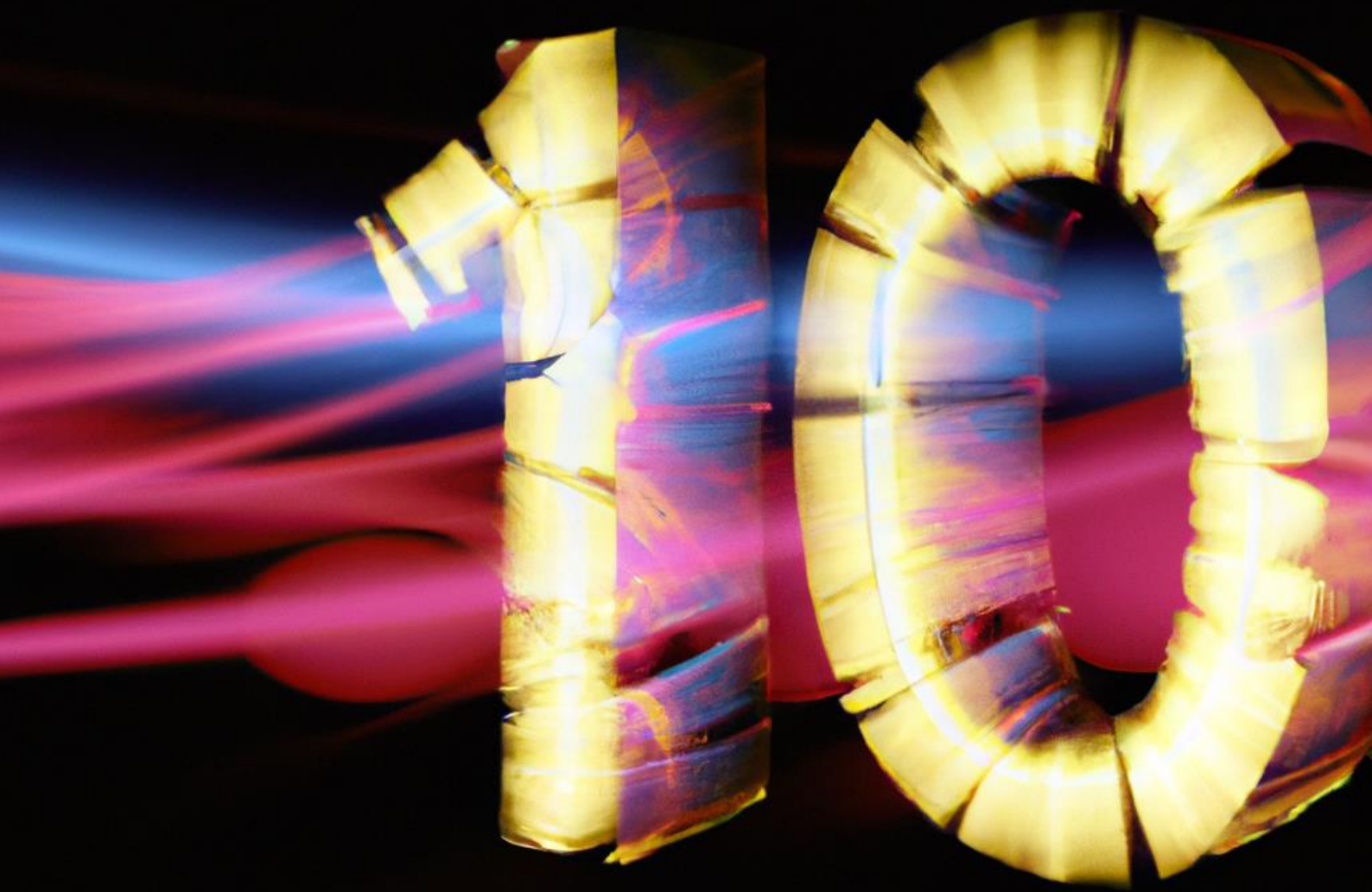
PLASMONICA 2023

Workshop on Plasmonics and Nano-Optics



Ten years of

PLASMONICA

5-7 July 2023

The Italian community of
plasmonics and nano-optics

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MILANO 1863
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This booklet is based on the AMCOS conference booklet by Maxime Lucas and Pau Clusella. The LaTeX template is freely available at https://github.com/maximelucas/AMCOS_booklet along with examples, additional codes, and information about its use and distribution policy.

The document was compiled on July 13, 2023. You can download the latest version of the booklet from the conference website at https://www.plasmonica.it/2023. Please address any comments (e.g. reporting errors) and suggestions on this booklet to attilio.zilli@polimi.it.

The digital art featured on the cover was created with the DALL·E 2 deep-learning model by OpenAI.

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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. A decade 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, ultrafast and nonlinear processes, chiral properties, surface-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, dissemination events (seminars and workshops),and outreach initiatives. 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	Antonino Foti, CNR–IPCF Messina
Paolo Biagioni, Politecnico di Milano	Nicolò Maccaferri, Umeå University
Michele Celebrano, Politecnico di Milano	Chiara Novara, Politecnico di Torino
Ilaria Rea, CNR–ISASI Napoli	Emilija Petronijevic, Sapienza Univ. Roma
Attilio Zilli, Politecnico di Milano	Attilio Zilli, Politecnico di Milano

Workshop scientific committee	
Leonetta Baldassarre, Sapienza Univ. Roma	Stefania D'Agostino, CNR–NANOTEC Lecce
Francesco De Angelis, IIT Genova	Emiliano Descrovi, Politecnico di Torino
Marco Finazzi, Politecnico di Milano	Carlo Forestiere, Univ. Federico II Napoli
Maria Caterina Giordano, Univ. di Genova	Fabrizio Giorgis, Politecnico di Torino
Francesca Intonti, Univ. di Firenze	Riccardo Sapienza, Imperial College London

Venue

The Politecnico di Milano main campus, where the Workshop will take place, is an extensive complex of buildings with its main entrance on Piazza Leonardo da Vinci 32. You can look up campus locations and accessibility paths on the interactive maps.

The *eduroam* **Wi-Fi** network is available everywhere on campus. Alternatively, if you have an **Italian SIM** card, you can connect to the *polimi* network through the following steps. Once redirected to the captive portal access the network as a guest. You will be prompted to insert your mobile telephone number and the **event code CBNT-PADM**. You will then receive an SMS containing the UserID and Password that you can use as temporary network credentials. If you have a **foreign SIM** card instead, you can ask for Wi-Fi credentials at the Welcome Desk.

Directions

The **opening day** (Wednesday) of the Workshop will take place in the *Rogers* lecture hall on the ground floor of building 11 (PoliMaps, Google maps). The remaining **oral sessions** on Thursday and Friday will be held in the lecture hall T.1.1 on the first floor of the building 13 (*Trifoglio*) (PoliMaps, Google maps). All **poster sessions** and the **sponsors'exhibition**, as well as coffee and lunch breaks, will be held in the *aula vetrata* on the entrance floor of the same building 13.

The main public transport links to the campus are:

- **Subway**: The Piola stop by the Green Line (number 2) of the metro network;
- **Train**: The Lambrate FS local railway station, at walking distance from the campus;
- **Bus**: The ground lines 39/62/90/91/93, all stopping in close proximity of the campus.

Detailed directions (in Italian) and maps can be found via the linked lecture hall names above.

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.

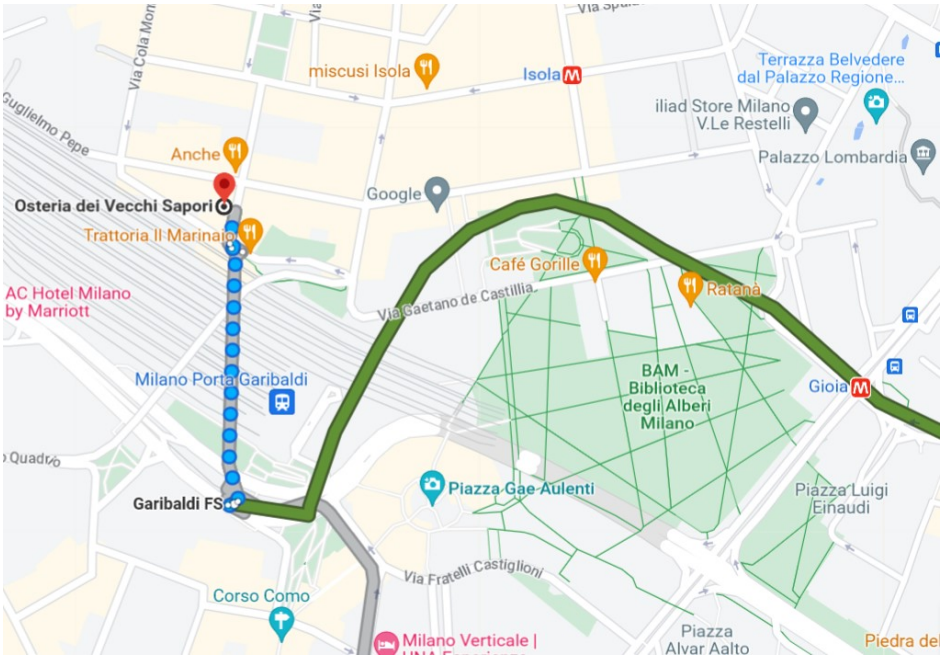
The recommended format for **posters** is A0 with portrait orientation. It can be printed locally at the campus print center PoliPrint. Please, hang your poster at the beginning of the half day (morning/afternoon) when your poster session is planned and bring them down with you by the end of the same half day.

All participants are welcome to follow and engage with our **social media** accounts, with the handle **@Plasmonica** on Twitter and Instagram. We also encourage you to include the hashtag #PLASMONICA2023 when tweeting about the Workshop.

Social dinner

The social dinner will take place at the **Osteria dei Vecchi sapori**, a traditional Milanese-style restaurant. The most direct route there from the conference venue is the Green Line (number 2) of the subway system from the Piola stop near the Politecnico campus to the Garibaldi FS railway station. From there on, you can follow the map below (clickable!).

Local tip: You may want to get there in advance and enjoy a sunset stroll (or an *aperitivo*) in the iconic Garibaldi neighborhood: discover the vibrant shops and cafes of Corso Como, the fast-rising skyline surrounding Piazza Gae Aulenti, the stylish greenery of the Biblioteca degli Alberi…But don't forget to be at the restaurant at 20:00 sharp!



Timetable

Wednesday, July 5th

12:30–14:00	**Registration and light lunch**	
14:00–14:15	**Opening remarks**	
14:15–15:45	**Session I: Applications of plasmonics. Chair: Maria Caterina Giordano**	
	Chiara Novara Politecnico di Torino	Aptamer-based detection of mycotoxins on SERS-active Ag-coated porous silicon-PDMS devices
	Valeria Nocerino CNR–ISASI and Univ. Parthenope Napoli	Plasmonic/dielectric nanostructured devices exhibiting ultra-high sensitivity to refractive index-based sensing
	Bruno Miranda CNR–ISASI and Univ. Federico II Napoli	A versatile plasmonic nanocomposite device for biosensing applications: from wearable sensors to food-quality monitoring
	Mirko Trevisani Univ. di Padova	Study of the excitation coupling mode on the emission of a plasmonic nanolaser
	Vittorio Scardaci Univ. di Catania	Plasmonic anisotropic silver nanoparticles for ultrafast fiber lasers
	Luca Salemi Univ. di Catania	Plasmonic nanoparticles as the scattering medium in colloidal random dye lasers
15:45–16:15	**Coffee break**	
16:15–16:45	**Alessia Pasquazi** Loughborough Univ.	Time-resolved nonlinear ghost imaging with Terahertz radiation: near-field microscopy and a path towards volumetry [invited]
16:45–18:00	**Session II: Atoms and molecules. Chair: Andrea Baldi**	
	Matteo Gardella Univ. di Genova	Large-scale Hybrid MoS_2/polymer films for enhanced photobleaching of dye molecules
	Jonathan Sepúlveda CSIC–UPV/EHU Donostia	Collective coupling strength of phononic and plasmonic nanoantenna modes with molecular vibrations
	Luca Nicoli Scuola Normale Superiore di Pisa	Fully atomistic modeling of plasmonic bimetallic nanoparticles
	Pietro Lombardi CNR–INO Firenze	Two-photon interference from distinct molecules on the same chip
18:00–19:00	**Round table of Plasmonica (in Italian)**	

Thursday, July 6th – Morning

9:00–10:30	**Session III: Nanofabrication and novel materials. Chair: Monica Bollani**	
	Franco Marabelli Univ. di Pavia	Displacement Talbot lithography to scale-up plasmonic metasurface fabrication
	Fritz Berkmann Sapienza Univ. di Roma	Suitability of highly doped group IV semiconductor for spectral narrow plasmonic MIR detection devices
	Cristina Mancarella Politecnico di Milano	Broadband and tunable multilayer metamaterials based on plasmonic nitrides, oxynitrides and transparent conductors
	Lorenzo Ramò Univ. di Genova	Thermal scanning-probe lithography for broadband on-demand plasmonics on transparent substrates
	Arrigo Calzolari CNR–NANO Modena	Tailorable materials for plasmonics in extreme conditions
10:30–11:30	**Poster session (A–D) and sponsors' exhibition**	
11:30–12:00	**Giuliana Di Martino** Univ. of Cambridge	A new era of materials characterization: can we achieve atomic sensitivity using visible light? [Invited]
12:00–13:00	**Session IV: Near-field optical microscopy. Chair: Leonetta Baldassarre**	
	Alfred J. Meixner Eberhard-Karls-Univ. Tübingen	Probing electron density shift at the metal–molecule interface induced by a static electric field by tip-enhanced Raman spectroscopy
	Nicoletta Granchi LENS, Univ. di Firenze	Detection of light transport regimes and localization in hyperuniform luminescent materials through near-field optical microscopy
	Andrea Mancini Istituto Italiano di Tecnologia, Milano	Phonon polariton vortices in suspended silicon carbide membranes
13:00–14:00	**Lunch break**	

Poster session A–D

No.	Presenter and poster title	
1	**Hira Asif** Akdeniz Univ. Antalya	All-optical control of ultrafast plasmon resonances in the pulse-driven extraordinary optical transmission
2	**Leonetta Baldassarre** Sapienza Univ. di Roma	Strong light–matter coupling in SiGe quantum wells embedded in terahertz patch antenna cavities
3	**Andrea Baldi** Vrije Univ. Amsterdam	Pulsed photothermal heterogeneous catalysis
4	**Stefania Benedetti** CNR–NANO Modena	Quantitative ultrafast electron-temperature dynamics in photo-excited Au nanoparticles
5	**Francesco Bertot** École Polytechnique Fédérale de Lausanne	Hybrid silicon-organic integrated terahertz detectors
7	**Monica Bollani** CNR–IFN Como	Nanofabrication and linear optical characterization of dielectric chiral metasurfaces
8	**Vittorio Bonino** Politecnico di Torino	High-Q Fano resonances in diamond nanopillars
9	**Lucrezia Catanzaro** Univ. di Catania	Tuning the aggregation of gold nanoparticles prepared by laser ablation with halide salt
10	**Daniele Ceneda** Sapienza Univ. di Roma	VO_2 perfect absorber by means of W doping
11	**Marcello Condorelli** Univ. di Catania	Silver nanoflower as a single plasmonic catalytic reactor for in situ photocatalysis
12	**Cristiano D'Andrea** CNR–IFAC Firenze	A wearable surface-enhanced Raman scattering patch for sweat monitoring
13	**Gauttam Dash** Jawaharlal Nehru Centre for Advanced Scientific Research, Bengaluru	Probing non-resonant coupling in exciton–plasmon hybrids using magnetic circular dichroism spectroscopy
14	**Maria De Luca** Univ. Federico II Napoli	Fe_3O_4@Au core satellite magnetic nanoparticles to enhance colorimetric immunosensor response
15	**Luisa D'Urso** Univ. di Catania	AgNFs as single-particle, multi-wavelength SERS active platforms

Thursday, July 6th – Afternoon

14:00–15:30	**Session V: Nonlinear nanophotonics. Chair: Tal Ellenbogen**	
	Agostino Di Francescantonio Politecnico di Milano	Coherent all-optical routing of upconverted light by a nonlinear metasurface
	Francesca Dodici Univ. di Padova	Design of ϵ-near-zero multilayers with enhanced Kerr-type nonlinearities
	Yigong Luan Politecnico di Milano	Surface vs bulk contribution to the second-harmonic generation in AlGaAs nanoresonators
	Huatian Hu Istituto Italiano di Tecnologia, Lecce	Free-electron third-order nonlinearities in heavily doped InGaAs nanoantennas
	Augustin Verneuil Univ. de Technologie de Troyes	Optimizing the extraction of second-harmonic light from a plasmonic array
15:30–16:30	**Poster session (F–M) and sponsors' exhibition**	
16:30–17:00	**Giancarlo Soavi** Friedrich-Schiller-Univ. Jena	Nonlinear plasmonics and exciton tuning in atomically thin materials [Invited]
17:00–18:00	**Session VI: Chiral plasmonics. Chair: Emiliano Descrovi**	
	Ventsislav Valev Univ. of Bath	Chiral optical harmonic scattering: theoretically predicted in 1979 and demonstrated four decades later
	Hanan Ali Univ. di Pavia	Circular dichroism in plasmonic array of elliptical nanoholes with square lattice
	Ben Olohan Univ. of Bath	Chirality in hyper-Mie scattering effects from CdTe nanohelices
	Alessandro Belardini Sapienza Univ. di Roma	Angle dependent output circular polarization degree characterization of self-assembled nanospheres coated with silver
20:00–	**Social dinner**	

Poster session F–M

No.	Presenter and poster title	
16	**Claudia Fasolato** CNR–IFN and Sapienza Univ. di Roma	Quantitative aggregation dynamics of responsive plasmonic colloids by real-time light transmission spectroscopy
17	**Marzia Ferrera** Istituto Italiano di Tecnologia, Genova	Nanohybrid platforms for strong light–matter interaction
18	**Carlo Forestiere** Univ. Federico II Napoli	Operative approach to quantum electrodynamics in dispersive objects based on a polarization modal expansion
19	**Martina Foschi** Istituto Italiano di Tecnologia, Genova	Antenna architecture based on plasmonic nanocone in a point contact–insulator–metal high frequency rectification system
20	**Alessio Gabbani** Univ. di Pisa	Plasmon-enhanced magneto-optical detection of sub-monolayers of single molecule magnets up to room temperature
21	**Michele Gherardi** Politecnico di Milano	SiGe dewetted Mie resonators
22	**Maria Caterina Giordano** Univ. di Genova	Large-scale Van der Waals heterostructures for photon harvesting
23	**Dihan Md. Nuruddin Hasan** North South Univ. Dhaka	Stimuli-responsive flexible silk-metamaterial for enhanced sensing of volatile organic compound (VOC) at mid-IR
24	**Felix Hecht** Friedrich-Schiller-Univ. Jena	Momentum-tuning of excitons in atomically thin transition metal dichalcogenides
25	**Pablo Ibáñez-Romero** Univ. Politécnica Madrid	CdZnO nanoparticles for SEIRA sensing in the mid-infrared
26	**Francesca Intonti** LENS, Univ. di Firenze	Influence of the fabrication process on the optical spectra of all-dielectric dewetted nanoparticles
27	**John Kerr** Univ. of Bath	Plasmonic nanohelices for surface-enhanced Raman spectroscopy with circularly polarized light
28	**Pan Li** Vrije Univ. Amsterdam	Nanoscale thermometry of plasmonic structures via Raman shifts in copper phthalocyanine
29	**Rustamzhon Melikov** Istituto Italiano di Tecnologia, Genova	Intracellular recording of rat primary neurons on commercially available plasmonic MEAs
30	**Elizabeth Mendoza-Sandoval** Univ. di Padova	Moiré photonic crystal to tailor nanolasing emission

Friday, July 7th

9:00–10:30	**Session VII: Metaphotonics. Chair: Francesca Intonti**	
	Theodoros Bouloumis Okinawa Institute of Science and Technology	A plasmonic metasurface for trapping and manipulating nanoparticles
	Cormac McDonnell Tel Aviv Univ.	Nonlinear plasmonic metasurfaces for efficient broadband THz beamshaping
	Andrea Vogliardi Univ. di Padova	Vector beams generated by metalenses
	Nils Henriksson Umeå Univ.	Probing temperature changes using non-radiative and radiative processes in hyperbolic meta-antennas
	Giuseppe Emanuele Lio LENS, Univ. di Firenze	Fano-resonant hybrid metastructures with ultra-high sensing performances
10:30–11:30	**Poster session (M–Z) and sponsors' exhibition**	
11:30–12:00	**Alessandro Alabastri** Rice Univ. Houston	Electronic and photothermal phenomena in optical metasurfaces [Invited]
12:00–13:00	**Session VIII: Ultrafast and active plasmonics. Chair: Cristian Ciracì**	
	Thorsten Feichtner Julius-Maximilians-Univ. Würzburg	Fast electrical modulation of a single plasmonic nano-rod resonance
	Alessio Gabbani Univ. di Pisa	Photochemical and electrochemical modulation of the infrared plasmonic response in metal oxide nanocrystals: an optical and magneto-optical investigation
	Ilya Razdolski Univ. of Bialystok	Active quantum plasmonics with non-thermal electrons on ultrafast timescale
	Alba Viejo Rodríguez Univ. of Luxembourg	Ultrafast dynamics driven by opto-acoustic excitations in free-standing nickel cavities
13:00–13:15	**Closing remarks**	

Poster session M–Z

No.	Presenter and poster title	
31	**Daniel Montesi** Politecnico di Torino	Automatization of SERS analysis towards point-of-care applications
32	**Quynh Nguyen** Vrije Univ. Amsterdam	Harvesting plasmonic hot holes
33	**Luca Nicoli** Scuola Normale Superiore di Pisa	Mixed QM/classical approaches for surface-enhanced Raman scattering
34	**Patrick O'Keeffe** CNR–ISM Roma	Generation of solvated electrons using visible light by excitation of diamond–gold nanoensembles
35	**Tadele O. Otomalo** Istituto Italiano di Tecnologia, Lecce	Effect of electron spill-out on the surface plasmon-polariton propagation at dielectric-magnetized plasma interface
36	**Alessandra Paladini** CNR–ISM Roma	Ultrafast dynamics of plasmonic and interband excited non-thermal electrons in 2D gold nanoparticle arrays
37	**Miriam Parmigiani** Univ. di Pavia	Surface-functionalized silver-coated gold nanostars for SERS and LSPR sensing of Fe(III)
38	**Jacopo Stefano Pelli Cresi** Istituto Italiano di Tecnologia, Genova	Ultrafast dynamics of surface plasmon polaritons in sub-wavelength hole arrays
39	**Michael Poloczek** Friedrich-Alexander-Univ. Erlangen–Nürnberg	Lithium niobate nanostructured resonator for directional emission of spontaneous parametric down-conversion
40	**Bernardo Santos Dias** Univ. of Amsterdam	Excitonic 2D Metasurface for Tunable Image Processing
41	**Serena Schiavi** Univ. di Pavia	Development of novel SERS platform based on polydopamine coated gold-nanostars-chips: fine tuning of the coating process and future perspectives
42	**Ankit Kumar Singh** Leibniz Institute of Photonic Technology, Jena	Ultrafast spatiotemporal chiroptical response of dielectric and plasmonic nanoparticles
43	**Sudarson S. Sinha** Istituto Italiano di Tecnologia, Genova	Plasmonic bowl-shaped nanopore using Raman Spectroscopy for sequencing of translocating DNA
44	**Zongyuan Tang** Politecnico di Torino	Bloch surface waves in resonant structures
45	**Francesco Verdelli** DIFFER, Eindhoven	Vibrational strong and ultra-strong coupling using surface lattice resonances

Abstracts – Talks

Aptamer-based detection of mycotoxins on SERS-active Ag-coated porous silicon-PDMS devices

Chiara Novara,[1,*] Alessandro Chiadò,[1] Niccolò Paccotti, [1] Paola Rivolo,[1] Francesco Geobaldo,[1] and Fabrizio Giorgis[1]

[1]*Dept. of Applied Science and Technology, Politecnico di Torino, Torino, Italy (*chiara.novara@polito.it)*

In the framework of food quality and safety assessment, the need for new reliable, fast and low-cost sensors suitable for on-filed detection of contaminants is growing rapidly [1]. Besides a high sensitivity, the identification of the target compounds in such complex matrixes also demands an excellent specificity. In this work, we combine the sensitivity of a Surface Enhanced Raman Scattering (SERS) microfluidic platform [2] with the specific recognition of the target enabled by aptamers to achieve the detection of mycotoxins in food matrixes. In detail, the functionalization of Ag nanoparticles (NPs) on porous silicon (pSi)-PDMS membranes with an aptamer for Aflatoxin B1 (AFB1) was first studied, investigating the effect of the length and orientation of the oligonucleotidic receptor on the recognition efficiency and on the SERS response of the sensor. An improved affinity for the AFB1 and the highest SERS intensity were observed using a 5' thiolated aptamer. As revealed by the SERS analysis, its orientation on the NPs allows its binding site to lie close to the Ag surface and to take advantage of a strong electromagnetic enhancement. Then, the detection of the AFB1 was performed through a competitive approach, monitoring the replacement of a 6-FAM-labelled "switch" sequence, hybridized into the aptamer binding site, by the AFB1 target (Figure 1a).The longest switch sequences exhibited the best performances, as they provided a stable pairing interaction with the aptamer but could be subsequently efficiently displaced by AFB1. Different concentrations of the mycotoxin were thus analyzed using the best aptamer-switch pair, allowing to calibrate the SERS response (Figure 1b). Finally, AFB1-spiked hazelnut slurry extracts were analyzed with the functionalized device, demonstrating its applicability to the SERS detection of the target in food matrixes at concentrations lower than the limit defined by the regulations (Figure 1c).

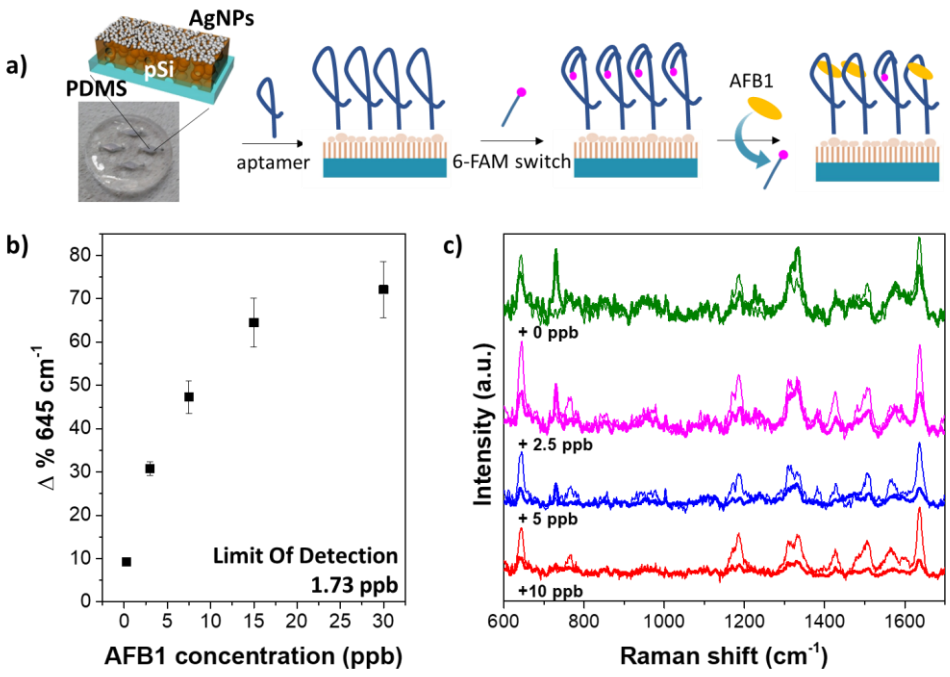


Figure 1: a) Scheme of the competitive assay for AFB1 detection on the Ag-pSi-PDMS membranes; b) Percentage decrease of the 645 cm^{-1} band of the 6-FAM-swtich hybridized with the 5'SH-aptamer after the incubation of the SERS substrates with different concentrations of AFB1; c) SERS analysis of the extracts of hazelnut slurries spiked with AFB1 at concentrations in the 10-2.5 ppb range together with a control sample without AFB1 (SERS spectra before and after AFB1 incubation are compared).

[1] J. Perumal, Y. Wang, A. B. E. Attia, U. S. Dinish, M. Olivo, Nanoscale **13**, 553–580 (2021).

[2] A. Chiadò, C. Novara, A. Lamberti, F. Geobaldo, F. Giorgis, P. Rivolo, Anal. Chem. **88**, 9554–9563 (2016).

Plasmonic/dielectric nanostructured devices exhibiting ultra-high sensitivity to refractive index-based sensing

Valeria Nocerino[1,3], Bruno Miranda[2,3], Principia Dardano[3], Maria Grazia Manera[4], Roberto Rella[4], Adriano Colombelli[4], Daniela Lospinoso[4], Luca De Stefano[3].

[1]Department of Engineering (DI), University of Naples Parthenope, Centro Direzionale Isola (C4), 80134, Naples (Italy). (valeria.nocerino@na.isasi.cnr.it)

[2]Department of Electrical Engineering and Information Technology (DIETI), University of Naples Federico II, Via Claudio 21, 80125, Naples (Italy).

[3]Institute of Applied Sciences and Intelligent Systems (ISASI), National Research Council (CNR), Via Pietro Castellino 111, 80131, Naples (Italy).

[4]CNR-IMM, Institute for Microelectronic and Microsystems, Campus Ecotekne, Via per Monteroni, 73100 Lecce, (Italy).

In the last decades, metallic nanostructures have played a key role in biosensing, as they exhibit unique properties that make them excellent optical transducers [1]. When their size is much smaller than the operating wavelength, they exhibit the well-known localized surface plasmon resonance (LSPR), whose position is strongly affected by the nanoparticles' size, shape composition, and surrounding medium refractive index. The combination of bottom-up and top-down fabrication strategies has been receiving increasing interest [2]. Large-scale fabrication of gold (Au) nanomushrooms (NMs) on glass and silicon substrates has been proposed as a novel platform for biosensing [3,4]. In this work, we show the combination of hybrid plasmonic/dielectric materials to significantly improve the sensitivity of large-scale plasmonic arrays. Precisely, we propose the optimization of the fabrication process of the AuNMs reported in [3], by substituting the pillar with dielectric Silicon Nitride. The fabrication involves the deposition of a 100 nm layer of Silicon Nitride, the thermal evaporation of a thin film of gold, and the thermal annealing during which the formation of gold nanoislands (AuNIs) takes place (Figure 1b). After these processes, the samples undergo a metal-assisted gas-etching to achieve 80 nm-high pillars below the gold nanoislands. This process is shown to significantly enhance the sensitivity of the device (Figure 1c). Indeed, the samples are tested before and after etching by exposing them to solutions with increasing refractive indexes and measuring the LSPR redshift as a function of the refractive index. An unprecedented sensitivity is therefore achieved for the etched substrates. AuNMs with the highest sensitivities have been tested both for gas sensing and biosensing applications. The results are very promising. Numerical simulations are also carried out to confirm the performance of the obtained nanostructured devices.

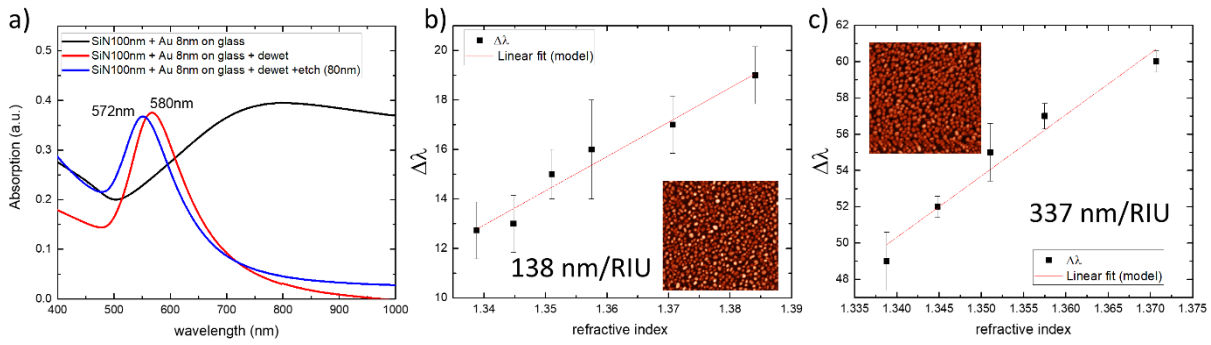


Figure 1: a) Absorption spectra of gold thin film, AuNIs, and AuNMs. b) AuNIs LSPR as a function of the refractive index; in the inset, AFM image of AuNIs. AuNMs LSPR as a function of the refractive index; in the inset, AFM image of AuNMs.

[1] V. Nocerino, B. Miranda, C. Tramontano, G. Chianese, P. Dardano, I. Rea, L. De Stefano,. *Chemosensors,* 2022.

[2] B. Miranda, K.-Y., Chu, P.L. Maffettone, A.Q. Shen, R. Funari, *ACS Applied Nano Materials*, 2020.

[3] J. Waitkus, Y. Chang, L. Liu, S.V. Puttaswamy, T. Chung, A. M. M. Vargas, S. J. Dollery, M. R. O'Connell, H. Cai, G. J. Tobin, N.Bhalla, and K. Du, *Advances Materials Interfaces*, 2023.

A versatile plasmonic nanocomposite device for biosensing applications: from wearable sensors to food-quality monitoring

B. Miranda,[1,2,*] V. Nocerino,[2,3], I. Rea,[2] P. Dardano,[2] C. Forestiere,[1] and L. De Stefano[2]

[1]*Dept. of Electrical Engineering and Information Technology, University of Naples Federico II – Naples, Italy (*bruno.miranda@unina.it)*

[2]*Institute of Applied Sciences and Intelligent Systems, National Research Council – Naples, Italy*

[3]*Dept. of Information Engineering, University of Naples Parthenope – Naples, Italy*

Recently, the development of flexible plasmonic sensors is growing strongly, as flexible sensors have many advantages, especially for their mechanical properties, adaptability to non-planar surfaces [1-3]. In this context, a 3D optical sensor has been developed, integrating gold citrate nanoparticles [4-6] into a polymer: PEGDA hydrogel. This hybrid sensor allows the detection of molecules in both label-free and non-label-free, exploiting the mechanical capabilities of hydrogels to swell in the presence of water, and the mechanism of MEF/SERS [1,7] thanks to the presence of noble metal nanoparticles. The proposed platforms are low-cost and scalable to the industrial levels with low detection limits and promising applications for the future.

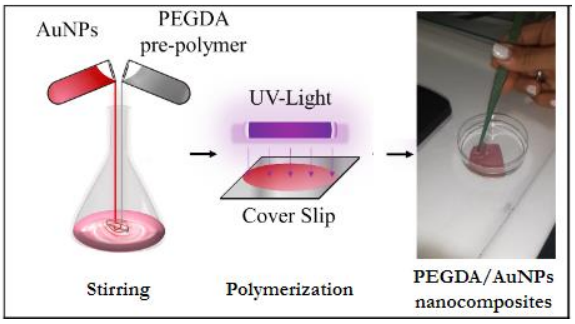


Figure 1: Simple fabrication strategy of hydrogel plasmonic nanocomposites embedding gold nanoparticles.

