POLITECNICO DI TORINO
Dipartimento di Scienza Applicata e Tecnologia

DiSAT chimica fisica materiali
Dipartimento di Eccellenza

SIOF Società Italiana di Ottica e Fotonica
Plasmonica & Nano-Ottica Working group

8th International Workshop on Plasmonics

July 7-8 | Torino, Italy

Politecnico di Torino

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PLASMONICA 2022 is organized by the Polytechnic University of Turin -PoliTo- and it is supported by SIOF (the Italian branch of EOS)

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• The total time allotted to each speaker is 18 minutes. You should plan to speak for 15 minutes and leave 3 minutes for questions.
• There are two projection screens 3.30 m wide in 16:9 format
• We kindly encourage the speakers to upload their presentations on the computer we provide. Please upload your presentation before your session and check there for compatibility issues. For any problem or special request please contact the session chair before the session starts.
• We provide the following equipment:
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• Poster boards are about 100 cm width x 120 cm height. Any poster fitting these limits are allowed. Some additional boards 120 cm x 150 cm are also available.
• In the workshop Program, please note the tag number assigned to your poster. This tag identifies the poster board where to hang your poster.
• All necessary material for attaching the poster to the poster board will be available at the Workshop desk.

Awards

At the end of the Workshop, the Best Oral Presentation and the Best Poster Presentation will be awarded by SIOF.

The award recipients are announced at the closing of the workshop

Workshop Location

The Politecnico di Torino main campus is a large complex of buildings in Corso Duca degli Abruzzi. It was opened in November 1958, after the former Industrial Museum was completely destroyed during World War II. The construction of the new Cittadella Politecnica in Corso Castelfidardo began in 1997 when Politecnico di Torino acquired the former Officine Grandi Riparazioni. The Cittadella is a single integrated complex of buildings of high architectural and urban value whose spaces are used by companies and management services, University and individual citizens

How to reach Politecnico di Torino

The easiest way to reach the conference location is by entering the Cittadella Politecnica of the Polytechnic University of Turin from the parking entrance located in Corso Castelfidardo 42bis, underneath the south bridge. It is ten minutes from the Porta Susa train station.

In alternative, you can take the Metro line from either Porta Susa or Porta Nuova train stations and get off at the "Vinzaglio" stop. Inside the Politecnico you will find signs carrying the Plasmonica 2022 logo pointing to the conference rooms (Classroom P). Support staff will eventually assist you to reach the conference site.

Workshop Program

Thursday 7th July		
8.30-9.00	**Registration**	
9.00-10.45	**Poster session & Welcome Coffe**	
10.45-11.00	**Workshop Opening**	
11.00-11.50 Invited	M. Petrov	All-dielectric thermonanophotonics: controlling light with heat
12.00-13.20	***Lunch***	
13.20-15.10	**Fundamental Plasmonics & NanoPhotonics** – *Chair*: Stefania D'Agostino	
	T. Giovannini	Do We Really Need Quantum Mechanics to Model Nanoplasmonics?
	A. Calzolari	Plasmonic by design
	M. Leonetti	Optical computation of the spin glass dynamics with a digital micromirror device
	L. Pattelli	Probing intensity correlations inside a scattering medium
	C. Triolo	Spontaneous and stimulated optical emission from CH3NH3PbBr3 perovskite: Role of excitons
	C. Vanzan	Energy transfer to molecular adsorbates by transient hot-electron tunnelling
15.10-15.40	***Coffe Break***	
15.40-16.30 Invited	C. I. Benea-Chelmus	Gigahertz free-space active photonics enabled by electro-optic metasurface modulators
16.30-18.20	**Novel Materials & Devices** – *Chair*: Michele Ortolani	
	E. Arigliani	Low loss polyethylene-loaded plasmonic waveguides for the mid-infrared
	S. Balestrieri	Plasmonic Nanodevice to generate force gradients to induce nanoparticles acceleration
	A. Gabbani	Magnetoplasmonics beyond metals: Transparent Conductive Oxide Nanocrystals Enable High Performance Sensing
	A. Mancini	Thin film Surface Phonon Polaritons dispersion in suspended Silicon Carbide Membranes
	N. Marcucci	Controlling resonant surface modes by arbitrary light-induced optical anisotropies
	F. Rusconi	Mid-infrared dielectric antennas on ENZ substrates
18.20	R. Tagliapietra	Characterization and analysis of biological assays by Enhanced Raman Spectroscopy
Social Dinner at «Snodo» Restaurant		

Friday 8th July		
8.30-10.40	**Metasurfaces & NanoParticles** – *Chair*: Alessando Belardini	
10.40-11.10	***Coffe Break***	
A. Calà Lesina	Time-domain topology optimization of wideband dispersive plasmonic nanostructures	
N. Granchi	Optical assessment of dewetted Mie resonators through Dark-field Scanning Microscopy	
H. Gupta	Bound State in the Continuum in Resonant hBN Metasurfaces	
M. Lipok	Assembly and optical properties of amyloid-gold hybrid nanomaterials	
C. Mancarella	Plasmonic and Photonic Multifunctional Metamaterials with Tunable Properties based on Alternative Plasmonic Materials	
S. Nic Chormaic	Single nanoparticle trapping using metamaterial-assisted optical tweezers	
E. Petronijevic	(Un)conventional experiments and simulations of chiro-optical effects in plasmonic	
11.10-12.00 Invited	S. Schlücker	Nanogold: A Journey From Ideal Dimers to SERS-based Lateral Flow Assays
12.00-13.20	***Lunch***	
12.30-14.00	**Round Table & Election Steering Committee Plasmonica**	
14.00-15.40	**Ultrafast & Non-Linear NanoPhotonics**– *Chair:* Carlo Forestiere	
F. De Luca	Surface charge modulated nonlinear response of heavily doped semiconductors	
A. Di Francescantonio	Dual-pump coherent control of the nonlinear emission by a plasmonic nanoantenna	
M. Romanelli	Ultrafast Dynamics of Photochromic Molecules Coupled to Plasmonic Nanoantennas	
A. Rossetti	Developing an Ultrafast Scanning Tunnelling Microscope	
A. Zilli	Second-harmonic generation of visible light by a monolithic LiNbO3 metasurface	
15.40-16.00	***Coffe Break***	
16.00-18.25	**Sensing** – *Chair*: Maria Caterina Giordano	
S. Bernatova	Optical force aggregation of gold nanorods for high sensitivity detection of molecular to nano-plastics particulate matter	
E. Cara	Reference-free X-ray fluorescence for the molecular quantification: determination of SERS enhancement factor	
C. D'Andrea	Surface-enhanced Raman scattering with nanophotonic and biomedical amplifying systems for a more accurate diagnosis of Alzheimer's disease	

	M. Iarossi	Probing Neurons Before and After Differentiation on Sharp-tipped Au Nanopyramid Arrays with SERS
	B. Miranda	Hydrogel-based Plasmonic Nanocomposites for Label-free and Non-label free Biomolecular Interactions Monitoring
	D. Montesi	Portable SERS device for early cancer diagnostics
	M. Najem	Barcode-like Aluminum Bowties towards an extended SEIRA sensing
	R. Polito	A confocal mid-infrared microscope for time-resolved difference spectroscopy of membrane proteins
18.25	**Workshop Closing & Award Ceremony**	

List of posters

Thursday 7th July Poster session		
1	H. Ali	Chiral Effect and Extraordinary Transmission in Metal Films with Elliptical Nanohole Arrays
2	L. Baldassarre	sSNOM characterization of the IR-active vibrational mode in highly strained hBN microbubbles
3	A. Belardini	Luminescence of molecules on plasmonic metasurfaces induced by chiral light
4	S. Benedetti	Control of the optical response of plasmonic nanoparticles on transparent conductive oxide through doping
5	S. Bertone	SERS specific and label free detection of tetracyclines
6	P. Biagioni	Towards polarization control in Bloch surface waves
8	L. Cascino	Surface Plasmons Effects on Azobenzene Photoisomerization
9	M. Condorelli	Ag Nanoflower as single-particle SERS active substrate
10	C. Deriu	Tailored Colloidal Nanostars for Surface Enhanced Raman Spectroscopy (SERS): Optimization of Formulation Components and Study of the Stabilizer-Nanoparticle Interactions
11	C. Forestiere	An Operative Approach to Quantum Electrodynamics in Dispersive Dielectric Objects Based on a Polarization Modal Expansion
12	A. Foti	Tip-enhanced Raman spectroscopy of polymer functionalized multiwalled carbon nanotubes
13	H. Garrone	Plasmonic gold nanostructured layer for photon absorption efficiency enhancement in Transition-Edge Sensors
14	M.C. Giordano	Large-scale photon harvesting in nanopatterned 2D semiconducting layers
15	N. Granchi	Engineering high Q/V photonic modes in correlated disordered systems
17	F. Intonti	Near-field hyper-spectral imaging of resonant Mie modes in a dielectric island

18	G. Lucchesi	Silver Nanowires Plasmon Enhancement of Photovoltaic Efficiency in Lead-Free Perovskite Solar Cells
19	M. Ortolani	Detection of strong light-matter interaction and near-field mapping on a single resonator
20	F. Pineider	Some interesting applications of ITO nanoparticles in thermoplasmonics
21	J. Segervald	Plasmonic metasurface assisted by thermally imprinted polymer nano-well array for surface enhanced Raman scattering
22	O. Tammaro	Magnetic metal-inorganic composite as new multimodal contrast agents: preliminary research design
23	M.E. Temperini	Infrared nanospectroscopy study of light-sensitive proteins with a plasmonic probe
24	A. Zilli	Quantitatively linking morphology and optical spectroscopy of single silver nanoparticles reveals surface composition changes
25	T. Venanzi	Mid-infrared photocurrent microscopy of vertical van der Waals semiconductor heterostructures

Fundamental Plasmonics & NanoPhotonics

Session Chair: Stefania D'Agostino

Do We Really Need Quantum Mechanics to Model Nanoplasmonics?

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Keywords: Quantum plasmonics, Spectroscopy and nano-imaging

Most properties of plasmonic nanostructures follow from the tunability of their optical response as a function of their shape and dimensions [1]. Such a feature is typical not only of metal nanoparticles but also graphene-based nanostructures, for which an additional tunability, based on electrical gating, can be exploited. The accurate description of the optical properties of the plasmonic substrates is crucial for a theoretical understanding of the physical phenomena occurring at the plasmon resonance frequency [2]. Here, we present an atomistic, yet classical, approach to predict the plasmon properties of nanostructures of complex shapes. Our approach is general enough to describe, at the same time and with the same level of accuracy, metal nanoparticles [3,4] and graphene-based nanoaggregates [5], being able to correctly reproduce the experimental trends.

Our classical approach show a remarkable potential for large scale nanoplasmonic simulations. In particular, by properly accounting for the atomistic discretization of matter, we can accurately describe the nanoplasmonics of systems dominated by quantum effects, such as subnanometer junctions [3,6] or by geometrical defects. In the selected test cases we will show how to engineer matter at the nanoscale to create very localized hot-spots, with potential application to single molecule detection [6,7].

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Plasmonic by design

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Keywords: Metamaterials

The manipulation of light on the deep subwavelength scale is essential for enhancing light-matter interactions and improving the performance of nanophotonic devices. In particular, hyperbolic metamaterials (HMMs) are highly anisotropic optical materials that behave as metals or as dielectrics depending on the direction of propagation of light. Their extraordinary optical properties made HMMs essential for a plethora of applications, ranging from aerospace to automotive, from wireless to medical and IoT. All these applications rely on the delicate balance between localization and loss of electronic excitations upon interaction with the impinging radiation. In this regard, the possibility to control and tune the optoelectronic properties of materials assumes a paramount relevance in the development of nanophotonics. Achieving the tunability of the electronic and optical properties of metal bulk and films is a difficult task. The coupling of optical properties with specific mechanical characteristics, chemical and thermal stability, CMOS compatibility, and low cost prevents the use of simple systems, such as noble metals. This calls for materials that show enhanced optical properties as well as tailorable mechanical and chemical properties.

Here, we adopted massive high-throughput techniques, based on density functional theory, to design and characterize tunable plasmonic materials that can be used as optical HMMS in the near-IR and visible range. Starting from simple transition-metal crystals (such as nitrides and carbides) [1,2], we investigate the role of composition, off-stoichiometry and structural disorder in TiNx compounds [3], and we provide an efficient strategy to fine engineering stable, easy-to-grow HMM superlattices [4,5], with selected optical and mechanical hardness (both ultrasoft and hard materials), see Figure 1. This new class of metamaterials may foster previously unexplored optical/mechanical applications in extreme conditions, e.g. in the fields of aerospace, satellites, and security systems.

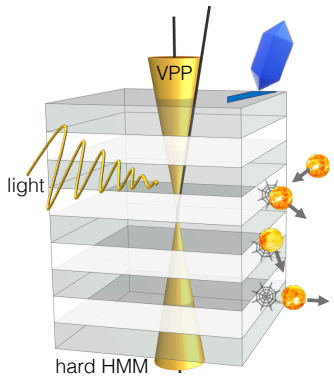

Figure 1: Pictorial scheme of mechanically hard HMM superlattice, which may sustain extraordinary volume-plasmon-polariton wave. Picture adapted from Ref. 5.

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Optical computation of the spin glass dynamics with a digital micromirror device

Marco Leonetti [1, 2], Luca Leuzzi[2,3], Erick Hormann[3], Giorgio Parisi[3], Giancarlo Ruocco[1,3].
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Keywords: Optical Computing, Light Diffusion, Digital Micromirror Devices, Complex photonics.

Optical computing is an emerging trend and it involves an optical layer paired with a traditional digital processing machine to improve performances while reducing computational costs and processing time. It promises parallel processing at high bandwidth that may be eventually performed in free space, with limited power consumption. Optical computation is an emerging scheme in quantum transport, quantum simulation [1], and machine learning. One of the advantages brought by optics is that certain simulations can be performed analogically, that is mapping the target mathematical problem on some optical observable which evolves "fast". For example, if the observable is light field, computation is performed in the time needed for a laser pulse wavefront to be shaped by a phase mask which can be as short as few femtoseconds: the calculation is in this case really performed at the "speed of light". A similar approach has bee for example, demonstrated for large matrix multiplication [2].

Spin glasses [3] serve as prototype models, capable of providing both equilibrium and off-equilibrium nontrivial phenomenology. In particular, the dynamics in an energy landscape with many equilibrium states and the origin of (multiple) relaxation times in finite dimensional systems are open questions in modern statistical mechanics. Complex systems from diverse fields fall into the spin glass universality class, e.g., brain functions, random lasers, and quantum chromodynamics. Indeed, novel methods for the calculation of the equilibrium states and of the dynamics of a spin glass system are highly sought after.

By exploiting last-generation optical modulation devices, millions of light rays can be driven simultaneously between several states within microseconds, thus potentially providing a scalable optical platform that only needs to be built around the relevant computationally hard problem.

In a recent paper [4], employing the experimental setup sketched in Fig. 1, we proposed an optical system to compute the dynamics of a given spin glass state. By implementing an analog optical calculation layer, we realized realize an optical spin glass (OSG) simulation. We observed that the overall intensity at P given points on a screen placed downstream of a strongly scattering medium shone with N coherent light rays from a single laser can be formally written as a spin glass Hamiltonian. Thus, we proposed scattering, coupled with an adaptive optical element, as an instrument to access the spin glass dynamics and employed for low and high complexity simulations. We demonstrate the optical supremacy of our approach with respect to digital computing.

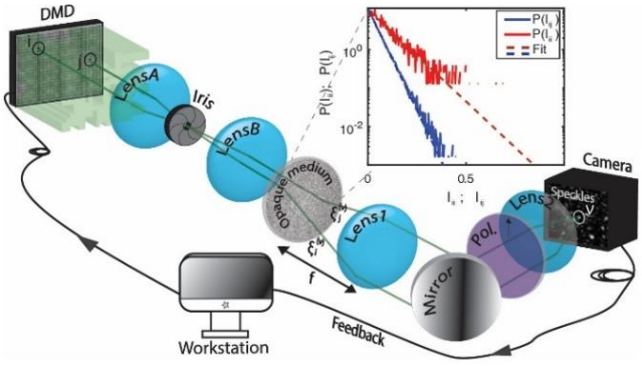

Figure 1 A sketch of the experimental setup. Light modulated by a digital micromirror device, in the State S in the super pixel mode, impinges on an opaque medium and thus each light ray is independently de-phased and attenuated. Transmitted light is measured on the camera. Intensity measure on a target is described from an equation identical to the SG Hamiltonian, where the role of the Jij matrix is played by the scattering matrix of the opaque medium.

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Probing intensity correlations inside a scattering medium

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Keywords: Spectroscopy and nano-imaging, Sensors and Biosensors

Speckle patterns generated by wave scattering are typically endowed with several universal properties. Inside a scattering medium, however, non-universal properties arise that depend on the material details and are still largely unexplored to date both experimentally and numerically due to physical inaccessibility and computational limitations. Here, we present an experimental study on the two-point intensity correlations of optical fields measured inside 3D random media, and validate it against rigorous numerical calculations [1]. To this purpose, we demonstrate a new experimental technique based on embedding DNA strings decorated with emitters separated by a controlled nanometric distance. In a typical turbid medium, the intensity emitted by each fluorophore will be proportional to the local excitation intensity. Their total emitted intensity can be then collected outside the sample without the need to resolve the position of the emitters, which are buried at sub-diffraction distances inside the scattering medium. The resulting probability distribution of the total fluorescent intensity is extremely sensitive to the number N of independent speckle patterns in which the sources are immersed [2]. By fitting the experimental distribution with its analytic model, the number of independent degrees of freedom of the field probed by the emitters is finally retrieved, free of any convolution or diffraction artifacts in spite of the nanometric distance between the fluorescent sources. When increasing the separation between the emitters, a transition should be observed from $N = 3$ degrees of freedom to 6, due to the fact that distant field values should be statistically independent. However, our experimental

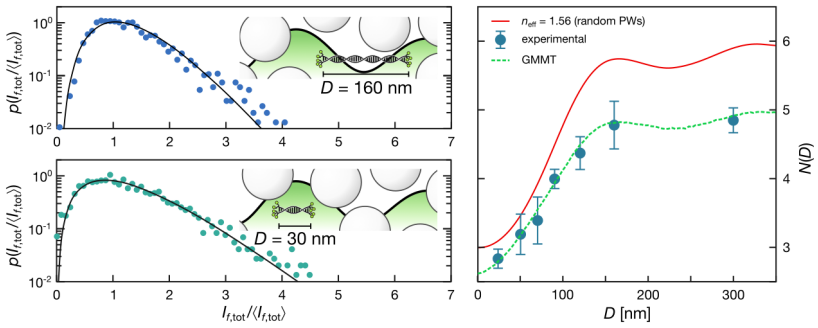

Figure 1: Degrees of freedom in a turbid medium (ZnO nanoparticles in a water-agarose). The average number of independent speckle patterns N is retrieved from intensity distributions (left), growing from $N(D = 0) = 3$ to $N(\infty) = 6$ for perfectly randomized speckle. The values inside the scattering medium (blue dots) remain below the expected trend (red), as confirmed by numerical calculations (green).

results show that the number of independent speckle components participating to the random field is lower (figure 1), despite the validity of mesoscopic regime assumptions [3]. This unexpected behavior is accurately reproduced by large scale 3D optical simulations based on Generalized Multiparticle Mie Theory (GMMT). The observed reduction of available degrees of freedom is due to the tightly constrained environment that is accessible to the fluorescent probes, which ultimately introduces preferred field oscillation directions in the regions between adjacent nanoparticles, causing a statistical bias on the observable polarization states.

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Spontaneous and stimulated optical emission from $CH_3NH_3PbBr_3$ perovskite: Role of excitons

Claudia Triolo[1], De Giorgi Maria Luisa[2], Lorusso Antonella[2], Cretì Antonella[3], Saveria Santangelo[1], Mauro Lomascolo[3], Marco Anni[2], Marco Mazzeo[2,4], Salvatore Patané[5].

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Keywords: Nano-imaging

Over the past decade, interest about metal halide perovskites has rapidly increased, as they can find wide application in optoelectronic devices, such as photovoltaic cells, light-emitting diodes, and optically pumped lasers. For these devices, the study and identification of emission mechanisms are crucial issues for determining the spectral properties of the device emission, and the factors influencing the stimulated emission threshold. In perovskites, the free-carrier (FC) recombination, excitons (EXs), and trap states (TSs) are regarded as the light-emitting species that contribute to the spontaneous emission process; their relative amount affects the spectral features of the optical emission. We have recently demonstrated [1] that the equilibrium condition between the densities of the photoexcited species, quantitatively expressed by Saha's equation, can be modified by the passivation of the TSs obtained by UV irradiating the sample under wet air conditions. This translates in an increase of electron–hole pairing to form bound neutral states, with EXs thus becoming the dominant species.

This contribution deals with the role of free and localized EXs in the spontaneous and stimulated emission from thermally evaporated thin films of $CH_3NH_3PbBr_3$ perovskite [2]. The optical features of the samples have been investigated from nano- to micro- scale by using different experimental approaches. The results highlight the correlation between morphological properties and spontaneous emission, which is spatially inhomogeneous in terms of intensity and wavelength of emission. A detailed line-shape analysis of the local photoluminescence (PL) emission allows quantifying the local contributions of the FC, EXs, and TSs to the spontaneous emission. As a general trend, EXs are confirmed as the dominant emitting species in passivated $CH_3NH_3PbBr_3$ perovskite films, whereas FCs play a minor role. Depending on the morphology, a further distinction can be done: free and localized EXs are the main emitters in the bottom layer and in the crystallites, respectively. Amplified spontaneous emission (ASE) measurements confirm the excitonic nature of emitting species. For higher excitation densities, the constant PL background is attributed to the localized EXs, while the occurrence of a competition between ASE signal and spontaneous emission of free EXs indicates that the ASE signal is due to stimulated emission from the free EXs.

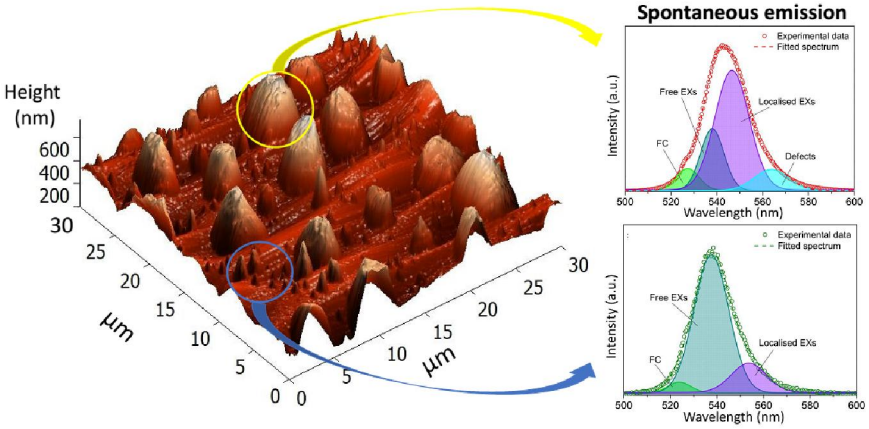

Figure 1: AFM images of thin films of $CH_3NH_3PbBr_3$ perovskite (nominal thick 50 nm) and line-shape analysis of PL spectra acquired on isolated crystallite and in correspondence of the bottom layer.

