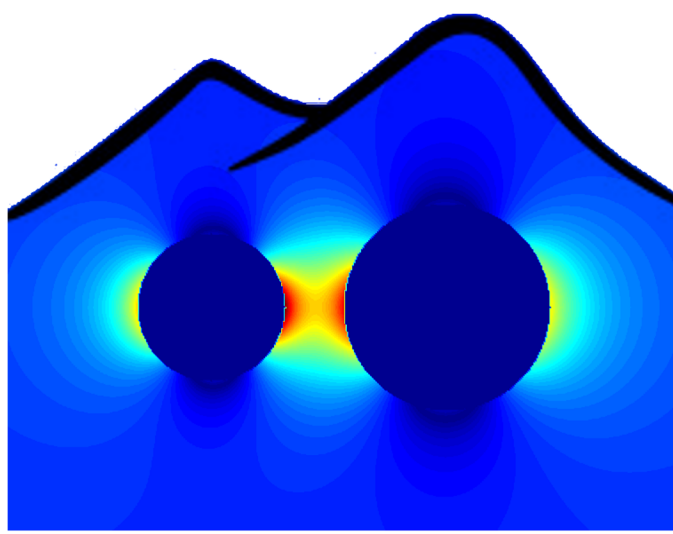
PLASMONICA 2019

June 19-21 2019 | Naples, Italy
San Marcellino & Festo Monastery
www.plasmonica.it/2019



Plasmonica is an annual conference aimed at bringing together a thriving community of researchers working on Plasmonics and Nanophotonics. In particular, the conference encourages early career researchers, PhD students, and post-docs to share their latest results, to discuss recent advances in the field, and to start new collaborations on challenging scientific problems.

Organizing Committee

- Vincenzo D'Ambrosio Università degli Studi di Napoli “Federico II”
- Luca De Stefano CNR-IMM - Napoli
- Carlo Forestiere Università degli Studi di Napoli “Federico II”
- Ilaria Rea CNR-IMM – Napoli

Scientific Committee

- Leonetta Baldassarre Università di Roma “La Sapienza”
- Paolo Biagioni Politecnico di Milano
- Michele Celebrano Politecnico di Milano
- Cristian Ciracì IIT Center for biomolecular nanotecnology
- Antonio De Luca Università della Calabria
- Emanuela Esposito CNR-IMM - Napoli
- Francesco De Angelis IIT - Genova
- Pietro G. Gucciardi CNR-IPCF Messina
- Francesca Intonti Università di Firenze
- Maria Grazia Manera CNR-IMM Lecce
- Giovanni Mattei Università di Padova
- Vito Mocella CNR-IMM - Napoli
- Riccardo Sapienza Imperial College London

Technical Committee

- Ambra Giannetti Institute of Applied Physics Nello Carrara
- Andrea Chiappini IFN-CNR

Supported by

Sponsored by

Oral Presentation Guidelines

- The total time allotted to each speaker is 15 minutes. You should plan to speak for 12 minutes and leave 3 minutes for questions.
- The projection screen has a 16:9 format and is 3.30 m wide
- We kindly encourage the speakers to upload their presentations on the computer we provide. Please upload your presentation before your session and check there for compatibility issues. For any problem or special request please contact the session chair before the session starts.
- We provide the following equipment:
    - Laptop (PC)
    - PowerPoint
    - Microphone
    - Laser pointer
    - Remote Control Presentation Clicker

Poster Presentation Guidelines

- Poster boards are about 80 cm width x 200 cm height. Any poster fitting these limits is allowed.
- In the workshop Program, please note the tag assigned to your poster. This tag identifies the poster board where to hang your poster.
- All necessary material for attaching the poster to the poster board will be available at the Workshop desk.

Best oral and poster awards

At the end of the conference SIOF and IEEE Photonic Society Italy Chapter will offer four prizes of **200 EUR**

- to the two Best Oral Presentations
- to the two Best Poster Presentations

The journal Sensors IMDI will offer a prize of **500 CHF** to the best presentation on plasmonic sensors.

All the winners will be announced at the closing ceremony of the conference

Special Issue of Sensors

Authors of papers presented at this conference and within the scope of Sensors (http://www.mdpi.com/journal/sensors) are invited to submit a technically extended version to the Special Issue of Sensors (Impact Factor 2.5):

Selected Papers from Plasmonica 2019 - 7th Edition of the Workshop on Plasmonics and its Applications

As an open access journal, Sensors have an Article Processing Charge (APC) of 1800 CHF for accepted papers.

The conference participants will receive a 10% discount on the publishing fees.