The optimization of the fabrication process has been carried out to satisfy the need for versatile platforms to be adopted *in-situ* (Figure 1). The integration of the nanocomposite into hollow microneedles starting from the knowledge of the optomechanical properties will be presented [8] for both label-free and non-label-free biosensing [9]. The optimization of the NPs density to have interacting or non-interacting NPs is proposed for applications in SERS biosensing. Finally, numerical optimization of the transduction mechanism is highlighted.

[1] B. Miranda, "Recent Advances in the Fabrication and Functionalization of Flexible Optical Biosensors: Toward Smart Life-Sciences Applications", in Biosensors, vol. 11, 2021, pp.107.

[2] B. Miranda, "A PEGDA hydrogel nanocomposite to improve gold nanoparticles stability for novel plasmonic sensing platforms", in Journal of Applied Physics, vol. 129, 2021, pp.101.

[3] Polavarapu," Towards low-cost flexible substrates for nanoplasmonic sensing" in Physical Chemistry, vol.15,2013, pp. 5288-5300.

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Study of the excitation coupling mode on the emission of a plasmonic nanolaser

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Introduction: Ordered arrays of nanoparticles can support hybrid extended resonant modes called Surface Lattice Resonances (SLRs) that are generated by the coupling of the localized surface plasmonic modes (LSPs) to the diffractive modes of the periodic structure. These modes can be used in nanolasers to achieve coherent emission from emitters coupled to the lattice by reducing the intrinsic ohmic losses of the LSPs. Controlling the lattice unit cell composition, symmetry and periodicity, it is possible to tailor the lasing properties [1, 2]. In this study, we investigated the effect of the incident angle, polarization, and dynamics of the excitation on the lasing properties at the *Γ* point of a 2D hexagonal nanolaser.

Results: The sample studied is shown in Fig. 1a and is made of a hexagonal array of Al tapered nanocones (lattice parameter a_0 = 475*nm*) coupled with an organic dye in a polymeric matrix. Figure 1b shows the measured optical band structure of the array. According to the incident angle with respect to the sample normal, at the excitation wavelength (532 nm), the photons can be coupled (A-B) or not coupled (C) to lattice modes. Figure 1c depicts the lasing emission taken with ps pulsed excitation above the lasing threshold at the *Γ* point (normal collection) at A, B, C excitation angles. The lasing peak intensity indicates that the emission can be enhanced by matching the incident wave vector to the SLR modes [3]. Additionally, by choosing the pump polarization, the coupling condition can be activated depending on the polarization state of the excited SLR modes. This is evident by comparing the lasing intensity for positions A and B. The dynamic effect is studied by pumping the sample with three different lasers, namely ps-pulsed laser, ns-pulsed laser, and cw diode. According to the pulse duration, the optical response can be modified. We found that when the excitation has the same or smaller duration with respect to the dye lifetime (5 ns), a lasing peak can be obtained at the *Γ* point. For longer pulses (or CW excitation) the competitive process of non-radiative intersystem crossing in the emitter inhibits the stimulated emission [4] and only directional fluorescence occurs.

Conclusions: Depending on the incident angle and the pulse duration, it is possible to couple the pumping beam to the nanoarray in a resonant way. This can largely modify the lasing emission, reducing the pumping threshold and increasing the lasing intensity.

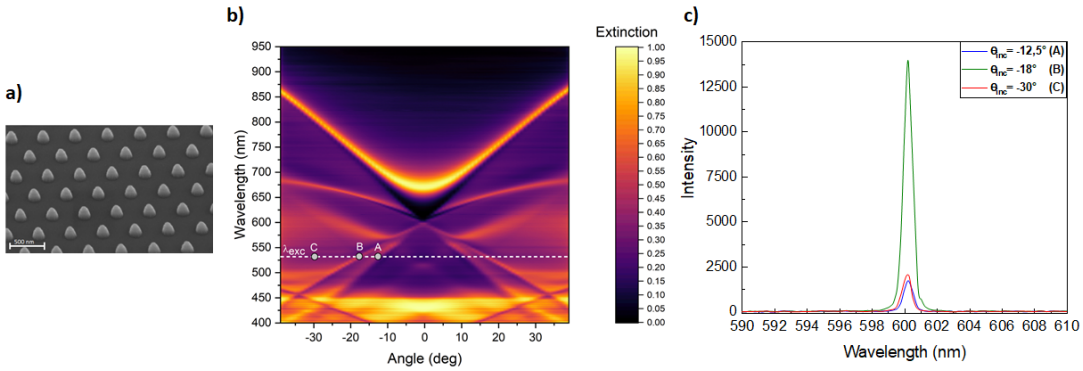

Figure 1: (a) SEM image in cross-section of the hexagonal array. (b) Experimental extinction map of the array coupled to the emitter, taken in TE polarization and along *Γ*M direction. The white line indicates the excitation wavelength (532 nm) and the gray dots are the coordinates of the incident angles investigated. (c) Lasing spectra collected at the *Γ* point (0°) at F = 1.4mJ/cm^2, TE polarization and different incident angles (A,B,C coordinates in panel b).

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Plasmonic Anisotropic Silver Nanoparticles for Ultrafast Fiber Lasers

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Plasmonic nanoparticles are continuously expanding their range of applications, which now include sensing, catalysis, imaging, nanomedicine, photonics, and optoelectronics, to name a few. Ultrafast lasers also find applications in a wide range of fields like medicine, telecommunications, sensing, materials processing and imaging. The generation of laser pulses requires an element that transforms a laser output into a train of short pulses. This element is called a saturable absorber, which is transparent to high intensity light. Here, we demonstrate the utilization of triangular silver nanoparticles, or nanoplates, as saturable absorbers for the generation of pulses in fiber lasers.

The saturable absorption properties are characterized by the z-scan technique, along with other non-linear optical properties (Fig. 1a). Silver nanoplates are then integrated into a fiber laser ring cavity by means of optical deposition onto an optical fiber connector or embedded within a polyvinyl alcohol (PVA) matrix. Here the non-linear absorption coefficient was first measured by power-dependent transmission measurements (Fig. 1b). Passive Q-switching and mode-locking were achieved in our devices at 1µm and 1.5µm wavelengths. For Q-Switching, we achieved pulse durations of 2µs, repetition rates in the order of 100 kHz and output power in the range of mWs (Fig. 1c,d). For mode-locking, we achieved pulse durations of ~300 ps, repetition rate in the order of 10 MHz and output power in the order of 10 mW. Our results demonstrate the feasibility of silver nanoplates as saturable absorbers in the near IR and as a viable alternative to traditional saturable absorbers.

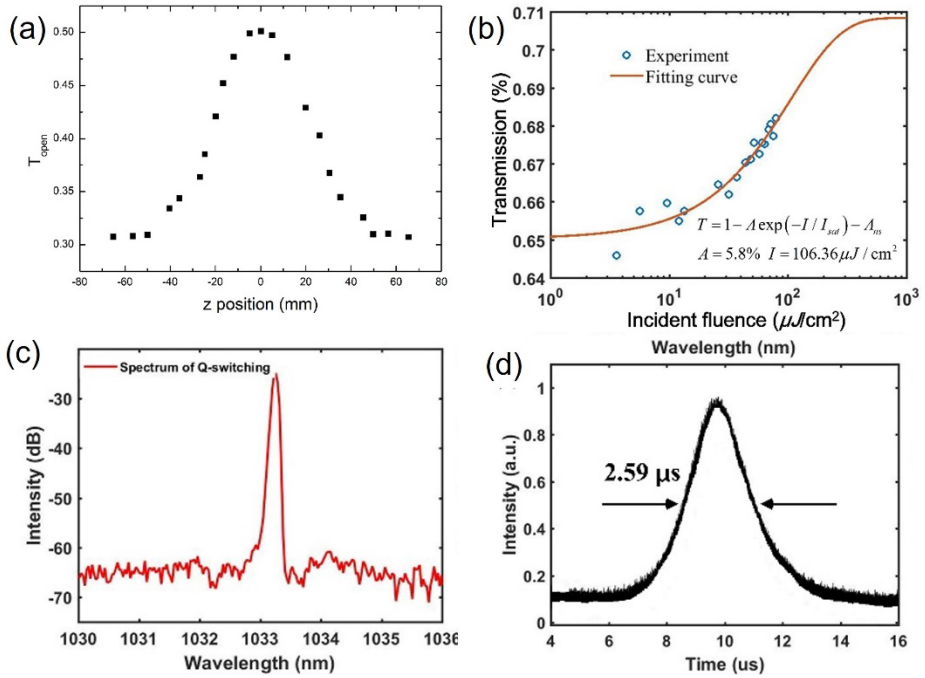

Figure 1: a) z-scan experiment results; b) power dependent transmission measurements; c) output spectrum for a Q-switched laser; d) pulse temporal profile for the Q-switched laser

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Plasmonic nanoparticles as the scattering medium in colloidal random dye lasers

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Plasmonic nanoparticles as the scattering medium in random lasers have been first demonstrated in 2005 by Dice and coworkers [1], proving favorable in comparison to dielectric particles due to two effects: a much higher scattering cross-section (i.e. per particle or per unit volume), and potential unspecified plasmonic enhancement effects in the near field of the nanoparticles. The two mechanisms have been partially tested by Popov et al. [2] using Au nanospheres of varying diameter embedded in a dye-polymer film, explaining all the observations by the scattering only. Further literature has explored the effect of various different plasmonic nanoparticles and system geometry, proving both coherent and incoherent random lasing [3,4].

However, since the localized plasmons are highly sensitive to details in the nanoparticles' size and shape and to the surrounding environment, to get a meaningful comparison of different materials and shapes one has to handle the plasmonic system with great care. For instance, an inappropriate choice of material properties, or reshaping of anisotropic particles under the pump laser, may lead to a large difference between calculated scattering cross-sections and the actual experiment.

In this work, we study the random lasing properties of Rhodamine 6G solutions with plasmonic nanoparticles, and attempt to carefully characterize the emission in relation to the properties of the plasmonic colloid, such as resonance wavelength, scattering cross section and efficiency, and electric field enhancement. To do so, we synthesize various plasmonic nanoparticles using a combination of chemical growth and pulsed laser techniques, characterizing the colloids experimentally and with numerical simulations.

The R6G-plasmonic colloids are then placed in a quartz cuvette and pumped with a 532nm pulsed laser, and their emission spectra are recorded keeping the same configuration of the system across all experiments. The emission spectra are then acquired and the laser threshold and bandwidth are studied in relation to the characteristics of the plasmonic nanoparticles.

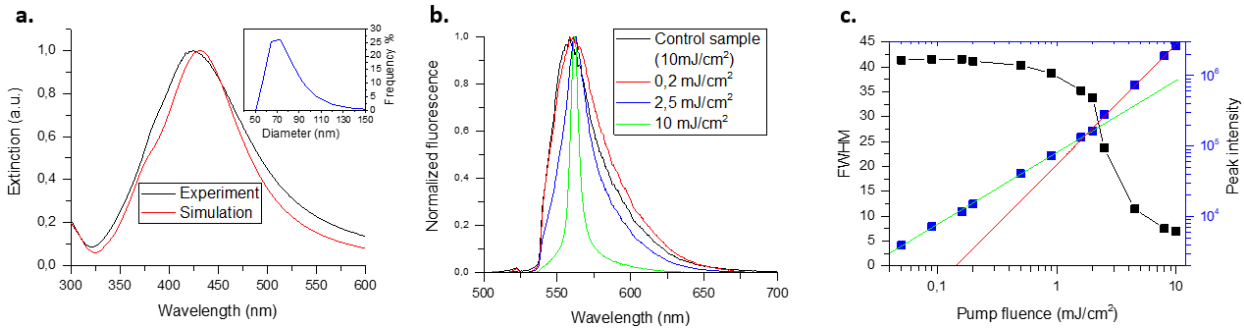

Figure 1: **a.** Experimental extinction spectrum and simulated extinction cross-section of Ag nanospheres of average diameter 70nm. The inset shows the DLS-measured size distribution. **b.** Normalized fluorescence spectra at various pump fluence, and **c.** bandwidth and peak intensity as a function of the pump fluence for the same Ag nanospheres suspended in a methanol solution of Rhodamine 6G 1mM. The control sample is the same solution without nanoparticles. Linear fits to the log-log plot of the peak intensity vs pump fluence are extended only to the points below (green) or above (red) threshold to aid visualization.

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Time Resolved Nonlinear Ghost Imaging with Terahertz Radiation: Near Field Microscopy and a Path Towards Volumetry

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Abstract: The development of innovative approaches to Terahertz (THz) imaging is a rapidly evolving field. THz spectroscopy, thanks to the possibility of detecting the field amplitude and phase, has already demonstrated unique capabilities in the spectral analysis of complex samples, opening up exciting possibilities for field-sensitive imaging systems [1].

In this framework recent works [2], we have proposed a nonlinear imaging approach denoted "Time-Resolved Nonlinear Ghost-Imaging". Our approach combines nonlinear frequency conversion, time-resolved measurements and full-wave single-pixel detection (as enabled by THz Time-Domain-Spectroscopy). Our results show not only that accurate field-sensitive time-resolved GI is feasible, but that it could overcome several intrinsic limitations of established techniques at any frequency. In this contribution, we will summarise the essential foundations and current advancement of our methodology, as well as a detailed analysis of the theoretical framework underlying the image reconstruction approach. Besides a demonstration of our method for the imaging of a semi-transparent sample, we show that how the imaging reconstruction performance can be improved through a careful choice of the image reconstruction scheme reaching deeply subwavelength resolution [3].

Moreover, we will discuss how our approach can enable volumetric hyperspectral imaging. By employing a backpropagation in an approach that recalls the principle of confocal microscopy, we investigated the three spatial dimensions thus isolating and identifying different semi-transparent materials in a complex geometry[4]. These result paves the way towards a full hyperspectral micro-volumetry, thus revealing the full spectroscopic nature of the morphological 3-D features.

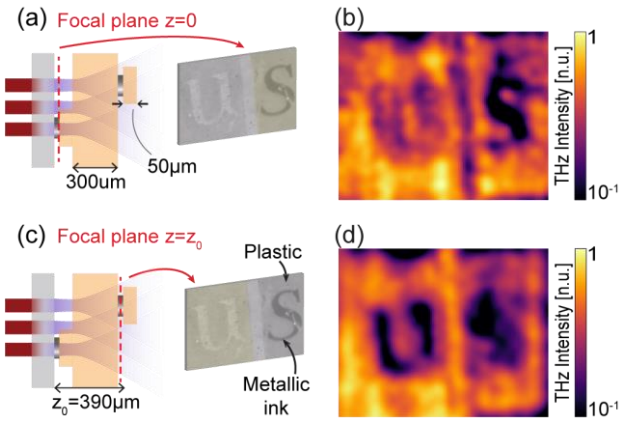

Figure 1: 3D reconstruction of a semi-transparent object with subwavelength metallic features. (a) Conceptual illustration of the imaging scheme and optical image with the focal plane highlighted (z=0 µm). Inset: microscope's optical image of the sample, 'S' letter's substrate highlighted. (b) image at the plane z=0, averaged between 1.6 and 2.4 THz. (c) Conceptual illustration of the imaging scheme and optical image with the focal plane highlighted (z=390µm). Inset: microscope's optical image of the sample, 'U' letter's substrate highlighted. (d) Hyperspectral image at the focal plane z=z0, averaged between 0.8 and 1.2 THz. In all panels the field of view was 2 mm x 2 mm with a 32x32 spatial sampling.

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Large-scale Hybrid MoS_2/polymer films for enhanced photobleaching of dye molecules

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New photon harvesting platforms are crucial to develop a new generation of photonic devices with impact in renewable energy conversion. Two-dimensional (2D) Transition Metal Dichalcogenides semiconductor (TMDs) layers that are characterized by exceptional optoelectronic properties tunable in the Visible and Near-Infrared spectrum represent a very promising platform in view of ultra-thin photonic devices [1]. Among them few-layer MoS_2, characterized by an electronic bandgap in the Visible and an high optical absorption coefficient, is particularly attractive for the light harvesting and photoconversion applications. Such intriguing optical response combined with high chemical reactivity qualifies this 2D semiconductor layer as a promising candidate in photoconversion and energy storage applications [2].
So far 2D TMDs devices mainly rely on exfoliated flakes with active areas limited to the μm^2 range, thus posing a serious issue in view of scalable photonic and photoconversion applications. Additionally, the application of 2D TMDs layer in photoconversion applications is still limited by their low overall photon absorption in the few-layer regime (~10%) [3], demanding for novel ultra-thin photon harvesting solutions. More conventional nanophotonic approaches to light harvesting in the ultrathin regime rely on functionalization of the surface with plasmonic nanoparticles [4]. Here we instead focus on the possibility of reshaping the TMD material itself as an active optical element featuring a flat-optics configuration that couples the incident light to the absorbing layer [5].
For this purpose we develop a hybrid 2D/polymeric flat-optics platform based on nanogrooved ultra-thin MoS_2 layers that extend uniformly over large area (cm^2) and promote enhanced photon absorption and conversion properties. Large-area periodic templates fabricated by Laser Interference Lithography (LIL) have been exploited to drive the formation of periodic gratings on transparent and flexible substrates. Furthermore we developed an original large-area physical growth approach of TMD films, based on the conformal deposition of ultra-thin MoS_2 layers supported on periodic templates. These hybrid polymer/MoS_2 nanoarrays feature a light absorption enhancement compared to a reference flat MoS_2 film, which is promoted by the excitation of the Rayleigh Anomalies (RA) arising at the evanescence condition when light is redirected parallel to the surface of the periodic nanogrooved layer.
As a demonstration of the surface functionalization and as its direct application we employed it in a prototypal photochemical reaction: the photobleaching of the Methylene Blue (MB) molecules in solution. We demonstrate a strong enhancement of the photochemical MB degradation by effectively tuning the RA mode in resonance to the molecular absorption band [6]. Therefore, these findings pave the way to the optimization of the platform for applications such as waste water treatment and energy storage where the diffractive anomaly can be easily tuned in resonance to a target molecule absorption band by tailoring the grating and illumination parameters.

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Collective coupling strength of phononic and plasmonic nanoantenna modes with molecular vibrations

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The increased sophistication of optical nanoantennas in the last decades has allowed for confining light to volumes well below the diffraction limit [1]. This strong field localization enhances the nanoscale interaction between the modes of the nanoantenna and molecular vibrations and excitons, opening new opportunities, for example, to change the chemical properties of molecules due to the formation of new polaritonic states [2, 3].

In this work, we compare the coupling of molecular vibrations at infrared energies with either phononic modes in nanoantennas made of polar materials (e.g., silicon carbide SiC) or with plasmonic modes in metallic (e.g., gold Au) nanoantennas. These nanoantennas couple with collective modes that involve the vibrations of many molecules. As a first step, we perform numerical simulations of the response of these nanoantennas coupled with molecules occupying a well-defined region (figure 1(a)), and we extract the coupling strength g by fitting the numerical spectra with a coupled harmonic oscillator model [4, 5]. However, performing a systematic analysis with this approach is computationally expensive because it requires one simulation for each spatial distribution of the molecules. Further, we consider an alternative approach that only requires performing a single simulation of the bare nanoantenna response without molecules [5, 6]. In this methodology, we obtain the coupling strength with an analytical expression that considers the overlap between the fields induced by the nanoantenna and the volume that the molecules occupy. We show in figure 1(b) the results of these two approaches, which are in excellent agreement. Notably, the coupling strength with the plasmonic nanoantennas is larger than with the phononic ones. However, it is easier to reach the strong coupling regime with the phononic nanoantennas because of the much weaker losses. This study can thus help to optimize the interaction of nanoantenna modes with collective molecular vibrations for strong-coupling experiments.

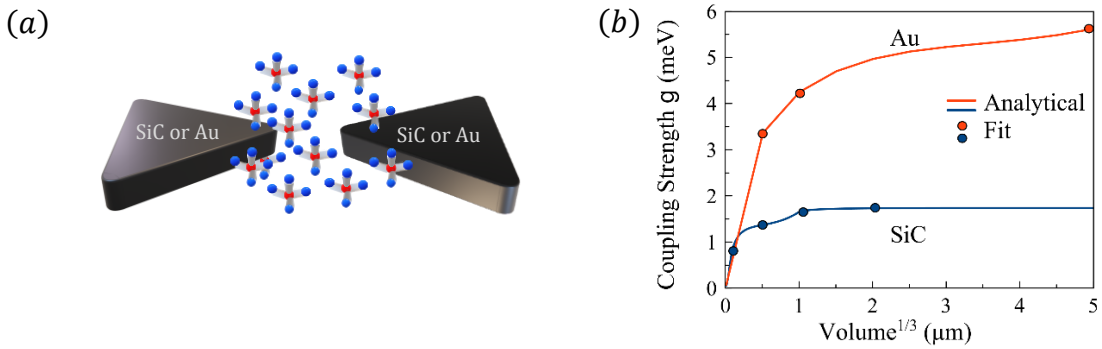

Figure 1: (a) Schematic representation of a phononic (SiC) or plasmonic (Au) bowtie nanoantenna coupled with molecules. (b) Coupling strength g for SiC (blue) and Au (red) bowtie nanoantennas interacting with molecules, obtained (dots) fitting the simulation with a coupled harmonic oscillator model and (solid line) using an analytical expression. The results are plotted as a function of the volume occupied by the molecules.

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Fully Atomistic Modeling of Plasmonic Bimetallic Nanoparticles

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In this contribution, we present the extension of the recently developed (frequency dependent fluctuating charges and fluctuating dipoles) ωFQFμ atomistic model[1] to treat the optical properties of bimetallic nanoparticles, with special emphasis on Ag-Au nanoalloys and core-shell systems.[2] ωFQFμ is a fully atomistic, classical approach, of which the theoretical foundations lay in Drude's theory of conduction, classical electrodynamics, interband transitions, and quantum tunneling. In particular, each atom of the nanostructure is endowed with an electric charge and an electric dipole moment, which vary as a response to an externally applied electric field. Charges account for the dynamics of the conduction electrons,[3] while dipoles model interband transitions. We show that by properly modeling the composition-dependent charge and dipole response, ωFQFμ can reproduce experimental trends for Au-Ag bimetallic nanoparticles (see for instance Fig. 1) of complex shape.[4–6]

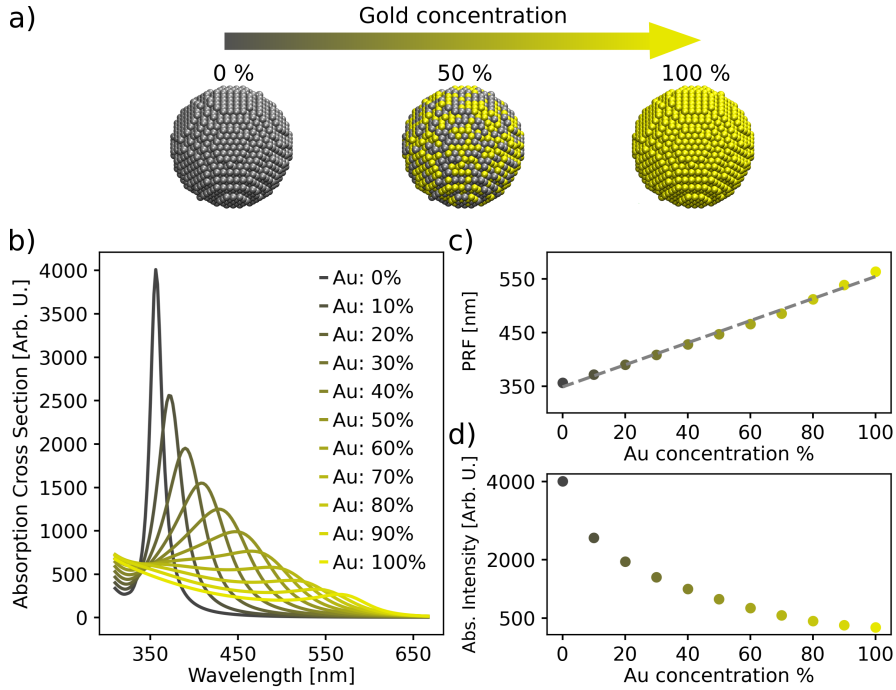

Figure 1: (a) Graphical depiction of spherical Au-Ag structures. (b) ωFQFμ absorption cross-section, (c) Plasmon Resonance Frequency (PRF) and (d) absorption intensity as a function of Au concentration.

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Two-photon interference from distinct molecules on the same chip

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Single molecules in solid-state matrices have been proposed as sources of single-photon Fock states back 20 years ago. Their success in quantum optics and in many other research fields stems from the simple recipes used in the preparation of samples, with hundreds of nominally identical and isolated molecules able to provide bright single-photon streams also at room temperature [1], which narrow down to their spectral Fourier-limit once placed in a cryogenic environment[2]. In the past years, such systems have proven unmatched coherent interaction properties, from non-linear behavior at the few photon level [3] to collective behavior for pairs of coherently coupled emitters [4]. Moreover, great potential for integration in hybrid photonic circuits has been demonstrated with different approaches [5,6]. All these elements make molecule-based single-photon sources promising emitters for application in quantum plasmonics.

Exploiting an organic molecule platform, in this contribution we demonstrate quantum two-photon interference from distinct single-photon sources located in a single chip. Hong-Ou-Mandel visibility of 97% for post-selected photons at zero delay and 40% integrating over the whole single-photon wavepacket is reported [7]. The work is made possible by the recently discovered effect of laser-induced charge-separated state formation in molecular matrices, responsible for a local Stark shift for the molecules therein embedded [8], persistent for hours after the shifting light is switched off.

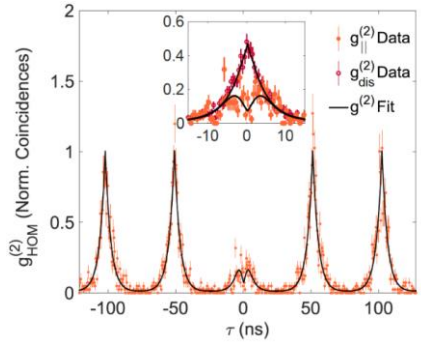

Figure 1: Coincidences histogram for Hong-Ou-Mandel interference experiments for photons emitted by distinct sources in the same chip. In the inset the case of molecules with nominally zero detuning (indistinguishable photons - orange dots) is compared to the configuration of largely detuned molecules emitting distinguishable photon wavepackets (red circles).

In the second part of the contribution, we will focus on a deeper understanding of the physical mechanism responsible for the frequency shift induced by the laser illumination. Investigating the interplay with controlled external electric fields, applied thanks to miniaturized electrodes built on the substrate, we can verify the Stark-effect nature of the shift and guess the charge dynamics inside the molecular medium responsible for it.

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Displacement Talbot lithography to scale-up plasmonic metasurface fabrication

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Plasmonic sensors are widely applied for the detection of contaminants and relevant (bio)markers and (bio)molecules for environmental, (bio)medical and food applications. Extensive efforts addressed the development of reliable and cost effective manufacturing solutions, enabling massive production of miniaturized sensing devices suitable for integration with other components into portable platforms. Despite this, the challenge is still open to find a grown technique combining suitable resolution, reproducibility, easy tunability in size and shape allowing, in parallel, low cost and limited time-consuming runs to pattern large areas in view of massive scaling-up, making the manufacturing affordable also for SME.

In this scenario, Displacement Talbot Lithography (DTL) is emerging as a promising manufacturing technique combining the requirements of high resolution, scalability, versatility, ability to pattern non-linear substrates on large areas at relatively low cost [1]. Consequently, DTL provides a promising route as a fast, robust and scalable process in the large volume manufacturing.

As a result, we decided to investigate DTL to scale-up the plasmonic metasurface developed by Plasmore and based on a multistep approach, combining nanosphere lithography and plasma-based processes [2]. Two main objectives have been identified:

1) Guarantee of an optical response reliable and standardized: the targeted application as a biosensing platform requires a high control over the fabrication parameters to obtain high reproducibility in terms of spectral position of the plasmonic resonance and sensitivity to refractive index changes of the environment;

2) Tunability of the plasmonic resonance spectral position: resorting to a nanofabrication technique compatible with large areas of high resolution patterns with tunable features, it is particularly interesting to broaden the eligible fields of application, boosting the knowledge transfer in cutting edge technologies.

These objectives will allow the detection of biological agents and (bio)markers in the field of cancer-related research, but also a high performance platform for contaminants analysis in the framework of the European Green Deal in relation to climate change and environmental degradation. In addition, an easy implementation within the modern food industrial chain could be feasible for safety and quality control [3].

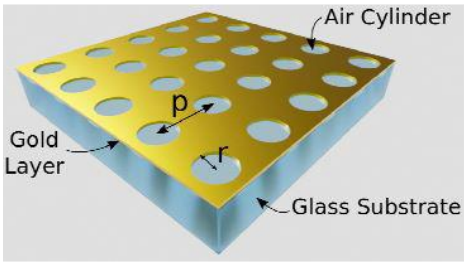

Figure 1: Scheme of the plasmonic metasurface, where "p" is the surface pitch and "r" is the hole radius.

Besides the usual morphologic characterization with SEM at different stages of the production process, the evolution of the optical response has been measured too and compared with the findings of FDTD simulations.

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Suitability of highly Doped Groupe IV semiconductor for spectral narrow plasmonic MIR detection devices

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Plasmonic antennas can be used to enhance light-matter interaction with possible applications in improving optoelectronic device performance. For example, plasmonic antennas offer the possibility for boosting hot carrier photodetection for selected wavelengths [1]. While for the visible and NIR wavelength region metals are well studied and suited for this task, in the MIR wavelength region metals exhibit large ohmic losses and long plasmon confinement lengths. In contrast, heavily doped semiconductors with their low electron density , if compared to metals, are promising candidates to replace metals and enable plasmonics in the MIR region [2, 3] . In particular, group-IV semiconductors such as SiGe, Ge and GeSn have the additional advantage of a non-polar lattice, free of infrared-active phonons. It was shown that and a plasma wavelength of λ_p = 2.6 µm could be achieved in n-type doped Ge with high carrier concentrations up to ND = 2.6 x 10^{20} cm^{-3} [4].

Nevertheless, to build fully functioning plasmonic hot-electron photodetectors there are stronger requirements that need to be met: not only the lowering of the plasma wavelength but also the increase of the crystal quality and therefore of the carrier mobility. A short relaxation time is crucial to achieve good device performance. Besides the material requirements, the design of the sensor needs to enable electrical contact, for which standard dipole nano-antennas are not suitable. Also, plasmonic modes that are typically used for hot carrier excitation e. g. localized surface plasmon resonances (LSPR) in general are rather broadband, which makes them less ideal for detectors with narrow spectral resolution. Coupling LSPR with a diffractive mode, e. g. a Rayleigh anomaly, leads to the formation of surface lattice resonance (SLR) with concomitant narrow extinction peaks of plasmonic nano-antennas, and this could prove crucial to achieve detector performance improvement in the MIR region.

By comparing different material growth approaches, as well as post-growth processing, we show the suitability of group-IV semiconductors for plasmonic applications in the MIR wavelength region. By optimizing the material parameters as well as the geometry of the antennas for the excitation of SLR, a sharp spectral behavior could been simulatively predicted and also shown in measurements (fig.1).

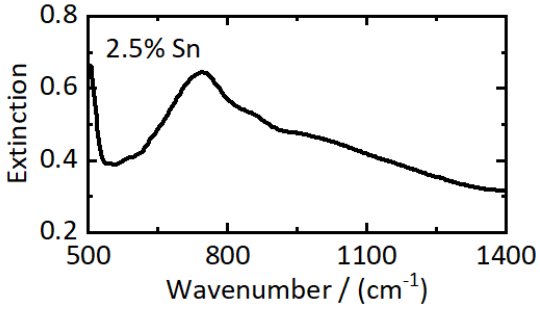

Fig. 1. Extinction spectra for a comb-like antenna made from $Ge_{0.975}Sn_{0.025}$, 3.5 µm pitch and a width of 1.3 µm.

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Broadband and tunable multilayer metamaterials based on plasmonic nitrides, oxynitrides and transparent conductors

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Plasmonics has been dominated for decades by noble metals because of the high-quality resonances in the VIS that they can support, pursuing unprecedented light-matter coupling. However, the impossibility to modulate plasmons in wider spectral ranges (fixed carrier density), has activated a rising concern to alternatives [1]. Transition metal nitrides are nowadays appointed as ideal substitutes to conventional metals because of low-cost, thermal stability, CMOS compatibility and modifiable plasmonic responses through VIS-nearIR by stoichiometry [2]. Oxynitrides are rising interest as well, due to the unique capability to cross twice the zero value of the real permittivity ε_1 (double epsilon-near-zero behaviour) in a wide spectral range, where new exotic phenomena arise, such as enhanced optical non-linearities or improved photocatalysis [3]. Further still, Transparent Conducting Oxides (TCOs) possess tunable carrier density, thus are promising for shifting the plasmonic features in the IR [1].

In this framework, the quest for uncommon and multiple functionalities to be designed at needs has stimulated the interest towards meta-structures based on alternative materials, finding application in energy conversion, biosensing or nanophotonics. Specifically, Hyperbolic Metamaterials (HMMs) show an anisotropic permittivity $\varepsilon(\omega)$ (parallel $\varepsilon_\parallel$ and perpendicular $\varepsilon_\perp$ to the HMM surface) due to the spatially-periodic alternation of conductors ($\varepsilon_1(\omega)<0$) and dielectrics ($\varepsilon_1(\omega)>0$) [4]. At the HMM region ($\varepsilon_\parallel<0$ $\varepsilon_\perp>0$), unique high-k waves are enabled, to promote for instance unprecedented light confinement.

Here, original multilayers (Fig.1a) merging titanium nitrides (TiN), oxynitrides (TiO_xN_y) and TCOs ($Ta:TiO_2$) have been developed in one-step by Pulsed Laser Deposition, to accomplish unconventional HMMs with exceptional optical tunability in VIS-IR (Fig.1b). The fundamental advantage is the capability to master stoichiometry and morphology directly at synthesis (Fig.1c), by acting on deposition parameters (e.g. background deposition gas). Great efforts have been devoted to materials characterization (structural, electrical and optical output) to understand the physics behind while keeping a material science outlook. Such novel HMMs can push the boundaries of nanophotonic research towards broadband, tunable and multi-resonant plasmonic systems, to be applied for engineered light manipulation, thermal management or solar absorption.

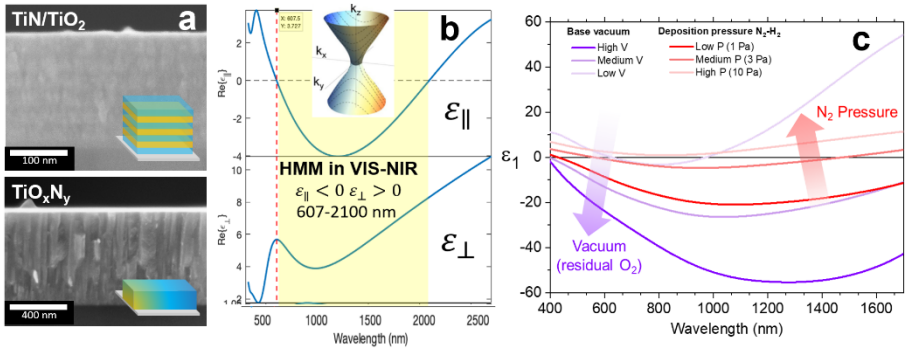

Figure 1: (a) SEM images of TiN/TiO_2 multilayers and TiO_xN_y films. (b) $\varepsilon_\parallel$ and $\varepsilon_\perp$ of HMM formed by TiN/TiO_2. (c) ε_1 of TiO_xN_y showing double epsilon-near-zero behaviour tunable in VIS-NIR with deposition conditions.

