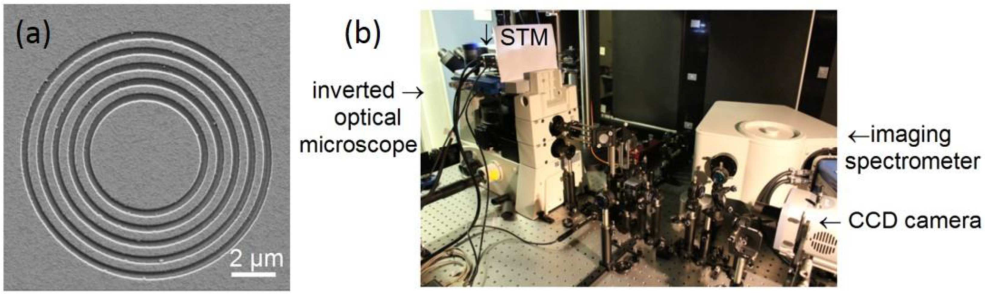

Figure 1 sample and experimental setup. (a) An SEM image of plasmonic lens consisting of 5 concentric slits etched in a 200 nm thick gold film on glass. (b) Experimental setup for imaging spectrometer detection.

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Optical Control of Plasmonic Devices for Single-Electron Nanotunneling

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We excite a gold bow-tie nanoantenna with 1.4-cycle pulses in the near-infrared regime (NIR) to trigger and control electronic transport at optical frequencies [1], as sketched in Fig. 1(a). The antenna with external leads attached to it provides a strong plasmonic field enhancement confined in a 8-nm wide feedgap, see Fig. 1(b), thus serving as an electronic circuit that exhibits a tunneling-like and highly nonlinear current-voltage characteristic. Biasing this structure with the electric field contained in single cycle pulses allows for electronic transport across the feedgap: cosine-shaped transients break the symmetry of the metallic nanostructure and lead to a finite total current.

An Er:fiber laser system generates phase-locked femtosecond pulses spanning more than one octave in the NIR, as presented in Fig. 1(c). Focused onto the nanoscale junction the optical field induces a net tunneling current through the gap. Figure 1(d) shows the currents of up to 0.6 A that we measured with lock-in detection as a function of the carrier-envelope phase (CEP) in a non-perturbative regime with pulse energies of only 80 pJ. This is possible because the free space bias is strongly enhanced by the broadband plasmonic resonance which is custom-tailored to perfectly complement the excitation spectrum, see Fig. 1(c). For the analysis of the attosecond dynamics of the transport it is furthermore crucial to control the plasmonic decay time and thereby conserve the few-cycle character of the excitation [2]. Figure 1(e) depicts how a short antenna response (from simulation) ensures a minimum retardation of the free-space driving field.

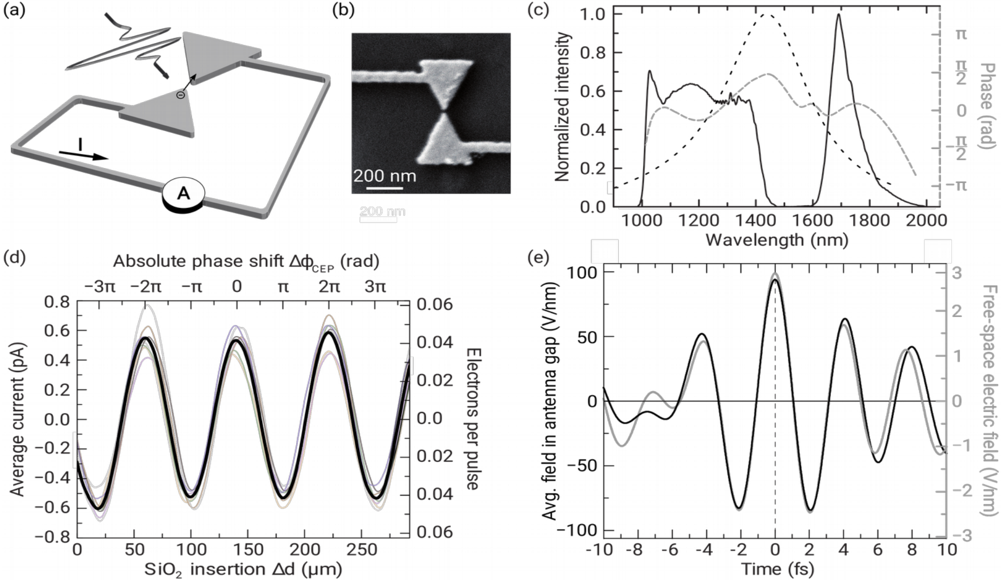

Figure 1: (a) Sketch of the experiment. (b) Scanning electron micrograph of the antenna. (c) Spectral intensity profile (black solid) and phase (grey) of the light pulses, compared to the antenna resonance profile (dashed). (d) Tunneling current for varied CEP. Thick line: average over 8 subsequent scans. (e) Electric field transient for maximum current injection in free space (black) and shaped by the plasmonic resonance (grey).

In order to gain full insight in the dynamics of the optical field that is actually present in the gap, we investigated the plasmonic decay time via third harmonic generation in an interferometric FROG setup [2]. For the bow-tie geometry we measure a dephasing time of less than 2 fs, i.e. shorter than one optical cycle of the driving pulse, which proves them to be a great ideal for providing simultaneously ultrabroadband and strong field enhancement.

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Microfluidic SERS chips for the selective detection of miRNAs in biological matrixes

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The employment of plasmonic nanostructures for Surface Enhanced Raman Scattering (SERS) based biosensing has been extensively explored [1], especially in the framework of early cancer diagnosis, which can benefit from the label-free nature and high sensitivity of SERS in a multiplexing approach [2,3].

In this work, we discuss the detection of miRNA222, an important cancer biomarker, on silver decorated porous silicon-PDMS membranes integrated in elastomeric multichamber microfluidic chips [4], investigating the effectiveness of different analysis configurations for the determination of miRNAs in cell extracts. A bioassay based on a two-step hybridization procedure was developed (Fig.1a). According to this functionalization protocol, a DNA probe, complementary to the target sequence, is divided in two shorter strands (half1 and half2). Half1 is immobilized on the Ag nanoparticles (NPs), in order to specifically capture the target miRNA, then, half2, modified with a Raman label at the 5' end, is incubated for the sensitive and label-free detection by SERS. After an accurate optimization of the protocol, its specificity for the target miRNA222 was confirmed by the analysis of mixtures of several miRNAs, even at high concentration, that simulate the effect of interfering sequences in real samples. In addition, a calibration curve was obtained, showing a decrease of the limit of detection for miRNA222, which was lowered of more than two orders of magnitude in comparison to the standard one-step hybridization protocol. Thanks to the new procedure, the analysis of cell extracts in the SERS microfluidic chip enabled the specific identification of the miRNA222 in the complex biological matrix (Fig.1b). In order to further improve the sensitivity, different analysis configurations were finally investigated. The effect of different Raman dyes (Cyanine 5/3 or Rhodamine 6G) and their labelling position (3' or 5') were studied. A significant boost of the SERS signal for the labelling at the 3' end (close to the NPs surface) compared to the 5' (far from the surface) was verified, due to a more efficient electromagnetic enhancement (Fig.1c). The combination of this improved sensitivity with the high specificity of the assay paves the way to the effective application of these SERS chips in the early detection of tumor markers.

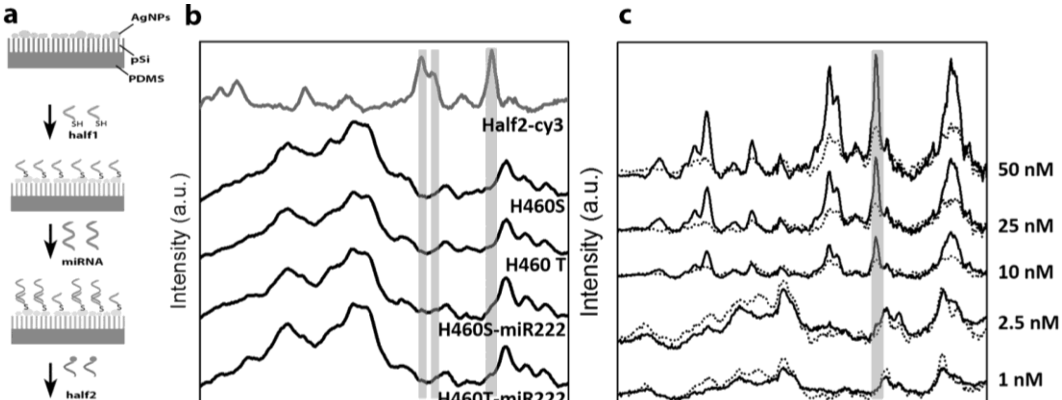

Figure 1: a) Scheme of the two-step hybridization assay; b) SERS spectra of the functionalized substrates incubated with total RNA (T) and small RNA (S) cell extracts obtained from H460 (miRNA222 not expressed) and miRNA222-transfected H460 cells; c) Comparison between SERS spectra acquired on samples incubated with different miRNA222 concentrations using a 5' (dotted line) or 3' (solid line) labelling position. All the spectra are averaged starting from 110 points SERS maps.

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Ultrafast Transient Optical Properties of Silver Nanoclusters

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As a nanoparticle get smaller (< 5 nm) its behaviour switches from nanoparticle-like (plasmonic response) to molecular-like (electronic transitions, dipole excitation and emission). In the case of thiolate capped silver nanoparticles with diameters < 2 nm they begin to assume stable structures containing a metal core surrounded by a layer of ligand bound silver atoms. The resulting structures turn out to allow facile synthesis and to be very stable over long periods [1] and have lead to their use in the fields of biosensing, bioimaging, catalysis and photonics. This is largely due to the fact that due to quantum confinement they exhibit properties which are not observed in molecules, larger nanoparticles or bulk materials.

In this work we concentrate on the ultrafast optical pump induced transmission changes of silver nanoclusters dispersed in a solvent in the UV range between 350 and 450 nm where both molecular-like transitions and plasmon bleaching are observed. Evidence for strong coupling between the plasmonic response of the metallic part of the nanocluster and the molecular transitions of the nanocluster are presented. A time-resolved polarisation dependent spectroscopic technique usually applied to rotational spectroscopy of fluorescent molecules shows very fast lifetimes (< 2 ps) of polarisation dependent signals indicative of coupling between the plasmonic and molecular responses of the nanoclusters.

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Enhanced Fluorescence Emission and Raman Scattering using Bound States in the Continuum of a Photonic Crystal Membrane

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The local enhancement of the electromagnetic field in photonic structures is very useful to manipulate light and boost nonlinear phenomena. In particular, high field enhancement factors can be generated in metallic nanoentities - such as metallic nanostructures, nanoparticles or nanoantennas - by exploiting localized surface plasmon polaritons at metal/dielectric interfaces. Nevertheless, plasmonic materials are not the only way to achieve optical field enhancement. The amplification in a structured dielectric surface is a relatively unexplored field that has received increasing attention in the last years [1-3]. It would be of great interest managing surface electromagnetic states in dielectric structures mimicking surface plasmon resonances in terms of spatial localization, high field intensity and dispersion characteristics, while avoiding heat dissipation produced by metallic absorption.

It has been demonstrated that a suitably designed photonic crystal (PhC) membrane can support Bound States in the Continuum (BIC) of radiation modes. These are resonant states of ideally zero line-width as a result of the interaction between trapped electromagnetic modes [4-6]. These special Fano resonances can completely decouple from the continuum of the free-space modes because of symmetry mismatch with far field radiation. However, fabrication imperfections partially break the symmetry of the lattice, thus allowing the coupling to the external incoming beam. At the bound state frequency, the electromagnetic field is ideally trapped with infinite life-time. Experimentally, this involves very narrow guided resonances, with high Q-factor and potential huge field intensity enhancement - up to 6 orders of magnitude [6]. Herein, we investigate the effect of the BIC-based field enhancement in the proximity of the PhC surface to boost the fluorescence emission of probe molecules dispersed on the surface. We also explore the possibility of amplifying the local field of resonant plasmonic nanostructures to exceed - with a combined excitation scheme - the sensitivity limits of surface-enhanced spectroscopies. Our results provide new solutions for light manipulation at the nanoscale, especially for sensing and nonlinear optics applications.

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Plasmonic silver-alkyne nanoclusters as putative intracellular SERS-active probes

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SERS-based spectroscopy is rising up as a powerful approach for intracellular *in vivo* imaging [1]. In this context, nanostructured materials carrying different Raman dyes have been proven to exhibit exciting features [2,3]. Among them, alkynes (compounds bringing C≡C triple bonds) could come out as new cutting-edge dyes due to their detectable, though weak, scattering in the cell-silent region (1800-3000 cm^{-1}) where the overlap with biomolecules cannot occur [4] beyond the possibility of obtaining alkyne-derivatized biomolecules.

Here we show a simple procedure to assemble colloidal silver-alkyne nanoclusters endowed with strong plasmonic behavior, which positively affects the alkyne's scattering. Nanoclusters are assembled from 10-20 nm AgNPs through a sulfur-silver chemistry under controlled conditions where the interparticle gap is chemically set by the crosslinker, *i.e.* DTT, while allowing the alkyne probe to bind the NP's surface. Electron microscopy reveals that nanoclusters are mainly formed by dimers and trimers (Figure 1a and b).

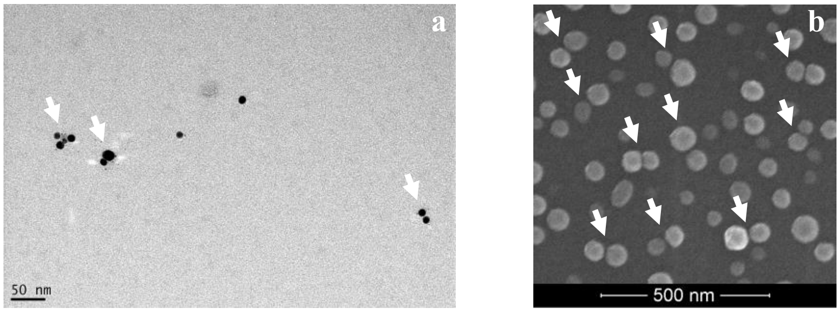

Figure 1: a) TEM and b) SEM micrographs of assembled silver-alkyne-DTT nanoclusters

Raman measurements demonstrate enhancement of the 2020 cm^{-1} signal related to the alkyne moiety, this one being silent or weak if not coupled to the plasmonic structures (Figure 2a). Such an enhancement is likely to rise out mainly from the nanometer gap of interparticle region as also supported by FTDT method-based simulations (Figure 2b).

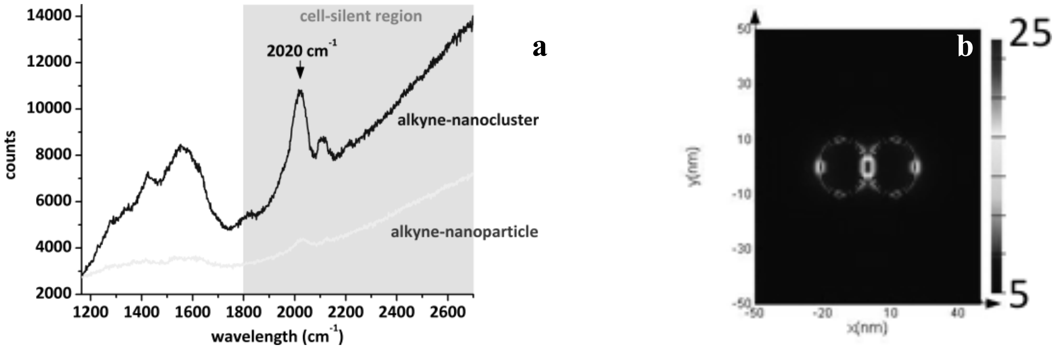

Figure 2: a) Raman scattering and b) FTDT simulation of the silver-alkyne-DTT dimers

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Deep-subwavelength hyper spectral imaging and tuning of individual disorder modes

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Optical localization in strongly disordered photonic media is an attractive topic for proposing novel cavity-like structures [1,2]. In fact, it has been argued that disordered PBG materials should be less sensitive to fabrication errors or defects and thus promise a more robust design platform [3]. The ability to fine-tuning the spectral resonance of the modes confined in the multiple-scattering regime without affecting their spatial intensity distribution is of the utmost relevance for cavity-like quantum electrodynamics experiments, where a single emitter is put in strong coupling with the random mode.

Here, by investigating the near-field of a two-dimensional disordered photonic system made of a GaAs slab patterned with randomly distributed circular air scattering centers, we retrieve near-field mode speckle patterns that extend over few microns and show several single speckles of the order of λ/10 size. Experimentally we perform a hyperspectral near-field imaging in the telecom window to directly investigate the spatial distribution of disordered induced localized optical modes. Exploiting the local perturbation induced by the near-field probe, which spectrally shifts the photonic modes proportionally to the mode electric field intensity [4]. Our findings demonstrate that the localized photonic modes, built up by disordered systems, show strong spatial non-uniformity with very small spatial features.

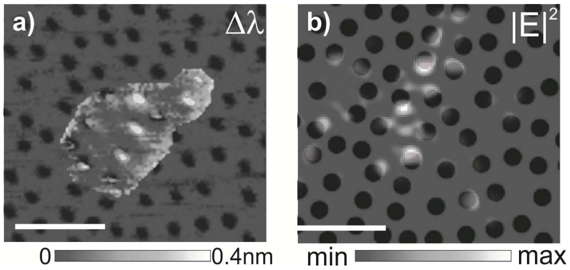

Figure 1: (a) Experimental spectral shift (Δλ) maps obtained by reporting the peak position of a mode centered around 1338 nm. (b) Electric field intensity maps obtained by FDTD calculations for a mode around the same spectral position as in a) in a medium with the same design characteristics of the investigated sample. The scale bar is 1 μm.

We also prove that a post-fabrication method based on laser assisted nano-oxidation of the GaAs slab, performed by near-field illumination, can be used for a gentle tuning of the localized photonic modes [5]. The novelty of this works lies on the experimental proof that the spectral tuning process does not modify the mode intensity distribution, which arises from the subtle balance creating stationary waves after multiple scattering by randomly placed scatters. This allows the exploitation of random localization both in the development of new optoelectronic devices and in the exploration of new routes for quantum electrodynamics experiments.

Our results pave the way for efficiently tailoring the light-matter interaction in random media, thus solving open questions at the frontiers of disordered photonics.

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Near-field Infrared Spectroscopy of Bacteriorhodopsin Hydration State in Single Purple Membranes

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The steady development of advanced high-resolution optical microscopies represents a promising tool to address important biological open-issues dealing with a variety of physiological and pathological processes. In this context, infrared (IR) nanospectroscopy is attracting much attention due to its capability to combine imaging capability with spectroscopic one at the nanometer level, providing the chemical and structural specificity needed to retrieve local functional information. Standard far-field IR spectroscopy is widely applied to the investigation of proteins since from the analysis of the lineshape of the amide-I (1620-1690 cm^{-1}) and amide-II (1500-1570 cm^{-1}) bands one can retrieve information on protein conformation, strongly related to their structure and functions [1]. Such studies, however, are performed on a large amount of identical proteins, preventing to study nanoscale heterogeneity.

Here we apply tip-enhanced near-field IR nanospectroscopy (AFM-IR) to investigate transmembrane proteins (TMPs) in their native membrane environment. Cell membranes display a high degree of intrinsic heterogeneity in terms of amount and types of TMPs, and, moreover, there can be a different local response of proteins to external stimuli or environmental factors. In our work we focus on bacteriorhodopsin (BR), which is the only TMP present in the cell membrane of Halobacterium salinarum (also named purple membrane) acting as light-activated proton pump [2]. Our sample are 5 nm-thick individual purple membrane patches deposited on ultraflat gold substrates. We perform IR nanospectroscopy using a setup that couples an atomic force microscope (AFM) with a broadly tunable mid-IR quantum cascade laser (Anasys Instruments). The local absorption spectrum is obtained by monitoring the amplitude of the cantilever oscillation induced by the sample thermal expansion. The strong confinement and enhancement of the optical field intensity at the nanogap between the gold-coated AFM tip and the metallic substrate allows to measure the IR spectrum of the membrane monolayer with a spatial resolution of about 30 nm [3]. We show that from the analysis of the lineshape of the amide-I band of 10^2 BR molecules we are able to reveal heterogeneity of the protein hydration, resulting in a heterogeneity of protein conformation [4]. The validity of the results is confirmed by a comparison with the far-field IR spectroscopy of purple membranes performed by standard Fourier transform IR spectroscopy (FTIR) and IR micro-spectroscopy, where not less than 20 purple membrane patches (10^6 BR molecules) are probed, hence preventing to assess local heterogeneity.

