PLASMONICA 2024

Workshop on Plasmonics and Nano-optics

Messina, 10-12 July 2024

ET IPSAN CIVITATEN IENEDICIMUS



The Italian Community of Plasmonics and Nano-optics



Università degli Studi di Messina





About

Plasmonica

Plasmonica was kickstarted in 2013 by a collective of young Italian physicists to provide a forum for researchers in nano-plasmonics – back then still a pioneering endeavor within the Italian landscape. Eleven years on, this community has thrived and vastly expanded its reach also internationally; its scope has correspondingly broadened to cover many active areas of nanophotonics, including nanoresonators, meta-optics, thermo-, magneto-, and quantum-plasmonics, optical forces at the nanoscale, ultrafast and nonlinear processes, chiral properties, surface- and tip- enhanced spectroscopies, and biological sensing.

Since 2015 *Plasmonica* has been affiliated to the Italian Society of Optics and Photonics (SIOF) as the Plasmonics and Nano-Optics Working Group. Nonetheless, its core mission remains the same: gathering the nanophotonics community in Italy – which is naturally spread over different disciplines such as physics, engineering, chemistry, and biology – as well as facilitating scientific collaborations, personnel exchange and dissemination events. Another distinctive feature of *Plasmonica* is its pledge to cater to early-stage researchers, by encouraging their scientific maturation and providing a platform to showcase their research. These values shape the two principal activities of the group, namely the organization of a **yearly workshop** and a **residential school** every two years. These in-person events are conducted in English, to foster the engagement with the wider international scientific community.

Credits

| Workshop organizing committee | Plasmonica steering committee |
|---|---|
| Alessandro Belardini, Sapienza Univ. Roma Maria Grazia Donato, CNR-IPCF Messina Antonino Foti, CNR-IPCF Messina Pietro G. Gucciardi, CNR-IPCF Messina Salvatore Patanè, Univ. di Messina Ilaria Rea, CNR-ISASI Napoli Rosalba Saija, Univ. di Messina | Antonino Foti, CNR-IPCF Messina Nicolò Maccaferri, Umeå University Chiara Novara, Politecnico di Torino Emilija Petronijevic, Sapienza Univ. Roma Attilio Zilli, Politecnico di Milano |
| Workshop scientific committee | |
| Leonetta Baldassarre, Sapienza Univ. Roma Stefania D'Agostino, CNR–NANOTEC Lecce Emiliano Descrovi, Politecnico di Torino Fabrizio Giorgis, Politecnico di Torino Riccardo Sapienza, Imperial College London | Paolo Biagioni, Politecnico di Milano Francesco De Angelis, IIT Genova Carlo Forestiere, Univ. Federico II Napoli Francesca Intonti, Univ. di Firenze Salvatore Savasta, Univ. di Messina |



The Workshop will take place in the auditorium Vittorio Ricevuto of the University of Messina at the Papardo University Campus in the northern part of the city. The Papardo Campus main entrance is in Viale Ferdinando Stagno d'Alcontres 31. You can look up campus location and accessibility on Google Maps.

The eduroam Wi-Fi network is available everywhere on campus.

How to reach the Campus

You can reach the Papardo campus by public transports (ATM Messina). The bus stop of the campus is indicated in the ATM timetable as "Viale Stagno D'Alcontres – via Archimede" (sometimes simply "Viale Stagno D'Alcontres") and is located in front of the main entrance at the intersection between Viale Ferdinando Stagno D'Alcontres and Via Archimede. The main lines are:



- 24. NB: It reaches the campus going through "La Panoramica dello Stretto" and not through via Consolare Pompea (aka "La Litoranea");
- **39 S. MARGHERITA PAPARDO**. NB: It reaches the campus going through "La Panoramica dello Stretto";
- 33 BIS PONTEGALLO PAPARDO. NB: Be careful not to catch the line 33;
- 32 PONTE GALLO MORTELLE TERMINAL MUSEO. It reaches the campus going through via C. Pompea (aka "La Litoranea");
- **31 TORRE FARO PAPARDO**. NB: It usually works as a shuttle between Torre Faro and Papardo but few rides per day can reach the central station through via C. Pompea.

Alternatively the line 1 - Shuttle 100 crosses Messina along its whole coast line (each 15 min). The

bus stop at the intersection between Viale Stagno D'Alcontres and via C. Pompea is at only 15 min walking from the Papardo Campus.

Tips: The MUSEO Terminal at "Annunziata" (Northern terminal of the TRAM line) usually offers more bus options to reach the Papardo Campus compared to Stazione Centrale/Cavallotti Terminal.

At each bus stop you can scan a QR code knowing the estimated waiting time.

You can also use the offical ATM App (**ATM MovUP**) or **Moovit** to find out about available public transport in real time.

After midnight the connection between Torre Faro and the city center is guaranteed by the night bus (each 30 min) **1N – Shuttle NOTTURNO**

Instructions for presenters

Contributed **talks** are allocated a 15 minutes time slot (12' talk + 3' questions). Please bring your slides in a USB stick and upload them to the lecture hall's computer well in advance of your talk.

The recommended format for **posters** is A0 with portrait orientation. Please, hang your poster at the beginning of the workshop. You can leave on the stands for the whole duration of the event and you will present when your poster session is planned.

All participants are welcome to follow and engage with our **social media** accounts, with the handle **@Plasmonica** on Twitter, Instagram and LinkedIn. We also encourage you to include the hashtag #PLASMONICA2024 when tweeting about the Workshop.

Social dinner

The social dinner will take place at the **Bellavista**, a restaurant which combines the flavors and culinary traditions of Sicily, with the innovation and creativity of Nouvelle Couisine, focusing on the freshness of raw materials and in particular of fish. The most direct route there from the conference venue is the bus line 31 from the Viale Stagno D'Alcontres – via Archimede stop near the Papardo campus to the "via Circuito" stop.

Local tip: You may want to get there in advance and enjoy a sunset stroll (or an *aperitivo*) facing the outstanding panorama of the Strait of Messina in the characteristic village of Torre Faro. It rises near *Capo Peloro*, a hilly promontory in the extreme north-eastern tip of Sicily, where the reliefs abruptly stop about 1.5 km from the sea to give way to a sandy beach. The Capo Peloro Lagoon is also a site of international importance, included in the UNESCO *Water Project* of 1972 in which more than 400 aquatic species live within the nature reserve, among which at least ten are endemic. But don't forget to be at the restaurant at 20:00 sharp!





Timetable

Wednesday, July 10th

| 12:30-14:00 | Registration and light lunch | | |
|-------------|--|---|--|
| 14:00-14:15 | Opening remarks | | |
| 14:15-14:45 | Marc Lamy de la Chapelle Univ. du Mans | Plasmonic sensors: Detection, identification and structural study of biomolecules [Invited] | |
| 14:45-15:45 | Session I: Non-linear optics. Chair: Salvatore Savasta | | |
| | Fritz Berkmann Sapienza Univ. di Roma | Ultra strong coupling of SiGe parabolic Quantum wells to THz microcavities | |
| | Augustin Verneuil Université de Technologie de Troyes | Plasmonic nanoantenna arrays for nonlinear optical sensing | |
| | Andrea Zappalà Univ. di Messina | Ultrastrong coupling between few molecules and a plasmonic nanocavity | |
| | Attilio Zilli Politecnico di Milano | Interferometric all-optical routing of the nonlinear emission by metasurfaces | |
| 15:45-16:30 | Poster session (A | L) and sponsors' exhibition with coffee | |
| 16:30-18:00 | Session II: Devices and Applications. Chair: Francesca Intonti | | |
| | Silvie Bernatova CNR – IPCF Messina | The optical manipulation of plasmonic particles as a promising approach for the detection of nanoplastics | |
| | Lucrezia Catanzaro Univ. di Catania | Plasmon resonance detection of gas adsorption isotherms | |
| | Giuliana Di Martino Univ. of Cambridge | Resetting the drift of Oxygen Vacancies in Ultra–Thin HZO Ferroelectric Memories | |
| | Antonio Ferraro CNR-NANOTEC Cosenza | Hybrid anticounterfeiting tag with multi security identification and authentication levels | |
| | Marco Leonetti CNR-NANOTEC Roma | Photonic Emergent Learning | |
| | Oisin McCormack Trinity College Dublin | All-dielectric qBIC-based metasurface for sensing applications | |

| Thursday, | July | 11 th - | Morni | ng |
|-----------|------|--------------------|-------|----|
|-----------|------|--------------------|-------|----|

| 9:00-9:30 | Pablo Albella Univ. of Cantabria | Optical Nanoantennas: from sensing to killing cancerous cells [invited] | |
|----------------------------|--|--|--|
| 9:30-10:30 | Session III: Nanofabrication and novel materials. Chair: Pietro Gucciardi | | |
| | Matteo Barelli Univ. di Genova | Self organized wrinkled nanorippled templates for large area flat optics metasurfaces in SERS, color routing and photocatalysis | |
| | Claudia Pernilla Hallqvist Politecnico di Milano | Nanocrystalline and Nanoporous TiO _x N _y Thin Films as Building Blocks for Solar Absorbers | |
| | Claudia Triolo Univ. of Reggio Calabria | An Ellipsometric study of dielectric/metal/dielectric electrode optical response for angular electroluminescence stability in Transparent-White-OLEDs | |
| | Antonella Lorusso Univ. del Salento | Dielectric/metal/dielectric electrode for angular optical response of semi-transparent perovskite solar cells | |
| | Poster session (A–L) and sponsors' exhibition with coffee | | |
| 10:30-11:30 | Poster session (A-L |) and sponsors' exhibition with coffee | |
| 10:30-11:30 11:30-13:00 | Poster session (A–L) Session IV: Light-matter interact |) and sponsors' exhibition with coffee tions at the nanoscale. Chair: Giuliana Di Martino | |
| 10:30-11:30 11:30-13:00 | Poster session (A–L) Session IV: Light-matter interact Stefania Benedetti CNR-NANO Modena |) and sponsors' exhibition with coffee tions at the nanoscale. Chair: Giuliana Di Martino Structure, electronic and plasmonic properties of amorphous Al:ZnO films for plasmonics in the mid-IR | |
| 10:30-11:30 11:30-13:00 | Poster session (A–L) Session IV: Light-matter interact Stefania Benedetti CNR-NANO Modena Lucia Cascino Univ. del Salento |) and sponsors' exhibition with coffee tions at the nanoscale. Chair: Giuliana Di Martino Structure, electronic and plasmonic properties of amorphous Al:ZnO films for plasmonics in the mid-IR The Polaritonic Index: A TD-DFT Approach for Polariton Chemistry | |
| 10:30-11:30 11:30-13:00 | Poster session (A–L) Session IV: Light-matter interact Stefania Benedetti CNR-NANO Modena Lucia Cascino Univ. del Salento Alessio Gabbani Univ. di Firenze |) and sponsors' exhibition with coffee tions at the nanoscale. Chair: Giuliana Di Martino Structure, electronic and plasmonic properties of amorphous Al:ZnO films for plasmonics in the mid-IR The Polaritonic Index: A TD-DFT Approach for Polariton Chemistry Direct determination of carrier parameters in indium tin oxide nanocrystals using concepts from magnetoplasmonics | |
| 10:30-11:30 11:30-13:00 | Poster session (A-L) Session IV: Light-matter interact Stefania Benedetti CNR-NANO Modena Lucia Cascino Univ. del Salento Alessio Gabbani Univ. di Firenze Nicoletta Granchi Univ. di Firenze | and sponsors' exhibition with coffee tions at the nanoscale. Chair: Giuliana Di Martino Structure, electronic and plasmonic properties of amorphous Al:ZnO films for plasmonics in the mid-IR The Polaritonic Index: A TD-DFT Approach for Polariton Chemistry Direct determination of carrier parameters in indium tin oxide nanocrystals using concepts from magnetoplasmonics Quasi-normal mode perturbation theory to achieve Q-factor optimization of resonances in disordered photonic systems | |
| 10:30-11:30 11:30-13:00 | Poster session (A-L) Session IV: Light-matter interact Stefania Benedetti CNR-NANO Modena Lucia Cascino Univ. del Salento Alessio Gabbani Univ. di Firenze Nicoletta Granchi Univ. di Firenze Thierry Taliercio Univ. di Montpellier | and sponsors' exhibition with coffee tions at the nanoscale. Chair: Giuliana Di Martino Structure, electronic and plasmonic properties of amorphous Al:ZnO films for plasmonics in the mid-IR The Polaritonic Index: A TD-DFT Approach for Polariton Chemistry Direct determination of carrier parameters in indium tin oxide nanocrystals using concepts from magnetoplasmonics Quasi-normal mode perturbation theory to achieve Q-factor optimization of resonances in disordered photonic systems Heavily doped semiconductor: the material to observe non-local effects | |

Thursday, July 11th – Afternoon

| 14:00-15:30 | Session IV: Plasmonic biosensors. Chair: Chiara Novara | | |
|-------------|--|--|--|
| | Cristiano D'Andrea CNR-IFAC Sesto Fiorentino | A SERS signal-off strategy for micro-RNA sensing with engineered molecular beacon | |
| | Daniel Montesi Politecnico Torino | Optimization of a microfluidic assay for the SERS detection of miR-320a | |
| | Maria Laura Sforza Sapienza Univ. di Roma | Gold nanorods array for pathogens biosensing and white light photothermal disinfection | |
| | Federica Zaccagnini Sapienza Univ. di Roma | Multifunctional FFP2 face mask for the simultaneous white light disinfection and detection of pathogens using hybrid nanostructures and metasurface- based optical absorbers | |
| 15:30-16:30 | Poster session (M–Z) and sponsors' exhibition with coffee | | |
| 16:30-17:30 | Session VI: Chiral and active plasmonics. Chair: Paolo Biagioni | | |
| | Leonardo Biancorosso Univ. di Trieste | Time-dependent quantum/continuum modelling of plasmon-enhanced electronic circular dichroism | |
| | Luca Bursi Univ. di Modena-Reggio Emilia | Linear, circular and trochoidal dichroism from chiral and achiral plasmonic nanostructures | |
| | Niccolò Marcucci CNR-IFAC Sesto Fiorentino | Metasurface enabled vortex beams from Bloch Surface Wave manipulation | |
| | Alberto Santonocito Univ. di Pisa | Design of a magnetically tunable Fabry-Perot metasurface based on ferromagnetic materials | |
| 17:30-19:00 | Round Table & election Steering Committee of Plasmonica (in italian) | | |
| | | | |
| 20:30- | | Social Dinner | |

Friday, July 12th

| 9:00-9:30 | Anna Chiara De Luca CNR – IEOS Napoli | Raman and SERS-bases imaging and sensing for biomedical applications [Invited] | |
|-------------|---|---|--|
| 9:30-10:30 | Session VII: Enahnced Raman spectroscopy. Chair: Cristiano D'Andrea | | |
| | Khouloud Abid CNR – IPCF | Photo-Induced Enhanced Raman Spectroscopy Beyond Two-Dimensional Materials | |
| | Mona Kebabová ISI – CAS, Brno | Nanosystems for molecular detection of biological samples using SERS | |
| | Shadi Rezaei Univ. di Messina | T-matrix calculations for optical trapping and enhanced spectroscopy of micro and nano-plastics | |
| | Serena Schiavi Univ. di Pavia | Boosting SERS performance with an ultra-thin coating of polydopamine for the detection of Methylene Blue | |
| 10:30-11:15 | Poster session (M–Z) and sponsors' exhibition with coffee | | |
| 11:15-12:30 | Session VIII: Metamaterials. Chair: Salvatore Patanè | | |
| | Stefano Campanaro Università di Modena e Reggio Emilia | Volume plasmon-polariton modes in all-dielectric hyperbolic metamaterials based on III-V semiconductors | |
| | Maria Grazia Donato CNR – IPCF | Photonic force microscopy in front of Epsilon-near-Zero surfaces | |
| | Julia Inglés Cerrillo ISOM, Univ.Politécnica Madrid | Phononic hyperbolic metamaterial with ZnO/ZnMgO heterostructures | |
| | Alice Sindoni Univ. di Padova | Spectral characterization of the optical Kerr effect in Au/Si ₃ N ₄ multilayer hyperbolic metamaterials | |
| 12:30-13:00 | | Closing remarks | |

