PLASMONICA 2018
July 4-6, 2018| Florence, Italy

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Book of Abstracts

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Conference Location

University of Florence, Lecture hall 8,
Via Gino Capponi 9,
Florence, Italy

PLASMONICA 2018
July 4-6, 2018| Florence, Italy

Via G. Capponi 9, Lecture Hall 8

Wednesday, 4th July

9:30 - 10:30	**REGISTRATION**
10:30 - 10:50	**OPENING**
10:50 - 12:50	**Nanoantennas** *Chairperson: Paolo Biagioni*
10:50 - 11:10	**T. Feichtner** – Double Modematching for Plasmonic Resonators
11:10 - 11:30	**S. D'Agostino** – Density Functional Tight Binding as a New Frontier for Quantum Plasmonics
11:30 - 11:50	**M. Pascale** – Plasmon Hybridization in the Full-Wave Regime
11:50 - 12:10	**M. Barelli** – Plasmon hybridization engineering in self-organized nanostrip dimers
12:10 - 12:30	**M. Khalid** – Analysis of Spherical Core-Shell Structures with Sub-nanometer Plasmonic Gaps
12:30 - 14:30	**LUNCH**
14:30 - 16:10	**Nonlinear Effects** *Chairperson: Michele Ortolani*
14:30 - 14:50	**A. Paladini** – Power Dependent Photoexcited Hot-Electron Dynamics in Plasmonics 2D Gold Nanoparticle Arrays
14:50 - 15:10	**F. Lotti** – Spectral filtering with linear and nonlinear plasmonic approaches
15:10 - 15:30	**M. Clementi** – Harmonic Generation in Silicon Rich Nitride Photonic Crystal Cavities
15:30 - 15:50	**T. Cesca** – Polarization-dependent nonlinear optical response of 2D ordered plasmonic nanoprism arrays
15:50 - 16:30	**COFFEE BREAK**
16:30 - 18:10	**Nanophotonics and Hybrid Plasmonics** *Chairperson: Costanza Toninelli*
16:30 - 16:50	**N. Caselli** – Fano profiles at exceptional points in photonic molecules
16:50 - 17:10	**S. Pazzagli** – Photostable single-photon emission from organic nanocrystals
17:10 - 17:30	**P. O'Keeffe** – Sensitizing Wide Band Gap Oxides to Visible Light using Plasmonic Metal Nanoparticles
17:30 - 17:50	**A. De Luca** – Extraordinary Effects in Quasi-Periodic Gold Nanocavities: Enhanced Transmission and Polarization Control of Cavity Modes
17:50 - 18:10	**L. Ghirardini** – Optimization and Control of the Second-Harmonic Generation in AlGaAs Dielectric Nanoantennas

Thursday, 5th July

9:00 - 10:40	**Bioplasmonics** *Chairperson: Silvia Vignolini*
9:00 - 9:20	**A. Foti** – In-liquid SERS detection of biomolecules and toxins by optical printing of gold nanorods
9:20 - 9:40	**C. Novara** – Porous plasmonic nanostructures for Surface Enhanced Raman Scattering: development of biosensing platforms
9:40 - 10:00	**C. Lofrumento** – Graphene Oxide-Functionalized SERS Substrates for a Simple Discrimination between Native and Fibrillar Lysozyme
10:00 - 10:20	**C. D'Andrea** – Tip-Enhanced Raman Spectroscopy Analysis of Amyloid Oligomers
10:20 - 10:40	**F. Capolino** – Achieving Giant Electric Field Enhancement: Introducing Longitudinal Epsilon-Near Zero and Two-scale Structures for spectroscopy
10:40 - 11:20	**COFFEE BREAK**
11:20 - 13:00	**Quantum Nanophotonics and Metamaterials** *Chairperson: Francesco Biccari*
11:20 - 11:40	**P. Lombardi** – Photostable Molecules on Chip: Integrated Single Photon Sources for Quantum Technologies
11:40 - 12:00	**B. Kalinic** – Shortening of Eu^{3+} Radiative Lifetime by near-field coupling with Hyperbolic Metamaterials
12:00 - 12:20	**N. Maccaferri** – Hyperbolic Control of the Free-Electron Plasmons Energy Landscape
12:20 - 12:40	**S. Checcucci** – A SiGe-based metasurface for high-efficiency near-infrared anti-reflection coatings
12:40 - 13:00	**M. Felici** – Spatially Selective Hydrogen Irradiation of Dilute Nitrides: A Versatile Nanofabrication Tool for Photonic Applications
13:00 - 15:00	**LUNCH and GROUP PHOTO**
15:00 - 16:40	**Thermoplasmonics and Photoacoustic Spectroscopy** *Chairperson: Cristiana Lofrumento*
15:00 - 15:20	**F. Ratto** – Design of an all-optical photoacoustic platform for the inspection of plasmonic particles
15:20 - 15:40	**G. Palermo** – Flexible Thermo-plasmonics: mechanically actuated control of the photo-induced heat generation
15:40 - 16:00	**S. Centi** – Cellular vehicles for delivery of gold nanorods to tumors
16:00 - 16:20	**A. Feis** – Photoacoustic spectroscopy of plasmonic nanoparticles
16:20 - 16:40	**A. Belardini** – Photoacoustic absorption reveals extrinsic chirality in self-organised polystyrene spheres partially covered by metal
16:40 - 17:20	**COFFEE BREAK**
17:20 - 19:30	**Poster Session / Round Table**
20:00	**SOCIAL EVENT: Apericena at THE GROVE (see below for the address)**

Friday, 6th July

9:00 - 10:40	**Polaritons and Terahertz** *Chairperson: Marco Felici*
9:00 - 9:20	**A. Macchi** – Extreme strong field plasmonics: MeV electron and XUV harmonic pulses from grating targets
9:20 - 9:40	**P. Biagioni** – Mid Infrared Nonlinear Plasmonics Using Germanium Nanoantennas
9:40 - 10:00	**C. Ciano** – Observation of Phonon-Polaritons in thin flakes of hBN on ultraflat gold substrates
10:00 - 10:20	**J. Fregoni** – Manipulating azobenzene photoisomerization through strong light-molecule coupling
10:20 - 10:40	**V. Giliberti** – Differential mid-IR tip-enhanced absorption spectroscopy to probe light-induced conformational changes of bacteriorhodopsin at the nanoscale
10:40 - 11:20	**COFFEE BREAK**
11:20 - 13:00	**Magnetoplasmonics and Scattering Phenomena** *Chairperson: Francesco Pineider*
11:20 - 11:40	**A. Gabbani** – Magnetic modulation of surface plasmons in magnetoplasmonic nanoparticles
11:40 - 12:00	**D. Loco** – Control of Optical Response of Tb^{3+} Bis-phthalocyaninato Complex close to Metal Nanoparticles
12:00 - 12:20	**E. Fantechi** – Magnetic-plasmonic heterostructured nanocrystals for innovative biomedical applications
12:20 - 12:40	**L. Pattelli** – Optimized density and spatial correlations for TiO_2 nanoparticle samples
12:40 - 13:00	**M. Leonetti** – Scattering Assisted single mode Transmission
13:00 - 15:00	**LUNCH**
15:00 - 16:40	**Bioplasmonic and Nanophotonic Devices** *Chairperson: Leonetta Baldassarre*
15:00 - 15:20	**S. Vignolini** – Bio-inspired Photonics: from nature to applications
15:20 - 15:40	**A. Capocefalo** – Bio-plasmonic functional aggregates of protein decorated gold nanoparticles
15:40 - 16:00	**G. Bruno** – Microfluidic multielectrode arrays for recording and drug delivery
16:00 - 16:20	**M. Mousavi** – Synthesis of Peroxiredoxin protein-templated plasmonic silver nanorings
16:20 - 16:40	**S. Perotto** – Flow-through dielectric ring resonators for biosensing
16:40 - 17:00	**CLOSING REMARKS**

Poster list. Thursday, 5th July

No.	Name	Poster title
1	Dario Balestri	Mechanical and electric control of random photonic modes
2	Martina Banchelli	Plasmonic Membranes as novel Bio-detection Substrates for Surface-Enhanced Raman Spectroscopy
3	Andrea Barucci	Magnetic Resonance Imaging of gold nanorods for hyperthermia therapy
4	Simone Berneschi	Silver ion exchanged soda-lime glasses for SERS platforms
5	Giulia Borile	Nanostructured Lab-on-Chip for Surface Plasmon Resonance biosensing in leukemia: from label-free cell detection toward diagnosis of mutations
6	Francesco Brasili	Synchrotron Radiation SEIRA signaling of a gold nanoprobe in sonicated cells
7	Beatrice Bricchi	Synthesis of Au nanoparticles with tuned plasmonic properties and integration in TiO2 hierarchical structures via single-step pulsed laser co-deposition
8	Angela Capocefalo	SERS active pH-nanosensor
10	Angela Capocefalo	Surface-Enhanced Raman Scattering of DNA-Nanoparticle assemblies
11	Maja Colautti	Photostable molecules on chip: a scalable approach to photonic quantum technologies
12	Maximilien Cottat	Surface-enhanced Raman detection of biomolecules with silver nanocubes and porous silver nanocubes
13	Stefano Danesi	Photo-Induced Heat Generation in Plasmonic vs Non-Plasmonic Nanoantennas
14	Marco Felici	Laser writing of the electronic activity of N- and H-atoms in InGaAs using near-field illumination
15	César de Julián Fernández	Magneto-Plasmonic Properties of Fe-oxide Capped Au Nanoparticles
16	Luca De Stefano	Gold-decorated biosilica nanodevices for nanomedicine
17	Marzia Ferrera	Temperature dependent optical constants of noble metals Au and Ag
18	Assegid Mengistu Flatae	Towards Ultrafast Single-Photon Sources based on Silicon-Vacancy Color Centers in Diamond
19	Antonino Foti	Low cost TERS tips fabricated by electrochemical etching of 125 μm diameter gold wires.
20	Antonino Foti	Evidences of molecular bending in STM-TERS tip-approach curves on different types of thiol self-assembled monolayers grafted on gold film

21	Lavinia Ghirardini	Plasmon-Enhanced Second-Harmonic Sensing in a Microfluidic Chip
22	Giulia Giannone	Molecular Plasmonic Switches via Density Functional Tight-Binding Theory
23	Nicoletta Granchi	Reconfigurable photonic molecules for sensing application
24	Tommi Isoniemi	Probing plasmon polaritons in hyperbolic metamaterials with electron energy loss spectroscopy
25	Giuseppe Lio	Design and Realization of a Nano-guided Hybrid system to implement a Photonic Transistor
26	Michele Magnozzi	Plasmonic properties of heated self-organized 2D arrays of Au nanoparticles
27	Michele Magnozzi	Plasmonic Properties of Self-Assembled Au/PNIPAM Core-Shell Nanoparticles Studied with Spectroscopic Ellipsometry
28	Maria Raffaella Martina	Development of a Plasmonic Device based on Langmuir-Blodgett films of Ag Nanowires
29	Artur Movsesyan	Plasmonic multi-resonances in simple geometric platforms
30	Alina Muravitskaya	Tunable Surface Plasmon Resonance of Silver Nanoparticles for Plasmon-Enhanced Fluorescence
31	Sara Nocentini	Optically tunable 3D photonic structures in rigid and soft polymers
32	Chiara Novara	Study of aptamer immobilization on plasmonic surfaces by SERS analysis
33	Fatima Omeis	Ultra-thin plasmonic nanopores for single molecule detection
34	Gaia Petrucci	Self-Assembly of Magnetic Nanoparticles over Plasmonic Nanoantennas
35	Francesco Pisani	Near Single Cycle Surface Plasmon Polariton Generation by Rotating Wavefront Pulses
36	Francesco Poggialini	Investigating Silver Nanoparticle Prepared by Pulsed Laser Ablation in Liquid as Simple, Cost-Effective and Reproducible SERS Substrates
37	Stefano Rossi	Grating-coupled Surface Plasmon Resonance (GC-SPR) optimization for phase-interrogation biosensing in a microfluidic lab-on-chip
38	Elisabetta Sepe	1D-Photonic Crystal Biochips for ERBB2 Cancer Biomarker Detection
39	Lorenzo Squillantini	Spin crossover nanostructures bistable behavior on surfaces
40	Roberto Tricarico	Radiative Plasmon Decay Rates in Nanoparticles
41	Cosimo Trono	SPR microfluidic platform based on multimode plastic optical fiber for the detection of sepsis biomarkers

42	Irene Vassalini	“Stainless” Gold Nanorods: Preserving Shape, Optical Properties, and SERS Activity in Oxidative Environment

Social dinner. Thursday, 5th July

The social dinner will take place in the Florence city center, at **The Grove** restaurant.

Address:

Piazza della Indipendenza 3/R,

50129 Firenze

(Distance from the conference venue about 800 m)

Session

Nanoantennas

Chairman

Paolo Biagioni, Politecnico Milano, Italy

Double Modematching for Plasmonic Resonators

Thorsten Feichtner[1], Katja Höflich[2], Silke Christiansen[2,3], Bert Hecht[1]
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Röntgen Research Center for Complex Material Research (RCCM), Physics Institute,
University of Würzburg, Am Hubland, D-97074 Würzburg, Germany
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[3]Helmholtz-Zentrum Berlin für Materialien und Energie, Lise-Meitnerpl. 1, 14109 Berlin, Germany

3D mode-matching is a powerful theoretical concept to understand and optimize the optical coupling between an arbitrary emitter and a plasmonic resonator. By introducing a second mode matching condition with an additional single emitter we take into account that the power transfered to the plasmonic resonator often is to be re-emitted efficiently to a receiver or detector (see Fig. 1a)). This allows to identify optimal geometries providing plasmonic modes, which are optimized to work as optical antenna, transducing and routing optical energy between light and matter[1]. Here, two applications of double mode-matching will be presented:

1) The coupling between a point-like two-level quantum emitter (QE) and the continuum of radiative modes. This leads to a set of novel optical antenna design guidelines for QE emission enhancement. Accordingly, a plasmonic cavity antenna (PCA) geometries is derived (see Fig. 1b)) and compared to an established dipolar two-wire antenna geometry (see Fig. 1c); [1]).

2) The the far-field coupling of nanometer-sized metal helices[2] to circular polarized light shows a rich and complex behavior. However, a 1D model based on 3D mode-matching can describe qualitatively the scattering behavior of the helical plasmonic nano resonator (see Fig. 1d)), providing a simple access to the design and fabrication of chiro-optical devices..

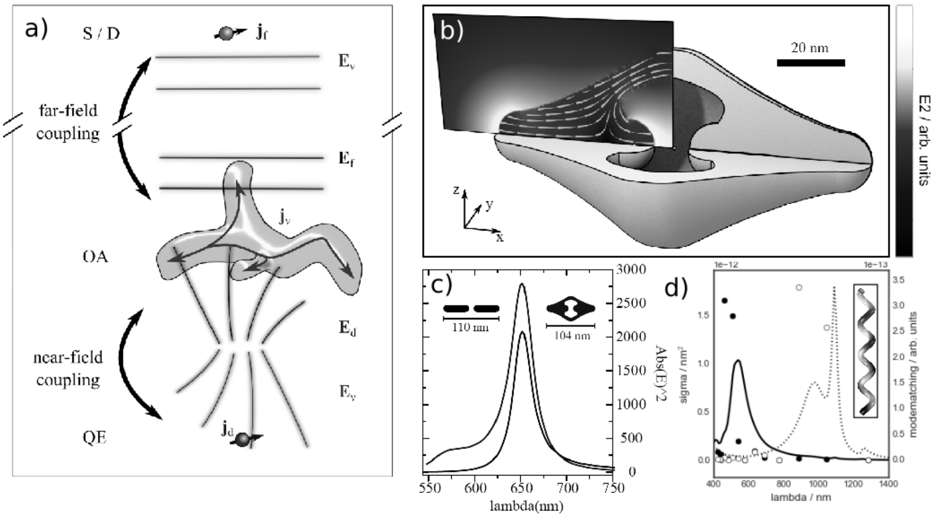

Figure 1: Double 3D mode-matching. a) An optical antenna (OA) couples to both a sending/detecting far-field dipole S/D with currents j_f and an near-field dipole (QE) showing currents j_d. The coupling can be described by the fields of the antenna mode E_v, and of the dipoles E_f, E_d. b) Antenna design carrying a doubly matched resonant mode. The originally rotational symmetric geometry is shown with a 90° cutaway for improved visualization. Additionally, the near-field intensity (greyscale) as well as the current direction (light arrows) are overlaid for a quarter cross section. c) Near-field intensity enhancement spectra in the center of b) as well as at the center of a two-wire dipole reference antenna (black). The small insets show the xy-plane cross section of both geometries. d) Numerically retrieved spectra (lines) of a plasmonic helix excited with even (dashed) and odd (solid) handedness as well as calculated coupling of 1D Fabry-Perot modes via 3D mode-matching (dots). The inset shows the charge density of the lowest order resonance.

References

[1] Feichtner, T., Christiansen, S., Hecht, B. (2017). Physical Review Letters, 119(21), 217401.
[2] Haverkamp, C., Höflich, K., Jäckle, S., Manzoni, A., Christiansen, S. (2017). Nanotechnology, 28(5), 55303

Density Functional Tight Binding as a New Frontier for Quantum Plasmonics

Stefania D'Agostino[1, 2] and Fabio Della Sala[1,3]
[1] *Center for Biomolecular Nanotechnologies@UNILE, Istituto Italiano di Tecnologia, Via Barsanti, 73010 Arnesano, Italy.*
[2] *Institute for Materials Science, TU Dresden, 01069 Dresden, Germany.*
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Computational methods from classical electrodynamics have been proved to be useful and powerful tools to design and optimize the properties of localized surface plasmons and their macroscopic interactions with absorbers or emitters put in their proximities. Anyways, state-of-the-art fabrication and characterization techniques are to date able to experimentally control light-matter interaction at sub-nanometer scales.

Thus theoretical schemes able to overcome the limits of the classical vision and to fully take into account quantum mechanical effects are needed[1].

In this work, we propose the Time-Dependent Density Functional Tight-Binding (TD-DFTB) as a new frontier for computational quantum plasmonics.

DFTB is based on the second order expansion of the Kohn-Sham energy functional around a reference density of neutral atomic species and it has been demonstrated to be an efficient scheme for describing the structural, electronic and optical properties of different nanoscale systems[2,3]. We performed a systematic investigation for plasmonics systems, analyzed the absorption spectra of silver tetrahedral closed-shell Agn clusters (n=10, 20, 35, 56, 84, 120) within the framework of TD-DFTB and compared the obtained results with the *First-Principles* Time-Dependent Density Functional Theory (TD-DFT) ones. We found out that, under an appropriate choice of the Slater-Koster parametrization, optical spectra result to be in a very good agreement with the reference ones (TD-DFT) and achievable within a total wall-time less than 0.2% the DFT one, this offering a concrete possibility to overcome the bottleneck of computational cost in quantum plasmonics.

In Table 1, the Total Wall-Times (TWT) required within both the approaches (TD-DFT and TD-DFTB/new parametrization), are compared for two different clusters.

Cluster	Theory	Total Wall Time (s)
Ag_{35}^{-5}	Standard DFT	44189
Ag_{35}^{-5}	Tight Binding	40
Ag_{56}^{-2}	Standard DFT	96762
Ag_{56}^{-2}	Tight Binding	125

Table 1: TWT table for simulations performed on identical systems with the same number of processors (NCPU = 4).

References

[1] R. Esteban et al., Nature Comm. 3, 825 (2012).
[2] C. F. A. Negre et al., J Phys Condens Matter. 25(12) (2013).
[3] R. Rüger et al., J. Chem. Theory Comput. 11, 157–167 (2015).

Plasmon Hybridization in the Full-Wave Regime

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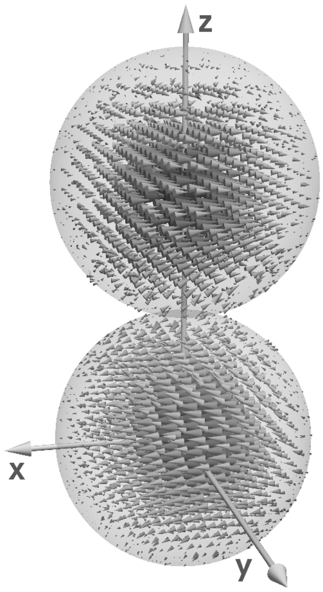
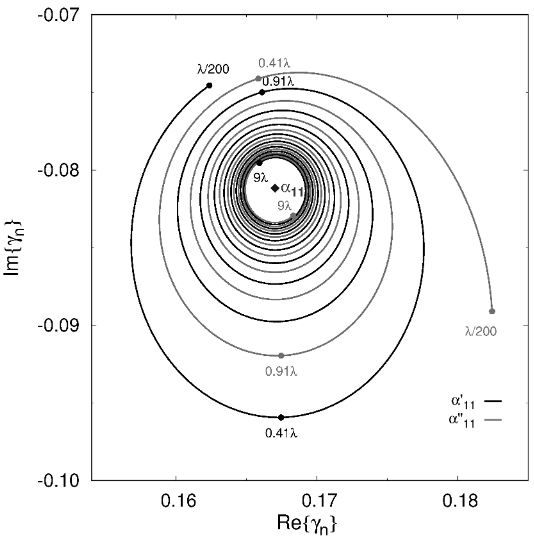
In the last few years, nanoparticle dimers have represented an ideal framework for the investigation of emerging physical phenomena at the nanoscale. In fact, they may support large electric field enhancement localized in the gap region. In addition, their properties can be tuned by varying the two radii and the interparticle-separation. Perhaps the most widely used theoretical approach to understand the properties of composite plasmonic structures, including a spheres' dimer, is the plasmon hybridization. It consists in the representation of the eigenmodes of the dimer in terms of the eigenmodes of the two constituent isolated spheres. However, the theory of plasmon hybridization has been so far limited to the electrostatic regime [1]. This fact imposes great limitations to the applicability of this theory, since real-world metal structures have dimensions comparable to the incident wavelength. For instance, the existing electrostatic mode hybridization theory cannot describe the radiative coupling between the spheres, nor the existence of photonic modes, which play a key role in the scattering from dielectric particles.

Here, by using spectral methods, we derive the first full-electrodynamic theory of modes hybridization in a spheres' dimer. The existing electrostatic plasmon hybridization can be seen as a limiting case of this approach. Specifically, the eigenmodes of a spheres' dimer are represented in terms of the modes of isolated spheres [2–4]. The eigenmodes of both the single spheres and the dimer of spheres are independent of the permittivity. Moreover, the field scattered by the dimer can be expressed in terms of modes of the isolated spheres, where the expansion coefficients are rational functions of the permittivity. The theory we developed represents an ideal framework for the analysis of the dimer's resonances: it enables us to classify the eigenmodes into plasmonic and photonic modes, to investigate the effects of near field and far field coupling on mode hybridization.



(a) Dipolar mode in a dimer of spheres with radius λ and edge-to-edge distance $\lambda/200$.



(b) Loci spanned in the complex plane by the dipolar eigenvalues of a dimer of spheres with radius λ, by varying the edge-to-edge distance from $\lambda/200$ to 9λ.

References

[1] E. Prodan, C. Radloff, N.J. Halas, P. Nordlander, A hybridization model for the plasmon response of complex nanostructures, American Association for the Advancement of Science, Science, 302, 5644, 419-422, 2003, doi :10.1126/science.1089171

[2] C. Forestiere and G. Miano, Material-independent modes for electromagnetic scattering, Phys. Rev. B 94, 201406 (2016).

[3] M. Pascale, G. Miano, and C. Forestiere, Spectral theory of electromagnetic scattering by a coated sphere, J. Opt. Soc. Am. B 34, 1524-1535 (2017).

[4] C. Forestiere, G. Miano, G. Rubinacci, A. Tamburrino, R. Tricarico and S. Ventre, Volume Integral Formulation for the Calculation of Material Independent Modes of Dielectric Scatterers, in IEEE Transactions on Antennas and Propagation, vol. PP, no. 99, pp. 1-1. doi: 10.1109/TAP.2018.2816604

Plasmon hybridization engineering in self-organized nanostrip dimers

Matteo Barelli[1], Maria Caterina Giordano[1,†], Stefano Longhi[2,], Andrea Mazzanti[2], Giuseppe Della Valle[2]
Francesco Buatier De Mongeot[1*]

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The engineering of self-organized plasmonic metasurfaces is demonstrated by a maskless technique employing defocused ion-beam sputtering and kinetically controlled metal deposition. Our approach enables the synthesis of periodic sub-wavelength gold nanostrips over large cm^2 area, in a reliable and controllable way. A multi-level variant of the self-organized approach led to high resolution manufacturing of vertically stacked nanostrip dimer arrays, designed by plasmon hybridization methods. In particular, we show the optical response of the nanostrip dimers in the so-called gap-plasmon configuration, demonstrating electric and resonance excitation in the visible (VIS) and near-infrared (NIR) spectrum [1]. The magnetic dipolar mode offers superior sensitivity and field-enhancement as compared to the more conventional electric dipolar one, and the translational invariance of the nanostrip configuration results into a high filling factor for the hot spots. The strong plasmonic response, tunable into the VIS and NIR spectrum, makes such gap-plasmon metasurfaces very attractive for surface-enhanced linear and nonlinear optical spectroscopies.

Recently we began exploring the possibility to exploit the nanopatterned soda-lime glass template to confine multi-metal plasmonic heterostructures with different geometries: (i) vertically or laterally stacked Ag/Au dimers in gap plasmon configuration and (ii) laterally stacked and connected Ag/Au "hut-like" structures. Those systems show promising and peculiar EM wave-front manipulation properties which makes them interesting for color routing applications.

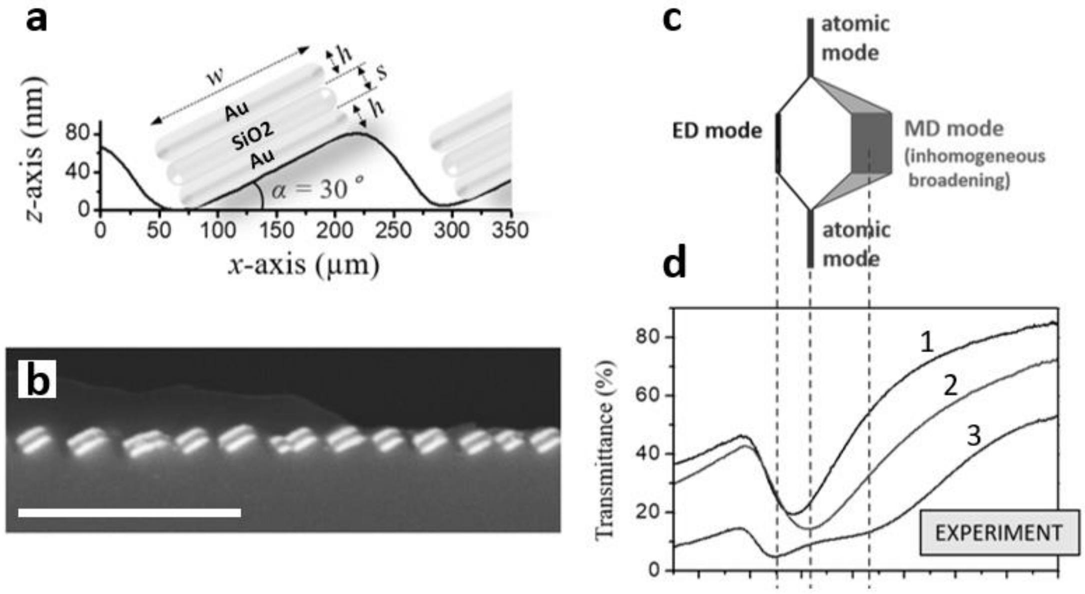

Figure 1: (a) Sketch of Au-silica-Au dimers confined on a faceted ripple pattern; w = 100 nm, h = 30 nm, s = 42 nm. (b) SEM image of Au-silica-Au dimers in cross-section view, scale bar correspond to 1 µm. (d) Cartoon of the hybridization mechanism taking place in the dimer configuration. (e) Optical spectra for transversal polarization (TM) of Au NWs (curve 1), Au-silica NWs (curve 2), Au-silica-Au dimers (curve 3) at normal incidence.

References

[1] Giordano, M.C., Longhi, S., Barelli, M. et al. Nano Research (2018) in press. https://doi.org/10.1007/s12274-018-1974-3

Analysis of Spherical Core-Shell Structures with Sub-nanometer Plasmonic Gaps

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We present a study of nonlocal optical properties of spherical core-shell structures (also known as nanomatryoshkas) with sub-nanometer core-shell spacing [1] using the quantum hydrodynamic theory (QHT). We consider several plasmonic systems of Na metal with dimensions SF × (R_1, R_2, R_3) where SF is the scaling factor, R1 is the radius of inner solid core and R2 and R3 indicate inner and outer radii of the shell, respectively, see Fig. 1(a). We apply state-of-the-art QHT which provides an elegant method to investigate near- and far-field optical properties of multiscale plasmonic systems [2, 3]. We study the effect of gap spacing and particle size on the optical properties of these core-shell structures. We present numerical results for different methods and find that the results calculated within QHT method are in excellent agreement with the Density functional theory (DFT) computations [4], performed using an in-house developed code. To show the potential of QHT as compared to the other methods, we also include in our analysis the results calculated using local response approximation (LRA) and Thomas-Fermi hydrodynamic theory (TF-HT).

Absorption efficiency spectra for five Na core-shell structures, with SF taking an integer value from 5 to 1, computed within the QHT are shown in Fig. 1(b). The lower panel of Fig. 1 presents a comparison for absorption spectra and induced polarization density, obtained by using different methods, for SF=4.

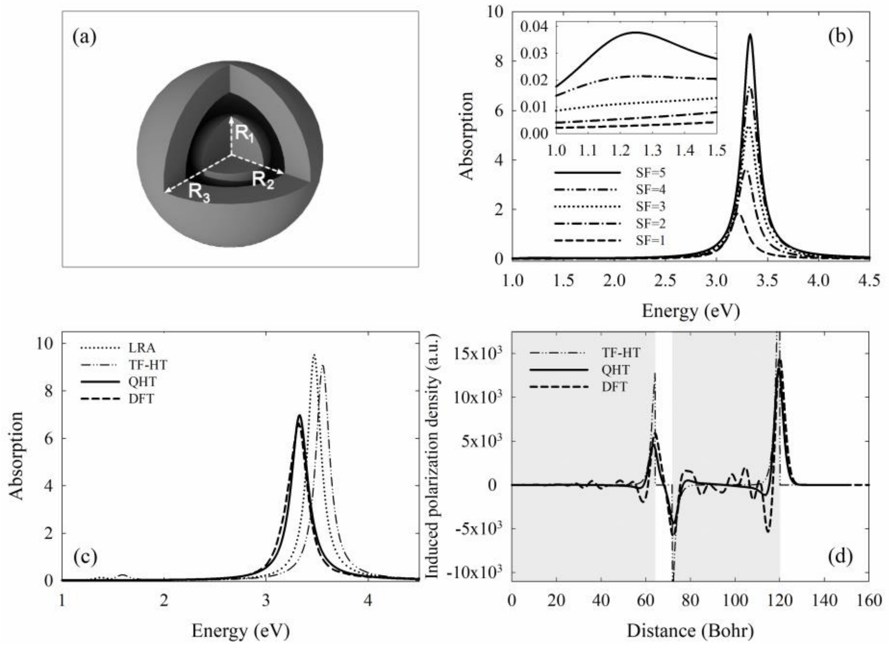

Figure 1: (a) Geometry of the structure (b) absorption spectra calculated using QHT for Na core-shell structures, with the scaling factor (SF) taking values from 5 to 1. (c) Absorption spectra and (d) induced polarization density for SF=4 calculated by using different theories.