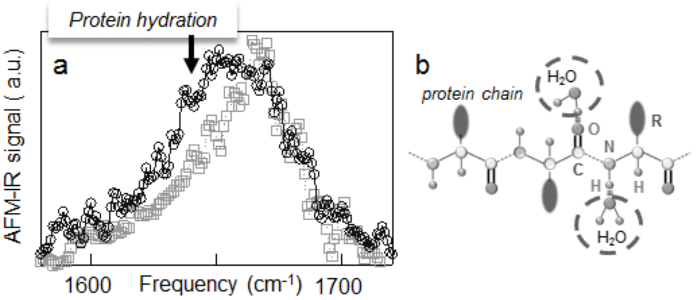

Figure 1: (a) Two selected AFM-IR spectra obtained on individual membrane monolayer patches showing the variation in the amide-I lineshape related to different local protein hydration. (b) In a generic protein, water molecules can bound either to the oxygen atom of the carboxyl group or to the hydrogen atom of the amino group, in both cases affecting the 3D patterns of folding of the protein, hence its amide-I absorption lineshape.

In perspective, one can think to push the capability of IR nanospectrscopy towards the investigation of the functional conformational changes of TMPs in an intrinsic heterogeneous cell membrane.

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Local Field Enhancement: Comparing Self-Similar and Dimer Nanoantennas

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Plasmonic nanoantennas are a key element to manipulate light at the nanoscale. Over the last decade, this class of nanostructures has received increasing attention because of their peculiar light-tailoring properties. Different effects including local field and emission enhancement, polarization rotation, angular emission redistribution, and high-efficiency single-photon collection are obtained by employing a variety of configurations ranging from plasmonic crystals to tightly coupled nanostructures such as bow-tie and Yagi-Uda antennas [1]. The quest for ever larger field enhancements, which are of paramount importance for a number of applications including sensing and light emission enhancement, has led to the design of a range of complex plasmonic nanostructures. Among the most promising ones, self-similar plasmonic nanolenses have been proposed and employed as an arrangement capable of boosting the local field enhancement, with projected gains in field intensity up to 6 orders of magnitude [2,3].

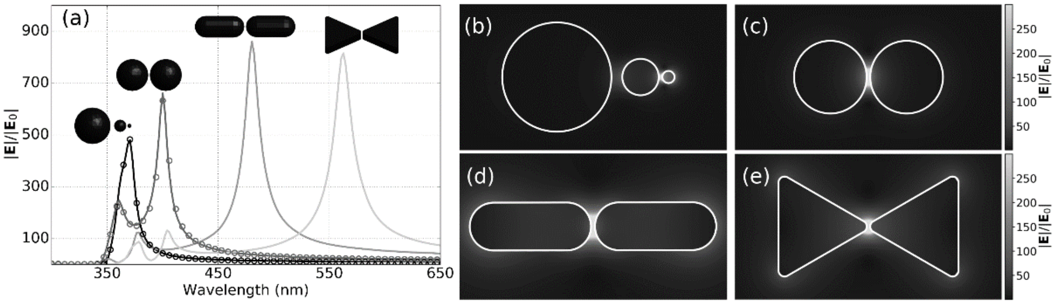

Figure 1: (a) Lines: the field enhancement spectra calculated with the BEM method in the quasi-static approximation. Dots: the field enhancement spectra calculated with the GMM approach. $|\mathbf{E}_0|$ and $|\mathbf{E}|$ represent the incident and local field amplitude moduli. (b-e) Field amplitude enhancement maps. The local fields are computed at the resonance wavelength and on the equatorial plane of each nanostructure: (a) self-similar nanolens; (b) sphere dimer; (c) rod dimer; (d) bowtie antenna.

In this context, we study self-similar nanolenses and compare them with standard bow-tie, rod and spherical dimer nanoantennas having comparable gap size. We show by full-field electrodynamics calculations that the field enhancement properties of self-similar nanolenses are comparable to those obtained by employing more traditional plasmonic nanostructures. Furthermore, we show that the predicted extreme local field enhancements are strongly hampered when radiative and ohmic losses of plasmonic materials in the visible are fully taken into account. We therefore demonstrate that, notwithstanding a significantly higher structural complexity, self-similar nanolenses are unable to improve the field enhancement obtained with standard plasmonic nanoantenna dimers [4,5].

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Material-Independent Modes for Electromagnetic Scattering from Nanoparticles

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Despite many advancement in the understanding of nanoparticles (NPs) electromagnetic scattering, several fundamental questions remain unanswered. First, the resonances in metal or dielectric NPs of size comparable to the wavelength are currently found either experimentally or numerically by exciting the NP with radiation of various frequencies and locating the peaks of the corresponding scattered power spectra. However, this procedure is flawed and can be often misleading. Generally speaking, a peak of the scattered power spectrum cannot be univocally associated to the action of a unique *resonant mode* but may arise from the interplay of several modes. The correct identification of the resonant modes is essential in the description of anomalous scattering behaviours such as the appearance of asymmetric resonant line-shapes, i.e. Fano-like resonances, where interference phenomena play a key role. Second, why silicon and metal NPs of comparable size exhibit deeply different resonant behaviours in the visible spectral range? For instance, magnetic modes in isolated metal nanospheres at optical frequencies have never been seen, but it is very well established that they can be excited in their silicon counterpart. Third, currently the solution of the scattering problem obtained by the majority of analytical and numerical method is often expressed in a form where the contributions of the material and of the geometry are interwoven and cannot be separated. For instance, in the Mie theory for the electromagnetic scattering from homogeneous spheres the electric size and the permittivity both appear in the argument of the vector spherical wave functions, and, as a consequence, the Mie expansion coefficients are complicated function of their combination. This fact makes the design of the material to achieve assigned constraints on the scattered field complicated.

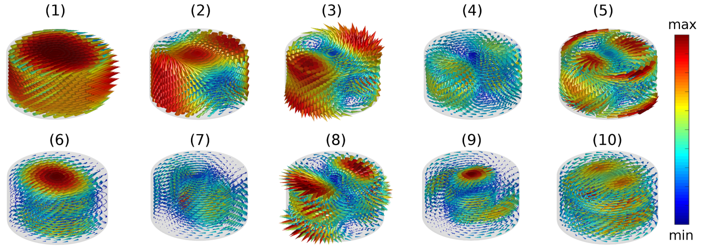

Figure 1: Cone plot of the the material-independent modes dominating the total scattered power of a cylinder of diameter equal to the incident wavelength and height equal to half of the wavelength.

Here, we introduce an alternative representation of the electromagnetic field scattered by a homogeneous object of arbitrary shape at a given frequency, in terms of a set of modes independent of its permittivity. With this modal basis the expansion coefficients of the scattered field are simple rational functions of the permittivity of the scatterer. Then, this spectral technique is applied to evaluate the resonance frequencies of the full retarded NP scattering. This approach allows one to unambiguously identify the modes that are responsible of both the peaks and the asymmetric lineshapes of the scattered power spectra. This approach also naturally highlights the role of plasmonic and photonic modes in any scattering process, and unveils the fundamental differences between the electromagnetic scattering properties of dielectric and metal spheres. Furthermore, we show how the simple dependence of the scattered field on the NP permittivity allows one to the design the NP permittivity to pursue a prescribed tailoring of the scattered field.

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Silica-gold nanodevices for biomedical applications

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Diatomaceous earth, also known as diatomite, is a fossil material of sedimentary origin, formed over centuries by siliceous skeleton (called "frustule") of aquatic unicellular microalgae, the diatoms, deposited on bottom of lakes or present in marine environments. Diatomite morphology can be very complex due to the presence of diatom frustules with different sizes (ranging from 2 μm to 2 mm) and shapes. The structure is highly porous and characterized by a large specific surface area up to 200 m2/g [1]. The main constituent of diatomite is amorphous silica, although it can contain impurities such as organic components and metallic oxides (MgO, Al_2O_3, Fe_2O_3) coming from environment [2]. Different strategies, including calcination processes and hot acid treatments, have been developed to remove impurities from frustules [3]. Due to large availability in many areas of the world, chemical stability, and non-toxicity, this fossil material has been widespread used in lot of industrial applications, such as food production, water extracting agent, production of cosmetics and pharmaceutics. Recently, diatom frustules have been exploited as an innovative platform in several biotechnological applications. In fact, the silica surface of diatoms, covered by reactive silanol (Si-OH) groups, can be modified with functional reactive groups ($-NH_2$, -COOH, -SH, -CHO) for the immobilization of biomolecular probes (DNA, antibodies, enzymes). Moreover, the porous structure allows the binding of a large amount of bioprobe molecules with respect to a flat surface, thus increasing sensitivity of biosensing. In the present work, we have investigated the potential of DNPs as a drug delivery system, improving their stability and biocompatibility by PEGylation, and cellular internalization by cell-penetrating peptide (CPP) bioconjugation.

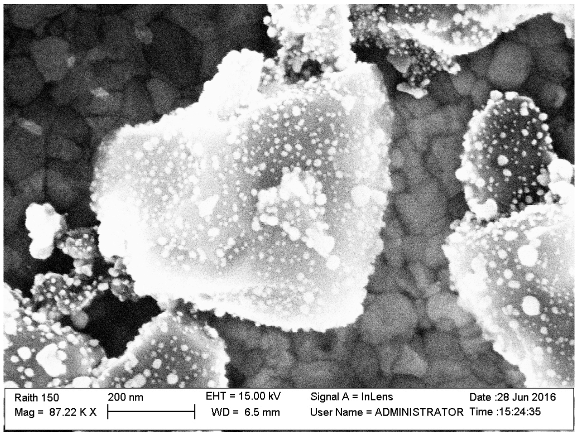

Figure 1: SEM image of hybrid silica-gold nanoparticles.

In this work, we present the fabrication and characterization of novel silica-gold nanoparticles, which can be used as nanovectors and imaging agents, simultaneously. In Figure 1, a SEM image of such samples is reported: a submicron silica nanoparticle is clearly covered by gold nanospheres.

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Efficient injection of hot electrons in water through plasmonic nanoelectrodes

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Free electrons represent simple but yet very powerful reducing chemical agents, showing reduction potential values higher than -5 eV with respect to the reference hydrogen electrode. This extraordinary reactivity makes them fundamental in several photochemical and electrochemical processes, acting as catalysts or intermediate states in a large variety of chemical, physical or biological processes [1].

Therefore, the opportunity to generate free electrons in water has been gaining attention since they open up new possibilities in various fields of chemical and physical sciences.

Nevertheless, even if extensive studies have been carried out on this topic since the 1970s, there are still several aspects that need to be clarified due to the wide range of energy and timescale involved in these processes [2].

Recently, plasmonic hot spots are emerging as an optimal tool for triggering electron driven processes, due to the capability of plasmonic nanostructures to harvest optical energy and to generate the so-called hot electrons, which are not in thermal equilibrium with their environment [3].

In this work we present an experimental and theoretical study of a novel architecture constituted by tridimensional plasmonic nanoelectrodes able to inject hot electrons into aqueous environments and to accelerate them in water by ponderomotive forces up to energies capable of the excitation or ionization of water molecules. This ability is enhanced by the peculiar out-of-plane structure of the nanoelectrodes, which extrude out of a metal baseplate, such achieving an intense plasmonic hot spot at the tip of the structure, while still maintaining electrical connection to an effective charge reservoir [4].

The actual injection of electrons is experimentally observed by measuring the current flow through the gold/liquid interface, while their acceleration is verified by the formation of a cavitation bubble for laser powers exceeding a proper threshold.

A complex model to describe the physicochemical phenomena involved is obtained through numerical methods, able to predict the critical electron density needed for bubble nucleation accurately matching experimental accurately matches experimental data, thus revealing a stronger efficiency in the energy transfer from the plasmonic hot spot to the free electron cloud in water with respect to vacuum [5].

Thanks to the high kinetic energy and large reduction potential, the wet hot electrons obtained with such technique may open up new opportunities in photo-catalysis, electrochemical processes and hot-electron driven chemistry.

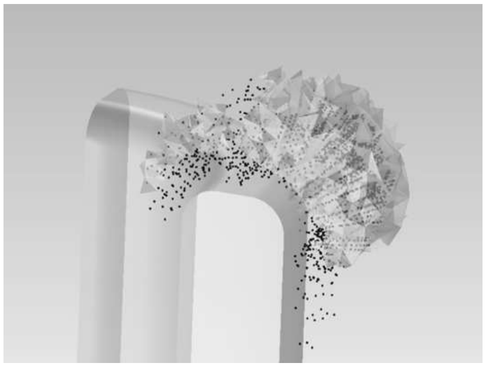

Figure 1: Sketch depicting emission of hot electrons from the tip of a 3D plasmonic nanoelectrode

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Tilted dipolar plasmonic antenna for super resolution imaging on LH2 light harvesting complexes

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Because of the intrinsic diffraction limit of the light, the study of ultrasmall fluorescent emitters like LH2 light harvesting complexes or emitting defects in 2-D materials require super resolution techniques.

Some of these techniques are based on near-field microscopy and their advantages, compared to far-field techniques, consist mainly on a local interaction with the emitters. They allow manipulation like coupling to plasmonic structures, injection of light or enhancement of fluorescence, below the diffraction limit [1,2]. Furthermore, the highly structured electric field close to the metallic probes allows the detection of out-of-plane oriented emitters, otherwise non detectable in far-field, resulting in enhanced sensitivity [2].

In our setup the plasmonic nanoantenna and the sample are scanned with nanometer precision and the excitation and collection of light are both provided by an inverted confocal microscope.

We report on the development of a new nanoantenna design, capable of providing the same enhancement of fluorescence and sensitivity, with improved optical and topographic resolution witht respect to the state of the art [3].

Our new tip design allows the employment of a resonant plasmonic antenna capable of providing a single spot interacting with the emitters.

The effectiveness of this new nanoantenna configuration has also been demonstrated by near-field super resolution measurements of 20 nm size molecular beads and terrylenediimide (TDI) single molecules embedded in a thin film of transparent polymer, providing a fluorescence enhancement of 10 times.

We also report on the application of this new near-field probe for the enhanced super resolution imaging of LH2 nanostructures. The tilt nanoantenna provides a single enhanced spot of 40 nm size and topography measurement with a nanometer precision in height.

We applied such tip for the implementation of a vertical plasmonic nanocavity, created between the probe scanning approximately 10 nm above the sample surface where a metallic layer has been deposited.

Since our experimental technique allows the positioning of a single emitter in such a plasmonic cavity with nanometer precision, we can characterize in detail its optical performances, exploring the potential for single photon source applications.

The results demonstrate the capability to efficiently apply nanoantennas as near-field probes for the study of LH2 systems, obtaining super resolution images and enhancement of fluorescence emission and sensitivity at the same time. They also show the potential for the realization of plasmonic cavities promising for higher levels of light confinement and enhancement of the Purcell factor.

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Bio-inspired strategies to target the tumor microenvironment with gold nanorods

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Gold nanorods and similar plasmonic particles have gained attention as contrast agents for key applications in biomedical optics, such as the photothermal ablation and photoacoustic imaging of cancer. [1,2] These particles feature a unique combination of intense optical absorbance in the near-infrared window, non-cytotoxicity and unique potential to home into tumors upon systemic injection, which rests on their capacity to pervade hyper-permeable lesions and to incorporate molecular probes of molecular targets of malignant cells. [3] However, the identification of suitable targets remains an outstanding issue, since the phenotypic features of malignant cells differ from case to case and are hardly accessible from the bloodstream, due to a complexity of biological barriers. [4] The aim of our work is to explore alternative routes that exploit the advantage of photo-thermics and acoustics to mitigate the need for a direct uptake of the plasmonic particles from the malignant cells. We propose innovative concepts to deliver gold nanorods to the tumor microenvironment (TME), which may combine high specificity and breadth of application.

In particular, we exploit the biological response to common faults of the TME. [5] The hyperproliferative profile of malignant cells entails a combination of high oxygen consumption and poor oxygenation, which generates chronic hypoxia. The cascade of biochemical processes that accompany the metabolic switch of hypoxic cells from aerobic respiration to fermentation results into the expression of transmembrane isoforms of carbonic anhydrase, which is an exclusive hallmark of chronic hypoxia. [6] We propose the conjugation of gold nanorods with inhibitors of carbonic anhydrase, as a multimodal tool to recognize and hit hypoxic cells. [5,6] The biological profiles of these particles display a strong dependence on environmental oxygenation, including endocytic uptake, cytostatic activity and optical sensitization.

In addition, the abnormal conditions of the TME activate a systemic reaction that involves the recruitment of various types of immune and stem cells, [7,8] which may serve as smart vehicles to deliver plasmonic particles to tumors [9,10]. In practice, these cells may be harvested from a patient, loaded with gold nanorods ex vivo and then re-injected into their host, so as to exploit their tumor-tropism. We found that macrophages loaded with polycationic gold nanorods retain their principal functions, in terms of viability and chemotaxis. An unique advantage of this strategy is the possibility to optimize most of the nano/bio interface in vitro. For instance, we analyze pros and cons of the introduction of a thin shell of organosilica, which is under inspection as an elegant solution to enhance the photostability (against reshaping [11]) and the optical stability (against plasmonic coupling [12]) of gold nanorods.

We are confident that our work shall provide new inspiration for the development of innovative strategies to deliver plasmonic particles to tumors.

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Following with a high sensitivity the adsorption of gases on nanoparticles by indirect nanoplasmonic sensing.

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The indirect nanoplasmonic sensing (INPS) lets us to follow the adsorption of gases on nanoparticles by measuring the shift in wavelength of the localized surface plasmon resonance (LSPR) signal of gold disks on which nanoparticles are deposited. Indeed during the adsorption of gas molecules on nanoparticles the dielectric properties at the surface of the nanoparticles are changed and it generates a shift of the LSPR wavelength of the underlying gold disk detector [1].

We describe in this work the different steps of the gold disks fabrication by electron beam lithography, the experimental set-up and present an accurate calibration of our LSPR gold sensor. Then we measure water adsorption isotherms by following the shift of the LSPR wavelength when water molecules adsorb/desorb on the gold disks surface, we were able to detect a few hundredths of an adsorbed water monolayer !

We show in a second part some results obtained by INPS on the adsorption/desorption of water on different carbon soot nanoparticles [2].

INPS associated to mass spectrometry can also be useful to follow quantitatively and with a high sensitivity the reactivity of gases (CO, NO_x, …) with metallic nanoparticles. (e.g. for catalytic reactions).

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Quantitative measurement of the optical cross-sections and optical sizing of individual nano-objects

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The optical properties of nano-objects (NOs) can be quantitatively described by the optical cross-sections (OCSs) corresponding to light absorption (σ_{abs}) and scattering (σ_{sca}). In particular, the OCSs of metallic NOs feature localized surface plasmon resonances sensitively depending on size, shape, and material of the NO and its surrounding environment, resulting in a rich phenomenology. However, while the spectral properties of the OCSs have been addressed in number of studies, their absolute value is hardly measured, as the few suitable techniques rely on not widely available laser-based set-ups as in Ref. [1].

In the attempt to reach a wider community, we have developed a simpler approach, based on a commercial microscope equipped solely with a camera or a spectrometer. We have applied our quantitation method to data obtained with two different techniques, each yielding complementary advantages. Firstly, micro-spectroscopy allows simultaneous acquisition of detailed spectral information as in Fig. 1a. On the other hand, automated analysis of conventional brightfield and darkfield images provides a high-throughput (> 100 objects per field of view) and high-sensitivity ($\sigma_{\mathrm{abs}} < 10\,\mathrm{nm}^2$) characterization, see Ref. [2, 3].

The measured OCS can be compared to numerical modeling (wherein a realistic description of the microscope illumination must be implemented) in order to retrieve the corresponding geometric parameters describing the NO. In perspective, sizing with purely optical means could provide significant advantages in terms of ease and cost with respect to electron microscopy. We have tested our method on a selection of model systems—including metallic (gold spheres and rods) and dielectric (polystyrene beads) NOs, both in a homogeneous optical environment and on an interface—with promising results, see Fig. 1b.

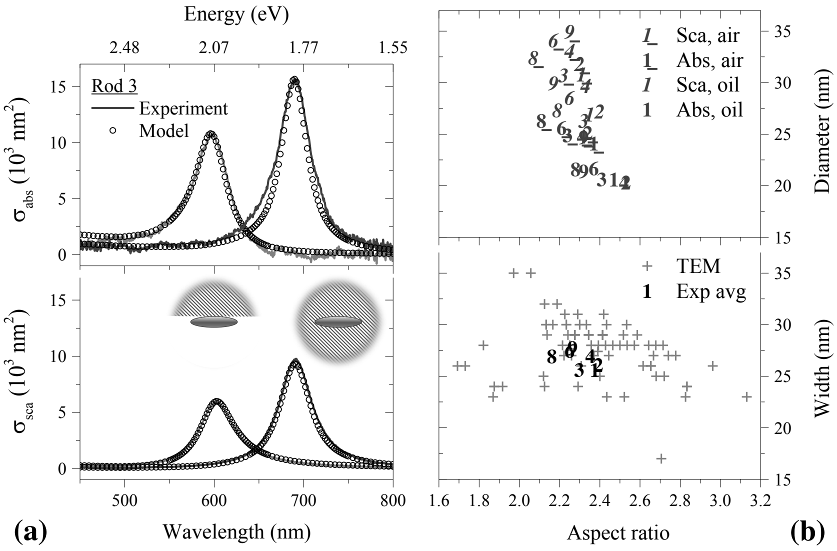

Figure 1: Cross-sections and optical sizing of individual gold nanorods. **(a)** Absorption (top panel) and scattering (bottom panel) spectra of the same rod, on a glass/air interface and a homogeneous glass/oil optical environment (short and long wavelength peak respectively). Numerical simulations (hollow circles) have been fitted to the experimental data (solid lines) by adjusting the aspect ratio and diameter of the rod. The resulting size estimates for seven rods (labeled with numerals) are reported in **(b)**, top panel. In the bottom panel the averages are compared to electron microscopy results (crosses) on the same rod batch.