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Energy transfer to molecular adsorbates by transient hot-electron tunnelling

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Keywords: Quantum plasmonics, Ultrafast nano-optics, Devices and Applications

In the last ten years the study metallic nanoparticles gained a lot of interest because of their opto-electronic features and especially to the presence of Surface Plasmon Resonance (SPR). This peculiar effect makes these nanosystems suitable for a broad variety of applications in biomedicine, catalysis, electronics, optics and more. [1,2]

A relatively new and highly promising way by which SPR can be exploited is hot-carriers mediated photocatalysis. As the SPR start to dephases, there is the generation of the so called hot-carriers which are out of equilibrium electrons (and holes) with higher (or lower) energy compared to the unperturbed system. Once formed, these carriers can migrate to the nanoparticle edges and their energy can be transferred to a molecule adsorbed on the surface, activating chemical reactions such as water splitting [3] and CO_2 reduction [4].

Although many theoretical advances have been made to determine the physics below this phenomenon [5,6], there still are an open debate on the precise interaction mechanism with the adsorbate. Our work aims to investigate one of the possible hot-carriers injection routes which implies the transient tunneling to the adsorbate and further energy release the molecular vibrational states.

To do that, we explored the interaction among hot-electrons (HEs) and a small molecule at the real time Time Dependent Density Functional Theory (rt-TDDFT) level. We represented the hybrid metallic nanostructure-molecule system through a minimalistic model composed on a linear chain of metal atoms interacting with a small molecule adsorbed on the edge. By simulating the real-time dynamics of a set of single HE on the metal chain, we observed that they can interact with the adsorbate by releasing part of their kinetic energy on some specific vibrational modes, with an efficiency strongly dependent on the molecular species and on the HE energies. We estimate that this effect would become significant when the contribution of all produced HE is taken into account, providing energy to the molecular vibrations in the order of a few tenths of eV. Our work suggests that, regardless their energy, all generated HE can compete to the activation of the motion involved in the photocatalyzed reaction and this process can cooperate with the currently accepted mechanism involving a direct electron transfer from the nanostructure to the adsorbed molecule. [7]

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Novel Materials & Devices

Session Chair: Michele Ortolani

Low loss polyethylene-loaded plasmonic waveguides for the mid-infrared

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Keywords: Devices and Applications, Sensors and Biosensors, Spectroscopy.

Plasmonic waveguides are crucial building blocks for on-chip photonic integrated circuits (PICs). They have recently attracted great interest in mid-infrared (mid-IR) molecule sensing [1], as the fingerprint absorptions of many molecules lie in this spectral range. However, some substances in chemical and biological sensing require addressing longer wavelengths (>7 µm). Moreover, the longwave IR (8-14 µm) atmospheric transmission window hosts a lot of additional applications such as low-loss and high bandwidth optical free-space communication, thermal imaging and remote explosive detection. Since PIC-ready quantum cascade technology became available recently [1] and due to the unsuitable, high losses of commonly used dielectrics and polymers, novel monolithic integration strategies and materials for on-chip devices are essentially needed, Polyethylene (PE) is a polymer of high interest for mid-IR and THz integrated photonics, due to its wide spectral transparency range from 2-200 µm [2,3] and its low refractive index. It is basically the mid-IR counterpart to PMMA in the near-IR.
In this work we provide the first demonstration of PE-based plasmonic structures in the mid-IR, together with their millimeter-scale propagation along the chip surface. We first identified suitable waveguide architectures and assessed the impact of geometrical factors via numerical simulations using the commercial software COMSOL, confirming low-loss transmission at a design wavelength of 9.12 μm (see Fig. 1a). Based on those results we could realize PE-based Dialectic-Loaded Surface Plasmon Polariton Waveguides (DLSPPWs) plasmonic waveguides. Analyzing them with a custom-made waveguide characterization setup, we determine coupling losses of ~4 dB. We obtain from them from applying the effective cut-back technique (Fig. 1b), which allows us to extract in this way low average waveguide losses of 11 dB/mm. To the best of our knowledge, this is the first demonstration of a low-loss DLSPPW at such wavelength. This result opens the pathway for novel PIC devices in the mid-IR, addressing various applications such as sensing and optical free-space telecommunication.

a) b)

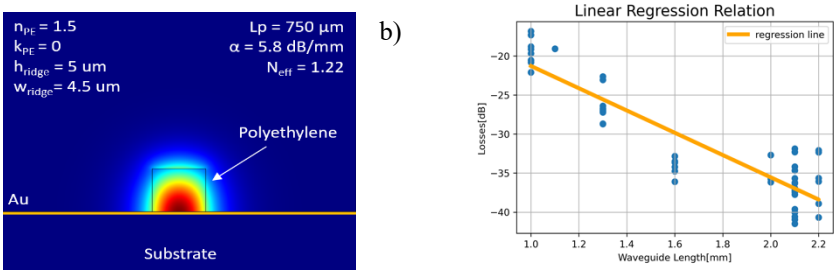

Figure 1: (1a) Cross sectional facet view of the simulated mode profile at 9.12 μm (relevant parameters given in the inset). (1b) Cut-back technique results for determining the coupling losses at 9.12 μm for typical PE-Au plasmonic waveguides of different lengths.

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Plasmonic Nanodevice to generate force gradients to induce nanoparticles acceleration

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Keywords: Plasmon-exciton polaritons, Hybrid metallo-dielectric nanophotonics, Devices and Applications

Optical forces are generated using electromagnetic field gradients and have proven to be a powerful tool for manipulating micro- and nano-objects [1].
An effective way to generate such gradients is to use the phenomenon of surface plasmonics, that is the amplification of the electromagnetic field due to the resonant interaction between a light beam and an interface between a dielectric and a metallic material [2]. By appropriately designing such plasmonic structures, it is possible to engineer the electromagnetic field distribution for effective manipulation of nano-objects. Thanks to these characteristics, plasmonic structures have many applications, especially in the medical and biological fields [3]. Moreover, in the last few years a line of research has developed in the aerospace sector aimed at designing plasmonic structures useful for generating optical propulsion for micro/nanosatellites.

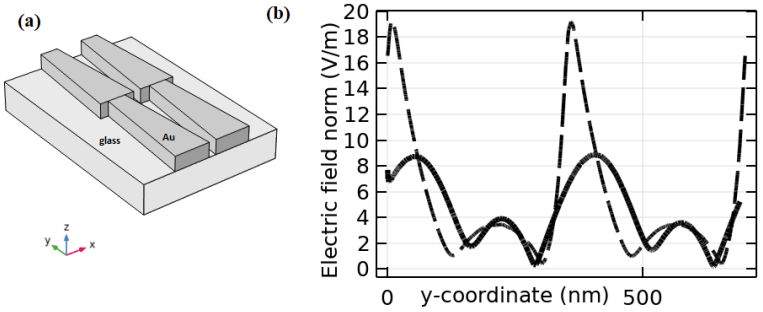

Figure 1: (a) a sketch of the gold scalene trapezoids structure with a glass substrate in array configuration. (b) 1D plot of the electric field amplitude in function of y-coordinate in trapezoids structure (dashed line) and rectangular structure (continuos line)

In this context, a very interesting structure is the one proposed by Rovey's group at the University of Illinois [4-5], in which two gold rectangular trapezoids are separated by a gap and placed on a glass substrate. When light illuminates this structure, the electromagnetic field resulting from plasmonic effects (in particular, from the combination of Localized Surface Plasmon and Surface Plasmon Polaritons) is such as to generate forces capable of ejecting nanoparticles (propellant) and thus inducing propulsion. In addition, the geometry of these structures allows the organization of elementary cells in an array configuration, i.e., to replicate them in a serial manner in order to amplify the force and obtain intensities suitable for the displacement of macroscopic objects. The array configuration, however, involves a spatial distribution of the force that is not optimal for maximising propulsion performance. In fact, in order to obtain effective ejection, it is necessary to induce a strong initial boost to the nanoparticles.

Therefore, we will describe a new type of plasmonic structure (Fig.1a) that overcomes the above limitations. In particular, the proposed system consists of two gold scalene trapezoids separated by a variable gap and placed on a glass substrate.

The optical characteristics of the proposed structures will be illustrated (Fig.1b) as a function of its geometrical parameters and compared with the field distribution described in the literature. In particular, we will see that the field distribution generated by a linear array of these structures no longer constrains the dynamics of the nanoparticles placed in the vicinity of the structure and that efficient nanoparticle motion is induced. Furthermore, the advantages of a circular array configuration (i.e. the individual structures are arranged to form a ring) will be detailed, showing the possibility of reducing the physical footprint of the structure while maintaining its performance. Finally, the dependence of the propulsive parameters (force, output velocity) will be optimized according to the geometrical parameters of the proposed array configurations.

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Magnetoplasmonics Beyond Metals: Transparent Conductive Oxide Nanocrystals Enable High Performance Sensing

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Keywords: Magnetoplasmonics, Spectroscopy, Sensors

Active modulation of the plasmonic resonance in nanostructures enables the improvement of plasmon-based sensors and optical modulators. Compared to other external tools employed to this purpose, magnetic field presents several advantages: it is fast, easy to implement in devices, and its action on free charge carriers is fully reversible as it does not damage or modify the plasmonic material. However, achieving large magnetic modulation of the plasmonic resonance without broadening the optical response represents a great challenge in material choice for magnetoplasmonics, hampering the application in devices. Indeed, noble metals nanocrystals (NCs) have sharp optical resonances, but weak magneto-optical signal, proportional to the cyclotron frequency (ω_C) [1]; on the other hand, nickel ferromagnetic nanodisks [2] or hybrid bimetallic nanostructures [3] have large magnetic modulation, but suffer from the high optical losses of the magnetic metal, thus broadening the plasmonic resonance.

To overcome such limitations, we propose a paradigm shift in material choice by employing transparent conductive oxides (TCO) NCs, which are able to support a plasmonic resonance in the infrared. The carrier density in these NCs is tunable in the range 10^{18}-10^{21} cm^{-3} by controlling the amount of aliovalent dopant introduced in the NCs. Among TCOs we synthesized Sn-doped In_2O_3 (ITO) and F^- and In- co-doped CdO (FICO) colloidal NCs, revealing a 20-fold and 40-fold enhanced magnetoplasmonic response compared to Au NCs, detected through Magnetic Circular Dichroism (MCD). Such enhancement is ascribed to the lower effective mass (m*) of free carriers in such TCOs with respect to most metals, which in turn boosts ω_C. FICO NCs have a reduced plasmon line width, which increases the magnetoplasmonic response with respect to ITO, while having a comparable m* [4].

Employing colloidal dispersions of FICO NCs in a proof of concept field-modulated refractometric sensing experiment we achieved a superior refractive index sensitivity with respect to metal-based magnetoplasmonic systems reported in the literature [1-3]. Our approach challenges the current state of the art of plasmonic refractometric sensing [5], with the advantage of not requiring curve fitting but simply tracking a change in magneto-optical signal at fixed wavelength.

Considering that non-magnetic TCOs have been used in this work, a further enhancement of the performance is potentially achievable by introducing magnetic dopants in plasmonic TCO NCs. These results open up a new route toward high performance magnetoplasmonic materials and devices, discarding current approaches based on metallic nanostructures.

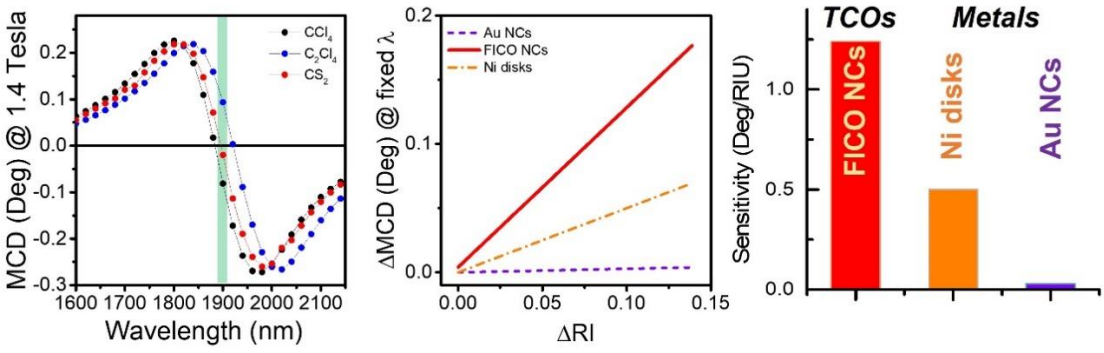

Figure 1: a) MCD of FICO NCs in three different solvents; b) MCD signal at fixed wavelength as a function of the solvent refractive index (RI) variation; c) RI magneto-optical sensitivity for FICO and ITO NCs compared with state of the art magnetoplasmonic nanostructures.

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Thin film Surface Phonon Polaritons dispersion in suspended Silicon Carbide Membranes

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Keywords: Spectroscopy and nano-imaging

Surface Phonon Polaritons (SPhPs) are surface waves originating from coupling of the electromagnetic (e.m.) field with optical phonons of a polar dielectric [1]. The SPhP dispersion in thin films splits in an upper and lower modes for thicknesses comparable to the e.m. field penetration length, leading to stronger wavelength compression compared to SPhPs in a semi-infinite surface. It has been shown that the in-plane thermal conductivity [2] and near-field radiative energy transfer [3] in suspended films of polar dielectrics are determined by the presence of SPhPs modes. The SPhPs dispersion was assumed to follow theoretical predictions. Here, we present the experimental retrieval of the SPhPs dispersion in 100 and 200 nm SiC suspended membranes through sSNOM polariton interferometry [4]. By recording spectra at different positions away from a slit etched in the membranes, the polariton decay can be followed. Through FFT in the tip position, the experimental dispersion can be retrieved. We show that measured values fit with theoretical predictions from both analytical models and transfer matrix calculations.

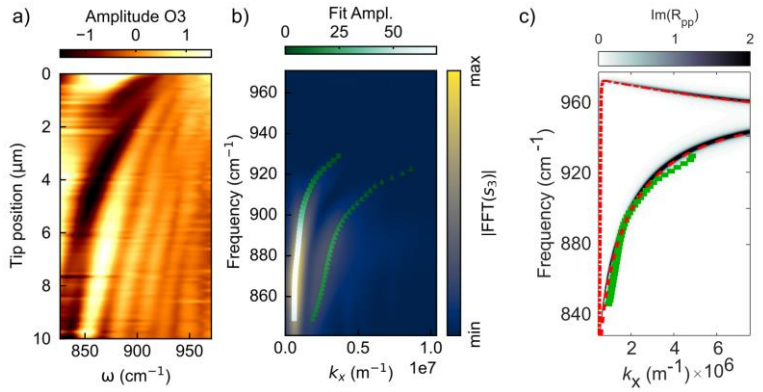

Figure 1: a) Nano-FTIR spectra at different tip positions with respect to a slit etched into a 200 nm SiC membrane. b) FFT of a) with respect to tip position fitted with a double Lorentzian (due to edge and tip launched SPhPs) at each frequency. c) The experimental dispersion relation extracted from b) is compared to analytical and transfer matrix calculations.

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Controlling resonant surface modes by arbitrary light-induced optical anisotropies

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Azobenzene-containing polymers are known to exhibit interesting and peculiar properties when irradiated. Thanks to the azo bond present in the molecular structure, azobenzenes can switch between a *trans*- and a *cis*-form, involving a variation in both the steric hindrance and the polarizability of the molecule [1]. Upon a proper choice of the illumination wavelength, the photoisomerization process can be made cyclic, thus leading to macroscopic effects on azopolymeric films such as surface relief grating formation [2-3] and birefringence [4-5].

In this work, we show how such a light-controlled birefringence can be successfully exploited to tune the optical response of a resonant nano-photonic structure for Bloch Surface Waves (BSW). The latter are surface defect modes sustained by one-dimensional photonic crystals (or planar multilayers). Here, we introduce an azopolymer-doped film deposited on top of a dielectric multilayer and use it as an arbitrarily-controlled anisotropic medium to tune some of the BSW properties. The azopolymeric film birefringence is produced by controlling the polarization state of an external illumination laser beam.

The cavity is constituted by a circular Distributed Bragg reflector (DBR), shown in fig. 1a, and it is combined with a circular diffraction grating to couple white illumination with the BSW. The fabrication is performed by means of a probe-assisted technique (NanoFrazor, Heidelberg) that uses an atomic force microscope (AFM) heated probe to induce a local evaporation of the polymer layer at high spatial resolution. Spectroscopic measurements are obtained on a modified inverted microscope, with oil-immersion collection optics, combined with a spectrometer. The measured spectrum of the cavity, shown in figure 1c, is monitored while a 532nm laser is used to excite the azopolymer with different polarization orientations.

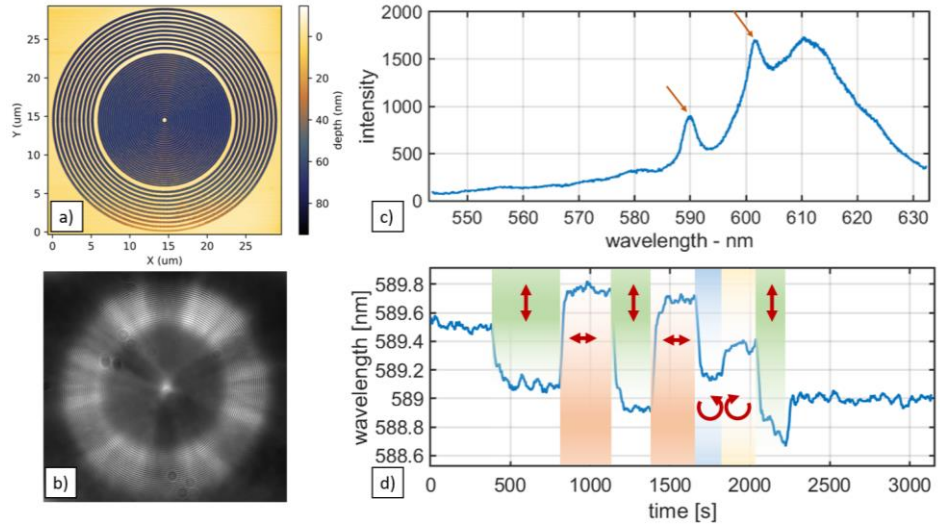

Figure 1: a) AFM image of the DBR circular cavity fabricated by means of a probe-assisted indentation technique. b) Image of the cavity obtained by Fourier-filtering the illumination beam. c) Spectrum measured at the centre of the cavity where two resonances are highlighted. d) Time evolution of the left most resonance peak upon variation of the laser polarization state.

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Mid-infrared dielectric antennas on ENZ substrates

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Keywords: mid-infrared; epsilon-near-zero; nanoantennas.

Nanoantennas play a major role in light manipulation at the nanoscale. This is achieved by exploiting their resonances, which present highly confined and enhanced local fields [1]. The traditional materials of choice for nanoantennas are noble metals, however there are intrinsic limitations associated to their use. In fact, plasmonic resonances suffer from ohmic losses, affecting the quality factor and the lifespan of the antenna itself. Moreover, magnetic resonances supported by metallic plasmonic antennas are weak, which is detrimental for specific applications such as those requiring enhanced optical chirality [2, 3].

In the last years, dielectric nanoantennas have been proposed as an alternative to plasmonic ones. While there are many demonstrations for dielectric nanoantennas working in the visible and near-infrared spectral range [3-6], their extension to the mid infrared (MIR) is not yet fully established. In particular, the epitaxial growth of crystalline semiconductor materials, which are the preferred choices for high-quality dielectric antennas working in the MIR, is typically performed on a semiconductor substrate with a refractive index close to the one of the nanoantennas. This environment configuration hinders the establishment of strong resonances for dielectric antennas in the MIR.

In this work, as a solution to this problem, we employ a highly doped InAs layer as the substrate [7]. By varying the doping of the InAs layer we obtain a material showing a zero crossing of the real part of the permittivity, the so-called epsilon-near-zero (ENZ) condition [8], that can be tuned over a broad wavelength range in the MIR. We then fabricate, exploiting standard e-beam lithography (Figure 1a), an array of dielectric nanoantennas in an undoped InAs layer deposited on top of the ENZ substrate. By designing the antenna array resonances to be spectrally overlapped with the ENZ frequency of the substrate, we observe a sharp resonance (Figure 1b). Numerical electromagnetic simulations also demonstrate that the associated field enhancements are expected to reach values similar to those obtained in the ideal situation consisting in the same antennas in vacuum. The demonstration of a dielectric platform displaying sharp resonances in the MIR opens new possibilities in surface-enhanced spectroscopy, biosensing, and chiroptical analysis.

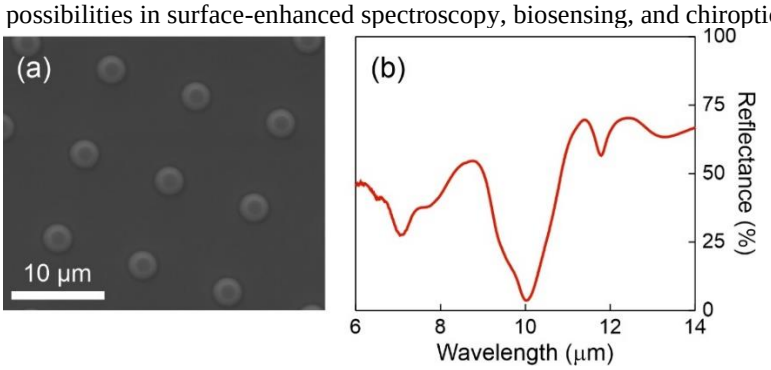

Figure 1: Scanning electron microscope top view of the InAs nanoantennas (panel a) and the experimental reflectance of the array (panel b).

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Session Chair: Alessando Belardini

Time-domain topology optimization of wideband dispersive plasmonic nanostructures

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Keywords: Ultrafast nano-optics, Nonlinear plasmonics, Metamaterials.

Topology optimization techniques enabled the inverse design of nanophotonic structures with desired optical properties. These techniques have been used to optimize dielectric integrated optical circuits and nanostructures using frequency-domain methods [1]. However, a time-domain formulation is computationally more efficient for handling dispersive materials. We introduce a new time-domain gradient-based topology optimization approach to design wideband dispersive plasmonic nanoantennas employing the Drude model [2]. We present several novel designs of 2D and 3D nanoantennas capable of boosting the enhancement/focusing of the electric energy at a specified domain of interest (see Fig. 1 for an example in 3D).