References

[1] V. Kulkarni, E. Prodan and P. Nordlander, Nano Lett. **13**, 5873-5879 (2013).
[2] C. Ciracì and F. D. Sala, Phys. Rev. B **93**, 205405 (2016).
[3] C. Ciracì, Phys. Rev. B **95**, 245434 (2017).
[4] E. Prodan, E. Lee and P. Nordlander, Chem. Phys. Lett. 360, 325-332 (2002).

Session

Nonlinear Effects

Chairman

Michele Ortolani, Sapienza – University of Rome, Italy

Power Dependent Photoexcited Hot-Electron Dynamics in Plasmonics 2D Gold Nanoparticle Arrays

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The generation of hot electrons in metallic nanostructures has attracted a great deal of attention in the literature due to the increasing interest in harvesting these electrons for purposes such as nanocatalysis or energy conversion [1]. In the first case it is possible to sensitize high band gap semiconductors to visible light using the localized surface plasmon resonance of the nanostructures (NSs), while in the second case efficiently harvesting hot electrons may lead to a route to overcome the Shockley-Quessier limit in photovoltaic energy conversion.

Here we use femtosecond photoexcitation of 2D arrays of gold NPs on a LiF substrate to investigate the ultrafast dynamics of these NSs. The timeline of the dynamics of a metallic NS following interband photoexcitation is the following: t = 0 - photoexcitation of a strongly non-thermal distribution of electrons; t = 0 – hundreds of fs - electron-electron scattering leading to thermalization of the electron distribution; t = 100 fs – 5 ps – electron-phonon scattering leading to exchange of energy between the hot electrons and the lattice; and t = 5 ps – hundreds of ps – phonon-phonon scattering in which energy is exchanged between the lattice of the metallic NS and the surroundings.

Transient Absorption (TA) spectroscopy can be used to investigate these dynamics thanks to the extreme sensitivity of the localized surface plasmon resonance (LSPR) to the instantaneous temperature of the electrons in the NS. As the electrons in the NS heat up following photoexcitation a bleaching of the LSPR is observed, while the cooling of the NSs causes the recovery of this signal. We have used TA measurements on a fs/ps timescale to obtain information on the electron thermalization [2] and hot-electron cooling [3] in the NSs. In this work a somewhat counterintuitive effect of faster electron thermalization with higher power optical pumping is observed, quantitatively analyzed, and compared with literature models [2,3].

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Spectral filtering with linear and nonlinear plasmonic approaches

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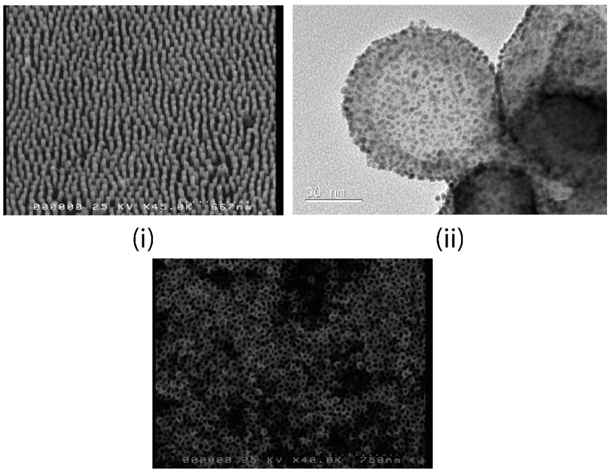
The development of metasurfaces and metamaterials made possible to engineer optical response by controlling nanoscale arrangements of plasmonic or dielectric objects. Not only linear reflection, transmission and absorption but also nonlinear optical properties can be engineered and enhanced with plamosmnic metamaterials [1].

In this work, we exploit these plasmonic metamaterial properties in order to create spectral optical filters in both the linear and non-linear regime, such as narrow band notch filters, bandpass and bandstop filters and intensity limiters. Geometrical configurations studied include (i) gold nanorods forming Fabry-Pérot cavities with tuneable effective refractive index, (ii) assemblies of dielectric, plasmonic and core-shell nanoparticles; (iii) plasmonic nanotube arrays. The transmission spectra of these geometries in general present features that, for a set polarisation, are constant for a wide range of angle of incidence, making them suitable for a variety of applications.

Taking advantage of the strong third-order nonlinearity of such metamaterials, which have been proven to exhibit an ultrafast response for controlling both the intensity and polarization of incident light [2], we extend the spectral filters for intensity limiting of nanosecond laser pulses.



(i) (ii)

(iii)

Figure 1: The various geometries analysed: (i) plasmonic nanorods; (ii) silicon nanoparticle with gold coating; (iii) plasmonic nanotubes.

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Harmonic Generation in Silicon Rich Nitride Photonic Crystal Cavities

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Photonic Crystal (PhC) cavities allow to confine light with ultra-high quality factor (Q) and low mode volume (V), enabling a significant enhancement of light-matter interaction. Thanks to this property, PhC cavities can be employed to achieve low-power on-chip frequency conversion, even under continuous wave (CW) pumping [1]. The state-of-art silicon-based PhC cavities, despite exhibiting high Q factors and nonlinear third-order susceptibility, suffer from parasitic effects such as two-photon absorption (TPA) and related free carrier absorption (FCA), which limit the performance of these devices at high powers. A possible way to overcome this limitation is to employ wide bandgap such as silicon nitride (Si_3N_4).

In order to provide a nonlinear response comparable to the one of silicon, the concentration of silicon can furthermore be increased by chemical vapor deposition (CVD) techniques. The resulting material, silicon rich nitride (SRN), exhibits a higher nonlinear coefficient than stoichiometric silicon nitride, low linear losses and negligible TPA [2]. Recently, SRN was successfully employed to fabricate PhC cavities with ultrahigh quality factor [3].

In this work, we report the simultaneous generation, obtained at low power under CW excitation, of second (SH) and third harmonic (TH) in a 2-dimensional PhC cavity, fabricated in a suspended membrane of SRN.

We exploited a line-width modulated design [3], modified in order to increase the optica power vertically coupled to the micro-resonator [4] to fabricate samples with a fundamental resonant mode at telecom wavelength ($\lambda_0 = 1546.3$ nm) and a good compromise between quality factor ($Q = 13{,}000$) and coupling efficiency ($\eta_C = 30\%$).

We performed imaging and spectroscopic measurements under different pumping regimes, in a modified resonant scattering (RS) apparatus [1,3,4]. From the analysis of SH and TH scaling trends, we estimated the normalized generation efficiencies $\rho_{SH} = 2.9 \cdot 10^{-7}\ \mathrm{W}^{-1}$ and $\rho_{TH} = 5.5 \cdot 10^{-5}\ \mathrm{W}^{-2}$. Our results show a substantial increase of the nonlinear process efficiencies compared with the bulk case, with improvements which are expected to scale as $(Q/V)^2$ and $(Q/V)^3$ respectively. Moreover, our study suggest the transparency of SRN at SH wavelength and the absence of TPA and related detrimental effects.

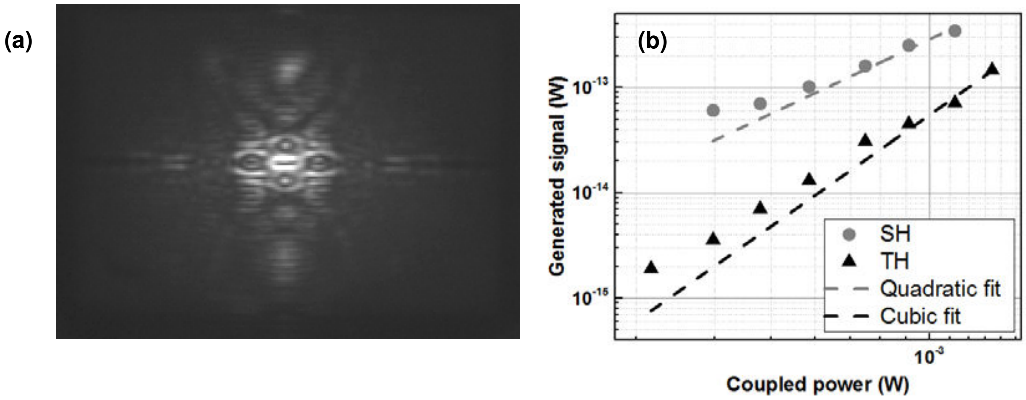

Fig. 1: (a) Image of the generated second harmonic, linear scale. (b) Scaling trends for SH and TH generation.

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Polarization-dependent nonlinear optical response of 2D ordered plasmonic nanoprism arrays

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Recent years have seen a tremendous burst of research activity towards the development of novel nonlinear optical (NLO) nanomaterials for many advanced applications in nanophotonics. To this regard, plasmonic nanoarrays attracted considerable attention for their strong and ultra-fast nonlinear optical response [1,2]. Besides this, an important requirement for NLO applications is the capability to control and modulate the material nonlinearity in a reversible way, by changing some external control parameters.

In the present work we report on the results of our recent investigation on the polarization dependence of the nonlinear optical response of bi-dimensional ordered arrays of plasmonic (Ag and Au) triangular nanoprisms, synthesized by nanosphere lithography on silica substrates (Fig. 1a). In particular, we studied the effects of dichroism in the nonlinear absorption of Ag nanoprism arrays (NPA) and the polarization-dependent second harmonic generation (SHG) properties of Au NPA. The nonlinear absorption characterization was performed with the z-scan technique [3] using a mode-locked ps Nd:YAG laser source (pulse duration < 20 ps, 10 Hz repetition rate) to excite the fast, electronic component of the nonlinear response of the NPA, while the SHG properties have been characterized with a mode-locked Ti:Sapphire laser producing 125 fs (FWHM) pulses at 100 MHz repetition rate.

In both cases, a continuous modulation of the nonlinear response is obtained, correlated with the 60°-symmetry of the NPA honeycomb lattice (Fig. 1b,c) and the behavior can be explained by taking into account the polarization-dependent local electric-field distribution in the nanoprism array, as demonstrated by finite elements method (FEM) simulations.

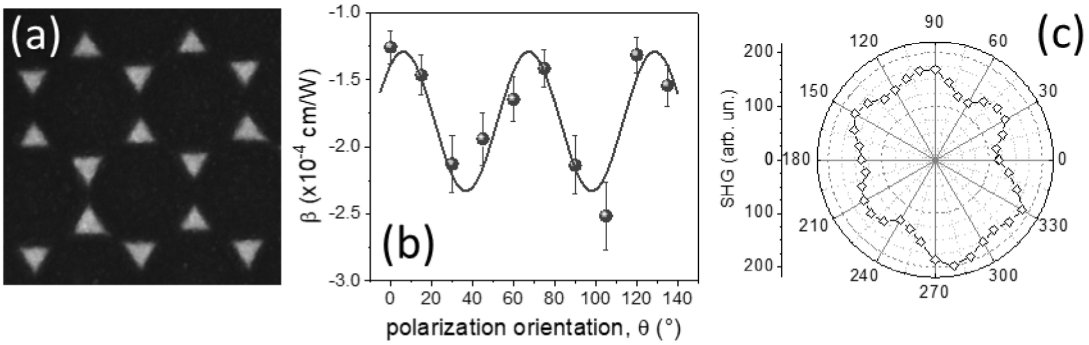

Figure 1: (a) SEM image of a nanoprism array. (b) Nonlinear absorption coefficient (β) as a function of the linear polarization orientation. (c) Polar plot of the polarization-dependent SHG signal.

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Session

Nanophotonics and Hybrid Plasmonics

Chairwoman

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Fano profiles at exceptional points in photonic molecules

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In photonics and plasmonics Fano profiles are the manifestation of the interference between a resonant mode and a spectrally wide background, whose phase difference generates a variety of lineshapes [1]. For coupled systems made of two resonant building blocks, two different regimes emerge, depending on the ratio of the coupling over the loss difference. The weak coupling regime (normal modes with equal frequencies but different losses) and the strong coupling regime (normal modes with different frequencies but identical losses). Notably, at the transition between the two exists a singularity, denominated exceptional point, where the two normal states coalesce into a single one. At this stage the breaking of parity and time-reversal symmetry occurs, thus giving rise to fascinating phenomena, including electromagnetic induced transparency, reversal of the pump dependence in coupled quantum cascade lasers and the non-reciprocal wave propagation in coupled waveguides [2-4]. However, since the exceptional point occurs exactly at the transition, it is quite elusive to be detected. To experimentally address it, the coupling to waveguide proposed so far was proved to work only in peculiar cases: if a large loss-detuning between the two resonators is present and if the waveguide is coupled only to the lower quality factor cavity [5]. Here, we extend the interference detection scheme by introducing a new class of (generalized) Fano lineshapes as a signature of the exceptional point occurrence in resonant scattering experiments [6]. We investigate photonic molecules and necklace states in disordered media by means of a near-field hyperspectral mapping. In a photonic system, as the one depicted in Fig. 1a), the modes of two coupled nanocavities were tailored close to the exceptional point by a post-fabrication control. We observe a wide class of generalized Fano profiles, as the ones of Fig. 1b), which nicely agree with the model and with finite-difference time-domain calculations.

Finally, in material science the presented approach could extend the characterization of composite nanoresonators, semiconductor nanostructures as well as plasmonic and metamaterial devices.

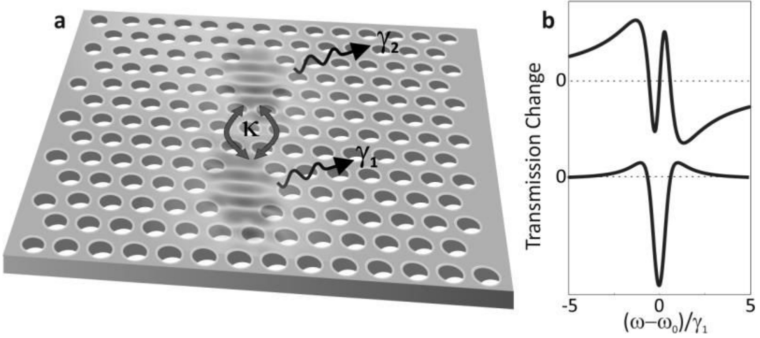

Figure 1. a) Schematics of the photonic molecule under investigation in a photonic crystal slab. The coupling κ was tuned to achieve the closer condition to the exceptional point. b) Transmission spectra in different spots of the photonic molecule near the exceptional point. They exhibit generalized Fano lineshapes.

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Photostable single-photon emission from organic nanocrystals

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Quantum technologies could largely benefit from the development of single quantum emitters in sub-micrometric size crystals providing single photons on demand. These are naturally prone to be deterministically integrated in complex nanostructures, such as photonic crystal devices, nano-guides and optical antennas. However, today-available single-photon sources embedded in nanocrystaline matrices - such as quantum dots or color centers in nanodiamonds - suffer from spectral instability [1,2], preventing their emitted photons to be used for basic quantum optics operations.

In this work we report on unprecedented performances of single-photon emission from organic nanocrystals (average size of hundreds nanometers) made of anthracene (Ac) and doped with dibenzoterrylene (DBT) molecules.

The growth procedure is based on reprecipitation, an easy and inexpensive method that we here adapted for a precise tuning of DBT concentration. Investigations on single molecules' photophysics demonstrate a single-photon emission with an uncorrected purity, $g^2(0)$, as low as 0.05 and a well-defined dipole orientation parallel to the crystal plane and the substrate. Single-photon emission around 785 nm from individual molecules is bright (with 1.5 MHz detected photon-rate at saturation) and photostable at room temperature. At cryogenic temperatures, 00-zero phonon lines show linewidths close to the lifetime-limited value (about 50 MHz) which are spectrally stable over time scale of hours. Such optical properties in a nanocrystalline environment make the proposed organic nanocrystals a unique single-photon source for integrated photonic quantum technologies.

Preliminary results on the manipulation and integration of the nanocrystals in different polymeric materials are discussed as possible writable system for applications in integrated quantum optics and nanophotonics.

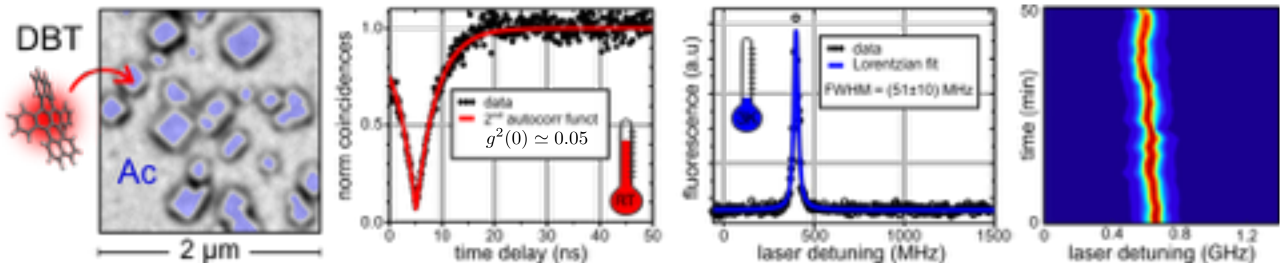

Figure (from left to right): Electron microscope image of the growth Ac nanocrystals doped with controllable DBT molecules concentration; Second order autocorrelation function measured from of a single DBT:Ac nanocrystal. The experimental coincidence reduction obtained at zero-time delay yields a uncorrected purity $g^2(0)$ as low as 0.05; Measured resonant excitation spectrum of a single DBT molecule in an Ac nanocrystal fitted with a Lorentzian profile; 2D plot representing the spectral time traces of a single DBT molecule showing the absence of spectral diffusion (Lorentzian peak center variation in time within the molecule lifetime-limited linewidth).

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Sensitizing Wide Band Gap Oxides to Visible Light using Plasmonic Metal Nanoparticles

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The possibility to sensitize wide band gap oxides to visible light has stimulated the research community in view of efficiently converting solar to chemical energy, with the aim of obtaining optimized materials for photo-catalysis [1]. Cerium oxide has been investigated due to the possibility for Ce ions to easily and reversibly switch between the 4+ and the 3+ oxidation states depending on the ambient conditions. In cerium oxide the presence of localized Ce 4f states between the filled O 2p valence band and the empty Ce 5d conduction band can make the material a very sensitive probe to identify possible charge transfer to/from neighboring metal atoms.

Pure CeO_2 absorbs light in the ultraviolet range (band gap 3.2 eV). To achieve a high efficiency for solar to chemical energy conversion, the material can be coupled with plasmonic nanoparticles (NPs). In this way the irradiation with visible light is sufficient to excite the localized surface plasmon resonance (LSPR) and to induce energy and/or charge transfer from the metal to the oxide [2, 3]. We have embedded mass selected silver NPs into a matrix of CeO_2. The resulting film exhibits significant absorption in the visible region of the spectrum (2 – 3 eV) which is much higher than expected for isolated spherical Ag NPs. Modeling of the plasmonic response as a function of the shape and position of the NPs allows us to explain this visible absorption.

Furthermore, we have used transient absorption (TA) spectroscopy to quantify the energy/charge transfer at the femtosecond/picosecond time scale between the plasmonically excited Ag NPs and the surrounding CeO_2. This was achieved by comparing the TA signals obtained by direct UV above-bandgap excitation with those of the plasmonic excitation of the Ag NPs by visible light. Evidence of signal associated with CeO_2 excitation in both cases reveals energy/charge transfer following plasmonic excitation. Furthermore we conclude that embedding the Ag NPs within the CeO_2 layers allows very high charge transfer efficiencies to be achieved with the added bonus of improved stability of the Ag NPs.

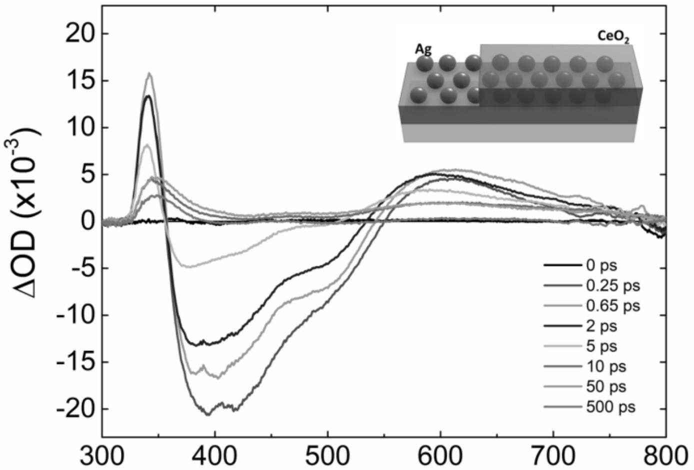

Figure 1: Transient absorption of Ag nanoparticles embedded in CeO_2.

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Extraordinary Effects in Quasi-Periodic Gold Nanocavities: Enhanced Transmission and Polarization Control of Cavity Modes

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Plasmonic quasi-periodic structures are well-known to exhibit several surprising phenomena with respect to their periodic counterparts, due to their long-range order and higher rotational symmetry [1]. Thanks to their specific geometrical arrangement, plasmonic quasi-crystals offer unique possibilities in tailoring the coupling and propagation of surface plasmons through their lattice, a scenario in which a plethora of fascinating phenomena can take place. In this work we investigate the extraordinary transmission phenomenon occurring in specifically patterned Thue−Morse nanocavities, demonstrating noticeable enhanced transmission, directly revealed by near-field optical experiments, performed by means of a scanning near-field optical microscope (SNOM) [2]. SNOM further provides an intuitive picture of confined plasmon modes inside the nanocavities and confirms that localization of plasmon modes is based on size and depth of nanocavities, while cross talk between close cavities via propagating plasmons holds the polarization response of patterned quasi-crystals. Our performed numerical simulations are in good agreement with the experimental results. Thus, the control on cavity size and incident polarization can be used to alter the intensity and spatial properties of confined cavity modes in such structures, which can be exploited in order to design a plasmonic device with customized optical properties and desired functionalities, to be used for several applications in quantum plasmonics.

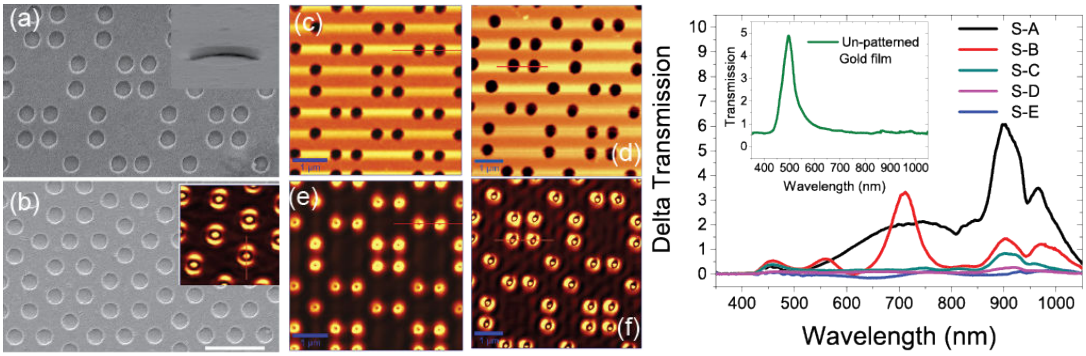

Figure 1: (a)-(b) SEM images of the quasi-periodic nanocavities. (c)-(d) AFM topographic scans of the Thue-Morse nanostructure under different polarization/wavelength excitation. (e)-(f) SNOM images of the Thue-Morse nanostructure under different polarization/wavelength excitation. (g) Enhanced Transmission measurements of the different samples.

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Optimization and Control of the Second-Harmonic Generation in AlGaAs Dielectric Nanoantennas

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Metal-less nanophotonics has been gaining increasing attention in the last decade, due to the favorable optical properties of high-permittivity nanostructures. Dielectric nanoparticles exhibit negligible dissipative losses together with strong multipolar resonances of both electric and magnetic nature [1–3]. This resonant behavior has been proven useful to manipulate the linear and nonlinear optical response of such nanoresonators in the visible and near-IR.

In this framework, we investigated all-dielectric $Al_{0.18}Ga_{0.82}As$-on-AlOx nanodisks for efficient second harmonic generation (SHG) pumped in the telecom range [4]. Our samples were fabricated from a [100] GaAs wafer, with a 400nm layer of $Al_{0.18}Ga_{0.82}As$ on top of an aluminum-rich substrate, resulting in arrays of nanopillars on top of an aluminum-oxide (AlOx) substrate (see figure 1.a). The linear and nonlinear optical response of such nanoantennas was modeled with finite element simulations in COMSOL [4].

We experimentally investigated the nonlinear properties of our sample with an ultrafast Erbium-doped fiber laser centered at 1554 nm (150 fs pulses, 80 MHz repetition rate), in a nonlinear confocal microscopy setup. We measured a conversion efficiency up to 10^{-5} for a 1.6 GW/cm^2 pump and a well-defined polarization dependence on the resonator geometry, in excellent agreement with the theoretical prediction [4,5]. These $Al_{0.18}Ga_{0.82}As$-on-AlOx nanostructures are among the most efficient SHG platforms so far demonstrated, but present an SHG angular distribution that does not couple efficiently to standard collection systems (see first inset in Fig. 1b). Here, we present the experimental validation of two strategies that enable the active reshape and control of the nonlinear emission of the nanopillars. The first is based on asymmetric gratings that reshape the SHG emitted by the pillar. The second is achieved by changing the incident angle of the pump beam with respect to the nanoantenna (see Fig. 1a). Figure 1b shows the collection efficiency as a function of the angle of incidence. More than a factor 10 enhancement is achieved at 45°, which is ascribed to the selection rules imposed by the SHG in the nanopillar [6].

Our results allow gaining further insight in the mechanisms underlying the nonlinear emission in these systems. The high conversion efficiency and radiation control show the potential these platforms in the nonlinear manipulation of light at the nanoscale, for the design of efficient integrated nonlinear nanophotonics active components.

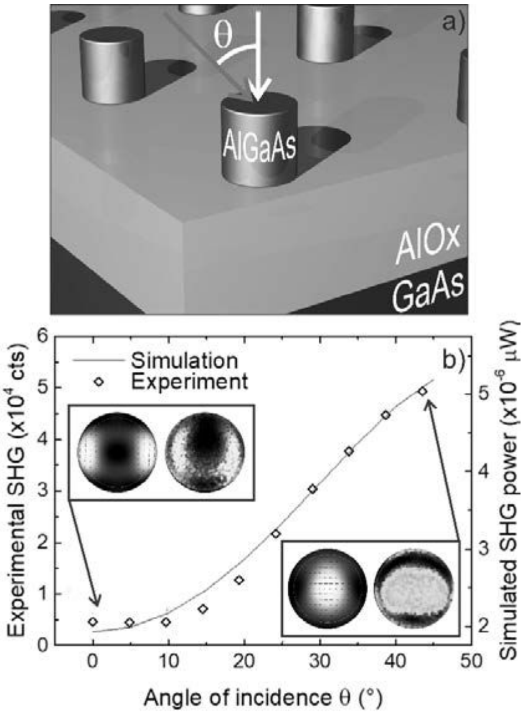

Figure 1: a) Sketch of the fabricated sample of AlGaAs nanodisks on top of a transparent (AlOx) layer. b) Change in the SHG emission with the variation of the incident angle (θ, see panel a) of the pump beam, due to a modification of the emission directionality. Inset: theoretical (left) and experimental (right) maps of the back focal plane.

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Session

Bioplasmonics

Chairwoman

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In-liquid SERS detection of biomolecules and toxins by optical printing of gold nanorods

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Optical forces can be used to aggregate plasmonic nanoparticles and achieve high sensitivity SERS biomolecular detection. Here we tailor this methodology to detect catalase and hemoglobin. We study the SERS signal in Bovine Serum Albumin as a function of the concentration to explore avenues in quantitative detection. We develop a hydrodynamic model of the aggregation process. Finally, we functionalize nanoparticles with specific aptamers for specific SERS detection of Ochratoxin A, a fungal toxin found in food commodities and wine.

Surface enhanced Raman spectroscopy (SERS) has proven to be an extraordinary tool for direct (label-free) detection of biomolecules [1]. We recently applied optically induced aggregation of gold nanorods to the SERS detection of aminoacids and proteins in liquid (LIQUISOR), showing the potential of this technique in the field of biomolecular sensing [2]. An ideal biosensor besides being highly sensitive must also feature high specificity and capability of quantitative determination of the amount of the target molecule in solutions. Here we show first experiments to show quantitative and high specificity detection with LIQUISOR. CTAB-coated gold NRs are added to the solution of biomolecules dissolved in PBS. Molecular interactions yield the formation of biomolecule-NRs complexes (BIO-NRCs) in solution. The optomechanical interaction with the laser beams is dominated by the radiation force (Fig. 1a). Positioning the laser spot close to the bottom of the microcell, the BIO-NRCs intercepted by the laser beam are pushed from the focal point towards the microcell surface where they stick, aggregate and generate a strong SERS emission of the embedded molecules. LIQUISOR has been used to detect Catalase (Cat) and Hemoglobin (Hgb), reaching sensitivities down to 10 nM (Cat) and 1 pM (Hgb). We develop a hydrodynamic model capable to describe optical aggregation of nanorods in liquid. Finally, nanorods functionalized with specific aptamers (DNA) were used to specific capture and SERS detection of Ochratoxin A (Fig. 1b) [3]. Control Experiments with non-functionalized nanorods mixed with OTA yield a signal 50 times smaller (Fig. 1c), proving the key role of aptamers in the capture of OTA.

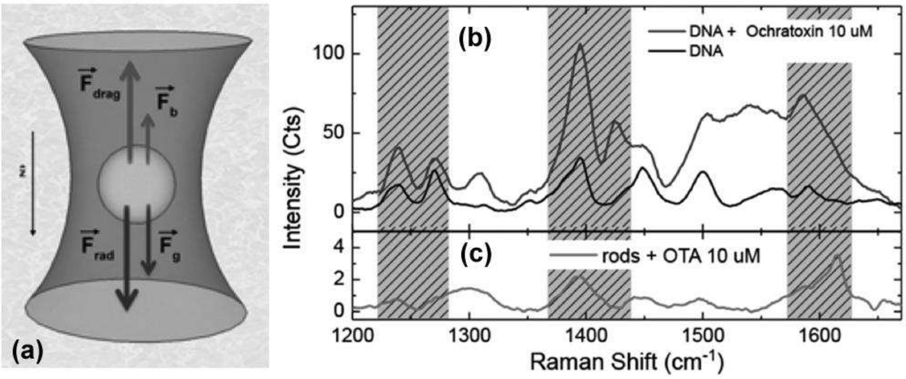

Figure 1: (a) Schematics illustrating all the forces acting on BIO-NRC, approximated here as a sphere. (b) SERS spectra of nanorods functionalized with DNA before (black) and after capture of OTA (gray). (c) Control experiment using non-functionalized rods yield a negligible signal.

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Porous plasmonic nanostructures for Surface Enhanced Raman Scattering: development of biosensing platforms

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The assembly of Surface Enhanced Raman Scattering (SERS) active plasmonic nanostructures in meso/macroporous spongiform matrixes yields functional hybrid nanosystems. Indeed, the combination of metals and dielectrics, the huge surface area and an improved stability of the particles embedded in the porous structure provide benefits in terms of SERS enhancement and bioanalyte pre-concentration or separation [1].