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Plasmonic Arrays of Nanostructures for Biosensing: Extended vs Localized Plasmons

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Revealing very low concentrations of a specific biological molecule is one of the key to early diagnosis of several diseases and, for this purpose, plasmonic nanostructures are very effective for the development of biosensors able to reveal concentrations of a specific molecule down to the picomolar (pM) range.

This work presents a comparison of the biosensing performances of two classes of plasmonic ordered arrays: (i) Nano Hole Arrays (NHA) and (ii) Nano Prism Arrays (NPA). They sustain different kinds of plasmons, i.e., extended and localized plasmons for the NHA and the NPA, respectively.

NHAs consist of an opaque metallic film patterned with a hexagonal array of circular subwavelength holes. Such nanostructure presents the Extraordinary Optical Transmission (EOT) phenomenon, which consists in observing at a certain wavelength a transmitted light intensity greater than the one that would pass through a single hole with equivalent area. The spectral position of this transmittance peak shifts as dielectric constant at the interface of the nanostructure changes and this represents the transduction mechanism for sensing purposes.

NHAs are produced by Nano Sphere Lithography (NSL) coupled to Reactive Ion Etching (RIE): a self-assembled monolayer (SAM) of polystyrene (PS) nanospheres (522 nm in diameter) is first obtained on a silica substrate. Then, the PS nanospheres are etched by RIE in Ar-O_2 atmosphere down to a 300 nm diameter and, finally, a Cr film 5 nm thick (as an adhesion layer) and 75 nm of Au are deposited by thermal evaporation.

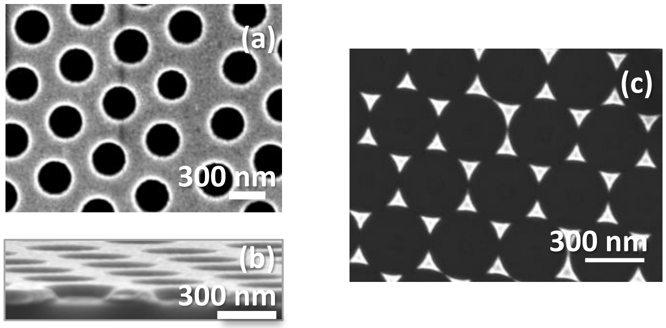

Figure 1: (a), (b) SEM images of a NHA; (c) SEM image of NPA

By employing FEM simulations, the bulk and local sensitivity of this NHA were computed, obtaining $S_{bulk} = 300\,\frac{nm}{RIU}$ and $S_{loc} = 3.5\,\frac{1}{RIU}$, respectively. These sensitivities indicate how much EOT peak shifts respectively, when the refractive index of the environment above the NHA is changed by 1 RIU and when only a thin layer of dielectric is added at the surface of NHA

The NPAs were fabricated with the same technique without performing the RIE step. FEM simulations for this NPA resulted in $S_{bulk} = 260\,\frac{nm}{RIU}$ and $S_{loc} = 8.9\,\frac{1}{RIU}$. So, in principle NPAs should be better transducers for sensing small molecules, with respect to NHAs, due to their shorter decay length of the near-field at the surface.

In order to test the sensing performances, NHAs and NPAs were functionalized with the same protocol to obtain a lable-free and specific biosensor for Biotin-Streptavidin receptor-analyte complex. First, a SAM of thiols is formed on the metallic surface, then Biotin is bound as the specific receptor. To prevent aspecific signal the exposed silica surface has been PEG-ylated. Finally, the functionalized nanostructures are incubated with different concentrations of Streptavidin (SA) from 100 pM to 10 μM, obtaining a sensing curve. A limit of detection (LoD) of 2 nM and of 200 pM has been obtained for the NHA and NPA, respectively. These results prove that, although NPA is more sensitive, both nanostructures can be used as a highly-sensitive, specific and lable-free biosensor for the streptavidin. Of course, the same detection scheme can be also used for other bio-molecules.

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Plasmonic enhanced chemical sensing with SnO_2 nanowires

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In the current work we demonstrated that conductometric gas sensors based on nanostructured metal oxides decorated with metallic nanoparticles show better performances when illuminated with visible light. In particular, we focused on SnO_2 bundle of nanowires (NWs) decorated with Silver nanoparticles (NPs).

In our research work we developed a convincing experimental evidence giving support to hypothetical plasmonic nature of the enhancement and to provide a detailed explanation of the chemo-physical process giving rise to the enhancement.

Sensors are composed of bundle of MOX nanowires grown by Vapor-Liquid-Solid and decorated by silver nanoparticles (~30 nm in diameter) by means of magnetron sputtering. The functional characterization towards H_2 (500 ppm) was performed at room temperature in 30% humid air. The sensors were tested in dark and under irradiation with light at constant irradiance along the visible spectrum (350-650 nm).

From UV-Vis measurement, we previously observed that such nanoparticles have a fundamental plasmon resonance mode around 500 nm and a higher frequency mode in the UV region.

From experimental results (Fig. 1) we can see that the response maxima correspond to the mentioned plasmon resonance modes, while in the case of bare SnO_2 NWs no enhancement is observed at any wavelength, confirming the plasmonic nature of the enhancement.

We explained the enhanced sensor response with an enhanced catalytic activity of the silver nanoparticles thanks to non-radiative decay of localized surface plasmon resonance.

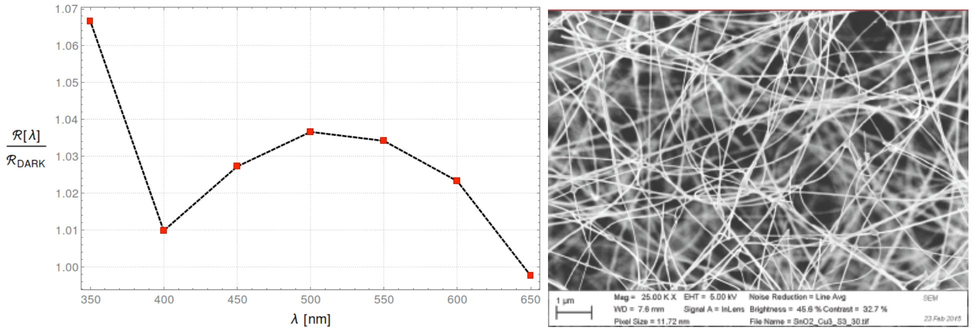

Figure 1: (Left) Relative response of Ag decorated SnO_2 NWs sensor towards 500 ppm of H_2. (Right) SEM image of SnO_2 bundle of NW.

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Self-organised flexible plasmonic arrays

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Rippled polydimethylsiloxane (PDMS) nanopatterned templates are formed by uniaxial wrinkling following air plasma treatment on pre-stretched samples. PDMS ondulations with height to width aspect ratios in the range of 1, remarkable long range order and periodicity from 300 nm to above one micrometer are so achieved.

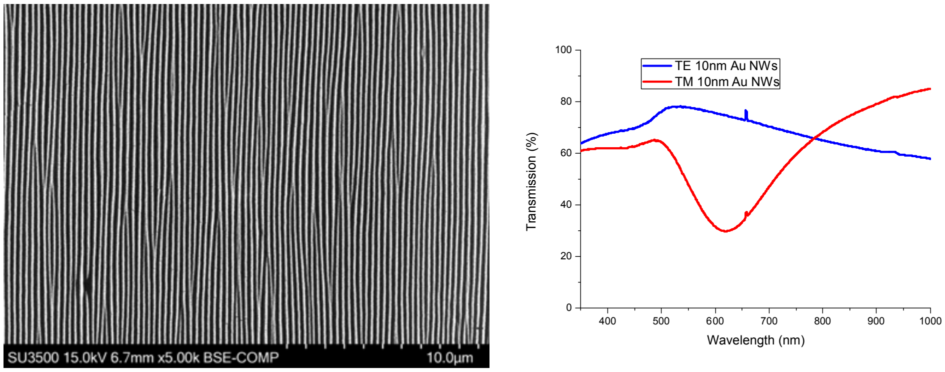

Figure 1 (a) SEM image in backscattering representing the Au NWs supported on PDMS nanoripples (scale bar 10 micrometers). (b) Optical extinction spectra of polarised light for polarization parallel (TE) and perpendicular (TM) to the NW axis.

The uniaxial PDMS modulations represent a natural platform for the confinement of plasmonic nanostructures when thermal deposition of Au is performed at grazing incidence. In this way Au nanowire arrays (NWs) endowed with monodisperse width distribution and length exceeding several tenths of micrometers are formed (Figure 1a). The NWs exhibit a strongly dichroic optical response due to the excitation of Localized Surface Plasmon Resonance (LSPR) when light is polarized orthogonal to their axis. The resonant wavelength can be tuned across the VIS-NIR spectral region by acting on the NWs width (140-250nm) and on the periodicity and aspect ratio of the flexible PDMS template. For light polarization parallel to the NWs axis, the optical spectrum is instead analogous to that of a continuous film, thus conferring to the NW array the performance of an IR wire grid polarizer (Figure 1b).

The tunability of the LSPR response can be exploited in order to match the pump laser in plasmon-enhanced spectroscopies. Test measurements demonstrate e.g. that Raman-SERS enhancement factors above 10^4 are easily achieved .

Also relevant is performance of the NWs as flexible conductive electrodes with sheet resistances in the range of 10-20 Ohm sq. the use of Au/PDMS nanowire arrays as flexible transparent electrodes.

n-type Ge-on-Si epilayers for mid-IR plasmonics with active doping above 10^{20} cm^{-3}

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Heavily-doped semiconductors have been proposed as a promising way to obtain high-quality and tunable plasmonic materials in the mid-infrared. Among them, Ge is very attractive for its compatibility with standard silicon foundry processes [1,2]. In order to cover the whole relevant mid-infrared fingerprint region, it would be desirable to obtain Ge epilayers with a doping density exceeding 10^{20} cm^{-3}. However, plasmonic devices require significantly thicker heterolayers with uniform doping compared to Ohmic contacts in CMOS and bipolar processes. Moreover, even higher activated doping densities well above 10^{20} cm^{-3} are required to cover the gas sensing window of 3 to 5 μm wavelength. The active doping in phosphorous-doped Ge is usually limited to 2-5 × 10^{19} cm^{-3} because the dopants tend to form neutral complexes with vacancies. In this work, we demonstrate plasma frequencies up to about 2700 cm^{-1} (3.7 μm wavelength) by exploiting post-growth laser thermal annealing (LTA) techniques to achieve full activation of the incorporated dopants. The samples are grown by low-energy plasma-enhanced chemical vapour deposition [3] on Si(001) substrates and consist of a ~ 600 nm thick Ge layer deposited at 450 °C at a rate of 1 nm/s with a GeH_4 flux of 20 sccm. The doping was obtained by adding PH_3 during the deposition. After the growth, the samples were treated by laser thermal annealing with a XeCl laser (λ = 308 nm, 160 ns pulse duration). The incorporated and activated doping densities have been measured by secondary ion mass spectrometry and Fourier-transformed IR spectroscopy, respectively. The as-grown material has an incorporated dopant density well above 10^{20} cm^{-3}, while the activated doping density is limited to about 2.5 × 10^{19} cm^{-3} (Fig. 1). After the annealing, the plasma edge of the material moves to higher frequencies up to about 2700 cm^{-1} (3.7 μm wavelength), which paves the way towards high-quality localized plasmon resonances over the whole mid-IR spectral window, thus merging plasmonic enhancement with the integrability and processability of semiconductor technologies.

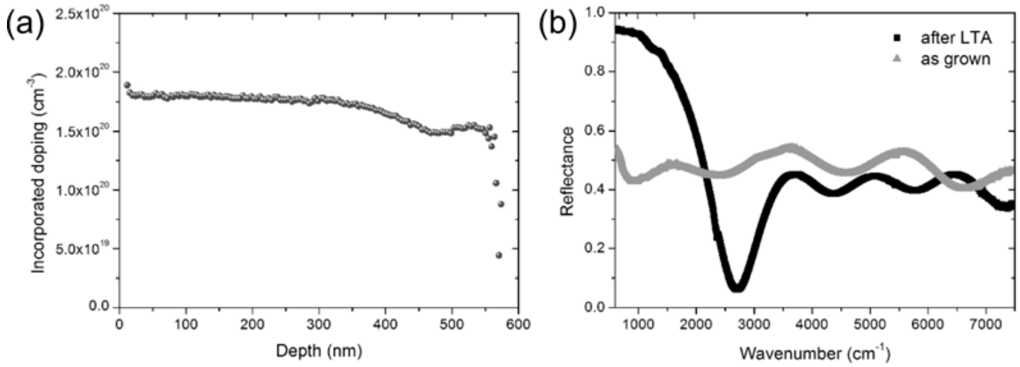

Figure 1: (a) incorporated dopants; (b) reflectance for the as-grown (grey) and annealed (black) samples.

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Tuning the optical properties of hybrid bio-plasmonic colloids

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The interaction of gold nanoparticles (AuNps) with the electromagnetic radiation is characterized by a resonant absorption in the visible spectral range, the Localized Surface Plasmon Resonance (LSPR). The dependence of the LSPR frequency on the AuNps size and shape, and on the dielectric constant of the environment, provides high versatility in the design of novel systems with the desired optical properties [1]. In particular, hybrid systems made up of AuNps conjugated with biomolecules exploit the synergic interaction between the plasmonic and the biological components, exhibiting enormous potential for nano-medicine and nano-biotechnology applications [2,3].

In this context, we studied the electrostatic adsorption of a globular protein on anionic AuNps and the colloidal aggregation in solution, subsequently induced by patch-charge interactions [4]. Lysozyme was employed to this aim: its robustness and structural stability within a wide range of environmental conditions make it suitable for our study, while, due to the high isoelectric point (pH 11.35), its positive charge allows to obtain stable aggregates at physiological pH. Furthermore, the employment of a functional protein as mediator of the aggregation let us exploit the specific interaction to the targeting ligand of the enzyme, besides the nonspecific ones which stabilize the aggregates.

Our work focused on the plasmonic properties of the system and the possibility to manipulate them, acting on the different degrees of freedom involved in the process [5]. The aggregation was characterized measuring the size and the surface charge of the aggregates by photo-correlation techniques supported by atomic force microscopy, while their LSPR was monitored by UV-Visible absorption spectroscopy. The catalytic activity of lysozyme confined in the clusters was also assayed. We investigated the effects of AuNps size and lysozyme-AuNps relative molar ratio and pointed out the conditions to obtain bio-plasmonic assemblies with the desired finite size (within few hundred nanometers), exhibiting colloidal stability. Correspondingly, it is possible to tune the plasmonic response of the system, which reflects the morphology of the formed clusters. In particular, the LSPR of the system can be selected within a large range of frequencies from visible to near-infrared spectral region (see figure 1), the latter suitable for *in vivo* applications. Moreover, the role of pH was investigated both as trigger for the lysozyme enzymatic activity and to modulate the protein net charge. Experiments, performed at different pH of the solution and supported by visual molecular dynamics simulations of the correspondent lysozyme charge distribution, showed the possibility to further handle the protein-AuNp interaction and in turn the morphology and the optical properties of the system. Noteworthy, we demonstrated the possibility to switch between aggregation and disaggregation of the formed clusters by changing the pH of the solution.

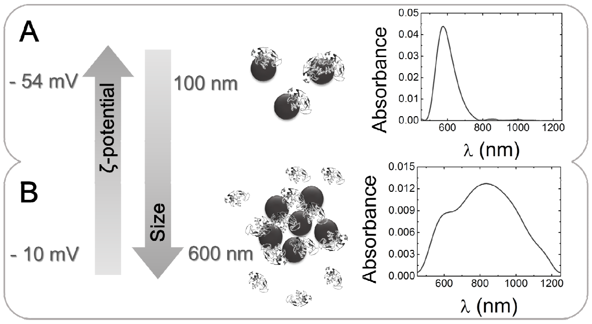

Figure 1: Scheme of the aggregation at increasing lysozyme-AuNps molar ratio, mediated by patch-charge interactions; representative absorption spectra of single AuNps (A) and clusters (B) are shown on the right.

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Resonant Gain Singularities in Hyperbolic Metamaterials

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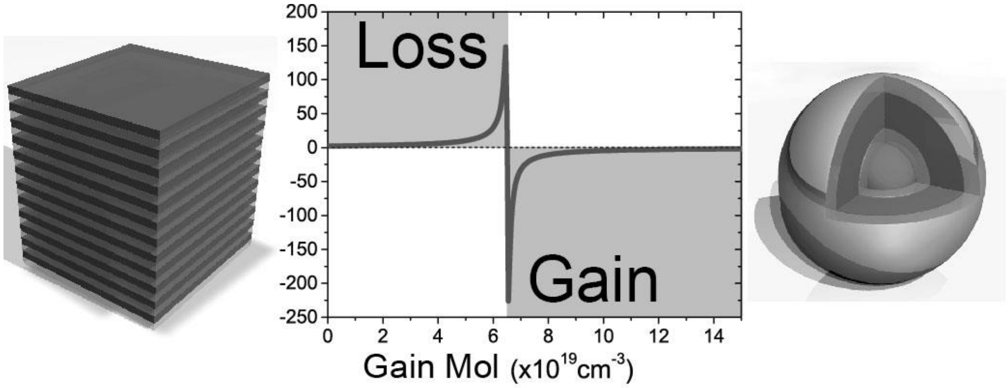
We present a detailed study on the *resonant gain* (RG) phenomenon occurring in metal/dielectric ultra-anisotropic subwavelength nanostructures, in which the simultaneous presence of a zero and a pole in, respectively, the in plane and out of plane dielectric permittivity, induces a huge amplification of the emitted photons resonantly interacting with the system. The presence of gain molecules in the considered nanoresonator systems makes it possible to obtain optical features that are able to unlock several applications. A specific hyperbolic metamaterial[1] (HMM) has been designed in the framework of the effective medium theory, in order to behave as an epsilon-near-zero-and-pole metamaterial,[2] showing extraordinary light confinement and collimation. Such a peculiarity represents the key to lead to a RG behavior, a condition in which the system is demonstrated to behave as a self-amplifying perfect lens. Very high enhancement and spectral sharpness of 1 nm of the emitted light are demonstrated by means of a transfer matrix method simulation. Finite element method-based simulations, together with an analytical model, clarify the electric field distribution inside the RG-HMM.[3] Counterintuitively, exceeding the resonant gain amount of molecules in both systems causes a significant drop in the amplitude of the resonance. Such a system configures as the ideal candidate for *Self-Amplifying.Perfect-Lenses*, capable of super-resolution and amplification of the signal at the same time and for *HMM self-collimater LASER*.



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Infrared detection of Plasmon-Polaritons in the two-dimensional electron system at the LAO/STO interface

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The metallic layer at the interface between a $LaAlO_3$ thin film and a $SrTiO_3$ substrate (LAO/STO) is known to host a two-dimensional electron system (2DES) when the LAO thickness is larger than four unit cells. It forms spontaneously due to the electronic reconstruction at the interface caused by the "polar catastrophe" which would occur by stacking negatively charged AlO_2 layers and positively charged LaO layers, even if this self-doping mechanism may be obscured by extrinsic doping caused by oxygen non-stoichiometry. Even if the conducting state at the LAO/STO interface has been characterized by numerous transport and magnetic measurements, the low-energy electrodynamics of the 2DES has been the object of very few experiments [1,2].

In the preset work we have repeated on the LAO/STO 2DES an experiment that some of us had previously and successfully performed on the 2DES which forms spontaneously at the surface of a Topologica Insulator (TI). This experiment [3] allowed us to detect the plasmon-polariton (PP) of the 2DES and to reconstruct its dispersion relation E(k) by using different samples with the surface patterned in form of parallel stripes of decreasing (micrometric) width. As the PP is confined within the metallic stripes, separated by the insulating ones, its wavevector k is exactly defined and suitable to match the E,k conservation law with the incoming photon.