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Thermal scanning-probe lithography for broadband on-demand plasmonics on transparent substrates

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High-resolution (HR) and deterministic fabrication of plasmonic nanostructures on transparent substrates is a crucial issue in photonics. Thermal scanning-probe lithography (t-SPL) is a mask-less technique that allows HR nanopatterning of thermally sensitive films by a sharp conductive probe heated in a controlled way. This way a deterministic nanolithography can be combined with pre-patterning and in-operando morphological characterization of the system all the while preserving delicate substrates (like two-dimensional materials) coated by a sacrificial polymer film [1, 2]. In order to precisely control the nanolithography process, the t-SPL system applies an electric bias between the scanning micromachined cantilever and the sample [3]; this condition is fulfilled by metallic and semiconducting substrates thereby limiting HR nanopatterning onto transparent dielectric substrates.
In this work we demonstrate that HR nanolithography t-SPL can be achieved also on challenging optically transparent dielectric substrates by intercalating an ultrathin layer of a transparent-conductive oxide (TCO) below the top polymer film employed as resist.
The insertion of the ultrathin TCO layer also enables the morphological characterization of the nanopatterns by high-resolution scanning electron microscopy, and the optimization of specific t-SPL fabrication recipes which were previously developed for conductive substrates. For different sizes of nanostructures we were effectively able to obtain a family of different gold plasmonic resonators, spanning the spectral range from 700 nm to 1350 nm. In this way we could engineer ordered arrays of plasmonic nanoantennas supported onto dielectric glass substrates. The nanoarrays support Localized Surface Plasmon Resonances tunable over a broadband spectral range from the Visible to the Near-Infrared by controlling the size and/or the shape of the nanoantennas. This non-invasive nanolithography thus opens new possibilites for engineering plasmonic nanoantennas onto fragile layers with impact in thermoplasmonics, sensing and nanophotonic applications.

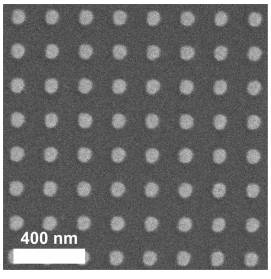

Figure 1: Scanning electron micrograph of an array of gold nanostructures obtained by t-SPL on glass coated with TCO.

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Tailorable materials for plasmonics in extreme conditions

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The manipulation of light on the deep subwavelength scale is essential for enhancing light-matter interactions and improving the performance of nanophotonic devices. The unique properties of plasmonic materials made them essential for a plethora of applications, ranging from energy to automotive, from wireless to medical and IoT. In particular, discovering multifunctional materials with tunable plasmonic properties, capable of surviving harsh environments (e.g., high temperature and pressure, and chemical or mechanical abrasion) is critical for advanced optical and telecommunication applications.

Here, we adopted massive high-throughput computational techniques, based on density functional theory, to design and characterize tunable plasmonic materials active in the near-IR and visible range. Starting from simple transition-metal crystals (such as nitrides) [1,2], we investigate the role of composition, off-stoichiometry and structural disorder in TiN_x compounds [3], and we provide an efficient strategy to fine engineering stable, easy-to-grow hyperbolic metamaterial superlattices [4,5], with selected optical and extraordinary mechanical properties (e.g. hard materials). Finally, by combining computational thermodynamics and first principles electronic structure techniques we propose high-entropy transition-metal carbides [6], which yielded plasmonic properties from room temperature to 1500K, as demonstrated by experiments performed on the archetype carbide $HfTa_4C_5$ (see Figure 1). This new class of plasmonic materials may foster previously unexplored optical/mechanical applications in extreme conditions, e.g. in the fields of aerospace, satellites, and security systems.

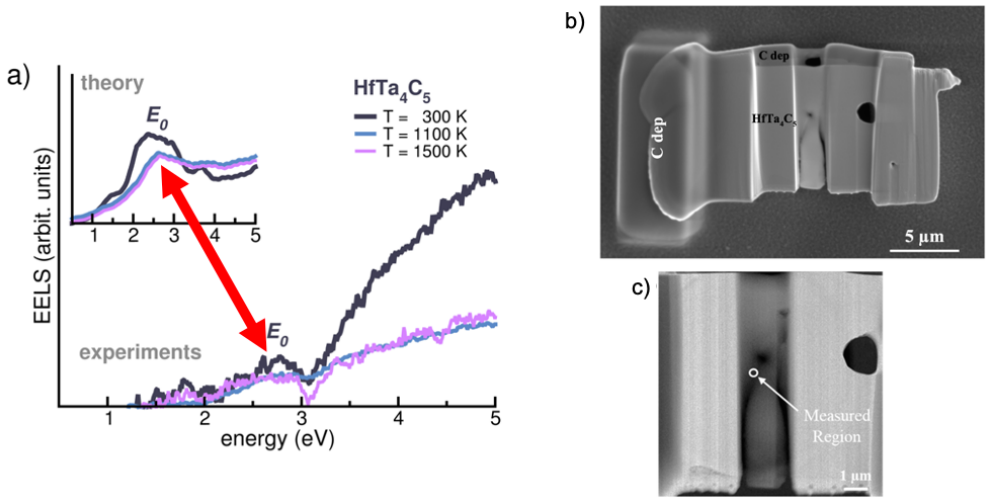

Figure 1: a) Experimental EELS spectra of $HfTa_4C_5$ as a function of temperature. Inset reports the corresponding theore- tical spectra, evaluated at the same temperatures. b) Ion milled electron transparent cross-section of sintered HfTa4C5 pellet fixed to Protochip Fusion Select Heating E-chip. (c) Monochromated STEM micrograph of the $HfTa_4C_5$ cross-section, which indicates the region where all EELS spectra were collected. Image adapted from Ref. [6]

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A new era of materials characterization: can we achieve atomic sensitivity using visible light?

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We just entered a new era of materials characterization, where atomic sensitivity can be achieved by plasmon-enhanced optical spectroscopy. During this talk you'll hear about a new characterization method where nanoparticle-mediated electrical contacts can "squeeze" light in the device active material, providing an innovative non-destructive technique able to characterise various device materials changes *in operando*. We will first discuss how 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].

You'll also see how light tracks both the migration of oxygen ions and phase change inside low energy consuming, ultrathin ferroelectric random access memory devices (FeRAMs), which has remained controversial so far. Specifically, hafnia-based oxides are an alternative to conventional bulk ferroelectrics and enable single-digit nm ferroelectricity. In them, *wake-up* and *fatigue* effects still cause unpredictable performance variation over consecutive electronic switching cycles, preventing large-scale commercialization. We achieve 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, capturing for the first time 1. *pre wake-up* stage where oxygen ions migration leads to phase change, 2. *wake-up* (i.e. increase of device remanent polarisation) due to phase change and 3. *fatigue* (i.e. decrease of device remanent polarisation) caused by further migration of oxygen ions in the new phase changed material [2].

We will then switch gear and hear about the first characterization of nanoscale MoS_2-based electrical switches at room temperature and in air, where accessing both Photoluminescence and Raman, together with Dark Field spectroscopy proved volatile threshold resistive switching due to the intercalation of metallic atoms from electrodes directly between Mo and S atoms, without the assistance of sulphur vacancies. Once again, our superb sensitivity is here able evidence the size of bridges till the atomic resolution, confirming the picture of many nanofilaments (1–2 Au atoms thick) penetrating spaces between atoms in MoS_2 rather than one filament growing along a grain boundary [3].

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Probing Electron Density Shift at the Metal-Molecule Interface Induced by a Static Electric Field by Tip-Enhanced Raman Spectroscopy

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A molecule chemically bound to a metal surface can share orbitals with the nearest surface atoms, leading to localized hybrid surface states by which electron density can be attracted from the surface atoms to the molecule or pushed from the molecule to the surface. This effect is fundamentally important for optoelectronics and organic electronics since it comes to play whenever molecules are chemisorbed to a metal surface and limits the efficiency and bandwidth of electronic devices. In SERS and TERS charge transfer can lead to the chemical signal enhancement [1]. STM assisted TERS allows for applying DC electric fields comparably high to the fields experienced by molecules in regular devices [2]. The influence of DC electric fields on tip enhanced Raman spectra has been reported by various authors who discussed different aspects such as reorientation of molecules [3], intensity changes and energy level shifts [4]. Here we report on our progress towards a better understanding of a scanning DC electric field on tip enhanced Raman spectra of small molecules directly bound to the metallic substrate [5].

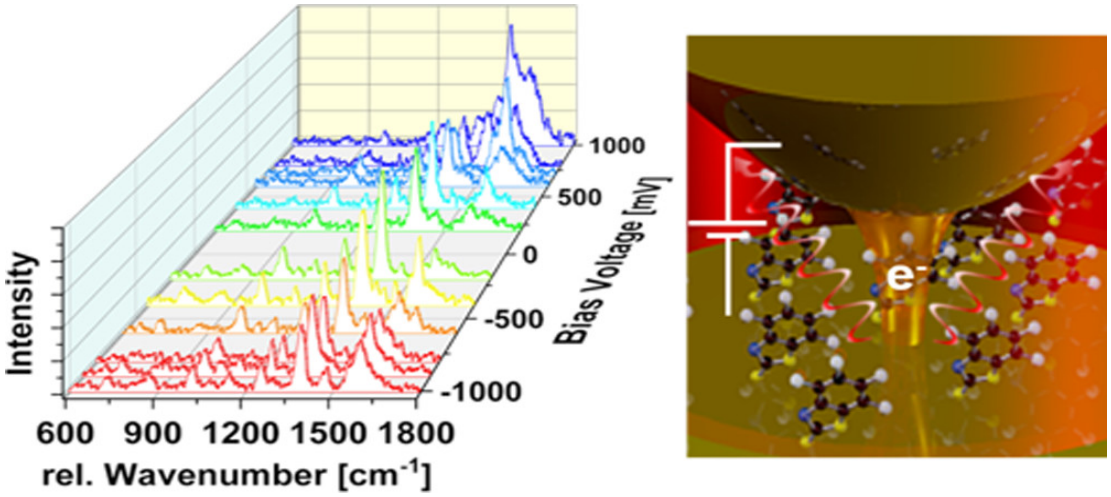

Figure 1: Tip-enhanced Raman spectra of 2-mercaptobenzothiazole (MBT) molecules on gold as a function of the bias voltage applied between the gold tip and the gold subsrate.

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Detection of light transport regimes and localization in hyperuniform luminescent materials through near-field optical microscopy

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Recently, disordered dielectric materials with structural correlations, which fill the gap between random structures and perfectly ordered photonic crystals, have generated an ever-growing interest. A special class of these materials are the Hyperuniform Disordered (HuD) photonic systems [1], that have recently been shown to display large isotropic photonic band gaps (PBG). Here, we present the realization dielectric slabs optically activated by embedded InAs quantum dots, patterned with a HuD network design in which it is possible to identify several Anderson localized states spectrally located at the PBG edges with relatively high quality factors (Qs) comparable with standard photonic crystal cavities, as well as spectral and spatial broadened modes in a diffusive light transport regime [2]. Interestingly, an accidental defect mode arising due to local peculiar topology is always detected as the first localized resonance at the lower PBG edge, and represents a fascinating peculiarity of HuD. Finally, engineered optical cavities in HUD photonic materials, exhibiting high-Q resonances of multipolar character, have been realized and considered as an advantageous alternative to photonic cavities thanks to the intrinsic geometrical statistical isotropy of the HuD environment upon which they are built [3]. Our samples display a network design capable of supporting three types of localized modes of different nature, coexisting within a small area and in a relatively narrow spectral window of the disordered correlated system (Fig.1a, from left to right): a i) topological defect (T), an ii) Anderson localized mode (A), and (iii) an engineered high Q optical cavity (Fig.1a) (D). These three different kinds of defect exhibit different localization properties, as it can be deduced by the theoretical predictions on the Inverse Participation Ratio (IPR) (Fig.1b). By performing on the sample Scanning Near-field Optical Microscopy (SNOM) (Fig.1c), which is capable of subwavelength resolution in the near-IR range, we build up a theoretical and experimental study on how light is confined in HuD networks, and unveil how different physical mechanism that lead to the formation of different kind of defects with different localization lengths and Qs. The possibility of detecting different light transport regimes and resonances through the analysis of the modes spatial profiles and the exploration of light localization and delocalization in a system, whose structuring place is at the junction between fully-ordered and completely random systems, can have a great impact on all-optical switching, implementations of linear-optical quantum information processors and single photon sources.

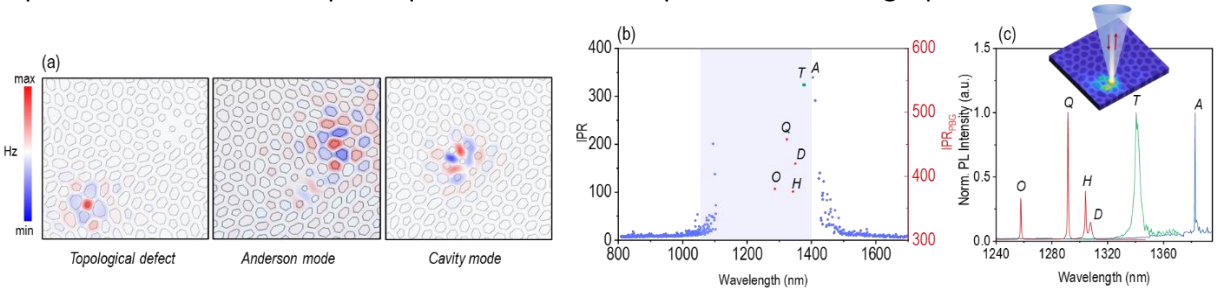

Figure 1: (a) Finite Element Method (FEM) simulation maps of the magnetic field component Hz of a topological defect, and Anderson mode, and a cavity mode. (b) FEM calculations of the IPR of the HuD modes, included the cavity modes (in red), mode T (in green) and mode A. (c) SNOM spectra of the cavity defects, of mode T and A.

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Phonon polariton vortices in suspended silicon carbide membranes

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Surface Phonon Polaritons (SPhPs) are mid-infrared surface waves originating from coupling of the electromagnetic field with optical phonons of a polar dielectric [1]. High SPhPs confinement in thin films arises due to hybridization of the modes supported by the top and bottom film interfaces and the associated dispersion can be retrieved by near-field measurements using scattering-scanning near field optical microscopy (sSNOM) [2]. Here, we use these highly confined surface modes to create deeply subwavelength optical vortices carrying intrinsic orbital angular momentum [3]. We show that by leveraging the sublinear SPhP dispersion the vortex topological charge can be multiplied by a small frequency increase because of the increased SPhP momentum. We experimentally generate SPhP vortices by fabricating appropriately designed Chromium ridges acting as SPhP launchers. We detect the vortex near-field signature by transmission sSNOM and quantify the measured order purity by defining a set of suitable reference functions. Moreover, we investigate high order vortices in which we detect the so called "deuterogenic" effect [4], in which multiple topological charges coexist at the same time.

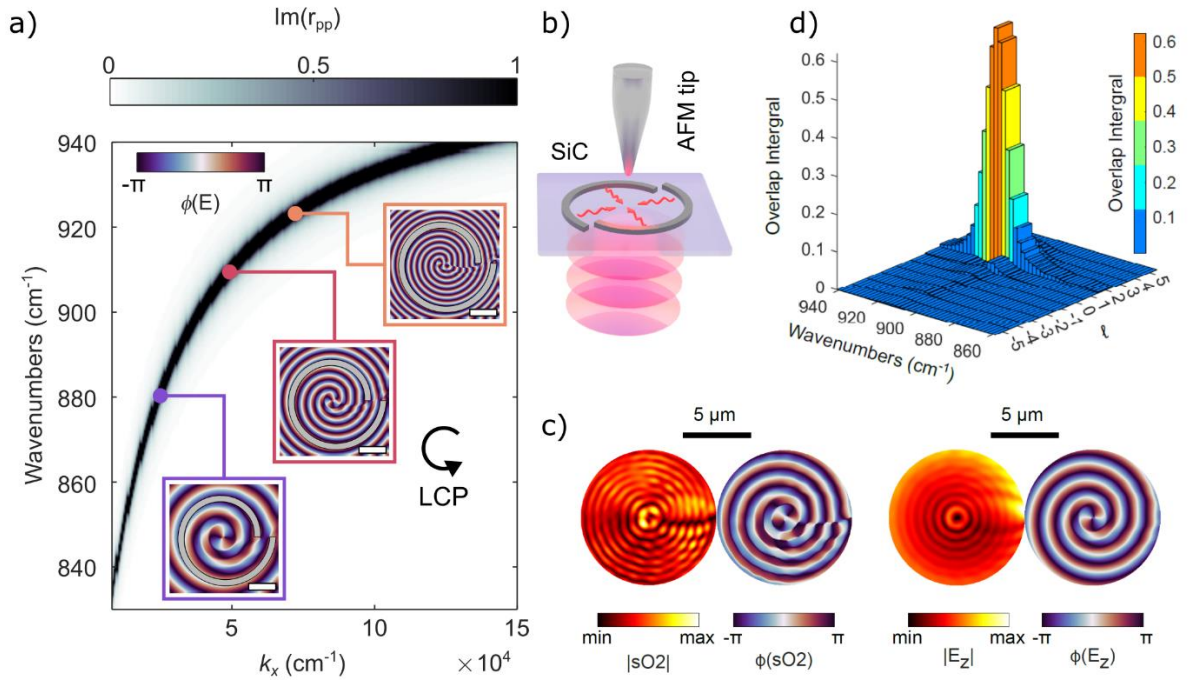

Figure 1: a) Calculated dispersion for a 100 nm SiC membrane together with simulated phase profiles of an order 2 SPhP vortex at different excitation frequencies. b) Sketch of the near-field measurement setup. c) Experimental (left) and simulated (right) amplitude and phase maps of a SPhP vortex with order -2. d) Calculated vortex purity for the data shown in c) as a function of vortex order and excitation frequency.

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Coherent all-optical routing of upconverted light by a nonlinear metasurface

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Recently, a strong drive towards the miniaturization of nonlinear optics has been motivated by the functionalities it could empower in integrated devices. For instance, near-infrared-to-visible upconversion of telecom photons is fundamental for optical communication and night vision, taking advantage of efficient silicon-based detection. Moreover, all-optical control of light can enable ultrafast optical information encoding. In this sense, optical metasurfaces are emerging as suitable platforms to multiplex such functionalities. In past works we devised metasurfaces for nonlinear light generation and polarization-based steering [1]. Here we propose a dual-beam scheme whereby a pulse at the telecom frequency ω (1550 nm wavelength) is mixed with its frequency-doubled replica at 2ω. Recently, we combined these pulses on individual dielectric and plasmonic nanostructures [2,3], exciting two coherent frequency-tripling pathways (Figure 1a): third-harmonic generation (THG, $\omega+\omega+\omega$) and sum-frequency generation (SFG, $\omega+2\omega$). Their coherent superposition at 3ω produces interference, which is allowed/suppressed depending on the symmetry of the system. Here we exploit a nonlinear, all-dielectric metasurface to lift symmetry constraints through diffraction, which steers radiation 3ω among different directions (Figure 1b). Moreover, interference modulates the power within each diffraction order (Figure 1c), depending on the relative phase between the two pumps. Therefore, by exploiting the phase as a tuning knob, the upconverted signal can be switched between opposite pairs of diffraction orders, e.g. (0,±1), with an efficiency >90% (Figure 1d,e). Notably, the phase shift necessary to have a complete switching corresponds to a delay Δt = 1.3 fs between the pumps. The steering can be also reconfigured by changing the polarization state of the pumps. The proposed approach can be envisioned as an all-optical method to reroute upconverted telecom photons in different k-space directions. The instantaneous timescale of the nonlinear interactions involved could enable the ultrafast reconfigurability of the metasurface, paving the way to GHz speed modulation of the optical signal.

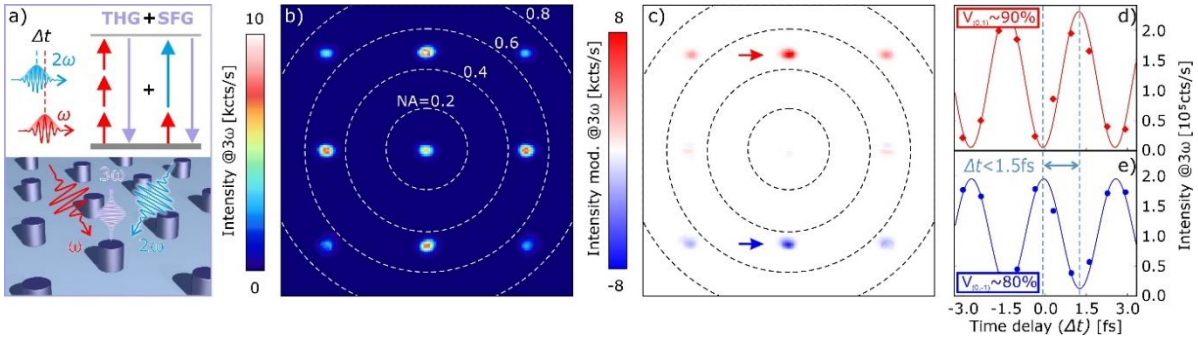

Figure 1: a) Frequency-tripling process based on ω + 2ω pumping scheme producing THG (3ω = ω+ω+ω) and SFG (3ω = ω+2ω). b) Back focal plane (BFP) map of the signal at 3ω emitted by the metasurfaces, showing the first and second diffraction orders. The first-order diffraction lobes appear at a numerical aperture NA = (λ/3)/p = 517 nm/1100 nm = 0.47, where p is the array periodicity. c) Modulation of the upconverted signal at 3ω, evaluated as the difference between the BFP maps acquired at a delay Δt between the ω and 2ω pumps of about 1.3 fs (see dashed lines in panels d and e). d,e) Upconverted power of the (0,+1) and (0,−1) orders of the metasurface (red and blue arrows in panel c, respectively) as a function of Δt, demonstrating switching with visibility (V) larger than 90%.

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Design of ϵ-near-zero multilayers with enhanced Kerr-type nonlinearities

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Introduction ϵ-near-zero (ENZ) materials have drawn the attention of many different fields of research such as nanophotonics, nonlinear optics and plasmonics thanks to their special linear and nonlinear optical response [1]. In these materials the real part of the dielectric permittivity becomes zero at a wavelength called λ_{ENZ}, a behavior which has been linked to extraordinary optical properties, including the enhancement of nonlinear optical phenomena such as the optical Kerr effect (OKE) [2]. This ENZ response can be obtained in artificial metamaterials such as periodic metal-dielectric multilayers, with λ_{ENZ} tunable by properly choosing the constituent materials and metal filling fraction. In these metamaterials, the generation of coupled surface plasmon polaritons at the metal-dielectric interfaces, leads to local intensity enhancement of the electric field in the metallic layers and thus, stronger nonlinearities [3]. The inclusion of a metal component however, also implies losses by absorption and reflection, which reduce the transmitted signal and application potential of the metamaterial. In this work we define a figure of merit (FOM) to evaluate the trade-off between these opposing effects, and study its evolution as a function of the constituent parameters of the multilayer to find an optimized design for multilayers with enhanced OKE. We then compare our predictions with both simulations and experimental data.

Sample design and characterization As example of the design procedure we followed, in Fig.1 we show the map of the FOM spectra for a four period Ag/Al_2O_3 multilayer with thickness of the Al_2O_3 layers fixed to 85 nm and Ag thickness in the range [10, 60]nm. We can notice bands of local maxima corresponding to the surface-plasmon modes supported by the metamaterial, and the decrease of the FOM at larger Ag thicknesses due to the stronger losses. Since working in the ENZ regime is another condition known to strongly boost the nonlinear response [4], we choose as our optimized Ag/Al_2O_3 multilayer the one in which λ_{ENZ} matches the FOM maximum (highlighted in Fig.1 with a white cross). We carry out this kind of analysis considering different thicknesses and materials and identify the more promising designs. We then synthesize these samples by magnetron sputtering depositions and experimentally measure the spectra of their OKE parameters with the z-scan technique. We also simulate the expected spectra with the method in [4] and find good agreement with experimental data. As predicted by the FOM, a strong nonlinear response peaked at λ_{ENZ} is found, even with small input field intensities. Moreover, the best performance is found in samples having higher values of the FOM at their λ_{ENZ}.

Conclusion Both simulated and experimental data show good agreement with our predictions, proving the efficiency of the FOM, as a useful predictive tool in the design of multilayers with optimized nonlinear optical response.

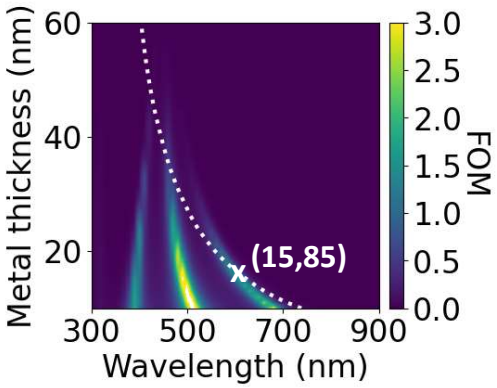

Figure 1: Figure of merit for a four period Ag/Al_2O_3 multilayer with Al_2O_3 layer thickness $t_d = 85nm$ as a function of the wavelength and Ag layer thickness. The dotted line highlights the value of λ_{ENZ}. The white cross corresponds to the sample $(t_m, t_d) = (15, 85)$ nm for which we achieve optimal overlap between λ_{ENZ} and the local maximum of the FOM.

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Surface vs bulk contribution to the second-harmonic generation in AlGaAs nanoresonators

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III–V semiconductors have been investigated intensively for nanoscale nonlinear optical processes due to their large bulk nonlinear susceptibility, negligible optical losses in the visible/near-infrared (NIR) range and ability to sustain strong Mie resonances. In III–V nanostructures, the bulk contribution to second-harmonic generation (SHG) is often reputed to be dominant [1]. However, a recent work reported that the surface contribution to SHG in GaAs metasurfaces can be comparable to the bulk one [2]. In this work, we investigate nanocylinders made of $Al_{0.18}Ga_{0.82}As$ to study the potential surface contribution to SHG. $Al_{0.18}Ga_{0.82}As$ exhibits and a broad optical transparency window up to 750 nm, which can significantly suppress two-photon absorption and prevent SH reabsorption in the near-infrared range [3]. The dependence of SHG on the polarization of the illumination at the fundamental wavelength of 1550 nm is studied systematically on a set of nanoantennas with variable radii from 183 nm to 207 nm with steps of 6 nm around the geometry supporting a magnetic dipole resonance [4].

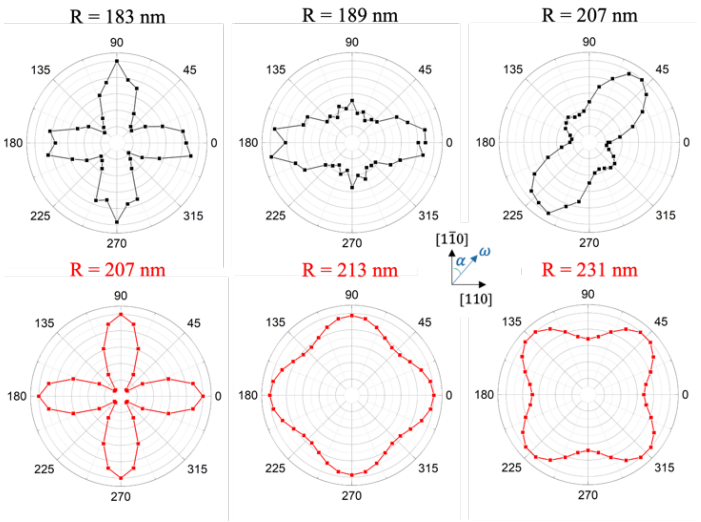

Figure1: Measured and simulated normalized SHG emission from nanocylinders of different radii *R* as a function of the linear polarization of the impinging illumination at the fundamental frequency. The polar plots at the top (black) display the measured SHG at *R* = 183 nm, *R* = 189 nm, and *R* = 207 nm. The polar plots at the bottom (red) display the calculated SHG at *R* = 207 nm, *R* = 213 nm, and *R* = 231 nm.

Figure 1 presents a comparison between measured and numerically calculated SHG for three radii. A nearly four-fold symmetry of SHG emission is observed at the radius of 183 nm, indicating a dominant bulk contribution. This is confirmed by the simulated polar plot by only considering the bulk contribution for a nanocylinder of 207 nm radius, which exhibits a magnetic dipole resonance at the wavelength employed in the SHG experiments, as already reported in [3]. A 24 nm deviation from the nominal radius can be ascribed to fabrication tolerances and is compatible with previous observations [3]. By simulating larger radii keeping this offset fixed, we retrieve a four-fold symmetry in the polar plots for all the radii that we investigated experimentally. Yet, the SHG signal obtained on cylinders with radius equal to 189 nm and 207 nm, only a two-fold symmetry of the emission pattern is observed. As already pointed out in previous works [2], this behaviour can bear the signature of a non-negligible contribution from the surface, which interferes with the bulk contribution of SHG.

This interplay between bulk and surface effects based on these platforms must be considered as a potential reason why the real-world performance of nano-optical systems may deviate from the design predictions. In addition, the presence of non-negligible surface SHG can be relevant for applications such as sensing, which is known to rely on surface sensitivity.

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Free-electron third order nonlinearities in heavily doped InGaAs nanoantennas

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Free electrons in plasmonic structures can provide extra degrees of freedom in modulating nonlinearities in the system when the nonlocal effect is considered (eqs. 1-3). The hydrodynamic model reveals that the third harmonic nonlinearity due to the free electrons could even be orders of magnitude higher than that of the conventional bulk $\chi^{(3)}$ when the free-electron density is low.[1] By employing this theory to heavily doped semiconductors, in the project NEHO, we aim to achieve advanced nonlinear integrated photonic circuits working in the mid-infrared by taking advantages of the high nonlinearity from the plasmonic aspect and low loss from the semiconductor aspect.

While the hydrodynamic theory has been used to successfully reproduce second order processes in noble metals [2,3], third order nonlinearities have remained unexplored experimentally, since in noble metals these are negligible compared to the crystalline lattice nonlinearities (i. e. $\chi^{(3)}$). Here, we use a proof-of-principle n-doped InGaAs antenna design (Fig. 1a) to demonstrate and achieve high hydrodynamic nonlinearity. The experiment shows that the third-harmonic nonlinearity has an evident doping dependence, which is predicted by hydrodynamic model. Numerical simulation reproduces the qualitative behavior observed experimentally. Moreover, from the simulation, we show both linear (Fig. 1b) and nonlinear (Fig. 1c) efficiencies, where the third-harmonic efficiency due to the free electrons is expected to be 3 orders of magnitude higher than that of the conventional bulk $\chi^{(3)}$ (Fig. 1c).

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

$$\mathbf{S}_{\mathrm{NL}}^{(2)} = \frac{e}{m}\mathbf{E}\nabla\cdot\mathbf{P} - \frac{e\mu_0}{m}\dot{\mathbf{P}}\times\mathbf{H} + \frac{1}{en_0}(\dot{\mathbf{P}}\nabla\cdot\dot{\mathbf{P}} + \dot{\mathbf{P}}\cdot\nabla\dot{\mathbf{P}}) + \frac{1}{3}\frac{\beta^2}{en_0}\nabla(\nabla\cdot\mathbf{P})^2 \tag{2}$$

$$\mathbf{S}_{\mathrm{NL}}^{(3)} = -\frac{1}{e^2 n_0^2}(\nabla\cdot\mathbf{P}(\dot{\mathbf{P}}\nabla\cdot\dot{\mathbf{P}} + \dot{\mathbf{P}}\cdot\nabla\dot{\mathbf{P}}) + \dot{\mathbf{P}}\cdot\dot{\mathbf{P}}\nabla\nabla\cdot\mathbf{P}) - \frac{1}{27}\frac{\beta^2}{e^2 n_0^2}\nabla(\nabla\cdot\mathbf{P})^3 \tag{3}$$

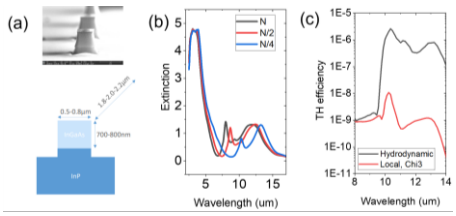

Figure 1: (a) Sketch and SEM picture of the plasmonic antennas. Linear (b) and nonlinear (c) efficiencies of the antenna. The comparison shows that the third-harmonic efficiency due to the free electrons is over 3 orders of magnitude larger than that due to the bulk $\chi^{(3)}$.

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Optimizing the extraction of second-harmonic light from a plasmonic array

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In recent years, metasurfaces have attracted much attention from the nano-optics community. Their collective behavior bears promise of flat optics miniaturization, new beam shaping capabilities and increased efficiency in a number of processes [1]. In particular, plasmonic metasurfaces have been employed to enhance nonlinear upconversion rates, with the best results being obtained using two surface lattice resonances (SLR) at the fundamental and harmonic wavelengths [2,3]. However, these designs are often based on sub-wavelength arrays to couple local modes to SLRs, only allowing the 0th diffraction order to be collected.

Here, we report on a periodic, plasmonic metasurface whose pitch can be optimized to allow maximal extraction of the second-harmonic generation (SHG) excited in the telecom wavelength (1550 nm) and emitted by the individual meta-atom, *i.e.* an L-shaped gold nanoantenna. In particular, we found that the SHG from the first horizontal diffraction order can be enhanced about a factor 2 by optimizing the metasurface pitch (see Figure 1a). Such enhancement is attributed to the optimized matching between the directional SHG emission by the individual nanoantenna and the diffraction orders of the metasurface.

We confirmed this by experimentally reconstructing the SHG radiation pattern of a single nanoantenna from different diffraction orders (see Figure 1b) through angular-resolved excitation (see Figure 1c). We obtained excellent agreement with the simulated radiation pattern using the finite elements method. In addition, the emission of a single particle in the Fourier plane was also directly imaged (see Figure 1d), yielding again very good agreement with the simulation.