Poster Sessions

Poster session A-M

Wednesday, July 10th 15:45–16:30 and Thursday, July 11th 10:30–11:30

| No. | | Presenter and poster title |
|-----|---|---|
| 1 | Lille Børresen Univ. of Cambridge | Collective emission effects from plasmonic nanocavity coupled dye molecules |
| 2 | Paolo Biagioni Politecnico di Milano | Polarization-resolved surface-enhanced sensing of single-stranded DNA with Bloch surface waves |
| 3 | Luca Bursi Univ. di Modena-Reggio Emilia | Quantitative analysisof emergence and evolution of plasmonic resonances in ultrasmall spherical nanoparticles and molecular systems |
| 4 | Gabriele Calusi Univ. di Firenze | Photonic band gap in Hyperuniform network over fabrication parameters |
| 5 | Carmelo Corsaro Univ. di Messina | SERS substrate based on hybrid structure of Graphene Oxide/Ag nanoparticles/Zirconia film |
| 6 | Giada Costanzo Univ. di Firenze | Diffraction limited focusing relaxation in metalens design for photovoltaics applications |
| 7 | Francesca Intonti LENS, Univ. di Firenze | Nano-imprint lithography of broad-band and wide-angle antireflective structures for high-power laser |
| 8 | Sephora Kamwe Sighano Univ. della Calabria and Univ. de Technologie de Troyes | Opuntia Ficus-indica extraction based anticounterfeiting tag functioning at Optical and Terahertz band. |
| 9 | Brad Kerrigan Univ. of Bath | Third Harmonic Chiroptical Scattering from Silver Nanohelcies |
| 10 | Yigong Luan Politecnico di Milano | Polarization encoding of nonlinear light in AlGaAs metasurfaces with attosecond precision |

Poster session M-Z

Thursday, July 11th 15:30–16:30 and Friday, July 12th 10:30–11:15

| No. | | Presenter and poster title |
|-----|---|---|
| 11 | Nabil Mahi Univ. of Djelfa | Angular plasmonic response of a periodic array of gold nanoparticles |
| 12 | Sonia Marrara CNR – IPCF & Univ. di Messina | Acoustically levitated Ag coated styrofoam particles for SERS spectroscopy of methylene blue |
| 13 | Tadele O. Otomalo Istituto Italiano di Tecnologia, Lecce | Computation of emitter-plasmon interactions using an axis-symmetric model for off-axis dipoles |
| 14 | Jyotsna Patra Indian Institute of Technology (ISM), Dhanbad | Influence of laser energy on particle size and localized surface plasmon resonance of copper nanoparticles by ns-laser ablation in liquid |
| 15 | Teresa Paviglianiti Univ. di Messina | Preparation of gel-supported plexcitonic nanohybrids and their optical characterization by 2D electronic spectroscopy |
| 16 | Michael Poloczek Friedrich-Alexander-Univ. Erlangen-Nürnberg | Lithium niobate nanostructured resonator for directional emission of spontaneous parametric down-conversion |
| 17 | Vittorio Scardaci Univ. di Catania | Magnetic Silver Nanoplates Grown by Laser Ablation and Irradiation |
| 18 | Claudia Skubisz Sapienza Univ. di Roma | Photo-acoustic technique with widely tuneable laser |
| 19 | Olena Turianska ENSTA-CNRS - Ecole Polytechnique, Paris | Plasmonic field enhancement in the ultra-intense, ultra-short laser-matter interaction with metallic nanoparticles |
| 20 | Federica Verde Istituto Italiano di Tecnologia, Roma | Protein fibrils monitored by mid-infrared nano-spectroscopy under THz irradiation |

Abstracts – Talks

Plasmonic sensors: Detection, identification and structural study of biomolecules

Aicha Azziz,¹ Qiqian Liu,¹ Marjan Majdinasab,¹ Celia Arib,¹

Mathieu Edely,¹ Marc Lamy de la Chapelle^{1,2,*}

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The development of reliable, sensitive and specific biosensors is a very active research field. Among all the technique, the Surface Enhance Raman Scattering (SERS) is one of most sensitive and has been widely used for ultrasensitive chemical analysis down to single molecule detection.[1] SERS is based on the exploitation of the optical properties of metallic nanoparticles and on the electromagnetic field enhancement localised at the vicinity of the nanostructures and created by the excitation of the Localized Surface Plasmon (LSP).

First, by controlling LSP, we are able to produce a highly sensitive sensor. We have determined the sensor characteristics such as its detection limit and its selectivity. We have determined that such sensor could be highly sensitive by reaching some detection limits lowest than the pico-molar. In this work, we have applied this sensor to the detection and the identification of specific proteins and we have been able to detect some specific disease biomarkers in body fluids (serum, saliva) paving the way to the potential disease diagnosis.[2,3]

Second, the biosensor specificity is provided by multiple and simultaneous biomolecular recognition events based on weak interactions which give an apparent affinity. Aptamers, single DNA strands, are new bioreceptors intensively used now in biosensor. Through the self-hybridisation of one part of its sequence, the aptamer forms a loop structure exposing some bases that interact specifically with the analyte thanks to electrostatic interactions. It is of primary importance to understand such interaction to optimize the analyte capture and to improve the sensing performances. In addition, molecular interactions are the basis of many biological mechanisms. It is therefore important to have a better understanding of these phenomena and to be able to answer to specific questions as: how does the interaction take place?, is it dynamic or static?, is there any specific conformation for the interaction? To answer to such questions, we study the interaction between aptamer or DNA strand with its analyte or its complementary strand by the combination of SERS and multivariate statistical analysis. We observe the DNA structure and its evolution during the interaction under different experimental conditions (in air or in buffer) and we are able to probe the strand conformations and orientations relatively to the surface.[4]

This work was supported by the European DeDNAed project (H2020-FETOPEN2018-2020, 964248) and by the project "Plasmon mediated biology: Exploitation of plasmonics to investigate and enhance biological processes and application to biomedical issues (acronym: BioPlasmonics)" funded by European Union – NextgenerationEU and Romanian Government, under National Recovery and Resilience Plan for Romania, contract no760037/23.05.2023, cod PNRR-C9-I8-CF-199/28.11.2023, through the Romanian Ministry of Research, Innovation and Digitalization, within Component 9, Investment I8.

^[1] K. Kneipp, et al., Phys. Rev. Lett. 78/9, 1667-1670 (1997)

^[2] M. Cottat, et al., J. Phys. Chem. C 119, 15532 (2015)

^[3] R. Yasukuni, et al., Nanophotonics 8(9), 1477 (2019)

^[4] W. Safar, et al., Nanoscale, **13**, 12443 (2021)

Ultrastrong Coupling of Si_{1-x}Ge_x Parabolic Quantum Wells to Terahertz Microcavities

Fritz Berkmann,[†] Tommaso Venanzi,[†] Leonetta Baldassarre,[†] Elena Campagna,[‡] Enrico Talamas-Simola,[‡] Luciana Di Gaspare,[‡] Cedric Corley-Wiciak,^{¶,§} Giovanni Capellini,^{¶,‡} Giuseppe Nicotra,[∥] Gianfranco Sfuncia,[∥] Andrea Notargiacomo,[⊥] Ennio Giovine,[⊥] Sara Cibella,[⊥] Michele Virgilio,[#] Giacomo Scalari,[@] Monica DeSeta,[‡] and Michele Ortolani^{*,†}

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 [#]Department of Physics, University of Pisa, Pisa, Italy
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Strong coupling in the THz range between a "matter" resonance and a "light" resonance is one suitable way to investigate the manipulation of quantum states via light. While this phenomenon was reported in several systems from the microwave range [1] up to the visible range[2], fully CMOS-compatible, room-temperature platform have not been shown yet.

Here we achieved ultra strong coupling between conduction-band inter-sub-band transitions (ISBTs) in Si(1-x)Ge(x) Quantum Wells and the optical cavity mode of a patch antenna. We developed a Parabolic Quantum Well epitaxial structure with energy-equidistant ISBT at $\omega_0 \simeq 3.1$ THz. This was embedded into hybrid metal-plasmonic patch-antenna microcavities with optical cavity modes varying from 2 to 5 THz, depending on the antenna length. These hybrid metal-plasmonic cavities, where the ground plane consist of a highly doped semiconductor, makes the fabrication suitable for CMOS-compatible fabrications. The SiGe parabolic quantum well spectrum is robust against carrier density and temperature variation, leading to a weak temperature dependence of the strong coupling in this system, allowing us to tackle room-temperature applications. Using group IV semiconductors such as SiGe, this platform has the additional advantage over III-IV semiconductors of the non-polar lattice and therefore no infrared active phonons, making it extendable up to 12 THz.

For the design of the cavities electromagnetic simulations were used which are in good agreement with the measurements (see Figure 1). In a first demonstration we could achieve an anti-crossing behaviour of the two coupled resonances. The measured rabi splitting Ω_R was shown to be almost temperature independent ($\Omega_R \simeq 0.7$ THz) and the strong coupling condition stayed intact up to room temperature. Due to a hight 2D electron density a coupling strength of $\Omega_R/\omega_0 \simeq 0.2$ was reached and therefore the systems enters the ultra-strong coupling regime [3]. These features makes the system suitable for further applications such as ultra-fast modulators or absorbers targeting the almost unemployed 5-12 THz range at room temperature.



Fig. 1: Reflection fitting showing the anti-crossing behaviour of the lower and upper polariton at 10K. Comparison between Measurements, Theory and Simulations with a Pitch of 2x the patch antenna size.

[1] Mi, X. "Strong coupling of a single electron in silicon to a microwave photon". Science 2017, 355, 156–158.

- [2] Baumberg, J. J. "Extreme nanophotonics from ultrathin metallic gaps". Nature Materials 2019, 7, 668–678.
- [3] Ciuti, C. "Quantum vacuum properties of the intersubband cavity polariton field". Phys. Rev. B 2005, 72,

Plasmonic nanoantenna arrays for nonlinear optical sensing

Augustin Verneuil,^{1,2} A.Zilli,² C. Vézy,¹ J. Béal,¹ M. Finazzi,² M. Celebrano² and A.-L. Baudrion^{1,*}

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Second-harmonic generation (SHG), the optical process whereby two photons at a fundamental frequency are converted into one at twice the frequency, is well known to be dipole-forbidden in centrosymmetric crystal lattices, such as in plasmonic metals. Thus, symmetry breaking is required for this phenomenon to be supported, which can be achieved in two ways: field gradients in the bulk of the material, or surface contributions.[1,2] This latter approach has received special attention due to its potential for sensing applications: indeed, a variation in the surface susceptibility tensor, mediated for instance by a biological binding event, could give rise to a larger change in the nonlinear signal,[3] compared to the refractometric approach usually employed in linear plasmonic sensors.

In this context, we experimentally investigate gratings of non-centrosymmetric V-shaped gold nanoantennas. The lattice parameters were chosen to overlap the diffraction orders with the maxima of the single particle SHG emission pattern (EP).[4] This opens a new opportunity to improve the sensing performance: as the EP depends on the local refractive index, but the diffraction pattern of our grating remains fixed, the overlap is affected, resulting in an enhanced modulation of the detected SHG power. To explore this possibility, we first investigate several gratings of varying constant period (fig. 2a,b). We also explore a continuously variable pitch lattice, supporting a broadened diffraction order (fig. 2c), in which the shift of the EP can be directly observed as the refractive index is changed (fig. 2d).



Figure 1: (a) Refractometric sensing experiment for different fixed pitch gratings. The lattice layout is schematized in the inset of (b), with the period varying in *x*. (b) The associated refractive index resolution for each configuration, in refractive index units (RIU). (c) Calculated array factor of the variable pitch array (VPA), showing the broadened (-1;0) diffraction order (inset: schematic of the lattice). (d) SHG emission in the (-1;0) diffraction order of the VPA for different RI. The white background represents the range where the array factor is roughly uniform.

[1] D. De Ceglia, M. A. Vincenti, C. De Angelis, A. Locatelli, J. W. Haus, and M. Scalora, Opt. Express 23, 2 (2015).

[2] G. Bachelier, J. Butet, I. Russier-Antoine, C. Jonin, E. Benichou, and P.-F. Brevet, Phys. Rev. B 82, 23 (2010).

[4] A. Verneuil, A. Di Francescantonio, A. Zilli, J. Proust, J. Béal, D. Petti, M. Finazzi, M. Celebrano, and A.-L. Baudrion, Nanophotonics (2024). DOI: 10.1515/nanoph-2023-0842.

^[3] Y. El Harfouch, E. Benichou, F. Bertorelle, I. Russier-Antoine, C. Jonin, N. Lascoux, and P.-F. Brevet, The Journal of Phys. Chemi. C **118**, 1 (2014).

Ultrastrong coupling between few molecules and a plasmonic nanocavity

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Ultrastrong coupling between light and matter is a regime of quantum light-matter interaction, which goes beyond weak and strong coupling to make the coupling strength comparable to the transition frequencies in the system [1, 2]. This regime has been achieved in a multitude of experimental setups, including superconducting circuits, organic molecules, semiconductor polaritons. It opens the way to the observation of new physical effects and to many potential applications (see, e.g., [3–6]). However, it is very difficult to achieve it with individual or a few quantum emitters, which is where novel quantum optical nonlinear effects can emerge. When it is reached with many dipole systems or by considering collective excitations, only nonlinear optical effects can be observed under ordinary excitation densities. Plasmonic nanocavities represents a unique setting where this regime can be achieve with a limited number of emitters [7]. Here we present a cavity-QED model beyond the rotating wave approximation able to properly describe systems of *N* emitters interacting with a plasmonic nanocavity in the ultrastrong coupling regime. We use this model and a generalized master equation approach [8] to calculate emission spectra under incoherent pumping of the molecules as a function of their number *N*, of the coupling strength, frequency detuning, and pumping power.

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Interferometric all-optical routing of the nonlinear emission by metasurfaces

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Motivation Optical resonances in nanostructures, such as metasurfaces, have shown great potential to enhance and control nonlinear optical processes, which are intrinsically weak at the nanoscale. There is presently a strong drive towards dynamically reconfiguring such resonant response, enabling versatile or broadband functionalities. Among several proposed physical mechanisms (electro-optic, mechanical,...) all-optical approaches stand out for their fast switching and contactless operation. Several pump-probe experiments have demonstrated various forms of *intensity*-based tuning, exploiting a transient alteration of the material properties, either via opto-thermo-optical effects or via the creation of hot electrons by photo-excitation. *Phase*, conversely, has received so far little attention as a control tool in this context.

Results We recently developed a two-pump scheme mixing a pulse at frequency ω in the telecom C-band (wavelength $\lambda = 1550$ nm) with its frequency-doubled replica. The sum-frequency generation (SFG, $\omega + 2\omega$) and third-harmonic generation (THG, $\omega + \omega + \omega$) processes are coherent and degenerate at 3ω – see inset of Figure 1. Because of their respectively even and odd nonlinear order, SFG and THG **E** fields have opposite parity, so that their interference is only allowed when some symmetry breaking takes place [1]. This can be realized either in the real (**x**) space via an asymmetric antenna geometry [2], or in the reciprocal (**k**) space via an asymmetric detection domain [3]. Here, I will focus on the latter strategy, whereby the diffraction orders of a periodic AlGaAs metasurface implement a directional filtering. The nonlinear emission is routed alternatively into either order of a mirror-symmetric pair depending the relative phase between the two pumps, as depicted in Figure 1. Thus, monitoring individual off-axis orders in optimized metasurface designs, we observed power modulations up to 90 %.

Outlook We are presently working towards leveraging the same metasurface system for modulating polarization rather than power, whose contrast is maximized when the SFG and THG **E** fields are perpendicular rather than parallel. Due to symmetry constraints, light of opposite handedness will be routed into opposite orders of a mirror-symmetric pair, providing a promising platform for chiral sensing.



Figure 1: Illustration of the directional routing of upconverted light by a periodic metasurface, controlled by the relative phase of the pumps. Inset: Energy diagrams of the nonlinear upconversion pathways brought to interfere.