In this work, we present three plasmonic nanostructures that take advantage from peculiar features related to their porosity: mesoporous silicon (pSi) decorated with Ag nanoparticles (NPs), graphene-metal based aerogels and flower-like Ag nanostructures. Densely packed and uniformly distributed silver NPs were synthesized *in situ* from $AgNO_3$ solutions on pSi-PDMS membranes (Fig.1a), either by immersion plating or in a controlled microfluidic environment [2]. Such nanostructures are featured by Localized Surface Plasmon Resonances in the whole Vis-NIR range, thanks to the high refractive index substrate, and present an optimal stability due to the direct growth of the NPs from the silicon pores. Aerogels based on reduced Graphene Oxide (rGO) decorated with Ag NPs (Fig. 1b) were obtained by exploiting a one-pot hydrothermal process followed by a freeze-drying step [3], by starting from an aqueous dispersion of commercial GO single-layer flakes and adding $AgNO_3$ with different reducing agents, such as trisodium citrate [4]. Their SERS application takes advantage from the synergic plasmonic and charge transfer enhancements obtained by coupling Ag NPs to rGO and from the high surface area of the 3D sponge-like nanostructured network, able to concentrate and adsorb biomolecules from highly diluted solutions. Flower-like porous nanostructured Ag NPs forming a nano-net architecture (Fig. 1c) were produced by using L-cysteine as reducing/stabilizing agent under mild condition, by following a modified procedure discussed in the recent literature [5]. These last structures can be easily immobilized on PDMS or on filter paper, and the presence of a multitude of sharp edges forming nanogaps, which act as Raman hot-spots, can be fruitfully exploited for SERS.

After the morphological and compositional characterization of the synthesized NPs, their SERS response was tested by using organic chromophores. A critical comparison concerning the Raman enhancements obtained for the three SERS-active substrates was performed, approaching single molecule detection regime. Finally, different surface grafting strategies for oligo-probes immobilization were developed and compared, exploiting the different surface chemistry of the metal NPs and rGO. The plasmonic nanostructures were then tested for the detection of miRNAs, a class of useful cancer biomarkers, through the application of an innovative two-step hybridization assay [6].

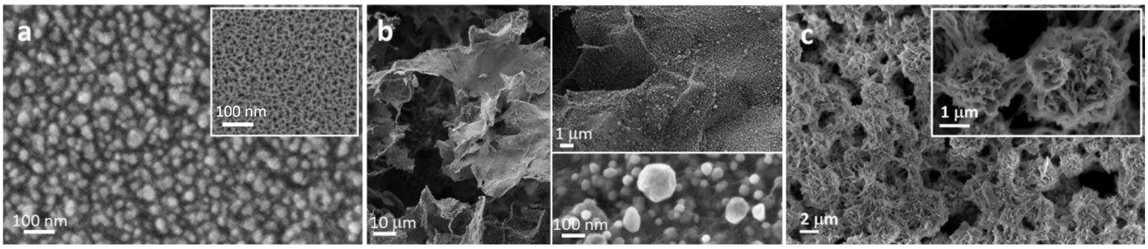

Figure 1: FESEM images of the porous plasmonic nanostructures: a) Ag NPs on pSi. The inset shows the porous matrix under the dense NP coverage; b) Ag NPs coated rGO aerogel at different magnification levels; c) flower-like Ag nanonet. A detail of the porous nanostructures is provided in the inset.

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Graphene Oxide-Functionalized SERS Substrates for a Simple Discrimination between Native and Fibrillar Lysozyme

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A variety of investigation methods have been proposed for the diagnosis of neurodegenerative disorders such as Alzheimer's and Parkinson's diseases even though a reliable procedure for early detection still lacks. In this context we explored the possibility to use a recently proposed sensor substrate [1,2] based on graphene oxide/silver nanocubes (GO/AgNCs) arrays for the identification of native and fibrillar aggregates of a model amyloid-prone protein, i.e. lysozyme.

The hybrid substrate was obtained by Langmuir-Blodgett assembly of a mixture of Ag nanospheres and nanocubes (AgNCNSs) followed by a controlled adsorption of graphene oxide (GO) sheets on the AgNCNSs array. The adsorption of lysozyme in its globular native form as well as fibrillar lysozyme with a high beta-amyloid content on the top of the GO surface was evaluated by means of Quartz Crystal Microbalance (QCM) measurements, which gave information on the kinetics and the mechanism of adsorption.

At the same time SERS experiments were performed on the hybrid GO/AgNCNSs arrays with adsorbed native and fibrillar lysozyme to investigate the protein conformation and aimed at discriminating between the two forms. For this purpose we carried out a Principal Component Analysis (PCA) on the whole set of the collected SERS spectra. The analysis showed a significant data grouping (Fig. 1), which we ascribed to different structures of lysozyme and/or the presence/absence of GO on the surface of the sensor substrate.

Further outcomes were:

- spectral differences ascribable to specific interaction sites of lysozyme with the silver surface;
- an additional signal amplification and improved signal uniformity supplied by the GO coating [3];
- more stable interactions of the fibrillar with respect to the native form of lysozyme;
- variability in the spectral region associated with protein secondary structures, deriving from the presence of β-sheet in the fibrillar form.

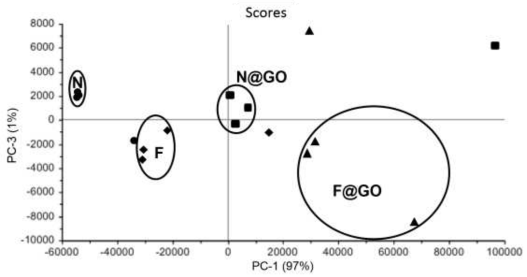

Figure 1: Scores plot of the whole collected SERS spectra (N: native lysozyme, F: fibrillar lysozyme)

Acknowledgements

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Tip-Enhanced Raman Spectroscopy Analysis of Amyloid Oligomers

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In this work we show how to benefit from Tip Enhanced Raman spectroscopy (TERS) as a surface-sensitive tool with spatial resolution on the nanoscale, to inspect the spatial organization and surface character of individual protein oligomers. Aggregation processes of aberrant proteins leading to the formation of amyloid oligomers and fibrils are considered primarily responsible for promoting synaptic failure and neuronal death associated with neurological disorders such as Alzheimer's and Parkinson's diseases [1]. Unravelling the relationship between structure and neurotoxicity of protein oligomers appears pivotal in understanding the causes of the pathological process, as well as in designing novel diagnostic and therapeutic strategies tuned toward the earliest and pre-symptomatic stages of the disease. Our TERS investigation provides compelling evidence of the presence of chemostructural determinants in the case of toxic oligomers, which sheds new light on the mechanism by which they cause cellular impairment. Specifically, we identified specific aminoacid residues that appear exposed on the surface of toxic oligomers while buried in the non-toxic forms, with obvious implications for the elucidation of the structural factors responsible for cell toxicity at the single residue level [2]. These residues, thanks to their outward disposition, might represent structural factors driving the pathogenic behavior exhibited by protein misfolded oligomers, including affecting cell membrane integrity and specific signaling pathways in neurodegenerative conditions.

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Achieving Giant Electric Field Enhancement: Introducing Longitudinal Epsilon-Near Zero and Two-scale Structures for spectroscopy

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Achieving giant field enhancement is crucial for a broad range of applications such as biosensing, surface enhanced Raman spectroscopy (SERS) and nonlinear optics [1,2]. To that end, various structures such as epsilon-near zero (ENZ) materials and plasmonic oligomers formed by chemical assembly [3,4] have been proposed. However, the ability of these structures in enhancing the local field is limited by their inherent loss. Here, we present two distinct structures for achieving giant field enhancement. The first structure is longitudinal ENZ (LENZ) structure which mitigates the loss compared to an analogous ENZ configuration. The second structure, called two- scale method, employs two complementary fabrication methods based on the Rayleigh anomaly using a periodic set of nanorods along with metallic oligomers to overcome the limited field enhancement obtainable with oligomers alone.

First, we establish that under TM wave incidence a uniaxially anisotropic ENZ film, with near zero *zz* entry of the permittivity tensor exhibits much stronger field intensity enhancement (*FIE*) than isotropic ENZ [5]. We consider a LENZ film with thickness $d = \lambda / 3$. In Fig. 1(a) we assume that the film has longitudinal permittivity of $\varepsilon_z = 0.001 + i0.1$ and transverse permittivity of $\varepsilon_t = \varepsilon_t' + i0.1$ at wavelength λ. In Fig. 1(b) we report the *FIE* just below the top surface of the film versus incidence angle and ε_t'. Notably, we observe that *FIE* is the lowest for the IENZ case (i.e., when $\varepsilon_t' \approx 0$) compared to LENZ cases with larger ε_t'.

Next, we report the field enhancement of a "two-scale structure" which consists of chemically assembled oligomers of gold nanospheres with a 1-2 nm sized gap between a periodic set of gold nanorods on a glass substrate, where the period of the structure is similar to that of the local surface plasmon resonance wavelength of the majority of oligomers [6]. We assume the structure shown in Fig. 1(c) is illuminated by a plane wave polarized along the nanorods. Fig. 1(d), shows the full-wave simulation results of the field enhancement defined as $FE = \left|\mathbf{E}^{\mathrm{tot}}(\mathbf{r})\right| / \left|\mathbf{E}^{\mathrm{inc}}(\mathbf{r})\right|$ for both the whole two-scale structure (FE_t) and for the linear trimer only (FE_o), versus wavelength. As observed, we get almost 2-fold stronger field enhancement from this structure compared to trimer alone. In our Raman spectroscopy experiments the maximum SERS enhancement (of the structure with the array of rods versus the one without rods) is 16, reaching total SERS values higher than 10^9.

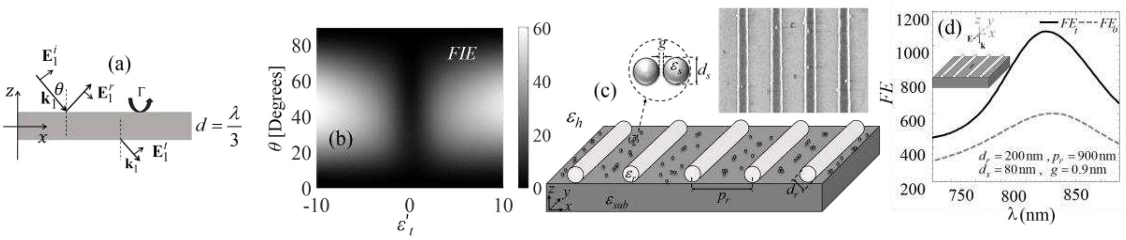

Figure 1: (a) Schematic of longitudinal epsilon near zero film. (b) *FIE* at $z = (d/2)^{-}$ as a function of ε_t' and incident angle θ. (c) The schematic of the proposed "two-scale structure" with rods and plasmonic oligomers. (d) Electric field enhancement for the two-scale structure and linear trimer versus wavelength

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Session

Quantum Nanophotonics and Metamaterials

Chairman

Francesco Biccari, University of Florence, Italy

Photostable Molecules on Chip: Integrated Single Photon Sources for Quantum Technologies

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Efficient quantum light sources and non-linear optical elements at the few photon level are the basic ingredients for most applications in nano and quantum technologies. On the other hand, on-chip integration is necessary to envision a scalable platform for quantum information and communication.

In this work we demonstrate the potential of a novel hybrid technology which combines single organic molecules as quantum emitters and dielectric chips, consisting of ridge waveguides and grating far-field couplers [1]. Dibenzoterrylene molecules in anthracene crystals are particularly suitable quantum systems for this task, due to outstanding photophysical properties [2,3] in samples as thin as few tens of nanometers. Here the emitters are integrated by spin-coating onto the photonic chip. We demonstrate at room temperature the emission of single photons from DBT molecules into ridge waveguides with a branching ratio up to 40%, corresponding to an estimated in-guide brightness around $50MHz$ for cw pumping at saturation intensity. These results are competitive with state-of-the-art single photon emission into propagating guided modes from solid state systems [4,5], while offering a novel platform with unprecedented versatility. Single waveguided photons can be readily processed on-chip or extracted into a quasi-gaussian mode in free space with overall efficiency around 16%. We also discuss options to further improve the collection efficiency and applications to quantum optics [6] and to study manybody-induced quantum correlation effects [7].

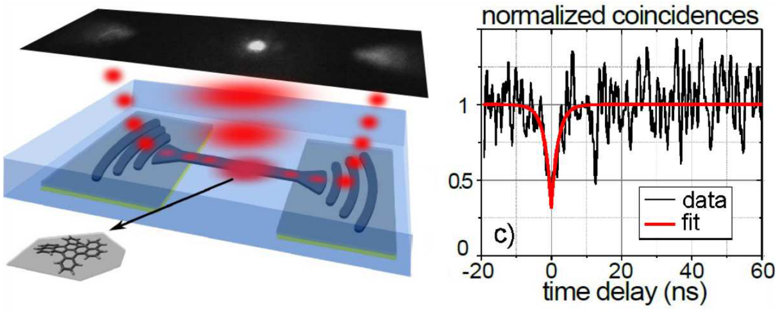

Figure 1: Cartoon and fluorescence image collected with an EMCCD camera showing signal from both the confocal excitation spot and the outcouplers; antibunching dip measured in correspondence of all output ports revels single-photon nature of the signal.

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Shortening of Eu^{3+} Radiative Lifetime by near-field coupling with Hyperbolic Metamaterials

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The emerging field of metamaterials proposes a new paradigm to engineer the optical response of a system and obtain properties which are not found in conventional materials [1]. A metamaterial consists typically in a unit block repeated periodically through space, deriving its properties not only from its constituent materials, but also from their geometry. Among different types of metamaterials, the class of hyperbolic metamaterials (HMMs) has gained interest in recent years for its peculiar properties which can be obtained even at optical frequencies [2]. HMMs are non-magnetic media characterized by a tensorial permittivity with principal components of different signs. This feature causes the isofrequency curve of a HMM to be hyperbolic instead of elliptical as in common materials. This means in turn that a HMM can sustain light modes with arbitrarily high wavevector, causing the photonic density of states in the medium to diverge. One of the simplest example of metamaterials with an engineered anisotropic optical dielectric permittivity is represented by a multi-layered system with alternating metal and dielectric thin films with subwavelength thicknesses. In the present work, we have fabricated and characterized two different types of multi-layered metamaterials, both with the same constituent materials (i.e. gold and alumina thin films) but with different metal filling fractions (f.f.=33% and f.f.=16%) in order to properly tune the epsilon-near-zero wavelength (λ_{ENZ}) in the visible region of electromagnetic spectrum. Finite element method simulation together with ellipsometric measurements have been used to characterize the peculiar optical properties of the two synthetized multilayers (see Fig. 1 A), pointing out that the ENZ wavelength is λ_{ENZ}=546 nm for the sample with 33% metal filling fraction and λ_{ENZ}=670 nm for the sample with f.f.=16%. A thin PMMA film (t~30 nm) doped with europium(III) thenoyltrifluoroacetonate complex (Eu-TTA) has been deposited by means of spin-coating technique on top of each sample. Therefore with respect to the Eu-TTA emission wavelength (λ_{em}=615 nm), the multilayer with f.f.=33% is in the hyperbolic regime, while the f.f.=16% is in the elliptic regime. Photoluminescence (PL) measurement have been performed to probe the photonic density of states in a multilayer, which can strongly influence the decay lifetime of fluorescent emitter placed nearby [3]. Preliminary results have shown that when the emitter is coupled with a metamaterial designed to be in the hyperbolic regime with respect of the emission wavelength, strong decrease of measured lifetime (up to a factor 3 – Fig. 1B) with a concomitant high increase of the PL intensity was observed suggesting that an efficient coupling between the HMM and the Eu^{3+} has been obtained.

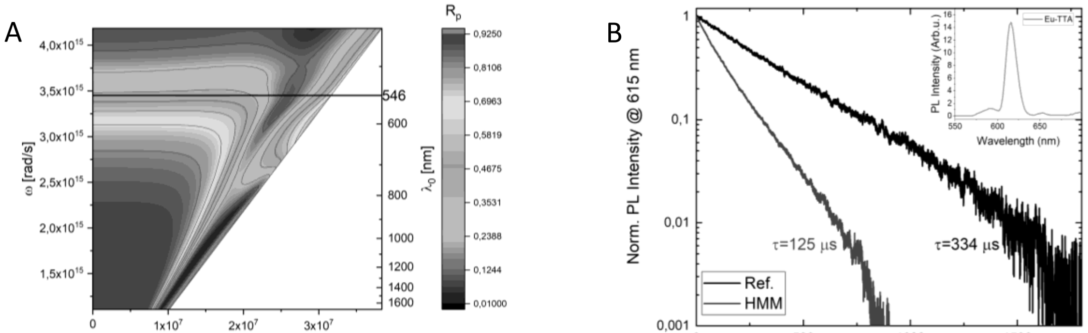

Figure 1: (A) Reflectance simulated spectrum for p-polarized light impinging on a 180 nm thick multilayer composed of four alternating alumina (t=30 nm) and gold (t=15 nm) layers. (B) PL decay curve of EuTTA doped PMMA layer deposited on SiO_2 substrate (Ref.) and on the HMM multilayer.

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Hyperbolic Control of the Free-Electron Plasmons Energy Landscape

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Besides its fundamental importance, manipulation of light at the nanoscale is of great interest for the prospect of real-life applications, such as energy harvesting and photovoltaics, wave-guiding and lasing, optoelectronics, biochemistry and medicine. Novel optical designs and architectures that modify the optical power flow through plasmonic nanostructures represent another crucial step towards a nanoscale manipulation of light-matter interactions. In this framework hyperbolic metamaterials (HMMs) have received great attention due to their unusual properties at optical frequencies that are rarely or never observed in nature[1-2], and their important applications such as negative refraction, resonant gain singularities, optical cloaking, super resolution imaging etc. Here we report on nanostructured plasmonic nanostructures made of a type II (metallic in-plane, dielectric out-of-plane) artificial hyperbolic metamaterial composed by a periodic stack of metallic and dielectric layers [3]. More in detail, we introduce a nanoantenna-based hyperbolic architecture for the manipulation of the optical power-flow, enabling the creation of well separated bands of either pure absorption or scattering (see Figure 1). The nanoantennas are directional, can be tuned to either absorb or scatter in different spectral ranges, and possess both an angular and a polarization-independent structural integrity, thus opening up new perspectives for application on a broad range of surfaces. Our findings open the pathway towards novel routes to exploit the light to energy conversion channels beyond what is offered by current plasmon-based architectures, possibly enabling applications spanning from thermal emission manipulation, theragnostic nano-devices, nano-fabrication and nano-manipulation, novel nano-antenna designs, plasmon-enabled molecular spectroscopy, photovoltaics and solar-water treatments, as well as heat-assisted ultra-dense and ultra-fast magnetic recording.

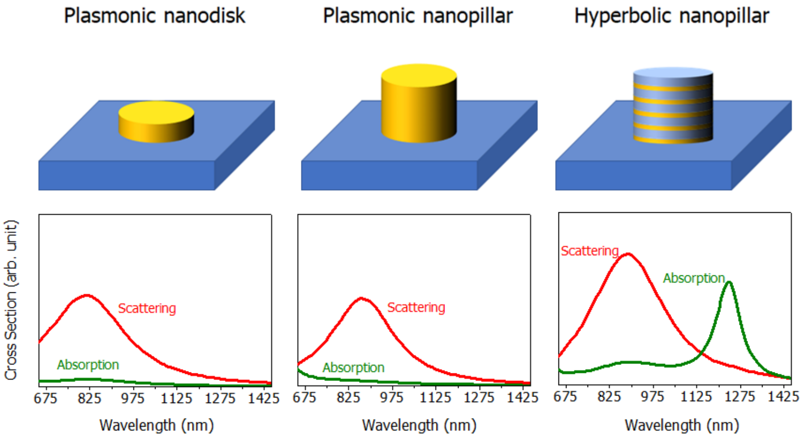

Figure 1: Scattering and absorption cross section of (i) a HMM nanopillar made of 5 bilayers of metal and dielectric on a glass substrate (left-panel), (ii) a classical plasmonic antenna on a glass substrate with the same shape and amount of gold (central-panel) and (iii) the same shape and size (right-panel).

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A SiGe-based metasurface for high-efficiency near-infrared anti-reflection coatings

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Abstract: Dielectric Mie resonators are gaining ground for light management at the nanoscale. However, fabrication remains costly and cumbersome. We demonstrate a simple self-assembly method based on solid-state dewetting for the fabrication of efficient anti-reflection coatings.

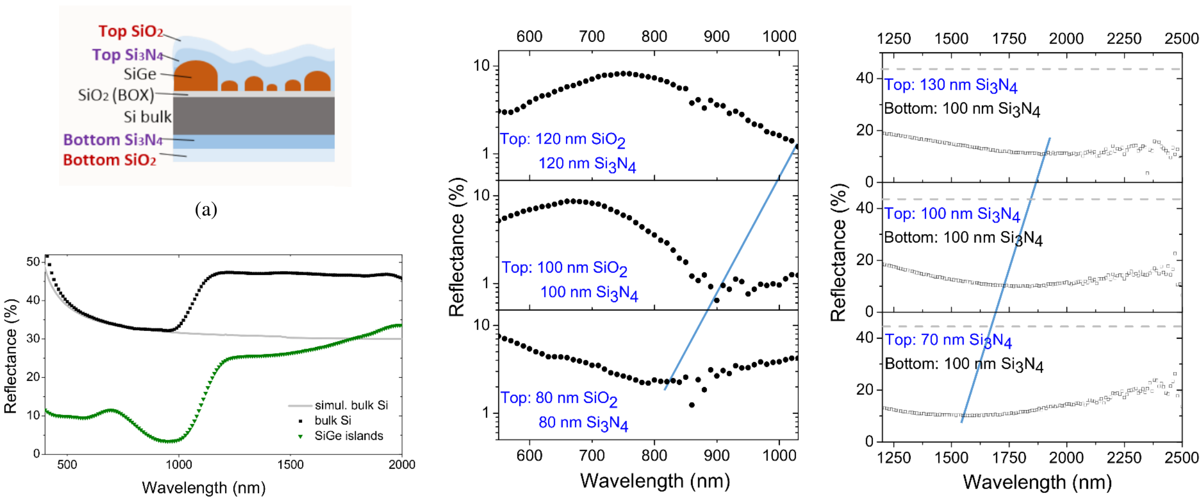
OCIS codes: 160.4760 Optical properties, 160.6000 Semiconductor materials, 220.4241 Nanostructure fabrication, 230.5750 Resonators, 240.6648 Surface dynamics, 290.1483 BSDF, BRDF, and BTDF, 290.1990 Diffusion, 290.4020 Mie theory, 310.1210 Antireflection coatings, 310.1860 Deposition and fabrication.

Dielectric particles exhibiting resonant Mie scattering have been under investigation in the last few years owing to their remarkable optical properties at visible and near-infrared frequencies [1]. Mirrors [2], lenses [3], polarizers and anti-reflection (AR) coatings [4] are few applicative examples.

State-of-the-art Mie resonators have been usually fabricated by top-down approaches (such as electron-beam lithography and reactive ion etching) however, for large scale applications, bottom-up methods are preferable for their easier scalability. To this end, solid-state dewetting of ultra-thin silicon films on insulator has been demonstrated as a viable alternative to top-down method [5]. The morphological instability giving rise to the dewetting phenomenon in thin films is mediated by the surface diffusion of atoms and occurs upon annealing at high temperature (even well below the melting point of the material) [6]. The final results are arrays of well separated islands, featuring a random spatial organization and a relatively large spread of sizes and shapes. The potential of this method in semiconductors has not been completely exploited and, for example, AR coatings formed by self-assembly have not yet been reported.

Here we demonstrate the potential of solid state dewetting of ultra-thin silicon on insulator (UT-SOI) structures coupled with germanium deposition, for the self-assembly of high-density, randomly organized, SiGe-based Mie resonators (Fig. 1a) as efficient AR coatings at near-infrared frequencies [7]. Angle-resolved measurements confirm that these excellent properties occur within an acceptance angle of about ±55 degrees (not shown). We would like to stress that this configuration, based on random distributed SiGe islands covered by thin layer AR coatings, allows several optical advantages with respect to conventional thin-films AR coatings. Very flat optical rensponse for all the working range, broad angle functionality, joined to a slight tuning of the minimum value of R, are the strengths of our devices.

The work is completed with a study of the spectral features of our AR coatings providing a precise discrimination between the main photometric parameters (total reflectance, specular reflectance, total transmittance and reflected scattering). We show that the dominant contribution to R comes from nearly-isotropic, back-scattering while that of specular reflectance is only a few per cent of it and we highlight a marked strong light trapping mediated by the SiGe islands within the Si substrate. In principle, this fabrication method can be performed at relatively low temperature [8] and it can be used on custom-made arbitrary SiO_2 layers [9] relaxing the need of a commercial UT-SOI. The enhanced coupling of the impinging light inside the resonators leads to AR coating on top of bulk silicon (Fig. 1b). Note that below the absorption edge of silicon the reflectivity presents a jump mostly due to the reflection of the back face of



(a)

(b)

(c)

(d)

Fig. 1: 1a) Sketch of the sample where random-distributed islands and thin coating layers are highlighted (sample optimized for AR above 1 μm). 1b) Reflectance at normal incidence for a wafer of silicon (black line, experimental) and for dewetted sample presenting random distribution of SiGe islands (green line, experimental). In both cases the sharp increase in reflectance is mostly due to the reflection from back face, as explained with the gray line where an infinite silicon bulk is considered (simulation). 1d) Reflectance (normal incidence) optimized for wavelengths below the silicon band gap. 1c) Reflectance (normal incidence) optimized for wavelengths above the silicon band gap. By engineering the thin capping layer a tuning of the minimum is possible (light blue line).

the sample, which is not AR coated (Fig. 1b, green line). Moreover, by adding ad hoc Si_3N_4 and SiO_2 layers, we target specific wavelength ranges optimizing the AR coatings for above band-gap wavelengths (1000-2500 nm) where R reaches 7-20%) and for below band-gap wavelengths (550-1000 nm) where R is reduced to few % (Fig. 1d and 1c respectively). Importantly the duration of the dewetting process does not depend on the sample size but only on the thickness of the thin Si(Ge) layer. Thus our C-MOS compatible [10] fabrication process opens the new possibility to implement efficient AR coatings on existing devices (e.g. photovoltaic cells, C-MOS and CCD cameras, Si- and Ge-based photo detectors, etc.).

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Spatially Selective Hydrogen Irradiation of Dilute Nitrides: A Versatile Nanofabrication Tool for Photonic Applications

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In the last few years, significant efforts have been aimed at the development of fully integrated nanophotonic devices, embedding all the elements required for the on-chip generation, manipulation, and detection of non-classical light states. A very promising route towards the achievement of this goal is provided by spatially selective hydrogen irradiation of dilute-nitride semiconductors (*e.g.*, GaAsN) [1]. Following H implantation, indeed, the formation of stable N-H complexes fully neutralizes the effects of N on the structural and electronic properties of these materials, resulting for example in a large, fully tunable redshift of their energy gap. This provides a simple route to the on-chip generation of single photons, via the fabrication of site-controlled GaAsN/GaAsN:H quantum dots (QDs) by H irradiation of lithographically pre-patterned samples [2]. These QDs emit single photons and can be easily integrated with nanophotonic devices, *e.g.*, PhC cavities, resulting in clear cavity-QED effects. Strikingly, spatially selective hydrogenation also provides a powerful tool for the realization of integrated optical elements for the routing and manipulation of single photons. Indeed, H irradiation has been shown to result in large variations of the refractive index of the material, *n* [1]. Over a broad wavelength range, comprising both the 1.3 μm and the 1.55 μm telecommunications windows, hydrogenated GaAsN is characterized by a systematic reduction of *n*, (>2% difference for a sample with a N concentration of ~2%). Such mismatch is sufficient to tightly confine NIR light within a sub μm-sized region, thus allowing for the realization of narrow GaAsN/GaAsN:H waveguides by spatially selective hydrogenation. Perhaps more interestingly, the ability to locally change *n* with sub-wavelength precision provides us with a unique tool for the optimization/modification/correction of the properties of pre-existing PhC structures. By defining a low-index, GaAsN region embedded within a PhC waveguide fabricated in hydrogenated GaAsN, we can for example define a novel type of PhC cavity (see Fig. 1), characterized by confined modes with Gaussian envelope functions and high ($>10^6$) computed *Q*-factors. These cavities, based on the well-established tenet that light must be "confined gently in order to be confined strongly" [3], are also inherently suited for the application of automated optimization algorithms [4].

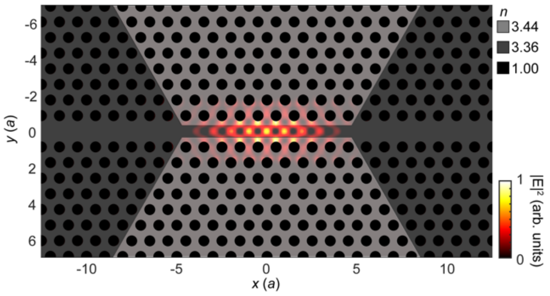

Figure 1: PhC cavity ($r/a = 0.29$) attainable by refractive-index engineering of a GaAsN epilayer (N concentration = 2.2%). The refractive index *n* of the untreated (light grey) and hydrogenated (dark grey) material are taken at 1.31 μm. The computed (by FEM calculations) intensity of the electromagnetic field associated with the fundamental cavity mode is superimposed to the structure.

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Session

Thermoplasmonics and Photoacoustic Spectroscopy

Chairwoman

Cristiana Lofrumento, University of Florence, Italy

Design of an all-optical photoacoustic platform for the inspection of plasmonic particles

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Over recent years, photoacoustic concepts have drawn much attention for new applications and innovative solutions in biomedical optics. In particular, photoacoustic imaging is penetrating the clinical arena as a non-invasive and versatile solution to combine optical contrast and ultrasonic depth of penetration and scalability of resolution. [1,2] The peculiar features of photoacoustic imaging have been demonstrated in a notable variety of setups, ranging from microscopy to tomography, that are already mature and competitive for translational developments. Most photoacoustic platforms rely on piezoelectric transducers that were developed within the venerable context of ultrasonography. However, the generation and propagation of acoustic signals in photoacoustics and ultrasonics differ in fundamental aspects that deserve innovative solutions and yield new opportunities. Here, we disclose our design and preliminary results for an all-optical photoacoustic flow spectro-cytometer that may be exploited in a broad variety of applicative domains, such as the detection of individual circulating cells in bio fluids as well as the inspection of colloidal suspensions of artificial particles in sols or aerosols. This setup rests on the implementation of an optical microcavity resonator [3] that may be coupled to a microfluidic interface and filled with any sample of interest. Then, its excitation with short optical pulses triggers a photoacoustic conversion within the cavity, which imparts a transient deformation of the glass resonator and its dielectric landscape, thus shifting its optical resonances. The advantages of this setup include its inherent feasibility for miniaturization and workability in air rather than water, as occurs with piezoelectric transducers for ultrasonography. We illustrate these features in the analysis of the spectral fingerprints of colloidal suspensions of plasmonic particles with volumes in the nL range and repetition rates in the kHz domain.