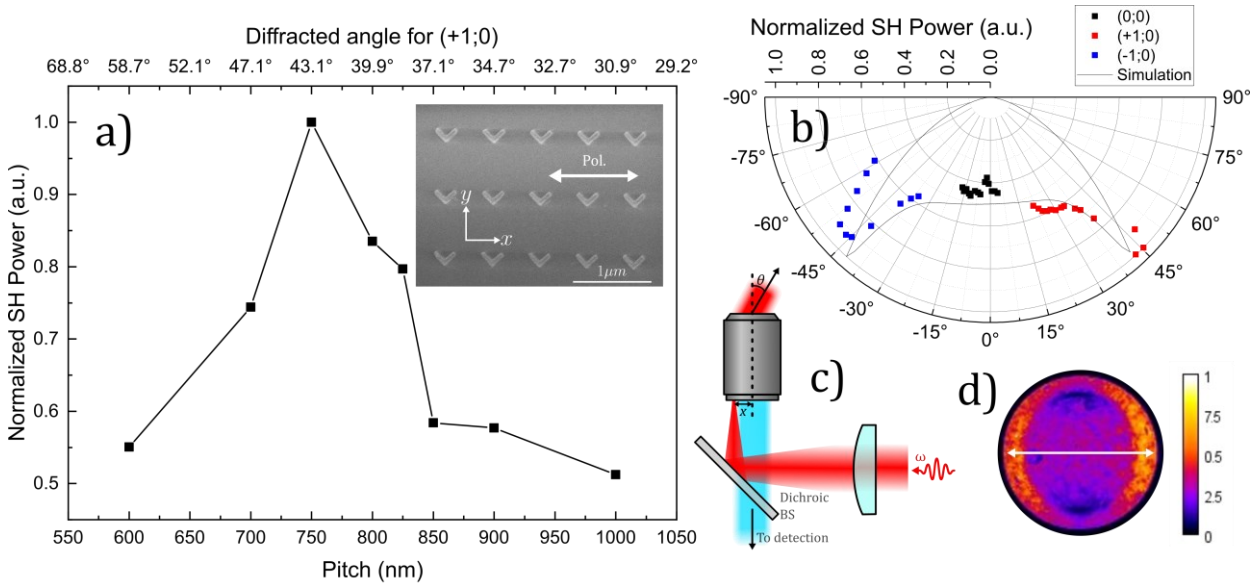

Figure 1: (a) SH power emitted at 775 nm by the metasurface in the (+1;0) diffraction order, measured as a function of the pitch in the x axis. Inset: SEM image of the metasurface, the double arrow represents the incident polarization. (b) Simulated and reconstructed emission pattern in the horizontal axis of the BFP (see cut in fig. 1d). (c) Sketch of the experimental setup for tilted excitation used in fig. 1b: a laser is focused on the back pupil of the objective, giving near collimated excitation. (d) Normalized SH power (a.u.) of a single nanoantenna in Fourier space.

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Nonlinear plasmonics and exciton tuning in atomically thin materials

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Graphene and related 2D materials represent a unique platform to study nonlinear optics at atomic scales [1]. In recent experiments, we have shown their potential impact for applications in ultrafast and broadband nanoscale frequency converters, triggered by electrical [2] and/or all-optical [3] switches. Further progress can be obtained thanks to integration with photonic devices, for instance in applications such as gas sensing [4], and metallic or dielectric metasurfaces.

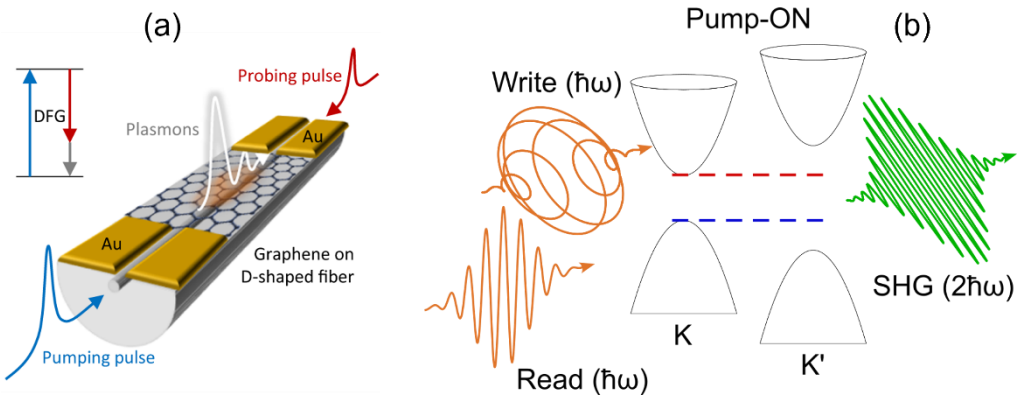

Figure 1: (a) Sketch of the photonic integrated device based on monolayer graphene on a D-shaped fiber for nonlinear plasmonic and ultrafast logic operations. (b) Schematic of nonlinear valleytronics to probe excitons in atomically thin semiconductors.

In this seminar I will discuss some of our recent results in the field of nonlinear plasmonic for logic operations in graphene based photonic devices (Figure 1a) and of ultrafast nonlinear spectroscopy of excitons and valleys in TMDs (Figure 1b). First, I will show that difference frequency generation (DFG) can be exploited to create gate tunable plasmons in an integrated photonic device, namely monolayer graphene on a D-shaped fiber. By tuning the Fermi Energy of graphene, we were able to shift the plasmon frequency and couple to the surface-optical phonons of the silica substrate, thus creating new plasmon branches. These could be independently tuned as a function of two distinct input voltages to realize logic operations (NOR, OR, AND) after proper filtering [5]. Second, I will discuss how nonlinear optics can be used to probe excitons in atomically thin semiconductors, focusing in particular on nonlinear valleytronics. 2D semiconductors such as transition metal dichalcogenides (TMDs) possess two energetically degenerate but non-equivalent valleys, which can be independently excited by circularly polarized light of opposite ellipticity. In this context, we have demonstrated that ultrafast coherent and nonlinear processes can provide distinct advantages for the realization of valleytronic operations such as the generation (write) and detection (read) of this binary state. In particular, we realized ultrafast generation of a valley population by the optical Stark effect, which we subsequently detected by valley induced second harmonic generation (SHG) [6]. Finally, I will discuss our approach and preliminary results towards the detection of momentum forbidden excitons, obtained by coupling monolayer TMDs with metallic metasurfaces.

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Chiral optical harmonic scattering: theoretically predicted in 1979 and demonstrated four decades later

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Back in 1979, Professor David Andrews hypothesized that the chirality of light scatterers could impact the intensity of light scattered at higher harmonics, which would be the most straightforward manifestation of chirality in nonlinear optics.[1] However, no one had been able to observe this phenomenon until recently, leading Andrews to consider it an "impossible theory". Our team's research has since led to groundbreaking discoveries in this area. In 2019, we published the first experimental observation of the effect, which we named Chiroptical (chiral optical) Harmonic Scattering, at the second harmonic wavelength, using Ag nanohelices.[2] This study resolved a 40-year-old scientific question. Our subsequent studies have further demonstrated the effect, from chiral Au nanocubes,[3] from semiconductor (CdTe) nanoparticles,[4] and at the third harmonic wavelength in collaboration with Andrews.[5] In Au cuboids,[3] we also set a sensitivity record, reporting the first chiroptical characterisation of a single nanoparticle floating freely in a liquid environment, a sensitivity that was further confirmed in Ag nanohelices.[6] Our findings open the way towards further nonlinear optical effects that could find future applications in healthcare.

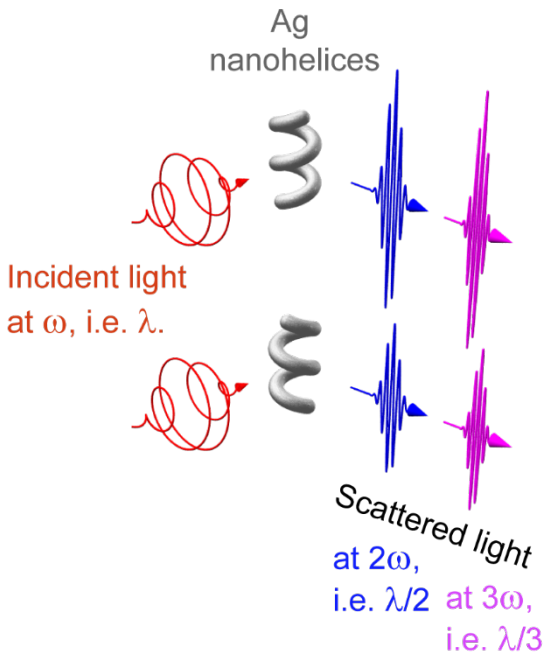

Figure 1: Diagram of chiral optical harmonic scattering from Ag nanohelices at the second- and third-harmonic.

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Chirality in Hyper-Mie scattering effects from CdTe nanohelices

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Recently, human-made nanotechnology based on lab-created inorganic nanoparticles (NPs) has progressed significantly in replicating the self-assembly processes of life[1]. Many of the building blocks of life are chiral – they lack mirror-symmetry – and, correspondingly, characterizing the chirality of inorganic NPs has become increasingly important. Here, we demonstrate nonlinear chiral optical effects in CdTe nanohelices; these effects are highly sensitive and can be used to explore the complex parameter space of such NPs.

To speed up chirality optimization as a function of geometry parameters, the volumes of solutions containing chiral NPs become smaller. Traditional chiroptical techniques (e.g. circular dichroism) are challenged by such small volumes. By contrast, nonlinear optical methods require only tiny volumes, typically in the focal point of a microscope objective. However, nonlinear optical methods are often technically hard to implement, and they have not been widely adopted outside the labs.

The discovery of hyper-Rayleigh scattering optical activity[2] opened the way for characterizing the nonlinear optical properties of small chiral NPs, suspended in isotropic liquid solutions (e.g. in Ag and Au NPs[3]). Here, we present an alternative for characterizing larger particles, based on hyper-Mie scattering optical activity, see **Figure 1**. We demonstrate a significant increase in the measured ellipticity of CdTe nanohelices[4], compared to the linear optical regime and show that our effect can determine the chirality of the helices in volumes as small as 1 µL. We also discuss the outlook for further nonlinear chiral light scattering effects and their ability to probe other types of materials.

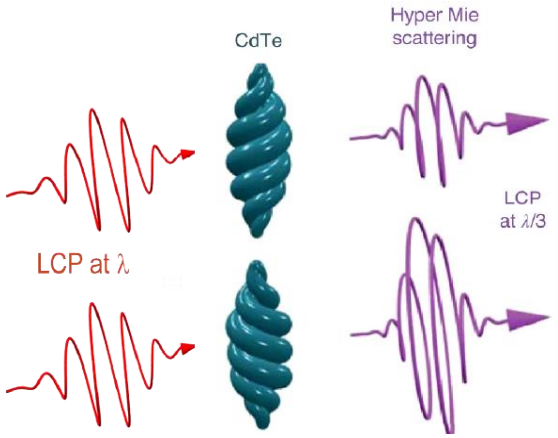

*Figure 1: **Third-harmonic hyper-Mie scattering optical activity.** (a): Left circularly polarized photons (LCP) at a wavelength λ are incident on the CdTe nanohelix. Light is then scattered at λ/3. The intensity of the scattered light is dependent on the handedness of the nanohelix.*

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Circular dichroism in plasmonic array of elliptical nanoholes with square lattice

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Abstract: We numerically studied the chiral properties of square 2D elliptic nanohole arrays in three different metallic metasurfaces (Ag, Au, and Al), from the near-IR to the ultraviolet spectral range. Circular dichroism arises in absorption spectra at the same wavelength region of extraordinary optical transmission. We elucidate the physical origin of absorption CD and we optimize the CD as a function of the geometrical parameters of the structure. The results suggest interesting applications for chiral biomolecule sensing.

Altering the electromagnetic properties at the nanoscale can be efficiently achieved by means of specially engineered metasurfaces. Particularly, when the symmetry of the metasurface is broken, its interaction with circularly polarized light can be controlled. Different absorption of left and right circular polarization is called circular dichroism (CD). Metasurfaces able to generate large CD are very interesting for both fundamental science and applications regarding ultrasensitive chiral molecule detection. Furthermore, it was recently shown that high-quality chiral metasurface samples can be created by using low-cost nanosphere lithography combined with tilted metal deposition [1]. In this work, we theoretically study CD in square arrays of elliptical nanoholes etched in thin metallic layers (Au, Ag, Al) [2] on a glass substrate. Fig.1 shows the metasurface structure used in our study at a normal incident on top of the surface. Transmission spectra display the well-known phenomenon of extraordinary transmission (EOT) from sub-wavelength hole arrays in a metal.

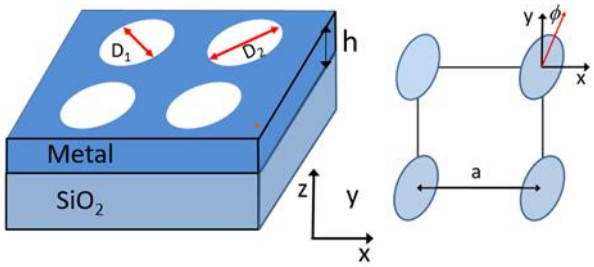

Figure 1: Scheme of the proposed structures studied in this work

The optical properties of elliptic nanoholes are numerically investigated by using two methods, 3D Finite Difference Time Domain (FDTD) simulation using Lumerical Ansys and Bloch-mode scattering matrix method in the open-source software known as Emustack [3]. To ensure convergence, we performed a comparison of the two methods. We calculate the optical spectra for circularly polarized light (RCP, LCP) to define the CD in absorption as

$$CD = (A_{LCP} - A_{RCP})/(A_{LCP} + A_{RCP}).$$

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Angle dependent output circular polarization degree characterization of self-assembled nanospheres coated with silver

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Abstract:

The addition of asymmetry introduced into plasmonic nanostructures can pave the path to chiro-optical phenomena. Especially, Circular dichroism which are often seen as different absorption of left and right polarization. Furthermore, fascinating characteristics emerge when the nanostructure alters the polarization state of the input beam. We present asymmetry in nanospheres and investigate its influence on electromagnetic response using broadband experimental data also characterize extrinsic chirality in a wide-tunable near-infrared region through observing simultaneously the input and transmitted beam polarization. We examine self-assembled asymmetric nanospheres coated with Ag using polystyrene nanospheres lithography which is low-cost manufacturing method. Our experimental setup is based on a laser with precise adjustable input and output polarization in the near infrared range. Activating the sample at different angle of incidence with linear, left, and right polarizations.

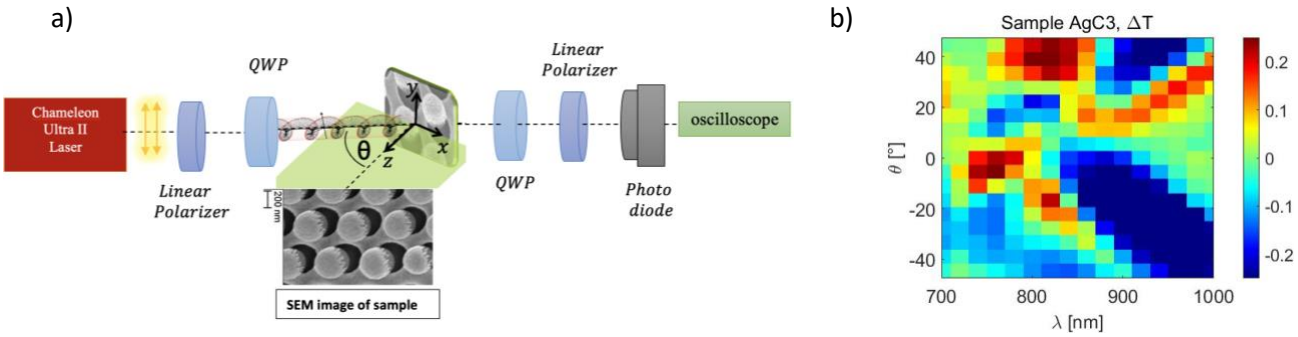

Figure 1. (a) Experimental setup. (b) Experimental (λ-θ) transmission dependence on the angle of incidence.

The circular polarization degree of the transmitted beam is then determined, showing resonance-governed circular polarization degree in the output, and illustrating the connection of intrinsic and extrinsic chirality.

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A Plasmonic Metasurface for Trapping and Manipulating Nanoparticles

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Introduction: Plasmonic structures are being used for many years in the field of trapping and manipulating particles in the Rayleigh regime [1]. Herein, we introduce a metasurface design fabricated on a gold film that exhibits a plasmonic Fano resonance [2]. Utilizing this unique feature and the strong optical forces arising from the plasmonic field, we trapped gold nanoparticles (AuNPs) 20 nm in diameter, as shown in Fig. 1a. We investigated the properties and the ideal excitation conditions for trapping with the metasurface, and achieved an extremely high trap stiffness value of 4.18 ± 0.2 (fN/nm)/(mW/μm^2) with very low excitation intensity [3].

Simulations and Fabrication: Extensive simulations were performed in order to define the geometry and tune the Fano resonance at the desired wavelength. In Fig. 1b, we plotted the generated electric field at a unit of the optimized metasurface for excitation wavelength 928 nm, which is the resonant wavelength. The simulations revealed the existence of two types of hotspots identified as Hotspot 1 (two identical and symmetric hotspots) and Hotspot 2. In the hotspots, the electric field is highly localized and thus, these are the locations where particles are trapped. Having the simulated dimensions of the metasurface, we fabricated an array of 16x16 metaunits using the focused ion beam milling technique. We also characterized the metasurfaces using microspectrophotometry.

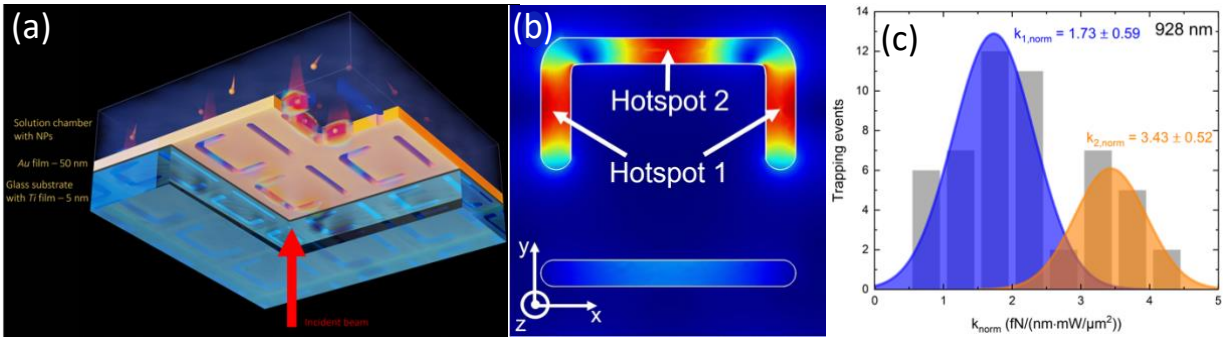

Figure 1: (a) Schematic of the metasurface etched on a gold film deposited on glass. During the experiment the metasurface is immersed in the solution of water with the AuNPs. (b) Simulated electric field of a metaunit. (c) Histograms of the trap stiffness values for the two hotspots.

Trapping Experiment: The AuNPs were suspended into water solution and a small amount of surfactant was added to avoid aggregation of the particles. We made a sample of the solution forming a liquid chamber on the metasurface, as shown in Fig. 1a. The excitation light was incident from the glass side. The plasmonic field extended into the solution was responsible for trapping and immobilizing the AuNPs. We used the trapping transient analysis to quantify the trap stiffness, i.e. how strongly a particle is trapped. In Fig. 1c, we plotted the experimental histograms of the trap stiffness when trapping with excitation wavelength 928 nm. Two Gaussian fits were performed that represent the particles trapped at the two hotspots of the metasurface. We also performed trapping with off-resonant excitation wavelengths 920 nm, 925 nm, and 930 nm. Very high stiffness values were obtained even for the off-resonant conditions.

Conclusions: A plasmonic metasurface was used for trapping AuNPs, resulting in stable trapping and very high trap stiffness values. Even though low incident intensities were used, we observed the presence of thermal effects destabilizing the trapping process. These effects would need to be investigated thoroughly and test the metasurface for trapping other particles, as well, such as proteins and quantum dots.

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Nonlinear Plasmonic Metasurfaces for Efficient Broadband THz Beamshaping

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Nonlinear plasmonic metasurfaces have been developed recently in order to generate broadband THz pulses through the interaction of ultrashort laser pulses with the nanostructured surface. These compact flat surfaces can be modified and designed on an extremely sub-THz wavelength scale, opening the door to tailored nonlinear fields and interactions. Recently, meta-atoms with C3 symmetry (Figure 1a) were used to generate broadband THz fields, where the phase and polarization of the emitted THz field can be tuned depending on the angle between the meta-atom and the pump linear polarization angle (Figure 1b) [1]. This led to the demonstration of many THz beamshaping applications, such as space-separated left and right hand circular polarization emission, tailored polarization dispersion in time and THz metagratings for dual polarization and beam steering (Figure 1c) [2]. Furthermore, C3 meta-atoms were used to generate nonlinear THz pulses with a toroidal topology, showing the first demonstration of such unique electromagnetic wave properties [3]. Recent nonlinear metagrating demonstrations have shown the ability to use amplitude shaping to control the emitted THz, resulting in holographically shaped beams such as Hermite-Gauss and Top-Hat configurations (Figure 1d) [4].

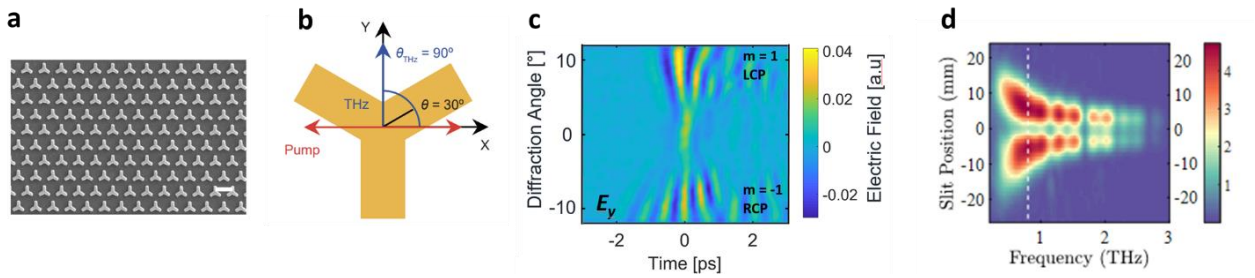

Figure 1: (a) Plasmonic metasurface with C3 symmetry meta-atoms for nonlinear THz generation [1]. (b) Relationship between the incident pump polarization angle and the emitted THz emission [1]. (c) Nonlinear generation of broadband THz pulses with space-separated left- and right-hand circular polarizations [1]. (d) Nonlinear generation of a broadband Hermite Gauss THz beam using C3 metagratings [4].

While the metasurface platform shows an unmatched ability to generate tailored nonlinear fields, the overall generated THz power still needs to be improved in order to show more suitability to the vast array of applications currently using THz waves. Recent results revealed that nanostructuring of the underlying epsilon near zero layer (ENZ) shows an order of magnitude improvement in the THz generation efficiency [5]. Further optimization of the metasurface material properties and the different photonic interactions comprising the complete metasurface, may lead to further increases in the efficiency, increasing the role of THz nonlinear metasurfaces as a suitable nonlinear platform. In the workshop we will present the advancements in beam shaping capabilities and conversion efficiency improvements.

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Vector beams generated by metalenses.

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By encompassing two emerging fields, structured optics and structured light, the design of a new generation of metasurface optics is expected to provide the key-elements of future optical architectures based on the manipulation of the spatial degrees of freedom of light. In particular, beams carrying orbital angular momentum (OAM) have gained increasing interest with formidable applications in a wide range of fields, such as particle tweezing, microscopy, high-capacity communications, and security. Our work proposes the design, fabrication, and characterization of new dielectric metaoptics able to generate orbital angular momentum beams with on-demand different vectorial behaviors acting only on the input polarization exploring different states of the Hybrid Poincaré Sphere (HPS).

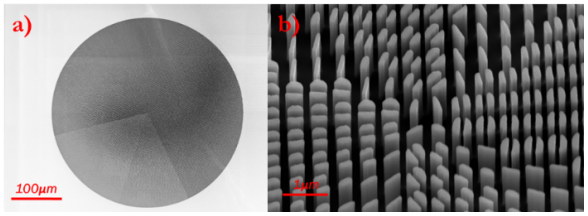

Fig. 1. a) Whole area of a fabricated metasurface (250 μm radius). b) Zoom of the metasurface central area. It

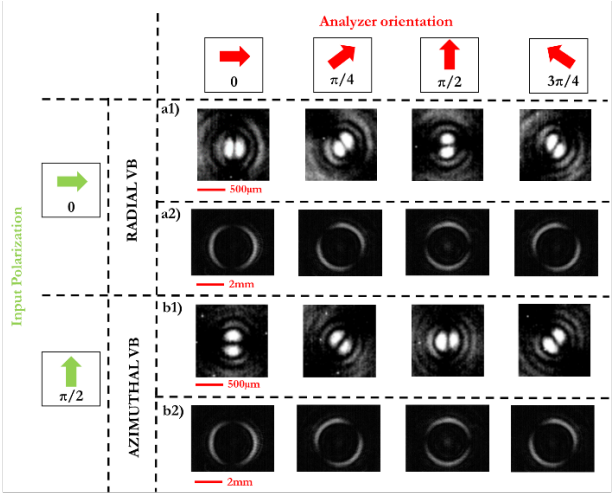

Fig. 3. a) Characterization of the generated radial (a) and azimuthal (b) vector beams (both fVBs (a1, b1) and PVVBs (a2, b2)) under different impinging polarization states and analyzer orientations.

Recently, it has been shown that by properly combining the control of both the geometric and dynamic phases acting on the pillars orientations and cross-sections, a dual-functional metalens (DFML) is able to generate different layouts. Imposing a general linear polarization state $|\alpha\rangle = |R\rangle e^{i\alpha} + |L\rangle e^{-i\alpha}$, the general formula of the output layout, $J|\alpha\rangle = \left(e^{i\phi^-} e^{-i\alpha}|L\rangle + e^{i\phi^+} e^{+i\alpha}|R\rangle\right)$, where $\phi^{\pm}$ are two phase equations maps that can be chosen independently [1]. In our case the first one generates focalized VBs (fVBs) into a desired position in space whereas the second generates perfect vortex vector beams (PVVBs) of controlled radius and width.

We designed and fabricated two metasurfaces working at wavelength of 1310 nm with radius of 250 μm, the first one generates a first order focalized Vortex Beams (fVBs) into a desired position fVB (l=±1) and a focal length f=1mm, the second one able to structure a first-order Perfect Vortex VBs with f=1mm and β=0.01rad. The characterization characterized showed the generated linearly-polarized Hermite-Gaussian VBs depending on the polarization orientation of impinging beamvector beam (Fig. 2).

The design significantly extends the functionality of standard spiral phase plates and *q*-plates, providing advanced optical elements for applications in microscopy, optical micromanipulation, and classical and quantum information, with unprecedented potential levels of compactness and integration into today's technology.

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Probing temperature changes using non-radiative and radiative processes in hyperbolic meta-antennas

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Plasmonics enables unrivalled concentration of light beyond the diffraction limit, leading to extremely confined and enhanced electromagnetic fields, which can be exploited in real-life applications, such as energy harvesting, wave-guiding and lasing, optoelectronics, and medicine. In this context, it was recently demonstrated that by using plasmonic hyperbolic meta-antennas one can achieve full control of absorption and scattering of light at visible and near-infrared frequencies [1], with potential applications of these architectures in magneto-optics [2], thermoplasmonics [3] and nonlinear optics [4]. Here, we explore the hyperbolic optical properties of multilayered hyperbolic Au-TiO_2 meta-antennas to probe changes in the temperature environment. We experimentally show that while the absorption decreases with increasing temperatures, the scattering remains unaltered (see Figure 1a). To explain these effects, we developed a finite element method (FEM) model utilizing the commercial software Comsol Multiphysics that simulates the temperature-dependent optical response of the meta-antennas, which reproduces very well the experimental findings (Figure 1b). The model was constructed by implementing a temperature-dependent complex dielectric function of gold [5]. In addition, we developed a semi-analytical approach providing further insights into the physics of these temperature-dependent optical processes, where we investigated the role of spectrally separated radiative and non-radiative processes when temperature is playing a role. Our work provides important knowledge regarding the opto-thermal properties of hyperbolic meta-antennas. Also, it provides a theoretical framework for simulating temperature-dependent light-matter interactions important in, for instance, opto-electronic applications based on switching mechanisms, such as all-optical logic gates.

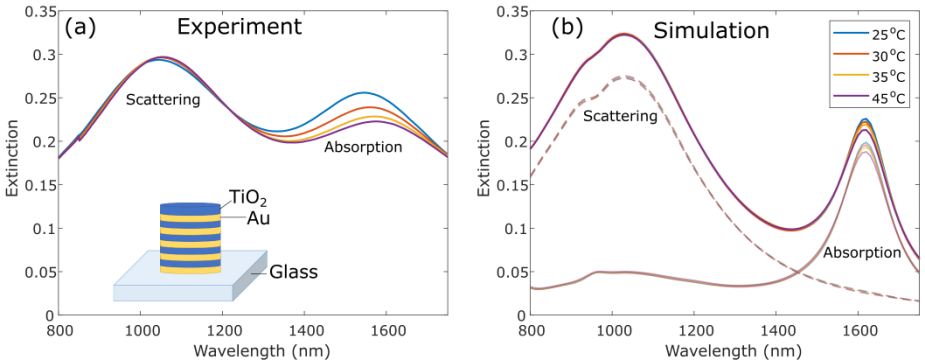

Figure 1: (a) Experimental and (b) calculated extinction spectra at different temperatures. The scattering (radiative) mode remains largely unaltered whereas the absorption (non-radiative) mode decreases with increasing temperatures. In (b), the transparent lines represent the contribution from scattering (dashed) and absorption (full). The inset in (a) is a sketch of the investigated geometry.

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Fano-resonant hybrid metastructures with ultra-high sensing performances

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Metamaterials-based sensors are of primary interest in physics, materials science, medicine, and biophysics thanks to their ability to detect very tiny amount of molecules spread into a medium [1]. Here, we report a detailed numerical study on the combination of epsilon-near-zero (ENZ) multilayer metamaterials [2,3] with all-dielectric metasurfaces resulting into Fano-Feshbach resonances and Rabi-analogue splits [4]. So far, a dedicated study of such systems has been missing. Following this, in this work we fill the gap by considering a polymeric metasurface, designed as a periodical array of rings with a cross in their center, placed on top of a silver (Ag) and zinc oxide (ZnO) epsilon near-zero optical nanocavity (εNZ-ONC) metamaterial. The accurate selection of the metasurface parameters allows the design of a sensor exhibiting an extremely high sensitivity of about 16000 and 21000 nm x RIU^{-1} depending on incoming polarization (p- or s- pol, respectively). This work paves the way for the development of novel groundbreaking devices for biomedical and environmental application based on plasmonic and photonic design principles.

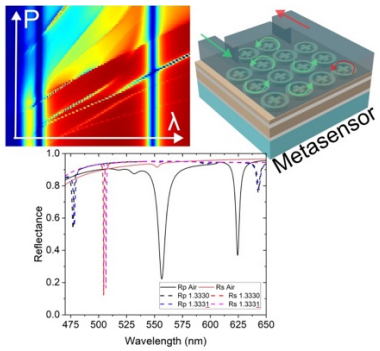

Figure 1: A novel metastructure was engineered for ultra-high sensitivity using epsilon near zero and Fano-Rabi physics. A metasurface made of rings with a cross in the center placed on a nanocavity metamaterial numerically achieved a high sensitivity of 16000-21000 nm x RIU^{-1} depending on incoming polarization.

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Electronic and photothermal phenomena in optical metasurfaces

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Nanostructured materials can interact with light, leading to various physical phenomena such as enhanced electric fields, high energy carrier generation, and heat dissipation. Optical metasurfaces can manipulate these effects by altering the shape, material, and arrangement of meta-atoms, the building blocks of metasurfaces, depending on the application. This presentation discusses recent research on the use of nanoscale optical metasurfaces in different systems, targeting extreme electromagnetic energy focusing, light rectification, and steam generation.

Excited plasmons decay over a sequence of events, transferring their energy to electron-hole pairs, and eventually to the particles' lattice as heat, causing a temperature rise [1]. Recently, we introduced an optothermal design featuring metallic bowtie antennas connected to a thermal sink, channeling electromagnetic energy into small, thermally isolated, and weakly absorptive reactors. This idea opens up possibilities for creating photothermally asymmetrical systems in which absorbing elements remain cool, while electromagnetically concealed structures heat up [2].

This strategy holds promise as the ability to produce heat in subwavelength regions can lead to enhanced nonlinear processes. For instance, we have illustrated how water desalination can benefit from high-temperature areas of limited size compared to homogenous thermal landscapes [3].

In this context, topologically optimized dielectric metasurfaces can achieve massive field enhancements in ultra-confined areas, boosting the efficiency of nonlinear optical processes, despite rejecting a portion of the input power [4]. In addition to light steering, an essential prerequisite for photothermal processes is efficient light-to-heat conversion, which underpins temperature increase. By utilizing TiN nanocavity arrays, we managed to dissipate approximately 90% of the solar spectrum within substrates only ~250 nm thick [5], laying the groundwork for ultra-thin optothermal devices.

However, in some applications, heat dissipation is unfavorable, and it's essential to harness hot carriers before they reach thermal equilibrium. We demonstrated how the spatial distribution of out-of-equilibrium carriers can be used prior to their decay to manipulate the optical properties of nanostructures at the ~ps timescale [6,7]. Furthermore, we showed that tapered conical nanoantennas can be manufactured in a point-contact metal-insulator-metal configuration to significantly enhance the hot electron extraction process near the visible range [8].

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Fast Electrical Modulation of a Single Plasmonic Nano-Rod Resonance

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Coupling of free electrons with electromagnetic fields near but below the plasma frequency of confined metallic nanostructures leads to plasmonic resonances. Their spectral response is strongly dependent on the geometry, i.e., for nanorods, changes in the aspect ratio of the cross-section to the length shift the resonance frequency. In this way, plasmonic resonances can be tuned from blue to infrared, but not actively.

Plasmonic resonances are fundamentally dependent on the metal density of free electrons n_0, since the resonance frequency of the system is proportional to the plasma frequency of the underlying material[1]. This gives rise to the idea of actively tuning n_0 by capacitive charging. Experimentally, however, this turns out to be very difficult to control, since the capacitance for a typical nanoresonator is in the order of magnitude of attofarads. Even for applied voltages in the order of tens of volts, compared to the large density of free electrons for metals ($n_0 = 5.9 \cdot 10^{28}\, m^{-3}$ in the case of gold), only a few hundred additional electrons can be pushed on or pulled off the surface of the resonator - which is about five orders of magnitude larger than the induced change. This makes plasmonic resonances extremely robust to applied voltages and plasmon resonance shifts difficult to observe.

To overcome the limitations of typical capacitive plasmon resonance changes, ion gels have been used to increase the capacitance due to the proximity of additional ions to the metal surface[2, 3]. However, one of the drawbacks of this approach is a long switching time compared to purely electrical methods, as well as hysteresis effects that can result from changes in surface chemistry[3].

Here, we demonstrate fast modulation of the plasmonic resonance of a single electrically connected gold nano-rod. We employ a lock-in amplifier to measure the relative change of scattering signal $\Delta S/S_0$ in the spectral range from 500 to 900 nm, while driving our structure with up to 50 kHz in frequency and up to 40 V in voltage amplitude. Results are of the expected order of magnitude according to existing theories. We discuss some of the theories in detail, like classical surface currents or the introduction of Feibelman parameters to account for non-classical electron spill-out at metal surfaces.