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The optical manipulation of plasmonic particles as a promising approach for the detection of nanoplastics

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Despite significant progress in the detection of nanoplastics, the detection of such particles still faces problems caused by the limitations of current detection methods and instruments. Herein, we present the optical method for fabricating a substrate using plasmonic particles to detect plastic nanoparticles. We summarize recent progress in our experiments using optical nanoimprinting of plasmonics nanoparticles to create the "active" aggregates (see Figure 1) that can be used for Surface Enhanced Raman Spectroscopy (SERS) detection of biomolecules in microfluidic circuits [1,2] and as plasmon-enhanced thermoplasmonic concentrators for nanoscale particulate matter such as nanoplastics. The principle of nanoimprinting is based on the dominance of the scattering force (compared to the gradient force) for plasmonic particles, that are pushed in the direction of propagation of the light beam. An aggregate comprising plasmonic particles is produced that can serve as a substrate for SERS and as a source of the temperature gradient attracting dielectric nanoparticles. In both cases, enhanced sensitivity is demonstrated, allowing the detection of nanoplastics/molecules of size/concentration orders of magnitude lower than what can be achieved by ordinary Raman spectroscopy.



Figure 1: Basic principle of nanoimprinting plasmonic particles by optical forces, followed by the formation of an aggregate that generates a temperature gradient that attracts the dielectric nanoparticles. a). The image of aggregate formed due to the plasmonic particles imprinting b). Raman spectrum of attracted nanoplastics due to the thermoplasmonic effect of the formed aggregate c).

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Plasmon resonance detection of gas adsorption isotherms

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Surface Plasmon Resonances (SPRs) are phenomena which consist in collective oscillations of electrons along the interface between a metal film and a dielectric layer [1]. This resonance condition is very sensitive to any changing of the refractive index above the surface of the metal film, making the SPR a powerful tool for detecting gas and biological analytes since the '80s [2].

Metal Nanoparticles (NPs) interact with light showing a similar phenomenon, called localized SPR (LSPR), which consists in the collective oscillation of electrons inside the volume of the NP. The involved resonance frequencies are generally strongly correlated to the optical properties of the surroundings [3,4].

In our work we investigated the LSPR response of silver nanoplates (NPTs), chemically grafted onto transparent substrates [5] and exposed to increasing quantities of water and/or organic vapors inside a vacuum chamber. Extinction spectra are obtained by using an "in situ" UV-Vis spectrophotometer as a function of the vapor pressure inside the chamber (figure 1a). We have also studied the sensitivity of different silver NPs grafted on silanated glass surfaces and exposed to different vapors and we supported the adsorption mechanism through Finite-Difference Time-Domain simulations.

As a result, figure 1b shows a Type IV adsorption isotherm observed by following the SPR shift of silver NPs as a function of ratio between the water vapor pressure and the vapor-liquid equilibrium pressure. Similar experiments have been conducted using organic vapors.

The huge sensitivity and the accessible and cost-effective measurement equipment make these effects promising candidates for various sensing applications, including the environmental monitoring.



Figure 1: a) Detection of water gas vapor through the red shift of the LSPR mode of silver NPTs deposited onto glass substrate. b) Water adsorption isotherm detected by following the shift of silver NPTs as a function of the ratio between water vapor pressure and vapor-liquid equilibrium pressure.

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Resetting the drift of Oxygen Vacancies in Ultra-Thin HZO Ferroelectric Memories

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We recently developed an innovative non-destructive technique able to characterise various device materials changes *in operando*. In the past, we probed few hundreds oxygen vacancies drift in thin (~5 nm) dielectric films during device switching just by the aid of visible light, an approach that helped to identify the breakdown mechanisms upon cycling in memristive device [1].

Using light, we also tracked both the migration of oxygen ions and phase change inside low energy consuming, ultrathin ferroelectric random access memory devices (FeRAMs). We achieved a single electrical cycle resolution investigation tool to study the nano-structural evolution when under continuous electronic switching in ambient conditions and track in *real- time* and *in-operando* the nanoscale kinetics of wake-up and fatigue [2].

Previously, simple and yet effective out-of-the-box methods were still needed to mitigate devices uncertainties due to vacancy migration inside the film under bias but now, thanks to our optical characterization, we can finally unlock routes to make better performing devices. We engineered ways to "reset" or revert the migration of oxygen vacancies inside ferroelectric oxide films. This control over nano kinetics inside the film allows to speed up wake-up, retard fatigue, and reduce leakage inside the film, unlocking novel potential towards unparalleled performance and enhanced device lifespan. We show the ability to manipulate wake-up by a factor of \sim 4× to \sim 24×, retard rate of fatigue by 4×, and reduce leakage by \sim 60% and polarisation loss by 20-80% [3].

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Hybrid anticounterfeiting tag with multi security identification and authentication levels

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The rise of counterfeiting is promoting a thriving research on different materials and technologies to prevent and limit such a phenomenon by developing new anti-counterfeiting identification tags [1]. Herein we report on the experimental demonstration of multi-level anticounterfeiting Physical Unclonable Function (PUF) tags realized on a flexible and conformable office paper substrate [2].



Figure 1: Camouflage anticounterfeiting tag with multi security level.

The first security level is guaranteed by the printing of a QR code which is hidden by a successive deposition of a metal/insulator/metal/insulator (MIMI) metamaterial. The QR code information can be read only by retro-illuminating the tags enabling a variation of the characteristic structural color exhibited by MIMI metamaterials.

Thanks to the intrinsic random morphologies of a paper substrate producing characteristic speckle patterns, a third "forensic" level is enabled by using a challenge response pair interrogation protocol proving their strong nature as physical unclonable function. This level works for the seller like a sample survey where, in case of doubt about the merchandise, he can ask to a forensic laboratory to test if the produced challenge response pairs are enrolled in the central authority.

The different security levels are intended to different possible users: the first and second one are accessible to customers and not specialized persons with a double check on the label genuineness by interrogating a specific repository where all the information, e.g Qr code and color association, are stored. The third is a forensic level because require sophisticated apparatus and experts in the field and can be adopted for legal actions.

The proposed physical unclonable functions represent an ideal candidate for the protection of goods thanks to their low cost and large-scale production possibilities.

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Photonic Emergent Learning

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Abstract: Here we present a new approach to write, read, and classify memory patterns: the photonic emergent learning. The writing paradigm is borrowed form a-physical- mathematical model for the biological memory, the emergent archetype, which we translated to photonics. In our approach the random patterns enclosed in the transmitted electromagnetic modes, are used as prototypes which are summed in constructive fashion in order write our target archetype-memory into our disordered optical memory (DOM). The DOM can work as a content addressable memory, retrieving at the lightning speed which memory in the library is the closest to an optically proposed query pattern. Moreover, the optical memories can be organized into super structures containing memories of the same thus efficiently delivering a classification task.



Figure 1: Writing procedure. Panel (C) reports the pattern to be written ϕ . The first step is the disorder characterization: we measure the transmission vector t^{ν} of all the output modes of the disordered medium, generating a huge library of random memories. Then we compute the similarity (panel A) between all the t^{ν} vectors and ϕ and perform a similarity-driven decimation. Then the Intensity of the selected modes are summed, realizing a macro-mode whose relative transmission vector t^{M} contains the arbitrary designed memory pattern ϕ . Panels on the right are relative to classification procedure (more details on [3]).

In the Hopfield scheme [1], an Emergent Memory is a memory structure realized aggregating noisy, imperfect or disordered memories used as prototypes[2].

Stochastic Emergent Learning (SES) [3] is a learning strategy which taps into the abundance of natural randomness to construct an emergent representation of the desired memory. Capitalizing a vast database of fully random patterns freely produced by a disordered, self-assembled structure, we select a set of prototypes that bear resemblance to the target memory through a similarity-based criterion. Subsequently, by performing a weighted sum of the synaptic matrices corresponding to these selected prototypes, we can effectively generate the desired pattern in an emergent fashion (See Fig. 1). Here, we will discuss on how to employ the scattering intrinsic patterns, the optical transmission matrices, to realize a SES-based optical hardware, the Disordered Optical Memory (DOM), capable of storing, preform pattern recognition, work as a content addressable memory, and classify query patterns, which are administered to the device by writing them thanks to a Digital Micromirror device on the propagating wavefront of a laser beam.

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All-dielectric qBIC-based metasurface for sensing applications

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Abstract: Plasmonic resonance-based sensors have inherent limitations due to high ohmic losses, reducing the quality factor of resonances and complicating multiplexing, where multiple resonance markers share the same spectrum. These ohmic losses also cause localized heating, posing challenges in biosensing applications where excess heat can damage or denature the analyte [1]. In contrast, all-dielectric nanostructures offer advantages such as perfect absorption, invisibility, directional emission, high field enhancement, and high compatibility with biosensing functional groups [2]. However, these benefits are often restricted as the regions with the highest field enhancement tend to be within the structure, limiting their accessibility for sensing [3].

The emergence of quasi-bound state in the continuum (qBIC) resonances in dielectric metasurfaces has sparked new possibilities for sensing applications. These qBICs, characterized by sharp Fano resonances with long optical lifetimes, are achieved by incorporating slight asymmetry into the design of nanoresonators [4]. The fabrication and control of these resonances offer unique opportunities for creating high-quality sensors.

In this study, a novel all-dielectric slotted-disk metasuface design [5] with qBIC resonances was modified to use Si_3N_4 nanoresonators, transferred onto a transparent fused silica substrate, and submerged in a water-based sensing buffer medium. This innovative design leads to high Q-factor and field enhancement that extends external to the structure, facilitating effective sensing. We present the preliminary results from the fabrication and characterization of these metasurfaces and compare with the simulated measurements. The realized design provides resonances that are robust, highly tune-able, and ideal for multiplexed sensing in the visible and near-infrared spectral regions.



Figure 1: Simulated transmission curve (blue) for the slotted-disk design (inset left), producing a 1nm FWHM qBIC resonance, with E-field enhancement external to the nanostructure (inset right).

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Optical Nanoantennas: from sensing to killing cancerous cells

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Optical antennas convert freely propagating light waves into highly localized excitations that strongly interact with matter. Specifically, plasmonic nanostructures functioning as nanoantennas have been utilized to achieve strong light-matter interactions at deep subwavelength scales. However, their ohmic losses can cause temperature increases in the nanoantenna and its surroundings, a well-known effect beneficial for applications like photothermal imaging, drug delivery, certain biosensing techniques, and cancer therapy. Conversely, this effect limits the power deliverable to a hot spot before the particle reshapes or melts, impacting nanoscale lighting or the emission properties of nearby targets. Metals also face challenges in generating optical magnetic responses. Recently, low-loss resonators made from high permittivity dielectric materials (non-plasmonic) have emerged as effective alternatives for applications such as sensing (including enantiomers), spectroscopy (SERS or SEF), and designing light-emitting devices for integrated photonics or optical nanocircuits, where tuning light propagation direction enhances performance.

In the first part of the talk, I will revisit and highlight the properties and strengths of plasmonic nanoantennas, focusing on recent developments in novel nanoheaters capable of delivering heat asymmetrically, desirable in photothermal cancer therapies and drug delivery [1-4]. In the second part, I will discuss the weaknesses of plasmonic nanoantennas for certain applications and emphasize non-plasmonic nanoantennas as a way to overcome these weaknesses. These novel nanoantennas not only produce significant near-field enhancement and good scattering efficiencies but also offer intriguing optical properties, such as the ability to excite nanoscale displacement currents leading to magnetic responses [5,6]. This allows tuning the amplitude and phase difference of electric and magnetic resonances independently, paving the way for designing new molecular sensors, including those of special interest in pharmacology that can enhance measurements of molecular chirality [7-9].

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Self organized wrinkled nanorippled templates for large area flat optics metasurfaces in SERS, color routing and photocatalysis

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Abstract: The nanofabrication of different flat-optics systems is controlled over a large-area (cm²) by a novel self-organized technique which exploits an ion-induced nanoscale wrinkling instability on glass templates to engineer tilted metallic and bimetallic nanostrips for different photonics and photocatalityc applications [1]. As a first demonstration we show that the self-organized patterns can act as quasi-1D gratings enabling the excitation of hybrid SPP modes confined at the Au/dielectric interfaces, with a resonant wavelength which can be tuned either by modifying the grating period, photon incidence angle or, potentially, the choice of the thin film conductive material. Surface Enhanced Raman Scattering experiments show promising gains in the range of 10³ which are competitive with state-of-the art lithographic systems [2]. Another interesting functionalization of the ripples glass template with bimetallic (Au and Ag nanostripes) leads to the fabrication of bidirectional nanoantennas (having two preferential directions of scattering) that are of key relevance for advanced functionalities such as color routing in an ultracompact flat-optics configuration.



Figure 1: Elaborated Scanning Electron Microscope (SEM) image of the bimetallic meta-surface detected in cross section configuration.

The typical design exploits the phase interplay between resonant optical modes within a single nanoantenna or between the different scattering elements in a nano-antenna array. Here we demonstrate an alternative approach, which doesn't require complex and/or restrictive collective geometries and morphological parameters, based on cross-polarized detuned plasmonic nanoantennas in a uniaxial (quasi-1D) bimetallic configuration [3]. Finally, the rippled glass template can be used to confine Au nanostripes that show a wavelength selective photocatalytic response in the photobleaching of polluting organic molecules such as methylene blue [4].

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Nanocrystalline and Nanoporous TiO_xN_y Thin Films as Building Blocks for Solar Absorbers

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In recent years, metal nitrides and oxynitrides, such as titanium nitride (TiN) and titanium oxynitride (TiO_xN_y), have drawn a lot of attention in the nanophotonic field as they are considered, along with other materials, a promising alternative to traditionally plasmonic metal materials (e.g., Au) [1]. Noble metals suffer from limited spectral tunability, incompatibility with CMOS technology and restricted integrability in photothermal devices [1-2]. On the contrary, TiN and TiO_xN_y exhibit good CMOS compatibility, high mechanical, thermal and chemical stability, and plasmonic tunable properties in the visible (VIS) and near-infrared (NIR) ranges. Furthermore, TiO_xN_y can exhibit unique properties such as the Double Epsilon-Near-Zero (D-ENZ) behavior, whereby the real permittivity ϵ_1 curve intersects the

zero line twice. Therefore, multi-resonant plasmonic, at different frequencies, can be achieved [1]. Exceptionally, TiO_xN_y optical constants can be tuned at the synthesis stage by manipulating its stoichiometry and composition [1-3]. However, the fine control of the composition is not trivial, since an excess of oxygen during the fabrication, leads to the formation of TiO_2 . Nevertheless, all the mentioned features are beneficial for energy harvesting applications, including solar absorption, where modulable optical properties and high thermal stability are required [2].



Figure 1: (a) Real permittivity of compact TiN and TiOxNy thin films. (b) Absorptance spectrum of TiN- TiO_xN_y -TiO₂ multilayer. (c) and (d) schematic representation and SEM image of the three-layer, respectively.

In this work, TiO_xN_y thin films with different stoichiometries and morphologies (compact/polycrystalline and nanoporous) were produced and characterized. The film synthesis was performed by pulsed laser deposition, starting from a TiN target, at room temperature and in different atmospheres/pressures: vacuum, O₂ and N₂-H₂ gas mixture. Compact TiO_xN_y thin films, with a thickness of 200 nm, deposited at increasing O_2 pressure (from vacuum to 2 Pa), exhibit a redshift of the real permittivity (Fig. 1a) along with the increment of O_2 gas pressure. Additionally, TiO_xN_y films deposited at a pressure higher than 1.5 Pa show the D-ENZ behavior. A porous TiO_xN_y film, with 1 μ m thickness, was produced at 50 Pa of N₂-H₂ to realize a broadband solar absorber, exploiting its nanostructure and plasmonic resonance. To further enhance TiO_xN_y absorbance and protect its porous structure from oxidation, TiO_xN_y was sandwiched between TiN and TiO₂ thin films (100 nm each) to form a three-layer structure (Fig. 1c and 1d). The produced multilayer exhibits promising solar absorption (up to 87%) in the UV-vis-NIR window (Fig. 1b). To conclude, TiO_xN_y optical properties were tuned in the UV-NIR range by controlling its stoichiometry and nanostructure at the synthesis stage. In addition, an example of TiO_xN_y solar absorber multilayer is shown. This work paves the way for the implementation of TiO_xN_y in nanostructured devices to improve light absorption such as metal-insulator-metal (MIM) structures, which we are currently simulating and realizing, and multilayer based on compact D-ENZ TiO_xN_y thin films.

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An Ellipsometric study of dielectric/metal/dielectric electrode optical response for angular electroluminescence stability in Transparent-White-OLEDs

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The integration of photonic structures into optoelectronic devices represents an ever-evolving great research field. In these devices, photonic structures allow manipulating the light propagation, acting on the reflection, absorption, transmission and polarization state of the light. Recently, a great interest has been paid to dielectric/metal/dielectric (DMD) electrodes, in which the suppression of the surface plasmon polaritons (SPPs) at the DM interface allows controlling the transparency degree of the structure in a wide range of wavelengths. This is a key parameter for electrodes in Transparent White Organic Light-Emitting Diodes (TWOLEDs), where DMD structures represent the most promising transparent electrodes as substitutes for ITO-based ones.