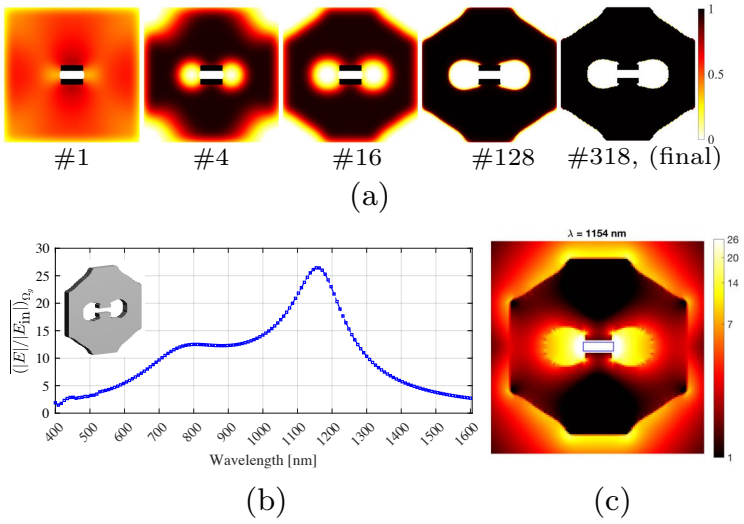

Figure 1: (a) Snapshots showing the evolution of a silver nanostructure during the optimization process subject to vertically polarized illumination. The design domain is pixelated and each pixel can attain, during the optimization, any permittivity between silver (black) and vacuum (white). The interpolation between metal and dielectric causes convergence issues due to plasmonic effects, which we relax by introducing an artificial damping in Maxwell's equations. (b) Field enhancement over the observation domain versus wavelength (the inset shows a 3D view of the nanostructure). (c) Field distribution at the wavelength of maximum performance $\lambda_0 = 1154$ nm.

Our method opens new opportunities for the automatic design and optimization of dispersive nanophotonic structures with a broadband optical response for applications in nonlinear plasmonics, integrated optics, plasmonic colouring and absorbers, epsilon-near-zero photonics, thermoplasmonics, biosensors, and ultrafast optics.

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Optical assessment of dewetted Mie resonators through Dark-field Scanning Microscopy

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Keywords: Metamaterials, Spectroscopy and nano-imaging, Devices and applications.

All-dielectric dewetted nano-particles have been widely studied and proposed as a valid alternative to plasmonic nanoparticles to improve light-matter interaction at the nanoscale, as they enable efficient manipulation of electromagnetic fields and can be used as building blocks for metamaterials and metasurfaces [1]. Recently, all-dielectric nanoparticles have emerged as candidate for beam-steering applications. Here, we clarify the crucial role of Mie nanoparticles illumination in the enhancement of their scattering directionalities. By combining for the first time dark-field spectroscopy with lateral (asymmetric tilted illumination) and controlled movement of the island under the collection objective (Figure 1a), the spatially and spectrally resolved radiation patterns of individual nanoparticles can be easily analyzed.In Fig. 1b we report the comparison between the experimental and simulated scattering cross-section for an island of radius R=190nm (SEM image in the upper right inset), where the magnetic quadrupole (Mq) and electric/magnetic dipole (Ed/Md) resonances can be detected. Lateral illumination results into a simple but powerful method to achieve and engineer beam-steering effects [2]; in fact, in this lighting condition different resonant modes show scattering intensities along distinct directions, as shown in the simulated polar plots of Mq and Ed/Md (Figure 1c). Through the hyperspectral approach, not only we are able to map in real space the distribution of multipolar modes and to reconstruct the scattering pattern, but also to spectrally isolate the two main Mie resonances contribution to the total scattering cross-section simultaneously in the same measurement. As shown in Figure 1d, the experimental spectra of Mq and Ed/Md (orange and purple lines) nicely agree with the theoretical contributions to the total scattering cross-section of Mq and Ed/Md (orange and purple dashed lines) . Our investigation tools result in an unprecedented ability in modeling and characterizing monocrystalline nanostructures and their optical properties of nanoantennas in sight of beam steering and light-matter interaction applications.

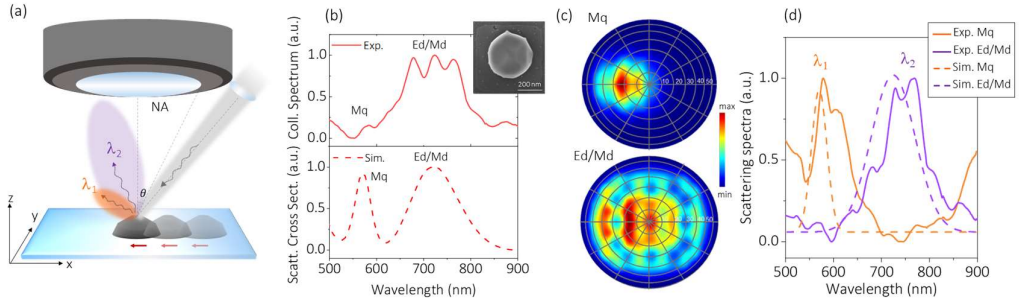

Figure 1: (a) Sketch of the dark-field scanning experiment. (b) Upper (Bottom) graph: experimental (simulated) scattering cross-section of an island of R=190nm, pictured in the SEM image of the inset. (c) Simulated polar plots of Mq and Ed/Md modes for the island illuminated laterally. (d) Contribution of Mq (orange) and Ed/Md (purple) to the experimental (continuous line) and simulated (dashed lines) scattering cross-section.

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Bound State in the Continuum in Resonant hBN Metasurfaces

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Keywords: Bound state in continuum BIC, polaritons, photonic crystals, 2D materials.

Optical Bound states in the continuum (BIC) is an emerging area of research interest that acquired a lot of attention in the last decade. The optical BIC states have been widely discussed in material systems such as photonic crystals, optical waveguides and fibers, 2D materials, and other optical systems. Eventually, in the last few years, optically detected BICs in photonic systems and nanofabrication were exploited as promising tools for breakthrough applications. Recent research [1] combines nanophotonics with imaging optics that extends the potential of dielectric metasurfaces for sensing applications by using a symmetric meta-unit composed of two elliptical dielectric nanoresonators [1]. The confinement of BIC to improve quality factor Q is still an important challenge in this field of research. We define Q as:

$$\text{Quality Factor } (Q) = \frac{\text{Central Frequency of the Resonance } (f0)}{\text{Full Width Half Maximum (FWHM) } (\Delta f)}$$

Here we are going to show the study of the resonance at (BIC) mode based on phonon polaritons and improve the quality factor (Q) using periodic meta-units composed of two elliptical hexagonal boron nitride (hBN) polaritonic resonators over the SiO_2/Si substrate as shown in Fig. 1a.
The wide bandgap (~6 eV), high-quality phonon polaritons, strong optical anisotropy, and high emission efficiency make hBN an ideal system for nanophotonics. hBN is a versatile platform to arbitrarily control polaritons at the nanoscale to achieve freeform, transformation, and meta optics [2,3].
Here in this research, the simulations are done under two directions of the electric field, E_X (horizontal) and E_Y (vertical), to selectively excite the modes of the structure. The rotation of the hBN resonators are showing significant dependence on the BIC modes because the component of E_X and E_Y varies with every rotation and orientation of resonators. Specifically, in each unit cell, the resonators are rotated by an angle θ in opposite directions. For $\theta = 0°$, the BIC state is a dark mode that cannot be excited with incident light. For increasing values of θ, we can increase the coupling of the original BIC mode with plane waves (quasi-BIC mode). In this simulation, we used $\theta = 0°, 10°$, and we observe that for 10°, a new resonance in the transmission spectrum (Fig. 1b) appears at about 43THz, indicating coupling to the BIC mode. To better estimate the Q we remove the effect of the substrate (Fig. 1c) and we find that Q increases from 140 (for the main resonances) to 430 for the BIC state. This enhancement in Q, is more than factor of *3* because, the main resonances are dominated by radiative losses, which can be reduced in the BIC state using the rotation angle to control coupling.
The high Q (BIC) modes represent the formation of strongly coupled phonon-polaritons and our result suggests a platform for future polaritonic devices.
We acknowledge the financial support of the European Research Council (ERC) under Grant Agreement No. ERC-2020-STG 948250 (*SubNanoOptoDevices*).

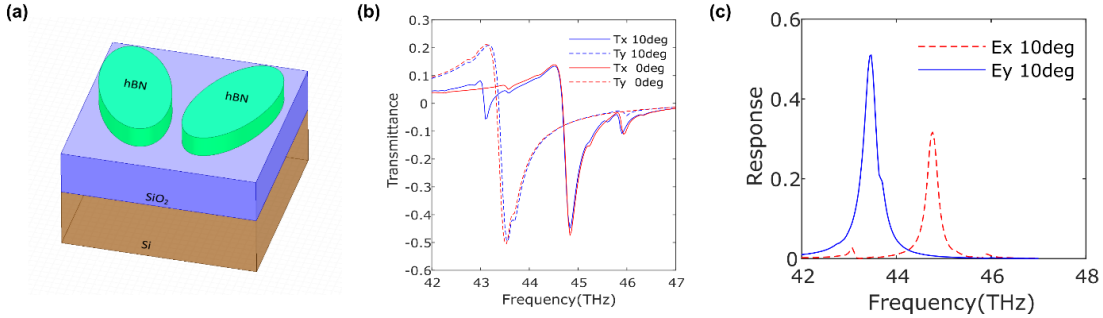

Figure. 1. a) Heterostructure of elliptical hBN over SiO_2/Si substrate. b) Transmittance vs Frequency curve T_X and T_Y for E_X and E_Y polarization at 0 and 10 degrees of hBN resonators rotation respectively. c) Response curve at degrees of rotation for E_X and E_Y polarization and represents BIC mode at E_X polarization.

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Assembly and optical properties of amyloid-gold hybrid nanomaterials

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Keywords: biosensors, spectroscopy

Hybrid nanomaterials are a group of nanomaterials built of both organic and inorganic part which can not only combine the beneficial effects typical for each of the components, but also exhibit new and unique properties [1]. Thus, they can find broad applications in fields such as bioimaging, drug delivery or photonics. One of the most interesting inorganic materials used for hybrid nanomaterials are gold nanoparticles, due to their characteristic plasmonic properties, desirable in fields like biosensing [2]. Kumar et al [3] has shown that anisotropic gold nanoparticles can also create hybrid nanostructures when they bind to organic fibrillar nanostructures called amyloids [4], which are protein aggregates present in neurodegenerative disorders like Alzheimer's disease or amyloidosis. Such nanomaterials are able to exhibit induced plasmon chirality (IPC) in their circular dichroism spectra due to chiral arrangement of anisotropic nanoparticles following the helical structure of fibrils. Surprisingly, our research on this topic has shown that there is also another possibility to induce plasmon chirality upon binding to amyloids and that it is possible with different shapes of anisotropic nanoparticles. Our hybrid amyloid-gold nanomaterials are made of chiral bovine insulin amyloids, acting as an organic matrix, and two types of achiral anisotropic gold nanoparticles: mini nanorods and bipyramids. What is interesting, we observed that upon binding to amyloids both types of nanoparticles show IPC of the same sign as intrinsic chirality of fibrils and without any chiral mutual nanoparticle arrangement meaning that observed IPC is based on the interaction with the chiral field of the matrix and not from the dipolar coupling between adjacent nanoparticles arranged in a chiral pattern. As a result, such gold-amyloid heterostructures could be efficiently used to sense the amyloid chirality in plasmonic wavelengths without any labelling them with fluorescent dyes, reported to influence the structure of protein aggregates [5]. However, staining the amyloid-gold heterostructures with one of amyloid-specific fluorophores like Thioflavin T or Congo Red, significantly enhanced IPC intensity leading to questions if amyloid-bound nanoparticles can sense not only the chirality of protein aggregates but also amyloid-bound dyes.

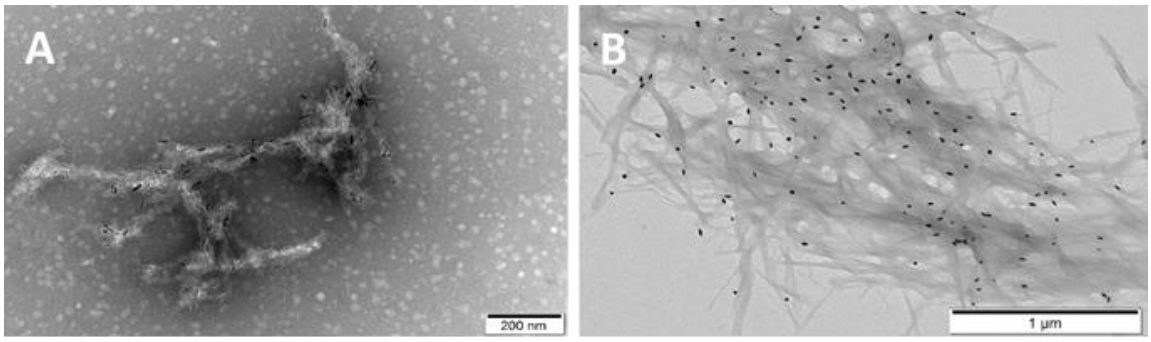

Figure 1: TEM images of amyloid-gold hybrid nanomaterials with gold nanorods (A) and bipyramids (B).

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Plasmonic and Photonic Multifunctional Metamaterials with Tunable Properties based on Alternative Plasmonic Materials

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Keywords: Metamaterials, Hybrid metallo-dielectric nanophotonics.

The current research in plasmonic nanotechnologies is focusing on nano-systems with intrinsic multifunctionalities, aimed at reaching large tunability of properties to fulfill at once multiple needs, spanning different applications (optoelectronics, biosensing, solar-energy harvesting). Indeed, several nanoarchitectures have been investigated to modulate optical characteristics of plasmonic metals outside the visible, enhance performances, and eventually activate novel functionalities. In this framework, a new class of artificial metamaterials is rapidly growing, in parallel with alternative materials (Transparent Conductive Oxides TCOs, or transition metal nitrides, e.g TiN) due to the possibility to adjust the carrier concentration, i.e. the plasmonic response from VIS to IR [1]. Hyperbolic metamaterials especially sustain unique "high-k modes" activated by the periodic alternation of conductors (e.g. noble metals) and dielectrics (e.g oxides) of subwavelength thicknesses [2]. Besides, when increasing the characteristic dimension of layers, one-dimensional (1D) photonic crystals can be achieved straightforward [3].

Here, a variety of novel multifunctional meta-structures have been developed, involving conventional metals (gold nanoparticles Au NPs), alternative materials (nitrides, TCOs) and original design routes (via pulsed laser deposition) with the aim to explore, from a material science perspective, electrical/optical responses resulting from unusual combinations of materials and properties (transparency, conductivity, tunable VIS-IR plasmonics, active modulation).

For instance, a metal-TCO nanocomposite has been obtained by integrating Au NPs in thin films of the less-explored Tantalum-doped TiO_2 (Ta:TiO_2) TCO, possibly operating as sensor or multifunctional transparent electrode. Indeed, the localized plasmon resonance of Au can be tailored in VIS-near-IR by exploiting the carrier concentration modulation in the TCO through the Ta content (Fig. 1a). Ta:TiO_2 has been also exploited for the fabrication of original transparent conducting multilayers synthetized directly in one-step by alternating conductive (compact) and dielectric (nanoporous) layers. Structural and electrical properties have been optimized to rule optical/plasmonic outputs as a function of deposition conditions, doping content and geometrical parameters. Applications are foreseen as hyperbolic platforms in the IR, while actively-modulated 1D photonic crystals can be easily accomplished by customizing compact/porous fraction (Fig. 1b-c). Finally, novel TiN-TiO_2 multilayers have been realized as potential hyperbolic metamaterials in the visible, with features that can benefit from the low cost, refractory nature and CMOS compatibility of TiN, along with the tunable plasmonic response through stoichiometry.

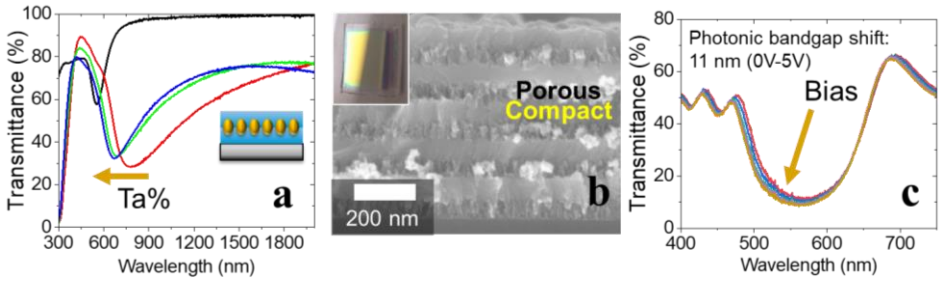

Figure 1: (a) Transmittance spectra of Au-TCO nanocomposites; SEM image (b) and transmittance spectra (c) of a Ta:TiO_2-based photonic crystal with external bias applied.

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Single nanoparticle trapping using metamaterial-assisted optical tweezers

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Keywords: nanoparticles, plasmonic structures, optical trapping.

Plasmonic nanostructures have been used to overcome Abbe's diffraction limit in optics and can provide very strong electric field gradients near metallic films [1,2,3]. This faciliates optical trapping of single (or clusers of) nanoparticles [4]. Achiving stable trapping with a low incident optical power can still be challening. In this work, we demonstrate a Fano resonance-assisted plasmonic optical tweezers for single nanoparticle trapping using an array of asymmetrical split nanoapertures on a 50 nm gold thin film [5]. We measured a large trap stiffness of 8.65 fN/nm/mW for 20 nm polystyrene particles at a near-resonance trapping wavelength of 930 nm. Notably, the trap stiffness on-resonance was enhanced by a factor of 63 compared to the off-resonance value, due to the effects of the cavity. We also attribute some of the trapping enhacement to thermally induced effects [6], which can be exploited to improve the trap performance and influence the particle motion. These results facilitate trapping with low incident laser intensity, reducing the risks of damage of biomolecules.

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(Un)conventional experiments and simulations of chiro-optical effects in plasmonic nanostructures

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Keywords: Metamaterials, Hybrid metallo-dielectric nanophotonics

Nanostructured materials with plasmonic layers can tailor and confine electromagnetic fields at the nanoscale, thus leading to different applications from flat optics and nanoscale light emitters to highly precise chip-scale sensors. Moreover, if the plasmonic layers are asymmetric, they can break the symmetry of light-matter interaction, opening new possibilities in chiro-optical interaction. Chirality, as a lack of mirror symmetry, presents a fundamental property of our world – most biologically important molecules are chiral. At the nanoscale, it leads to different interaction with circular polarizations of opposite handedness, usually defined as circular dichroism (CD). Nanostructured components can be designed in order to enhance the chiro-optical effects in the near of far-field, or to emit desired circular polarization into desired direction. On the other hand, experiments for the improvement of chiral sensing ideally involve chiro-optical characterization of nanostructures without and with molecules, while the measurements of circularly polarized emission require additional optical components on the pathway of the emitted light.

From the design point of view, 3D asymmetric geometries are modelled and optimized by numerical solvers, depending on the possibilities of the fabrication technique in use. We focus on the possibility of low-cost fabrication of asymmetric nanostructures by tilted deposition of metal. Specifically, we model plasmonic elliptical nanohole as periodically repeated unit cells with ellipses tilted from the periodic symmetry lines; such periodic metasurfaces possess intrinsic chirality [1] and can further emit high degree of circularly polarized light [2]. Plasmonic nanostructures can also enhance chiral near-field effects in single [3] and periodic [4,5] geometry. Instead, novel quasi-random simulation approach is needed for nanostructures obtained with self-assembled growth from randomly positioned seeds; we used it to explain reflection CD in self-assembled nanowires asymmetrically covered by Au [6].

In order to prove chiro-optical behaviour of plasmonic designs, we use both conventional and unconventional characterization techniques. The first ones involve transmission or reflection measurements of the circularly polarized input [6,7]. Moreover, we are now able to characterize the polarization state of the transmitted beam, by exciting the nanostructure with an input beam which is widely tunable in wavelength, polarization state and direction. It must be, however, noted that molecular CD arises from the different absorption of left and right circular polarizations. For direct measurements of absorption of nanostructures, we rely on unconventional characterization by means of photothermal effects. Namely, we use photo-acoustic [8,9] and photo-deflection [10,11] technique to measure the nanostructure absorption response under left or right circularly polarized excitation.

The subject of current work is chiro-optical characterization of nanostructured plasmonic samples which are coupled with chiral molecules. To this end, we first characterized chiral molecules in solutions, by measuring fluorescence detected circular dichroism from cuvettes [12]; in this case, a large volume of chiral molecules is excited in blue range by left or right circular polarization, and the fluorescence intensity difference is detected. The next step is the deposition of emitting molecules on plasmonic nanostructured samples, and characterization of the final chiro-optical response. Led by vast experience in near-field simulations of chiral field around plasmonic nanostructrues, we believe that our approach can be extended toward sensing of low volumes of chiral molecules deposited on the top of resonant plasmonic nanostructures.