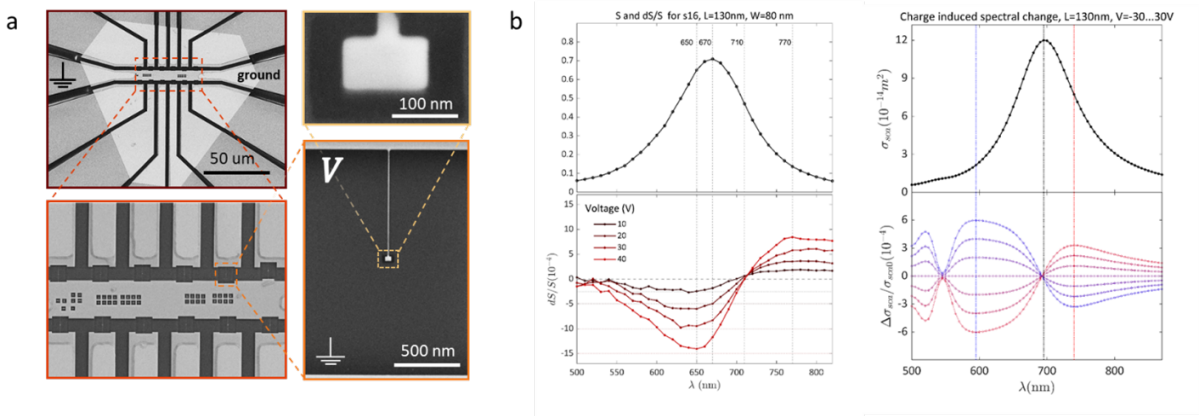

Figure 1: a) Gradually zoomed in SEM images of one of the electrically connected gold nano-rods for capacitive charging. b) Unbiased scattering spectra S_0 (top) and relative change of scattering $\Delta S/S_0$ under applied potentials (bottom), in experiment (left) and finite element simulation incorporating a surface charge density (right).

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Photochemical and Electrochemical Modulation of the Infrared Plasmonic response in Metal Oxide Nanocrystals: an Optical and Magneto-optical investigation

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Infrared (IR) light is attractive for nano-optics, as the low loss windows of optical fibers for telecommunications fall in the near IR, and vibrational modes of molecules have absorption fingerprints in the medium IR. Doped metal oxide (MO) nanocrystals (NCs) represent a unique platform for infrared plasmonics, as they provide tuneable carrier density, covering a wide spectral range, from 1.5 to 10 μm.[1] Their plasmonic response can be modulated synthetically by controlling the amount of aliovalent dopant introduced in the crystal structure, or by controlling its spatial distribution in core@shell NCs. Remarkably, the spectral response can be further tuned through post-synthetic approaches, such as photo-doping or the application of an electrochemical potential.[2]

In this work we prepared 10 nm indium tin oxide (ITO) NCs by colloidal chemistry and we exploited both the control of the dopant content as well as its spatial segregation to tune the plasmonic response. We developed a fitting approach based on optical and magneto-optical spectroscopy[3] to extract carrier parameters in homogeneously doped ITO NCs, and to determine the correlation between Sn dopant content and the ability of dopants to introduce free electrons in the semiconductor lattice.

Photo-chemical and electrochemical modulation were also implemented in-situ in a magneto-optical spectroscopic setup, studying the effect of such modulation on free carrier parameters.

Finally, we designed a core@shell In_2O_3@ITO NC with a plasmonic frequency that matches the vibrational signals of surface-bound oleate molecules (around 1500 cm^{-1}). A Fano-like interference between the plasmon and the molecular vibration was observed on a colloidal dispersion of such NCs. Applying a photo-chemical stimulus we can control the detuning between the plasmon and the vibrational modes, thus modulating the interference effect.

Our results are expected to deepen the understanding of the correlation between structural and carrier parameters and the plasmonic response of MO NCs, enabling their use in applications such as redox sensors,[4] surface enhanced infrared spectroscopy[5] and electrochromic windows.[6]

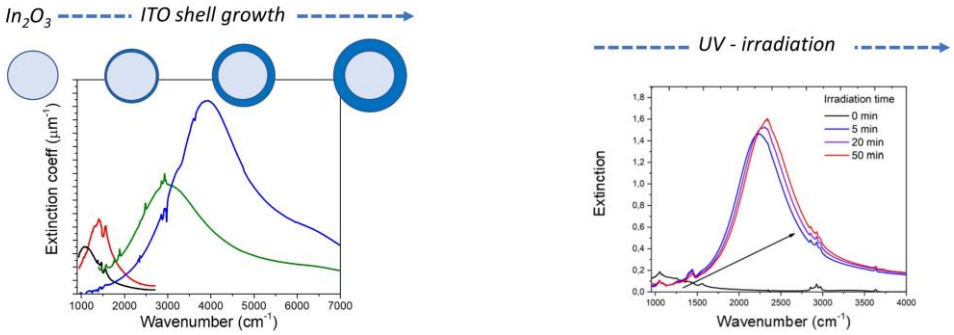

Figure 1. Effect of ITO shell thickness on the optical response of core@shell In_2O_3@ITO NCs (left), and effect of UV-irradiation time on the optical response of In_2O_3 NCs.

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Active quantum plasmonics with non-thermal electrons on ultrafast timescale

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Active plasmonics, where plasmonic excitations can be controlled with an external means, represents an attractive research direction of modern nanophotonics. Among the vast variety of approaches, optical excitation with femtosecond laser pulses stands out from the rest for bringing the active modulation onto the ultrafast timescale. Yet, direct laser illumination of metallic nanostructures results in their significant heating, often leading to the deterioration of their photonic properties. As such, the development of non-dissipative, heating-free methods for optical control of plasmonic systems is highly desirable.

In this work, we introduce laser-driven injection of non-thermal electron population into plasmonic metal and observe strong variations of the electronic density on the sub-picosecond timescale. Experimentally, we employ a back pump-front probe approach to realize an injection of highly energetic laser-excited electrons into Au from the adjacent 10 nm-thin Fe layer. Similar configuration has been used previously for the generation of laser-induced femtosecond spin current pulses in epitaxially grown MgO[001]/Fe/Au multilayers [1, 2]. The front surface of the 90 nm-thick Au film was periodically corrugated using electron beam lithography, allowing for the free-space excitation of a quasi-propagating plasmon-polariton mode with a delayed probe beam. In the detection arm, the 50 fs-long probe pulses (spectral width about 60 nm) were recorded using a monochromator and a fast CCD camera (Princeton Instruments), providing 2D-type of information in both temporal and spectral domains. We argue that this dedicated time-resolved spectroscopic approach is ideally suited for studying transient variations of the surface plasmon dispersion upon perturbations with external stimuli.

In the experiments, we observe ultrafast variations of the reflectivity of the probe beam on the order of 1% around the resonant wavelength (795 nm at 45 degrees of incidence). Notably, these variations are largely antisymmetric in wavelength, indicating the dominant impact of the shift of the surface plasmon resonance. In turn, symmetric variations are suppressed, highlighting the negligible contribution of the Au heating. Further, the effect is operative on the 300 fs-timescale, too quick for the heat transport across the metallic bilayer. Instead, we argue that the observed resonance shift is driven by the response of the native electronic density in Au to the super-diffusive transport of hot electrons injected from Fe. In particular, we found shifts up to about 0.15 nm, and scaling linearly with the 800 nm-wavelength pump pulse energy (and thus the number of injected non-thermal electrons). Within the Feibelman formalism [3] routinely employed for the electron spill-out effects, this shift corresponds to the variation of the Feibelman $d_\perp$ parameter of about 20 times, from -0.5 Å [4] to about +1 nm. These extremely strong and ultrafast variations illustrate the immense capabilities of the non-thermal electron injection for active plasmonics. In fact, this response of the electronic density in Au to the non-thermal electron injection that drives the surface plasmon dispersion shift can be seen as a manifestation of quantum plasmonics on the femtosecond timescale. These results pave the way towards ultrafast active plasmonics with indirect excitations, reducing the undesirable thermal effects and instead promoting other, less dissipative nanophotonic interactions.

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Ultrafast dynamics driven by opto-acoustic excitations in free-standing nickel cavities

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Light manipulation at the nanoscale has opened a previously unseen horizon for real life technology applications such as biosensors, energy harvesting devices or optoelectronics. In particular, light can be used to process information with extremely reduced energy consumption. Photonic technologies furthermore allow to overcome fundamental limitations of conventional electronics, such as bandwidth, clock-time and heating of the device [1].

In this context, the coupling of optical and acoustic properties has opened a new perspective in this field, providing an exciting alternative to electrical switching or passive optical devices. Opto-acoustic light matter interaction has already proven the capability for reflectance modulation [2] or magnetization dynamics control [3,4].

In this work we focus on the study of the opto-acoustic response of single picosecond-laser-produced ferromagnetic Ni cavities, i.e. free-standing nickel film, with a lateral dimension of 10 µm (Figure 1). The generation of acoustic waves in the cavity results from the mechanical stress induced by the pump pulse (515 nm, 50kHz) in the structure, while a visible probe pulse (500-950 nm, 100kHz) monitors the relaxation dynamics of the system. The transient reflectivity pump-probe measurement is carried out at room temperature. A Cassegrain objective has been implemented in the setup allowing both to image single structures and measure the transient signal from them. The spot size diameters and the energy densities of the pump and probe pulse are set to 8.6 µm and 4.76 mJ/cm^2, and 5 µm and 330 µJ/cm^2, respectively. The use of a free-standing Ni film cavity [5], in comparison to a nickel film on a glass substrate (Figure 2), could prove the generation of a greater number of acoustic echoes for the same scanning delay as well as a slower decay of those. We envision that this type of structures could be used to actively control the magnetization dynamics through low-dissipative acousto-optical switching processes, enabling the development of next-generation light-driven ultrafast spintronic devices with THz bandwidth.

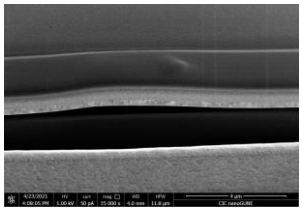

Figure 1: SEM image of the Ni cavity: Transversal cut view.

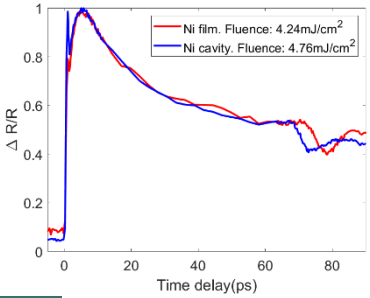

Figure 2: Normalized transient reflectivity spectra of a Ni film on a glass substrate (red curve) and a free-standing Ni cavity (blue curve).

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Abstracts – Posters

All-optical control of ultrafast plasmon resonances in the pulse-driven extraordinary optical transmission

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Abstract: Understanding the ultrafast processes at their natural-time scale is crucial for controlling and manipulating nanoscale optoelectronic devices under light-matter interaction [1]. In this study, we demonstrate that ultrafast plasmon resonances, attributed to the phenomenon of Extraordinary Optical Transmission (EOT), can be significantly modified by tuning the spectral and temporal properties of the ultrashort light pulse [2]. In this scheme, all-optical active tuning governs spatial and temporal enhancement of plasmon oscillations in the EOT system without device customization. We analyze the spectral and temporal evolution of the system through two approaches. First, we develop a theoretical framework based on the coupled harmonic oscillator model, which analytically describes the dynamics of plasmon modes in the coupled and uncoupled state [3]. Later, we compare the evolution of the system under continuous wave and pulsed illumination. Further, we discuss time-resolved spectral and spatial dynamics of plasmon modes through 3D-FDTD simulation method and wavelet transform. Our results show that optical tuning of oscillation time, intensity, and spectral properties of propagating and localized plasmon modes yields a 3-fold enhancement in the EOT signal. The active tuning of the EOT sensor through ultrashort light pulses pave the way for the development of on-chip photonic devices employing high-resolution imaging and sensing of abundant atomic and molecular systems.

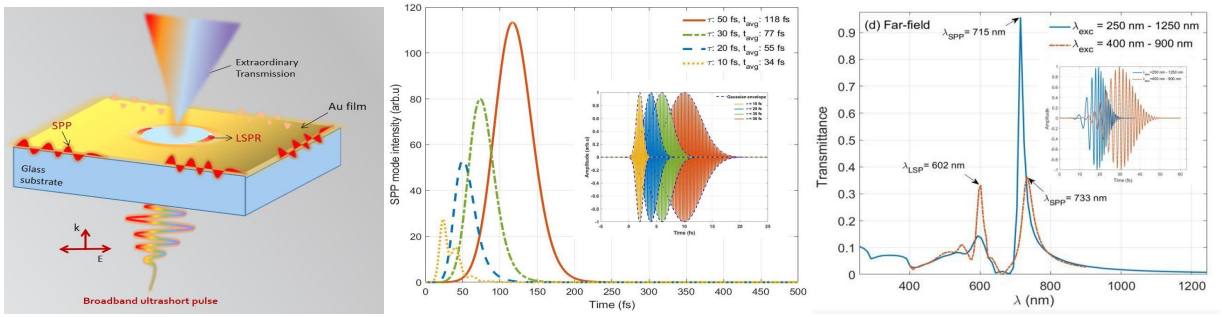

Figure 1: Left: Schematic representation of EOT device. Mid: Field-time profile of SPP for various pulse duration. Right: Extraordinary transmission spectra of Au hole array system for different spectral bandwidth of incident light.

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Strong light-matter coupling in SiGe quantum wells embedded in terahertz patch antenna cavities

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Optical antennas and optical cavities can convert the energy of free propagating radiation to localized energy (and vice versa) thus increasing the efficiency of light-matter interactions, as demonstrated by the enhancement of spontaneous emission (Purcell effect) or by the achievement of strong light matter interaction. In an optical cavity, the strong coupling of light with matter can be observed by measuring the spectral or spatial modifications of one of the photonic cavity modes resonant with an electronic transition that has an infrared-active dipole moment (and that occurs in the matter filling the cavity).
Typically, the strong coupling regime is achieved when the a-priori degeneracy between the energies of electronic and photonic modes is lifted, and two polariton states are created with hybrid light and matter character. Recently, intersubband transitions (ISBTs) in semiconductor quantum wells (QWs) have become an ideal model system for strong-coupling studies due to the relatively low value of the electromagnetic frequency in the mid-infrared and terahertz ranges where ISBTs are observed [1-3].
In this work, we realize a stack of 21 identical $Si_{1-x}Ge_x$ QWs grown by chemical vapor deposition on a Si wafer [4]. We then fabricate metal-semiconductor-plasmonic conductor cavities entirely filled with the parabolic QWs with the shape of a square patch antenna to increase radiative coupling to incoming electromagnetic beams. By means of FTIR spectroscopy we have first studied the ISBTs and antenna resonances, and then proceed to demonstrate the strong coupling regime on a silicon-based material platform, with the added advantage of high transparency up to ~12 THz due to the lack of polar optical phonons in group-IV materials.

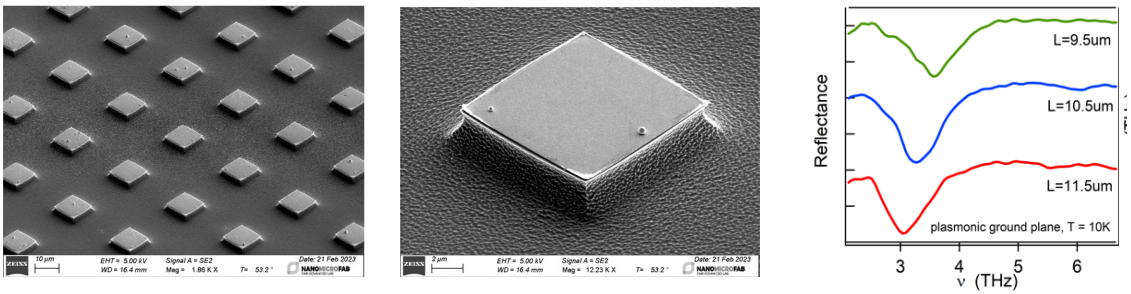

Figure 1: from left to right: Scanning electron microscope images of test cavities, obtained by subsequent steps of electron-beam lithography, Ti/Au evaporation and deep reactive ion etching, on a test Ge-on-Si epitaxial layer. The etching depth is 2.0 microns, the square patch size spans the 9 to 12 microns range. Measured extinction spectra of test THz cavity arrays by FTIR spectroscopy at normal incidence (array size 2x2 mm^2, undoped quantum wells, heavily doped N^{++} Ge ground plane

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Pulsed Photothermal Heterogeneous Catalysis

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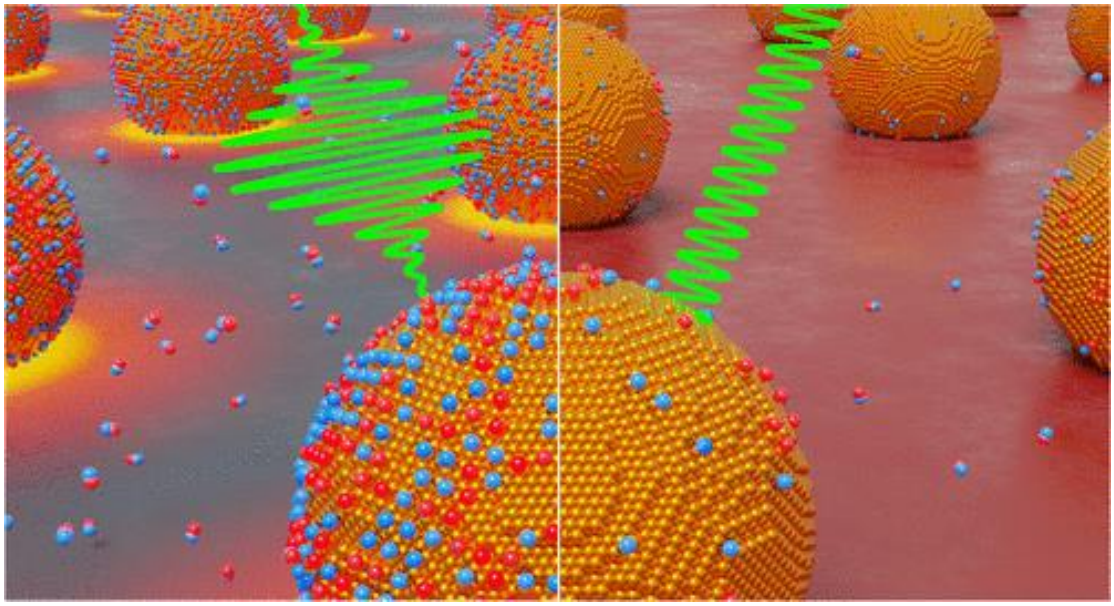
Anthropogenic climate change urgently calls for the greening and intensification of the chemical industry [1]. Most chemical reactors make use of catalysts to increase their conversion yields, but their operation at steady-state temperatures limits their rate, selectivity, and energy efficiency.

Here, we show how to break such a steady-state paradigm using ultrashort light pulses and photothermal nanoparticle arrays to modulate the temperature of catalytic sites at timescales typical of chemical processes [2].

Using heat dissipation and time-dependent microkinetic modeling for a number of catalytic landscapes, we numerically demonstrate that pulsed photothermal catalysis can result in a favorable, dynamic mode of operation with higher energy efficiency, higher catalyst activity than for any steady-state temperature, reactor operation at room temperature, resilience against catalyst poisons, and access to adsorbed reagent distributions that are normally out of reach.

Our work identifies the key experimental parameters controlling reaction rates in pulsed heterogeneous catalysis and provides specific recommendations to explore its potential in real experiments, paving the way to a more energy-efficient and process-intensive operation of catalytic reactors.



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Quantitative Ultrafast Electron-Temperature Dynamics in Photo-Excited Au Nanoparticles

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When localized surface plasmons (LSPs) are excited in metal nanoparticles (NPs), a non-thermal electron population is generated. This out-of-equilibrium gas is characterized by a broad energy distribution that thermalizes on a sub-picosecond time scale via electron–electron and electron–phonon collisions, giving rise to a high-temperature electron gas. The hot gas eventually releases its excess energy to the ion lattice through electron– phonon scattering on the picosecond (ps) time scale, and the lattice heat is then dissipated to the environment via phonon–phonon interactions within few hundred ps [1,2]. The measurement of the evolution of the electron gas temperature is fundamental for the comprehension of these dynamic processes that are at the basis of light-induced phenomena, like photocatalysis and solar energy conversion.

In this work we report the measurement of the ultrafast electron-temperature (ϑe) dynamics of plasmonic Au NPs [3]. Experiments were performed in pump-probe configuration by photo-exciting the NPs close to the LSP resonance and collecting ultrafast time-resolved photoemission spectra (tr-PES) at SPRINT Lab (CNR-IOM). ϑe is deduced by fitting spectra around the Fermi edge of Au NPs as a function of the time delay between pump and probe, providing a direct picture of the ultrafast electron dynamics (Figure 1). A fast evolution of the electronic temperature occurs within the first ps after excitation, with a peak at about 800 fs delay, followed by its gradual relaxation toward environment temperature. While the general trend is in agreement with the current understanding of ultrafast relaxation dynamics, the emerging of discrepancies with theoretical predictions underscore the key role of direct ultrafast measurement of ϑe in order to correctly evaluate the transient response of nanosystems. Our quantitative, model-free measurement of the electron-temperature dynamics represents a major advancement for significantly improving the future understanding of processes in nanosystems.

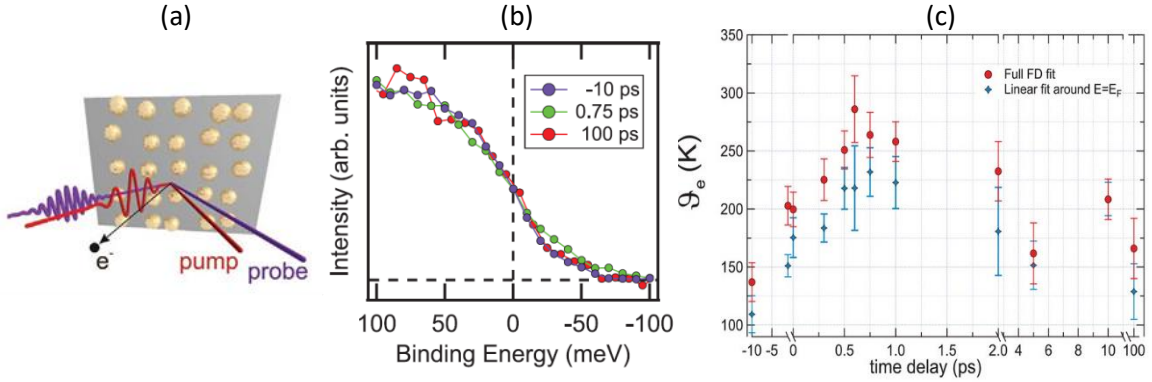

Figure 1: (a) Schematic diagram of the experimental Tr-PES setup. (b) Tr-PES spectra acquired in correspondence of three representative delay times. (c) Ultrafast electron-temperature (ϑ_e) as a function of delay time after pump excitation as obtained by Tr-PES spectra.

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Hybrid silicon-organic integrated terahertz detectors

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Abstract: Silicon-organic and plasmonic-organic hybrid integrated photonic circuits have recently shown unprecedented capabilities for the on-chip electro-optic (EO) detection of electromagnetic waves [1]. Only recently modern nonlinear (NL) polymers have been combined with hybrid photonic-plasmonic integrated circuits to obtain high-performance detection of terahertz (THz) waves [2], with effective operations to frequencies up to a few THz, far beyond commonly employed microwaves solutions [3]. In this work, we propose a novel design and fabrication process for THz detectors exploiting silicon slot waveguides [4], with the aim of overcoming the main limitation of these platforms, i.e. the high optical loss (about 0.5 dB/μm) affecting the near-infrared probe beam in the plasmonic interaction region, and extending their range of applications in terms of operation frequencies and on-chip functionalities.

Device operation: The device features a gold bow-tie antenna structure deposited across a silicon strip waveguide (see Fig. 1a), which the optical probe beam travels through. As such, the waveguide hosts the nonlinear interaction between THz and probe electric fields. Here, we propose two alternative configurations for its realization: a plasmonic and a slot design (see Fig. 1b and c), compared in terms of enhancement of the incident THz field and transmission T for the optical probe through the interaction region (see Fig. 1d and e respectively). The intensity response of the detector to the THz field is linear, as described by the EO operator $\hat{S}_{eo}(t)$ [2], while that of the optical signal after the interaction region is computed as $I_{out} = I_{in}e^{-\alpha l_{gap}} = I_{in} * T$ (with l_{gap} = length of the interaction region), analyzed estimating the transmission T. Since both quantities should be maximized to optimize the response of the device, a representative figure of merit (FOM) to compare the two configurations is given by their product, i.e., $FOM = \max(\hat{E}_{THz}) * T$, depicted in Fig. 1f for different separations between the antenna pads. The enhanced FOM for the slot configuration is promising for devices that exploit complex on-chip detection schemes beyond the single field detector, where the total loss of the architecture as a whole is relevant.

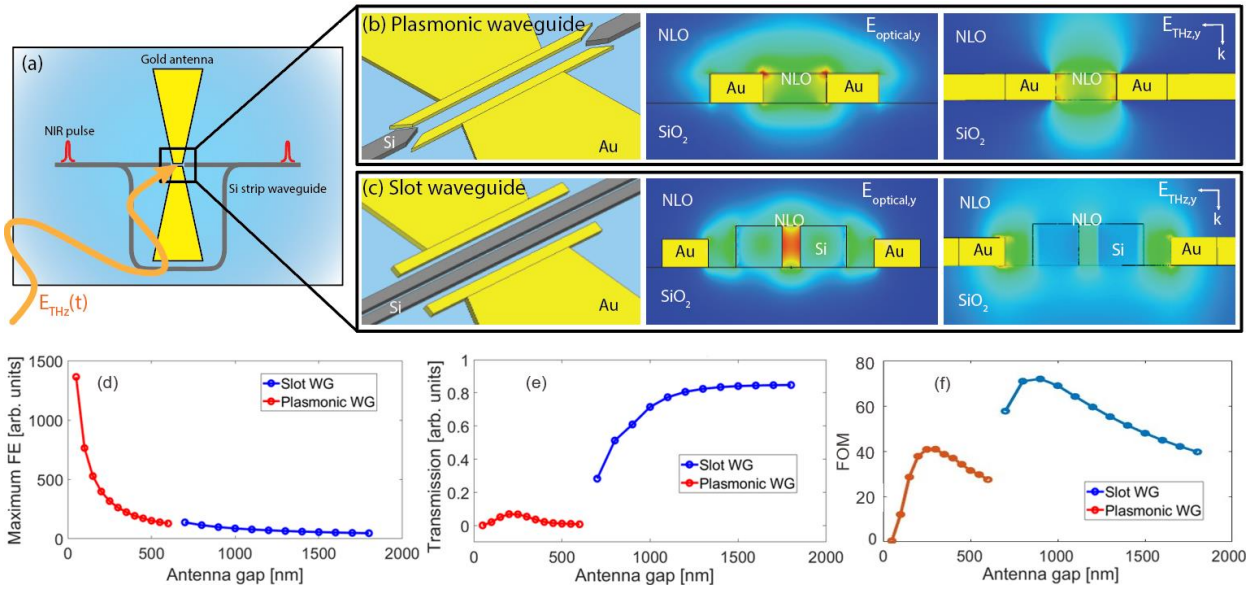

Figure 1: a) Schematic of the integrated THz detector. b-c) Zoom box for the plasmonic and slot interaction region respectively with schematic, excited fundamental mode and produced field enhancement. d-e-f) Comparison in terms of THz field enhancement, Transmission of the NIR pulse and FOM respectively.

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Nanofabrication and linear optical characterization of dielectric chiral metasurfaces

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Chirality refers to the geometrical property of a structure consisting in the absence of any mirror symmetry plane [1]. Chiral geometries can induce optical effects such as optical rotation (OR) or circular dichroism (CD), which consist in the differential absorption of left-handed and right-handed circularly polarized (LCP and RCP) light [2]. In this context, optical chiral metamaterials have recently attracted considerable attention; in fact, through specific design the chiroptical response of chiral metamaterials can be several orders of magnitude higher than that of natural chiral materials [3], offering new and exciting opportunities for fundamental research and practical applications such as, e.g., chiral bio-detectors [4], and polarization conversion [5]. In this work we report the fabrication steps of a chiral silicon metasurface embedded in silica supporting symmetry-protected bound states in the continuum (BICs). By breaking the symmetry of the system, a quasi-BIC mode with a very high Q-factor (10^5) is designed [6]. The chiral geometry enables selective excitation of the high-Q mode and high non-linear CD in third-harmonic generation (up to 99.9%). The metasurfaces are fabricated on a silicon-on-insulator (SOI) with a device layer of 220 nm and SiO2 box of 1 um over an area of 25x25 µm^2 by a combination of electron-beam lithography and reactive ion etching. They consist of a periodic square array of two asymmetric Si cuboids with equal height (H) of 220 nm, equal width (W) of 337 nm, length (L) of 550nm, asymmetry parameter $\alpha = \Delta L/L = 0.33$, and pitch (P) of 850 nm along both axes (Figure 1). Modelling the nanofabrication uncertainties on the gaps of the chiral metasurface [7], the imperfections of the etchings process, or the modification of the asymmetry factor, we found that the proper engineering of the gap between the nanostructures of the unit cell is the most important parameter to achieve a high-quality factor and enhanced optical dichroism.

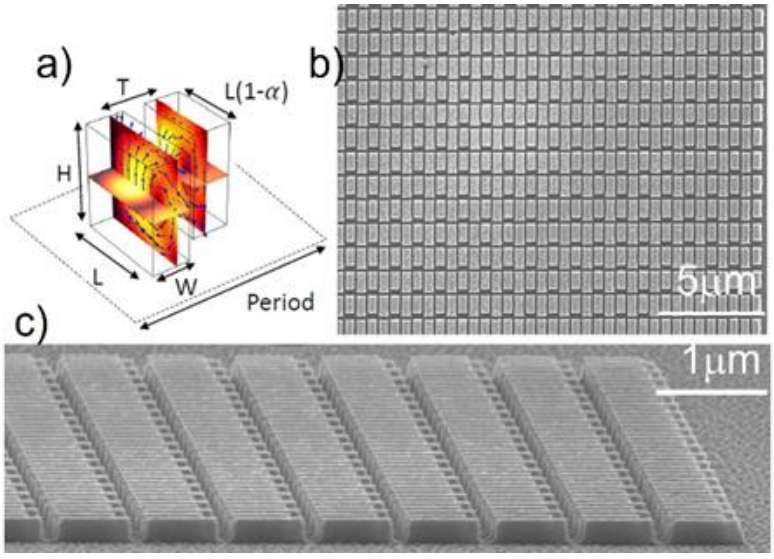

Figure 1: a) Layout of the single cell of the array consisting in two asymmetric cuboids. b) Top view of the metasurface by scanning electron microscopy (SEM) characterization c) Tilted SEM close-up of the metasurface

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High Q-factor Fano resonances in diamond nanopillars

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Abstract: Metasurfaces, consisting of nanoresonators known as meta-atoms, have shown great potential in replacing bulky optical components with ultrathin, integrable, and high-performance devices [1]. Diamond, with its unique electronic properties and high refractive index, is an ideal material for photonic applications [2-3]. In this work, we report on the optical behavior of diamond nanopillars on a glass substrate and demonstrate the excitation of Fano-like resonances with a Q-factor as high as 3.5 × 10^5, among the highest reported for dielectric metasurfaces [4]. We investigate the dependence of the resonance on geometrical and environmental parameters and show that diamond metasurfaces can be used as a refractive index sensor with sensitivity up to 72.21 nm per refractive index unit (RIU) and linearity over a wide range of refractive indexes. Our findings demonstrate that diamond-based metasurfaces are a valuable nanophotonic platform for controlling light propagation at the nanoscale, enabling both linear and nonlinear effects.

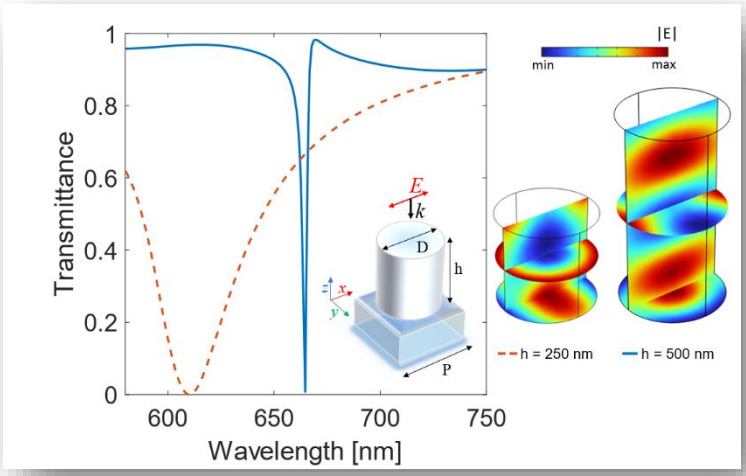

Figure 1: Diamon nanopillars on glass substrate that support very sharp resonances when illuminated by a plane wave electromagnetic radiation. The Q-factor is dramatically enhanced when specific geometric conditions are satisfied.

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Tuning the Aggregation of Gold Nanoparticles prepared by Laser Ablation with Halide Salt

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Abstract

Gold nanoparticles (NPs) have been largely studied due to their surface plasmon resonance properties that are strongly dependent on size, shape and coupling effects between NPs as well as their dispersive medium [1,2]. Thanks to their unique optical properties, gold NPs and their aggregates are applied in different fields like medicine [3], energy [1] and sensing [4].

Here, we studied the surface plasmon resonance properties of strongly coupled gold NPs obtained by "in water" laser ablation and aggregated by adding potassium bromide.

Unlike other classical chemical synthesis methods of nanoparticles, laser ablation in liquids provides a unique way to obtain surface-clean and ligand-free nanoparticles, ready to be used [5].

The aggregation of gold NPs was analysed under different experimental conditions such as salt concentration, temperature and laser irradiation.

The extinction spectra (figure 1a) show two peaks which red-shifted by increasing salt concentration. Supported by Finite-Difference-Time-Domain simulations we can hypothesize the formation of small nanoparticle chains which became longer by increasing potassium bromide concentration as also demonstrated by electron microscope data. Figure 1b shows the effect of temperature on the aggregation process which seems to be suppressed at higher temperatures.

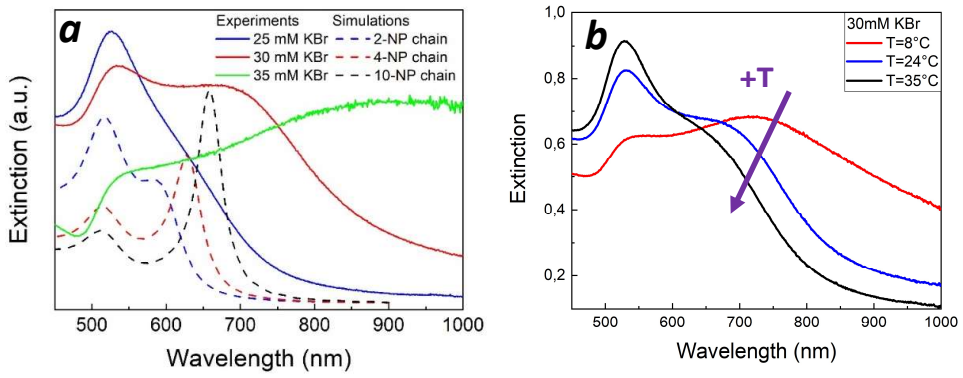

Figure 1: a) Comparisons between experimental and simulated extinction spectra of gold aggregates. b) Extinction spectra of gold aggregates at different temperature in 30mM of potassium bromide.

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VO_2 Perfect Absorber by means of W doping

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Abstract: We performed infrared optical characterization of W-doped VO_2 films with increasing W doping percentage, deposited on sapphire substrates using PLD. This resulted in a temperature-tunable VO_2 perfect absorber, with a reflectance of 0.02% at room temperature.