The Special Issue website can be reached at:

http://www.mdpi.com/journal/sensors/special_issues/Plasmonica 2019

sensors

an Open Access Journal by MDPI

Conference Location

The conference will be held at San Marcellino and Festo Complex, a prestigious historic monastery in the heart of Napoli. The construction of the chiostro began in 1567, when the monasteries of Santi Marcellino e Pietro and Santi Festo e Desiderio (both dating back to the VIII century) were unified, and ended up in 1772. It has a rectangular courtyard surrounded by a portico (three pillared arches) with decorations in piperno; an eight-twentieth-century garden decorated with various fountains in piperno and marble stands in the center. On the south side, there is access to the splendid church of San Marcellino e Festo, now crown jewel of the University Congress Center.

How to reach San Marcellino & Festo Monastery

The easiest way to reach the conference venue is by entering the main building of the **University of Naples "Federico II"** (picture on the left), whose address is:

Corso Umberto I, 40, Napoli

It is two minutes walk from the "Università" stop of the Metro 1. You can take the **Metro 1** from the Napoli central station (Napoli Centrale). Inside the University you will find signs with the Plasmonica2019 logo that will guide you to the San Marcellino & Festo Monastery. You can also ask to the university staff that will guide you to the San Marcellino and Festo complex. The address of the monastery is

Largo San Marcellino, 7, Napoli.

Social Dinner


The conference dinner will take place on June 20th at 20:30 at the restaurant 'Antonio & Antonio' which is located on the beautiful Napoli waterfront.

The address is Via Partenope 26, Napoli

Please note that

- the cost of the social dinner is of additional **25 EUR** for any conference participant
- Guests are welcomed. The cost of the social dinner for a guest is of 30 EUR. If you would like to bring more than one guest please let us know by sending a mail to workshop@plasmonica.it
- If you have food allergies or you prefer a vegan option please let us know!
- The regular menu includes
    - Welcome drink (prosecco)
    - Assorted pizza slices (spicchi di pizza assortiti)
    - Seafood Risotto (Risotto alla pescatora) or a vegetarian option
    - Babà
    - Limoncello;
    - Wine and Water;

Conference Program

	Wednesday June 19		
	9:30-10:30		**Registration**
	10:30-10:45		**Opening**
De Angelis	10:45-11:30	Quidant	Putting Nanoplasmonics to work!
			Biosensors
	11:30-11:45	Romano	Exponential sensitivity of a bound-state-in-continuum photonic crystal sensor
	11:45-12:00	Santoro	Exploring dimensionality for biosensing
	12:00-12:15	Alessandri	Plasmonic Hydrogels for Pan-Specific Capture and Ultrasensitive Raman Detection of Persistent Organic Pollutants
	12:15-12:30	Di Meo	Plasmonic Metasurface based on Cross-Shaped Nanoantennas for Biosensing Applications
	12:30-14:30		**Lunch**
Alessandri			**Plasmonics for Chemistry and Bio-Chemistry**
	14:30-14:45	Baldi	Plasmonics for Chemistry: sensing and driving chemical reactions using plasmons
	14:45-15:00	Garma	Electrophysiology for the masses: a cost-effective ecosystem for the study of electrogenic cells
	15:00-15:15	Guido	Control of Coherences and Optical Responses of Pigmenta Protein Complexes by Plasmonic Nanoantennae
	15:15-15:30	Hernandez	Remotely Generated Hot-Electron using Surface Plasmon Polaritons
	15:30-15:45	Della Ventura	Plasmonic Enhanced Fluorescence as an Effective Biosensing Platform: Detection of Immunoglobulins in Urine for POC Applications
	15:45-16:00	Sepe	Study of the Fluorescence Emission at the Surface of 1D-Photonic Crystal Biochips
	16:00-16:30		**Coffee Break**
Baldi	16:30-16:45	Jensen NKT Photonics	Towards the ultimate light source
			SERS/SEIRA
	16:45-17:00	Zito	Surface-Enhanced Raman and Fluorescence Spectroscopy with an All-Dielectric Metasurface
	17:00-17:15	Caprara	SERS spectroscopy as a high-performance technique to monitor the DNA melting profile
	17:15-17:30	Novara	In situ growth of silver nanoparticles on PDMS membranes for multi-wavelength SERS biosensing platforms
	17:30-17:45	Giordano	Plasmon engineering in self-organized metasurfaces for broadband Surface Enhanced Infrared Absorption (SEIRA) spectroscopy
Celebrano			**Aperiposter Session**
	17:45-17:55	Ferraro	Best Doctoral Thesis Award: From basic to advanced: design, fabrication and characterization of functional Terahertz devices
	17:55-19:00		**Poster Session**