In this work, DMD structures (consisting of WO₃/Ag/WO₃ layers) were produced via UHV thermal evaporation and investigated for transparent electrodes in TWOLED applications. The optical response in the visible range was studied with Variable Angle Spectroscopic Ellipsometry (VASE), as the thicknesses of the dielectric layers varied. VASE data allowed understanding the relation between the transparency degree of the DMD structures and the polarization state of the output light. The Poincaré-sphere representation proves that the polarization of light changes from linear to circular state passing through elliptical ones and the dielectric layer thicknesses determine the working wavelength range of the DMD. Interestingly, the maximum transmittance of the DMD electrode occurs at specific critical values of the wavelength and angle of incidence, where the light reflected is fully p-polarized, miming the Brewster angle of a simple dielectric plane but in TM mode. The electroluminescence (EL) spectrum of a p-i-n TWOLED device, which integrates an optimized DMD structure working as upper electrode, was measured at viewing angles of 0°, 30°, and 60°. An analysis on the optical modes that contribute to the power dissipation in TWOLED reveals that the reduction of plasmonic and waveguided modes is due to the antireflection properties of the DMD electrode. The result is a very large angular stability of the EL signal from TWOLED, with negligible color coordinates variation in an escaping light visual cone of 120°, thus paving the way for a new generation of transparent white lighting sources.



Figure 1: Architecture of the TWOLED device with DMD structure as upper transparent electrode; Electroluminescence signal from TWOLED device as a function of wavelength and varying the viewing angle (0°, 30° and 60° with respect to the normal direction to the surface); CIE coordinates of the output light and a picture of an operating TWOLED in a tilted viewing angle.

Dielectric/metal/dielectric electrode for angular optical response of optoelectronic devices

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Recently, very efficient dielectric-metal-dielectric (DMD) electrodes have been proposed as transparent electrode in optoelectronic devices and many efforts have been done to overcome the losses due to the surface plasmon polaritons at the metal-dielectric interface as well as on the possibility to reach high transmittance by matching the refractive index and the thickness of each layers. In this work, the study of the electromagnetic wave propagation into DMD electrodes has been done by Variable Angle Spectroscopic Ellipsometry useful for reaching the right trade-off between the transparency and the conductivity of such electrodes. Semi-transparent solar cells and transparent organic light emission diodes have been fabricated by utilizing the engineered DMD electrode showing high optoelectronic performances.



Figure 1: Scheme of Variable Angle Spectroscopic Ellipsometry of DMD electrode and transparent optoelectonic devices.

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Structure, electronic and plasmonic properties of amorphous Al:ZnO films for plasmonics in the mid-IR

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Transparent conductive oxides like Al-doped ZnO (AZO) are a class of materials that combine high transparency and low resistivity. Additionally, they show an interesting tunable plasmonic response in the near infrared range with an epsilon-near-zero behavior [1]. When conducting films are grown amorphous they can overcome poor CMOS compatibility, discontinuity and poor mechanical stability typical of noble metals. The intrinsic absence of grain boundaries allows for the growth of extremely thin smoother films with improved electronic and transport properties. Even though amorphous conductors are known, a theoretical and experimental understanding of the influence of structural disorder on the electronic and optical properties of the films is completely missing.

We have performed DFT calculations that predict electronic modifications with broadening of the valence and conduction edges due to amorphization [2]. The role of symmetry breaking and long/local order scale ranges in the amorphous structure can explain the occurrence of a defect related midgap feature, whose origin is still debated (Fig. 1a). We have then grown amorphous AZO films by RF magnetron sputtering by increasing Ar pressure and characterized their electronic and optical properties as a function of the degree of disorder. By XRD and TEM we have determined the degree of disorder (Fig. 1b,c) and the appearance of nano-voids, proved also by positron annihilation spectroscopy [3]. Preliminary photoemission measurements confirm the electronic modifications predicted by DFT. Indeed, a broadening of the valence band edge and the occupied states at the Fermi level (FL) in the amorphous AZO are observed. In order to address the plasmonic response of the AZO films, optical reflection measurements were performed via FTIR spectroscopy. Already in the reflectivity curves it is possible to identify a large spectral weight in the mid-infrared region, at variance with what is found on the quartz substrate (Fig. 1d). Such strong spectral weight, that could be linked to the DFT-predicted mid-gap states, shows some dependence on the degree of disorder. The reflection spectra were fitted with a Kramers-Kronig constrained Drude-Lorenz model in order to obtain the complex permittivity.

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Figure 1: (a) DFT calculation of DOS on polycrystalline and amorphous AZO films; (b,c) FFT analysis of HRTEM images of AZO films grown at 5 and 100 mTorr respectively; (d) Reflectivity for increasing Ar pressure.

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The Polaritonic Index: A TD-DFT Approach for Polariton Chemistry

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Light-matter interactions at the nanoscale are crucial for fields like quantum chemistry and nanophotonics. This research is grounded in the field of polaritonic chemistry, that focuses on controlling chemical reactions through the creation of light-matter interactions known as polaritons or plexcitons. Inspired by the groundbreaking work of Ebbesen et al. [1], we employed TD-DFT to achieve a comprehensive understanding of the coupling mechanisms between a photoswitch and a silver nanocluster [2-3].

In line with recent findings of strong coupling between surface plasmon-polaritons and excitons leading to hybrid states (polaritons) [4], this work explores the emergence of these states and their impact on the photoswitch potential energy landscape. We introduced a novel figure of merit, the *Polaritonic Index* (PI), to identify all hybrid excitations and differentiate between polaritonic states (Figure 1) and charge-transfer states. Polaritonic states are confined to the barrier region between the two stable configurations of the thermal isomerization of the analyzed molecule, while charge-transfer excitations appear along the entire isomerization pathway. This suggests potential new pathways for the investigated isomerization process.

This work highlights two key points. First, it demonstrates the need for advanced theoretical models to capture the complex interactions between metal and molecule in this system. Second, it paves the way for utilizing polaritonic chemistry to manipulate light-sensitive molecules opening doors for future applications.



Figure 1: Comparison between the absorption spectra of the isolated Ag_{20} , an intermediate isomer of azobenzene thermal isomerization (#19) and the hybrid system. Inset: transition densities of the lower and upper polaritonic states.

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Direct determination of carrier parameters in indium tin oxide nanocrystals using concepts from magnetoplasmonics

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Indium Tin Oxide (ITO) is the prototype conductive oxide, which has recently gathered interest in nano-optics,¹ owing to the excellent plasmonic properties displayed by ITO nanocrystals (NCs) in the infrared spectral region. Unlike noble metals, the plasmonic resonance frequency in spherical ITO NCs can be tuned synthetically by controlling the tin content.² Nanostructuration typically introduces several challenges in the characterization of electronic parameters in NCs, hampering advanced material design. Indeed, while films of doped oxides are routinely studied through electrical experiments, these cannot be reliably applied to NCs, since the insulating ligand layer forces charge hopping and results in a complex (albeit interesting) behaviour. Moreover, the surface potential creates a depletion region near the surface, which typically requires core@shell models with a purely dielectric shell to fit the extinction spectrum.³

In this work,⁴ we present an integrated approach (Figure 1) based on magneto-optics, singleparticle Electron Energy Loss (EELS) spectroscopy and ¹¹⁹Sn Solid State Nuclear Magnetic Resonance (SSNMR) spectroscopy to extract the fundamental electronic parameters of a series of ITO NCs with variable tin doping. Our methodology overcomes the limitations of standard fitting approaches based on extinction spectroscopy, which can only determine the ratio between carrier density and mass. Conversely, exploiting concepts from magnetoplasmonics^{5,6} we determined the carrier effective mass directly on the NCs, discarding the use of literature values. The effective mass was found to deviate from the parabolic approximation at high carrier density. This approach can be generalized to other plasmonic heavily-doped semiconductor nanostructures and represents, to the best of our knowledge, the only method to date to characterize the full Drude parameter space of 0-D nanosystems.

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Figure 1: Scheme of the multitechnique approach employed in this work to extract the relation between carrier mass and carrier density in a series of chemically prepared ITO NCs with variable Sn content.

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Quasi-normal mode perturbation theory to achieve Q-factor optimization of resonances in disordered photonic systems

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Photonic crystal cavities nowadays are the most widespread and versatile devices conceived to mold the flow of light at the nanoscale. Other photonic systems, based on random distributions of point scatterers, have emerged and proposed as complementary alternative to ordered photonics [1]. They have been investigated for their basic physical insights, such as Anderson localization, and envisioned for several applications, due to their capability of exhibiting a higher density of modes in a small spatial domain with respect to their ordered counterparts [1]. The main disadvantage, mainly in purely random photonic systems on slab operating at telecom wavelengths, is represented by the low Q factors that Anderson modes exhibits (typically \approx 200). While the problem of Q factor optimization of photonic crystal cavities have been accomplished widely and successfully [2], in the case of Anderson modes localized in random structures, further complicated by the lack of an in-plane photonic band gap, it has never been addressed. Here, we propose a gradient-based automated optimization approach to maximize the Q of a selected Anderson mode supported by a dielectric slab randomly patterned with air holes (Fig.1a). The method uses the theoretical framework of guasinormal modes (QNMs) [3] and relies on first-order non-hermitian perturbation theory to efficiently compute the gradients of Q relative to arbitrary material boundary displacements. Given its first order nature, the method requires only the calculation of the complex eigenfrequency and field profile of the QNM of interest. The optimization process, which determines a shift in the position of all holes in the structure (Fig.1b) to produce a Q-factor enhancement from 200 to 105 as well as a negligible average wavelength shift (Fig.1c). By monitoring the spatial distribution of the mode along the optimization we observe the mode central location and spatial distribution to change dramatically (Fig.1d), with a final spatial localization comparable with the one achieved in engineered photonic-crystal cavities (Q/V \approx 10⁶ µm-3) [4]. Our result might be relevant for the employment of random structures for lasing an sensing applications and constitute an important step toward the full engineering of the random photonic platform.



Figure 1: Results of the optimization process applied to a random design (slab thickness d=180 nm, hole radius r=110nm). (a) Simulated electric field intensity of the Anderson mode in the initial configuration; (b) Holes distribution in the random design from the initial configuration (red) to the final one (blue). (c) Evolution of the resonant wavelength and Q of the Anderson mode during the optimization process. (d) Simulated electric field intensity maps of the Anderson mode in the final configuration.

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Heavily doped semiconductor: the material to observe non-local effects

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Abstract: Non-locality is the effect of the field at a given point, **r**, but especially the variation of the field around that point, on the polarisation and current densities. Therefore, non-locality appears in very small metallic nanostructures a few tenths of a nm, where their size is similar to the average free path of the electrons. It is therefore difficult to carry out experimental observations. Heavily doped semiconductors, however, have a longer mean free electron path, making it possible to observe a strong non-local effect for relatively small nanostructures. Figure 1 shows the wavelengths of the volume plasmon modes (diamonds) measured by attenuated total reflectance (ATR) on heavily Si-doped InAsSb grown by solid source molecular beam epitaxy on GaSb substrate [1]. The InAsSb:Si films thickness varies between 20 nm and 200 nm.





Model: We apply the Hydrodynamic Drude Model (HDM), which introduces an electron quantum pressure with the parameter, β , into the equation of motion of the free electron gas. [2] This model provides an accurate description of the non-local effects and accurately describe the ultra-confined light of the plasmonic mode. This approach is well suited for implementation in electromagnetic modelling such as RETICOLO. [3] We can see a very good agreement between the HDM model and the experimental data in Figure 1. The unique fitting parameters are β and γ , the damping term. The carrier density of the InAsSb:Si is n_0 and the dielectric high frequency constant ε_{∞} . For n_0 , the plasma wavelength, λ_p , is expected to be close to 9 μ m. [4] The non-locality introduces two main effects that we can observe experimentally and model with the HDM. First, it is possible to measure bulk plasmon modes up to the 7th order at shorter wavelengths than λ_p . Second, the decrease of the thickness induces a large blueshift of the bulk plasmon modes once the thickness is less than 200 nm.

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A SERS signal-off strategy for micro-RNA sensing with engineered molecular beacon

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Abstract: Micro-RNAs (miRNA) are a class of small non-coding RNA molecules, ranging from 17 to 25 nucleotides in length. They have recently emerged as promising class of biomarkers for the detection of various diseases, including cancer or inammatory chronic diseases [1,2].

In this work, a novel biosensor based on surface-enhanced Raman spectroscopy (SERS) is presented for the specific detection of a miR-183, a miRNA biomarker associated with chronic obstructive pulmonary disease (COPD) [3]. The adopted strategy exploits a signal-off mechanism, utilizing an engineered molecular beacon (MB) as the oligonucleotide biorecognition element immobilized on a SERS substrate. This substrate comprises silver nanowires deposited on a polytetrafluoroethylene (PTFE) membrane and is coupled with a multi-well low-volume cell, enabling the analysis of micrometric liquid amounts (Figure 1).

The designed biosensor offers highly sensitive and specific detection capabilities, achieving detection limits down to femtomolar concentrations. Additionally, it allows for reuse after a regeneration cycle using a protocol based on HCl, which permit a second detection cycle, with a good recovery of the initial MB signal (83%) and a reproducible signal after hybridization [3].



Figure 1: The schematic representation illustrates: i) the coupling between the SERS substrate and the micro-well cell for liquid experiments (left); and ii) the SERS signal-off mechanism, wherein the hybridization between the molecular beacon and the target miRNA increases the distance between plasmonic AgNWs and the label molecules, resulting in a decrease in the SERS intensity (right).

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Optimization of a microfluidic assay for the SERS detection of miR-320a

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The development of sensing platforms able to carry out the in-field detection of a target analyte plays a key role in the spread of point-of-care applications. In the framework of early cancer diagnostics, Surface Enhanced Raman Scattering (SERS) spectroscopy, combined with microfluidics, represents a promising tool for the on-site analyses of micro-RNAs (miRNAs) as tumor biomarkers. In this work, a microfluidic assay for the SERS detection of miR320a was developed and optimized. In detail, porous silicon (pSi) membranes covered with Ag nanoparticles (AgNPs) were employed as SERS-active elements and integrated in polydimethylsiloxane (PDMS) multi-chamber microfluidic chips [1]. For the detection of the target miRNA, the surface of the AgNPs was functionalized according to a previously optimized two-step hybridization assay [1,2]. An automated injection system consisting of three syringe-pumps controlled by a custom script was used to perform the incubation of the analyte solution, by automatically flowing the liquid back and forth into the microfluidic chip during the sample incubation step (Figure 1a). A careful optimization of the parameters involved in such dynamic incubation (i.e. incubation time, analyte volume and flow rate) was carried out in order to maximize the intensity of the SERS signal. The optimized protocol was then employed to perform the detection of several concentrations of miR320a in buffer solutions, resulting in a sevenfold increase in the sensitivity of the bioassay in terms of Limit of Detection (LOD) compared to a reference assay exploiting SERS-active substrates not integrated in microfluidic chips (Figure 1b). Such a result demonstrates that the automatic and dynamic incubation of the sample solution can significantly improve the SERS detection of miRNAs as cancer biomarkers. Thus, the portable and easy-to-handle platform here developed shows a great potential towards clinical applications.



Figure 1: a) Schematic representation of the microfluidic setup employed for the SERS detection of miR320a. b) SERS spectra relative to the analysis of several concentrations of miR320a by means of the microfluidic (black curves) and reference (red curves) assay. Spectra were normalized to the acquisition conditions. The light blue bar highlights the main vibrational band of Rhodamine Green X at 648 cm⁻¹ employed as Raman reporter.

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Gold nanorods array for pathogens biosensing and white light photothermal disinfection

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Inadequate water sanitation and management expose human and environmental health to severe risks, thus pushing the need of fast and effective point-of-use strategies and devices for an accessible and reliable water management.

The present work aims to meet these demands by developing a gold nanorods (AuNRs) array for pathogen detection or disinfection purposes.