Vanadium dioxide is a type of phase change material that is known for its fast structural phase transition from monoclinic to tetragonal, resulting in a significant change in resistivity. VO_2 has attracted major attention due to its low transition temperature of 68°C and the ability to modify its properties by adjusting various parameters such as temperature, strain, pressure, doping, and electromagnetic or electrostatic fields. This has led to the development of many applications, such as smart window coatings, perfect infrared absorbers, and thermal emitter modulators [1-3].

Various methods have been proposed to reduce the phase transition temperature of VO_2 to approach room temperature, including introducing stress variations within the lattice structure or doping [4-5]. This study aims to investigate the optical characteristics of several W-doped VO2 samples using Pulsed Laser Deposition on a sapphire substrate.

The films were deposited at 550°C and 1 $\times 10^{-2}$ mbar oxygen pressure, with a thickness of 480 nm. The optical characterization was carried out in the infrared range using Fourier-transform infrared spectroscopy in reflection mode with an incidence angle of 15° and linear s-polarization. The samples were heated to 100°C, and several spectra were collected at different temperatures during the cooling process to room temperature showing that the transition temperature dropped as the doping concentration of W increased and a small percentage of 0.75% was sufficient to achieve a minimum reflectance signal of about 0.02% at the wavelength of ~12 µm at room temperature.

The study demonstrates that the critical temperature of VO_2 can be easily tuned by a small percentage of W doping. The use of the PLD deposition method also allowed for the realization of a perfect absorber at 12 µm at room temperature. This development marks a significant step forward in the practical application of VO_2 for IR device applications, as confirmed by the Thermal-Optical FT-IR

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Silver Nanoflower as a single plasmonic catalytic reactor for in Situ Photocatalysis

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In this work, we successfully synthesized silver nanoflower (AgNFs) via a facile wet chemical method and studied plasmon stimulated catalysis of a probe molecule attached to their surfaces[2]. We followed the reaction OF 4-Nitrothiobenzene to 4,4'dimetilmarcaptoazobenzene[1]. To obtain high catalytic properties, we deposed single AgNFs by drop-casting a diluted colloidal dispersion of each nanoparticle on a silicon wafer. The reaction processes were monitored and identified through in situ surface-enhanced Raman spectroscopy based on the confocal Raman microscope system. Moreover, to asset if the reaction is strictly related to the excitation wavelength and to the hot electrons production, tougher than thermal effects, we excited the system with three different wavelength , 532 nm, 633 nm , 785 nm. This study provides a simple and fast method to improve the catalytic property of the noble nanoparticles.

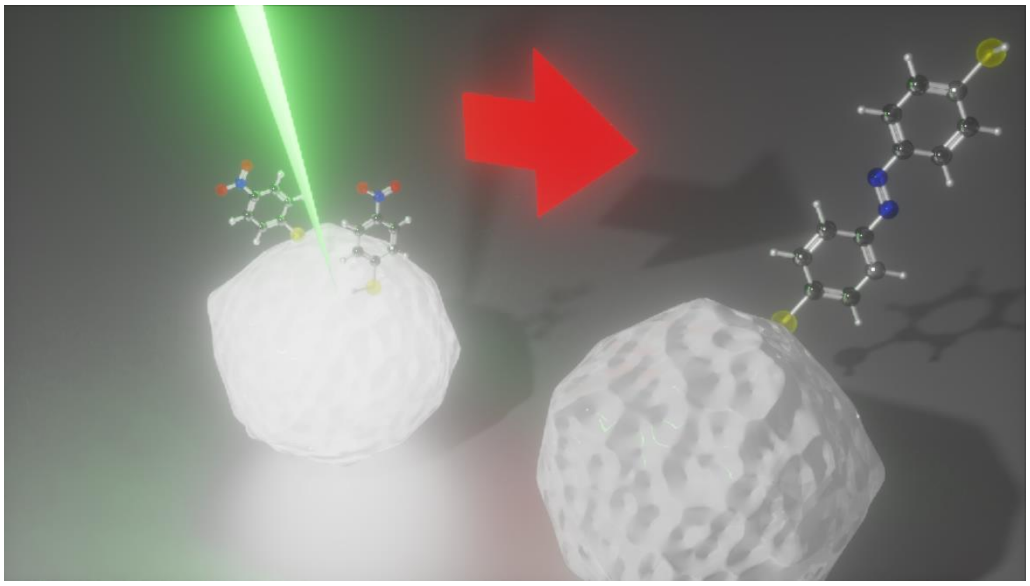

Figure 1: Graphical representation of the plasmon stimulated catalytic process.

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A Wearable Surface-Enhanced Raman Scattering Patch for Sweat Monitoring

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Abstract: In the recent decades, wearable sensors have been the subject of a major technological efforts that turned them into advanced biosensing platforms or *lab-on-chip* for continuous monitoring of multiple health parameters. Devices originally developed to track biomedical parameters (i.e., glucose concentration in blood of diabetic patients) or physical exercise activity (i.e., heart rate, burned calories, steps count) now allow real-time sensing of physiological information about metabolism and health of individuals. Compared to other biofluids (blood, interstitial fluid, tear, saliva and urine) sweat contains a broad variety of biomarkers (electrolytes, proteins, metabolites, etc.) and can be non-invasively sampled by placing a sensor patch on the skin [1].

Plasmon-enhanced vibrational spectroscopies, such as Surface-Enhanced Raman Scattering (SERS), due to the local amplification of the electromagnetic field in proximity of noble metal nanoparticles, allow the label-free detection and characterization of analytes at sub-micromolar concentration [2]. Recent advancement in flexible and biocompatible SERS-active substrates production, together to a broad availability of commercial handheld Raman spectrometers, paved the way for the development of non-invasive platforms for healthcare based on SERS sweat spectra monitoring [3, 4].

Here we describe the development of a wearable SERS patch for sweat biomarkers monitoring. The plasmonic core of the chip, obtained by depositing silver nanowires on a flexible PTFE porous membrane [3, 4], was integrated with biocompatible protective and adhesive layers and tested with a simulated sweating systems designed to mimics the sweat secretion by the skin. Once the initial characterization with artificial sweat was done, the biocompatible SERS patch was applied on volunteer's harm for real sweat sampling during physical exercise activity.

The results demonstrate that our SERS patch allows to direct and label-free detect urea and lactate at physiological concentration in combination with the evaluation of the sweat pH in the range between 4 and 9.

Funding: This research was produced with the co-funding European Union – Next Generation EU, in the context of The National Recovery and Resilience Plan, Investment Partenariato Esteso PE8 "Conseguenze e sfide dell'invecchiamento", Project Age-It (Ageing Well in an Ageing Society) and of EU project ECS00000017 'Ecosistema dell'Innovazione' Tuscany Health Ecosystem (THE, PNRR, Spoke 4: Nanotechnologies for diagnosis and therapy).

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Probing Non-resonant Coupling in Exciton-Plasmon Hybrids Using Magnetic Circular Dichroism (MCD) Spectroscopy

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Keyword- Magnetoplasmonics, Plasmonitronics, Spintronics, Exciton-Plasmon Hybrid

Exciton-plasmon hybrids have emerged as promising systems for a wide range of applications in optoelectronics, sensing, and energy harvesting due to their unique optical properties. In these systems, the strong energy space coupling between excitons and surface plasmons leads to the formation of hybrid states that exhibit new optical phenomena. Recently it is discovered that the strong energetic coupling is not necessary for forming exciton-plasmon hybridization, and in semiconducting plasmonic materials like metal oxides (In_2O_3, TiO_2) or metal chalcogenides (Cu_xSe), where both exciton and plasmonic absorptions coexist far apart in energy, this exciton-plasmon coupling can be achieved under the application of a strong magnetic field.[1 2] While the discovery effectively opens up the field of plasmonitronics, where the magnetoplasmonic modes can be used as a new degree of freedom in photonic, optoelectronic and quantum-information processing devices, till now it is limited within a single interface-free material, and no evidence of non-resonant exciton-plasmon coupling is found across different materials. In this study, we present a comprehensive investigation of the cross-platform non-resonant coupling between excitons and surface plasmons in hybrid systems, namely, colloidal In^{3+} doped CdO-$CsPbBr_3$ [3] and Cu_xS-$CsPbBr_3$ heterostructures using MCD spectroscopy. MCD is a powerful tool for probing the electronic and magnetic properties of materials and has been widely used to study exciton and plasmon properties in various systems. Here the surface plasmons in In^{3+} doped CdO and Cu_xS influence the band edge Zeeman splitting of $CsPbBr_3$ as shown in figure 1(a). It is observed that the nature of the plasmon resonance (i.e., electron or hole oscillation) plays a crucial role in determining the MCD signal, and the exciton band edge MCD amplitude is significantly reduced in the heterostructures (figure 1(a)). These modifications can be tuned by rendering more control via easy exciton band gap tunability and modulation of plasmon resonance which can lead to next generation plasmonitronic materials.

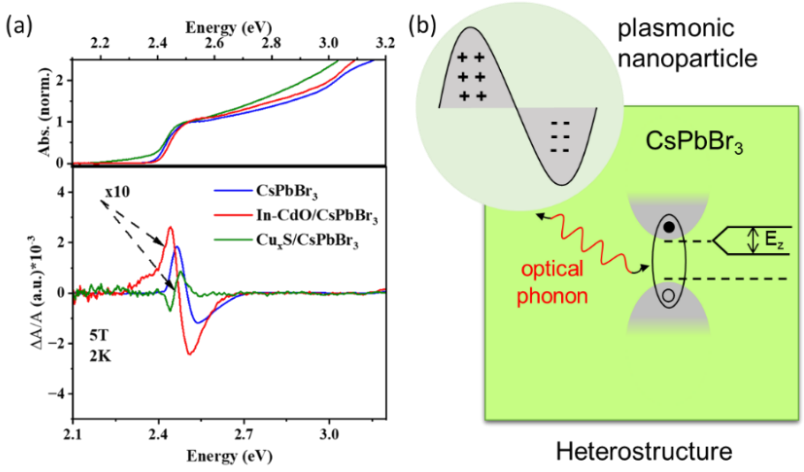

Figure 1: (a) MCD spectra comparison of $CsPbBr_3$, In-CdO/ $CsPbBr_3$ and Cu_xS/ $CsPbBr_3$ heterostructures obtained at 5T and 2K showing reduced amplitude and reversed sign in the heterostructure as compared to parent perovskit (b) schematic representing magnetic plasmonic modes influencing band edge Zeeman energy of $CsPbBr_3$

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Fe_3O_4@Au core satellite magnetic nanoparticles to enhance colorimetric immunosensor response

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Over the past two decades, gold-decorated magnetic nanoparticles (Fe_3O_4@Au) have been widely studied for their potential applications in biosensing due to their unique properties[1]. Localized surface plasmon resonance (LSPR) of gold nanoparticles and magnetic properties of the core (Fe_3O_4) have been utilized to develop a variety of biosensing platforms with high sensitivity and specificity[1,2].
Fe_3O_4@Au nanoparticles can be synthesized by various methods, such as seed-mediated growth, electrostatic self-assembly, and co-precipitation. Among them, the seed-mediated growth method is a widely used approach due to its high yield and reproducibility. In this method, gold nanoparticles are first synthesized by reducing gold ions in the presence of a stabilizer, and then they are attached onto the surface of Fe_3O_4 nanoparticles by using a reducing agent. The size, shape, and distribution of the gold nanoparticles can be tuned by adjusting the reaction conditions, such as the ratio of gold to iron precursor, the reducing agent, and the reaction time. Fe_3O_4@Au nanoparticles can be used for magnetic separation and concentration of analytes. Due to the magnetic properties of the Fe_3O_4 core, the nanoparticles can be easily manipulated by an external magnetic field, allowing for the separation and purification of analytes from complex matrices, such as blood or urine[1,3].
In this scenario, we were able to coat clustered magnetic nanoparticles (250 nm linear size) with gold nanoparticles (20 nm diameter) so to have Fe_3O_4@Au nanoparticles with magnetic core and gold surface[4], which we used for LSPR, but also to immobilize antibodies (anti-human IgG) with a photochemical technique[5] setup in our group (PIT, photochemical immobilization technique). Fe_3O_4@Au nanoparticles were used in a sandwich scheme to enhance the response of a nanostructured gold surface[6], the latter realized with high density of gold nanoparticles (30 nm diameter, 300 ± 20 AuNPs per μm^2). Gold nanoparticles were randomly placed onto a glass coverslip via an electrostatic self-assembly technique, and subsequently functionalized by PIT with anti-human antibodies to detect human IgG. The change of the absorption spectrum of the nanostructure – resulting from the detection of the target (human IgG) – was enhanced by Fe_3O_4@Au nanoparticles that bound the target from the top (sandwich) in presence of a magnetic field, which we used to overcome the passive diffusion. Thanks to this scheme, preliminary results obtained with human IgG in water demonstrated that a limit of detection of 1 ng/mL can be achieved with a measurement carried out in only 10 minutes, thereby paving the way to applications in rapid tests for mass screening.

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AgNFs as single-particle, multi-wavelength SERS active platforms

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Surface Enhanced Raman Spectroscopy (SERS) has been successfully employed in several fields of interest such as biosensing, in-situ catalysis studies, and archeology. Usually, the greatest contribution to the Raman enhancement is explained by an electromagnetic mechanism [1]. To amplifying the SERS effect, the research studies report the production of nanostructures that allow the creation of hot-spots on the surface [2]. Furthermore, the possibility of amplifying Raman signals is linked to the excitation wavelength of the laser used [3]. In this work, we present a SERS active substrate with a high enhancement in a wide range of excitation wavelengths. We propose Silver Nanoflowers (AgNFs), metal microparticles with a nanorough surface that creates a pattern of petals. Thanks to their dimension is possible, by using a Micro-Raman spectrometer, to quickly find a single microparticle and study the signal enhancement of an analyte adsorbed onto its surface. The SERS properties at a single-particle level were studied using a standard molecule 4-mercaptobenzoic acid (4-MBA). Because of the AgNFs extinction spectra cover the entire visible range, we were able to study the enhancement for the single AgNF with 532, 633, and 785 nm laser wavelengths (Fig.1), finding a maximum enhancement factor in the order of 10^8- 10^9, due to several number of hot-spots on the tips and between the petals. This suggests that the AgNF could be an excellent SERS substrate on the entire visible and near infrared spectral region and demonstrates that such nanomaterial can be easily used to study analytes at low concentrations with any exciting wavelength, opening the possibility to study several biological and medical interest analytes without the interference of not desired optical phenomena such as luminescence.

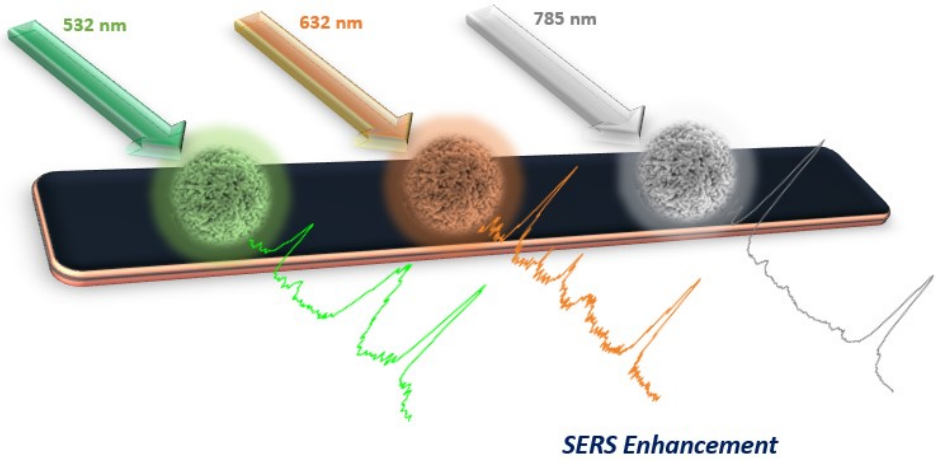

Figure 1: Representative scheme of the SERS study conducted on single AgNFs with different excitation wavelengths.

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Quantitative aggregation dynamics of responsive plasmonic colloids by real-time light transmission spectroscopy

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In the last decades, optical transmission spectroscopy has emerged as a candidate technique for the study of colloidal systems in terms of particle size, shape, concentration, and aggregation level, since the optical extinction spectrum, beside the absorption properties, contains quantitative information about the light scattering processes [1].

The behavior of colloidal suspensions is dictated by the interplay of a variety of short- and long-range forces and can be controlled by functionalizing the particles surface with suitable stimuli-responsive ligands [2]. The active control of the self-assembly is of interest for many types of colloidal systems. Among these, plasmonic noble metal nanocolloids exhibit aggregation dependent optical properties and visible near field enhancement capability [3]. These features are of great interest in a wide variety of applications, from biosensing application to the development of responsive nanobiomaterials. Indeed, the remarkable optical properties of plasmonic nanocolloids make them an ideal testbench for developing novel spectroscopy-based investigation approaches.

Here, we will discuss the development of a real-time optical transmission spectroscopy setup, suitable for time-resolved measurements in the millisecond time scale, to study the temporal evolution of colloidal systems in presence of external stimuli (see *e.g.* Figure 1). We will present the application of the proposed experimental design to the study of the stimuli-triggered aggregation dynamics of plasmonic nanoparticles. These results are a solid preliminary step to the investigation and, ultimately, the design of active biocompatible plasmonic nanomaterials.

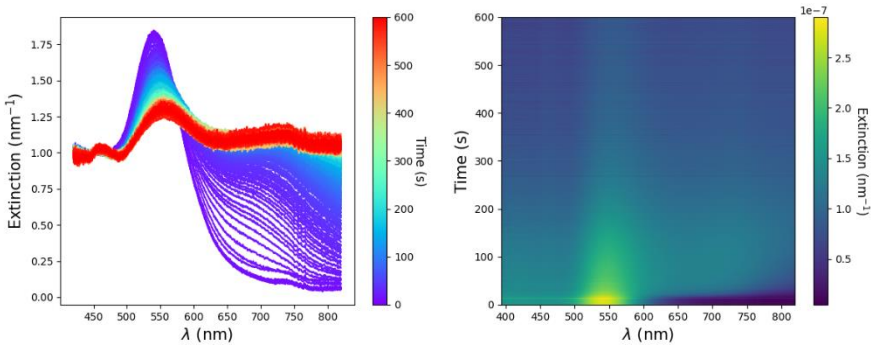

Figure 1: Evolution of the optical extinction spectra of citrate-capped 60 nm gold nanoparticles when the colloid pH is abruptly brought from pH 6.5 to pH 2 through HCl addition at t = 10s. Left: spectra normalized to the extinction at 450 nm. Right: color map of the data, showing the rapid evolution of the extinction spectral shape.

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Nanohybrid platforms for strong light-matter interaction

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Many systems and processes in nature and technology are driven by light-matter interaction. For instance, the energy exchange between electromagnetic radiation and a quantum emitter is at the root of several relevant applications and devices, spanning from sensing and photocatalysis, to optoelectronics and quantum information [1]. In particular, the interplay between the electromagnetic field and the quantum states of matter can be controlled and engineered to obtain an exchange rate of energy faster than any other competing relaxation process. The system enters in the so-called "strong-coupling" regime, and new hybrid light/matter states, i.e. polaritons, are formed [2,3], which, in turn, offer huge potential for a wide class of technological applications, including quantum computing, non-linear photonics and polariton chemistry [4,5].

Among the various metamaterials and metasurfaces, plasmonic arrays of subwavelength holes milled through metallic films revealed promising platforms to be combined with quantum emitters in order to achieve strong coupling. Indeed, they combine the required field confinement along with an open architecture, which facilitates both the placement of the material and the excitation and probing of polaritons [6-8]. In addition, the optical properties of the 2D nanohole arrays can be properly tuned by playing with their symmetry and geometry.

Here, we investigate the optical properties of periodic arrays of nanoholes milled in metallic films combined with quantum emitters. Steady-state transmittance spectroscopy is exploited to investigate the radiative properties of the hybrid heterostructures and to assess the presence of the anti-crossing behavior, as one of the distinctive fingerprint of strong-coupling regime. Particular attention is devoted to the roles played by the plasmonic array symmetry on the interaction strength with the quantum emitter. A quantitative evaluation in terms of Rabi splitting energy obtained with the various configurations is presented. This work is stimulating toward further studies on the symmetry-dependent properties of plasmonic arrays of nanoholes and can set the base for investigations on the design and fabrication of novel nanohybrid architectures featuring strong light-matter interaction, and their exploitation towards functional devices.

Acknowledgement

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

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In the last twenty years, there has been a large interest for macroscopic quantum electrodynamics in the presence of metal and dielectric structures motivated by the prospect of using plasmonic and photonic devices for quantum optics and quantum technology applications. In this work, we propose an “operative" full wave approach to evaluate the macroscopic electromagnetic response of a dispersive dielectric of finite size in unbounded space that does not involve a complete diagonalization of the Hamiltonian. We use the Heisenberg picture to describe the time evolution of the observables of the matter and of the electromagnetic field. We keep the matter and the electromagnetic field distinct. We use a Hopfield type model to describe the matter and the coupling with the electromagnetic field. We expand the matter field observables through the electroquasistatic (longitudinal) modes [1] and the magnetoquasistatic (transverse) modes [2] of the object. These modes are size-independent, and do not depend on the material. They are the natural modes of the polarization field in the small size limit. We apply the Coulomb gauge, and we use the transverse plane waves to represent the radiation field observables. The separation between matter and electromagnetic field allows us to include on an equal footing both electromagnetic field and matter fluctuations in a self-consistent QED Hamiltonian. The expansion of the matter field observables in terms of the static longitudinal and transverse modes of the object allows to diagonalize the Coulomb and Ampere interaction energy terms of the Hamiltonian. Using this approach, we obtain a general expression for the time evolution of the polarization density field observable as functions of the initial conditions of the matter field observables and of the electromagnetic field observables. It is a linear integral operator whose kernel is a linear expression of the impulse responses of the dielectric object that we obtain within the framework of classical electrodynamics [3]. The electric field observable is expressed in terms of the polarization density field observable by means of the dyadic Green’s function for the free space. The statistical functions of these observables are integral operators of the statistics of the initial conditions of the matter field observables and of the electromagnetic field observables. The kernels are linear or multilinear expressions of the impulse responses of the dielectric object. The use of the static modes significantly reduces the computational burden for the evaluation of the impulse responses of dielectric objects with small sizes.

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Antenna architecture based on plasmonic nanocone in a point contact-insulator-metal high frequency rectification system

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High frequency rectification with the aim of solar energy harvesting can be traced back to 1971, when R.L. Bailey [1] proposed an alternative to standard photovoltaic technology able to convert solar energy to electric power. A rectifying antenna or rectenna, is a device composed by a receiving antenna connected to a rectifying diode, in which the electromagnetic radiation received by the antenna is converted into a DC signal by the diode. To adapt this technology, successfully employed in microwave rectification [2], to optical frequencies (PHz) a nano-antenna and ultra-high-speed diode are needed. While there are a lot of options regarding nano-antennas, few diodes can operate at high frequencies. For this purpose, the solution mostly employed is the Metal Insulator Metal (MIM) diode that, owing to the tunnelling process associated to the electrons going through the thin insulator, can in principle respond at the time scale of femtoseconds, namely at high frequency radiation. In the past decades a lot of efforts were made to achieve efficient optical rectennas. Among all, a boost in efficiency was achieved by merging the antenna and diode components into a single architecture and exploiting geometrical and material asymmetries [3-4]. Following this path, we introduce a rectenna architecture based on a patch antenna, a three-layer metal-insulator-metal system (Au-SiO_2-Au), modified by a gold plasmonic nanocone and two additional thin layers (Ti and TiO_2) (Figure 1). In this system the patch antenna will serve as receiving antenna and as support for the plasmonic nanocone that, with the addition of the two thin layers, will complete a point contact-insulator-metal rectification system. When excited with a linearly polarized plane wave, we expect our system to convert the receiving radiation into TM modes within the insulating layer of the patch antenna. Under this condition, the metallic conical structure inserted in the insulating layer responds by forming a TM_0 mode (also known as radial mode). This kind of mode can realize adiabatic compression, leading to a strong Surface Plasmon Polaritons (SPPs) concentration at the apex of the cone. Finally, this large SPPs concentration can be associated to an abundant presence of hot-electrons available for tunnelling through the thin insulating layer, namely photocurrent. Given the aforementioned scenario, here we have been focusing on the geometrical design of the architecture, especially on electromagnetic simulations through which we aim at maximizing the SPPs presence at the cone apex. This is indeed the first step on which the correct functioning of our rectenna architecture is based.

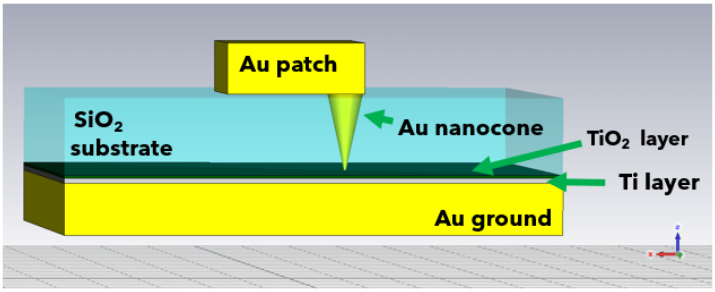

Figure 1: Illustration of the patch antenna modified by inserting a plasmonic nanocone in the SiO_2 substrate and by the Ti and TiO_2 layers placed at the interface between the SiO_2 substrate and the ground.

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Plasmon-enhanced Magneto-optical detection of sub-monolayers of Single Molecule Magnets up to room temperature

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Plasmonic nanoantennas enable sub-wavelength electromagnetic field confinement, allowing the identification of trace amounts of molecular compounds in plasmon-enhanced spectroscopies.[1] Despite extensive works have been reported on optical properties of molecular-plasmonic hybrid systems, there are very few studies on the plasmonic enhancement of the magneto-optical response of molecules.[2]

Here we design nanoarchitectures composed of molecular magnets deposited on gold nanodisk antennas through an established thermal sublimation method. In a preliminary work, we demonstrated a significantly boosted magneto-optical detection of a thin film of a terbium(III) bis-phthalocianinato (TbPc2) single-molecule magnet. We tracked down the origin of this enhancement to nanoantenna effects at the optical level, reporting a 5-fold amplification of the magneto-optical response of a few nanometers layer of TbPc2 molecules at 1.5 K.[3]

In this work, we tune the plasmonic resonance frequency of the nanodisks, and study its effect on the magneto-optical response of the hybrid TbPc2@Disk nanostructures. The spectral detuning between the two resonances was optimized, allowing to detect sub-monolayers of TbPc2 up to room temperature. Remarkably, the same quantity of TbPc2 deposited on glass does not provide any magneto-optical signal at room temperature, while such a thin layer of TbPc2 can be clearly detected through magneto-optics in the hybrid TbPc2@Disks system.

Our results can enable strong magneto-optics enhancement in single molecule magnet thin films, giving access to routine investigations in the sub-monolayer regime, which is currently challenging even for the cutting-edge synchrotron-based X-ray magnetic spectroscopy methods. This could give a tremendous boost to the design and fabrication of readout-enabled molecule-based magnetic devices.

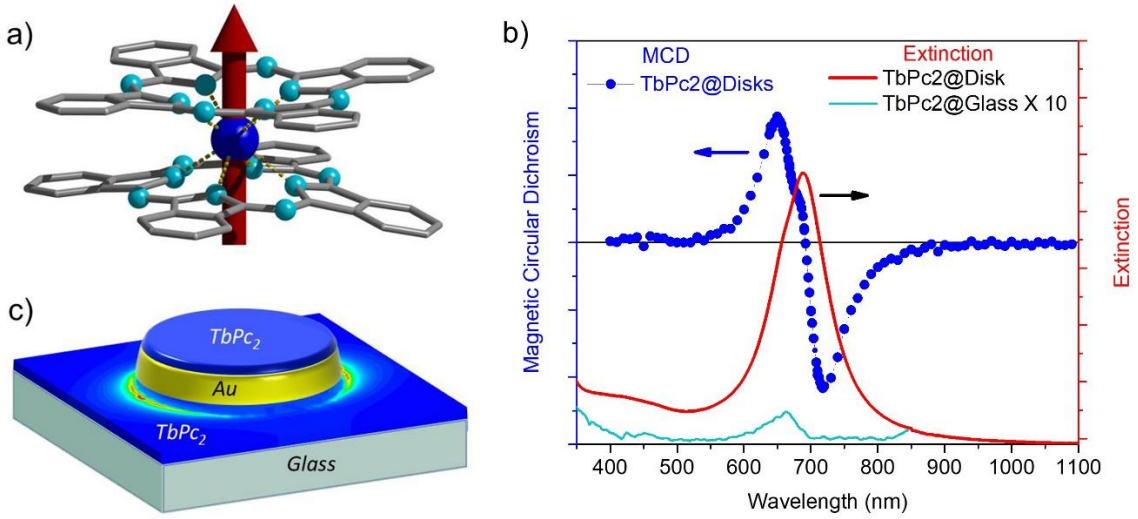

Figure 1: (a) TbPc2 molecule; b) optical (red) and magneto-optical (blue) response of the TbPc2@disk hybrid nanostructure, and optical extinction spectra of the same quantity of TbPc2 deposited on glass.

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SiGe dewetted Mie Resonators

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Solid state dewetting has been investigated in the last 50 years, being thin film stability a very relevant issue for polymers, metals, and semiconductors [1]. In analogy with liquid films breaking into tiny droplets, soft matter and solid films are unstable and break into islands when annealed at temperatures well below their melting point. The thermally activated surface adatom diffusion together with the intrinsic defectivity of the thin layer leads to local thinning of the layer, bringing its top surface in contact with the substrate. At this point, around these heterogeneously distributed holes, a rim forms and starts receding with a speed proportional to the Laplacian of the surface curvature [2]. While the rim moves, the underlying Rayleigh-like instability emerges, leading to the formation of fingers that eventually break into islands [3]. When practical applications are concerned, a templated dewetting approach is the key to tune size and density of the islands, overcoming the randomness of a phenomenon that is intrinsically stochastic: ordered arrays of individual islands can be obtained in SiGe alloys by patterning the thin layer before annealing by electron beam lithography and reactive ion etching [4,5]. Here we show that templated SiGe dewetting produces monocrystalline, sub-micrometric particles featuring strong light scattering supported by Mie resonances. Although the scattering properties of these systems have been qualitatively investigated, a precise study on the impact given by the effective complex morphology of a dewetted nanoparticle to the Mie scattering properties is still missing. In this work, by using morphological characterization, phase field and light scattering simulations, we provide a realistic modelof the single scatterer optical properties. Dark-field scanning hyperspectral imaging experiments are then performed allowing to map in real space the distribution of multipolar modes and to reconstruct the scattering pattern also at angles wider than the numerical aperture of conventional microscope objective lenses. We find an excellent agreement between the experimental and theoretical scattering cross-sections.

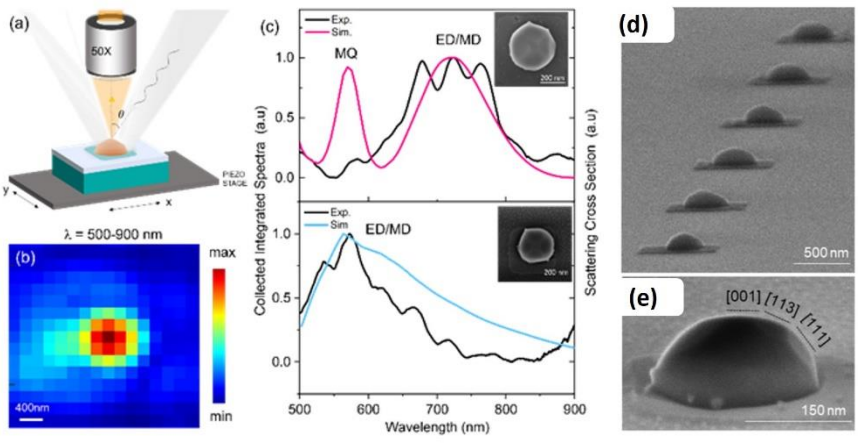

Figure 1: a) Sketch of the Dark-field scanning setup. b) Hyperspectral map of an island with R ≈ 190 nm filtered around the wavelength range 500-900 nm. c) Comparison between the collected integrated spectra and the simulated scattering cross section for island of R ≈ 190. d) SEM image of islands acquired with a tilt angle of 45 degrees with respect the sample normal to highlight the faceting of each scatterer. (e) SEM image of of a single island, where the faceting planes {001}, {113} and {111} are labeled (upper panel) and R ≈ 80nm (lower panel).

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Large-scale Van der Waals heterostructures for photon harvesting

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Two-dimensional (2D) Transition Metal Dichalcogenide semiconductor (TMDs) layers have recently attracted diffuse interest owing to their exceptional optoelectronic properties, simply tunable by tailoring the number of layers and/or by assembling van der Waals (vdW) heterostructures [1,2]. Interestingly, vdW heterostacks based on MoS_2 and WS_2 layers gives rise to a type II heterojunction that promotes carrier separation across the junction with impact in photonics and energy conversion applications. However, the inherent low photon absorption in the atomic layers demands for novel photon harvesting schemes able to achieve effective light coupling to the few-layer semiconductor. Flat-optics media supporting Lattice Resonances offer a promising opportunity in this respect, promoting strong in-plane light scattering and confinement [3]. In parallel, there is an urgent request to scale-up the lateral size of the 2D layers controlling their stacking in a deterministic way.

Here we demonstrate a novel approach for the maskless growth of large area (cm^2 scale) TMDs van der Waals heterostructures confined onto transparent periodic lattices. An original physical deposition process based on the ion beam sputtering of bulk TMDs targets has been exploited to control the growth of tilted WS_2 nanostripe arrays conformally coated by a continuous few-layer MoS_2 film. Under this condition narrowband photonic anomalies are excited at the interface of the periodic lattice, thus steering the light parallel to the ultra-thin semiconductor layers [4]. In parallel a modulation of the refractive index on the surface is promoted by the periodic WS_2 nanostripes, acting as optical sensitizers. We thus observe a strong resonant and non-resonant enhancement of the photon absorption in in the ultra-thin vdW layers up to the 250%, relatively to the flat reference heterostructure film [5]. Additionally, the capability to control the out of plane tilt of the 2D layers promotes directional light scattering properties, enhanced in the flat-optics configuration. These figures demonstrate that the large-area vdW heterostructures nanoarrays represent a promising scheme for various applications from photonics to photoconversion and energy storage.

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Stimuli-responsive Flexible Silk-Metamaterial for Enhanced Sensing of Volatile Organic Compound (VOC) at Mid-IR

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Abstract: Metamaterial platforms are limited for monitoring transient events, i.e., exposure to volatile organic compound (VOC) and biomolecular activities with large chemical-specificity and differential response, particularly in flexible applications. Here, we report a robust, flexible and stimuli responsive hybrid Silk-Metamaterial architecture for fast and repeatable detection of VOCs particularly suitable in biocompatible applications. By utilizing the "super-modes" existent in the nano-pillar cavity architecture, chemical sensing in vapor phase and liquid phase is demonstrated at mid-IR extending the capabilities of surface enhanced absorption (SEIRA) spectroscopy. The platform is highly disposable and biocompatible and can be robustly integrated for a range of flexible applications.