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Ultrafast & Non-Linear NanoPhotonics

Session Chair: Carlo Forestiere

Surface charge modulated nonlinear response of heavily doped semiconductors

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Keywords: Nonlinear Plasmonics

In the context of near- and mid-infrared plasmonics based on heavily doped semiconductors [1], we apply a hydrodynamic perturbative approach within the Thomas-Fermi approximation [2, 3] to investigate the effects of surface charge depletion, obtained through the application of a static bias [4, 5], on the free electron (FE) nonlinear response of these materials. This, under the influence of external electric- and magnetic- fields $\mathbf{E}(\mathbf{r},t)$ and $\mathbf{H}(\mathbf{r},t)$, can be modeled through the following constitutive relation:

$$\ddot{\mathbf{P}}+\gamma\dot{\mathbf{P}}=\frac{n_0e^2}{m}\mathbf{E}+\beta^2\nabla(\nabla\cdot\mathbf{P})-\frac{1}{3}\frac{\beta^2}{n_0}(\nabla\cdot\mathbf{P})\nabla n_0+\mathbf{S}^{(2)}_{\mathrm{NL}}+\mathbf{S}^{(3)}_{\mathrm{NL}}. \tag{1}$$

where $\mathbf{P}(\mathbf{r},t)$ is the polarization field, $n_0(\mathbf{r})$ is the equilibrium charge density, $\beta(\mathbf{r})^2=\frac{10}{9}\frac{c_{\mathrm{TF}}}{m}n_0(\mathbf{r})^{2/3}$, with $c_{TF}=\frac{\hbar^2}{m}\frac{3}{10}(3\pi^2)^{\frac{2}{3}}$, and second- and third-order nonlinear sources are:

$$\begin{aligned}\mathbf{S}^{(2)}_{NL}=&\frac{e}{m}\mathbf{E}\nabla\cdot\mathbf{P}-\frac{e\mu_0}{m}\dot{\mathbf{P}}\times\mathbf{H}+\frac{1}{en_0}(\dot{\mathbf{P}}\nabla\cdot\dot{\mathbf{P}}+\dot{\mathbf{P}}\cdot\nabla\dot{\mathbf{P}})-\frac{1}{en_0^2}\dot{\mathbf{P}}(\dot{\mathbf{P}}\cdot\nabla n_0)\\&+\frac{1}{3}\frac{\beta^2}{en_0}\nabla(\nabla\cdot\mathbf{P})^2-\frac{1}{9}\frac{\beta^2}{en_0^2}(\nabla\cdot\mathbf{P})^2\nabla n_0,\end{aligned} \tag{2}$$

$$\begin{aligned}\mathbf{S}^{(3)}_{NL}=&-\frac{1}{e^2n_0^2}\Big[\nabla\cdot\mathbf{P}(\dot{\mathbf{P}}\nabla\cdot\dot{\mathbf{P}}+\dot{\mathbf{P}}\cdot\nabla\dot{\mathbf{P}})+\dot{\mathbf{P}}\cdot\dot{\mathbf{P}}\nabla\nabla\cdot\mathbf{P}\Big]\\&+\frac{2}{e^2n_0^3}(\nabla\cdot\mathbf{P})\dot{\mathbf{P}}(\dot{\mathbf{P}}\cdot\nabla n_0)-\frac{1}{27}\frac{\beta^2}{e^2n_0^2}\nabla(\nabla\cdot\mathbf{P})^3+\frac{4}{81}\frac{\beta^2}{e^2n_0^3}(\nabla\cdot\mathbf{P})^3\nabla n_0,\end{aligned} \tag{3}$$

where m is the electron effective mass, e the elementary charge (in absolute value), μ_0 is the magnetic permeability of vacuum and γ is the damping rate. Here, contributions proportional to ∇n_0 tackle the non-zero gradient of the equilibrium charge density. We study FE third-harmonic generation (THG) solving Eqs.(1-3) numerically [2]. For a semi-infinite slab (see Fig.1), we predict a one order of magnitude increase of the efficiency of FE THG when the equilibrium charge density at the surface, n_0^{surf}, is 25 smaller than that in the bulk, n_b. The efficiency enhancement factor, ζ, can grow up to two orders in correspondence with the plasmonic resonance of a nanopatterned structure.

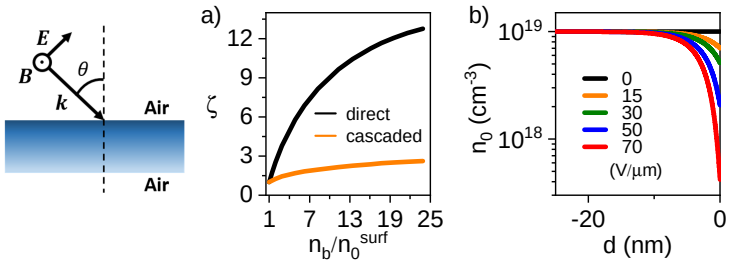

Figure 1: (a) Enhancement factor ζ, for $\theta=60°$, as function of the depletion factor n_b/n_0^{surf}, in the case of cascaded and direct THG from a doped ($n_b=10^{25}\ m^{-3}$) indium phosphide slab; (b) $n_0(\mathbf{r})$ as a function of the distance d from the surface of the slab for different applied external bias.

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Dual-pump coherent control of the nonlinear emission by a plasmonic nanoantenna

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The present drive towards the miniaturization of nonlinear optics is motivated by the number of functionalities it could bring about in integrated devices, such as frequency conversion, biochemical sensing, and active optical signals control. The main hindrance to the technological deployment of nonlinear optics is the perturbative character of nonlinear optical interactions, whose intrinsic weakness is compounded at the nanoscale by the small volume of matter involved. This fundamental limitation can be mitigated by exploiting the localized plasmonic or photonic (i. e. Mie-type) resonances supported by metallic or dielectric nanoantennas, respectively, which lead to a confinement and an enhancement of optical electromagnetic fields. Thanks to the advanced nanofabrication techniques currently available, these platforms are driving the expansion of the nonlinear nano-optics and meta-optics fields since the last decade.

Recently, we explored a wave mixing process excited by a pulse of angular frequency ω, corresponding to the telecommunication wavelength $\lambda = 1550$ nm, and its second-harmonic generation (SHG) replica pulse at 2ω. When the two pump pulses are temporally and spatially superimposed on an optical nanoantenna, sum-frequency generation (SFG) is observed at $3\omega = \omega + 2\omega$. This output is coherent and degenerate in frequency with the third-harmonic generation (THG) at $3\omega = \omega + \omega + \omega$ seeded by the pump at ω alone, as illustrated by the energy diagrams in Figure 1. We have already investigated the interplay between these two frequency-tripling pathways in AlGaAs nanocylinders [1]. Here we focus on a gold dimer where a V-shaped nanoantenna [4], tuned to resonate at ω, is electromagnetically coupled to a rod resonating at 2ω. The geometry of the dimer was initially devised to limit the destructive interference in the far-field of the second-harmonic emission and to boost the conversion efficiencies of SHG and THG [2, 3]. Here, its asymmetry unlocks the coherent cross-talk between THG and SFG, which produces a nonzero net interference between SFG and THG. The interference is visible in delay traces (see the inset in Figure 1) which exhibit a power modulation of the total signal at 3ω up to a factor of 2.

The range of modulation can be explored by varying the delay τ of about 1.5 fs. This effect, that was forbidden in the AlGaAs platform due to the cylindrical symmetry of the nanoresonators, is not a mere byproduct of the frequency degeneracy between THG and SFG. Instead, it can be exploited to implement an all-optical signal control. Indeed, the dephasing between pumps needed to achieve such modulation could be imparted with an electro-optic device, thereby providing a practical avenue for ultrafast modulation and coherent control of the up-converted signal.

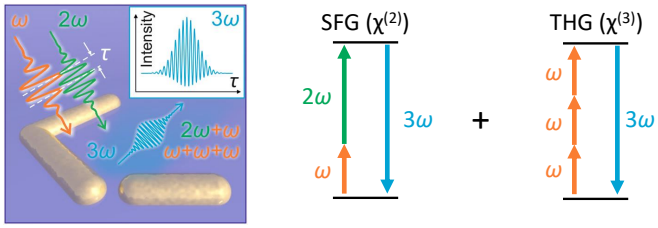

Figure 1: The concept of the $(\omega, 2\omega)$ experiment on the asymmetric plasmonic nanostructure is displayed on the left. The inset displays an idealized interference measurement as a function of the delay τ between the two pumps. The energy diagrams of the wave mixing processes are shown on the right.

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Ultrafast Dynamics of Photochromic Molecules Coupled to Plasmonic Nanoantennas

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Keywords: Quantum plasmonics, Ultrafast nano-optics, Plasmon-exciton polaritons

Molecular polaritons are hybrid light-matter states that emerge when a molecular transition strongly interacts with the light modes of a resonator [1]. At optical frequencies, this interaction opens up new possibilities to tailor the energetics and the morphology of the molecular electronic states, even allowing to enhance or suppress the photophysical and photochemical processes of molecules [2,3]. However, achieving such control on ultrafast timescales in collective molecular ensembles requires a deep understanding of the coupled dynamics stemming from the interaction between many molecules and localized optical excitations. In this work, by combining quantum mechanical modelling and pump-probe spectroscopy, we shed light on the ultrafast dynamics of a hybrid system composed of photo-switchable dye molecules coupled with optically anisotropic plasmonic nanoantennas, which allow us to selectively switch between two regimes where the light-matter interaction is either weak or strong. Our synergistic approach reveals an ultrafast relaxation dynamic of polaritonic states, collapsing from a collective coherent excitation to a localized molecular state undergoing vibrational relaxation.

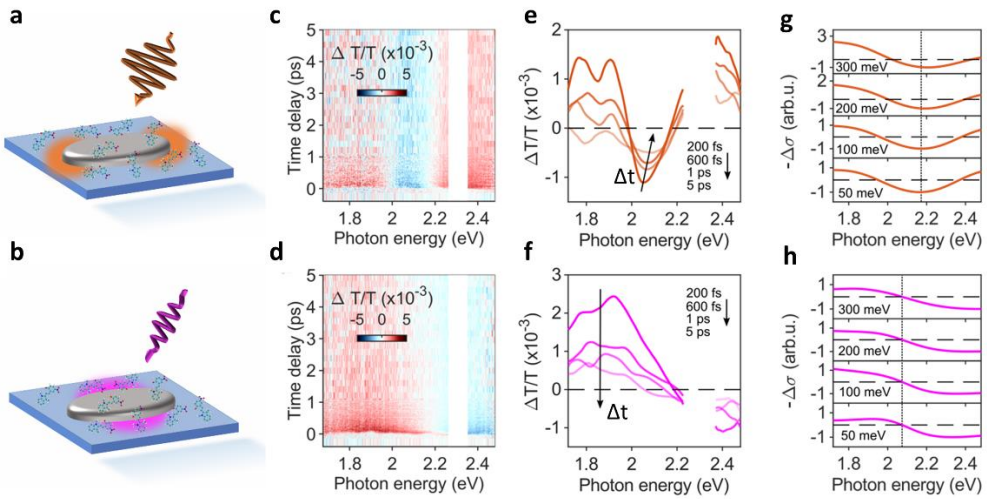

Figure 1: **a,b** Sketch of the hybrid system displaying the two dipolar plasmon resonances along the long (**a**) and short (**b**) axis of the nanoantenna. **c,d** Pump-probe transient transmission ΔT/T upon excitation along the long (**c**) and short (**d**) axis. **e,f** Spectral cuts of the corresponding maps (**c,d**) at 200 fs, 600 fs, 1 ps and 5 ps. **g,h** Simulated transient transmission for the two cases considering the frequency relaxation of the localized molecular state. Frequency shifts of 50, 100, 200, 300 meV are shown.

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Developing an Ultrafast Scanning Tunnelling Microscope

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Keywords: Ultrafast Nano-Optics, Spectroscopy and Nano-Imaging

Scanning tunneling microscopy (STM) is a well-established experimental technique that allows to investigate the electronic properties at the surface of condensed matter systems with atomic spatial resolution. The working principle is the following: when a metallic tip is brought a few nanometers away from a sample and a voltage is applied, a net electron current flows across the nanojunction due to quantum tunnelling. If the voltage is applied electronically, only quasi-static electronic properties can be studied. However, electron dynamics in condensed matter systems takes place on the femtosecond timescale ($1fs=10^{-15}s$), which is several orders of magnitude faster than the speed at which electronic devices operate so that dynamic phenomena are elusive in traditional STM.

Interestingly, state-of-the-art ultrafast laser technology allows the generation of optical pulses lasting only one cycle of the carrier wave. The interaction of such electromagnetic transients with metallic nanostructures enables extremely nonlinear optical phenomena even at minute pulse energies of a few picojoules, due to field enhancement effects. In this extremely nonlinear regime of light-matter interaction, field-induced tunnelling of electrons across a nanoantenna junction has recently been demonstrated [1]. These tunnelling currents are coherent with the driving radiation and can be controlled by varying the carrier-envelope phase (CEP) of the laser electric field.

In this context, we propose here the realization of an ultrafast scanning tunnelling microscope, where the electric field of near-infrared single-cycle laser pulses is exploited to drive electron currents across an STM junction thus enabling femtosecond temporal resolution.

A custom-made Er:fibre laser system, operating at a repetition rate of 40MHz, provides a supercontinuum spanning from 850nm to 2200nm [2]. After compression, we measured a laser pulse duration of 5fs, which corresponds to only one oscillation of the central carrier wave at 1500nm. The CEP of the laser field is passively stabilized and can be controlled with a feedback loop based on f-2f interferometry. The laser pulses are focused onto the STM tunnelling junction and a laser-induced tunnelling current is measured through lock-in detection. In order to assess the nature of the laser-induced tunnelling current, we sweep the CEP while acquiring tunnelling current values and we observe a modulation coherent with that of the optically-induced voltage transient. This proof is crucial for the establishment of the ultrafast STM technology.

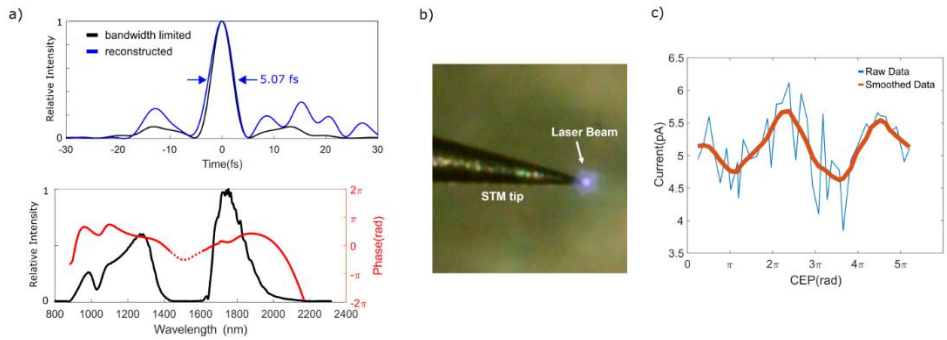

Figure 1: a) (top) Reconstructed laser electric field after compression (blue line) and comparison with bandwidth limited pulse with the same spectrum (black line). (bottom) Reconstructed spectrum and spectral phase of the laser. b) Image of STM tip with the laser beam scattered at the tip apex. c) Measured tunneling current as a function of the laser carrier-envelope-phase (CEP).

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Second-harmonic generation of visible light by a monolithic $LiNbO_3$ metasurface

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Metasurfaces (MSs) are planar arrays of sub-wavelength elements ("meta-atoms") whose optical response can be finely tuned through the geometry and arrangement of the meta-atoms. They hold promise to miniaturize many bulk ($\sim$ mm) optical elements so to integrate their functionalities in compact optoelectronic devices. Nonlinear optics is a fast-rising field of application of MSs, for purposes such as frequency mixing and up-conversion, and generating entangled photon pairs. Nonetheless, the sub-wavelength thickness of MSs along with the intrinsic weakness of nonlinear interactions mean that the efficiency of such processes is often very low. One must thus carefully engineer the resonant behavior of the MS to enhance light–matter interaction in such small volumes and control the directionality of the nonlinear emission.

Crystalline lithium niobate ($LiNbO_3$) is a ferroelectric material widely employed for optoelectronics and nonlinear optics thanks to its high refractive index, broad transparency window, and large electro-optical response and second-order nonlinearity. Following steady advances in nanofabrication techniques, $LiNbO_3$ is attracting much attention as a promising platform for metal-less nano- and meta-photonics and a valid alternative to the well-established narrow band-gap semiconductors (particularly III–V compounds and alloys) [1].

I will report highly directional second-harmonic (SH) generation of visible light by a monolithic $LiNbO_3$ MS [2]. The experiment is schematically depicted in Figure 1a: excitation occurs from the substrate side and SH is generated in the forward direction. The MS was milled on a commercially available z-cut $LiNbO_3$ substrate via dual-beam focused ion beam lithography, achieving the fabrication of small (175 nm radius) and tall (440 nm) meta-atoms ("pillars") with steep (80°) side walls arranged in a square grating (590 nm pitch) as displayed in Figure 1b. Pumping with an 80 MHz train of 140 fs laser pulses with 500 MW/cm^2 peak intensity, we measured SH conversion efficiencies (SH power/exciting power) up to 2.4×10^{-8} — in line with previous reports of SH generation in the infrared [3]. The numerically-assisted design of the MS [4] exploits the resonant modes of the single pillar: a magnetic dipole at the exciting wavelength of 820 nm, along with an electric dipole and a magnetic quadrupole at the SH wavelength of 410 nm. The interplay between the single-pillar emission and the grating mode of the MS brings about an efficient ($\sim$ 20 dB) rerouting of the SH emission from the normal direction into the first diffraction orders at an angle of 45°. The diffraction orders that lie along the pump polarization dominate, thereby encoding the pump polarization into a given SH emission direction. Such light steering capability suggests a blueprint of a nonlinear diffractive MS for applications like nonlinear holography with polarization encoding.

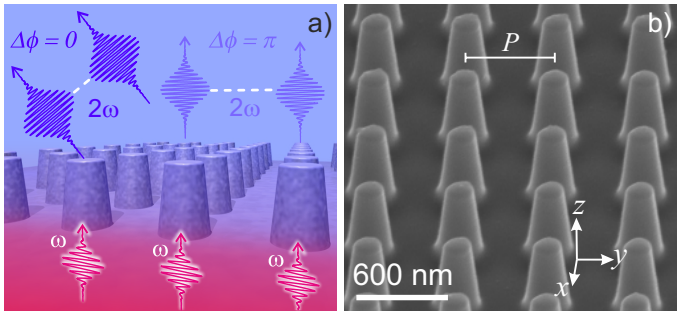

Figure 1: (a) Sketch of harmonic generation and steering by the metasurface. (b) Scanning electron micrograph of the metasurface. The extraordinary axis of $LiNbO_3$ lies along the z direction.

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Sensing

Session Chair: Maria Caterina Giordano

Optical force aggregation of gold nanorods for high sensitivity detection of molecular to nano-plastics particulate matter

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Keywords: Optical printing, plasmonic particles, sensor.

Optical nanoimprinting provides a versatile platform to print nanometer size particles into arbitrary configurations with very high precision. We used dipole approximation [1-3] to calculate optical forces acting to nanoparticles for a focused laser beam, where two main optical force components are identified [4-5]: the gradient force, which attracts particles toward the high-intensity focal spot, and the scattering force, which tends to push particles along the beam propagation direction. In the case of metallic nanoparticles, optical forces are dominated by radiation pressure [6] and can be used to efficiently push nanoparticles along the beam optical axis onto a substrate [7-10]. In this context, optical forces can be applied to optically print nanoparticles into patterns of "active" aggregates [7-8] on surfaces such as glass (Fig. 1), polymers [11] and graphene [12].

Here, we summarize recent progress in our experiments that use optical nanoimprinting of plasmonic nanoparticles to create the "active" aggregates that can be used for Surface Enhanced Raman Spectroscopy (SERS) detection of biomolecules in microfluidic circuits [13] and as plasmon-enhanced thermophoretic concentrators for nanoscale particulate matter such as nanoplastics. In both cases enhanced sensitivity is demonstrated, enabling the detection of nanoparticles/molecules of size/concentration orders of magnitude lower than what can be done by Raman spectroscopy or Raman Tweezers [14].

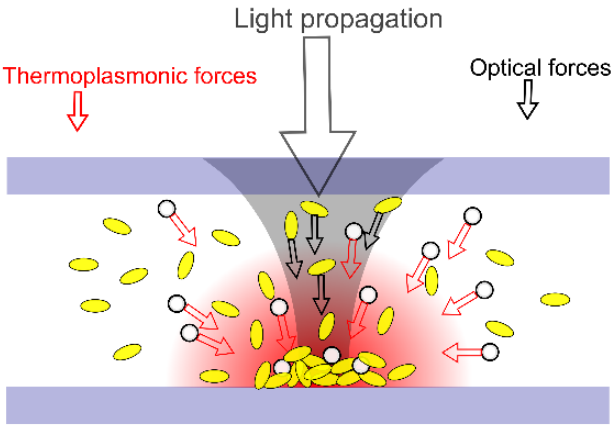

Figure 1: Basic principle of an "active" aggregate fabrication. Optical forces are used to push metal nanorods (yellow ellipses) mixed to either molecular or nanosize particulate matter (white circles), in order to generate either SERS-active hot spots or thermophoretic concentrators of particles.

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Reference-free X-ray fluorescence for the molecular quantification: determination of SERS enhancement factor

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Keywords: SERS, enhancement factor, sensors.

The enhancement factor (EF), indicating the magnification of the Raman signal of molecules interacting with the surface of plasmonic nanostructures, is a crucial parameter in the field of surface-enhanced Raman spectroscopy (SERS). Metrological calculation of EF requires a careful evaluation of both the signal intensities and the number of molecules in SERS and normal Raman conditions. The determination of the surface density of molecules adsorbed on the substrate is fundamental to estimate the number of active molecules contributing to the enhanced Raman signal on a plasmonic substrate and, for this reason, strongly impacts the estimation of the enhancement factor. A viable methodology for this challenging task is reference-free X-ray fluorescence (RF-XRF). We determined the EF using 7-mercapto-4-methylcoumarin (MMC) as probe molecule on gold-coated silicon nanowires, as schematized in Figure 1, integrating SERS and normal Raman spectroscopy with synchrotron radiation based RF-XRF data that provide an absolute quantitative measurement of the molecular surface density [1]. In addition, the surface coverage of MMC on the substrate is modelled by molecular mechanics (MM) and molecular dynamics (MD) simulations. RF-XRF analytical quantification can be extended to other molecules or common analytes for SERS or fluorescence spectroscopy. The adoption of standardized methodologies for the characterization of nanostructured systems promotes inter-laboratory comparison and boosts the applicability and progress of SERS.

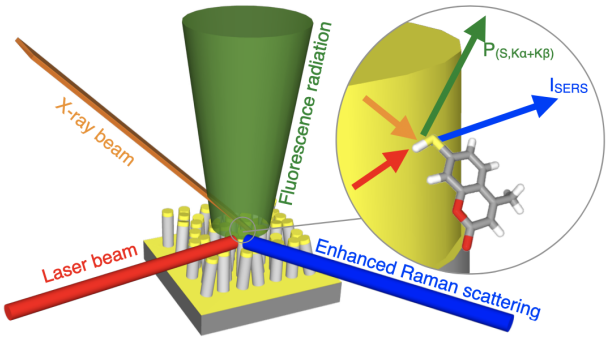

Figure 1: Schematic representation of the RF-XRF measurement where the incident X-ray beam excites the fluorescence radiation on the plasmonic substrate, constituted of gold-coated silicon nanowires. The same substrate was used for SERS analysis of MMC.

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Surface-enhanced Raman scattering with nanophotonic and biomedical amplifying systems for a more accurate diagnosis of Alzheimer's disease

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Keywords: Surface Enhanced Raman Scattering, Spectroscopy, Sensors and Biosensors, Alzheimer's disease

Alzheimer's disease (AD) is the most common neurodegenerative disorder in the elderly with an incidence that progressively increases worldwide [1]. One of the main neuropathological hallmarks of AD is the presence of amyloid-β protein (Aβ) aggregates which forms extracellular amyloid plaques [2]. At present, clinical diagnosis of AD relies on NINCDS-ADRDA (National Institute of Neurological and Communicative Diseases and Stroke/Alzheimer's Disease and Related Disorders Association) criteria that permit to classify the disease as possible or probable, but not definite (which still requires neuropathological examinations) [3]. This is partially due to the fact that the clinical, laboratory and instrumental biomarkers investigated are not specific for AD and can be altered in other neurodegenerative conditions [4].