	Thursday June 20		
Baldassarre	09:00-09:45	Reich	Plasmonic nanoparticle crystals: Exploring the limits in light-matter coupling
	Alternative Plasmonic Materials and Dielectrics Resonators		
	09:45-10:00	Li Bassi	Nanoengineered TiO2 and Ta:TiO2 films with enhanced optical/electrical properties for advanced photoconversion and plasmonics
	10:00-10:15	Ciano	Surface Plasmon Waveguides in the THz range for photoluminescent and nonlinear emitters based on Ge/SiGe Quantum Wells
	10:15-10:30	Setaro	Plasmon-Assisted Phenomena in Gold-Carbon Nanotubes Hybrids
	10:30-11:00	**Coffee break**	
Bollani - Sapienza	11:00-11:15	Vitucci Crisel Instruments	THz technology for imaging: from Time Domain Spectroscopy (TDS) to THz Quantum Cascade Laser (THz QCL) Imaging
	Cavities and Resonators		
	11:15-11:30	Sapienza	Dielectric nanocavities for enhanced Purcell effect and strong directionality
	11:30-11:45	Mancini	Near-field spectroscopy of Phonon Polariton resonators
	11:45-12:00	Caligiuri	A Semi-Classical view on the Occurrence and Hybridization of Resonant Tunnelling Epsilon-Near-Zero Modes in Metal/Insulator Nanocavities
	12:00-12:15	Zambrana-Puyalto	Enhanced single molecule detection using Plasmonic Nanochannels and Zero-Mode Waveguides
	12:15-12:30	Piccotti	Two-dimensional nanostructure arrays for plasmonic nanolaser devices
	12:30-14:30	**Lunch**	
Mattei	**Multiphysics systems**		
	14:30-14:45	Gabbani	Coupling Plasmonics with Magnetism in Magnetoplasmonic Hybrid Nanoalloys
	14:45-15:00	Patti	Chiral optical forces and optical trapping of optically active particles
	15:00-15:15	Polito	Difference nanospectroscopy of Proteins in Cell Membranes Located in a 10-nanometer wide Plasmonic Nanogap
	15:15-15:30	Ferrera	Plasmonics of Au Nanoparticles in a Variable-Temperature Thermodynamic Bath
	15:30-15:45	Gillibert	Polarization-dependent thermoplasmonic response of anisotropic metal nanoparticles
	15:45-16:00	Behel	Second Harmonic Scattering from Hybrid Gold & Dielectric Nanoparticles
	16:00-16:30	**Coffee Break**	
Intonti	**Probing and Imaging**		
	16:30-16:45	Isoniemi	Probing resonant modes in hyperbolic metamaterial nanostructures with electron energy loss spectroscopy
	16:45-17:00	Triolo	Near-field imaging of surface-plasmon vortex-modes around a single elliptical nanohole in a gold film.
	17:00-17:15	Zilli	Quantitative measurement of the optical cross-sections of single nano-objects
	17:15-17:30	Leonetti	Scattering Assisted Imaging
	17:30-18:30	**Round Table**	
	18:30-18:45	**Election Steering Committee Plasmonica**	
	20:30	**SOCIAL DINNER, Antonio & Antonio Restaurant**	

	Friday June 21		
Cirac'i	09:00-09:45	A. Alù	Plasmonic metamaterials
	Modes & Topology		
	09:45-10:00	Pascale	Full-wave mode hybridization in Nanoparticle Dimers
	10:00-10:15	Picardi	Dipolar sources for directional and selective excitation of guided modes
	10:15-10:30	Garcia-Etxarri	Topological photonics: Mistaken paradigms and new opportunities
	10:30-11:00	**Coffee Break**	
Finazzi	11:00-11:15	Calvano (Ansys)	Metamaterial Simulation with ANSYS
	Non Linear Effects		
	11:15-11:30	Savo	Nonlinear Light Generation in Disordered Micro-Balls
	11:30-11:45	Rocco	Efficient Second Harmonic Generation in Dielectric Nanoantennas with Epsilon-Near-Zero Substrate
	11:45-12:00	De Luca	Parameter-free hydrodynamic treatment of Difference-frequency Generation in plasmonic nanostructure
	12:00-14:00	**Lunch**	
De Luca	**Quantum Effects**		
	14:00-14:15	Tricarico	Field Quantization in Arbitrarly-Shaped Metal Nanoparticles
	14:15-14:30	Giannone	Molecular Switches interacting with Localized Surface Plasmons: a Density Functional Theory Approach
	14:30-14:45	Della Sala	Ab initio Plasmonics of Externally Doped Silicon Nanocrystals
	14:45-15:00	D'Agostino	The Role of Quantum Mechanical Effects in Metal-Molecule Interactions
Esposito	**Metasurfaces & Gratings**		
	15:00-15:15	Chowdhury	Large-area nanostripe gratings for flexible NIR plasmonics and optoelectronics
	15:15-15:30	Marabelli	Anomalous effective permittivity of Vogel spiral metamaterials
	15:30-15:45	Occhicone	Mid-infrared Bloch Surface Waves for Sensing Biomolecules by their Fingerprints
	15:45-16:00	Papari	Sensing using Surface Plasmon Polaritons in THz metagrids
	16:00-16:15	**Conference Awards**	
	16:15-16:30	**Closing Remarks**	

Keynote Regular Session Coffee-break/lunch/aperitif Opening/Closing Awards

Wednesday June 19

Putting Nanoplasmonics to work!