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Flexible Thermo-plasmonics: mechanically actuated control of the photo-induced heat generation

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The physical control of the photo-induced heat generated by an amorphous arrangement of homogenously distributed gold nanoparticles (AuNPs), immobilized on a biocompatible flexible elastomer, is presented. The macroscopic application of a mechanical strain to the polydimethylsiloxane (PDMS) tape, supporting the particles, leads to a nanoscale modification of their mutual inter-distance. As a result, the strong variation of the particles near-field coupling gives rise to a macroscopic change of the photo-generated heat. A fine control of the amount of generated heat is thus possible by stretching the initially isotropic sample of only a few-percent. Due to the anisotropy of the stretching procedure, the plasmon band shift, and thus the heat generation, results to be strongly polarization-dependent. This system, exploiting for the first time the possibility to mechanically act on the photo-generation of heat, holds promises for the development of optically-active thermal patches, usable for biomedical applications, and flexible platforms for microfluidics and lab-on-a-chip devices.

Cellular vehicles for delivery of gold nanorods to tumors

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Over recent years, gold nanorods (GNRs) have emerged as a promising material in biomedical optics and have been proposed as contrast agents for the photothermal therapy and the photoacoustic imaging of tumors [1,2]. A pioneering approach to target tumors is the use of cellular vehicles, i.e. cells of the immune system that exhibit an innate tropism to tumors and that can be serve as Trojan horses [3,4]. This strategy relies on cell types, such as tumor-associated macrophages, mesenchymal stem cells or T cells, that are recruited by or naturally traffic to the microenvironment of tumors and that can be isolated from a patient and loaded with plasmonic particles in vitro. In this work, GNRs were synthesized and designed to combine high optical and photo-stability and the ability to accumulate into cells of the immuno system. Particles were PEGylated and conjugated with cationic moieties. Different cationic compounds were tested and the cell viability, uptake and exocytosis of the particles were studied on different cell types. The cytotoxicity test was based on a colorimetric WST-8 assay while the intra- and extra-cellular amount of gold and the optical absorbance of the cells were quantified by spectrophotometry. Moreover, we investigated the effect of GNRs on the cell migration and the production of cytokines in the presence of pro-inflammatory stimuli, which provide a functional overview on the feasibility of this approach to target tumors.

A tridimensional model was also developed to observe the recruitment of bone marrow-derived mesenchymal stem cells, pre-loaded with GNRs, towards tumor spheroids by confocal microscopy.

These experiments allowed us to establish the best conditions to prepare multifunctional cellular vehicles displaying plasmonic features for photothermal and photoacoustic applications.

Acknowledgments

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Photoacoustic spectroscopy of plasmonic nanoparticles

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Optical properties of plasmonic nanoparticles should be determined in the widest possible wavelength range if a complete picture of their response to light has to be drawn. The experimental techniques that can be employed to this aim are manifold. In particular:

- σ_E (λ), the extinction cross section, can be determined by ordinary spectrophotometry with some accuracy - provided the nanoparticle number is known;
- σ_A (λ), the absorption cross section, must be measured by photothermal methods, like photoacoustic spectroscopy, as these are selectively sensitive to light absorption;
- σ_S (λ), the scattering cross section, can be obtained by very accurate light scattering measurements. Alternatively, it can be obtained by the difference between the former cross sections, through the relationship $\sigma_E(\lambda) = \sigma_A(\lambda) + \sigma_S(\lambda)$. [1]

We will show that laser-induced photoacoustic spectroscopy has the capability to yield $\sigma_A(\lambda)$, when the photoacoustic signals are properly calibrated by the use of calorimetric references. Benchmark measurements on gold nanospheres of various size (10, 61 and 93 nm diameter) will be first discussed. An example of this measurement, which we refer to as a photoacoustic excitation profile, is shown in Figure 1. The experimental results are in agreement with Mie theory simulations. [2]

Then, the application of the method to gold nanoshells, with silica core and different core and shell dimensions, will be presented. We observe a decrease of the σ_A / σ_E ratio as the overall diameter increases, and different spectral distributions for σ_A and σ_S, the latter being red-shifted.

Recently we have investigated materials with localized surface plasmon resonances in the near-infrared range. Results will be shown for non metallic plasmonic nanoparticles, namely, copper sulfide nanoflakes, and for silver nanowires with micrometric length. [3] Remarkably, the extinction at 1064 nm of the latter systems results to originate completely from scattering, as predicted by finite elements method simulations. Implications for surface-enhanced Raman spectroscopy will also be discussed.

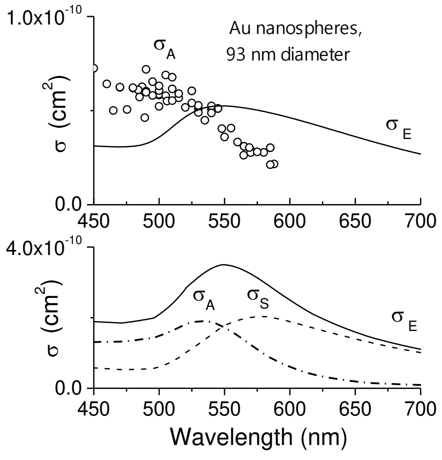

Figure 1: (*upper panel*) Photoacoustic excitation profile of 93 nm diameter gold nanospheres in aqueous dispersion. (*lower panel*) Simulated absorption, scattering and extinction cross sections.

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Photoacoustic absorption reveals extrinsic chirality in self-organised polystyrene spheres partially covered by metal

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Self-assembled approach allows realizing plasmonic metasurfaces with a low cost reliable procedure. In order to measure the absorption properties of these structures usually extinction measurements were performed by looking at transmitted signal and eventually at reflected signal. In these kind of structure realized by a bottom-up approach a certain amount of disorder is inherently present, although well controlled and limited, that gives rise to scattering losses that can disturb the extinction measurements. Direct measurements of absorption by induced thermal heating can overcome this problem.

Here we use the photoacoustic absorption (PA) technique [1-2] in order to direct measure the absorption in self-assembled metasurface composed by polystyrene spheres partially covered by few nanometers of metal (Cr, Ag, Au).

The spheres (starting diameter of 530 nm), deposited on a glass substrate are self-organized in a hexagonal lattice. The diameter of the spheres are then reduced by selective etching up to 450nm and partially coated by 50 nm metal evaporated by an glancing angle of 45°. The 2-D periodical arrangement of the spheres can be seen in the fig.1.

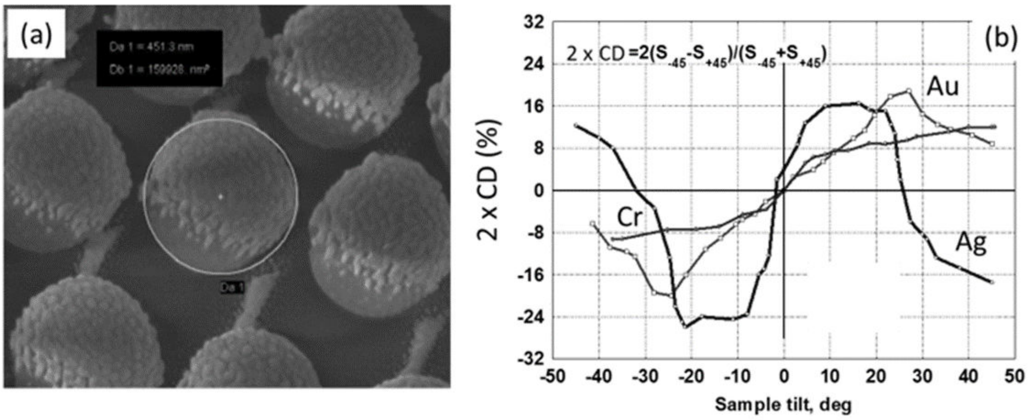

Figure 1: (a) SEM image of the realized metasurface. (b) circular dichroism as a function of incidence angle for different metals (Cr, Ag, Au).

In our PA measurements [1] the laser pump beam is circularly polarized so that the PA signal reveals a strong circular dichroism strongly dependent on incidence angle and on plasmonic resonances due to matching of proper material and pumping wavelength.

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Session

Polaritons and Terahertz

Chairman

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Extreme strong field plasmonics: MeV electron and XUV harmonic pulses from grating targets

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How strong a surface plasmon (SP) may be? Although no clear theoretical answer is available [1], we found experimental evidence of propagating SPs generated by ultra-high contrast femtosecond laser pulses coupling with grating targets at intensities $> 10^{19}$ W cm^{-2}, high enough for the electron dynamics to be strongly relativistic. SP excitation was first inferred by enhanced emission of MeV protons [2] and later by the "surfing" acceleration of multi-MeV, high charge electron bunches by trapping in the SP field [3].

Recently we demonstrated enhancement of electron emission by choice of the grating profile [4] (obtaining up to 650 pC bunch charge for femtosecond duration at the source) and strong emission of high harmonics (HH) in the XUV range (up to the 40th order of 0.8μm laser driver) collinear to the multi-MeV electron bunch [5, 6]. Dynamical enhancement of the XUV signal by tailoring the target density profile on a nanometric scale using a femtosecond prepulse was also shown. Experimental results are reproduced accurately by simulations which evidence the enhancement of HH attosecond pulses by nano-bunching of electrons in the SP field (similarly to Free Electron Laser operation). Prospects to decrease the duration of the SP-enhanced emissions in the sub-optical cycle range have been also proposed [7] and are under current experimental investigation. These findings may enable the development of intense, synchronized, (sub-)femtosecond sources of electrons and XUV photons for applications in ultrafast radiography, and stimulate the extension of plasmonics to the relativistic, extremely high field regime.

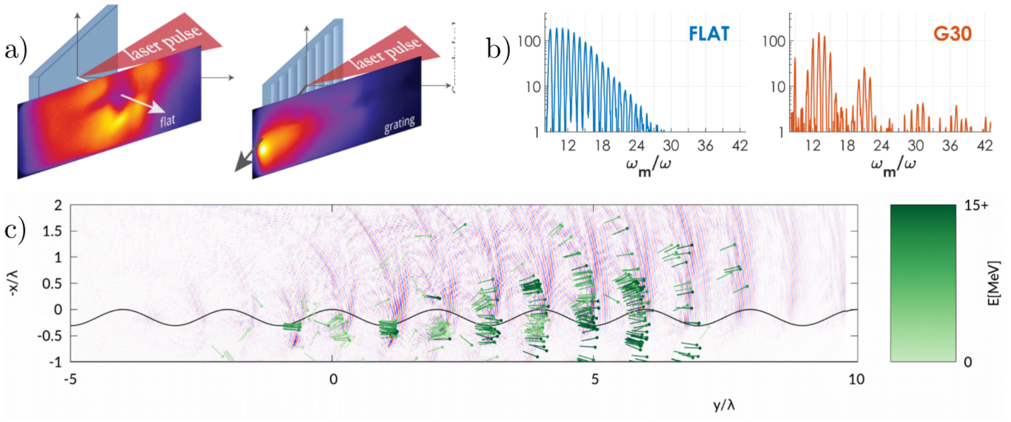

Figure 1: a): experimental angular distributions of electrons from a flat target and a grating target (G30) irradiated at the resonant angle (30°) for surface plasmon (SP) excitation, showing a transition from diffuse emission to a collimated near-tangent jet. b): experimental high harmonic (HH) spectrum in specular direction from a flat target and near tangent for G30, showing diffraction and enhancement of HHs. c): simulation showing the bunching of SP-accelerated electrons (green arrows) and attosecond EM pulses (field frequencies below 8th HH order are filtered out).

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Mid Infrared Nonlinear Plasmonics Using Germanium Nanoantennas

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Recent advances in semiconductor film deposition allow for the growth of heavily-doped Ge with effective plasma frequencies above 60 THz, corresponding to wavelengths below 5 µm. This paves the way for mid-infrared nanoplasmonics with applications in integrated telecommunication systems and enhanced molecular sensing in the so-called vibrational fingerprint spectral region [1]. In this work, we demonstrate that Ge antenna structures are also suitable for nonlinear optical processes such as third-harmonic generation (THG) in the mid infrared [2], owing to the strong resonant enhancement. Sub-wavelength-confined light emitters are of high interest for experiments targeting single molecules or other isolated quantum systems.

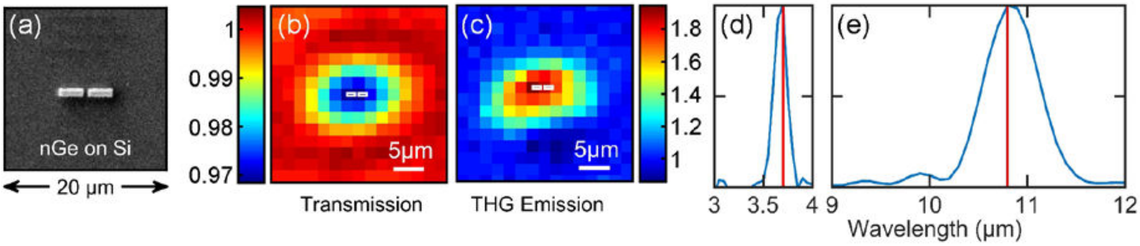

Figure 1: (a) SEM image of a Ge nanoantenna; (b) linear transmission map of a resonant gap antenna illuminated with a central wavelength of 10.8 µm; (c) THG map normalized to the Si substrate background emission; (d) and (e) normalized THG and excitation intensity spectra, respectively.

Doped single-crystalline Ge films are grown via low-energy plasma-enhanced chemical vapor deposition (LEPECVD) on intrinsic Si substrates [3] and are used to fabricate resonant gap antenna structures via electron beam lithography as demonstrated in Fig. 1(a). The optical system is driven by a Yb:KGW femtosecond laser equipped with optical parametric amplifiers. Intense few-cycle pulses tunable in the mid-infrared spectral range are obtained via difference frequency generation in GaSe. Excitation fields of up to 20 MV/cm are reached in the focus of a Cassegrain-Schwarzschild reflecting objective. A second objective images the antenna in transmission geometry. A liquid nitrogen cooled mercury cadmium telluride detector collects the emission while the sample is confocally scanned. This allows addressing single antennas and mapping their linear and nonlinear response. Fig. 1(b) demonstrates the transmission image at the fundamental excitation wavelength (10.8 µm, see Fig.1(e)), with marked extinction due to the resonant scattering, while Fig. 1(c) plots the corresponding THG emission at 3.6 µm wavelength (Fig. 1(d)). By varying the antenna length, we confirm the role of the localized plasmon resonances in achieving a strong THG, which represents the first demonstration of third-harmonic conversion from single sub-wavelength plasmonic structures resonant in the mid-infrared [4].

This research has received funding from the European Union’s Seventh Framework Programme (g.a. n° 613055) and from the Deutsche Forschungsgemeinschaft (Emmy Noether Program BR 5030/1-1).

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Observation of Phonon-Polaritons in thin flakes of hBN on ultraflat gold substrates

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Hexagonal boron nitride (hBN) is a layered polar van der Waals crystal very attractive for nanoscale optical devices at infrared frequencies as it can sustain phonon-polariton (PhPs) within its mid-infrared (mid-IR) reststrahlen bands [1]. PhPs are collective modes originating from the coupling between light and optical phonons and, due to their capability of providing strong field confinement, can be exploited for a variety of applications in the mid-IR. Scattering-type near-field optical microscopy based on an atomic force microscope (AFM) has allowed to determine the dispersion relations in hBN [2], using the AFM metallic tip to provide the momentum required for launching polaritonic waves. Edges in patterned flakes, defects and metallic nanostructure can also be used to overcome the momentum mismatch between free-space propagating radiation and PhPs. Recently, it has been shown that PhPs can be detected also with a near-field AFM-based technique that exploits a mechanical detection scheme (AFM-IR) [3,4].

By means of the AFM-IR technique we study a sample consisting in few layers of hBN deposited on ultraflat gold substrate. With respect to previous work, where the hBN flakes are deposited on dielectric materials and/or adjacent to graphene layers, we aim here at studying the effect of a metallic layer adjacent to the hBN. We exploit the resonantly enhanced infrared nanospectroscopy scheme, based on a quantum cascade laser coupled to the AFM, to detect the amplitude profile of polariton standing waves with a lateral resolution of 30 nm. Thanks to the strong field confinement between the gold-coated AFM tip and the gold substrate, we were able to measure the excitation spectra of several samples with thickness ranging from 4 nm up to 80 nm, showing a circular shape. The same PhP excitation pattern of different circular symmetry appears at different frequencies within the upper reststrahlen band of hBN (1370-1610 cm^{-1}), according to thickness and radius of the flakes. We interpret these patterns as PhP standing waves and therefore we compare the line profile obtained from the AFM-IR maps (fig. 1 (b-e)) with the prediction of intensity profiles of standing waves in a circular membrane based on the elastic response theory. The diametrical amplitude profiles for standing waves of this kind are given by the squared $J_0(r\,\alpha_{0j}/a)$ and $J_1(r\,\alpha_{1j}/a)$ Bessel function of the first kind, where r is the radial coordinate, a is the radius and α_{ij} is the j-th root of the equation J_i=0. The symmetry of polariton standing waves is found to be extremely robust against geometrical imperfections.

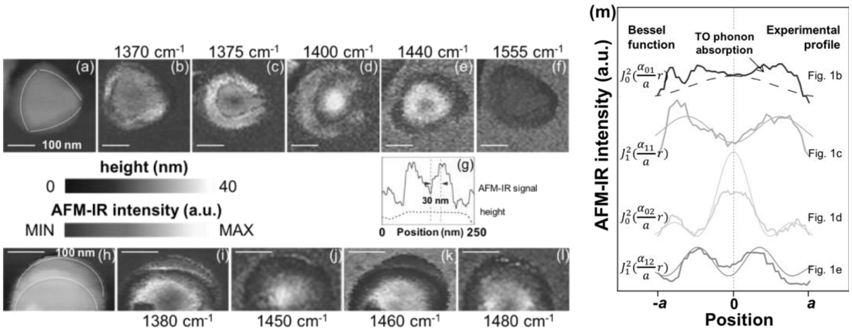

Figure 1: Topography (a and h) and polaritonic standing waves (b-f and i-l) of two samples of hBN with thickness 19 nm and 26 nm, respectively. (g) Amplitude profile of the polariton standing wave of panel (e) showing a lateral resolution of 30 nm. (m) Line profiles of the AFM-IR maps of panels (b-f) and the square of the Bessel functions.

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Manipulating azobenzene photoisomerization through strong light-molecule coupling

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Recent achievements of strong light-matter couplings [1][2] had unprecedented impact in its applications, ranging from enhanced optical response to quantum information, sensing and polaritonic chemistry [3]. The latter aims to study how the electronic states of molecules are modified by the coherent coupling of molecules with an electric field. The modulation of Polaritonic Potential Energy Surfaces through light-matter coupling brings the possibility to control the quantum yields of photochemical reactions, recently shown on model molecules [4]. Our goal is the theoretical investigation of polaritonic-induced effects on quantum yields of photochemistry: non-adiabatic dynamics methods have been developed to simulate photochemical reactions extensively[5], providing a good starting point for polaritonic chemistry. In our work, we rely on a validated quantum mechanical atomistic approach,*i.e.* the Direct Trajectory Surface Hopping[6] method. We extend it to characterize the polaritonic states in azobenzene, stressing out how the molecular properties affect the coupling conditions. Finally, we compare these effects in different simulations of azobenzene photoisomerization in the strong coupling regime[7].

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Differential mid-IR tip-enhanced absorption spectroscopy to probe light-induced conformational changes of bacteriorhodopsin at the nanoscale

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Standard vibrational mid-infrared (mid-IR) spectroscopy is widely applied to transmembrane protein receptors in order to gain insights on the dynamics and conformational changes that are at the base of their function as ion pump or channel. Here we apply mid-IR tip-enhanced absorption spectroscopy to the investigation of functional conformational changes of bacteriorhodopsin, a transmembrane protein acting as proton pump across the cell membrane of Halobacteria when illuminated with green light.

We used a photo-thermal induced mechanical resonance platform equipped with a mid-IR quantum cascade laser coupled to an atomic force microscope (AFM-IR) [1]. The samples are ~ 5 nm-thick flakes of purple membranes, i.e. cell membranes densely filled with bacteriorhodopsin (BR). Purple membranes are deposited on ultraflat gold substrate so that to exploit the strong field enhancement at the nanogap between the substrate and the gold-coated AFM tip. We performed differential nanospectroscopy by acquiring AFM-IR spectra under green (565 nm) and blue (420 nm) illumination. The green light activates the BR photo-cycle, while the illumination in the blue brings the proteins back to a resting state. The feasibility of detecting the light-induced protein conformational change with the AFM-IR technique is confirmed in Figure 1a where we benchmark the difference spectrum (green-blue) normalized to the absorption ($\Delta A/A$) obtained on a 1 μm-thick film of unoriented purple membranes to that obtained by standard Fourier transform IR spectroscopy (FTIR). In Figure 1b we report the results obtained for a membrane bilayer, i.e. two overlapping membrane flakes of less than 1 μm^2 area (see topography map in Figure1c). The main spectral features related to the light-induced proton pump process, like the negative difference band around 1522 cm^{-1} and the positive difference band around 1760 cm^{-1} (see vertical dashed lines), are both clearly seen in the $\Delta A/A$ spectrum. The use of a nanospectroscopy platform enabled us to measure the conformational changes of proteins embedded in two overlapping membrane flakes of less than 1 μm^2 area, with a dramatic increase of sensitivity (in terms of number of probed molecules) compared with standard mid-IR spectroscopy [2], including surface-enhanced mid-IR spectroscopy [3].

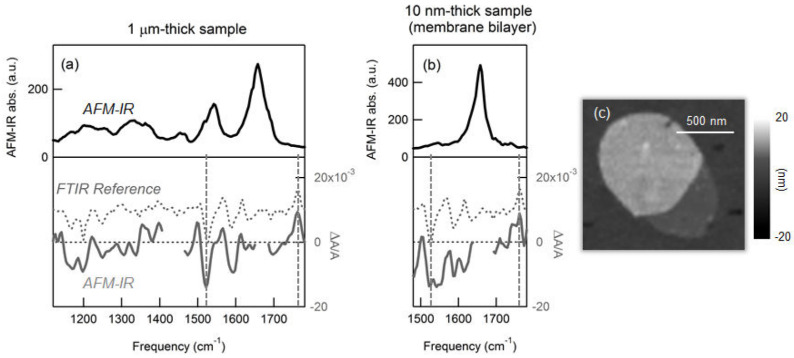

Figure 1: (a) AFM-IR absorption A and corresponding $\Delta A/A$ obtained on a 1 μm-thick sample of purple membranes. (b) Same as (a) but for 10 nm-thick membrane bilayer deposited on ultraflat gold substrate. The dashed curves represent the FTIR $\Delta A/A$ obtained on a thick sample of unoriented purple membranes. A smoothing algorithm and a baseline correction have been applied to obtain the final AFM-IR $\Delta A/A$ spectra. (c) AFM topography map of two overlapping membrane flakes.

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Session

Magnetoplasmonics and Scattering Phenomena

Chairman

Francesco Pineider, University of Pisa, Italy

Magnetic modulation of surface plasmons in magnetoplasmonic nanoparticles

Alessio Gabbani[1], Elvira Fantechi[1,2], Vincenzo Amendola[3], Angshuman Nag[4], Massimo Gurioli[5], Andrea Caneschi[2,6], Claudio Sangregorio[7], Francesco Pineider[1,2].
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The modulation of the optical response of plasmonic nanoparticles (NPs) by means of an external magnetic field, i.e. magnetoplasmonics, can trigger interesting improvements in the design of optical switches, modulators or more efficient refractometric sensors [1,2]. The enhancement of this magnetic modulation is a challenging goal in magnetoplasmonics. In a previous work, our group proved the ability of Magnetic Circular Dichroism (MCD) to detect small magnetic field-induced energy shifts of the plasmonic modes in simple Au NPs, which were described in terms of cyclotron splittings [3,4]. Nevertheless, the MCD signal of Au NPs is small and it can be further enhanced through the design and preparation of new magnetoplasmonic NPs with large magneto-optical signal. In this contribution we present two main strategies explored to this purpose.

The first approach is the preparation of hybridized magnetoplasmonic NPs, by alloying Au with magnetic metals (Fe, Co or Ni) and exploiting the interaction between the conduction electrons of Au and the spin polarized electrons of magnetic metals to increase the magnetic modulation. Recently, our group measured the MCD spectrum of AuFe nanoalloys prepared by laser ablation [5] and the MCD signal was roughly one order of magnitude higher than that of pure Au NPs. Motivated by these promising results we exploited colloidal chemistry approaches to synthesize Au_3M (M = Fe, Co, Ni) intermetallic nanoalloys. The nanoalloys were characterized structurally, magnetically and optically in order to optimize their properties for MCD experiments.

The second approach consists in the use of a different kind of plasmonic material, n-doped Indium-Tin-Oxide (n-ITO) NPs, which display a sharp plasmonic absorption in the Near-Infrared region of the spectrum [6,7]. Thanks to their low peak width and to the lower electron effective mass of n-ITO with respect to Au, the magnetic modulation of surface plasmons in n-ITO NPs is at least one order of magnitude higher than in simple Au NPs, as we found from MCD investigations.

This work has been financed by the EC through grant 737093 — FEMTOTERABYTE — H2020-FETOPEN-2016-2017.

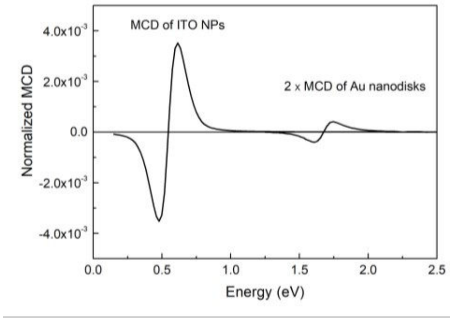

Figure 1: MCD signal of n-ITO NPs compared with that of Au nanodisks.

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Control of Optical Response of Tb^{3+} Bis-phthalocyaninato Complex close to Metal Nanoparticles

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$[TbPc_2]^0$ complexes represent one of the most representative mononuclear metal complexes behaving as single molecular magnets (SMMs) (i.e., characterized by large magnetic anisotropy, slow relaxation of the magnetic moment and quantum tunneling of magnetization). [1, 2] Due to this property they are expected to play an important role in technological applications in material sciences in the field of information storage on miniaturized devices.

In this context, the enhancement of light-matter interactions induced by the vicinity of plasmonic nanoantennas can boost the technological appeal of single molecule magnets, and even reveal novel fundamental phenomena in their behaviour.

In this contribution, we present a study on the peculiar spectroscopic properties of the $[TbPc_2]^0$ in proximity of a gold nanodisk, analyzing the role of the metal through a multiscale quantum/classical description of the Tb^{3+} complex–nanodisk system. Within this framework, an accurate representation of the interaction between the molecular probe and the metal nanostructures is achieved, describing the Tb^{3+} complex electronic properties with time-dependent density functional theory (TDDFT) and the gold nanodisk with a polarizable continuum model. [3, 4]

We will show that a significant enhancement in light absorption from $[TbPc2]^0$ takes place when the molecule is placed in proximity of the metal nanoparticle, especially when the molecular and the plasmonic resonances overlap. This study suggests promising outcomes in plasmon-enhanced spectroscopic experiments on single molecule magnets, especially with magneto-optical techniques.

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Magnetic-plasmonic heterostructured nanocrystals for innovative biomedical applications

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One of the most prized goals in the current landscape of nanotechnology is the design and realization of multifunctional heterostructured nanocrystals (HNCs), that combine the different physical properties of two or more inorganic constituents within a single nanosystem.[1] Within this framework, magnetic-plasmonic (MP) HNCs has recently attracted strong interest, due to the new exciting properties that can arise from the direct interaction of magnetic and plasmonic counterparts, and to the enormous potential of this class of nanomaterials in a wide range of applications, such as catalysis, optics, electronics, sensing, and, above all, biomedicine.[2] Indeed, both gold- and iron oxide-based nanoparticles (NPs) are well known as contrast agents for imaging, heat mediators for hyperthermic antitumoral therapy, drug delivery agents and elements in biosensing devices.[3] The integration of magnetic and plasmonic properties in a single nanosystem represents then an extremely powerful tool for the improvement of these applications, thanks to both synergistic action and multifunctionality, and for the development of new ones. Moreover, the study of the interaction between magnetic and plasmonic domains is extremely challenging also from a fundamental viewpoint. However, despite the great interest for MP-HNCs, their mechanism of formation and the synthetic parameters controlling their morphology are still not fully understood, especially concerning systems composed of Au and iron-based ferrites.

In this contribution, we present the synthesis and the characterization of physical properties of Au-Fe_3O_4 HNCs.[4] We demonstrate that a precise control over their size and morphology can be achieved by a seeded-growth thermal decomposition synthetic strategy, in which iron oxide nucleates onto preformed Au NPs. The formation of Au-Fe_3O_4 HNCs was found to be highly sensitive to the different reaction parameters and a morphology-dependent red-shift of the plasmonic resonance was observed. Preliminary hyperthermic characterization shows that Au-Fe_3O_4 HNCs can act as multifunctional heat mediators for hyperthermia under both magnetic and laser actuation. Finally, we will present a strategy for the realization of MP-HNCs composed of Au and different spinel ferrites, and the investigation of their physical properties.

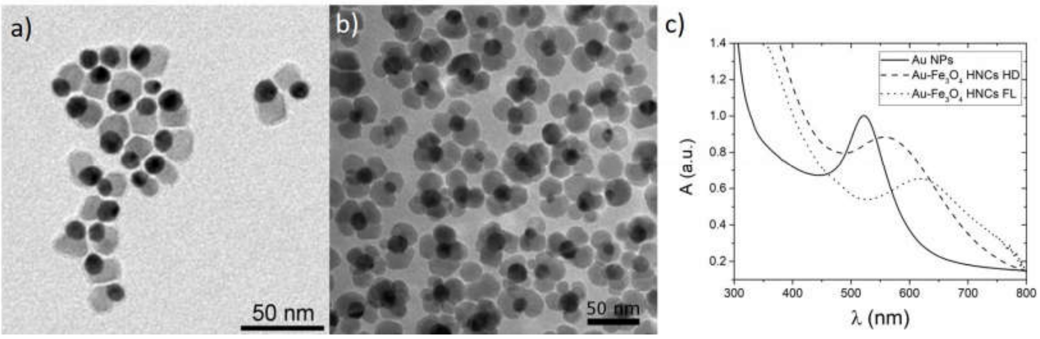

Figure 1: TEM images of Au-Fe_3O_4 HNCs with a) heterodimer (HD) and b) flower-like (FL); c) UV-VIS spectra of Au-Fe_3O_4 HNCs with different morphology obtained from iron(III)acetylacetonate.

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Scattering-assisted localization microscopy

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Super-resolution fluoresce microscopy techniques break the diffraction limit in biological systems, promising a resolution ultimately limited only by the size of the emitting molecules [1]. These methods, however, demand high numerical aperture (NA) lenses, in turn involving short working distances (typically below 1mm), while their imaging capability rapidly decays in turbid samples. Here we demonstrate that the unavoidable light scattering arising in bio systems, can be exploited to generate sub-diffraction images[2] using low NA and long working distances. In the Scattering-Assisted localization Microscopy (SAM) [3], the resolution is defined by the grain size of the speckle pattern on a sample rather than by the collection optics. We report a four-fold increase in resolution compared to the theoretical diffraction limit, enabling, as an example, the detection of micron-sized Beta Amyloid plaques in brain tissues using a lens of 25 mm working distance and minimal laser power.