In this work, we present an innovative approach in which a seed amplification assay (SAA) capable to detect traces of pathological Aβ species in the cerebrospinal fluid (CSF) of patients with AD [5] is combined with Surface Enhanced Raman Spectroscopy for the ultrasensitive analysis of CSF collected from extensively-characterized patients with AD or other neurological conditions.

Our findings show that SERS analysis of SAA end products through an optimized low-cost silver nanowires/PTFE SERS-active substrate [6,7], supported by machine learning approach [8] and correlated with the other clinical, instrumental and laboratory findings, could reveal chemo-structural information useful to distinguish AD from other neurological diseases in living patients.

Acknowledgment:
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Probing Neurons Before and After Differentiation on Sharp-tipped Au Nanopyramid Arrays with SERS

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Keywords: Surface Enhanced Raman Scattering, Sensors and Biosensors, Devices and Applications,

The development of local plasmonic nano sensors which enable the investigation of cellular processes has attracted great attention for both fundamental research and real biological applications[1], [2]. Here, we report on an effective biointerface to monitor the activity of cells over time and probe their stage of differentiation with Surface Enhanced Raman Spectroscopy (SERS). In particular, the investigation is focused on ND7/23 neuronal cells and the discrimination is carried out through principal component analysis (PCA) of the SERS spectra collected from undifferentiated and differentiated neurons. We show that Au nanopyramids (AuNPs) array with sharp tips are realized with a large-scale fabrication route based on colloidal lithography (Figure 1a-c)[3]. By tuning the length (L) and the height (H) of the Au NPs it is possible to realize a SERS substrate with a plasmonic resonance at 785 nm, which can be used to perform SERS on neurons in a non-destructively way (Figure 1d-e). From the PCA analysis we demonstrate that it is possible to discriminate between the two groups, which are morphologically different since differentiated neurons have axons and dendrites (Figure 1f-g). We discuss that the collected Raman maps contain information on lipids and proteins of the cells membrane and intracellular DNA/RNA fragments.

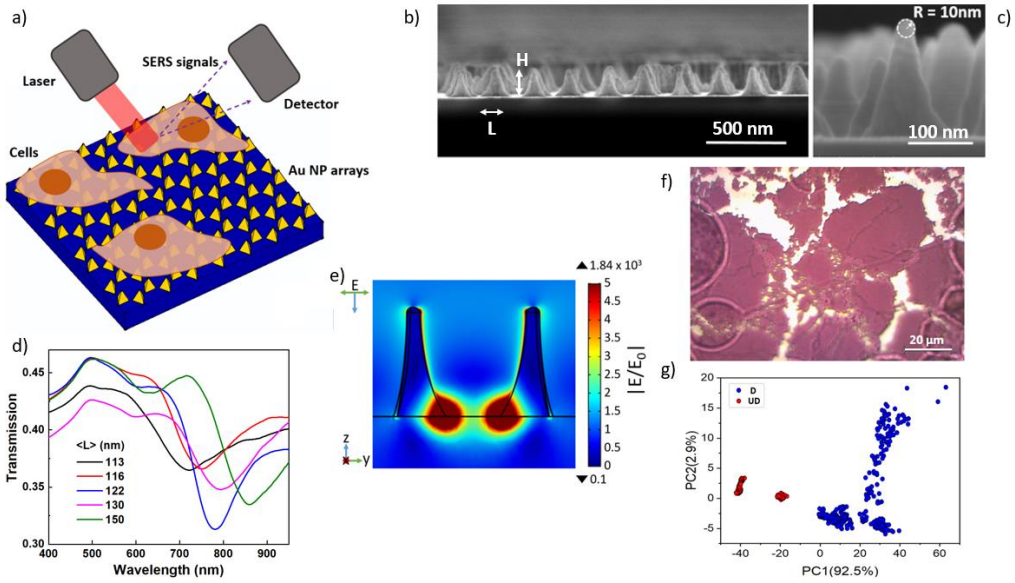

Figure 1: a) Sketch of the Au NPs array as biosensing platform of cells with SERS. b)-c) SEM image of the Au NPs array and a magnification of a single nanostructure respectively. d) Transmission spectra as a function of the lateral size. e) Electric field distribution at the resonant wavelength 780 nm. f) Microscope image of a differentiated neuron on the SERS substrate. g) PCA biplot obtained from the analysis of the SERS spectra of differentiated and undifferentiated neurons.

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Hydrogel-based Plasmonic Nanocomposites for Label-free and Non-label free Biomolecular Interactions Monitoring

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Keywords: Metal-enhanced fluorescence; Sensors and Biosensors; Devices and Applications.

Localized Surface Plasmon Resonance (LSPR)- and Metal-Enhanced Fluorescence (MEF)-based biosensors show unique benefits compared to other sensing technologies [1], [2]. LSPR biosensors, based on noble metal nanoparticles (NPs), exhibit resonances confined within the surroundings of NPs and highly sensitive to the local variations [3]. Moreover, the combination of plasmonic NPs with fluorescent dyes enables the design of MEF biosensors. Flexible optical biosensors represent promising devices capable of adapting to non-planar surfaces and easy to integrate with complex microfluidics and microelectronics systems. In this context, we propose the fabrication of a 3D optically responsive nanocomposite materials based on spherical gold nanoparticles (AuNPs) embedded in Poly-(ethylene glycol) diacrylate (PEGDA) hydrogels with varying MWs (700 Da and 10000 Da) (Figure 1).

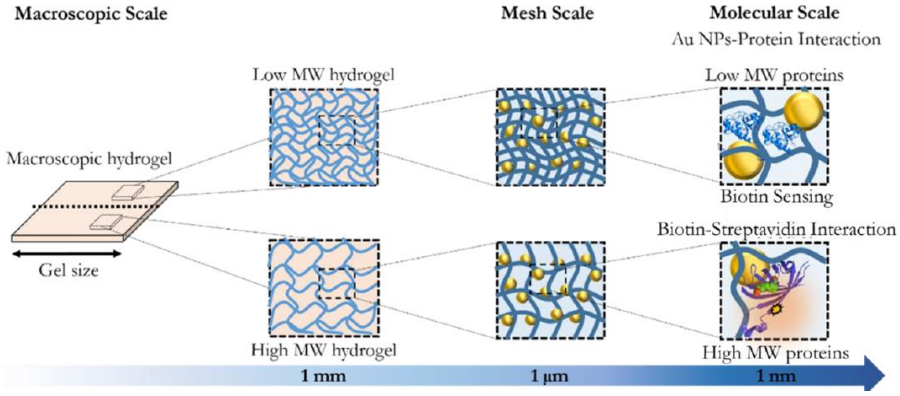

Figure 1: Schematics of PEGDA/AuNPs nanocomposites at different size scales.

We exploit the different mechanical properties of the selected polymers to design optically-bioresponsive platforms with different detection mechanisms. Low-MW nanocomposites can be used as refractive index sensors for small molecules, as hormones, while high-MW hydrogel nanocomposites with high swelling capability can be used to specifically recognize large molecules with specific plasmon coupling and decoupling. Moreover, we use a labelled molecule to prove that these platforms can be used also as MEF sensing systems [4], [5]. The AuNPs physically entrapped within the hydrogel network act as sensitive transducers of the variations in hydrogel swelling ratio. Moreover, the well-known metal-enhanced fluorescence phenomenon was investigated within the nanocomposite to validate the functionalization scheme and to further improve the performance of the transducer showing a Cy3 fluorescence intensity enhancement of one order of magnitude. We envisage that our work could pave the way to the design of integrated nanoplasmonic platforms for multiplexed sensing with implications in rapid and low-cost healthcare monitoring, water cleaning, and environmental monitoring.

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Portable SERS device for early cancer diagnostics

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Keywords: SERS, miRNA, early cancer diagnostics

In this work, a polydimethylsiloxane microfluidic device integrating porous silicon (pSi) membranes decorated with silver nanoparticles (AgNPs) was used as a portable SERS biosensor for the detection of microRNAs (miRNAs), short regulatory non-coding RNA sequences typically over- or under- expressed in connection with several diseases including oncogenesis. A two-step hybridization assay was exploited [1,2]: in the first step, one half (half1) of a complementary DNA probe is immobilized on the AgNPs through a thiol group to capture the miRNA from the sample. In the second step, the miRNA is bound by the second half of the probe (half2), which is labelled with a Raman reporter, thus enabling the highly sensitive and label-free detection of the target. Commercial and custom Raman dyes featured by different molecular sizes and electronic resonance wavelength were compared as Raman reporters. In order to study the dependence of the assay sensitivity on the reporter-to-surface distance, different concentrations of miRNA were analyzed by changing the position of the reporter along the half2 sequence. The results were interpreted taking into account the near-field plasmonic response of the SERS nanostructures by modeling a simplified system (Ag hemispheres dimers on pSi) by 3D Finite Element Method. The electromagnetic near-field intensity was calculated for representative NP diameter-gap size combinations (Figure 1a, b, c) and analyzed inside and outside the inter-particle gap, evaluating the impact of the highlighted differences on the detection of miRNAs at high and low concentration. The optimized functionalization protocol was successfully used to detect several miRNAs involved in lung cancer (i.e. miR-222, miR-214, miR-146a, miR-148b, miR-320a and miR-20a), even in cancer cell extracts. In-chip miR-214 detection using a portable Raman spectrometer was demonstrated at picomolar concentrations (Figure 1d), confirming the potentialities of SERS-based microfluidics for low cost and reliable early cancer diagnostics.

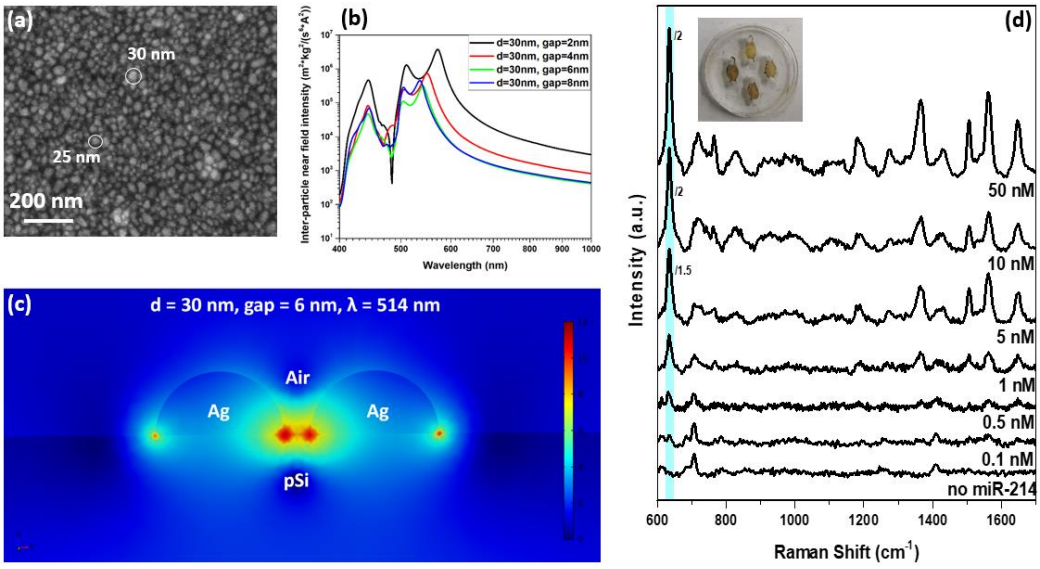

Figure 1: (a) FESEM image of the AgNPs on pSi. (b) EM near-field intensity calculated in the inter-particle gap between the AgNPs and (c) its distribution under 514 nm excitation. (d) In-chip SERS detection of different concentrations of miR-214 through a portable Raman spectrometer.

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Barcode-like Aluminum Bowties towards an extended SEIRA sensing

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Keywords: Plasmonics, Metallic nanoantenna, Surface enhanced IR absorption spectroscopy, sensing application.

Surface-enhanced infrared absorption (SEIRA) spectroscopy shows a promising potential to detect characteristic features of any molecules down to some low concentrations per individual nanoantenna [1]. Aluminum bowtie-shaped (Al-BT) nanoantennas are excellent building blocks for a wide-spectrum SEIRA, thanks to the facility to engineer tunable localized surface plasmon resonance (LSPR), by varying their triangle side-length (L) and gap (g), and to provide an outstanding near E-field by "lightening-rod effect" at their sharp apex [2]. In line with this, Al BT barcode-like plasmonic transducer is tailored to cover a wide IR spectrum ranging from 1000 to 10.000 cm^{-1}. Al-BT are fabricated by electron-beam lithography followed by metallization and lift-off within a metal-insulator-metal (MIM) structure with respective thicknesses of 200 nm of Al, 20 nm of SiO_2, and 50 nm Al-BT as illustrated in fig.1a. For a wide-coverage purpose, L is swept from 0.3 to 2.0 µm with a step of 0.1 µm, g is maintained at 100 nm. To investigate the spectral response of these periodic Al-BT arrays, FDTD solver (Lumerical) is employed. The excitation source is polarized along the BT main axis to enhance the electrical field into the gap where it is strongly localized [3]. Fig.1b SEM image shows an Al-BT array with gaps of 20 nm and a ~ 10^3 near-field enhancement from FDTD simulations. For each L value, one main plasmonic resonance peak is detected and usually referred to as strong dipolar coupling. Al-BT are optically characterized under 36x IR Fourier Transform IR (FTIR) spectrometer. Fig.1c confirms a good agreement between simulation (FDTD) and experiment (FTIR). Fig.1 is the SEIRA demonstration of 5 IR lines of vanillin, L is varied from 1.4 to 2.0 µm (step of 0.1 µm). The enhancing effect occurs only when the resonant interaction between both excitations (antenna and molecular vibration) is fulfilled and it is marked by a Fano-like asymmetric profiles. The asymmetry of the line shapes is reversed when the narrow vibration is located to the right or to the left of the broadband plasmonic resonance. Matching the state-of-art of SEIRA, an enormous enhancement factors of 4 orders of magnitude are achieved only by probing 2.5 × 10^4 molecules per tip with Al BT [1]. Such result is extremely encouraging for a lab-on-chip detection using a single plasmonic platform [4].

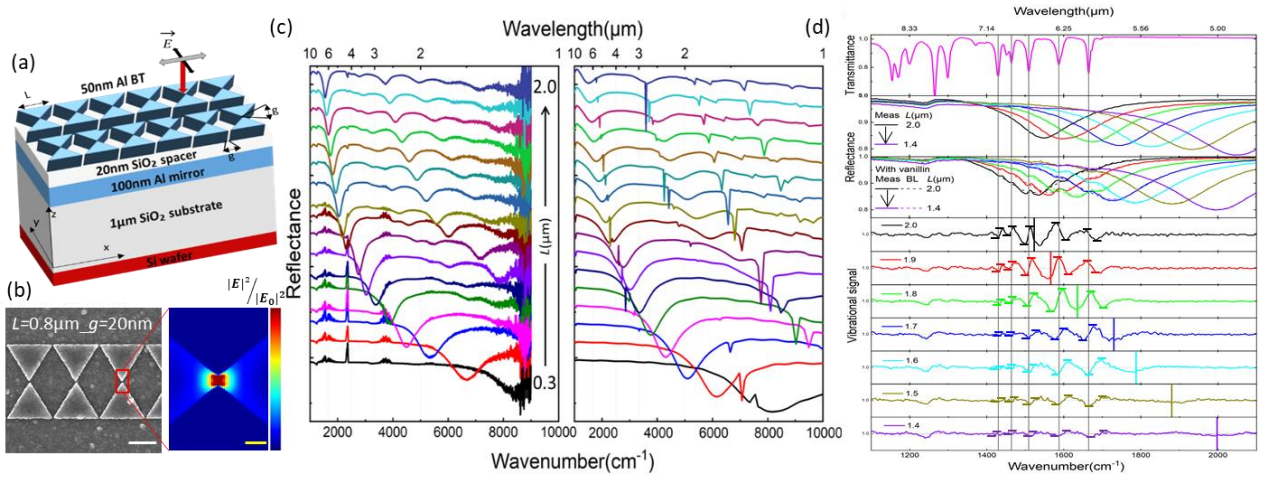

Figure. 1(a) CMOS-compatible MIM structure schema. (b) SEM image of fabricated BT with the corresponding near-filed localization. White and yellow scales are 0.5 µm and 20 nm long, near field $|E|^2/|E_0|^2$max ~ 10^3. (c) FTIR (left) vs FDTD (right) results for all Al-BT sizes with a 100nm gap. (d) SEIRA demonstration with 5 IR lines of vanillin as trial molecule.

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A confocal mid-infrared microscope for time-resolved difference spectroscopy of membrane proteins

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Keywords: Spectroscopy and nano-imaging

Rhodopsins are fundamental cell receptors that can act as ion pumps and channels through the cell membrane, playing key roles in communication and signal transduction between cells. They perform their function through a cyclic series of conformational changes, i.e., the rhodopsin photocycle, that can be triggered by external stimuli, including visible light as in Bacteriorhodopsin (BR) [1].

Mid-IR time-resolved difference spectroscopy, thanks to its frequency-resolved sensitivity to vibrational motions, can be employed to reveal details of the protein conformation and of its subtle changes occurring during the rhodopsin photocycle [2]. The usual approach consists in activating the rhodopsin photocycle many times with identical starting conditions for signal averaging. This approach allows one to obtain enough high signal-to-noise to isolate the extremely small ($\leq 10^{-3}$) light-induced differences in mid-IR absorption. The time between subsequent photocycles should then be longer than the return time of the given protein to the dark-adapted state. This return time ranges from a few tens of milliseconds for Bacteriorhodopsin (BR) to many minutes for BR slow-mutants or other rhodopsins, extending the total experimental time up to several days [3].

We have developed a confocal microscope integrating an external-cavity tunable quantum cascade laser (QCL) source with a parallel confocal visible-light illumination channel for monitoring the conformational changes of BR. Our in-house developed confocal microscope operates in the wavelength range between 5.8 and 6.3 μm and can be used to study slow-photocycle rhodopsins because the visible-illuminated sample area can be replaced at each measurement. The protocol for sample replacement allows one to perform time-resolved studies rigorously starting from the dark-adapted states of rhodopsins. The measured diffraction-limited lateral resolution is 19 μm. Mid-IR absorbance differences of the order of 10^{-5} can be detected with 30 ms time resolution using cryogen-free HgCdTe detectors and lock-in amplification at the QCL repetition rate.

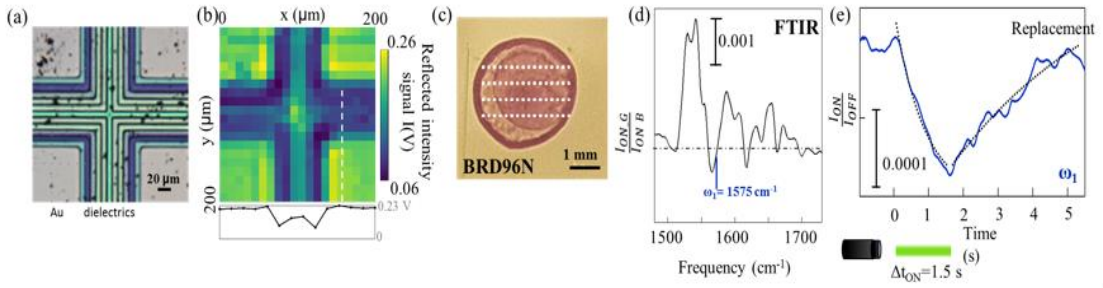

Figure 1: Performance of our custom QCL microscope. (a) Visible image of a target sample with 8 μm wide dielectric and metallic crosses. (b) IR reflectance at λ = 6.1 μm taken with our microscope (reflective objective with NA=0.4); pixel size is 10 μm. (c) A dried droplet of cell membranes loading the slow mutant BR D96N, with return time to the dark-adapted state longer than 3 s. (d) FTIR difference spectrum of the slow mutant BR D96N. (e) Time-resolved trace with 30 ms resolution acquired at ω_1=1575 cm^{-1} on the slow mutant BR D96N, replacing the sample area at each photocycle start (sample and point grid like that shown in panel c).

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Poster session

Chiral Effect and Extraordinary Transmission in Metal Films with Elliptical Nanohole Arrays

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Keywords: Quantum plasmonics, Metamaterials, Sensors and Biosensors

In this work, we theoretically study the Circular Dichroism (CD) properties of square and hexagonal elliptical nanoholes arrays on glass supported thin metallic layers (Au, Ag, Al). We consider these geometries because of their computational simplicity (square lattices) and technological relevance (hexagonal lattices), knowing that the hexagonal arrangement is easily fabricated by low-cost nanosphere lithography [1], hence its suitability for chiroptical sensing applications. Fig.1 shows the metasurface structures used in our study, illuminated with a plane wave at normal incident coming towards the nanostructured top side. We investigate the optical properties of elliptic nanoholes by using two methods. We first employ 3D Finite Difference Time Domain (FDTD) simulation using the Lumerical commercial software. We set perfectly matched layers in the z-direction and periodic boundary conditions in x,y directions. We then adopt a Bloch-mode scattering matrix method using the open-source software Emustack [5]: in this method, a finite element approach is applied to calculate the Bloch-modes in each 2D layer of the proposed structure. Both mentioned methods allow to calculate the relevant optical properties including CD spectra and field profiles. Finally, to ensure the convergence, we perform a comparison of the results obtained with the two different approaches. We underline that the performed simulations are always guided by symmetry considerations, suggesting that the maxima of the CD signal are expected for a nanohole rotation of 22.5 degrees for the square lattice and of 15 degrees for the hexagonal lattice respectively.

The main goal of our work is to determine how maximum CD is depending on varying the structure parameters including the type of metal, the film thickness, and the chosen 2D lattice. The obtained transmission spectra display the well-known phenomenon of extraordinary transmission (EOT) from sub-wavelength hole arrays in a metal [2-4]. We find that strong resonant features in the CD spectra arise due to coupling of the incident waves to surface plasmon at metal/glass interface. The CD can be optimized to reach high values with proper choice of the structure's parameters. Gold metasurfaces are useful for CD resonances above 600 nm while aluminum metasurfaces are convenient for achieving CD resonances in the short-wavelength range of the visible regime and in the near UV, which have interesting applications for sensing of biomolecules.