R. Quidant [1, 2]
(1) *ICFO- Institut de Ciencies Fotoniques, Barcelona*
(2) *ICREA- Institució Catalana de Recerca i Estudis Avançats, Barcelona*

Fifteen years of very active research in the field plasmonics have enabled us to considerably advance light control on the nanometer scale. Beyond the original *peak of inflated expectation*, the assets of nanoplasmonics over other technologies became clearer along with its limitations. More recently, the field has entered into the "*slope of enlightenment*" in which the actual contribution of metallic nanostructures to future technologies has been better identified. In this talk, we will review different aspects of our research where metallic nanostructures are used as an enabling tool towards novel photonic functionalities.

1. On-a-chip biosensing with optical nanoresonators — Owing to the subwavelength confinement of plasmonic fields, the resonances of optical nano-antennas are extremely sensitive to tiny changes of their surroundings, as for instance induced by the binding of molecules at their surface. This makes them very good candidates for compact, sensitive and low cost biosensing. While last two decades have witnessed a diversity of nano-optical systems with outstanding sensitivity, their implementation into a real analytical device is only at its infancy. In this context, we present here our latest advances in the optical, label-free detection of biomarkers based on gold and silicon nanoantennas integrated into a state-of-the-art microfluidic platform [1-3].

2. Nanoscale heat control and its applications – Recent years have witnessed a growing interest in controlling temperature on the nanoscale motivated by applications to different fields, including information technology, chemistry and medicine. Under illumination at its plasmon resonance, a metal nanoparticle features enhanced light absorption, turning it into an ideal nano-source of heat, remotely controllable by light. Such a powerful and flexible photothermal scheme sets the basis of the emerging and fast-growing field of *thermoplasmonics*. In this second part of the talk we first briefly present the specificities of heat generation in metal nanoparticles. We then focus on the experimental methods that have been developed to further understand and engineer plasmonic-assisted heating processes on the nanoscale. Finally, we present a selection of applications, focusing on reconfigurable planar optics, 3D printing and biomedicine [4, 5].

References

[1] O. Yavas et al, ACS Sensors **3**, 1376 (2018)
[2] O. Yavas et al, ACS Nano **13**, 4582 (2019)
[3] J. Garcia et al, ACS Photonics **5**, 3673 (2018)
[4] A. Powell et al, Nano Lett. **18**, 6660 (2018)
[5] De Miguel et al, Nano Lett. **19** 2524 (2019)

Biosensors

Exponential sensitivity of a bound-state-in-continuum photonic crystal sensor

Silvia Romano[1*], Gianluigi Zito[2], Sofía N. Lara Yépez[1], Erika Penzo[3], Stefano Cabrini[3], Giuseppe Coppola[1], Ivo Rendina[1], Vito Mocella[1]

[1]*Institute for Microelectronics and Microsystems, National Research Council, CNR-IMM – Unità di Napoli, Napoli, Italy*
[2]*Institute of Protein Biochemistry, National Research Council, CNR-IBP, Napoli, Italy*
[3]*Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, USA*

**silvia.romano@na.imm.cnr.it*

Keywords: photonic crystal, field enhancement, bound states in continuum, biosensors

Optical biosensors are widely-used devices that offer great advantages over conventional detection techniques in many crucial applications from health-care and food quality control to environmental analysis and industrial process monitoring [1], [2]. A widespread class of label-free photonic biosensors exploits optical resonance effects where the shift in the resonance wavelength in response to a change of the refractive index (RI) of the medium surrounding the sensing area gives information about the analyte. Based on this mechanism, surface plasmon resonance (SPR) and localized SPR (LSPR) devices are widely employed and are typically characterized by high values of sensitivity ($S = \Delta RI/\Delta\lambda$) [3]. However, the large plasmonic optical losses, leading to resonance broadening, strongly affect their main figure of merit (FOM), commonly defined as the ratio between the sensitivity and the resonant peak width. In addition, these high optical losses induce local heating that can cause damages to the biological material under investigation and to the nanostructure itself by altering its photonic properties. For this reason, great efforts have been made to overcome the limits of the conventional plasmonic devices, taking advantage of near-field enhancement in loss-free dielectric material [4], [5].
It has been demonstrated that an all-dielectric photonic crystal metasurface (PhCM) can support Bound States in Continuum (BIC), resonant states of infinite lifetime, experimentally involving very narrow coupled resonances, with a high Q-factor and a possible extremely large field intensity enhancement, up to 6 orders of magnitude larger than the intensity of the incident beam [6], [7]. Herein, the design and realization of an innovative sensing platform for bulk and surface measurement is reported[8]. The device exploits a normal-to-the-surface optical launching scheme to easily excite high Q-factor resonances associated with BICs supported by the PhCM. The sensing performances of the device and the capability of the metasurface resonance, showing a large near-field amplification, to sense the perturbation of the dielectric environment have been characterized. In addition, the ultra-high figure of merit of the device enables the recognition of protein-protein interaction and the detection of low molecular weight molecules[9], [10]. Finally, we provide more insight into the physics underlying the sensing mechanism by theoretically and experimentally investigating the exponential-growth sensitivity curve of our BIC-based device. In particular, the impact of the system symmetrization (substrate/PhCM/analyte) on the performance of the sensing mechanism has been studied. This behavior is explained in terms of the physical superposition of the field with the surrounding medium under investigation and paves the way to the design and realization of novel high-performances all-dielectric sensing platform.