SAM relies on the diffraction-free size of the Enhanced Speckle Grains (HSG) obtained through a wavefront shaping optimization protocol. In SAM the optimization protocol serves to enhance the signal from a fluorescent volume embedded in the turbid sample and on the localization of the emission “barycenter”. This basic protocol is iterated many times at random locations (different fluorescent targets) in the region of interest to be imaged, in order to capture information in the whole field of view. The result, for two fluorescent beads embedded in a diffusive titanium dioxide layer, and for a beta amyloid plaque embedded into a mouse brain is shown in Figure 1.

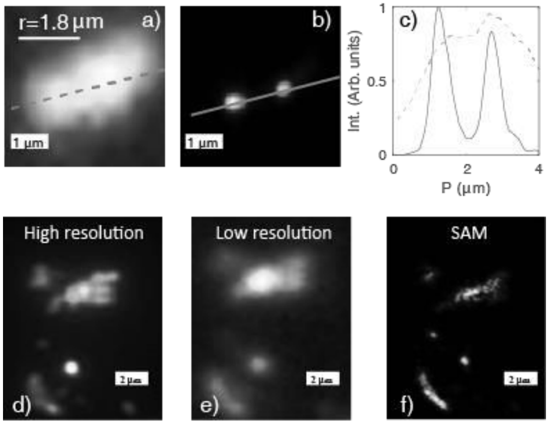

Figure 1: SAM compared with Wide Field (WF) microscopy. (a) : Two 0.5 µm beads as seen by a long working distance (NA=0.15) lens. (b) The same field (where the two beads clearly resolved) after the SAM image reconstruction has been performed. (c) Intensity profile along the line indicated in the figures (dashed line for the WF and continuous line for the SAM profile). In (d-e-f) we compare images of a group of amyloid-beta plaques in a mouse-brain imaged with an High numerical aperture objective (d, NA=0.8) a low numerical aperture objective (panel (e, NA=0.2) and with SAM (panel (f), obtaining with the low numerical aperture objective NA=0.2 objective).

In summary we are able to exploit small speckles and large angle K-ectors generated by a diffusive sample to improve resolution of a low numerical aperture long working distance lens. The technique has a straightforward application to retina imaging or to similar systems where short working distances are forbidden.

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Session

Bioplasmonic and Nanophotonic Devices

Chairwoman

Leonetta Baldassarre, Sapienza - University of Rome, Italy

Bio-inspired Photonics: from nature to applications

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Abstract

The most brilliant colours in nature are obtained by structuring transparent materials on the scale of the wavelength of visible light. By controlling/designing the dimensions of such nanostructures, it is possible to achieve extremely intense colourations over the entire visible spectrum without using pigments or colorants. Colour obtained through structure, namely structural colour, is widespread in the animal and plant kingdom [1]. Such natural photonic nanostructures are generally synthesised in ambient conditions using a limited range of biopolymers. Given these limitations, an amazing range of optical structures exists: from very ordered photonic structures [2], to partially disordered [3], to completely random ones [4].

In this seminar, I will introduce some striking example of natural photonic structures [2-4] and review our recent advances to fabricate bio-mimetic photonic structures using the same material as nature. Biomimetic with cellulose-based architectures enables us to fabricate novel photonic structures using low cost materials in ambient conditions [6-7]. Importantly, it also allows us to understand the biological processes at work during the growth of these structures in plants.

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Bio-plasmonic functional aggregates of protein decorated gold nanoparticles

Angela Capocefalo[1], Francesco Brasili[1,2], Damiano Palmieri[2], Ester Chiessi[2], Gaio Paradossi[2], Federico Bordi[1], Paolo Postorino[1] and Fabio Domenici[2]
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Bio-plasmonic systems made up of gold nanoparticles (AuNPs) conjugated with proteins exhibited enormous potential for nano-medicine and nano-biotechnology [1,2]. The synergistic interplay between the plasmonic and the protein components can be exploited to modulate the spatial organization, the Localized Surface Plasmon Resonance (LSPR) of AuNPs (i.e. the NP plasma electrons oscillation modes in resonance with the incident light) and the functionality of the system [3].

In this context, we have fabricated and characterized a nanostructured system based on the self-assembly in solution of AuNPs into clusters. The aggregation process is electrostatically activated by the adsorption of lysozyme (Lyz), a globular protein with enzymatic activity, onto the AuNPs surface.

We optimized a strategy to obtain stable assemblies with finite size, providing the possibility to tune both their optical response and functional activity by acting on the parameters which affect the surface ζ-potential of Lyz decorated AuNPs and in turn the size of the aggregates. Noteworthy, the system shows a significant catalytic activity, as assayed by monitoring its lysis efficiency on *Micrococcus lysodeikticus* bacteria (Figure 1). In particular, an enhancement of the enzymatic activity of adsorbed Lyz occurs when AuNPs aggregate.

On the other hand, bringing the system out of equilibrium by inducing the unfolding of the protein exploiting the thermo-plasmonic effect, we will discuss the possibility to obtain an intriguing novel gel-like plasmonic material.

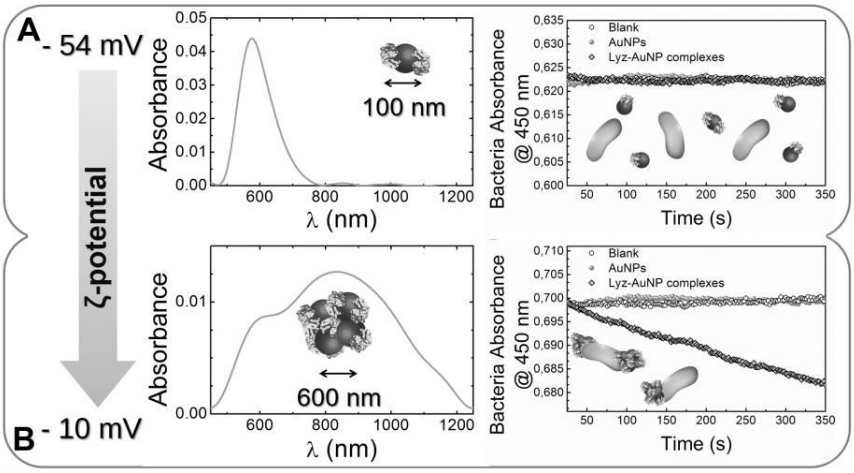

Figure 1: Scheme of the modulation of the properties of Lyz decorated AuNPs complexes at increasing the surface ζ-potential; representative absorption spectra and activity assays of single (A) and aggregated (B) AuNPs are shown.

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Microfluidic multielectrode arrays for recording and drug delivery

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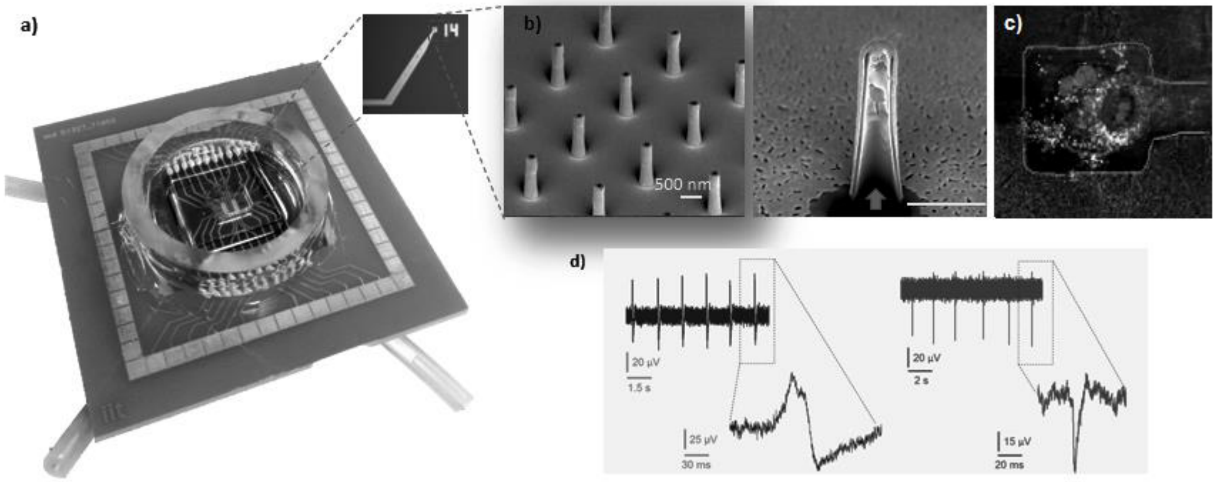
The study of the intracellular compartment requires devices that can not only monitor the bioelectric activity, but also control and observe the biochemical environment at the biomolecular level. Up to now the electrical activity of excitable cells, in particular that of a whole cells network has been studied with multi electrode array (MEA) devices. To overcome the intrinsic limitations of this method, such as low accuracy and low signal to noise ratio, 3D nanoelectrodes were developed on the planar surface in order to improve the interface with cells.[1] A novel fabrication technique for producing 3D vertical nanostructures that can be tuned in material and shape has recently been shown by our group.[2] This technique enables the fabrication of 3D hollow nanoantennas with high control over geometry and layout by means of a focused ion beam (FIB) procedure. These plasmonic vertical structures have shown to be suitable for enhancing the electrical recording of electrogenic cells and for performing selective intracellular drug delivery.[3,4] To further increase the capabilities of MEAs, here we combine these 3D hollow nanoantennas on top of MEA electrodes fabricated on thin silicon nitride membranes in order to combine the improved electrical recording with a controlled delivery over the cells. The goal of *in vitro* devices is to replicate as closely as possible aspects of the true *in vivo* microenvironment, this platform could be applied to make *in vitro* assays more realistic and capable of a precise manipulation of the microenvironment to deliver soluble factors to cells. The nanoantenna's hollow shape, in fact, allows to have a controlled delivery of molecules during cell signal recordings, providing the device with great versatility and allowing the exploitation of different approaches and techniques such as disease diagnosis, single cell analysis, drug screening, proteomics and other biological applications. The device configuration could provide flexibility in controlling the critical biochemical factors that influence cells behavior, allow for the partial differentiation of cells in a single system, provide for the establishment of biochemical gradients in two- or three-dimensional cultures, and at the same time allows for high quality intra and extracellular recordings.



This figure shows a) the final device,b) SEM images of the nanoantenna, c) selective delivery on the electrode and d) intra and extracellular recording.

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Synthesis of Peroxiredoxin protein-templated plasmonic silver nanorings

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Fabrication of metal nanostructures smaller than 10 nm in diameter is challenging through traditional top-down nanofabrication techniques. As an alternative to the top-down approach, bottom-up methods are quickly emerging as viable strategies, where nanostructures form through self-assembly of molecular components [1, 2]. There are indeed several examples in nature of self-structuring matter at the nanometer scale through well-ordered reactions and self-organization. Further, such examples display other properties that are valuable in nanotechnology, such as self-maintenance of non-equilibrium conditions, feedback loops, reaction-diffusion processes, compartmentalization and communication [3].

Here we show that the ring-shaped protein 2-Cys peroxiredoxin I from the human parasite *Schistosoma mansoni* (*Sm*PrxI) can guide the synthesis of colloidal silver nanorings with plasmonic cavities. Ring-shaped proteins possess several interesting features, *i.e.* four independent solvent-accessible surfaces available for biofunctionalization, natural abundance and relatively high structural stability compared to the large majority of biomolecules [4, 5]. Our approach is based on a wet chemistry method where Ag^+ (silver ions) are adsorbed on the surface amino acids of the ring-shaped protein *Sm*PrxI before undergoing chemical reduction through sodium borohydride to obtain metal nanorings. Absorbance spectroscopy, electron microscopy and energy dispersion spectroscopy show seeding growth of silver along the Peroxiredoxin scaffold leading to metal nanorings with outer and inner mean diameters of 27.2 and 3.5 nm, respectively. A schematic representation and Transmission Electron Microscopy (TEM) images of SmPrxI-Ag nanoring are shown in figure 1. These data indicate that the *Sm*PrxI ring complex acts as molecular scaffold where a controlled seeding growth of metal Ag^0 occurs. The cavity offers electric field enhancements as predicted by numerical simulations. These data stands as a proof-of-concept of hybrid protein-metal plasmonic nanopore.

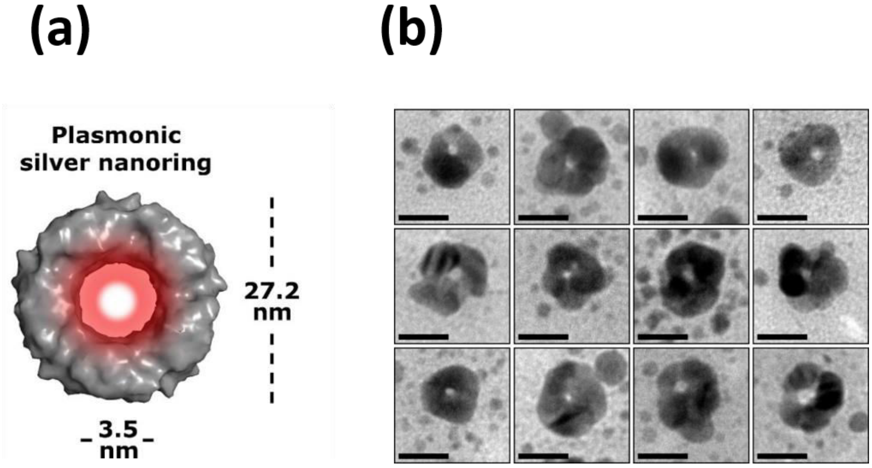

Figure 1: (a) Schematic image of SmPrxI-Ag nanoring (b) TEM micrographs at 80 keV of *Sm*PrxI-Ag sample after reduction. Mean outer and inner diameters are 27.2 nm and 3.5 nm, respectively. In a number of cases, nanorings are found decorated with small particles. Scale bars= 10 nm.

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Flow-through dielectric ring resonators for biosensing

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In the wide field of single particle detection, purely optical methods are recently gaining considerable attention. In particular, optical sensing with whispering gallery mode (WGM) resonators shows prospects for the unique sensitivity to extremely small objects, down to the single molecule level, and a number of technologically relevant advantages. These include great stability and robustness in aqueous environments, multiplex operations, scalability, reduced fabrication costs, and the potential for integration in point-of-care and portable devices.[1-3] One of the most challenging issues in sensing application lies in the background noise that affects the limit of detection of the system. In fact, although great efforts have been made to suppress any source of noise in the optical measurement, the detection of single molecules, biomarkers, and proteins remains very challenging when using a conventional WGM resonator and requires a very sophisticated experimental setup. Here we propose a background-free system for single particle detection.

Specifically, a silicon nitride ring resonator on a silicon dioxide membrane with a passing-through hole. The hole in resonating structure will work as a point-source thanks to the electromagnetic field confinement in a subwavelength volume.

Here, we propose the theoretical validation of the model performed with a 3D finite element method solver (COMSOL) and experimentally demonstrate the localized field enhancement within the subwavelength volume.

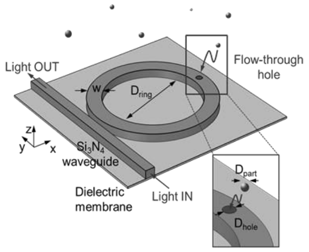

Figure 1. Sketch of the flow-through dielectric ring resonator

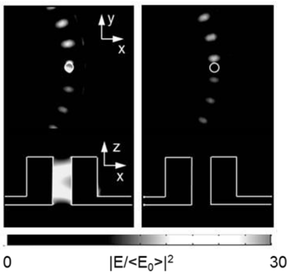

Figure 2. Theoretical analysis of the field distribution within the perforated ring resonator.

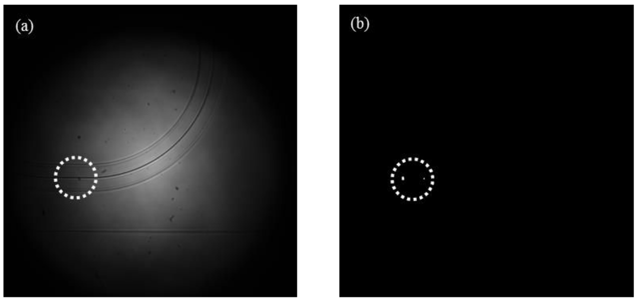

Figure 2 – (a) White light image of the resonating structure. (b) Localized emission from the resonating structure. Light coupling by means of lensed fiber in side-coupling configuration.

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Poster Session

Plasmonic Membranes as novel Bio-detection Substrates for Surface-Enhanced Raman Spectroscopy

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A novel substrate based on hydrophobic membranes decorated with a 2D-assembly of silver nanowires (AgNWs) is presented. Here we are aimed at implementing a SERS biosensor obtained by simple and cost-effective fabrication procedures, ensuring a highly sensitive, reproducible and uniform SERS signal from biomolecules in trace amounts [1,2].

The choice of high-aspect-ratio silver nanostructures is justified by the advantage of their facile synthesis and exceptional capability of self organizing into complex 2D assemblies with high degree of hot spot formation and improved electromagnetic enhancement of the Raman scattering [3]. A low-density clustered layer of AgNWs was achieved either by filtration through a porous Teflon membrane or by ink-jet printing on the surface of the membrane. The resulting high contact angle of a drop of aqueous solution on top of the AgNWs-decorated membrane upon evaporation allows the molecules to concentrate into small spots on the surface. Thereby a large number of molecules can get in close proximity to the hot spot regions of the plasmonic nanowires yielding an enhancement factor of the Raman intensity of the species of about 10^5.

The novel AgNWs-decorated membranes were efficiently tested as a SERS bio-detection platform on proteins, oligonucleotides and amyloid oligomers. Thus, thanks to a simple and low-cost fabrication procedure, a high sensitivity and reproducibility as well as an overall performance improvement due to analyte concentration on the SERS hot spots, the proposed substrates can be used as effective tools for SERS analysis of molecules of biomedical interest.

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Magnetic Resonance Imaging of gold nanorods for hyperthermia therapy

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The aim of this work is to explore the synergistic use of plasmonic particles as gold nanorods with advanced Magnetic Resonance Imaging (MRI), in order to map temperature during irradiation with a near infrared laser coupled to fiberoptic delivery, in a setup simulating a photothermal treatment of cancer. Advanced MRI [1], unlike current methods as infrared thermography or the use of insertion probes as thermocouples, thermistors, etc., provides a mini invasive measurement of temperature in three dimensions and near-real time, which is a critical issue for a photothermal treatment to ensure efficacy and minimize side effects.

Here, we report on the design and fabrication of gold nanorods developed for this purpose [2], along with the first experimental results obtained by implementing a plastic phantom mimicking in vivo measurement conditions and enabled by additive manufacturing [3].

Preliminary measurements were performed with different suspensions of gold nanorods with 1.5 and 3 T clinical scanners, demonstrating the feasibility of monitoring temperature with advanced MRI.

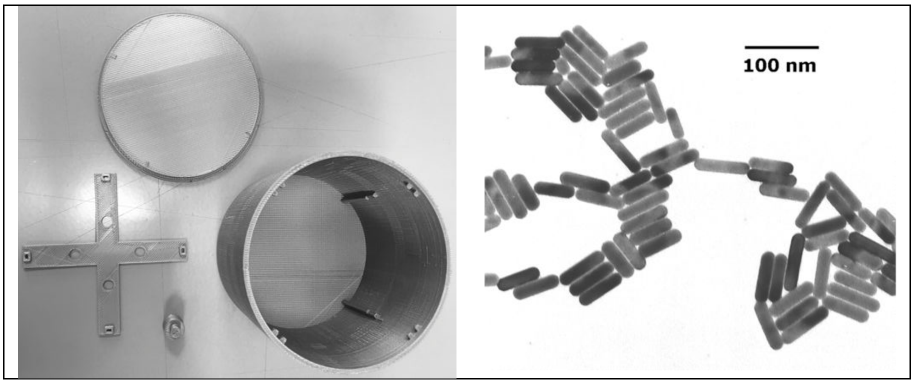

Figure 1: Left panel) Phantom; Right panel) TEM image of Plasmonic gold nanorods developed by authors at IFAC-CNR.

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SILVER ION EXCHANGED SODA-LIME GLASSES FOR SERS PLATFORMS

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Ion exchange in silver nitrate is gaining an increasing interest in plasmonics due to the possibility to induce the formation of silver nanoparticles in the glass matrix by an *ad-hoc* thermal post-process. Here we report the application of this technology in soda-lime glasses for the fabrication of SERS platforms both in planar and fiber configurations.

Commercially available soda-lime glass (SLG) slides of dimensions (75 mm × 25 mm × 1.3 mm) and composition (in wt.%) 73.24% SiO_2, 14.07% Na_2O, 6,45% CaO, 4.08% MgO, 1.46% Al_2O_3, 0.18%, K_2O and 0.09% Fe_2O_3 supplied by Gold Star, Chance Propper LTD. were used as substrates. After a standard cleaning procedure, the glass samples were immersed for 4 h in a molten salt bath of $NaNO_3$:$AgNO_3$ (95:5 mol.%) mixture at the temperature of 390 °C. Then, the resulting silver ion-exchanged glass samples (labelled as SLG1, SLG2, SLG3 and SLG4) were annealed at 550 °C for the different time intervals of 45 min and 3, 6 and 16 h, respectively. Finally, the annealed specimens were etched in 4% HF solution in order to remove about 350 nm of material and expose the Ag nanoparticles for SERS applications

Commercially glass bar made available by Effetre Murano s.r.l., with a composition of 70,06% SiO_2, 17,53% Na_20, 8,87% CaO, 3,54% K_2O, and Fe_2O_3 traces of around 0.27%, was drawn at the Polytechnic of Turin in order to obtain an optical fiber with a diameter of around 130 µm. The tip of the fiber was ion-exchanged under the same conditions of molten salt and temperature already adopted for the planar samples. The ion-exchange duration was around 4 h and 30 min. Subsequently, the fiber tip was annealed at the temperature of 550 °C for 45 min.

Atomic Force Microscopy (AFM), UV-Visible (UV-Vis) and SERS characterization of the aforementioned nanocomposite substrates showed the presence of Ag nanoparticles ranging in size from few nm to a few tens of nm, depending on the annealing conditions. SERS effect was observed on the fiber tip covered by 4-mercaptobenzoic acid (MBT) at 10^{-6} M by using a micro-Raman spectrometer with a 638 nm excitation wavelength, a 50xLWD objective and a 1200 gr/mm grating.

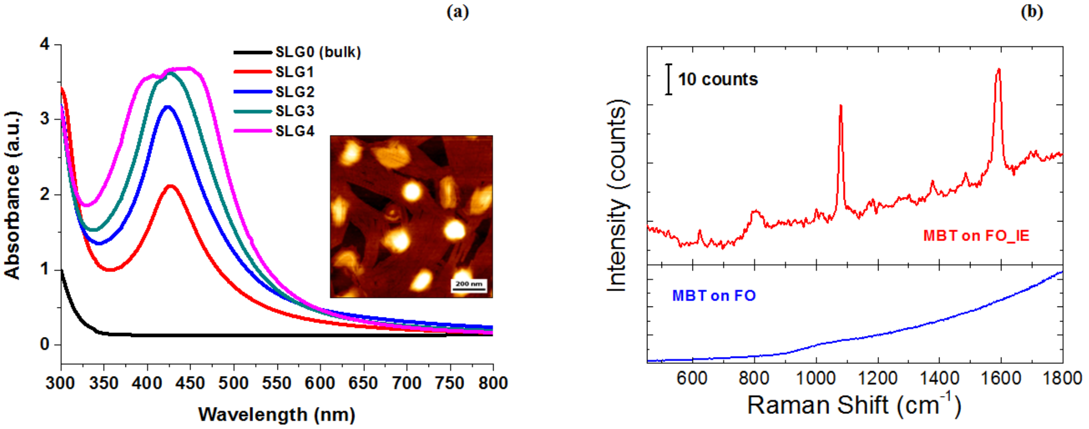

Fig. 1: (a) Absorbance spectra of the SLG samples. The inset shows a particular of the SLG4 surface kept by the AFM. The presence of Ag nanoparticles is clearly visible; (b) SERS spectra of the MBT on ion-exchanged (IE) glass fiber optic (FO) tip (red line) compared to the signal acquired by the MBT on the same optic fiber before the ion exchange (blue line).

Nanostructured Lab-on-Chip for Surface Plasmon Resonance biosensing in leukemia: from label-free cell detection toward diagnosis of mutations

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Surface Plasmon Resonance SPR-based sensors, with the advantage of being label-free, enzyme-free and real-time, are of growing interest in biomedical research [1]. This kind of sensors are widely recognized as trustworthy tools for detecting biological specimens but are conventionally limited to single marker analysis and usually applied to molecular interactions. Nanostructured SPR biosensors combined with microfluidic chambers [2] and simple detection device are here proposed as an innovative approach to leukemia research. Acute leukemias are the most common type of pediatric tumor and improved drug screening towards personalized therapy as well faster and cost-effective diagnosis assay are of great clinical interest [3]. Here we show the application of a grating-coupled SPR based on phase interrogation biosensing to address these clinical needs. On one hand, a label-free leukemia cell counting and cell-drug interaction protocol have been developed and successfully applied. On the other hand, we implemented the sensing area for multiple analysis in parallel for enhanced throughput, using a strategy based on grating multiplexing in smaller regions while maintaining the compactness and sensitivity of the system [4].

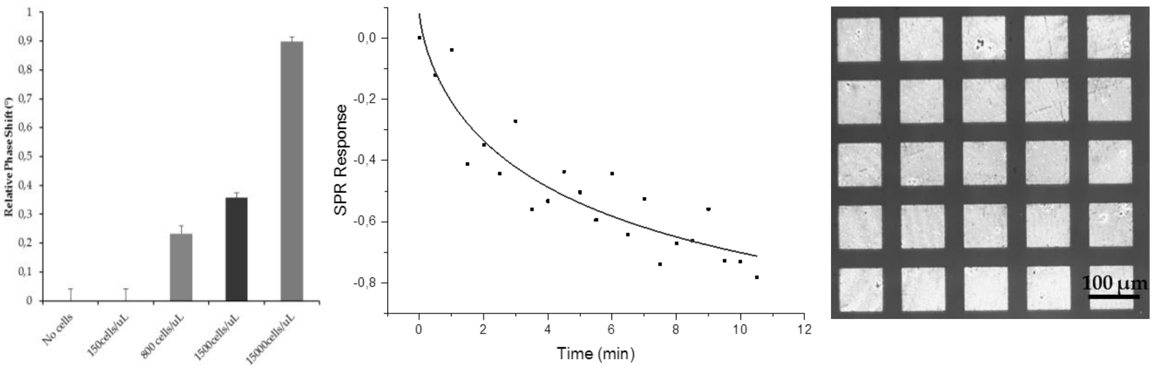

Figure 1. (Left) Calibration between cell number and relative phase shift. (Middle) SPR response decrease upon administration of trypsin to a confluent cell layer. Trypsin has been used as a gold standard for cell detachment from the gold surface. (Right) Optical microscope image of multiplexing of sensing area.

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Synchrotron Radiation SEIRA signalling of a gold nanoprobe in sonicated cells

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Novel nanostructured vectors based on gold nanoparticles (AuNPs) have demonstrated their capability to combine selective high-performing detection and therapeutic strategies at the single cell level [1]. The resonant absorption of light by AuNPs and the resulting strong electromagnetic fields, localized at the metal-dielectric interface, provide a huge amplification of the spectroscopic signal of molecules in the proximity of the gold surface. On this mechanism rely the so-called surface enhanced spectroscopies, such as Surface Enhanced Infrared Absorption (SEIRA), which benefit of a remarkable improvement of the sensitivity [2].

By taking advantage of Synchrotron Radiation (SR) and Fourier Transform Infrared micro-spectroscopy in providing high sensitive single cell signalling, we focused on the internalization and detailed recognition of a plasmonic nanovector [3]. To this aim, we treated the murine fibroblasts (NIH-3T3) model cell line with a probe made up of AuNPs conjugated with the IR marker 4-aminothiophenol (4ATP-AuNPs). The uptake was obtained by the so-called transient sonoporation (figure 1A), i.e. the ultrasound (US) induced temporary permeabilization of the cell membrane, intensively studied in designing improved anticancer strategies [4].

The characterization of the IR signal fingerprint of 4ATP-AuNPs assembled on flat silicon wafers enlightened a two order of magnitude enhancement of the absorbance at 1586 cm^{-1}, corresponding to the C-C stretching of the phenyl ring. The strong, selective and stable signal provided by the coupling between SR and SEIRA allowed to ascertain the vector inclusion within single cells, whose spectral profile exhibit comparatively evident changes in both shape and intensity when treated with the nanoprobe. The capability of AuNPs to improve the sensitivity in the detection of cell viability, providing a strong enhancement in the specific spectral range, was pointed out. Eventual occurrence of cytotoxic and genotoxic effects of the US mediated internalization of 4ATP-AuNPs have been also evaluated.

Our benchmark study provides a novel detection method with the main asset of non-destructivity with respect to the traditional, fluorescence based ones. We are confident that our results can provide novel hints towards US- and photo-based nanomedicine combined strategies for diagnostics as well as drug delivery-based therapeutics.

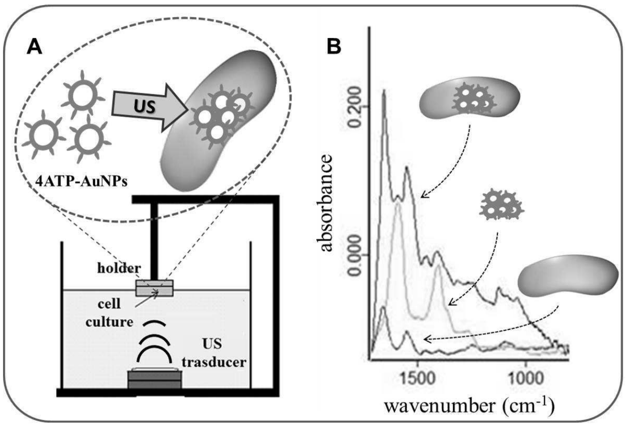

Figure 1: (A) Scheme of the US exposure setup employed for the uptake of 4ATP-AuNPs within cells and (B) representative IR spectra, from the bottom: untreated cell, 4ATP-AuNPs and cell treated with 4ATP-AuNPs.

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Synthesis of Au nanoparticles with tuned plasmonic properties and integration in TiO_2 hierarchical structures via single-step pulsed laser co-deposition

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Metallic nanoparticles (NPs) possess interesting optical properties due to size confinement, which enables the activation of the localized surface plasmon resonance (LSPR) [1]. Engineering NPs by tuning their size and shape will allow to set specific LSPR wavelengths, with a potential for several applications in the fields of optoelectronics and spectroscopy. Moreover, plasmonic NPs can be integrated in wide band gap semiconductors photoanodes (such as TiO_2) in order to enhance the photoresponse, by promoting light absorption in the visible range as well as light trapping and scattering effects, with applications in photocalysis, photovoltaics and chemical sensors [2].

Here, we demonstrate the controlled synthesis of surface-supported plasmonic Au NPs by vapor phase pulsed laser ablation. Au NPs have been deposited at room temperature by varying a number of process parameters – including background gas pressure and the number of laser shots - in order to tune average diameter (from 5 up to 15 nm) and substrate coverage. Optical analysis has shown the dependence of the plasmonic behaviour on the NP size and average distance, enabling to tune the LSPR wavelengths from 540 up to 640 nm [3].