Keywords: ***Biocomaptible, Flexible, Metamaterial, , Mid Infrared, Silk, Stimuli-responsive***

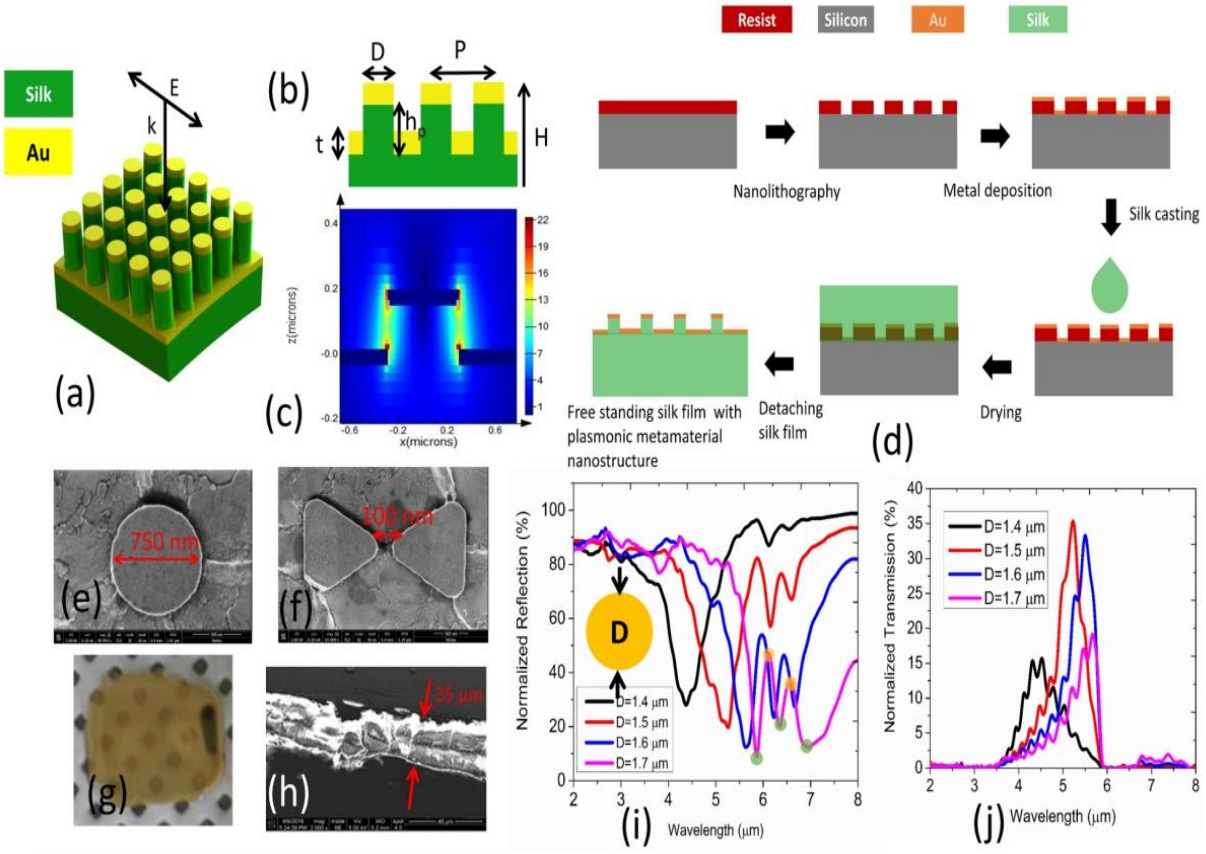

Figure 1: (a) 3D schematic of the free standing, flexible silk film with plasmonic nanostructure (b) Dimensional parameters of the structure (c) Electric field enhancement induced by the vertical coupling between the top and bottom layer, observed at the XZ plane. Incident polarization is maintained along x-axis (d) Detailed steps of the transfer process (e) Suspended disk nanostructure (f) Suspended bow-tie nanostructure (g) Flexible silk membrane containing the nano-pillar cavity structures (h) SEM cross-section of the flexible silk membrane (i)Diameter dependent characteristics of the suspended disk nanostructures on silk nano-pillar in reflection mode (j) Corresponding transmission characteristics of the disk nanostructures

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Momentum-Tuning of Excitons in Atomically Thin Transition Metal Dichalcogenides

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The optical properties of transition metal dichalcogenide (TMD) monolayers are dominated by strongly bound electron-hole pairs, the so-called excitons, due to the reduced dimensionality and the associated inherently weak Coulomb screening. Thus, the emission caused by the recombination of the excitons at the K-point of the Brillouin zone is the predominant feature of the photoluminescence (PL) spectrum. Up to now, there have been several elaborate approaches to tuning the wavelength of the PL signal, which involved the application of uniaxial strain [1], temperature control of the sample [2], or application of a gate voltage [3]. While all these methods achieve the goal of shifting the emission wavelength, they also drastically change the physics of the system, *e.g.,* the phonon scattering time, the nonlinear susceptibility tensor, or the exciton-trion ratio. Recently, a less invasive method was proposed by Simbulan *et al.* which used a light source with well-defined orbital angular momentum to provide additional finite momenta to open the light cone which led to an enhancement of momentum-forbidden exciton transitions [4].

In this work, we follow this approach but instead of the complex shaping of the incident light into a helicoidal wavefront, we integrate different TMDs ($MoSe_2$, WSe_2, WS_2) on dielectric linear chirped nano-gratings (see Fig. 1a)) which provide additional momentum to the system. Depending on the local groove density of the grating the provided momentum and accordingly the enhanced PL emission wavelength varies along the structure (Fig. 1b)). With further tailoring of the grating dimensions this method could be extended to directly probe the exciton dispersion in different TMD monolayers which in turn could provide valuable information for the understanding of fundamental processes such as exciton diffusion.

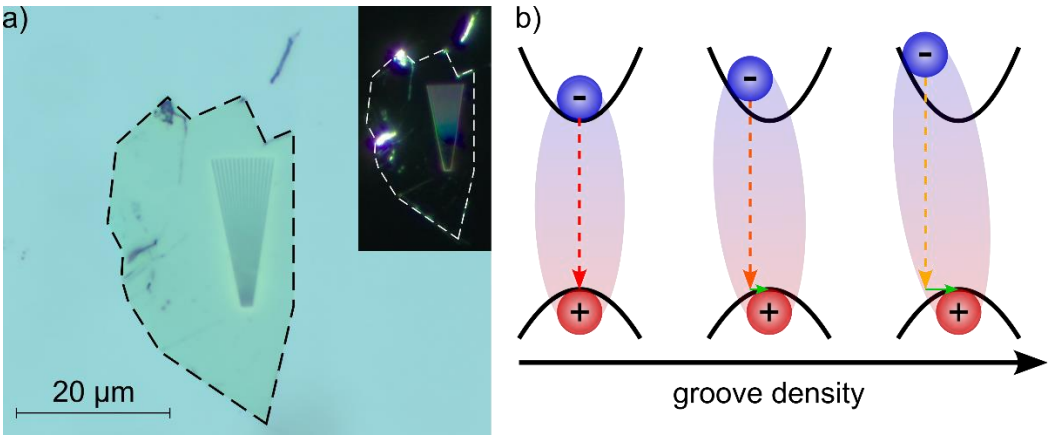

Figure 1: a) Microscopy picture of a $MoSe_2$ monolayer (green area) transferred on a linear chirped nano-grating. The inset shows the dark-field image of the same sample, where no defects are visible in the TMD/grating area. b) For an increasing groove density, the grating provides more momentum (green arrows), leading to a blue shift of the emitted PL signal (dashed arrows) of the TMD.

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CdZnO nanoparticles for SEIRA sensing in the mid-infrared

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Resonant Surface Enhanced Infrared Absorption (SEIRA) relies on the resonant coupling of a broadband plasmonic mode supported by a metallic micro or nanostructure and the narrowband absorption minimum of the analyte to detect. With this method, enhancements up to a factor 7 in the signal of the analyte have been reported [1]. However, most reports rely on noble metals that suffer from high losses in the mid-IR range [2], and complex lithography is required to place the plasmonic resonances at the desired wavelengths. In this study, we report a novel, lithography-free approach for resonant SEIRA sensing. We employ self-assembled nanoparticles (NPs) made of $Cd_{1-x}Zn_xO$ –a material characterized by its low losses in the mid-IR [3]— deposited on GaAs.

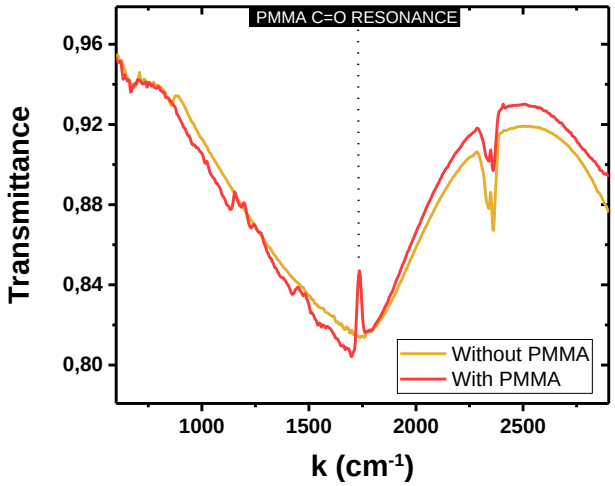

Figure 1: Transmittance spectra of the $Cd_{0.9}Zn_{0.1}O$ NPs on GaAs, with and without a layer of PMMA on top.

Resonant coupling between the localized surface plasmons (LSPs) supported by the NPs and the sharp absorption minimum presented by PMMA resist is demonstrated. The low energy resonance of the LSPs [3] is dependent on the refractive index of the substrate. For GaAs (n=3.3), it is found at around 1750 cm^{-1}, well below the plasma frequency of $Cd_{0.9}Zn_{0.1}O$ (~ 4000 cm^{-1}). This energy matches that of the C=O absorption in the PMMA. Figure 1 presents the transmission spectrum of a $Cd_{0.9}Zn_{0.1}O$/GaAs sample before and after the deposition of a thin layer of highly diluted PMMA. Here, the PMMA absorption band appears as a sharp, well-defined maximum in the middle of the broadband LSP. This paradoxical behavior where an absorptive mode appears as a non-symmetrical maximum is typical of this type of resonant coupling, as first described by Fano and shown in most successful SEIRA experiments [4].

This approach is not restricted to GaAs substrates. Tunability of the resonance by growing CdZnO NPs on other substrates with different refraction indexes can be achieved, thus opening the possibility to fingerprint other analytes with resonances in this spectral range.

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Influence of the fabrication process on the optical spectra of all-dielectric dewetted nanoparticles

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All-dielectric, sub-micrometric particles obtained through solid state dewetting have been shown to support Mie resonances together with a high quality monocrystalline composition [1]. Recently, a precise study on the impact given by the effective complex morphology of a SiGe dewetted nanoparticle to the Mie scattering properties has been provided and carried on through a novel experimental technique called Dark-field Scanning Optical Microscopy [2]. In this work, by means of the same technique and of light scattering simulations, we reveal how the presence of a Si-based pedestal under the dewetted nanoparticle, resulting from the electron-beam lithography process, accounts for a sharp peak at 450 nm in the total scattering cross-section and strongly influences its features, see Fig. 1(b). The FDTD simulations reported in Fig. 1(a) do not reproduce the short wavelength peak. However, by adding in the dielectric simulation windows a thin Si-based pedestal below the dewetted island, Fig. 1(c), evidenced also by SEM images, the FDTD scattering cross sections agree much better with the experimental dark-field spectrum. In conclusion, we demonstrated through simulations and dark-field spectra that a Si-based pedestal, deriving from the fabrication process, is present under dewetted nanoparticles, and that it influences the scattering cross-section of the nanoparticle itself.

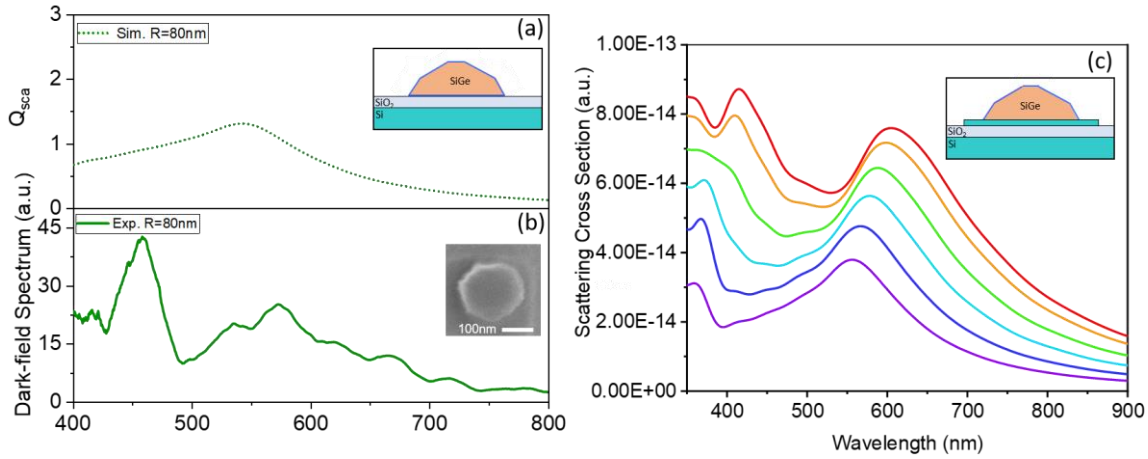

Figure 1: (a) FDTD Normalized scattering cross-section of a SiGe dewetted island with 80 nm radius. The inset shows the dielectric window used for the FDTD simulations (b) Normalized dark-field spectrum of the islands of a SiGe dewetted island with 80 nm radius. The inset shows the top view SEM images of the investigated islands. (c) scattering cross-section of a SiGe dewetted island with 80 nm radius sitting atop the Si pedestal as a function of t, the pedestal thickness. The inset shows the dielectric window used for the FDTD simulations.

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Plasmonic nanohelices for surface enhanced Raman spectroscopy with circularly polarized light

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Recently, Raman spectroscopy has become important for environmental analysis, however the Raman effect is intrinsically very weak. To overcome this limitation, advanced surface enhanced Raman scattering (SERS) substrates have been proposed by researchers but these are difficult to compare to one another. Here, we demonstrate a high-performance SERS substrate and, for meaningful comparison, we benchmark its properties to a commercially available product. Our substrate couples efficiently to circularly polarized light allowing the observation of two previously unknown ways to detect the chirality of nanostructures.

In response to environmental challenges Raman spectroscopy is becoming a key tool to fingerprint and identify molecules associated with pollutants (such as viruses, bacteria and toxins) [1]. To meet these challenges, SERS substrates must produce strong and reproducible signal enhancements over large areas and with a low fabrication cost. Moreover, through practical assessment of their properties, such substrates need to be comparable. Here, we show that dense arrays of plasmonic nanohelices, which are of interest for many advanced nanophotonics applications, also present excellent SERS properties [2]. We compare the performance of the nanohelices to commercially available conglomerates of Au nanoparticles.

Figure 1A shows the dimensions of the left-handed Ag nanohelices; at a length of ≈100 nm these are the smallest helical structures used of SERS [3]. The SERS properties of the helices are demonstrated through two new methods for probing near-field enhancement generated with circular polarization at chiral metasurfaces, see Figure 1B. The first method is based on a single, element specific, achiral molecular vibrational mode (i.e., a single Raman peak), see Figure 1C. The second method is based on the Raman spectra of achiral molecules (crystal violet), see Figure 1D.

We believe these advanced plasmonic materials are set to find broad applications in surface enhanced Raman spectroscopies for environmental science applications. One such application they could benefit is Hyper Raman spectroscopy. Hyper Raman's very weak signal limits its use as a complimentary technique to standard Raman but our hope is that these substrates could allow wider use of the technique.

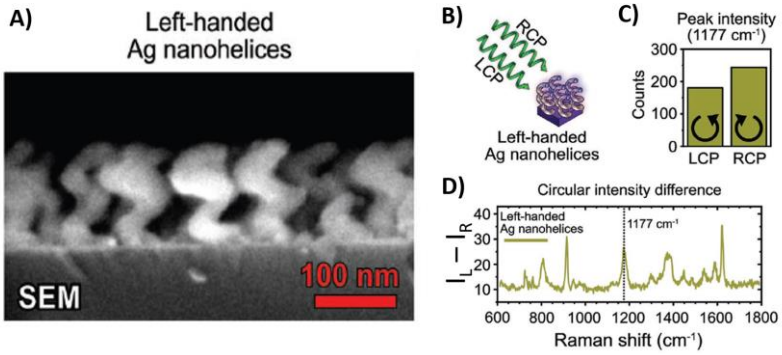

Figure 1: Imagery and data related to left-handed Ag nanohelices. A) Side view SEM of the nanohelices. B) Diagram of illuminating nanohelices with left- and right-handed circularly polarized light (LCP and RCP, respectively) at 532 nm. C) Peak intensity of the Raman vibrational mode at 1177 cm^{-1}, for LCP and RCP illumination. D) The circular intensity difference (CID, defined as $I_L - I_R$) spectrum of crystal violet for dense arrays of nanohelices; irradiance 1.7 kW cm^{-2}. [2]

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Nanoscale thermometry of plasmonic structures via Raman shifts in copper phthalocyanine

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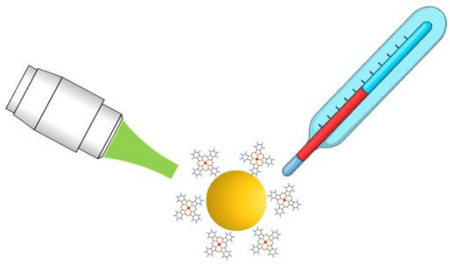
Abstract: Temperature measurements at the nanoscale are vital for the application of plasmonic structures in medical photothermal therapy and materials science, but very challenging to realize in practice. In this work, we exploit a combination of surface enhanced Raman spectroscopy together with the characteristic temperature dependence of the Raman peak maxima observed in β-phase copper phthalocyanine (β-CuPc) to measure the surface temperature of plasmonic gold nanoparticles (NPs) under laser irradiation. We begin by measuring the temperature dependent Raman shifts of the three most prominent modes of β-CuPc films coated on an array of Au nanodisks over a temperature range of 100 K to 500 K. We then use these calibration curves to determine the temperature of an array of Au nanodisks irradiated with varying laser powers. The extracted temperatures agree quantitatively with the ones obtained via numerical modelling of the electromagnetic and thermodynamic properties of the irradiated array. Thin films of β-CuPc display low extinction coefficients in the blue-green region of the visible spectrum as well as exceptional thermal stability, allowing a wide temperature range of operation of our Raman thermometer, with minimal optical distortion of the underlying structures. Thanks to the strong thermal response of the Raman shifts in β-CuPc, our work opens the opportunity to investigate photothermal effects at the nanoscale in real-time and over single-nanoparticles.



Intracellular recording of rat primary neurons on commercially available plasmonic MEAs

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Technologies that control and monitor neural activity are crucial to understand the functions of neural circuits. Micro-electrode arrays (MEAs) play a significant role for both spatial and temporal monitoring of neural activity from neurons cultured on MEAs. The combination of plasmonic laser poration and MEAs will offer advanced electrophysiology and neurotoxicity assessments on neurons, allowing for screening compound effects in acute and chronic conditions with outstanding intracellular signal quality on neurons. As a foremost candidate for optical poration, plasmonic materials such as Au, Pt with nanostructures such as dots, rods and various shapes have been utilized on MEAs [2-4]. Currently, significant results have been obtained by active and passive microelectrode arrays (MEAs) with engineered nano- and micro-structures or 3D nanostructures [6], although very few successful approaches have been reported for neuronal cells [5]. However, the practical implementation of 3D nanostructures is limited due to complex and expensive procedures that are not well suited for large scale production. Here, we investigate and optically porate rat primary neurons grown on commercially available PedotCNT MEAs.

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Moiré photonic crystal to tailor nanolasing emission

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Moiré lattices are made of two superimposed identical two-dimensional periodic structures with a relative rotation angle. The interest in such lattices stems from the possibility to obtain a large class of optical phenomena related to a tailored design of the optical band structure for particular values of the rotation angles. In this work, we study the optimization of the electromagnetic properties of a Moiré photonic lattice made by two plasmonic honeycomb sublattices to tailor the emission and absorption properties of light emitters coupled to them. In particular, we focus on the band flattening effect exhibited at certain twisting angles (magical angles) related to novel phenomena such as localization and delocalization of light [1]. We characterize the local density of optical states (LDOS) within the system by calculating its associated dyadic green function $\overleftrightarrow{G}$ [3], which, in turn, is determined considering the Couple Dipole Approximation (CDA) to simulate the optical response of the photonic crystals. In particular, the CDA semi-analytic method was chosen over other numerical methods, such as the Finite Element Method (FEM), due to its lighter computational load to simulate experimentally nanofabricated larger systems in size [2]. Fig. 1 shows that the extinction map of an AA stacked plasmonic crystal of aluminum spheres obtained using CDA is in good agreement with the numerical result obtained using FEM, demonstrating the validity of the application of CDA to study the optical response of the Moiré photonic lattice with null rotation angle. Subsequently, the calculation of the LDOS, derived from a semiclassical treatment of radiation of the nanoparticles, is used in Fermi's Golden rule to characterize the radiation of the light emitter that is inside the photonic cavities. Finally, the present project aims to study the optimization of flat bands on the optical analog of a twisted graphene bilayer at a magic angle 1.1°, which gives rise to the novel phenomenon of stopped light nanolaser [4].

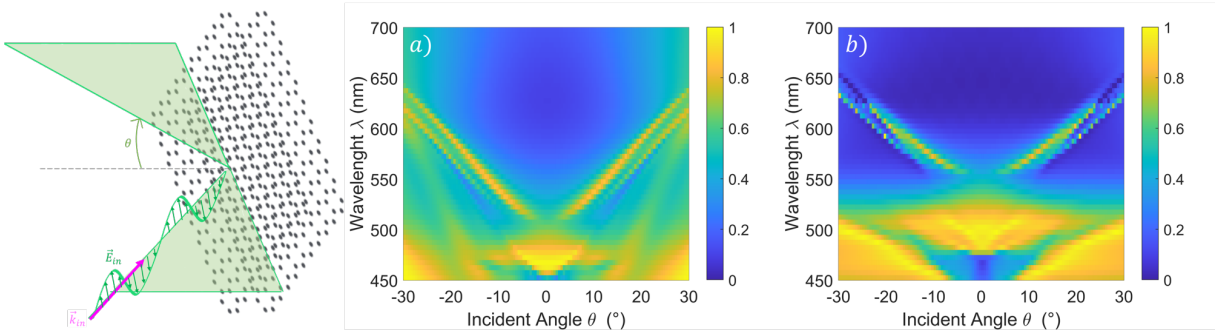

Figure 1: Illustration of the simulated plasmonic Moiré lattice at null rotation. Extinction map as a function of the incident angle and the wavelength of the incident electric field by a) CDA and b) FEM.

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Automatization of SERS analysis towards point-of-care applications

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The integration of plasmonic nanostructures into miniaturized devices combined with the availability of portable Raman spectrometers fosters the development of *on-site* sensing applications of Surface Enhanced Raman Scattering (SERS) [1]. In this context, the automatization of the whole analytical procedure is highly desirable as the measurement has to be performed by non-specialized users. In this work, we present the development and optimization of an automatic setup for SERS analyses. The described system includes a motorized sample injection module, a support for the proper positioning of the Raman probe on the SERS-active platform, the microfluidic chip and a portable Raman spectrometer, as well as a single custom script that allows for syringe and spectrometer control and data processing (Figure 1a). As a proof of concept, the system is tested for the detection of miRNA tumor biomarkers. The SERS chip, containing Ag-coated porous silicon membranes, is functionalized following a two-step hybridization assay [2]. Then, the device is connected to the automatized injection system and the sample containing the target is repeatedly flown in and out from the chip chambers. After the optimization of the injection, incubation and acquisition parameters, the performances of the portable automatized system and of the laboratory-scale procedure involving a bench spectrometer were compared by analyzing several miR-214 concentrations. The analyte was efficiently concentrated at the SERS-active surface though the dynamic incubation procedure (Figure 1b). Actually, the described improvement resulted in a comparable sensitivity for the assay performed with the portable setup operating in automatic mode or analyzed by a bench Raman microscope. The *in-chip* analysis of miR-214 and its quantification by an entirely automatized procedure was thus demonstrated, promoting *in-field* SERS-based sensing featured by a small, robust and easy to handle platform.

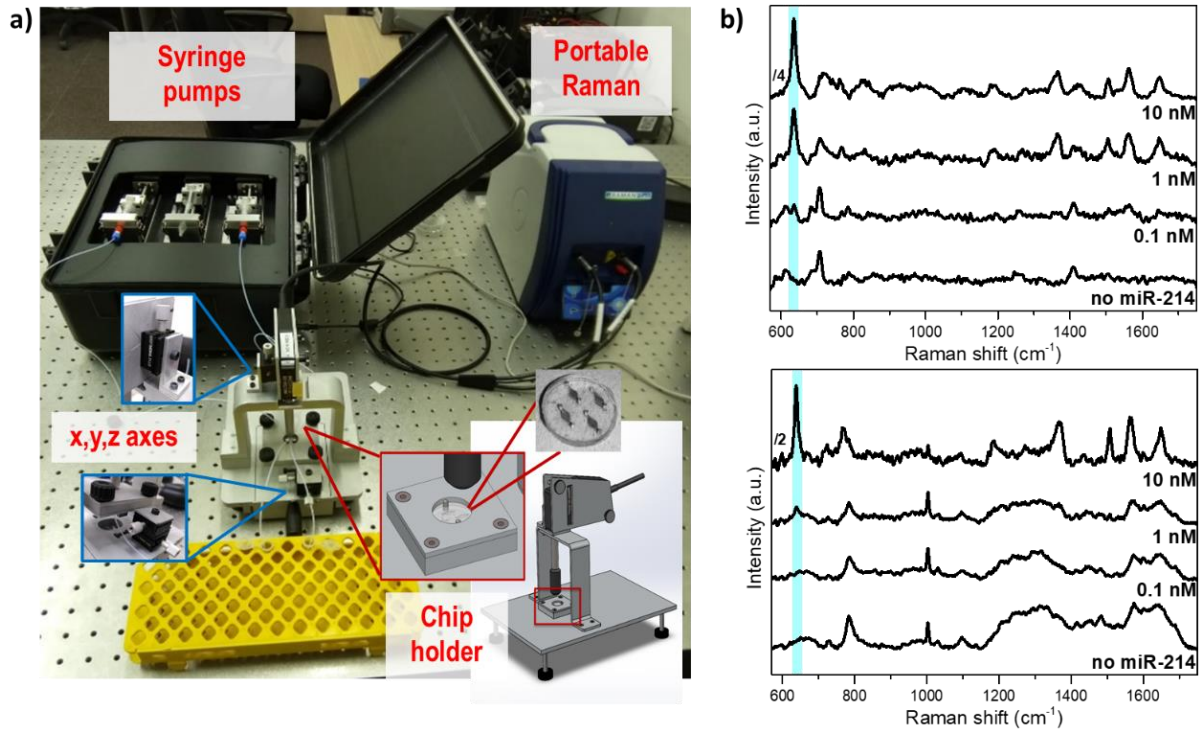

Figure 1: a) Microfluidic and Raman integrated setup for automatized SERS analyses; b) SERS detection of miR-214 ($\lambda_{exc.}$= 532 nm) at different concentrations performed using the developed portable and automatic setup (top) or through the laboratory-scale procedure (bottom).

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Harvesting plasmonic hot holes

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Noble metal nanoparticles (NPs) exhibit exceptional light scattering and absorption, thanks to so-called localized surface plasmon resonances (LSPRs). These resonances originate from light-driven oscillations of free electrons and can be used in a variety of applications, from opto-electronics to photochemistry and optical sensing.

Recently, plasmonic nanostructures have been thoroughly investigated for their potential application in photocatalysis thanks to their ability to generate hot electrons and hot holes upon excitation with light. These non-thermalized charge carriers can be harvested to drive redox reactions at the surface of the metal, but it remains unclear how efficient this process is, particularly considering their very short lifetime.

In this study, we investigate the light-driven synthesis of Au@Ag core@shell structures, where the growth of the Ag shell is facilitated by hot holes originating from interband transition in the Au cores. Previous studies have suggested that the mean free path of a d band hole is limited to 4 nm, which makes the growth of the Ag shell challenging, particularly for large Au NPs and thick Ag shells.[1–3]

To elucidate the photochemical role of the mean-free path of d-band holes, we study the Ag shell growth over Au nanoparticles of varying sizes and compare the rates in the dark and under plasmon excitation. Our results show significant differences in the reaction rates on AuNPs of different diameters.

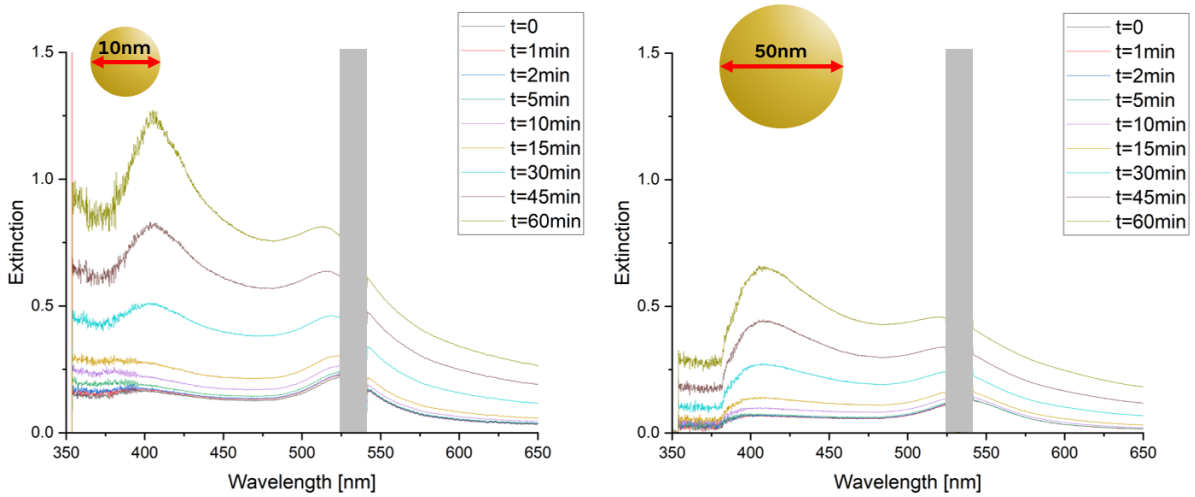

Figure 1: Time evolution of the extinction spectra measured during Ag shell growth on (left) 10 nm and (right) 50 nm Au nanoparticles. The reactions are conducted under 532 nm laser irradiation.

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Mixed QM/Classical Approaches for Surface-Enhanced Raman Scattering

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Surface enhanced Raman scattering (SERS) is a widely used analytical technique, which takes advantage of the huge enhancement of the Raman signal of a target molecule adsorbed on metal nanoaggregates [1]. In this contribution, we present a novel theoretical approach to treat surface-enhanced spectroscopies, in which the plasmonic structure (either metallic or graphene-based) is described by means of fully atomistic, classical, electromagnetic models, which have recently been developed by the present authors [2-4], while the adsorbed molecular system is treated at the quantum mechanical (QM) level. The atomistic, yet classical, approaches are able to predict the plasmonic properties of nanostructures of complex shapes, and are general enough to describe, at the same level of accuracy, metal nanoparticles [2,4] and graphene-based nanoaggregates [3,5]. Indeed, our classical model shows a remarkable potential for large scale nanoplasmonic simulations (more than 1 million atoms), also for systems dominated by quantum effects, such as subnanometer junctions [2,4] or by geometrical defects [5,6]. In this contribution, we couple our classical model to a QM description of the adsorbed molecular system, and we extend the resulting approach to the prediction of SERS signals [7]. The robustness and reliability of the developed method are demonstrated for selected test cases and comparison with available experimental spectra.

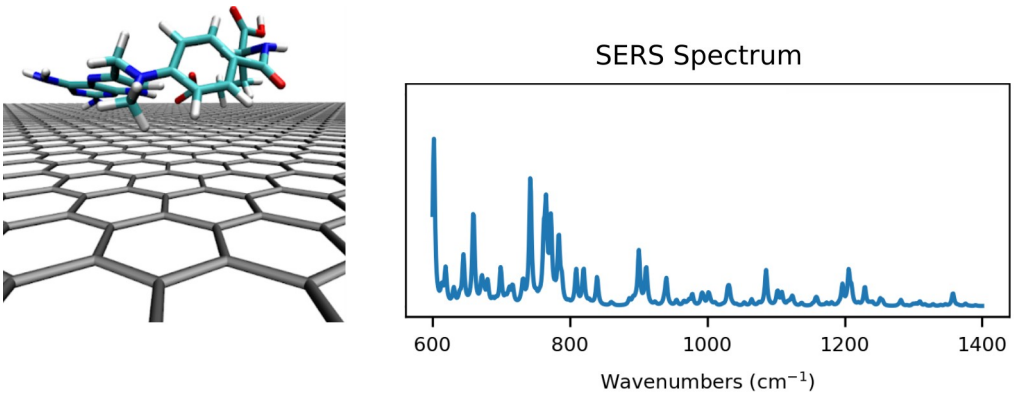

Figure 1: Graphical depiction of methotrexate adsorbed on a graphene disk (left) and the corresponding calculated SERS spectrum (right).

Acknowledgments: This work has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No. 818064).

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Generation of solvated electrons using visible light by excitation of diamond-gold nanoensembles.

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Combining plasmonic metal nanoparticles with wide bandgap semiconductor materials has been demonstrated to be an effective way to sensitise these materials to sub bandgap light [1]. This is often used as a strategy improve the photocatalytic properties of these materials.

In this work we focus our efforts on diamond as it has the very interesting property of having a negative electron affinity at its surface when it is hydrogenated. The result is that when electrons are excited into the conduction band in the vicinity of a diamond/vacuum or, indeed, a diamond/water interface they are ejected from the diamond into the vacuum or water. This property can lead to numerous useful applications such as a cold cathode or as a clean source of solvated electrons. The problem is that diamond has a band gap of 5.5 eV and therefore this process only works with VUV light ($\lambda < 213$ nm).

We have fabricated two separate systems based on the combination of plasmonic nanoparticles with diamond which show that the exciting the plasmonic resonance of the metal nanoparticles can lead to a strong enhancement of the emission of electrons from the diamond surface. The process is demonstrated using an array of nanoparticles embedded below the surface of a thin film of diamond for the emission of electrons into vacuum using visible light. The increased electron emission efficiency was verified by photoemission and photoconducibility measurements. Initial attempts with Aluminium as the plasmonic material were not successful [2] while successive fabrication using silver showed the required properties. Furthermore, a second system involving nanodiamonds coupled with gold nanoparticles in aqueous solution has been shown to be source of solvated electrons following interaction with visible light. In this case the presence of solvated electrons was verified by using an ultrafast pump-probe experiment in which a visible light pump was used to excite the plasmon resonance of the gold nanoparticles while the white light probe was used to optically detect the formation of the solvated electron in the first picoseconds after the excitation.

Based on the details of the above measurements we discuss the mechanisms which could explain the results observed in the two systems.