References

[1] S. M. Borisov and O. S. Wolfbeis, "Optical biosensors," *Chem. Rev.*, vol. 108, no. 2, pp. 423–461, 2008.
[2] F. S. Ligler and F. S. Ligler, "Perspective on Optical Biosensors and Integrated Sensor Systems," *Anal. Chem.*, vol. 81, no. 2, pp. 519–526, 2009.
[3] J. Homola, S. S. Yee, and G. Gauglitz, "Surface plasmon resonance sensors: review," *Sensors Actuators B Chem.*, vol. 54, no. 1, pp. 3–15, 1999.
[4] E. De Tommasi, A. Chiara De Luca, S. Cabrini, I. Rendina, S. Romano, and V. Mocella, "Plasmon-like surface states in negative refractive index photonic crystals," *Appl. Phys. Lett.*, vol. 102, 2013.
[5] J. B. Khurgin, "How to deal with the loss in plasmonics and metamaterials," *Nat. Nanotechnol.*, vol. 10, no. 1, pp. 2–6, 2015.
[6] C. W. Hsu, B. Zhen, A. D. Stone, J. D. Joannopoulos, and M. Soljacic, "Bound states in the continuum," *Nat. Rev. Mater.*, vol. 1, no. 9, 2016.
[7] V. Mocella and S. Romano, "Giant field enhancement in photonic resonant lattices," *Phys. Rev. B*, vol. 92, no. 15, p. 155117, 2015.
[8] S. Romano *et al.*, "Surface-Enhanced Raman and Fluorescence Spectroscopy with an All-Dielectric Metasurface," *J. Phys. Chem. C*, vol. 122, no. 34, pp. 19738–19745, 2018.
[9] S. Romano *et al.*, "Optical biosensors based on photonic crystals supporting bound states in the continuum," *Materials*

Exploring dimensionality for biosensing

Francesca Santoro

Italian Institute of Technology, Naples, 80125, Italy
francesca.santoro@iit.it

The interface between biological cells and non-biological materials has profound influences on cellular activities, chronic tissue responses, and ultimately the success of medical implants and bioelectronic devices. For instance, electroactive materials in contact with cells can have very different composition, surface topography and dimensionality. Dimensionality defines the possibility to have planar (2D), pseudo-3D (planar with nano-micropatterned surface)[1] and 3D conductive materials (i.e. scaffolds) in biosensing devices. Their success for both *in vivo* and *in vitro* applications lies in the effective coupling/adhesion of cells/tissues with the devices' surfaces. It is known how a large cleft between the cellular membrane and the electrode surface massively affects the quality of the recorded signals or ultimately the stimulation efficiency of a device.

However, this field is hindered by lack of effective means to directly visualize in 3D cell-material interface at the relevant length scale of nanometers. In this work, we explored the use of ultra-thin plasticization technique[2] to cells for the first time on materials which differ in dimensionality[3], particularly focusing on the optimization of this procedure for 3D cell-materials interfaces which have been unexplored so far. We have characterized how cells differently elongate and deform their membranes in response to the dimensionality of the electroactive materials and the relevant processes at the biointerface. In this way, we are able to define a set of optimal conditions for cell-chip coupling which enable an appropriate approach for designing bioelectronics platforms for both in vivo and *in vitro* applications in 3 dimensions.

1. Santoro, F., Zhao, W., Joubert, L.-M., Duan, L., Schnitker, J., van de Burgt, Y., Lou, H.-Y., Liu, B., Salleo, A., Cui, L., Cui Y., Cui B., Revealing the Cell–Material Interface with Nanometer Resolution by Focused Ion Beam/Scanning Electron Microscopy. ACS Nano, 2017
2 Li X., Matino L., Zhang W., Klausen L., McGuire A., Lubrano C., Zhao W., Santoro F., Cui B., A nanostructure platform for live cell manipulation of membrane curvature, Nature Protocols, just accepted.
3 Iandolo D., Pennacchio F. A., Mollo V., Rossi D., Dannhauser D., Cui B., Owens R. M., Santoro F., Electron Microscopy for 3D Scaffolds–Cell Biointerface Characterization, Advanced Biosystems, 2018.