The LAO/STO grown and patterned in form of stripes at the Chalmers University of Gothenburg has been measured at Sapienza University of Rome and at the SOLEIL synchrotron in Paris. A first set of samples, with micrometric stripes, has not shown the PP absorption due to the overwhelming absorption of STO phonons in the Terahertz range. New samples with sub-micrometric widths (100 and 200 nm) have therefore been prepared to displace the PP absorption towards higher frequencies, and SRO/STO striped samples have also been prepared for comparison with a conventional ultrathin metal. The encouraging results thus obtained will be shown and discussed in our poster.

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Thermophilic rearrangement of bio-plasmonic aggregates: morphological and plasmonic related evidences

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The peculiar interaction of metallic nanoparticles with the electromagnetic radiation paved the way to design novel nano-architectures whose optical properties can be tuned by controlling their structure and the features of the surrounding environment [1]. The research of the last few years heads up to the idea of creating hybrid assemblies made up of metallic nanoparticles and biomolecules with promising applications in the field of nano-medicine and nano-biotechnology, providing a new and powerful tool for innovative diagnosis and therapeutical approaches [2-4]. We recently developed a bio-plasmonic system based on the colloidal aggregation in solution of anionic gold nanoparticles (AuNPs) mediated by lysozyme [5]. The aggregation is driven by patch-charge interactions [6], induced by the adsorption of the positively charged protein on the AuNPs surface. We demonstrated that the optical properties of the system can be tuned through the clusters morphology, acting on several parameters such as the AuNPs size, the Lysozyme-AuNPs relative molar ratio and the pH of the solution.

Proceeding from these, here we would consider also the role of the temperature as a further tool to fine tuning the structural morphology together with the plasmonic properties of the aggregates. In this framework, the thermally enhanced diffusion of the NPs within the clusters can affect aggregate stability and shape, and thereby the own plasmonic profiles. On the other hand, the unfolding of the protein, induced by the increasing temperature and its consequent relaxation on the AuNps surface [7], implies a redistribution of the surface charge, together with an increase of the hydrophobic interactions. Lysozyme unfolding can thus be employed to change the nature of the interaction which holds the aggregates, switching from electrostatic to hydrophobic. As a first step in this direction we undertook a combined study of the temperature effects on the localized surface plasmon resonance and on the size of preformed Lysozyme-NPs aggregates.
The plasmonic profile and the related inter-particles plasmonic bands which arise due to the NPs aggregation were monitored by UV-Visible Absorption Spectroscopy at varying the temperature from 20°C to 90°C, while information on the aggregates size has been obtained by Dynamic Light Scattering experiments. The combination of these techniques allowed us to disentangle the two abovementioned aspects, which can interplay in the stability of the clusters, leading to their disaggregation or resulting in the cluster reorganization, depending on the Lysozyme-AuNPs relative molar ratio. It is well known that the localised heating can be also induced by the plasmonic absorption, hence our work sets the foundations to realize a “thermo-plasmonic based annealing”.

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Plasmonic Effects and Localized Melting in Self-Assembled Dye-Stabilized Gold Nanoparticle Systems

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Metal nanoparticles (NPs) exhibit many fascinating properties which are widely exploited for applications in different fields, such as surface enhanced Raman spectroscopy [1], biosensors [2], biomedicine [3], and biodiagnostics to name but a few. Many of these applications are based on the NPs' remarkable property of strongly enhancing the local electromagnetic near–field and this, together with the effect of the LSPR (Localised Surface Plasmon Resonance), can lead to light absorption and scattering of NPs to be extremely intense. Controlling the plasmonic response of NPs and metal nanostructures is the first step to exploit the features of the plasmon resonance that are central to many of the above mentioned applications. This has led to the synthesis of a plethora of shapes of metal NPs such as rod, prisms, stars, cages, core shell and more, with plasmonic responses ranging from the visible to the IR. Another important way to control the plasmonic resonance of the system is to take advantage of the interaction between closely spaced NPs which lead to a coupling of their plasmonic response [4,5]. This can be described in terms of a hybridisation model that leads to strong changes in the frequency of the LSPR. In the case of linear structures the LSPR splits into two contributions generated when the polarization of the electromagnetic field is perpendicular to the inter-axis of the NP 'chain' (blue shift – transverse plasmon) and when the polarization is aligned along the axis (red shift – extended plasmon). The precise spectral energy and shape of the extended plasmon resonance depend on the inter-particle distance, the particle disposition and the number of particles involved. Extremely precise control has been gained over the gaps between NP dimers by means of chemical synthesis and the use of linker molecules which can be carefully tailored to change the gap size [6]. Moreover the LSPR can be used to monitor shape and morphology of functionalized metal NPs during synthesis/modification processes.

In this work [7] we present the ultra-fast transient absorption characterization of AuNPs stabilized by Rhodamine B Isothiocyanate [8,9], studying how the self-assembled nanostructures and the NP-NP interactions in solution can affect the time-resolved response of the LSPR following photoexcitation at low intensities (< 100 μJ/cm^2). On the other hand, the interaction of more intense light (> 1 mJ/cm^2) with the NPs can lead to the "melting" of the NP systems, modifying their morphology by reshaping spherical NPs into nanorods, nanotriangles or larger nanospheres. Therefore, we have studied how to take advantage of the extended plasmon resonance to control the morphology of the melted nanostructures by irradiating the system at different wavelengths allowing us to selectively excite self-assembled NP chains of different lengths.

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Optimization of plasmonic metal-elastomer nanostructures for Surface Enhanced Raman Scattering

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Surface enhanced Raman scattering (SERS) is one of the leading label-free techniques in the field of biosensing, because of its great sensitivity that can reach the single molecule detection [1]. This key feature is due to the presence of plasmonic nanostructures that increase the Raman signal coming from the nearby molecules. To fully exploit this potential for biomedical applications, there is a constant evolution of the SERS substrates. Recently, the fabrication of plasmonic nanostructures constituted by Ag nanoparticles (NPs) on flexible elastomeric polydimethylsiloxane (PDMS) matrices has been reported [2,3]. These substrates, whose plasmonic properties can be finely tuned, can potentially fulfill the need for flexible/wearable biosensors. Unfortunately, the poor compatibility of these systems with biological buffers limits their practical bio-application. In particular, the Ag NPs deposited by sputtering tend to detach from the surface and aggregate when exposed to water and salt-based buffers, reducing the SERS efficiency [4]. In this work, in order to fix the silver NPs on the PDMS substrate, two different strategies were investigated. The first one consisted in the chemical functionalization of the PDMS surface before sputtering, whereas, the second involved the direct *in situ* synthesis of the NPs by using the residual Pt-catalyst of the curing agent. For this last, different parameters, such as the prepolymer to curing agent ratio, temperature of incubation, PDMS thickness, and the presence of ethanol were evaluated in order to identify the optimal synthesis conditions. All the samples were characterized by means of FESEM imaging and spectrophotometric analyses. Finally, the efficiency of the plasmonic nanostructures has been evaluated by checking the detection of low-concentrated solutions of Rhodamine 6G (R6G) in SERS regime. Among the functionalized samples, the one modified by 3-mercaptopropyltrimethoxysilane (MPTMS) gave the best results in terms of retention of NPs spatial arrangement, even after its incubation in Tris-EDTA buffer containing 1M NaCl, as assessed by spectral transmittance analyses (Fig.1a). The plasmonic dips remained almost unaffected before and after the incubation. The best results of the *in situ* synthesis were obtained by the incubation of the PDMS (3:1) in aqueous $AgNO_3$ solution at 30 °C for 48 hours. The related NPs showed an average size of ~50 nm (Fig.1b) and allowed the detection of R6G at 10^{-14} M (Fig.1c). Moreover, this sample was effectively used as silvered flexible substrate for the in-liquid transfer of a CVD-grown single layer graphene (SLG), in view of a future exploitation of the extra SERS chemical enhancement provided by the presence of SLG (Fig.1c,d).

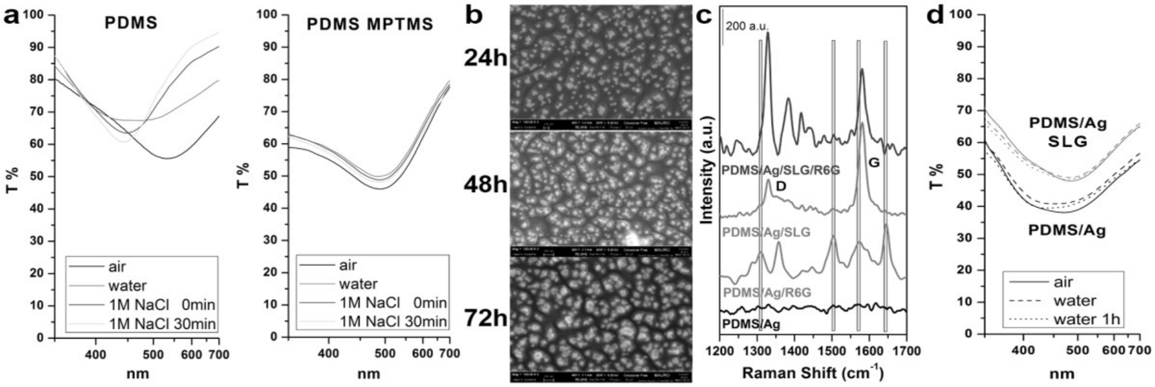

Figure 1: a) Transmittance spectra of PDMS (left) and PDMS-MPTMS (right) Ag NPs substrates incubated in different buffers. b) FESEM imaging of NPs synthetized *in situ* on PDMS (3:1) at 30 °C over time. c) SERS detection of 10^{-14} M R6G with the *in situ* synthesized Ag/PDMS and PDMS/SLG/Ag. d) Transmittance spectra of silvered PDMS before and after the SLG transfer in air, water and after 1h incubation in water.

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Nano-infrared photo-expansion spectroscopy of phonon-polaritons in few-layer h-BN

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Hexagonal boron nitride (h-BN) is a layered polar van der Waals crystal that sustains hyperbolic phonon polaritons (PhPs) [1]. Scanning probe near-field optical microscopy (SNOM) technique is having an exceptional impact for study the dispersion relation in h-BN by both launching and observing hyperbolic phonon-polaritons within the Reststrahlen band, i.e. the frequency region in which is negative the real part of the in-plane permittivity $\mathrm{Re}(\varepsilon_{\parallel})$ (lower Reststrahlen band, 760-825 cm^{-1}) or that of out-of-plane permittivity $\mathrm{Re}(\varepsilon_{\perp})$ (upper Reststrahlen band, 1360-1614 cm^{-1}) [2]. The great interest in such material is also justified by the easiness to prepare single-crystalline layers by mechanical exfoliation [3].

The aim of this work is to observe phonon-polaritons waves in h-BN using AFM mechanical detection (based on photo-thermal effect) to probe the absorption at mid-IR frequencies. Indeed, by monitoring the cantilever deflection as the wavelength of the laser is scanned, we obtain the absorption spectrum of the portion of sample below the tip. Alternatively, we can get absorption map by scanning the sample setting a single frequency [4]. The setup employed consists in a mid-IR tunable quantum cascade laser (900 cm^{-1}-1900 cm^{-1}), working in pulse mode, coupled to the AFM head from Anasys.

Here we study a sample consisting in few layer of h-BN in solution, deposited on Au substrate. The AFM tip, also gold coated, works as an optical antenna and provides the energy and the momentum required for launching polaritonic waves. Thanks to the strong field confinement between tip and substrate and the mechanical resonantly-enhanced detection scheme, we were able to measure the absorption spectra of several samples with thickness ranging from 4 nm up to 40 nm, confirming results obtained on thicker, nanofabricated samples [5].

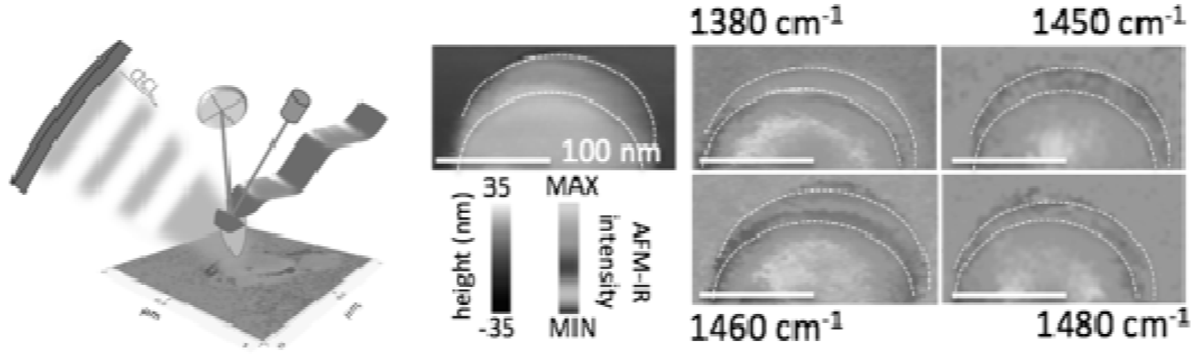

Figure 1: (left) Sketch of the AFM tip-laser coupling on a nanometer sample; (right) Topography and AFM-IR absorption maps taken at 1380 cm^{-1}, 1450 cm^{-1}, 1460 cm^{-1} and 1480 cm^{-1} on a 26 nm thick flake of hBN.

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2D and 3D Plasmonic nanostructures prepared by physical methods: modeling and functional characterization

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There is great interest in assembling gold nanoparticles (NPs) onto flat 2D substrates or suitable 3D structures for investigating Localized Surface Plasmon resonance (LSPR) based phenomena. The unique optical properties of metal nanostructures, that are absent in the bulk or flat surfaces, give rise to intense absorption bands, with their intensity and position depending markedly on the size, shape, distribution and on the refractive index of the environment surrounding the nanoparticles, as predicted by Mie Theory. These properties makes the metal nanostructured interfaces suitable transducers for gas or bio-sensing applications.

The use of LSPR based phenomena for chemical and biological sensing is of special interest, because it allows the label-free detection of extremely small concentrations of target molecules. Due to relatively short (≈ 30 nm) electromagnetic field decay length of the metallic nanoparticles, their surface sensitivity is much higher , in comparison to that of flat SPR sensors, using thin metallic films as transducers [1].

In this work, the results achieved in the preparation of suitable plasmonic transducers by physical methodologies are presented. In particular, the different strategies adopted for the realization of a distribution of Au NPs over large areas of flat glass substrates or 3D silica nanowires prepared onto quarts support with physical preparation techniques like de-wetting and pulsed laser deposition are presented. Optical properties of the realized nanostructures are related to their shape and distribution both in a two-dimensional and three dimensional configuration. A modelling of these architecture is also presented supported by morphological and structural information, will help to predict and realize a proper design of the investigated materials tailored on the nanoscale. Optical and morphological properties will be correlated with functional properties of the realized nanostructures by showing how they can be used as a proper transducers for optical sensors.

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Silver Nanoplatelets : a promising dual SPR-SERS substrate for plasmonic sensing

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Metal nanoparticles possess intriguing chemical and physical properties that can be exploited for advanced applications in different fields [1]: among them sensing is one of the most promising since plasmon resonance strongly enhances system sensitivity. Bottom up syntheses combined to surface functionalization strategies allow for design and build up highly sensitive, optically stable and biocompatible metal nanoparticles to be used for detection of low concentrations (< nM) biomolecules in aqueous media. [2]. Herein, we demonstrate the successful use of silver nanoplatelets in proteomics and, in particular, their ability to detect two amyloidogenic proteins (Human Islet Amyloid Polypeptide and Beta Amylin) at nanomolar concentration. The used synthetic strategy is based on the combination of selective ligands adhesion and seeded growth. [3] resulting in tunable plasmon resonance associated to controllable geometrical features, as reported in figure.

Silver nanoplatelets are stable in aqueous solution and show enhanced plasmon resonance as well as Surface Enhanced Raman (SER) effect. The plasmonic features have been tested by evaluating related figure of merits (FOM) and dipole sensitivity [4], while SER effect has been studied using different analytes down to nanomolar concentrations.

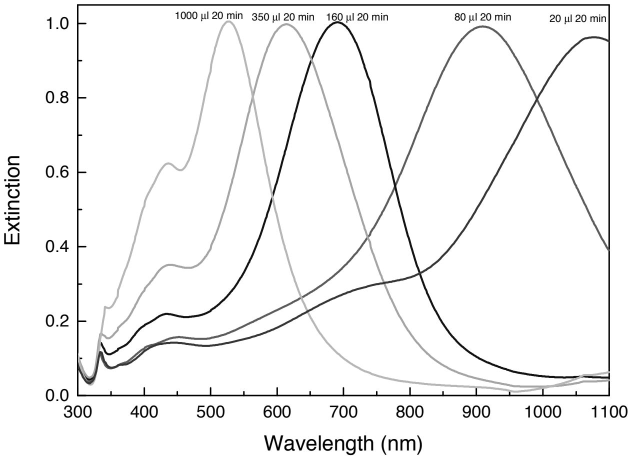

Figure 1: Tunable surface plasom resonance of silver nanoplatelets upon varying growth conditions.

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Nanoscale Study of the Tarnishing Process in Silver Nanoparticles

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Silver is the ideal material for plasmonics because of its low loss at optical frequencies, though is often replaced by a lossier metal, gold. This is because of silver tendency to tarnish, an effect which is enhanced at the nanoscale due to the large surface-to-volume ratio. Despite chemical tarnishing of Ag nanoparticles (NPs) has been extensively studied for decades, it has not well been understood whether resulted by sulfidation [1] or oxidation processes [2,3].

This intriguing quest is herein rationalized by studying the atmospheric corrosion of electron beam lithography-fabricated Ag NPs, through nanoscale investigation performed by high-resolution transmission electron microscopy (HRTEM) combined with electron energy loss (EEL) and energy dispersive X-ray (EDX) spectroscopies.

We demonstrate that tarnishing of Ag NPs upon exposure to indoor air of an environment located inside a rural site, not particularly influenced by naturally and human-made sulfur sources, is caused by chemisorbed sulfur-based contaminants rather than via an oxidation process. Furthermore, we show that the sulfidation occurs through the formation of crystalline Ag_2S bumps onto Ag surface in place of a homogenous growth of a silver sulfide film. From a single 2D Z-contrast scanning transmission electron microscopy (STEM) image, a method for 3D reconstruction of silver nanoparticles with extremely high spatial resolution has been derived thus establishing the preferential nucleation of Ag_2S bumps in proximity of lattice defects located on the NP surface (Fig. 1). Finally, we also provide a straightforward and low-cost solution to achieve stable Ag NPs by passivating them with a self-assembled monolayer of hexanethiols. The sulfidation mechanism inhibition allows to prevent the increased material damping and scattering losses.

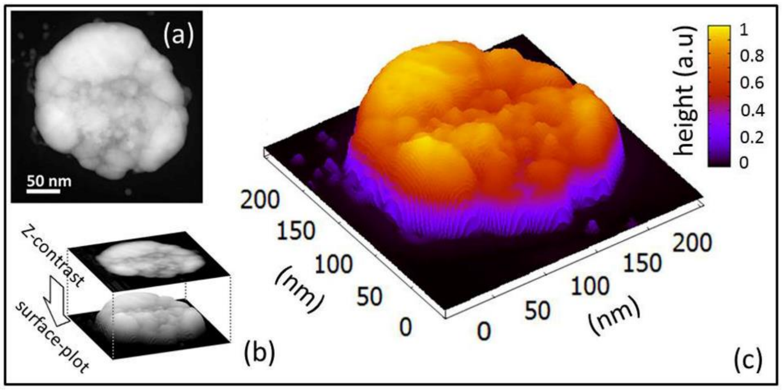

Figure 1: (a) Z-contrast STEM image of single Ag ND (48 hours of exposure to air at ambient conditions). (b) 3D reconstruction method of a silver nanodisk from the intensity variation of 2D Z-contrast STEM image reported in panel a. (c) Temperature scale palette 3D surface plot showing ND morphology including Ag_2S bumps in proximity of silver grain boundaries.

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Numerical analysis and characterization of photothermal effects in colloidal plasmonic nanoparticles

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Strong local absorption in plasmonic nanoparticles leads to a temperature increase, that is usually avoided in pure photonic applications, or at most exploited for modulation, according to thermo-optic effect [1]. Recently, the temperature increase in metal nanoparticles (NPs) has been exploited in nanomedicine science as nanosurgery tool, local thermal assisted drugs delivery systems or in cancer therapy [2-4]. In these cases, a nanoheater source with a remote control is obtained by irradiating plasmonic NP solutions at their resonance frequency [5]. In this work, we analyze thermodynamics computing of temperature profiles inside and outside plasmonic structures under illumination. In particular, photoinduced temperature increasing of a single nanosphere and a single nanorod suspended in water and clusters of NPs in colloidal water solution have been investigated.