When AuNRs (and plasmonic nanoparticles in general) are irradiated by a visible electromagnetic wave, Localized Surface Plasmon Resonance occurs. The resonance frequency (v) depends on the medium's refractive index (n) surrounding the AuNRs. Moreover, when incident photons with frequency v are absorbed, they cause plasmon excitation. To restore the equilibrium condition, energy is dissipated producing localized heating, turning AuNRs into light-to-heat transducers (photothermal conversion).[1]

Here, the dependence of v from n is exploited for biosensing[2-3], while the photothermal (PT) properties are used for achieving white light PT disinfection.[1] To this end, AuNRs are immobilized on a glass substrate by the electrostatic Layer-by-Layer assembly method, thus giving rise to AuNR arrays whose optimal morphology determines optical properties close to the ones of a colloidal dispersion. The AuNRs array is then functionalized, by physisorption, with an antibody (Ab) suitable for the specific recognition of the Escherichia coli pathogen. The univocal antigen-antibody interaction, occurring on the AuNRs array, determines a n change, causing a v variation. The v difference corresponds to an optical shift (colorimetric change or $\Delta\lambda$) in the absorption spectrum of the AuNRs. As a result, the $\Delta\lambda$ values linearly increase as a function of the *E. coli* concentration with a detection limit of 1 CFU mL⁻¹. Interestingly, the AuNRs-based biosensor is specific and versatile. Indeed, the contamination with Yersinia ruckeri does not determine any significant $\Delta\lambda$. Furthermore, functionalizing the AuNRs array with an anti-Salmonella Typhimurium antibody, followed by contamination with S. Typhimurium (10³ CFU mL⁻¹) demonstrates the biosensor adaptability for detecting various pathogens in drinkable water. The AuNRs array is also investigated as a thermo-optical transducers for white light photothermal (PT) disinfection. Remarkably, a PT efficiency of 43.5% is obtained under white light irradiation, producing a temperature increase (ΔT) of 50 °C in an irradiation time of 3 min. Experiments performed by contaminating the substrate with E. coli cells demonstrate the AuNR array's capability to reduce bacteria's viability upon white light illumination. The PT heating of the AuNR arrays can also generate a temperature increase suitable for disinfecting medical tools.

The proposed AuNR arrays are pioneering new solutions for more environmentally friendly and affordable pathogen detection and disinfection procedures, that are also suitable for improving the water management and, therefore, the quality of life in less developed countries.

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Multifunctional FFP2 face mask for the simultaneous white light disinfection and detection of pathogens using hybrid nanostructures and metasurfacebased optical absorbers

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The Covid 19 pandemic has promoted increased personal protective equipment (PPE) production. Face masks and antigen tests have been crucial in controlling the pandemic's spread among PPE. FFP2 face masks have rapidly become the first choice for indoor use since they provide 94% filtering efficiency for viruses and bacteria. Moreover, a rapid and facile recognition of the virus became an urgent task faced with rapid antigen tests. However, the difficulty of medical waste disposal contributed to environmental pollution. New methodologies are continuously developed to minimize the environmental impact. A new generation of an FFP2 smart face mask is achieved by integrating broadband hybrid nanomaterials (Ag@Au NPs) and a self-assembled optical metasurface (Figure 1). The multifunctional FFP2 face mask shows simultaneously white light-assisted on-demand disinfection properties and versatile biosensing capabilities. These properties are achieved by a powerful combination of white light thermoplasmonic responsive hybrid nanomaterials, which provide excellent photo-thermal disinfection properties, and optical metasurface-based colorimetric biosensors, with a very low limit of pathogens detection. The realized system is studied in optical, morphological, spectroscopic, and cell viability assay experiments and environmental monitoring of harmful pathogens, thus highlighting the extraordinary properties in reusability and pathogens detection of the innovative face mask.



Figure 1: Photo of the Ag@Au NPs face mask incorporating the metasurface-based biosensor technology.

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Time-dependent quantum/continuum modelling of plasmon-enhanced electronic circular dichroism

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Optical properties of a molecule can be dramatically modified by close metal nanoparticles (NPs), in presence of an external electromagnetic perturbation. Plasmonic effects can be used to enhance weak molecular signals and among those circular dichroism (CD) is central in many chemical-physical applications. The presence of the NP can affect the CD signal by determining two specific responses: enhancement/quenching of one or more molecular peak(s); promoting the appearance of a peak in correspondence of the plasmonic resonance¹. We propose a multiscale method to effectively study the electronic circular dichroism (ECD) of a chiral molecule interacting with a non-chiral NP under the influence of an external field. We obtain the ECD spectra of the molecule by means of the propagation of the timedependent Schroedinger equation^{2,3}. This multiscale method is characterized by a quantum description of the chiral moiety at DFT and TDDFT level, whereas the NP is treated according to a polarizable continuum model extended to nanoparticles (PCM-NP)⁴. In particular, we calculated and analyzed the ECD spectra of methyloxirane (MOX) and peridinin (PID) in presence of an Au NP of 2.5 nm radius to study the effects at different distances and laser polarizations of the presence of the plasmonic NP on the ECD spectra. The gap in energy between the plasmonic and molecular excitation and the coupling between the laser pulse and electric and magnetic dipole of MOX or PID proved to be the main factors determining the optical response of the system. This method paves the way to a quantum-chemistry systematic investigation of plasmon-assisted ECD molecular spectra, also of biological relevance, and to propose novel routes for experiments.



Figure 1: Sketch Representation of peridinin (PID), methyloxirane (MOX) and the NP.

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Linear, circular and trochoidal dichroism from chiral and achiral plasmonic nanostructures

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Plasmonic nanoantennas have considerably stronger polarization-dependent optical properties than their molecular counterparts, inspiring photonic platforms for enhancing molecular dichroism and optical activity, achieving negative refraction, and providing fundamental insight into light-matter interactions [1]. Here we will discuss some of such insight mainly from the point of view of the theoretical modeling. Namely, we will review the modulation of visible light scattering from achiral gold half-rings and chiral pinwheels when switching between evanescent surface wave excitation produced from the total internal reflection of left-handed and right-handed circularly polarized light [2]. This effect is driven by a differing relative phase between the in-plane transverse and longitudinal field oscillations of the evanescent wave depending on the incident light handedness (see panel a in the Figure). That will be presented in light of the nanostructures' sensitivity to the trochoidal, or cartwheeling, field motion of the evanescent waves, which leads to trochoidal dichroism [3]. Finally, even achiral nanoparticles can yield strong optical activity when they are asymmetrically illuminated from a single oblique angle instead of evenly illuminated. This effect, called extrinsic chirality, results from the overall chirality of the experimental geometry and strongly depends on the orientation of the incident light. Although extrinsic chirality has been wellcharacterized, an analogous effect involving linear polarization sensitivity has not yet been discussed. Here we report the differential scattering of rotationally symmetric chiral plasmonic pinwheels when asymmetrically irradiated with linearly polarized light [4]. Despite their high rotational symmetry, we observe substantial linear differential scattering that is maintained over all pinwheel orientations (see panel b in the Figure). We demonstrate that this orientation-independent linear differential scattering arises from the broken mirror and rotational symmetries of our overall experimental geometry. Our results underscore the necessity of considering both the rotational symmetry of the nanoantenna and the experimental setup, including illumination direction and angle, when performing plasmon-enhanced chiroptical characterizations. L. Bursi acknowledges financial support from project PNRR-M4C2INV1.5, NextGenerationEU-Avviso 32772021 -ECS_00000033-ECOSISTER-spk6.



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Metasurface enabled vortex beams from Bloch Surface Wave manipulation

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In the ever-evolving landscape of communication and information technologies, Orbital Angular Momentum (OAM) has emerged as a captivating phenomenon with promising applications. Central to unlocking the full potential of OAM are the innovative techniques developed for generating optical vortices [1]. Metasurfaces are one of such techniques that have proven to be particularly effective for manipulating light properties, such as polarization, phase, and amplitude [2]. It has also been shown that, with particular metasurface gratings, it is possible to obtain a chiral-sensitive diffraction, by exploiting the phase discontinuities introduced by the metasurface nanoparticles [3].

While metasurfaces are typically utilized as transmissive optical elements, in this work we show that, with the appropriate design, they can act similarly to traditional gratings and be combined with surface propagating modes like Bloch Surface Waves (BSWs) or Surface Plasmon Polaritons. In particular, we exploit a chiral sensitive metasurface grating in combination with a transverse magnetic (TM) BSW in order to generate vortex beams with arbitrary spin and orbital angular momentum. Thanks to its circular design, such platform is particularly attractive for the manipulation of the field generated from single photon emitters.

The metasurface grating is studied with FDTD simulations and consists of a sequence of Gold, rod-shaped nanoparticles, arranged azymuthally and designed to interact with a TM-BSW propagating from the center of the structure outward, as depicted in Fig.1.a, and outcoupling in the far field only one of the two circular polarizations. By introducing an azimuthally dependent, spiral shaped, phase delay in the outcoupling mechanism, as proposed in [4], we are then able to control also the OAM of the output beam by varying the topological charge of the metasurface.



Figure 1: a) Diffractive structure composed of Gold nanorods of size 75nm x250nm x 60nm, with a grating period of 347nm and scatter tilt of 60°. The structure has a topological charge m = +2, and is designed to interact with a transverse magnetic Bloch Surface Wave propagating radially from the center of the structure. b) Light collected in the far field above the grating, represented in a double HSV colormap: the color Hue (from green, to red) corresponds to the polarization state expressed as the ratio between the Stokes parameter (S3) and the total intensity (S0), while the color Value corresponds to S0. In the image the Field is shown to be mainly RHC polarized, and the inset on the bottom right corner shows a vortex phase profile, with OAM number l = +1. The cyan dashed line highlights the region of maximum intensity.

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Design of a magnetically tunable Fabry-Perot metasurface based on ferromagnetic materials.

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Metasurfaces exhibit unique wave manipulation capabilities. Although static metasurfaces have been extensively studied, the practical realization of their full potential in optical applications requires the development of reconfigurable metasurfaces able to dynamically adjust their optical response in real time [1]. The utilization of magnetic fields emerges as a promising solution, offering rapid and reversible control over metasurfaces optical response without mechanical action [2-4].

We propose the simulation and design of a magnetically tunable Fabry-Perot (FP) metasurface to address the challenges of controlling nanocavity lengths in nanoscale devices, surpassing limitations of traditional mechanical methods that are irreversible and imprecise [5].

The design consists of two main elements: a multilayered substrate and a magnetic disk-shaped metaatom supporting localized surface plasmon resonance (LSPR) (Fig.1). The layered structure is made of an Aluminum (Al) substrate, covered by a thin layer of ferromagnetic Cobalt (Co) which in turn is coated by a layer of amorphous silica (SiO₂) with a thickness of the order of $\lambda/2$ of the LSPR of the regularly spaced Co nanodisks, placed on top of the SiO₂ layer.



Figure 1: (a): Unit cell of the simulated system and (b) schematic representation of the simulated metasurface showing the periodic arrangement of unit cells. (c) Reflectance spectrum of the metasurface for a perpendicularly incident electromagnetic wave with an external DC magnetic field H collinear (+) or anticollinear (-) with respect to the incident EM wave.

The Co disks and the Co layer geometrically define FP nanocavities within the SiO₂ layer. Their resonant modes dictate the reflectance and absorption properties of the metasurface (Fig.1 c), with the presence of minima in the reflectance spectrum at the FP cavity resonances. The application of a magnetic field perpendicular to the metasurface gives origin to off-diagonal elements in the dielectric tensor of Co. This induces a shift in the nanocavities resonant modes through the hybridization of the Co nanodisks LSPRs and Co layer surface plasmon polaritons (SPPs), both magnetically tuned, with the FP modes. This hybridization corresponds to a change in the effective length of the nanocavities. Consequently, a corresponding shift in the minima of the reflectance spectrum is observed (Fig.1 c). By adjusting the size and distances of the Co disks and the layers thicknesses, the collective effect of regularly spaced, interacting FP cavities on the metasurface effectively magnifies the effect of the magnetic field in the reflectance spectrum with respect to isolated or irregularly distributed cavities. The results of this study lay the ground for the exploration of magnetic field-tunable FP metasurfaces, prompting the realization of optical devices, e.g. metalenses, wedges and filters with tunable optical response.

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Raman and SERS-bases imaging and sensing for biomedical applications

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Surface-enhanced Raman scattering (SERS) has garnered increasing research interest due to its excellent resolution, high sensitivity, and rapid detection of low-concentration analytes, particularly in biomedicine. This discussion will cover recent developments and applications of SERS-based nanosensors and nanoreporters developed in our laboratory for imaging, biochemical monitoring, medical diagnostics, and therapy. Diseases such as cancer induce changes in the molecular composition of affected cells, including alterations in lipid and protein levels, all of which are reflected in Raman spectra. Additionally, I will demonstrate the significant benefits of SERS-based approaches for identifying, classifying, and monitoring cancer cells in in-vitro experiments and preclinical studies, providing label-free biochemical information [1]. The application of Raman/SERS imaging in combination with other imaging techniques, such as digital holography, for label-free and non-destructive identification of circulating tumor cells in liquid biopsy will also be discussed [2]. The applications of SERS nanosensors for protein detection, local quantification, and controlled release of drugs in living cancer cells will be presented [3,4].

Keywords: Raman imaging, Correlative imaging, SERS, Biosensors, cancer.

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Photo-Induced Enhanced Raman Spectroscopy Beyond Two-Dimensional Materials

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Abstract: After the exfoliation of graphene, various two-dimensional (2D) materials, especially transition metal dichalcogenides (TMDCs), have been synthesized via many techniques that are grouped into two approaches: bottom-up and top-down. The former ones have shown fascinating potential in different application fields like sensing, solar cells, hydrogen evaluation, and so on. In particular, good results are reported using these materials as electrochemical, optical, and plasmonic sensors for low molecular concentrations. Recent advancements in enhanced Raman spectroscopies (ERS) like surface-enhanced Raman spectroscopy (SERS), tip-enhanced Raman spectroscopy (TERS) or photo-induced enhanced Raman spectroscopy (PIERS) have extended the capabilities to probe the local electromagnetic field and chemical enhancements of TMDCs materials enabling the detection and analysis of subtle structural and chemical changes at the nanoscale level. PIERS offers a versatile and powerful platform for probing the vibrational properties and structural characteristics of molecular analytes adsorbed on the AuNps-TMDCs hybrid system leading to an enhancement in the Raman signals due to the synergic effects combination of Raman spectroscopy and photoexcitation techniques triggering highly efficient charge transfer processes between the metal and the TMDC. In this framework, we used two different kinds of TMDCs nanosheets for our experiments, namely WS2 and MoSe2 nanosheets, which were exfoliated through liquid-phase exfoliation (LPE) followed by liquid cascade centrifuge (LCC) and subsequently coated with either gold nanoparticles (AuNPs) or gold nanorods (AuNRs), respectively. The first hybrid system was tested as PIERS platform and its efficiency was analyzed monitoring the scattering intensity of 4-mercaptobenzoic acid (MBA) molecules adsorbed on the substrate. The UV pre-irradiation step in this case gives an increase of the charge carriers' density $\approx 1.8\%$ with an overall PIERS signal enhancement is $\sim 10^6$, whereas the photoactivation of WS2 yields a signal improvement of factor 4 with respect to SERS before UV irradiation.¹ On the other hand, MoSe2 nanosheets, coated with AuNRs, were tested with methylene blue (MB). In this case, the PIERS signal is about three times stronger with respect to normal SERS.

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Figure 1: Descriptive scheme for the PIERS effect on AuNps-WS₂ with MBA molecules ¹

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Nanosystems for molecular detection of biological samples using SERS

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Abstract:

Sensitive and accurate detection of analytes and/or bacteria is a crucial step in identifying dangerous compounds or pathogens, whether in the clinical field or food safety. Utilizing advanced methods such as Surface-Enhanced Raman Spectroscopy (SERS) would help with identifying bacteria or analytes with high sensitivity and accuracy.

Manufacturing of high-quality nanoparticles (NPs) are fundamental for detection via SERS to ensure sensitive and reproducible SERS detection. To ensure high quality and easy application of the NPs, the NPs should be cost-effective and simple to reproduce the fabrication process. To optimize the method, the focus is on the synthesis and characterization of metal NPs that enhance Raman signal by a localized plasmon resonance in SERS, where the main part of the experimental work consists of the synthesis of gold (Au) and silver (Ag) NPs and their characterization and use for analysis of chemical and biological samples by SERS. The SERS-active Ag-NPs and Au-NPs were tested with pathological bacteria *Staphylococcus aureus* and *Escherichia coli*, which were exposed to the stressful environment of the deionized water. The physiological stress led to the release of biomarkers, specifically adenine which exhibits a characteristic SERS peak at 730 cm⁻¹. The experiments proved that the NPs synthesized through a simple, rapid and cost-effective method were suitable for a qualitative detection of adenine released by the bacteria with a commercial available Raman spectrometer, see Figure 1.