Plasmonic Hydrogels for Pan-Specific Capture and Ultrasensitive Raman Detection of Persistent Organic Pollutants

Ivano Alessandri[1,2,3], Nicolò Bontempi[2], Stefania Federici[2,4], Matteo Ferroni[1,5], Alessandra Gianoncelli[2,6], Irene Vassalini[1,2,3]

[1]*Department of Information Engineering (DII), University of Brescia, via Branze 38, 25123 Brescia, Italy. E-mail: ivano.alessandri@unibs.it*

[2]*INSTM, UdR Brescia, via Branze 38, 25123 Brescia, Italy*

[3]*INO-CNR, via Branze 38, 25123 Brescia, Italy*

[4]*Chemistry for Technologies Laboratory, Mechanical and Industrial Engineering Department (DIMI), University of Brescia, via Branze 38, 25123 Brescia, Italy.*

[5] *IMM-CNR, via Gobetti 101, 40129 Bologna, Italy*

[6]*Department of Molecular and Translational Medicine, University of Brescia, Viale Europa 11, 25123, Brescia, Italy.*

Keywords: Plasmonic and Dielectric Nanoantennas, Sensors and Biosensors, Devices and Applications

Water purification and quality monitoring is one of the hottest topics in environmental science. [1] Surface Enhanced Raman Scattering (SERS) can represent a unique tool for ultrasensitive detection of water pollutants. [2-5] Here we demonstrate that non-toxic plasmonic hydrogels, made by a rational synergistic combination of different functional units (optical nanoantennas, receptors, water-absorbing matrix), are able to efficiently capture and detect different types of organic pollutants, including polychlorinated biphenyls, pharmaceutic compounds and organic dyes. Two major results are highlighted:

-The general affinity of β-cyclodextrin receptors towards benzene and heterocyclic rings makes these nanocomposite hydrogels universal scavengers for the most common organic pollutants. In the present case, these receptors have been linked to silver plasmonic nanoantennas and embedded in alginate beads that can be directly dispersed and recovered from real water, as well as other common solvents (ethanol, acetone…) utilized in extraction protocols, which makes this approach easily extensible to a wide range of analytical targets and methods.

- The alginate drying-induced self-assembly of the Ag@cyclodextrin receptors enables ultrasensitive detection of pollutants by SERS. Unlike conventional SERS, here the Raman fingerprints of the low-concentrated pollutants can be reconstructed by principal component analysis. This indirect-detection approach boosts the Raman sensitivity, getting rid of common pitfalls that usually prevent the reproducibility of SERS analysis.

For example, in the case of polychlorinated biphenyls, the treatment of SERS spectra by principal component analysis allowed to extend the detection limit to the level of 1 ng/L, which is unprecedented and two orders of magnitude lower than that requested by current legislation.

References

[1] P.J. Vikesland, Nat. Nanotechnol. **13**, 651-660 (2018).
[2] I. Alessandri, J. R. Lombardi, Chem. Rev. **116**, 14921−14981, (2016).
[3] I. Alessandri, J. Am. Chem. Soc. **135**, 5541–5544, (2013).
[4] N. Bontempi, I. Vassalini, I. Alessandri, J. Raman Spectrosc. **49**, 943-953, (2018).
[5] N. Bontempi, I. Vassalini, S. Danesi, I. Alessandri, Chem. Commun. **53**, 10382-10385 (2017).

Plasmonic Metasurface based on Cross-Shaped Nanoantennas for Biosensing Applications

*Valentina Di Meo[1,2], Alessio Crescitelli[1], Andrea Caporale[3], Mohammed Janneh[4], Elia Palange[4], Andrea De Marcellis[4], Marianna Portaccio[5], Maria Lepore[5], Ivo Rendina[1], Menotti Ruvo[3], Emanuela Esposito[1]**

[1] Institute for Microelectronics and Microsystems, National Research Council, Naples, Italy*
[2] CeRICT scrl, Benevento, Italy*
[3] Institute of Biostructure and Bioimaging, National Research Council, Naples, Italy*
[4] Department of Industrial and Information Engineering and Economics, University of L'Aquila, Italy*
[5] Department of Experimental Medicine – University of Campania "L. Vanvitelli", Naples, Italy*
**corresponding author: emanuela.esposito@cnr.it*

Keywords: Label-free biosensor, plasmonic nanoantennas, metasurface, nanotechnology