Moreover, preliminary experimental thermodynamical characterization of a colloidal NP solution lit up at plasmonic resonance frequency has been performed exploiting the temperature dependence of quartz piezoelectric resonance. In this case, the mechanical resonance of a vibrating piezoelectric quartz crystal has been measured by means of a quartz crystals microbalance by varying the temperature and then after has been related to optical irradiation of a NP solution.

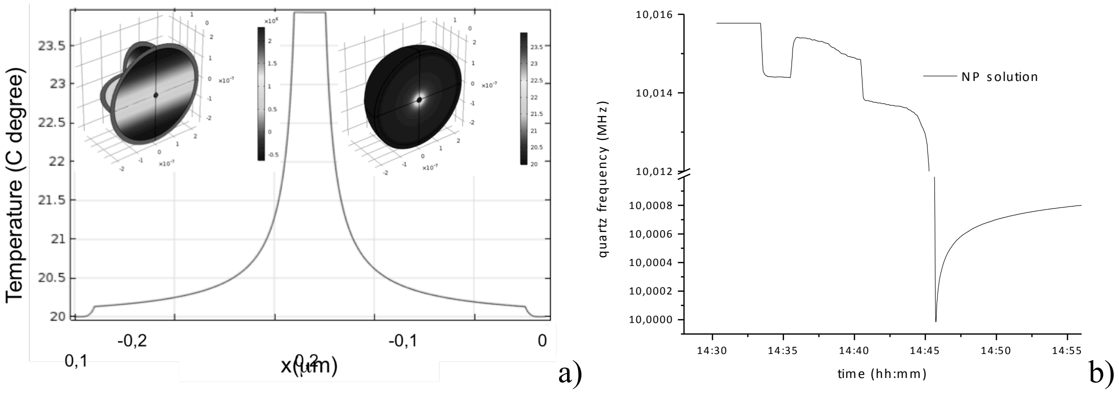

Figure 1: a) Photoinduced temperature increasing of a single spherical nanoparticle; the electromagnetic field and the themperature distribution are in the captions. b) Photoinduced frequency increasing of quartz resonance in presence of nanoparticles solution

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Inverse Identification of the Optical Properties of Hybrid Spherical Nanoparticles

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In this work, we present the inverse identification of the optical properties of a hybrid spherical gold nanoparticles with dicarboxylic polyethylene glycol (PEG) inclusions in a water colloidal solution. In particular, we estimated the value of PEG volume concentration that minimize the norm of the difference between theoretical and experimental absorption power spectra in the range 400-900 nm, exploiting a Genetic Algorithm Optimization (GAO). Gold nanoparticles have been synthesized by directly adding PEG during the synthesis process. Due to its chemical characteristic, PEG acted as a surfactant, but also as a stabilizer agent. The formation of the PEG-AuNPs was observed as an instantaneous color change of the solution from pale yellow to bright red [2]. In our previous work, we have demonstrated that PEG was inside and around the gold core of the nanoparticle.

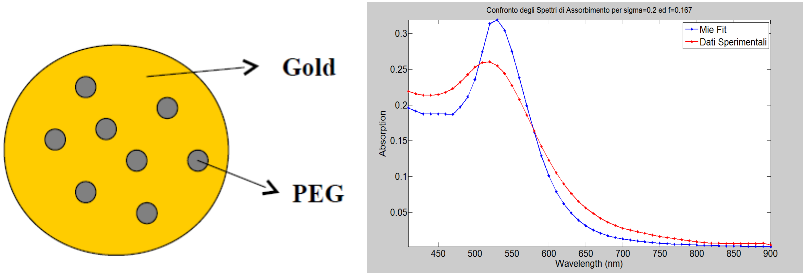

Figure 1: Comparison between he experimental (red curve) and theoretical calculated absorption (blue line) using the optimum volume concentration found by the Genetic Algorithm.

Absorption spectra were recorded using a Cary 100 (Agilent) Spectrophotometer in the 400-900 nm range. Since the size of the particles in solution was much smaller than the incident wavelength, the theoretical absorption spectrum has been obtained by using the Mie theory [1] in the electrostatic limit. The sphere permittivity $\varepsilon_{\text{eff}}(\omega)$ has been described by using the Maxwell-Garnett effective medium theory [1]

$$\varepsilon_{\text{eff}} = \varepsilon_{\text{Au}} \frac{2\delta_i(\varepsilon_i - \varepsilon_{\text{Au}}) + \varepsilon_i + 2\varepsilon_{\text{Au}}}{2\varepsilon_{\text{Au}} + \varepsilon_i - \delta_i(\varepsilon_{\text{Au}} - \varepsilon_i)},$$

where δ_i is the volume concentration of the inclusions, ε_{Au} is the gold permittivity [6], $\varepsilon_i = 1.468$ is the permittivity of the PEG inclusions.

In Figure 1, we show the comparison between the experimental (red curve) and theoretical calculated absorption (blue line) using the optimum volume concentration found by the GA.

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Origin of the chiral plasmonic behaviour in helix based “composite” metamaterials by FIBID

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Chiral metamaterials are a new class of metamaterials where a specific chiral geometry induces an optical response to the incident light field resulting from a mixture of electric and magnetic dipoles. This leads to many intriguing phenomena and applications, such as strong circular dichroism or optical rotatory dispersion, and provides interesting potential applications as broadband circular polarizers or to enhance the optical response of chiral molecules by superchiral light, offering also a simpler route to negative refraction

Here, we discuss the origin of plasmonic resonances1 in the composite carbon-platinum alloy nanohelices fabricated by deposition induced by focused ion beam (FIBID) shown in fig 1.

TEM analysis has shown that the Pt-nanohelix consists of Pt grains (average diameter 5nm) embedded in a carbon matrix1.

Mie theory2 predicts an absorptive resonance frequency for localized surface plasmon (LSP) from Pt nanoparticle (diameter 5nm) in vacuum at 210 nm, which redshifts up to 370 nm when considering the carboneous matrix matrix. Putting nanograins in strong proximity inside a nanocluster, collective interactions between plasmonic dipoles, induced by the small or null interparticle distance, are expected to broaden and redshift the plasmonic resonance.3 The assembly of the achiral Pt/C nanoclusters into a chiral fashion along the helical path (meta-atom) is expected to result into circular dichroism and optical activity.4,5

Moreover, plasmon hybridization takes place when multi meta-atoms are stacked along the helix axis, leading to the new mode generation and tailoring the chiro-optical properties of the nanostructures.6-8

Further technological evolution on the growth of 3D nanohelices lead us to controlling also complex intertwined chiral structures such as Triple-Helical Nanowires9,10, where the mutual coupling between surface plasmon modes, excited by incident light in individual helical nanowires arranged in close proximity (~100 nm), led to hybridization phenomena among the plasmon modes in all of the spatial directions (full 3D hybridization), broadening the region of circular dichroism selectivity in the transmission spectra (figure 1).

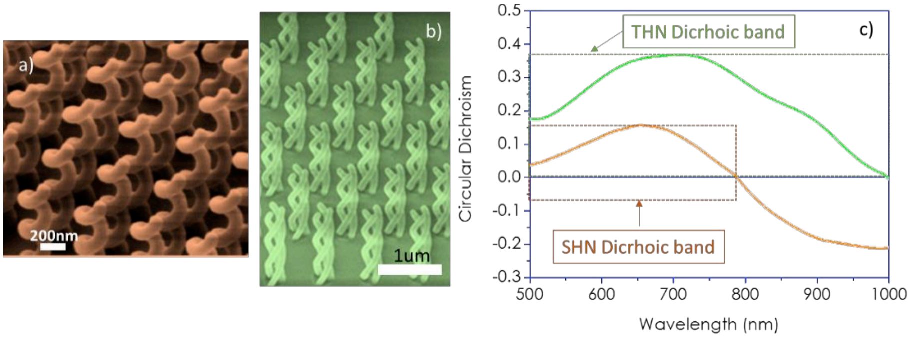

Figure 1. a) Single helix nanostructures, b) Triple helix based metamaterials, c) circular dichroism for single and triple nanohelix systems with highlighted dichroic band.

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Narrow and broad band terahertz transmission filters

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A great deal of scientific and research effort has been recently directed to the development of novel technologies for the terahertz (THz) spectrum, stimulated by the significant advances in THz sources and the numerous applications that span from short-range wireless communications to life-science, defense, and security [1]. The deployment of these technologies relies, among other, on the engineering of novel components for THz-wave manipulation, such as polarization control, phase or amplitude modulation, and filtering [2, 3].

A traditional component for THz passband filtering is based on cross-shaped frequency-selective surfaces (FSS) [4], which can be either free-standing or patterned on a dielectric substrate. The introduction of the polymer substrate induces guided-mode resonances (GMR), which appear at higher frequencies with respect to the FSS peak and show extremely narrow linewidths, with quality factors in some cases exceeding 100 [5,6]. Guided-mode resonances (GMR) manifest as narrow-linewidth transmission or reflection bands when waves diffracted from a grating couple to propagating modes in an adjacent dielectric substrate. Recently, such structures were proposed for the design of narrowband filters operating at terahertz (THz) frequencies, suitable for applications in telecommunications, radar science, or imaging [7].

Here, we investigate, both theoretically and experimentally, the properties terahertz filters based on metallic frequency-selective surfaces (FSS), as shown in Fig. 1(a), which are patterned via photolithography on thin films of the low-loss cyclo-olefin polymer Zeonor. Filters with very high quality factors are designed and their spectral response is studied under different conditions, such as oblique incidence, rotation of the polarization plane, and bent configurations. Contrary to the filtering response of standard free-standing FSS-THz filters, we observe extensive tunability of the GMR frequencies by means of mechanically rotation, as well their suppression by bending the flexible substrate, as demonstrated in Fig. 1(b). The fabrication cost of the filters is low and can be scaled to mass production processes.

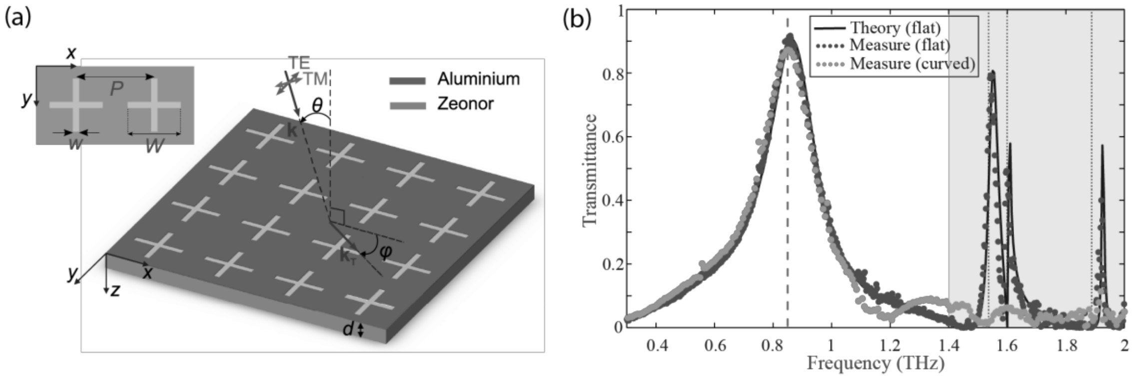

Figure 1: (a) Schematic layout of the investigated FSS-THz filter. (b) Filter power transmittance in both flat and bent configurations.

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Azobenzene photoisomerization in the strong coupling regime

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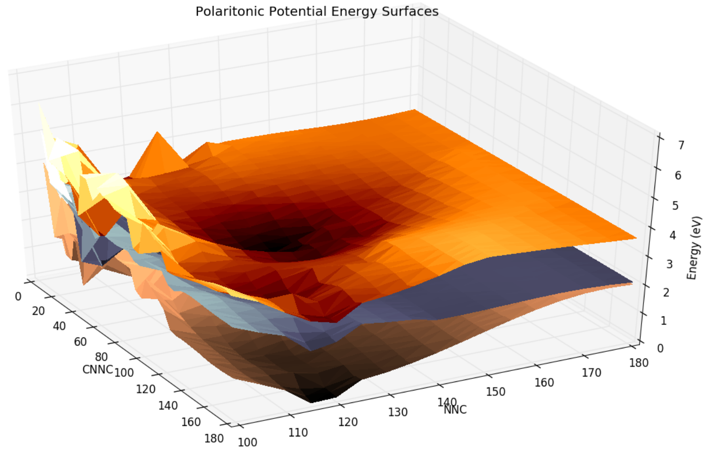
The experimental achievement of single-molecule strong coupling regime in nanocavities for organic molecules [1] has risen a deep interest in the theoretical comprehension of such phenomenon [2]. Such regime can be achieved as the resonant frequency of a cavity couple with the excited states of a molecule. Under this condition, the Rabi oscillations of a single molecule inside the cavity are much faster than the dissipation effects. Therefore, the coupling allows stable hybrid light-matter states to be formed (polaritonic states), together with a change in the shape of the bare molecule potential energy surfaces of the excited states. Various theoretical treatments on model molecules show the possibility to manipulate the nonadiabatic dynamics through cavity femtochemistry [3]. To this aim, we present the formation of polaritonic states of a photopolarizable molecule at different resonant energies. Such states are computed on the basis of an atomistic, quantum mechanical (CI) wavefunctions, specifically parametrized in the past for azobenzene [4],[5]. This approach guarantees a good compromise between accuracy and computational cost. We focus on the photochemical properties of azobenzene, retrieved through a direct trajectory surface hopping (DTSH) dynamics on these new hybrid-matter states. The results are then compared to the state-of-the-art literature references for the photochemistry of such molecule.



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Nanoporous Aluminum for UV plasmonic enhanced spectroscopy

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During the last decade, Localized surface plasmon resonances (LSPRs) have been explored extensively for their various technological applications such as surface-enhanced Raman spectroscopy (SERS), metal-enhanced fluorescence, plasmon enhanced light harvesting, and photocatalysis. [1-4] Up to now, plasmonics applications were mainly focused on the Ag and Au systems because of their optical properties. They can easily support surface plasmons in the visible and near-infrared (NIR) spectral range, but their application is limited down to 350nm due to the intrinsic properties of the metals. On the contrary, now there is increasing interest in extending the plasmonics down to UV and deep-UV (DUV) wavelengths. For instance, UV and DUV excitations can be utilized to extend the application of Raman spectroscopy to some biomolecules that have small Raman cross sections in the visible and NIR regions. [5] Unfortunately, interband transitions introduce a dissipative channel for Au and Ag plasmon resonances at wavelengths shorter than 550 and 350 nm, respectively. Aluminium (Al) has recently been suggested as promising plasmonic material in the UV and DUV regions because it has negative real part of dielectric function down to a wavelength of ≈100 nm. [6] The excellent optical properties of Al make it an excellent material for UV nanoantennas, [7] DUV SERS, [5,8] light emission enhancement of wide-bandgap semiconductors, [9] and improvement of light harvesting in solar cells. [10] Controllability of LSPR energies is highly required for plasmonic applications. For instance, DUV-SERS of adenine on Al nanostructures requires their resonance peaks close to the excitation wavelength to ensure high-electromagnetic nearfield enhancement. [5,8] Al NPs are generally designed with the help of electron beam lithography (EBL) and focused ion beam (FIB) lithography in order to obtain well-controlled structures. [7] However, these approaches involve a slow process and are not cost effective, so that they are not practical for large area (square cm) fabrication.

Porous metal films have recently attracted increasing interest due to the unique properties related to their very high specific surface area. While several examples of porous metal applications exist in the Vis / Infrared spectral regions, studies in the UV region have not been reported so far. Here we present the plasmonic properties of nanoporous aluminum prepared from a Ag/Al alloy by means of a challenging chemical dealloying procedure (Fig.1). The optical properties and the expected enhanced spectroscopy behaviors will be present.

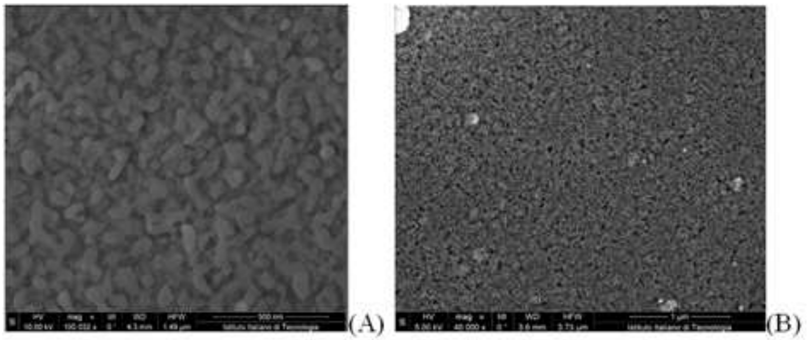

Fig. 1. SEM micrographs illustrating two different nanoporous Al films obtained under different dealloying conditions.

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Design and Optimization of a Plasmonic Grating to Enhance Silicon Photodetectors Performances in the Near-Infrared

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Silicon photomultipliers (SiPMs) have obtained a growing attention as an alternative to photomultiplier tubes in the detection of low photon fluxes, thanks to a number of advantages typical of solid state detectors such as compactness, ruggedness, ease of use, low operational voltage, insensitivity to magnetic fields.

Fondazione Bruno Kessler (FBK, Trento) has a well-established history of SiPM development and characterization, in particular for light detection from scintillators used in time-of-flight positron emission tomography, which typically ranges between the blue and the near-ultraviolet regions [1].

FBK now aims to develop new technologies with sensitivity peaked at higher wavelengths, towards the red and even near-infrared spectral region, in order to expand the photodetectors field of application.

These new devices could bring all the benefits of SiPM to microscopy techniques for biological applications, usually working with low photon signals and small S/N ratios, like Second and Third Harmonic Generation Microscopy (SHG, THG) and Stimulated Emission Depletion Nanoscopy (STED) [2-4]. However, shifting the sensitive range to the NIR is challenging, due to longer absorption depths and lower absorption coefficients of Si.

In order to overcome this problem, we propose an aluminum-based plasmonic grating working in the NIR range, which exploit Surface Plasmon Resonance to localize the field at the photodetector surface, therefore enhancing the absorption efficiency of NIR photons by several times.

We present design and optimization of this device by means of Finite Elements simulations (COMSOL Multiphysics®), by which we achieved the expected increased absorption efficiency, easily exceeding five times that of a standard SiPM.

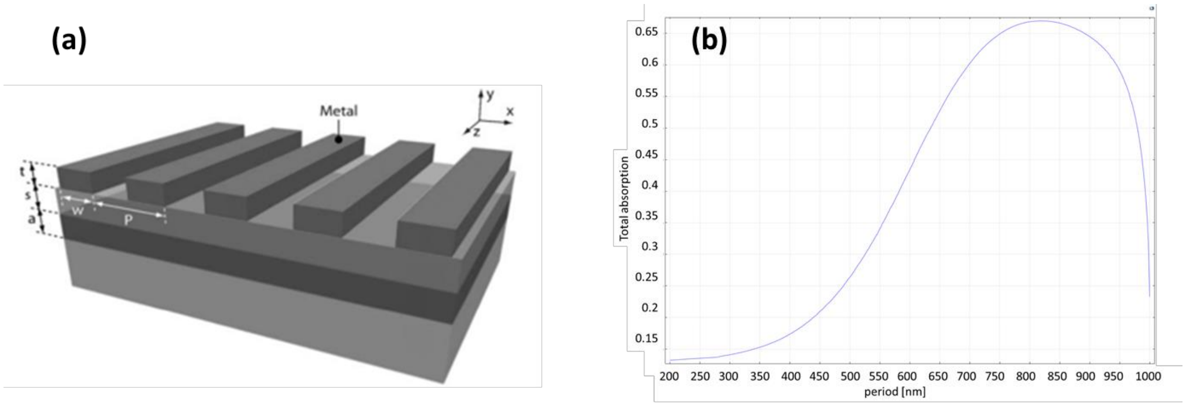

Fig. 1. **(a)** Scheme of the plasmonic-enhanced device. The gold slits are placed on an oxide/nitride spacer layer in order to optimize the distance between the slits and the detector active layer. **(b)** an optimization step, in which the total absorption by the structure is investigated as a function of the grating period.

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Plasmonic Dimers Analysis within Density Functional Tight Binding Method

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Electrodynamics methods have been proved to be useful and powerful tools to theoretically study localized and delocalized surface plasmons [1]. The recent progress achieved in fabrication techniques to control subnanometer structures and features has lead to search for more rigorous approaches able to theoretically describe nonlocality or the spill-out of conduction electrons, effects well visible in very narrow junctions or subnanometers gaps [2].

Standard atomistic ab-initio *Time-Dependent Density Functional Theory* (TD-DFT) is the most suitable approach for a complete quantum mechanical treatment of plasmons [3] but it becomes computationally unaffordable for particle sizes of several hundreds of atoms.

Here we alternatively propose a *Time-Dependent Density Functional Tight-Binding Method* (TD-DFTB) study [4] on silver dimers done using an optimized Slater-Koster parametrization. More in detail, we study the plasmonic response of dimers of closed-shell Ag_n (n=10, 20, 35, 56, 84 and 120) tetrahedral clusters (tip-to-tip configuration) as a function of the nanogap size (from 2 Å to 20 Å). Atom positions are fixed to the ones obtained by relaxing the isolated clusters within standard DFT (TURBOMOLE code) and geometries are re-optimized only for the smallest gaps (2 Å and 4 Å).