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Effect of electron spill-out on the surface plasmon-polariton propagation at dielectric-magnetized plasma interface

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Surface plasmon-polaritons (SPPs) propagating at dielectric-metal interfaces, due to the coupling of light with the collective oscillation of free electrons, satisfy the Lorentz reciprocity principle which is exhibited by the symmetrical propagation of the SPPs in opposite directions. This reciprocity can be broken when external magnetic field is applied to the system and may result in the creation of unidirectional SPP propagation within a certain frequency gap [1]. This phenomenon has attracted a substantial interest in the community since it carried a significant application prospect in the fields of sensing and communication. Recent works, have however, shown that this unidirectionality does not hold if one accounts for nonlocal effects in the optical response of the plasmonic system [2,3]. Contrarily to the local response approximation (LRA) model, nonlocality prevents the existence of unidirectional band gaps, since nonlocal dispersion would in principle always provide a back propagating mode. This underlines the importance of consideration of more realistic material models in the theoretical study of SPPs. Here we investigate SPP propagation in the presence of externally applied magnetic field, within the framework of quantum hydrodynamic theory (QHT), which accounts for both nonlocality (beyond the Thomas-Fermi approximation) and electron spill-out. Contrarily to Thomas-Fermi nonlocal dispersion predictions, the QHT appears to restore the existence of the unidirectional gaps. The results given by the QHT are compared with previous results, Fig. 1(**a**).

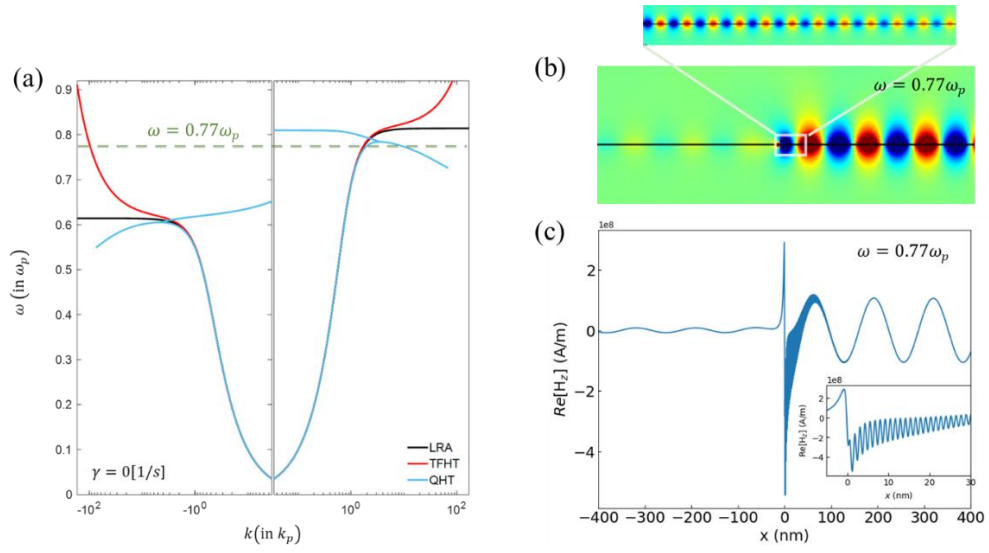

Figure 1: **(a)** Dispersion diagrams calculated for the SPP propagation at the air-magnetized Na interface based on the local response approximation, LRA (black curve), the Thomas-Fermi hydrodynamic theory, TFHT, nonlocal model (red curve), and the Quantum hydrodynamic theory, QHT, model (light-blue curve). **(b)** Real part of the magnetic field distribution at $\omega = 0.77\omega_p$ [green dashed line in **(a)**] calculated with QHT framework. **(c)** The one-dimensional profile of the field extracted from **(b)** at 0.5 nm below the interface. Indicates field interference pattern on the right of the dipole source due to the contributions from the two crossing points [green dashed line in **(a)**] in the positive k of the QHT dispersion curve.

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Ultrafast Dynamics of Plasmonic and Interband Excited Non-Thermal Electrons in 2D Gold Nanoparticle Arrays

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The generation of excited non-thermal electrons in plasmonic nanostructures has been the subject of a great deal of papers mainly due to increasing interest in harvesting these electrons for applications such as photocatalysis, energy conversion, and nanophotonics [1-3]. One of the main difficulties in designing efficient energetic electron devices is the intrinsic ultrashort lifetime of these highly energetic carriers, which generally only live tens to hundreds of femtoseconds before being thermalized into a Fermi-Dirac distribution.

Here, we have used a combined experimental and theoretical approach [4] to investigate the dynamics of non-thermal electrons generated following either plasmonic or interband photoexcitation. In particular, an array of gold nanoparticles deposited on a LiF substrate has been investigated through femtosecond pump-probe spectroscopy and the experimental measurements have been post-processed guided by the extended two-temperature model.

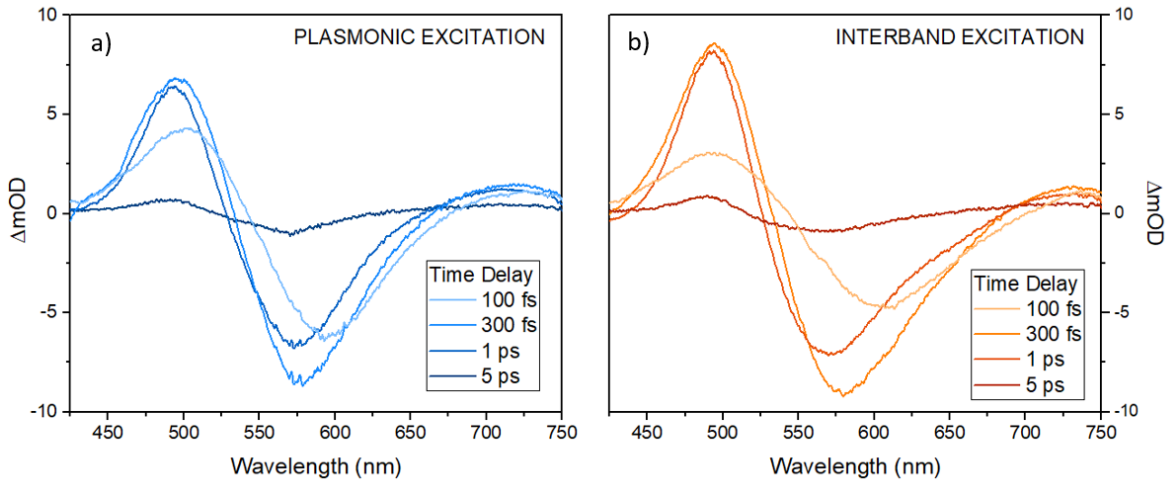

Figure 1: Transient absorbance spectra acquired at increasing time delays (100 fs, 300 fs, 1 ps, 5 ps) between the pump and the probe pulses, following a) plasmonic and b) interband excitation at 570 nm and 410 nm, respectively.

The analysis has shown that the appearance time of plasmonicly excited non thermal electrons is significantly faster than that of the interband excited carriers. This result has been discussed in light of the different processes involved in the generation of the non-thermal electronic distribution following photoexcitation. The possible role of spatially localized carriers due to the action of hot spots has also been discussed.

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Surface-functionalized silver coated gold nanostars for SERS and LSPR sensing of Fe(III)

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Iron is one of the most common and important elements on earth and it plays critical roles in many natural and biochemical processes[1,2]. Iron concentration is therefore an important parameter for water environmental quality and, with the rapid development of modern industry, this topic is gaining more and more relevance. Convenient, rapid, high sensitive and on-site iron determination is thus important for environmental safety and human health, and nanotechnology may offer some options.

In this regard, we developed a sensing system for the detection of Fe(III) in water, based on 7-mercapto-4-methylcoumarine (MMC) stabilized silver coated gold nanostars (GNS@Ag@MMC)[3], exploiting a redox reaction between the Fe(III) cation and the silver shell of the nanoparticles. This sensor can detect Fe(III) by simultaneously monitoring changes in the LSPR and SERS spectra of GNS@Ag@MMC as a function of added Fe(III). The specific selectivity of the GNS@Ag@MMC sensor towards iron has been verified monitoring the LSPR and SERS response to other cations.

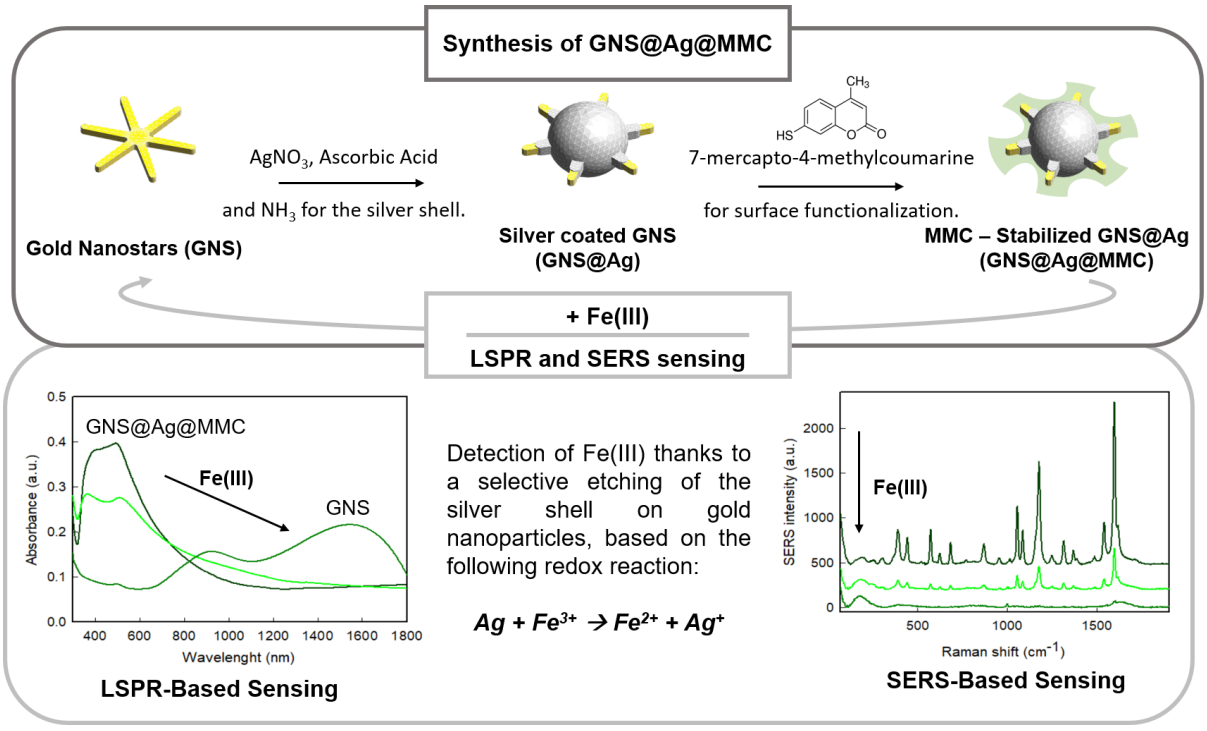

Figure 1: Schematic representation of GNS@Ag@MMC synthesis and LSPR and SERS –based detection of Fe(III).

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Ultrafast dynamics of Surface Plasmon Polaritons in Sub-Wavelength Hole Arrays

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Light-matter interaction has a fundamental role in numerous fields of science and technology. Nowadays, new techniques and technologies permit light control and manipulation at the nanoscale, giving access to novel regimes of interaction with matter. In this view, the "strong coupling" condition is reached when the exchange rate of energy between a confined electromagnetic field and a quantum emitter is faster than any other relaxation process. Only then, the overall system can exhibit novel *hybrid states* endowed with inherently different physico-chemical properties, which no longer belong to its separate components. The investigation of these system has massively involved the scientific community in a large variety of applications such as lasing [1], quantum information [2], and chemical reactions [3]. For these purposes, different kind of photonic cavities has been and can be designed and investigated; among them, open cavities sustaining Surface Plasmon Polaritons (SPPs) represent one of the most promising platforms due to its ease of material placement and polariton exploitation into the chemistry and material science domains [4].

Here, we present the steady and time-dependent characterization of an open optical cavity that can be combined in the visible range with an appropriate quantum emitter (dye molecules, low dimensional semiconductors, etc). The aforementioned system consists of a nano-patterned surface made on a metallic thin film (e.g. Au, Ag, or Al) where the periodicity of the holes defines the SPP modes propagating at the metal/dielectric interface. Therefore, by controlling the geometry of the pattern, it is possible to easily overlap the plasmonic resonances with the nanomaterial elementary excitation(s), thus promoting hybrid state formation. This work is in line with recent transient reflectivity results obtain on different plexciton systems [5], [6], and provides a wider investigation of the available SPP platforms.

Acknowledgement

The authors acknowledge support by the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program "REPLY ERC-2020_COG Grant agreement No. 101002422".

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

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Lithium niobate ($LiNbO_3$) has been intensively employed in photonics due to its broad transparency window in the visible and near-infrared and its strong electro-optical response [1]. Recent technological progress in nanofabrication has enabled structuring $LiNbO_3$ at the nanoscale, leading to ground-breaking advances in the fields of nano-optics [1]. In particular, due to its strong second-order nonlinear optical response, applications to nonlinear nano-optics are flourishing [1,2]. For example, $LiNbO_3$ metasurfaces were specifically designed for the generation of photon pairs via spontaneous parametric down-conversion (SPDC) [3]. In this quantum process, a second-order nonlinear material interacts with an incoming photon, generating two entangled photons whose energies summed are equal to the input one. We report here on the realization and optical characterization of a $LiNbO_3$ nanostructured resonator for SPDC as an ultimately compact source of photon pairs. One key issue of SPDC in nano-devices is the short interaction length, yielding a broad angular and spectral range of emission. In addition, the small volume of material inherently yields weak signals. Therefore, we tailored the resonant behaviour of the nanostructure for an efficient and highly directional emission of SPDC. Numerical studies of the eigenmodes of a 500 nm-high $LiNbO_3$ cylinder have been conducted to obtain an eigenmode with a directional emission, allowing for efficient collection. The electric field norm distribution of this eigenmode with a Q-factor of 14 is shown in Figure 1a. The directionality of this mode was further improved by carving an annular groove, tightening the emission to a numerical aperture (NA) of NA≈0.2. The SPDC emission simulated at λ= 1450 nm via an analytical nonlinear polarization density vector adapted to the simulated distribution of the pump field is shown in Figure 1b with the two lobes indicating its directionality. To suppress competing whispering-gallery-like eigenmodes, we introduced two lateral cuts, visible in the scanning electron micrograph of a fabricated resonator in Figure 1c. The resonators are directly milled in a 500 nm-thick $LiNbO_3$ film on a silica substrate by a focused (Ga^+) ion beam (FIB) machine, resulting in sharp spatial features. An example of a photon correlation measurement on a single resonator can be seen in Figure 1d, where a distinct coincidence peak indicates the generation of photon pairs. A coincidence rate exceeding 300 Hz/W was achieved, sizably more than in the only other report – to the best of our knowledge – of SPDC in $LiNbO_3$ particles (15 Hz/W in 4 µm sized microcubes) [4]. Designs like the one we propose here can find application in integrated devices as miniaturized room-temperature sources of non-classical light for quantum technologies.

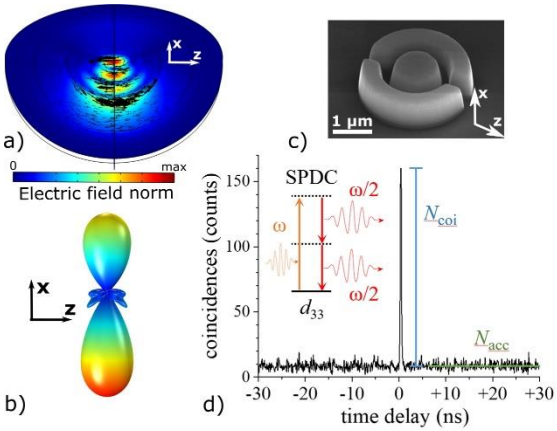

Figure 1: a) Electric field norm distribution of the eigenmode aimed at (wavelength λ= 1450 nm) simulated with a finite-element method. b) Far-field distribution of the simulated SPDC emission at λ = 1450 nm based on an analytical SPDC source distribution. c) Scanning electron micrograph of the nanostructure with groove and cut. d) Example of a photon correlation measurement on a single resonator (excitation 5 mW power at wavelength 785 nm, 10 min exposure time). At zero time delay, a peak of "true" coincidences N_{coi} emerges against the background of accidental coincidences N_{acc}. Inset: Energy level diagram of degenerate SPDC pumped at a frequency ω.

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Excitonic 2D Metasurface for Tunable Image Processing

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Edge detection is a central process in Computer Vision, Artificial Intelligence and Augmented/Virtual Reality, allowing operations such as object recognition and detection, classification, and image compression. These new technologies rely on processing of large image files and may require real-time operation, leading to large energy consumption and an ever-increasing demand in hardware processing power. Recently, several optical analog computing alternatives based on metasurfaces have been presented, which allow performing mathematical operations at the speed of light with extremely low power consumption [1]. While very promising, these initial demonstrations are limited to passive operations, which are imprinted in the metasurface's nanoscale geometry and constituent materials. At the same time, active tuning of the mathematical operation performed by the metasurface would greatly enhance the applicability in real world technologies.

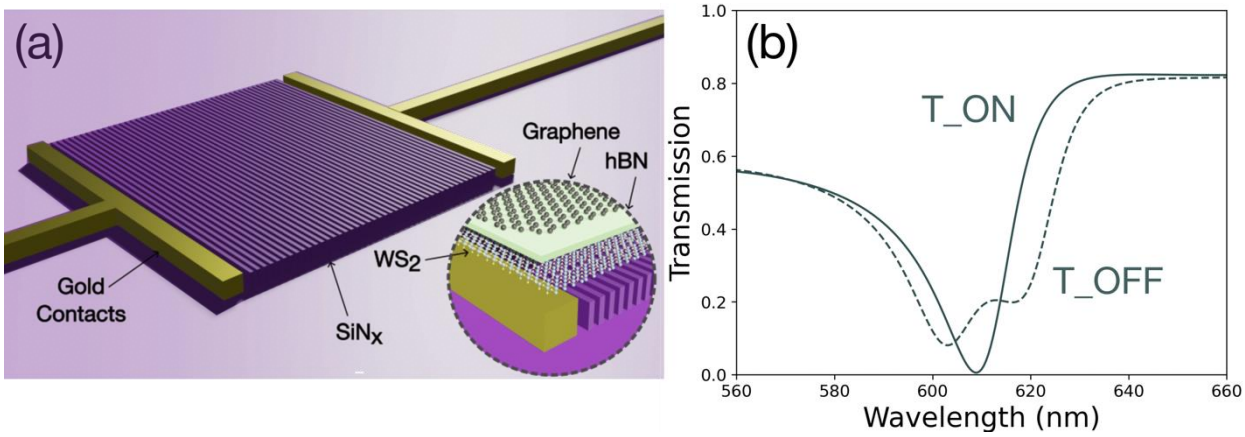

Figure 1: (a) Illustration of the metasurface composed of SiN_x nanobeams capped with a WS_2-hBN-graphene structure. (b) Transmission spectra of the metasurface device, showing the large modulation induced by the excitation or suppression of the excitonic resonance.

Transition metal dichalcogenides are 2D Van-der-Waals materials which support excitonic resonances at room temperature due to their high binding energies. These materials display large changes of their optical properties at the exciton wavelength when the material's carrier density is increased through electrostatic gating, making them ideal for applications in active nanophotonic devices [2]. Here, we propose an active metasurface performing a switchable second-order spatial differentiation by leveraging the coupling between a Fano resonance supported by a SiN_x nanobeam structure and an exciton resonance in a monolayer WS_2 (Figure 1 (a)). The WS_2 layer is combined with an hBN and graphene electrode to form a parallel plate capacitor, which enables the modulation of the charge carrier density. This provides active tuning of the coupling strength between the Fano resonance and the excitonic resonance.

We employ the Finite-Difference Time-Domain method to simulate the spectral response of the device (Figure 1 (b)), and a modulation of 20% and 40% is obtained in transmission and reflection, respectively. This modulation allows the mathematical operation to be turned ON or OFF. Experimental measurements of the nanobeam's transmission show good agreement with the FDTD simulations. Looking forward, we are developing a new 2D stamping technique to transfer monolayers onto nano patterned surfaces, which will allow combination of metasurfaces with 2D material heterostructures.

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Development of novel SERS platform based on polydopamine coated gold-nanostars-chips: fine-tuning of the coating process and future perspectives.

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Here in this contribution we describe the process of coating of gold nanostars (GNS) SERS chips with an ultra-thin layer of polydopamine (PDA). PDA is a versatile biopolymer with great adhesive properties [1] that spontaneously self-polymerize from dopamine (DA) in weak alkaline media and in presence of oxygen [2]. The final goal of the project is to exploit adhesive properties of PDA to increase affinity of SERS chips towards given targets.

The process of the PDA layer formation was carefully studied with different techniques (Figure 1):

1. The thickness and the spatial homogeneity of the PDA layer have been analyzed by varying the polymerization conditions.
2. SERS measurement using a model Raman reporter allowed to evaluate the effect of PDA layer thickness on the enhancement factors of the substrate.

To complete the investigation, we performed similar experiments on colloidal samples of GNS, using Uv-Visibile, SERS and TEM characterization.

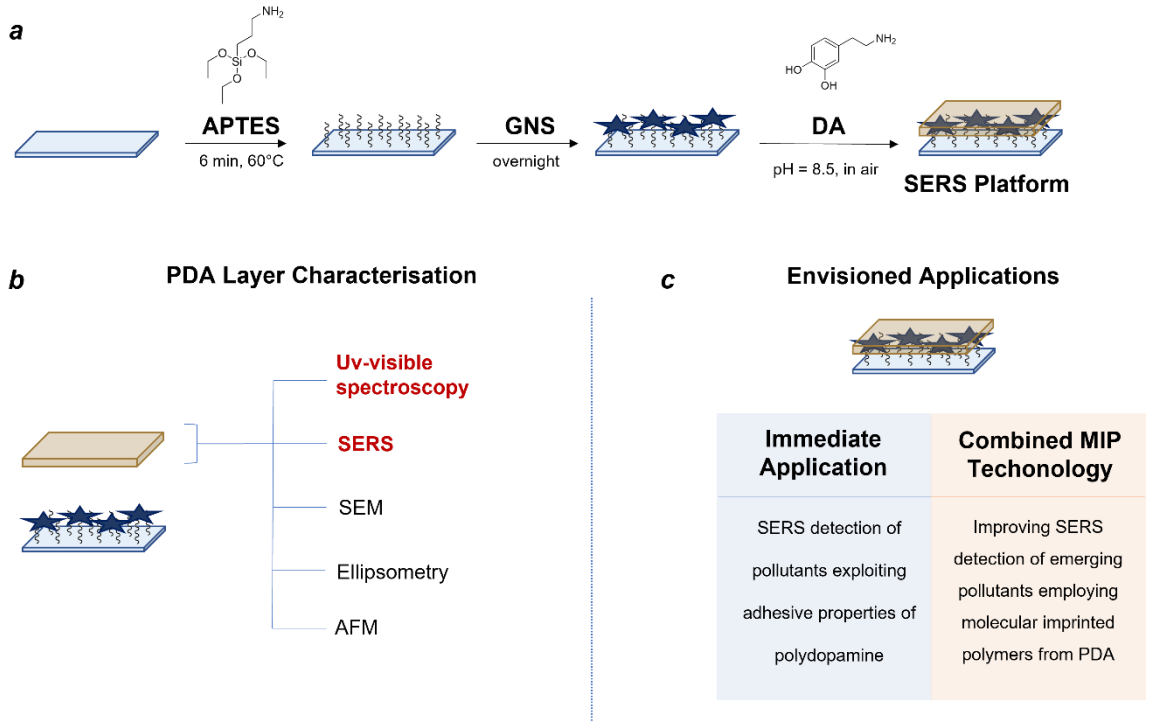

Figure 1: schematic representation of the SERS-chip synthetic path (a), substrate characterization techniques employed (b) and the currently studied applications.

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Ultrafast spatiotemporal chiroptical response of dielectric and plasmonic nanospheres

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The study of nanostructure-enhanced chiroptical light-matter interactions is progressing towards the detection of chiral molecules at ultralow concentrations and ultrafast time scales. The understanding of the temporal response of the chiral molecule, the spatiotemporal response of the nanostructure and response of molecules in presence of the nanostructure becomes important for the determination of the molecular chirality and quantitative estimation of the chirality parameters.

Using Mie theory and the finite difference time domain method, we theoretically study the spatiotemporal response of a dielectric (silicon) and plasmonic (silver) nanosphere for an ultrashort pulse excitation (see Fig.1a). We show that while the optical chirality enhancement (OCE) by plasmonic spheres requires the presence of the incident (the pulsed excitation) and scattered fields, dielectric nanospheres can provide OCE even after the incident light (excitation) completely vanishes as long as the dielectric NPs support resonant electric (a_1) and magnetic (b_1) modes. The OCE in the scattered field of the dielectric particle is observed due to the interference of the fields of electric and magnetic modes (see Fig.1b). We further demonstrate spectral tuning of the spatial distribution of OCE by controlling the phase between the electric and magnetic resonant modes in a dielectric nanosphere.

The work highlights the understanding and manipulation of the ultrafast and nanoscale spatiotemporal evolution of the near-field OCE around resonant nanospheres excited by fs-pulsed excitation and may find applications in spatiotemporal control of the chiroptical response of nanostructures.

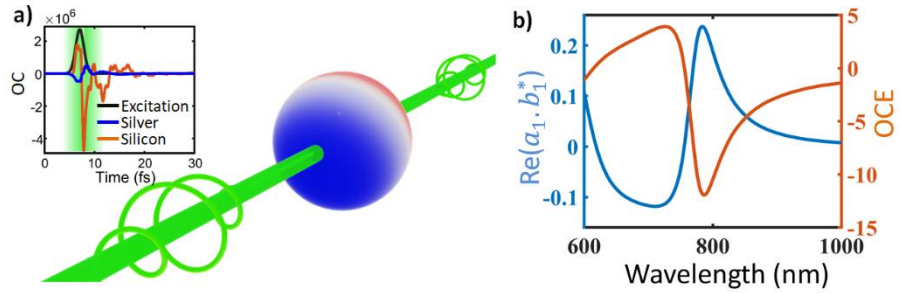

Figure 1: a) A schematic showing an ultrafast optical illumination of a nanosphere and near field optical chirality (OC). The time-dependent OC in the scattered field for the silicon and silver nanospheres is shown in the inset. b) The effect of electric (a_1) and magnetic (b_1) dipole mode interference (blue, left axis) on the OCE spectrum (red, right axis) obtained at a point in the equatorial plane for silicon nanosphere.

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Plasmonic bowl-shaped nanopore using Raman Spectroscopy for sequencing of translocating DNA

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Label free detection in a single-molecule regime is a great challenge. It is now well-recognized technique to perform an experiment in a single molecular regime however, that is labelled with fluorescent molecule. Out of several label free detection, Raman spectroscopy is an emerging method due to its selective signals in fingerprint regime. Plasmonic nanopores are on the other hand, useful to control the spatial confinements in single molecule regime. A nice composition of these two methodologies could be useful for the achievements of the detection and sequencing of DNA and proteins in single molecular regime. The ability of recognizing the sequence of DNA in single nucleotide regime or sequence of proteins in single amino acid level have been demonstrated. In these cases, a single polymeric unit is absorbed on plasmonic surface and delivered through a plasmonic pores. Here, we demonstrated on bowl-shaped gold nanopores capable of direct Raman detection of single λ-DNA molecules in flow through pore. The bowl shape allows two advantages in these experiments. The foremost optical effect enables to focus the incident laser into the nanopore to generate a single hot spot with no cut off in pore size. The second one is the trapping of the particle due to its shapes. The curved surface allows the electrical trapping of the molecule efficiently and guide the unidirectional movements. Therefore, we achieved ultrasmall focusing of NIR light in a spot of 3 nm that enables to detect 7 consecutive bases along the DNA chain during the translocation. Furthermore, we found a novel electro-fluidic mechanism to manipulate the molecular trajectory within the pore volume so that the molecule is pushed toward the hot spot thus improving the detection efficiency[1].

[1] †Y. Zhao et al.

Bloch Surface Waves in Resonant Structures

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Introduction

With the development of integrated photonics, Bloch Surface Waves (BSW) are attracting more and more attention as an alternative to plasmonic platforms. Being evanescently bound to a surface, BSW require energy and momentum matching for coupling from free-space radiation. Generally, oil immersion optics and diffraction gratings [1-2] are the two main methods used to this aim.

In this work, we introduce resonant structures equipped with grating couplers on the surface of one-dimensional photonic crystal (1DPC) to provide BSW excitation. We show experimental characterization of linear Fabry-Perot cavities inscribed within thin polymeric film tailoring all-dielectric 1DPC.

Experiment

Fabrication of the surface corrugations is performed by means of a probe-assisted technique (NanoFrazor, Heidelberg) that uses an atomic force microscopy (AFM) heated probe to induce a local evaporation of the polymer layer at high spatial resolution. The PPA film is spun with a thickness of approximately 60 nm and then patterned with linear cavities surrounded by linear grating couplers.

The optical characterization is performed on a modified inverted microscope, equipped with oil-immersion optics. Both illumination and collection are performed through a NA=1.49 objective. Illumination is provided by using polarization-controlled white-light from a halogen lamp. In order to assure a better control on the BSW coupling, the illumination beam can be selectively moved across the objective back focal plane, in order to steer the incidence angle on the 1DPC. In this way, BSW can be coupled in Kretschmann-like fashion, exploiting the objective as a cylindrical prism, with no need of grating couplers. Instead, an almost-normal incidence can be used in case grating couplers are present. Collected light is Fourier-filtered with a beam blocker in order to let only light propagating at large angles to reach the image plane. In Figure 1(a) the dark-field of a linear cavity is shown, with the central bright line representing the scattered light from the cavity mode. This image is projected onto the entrance slit of the spectrometer, which is aligned with the spacer, thus allowing space-dependent spectral measurements. In Figure 1(b), a typical spectrum of the cavity mode is shown, with a peak at 2.16 eV that is well matching the resonance expected from calculations (2.11 eV).

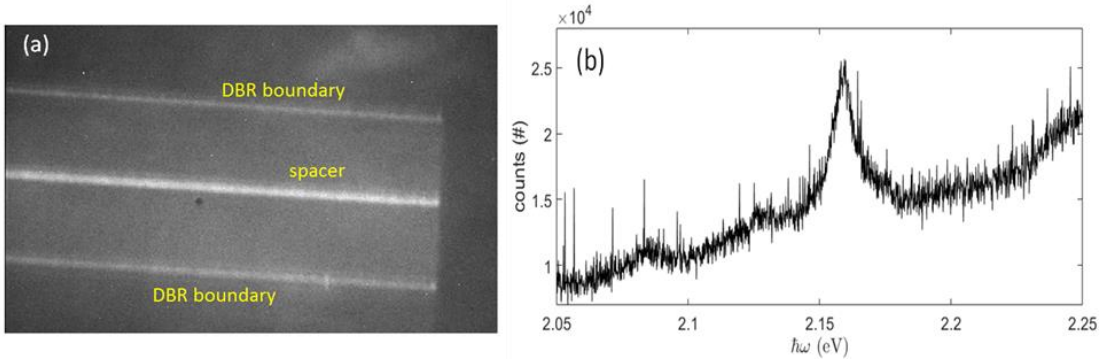

Figure 1. (a) Dark-field image of the linear cavity upon illumination through BSW coupled through oil-immersion objective; (b) scattering spectrum measured corresponding to the bright spacer appearing in the centre of the cavity.

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Vibrational Strong and Ultra-Strong Coupling Using Surface Lattice Resonances

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Plasmonic particles arranged in periodic arrays support narrow optical modes known as surface lattice resonances (SLRs). SLRs are the result of the coherent scattering by nanoparticles enhanced by in-plane diffraction in the array.[1] These plasmonic arrays act as open optical cavity with good field confinement on the surface, making them an interesting and accessible tool to investigate light-matter coupling. In our work, we optimize these arrays to overlap their SLRs with molecular vibrations of thin molecular films and liquids to achieve the strong light-matter coupling regime. These arrays undergo vibrational strong coupling (VSC) with the C=O bond of poly(methyl metacrylate), with a splitting of 76 cm^{-1} (see Fig. 1a),[2] and ultra-strong coupling with the OH^- bond of water/sodium hydroxide, with a splitting of 550 cm^{-1} (see Fig.1b), which is 16% of the energy of the hydroxyl vibration.[3] Despite a clear measurement of the Rabi splitting in the infrared spectra for both the strong and ultra-strong coupling, spontaneous Raman spectroscopy, micro-Raman imaging, and stimulated Raman measurements do not show any polariton signatures (Figs. 1c). Our results introduce SLRs as a novel platforms to investigate light-matter phenomena under strong coupling regime, such as polaritonic chemistry. These plasmonic arrays maintain the spectral position of their SLRs for a long period of time and are easy to fabricate on large areas, making them ideal for possible industrial applications.

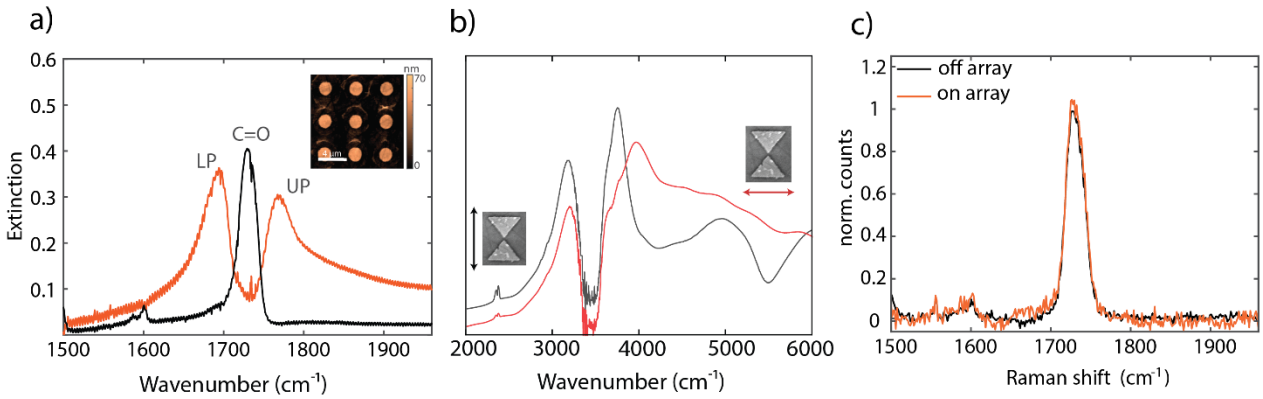

Figure 1: a) Extinction measurement of bare PMMA (black) and strongly coupled system (orange). The array of gold microdisks is shown as an inset. b) Extinction measurements of the ultra-strong coupled system. The TE (black curve) and TM (red curve) polarizations are shown as insets. c) Spontaneous Raman measurement on the bare polymer film (black curve) and on the strongly coupled system (orange curve).

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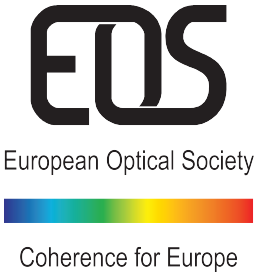

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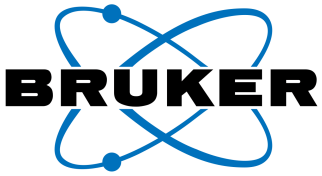

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