In last years, surface enhanced infrared (IR) absorption (SEIRA) spectroscopy has obtained a remarkable attention as a significant tool for the unequivocal identification of molecular species. SEIRA technique allows the detection of very small molar concentrations (such as monolayers) of the analytes covering the metasurface that acts as the effective sensor for this spectroscopic method. The growing attention of this technique is also due to its significant signal enhancement obtained using resonant plasmonic Nano Antennas (NAs) [1]. Metallic NAs transform propagating optical radiation into enhanced optical fields localized on nanometric regions of their surface, giving arise to localized surface plasmon resonances [2]. SEIRA based on resonant metallic NAs has a great potential for sensing applications, merging the specificity of IR spectroscopy with the high sensitivity assured by plasmonic nanostructures [1]. In this work, we report on the design, fabrication and experimental characterization of plasmonic metasurfaces based on 2D arrays of gold cross-shaped NAs as SEIRA employable in biosensing applications such as the vibrational detecting of bio-chemical analytes. The realized plasmonic metasurfaces constitute a biosensing chip with a large (several mm^2) active area. The cross-shape designed NAs are insensitive to the polarization of the electromagnetic radiation impinging the active area and guarantee, at the same time, a significant near-field signal enhancement due to the coupling between neighbour NAs. The resonance peak of the plasmonic metasurface can be tuned by varying only the length (L) of NAs. As shown in Figure 1, the sensor is used to detect small molecules (Figure 1a), with molecular weight (MW) of less than 500 g/mol and a polymer (PMMA) with MW ~ 95,0000 g/mol (Figure 1b) in the mid-infrared range. In presence of a layer of PMMA that contains repeated carbonyl groups, the SEIRA enhancement has been found to be as high as 48,000 relative to the absorption peak at 1720 cm^{-1}, arising from the stretching vibration of the carbonyl group of the PMMA. For small molecules (Pentinyl Cisteina Amide) containing triple bond groups resonating at about 2100 cm^{-1} a sensitivity of 600 nm/RIU has been found for amounts of immobilized compound as low as 0.7 fmoles.

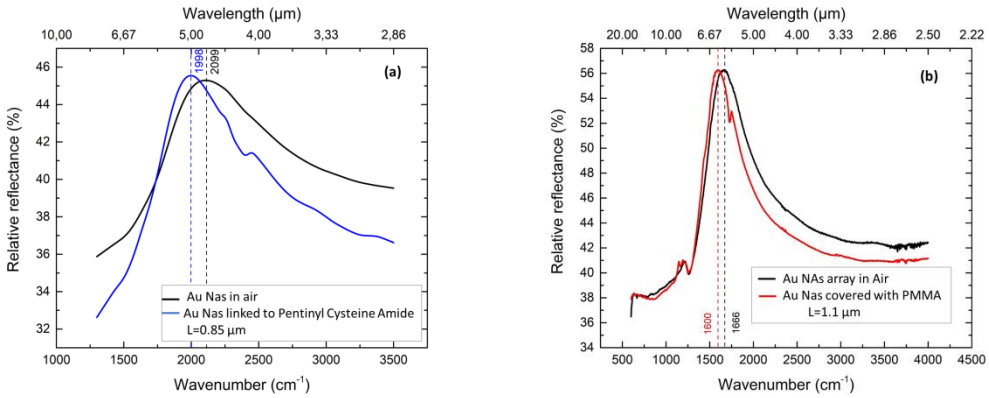


Figure 1: Reflectance curve of NAs array (black) in air versus reflectance curve (blue) of NAs array linked to Pentinyl Cystein Amide (a) and reflectance curve (blue) of NAs array covered with a 50 nm PMMA layer (b).

References

[1] F. Neubrech, C. Huck, K. Weber, A. Pucci, H. Giessen, Surface-Enhanced Infrared Spectroscopy Using Resonant Nanoantennas, Chem. Rev. 117, 5110−5145 (2017).
[2] J. Homola, S.S. Yee, G. Gauglitz, Surface plasmon resonance sensors: review, Sens. Actuators B 54, 3-5 (1999).

Plasmonics for Chemistry and Bio-Chemistry

Plasmonics for Chemistry: sensing and driving chemical reactions using plasmons

Andrea Baldi[1]
[1]*DIFFER – Dutch Institute for Fundamental Energy Research, Eindhoven, The Netherlands,*
a.baldi@differ.nl

Keywords: Sensor and Biosensors, Thermo-Plasmonics, Devices and Applications.

Metal nanoparticles can sustain localized surface plasmon resonances, which are light-driven resonant oscillations of their free electrons. Thanks to their strong spectral dependence on the nanoparticle size, shape, composition, and dielectric environment these resonances can be used as nanoscale probes for a large range of chemical and physical processes. Furthermore, their non-radiative decay into "hot" charge carriers and heat can be exploited to accelerate and modify chemical reactions at the metal nanoparticle surface [1].

Here, I will first show how we use plasmon resonances to study hydrogen absorption in individual metal nanocrystals in an environmental transmission electron microscope. Such single-particle approach offers unprecedented insight into the phase transition of nanomaterials used for energy storage [2–5]. Additionally, I will present how we use localized surface plasmon resonances to probe charge equilibration reactions in metal@semiconductor core@shell nanoparticles. Detailed characterization of the plasmon resonance peaks allows us to challenge the established understanding of charge equilibration in hybrid metal@semiconductor nanostructures [6]. Finally, I will demonstrate how plasmon resonances can be exploited to drive the synthesis of hierarchical nanostructures in solution and discuss the relative contributions of photo-thermal heating versus non-thermal processes such as near-field effects and hot charge carriers [7].