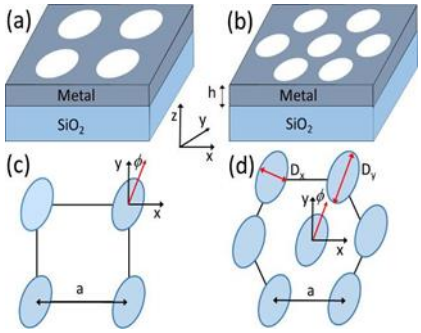

Figure 1: Scheme of the proposed structures studied in this work

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sSNOM characterization of the IR-active vibrational mode in highly strained hBN microbubbles

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Keywords: Spectroscopy and nano-imaging

Hexagonal Boron Nitride (hBN) is a layered material with a large bandgap and with high mechanical strength. It is often used as an encapsulating layer for various 2D materials and as insulator in van der Waals heterostructures. Defect states in the hBN wide bandgap display bright, room-temperature single photon emission that can be activated and tuned by applied strain [1]. hBN possesses a dipole-active transverse optical (TO) phonon mode at 1360 cm^{-1} that corresponds to in-plane atomic motion [2], and that could be used to quantify strain in hBN.

Here we report on a method to mechanically deform hBN based on the low-energy hydrogen (H) or deuterium (D) ion irradiation of multilayer flakes. H/D-ion treatments lead to the formation of nano/micrometric bubbles or wrinkles, that produces a ~2% tensile strain. We employed an infrared (IR) scanning near-field optical microscope (SNOM) to perform nanoscale Fourier transform IR (nano-FTIR) measurements of the in-plane TO mode of hBN. Across the bubble diameter, we observe large shifts of the IR-active mode. With the support of numerical modeling of the strain distribution, we extract the Grüneisen parameters of hBN [3].

The infrared spectra were collected with a SNOM microscope (NeaSNOM from NeaSpec). Measurements were taken by averaging ten interferograms with an 8 cm^{-1} spectral resolution. The demodulated phase and amplitude signals are normalized to the reference quantities measured on an Au patches in the vicinity of the flakes of interest. In Figure 1 a) we show the AFM image of a circular hBN bubble. The normalized near-field amplitude S(ω,r), as obtained with a spectral line scan along the red line, is reported in Figure 1 b)- c) demodulated at two different harmonics n = 2 (b) and n= 3 (c). We note the clear red-shift of the TO mode for the both demodulation harmonics, due to the strain increase from the edge towards the center of the bubble. Using n=3 we suppress the background far-field scattering and the signal from the TO mode of un-strained bulk material underneath the bubble, collecting the scattered signal only from the thin layer (2-12 nm [3]) that forms the bubbles.

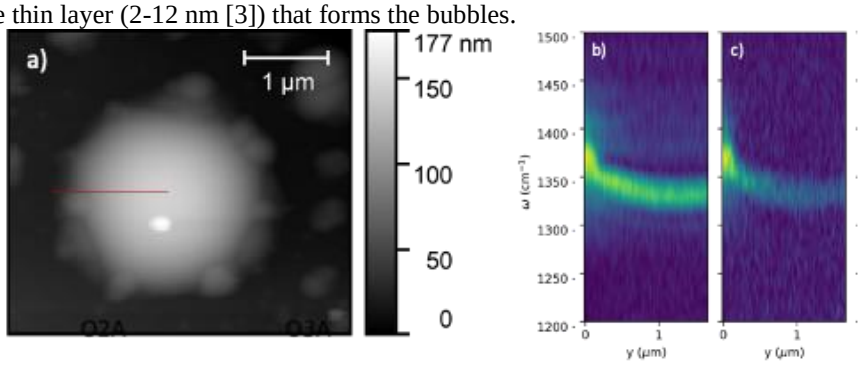

Figure 1: (a) AFM image of a bubble found on a thick hBN flake. One can see that small bubbles may form at the large bubble edge. Spectral line scan of the near field amplitude S(□,r) demodulated at harmonics with n=2 (b) and n=3 (c), collected along the red line.

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Luminescence of molecules on plasmonic metasurfaces induced by chiral light

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Keywords: Sensors and Biosensors, Metamaterials.

Chirality, the lack of mirror symmetry, is a key element for the expression of life. In fact, practically all the molecules in biological processes are chiral (e.g., DNA, sugars, amino acids). Thus, the possibility of detecting weak concentrations of chiral molecules is important for various applications ranging from the field of biochemical, medicine to agri-food). With its left and right circular polarization states, the light can be used to effectively study the properties of chiral molecules. For example, many chiral molecules absorb left and right circularly polarized light in different ways and this gives rise to a phenomenon called circular dichroism (CD). Unfortunately, the CD signal is usually very weak, so there is a need to use a high concentration of molecules to be able to see it. There are some methods that can increase the sensitivity of light in the detection of chiral molecules: one possibility, is to measure the CD as a difference in the emission properties of luminescent chiral molecules [1]. Another method that increases the sensitivity to CD, is the coupling of the light with plasmonic metasurfaces [2]. Here we would like to merge the two approaches, by measuring, under circular polarized light, the luminesce of molecules when them are deposited on specific plasmonic metasurfaces.

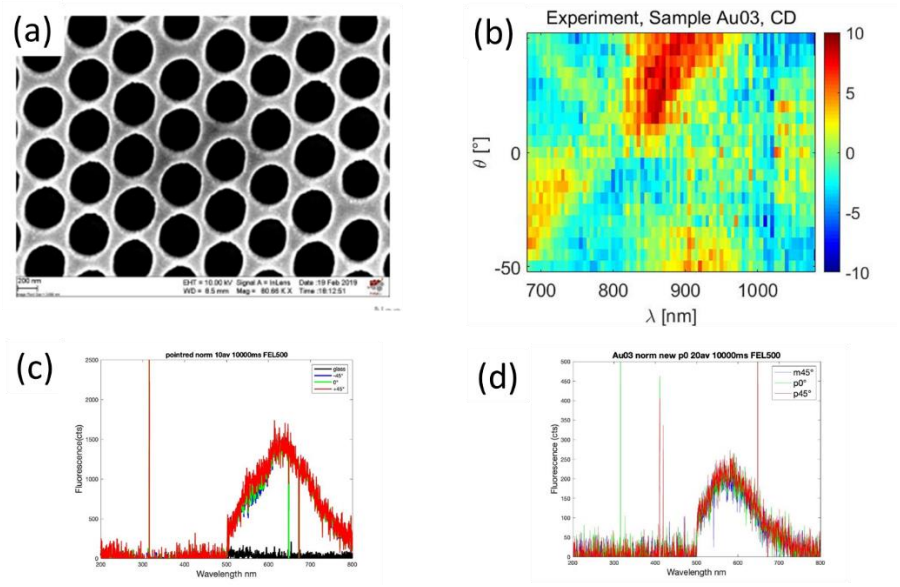

Figure 1: (a) SEM image of the plasmonic nanostructures; (b) Circular dichroism measured in extinction detected by measuring the transmission of the nanostructures as a function of wavelength and incidence angle; (c) luminescence spectrum of the organic molecules deposited on glass for different polarization states of the pump at 405nm; (d) luminescence spectrum of the organic molecules deposited on the nanostructures for different polarization states of the pump at 405nm impinging at normal incidence.

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Control of the optical response of plasmonic nanoparticles on transparent conductive oxide through doping

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Keywords: Hybrid metallo-dielectric nanophotonics

Transparent conducting oxides (TCOs) like Al:ZnO (AZO) have been extensively studied recently because of their peculiar properties of combining high transparency and low resistivity due to the n-type doping leading to a degenerate wide bandgap semiconductor. Furthermore, they can be used for epsilon-near-zero materials and to exploit their plasmon resonance in the near to mid infrared. One of the most interesting features of this class of materials is that their response can be easily tuned both from an electrical and an optical/plasmonic point of view by controlling the dopant concentration in the material [1]. In particular, this aspect can be interesting when the TCO is coupled with plasmonic nanoparticles (NPs) like Au. The excitation of plasmon resonance in Au NPs can induce the decay through hot electron generation and their injection in the oxide. This charge injection can modify the optical response of the TCO. On the other side the tuning of the optical and electrical properties in the oxide can be exploited to modify the response of the NPs in contact with the TCO [2]. This control is extremely promising for the realization of innovative plasmonic and opto-elctronic devices.

In this work we present our study on the hybrid system based on Au NPs deposited on AZO film. We have prepared the AZO substrate by magnetron sputtering in co-deposition, controlling in a highly reproducible way the dopant concentration and therefore the film response. We have investigated the optical response of the system when the AZO dopant concentration is varied between 0 and 4 at% by spectroscopic ellipsometry, correlated with surface morphology by AFM. The dielectric function of AZO reveals doping-induced band gap shift and the appearance of increasing free carriers, confirmed by Hall measurements. When Au NPs are added, we observe a blueshift of the localized surface plasmon resonance of Au NPs as a function of increasing Al doping of the substrate (Figure 1), ascribed to the occurrence of a charge transfer from AZO substrate to Au NPs and the doping-dependent variation of the polarizability of the substrate [3]. We expect that embedding Au NPs efficiently in TCO we could obtain also a variation of the optical response of the substrate inducing a mutual TCO/NPs relationship, which can potentially be exploited to tailor the ENZ regime.

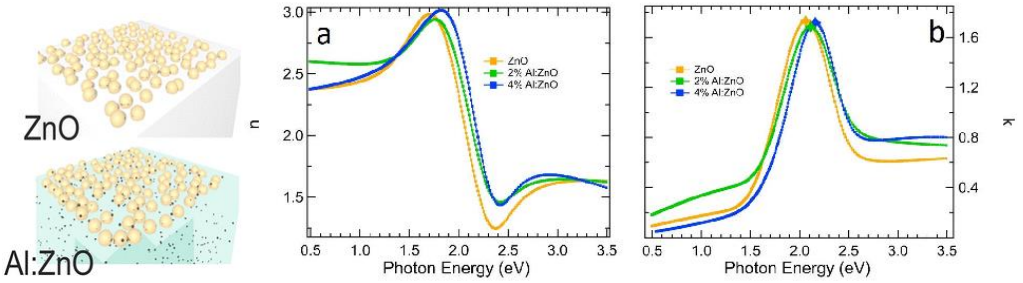

Figure 1: Schematic of the evolution of the optical properties of Au NPs on top of AZO film as a function of the TCO doping level.

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SERS specific and label free detection of tetracyclines

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Keywords: SERS substrate, Raman, bioassay

In the last years antibiotics became more and more used for applications ranging from healthcare, to animal breeding and agriculture. Among them tetracyclines are some of the most known and exploited. The use of these pharmaceutical compounds results to be very important for the resolution of several diseases and infections but it is also worth to mention some possible drawbacks. Among them there are the increasing drug-resistance of pathogens and the health risks, linked to an involuntary over exposure to these drugs from contaminated water and food [1]. For these reasons finding good strategies to identify and detect these molecules even in complex matrix results to be essential. In this work, Surface Enhanced Raman Scattering (SERS) was selected to perform the detection of tetracyclines. To this aim, different thiol-modified aptamers were immobilized on Ag-decorated porous silicon (pSi) membranes on polydimethylsiloxane (PDMS) (**Fig.1A**) to enhance the Raman scattering signal by exploiting the SERS effect [2,3]. Among the tested aptameric sequences, A8 was selected for the development of the detection assay thanks to its greater sensitivity and tetracycline binding affinity compared to the other tested sequences. As a result of the specific interaction with its target, this short molecule acquires a peculiar folded 3D structure capable to interact and block the analyte of interest close to the nanostructured surface. Several optimization of all the steps of the bioassay were performed and in the end the Tetracycline (TC) was detected at a concentration as low as 93 ppb (**Fig.1B)**, which results to be lower than its maximum residue levels in food defined by regulations. Furthermore, the specificity and selectivity of the assay was tested, challenging the system with other antibiotic solutions (e.g. sulfonamides). In this case no relevant signals were detected. Preliminary analysis were also performed in a microfluidic chip, using an automated procedure and a portable Raman spectrometer. Encouraging results have been reached with this methodic, paving the way for the on-site biosensing analysis of antibiotics in food matrix and raw materials.

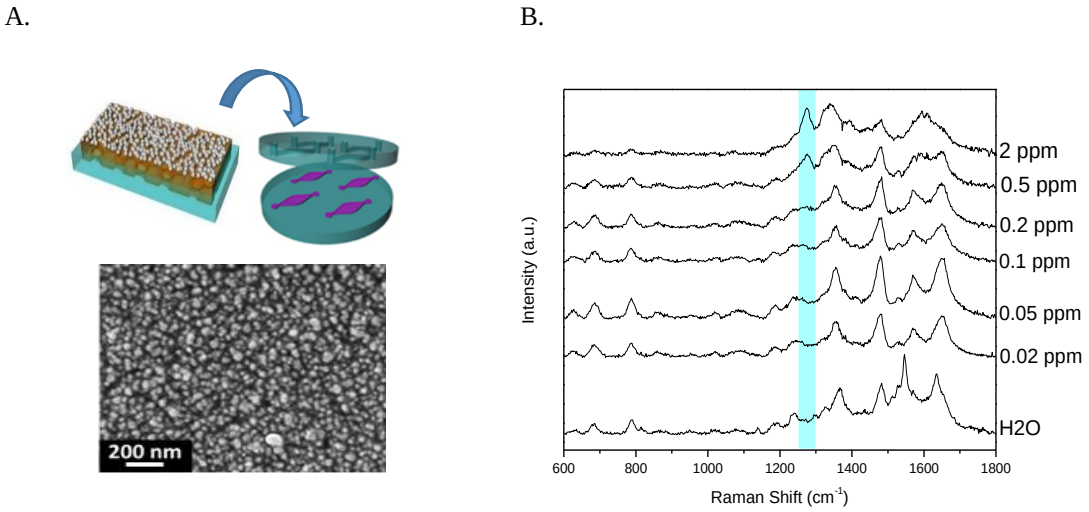

Fig.1: A. Schematic representation of the SERS substrate integrated in microfluidics (top); FESEM picture of the plasmonic nanostructures. B. Average spectra of SERS maps obtained by incubating different concentrations of Tetracycline (2-0.02 ppm) on the surface of the A8-functionalized SERS substrate. The main TC peak (indicated with a light blue line) can be observed at 1273 cm^{-1}

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Towards polarization control in Bloch surface waves

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Keywords: Photonic crystals, surface waves, polarization.

Bloch Surface waves (BSWs) are supported by semi-infinite one-dimensional photonic crystals, where both the transverse electric (TE) and the transverse magnetic (TM) eigenmodes can be sustained. Thanks to the high sensitivity to the local refractive index, platforms supporting BSWs are widely used for sensing analytes located close to the surface [1,2]. Moreover, the resonant frequencies of the modes can be tuned by a proper design of the 1DPC, acting on the materials (i.e. the refractive index) and the thicknesses of the layers. A further step in surface-enhanced spectroscopies using BSWs would be the control over the wave polarization, which can be attained by engineering the overlap between the TE and TM modes.

In this framework, we recently proposed a platform [3] that allows for the generation of "superchiral" surface waves, carrying an enhanced optical chirality that can be exploited for chiroptical sensing. Here we experimentally fabricate a 1DPC that simplifies the previous design by reducing the number of layers while keeping a similar polarization performance. We experimentally demonstrate the energy and momentum superposition of the TE and TM modes, paving the way to their coherent superposition for surface-enhanced polarization-sensitive spectroscopies in the visible-UV range.

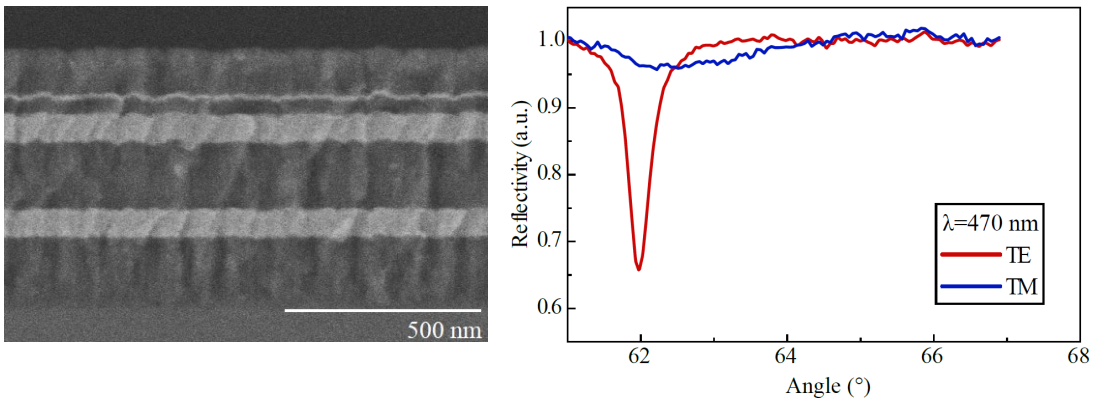

Figure 1: SEM image of a photonic crystal multilayer (left) and experimental reflectivity data as a function of the incident angle (excitation of surface modes appears as a dip due to material absorption)

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Surface Plasmons Effects on Azobenzene Photoisomerization

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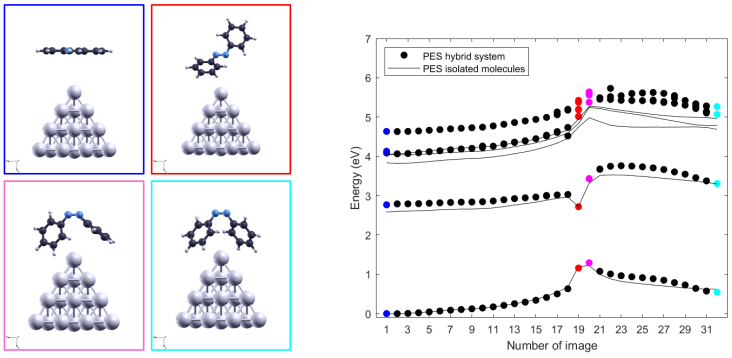
Keywords: Polariton Chemistry, Molecular Plasmonics

Photoisomerization as other photochemical processes can be importantly modified by strong coupling interactions between molecule excitations and photonic modes. In this non-perturbative regime of interaction, the emergence of hybrid light-matter states, i.e. polaritons, offers thus a new platform to manipulate the chemical pathway and kinetics [1, 2].

The theoretical approaches used to handle such hybrid states are generally classical or semiclassical but these must be necessarily overcome in polariton chemistry studies.

In this work we propose a fully quantum mechanical analysis in which both the metallic nanoparticle, responsible for the photonic component, i.e. the localized surface plasmon (LSP), and the molecule are treated atomistically via Density Functional Theory (DFT) and Time-Dependent DFT [3]. In more details, we propose an investigation of a sub-nanometer interaction between an azobenzene molecule and an Ag_{20} tetrahedral cluster, by considering the effects of interaction on a set of 30 representative intermediate states along the minimum-energy pathway calculated with NEB method [4] for the trans to cis photoisomerization process.

As shown in Fig. 1b, reporting the first polaritonic PESs (PoPESs), the presence of metal does not affect in a considerable way the ground state and the first excited PES. However, the plasmon acts mainly on the second and third excited states with a blueshift and a perturbation of the curves profile. An in-depth analysis done by considering the transition densities, the natural transition orbitals and the transition contribution maps of excitations, has revealed the appearance of the bonding and antibonding polaritonic states as well as net charge-transfer excitations. In conclusion, in this work we show that ab initio modeling of the strong coupling between molecular excitations and LSP can disclose a picture of polaritonic chemistry richer than what expected only on the basis of Jaynes-Cummings-like Hamiltonians.



(a) (b)

Figure 1: (a) Sketches of hybrid systems. (b) The PES of isolated molecules are represented by the black continuous line and the PES of hybrid systems are represented by black points. The colored dots refer to the configurations shown on the side.

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Ag Nanoflower as single-particle SERS active substrate

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Keywords: Surface-enhanced Raman scattering,

Surface-enhanced Raman scattering (SERS) has received plentiful attention from all scientific communities for several years, due to the high range of non-destructive applications. Raman spectroscopy has been successfully employed in biosensing [1], in-situ catalysis study, archeology, and so on. However, the low sensitivity of the technique has hindered its application when low concentrations are involved. For this reason, the magnification of Raman signals due to the SERS effect is the core of scientific research in this field of interest. The maximum enhancement factor (EF) calculated theoretically is 10^{14} [2] which corresponds to a limit of detection (LOD) of attomoles. Up to now a lot of different types of metallic nanoparticles were produced in trying to match the theoretical enhancement. However, the relatively, low homogeneity and low reproducibility of the SERS substrate hinder its practical applications. In this work, we present a novel approach to the study of the enhancement factor of SERS active substrates. We synthesize Ag Nanoflowers (AgNFs) which are spherical silver micro-particles with a diameter of 2 µm with a nano-rough surface [3] (figure 1 (a)). Such Ag NFs are spin-coated onto a silicon substrate. Thanks to their dimension it is possible by a micro-Raman apparatus, to optically localize a single micro-particle and study the enhancement and stability of the signals. The SERS properties at the single-particle level were studied using 4-mercaptobenzoic acid (4-MBA) as a standard molecule. We also evaluated the impact on the EF of the laser excitation laser line, of nanostructure size, and surface roughness by finding, in this last case, a decrease in EF as size and roughness decrease Fig 1. By systematically studying the enhancement for several-single Ag NFs, we find an enhancement factor in the order of 10^8- 10^9 which result to be 3 order of magnitude higher than the classical Ag sphere (AgNPs).

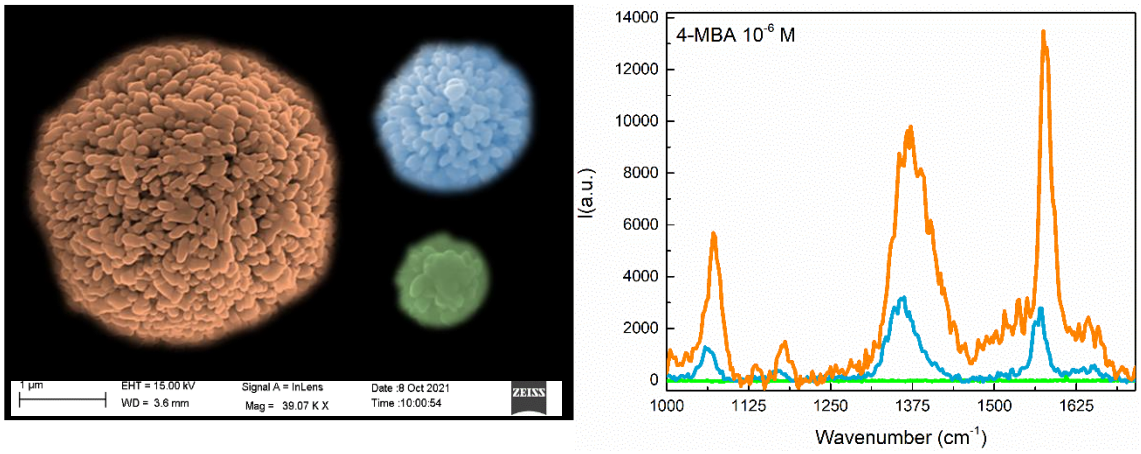

Figure 1: Left, SEM image (colorized) of AgNFs produced with different experimental parameters which influence the dimension and roughness of the surface, right SERS spectra of the 4-MBA using the three different nanostructures, the color of the spectra correspond to that of the nanostructures.