A red-shift in the plasmonic peak can be clearly seen in Fig. 1b by reducing the interparticle distance until 6 Å, this being due to the clusters mutual depolarization. For smaller distances, a blue-shift effect appears for these structures, this proving the onset of a quantum mechanical effect already evidenced in literature within other approaches [5]. Moreover, it should be noted as the coupling effects, both in the near-field and in the near-touching regimes, become more evident as the number of interacting atoms becomes larger (Fig. 1b). With a computational cost much smaller with respect to standard TD-DFT one, TD-DFTB seems thus to be a useful method to overcome the limits of classical description and thus to favor the spread of computational quantum plasmonics.

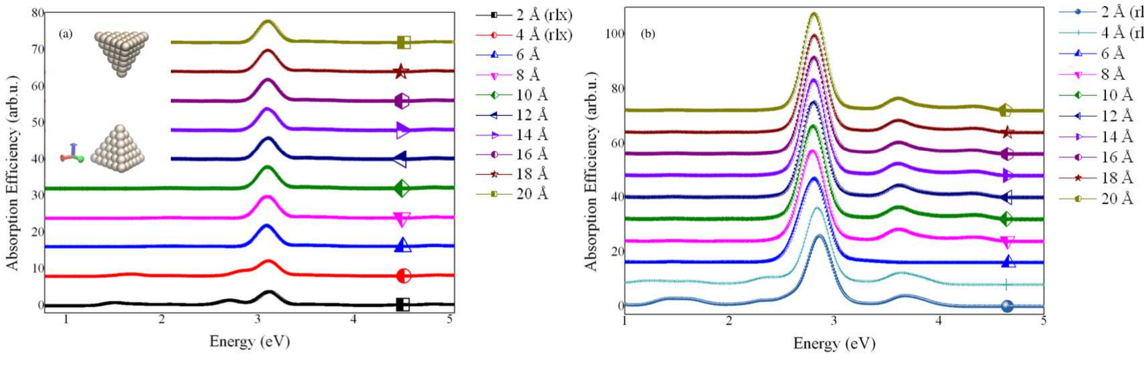

Figure 1: TD-DFTB efficiency calculated for dimers of tip-to-tip closed-shell Ag20 (a) and Ag120 tetrahedra (b). Separation gaps from 2 Å to 20 Å are analysed with the spectra reported from the bottom to top side of the panels, respectively. Geometries are sketched in the inset.

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Development of a multiphoton-multicolor and super-resolution STED microscope for in vivo experiments

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Two-photon excitation (2PE) microscopy [1] has proven an excellent technique for in vivo fluorescence imaging of deep structures and tissues due to low absorption and scattering of infrared light.

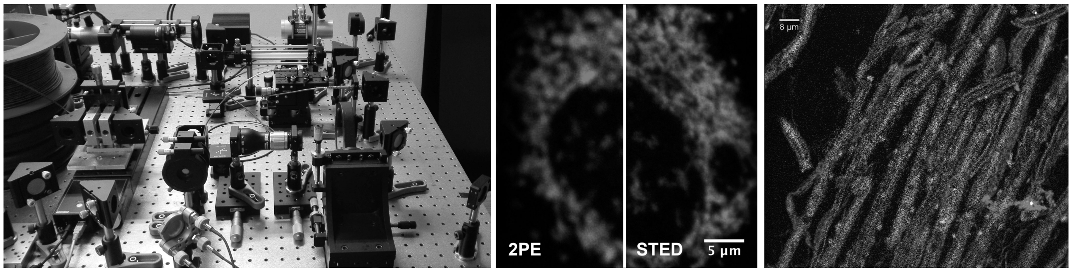
The combination of two laser beams introduces the possibility of further imaging capabilities, such as simultaneous excitation of three fluorophores at same time (multiphoton-multicolor [2]) or sub-diffraction resolution of cellular structures (Stimulated Emission Depletion, STED [3]).

Here we present a cost-effective solution that combines both techniques by use of a homemade optical bench equipped with a pulsed laser split into two beams by an Optical Parametric Oscillator (OPO).

Preliminary experiments were successfully performed with the multiphoton-multicolor technique, setting proper conditions to perform experiments for the study of neutrophil mobilization in skull bone marrow of diabetic mice.

In the STED configuration, we successfully tested the fluorescence depletion effect and the optical generation of a doughnut-shaped point-spread-function by the depletion laser, both conditions required to obtain super-resolution.

A preliminary super-resolution performance was obtained by visualizing the outer mitochondrial membrane stained with Alexa 647 dye



(**Left)** 2PE-STED microscope optical path; (**Center)** Super-resolution obtained in HeLa cells by visualizing TOMM20 mitochondrial protein stained with Alexa 647: A-B) whole HeLa cell image; **(Right)** Murine sciatic nerve. The myelin sheats are observed in third harmonic generation.

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Hybrid metal-dielectric nano-pillar array structures

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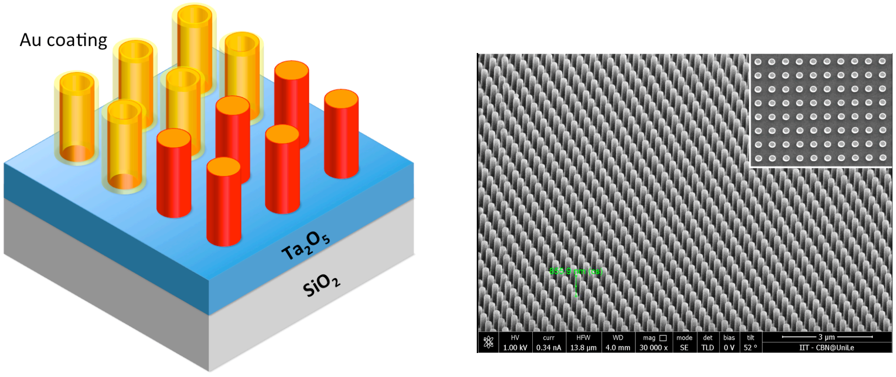
In this work, we propose an optimized nano-imprint protocol for the fabrication of a two-dimensional (2D) array of polymethyl-methacrylate (PMMA) nano-pillars deposited on a sputtered tantalum pentaoxide (Ta_2O_5) slab supported by a silicon dioxide (SiO_2) substrate. A sketch of the proposed device is shown in Figure 1(a). The sub-micron PMMA pillars were realized by using nano-imprint lithography (NIL). In order to optimize the NIL process, several tests were performed by varying temperature and pressure, allowing us to achieve uniform and high-resolution pillars. Figure 1(b) shows the SEM picture of the 2D array with PMMA pillars whose periodicity p is set equal to 450 nm. The master template used in the imprint process of the PMMA was made of Silicon substrate patterned with a 2.5 mm x 2.5 mm area of holes having the same geometrical parameters of the replicated 2D pillar array. The fabricated periodic array permitted to phase-match the incident plane wave and the guided discrete modes leading to the excitation of guided mode resonances (GMR) [1-2]. The optical response was investigated by means of numerical simulations carried out by means of DiffractMOD (RSoft) that implements the Rigorous Coupled-Wave Analysis (RCWA) method.
This platform was used as starting point to realize hybrid structure where the pillar were coated by means of both thick and thin gold layers as sketched in Figure 1(a).

The fabricated hybrid nano-pillars are mechanically stable and they can be fully exploited for the realization of novel metallic-dielectric core/shell structures for sensing, surface-enhanced Raman spectroscopy and light-matter interactions.



(a) (b)

Figure 1: (a) Sketch of the proposed device consisting of PMMA pillars realized on a Ta_2O_5 slab supported by a glass substrate without (right) and with (left) gold coating. (b) Bird's eye SEM picture of the fabricated PMMA nanostructures (p = 450 nm); (inset) in-plane detail of the 2D PMMA nano-pillar arrays.

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Investigation of Cell Membrane Dynamics by 3D Nanoplasmonic Electrodes

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Nanoscale electroporation of cell membrane by nanopillars finds promising applications such as intracellular drug delivery and intracellular recording of action potentials. Compared to conventional bulk electroporation, nanoscale electroporation exhibits low poration voltage and high cell viability.[1] On the other hand, the pore size and resealing time of the membrane on the nanopillars remain unclear, though they are critical to the applications. In bulk electroporation, such pore dynamics are usually studied by fluorescence microscopy of dye molecules transfected into the cell through pores. However, it can be hardly applied to the nanoscale electroporation because of fluorescence background from the nanopillar substrates and from the cells.[2] In this work, we used gold nanoantenna array as three-dimensional (3D) nanoplasmonic electrodes for *in-situ* probing the membrane dynamics by surface enhanced Raman spectroscopy (SERS) as well as for electroporating the membrane. The gold nanoantennas made of gold-coated vertical polymer nanotubes and were used as nanopillar electrodes. They exhibited strong electric field on their tips due to plasmonic resonance[3] that could enhance Raman scattering signals of molecular changes of the cell membrane attached on the antenna during the electroporation as shown in Figure 1 below.[4]

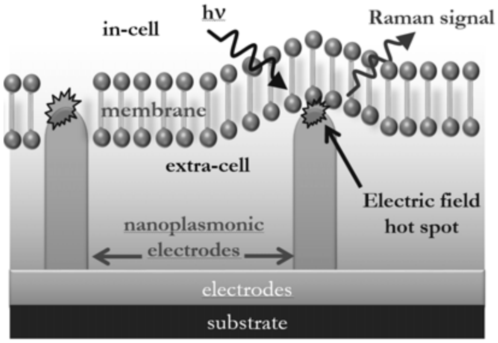

Figure 1. Sketch of the 3D nanoplasmonic electrods

The experiment was implemented by culturing cells on the nanoantenna substrate which was housed by a microfluidic chamber with one electrode connected to the nanoantenna and the grounding electrode being in the cell culture. The nanoantenna on which cells grew were excited by a 785 nm laser at a backscattering setup of a Raman spectrometer and the SERS spectra were collected by a water-immersion objective focusing on the nanoantenna tip where the membrane was attached. Each SERS collections lasted for 30 minutes during which the electroporation was carried out 10 minutes after collection start by applying pulse voltages of 0.5 - 4.5 V to the nanoantenna for 10 seconds.

In analyzing the time-resolve changes of SERS peak intensity and shift, we found that, during the electroporation at voltages no less than 3 V, intensity drop of SERS baseline was due to membrane moved off the nanoantenna. It could be related to microbubbles generated during the electroporation. Peak shift of phospholipids because of changes of phosphorlipid molecule orientation with respect to the electric field suggested pore opening and closing.[5] More importantly, the intensities of both phosphorlipid and protein peaks after electroporation fluctuated in a time scale of 5 – 10 mintues, which was in agreement with the time scale of membrane resealing in bulk electroporation revealed by the fluorescence microscopy. Our results suggest the nanoantenna array as a good label-free platform for studying cell membrane dynamics.

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Dexter-like energy transfer between metal quantum clusters and Er^{3+} ions in silica

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Among the trivalent rare-earth ions, Er^{3+} has emerged as a key element in the field of optical communication technology because of its sharp and thermally stable radiative emission at 1.54 µm. Finding effective strategies for improving the luminescent emission performances of Er^{3+} ions in silica is therefore of paramount importance in the field of photonics and optoelectronics [1].
To this aim, an interesting possibility is given by ultra-small metal quantum clusters (QCs). Noble metal QCs can indeed efficiently absorb light through broad-band interband transitions and transfer energy to a nearby emitter, thus acting as efficient nanoantennae for the emitter excitation [2,3].
In the present work, we compare the sensitization effect of Au, Ag and AuAg QCs produced in silica by ion implantation and subsequent thermal annealing. The results demonstrated that an enhancement of more than one order of magnitude amplification of the characteristic Er^{3+} photoluminescent (PL) emission intensity at 1,54 µm can be achieved when ultra-small metal quantum clusters (made of 5-20 atoms) are formed [Figure 1A].

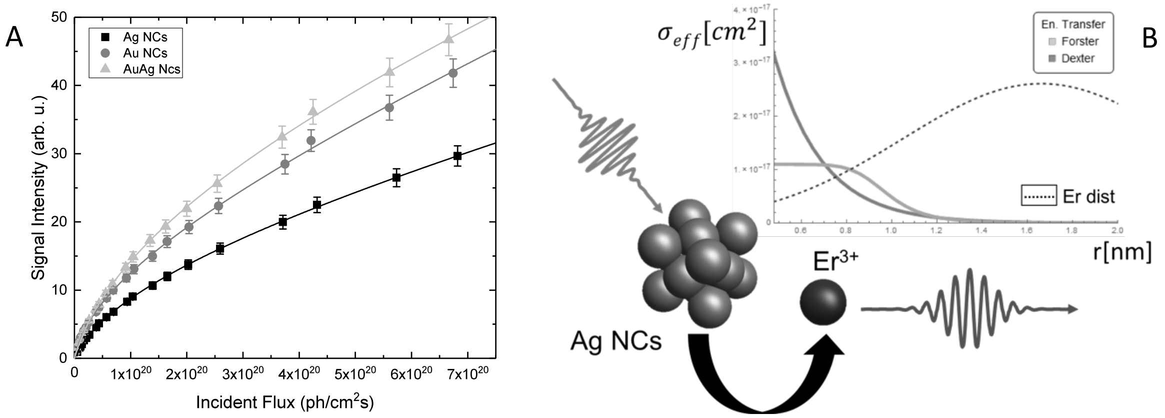

Figure 1: (A) PL intensity at 1.54 µm as a function of the photon flux for the samples indicated in the legend. (B) Schematic representation of the energy transfer mechanism.

Moreover, we developed a phenomenological model based on a Dexter-like energy-transfer mechanism [4] that allowed us to determine the important photophysical parameters (i.e. sensitization cross-section, interaction distance, fraction of active clusters) of the sensitization process between noble metal QCs and Er^{3+} ions in silica [Figure 1B]. The analysis pointed out that despite a limited fraction of quantum clusters (<5%) is involved in the sensitization process, the boost of the effective cross-section (more than 3 orders of magnitude higher than the intrinsic excitation cross-section of Er in silica) leads to a large enhancement of the Er^{3+} PL emission.

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Plasmonic spectroscopy of silver based bimetallic clusters under reactive atmosphere

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The structural and optical properties of small iron-silver clusters have been investigated by TEM and *in situ* plasmonic spectroscopy, respectively. The optical absorption spectra is dominated by a broad surface plasmon resonance (SPR), the features of which are dependent on the sample aging and the surrounding environment. These clusters have been synthesized by laser vaporization and co-deposited in silica and are expected to segregate at the nanoscale. Segregation is confirmed by the combination of HRTEM observations, optical analysis. Iron oxidation in ambient air leads to the formation of an amorphous or partially crystallized magnetite (Fe_3O_4) shell surrounding a crystalline silver core. Consequently the particles display both plasmonic absorption corresponding to the silver nanospheres in an oxide environment.

Changes in the oxidation state of iron induced by the exposure to oxidizing or reducing atmospheres could be followed through their optical response (figure 1). The optical spectra were measured with a new *in situ* transmission spectroscopy setup, based on the highly sensitive Spatial Modulation Spectroscopy (SMS) technique [1].

We have demonstrated that changes in the surface plasmon resonance of clusters provide information about the restructuring processes that occur when they are exposed to a reactive environment. Our approach could be extended to the investigation of catalytic processes. Moreover, segregated Ag-Fe clusters may be promising as a bifunctional system for magneto-optical devices.

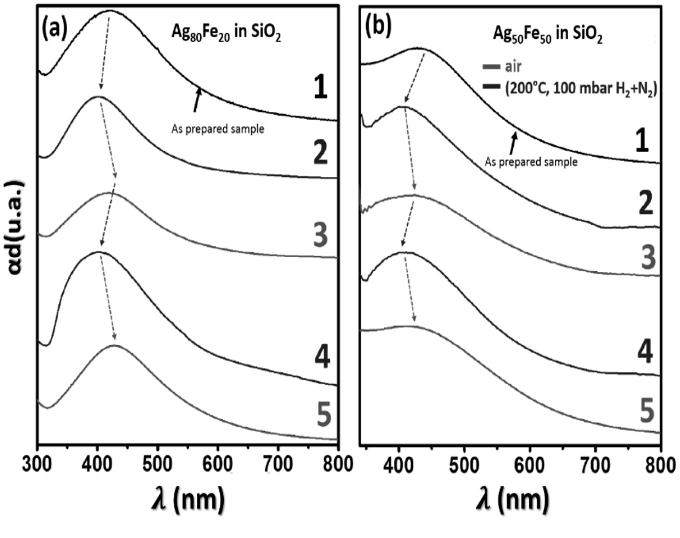

Figure 1: Absorption spectra of silver-ion clusters embedded in silica. (black (1)): just after the sample synthesis; (dark gray (2) and (4)): after annealing under reducing atmosphere; (light gray (3) and (5)): after being placed in air

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Grating-coupled hyperbolic metamaterials

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Optical metamaterials composed of sub-wavelength metal–dielectric multilayers are receiving an increasing amount of attention due to their striking electromagnetic properties [1]. The possible extraordinary applications include negative refraction, sub-wavelength imaging, spontaneous emission enhancement, biosensing, and nanoscale light confinement. In addition, such anisotropic media support hyperbolic dispersion relations rather than the elliptical ones commonly displayed by conventional dielectric media, as well as the propagation of highly confined modes (high-k modes) across the multilayer structure. These modes are conventionally known as volume plasmon polaritons (VPPs) or bulk Bloch plasmon polaritons (BPPs). The absolute values of modal indices of VPP modes are larger than those of the surface plasmon polaritons (SPPs) and vary from positive to negative. Since VPPs (or BPPs) are highly confined within the entire structure, the excitation, collection and control those modes at optical frequencies is very challenging. Here, we theoretically and experimentally demonstrate the excitation of both surface and bulk plasmon polaritons in HMMs through a grating coupling technique based on the excitation of SPPs, namely a hypergrating, which is a combined structure of a metallic diffraction grating and an HMM. We present a complete overview on the excitation of VPP modes in multilayered Au/Al_3O_2 metamaterials using 1D and 2D metallic diffraction gratings. We further compared our predictions using different numerical methods with experimental results. We show that a stack of metal-dielectric nanolayers, in addition to the long- and short-range plasmon polaritons, guides also an entire family of modes strongly confined within the multilayer—the bulk plasmon polariton modes. Reflection measurements as a function of incident angle and excitation wavelength show the existence of both surface and bulk plasmon polaritons inside the hypergrating. Moreover, we find a special configuration where almost-zero-reflection is reached, finding potential applications in plasmonic-based sensors near topological darkness [2]. The proposed configuration is expected to find potential applications in bio-chemical sensors [3], integrated optics and optical sub-wavelength imaging.

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Temperature-dependent plasmonic properties of self-assembled Au NPs arrays

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The exploitation of the localized surface plasmon resonance (LSPR) of noble metal nanoparticles (NPs) as an efficient mechanism to convert electromagnetic radiation into heat makes it possible to turn such NPs into nanoscale heat sources, with considerable scientific and technological applications [1]. In this relatively recent field, christened thermoplasmonics, novel challenges have arisen from both a theoretical and experimental point of view. One of the most intriguing issues is related to the variation of the physical properties of the nanoparticles (dielectric response, electron-phonon coupling etc.) with temperature. This topic has a twofold valence: on one hand, a knowledge of the temperature-dependent response would allow to better design nanoparticle systems for variable-temperature applications; on the other hand, temperature dependent properties may be directly exploited for nano-thermometry applications. For example, it is generally known that heated Au nanoparticles (NPs) exhibit a quenched, broadened and redshifted localized LSPR with respect to room-temperature analogues [2]. Thus, a more precise determination of such temperature-dependent plasmonic properties is needed whenever the LSPR is used as a detection tool (e.g. for molecular species, or temperature measurement).

In this work, we systematically investigate the variations of the plasmonic response of Au NPs at various temperatures between RT and 375 °C, by means of spectroscopic ellipsometry. Our samples consist of self-assembled arrays of sub-20-nm Au NPs laid onto a nanopatterned insulating substrate (Fig. 1, Left) [3]. Subjecting the NPs to cyclic temperature variations, we systematically observed a temperature-dependent broadening and damping of the LSPR. When attempting to reproduce the plasmonic response of the system introducing temperature-dependent bulk-Au dielectric functions, we notice that systematic discrepancies arise for increasing temperature. We suggest that often-neglected temperature dependent additional surface contributions to plasmon damping are responsible for the effect.