Then, we demonstrate a single-step synthesis approach for the integration of plasmonic Au NPs within TiO_2 hierarchical nanoporous films, by means of laser ablation of a composite TiO_2-Au target. Specifically, we report the fabrication and characterization of Au NPs-decorated TiO_2 forest-like systems (Fig.1a) with tunable porosity and density while varying the Au content (from 0.5 up to 5% at.). Moreover, the effect of post-deposition thermal treatment has been studied as a mean to control TiO_2 crystallization and Au NP nucleation and growth.

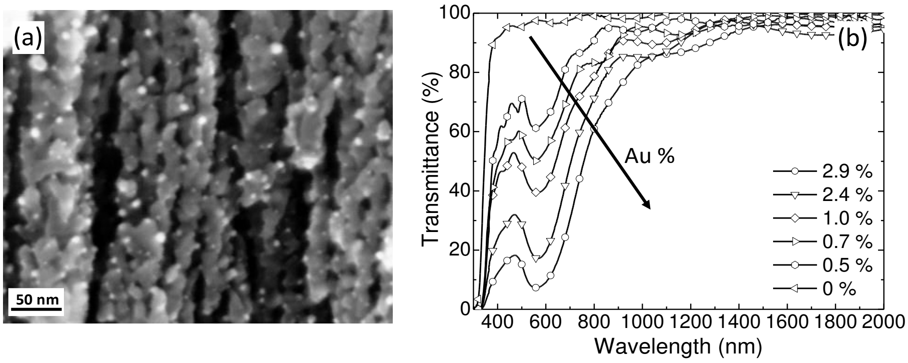

Figure 1: (a) SEM images of Au-TiO_2 integrated structure; (b) Optical transmittance of annealed Au-TiO_2 films with different Au content.

Optical analysis shows the onset of characteristic plasmonic resonance of Au NPs with the increase of film absorption in the visible range (Fig. 1b). Preliminary tests of photodegradation of methyl orange dye show that Au NPs integration in TiO_2 films results in a significant improvement of the catalytic activity. Our results suggest the potential of this approach for the synthesis and the integration of metallic NPs within wide band gap semiconductors, while paving the way toward novel plasmonic-based devices.

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Surface-Enhanced Raman Scattering of DNA-Nanoparticle assemblies

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The great interest in DNA-coated colloids and the large number of applications in different branches of science, have contributed to deepen their properties for the realisation of innovative nanomaterials [1, 2]. Among the common spectroscopic techniques, Surface Enhanced Raman Spectroscopy (SERS) [3, 4] reveals to be the most promising for the study of the optical properties of such hybrid biosystems, thus, for the detection of specific targets and for the implementation of high-quality biosensors.
Combining the high sensitivity and the surface-selectivity of a metal nanostructure, SERS allows for a rapid and precise detection of several biomolecules. The presence of a metal core, able to support the localised surface plasmon resonance, is a key prerequisite for the observation of SERS phenomenon. Indeed, the well-known 'nanoantenna' effect, able to create a strong intensification of the electromagnetic field in the vicinity of the metal surface, makes possible the spectroscopic characterisation of macromolecules even at very low concentration, overtaking the limit of conventional Raman technique.
In our lab we have provided for the realisation of DNA-nanoparticle systems, consisting of metal gold nanoparticles (NPs) functionalised with two different and purposely-defined DNA strands of 12-bases, covalently attached on the NP surface. Covalent bonds were induced by the presence of a thiol group at the end of each sequence, assuring not only a harder and more reproducible bond but also a more controllable adherence. Thanks to UV-Visible measurements, we have tested the DNA-NP attachment for both the two different DNA chains, observing a red shift in the plasmonic absorption band respect to the gold NP stock solution. It has been possible an ensuing study of spectroscopic features of these binary systems through the use of SERS which has allowed us to obtain a coherent and reproducible signal.
In addition, taking advantage of the programmability and the base-pairing specificity (A-T, C-G) of DNA strands, we have promoted an aggregation process by adding to the solution of NPs, functionalised with the two 12-base DNA sequences, a 24-base 'bridge' complementary to the two chains, as shown in Fig.1.

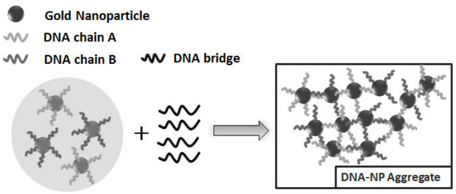

Figure 1: Sketch of the system studied: a solution of gold NPs functionalised with two distinct 12-base DNA chains (A and B) is realised. Then a DNA 24-base 'bridge', complementary to the two sequences, is added to the solution allowing the system to hybridise and to form mesoscopic aggregates.

The aggregates so formed have provided to the presence of 'hot spots', localized regions between two or more NPs, which allow an intensification of Raman signal up to 10^8. A SERS spectrum of the hybridised system has been obtained through a direct and label-free method which guarantee the extrapolation of the real vibrational signature of DNA molecules without the use of any fluorescent reporter [5].
In this framework, the still unknown and not totally investigated properties of DNA-colloids open a vast scenario of possible theoretical and experimental implementations as well as future developments in nanotechnology and materials science.

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SERS active pH-nanosensor

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The extraordinary optical properties of gold nanoparticles (AuNPs), together with their rewarding chemical stability and ease of functionalization, make them an invaluable platform to develop ultrasensitive and molecular specific chemical sensors [1]. Taking advantage of the strong electromagnetic fields confined at the AuNPs surface, vibrational spectroscopies benefit of a huge amplification of the signal from molecules located at the metal interface, resulting in a remarkable sensitivity increase. In particular, Surface Enhanced Raman Spectroscopy (SERS) emerged as a powerful analytical tool with detection limits lowered down to the single molecule recognition [2].

In this framework, we developed and characterized a plasmonic pH-nanosensor by conjugating AuNPs with the pH-sensitive molecular probe 4-mercaptobenzoic acid (4MBA), which shows a SERS signal depending on the protonation degree of the carboxylic group. Exposing the AuNP-4MBA nanosensors to solutions at varying pH, we identified the dynamic range of sensitivity, which is centered around the pKa value of the molecule, as a function of the relative intensity of selected pH-dependent SERS bands (Figure 1B). From the comparison of the obtained calibration curve with a standard acid-base titration curve of the free molecule (Figure 1A), we enlightened an increase of the molecule pKa when measured by SERS at the interface of the plasmonic nanostructure. In particular, for AuNPs with a diameter of 60 nm, the pKa value results around pH 6, making this system suitable for pH measurements in physiological environment, at the single cell level [4].

Proceeding from this, we will investigate how the AuNPs curvature and plasmonic affect the acidic properties of the molecule. To this purpose, we will further characterize the system at varying the AuNPs size as well as the core material, with the final aim to reach a modulation of the working point of the nanosensor.

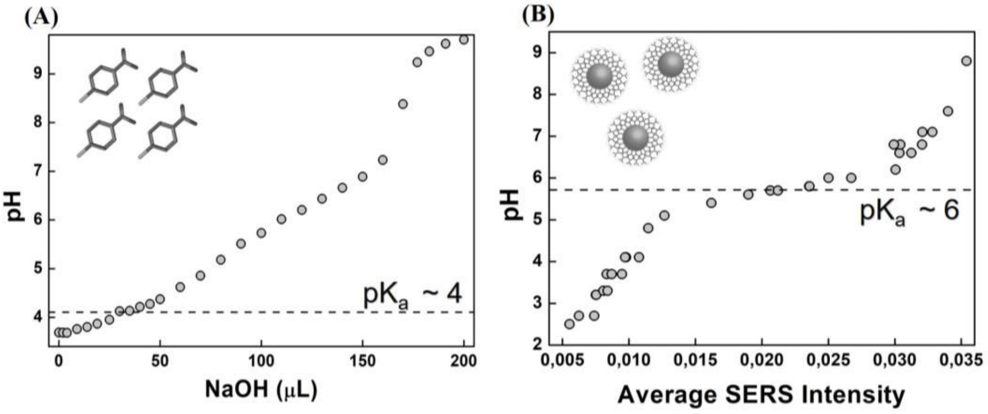

Figure 1: **(A)** Acid-Base titration curve for free 4MBA. The pKa value corresponding to the dissociation of the carboxylic group is around pH 4. **(B)** SERS titration curve for the AuNP-4MBA nanosensor. On the horizontal axis is reported the ratio between the intensities of β(COO-) (at 850 cm^{-1}) and aromatic ring vibration signal. The second one has been taken as reference, since it is pH independent. The pKa value for the molecule confined on the nanostructure shifts to pH 6.

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Photostable molecules on chip:
a scalable approach to photonic quantum technologies

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The efficient interaction of light with quantum emitters is crucial to most applications in nano and quantum technologies. In this context, we demonstrate the potential of a novel hybrid technology which combines single organic molecules as quantum light sources and dielectric chips.

Dibenzoterrylene molecules in anthracene crystals (DBT:Ac) are particularly suitable quantum systems for this scheme, due to outstanding photophysical properties [1]. Long-term photostability is combined with a convenient operating wavelength in the near-infrared (780 nm), lifetime-limited emission in the zero phonon line at cryogenic temperatures [2, 3], and easy fabrication methods.

Here the emitters are integrated by spin-coating onto a ridge waveguide supplied with grating far-field couplers (see fig. 1, [4]). We demonstrate at room temperature the emission of single photons into the photonics structure with a branching ratio up to (40 ± 3)%. The overall single-photon source efficiency is estimated around (16 ± 1)%. These results offer a competitive platform for on-chip processing of single waveguide photons.

We also discuss preliminary studies on a novel photonic scheme, where nanocrystals of DBT:Ac [5] are directly embedded in a polymeric suspended waveguide. Direct laser writing fabrication allows for high resolution at the nanoscale of the guiding structure and for the scalable integration of the sources. This technique is promising for an improvement of the collection efficiency and for the design of a versatile photonic architecture with applications to quantum technologies for communication and solar energy [6–8].

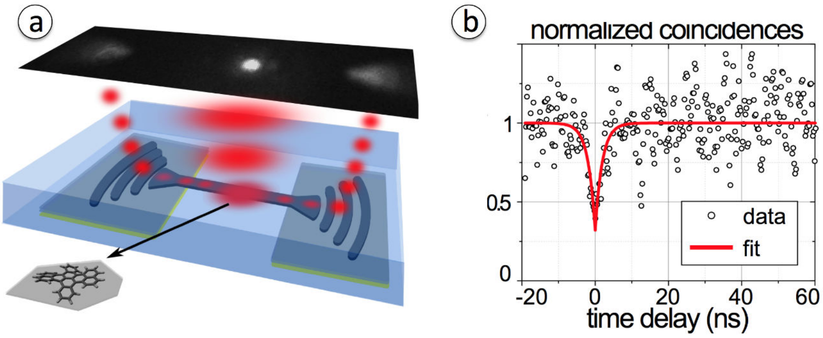

FIG. 1. *Integrated single photon source.* (a) Cartoon of the ridge waveguide and the spin-coated emitters (arrow). On the top, a florescence image collected with an EMCCD camera shows signal both at the confocal excitation spot (central) and at the outcouplers. (b) Anti-bunching dip measured at the grating far-field couplers.

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Surface-enhanced Raman detection of biomolecules with silver nanocubes and porous silver nanocubes

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Surface enhanced Raman spectroscopy (SERS) has been proposed for detection and analysis of biomolecules at low concentration. A common approach of SERS detection of biomolecules is mainly based on inducing the formation of aggregates of plasmonic nanoparticles in solution, which can lead to the generation of effective hot-spots with a random distribution. However, an irregular arrangement as well as a high variability in the SERS response of these hot-spots are frequently responsible for scarce signal reproducibility. Moreover, uncontrolled clustering of plasmonic nanoparticles can produce high photoinstability, inducing photothermal and photodegradation processes and affecting the Raman signal. Here, we describe a novel strategy to detect intense, stable and reproducible SERS signals from biomolecules in physiological buffer by using isolated silver nanocubes [1] as well as porous Ag/Au nanocubes obtained by galvanic replacement. A theoretical simulation based on the Finite Element Method (FEM) was performed to estimate the E-field distribution on the surface of both substrates. SERS spectra of model biomolecules were achieved and the impact on their structure caused by the excitation of the nanoparticles was evaluated. Using this type of nanoparticles, we were able to measure SERS spectra in physiological buffer with a limit of detection in the nanomolar range.

Acknowledgements

We thank the financial support from the Russian Foundation for Basic Research (grant 18-52-7803) and by the CNR within the project "Hybrid plasmonic nanostructures for biomedical sensing and imaging-HYPNOSIS" (2018-2020 RFBR/CNR bilateral project).

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Photo-Induced Heat Generation in Plasmonic vs Non-Plasmonic Nanoantennas.

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Light-to-heat conversion in plasmonic and non-plasmonic nanonatennas is a key topic for many applications, including photo-thermal therapy, Raman sensing, laser writing and nanofabrication. Especially in the case of non-plasmonic systems, heat generation and propagation is increasingly debated, and contradictory results have been reported so far.

Some authors observed that non-plasmonic silicon nanoantennas generate heat even more efficiently than the metallic counterparts [2,3], while other authors claim that resonant silicon nanoantennas are nearly unaffected by temperature rise [4,5].

Here we report an experimental evidence and a Finite Element Analysis of temperature distribution and heat flow in SiO_2/Si core/shell systems (silicon nanoshells) irradiated with different continuous wave lasers (λ=532, 633 and 785 nm) [1]. The complex interplay among optical properties, morphology, degree of crystallinity of the nanoshells, thickness dependence of thermal conductivity and interactions with the substrate has been elucidated. This study, for the first time to our knowledge, reveals that all of those parameters can be properly combined to obtain either stable nanoantennas for surface enhanced spectroscopy or highly efficient sources of local heating. The optimal balance between thermal stability and field enhancement was found for crystalline Si shell layers with thickness ranging from 40 to 60 nm, irradiated by a NIR laser source. On the other hand, non-conformal amorphous or crystalline shell layers with thickness >50 nm can reach very high local temperature (above 1000 K) also when irradiated with low power density (less than 1 mW/μm^2) laser sources. This work provides a general approach for an extensive investigation of the opto-thermal properties of high-index nanoantennas.

A comparison with the optical and thermal proprieties of plasmonic systems has been done. The opto-thermal performances show that, in some cases, resonant silicon nanostructures enable a light-to-heat conversion even higher compared to the plasmonic counterparts.

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Laser writing of the electronic activity of N- & H-atoms in InGaAs using near-field illumination

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In 21st century, introduction of nitride semiconductors has brought a boom in telecommunication industry, and this has opened the door for nano-light emitting devices (nano-LEDs) in the field of Information and Communication Technologies (ICT), cyber security, energy and materials for environment, like sensors and photovoltaics. And, now at present in our work, we are trying to integrate the quantum communication protocols with present optical fiber technology requires single photon sources operating at 1.31µm and 1.55µm wavelengths (0.95eV and 0.79eV respectively), where optical losses and dispersion of silica fibers are minimal. Incorporation of 1-2% N-atoms strongly affects the structural and electronic properties of III-V compounds and also induces a large reduction of the band gap energy.

In our technique, we used a focused laser beam to study the electronic activity of N- and H-atoms in (InGa)(AsN)/GaAs SQW. We used a focused laser beam for laser annealing and then characterizing it using micro-photoluminescence (µPL) which provides live characterization and we can control the dissociation of N-H bonds, and thus the band-gap energy of (InGa)(AsN).

In this study, we used a 5nm nm $(\mathrm{In}_{0.21}\mathrm{Ga}_{0.79})(\mathrm{As}_{0.975}\mathrm{N}_{0.025})$ QW/GaAs SQW sample grown by metal-organic vapour phase epitaxy (MOVPE) on a GaAs substrate. The sample was mildly annealed at first at 600°C for 10 seconds, and then hydrogenated with a H-dose of 5×10^{17} ions/cm^2 at 300°C. Upon hydrogenation, N-H complexes causes expansion of host lattice which causes blue-shift. It may turn tensile strain of InGaAsN into compressive strain. After hydrogenation, we observed a blue-shift of 220 meV. Then, we used a range of power to understand the N-H dissociation caused by laser annealing (using objective lens x100). We got a red-shift of 120-130 meV (fig.1), but the limitation of this technique is that it completely burns out the sample as shown by AFM because of lack of heat dissipation, shown in fig.2.

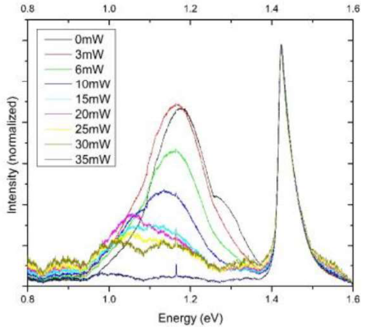

Fig.1. Laser annealing with different powers ranging from P=3mW to P=35mW for a time period of t=7 seconds.

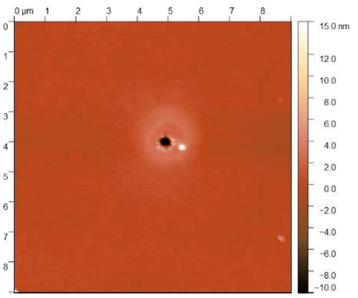

Fig.2. For P=35mW and t=7seconds, Arsenic (As) desorption happens, and a hole is created (observed by AFM).

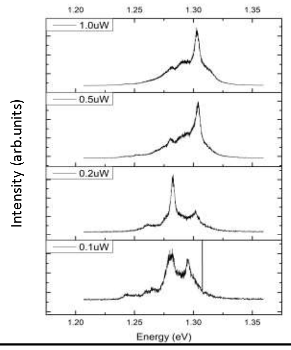

Fig.3. Using SNOM, P=1.8mW and t=5 seconds, sharp dots are observed which are measured under different powers using µPL.

This leads us to a technique called “near-field scanning microscopy” (SNOM), a better replacement to laser annealing using objective, in which light is focused using a dielectric tip in much smaller area, and so the quantum dots made are much smaller (~200nm) as compared to dots made by laser annealing using objective lens (~500nm). This technique works on the principle of exploiting near field, which has already been used for GaAsN, and reported [1]. Using SNOM, we made dots in InGaAsN QW, shown in figure (3), which are highly confined.

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Magneto-Plasmonic Properties of Fe-oxide Capped Au Nanoparticles

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Magneto-plasmonics is a novel discipline involving nanostructured materials composed by the combination of components that exhibit plasmonic and magnetic activity. The number of applications that profit of the plasmonics or magnetic properties is increasing day-by-day, involving information storage, telecommunications, energy, catalysis and in particular environment and health technologies[1]. Core@shell nanoparticles, composed by plasmonic noble metals and magnetic Fe oxide moieties, constitute one of the more investigated class of magneto-plasmonic nanostructures. Originally their study was motivated by their novel magneto-optical properties, but actually they are promising multifunctional nanomaterials to be employed in biomedicine, in magnetic and photo-thermal therapies and imaging, and in photo-magneto-catalysis. In particular, a very interesting theme of investigation is the interaction between magneto-optical characteristics of the magnetic moiety and the plasmonic resonance, which can give rise to new properties and modify the existing ones.

In this work we are interested primarily in the magneto-optical features of the core@shell hybrid system. Magneto-optics studies the modification of the optical properties of magnetized matter. Among the magneto-optical features, we have measured the Magnetic Circular Dichroism (MCD), which shows the difference in the optical absorption of the left- and right-circularly polarized states of the light crossing a magnetized medium [2]. Even if recently we shown that the MCD response of bare Au nanoparticles is not negligible [3], it is very weak when compared with a magnetic system like a Fe oxide. Most importantly, the presence of a magnetic oxide surrounding the noble metal leads to a very large total optical absorption and a consequent strong damping of the plasmonic resonance. The aim of this study has been the realization of a new magneto-plasmonic hybrid system, whose magnetic component surrounding the plasmonic moiety, does not affect in a destructive way the magneto-optical response due to the localized surface plasmon resonance: to achieve this result, we have capped 6.5 diameter Au cores with a very thin film of Fe oxide. In order to get a better understanding of the trend in the magneto-optical properties, we have synthesized two nanostructured magneto-plasmonic core-shell system with different shell thickness, 1 nm and 1.5 nm thick Fe oxide layer, and it has been possible to follow the evolution of the interaction between plasmonic and magneto-optical features with the change of the surrounding dielectric material. The hybrid nanoparticles have thus been analyzed using classic optical and magnetometric techniques, focusing on the magneto-optical properties.

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Gold-decorated biosilica nanodevices for nanomedicine

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In recent years, theranostic nanomedicine is emerging as the next generation of healthcare weapons for timely diagnosis and fighting of cancer [1]. An integrated system of nanoparticles (NPs) could be a theranostic nanodevice able to deliver both diagnostic imaging agents and therapeutics at the same time; moreover, the high surface area-to-volume ratios, high loading capabilities and the possibility to modify NPs surface with targeting ligands allow increasing the local concentrations of a contrast imaging agent or a therapeutic at the target of interest, reducing systemic toxicity. To date, a variety of NPs were proposed for nanomedicine. Semiconductor quantum dots, magnetic and colloidal gold NPs were suggested for fluorescent, magnetic and photoacoustic imaging, respectively. Nanovectors made of synthetic porous silica were successfully demonstrated as carriers for drug delivery, even if their long-term safety was not yet demonstrated [2]. More recently, natural porous silica micro- and nanovectors were obtained by diatomite, a material of sedimentary origin formed by diatom remains; targeted drug delivery inside cancer cells, with high biocompatibility and cellular uptake was demonstrated [3]. In this contest, we explored the fabrication of hybrid multifunctional nanodevices made of polyethylene glycol (PEG)-modified diatomite NPs (PEG-DNPs) covered by gold NPs (AuNPs) [4]. In the NPs complex, PEG-DNPs have the function of nanovectors for delivery of therapeutics and AuNPs of imaging contrast agent.

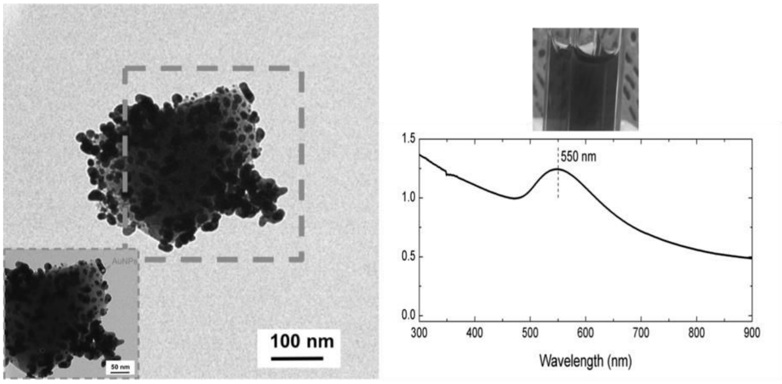

Figure 1: TEM images and UV-VIS absorption spectrum of AuNPs/PEG-DNPs.

In order to realize DNPs decorating with AuNPs (AuNPs/PEG-DNPs), a direct wet chemistry based on one-pot synthesis approach without any prefabricated templates, was developed. The average diameter of AuNPs/PEG-DNPs was estimated as 490 (50) nm, comparable with that of bare PEG-DNPs. TEM analysis, performed to evaluate morphology of nanocomplex, revealed a coating of gold NPs, mainly nanospheres, on PEG modified porous silica surface. UV-VIS absorbance spectrum of AuNPs/PEG-DNPs was characterized by an absorption peak to 550 nm due to coherent localized plasmon oscillations of electrons. Preliminary tests of uptake in cancer cells demonstrated a perinuclear localization of AuNPs/PEG-DNPs.

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Temperature dependent optical constants of noble metals Au and Ag

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In recent years, metallic nanoparticles have been exploited as nanoscale converters of electromagnetic energy into heat.

This approach has the advantage of providing heat on a very local scale, in a remotely controllable way and possibly on an ultrafast time scale. This can be very useful for biomedical applications, such as local hyperthermia and for other applications, such as heat-assisted magnetic recording [1].

The presence of a Localized Surface Plasmon Resonance (LSPR) provides an extra degree of freedom in tailoring the optical absorption of nanoparticles with respect to the material's bulk counterparts. For this reason, the noble metals Au and Ag are the most widely exploited for thermoplasmonics.

In order to model the thermo-optical response of metal nanoparticles, it is necessary to know in detail the dielectric function of the constituent materials as a function of temperature.

Here, we present a study of the temperature dependence of the dielectric function of Au and Ag optical thick films deposited by means of Molecular Beam Epitaxy in UHV ($P=10^{-9}$ mbar). The investigation was performed by spectroscopic ellipsometry (SE) under high-vacuum conditions ($P=10^{-7}$ mbar), employing a portable roll-on/roll-off vacuum chamber set within the arms of a J.A. Woolam M-2000 ellipsometer [2]. The investigated temperature range is between room temperature and 623 K; the optical spectral range is 245-1700 nm.

As a function of increasing temperature we observe definite changes in the dielectric function of the metals.

In the case of Au, we can notice both a broadening of the interband transitions and a significant increase of the intraband contribution (so called Drude tail).

In the case of Ag, interestingly, we observe that an absorption peak in the 310-350 nm wavelength range progressively splits off from the interband transitions, while in the free electron region the changes are less marked. The extra-peak which appears at energies just below the so called X-point must be kept into account in thermoplasmonics measurements/modelling as it directly affects the Ag LSPR spectral range [3].

Our data show that accurately evaluating the temperature dependence of the dielectric function is mandatory to correctly model the thermo-optical properties of metallic nanoparticles systems.

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Towards Ultrafast Single-Photon Sources based on Silicon- Vacancy Color Centers in Diamond

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Narrow-band ultrafast solid-state single-photon sources would play an important role in quantum photonic technologies. We currently develop techniques for the fabrication and optical characterization of single-photon sources based on the silicon vacancy (SiV) color center in diamond [1] and introduce resonant plasmonic nanostructures to modify the photonic environment of the SiV center for ultrafast bright single-photon emission [2].

The SiV center is a promising single-photon source as most of the fluorescence signal is concentrated in a narrow zero-phonon line (> 90 %) at 738 nm, with a room temperature line-width down to about 1 nm. Moreover, the SiV exhibits a short excited-state life-time (~ 1 ns) and a very small inhomogeneous broadening [1]. The photonic environment around a SiV color center can be manipulated using plasmonic nanocones to control the emission rate, the quantum efficiency, the angular distribution and the polarization of the emitted photons.

High- quality plasmonic gold nanocones exhibiting a very sharp tip radius of curvature down to 10 nm are fabricated by electron beam- induced deposition (EBID) of an organometallic precursor followed by sputtering deposition of a gold layer [2]. The dimensions of the nanocones are precisely determined to spectrally match the localized surface plasmon mode with the SiV color center.

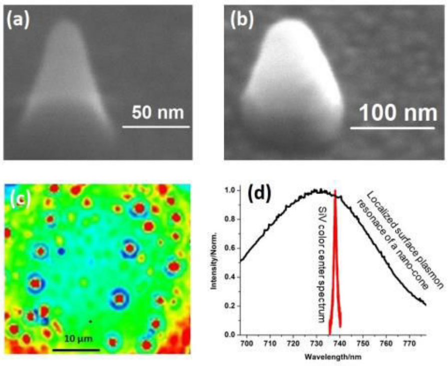

Figure. (a) Platinum based nanocone fabricated by EBID. (b) Gold plasmonic nanocone. (c) SiV color centers in diamond. (d) Spectral matching of plasmon resonance of the nanocone with the SiV color center.

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Low cost TERS tips fabricated by electrochemical etching of 125 µm diameter gold wires

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Tip Enhanced Raman Spectroscopy (TERS) has become a well-assessed technique for nano-spectroscopy, capable of single molecule sensitivity and sub-nanometer spatial resolution. The demand of efficient, stable and reproducible probes for TERS is increasing. The tip is a crucial element in TERS, since it directly influences spatial resolution, reproducibility, and signal enhancement. Gold, thank also to its chemical inertness, is the most common material used for the visible range in plasmonics. At present, the best way to produce high performing and reproducible TERS probes with radius of curvature lower than 50 nm is exploiting electrochemical etching of bulk gold wires with 250 µm of diameter [1]. In this work we have tailored a two-steps electrochemical etching fabrication procedure of highly efficient TERS-active tips [2] to gold wires of 125 µm diameter.

Gold wires are etched in a solution of hydrochloric acid and ethanol, 1:1 v/v. The experimental setup is shown in Fig. 1. The gold wire is placed at the center of a platinum ring, which is dipped few millimeters below the air/liquid interface (Fig. 1b). An adjustable DC voltage generator provides tension between the electrodes. At the beginning of the etching process, occurring mainly at the meniscus, the voltage is set at 5 V for a fixed time and then it is decreased at 2.1-2.3 V till the detachment of the immersed part of the wire. The entire procedure is inspected through a stereo microscope (Fig. 1c).

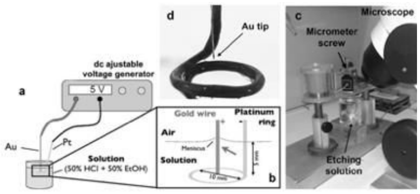

Figure 1: (a) Sketch of the etching experimental setup. The zoomed area (b) shows the details of the tip immersion zone. (c-d) Photograph of the etching setup.

SEM image in Fig. 2 shows a typical double-tapered tip with a radius of curvature of ~12 nm, obtained after this two-steps etching process. A statistical analysis highlights on average this procedure yields ~ 50 % of tips with r < 35 nm and ~66 % of tips with r < 80 nm while ca. 25% are blunt tips.

Finally we successfully test our tips TERS efficiency (in an STM configuration) on different dye molecules grafted on flat gold substrates, namely Methylene Blue (MB), Rhodamine 6G (R6G), Crystal Violet (CV) and Alizarin red s (AZ-s). Using a laser diode emitting at 638 nm we can achieve TERS enhancement factor of 5×10^4 with CV molecules. These probes can be used also for TERS characterization of biological samples such as amyloid oligomers [3].

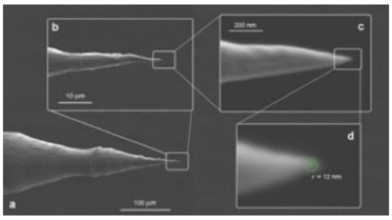

Figure 2: SEM images of a double tapered tip with subsequent zooms ((b), (c) and (d)) on the apical part showing a radius of curvature r ~ 12 nm.

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Evidences of molecular bending in STM-TERS tip-approach curves on different types of thiol self-assembled monolayers grafted on gold film

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Self-assembled monolayers (SAMs) are ordered assemblies spontaneously formed at metal surfaces. Highly ordered SAMs on gold can be formed by Azobenzene thiols, which are linear molecules oriented almost perpendicularly with respect to the substrate surface. Tip-enhanced Raman Spectroscopy (TERS), thanks to the huge field amplification occurring in the near-field region underneath a nano-sized metal tip, can amplify the extremely weak Raman signal of Azobenzene SAMs, allowing also a chemical surface characterization of the sample at the nanoscale [1]. It was demonstrated in a previous work [2] that the electric field inside the gap formed between a gold tip and a gold film, in scanning tunneling mode TERS, can bend the Azobenzene molecules grafted on the substrate. This changes the orientation of the Raman tensor and consequently it affects TERS intensity. Experimental results fit very well with a phenomenologically model developed within the picture of the scattering dipole model [3] taking into account a molecular torque induced by the interaction of the external electric field with the molecular dipole [2].