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Tailored Colloidal Nanostars for Surface Enhanced Raman Spectroscopy (SERS): Optimization of Formulation Components and Study of the Stabilizer-Nanoparticle Interactions

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Keywords: Surface Enhanced Raman Scattering, Spectroscopy and nano-imaging.

While the effects of morphology and composition of plasmonic substrates on the SERS response are widely studied in the literature, surface chemistry and, more specifically, the role of pre-adsorbed species on colloidal substrates (*i.e.*, stabilizers and synthesis by-products) are typically less explored. In this work [1], a surfactant-free synthesis of sparingly capped bimetallic colloidal AuAg (18:1) nanostars [2,3] was selected as a basis to *(1)* examine the effect of varying stabilizers and *(2)* systematically assess the impact of the resulting surface environment on SERS intensity. The latter entailed the characterization of the colloidal formulations in terms of optical reproducibility, suitability for analytical applications, long-term colloidal stability, and SERS performance. Emphasis was given to the elucidation of the stabilizer-metal interactions, which were studied by Electrophoretic Light Scattering (ELS) and infrared spectroscopy.

It was found that the capping process is the result of chemisorption to an essentially neutral alloy, and that the capping environment has effects on the SERS response that can overtop those caused by nanoparticle morphology (*Figure 1*). Model stabilizer citrate was found to weakly chemisorb (-4.36 ± 0.08 kJ/mol and -4.58 ± 0.05 kJ/mol at 10 and 20 °C, respectively) to the bimetallic surface in a positively cooperative fashion ($n_{Hill} > 1$), via unidentate mode.

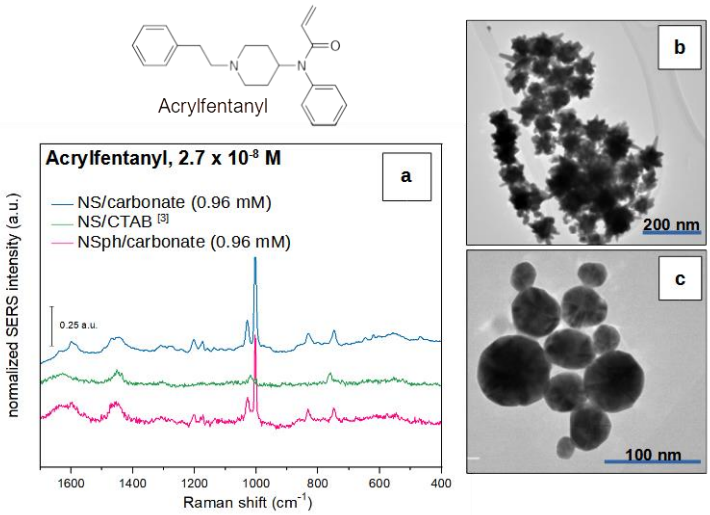

Figure 1: Non-ideal probe acrylfentanyl (2.7 x 10^{-8} M, *a*) was studied with three different SERS substrates: carbonate-capped nanostars, NS (*b*, TEM micrograph), CTAB-capped NS, and carbonate-capped nanospheres (Au:Ag 18:1; *c*, TEM micrograph). All samples were measured with the same acquisition parameters and under the same aggregating agent conditions ($MgCl_2$ 1.78 mM); pH was 6.0-6.5 for all formulations.

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An Operative Approach to Quantum Electrodynamics in Dispersive Dielectric Objects Based on a Polarization Modal Expansion

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Keywords: Please specify up to three keywords chosen among the conference topics.

In this paper we deal with the macroscopic electromagnetic response of a finite size dispersive dielectric object, in unbounded space, in the framework of quantum electrodynamics using the Heisenberg picture. We apply a Hopfield type scheme to account for the dispersion and dissipation of the matter. We provide a general expression of the polarization density field operator as functions of the initial conditions of the matter field operators and of the electromagnetic field operators. It is a linear functional whose kernel is a linear expression of the impulse response of the dielectric object that we obtain within the framework of classical electrodynamics. The electric field operator is expressed as a function of the polarization density field operator by means of the dyadic Green's function for the free space. The statistical functions of these operators are classical functionals of the statistics of the initial conditions of the matter field operators and of the electromagnetic field operators, whose kernels are linear or multilinear expressions of the impulse response of the dielectric object. We keep the polarization and the electromagnetic field distinct to enable the treatment of the polarization and electromagnetic fluctuations on equal footing. We expand the polarization density field operator in terms of the static longitudinal and transverse modes of the object to diagonalize the Coulomb and Ampere interaction energy terms of the Hamiltonian in the Coulomb gauge. We expand the radiation fields in terms of the transverse plane wave modes of free space. Few static longitudinal and transverse modes are needed to calculate each element of the impulse response matrix for dielectric objects with sizes of the order up to $\min_{\omega}\{c_0/[\omega\sqrt{|\chi(\omega)|}]\}$ where $\chi(\omega)$ is the susceptibility of the dielectric. We apply the proposed approach to different scenarios describing the dielectric susceptibility by the Drude-Lorentz model.

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Tip-enhanced Raman spectroscopy of polymer functionalized multiwalled carbon nanotubes

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Tip-enhanced Raman Spectroscopy (TERS) combines the high specificity and sensitivity of plasmon-enhanced Raman spectroscopy with the high spatial resolution of scanning probe microscopy. TERS has gained a lot of attention from many nanoscience fields since this technique can provide chemical and structural information of surfaces and interfaces with nanometric spatial resolution [1-3]. Multiwalled carbon nanotubes (MWCNTs) are very versatile nanostructures that can be dispersed in organic solvents or polymeric matrices giving rise to new nanocomposite materials showing improved mechanical, electrical and thermal properties. Moreover, MWCNTs can be easily functionalized with polymers in order to be employed as specific chemical sensors. In this context, TERS is strategic since it can provide useful information on the cooperation of the two components at the nanoscale for the optimization of the macroscopic properties of the hybrid material. Nevertheless, efficient TERS characterization relies on the geometrical features and material composition of the plasmonic tip used [3]. In this work, after comparing the TERS performances of commercial Ag coated nanotips and home-made bulk Au tips on bare MWCNTs, we show how TERS can be exploited for characterizing MWCNTs mixed with conjugated fluorene copolymers. Notably the distribution of the polymer with respect to the MWCNTs was imaged at the nanoscale (Figure 1) while the analysis of the TERS spectra can give useful information to the understanding of the polymer/CNT interaction process at the local scale [4].

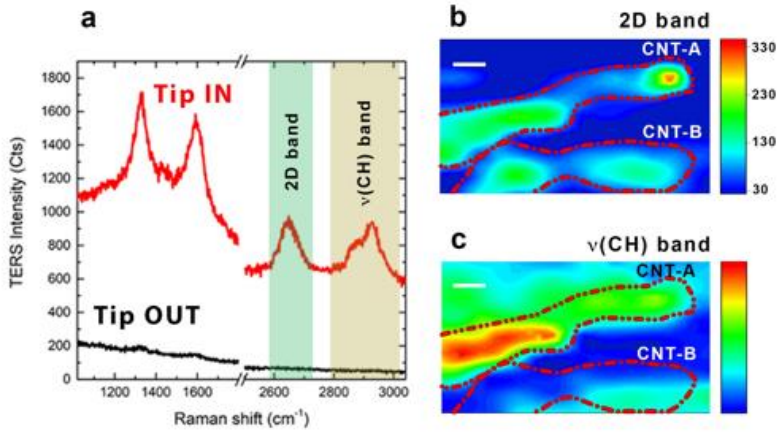

Figure 1: (a) Raman signal of polymer functionalized MWCNTs on gold substrate observed with (red line) and without (black line) the TERS tip in close proximity to the sample surface. TERS imaging of (b) the 2D band of the MWCNT, (c) the CH stretching mode of the polymer. Red dashed lines in the two maps are the contours of the MWCNTs localized from the images in panel (b), while the scale bar is 25 nm.

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Plasmonic gold nanostructured layer for photon absorption efficiency enhancement in Transition-Edge Sensors

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Keywords: Transition-Edge Sensors, photonics, plasmonics.

Transition-Edge Sensors (TESs) are outstanding calorimeters based on the steep superconductive transition of a metallic film. Among photon detectors, they are renowned for the intrinsic energy resolutions and the low dark counts rate. They are usually applied to detect electromagnetic energy from gamma-ray to visible and submillimeter wavelengths, but their use go further.

In the optical and near-infrared range of wavelengths, INRiM's TESs can actually perform photon energy measurements with a resolution around 100 meV [1].

For many applications in which rare events or all the events has to be detected, TESs should have the highest possible detection efficiency and low dark count rates. This is the case for quantum optics experiments [2], but also, f. i., for dark matter search experiment, like MuDhi (Multilayer Dielectric Haloscope Investigation) experiment [3], which is looking for dark photons in the mass range of 1.5 eV/c^2.

INRiM is developing TESs for near-infrared wavelengths based on metallic bilayers of titanium and gold. The first is a superconductive metal with a low critical temperature (T_C), while the second is required to reduce the T_C of this device depending on the relative thicknesses. The energy resolution depends both on the TES volume and (more strongly) on the T_C and thus materials and geometry are already defined. To reduce losses due to photon reflection and transmission, i.e. to enhance the TES absorption, preserving the other TES properties, INRiM will evaluate two different approaches. The first consists in the design and fabrication of a TES embedded in a microcavity to enhance the quantum efficiency above the 80%. The drawback of this solution is that it requires the fabrication of many different dielectric layers above and under the TES, including a mirror to create the cavity under the TES.

The second solution to be followed concerns manufacturing of plasmonic nanostructures. A suited periodical corrugation on a metallic layer allows the coupling of external electromagnetic waves with Surface Plasmons Polaritons (SPPs), increasing its absorption even with a mismatch of the wave number vector at the metal surface. A gold layer 100 nm thick, with a series of trenches 260 nm wide and distant 1490 nm from one to the other [4], will be fabricated on top of the TES. From simulations performed with neural networks [4], this geometry has shown to be the one maximizing the absorption for photons with a wavelength of 1550 nm. In this configuration, photons will be absorbed from the gold nanostructured layer, converted in SPPs that will propagate thanks to the grating and efficiently converted in thermal heat and detected by the TES. The overall process is expected to enhance the collection efficiency from around 50% of the original TES up to theoretically 98% thanks to the SPPs mediation.

Preliminary results will be reported as a first step for the future investigation on plasmonic nanostructures that will potentially lead to a TES with maximum absorption efficiency.

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Large-scale photon harvesting in nanopatterned 2D semiconducting layers

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Two-dimensional (2D) Transition Metal Dichalcogenide semiconductor (TMDs) layers, such as MoS_2, have recently attracted diffuse interest owing to their exceptional optoelectronic properties, simply tunable by tailoring the number of layers and/or by assembling Van der Waals heterostructures [1,2]. This has recently allowed the development of ultra-thin devices featuring a variety of properties ranging from photodetection and solar energy conversion, to quantum optics. However, the inherent low photon absorption in the atomic layers demands for novel photon harvesting schemes able to achieve effective light coupling to the few-layer semiconductor. Flat-optics nanogratings supporting Lattice Resonances offer a promising opportunity in this respect, promoting strong in-plane light scattering and confinement. In parallel, there is an urgent request in view of applications to scale-up the growth of 2D layers and devices, that generally relies onto mechanically exfoliated flakes, whose size is limited at the microscale.

Here we demonstrate a novel flat-optics scheme based on nanoscale re-shaped few-layers MoS_2 forming ultra-thin periodic nanogratings. These 2D nanopatterned layers homogeneously extend over large scale (cm^2) thanks to a physical deposition growth combined with Lloyd Lithography, thus enabling polarization-sensitive excitation of Rayleigh Anomalies (RA) [3,4]. This configuration enables the efficient light coupling to the ultra-thin TMDs layer by tuning of the RA mode across the exciton transitions, with a following enhancement of the photon absorption exceeding 400%, relative to the flat layer. Additionally, a non-resonant Guided Modes Anomalies is launched into the transparent substrates, thus inducing a broadband photon absorption enhancement in the whole visible spectrum. The superior photo harvesting performances achieved are very promising in view of large scale photonics and energy conversion applications.

As a step forward, arbitrarily defined ultra-thin semiconducting MoS_2 nano-paths has been recently achieved thanks to a novel *additive* nanofabrication process, based on the thermal - Scanning Probe Lithography [5]. We demonstrate the possibility to employ these high-resolution few-layer nanocircuits as a building block for ultra-thin integrated electronic and photonic devices.

These additive and non-invasive 2D-TMD nanolithography approaches are thus very promising for the integration of 2D TMDs layers in scalable photonics, electronics and quantum technologies.

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Engineering high Q/V photonic modes in correlated disordered systems

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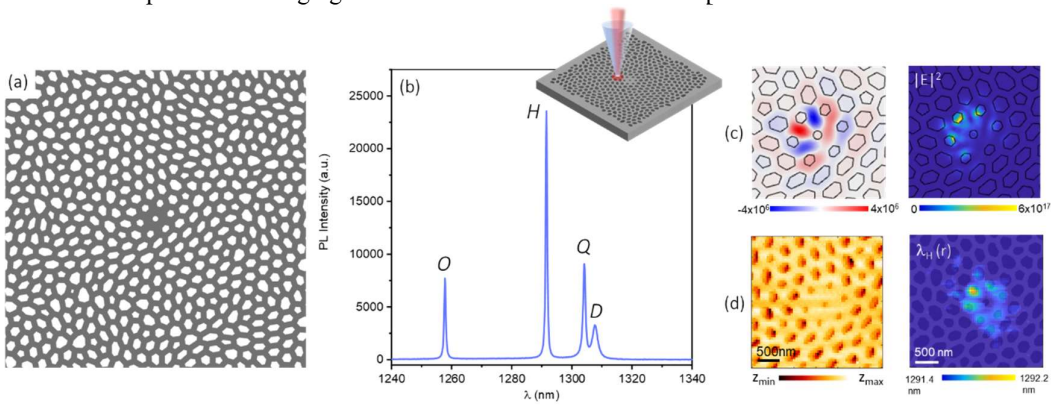
Keywords: Spectroscopy and nano-imaging, Metamaterials, Devices and applications.

Located in-between random structures and perfectly ordered photonic crystals, there is a special class of disordered photonic heterostructures, called hyperuniform disordered (HuD) photonic structures [1]. These systems have recently been shown to display large isotropic band gaps (BG) as well as optical transparency, to mention two of the most fascinating an promising features.

It was recently demonstrated that HuD photonic materials display several localized states with relatively high Q factors [2]. However, their spatial position is not predictable a priori. Here we experimentally benchmark through near-field spectroscopy the engineering of high Q/V resonant modes in a defect inside a HuD luminescent pattern. These deterministic modes, coexisting with Anderson-localized modes, are a valid candidate for implementations in optoelectronic devices due to the spatial isotropy of the HuD environment upon which they are built.

We engineer the defect inside the HuD luminescent pattern and deterministically control its spatial location in a correlated disordered environment and optimize the light confinement (as it has been recently proposed only theoretically in [3]). The central defect is designed (Fig.1a) in order to support several resonant modes with the Finite Element Methods (FEM) distributions of the magnetic field component Hz: dipole-like (D), hexapole-like (H), quadrupole-like (Q) and octupole-like (O) and so on [3]. By tuning the structural parameters such as the width of the dielectric veins in the HuD network and the radius of the central hole of the defect, we achieve a fine control over every spectral resonance to find the best condition that maximizes the Q factor for every mode. We experimentally benchmark this engineering through Near-field scanning microscopy (SNOM), used in illumination-collection configuration and capable of subwavelength resolution in the near-IR range. In Fig.1b we report a typical near-field PL spectrum of the cavity, displaying the 4 predicted resonances. An example of FEM simulation maps is shown in Fig.1c, that are the Hz (left panel) and electric field intensity (right panel) maps of mode H. In a SNOM scan it is possible to acquire the topography of the sample (Fig.1d) and to map the LDOS distribution of the modes by fitting the peaks of the experimental spectrum and reconstructing the spectral shift maps. An example of spectral shift map, that constitutes a faithful reproduction of the electric field intensity of the mode, as confirmed by the FEM map in the right panel of Fig.1c, is reported in the right panel of Fig. 1d for mode H. An excellent agreement between the experimental imaging of the LDOS and the theoretical maps is achieved for all resonances.



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Near-field hyper-spectral imaging of resonant Mie modes in a dielectric island

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Keywords: Spectroscopy and nano-imaging, Metamaterials, Devices and applications.

All-dielectric sub-wavelength sized Mie resonators have emerged in the last decade as promising building blocks for optoelectronic devices, since they provide the possibility to efficiently redirect and concentrate light with low absorption losses [1]. The optical modes in high-index dielectric nanoparticles originate from the excitation of optically induced displacement currents and can be both magnetic and electric in nature. The exploitation of higher order multipolar modes offers opportunities for directional and polarization controlled emission from nanoemitters. However, the investigation of the intricacies of the Mie resonances at the sub-wavelength scale has been hampered by the limitations of conventional near-field methods. In this work, we address the spatial and spectral mapping of multipolar modes of a Si island by near-field hyper-spectral imaging. A dewetted Si resonator [2], with diameter of 320 nm and sitting atop a 2 μm SiO_2 substrate, Fig. 1a), is investigated through scanning near-field optical microscopy (SNOM), Fig. 1b). The normalized near-field spectrum collected on top of the resonator, illuminated by a tilted supercontinuum laser source, is reported in Fig. 1c), together with the finite difference time domain (FDTD) near-field spectrum. Simulated and experimental spectra are in good agreement, allowing to identify the main higher order multipolar resonances that result from the resonant modes of the antenna. Fig. 1d) shows the near-field map of the resonance at 730 nm, that is in excellent agreement with the FDTD map of the same resonance, Fig. 1e). Experimental and simulated maps of all Mie modes show striking similarities in the spatial distribution of the hot spots.

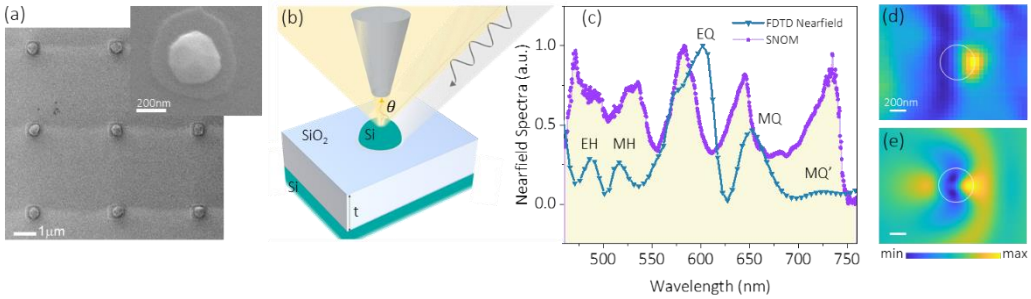

Figure 1: a) SEM image of a Si resonator. b) Sketch of the experimental setup: the tilted illumination from the supercontinuum laser is scattered by the island and the scattered light (yellow cone) is collected by the near-field probe. c) Normalized SNOM scattering spectrum collected on top of the dewetted island (purple) and corresponding FDTD spectrum (dark green); the spectral positions of different high order resonances (magnetic and electric quadrupole and hexapoles) are indicated. d) and e) SNOM and simulated maps relative to mode MQ'.

The combination of numerical and experimental results allows a full comprehension of the sensitivity of magnetic light with respect to the thickness of the substrate and the angle of illumination [3]. Moreover, this detailed analysis indicates how such sensitivity affects the near-field scattering pattern of the antenna, suggesting a novel approach to control the position of the localized electric field maxima to engineer an important aspect of the coupling between emitters and antenna: instead of placing the emitter on the hotspot, the hotspot can be moved on the emitter position, offering a versatile tuning tool to control the absorption of the emitter itself.

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Silver Nanowires Plasmon Enhancement of Photovoltaic Efficiency in Lead-Free Perovskite Solar Cells

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Keywords: Metamaterials, Devices and Application.

We construct a non-toxic and low environmental impact perovskite combined with silver nanowire to modify the photovoltaic properties. Perovskites are organic-inorganic materials with a ABX_3 structure (where A = monovalent organic cation, B = divalent metal, and X = halide) suitable for various fields of application such as solar cells, light emitting diodes and sensors due to their strong light absorption, band gap, excitation lifetime and dielectric properties [1].

The chemical composition of the new Perovskite Solar Cell (PSC) active layer was chosen according to DFT/LDA calculations [2] substituting the more commonly used lead with magnesium to obtain a $CH_3NH_3MgI_3$ perovskite active layer. The addition of silver nanowire will modify the photogenerated current in the resulting device and thus to obtain higher efficiency.

Different architectures are proposed incorporating the silver nanowires in different layer of the devices. The nanowires are incorporated in the structure both by means of Langmuir-Blodgett and drop-casting technique depending on the layer position. Morphological characterization allows to evaluate the surface density and the packing of the nanowires in the layer; the UV-visible spectroscopy characterization show the presence distinct peaks due to the presence of the silver surface plasmon resonance

The photophysical characterization allowed for evaluate the properties of photoluminescence and the band gap of the entire device as a function of the preparation procedure. The efficiency and stability of the solar cells were estimated from I-V curves as a function of irradiation and storage time. The results of the nanowires containing device reveal an increase of the photogenerated current value and of the photodegradation stability.

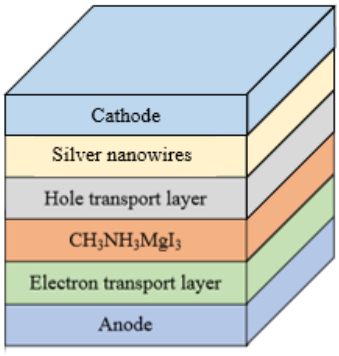

Figure 1: Architecture example of the perovskite solar cell device.