The further research will focus on experiments with different bacteria and different stress conditions (such as antibiotics) to further explore possibility of using SERS at POC (point of care settings) for identification of bacteria sensitivity to antibiotics. Mainly, we will investigate possibility to detect metabolites which are produced by bacteria under the stress. Here as a complementary technique, we will use CARS spectroscopy to detect metabolites and biomarkers in selected samples.



Figure 1 Illustration of our experimental setup. Figure courtesy of Martin Kizovský (Institute of scientific instruments, The Czech Academy of Sciences)

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T-matrix calculations for optical trapping and enhanced spectroscopy of micro and nano-plastics

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In the last decade micro and nano-plastics have raised a growing interest in the scientific community due to their ubiquitous presence in the environment and due to their potential toxicity for the human health and the ecosystem [1]. Since their identification is very challenging, especially for smaller particles, it is crucial to find accurate detection and characterization methods.

Recently, Optical and Raman tweezers have proved to be an efficient tool to trap, manipulate and characterize micro and nano plastics, allowing a contamination-free investigation [2,3]. Great scientific interest has also been directed towards the development of sensitive SERS structures with the aim to enable a better detection and particle characterization thanks to hot spots formation and electromagnetic field enhancement [4]. Computational methods capable of efficiently simulating the enhanced optical response of micro and nano-plastics in presence of metal nanoparticles could be very helpful in the design of SERS substrates and in the development of SERS detection methods. To this end, we study the near and far-field optical properties of nano clusters composed by nano-plastics particles coupled with metal nanoparticles, using the Transition matrix (T-matrix) method based on the multipole field expansion formalism [5]. This approach allows an accurate description of the optical forces acting on model metal-plastic nano-clusters and appears as a useful tool to address the experimental effort in the detection ad characterization of trapped plastics nanoparticles.

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Boosting SERS performance with an ultra-thin coating of polydopamine for the detection of Methylene Blue

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Polydopamine (PDA) is a versatile biopolymer with great adhesive properties [1] that spontaneously self-polymerizes from dopamine (DA) in weak alkaline media and in presence of oxygen [2]. In this contribution we describe the coating process of silver nanoparticles (AgNPs) with an ultra-thin layer of PDA (schematic representation in figure 1a) to increase SERS signal of Methylene Blue (MB), as hypothesised on the basis of the well-known affinity between PDA and MB [3]

The control of the thickness is crucial since the SERS enhancement is strictly dependent on the distance between the target molecule and the plasmonic substrate. Four different thicknesses were obtained, labelled as @PDA003/006/012/031 stating for the different amounts of DA monomer employed (mg/mL). From the TEM images reported in figure 1b polydopamine coating on the silver nanoparticles can be clearly observed.



Figure 1: a) PDA coating process of silver nanospheres. b) TEM images of AgNP@PDA031 on the left and AgNP@PDA012 on the right.

The substrates have been characterised with TEM microscopy, Dynamic Light Scattering (DLS), Uv-Visible and Raman spectroscopy, demonstrating that huge increase in the SERS signal of MB can be obtained with a careful tuning of PDA thickness if compared to bare AgNPs.



Figure 2: a) Uv-visible normalised spectra of bare AgNPs and PDA coated AgNPs with different shell thicknesses. b) SERS intensity trend of Methylene Blue 10⁻⁶ M at 1624 cm⁻¹ as PDA thickness increase. c) SERS spectra of Methylene Blue employing respectively AgNPs and AgNP@PDA003 as SERS substrate.

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Volume plasmon-polariton modes in all-dielectric hyperbolic metamaterials based on III-V semiconductors

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Hyperbolic metamaterials (HMMs) have gained particular attention because they allow for the propagation of electromagnetic waves with arbitrarily large wavevectors, which would be evanescent in ordinary materials. These high-k modes, called volume plasmon-polaritons (VPPs), enable advanced applications such as superlenses, sub-wavelength imaging and super-Planckian thermal emission. HMMs are characterized by extreme optical anisotropy, as they behave as metals in one direction and as dielectrics in the perpendicular direction. They are most often realized by alternating layers of metallic and dielectric systems, where plasmonic resonances are used to couple light with the metallic component of the stack. When regular metals are employed, the resulting metamaterials are generally hyperbolically active in the visible-UV range, because of their high electron density. However, HMMs working in the IR-to-THz electromagnetic range would be of great technological interest for applications in infrared optoelectronics. Recent experimental reports [1] have shown the feasibility of fabricating multilayer HMMs working in the infrared spectrum using some III-V semiconductors, where intrinsic and doped compounds serve as dielectric and metallic layers respectively.

In this work [2], we undertake a comprehensive investigation of volume plasmon polaritons within hyperbolic metamaterials. Initially, we integrate ab initio atomistic simulations based on DFT+U and the effective medium approximation to theoretically demonstrate the capability of realizing hyperbolic metamaterials using only III-V semiconductors. The obtained results are in excellent agreement with the experimental findings. However, this approach provides insights only into the first-order VPPs, so we expand beyond the limitations of effective medium theory by employing the transfer/scattering matrix method for electrodynamics simulations. This allows us to explore volume plasmon polaritons of higher orders and also to predict not only the resonance peaks of transmission and reflectivity but also the electromagnetic field within the metamaterial. Moreover, by leveraging the study of the photonic band structure of the metamaterial, we systematically identify optimal excitation conditions for these resonances, independently of external environmental factors. Thanks to this methodology, we achieve a highly efficient design of hyperbolic metamaterials to effectively harness these plasmonic resonances.



Figure 1: Scheme of the superlattice model used to design the HMMs. ε_{\parallel} and ε_{\perp} are the parallel and the perpendicular components of the effective dielectric tensor, respectively; $\varepsilon_{m/d}$ and $d_{m/d}$ are the complex permittivity and the thicknesses of component metallic and dielectric layers.

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Photonic force microscopy in front of Epsilon-near-Zero surfaces

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Optical tweezers are an extremely sensitive tool for the study of force fields in front of surfaces, allowing force sensing in the femtonewton range [1]. This technique is ideal to probe light-induced forces in front of Epsilon-near-Zero (ENZ) metasurfaces, in front of which the levitation of an electrical dipole has been theoretically shown [2].

In this work, we use both a theoretical and experimental approach to study optical forces on nano and micron-sized particles in front of ENZ surfaces and, as a comparison, in front of ordinary dielectric and metallic surfaces. Repulsive-attractive optomechanics on the trapped particle is theoretically shown, depending on the composition and shape of the trapped particle and on the properties in front of which the particle is trapped [3]. Measurements carried out by using a dielectric micron-sized particle and two laser beams, one to trap the particle and one to periodically excite the surface, show a repulsive force in front of multilayered ENZ metasurface. The force is strongly dependent on the wavelength of the beam used to excite the surface and show a non-linear dependence on its power. The role of short-range forces, such as van der Waals and Casimir forces, is evaluated as not effective in determining this peculiar behaviour. We suggest that the repulsive force is due to the combination of a thermophoretic force and ENZ repulsion.

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Phononic hyperbolic metamaterial with ZnO/ZnMgO heterostructures

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Hyperbolic metamaterials (HMMs) exhibit opposite signs of the real part of the dielectric function along the directions parallel (ε_{\parallel}) and perpendicular (ε_{\perp}) to the surface plane. Type I HMMs ($\varepsilon_{\parallel} > 0$ and $\varepsilon_{\perp} < 0$) have been of special interest given their negative refraction capabilities [1,2]. Various approaches have been explored to achieve Type I HMMs, including arranging materials in periodic structures [3,4], designing plasmonic structures [2] and, only recently, the first phononic HMM was demonstrated using superlattices supporting surface phonon polaritons (SPhPs) [5]. Given the higher quality factor observed in SPhP materials compared to plasmonic materials [6], phonon modes hold promise for attaining low-loss, sub-diffraction-limited optical modes using SPhP excitations, hence our focus on this approach.

This study presents the demonstration of a Type I phononic HMM formed by ZnO/ZnMgO heterostructures. Our approach begins by designing the heterostructure using the transfer matrix method (TMM) to find the conditions that the structure needs to satisfy so that a Type I HMM spectral region exists. For this purpose, the HMM is studied as function of three parameters: the doping level of the ZnO quantum wells (QWs), the thickness ratio of QWs/barriers (d_{ZnO}/d_{ZnMgO}) and the Mg concentration ([Mg]) in the $Mg_xZn_{1-x}O$ layers. Once the optimal parameters are identified, we fabricate that structure and characterize it experimentally by carrying out reflectance measurements in a Fourier Transform Infrared (FTIR) spectrometer, using a *p*-polarized incident light and an incidence angle ranging from 30 to 85 degrees. We then fit the experimental measurements, obtaining the dielectric functions of the two constituent materials, ϵ_{ZnO} and ϵ_{ZnMa0} , from which we obtain ε_{\parallel} and ε_{\perp} by employing effective medium theory (EMT). Finally, we verify that this effective dielectric function exhibits a Type I HMM behaviour in a specific region.



Figure 1: Reflectance spectra under *p*-polarization at 45° angle of incidence. The red curve is the experimental result, and the black curve is the fitted reflectance spectra calculated by EMT.



Figure 2: Calculation of the effective dielectric function for the study of the HMM Type I region.

The results of this work indicate that achieving a Type I HMM in ZnO/ZnMgO heterostructures requires undoped ZnO QWs, and that an enhanced response (i.e. a higher HMM figure of merit) is achieved when the thicknesses of the quantum wells and barriers are closely matched and when a high Mg concentration is incorporated. Thus, this study presents a method of obtaining a phononic Type I HMM by tuning its effective dielectric function. The optimal parameters for obtaining a Type I HMM in ZnO/ZnMgO heterostructures are identified and this phenomenon is demonstrated experimentally for a particular sample with undoped QWs, d_{ZnO}/d_{ZnMgO} =4/5 and [Mg] = 32%.

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Spectral characterization of the optical Kerr effect in Au/Si₃N₄ multilayer hyperbolic metamaterials

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In recent years, the research field of metamaterials (MMs) has flourished thanks to the widespread interest in their different applications in nanoscience and nanotechnology. In fact, MMs offer the possibility to engineer their optical functionalities by accurately designing their structural nanometric building-blocks on a sub-wavelength scale. In particular, hyperbolic metamaterials (HMMs) exhibit a region of vanishing permittivity called epsilon near-zero (ENZ). In this work multilayer HMMs are crafted with an ENZ that is widely tunable in the visible and near-infrared spectral range through the control of their metallic filling fraction f_m [1]. Here enhanced light-matter interactions and strong nonlinear optical phenomena arise, thus allowing for applications that require lower powers and smaller footprints [2].

The aim of this work is the spectral characterization of the nonlinear optical Kerr effect (OKE) of multilayer hyperbolic metamaterials (MHMs) obtained by magnetron sputtering deposition of alternating layers of Au and Si₃N₄. Two MHMs with metallic filling fraction $f_m = 30\%$, 10% are realized, thus tuning their ENZ wavelength respectively in the visible at $\lambda_{ENZ}^{MHM30} = 603$ nm and near-infrared at $\lambda_{ENZ}^{MHM10} = 914$ nm spectral regions, in order to obtain enhanced nonlinear optical properties at these accurately selected spectral positions.

The OKE is spectrally studied in the picosecond excitation regime in the visible and near-infrared spectral range through the coupling of a Nd:YAG laser, with its third harmonic beam at $\lambda = 355$ nm as a source, and an Optical Parametric Amplifier (OPA) that allows for the spectral exploration of the nonlinear response of the MHMs. The z-scan technique [3] is adopted, where the two configurations of open aperture (OA) and closed aperture (CA) work simultaneously to retrieve the nonlinear absorption coefficient β and nonlinear refractive index n_2 . In Figure 1 are reported the measurements performed on the MHM10 at a wavelength near its ENZ spectral position. Here the MHM exhibits a clear and remarkable nonlinear behavior that was not previously observed in its constituent materials at the considered wavelength, thus completely owing its nonlinear response to the nanoscale combination of Au and Si₃N₄.



Figure 1: Z-scan Normalized Transmittance data of the MHM10 in OA (a) and CA (b) configurations, acquired at $\lambda = 900$ nm and $I = 7.4 \times 10^8$ W/cm². Experimental data is reported in black and its fit is represented by the red solid line. The resulting nonlinear parameters β and n_2 are explicited.

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Abstracts – Posters

Collective emission effects from plasmonic nanocavity coupled dye molecules

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Using plasmonic structures to concentrate light into extremely small mode volumes, creating intense optical 'hot-spots', can massively enhance signals from individual molecules [1]. By coupling together such hot-spots containing dye emitters, we probe here fundamental questions about extreme-scale dipole-dipole interactions in the nonlinear pumped regime.

Self-assembled monolayer aggregate (MLagg) gold nanoparticle (AuNP) films are assembled with cucurbit[7]uril (CB) scaffolding molecules that define a precisely uniform 1 nm separation between the Au facets [2]. CB host molecules also allow incorporation of guest rhodamine B (RhB) emitters. Under 633nm laser excitation, imaging reveals the spatial dependence of emission in these systems. Notably, dyes coupled through the plasmonic cavity exhibit a non-linear power dependence, suggestive of collective emission phenomena beyond simple fluorescence.



Figure 1: Array of close-packed Au NPs separated by 1nm gaps to form coupled nanocavities, with rhodamine B dye emitters placed within each nanocavity scaffolded with CB.

We show the influence of coupling and disorder in this system. Particularly surprising is that emission from RhB emerges from regions far outside the pumped laser excitation spot, indicating a transition to a collective emission regime [3] under specific excitation conditions. Statistical analysis of spatially resolved PL images as well as coherence measurements demonstrate consistent behavior between samples, supporting the presence of collective emission phenomena.

The simplicity of self-assembled MLagg fabrication thus offers a promising approach for generating structures exhibiting collective emission behavior at room temperature. Moreover, the observed nonlinear power dependence of dye molecule emission coupled with Raman enhancement underscores the significance of plasmonic nanocavities in enhancing spectroscopic techniques. Future investigations will focus on comparing these findings with other emitting molecules to elucidate underlying mechanisms.

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Polarization-resolved surface-enhanced sensing of single-stranded DNA with Bloch surface waves

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One-dimensional photonic crystal multilayers are well-established and fully consolidated tools in the palette of nanophotonic design, yet they still offer exciting and unexplored possibilities with novel ways to control the local density of optical states in the energy-momentum space. Of particular interest for surface-enhanced sensing applications is the possibility to excite Bloch surface waves at the top layer of a truncated photonic crystal multilayer, which are solutions of the Maxwell equations that propagate along the surface but are exponentially confined along the perpendicular direction. The associated strong field confinement and enhancement at the surface makes them particularly suitable for molecular sensing and spectroscopy, both on-resonance (surface-enhanced absorption) and off-resonance (refractometric sensing) with the electronic or vibrational transitions of the investigated molecules.

In a series of recent works, we have discussed how to engineer the top layer of the truncated photonic crystal multilayer to tune the local refractive index and superimpose the dispersion relations of the TE and TM modes over a broad spectral range. By means of analytical and numerical analysis, we highlighted the superior performance that the combination of the two modes guarantees in chiral sensing [1,2] and in the optical sorting of chiral molecules [3]. While the experimental validation of those concepts is still ongoing [4], in this contribution we focus on a recent experiment in which we sensed the refractometric response of a molecular layer with both the TE and TM modes in order to assess the anisotropy (birefringence) that is a signature of the molecular orientation. Specifically, we follow the growth of single-stranded DNA chains on the sample surface by rolling circle amplification, an enzymatic reaction mediated by polymerase. By monitoring the spectral shift of both the TE and TM surface modes in the functionalized photonic crystal multilayer, we were able to assess the molecular orientation of the DNA chains exploiting the surface enhancement provided by Bloch surface waves.