In this work we extended our investigations combining different techniques to achieve the variation of TERS intensity as a function of the electric field: (i) changing the tip-to-sample distance or (ii) changing the bias voltage keeping the tunneling current constant. Furthermore we also compared our results probing Azobenzene SAMs with differently long alkyl chain, namely with 6 (C6) or 11 (C11) carbon atoms. Despite the fact the molecules are very similar from a chemical point of view, experimental results highlight a clear different behavior between the two molecules (Figure 1). The differences however can be explained considering, within the molecular bending model framework, different elastic properties for the two SAMs. In addition the bending model was improved taking into account also the dielectric properties of both monolayers. Finally the parameters retrieved from the experimental fits are critically discussed and compared.

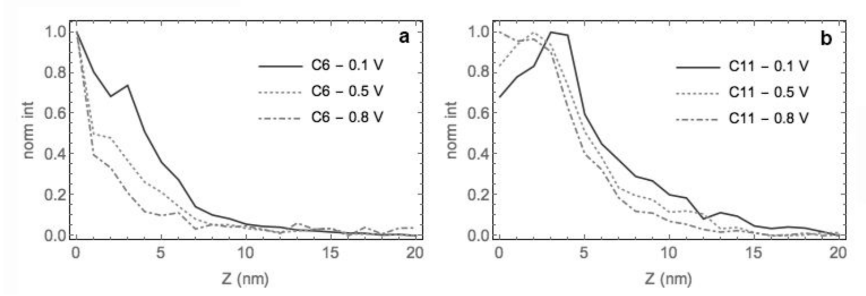

Figure 1: TERS tip-approach curves at different bias voltage for (a) C6 and (b) C11.

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Plasmon-Enhanced Second-Harmonic Sensing in a Microfluidic Chip

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Second Harmonic Generation (SHG) is nowadays a renowned technique for the background-free and non-damaging investigation of living tissues. In the miniaturization process of nonlinear sources, the field enhancements provided by plasmonic nanostructures can effectively compensate for the lack of phase-matching at the nanoscale, making sensing platforms based on plasmonic nanoantennas as nonlinear sources a viable technological option [1, 2]. In fact, nonlinear optical processes are expected to substantially boost the sensitivity of plasmonic sensing platforms [3].

During the last decade, the design criteria that plasmonic antennas should satisfy to provide a suitable SHG efficiency have been the subject of a thorough optimization. We recently reported a multi-element single-crystalline gold nanoantenna designed for efficient SHG at the nanoscale in the near-infrared spectral region [4], and we expanded its paradigm for SHG enhancement to extended metasurfaces of single-element nanoantennas that can be fabricated by standard electron-beam lithography for the specific purpose of nonlinear sensing applications. This allowed realizing a nonlinear platform that can be excited by a weakly-focused light, suitable for integration in standard sensing devices employing low NA optical components [5].

Our first prototypical sensing platform integrates these arrays of non-centrosymmetric plasmonic nanoantennas in a microfluidic chip, as sketched in Figure 1. By monitoring the SHG and reflectance signal variations in response to the flow of solutions with different refractive indices, we characterize the linear and nonlinear sensing performance of the device. We also exploit the normalization to a real-time reference signal kept at a constant refractive index to compensate for possible fluctuations of the pump laser, thus increasing the stability of our measurements. We compare the linear and nonlinear sensing performance of our platform through a figure of merit (FOM) that accounts for the relative change in the measured intensity against the variation of the environmental refractive index n, while the resolution is quantified as the minimum detectable refractive index variation (Δn_{min}). Although the signal-to-noise ratio achieved in both regimes allows attaining the same resolution of $\Delta n_{min} \sim 10^{-3}$, the platform operation in the nonlinear regime features a sensitivity (i.e. the FOM) that is up to 3 times larger than the linear one.

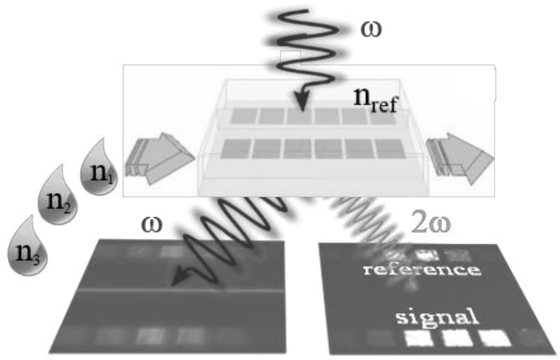

Figure 1: Sketch of the sensing platform. The antenna arrays in the channel are used as sensors, while their reference copy is kept at a constant refractive index n_{ref}, under PDMS. The nonlinear emission (2ω) along with the reflectance (ω) from the sensor depends on the refractive index of the flown solutions (n_1, n_2, n_3).

Thanks to the surface sensitivity of plasmon-enhanced SHG, our results show that the development of SHG sensing platforms with sensitivity performance exceeding that of their linear counterparts is within reach.

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Molecular Plasmonic Switches via Density Functional Tight-Binding Theory

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Quantum plasmonics represents a frontier field between the macroscopic world of photonics and the atomistic one of molecular electronics [1]. Optical nanoantennas with sub-nanometer gaps or put in close proximities of quantum systems, face the promising regime of quantum plasmonics in which a quantum mechanical tunnelling becomes responsible of an electron transfer outside the metallic boundaries. The fascinating connections between molecular electronics and plasmonics are gaining a huge interest in the scientific community and the electro-optical control at the nanoscale of the properties of hybrid metal-molecule systems is becoming a crucial topic.

Here, we attempt a quantum mechanical approach to the problem by proposing a *Time-Dependent Density Functional Tight-Binding* (TD-DFTB) [2] study on the physics of interactions between an optically switchable molecule and a localized surface plasmon excitable in a cluster of a few silver atoms. The plasmonic system is composed by a tetrahedral cluster of Ag_{20}, whose plasmonic response is reported in the TD-DFTB absorption spectrum (black filled curve) of Fig. 1. The molecular system is a molecular photoswitch, the stilbene molecule in its *trans-* configuration, functionalized with a benzene ring and a COOH carboxylic group whose plasmonic response is reported in the TD-DFTB absorption spectrum (grey filled curve) of Fig. 1. As it is evident from the spectra, the molecule is optically active in a spectral range overlapping the Ag_{20} one. The black curves in Fig. 1 correspond to the TD-DFTB absorption spectra of the whole system, sketched in the inset, with each curve corresponding to a different explored distance, going from 5 Å to 2 Å.

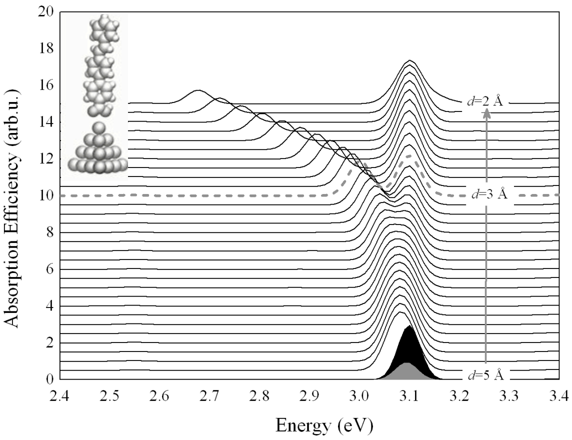

Figure 1: TD-DFTB absorption spectra for a COOH-B-TS molecule put at several distances from an Ag_{20} cluster and oriented perpendicularly to the tetrahedron basis.

The effect of the interaction between the localized surface plasmon of the Ag_{20} cluster and the molecule excitation leads to the appearance of a Rabi-splitting with two well distinguished peaks revealing remarkable strong coupling phenomena, studied by analysing the electronic densities.

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Reconfigurable photonic molecules for sensing application

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Among the numerous nanophotonic platforms investigated during the past decade, photonic crystal cavities represent an excellent toolbox for metrology and sensing applications, due to their ultranarrow resonances localized in diffraction-limited dielectric volumes. A key requirement is the design and control of adjacent nano-cavity modes at the target wavelengths, within an accuracy which is not directly obtainable because of the intrinsic fabrication imperfection. Therefore, post-processing tuning strategies are mandatory in order to create real quantum optics devices. Among the many post-fabrication techniques available it has been recently proposed mechanical actuation with near-field probe [1]. Contact forces induced by the near field tip are employed to tune and probe the optical resonances of a reconfigurable photonic crystal molecule. So far the photonic molecules studied consist of two nominally identical photonic crystal cavities (L3) realized on two parallel membranes separated by a distance *d* along the growth direction. It was shown that the pressure induced by the near field tip is exploited to control the spectral properties of the coupled cavities in an ultrawide spectral range, demonstrating a reversible mode shift. Besides, by monitoring the coupling strength variation due to the vertical nanodeformation of the dielectric structure, this system acts as an optical force sensor with nano-Newton sensitivity.

Here we wish to exploit the in-plane coupling between 4 L3 cavities on double membrane (8 cavities in total) in order to relate the *xy* position of the near-field tip to the induced spectral shift of the coupled modes (fig 1(a)). In this way we expect to realize an optical nanosensor with spatial resolution. The 4xL3 double membrane system is studied from an analaytical point of view and also with Finite Difference Time Domain simulations. The developed model gives full information about the coupled modes of the complex structure. Preliminary near-field characterization shows coupling between the L3 cavities with coupled modes extended in the entire *xy* plane and with vertical spatial parity. The antisymmetric coupled modes spectral configuration and spatial distribution is confirmed both by theoretical and experimental data (fig. 1 (b) and (c)). The analytical model allows a feasibility study in which we demonstrate that mechanical actuation on left and upper cavities unambiguously induces very different coupled modes shifting, showing the importance of double membrane photonic molecules for sensing applications. We propose the investigated structure as a promising platform for force optical sensors with spatial resolution.

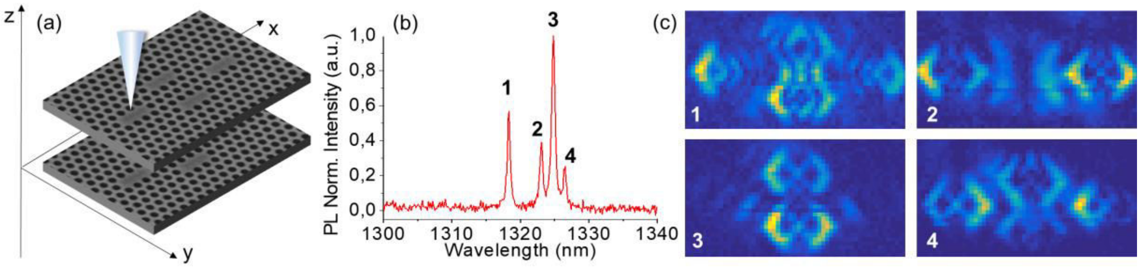

Figure: (a) Sketch of the 4xL3 double membrane structure with near field probe on the left cavity. (b) Experimental near-field photoluminescence (PL) spectrum of a 4xL3 double membrane sample. 1, 2, 3 and 4 indicate the antisymmetric coupled modes of the structure. (c) PL intensity maps acquired at the wavelengths of the 4 modes.

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Probing plasmon polaritons in hyperbolic metamaterials with electron energy loss spectroscopy

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Optical metamaterials are composed of sub-wavelength structures and exhibit unusual electromagnetic properties. These materials can enable applications with sub-wavelength imaging, negative refraction and nanoscale light confinement. One class of them, hyperbolic metamaterials (HMM), are highly anisotropic media with opposing signs of permittivity tensor components in different directions. As such, the motion of free electrons is confined in one or two spatial dimensions, and the dispersion relation of HMMs is hyperbolic [1]. One way to realize these is to deposit alternating metal and dielectric layers. In addition to surface plasmon polaritons, HMMs can support bulk Bloch plasmon polaritons (BPPs) localized inside the multilayer structure that are essentially coupled modes of plasmon oscillations on interfaces inside the material.

These polariton modes can be excited optically with the help of gratings, but excitation with electrons [2] can provide nanoscale resolution, produce additional resonances and separate the effect of the grating from the BPP modes. We have used electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM) to characterize plasmon resonances of HMM structures produced with focused ion beam milling. Aloof beam measurements close to the nanostructures reveal low-energy resonances dependent on excitation location in relation to the multilayer (Fig. 1).

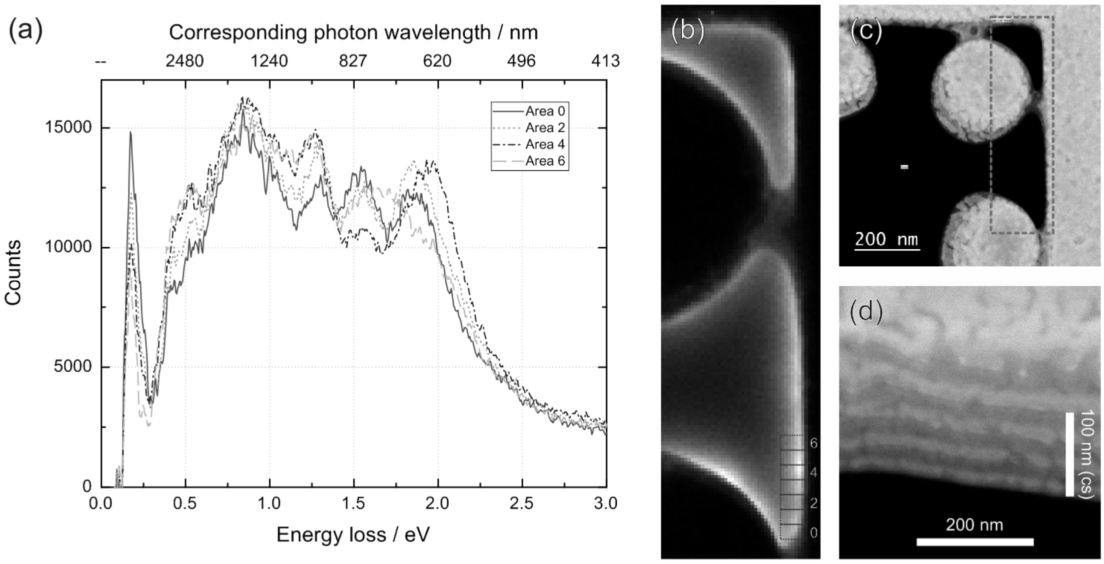

Figure 1: (a) EELS spectra from a HMM Au-Al2O3 multilayer structure at areas marked in the (b) STEM EELS map of energy loss at 1.75-1.85 eV. (c) STEM HAADF image with the EELS image area marked. (d) Scanning electron micrograph of the multilayer edge at a 52° angle.

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Design and Realization of a Nano-guided Hybrid system to implement a Photonic Transistor

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The interplay between quantum dots and plasmonic nanoantennas may have a critical role in the behavior of novel-concept photonics. In this work, the design and first implementation of a photonic-plasmonic transistor is reported. A mixed top-down and bottom-up nanofabrication approach has been used to realize a prototype including a nano-guided hybrid system able to promote the interaction between gold nanostructures and quantum dots in a plasmonexciton exchange procedure. In particular, photopolymerization by evanescent waves has been exploited to fabricate a polymer ridge containing quantum dots directly on top of the hybrid system. A first characterization of the prototype, performed by fluorescent spectrometry, has evidenced a sensitive enhancement of the emission of the quantum dots located in proximity of the apices of Au nanotapers. This enhancement can be efficiently exploited to modulate and route optical signals at high frequency in the novel photonic device.

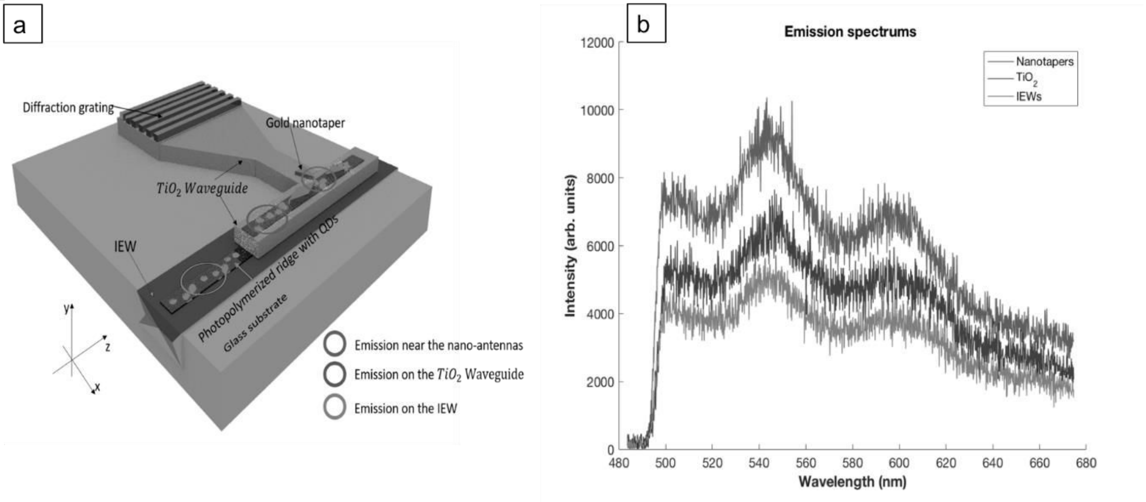

Figure 1: a) The photopolymerized ridge onto the main arm,(orange spheres on the brown layer). The circles represent the areas where it has been used the confocal microscope to collect the emis- sion of QDs into the spectrometer. b)The graph shows the emission in three different cases: close to nanoantennas (blue line), on the TiO_2 ridge (green line), on the IEW (red line).

Plasmonic Properties of Self-Assembled Au/PNIPAM Core-Shell Nanoparticles Studied with Spectroscopic Ellipsometry

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The ordered assembly of nanoparticles is a key challenge in nanoscience. A convenient approach in this regard is to use self-assembly methods, that allow to create ordered arrays of nanoparticles on a relatively large scale (cm^2) and at a low cost [1]. Such platforms of uniformly-spaced, regularly-shaped nanoparticles can find applications from sensoristics to photovoltaics, provided that their optical response is well understood [2].

Here, we present the spectroscopic ellipsometry (SE) data and analysis of a self-assembled system of core-shell nanoparticles, with gold as a core and the thermoresponsive polymer PNIPAM as a shell. The nanoparticles are arranged on an hexagonal lattice and deposited on glass. The interparticle distance is enough to avoid particle-particle interactions, thus the plasmonic properties of the lattice are dominated by the single-particle response. This Au/PNIPAM system is well suited to investigate the variation in the plasmonic response of Au nanoparticles when surrounded by a dielectric environment (PNIPAM), whose refractive index change with temperature.

For the data analysis and interpretation of the SE spectra, since commonly-used Effective Medium Approximations (EMA) don't provide enough accuracy, we applied a model that explicitly takes into account the key morphological parameters of our system (NPs size, shape, interparticle distance, distance from substrate) [3, 4, 5]. The main spectral feature of the SE data, caused by the plasmonic resonance, is correctly matched by the model. Thus, our approach provides detailed information about the optical properties of this system of nanoparticles, and more in general, it constitutes a flexible tool to investigate 2D arrays of plasmonic particles.

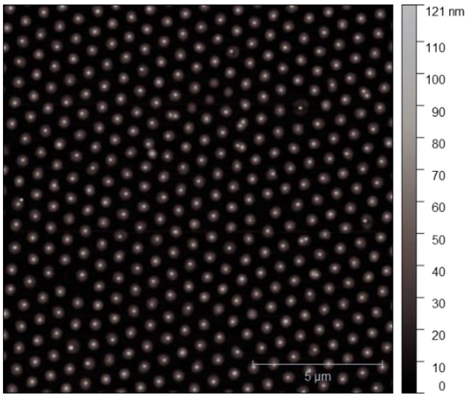

Figure 1: AFM image (15x15 µm^2) of the hexagonal lattice formed by Au/PNIPAM particles

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Plasmonic properties of heated self-organized 2D arrays of Au nanoparticles

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Metal nanoparticles (NPs) have the interesting property of behaving as efficient converters of EM radiation into heat. While this can occur via interband photoexcitation, the presence of a Localized Surface Plasmon Resonance (LSPR) provides an extra degree of freedom to tune and optimize the degree of heating acting on the particles' morphological parameters [1].

The photothermal properties of metal nanoparticles have attracted considerable interest in the last few years due to the appealing possibility to exploit them as nanoscale heaters externally triggered by light. Most of those applications are based on gold nanoparticles due to their tunable plasmon resonance from the visible to the NIR, low reactivity, and possibility of functionalization with many chemical compounds.

Measuring the temperature of EM-heated NPs is a challenging task. For steady-state illumination, rather complex methods have been devised, whereas for ultrafast heating it typically relies on more or less sophisticated models that often do not fully capture the complex temperature-dependent behavior of these nanosystems. Knowing from an independent experiment the NPs temperature-dependent behavior would represent a step forward in understanding their thermoplasmonics response, especially when ultrafast processes are involved. Whereas the temperature-dependent optical response of bulk materials is relatively well investigated [2], much less is known about the nanoparticle analogues, where surface and finite-size effects may strongly affect the plasmonic response.

We report a temperature-dependent investigation of the optical response of densely-packed 2D arrays of gold nanoparticles supported on an insulating nanopatterned substrate [3]. The study was performed by spectroscopic ellipsometry (SE), in the 245-1700 nm spectral range, under high-vacuum conditions and in the 25 °C to 350 °C temperature interval [4]. Using a dedicated effective medium approximation developed for this kind of systems [3], we are able to reproduce the complex anisotropic optical response of this system employing morphological parameters deduced by *ex-post* AFM analysis and feeding into the model the temperature-dependent dielectric functions of Au, deduced in a dedicated experiment. The model yields a very good agreement with experimental data at relatively low temperature.

Though the appropriate T-dependent optical constants are systematically employed, the model is no longer able to reproduce the data obtained at the highest temperatures, underestimating the weight of the so-called Drude tail in the IR spectral range.

Indeed, a satisfactory agreement is attained introducing an effective correction to the Drude term of the dielectric function that keeps into account morphological effects affecting the NP surface, such as softening or melting, that enhance the surface electron scattering rate.

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Development of a Plasmonic Device based on Langmuir-Blodgett films of Ag Nanowires

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The aim of this work is the set-up of a device for early diagnosis in the field of neurodegenerative diseases by exploiting the plasmonic properties of silver nanoparticles and based on Surface-Enhanced Raman Spectroscopy (SERS).

The selected platform is composed of gold, silver or quartz surfaces covered with single/multi layers of silver nanowires (AgNWs), which were transferred from the air/water interface to the solid substrate by means of the Langmuir-Blodgett technique.

Specifically, the silver nanowires deposited at the air/water interface form a stable layer allowing for the acquisition of Langmuir isotherms along several compression/expansion cycles of the AgNWs monolayer. The nanowires are organized in ordered clusters as evidenced by Brewster Angle Microscopy (BAM) images acquired at different surface pressures. By following the above procedure, we observed that an assembly of AgNWs is possible even without thiolation of the nanostructures as commonly reported in literature. [1]

Afterwards, the silver nanowire clusters were transferred by the Langmuir-Blodgett technique at selected surface pressure on silver and gold QCM sensors (fig. 1). Samples with increasing numbers of layers were further characterized by QCM measurements for the determination of the adsorbed mass and by Atomic Force Microscopy (AFM) to evaluate the morphology of the surfaces. UV-Vis-NIR spectroscopy was performed on AgNW samples transferred on quartz slides to explore the plasmonic properties of the system.

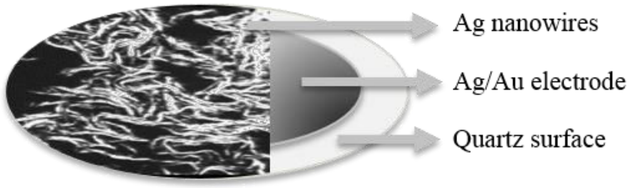

Figure 1: Sensing platform composed of AgNWs (BAM image) transferred on a QCM sensor.

The SERS efficiency of the device was tested on myoglobin as model protein to compare the SERS spectra on varying the number of deposited nanowires. More intense SERS signals were acquired from the substrate containing 5-layers of deposited AgNWs with respect to the substrate containing a lower number of AgNW layers. In addition, more homogeneous SERS signals were obtained as compared to those produced by using different SERS substrates [2].

The presented nanostructured system paves the way towards the construction of promising devices for the advantageous functionalization with proper receptors for the early diagnosis of neurodegenerative diseases by SERS analysis.

Acknowledgements

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Plasmonic multi-resonances in simple geometric platforms

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Localized surface plasmon resonance (LSPR) is generated when light interacts with metallic nanoparticles [1]. A broad range of applications in sensing, lasing, healthcare, tumor treatment and etc. benefit from the tunability of LSPRs based on the nanoparticles size, shape and material, refractive index of the surrounding medium sensitivities [2]. A plasmonic system may exhibit several resonances for different spectral positions. Complex nanostructures such as nanorings, nanostars, nanocrosses, core-shell nanoparticles and nano-clusters of nanoparticles have been developed in order to obtain multi-resonant systems, which are useful for many applications [3-5].

In this work we study a simple nanocylinder and show that it can be used as a multi-resonant system. We demonstrate a method to characterize the different modes of a single gold nanocylinder. We also show a novel approach to observe the plasmonic excited modes using extinction and dark-field spectroscopies. Fig.1 shows the experimental and simulated extinction spectra obtained for a gold nanoparticle illuminated at 50° incidence. The commercial software of Lumerical Solutions, Inc is used for numerical simulations, based on the finite difference time domain method [6]. We show a simultaneous excitation of out-of-plane, in-plane, dipolar and multipolar modes.

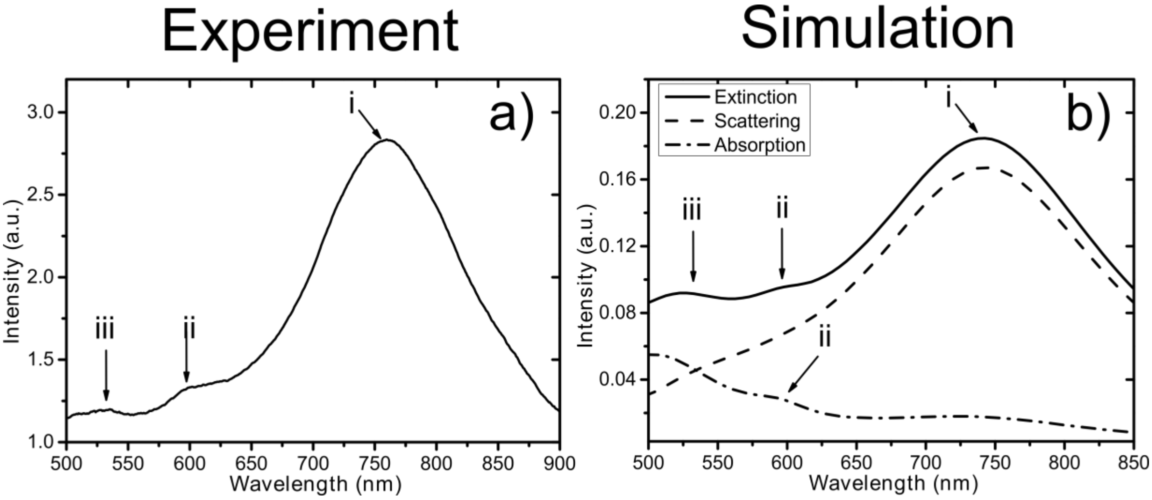

Figure 1. (a) Experimental extinction spectrum of 170nm diameter and 50nm height gold nanocylinder. Illumination is at 50 degree respectively to the normal, (b) corresponding numerical simulation.

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Tunable Surface Plasmon Resonance of Silver Nanoparticles for Plasmon-Enhanced Fluorescence

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Plasmon-enhanced fluorescence of molecular probes is a highly developing field providing a number of new methods in chemical and biomedical analysis. The heightened electromagnetic fields near nanostructured metallic surfaces enhance the excitation rate of the fluorescent species placed in the near field. At the same time, the close vicinity of the metal nanostructures changes fluorescence quantum yield due to density of states effect and possible energy transfer to metal surface [1]. Fluorescent enhancement depends on different factors, like size and shape of the metallic nanoparticles, its extinction properties, distance between them and fluorophore. The optimal distance usually is a result of the balance between the nonradiative energy transfer which dominates on the short distance and radiative processes. There are number of ways to control this distance and optimize the enhancement. Majority of them are based on the chemical or vacuum deposition of the dielectric spacer between the metal nanoparticle and fluorophore.

The effect of this dielectric spacer and, then, surrounding refractive index on the localized surface plasmon resonance (LSPR) position was studied before [2, 3], but this factor is rarely taking in account in the studies of fluorescence enhancement (or Raman enhancement). With a growing of the dielectric layer the LSPR band shifts to a longer wavelength and increase in intensity. These change accords with an electromagnetic theory. Then surrounding medium allows to control the plasmon peak position and its intensity. However, the influence of the dielectric layers of different thickness on the fields distribution, radiative and nonradiative processes need further investigation. We report on the study of the change of electric field distribution around the silver nanoparticle covered with dielectric layers. Finite difference time domain method was used for numerical simulations [4]. Experiments were made on the deposited colloidal silver film. As a spacer we used polyelectrolyte layers which allows to control the thickness in nanometric scale. We confirm the significant extinction increase and red shift with a number of layers and study the fluorescence change. Simulations show that the maximum of the electric field relocate from the bottom to the middle part of the nanoparticle, which can result in change of the fluorescence enhancement efficiency. Usually dipolar mode is localized near the substrate, however the equalization of the local refractive index result in the redistribution of the field. The results show that it is possible to tune the metal nanoparticle resonance for the need of the experiment. For each combination of the nanoparticle and label, the optimized distance between them depends on the refractive index of the spacer as well.

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Optically tunable 3D photonic structures in rigid and soft polymers

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Polymeric matrices offer a wide and powerful platform for integrated photonics, alternative to the well-established silicon photonics technology. The possibility to integrate, on the same chip, different customized materials allows for many functionalities, like the possibility to dynamically control the spectral properties of single optical components. Within this context, we will report the fabrication and characterization of three dimensional photonic structures made of a combination of both rigid and tunable elastic polymers. By using a 3D photolithographic technique (direct laser writing) [1], in a single step process, every building block of the polymeric circuit is fabricated with nanometric resolution.

Using this platform, a new type of operation was introduced through the integration of tunable photonic components, made by liquid crystalline networks (LCN) that can be actuated and controlled by a remote and non-invasive light stimulus [2]. Depending on the architecture, it is possible to integrate them as elastic actuators or as constituents of the photonic structure itself.

We demonstrated a grating structure with sub-millisecond time response for optical beam steering exploiting an optically induced reversible shape-change (Figure 1a). By creating a structured material out of photo-responsive polymer (LCN), we show that it is possible to induce mechanical deformation, and hence a huge change in the optical response of the material, by simply shining light on it.