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Detection of strong light-matter interaction and near-field mapping on a single resonator

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Keywords: Spectroscopy and nano-imaging, Plasmon-exciton polaritons, Thermo-Plasmonics

We present a novel approach, alternative to near-field SNOM techniques [1], capable of detecting the spectral response of a single metal-insulator-metal (MIM) cavity in the mid-IR range, and of mapping the electromagnetic fields buried within. We achieve this by inserting a 150-nm-thin layer of polyethylene (mid-IR transparent [2]) inside a metal-semiconductor-metal resonant cavity. The semiconductor is a single InGaAs/AlInAs quantum well (QW) which either (i) exhibits an intersubband (ISB) transition in the mid-IR (heavily doped sample) or (ii) passively sets the resonance (undoped sample , empty cavity). By shining a tunable mid-IR quantum cascade laser (QCL) on the system, the cavity absorbs energy at its resonance frequencies. By changing the patch antenna dimensions, the cavity resonance can span across the ISB transition. The energy is absorbed and transformed into heat and transferred to the polymer layer, which in turn expands and allows an AFM detection of the system's spectral response.

As a test bench, we choose to compare a simple bare cavity, where the QW is not doped and acts as a simple passive dielectric, with a loaded cavity, where the QW is highly doped and can enter the strong-coupling regime, where the photonic mode and the ISB transition strongly interact together revealing a polaritonic behavior (see image, right panel). By comparing the spectra with FTIR far-field measurements, we see that the Rabi splitting is approximately the same, proving that the proposed photothermal technique can probe the same global physical observables that are measured by purely optical techniques.

We further show that polymer photoexpansion can also be used to map the EM fields inside the cavity, accessing a region that is inaccessible by any other technique. 2D maps of the magnetic fields for the 1st and 2nd order resonances are collected and show the typical field distribution of the magnetic field.

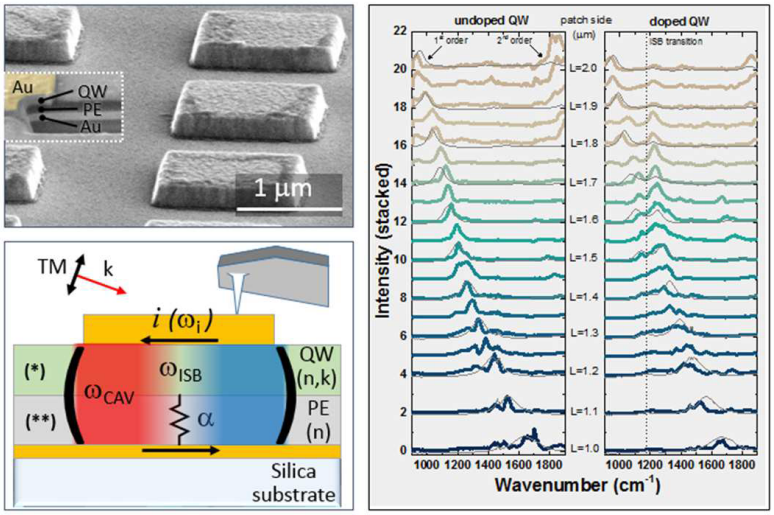

Figure 1. Left: MIM resonators containing a quantum well and a photo-expanding polymer layer. Right: AFM-IR spectra of single resonators (thick curves) compared to FTIR spectra of arrays (thin)

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Some interesting applications of ITO nanoparticles in thermoplasmonics

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Keywords: Thermoplasmonics, Devices and Applications

Interest in thermoplasmonics has been soaring over the last decade. Several very promising applications have been proposed and partly demonstrated in the fields of nanomedicine, catalysis, and solar light harvesting [1]. Classical plasmonic metals -gold in particular- are by far the most employed materials for thermoplasmonics. However, the quest for materials with improved or novel properties is open and several alternatives to coinage metals have been proposed [2]. Among these, Indium Tin oxide (ITO) is an impressive contender: not only it is able to sustain sharp plasmon resonance around the NIR telecom region in nanoparticles as small a 5 nm, but it is completely transparent over the whole visible region, thanks to the high bandgap. Thus, ITO nanoparticles are strong IR absorbers which remain invisible to the naked eye: two features that are rarely seen together in most materials.

Here we show some applications that take advantage of these peculiar properties. First, we developed an ITO nanoparticle-based printable ink that can be used to watermark invisible, hard to replicate codes as anticounterfeiting measures. The codes can then be retrieved with an infrared camera within fractions of a second of illumination with an IR bulb (Figure 1). The small size (7 nm) of the ITO nanoparticles affords negligible scattering, which results in a twofold advantage: *i)* the nanoparticles dispersed in the transparent matrix of the ink display no optical contrast, contributing to the invisibility of the code and *ii)* virtually all radiation is absorbed and available for conversion into heat [3].

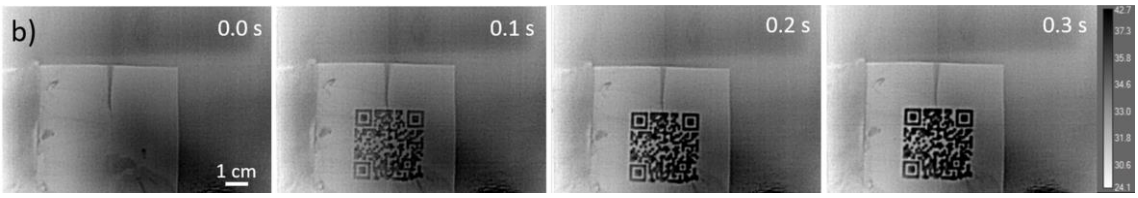

Figure 1: Invisible ITO NP-based QR code that can be read through an infrared camera.

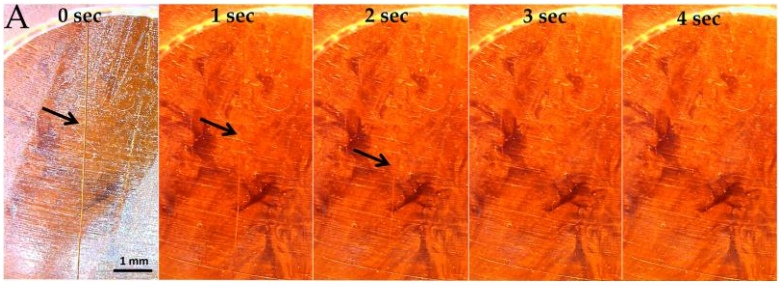

Figure 2: Self-healing polymer loaded with ITO NPs.

We also tested the heating capability of ITO nanoparticles by embedding them in a heat-triggered self-healing polymer [4]. We found that at relatively low loading values (<5% w/w) the nanoparticles induce full recovery of mechanical damage within seconds of IR illumination (Figure 2). Also in this case, the visual features of the polymer were not affected by the addition of nanoparticles.
We believe that transparent conductive oxides such as ITO can be extremely promising materials for thermoplasmonics, especially in cases where the interaction with visible light must be minimized.

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Plasmonic metasurface assisted by thermally imprinted polymer nano-well array for surface enhanced Raman scattering

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Keywords: plasmonic metasurface, nanotrenches, SERS

Plasmonic nanometasurfaces/nanostructures possess areas sustaining dramatically enhanced electromagnetic fields relative the incoming light. The enhancement is due to charge separation of free electrons in the conductive band at resonant oscillations, and has been extensively applied in various applications, such as surface enhanced Raman spectroscopy (SERS)[1,2], as chemical- and biomedical sensors[3,4] and as photo catalysis and photovoltaic cells[5,6]. Metasurfaces containing plasmonic nanostructures can be fabricated through a number of techniques, including electron beam lithography[7,8], laser interference lithography[9,10], focused ion beam milling[11,12], wet chemical synthesis[13,14], embossing[15,16], and annealing of thin films and patterns[17,18]. Each technique has strengths and limitations, where in general the fabrication of uniform nanostructured metasurfaces is a complicated and costly procedure, which mitigates a wide-spread use of this technique in ubiquitous applications.

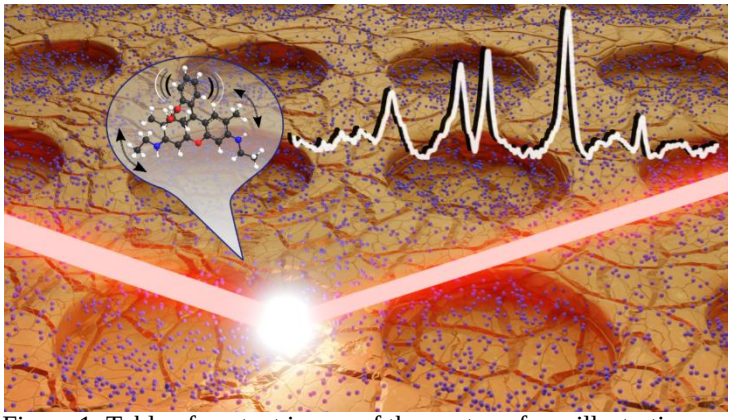

Figure 1: Table of content image of the metasurface, illustrating the detection of rhodamine 6g molecules by SERS.

Here, we present a facile and scalable method to fabricate an active nanotrench plasmonic gold substrate. The surface comprises sub-10 nm plasmonic nanogaps and their formation is assisted by a pre-fabrication of nano-imprinted polymer nano-well arrays. By optimizing substrate material, imprinting process and film deposition, the plasmonic metasurface is optimized to maximize the density of the nano-trenches, and we show that the surface Raman enhancement due to plasmonic resonances correlates well with trench density and reach meritorious enhancement factor $>10^5$ over large surfaces. We further show that the electric field strength at the nanotrench features are well explained by finite element method simulations using COMSOL Multiphysics. The plasmonic substrate is transparent in the visible spectrum and conductive. In combination with scalable bottom-up fabrication the plasmonic metasurface open up for a wider use of the sensitive and reliable SERS substrate in applications such as portable sensing devices and for future internet of things.

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MAGNETIC METAL-INORGANIC COMPOSITE AS NEW MULTIMODAL CONTRAST AGENTS: PRELIMINARY RESEARCH DESIGN

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The design of new multimodal contrast agents (MCAs) is still challenging. Despite the huge interest in this research field, major progress is still needed to achieve a real and scalable process. The ideal process should be able to combine different phases within the same diagnostic tool, overcoming the additional synthetic steps and high-cost procedures. In detail, in the case of the multimodal approach to combine SERS and MRI signals, a great interest is focused on the synthesis of Au-Fe nanoalloys as MCAs, exploiting their magneto-plasmonic behaviour. However, the production of a Au-Fe nanoalloy as single unit is tricky because a precise control of particle size, composition, and surface property is required. One possible strategy is to use supports, such as zeolites, in the synthetic design to simplify the process.

In this view, our idea is to design a novel strategy to obtain nanoalloys by exploiting prior knowledge in the synthesis of metal-inorganic nanocomposites. As the first step, we started studying the production of Fe NPs supported by an inorganic matrix obtained from zeolite precursor. The employed raw materials are commercial and/or natural zeolites (price per kg, some dozens of dollars). The zeolites are treated following a patented process. In detail, they are repeatedly exchanged with transition metal ions (here, Fe^{2+}) and then subjected to chemical reduction by thermal treatment at a relatively mild temperature under reducing atmosphere. Already after the cation exchange steps, it is visible the formation of small Fe NPs embedded in the zeolite structure, while the final product, after the thermal treatment is represented by a metal-inorganic nanocomposite, where nanoparticles of Fe^0/ Fe_3O_4 are dispersed within a ceramic matrix due to zeolite collapsed structure. The future steps involve the addition of the second metallic component (Au) during the cation exchange steps, in order to obtain an Au-Fe alloy. Once obtained this alloy, we will conduct a study on the effect of the thermal treatment to define the best applicability conditions (presence or not of an amorphous matrix). The simplicity of the process together with the versatility of the materials obtained has already produced excellent results in various fields.

Infrared nanospectroscopy study of light-sensitive proteins with a plasmonic probe

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Infrared (IR) spectroscopy in the mid-IR range (wavelength 5-20 μm) is broadly applied for the study of functional processes of biomolecules, as it can provide a label-free sensitivity to chemical bond orientation and length due to the specificity of vibrational fingerprints. However, the IR techniques are limited in terms of sensitivity and they require large quantities of molecules to probe, while preventing the possibility of investigating the intrinsic heterogeneity of the biological matter at the nanoscale. In the last years, various approaches have emerged to bring the IR spatial sensitivity at the nanometer size, taking advantage of plasmonic scanning probes. Here we present the photothermal-induced resonance (PTIR) method, also called AFM-IR, that couples the radiation emitted by a quantum cascade laser in the mid-IR range and a gold-coated tip of an atomic force microscope (AFM). The laser beam is focused on the AFM probe, which operates in contact mode with the sample. The laser emission wavelength is scanned in the IR range of interest (here 5 to 11 μm) and the thermal expansion generated by the local IR absorption results in a wavelength-dependent change of the indentation depth Δδ (Fig.1a) that is proportional to the IR absorption spectrum of the object under the AFM tip [1]. We apply the AFM-IR method to study two light-sensitive proteins, the Bacteriorhodopsin (BR) and the Channelrhodopsin-2 (ChR2). The latter are transmembrane proteins embedded in the lipid cell membrane that are involved in functional process of the host organism since they act, respectively, as proton pump and ion channel in response to the absorption of visible light at a specific wavelength. We investigate single membrane patches loaded with light-sensitive proteins and deposited on an ultraflat gold surface to exploit the plasmonic field enhancement in the nanogap between the gold-coated tip and the metallic surface (Fig.1b), reaching the sensitivity of monolayer samples (5 nm). The difference nanospectroscopy results we get are benchmarked with conventional micro-FTIR measurements and they display common features known to be related to the vibrational modes involved in the protein activity (Fig.1c) [2,3]. We conclude that the protein activity is preserved and measurable with our nanospectroscopy approach at the level of the single membrane patch.

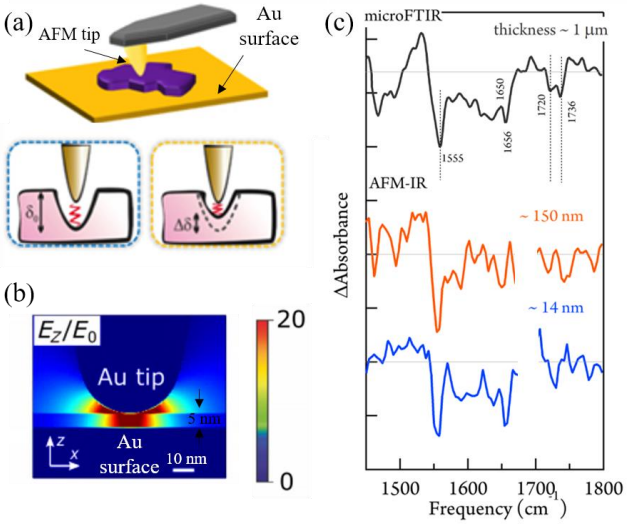

Figure 1: (a) Schematic sketch of AMF-IR technique. (b) Electromagnetic simulation of the IR radiation enhancement in the plasmonic nanogap. (c) Difference-absorbance results obtained on ChR2 sample with FTIR and AFM-IR measurements.

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Quantitatively linking morphology and optical spectroscopy of single silver nanoparticles reveals surface composition changes

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The cross-sections for optical scattering (σ_{sca}) and absorption (σ_{abs}) of an object quantify the strength of its interaction with light. Yet it is challenging to measure accurately the magnitude of σ_{sca} and σ_{abs} at the single nano-object level, with only a handful of quantitative reports of σ_{sca} in literature. We devised a rather general experiment and analysis workflow for measuring, simultaneously and accurately, σ_{sca} and σ_{abs}, by correlating a transmission and a scattering image or spectrum measured under incoherent widefield illumination. In parallel, we developed a numerical and analytical toolbox to simulate the experimental σ_{sca} and σ_{abs}, that is, modelling our high-numerical aperture, incoherent illumination. In order to assess the accuracy of our method in its spectroscopic version, we tested it on nanoparticles (NPs) whose morphology was precisely determined via correlative electron microscopy and used as input for quantitative simulations.

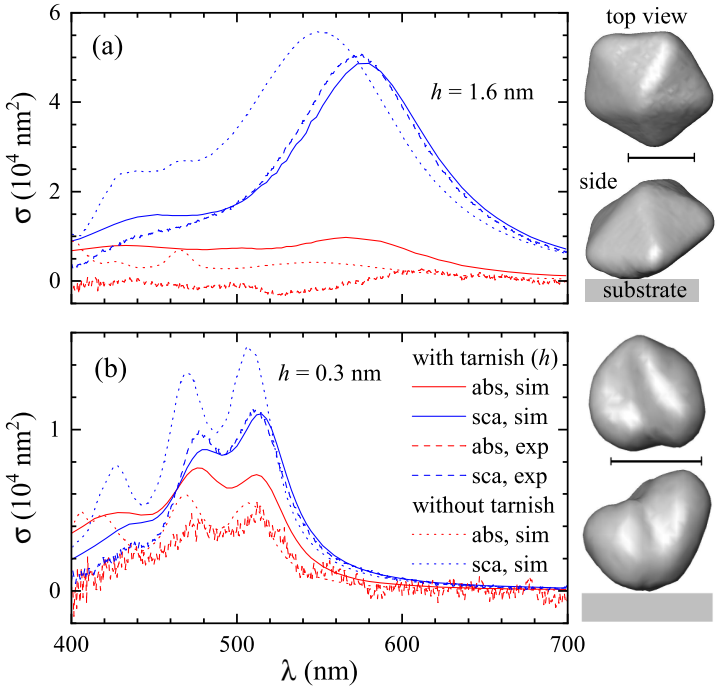

Figure 1: Scattering (blue) and absorption (red) cross-section spectra of two NPs (a,b). Experiments (dashed lines) are compared to numerical simulations including (solid) or not (dotted) a superficial tarnish layer of thickness h. Tomographic reconstructions are shown to the right of the respective graphs; the scale bars are 40 nm. From [3].

We investigated two exemplary silver NP colloidal systems: cubes [2] of 75 nm nominal edge length and nanohedra obtained by photochemically driven wet synthesis [3] including tetrahedra, decahedra (Figure 1a), and irregular shapes (Figure 1b). For most studied NPs, simulations exhibited a sizable blue-shift of the plasmonic peaks as well as a larger σ_{sca}, suggesting some aspect of the system was not included or reproduced well in the numerical model. Similar discrepancies are frequent in literature, and typically justified by invoking organic contaminants or water condensation at the NP surface. We tested systematically (on 11 cubes and 20 nanohedra) these hypotheses and explored several other possibilities, including realistic modifications of morphology and material properties. While most of these changes can red-shift the simulated peaks enough to match the experiments, at the same time they increase σ_{sca} in magnitude, moving simulations further away from experiments. Conversely, as shown in Figure 1, the presence of a thin (up to 2 nm) absorptive layer (which could easily evade detection in electron micrographs) brings about a consistent agreement. We tentatively identify it as tarnish (Ag_2S), which is commonly found on silver surfaces as a result to the exposure to atmospheric traces of sulfur e. g. as H_2S. Our results on the one hand demonstrate the accuracy of our method for measuring cross-section magnitudes and, on the other hand, showcase the potential of quantitative optical characterization to reveal fine details that could hardly be accessed otherwise.

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Mid-infrared photocurrent microscopy of vertical van der Waals semiconductor heterostructures

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Van der Waals semiconductor heterostructures can be used for the detection of mid-infrared radiation. This class of materials possess extraordinary mechanical and optical properties. The most important properties related to devices for light detection are 1) the ease in the fabrication of vertical heterostructures without lattice-matching constrains (this includes CMOS compatibility), 2) the cleanness and flatness of the surface in the few-layer limit, and 3) the high light-absorption for nanometric thicknesses due to the strong confinement of the carrier wavefunctions in the 2D plane [1]. For these reasons, investigating van der Waals semiconductors for infrared radiation detection is particularly appealing. So far, mostly thermal effects have been used for the detection of infrared radiation [1]. However, the experimental observations of intersubband transitions in few-layer InSe make plausible to use these materials for resonant detectors [2], such as quantum well infrared photodetectors. Here we share the preliminary results of a InSe/MoS_2 heterostructure where the 10-layer InSe flake acts as active material for infrared absorption and the MoS_2 layer as barrier to reduce the dark current.

We fabricate heterostructures made of few-layer InSe/MoS2 exploiting graphene as ohmic contacts to on-chip gold electrodes [3]. Figure 1(a) shows a Scanning Electron Microscope (SEM) image of one InSe/MoS_2 device. As passivation layer we use a hBN flake that is fully transparent in the mid-IR apart for its transverse optical phonon at 1370 cm^{-1}, i.e. outside our measurement range. Figure 1(b) shows the I-V characteristic of the device that shows a diode-like behavior (fit with the Shockley diode equation). The InSe flake is intrinsically n-doped and the potential barrier is given by the band offset between the MoS_2 and the InSe layer. As the last step, we assembled a tunable Quantum Cascade laser-based infrared microscope with long working distance Cassegrain objectives coupled to a cryostat that allows us to perform low temperature photocurrent microscopy (laser IR spot of about 10 μm). The repetition rate of the Quantum Cascade laser is 78 kHz. Preliminary results are shown in figure 1(c). We observe a photocurrent signal at 1650 cm^{-1} (6 μm). The signal is likely due to a photo-thermoelectric effect but further investigations are needed. We note that the photocurrent at zero and negative voltages is high with respect to the dark current in figure 1(b). The future steps of this research are to implement a gate voltage to tune the doping and the band alignment in order to maximize the infrared response of the device, vary the thickness of each layer, and design the electrical contacts to act as plasmonic antennas in the mid-infrared.

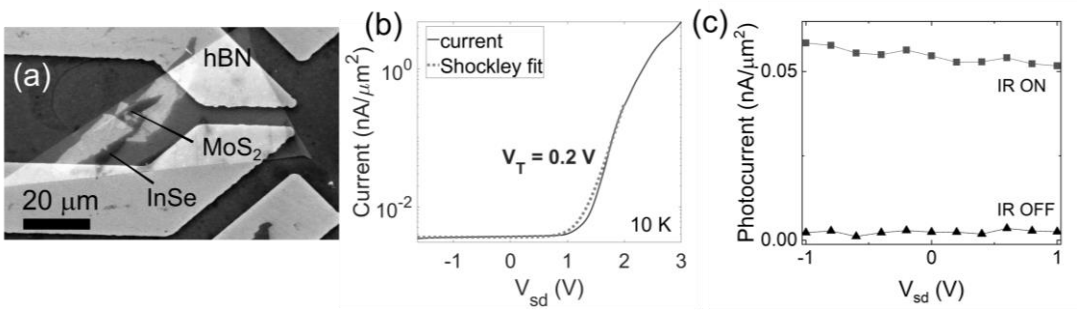

Figura 1: (a) SEM image of the device InSe/MoS_2 device. (b) Low-temperature DC transport measurement at zero gate voltage. A diode-like behavior is observed. (c) Low-temperature infrared photocurrent measured at 6 μm and at 78 kHz repetition rate. We observe an infrared photocurrent signal that does not depend strongly on the applied voltage and is probably due to a photo-thermoelectric effect.

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