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Quantitative analysis of emergence and evolution of plasmonic resonances in ultrasmall spherical nanoparticles and molecular systems

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An attractive trend in plasmonics focuses on the use of plasmons supported by ultrasmall nanostructures - a few nanometers large down to the molecular limit, represented by proper molecular systems. In this size range, quantum confinement, non-locality, and the details of electronic structure significantly alter the optical response of nanostructures compared to classical theories. In ultrasmall nanoclusters and molecular systems, plasmonic resonances are mixed with single-electron transitions, making it difficult to identify excitations with a dominant plasmonic character. Here, using the generalized plasmonicity index (GPI) [1], we quantitatively investigate the evolution of plasmon resonances in jellium nanospheres as a function of size, lattice background permittivity and conduction electron density [2]. Moreover, we thoroughly investigate the connection between the *plasmonicity* – i.e., the plasmonic character – of such resonances and their degree of quantum effects and we present a simple classical model that elucidates the fundamental physical mechanisms underlying the GPI [2]. Finally, we analyze the effect of molecular plasmonic excitations, supported by ultrasmall graphene nanoislands, on selected target molecules placed nearby [3]. Our work provides a quantitative foundation for the further design and optimization of ultrasmall nanostructures for quantum and molecular plasmonics applications. L. Bursi acknowledges financial support from project PNRR-M4C2INV1.5, NextGenerationEU-Avviso 32772021 -ECS_00000033-ECOSISTER-spk6.

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Photonic band gap in Hyperuniform network over fabrication parameters

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Recently, disordered dielectric materials with structural correlations, which are halfway between random structures and perfectly ordered photonic crystals, have generated an ever-growing interest. A subclass of these materials are the Hyperuniform Disordered (HuD) photonic systems, that have recently been shown to display large isotropic photonic band gaps (PBG) [1]. Recently, dielectric slabs optically activated by embedded InAs quantum dots and patterned with a HuD network design have been experimentally investigated, allowing to characterize light transport regimes as well as to identify several Anderson dielectric localized states spectrally located at the lower PBG edge [2]. Here, we show a Near-field Optical Microscopy (SNOM) analysis of air modes located at the upper PBG edge of similar photonic samples (Figure 1a). To do so, we characterize the tuning of the PBG by changing a fundamental structural parameter of the structure: the wall thickness (T, namely the ratio between the wall of a dielectric cell and the scale length a, defined as $a = \frac{L}{\sqrt{N}}$ with L the length of the side and N, the number of points in the pattern). We used SNOM setup, which is capable of subwavelength resolution in the near-IR range, to reveal the spatial extention of the electromagnetic field in an illumination/collection configuration. A SNOM hyperspectral map filtered around a broad wavelength interval (1040-1299 nm) is shown in Figure 1b, displaying several Anderson air modes; two typical spectra acquired in the red spots, corresponding to the two modes maximum intensity positions, have been overlaid. Figure 1c shows five typical spectra of samples with three values of T=0,34; 0,40; 0,46; the band gaps have been highlighted in different colours. The limits of the PBGs are set by detecting the upper (air) and lower (dielectric) modes at the edges and, coherently with the expected behavior of conventional photonic crystals bandgaps, we can observe that the band gap becomes narrower by increasing T [3]. The possibility of understanding the effect of changing the fabrication parameters on the photonic band gap and the modes near it can extend the plethora of possible applications based on HuD platforms.



Figure 1: (a) SEM image of HuD sample. (b) SNOM Hyperspectral map, $10 \times 10 \ \mu m^2$, filtered around a broad wavelength interval (1040-1299 nm) for the sample with T=0,46 and two spectra acquired in the red points of the map. (c) Different spectra obtained for T=0,34; 0,40; 0,46 respectively in blue, green, red. Shaded spectra overlapped to the red and green ones highlight the upper modes of the PBG. The highlighted areas are the photonic band gaps.

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SERS substrate based on hybrid structure of Graphene Oxide/Ag nanoparticles/Zirconia film

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Graphene oxide (GO) is widely used as a platform to assemble various metal or metal oxide nanostructures to generate functional materials with unique properties. GO is known for its high surface area, and excellent 2D conductivity. High surface area and functional groups of GO promote adsorption of various molecules and anchoring of nanoparticles, while carbon network promotes electron delocalization and shuttling that aids in fluorescence quenching [1,2]. The hydrophilic graphene oxide sheets can adsorb analyte molecules nearby the plasmonic nanoparticles, while zirconia favors the formation of nucleation centers to which Ag NPs adhere, forming conglomerates visualized in SEM images.



Figure 1: UV-Vis spectra of individual systems and their ternary mixture (a); SEM image of the investigated system.

In this work, we present the surface-enhanced Raman scattering (SERS) substrate based on Graphene Oxide/Ag nanoparticles/Zirconia (GO/AgNPs/ZrO₂) films prepared by a low cost and simple method. The structural, optical and morphological properties have been investigated by micro-Raman, UV-vis absorption spectroscopies and Scanning Electron Microscopy, operating in Transmission mode (STEM). The hybrid GO/AgNPs/ZrO₂ composite presents high sensitivity and well stability with crystal violet (CV) molecules as a probe. To show the potential for practical application, SERS detection of bacteria was realized. The main advantages of SERS for this purpose are the sensitivity of the technique and the resolution of the spectra, which combined with multivariate statistical analysis, allowed to investigate the complexity of bacterial cells [3].

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Diffraction limited focusing relaxation in metalens design for photovoltaics applications

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At the center of the most recent technological advancement are optical devices, such as lenses, mirrors, filters, etc., which enable light manipulation. With the rapid advancement of nanotechnology, due to the increasing request for lightness, compactness and flexibility, this control is being moved at the microand nano-scale, and metalenses are at the center of this scenario. A Metalens is an ultra-flat metasurface composed of periodically arranged dielectric or metallic nano-units with varying geometrical parameters. By engineering their structure an abrupt phase change can be introduced on a scale of the incident wavelength along the optical path, allowing for new degrees of freedom for controlling wavefronts [1,2].

To achieve a more compact system for space applications, the goal is to design an optical system for harvesting light in a broad spectral range able to focus sunlight onto small, highly efficient, multijunction solar cells. In this work, we show how, in order to increase in a wide spectral range the achromaticity performances of a metalens, we optimize the amount of light reaching the solar cell, by relaxing the diffraction-limited conditions, since it is not mandatory to achieve subwavelength image resolution. To quantify the performance of our design, i.e. the metalens factor of merit (FoM), we illuminate the metalens, placed in the xy plane, with a broadband planewave propagating along the z direction. For each wavelength, the amount of light that reaches the solar cell with a size equal to half the radius of the metalens, is normalized to the amount of light that reaches the solar cell without the metalens. To improve the FoM, we propose to release the diffraction-limited focusing condition by changing the phase profile of the metalens.



Figure 1: Electric field intensity along the x-z plane produced by a metalens (positioned at z=0) with a diffraction limited phase profile (A), and a metalens with a phase profile where the diffraction limited condition is relaxed (B). C) FoM obtained at different z for the two-phase profiles, for metalens with NA = 0.45 and R= $11 \,\mu m$.

To verify that the relaxation of the diffraction-limited condition would improve the FoM, different metalenses (designed with dielectric cylindrical pillars as meta-units) were analyzed by changing the numerical aperture (NA = 0.22, NA = 0.45, NA = 0.60) and lens radius (R = 11 μ m, R = 22 μ m). All metalens with the relaxed phase profile show a larger FoM, as shown in Figure 1C) for NA=0,45 and R=11 μ m, thus improving light harvesting. The future objective is to extend the analysis to lenses with larger diameters by trying to increase the degrees of freedom of the system by changing the geometry of the nano-scatterer.

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Nano-imprint lithography of broad-band and wide-angle antireflective structures for high-power lasers

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Antireflection coatings [1] (ARCs) are devices that reduce the impact of impedance discontinuity for light propagation across two media featuring a different dielectric constant. They are commercial devices exploited in many applications, including imaging, photovoltaic, extreme UV optics and high-power lasers.

In this work we report on the fabrication of broad-band and wide-angle ARCs on glass and fused Silica (FS) and their applicability to high-power lasers at visible and near-infrared frequencies. They are obtained via sol-gel spin-coating followed by nano-imprint lithography of metal-oxides (MOx-NIL) [2,3] [Fig. 1a)].The metastructures are composed of methylated silica (MSA, Si₄O₇Me₂) and are shaped as tapered nipple-dimple arrays, a 3D double structure of intercalated pillars and holes arranged in a triangular pattern, see Fig. 1b).



Figure 1: (a) MOx-NIL fabrication process. (c) Tilted view at 50 degrees of the MSA replica used at visible frequency. (c) Transmission measurements with unpolarized light at normal incidence for double face ARC on glass.

Fig. 1c) shows light transmission (T) measurements for double face ARCs that accounts for their broadrange character. ARCs on FS and glass display the same behavior. T can reach values as high as 99.8% and has an achromatic character with T > 98% from 400 to 1200 nm and > 96% from 800 to 2500 nm. The performances of the presented broad-band and wide-angle ARCs [4] are comparable or superior to the existing state of the art, showcasing the exploitability of our devices also for high-power lasers. The sustainability and simplicity of our fabrication process together with its compatibility with plateto-plate and roll-to-plate fabrication account for its high market readiness.

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Opuntia Ficus-indica extraction based anticounterfeiting tag functioning at Optical and Terahertz band

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Anti-counterfeiting methods [1] are developed in response to the counterfeiting activities that continue to cause damage around the world. Several approaches are emerging for the fabrication of new anti-counterfeiting tags, combining the use of new techniques and materials, in order to make it more difficult to reproduce. We propose a novel technology, using cheaper materials and a simple fabrication process, while increasing levels of security.

We used Opuntia Ficus-indica (OFI) plant extract, with its distinctive fluorescent properties as a key material to provide the first security level of the tags. Indeed, it show a distinctive red emission when excited with UV light source. Polyvinyl alcohol (PVA) was combined with titanium dioxide (TiO2) to realize a flexible substrate that can be easy integrated on product packaging. The OFI fluorescent extract was mixed with polymethyl methacrylate (PMMA) and sprayed on the substrate to realized not deterministic deposited fluorescent droplets. We fabricated 10 tags and then we took three photos of each tag at three angles: 0°, 45° and 90°. Scale Invariant Feature Transform (SIFT) image recognition algorithm is used to analyze these photos and recognized unique features. The analysis shows that a range of 130 to 1502 features is recognized when a tag is compared to itself whatever the angle taken. Instead of a maximum of 16 features being detected when two different tags are compared, namely at least one order of magnitude lower. Higher number of features makes the tag stronger and more difficult for counterfeiters to reproduce.

A logo undetectable in the visible spectrum has been sputtered to the anti-counterfeit tags to provide a second level of security. It consists of a 6-square patch array of 25 nm thickness of indium tin oxide (ITO) [2]. This logo is visible in terms of reflection in terahertz spectroscopy [3] at 0.3-10 THz frequency range. Thanks to the transmission line circuit model [4], the evaluation of the reflectance behavior of the ITO shows that each patch array in the logo has a unique and unpredictable response because of its distinct electro-optical characteristics. Due to the difference in their thickness caused by the fluorescent dots on the substrate, the different patches are then unique. Thus, it would be impossible to reproduce them, giving an anti-counterfeiting tag which are doubly protected and impossible to replicate.

These low-cost anti-counterfeiting tags will help producers to protect their works easily. For the first level of security, it is only necessary take a photo with a smartphone, therefore consumers could easily verify the authenticity of products. by comparing the taken photon with the one stored into the database. Indeed, they can use a specific application to compare the taken photo with the one stored into a secure database. The second level requires advanced instrumentations and high skill therefore it is accessible only to expert in case of doubt on the first level.

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Third Harmonic Chiroptical Scattering from Silver Nanohelcies

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Nonlinear chiroptical activity has been of interest in recent years due to promising applications such as controlling light with chiral-photonics [1], sensitive chemical analysis [2] and photo-reactions [3]. Being able to detect these signature may also lead to the ability to characterise chiral materials in volumes multiple orders of magnitude smaller than those used required for conventional linear circular dichroism measurements [4]. This would be advantageous to research in pharmacology, where drug yields maybe small, time consuming and expensive to produce.



Figure 1: Experimental setup used to measure the nonlinear chiral response of Ag nanohelcies

Here we present experimental results showing that when Ag nanohelices of different handedness dispersed in water are excited with circularly polarised light from a 1095nm fs pulsed laser, a nonlinear chiral response is observed both parallel and perpendicular to the incident beam. When varying the incident power the observed signal is cubic which is consistent with that of third-order nonlinear scattering. From the observed difference in scattering for the two enantiomers we are able characterise the chiroptical activity in terms of a value known as the third harmonic ellipticity, measuring values of -2° and 6° for left-and right-handed nanohelcies respectively. The measured values of the ellipticity provides a clear way of discriminating between the two enantiomers of sample due to their differential response to circularly polarised light.

Using the calculated values of the ellipticity it is also possible to produce a nonlinear spectra by varying the wavelength to further characterise the nonlinear response of the Ag nanohelices providing a nonlinear analogue to the linear circular dichroism spectra. Further work to improve the measured signal will allow for the concentration of the sample to be continually reduced, whilst also providing a high throughput method of analysing chiral materials which may prove valuable to pharmacological and health sciences.

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Polarization encoding of nonlinear light in AlGaAs metasurfaces with attosecond precision

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All-optical control using metasurfaces has emerged as a frontier in photonics, offering unprecedented capabilities for light manipulation at the nanoscale. Recent advances have extended these capabilities to nonlinear regimes, where upconversion processes can enable all-optical signal modulation. For example, we have recently demonstrated that the upconverted light can be effectively routed among diffraction orders of a metasurface via nonlinear interferometry.¹ Here, using the same platform of Al_{0.18}Ga_{0.82}As nonlinear metasurface² we extend control to the polarization state of the upconverted light. This is achieved by controlling the phase delay between two frequency-degenerate nonlinear processes, namely Third- Harmonic Generation (THG) and Sum- Frequency Generation (SFG). We can toggle the polarization state between two opposite diffraction orders from linear to circular with opposite handedness by finely controlling the pulse delay. In addition, we also show that our approach offers the flexibility to switch the circular states among various sets of diffraction orders by modifying the polarization of one of the pump beams.



Figure 1: (a) Diagram of the experimental excitation and detection scheme. (b) Scanning electron micrograph of the investigated metasurface. (c,d) Energy diagrams of THG and SFG with numerical simulation of the angular distribution of emitted power in the far field. (e) Experimental characterization of the polarization state for different relative phase delay $\Delta \phi$ between the ω and 2ω pumps.

To investigate this experimentally, we introduced a ω +2 ω dual-beam pumping scheme, whereby а femtosecond telecom pulse at 1556 nm combines with its frequencydoubled replica at 778 nm. The relative phase delay between two beams is modulated via a liquid crystal retarder with attosecond precision (150 as) (see Figure 1a). This way, we can modulate the relative phase delay between SFG and THG from 0 to 2π . To modulate the polarization states, we first simulate the back-focal plane images of THG and SFG for a metasurface with 1000 nm periodicity (see panel b) when the two pump beams are copolarized (see panel c,d). We retrieve that SHG and SFG are orthogonal at specific diffraction orders. In our experiment, we carefully balance the

power between THG and SFG, then modulate the relative phase delay via a liquid crystal retarder. Eventually, the polarization state is measured via rotating-waveplate polarimetry³ (see panel a). Interestingly, breaking the mirror symmetry in the detection domain allows us to observe a chiral output. We can modulate the polarization between linear and circular states at orders where the electric fields of SFG and THG are orthogonal, and the opposite polarization states are generated in the orders symmetrically positioned across the optical axis. The quality of circularly polarized light is determined by the degree of circular polarization, and we can obtain up to 83% for a specific order.