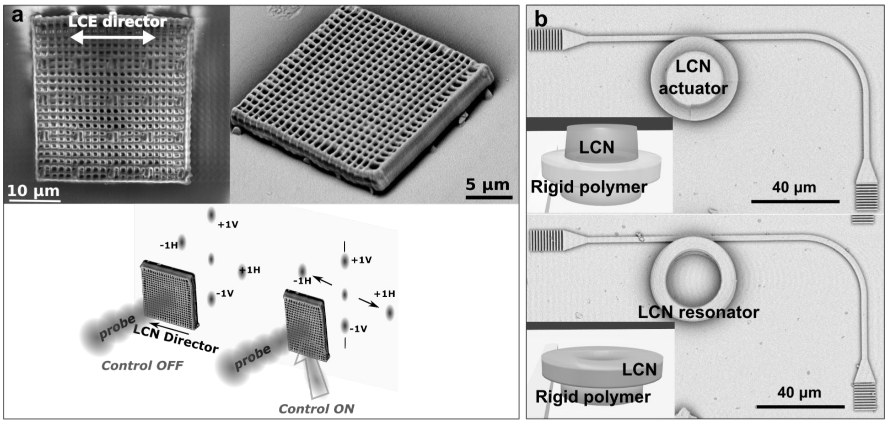

Figure 1: a) Scanning electron microscope (SEM) images of LCN grating beam steerers and light controlled working mechanism. b) On the top, SEM image of the waveguide coupled to Ip-Dip WGM resonator with LCN actuator placed on the top. On the bottom, SEM of the waveguide coupled to LCN ring.

Further optical functionalities can be addresses through integrated photonic circuits where monomodal waveguides and whispering gallery mode resonators (WGMR) enable signal manipulation and filtering. Tunability has been obtained following two different strategies (Figure 1b): in one case the LCN is used as mechanical actuator that slightly and finely changes the shape of the polymeric WGMRs, while in the second case the LCN is used as truly photonic material to fabricate the WGMR itself. For the first time, the spectral response of high quality factor photo-responsive deformable resonators, is remotely and reversibly controlled by a local and non-invasive light stimulus.

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Study of aptamer immobilization on plasmonic surfaces by SERS analysis

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Surface-enhanced Raman Scattering (SERS) is an excellent technique that can be used to develop diagnostic assays for the sensitive detection of small molecules in complex samples, taking advantage of plasmonic nanostructures [1]. This sensitivity can be further enhanced by combining SERS with the most advanced molecular recognition systems, such as aptamers, DNA or RNA sequences that fold into a 3D structure, creating an artificial receptor able to bind specific target molecules [2-3].

In this work, the immobilization of a model aptamer, previously used for mycotoxin detection [4], was studied by SERS analysis, taking into account the different Raman signal acquired when oligos approach the plasmonic nanostructures with different orientations. In particular, different synthetic oligos carrying a thiol group at the 3’ (Fig. 1a) or at the 5’ terminal (Fig. 1b) were grafted on porous silicon membranes, decorated with Ag nanoparticles (NPs), by adopting previously optimized methods [5]. The immobilization was assessed by SERS mapping, using both labelled and unlabelled aptamers. The presence of a Raman reporter at the free terminal allowed to understand that the two aptamers bind to the surface with different orientations, preserving their folded structure, predicted by bioinformatics tools. Indeed, in the label-free configuration, it was possible to recognize that the two aptamers reached a similar surface coverage (Fig. 1c, top). However, the results obtained by grafting the labelled aptamer at its 5’ end, showed that the Raman signal of the reporter was significantly higher in comparison to the 3’ terminal (Fig. 1c, bottom). This can be explained by a lower distance of the reporter from the Ag NPs for the 5’ thiolated sequence in comparison to the other one, suggesting that the aptamers bind according to the schemes in Figure 1b and 1a, respectively. This effect is related to the higher electromagnetic enhancement for molecular oscillators close to the plasmonic NPs.

The uniformity of the coverage was then investigated by comparing the SERS signal variability over the mapped surface. A greater fluctuation of the SERS intensity was detected in case of the 5’ thiolated aptamer, probably due to a higher conformational variability for the oligo interacting with the silver surface. For this reason, a third aptamer, whose sequence was shortened at the 3’ terminal, maintaining the target binding site, was tested. The reduced distance of the Raman reporter from the surface and the vertical orientation of the aptamer boosted the SERS intensity, while keeping a good signal uniformity, showing that such functionalization is suitable for the subsequent use in competitive SERS assays for aflatoxins detection.

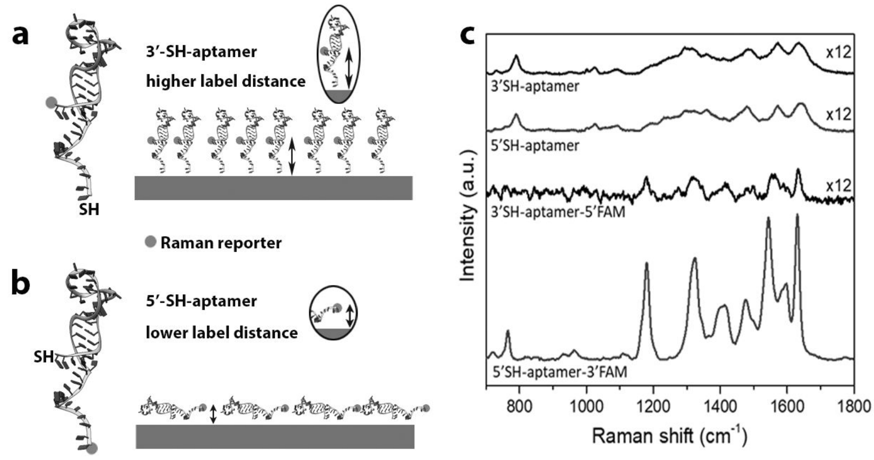

Figure 1: Scheme of the aptamer immobilization at the 3’ (a) or 5’ end (b). (c) Average SERS spectra acquired on the samples functionalized with the 6-FAM labelled and unlabelled aptamers.

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Ultra-thin plasmonic nanopores for single molecule detection

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In the past two decades, many research groups in the world paid a significant attention to the development of nanopore-based sensors [1]. This remarkable recognition is due to fascinating perspectives in biotechnology and nanomedicine, such as detecting extremely small DNA molecules and proteins at the single/few entities limit [2]. Among the various geometries and materials used in order to realize efficient nanopore sensors, plasmon-based architectures are the least explored due to the intrinsic challenge in the fabrication procedures, which practically hinder a large-area reproducible production of extremely small pores (i.e. 2-10nm) [3].

In this work, we aim to study the optical response of extremely thin silver nano-disks with a pore at the center fig.1 (a). For a normal incident light, the absorption spectra of a disk of 7nm thickness and 130nm diameter with three different pore sizes (d=2,8,14 nm) show two resonant peaks, one near 500 nm and the second around 1 μm as shown in fig. 1 (b). The electric field intensity map of the first resonance (normalized to the impinging radiation) indicates that the light is concentrated and enhanced up to 200 times at the center of the pore (see fig. 1 (c)). As expected, the peak position is increasingly red shifted by widening the pore size. The second resonance shows a clear dipolar character as well as a remarkable concentration at the center of the pore fig.1 (d).

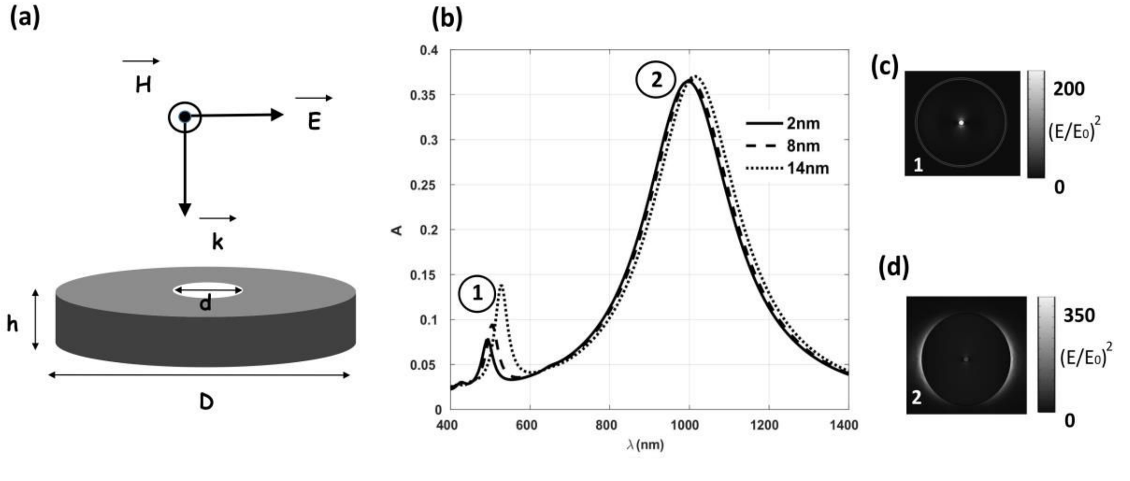

Figure 1: (a) Schematic representation of the 7 nm thickness silver nano-disk of diameter 130 nm with a pore of few nanometer hole at the center. (b) Absorption spectra of a 2,8,14 nm pore diameter. (c) and (d) are respectively the maps of the electric field intensity of resonance (1) and (2) pointed out in (b).

As a conclusion, the optical response of this structure is a promising starting point in the process of developing an efficient sensor for single molecule detection and DNA sequencing. These silver nano-disks with the pore will be fabricated and integrated in a device in order to be characterized, optimized and utilized in the detection procedure.

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Self-Assembly of Magnetic Nanoparticles over Plasmonic Nanoantennas

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Metallic nanostructures supporting localized surface plasmons are able, thanks to their shape, size and composition, to collect, enhance and confine the external electromagnetic field carried by the incident light. The use of the magnetic field can add an extra functionality, leading to optically-controlled nanomagnetism [1].

Through a proper combination of nanostructured plasmonic surfaces with magnetic materials, magnetoplasmonic nanoantennas can be realized. The plasmonic nanostructures can focus the electromagnetic field in nanometric hot-spots around themselves, and by assembling the magnetic material in these points we aim at tailoring light-matter interactions at the nanoscale.

As a magnetic material we chose to use magnetic nanoparticles (MNPs) because of their easiness in tuning their magnetic properties just by varying nanoparticles' size and composition, acting on basic synthetic parameters. The synthesis is performed by thermal decomposition of organometallic precursor in high-boiling solvents, a method that leads to a colloidal solution of nanoparticles with a narrow size distribution [2]. The nanoparticles are then characterised structurally, magnetically and optically.

The nanostructured surfaces are realized by Göteborg University through soft lithographic techniques (i.e. hole-mask colloidal lithography using polystyrene nanospheres) [3].

The magnetic nanoparticles are then assembled in monolayers on the plasmonic surfaces by means of linear bifunctional molecules: exploiting the high affinity of thiols for gold, self-assembled monolayers of molecules are realized upon the gold nanostructures, leading to regular surfaces that expose the other moieties, which will bind to the nanoparticles' surface.

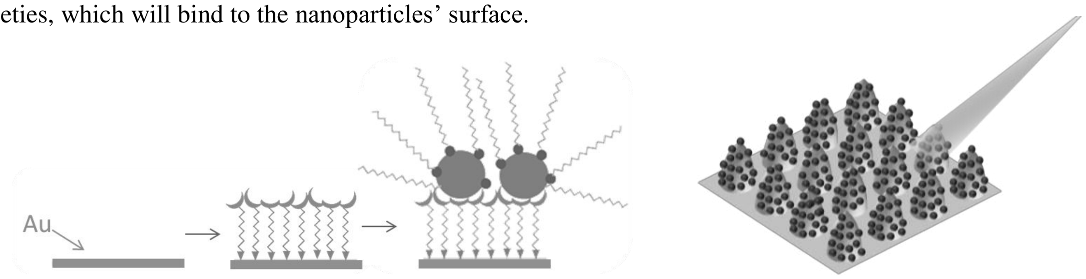

Figure 1: Sketches of the assembly of MNPs on gold nanostructures.

The assembled systems are characterised topologically, structurally, magnetically and optically. Finally, using a homebuilt Magnetic Circular Dicroism apparatus (MCD) we can check the effective interplay of light and magnetism to see how the two materials interact [4].

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Near Single Cycle Surface Plasmon Polariton Generation by Rotating Wavefront Pulses

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A concept for the efficient generation of surface plasmon polaritons (SPPs) with a duration of very few cycles is presented [1]. The scheme is based on the coupling of a laser pulse with wavefront rotation [2] (WFR) with a grating target, so that the resonance condition for SPP excitation is satisfied only for a brief time interval (Fig.1). The feasibility and robustness of the technique is investigated by means of simulations with realistic parameters. In optimal conditions, we find that a 29.5 fs pulse with 800 nm wavelength can excite a 3.8 fs SPP (~1.4 laser cycles) with a peak field amplitude 2.7 times the peak value for the laser pulse (Fig.2).

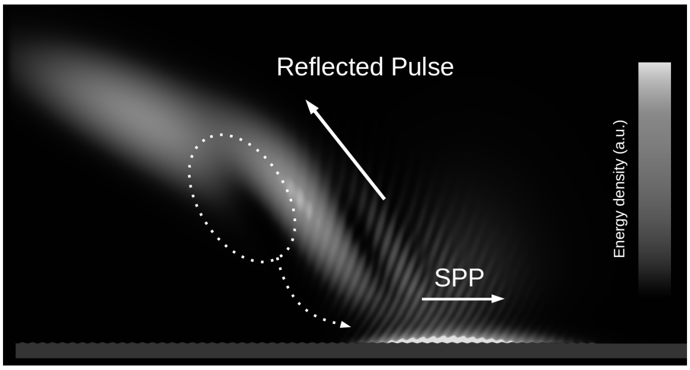

Figure 1: WFR pulse impinging on a grating and generating a SPP. The duration of the latter is proportional to the time in which the resonance condition is satisfied.

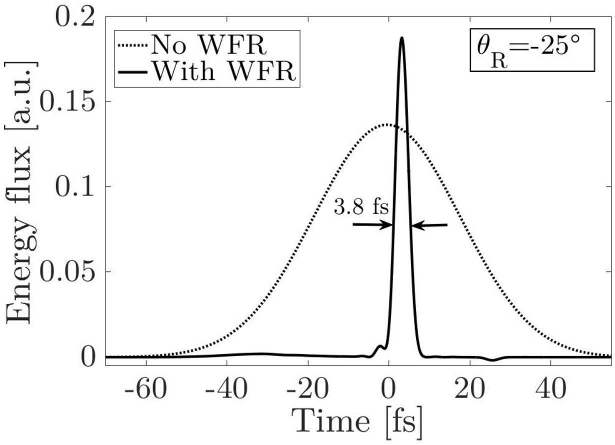

Figure 2: Energy flux of a SPP generated by a WFR pulse compared to one generated without WFR.

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Investigating Silver Nanoparticle Prepared by Pulsed Laser Ablation in Liquid as Simple, Cost-Effective and Reproducible SERS Substrates

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Colloidal noble metal nanoparticles (NPs) are of great interest for numerous applications in a wide range of disciplines, form materials science to medicine. Properties such as size, shape and composition dictate the behavior of these nanostructures and their knowledge is fundamental for an optimal application.

This is particularly true when metallic NPs are used as a tool to improve the performances of a spectroscopic technique, like in the case of Surface Enhanced Raman Spectroscopy (SERS) [1]. In SERS, the Raman signal of molecules deposited on nanostructured metal substrates can be enhanced by several orders of magnitude, depending on the shape, size and spatial density of the deposited nanoparticles. For SERS, silver (Ag) is the most universal substrate due to the broad plasmon resonance in the visible/near infrared region, high stability and easy preparation [2].

Metallic nanoparticles can be prepared by a chemical approach (Bottom-Up) that involves the reduction of metal ions and subsequent growth of nanostructures, or a physical approach (Top-Down) that generates nanostructures by fragmenting a bulk metallic target, generally by laser ablation.

While most of the works involving SERS have used colloidal dispersions of Ag nanoparticles, prepared by chemical reduction of Ag^+ salts, or Ag-coated roughened substrates, few publications proposed the use of nanoparticles prepared by pulsed laser ablation in liquid (PLAL). In this method, a metallic target is immersed in a suitable solvent, that can contain a stabilizing salt or compound, and irradiated with sufficiently powerful and consecutive laser pulses in order to produce a suspension of nanoparticles.

PLAL shows some advantages when compared to conventional chemical preparation methods, namely the absence of reagents in the suspension and a higher control over the NP morphology by changing the ablation conditions.

In this study, we present, as part of an ongoing project, the investigation of Ag-NPs prepared by PLAL as a substrate for SERS.

Various batches of NPs were prepared, varying the ablation conditions, and characterized. The same NPs were then used to prepare SERS substrates and their efficiency was tested using standard solutions of organic dyes.

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Grating-coupled Surface Plasmon Resonance (GC-SPR) optimization for phase-interrogation biosensing in a microfluidic lab-on-chip

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Surface Plasmon Resonance (SPR) refers to the collective oscillation of conduction electrons at the interface between a conductor material (i.e. gold) and a dielectric (i.e. nucleic acids or proteins) upon light interaction. SPR-based sensors, with the advantage of being label-free, enzyme-free and real-time, are of growing interest in biomedical research [1]. Plasmonic biosensors have been developed to reach higher sensitivity, while offering a cost-effective and versatile instrumentation [2]. Here we describe a sensing platform based on phase-interrogation method, which entails the exploitation of a nanostructured sensor based on a grating coupler [3]. The azimuthal rotation of the grating was found to have a deep impact on the enhancement of the plasmonic response in respect to the null rotation [4]. This technique is particularly suitable for integration of the plasmonic sensor in a lab-on-chip platform and can be used in a microfluidic circuit to ease the sensing procedures and limit the injected volume [5]. The proposed sensing platform, based on polarization scan, is very cost-effective and can be miniaturized for direct in-field use. Numerical simulations by Chandezon method were used to evaluate the contribution to the sensitivity of polar and azimuthal angles. The careful determination of suitable experimental parameters by numerical simulations lead to a 30 to 50% enhancement of sensitivity opening new possibilities for applications in biomedical research field.

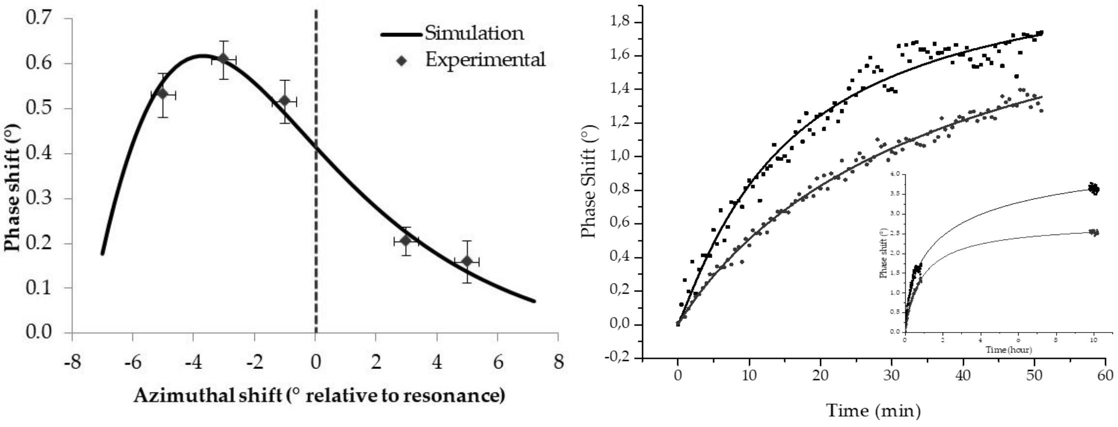

Figure 1. (Left) simulated curve versus the experimental data (dots) of the phase shift for azimuthal rotation. The dotted vertical line represents the resonant azimuth for the given parameters in milliQ water. Azimuthal shift from resonance enhances phase shift in response to 200mM NaCl solution in milliQ water. (Right) Biotin-SH functionalization shows higher phase shift for optimized condition in the first hour of the experiment and after several hours when the functionalization is almost completed (inset). Data were fitted with Hill curves obtaining values of the reduced $X^2 > 0.999$.

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1D-Photonic Crystal Biochips for Erbb2 Cancer Biomarker Detection

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Different kind of disposable biochips are nowadays available for several clinical applications, ranging from cancer to cardiovascular diseases. The optical biochips we developed, are a promising tool for the detection of cancer biomarkers, in our specific case of the ERBB2 cancer biomarker. ERBB2 is a tyrosine kinase receptor that regulates a variety of cell activities such as proliferation, growth and differentiation [1]. The reason of the wide use of ERBB2 is that its amplification and overexpression occur in 20–30% of breast cancers, that are the most common for women. Although the method, established by international guidelines, that sets the limits to adopt a target therapy based on the Trastuzumab administration, is accurate and highly standardized, it depends on semi-quantitative scores and yields a discontinuous scale.

Herein, we present an alternative analytical method, able to overcome these drawbacks by making use of such novel biochips based on one-dimensional photonic crystals (1DPC) to precisely quantify low concentrations of ERBB2 cancer biomarker in biological complex matrices. To achieve this goal, such biochips are mounted on an optical platform, which we developed, that combines both label-free and fluorescence detection modes. The 1DPC biochips are properly designed to sustain a Bloch surface wave (BSW), whose excitation is obtained by a prism coupling system, like in the surface plasmon resonance (SPR) technique [2]. As in SPR, the excitation of such surface wave leads to a dip in the angular reflectance spectrum, whose position shifts depending on the refractive index changes, due to biomolecular interactions that take place at the surface. Furthermore, by adding fluorescence labels at the 1DPC surface, the enhanced fluorescence mode, can be exploited to obtain further information with the advantage of allowing a lower limit of detection (0.3 ng/mL) with respect to the label-free approach (16 ng/mL) [3].

The herein proposed disposable biochips, together with the reading platform, enable to successfully discriminate ERBB2 levels in several different lysates overexpressing. The results obtained suggest that our method would have promising applications in the breast cancer treatment, since it is well below the threshold set by the FDA (15 ng/mL), which defines limit acceptable concentration of ERBB2.

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Spin crossover nanostructures bistable behavior on surfaces

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Spin crossover (SCO) complexes are molecules able to change their magnetic state by varying the temperature [1] or via external stimuli such as pressure [2] or light irradiation [3]. Molecular electronics aims to substitute the standard inorganic materials with molecular materials [4] and SCO molecules have been proposed by several groups of the molecular magnetism community [5], as good candidates for the development of multi-functional molecular electronics [6]. My PhD is focused on the nano-structuration of SCO molecules by sublimation in UHV [7] with the purpose of integrating them in molecular devices. The chemical and magnetic characterization of SCO-based 2D nanostructures are fundamental prerequisites for the realization of these multifunctional devices. I will show the characterization of the bis[hydrotris (1,2,4-triazol-1-yl)borate]iron(II) spin crossover complex [8]. Nanostructuration has been carried out on Au single crystal and HOPG. Firstly, the complex has been characterized with XPS [9] in the bulk and, subsequently, in the sublimated film, confirming the intactness of the system after nanostructuration. Then, the magnetic behaviour of the SCO has been studied by X-ray Absorption Spectroscopy at variable temperature [10] and under light irradiation. This powerful investigation has confirmed the spin crossovering at the nanoscale, showing remarkable differences between the two investigated surfaces.

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Radiative Plasmon Decay Rates in Nanoparticles

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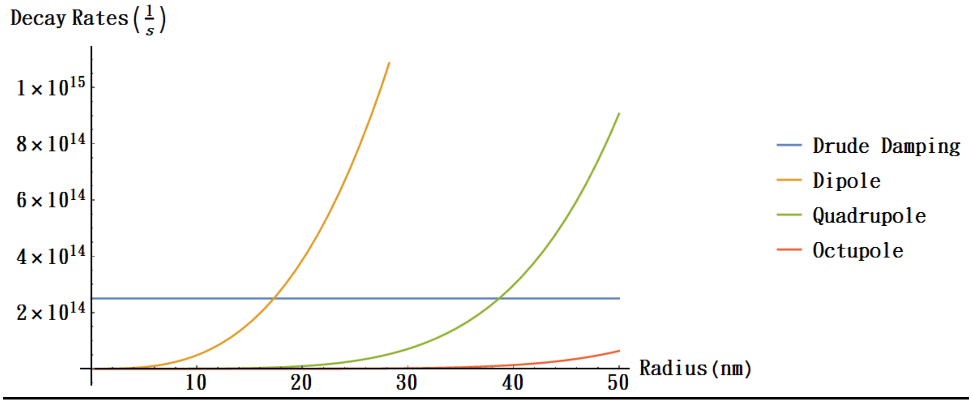
In the transient analysis of the electromagnetic scattering from nanoparticles, the understanding of the damping mechanisms and the calculation of the lifetimes of the plasmon modes are of central importance. So far, this problem has only been addressed in the limit of small particles, where the lifetimes are calculated in the electro-quasi-static approximation. However, when the size of the particles is comparable to the incident wavelength, the electro-quasi-static approximation breaks down, and the continuum of radiative modes have to be rigorously included in the model.

In this work, we focus on the problem of calculating the radiative decay rates of the plasmon modes in the full-wave regime and, by using an electro-hydrodynamical Hamiltonian formulation, we are able to deal with particles of every size and shape. As an example, we investigate the case of the single sphere, and we derive the associated lifetimes as functions of the radius.



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SPR microfluidic platform based on multimode plastic optical fiber for the detection of sepsis biomarkers

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A plastic optical fiber (POF) biosensor, based on surface plasmon resonance (SPR) and integrated into an ad-hoc developed thermostated microfluidic platform, is presented. The POF (1 mm in diameter) was side-polished in order to expose the fiber core; then, a buffer layer (photoresist Microposit S1813, with a refractive index greater than the one of the fiber core) was spinned on the fiber core and, finally, a gold film was sputtered, as the plasmonic responsible layer.

The microfluidic platform is constituted by: 1) an aluminum bottom part (30 mm × 30 mm × 15 mm) containing the housing for the sensor head, the groove housing for the POF and the housing for a thermistor for the temperature detection; 2) a PDMS top part (20 mm × 20 mm × 10 mm) containing the flow channel (9.5 mm × 2 mm × 1 mm, volume 20 μL) and the fluidic inlet and outlet. The platform is in contact with a TEC system based on Peltier cells, which allows stabilizing the temperature of the flow-cell at (23 ± 0.1) °C.

C reactive protein (CRP) is an important protein biomarker: high levels of CRP in serum are observed after trauma, tissue necrosis, infection, and myocardial infarction and are associated with an increased risk of cardiovascular diseases [1]. In the case of infection and acute inflammatory events, such as sepsis, CRP concentration may increase up to 1000-fold, whereas its concentration in healthy human serum is lower than 1 mg L^{-1}.

The SPR-POF sensor platform integrated into the microfluidic system was initially tested and validated by performing a model IgG/anti-IgG assay in buffer and in serum [2]. Afterwards the sensing platform was applied to the detection of CRP spiked in serum at increasing concentrations ranging from 10 μg L^{-1} up to 500 mg L^{-1}. A working range of 0.006–70 mg L^{-1} and a LOD of 0.009 mg L^{-1} were achieved [3]. These results are among the best compared to other SPR-based biosensors for CRP detection, especially considering that they were achieved in a real and complex medium, i.e. serum. Since the sensor performances are those requested for many clinical purposes, the whole biosensing platform could well address the continuous request of the physicians for high sensitive, easy to realize, real-time, label-free, portable and low cost sensing platforms for future lab-on-a-chip applications.

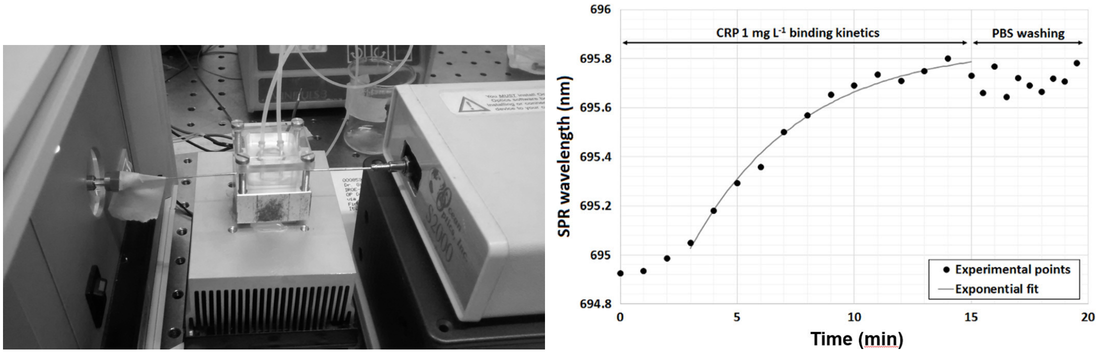

Figure 1. Left: picture of the experimental setup with the POF integrated into the thermostated flow-cell, the white light source and the spectrometer. Right: sensor response curve during the binding interaction of the specific antigen (CRP 1 mg L^{-1}) with the immobilized anti-CRP antibody.

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"Stainless" Gold Nanorods: Preserving Shape, Optical Properties, and SERS Activity in Oxidative Environment

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Gold nanorods (Au NRs) are intensively investigated as SERS-active materials. Their localized surface plasmon resonance (LSPR), which gives rise to a strong enhancement of the local electromagnetic field near their surface, can be tuned over a wide range of wavelengths (from Vis to NIR) by adjusting their aspect ratio. As a result, they can be suitably designed to match the energy of different Raman laser sources and control charge-transfer processes with specific target molecules.

However, one of the main limitations to the application of gold nanorods (Au NRs) as Surface Enhanced Raman Scattering (SERS) probes for in situ monitoring of chemical and biochemical processes is their instability in oxidative environments, like those occurring in degradation of organic pollutants, as well as in monitoring of cellular oxidative stress. Oxidative environments induce progressive anisotropic shortening of the NRs, which are eventually dissolved once this process has been completed. As a result, the SERS response is not reproducible and progressively vanishes during the experiment. Finding SERS-active Au NRs that can tolerate harsh conditions without altering their optical properties and SERS response is a key step toward a full exploitation of their unique capabilities.

Here we will compare the resistance to oxidation of two types of Au NRs (type A and B), obtained respectively through traditional, hexadecyltrimethylammonium bromide (CTAB)- and binary-surfactant mixture routes. A careful control of the key parameters influencing the oxidation process (size of the NRs, concentration of the free Br- ions) allowed the selection of Au NRs that can tolerate oxidative environment without any modification of their optical properties. Their superior performance is demonstrated in a series of SERS experiments under oxidative conditions, in which the degradation of different organic dyes (methylene blue and crystal violet) can be monitored through several detection cycles carried out on the same clusters of Au NRs.[1]

These hallmarks make these "stainless" Au NRs attractive tools for ultrasensitive diagnostic under real working conditions and were also exploited for developing 3D SERS-active platforms based on cellulose supports.

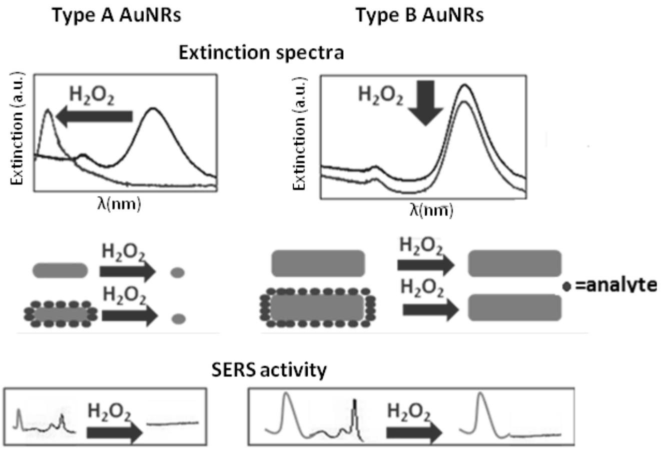

Figure 1. Comparison between the behavior of Type A and Type B AuNRs, before and after the addition of an oxidant: extinction and SERS spectra.

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