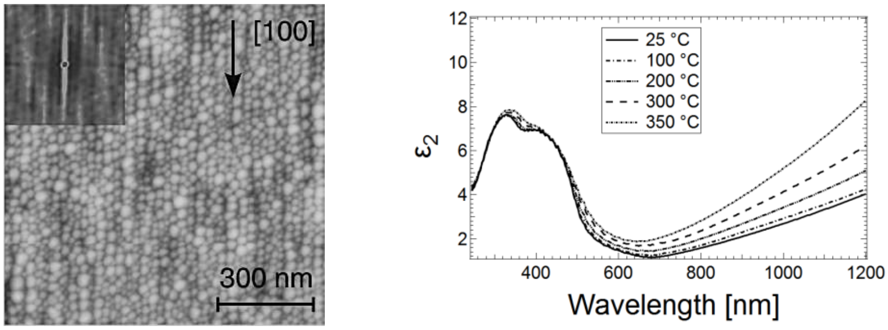

Figure 1: Left: AFM image of Au NPs arrays on rippled LiF substrate. Inset: 2D autocorrelation function. Right: ε_2 of a Au film extracted from ellipsometric spectra at different temperatures in high vacuum.

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Ultrafast laser-induced nanoparticle melting

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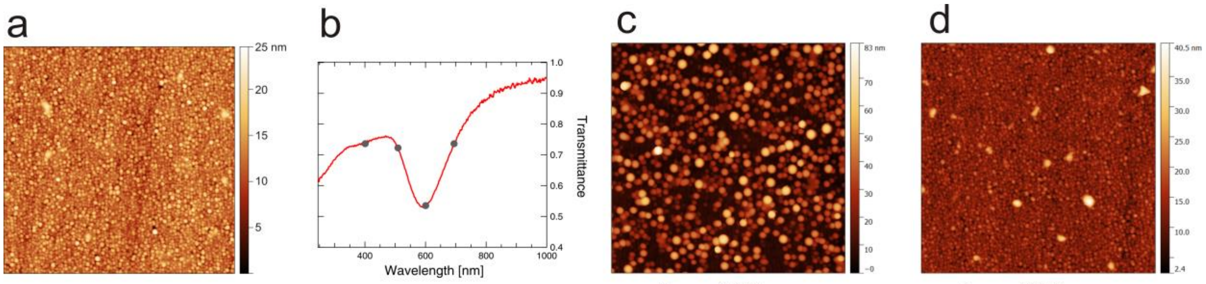
Nanometric noble-metal particles have long been known for their appealing plasmonic response, yet they may also be exploited as highly efficient light-driven nanoheaters, with important fallouts in fields as diverse as cancer therapy or nanofabrication. The nanoscale conversion of electromagnetic (EM) energy into heat can lead to fast and efficient heating of both the nanoparticles and their environment. For sufficiently high radiation intensity, nanoparticle melting, metal welding or material evaporation can take place. The localized surface plasmon resonance (LSPR) plays a major role in the nano-heating effect, providing an efficient mechanism to dissipate EM energy within the particles.

In this contribution, we explore the effects of pulsed-laser irradiation on ordered 2-dimensional arrays of Au nanoparticles. The arrays are fabricated by bottom-up techniques and consist of 20-nm Au nanoparticles, arranged in the form of coherently-aligned many-particle chains with high surface density onto an insulating nanopatterned substrate [1]. The interparticle gaps are systematically in the few-nm range, implying a strong near-field EM coupling of neighbouring NPs. The as-fabricated systems exhibit a NP density of 10^{11} cm^2, and a LSPR for excitation along the NP chains of 600 nm.

The 2D arrays were irradiated with ultrashort laser pulses (50 fs) of variable intensity and wavelength. The energy per pulse varied between 1 μJ and 10 μJ, onto a 700-μm-diameter spot, while two different irradiation wavelengths were chosen, 400 nm and 600 nm, corresponding to Au interband excitation and the LSPR. Atomic-force microscopy images recorded following the irradiation show that interband irradiation is almost tenfold more efficient than plasmonic irradiation in inducing nanoparticle melting, in apparent contradiction with calculated absorption cross-sections for EM radiation. We suggest that the different localization of the heat sources within the NPs (surface hot-spots for LSPR vs more homogeneous bulk heating for interband irradiation), and the onset of non-thermal melting effects are to be held responsible for this behaviour.



λ_{melt}=400 nm λ_{melt}=600 nm

Figure 1: panels a, b: AFM image and extinction spectrum of as-deposited Au nanoparticles array (2×2 μm^2). Panels c,d: AFM images of the 2D arrays after irradiation with 4μJ pulses @ 400 nm and 600 nm, respectively

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Plasmon-Enhanced Fluorescent molecules: towards Single-Molecule Imaging sensing

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The effect of coupling a molecule to resonantly excited plasmonic nanoparticles (NPs) is an active area of research. Collectively, these effects will lead to altered molecular optical properties.

The resonant charge oscillations associated with the excitation of Localised Surface Plasmon Resonances (LSPR), give rise to a large local electric field enhancement near the nanoparticle surface. Molecules placed in the nanoparticle near field can couple to this enhanced electric field, yielding several important effects [1]. First, the NPs can act as an optical antenna, efficiently concentrating incident radiation in its near-field, and causing an increased excitation rate of the molecule due to enhanced local power [2]. These highly confined fields, generally referred to as "hot spots", have been used in several near-field spectroscopies and imaging techniques, such as near-field scanning optical microscopy (NSOM) and surfaced-enhanced Raman spectroscopy (SERS). Second, there will be an increased density of photonic states accessible to the nearby molecule, and therefore, it will have an enhanced radiative decay rate according to Fermi's Golden Rule. With an enhanced radiative decay rate, the quantum yield of the molecule will increase, and the photostability of the molecule will also increase [3], with important consequences in improved Fluorescence sensing and imaging. These factors are extremely sensitive to excitation and emission frequencies, respectively, as well as to the NPs shape and size, and to the distance between the NP and fluorophore. Thus, a comprehensive understanding these parameters of the specific NP-fluorophore system being studied is of vital importance for optimizing fluorescence enhancement.

Nanocomposites consisting of a metal core, a silica-spacer shell with controlled thickness, and a dye-labelled shell are realized in this study. Metal (Au,Ag) nanoparticles of varied sizes and coated with silica shells of controlled thickness were synthesized. A silica shell offers chemical inertness, electronic insulation, and robustness, and it can be synthesized cheaply, so silica shells were used as spacers for varying the distance between the fluorophores and metal nanoparticles. The overlap between absorption/emission band of fluorophore system and plasmonic band of metal NP is varied by properly engineering the plasmon spectral position. Time-resolved fluorescence spectroscopy is employed to study the size and distance effects on plasmon enhanced fluorescence. The decay behavior is demonstrated to be sensitive to the interaction between the fluorophore and nanoparticle and can provide detailed information on the coupling mechanism.

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Angular plasmon response of metal monomers and dimers nanoparticles

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We study theoretically and numerically bidimensional square gratings of monomers and dimers of gold nanocylinders supported on a dielectric substrate, under plane wave illumination as a function of the angle of incidence and of the polarization. The number of parameters investigated makes that system a rich platform for the investigation of how grating coupling, and in particular edge diffraction which corresponds to the grazing propagation of a particular diffracted order, influence the surface plasmons response of nanoparticles. In particular, the considered periods are comparable to the range of incident wavelength, which makes the interpretation of the observed phenomena complex due to the large number of diffraction orders coming into play.

Microfluidic growth of Ag nanoparticles onto porous silicon/PDMS surface for reliable SERS detection

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Thanks to the miniaturized environment, microfluidics can offer an improved control over the growth of nanoparticles (NPs) particularly in terms of increased uniformity [1]. An in-flow synthesis process can be therefore advantageous to fabricate plasmonic NPs for Surface Enhanced Raman Scattering (SERS), which requires reproducible and uniform NPs arrangements aimed to obtain a repeatable Raman enhancement [2].
In this study, silver NPs are synthesized in elastomeric microfluidic chips (polydimethylsiloxane, PDMS) hosting ultra-thin porous silicon (pSi) membranes [3]. The NPs growth is investigated through the evolution of UV-Vis transmission spectra presenting Localized Surface Plasmon Resonances (LSPRs). The intrinsic reducing properties of the pSi towards the silver cations are exploited for the NPs synthesis. A motorized syringe is connected to the microfluidic chip and drives the injection of a $AgNO_3$ solution into the reaction chamber (Fig.1a). Synthesis parameters, such as the silver nitrate concentration, the solvent and the flow rate, are systematically varied in order to understand their influence on the NPs growth and morphology. At medium/high salt precursor concentrations (10^{-2} – 10^{-1} M) the appearance of a plasmonic dip over the pSi-PDMS spectral features is already evident after the first minute of reaction and a continuous red-shift combined with a broadening of the LSPRs is observed at increasing contact times until a saturation regime is reached at around 20 minutes (Fig1.b I-V). In order to compare the microfluidic results with static synthesis conditions, the immersion plating of an open pSi-PDMS membrane attached to a plastic cuvette is performed. In this case, a reduced growth rate is observed, as shown by the slower evolution of the plasmonic resonance (Fig1b VI), together with an altered morphology of the NPs. In fact, FESEM imaging reveals that under dynamic conditions the obtained NPs are smaller and more uniformly distributed on the pSi surface, in comparison to the larger and isolated particles obtained by static dipping, in agreement with their optical responses (Fig.b V-VII). Such differences are reflected in the SERS properties of the samples, which are tested with 4-mercaptobenzoic acid (4-MBA) as probe molecule. A high Raman signal intensity fluctuation is detected for the immersion plated substrates, while a higher average intensity and a better homogeneity characterize the in-flow synthesized ones. These results show the potentialities of the microfluidic process for the *in situ* fabrication of reliable SERS substrates.

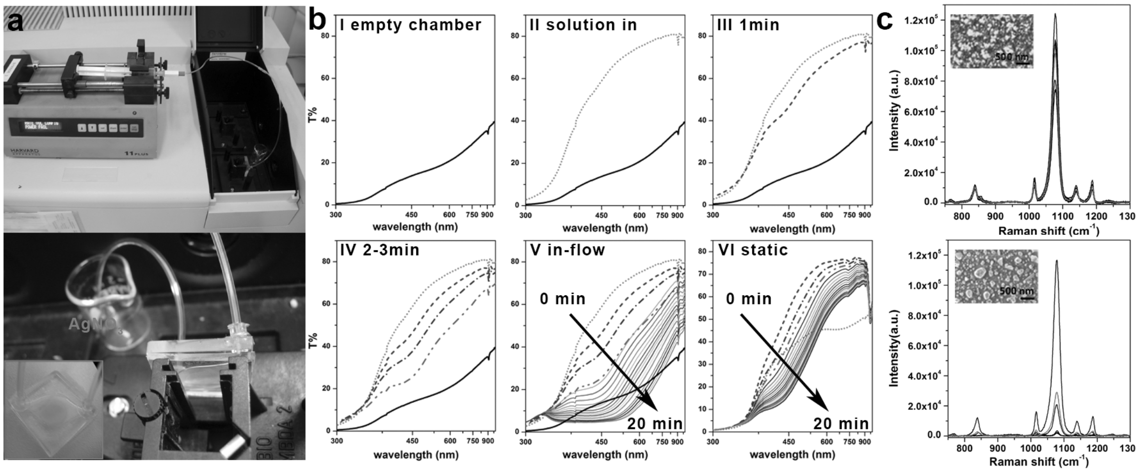

Figure 1: a) Set-up for the in-situ monitoring of the growth of AgNPs; b) UV-Vis transmission spectra acquired during the synthesis of AgNPs: I-V) in the chip at different reaction times (0 to 20 minutes); during the static synthesis VI) reaction times from 0 to 20 minutes. c) SERS spectra of 4-MBA measured on the immersion plated (bottom) and in-flow synthesized (top) samples.

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Mid-Infrared Scanning Nanoantennas for Near-Field Photoexpansion Microscopy

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Scanning probe microscopy (SPM) has developed in the last decade into a nano-optics tool, thanks to the incorporation of plasmonic structures capable of enhancement and confinement of the radiation electric field at the probe tip [1]. The fine positioning of SPM tips by piezo stages on the sample surface has allowed the control of light fields at the nanoscale with simultaneous atomic force microscopy (AFM) and scanning near-field optical microscopy (SNOM) imaging of nanostructures. In the mid-infrared range [2], the presence of narrow vibrational lines in both soft and hard condensed matter, jointly with the recent development of external-cavity tunable quantum cascade lasers, provides novel opportunities to perform label-free spectroscopy of biochemical reactions and of inhomogeneous electronic states in nanomaterials.

Infrared nanospectroscopy probes are typically constituted by pyramidal AFM tips made of silicon, coated with a gold film just thicker than the skin depth of gold (about 30 nm). While these probes provide a reasonable (geometric) field confinement at the tip apex in a broad infrared bandwidth, they are definitely not optimized for high field enhancement, as recently demonstrated by the direct comparison with gold nanorod antennas attached to silicon cantilevers [2]. Moreover, gold-coated silicon probes display a very high thermal conductivity, which is detrimental to photoexpansion techniques that exploit local heating as the nanoscale spectroscopy and imaging contrast mechanism [3]. In order to solve these and other issues, we have recently devised and fabricated novel SNOM probes [4]. In this work, we present a new type of infrared nanospectroscopy probe constituted by a tilted triangular silicon nitride membrane with a finite-size triangular metal patch at the apex (see Figure 1), acting as a scanning bow-tie infrared nanoantenna [1]. The metal employed is palladium, which features good optical conductivity in the mid-infrared range.

The calculated near-field enhancement is in excess of 80, while it is estimated to be below 20 for gold-coated pyramids [2]. The thermal conductivity and heat capacity of the present probe are estimated to be orders of magnitude lower than those of gold-coated silicon pyramids. This has been demonstrated by a photoexpansion nanospectroscopy experiment on a purposely patterned poly-methylmethacrylate nano-wedge deposited on a gold surface. The dependences of absorption peak intensity on wedge thickness in the 40-400 nm range were measured with both types of probes and they show different scaling laws.

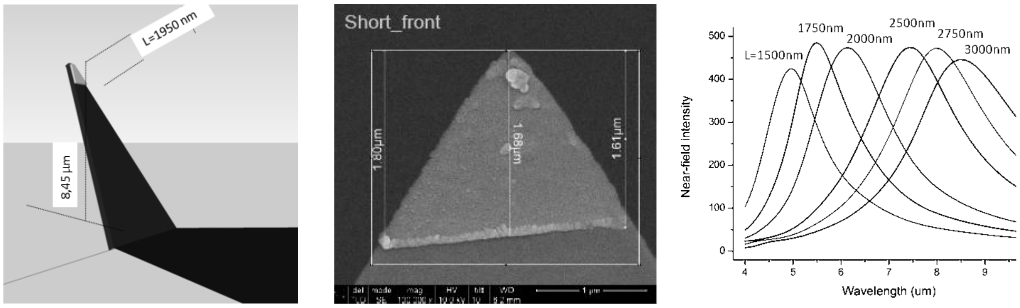

Figure 1: Design of a mid-infrared scanning plasmonic nanoantenna realized on a silicon nitride membrane probe tip. The length L of the triangular Pd patch at the probe tip is 1.95 µm (tilting correction was applied to the center SEM image) and produces a resonant field enhancement at $\lambda = 5.8$ µm (right panel).

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Transient Absorption as a Time-Resolved Measurement of Temperature in 2D Gold Nanoparticle Arrays

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The dynamics of photoexcited noble metal nanoparticles (NPs) and nanostructures (NSs) takes place on a number of different timescales: electron - electron scattering (100s of femtoseconds), electron - phonon coupling (less than 10 picoseconds) and phonon-phonon coupling (100s of picoseconds) [1]. The purpose of this work is to use the Femtosecond Transient Absorption Spectroscopy (FTAS) to monitor all of the above timescales following interband photoexcitation of 2D arrays of gold nanoparticles. The electronic heating of the NP array leads to a strong change in the dielectric constant of the material and thus to a change of the plasmonic response of the NS in time. In gold spherical particles this typically leads to a bleaching of the central part of the resonance and a simultaneous increase in the wings of the resonance (photoinduced absorption) [2]. In non-spherical particles the transient response is more complicated. In the case of the 2D arrays probed in this work the possibility to control the polarisation of the probing light permits us to selectively probe either the transverse (electric field perpendicular to the major axis of the NPs) or the longitudinal (electric field parallel to the major axis of the NPs) plasmon resonances. This makes it possible to separate these contributions to the FTAS and to better understand the transient response of the material. The temporal development of the bleaching/photoinduced absorption of the plasmon reflects the dynamics described above with the rise-time of the signal being related to the electron-electron scattering and the decay occuring on the two timescales related to the electron-phonon and phonon-phonon scattering times. An in-depth analysis of these signals both in transmission and in reflectance has allowed us to gain a detailed insight into these dynamics for 2D AuNP arrays.

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Gain assisted thermo-plasmonic effects in gold nanoparticles solutions

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We report a detailed characterization of the photo-induced heating in gain assisted gold nanoparticles (AuNPs) colloidal solutions. AuNPs, with sizes ranging from 14 to 48 nm and concentration of $2.5 \cdot 10^{-10} M$, were exposed to different intensity values of a resonant green laser (532 nm) to estimate the optimal condition to achieve the maximum temperature variation with the least laser dosage. By adding in the solutions an organic dye, Rhodamine 6G (R6G), whose emission band overlaps to the Localized Surface Plasmon Resonance (LSPR), we found that, in the case of smaller NPs, the contribution to the photo-thermal efficiency is enhanced due to a strong coupling effect between the gain medium and AuNPs, related to an increasing of the extinction cross section of the whole gain-assisted system. On the other hand, for the AuNPs characterized by a larger diameter, an opposite behaviour has been found: a loss compensation mechanism, based on a resonant energy transfer process from gain units to plasmonic nanoparticles, limits the increasing of the absorption cross section with a consequent lowering of the photo-thermal efficiency. The presented quantitative analysis results fundamental in bio-medical applications as well as in integrated plasmonic devices based on loss compensation effects, where the impact of undesirable thermal effect can not be ignored.

Development of spatial modulation spectroscopy of single nano-objects in liquid environments for biosensing applications

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Research and applications in medicine and molecular biology increasingly depend on the development of rapid, accurate and highly sensitive methods for detecting target analytes in solution. One of the currently most promising approaches is the development of sensors based on Localized Surface Plasmon Resonance (LSPR) of noble metal nano-objects, which is very sensitive to the object's immediate environment. In particular, it would be very interesting to measure the response of individual objects in liquid in order to detect minute changes in the presence of weak concentrations of analytes that would otherwise be lost against the background of ensemble measurements.

Here we report on the development of a new setup based on the spatial modulation spectroscopy (SMS) technique [1] to measure the response of individual nano-objects on a substrate in a liquid environment. We have also developed a method for the preparation of stable samples of individual gold nano-objects deposited on a silanized glass substrate for measurements with this setup. We will present the results that we have obtained so far in liquid environments of different optical indices, with a focus on gold bipyramids (figure 1). We will also show that bipyramids are of particular interest due to the ability to tailor their LSPR response via synthesis parameters as well as the amplification of the electric field near their tips in the so-called "hot spots", which makes them particularly sensitive to the local environment in these regions.

Looking ahead, we will discuss the prospects of further development of the setup, such as backscattering and real-time dynamic flow measurements. We will also discuss the possibility to produce samples with functionalized gold nano-objects and the potential interest of other types of probes for biosensing applications.

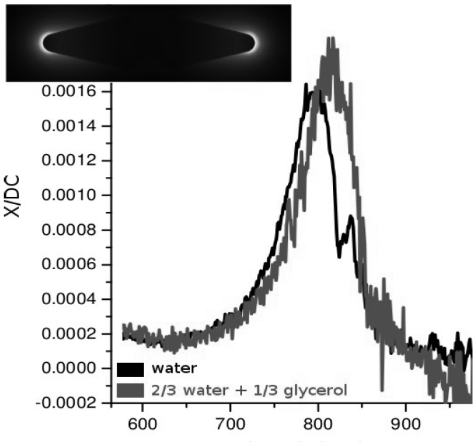

Figure 1: *LSPR shift of a bipyramid after adding glycerol to water. Silanized sample. Inlay: FEM calculations showing hotspots under LSPR.*

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Density functional theory investigation of electron over-rich silicon clusters

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Heavily doped semiconductor nanocrystals are promising materials for nanoscience applications [1]. One the simplest models for such systems is that of a charged semiconductor cluster [2]. Hence, we have performed density functional theory calculations to study the electronic properties of silicon clusters doped with an increasing number of excess electrons (up to $24e^-$).

To this purpose, we have considered clusters of different dimensions both isolated and embedded into an external polarizable medium. We have found that stable ground-state configurations are only achieved when a polarizable environment as well as proper positive external counter charges are included. Time-dependent density functional theory calculations have been also performed to study the effect of excess electrons on the optical properties of the clusters (see Fig 1).