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Angular plasmonic response of a periodic array of gold nanoparticles

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

Keywords: plasmonics; angle-resolved measurements; collective dipolar resonance; vertical mode; nanoparticles array

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Acoustically levitated Ag coated styrofoam particles for SERS spectroscopy of methylene blue

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Acoustic levitation is a fascinating technology that relies on the use of sound waves to support, manipulate, and move objects of various shapes and sizes without any physical contact. Acoustic tweezers in air consist of arrays of ultrasonics transducers emitting sound waves at kHz frequency. The waves are focused and interfere at specific points in space, creating an acoustic trap in which particles can be trapped and maneuvered. Specifically, the setup we used is a standing wave acoustic levitator called TinyLev, consisting of two opposite arrays of emitters, each containing 36 transducers emitting at a frequency of 40 KHz [1]. The dynamic of trapped particles can be studied to calculate the trapping stiffness of the trap [2]. Moreover, they can be also spectroscopically studied by coupling the transducers arrays to a Raman spectrometer. In this work, we trap Ag-coated styrofoam particles, produced by Ion Beam Sputtering [3], to be exploited for surface-enhanced Raman spectroscopy (SERS)[4]. More specifically, a thin layer of silver was deposited on styrofoam 1.5 mm particles by means of Ion beam sputtering. Then, the particles have been immersed in methylene blue water solutions at 10⁻⁵ M for 50 min and after drying they were levitated in an acoustic trap coupled to a portable Raman spectrometer. We observe a 30 fold amplification of the Raman signal of methylene blue molecules absorbed on the surface of the particle compared to the detected signal of a reference bead with no Ag. This approach can open a new route for the contactless manipulation of SERS platforms for the detection of contaminants dispersed in the environment.



Figure 1: a) Ag-coated styrofoam particle trapped in the Raman Acoustic Tweezers. b) Raman signals of Methylene Blue (MB) [blue line, y scale on the right], Red Polystyrene (PS) Bead with MB [black line, y scale on the left), Ag-coated Red PS Bead with MB [red line, y scale on the left].

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Computation of emitter-plasmon interactions using an axis-symmetric model for off-axis dipoles

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Emission properties of quantum emitters can be influenced by several factors near plasmonic nanoparticles (NPs) such as near- and far-field coupling, the dipole position, or orientation. Therefore, equally to the experiments, developing theoretical models that help understand and control these multifaceted factors becomes crucial for developing advanced plasmonic devices and applications.

For axially-symmetric systems, i.e. for most NP systems, such as spheres, rods, cylinders, dimers, NP-on-mirror, and so on, it is possible to expand the fields in cylindrical harmonics and compute the response on a two-dimensional cross-section separately for every harmonic [1]. While this is relatively simple for emitters placed on the symmetry axis, where only one or two harmonics are necessary [2, 3], this is less straightforward for off-axis dipoles. The vector field of a off-axis dipole can be described by performing multipole expansion either in spherical harmonics [4] or using toroidal functions [5]. However, the latter often requires large harmonic mode numbers, especially for dipoles in close proximity to plasmonic systems. The former requires complicated functions to be implemented and it is only limited to the quasi-static approximation.

In this poster, we propose an alternative formulation based on the Fourier expansion of the delta function associated to the dipole currents along the azimuthal direction. Its variational formulation is established and has been implement in Finite Element Method (FEM). We benchmark our method against the standard Mie theory method, for a single dipole near a spherical plasmonic NP, obtaining a perfect overlap [Fig. 1(a)-(c)]. We have then applied the model to study the interaction of an ensemble of emitters (up to N = 80 dipoles) and a spherical gold NP. The results show that decay rates of the system increase with the increasing number of emitters, in line with the previous reports. On the macroscopic level, such a system is subject to effective results which depend on the locations, orientations, and phases of the emitters. We then performed vast computations for randomly varying phases of the emitters near the NP by fixing the emitter-emitter separation, s, and emitters-NP separation distance, d [Fig. 1(d)]. As expected, the averaged non-radiative [Fig. 1(e)] and radiative [Fig. 1(f)] decay rates are well fitted with the estimation, $\gamma_N = N\gamma_0^1$, where γ_0^1 is the decay rate of a single emitter near the plasmonic NP. We have also extended the model to a plasmonic-dimer-based one where we observed the infamous Dicke effect-like cooperativity which scales with N^2 for random but ordered emitters placed inside the dimer gap.



Figure 1: (a) Illustration of the gold NP and an offaxis dipole. (b) The normalized total spontaneous emission decay rate, γ_{tot} . The red dashed curve is for the case of the system schematized in (a) and is calculated using the 2.5D model. The solid black curve is calculated using the analytical Mie theory for a dipole normal to the surface of a spherical gold NP. (c) The same as in (b) but for the radiative decay rate, γ_r . (d) A scheme exemplifying the multiple dipoles distributed around the spherical gold NP. The colored histograms show the distribution of the (e) non-radiative and (f) radiative emission decay rates depending on the randomness of the oscillation phases of the dipoles in the ensemble near the NP. The connected blue symbols are the average of the emission rates for each sample. The red line is an estimation of plasmon-assisted emission rates, $\gamma_N = N\gamma_0^1$.

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Influence of laser energy on particle size and localized surface plasmon resonance of nanoparticles by ns-laser ablation in liquid

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Abstract: Laser ablation of solid in liquid media is a clean and simple method to produce nanoparticles and nanostructures. It offers a variety of laser parameters such as laser energy, wavelength and pulse width which could be used to tune the properties of nanostructures. In this work, we investigated the effect of laser energy on concentration, LSPR and size of copper nanoparticles fabricated via pulsed nslaser ablation of copper in liquid medium and studied how the laser energy can be used to control such fabrication. Laser ablation on solid copper kept inside deionized water was performed by varying the laser energy of a pulsed nanosecond laser of fundamental wavelength (1064 nm) having pulse duration of 7ns. The ablation process was carried out for a duration of 25 minutes. UV-Vis absorption spectroscopy and TEM were used to study the properties. A correlation between the localized surface plasmon resonance behavior and particle size with the incident laser energy were observed.



Figure 1: Setup of pulsed laser ablation inside liquid.

Preparation of gel-supported plexcitonic nanohybrids and their optical characterization by 2D electronic spectroscopy

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Plasmonic nanostructures have the unique ability to confine and manipulate light at the nanoscale due to their support of localized surface plasmons, which are collective oscillations of free electrons in metallic nanoparticles. When excitonic molecular media are placed near these plasmonic nanoparticles, strong interactions can create hybrid states known as "plexcitons".^{1,2}

Plexcitons exhibit novel photophysical properties, presenting significant opportunities for manipulating light-matter interactions at the nanoscale. Tuning the plasmonic nanostructures and excitonic systems, the optical and dynamic properties of plexcitons can be tailored, opening new avenues in integrated optics, optoelectronics, imaging, and sensing.



Figure 1. a) Gold nanoparticles and TPPS dye used in this work. b) example of 2DES maps collected for the systems.

To avoid precipitation issues and increase the sample stability, the functionalized NPs have been transferred from water suspensions to suitably selected gel matrixes, able to preserve the nanohybrids' properties and prevent NPs' aggregation and precipitation. The samples in the gel matrixes were revealed to be stable enough to be studied by linear and nonlinear optical techniques.

We investigated the ultrafast relaxation dynamics of these nanohybrids using 2D electronic spectroscopy (2DES), providing unprecedented detail in characterizing the coherent and incoherent dynamics of plexcitonic states (Figure 1B). The results from 2DES were compared with uncoupled species under identical conditions, revealing significant changes in photophysical and dynamic properties due to plasmon-exciton coupling.

This research marks a significant step in understanding the dynamics of colloidal plexcitonic nanohybrids, contributing to the broader research on nanomaterials with strong light-matter coupling.

Our study focuses on gel-supported colloidal nanohybrids made of colloidal cationic gold nanoparticles (NPs) and tetra sulphonate phenyl porphyrin (TPPS) dyes (Figure 1a). By manipulating the relative ratio between NPs and dyes, it is possible to induce variations in their mutual supramolecular interactions and selectively activate or deactivate two different sets of plexcitonic resonances, which arise from the coupling between different states of the porphyrin dye and gold NPs (Figure 2).^{3,4}



Figure 2 Absorption spectra of a) TPPS in monomeric and J-aggregate form and plexcitonic samples.

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Lithium niobate nanostructured resonator for directional emission of spontaneous parametric down-conversion

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Lithium niobate (LiNbO₃) is highly demanded in photonics due to its broad transparency window in the visible and near-infrared and its strong electro-optical response [1]. Recently, ground-breaking results in the fields of nano-optics have been achieved due to novel techniques in nanofabrication allowing for structuring LiNbO₃ at the nanoscale [1]. In particular, due to its strong second-order nonlinear optical response, applications to nonlinear nano-optics are flourishing, for example metasurfaces for the generation of photon pairs via spontaneous parametric down-conversion (SPDC) [2,3]. In this quantum process, a second-order nonlinear material interacts with an incoming photon, generating two



Figure 1: a) Scanning electron micrograph of the nanostructure with geometrical features (groove and lateral cuts). b) Electric far field norm of the SPDC emission (wavelength λ = 1450 nm) calculated with the Green function method. c) Power dependence of the coincidence count rate measured from a disk resonator and its corresponding linear fit. d) Coincidence counts of one resonator for different numerical apertures of collection (excitation 5 mW power at wavelength 725 nm, 5 min exposure time). The peak value corresponds to a coincidence count rate of 1kHz/W.

entangled photons with conservation of energy and momentum. We report here on the realization and optical characterization of a LiNbO3 nanostructured resonator for SPDC as an ultimately compact source of photon pairs. One key feature of SPDC in nanodevices is the short interaction length, resulting in a broad angular and spectral range of emission. Therefore, we designed a nanostructure with resonant behaviour for efficient and highly directional emission of SPDC. Via eigenmode studies, we tailored the resonance and introduced geometrical features for optimizing the resonant behaviour. A scanning electron micrograph of a fabricated resonator is shown in Figure 1a. The resonators are directly milled in a 500 nm-thick LiNbO₃ film on a silica substrate by a focused (Ga⁺) ion beam, resulting in sharp spatial features. We calculated the SPDC emission of this resonator at 1450 nm using the Green function method [4] and obtained a highly directional emission pattern with a numerical aperture (NA) of ≈ 0.2 as visible in Figure 1b. Coincidence measurements have been conducted for measuring the generation of photon pairs from several single resonators. A coincidence count rate of $\approx 1 \text{ Hz/mW}$ input power was found as can be seen Figure 1c. We also performed coincidence in measurements on a single resonator for different numerical apertures of collection, trying to deduce the angle of emission, as shown in Figure 1d. The theoretical emission pattern yields a sharper directionality than the measured one. Notably, a peak coincidence rate of 1 kHz/W was achieved,

sizably exceeding the only other report – to the best of our knowledge – of SPDC in LiNbO₃ particles (15 Hz/W in 4 μ m sized microcubes) [5].

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Magnetic Silver Nanoplates Grown by Laser Ablation and Irradiation

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Noble metal nanoparticles (NPs) have demonstrated viable applications in a number of different fields thanks to their strong interaction with electromagnetic radiation. Bifunctional Magnetic plasmonic materials have also shown broad interest, due to the simultaneous presence of both magnetic and plasmonic properties. Here, we report the synthesis and characterization of anisotropic silver nanoparticles, or nanoplates, and their characterization.

Silver nanoplates were synthesized based on a previously reported method [1], which has been modified to include Fe(III) ions. Spherical nanoparticles were initially produced by laser ablation in water, in presence of citrate. After that, a small amount of Fe(III) is added to the solution, to which H_2O_2 is slowly under irradiation by a 515 nm LED. The surface plasmon resonance of the initial spherical nanoparticles, located at 393 nm, broadens and red-shifts to around 600 nm, showing the typical features of silver nanoplates (Fig. 1) [2].



By TEM, SEM and AFM we estimate a nanoplate average size of 80 nm and thickness around 15 nm. XPS and EDX measurements show that Fe(III) ions are present on the nanoplate surface in concentration around 2%. Combined magnetometric measurements, high resolution TEM and local EDS elemental analysis show that Fe(III) ions are homogeneously distributed throughout the NPTs and are present as two subpopulations, i.e. free paramagnetic ions and coupled ferrimagnetic Fe₂O₃. (Fig. 2). Despite the low magnetic moment per unit mass shown by these nanosystems, this synthetic approach seems promising to obtain bifunctional magnetic plasmonic units.

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Photo-acoustic technique with widely tuneable laser

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Chirality, an intrinsic property of certain entities in the universe, is characterized by the absence of mirror symmetry. The chirality is crucial as it influences molecular interactions and properties. Circular dichroism (CD), measured using circularly polarized light, is a standard technique, but its sensitivity is often limited. Here, we explore extrinsic chirality [1], using photo-acoustic spectroscopy (PAS)[2].PAS allows direct measurement of local absorption, by monitoring the heat produced and transferred to the surrounding air, regardless the transmitted, reflected and scattered light that flows away from the sample. In the study to study extrinsic chirality, the sample is a silver-coated self-assembled metasurfaces, introducing a new PAS setup [3] (fig. 1a) that employs an oblique-incidence laser that covers a spectral range from 680 nm to 1000 nm. The light emitted by the source undergoes modulation via a mechanical chopper operating at a fixed frequency of 81 Hz. The impinging light has a spot diameter of 1.2 mm and is polarized either with linear horizontal polarization or RCP and LCP. The experimental results reveal that the CD trends dependent on the angle of incidence and wavelength, indicative of extrinsic chirality. The study enabling simultaneous analysis of multiple wavelengths and providing valuable insights into chiral metas urfaces. In Figure (1b) show the trend obtained by the measurements, for wavelengths longer than 800 nm the CD gradually increases from 0% at normal incidence, to positive values for positive angles of incidence, and changing to negative values as the incidence angles become more negative. The sign reversal is a characteristic feature of extrinsic chirality. For wavelength of 800 nm, as can be seen in (fig. 1b), all trends converge to a value of 0%, suggesting a unique behavior of the sample at this wavelength, showing an inverse process for wavelengths shorter than 800nm.



Figure 1: (a) schematic of the experimental setup ; (b) CD dependence on the angle of incidence for the sample.

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Plasmonic field enhancement in the ultra-intense, ultra-short laser-matter interaction with metallic nanoparticles

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In this work we perform numerical and experimental study of plasmonic resonance to enhance locally the intensity of a laser matter interaction. The goal is to use plasmonic effects on metallic nanoparticles to reach relativistic intensities on few optical cycles regime. These resonances for copper and gold nanoparticles are optimum at shorter wavelengths, around the second harmonic of the Ytterbium doped fiber laser (515nm). Laser parameters in the experiment were a time about 180fs and power was 20W with a maximum pulse energy was 2mJ. A study was done for gold and copper spherical nanoparticles with different diameters 500nm 100nm, 50nm and 25nm. We use Finite-Difference Time-Domain (FDTD) simulation to confirm the plasmonic electric field enhancement from gold and copper nanospheres. Particles around 100 nanometer ion diameter show higher enhancement. Experimental tests with the Ytterbium laser will possibly be performed in June and compared to the simulations. Basically, reflectivity will be measured experimentally for different sizes of nanoparticles compared to simulations.
Protein fibrils monitored by mid-infrared nano-spectroscopy under THz irradiation

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Introduction: Long-range structural vibrations of proteins involve subdomains of hundreds of atoms with corresponding frequencies in the THz range ^[1]. Recent studies have investigated the possibility to use high-field THz sources to disassemble supramolecular complexes ^[2]. This issue would be of great relevance for amyloid fibrils, i.e. ordered supramolecular protein complexes linked to neurodegenerative diseases such as Parkinson's and Alzheimer's. In this work, we monitored the effect of THz radiation of protein conformation by looking at the amide-I band falling in the range 1610-1700 cm⁻¹, known to be the most sensitive mid-IR protein absorption band sensitive to protein conformation and to the formation of protein fibrils. We observe, as the effect of THz irradiation, a weakening of the inter-molecular forces, here directly induced by THz absorption.

Results: Fig. 2 (a) shows a comparison between FTIR absorbance spectra in the amide-I range of alphasynuclein proteins in the oligomeric form (start of the aggregation process, black curve) and once mature fibrils have formed (red curve). In Fig. 2 (d) we report the AFM-IR spectrum of the same sample calculated from the difference between the spectrum acquired during THz radiation for 10 minutes and that acquired with THz turning off. An increase of the non- β structures and a decrease of the β sheets contribution under THz irradiation can be noticed. This observation corresponds to the breaking of intermolecular bonds, which could possibly lead to disassembly of the fibrils by THz radiation^[2].



Figure 1: a) FTIR absorbance spectra of alpha-synuclein proteins in the oligomeric form and mature fibrils with its AFM topographic map; b) scheme of AFM-IR set up; c) optical path scheme of THz; (d) AFM-IR spectrum acquired on an isolated agglomerate of protein fibrils; (e) AFM-IR difference-spectrum (THz ON-THz OFF).

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