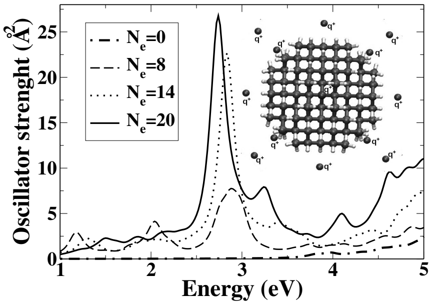

Figure 1: Absorbance spectra of $Si_{35}H_{36}$, showing a redshift, narrowing and enhanced intensity peak of the plasmon peak as doping increase

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Tunable plasmonic nanostructures arrays: a template mediated low cost approach

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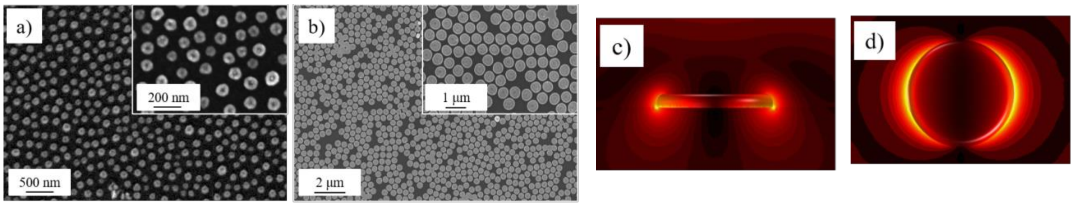
In the last years, many studies have been performed on metal nanoparticles because of their possible applications as chemical and biological sensor [1]. Unfortunately, the most used fabrication methods for metallic nanostructured systems, such as EBL and FIB, are less accessible choices for scientists and industrial applications due to their critical drawbacks, like low speed and high-cost. In this work low cost fabrication methods have been developed to realize planar distribution of metal nanostructures on glass substrates with tailored optical functionalities for biochip sensing purposes. In order to achieve sharp LSPR resonances in the visible and IR range, the geometry of the fabricated nanostructures have been optimized through numerical modelling. The proposed deposition technique are revisited method based on the known nano sphere lithography (NSL), or colloidal lithography techniques. Particularly suited for the creation of large-areas and low-cost nano-optical devices, these fabrication methods are providing interesting alternative to sequential and very expensive manufacture techniques. Nano-sphere lithography, colloidal lithography using shadow-angle evaporation, as well as hole-mask colloidal lithography, enable parallel surface patterning of large-areas, allowing the creation of complex plasmonic systems with variable shapes and distributions. Owing to their advantages, we used these high-throughput methods for the realization of optical devices with possible sensing applications. Planar distribution of gold nano-disk have been fabricated using both lithographic techniques. The size of the nanostructures was directly controlled by the diameter of the latex spheres acting as a mask, while their average distance, in the electrostatic deposition, was controlled by the salt concentration of the colloidal solution (Figure 1 a,b). The optical response of the fabricated nanoparticles was investigated through absorbance measurements in the Visible-IR spectra (Figure 1e), and qualitatively explained using different numerical models based on finite element analysis. The optical properties and the sensing capabilities of different metal nanostructures have been investigated, exploring several key parameters for sensitivity enhancement of traditional biosensors based on Localized Surface Plasmon Resonances (LSPR).



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Plasmonics enables Nanotheranostic Systems: Synthesis, Photophysics and Cancer Phototherapy

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During the last decade, the unique properties of nanostructures based systems have been extensively investigated, with particular emphasis on the field of biomedicine and cancer prevention, both diagnosis and treatment [1]. In Photodynamic Therapy (PDT), a non-invasive cancer treatment based on a phototriggered drug, the employment of nanomaterials overcomes most of the limitations of the conventional approaches related to the use of free photosensitizing agents [2,3]. Moreover, the outstanding properties of plasmonic nanostructures, including the high photothermal conversion efficiency, provide a great potential as phototherapeutic nanoagents [4]. In this context, we have developed multifunctional nanoplatforms based on a phosphorescent cyclometalated Ir(III) complex as photosensitizer/sensing probe and hybrid nonbiodegradable nanoparticles of different shape for simultaneous and multimodal light-activated synergistic therapy [5-7]. Here, we will also present new approaches based on novel nanostructures that will allow one and two-photon excitation of the photosensitizing agents coupled with thermal activation processes.

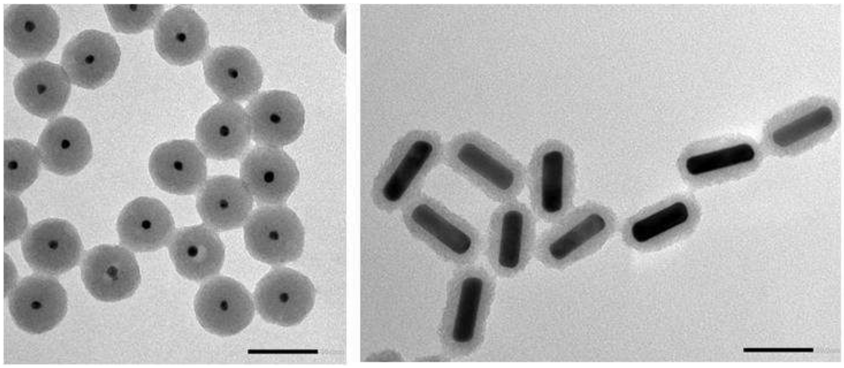

Figure 1: TEM images of multifunctional theranostic gold-silica-based nanostructures (scale bar: 50 nm).

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Increasing Organic Solar Cells (OSCs) efficiency through plasmonic anisotropic gold nanoparticles incorporated in the hole transport layer

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Organic solar cells (OSCs) are a promising alternative to the well-know silicon devices for the conversion of solar radiation into electricity. Low cost, lightweight, flexibility of their components and the compatibility of fabrication processes with roll-to-roll technology are interesting features that stimulate the research in this field. The main factor that limits OSCs marketability is the not still high enough efficiency respect to silicon cells. Short exciton diffusion lengths and low charge mobility typical of organic semiconductors impose a limited active layer thickness in OSCs, generally below 100 nm, reducing light absorption. A most useful method to enhance the absorption of sunlight without increasing the thickness of the active layer is the addition of plasmonic nanoparticles. Two main effects can be exploited: light-scattering that increases the light path inside the cell and near field enhancement that boosts the absorption cross section of materials.

Gold nanoplates coated with polyvinylpyrrolidone (Au-PVP NPLs) were incorporated in the hole transport layer (HTL) of an organic bulk heterojunction solar cell with the aim to enhance efficiency exploiting plasmonic effects. The reason for the introduction of anisotropic gold nanoparticles was dictated by their plasmonic resonances that are in a spectral region where absorption of the active layer of the solar cell is low. In this way some of the energy otherwise lost in the absence of nanoparticles can be recovered. In addition, given the thickness of the NPLs (~15 nm) and the fact that they tend to assume a flat orientation with respect to the cell substrate [1], they do not interfere with the cell morphology. A reference device with the following architecture was used: Glass/Indium Tin Oxide (ITO)/ Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) / Poly(3-hexylthiophene-2,5-diyl) (P3HT):[6,6]-phenyl C_{61} butyric acid methyl ester ($PC_{61}BM$)/Aluminum (Al). The PEDOT:PSS layer constitutes the HTL of the solar device, the P3HT:$PC_{61}BM$ blend is the active layer, while ITO and Al are the anode and cathode, respectively.

Au-PVP NPLs were synthesized using a versatile, template-free synthesis [2]. The PVP allows both to obtain anisotropic shape and to avoid that the gold nanoparticles could act as charge recombination centers when introduced in PEDOT:PSS. Au-PVP NPLs were optical and morphological characterized by UV- VIS- NIR spectrometry and Transmission Electron Microscopy, respectively. Solar cells with different concentration of Au-PVP NPLs in the HTL were prepared. Electric characterizations were performed under an irradiance of 1000 W/m^2 at air mass (AM) 1.5G. The addition of Au-PVP NPLs in PEDOT:PSS induced an increase of the efficiency up to 14% respect to the reference cell without nanoparticles, demonstrating that the Au-PVP NPLs can be effective in the enhancement of efficiency of OSCs.

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Excitation of coherent vibrations of nanoparticles of different shapes

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Changing the shape of a nanoparticle (NP) is a very powerful means of finely tuning the plasmonic properties of the system. The particle shape has a dramatic effect on the position of the plasmonic resonance and also additional resonance modes appear due to a reduction of the symmetry of a particle. For example, the peaks of the UV-Vis extinction spectra of Ag nanotriangles (NTs) have been assigned as an in-plane dipole peak, an in-plane quadrupole (or higher order: octapole, decapole, etc.) peak, and out-of-plane dipole and quadrupole resonances [1].

Time-resolved pump and probe spectra of NPs with different shape show a spectral modulation as a signature of a mechanical vibration induced by the pump pulse, as described by Hartland [2] and L. Bonacina et al. [3] in their works on Gold Nanorods and Silver Nanotringles, respectively. Symmetric vibrations of the particles are responsible for this modulation and affect the plasmon peak of the NP (see figure).

In this work we investigate the coupling between these coherent vibrations and the local surface plasmon resonances of different kinds (Silver and/or Gold) of lower symmetry (relative to spheres) NPs, as nanotriangles, nanorods, core-shell NPs, multi-face NPs (hexagonal, octagonal, etc.).

The dynamics of the plasmon resonances of these materials are probed through femtosecond transient absorption spectroscopy (FTAS). The NPs dispersions are excited with a pump pulse and the extinction is monitored by a white light probe (400-800 nm).

The results confirm that the coherent vibrations are strictly correlated with the shape on the NPs under investigation and show how the vibrations and plasmon resonance of the NPs interact as shown in the FTAS spectrum reported in Fig. 1.

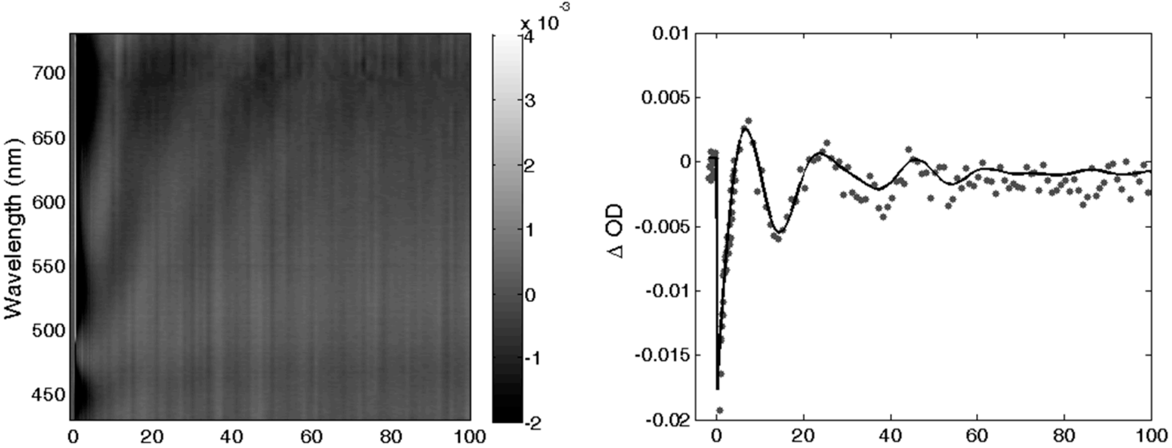

Figure 1: FTAS Spectrum of Ag nanotriangles in the first 100 ps after photoexcitation and a cut of the time response of the plasmon bleaching at 680 nm showing the oscillations due to the coherent vibrations.

The shift and/or broadening of the plasmon peak can be ascribed to the geometry alteration due to the mechanical vibration of the NPs induced by the vibrations of the NPs.

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Plasmon vortices around isolated nanoholes cratered on a gold film: polarization dependent coupling of SPPs and excitation beam

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Understanding the role of surface plasmon polaritons (SPP) in extraordinary light transmission through subwavelength holes in metallic layers [1,2] is crucial for the development of subwavelength optics and nanophotonics [3].

It has been shown that nanoholes in Au thick films act as point like sources of SPPs in near-field. SPPs propagate in directions determined by the polarization of incident beam and interference fringes are produced [4]. The resulting light can be controlled by changing the polarization and angle of incident light beam [4]. In this context, we study the electromagnetic near-field distribution around isolated elliptical nanoholes in 88 nm thick Au film using near-field scanning optical microscopy by changing the polarization directions of both the exciting and revealed light. We performed transmission-mode SNOM measurements. The measurements show interesting optical effects related to de-polarization process of incident light through the elliptical nanohole. Specifically, when the incident and collected light are cross-polarized, the near-field intensity around the hole exhibits a vortex-like interference pattern as shown in Fig. 1(a).

A comparison with near-field transmitted light intensities and interference patterns detected at wavelengths were SPPs play a negligible role, provide indication that the observed effects origins from SPPs.

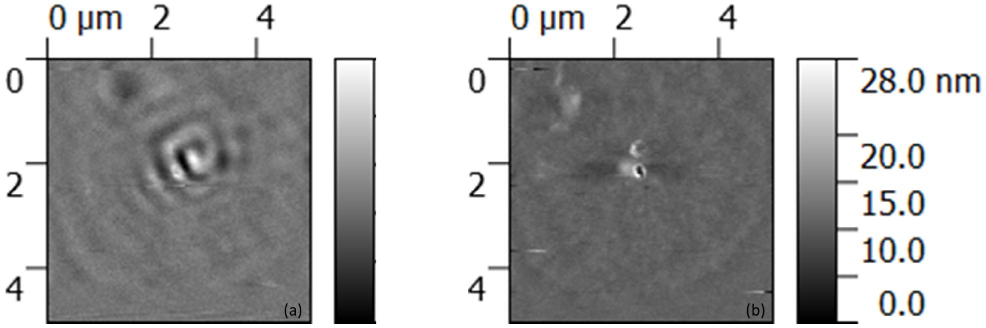

Figure 1: 5μm × 5μm (a) SNOM and (b) AFM images of a single nanohole in a gold 88 nm thick film. The optical pattern is obtained by illuminating the sample at 632 nm in transmission mode. The incident and collected light are cross-polarized in order to enhance only the de-polarized component of the transmitted light.

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Spin-orbit interactions of light in the near field of metal nanoparticles

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Light carries both spin and momentum. Spin-orbit interactions of light come into play at the subwavelength scale of nano-optics and nano-photonics, where they determine the behavior of light [1,2]. These phenomena, in which the spin affects and controls the spatial degrees of freedom of light, are attracting rapidly growing interest [3,4]. Here we investigate spin-orbit interactions in the near field of metal nanostructures supporting localized surface plasmons. These systems can confine light to very small dimensions below the diffraction limit, leading to a striking near-field enhancement. In contrast to the propagating evanescent waves of surface plasmon-polariton modes, the electromagnetic near-field of localized surface resonances does not exhibit a definite position-independent momentum or polarization. All the calculations have been carried out beyond the quasistatic approximation, using the Mie theory implemented within the T-matrix formalism [5]. We find that the spin of the incident light can control the rotation direction of the canonical momentum.

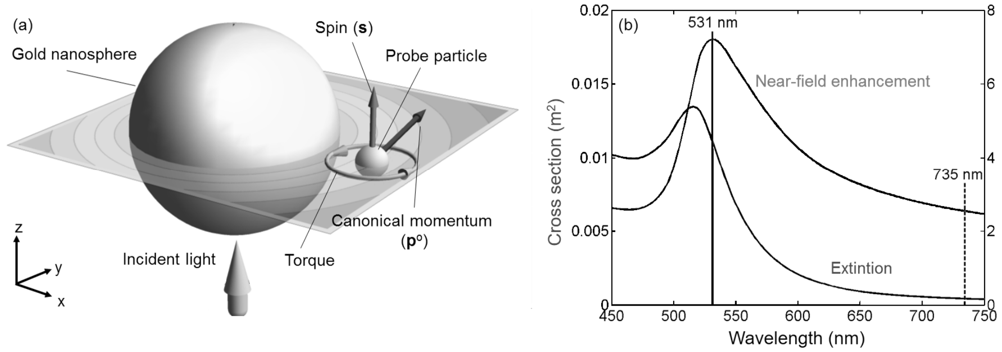

Figure 1: (a) Schematic representation of the configuration used for the scattering calculation. The incident field propagates along the z-axis. The force and torque produced by the orbital and spin momentum, respectively, are calculated by considering a probe-particle near the gold nanosphere. (b) Near-field enhancement |E⁄E_0 |^2 calculated on the equatorial plane, at a distance d=4 nm from the particle surface, and the extinction efficiency cross section spectra for a gold spherical nanoparticle (radius a=40 nm), calculated beyond the quasistatic approximation, by employing the Mie theory implemented within the T-matrix formalism. The resonance condition occurs in correspondence of the maximum near-field enhancement of the optical field at λ=531 nm (black vertical line). The dotted vertical line indicates an out-of-resonance wavelength (λ=735 nm), where we also calculated the canonical and spin momenta.

Our results represent an interesting example of spin-orbit interactions of light for complex evanescent fields. Investigation of optical forces and torques around nanoparticles and nanostructures is interesting for experimental studies and applications, since the huge light concentration around metal nanoparticles can give rise to very strong optical forces and torques, even with moderate illumination. The present study can be extended to more complex nanostructures, considering for example metal nano-dimers were very high field-amplification effects in the dimer gap can be obtained at specific wavelengths.

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Collective Enhanced IR-SR Absorption microscopy for conformational studies of protein of biomedical interest

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Despite its potential for biomolecule characterization, FTIR microscopy (FTIRM) of sub-micromolar samples using conventional approaches is extremely challenging. A promising method for increasing the technique sensitivity is to take advantage from the electric field enhancement associated with the excitation of plasmonic resonances from ad-hoc shaped metallic structures. Furthermore, the enhancement of the Mid-IR signal can be increased in respect of using isolated structure by exploiting the collective resonant excitation of nanoantennas assemblies, a technique called Collective Enhanced IR Absorption (CEIRA) [1,2].

In our study, structures were simulated, designed and produced to enhance the absorption in the 1400-1800 cm^{-1} range since our aim was to detect conformational variations in biologically relevant proteins. These kind of proteins can be expressed in-vitro through recombinant technology, although the yield after purification is low (>200-300 µg of protein). Moreover, mutated forms are very difficult to crystalize. Thus we thought that by the Collective Enhanced IR Absorption (CEIRA) approach, even in combination with synchrotron radiation, we can get conformational details about these proteins from a very low amount of sample. Gold nanoantennas arrays were directly fabricated on CaF_2 by electron beam lithography (EBL). Two different strategies for protein deposition were tested: (i) physisorption of a very thin layer and (ii) surface functionalization by exploiting thiols chemistry and amide coupling immobilization protocol. We found out that with the first we can get ~10-20 nm thick layers, whereas the functionalization produces a monolayer, as can be seen in Figure 1A. We obtained data from monolayers of reference proteins, Bovine Serum Albumin (BSA) and Concanavalin-A (Con A), and by comparing them to the reference spectra collected on bulk sample (Figure 1B), and we confirmed that it is possible to discern the difference in conformation of the two protein. We also managed to measure Epidermal growth factor Receptor (EGFR) (Figure 1C), a protein involved in the progression of lung cancer.

We believe that a platform with this sensitivity, few hundreds of molecules, has really the potentialities to become the base of an advance high-throughput tool, even exploiting microfluidic and the new Quantum Cascade Laser sources.

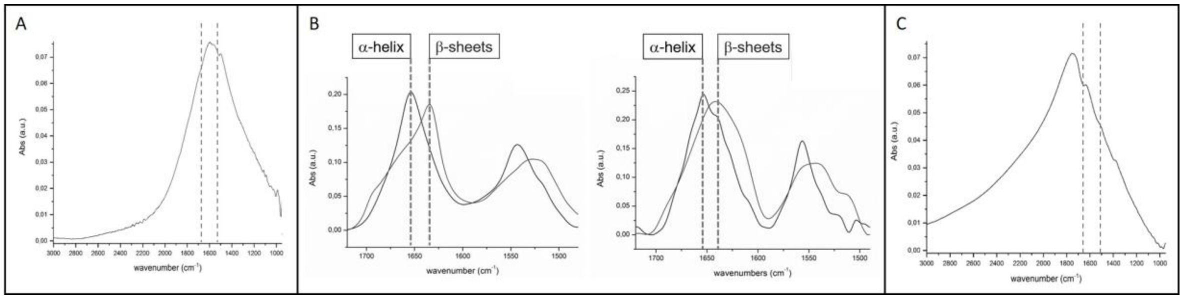

Figure 1: (A) CEIRA resonance curve with a monolayer of BSA. (B) Reference spectra in the AmI-AmII range of BSA (black curve) and Con A (gray curve) acquired on bulk (left) and monolayer spectra extracted from the resonance curves (right). Peak position of main protein conformations is highlighted in the picture. (C) CEIRA resonant peak of EGFR dropped nanoantennas. AmI and AmII highlighted with dashed lines.

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