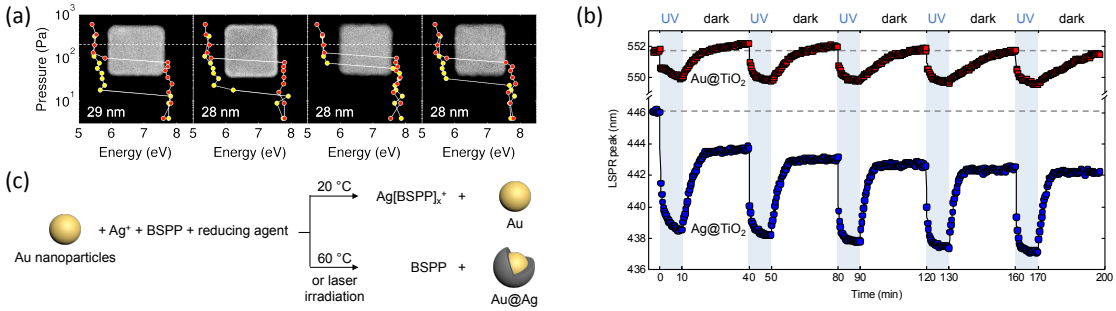


Figure 1: (a) Hydrogen loading (*red dots*) and unloading (*yellow dots*) isotherms for four individual palladium nanocrystals. The isotherms are plotted as the H_2 gas pressure versus the bulk plasmon energy of the nanoparticles, as measured by electron-energy loss spectroscopy in the TEM. The plasmon energy varies between 7.8 eV in Pd and 5.5 eV in PdH_x indicating 1st order phase transitions. (b) Plasmon resonance shifts measured for solutions of core@shell Au@TiO_2 and Ag@TiO_2 nanoparticles, under five cycles of UV irradiation followed by charge equilibration in the dark. The blue shifts under UV irradiation are due to electron accumulation in the TiO_2 shells. (c) Schematic of the chemical reaction used to quantify the relative contribution of photo-thermal heating and non-thermal effects in plasmon-driven synthesis of core@shell Au@Ag nanoparticles.

References

[1] J. A. Dionne, A. Baldi, B. Baum, C.-S. Ho, V. Jankovic, G. V. Naik, T. C. Narayan, J. A. Scholl, and Y. Zhao, MRS Bulletin **40**, 1138-1145 (2015).
[2] A. Baldi, T. C. Narayan, A.-L. Koh, and J. A. Dionne, Nature Mater. **13**, 1143-1148 (2014).
[3] T. C. Narayan, A. Baldi, A.-L. Koh, R. Sinclair, and J. A. Dionne, Nature Mater. **15**, 768–774 (2016).
[4] T. C. Narayan, F. Hayee, A. Baldi, A.-L. Koh, R. Sinclair, and J. A. Dionne, Nature Comm. **8**, 14020 (2017).
[5] F. Hayee, T. C. Narayan, N. Nadkarni, A. Baldi, A. L. Koh, M. Z. Bazant, R. Sinclair, and J. A. Dionne, Nature Comm. **9**, 1775 (2018).
[6] M. Parente, S. Sheikholeslami, G. V. Naik, J. Dionne, and A. Baldi, J. Phys. Chem. C **122**, 23631-23638 (2018).
[7] R. Kamarudheen, G. W. Castellanos, L. P. J. Kamp, H. J. H. Clercx, and A. Baldi, ACS Nano **12**, 8447-8455 (2018).

Electrophysiology for the masses: a cost-effective ecosystem for the study of electrogenic cells.

Leonardo D. Garma[1], Laura M. Ferrari[2], Michele DiPalo[3], Francesco Greco[2], Francesca Santoro[1]

[1]*Center for Advanced Biomaterials for Healthcare, Istituto Italiano di Tecnologia, Naples, Italy,*

Leonardo.garma@iit.it

[2]*Center for Micro-BioRobotics@SSSA, Istituto Italiano di Tecnologia, Pontedera, Italy*

[3]*Istituto Italiano di Tecnologia, Genoa, Italy*

Keywords: Sensor and Biosensors, Devices and Applicationss.

In vitro multi-electrode array (MEA) technology is nowadays involved in a wide range of applications beyond neuroscience, such as cardiac electrophysiology and bio-interface studies. However, the cost of commercially available acquisition systems and MEAs severely limits its adoption outside specialized laboratories.
Thus, the availability of low-cost tools is important to allow research labs worldwide to exploit this technology. In particular, cost-effective solutions would enable non-specialized labs to incorporate electrophysiological measurements as a routine procedure.
Here, we present a multifunctional comprehensive multifunctional *in vitro* MEA acquisition system[1] and PEDOT:PSS-based inkjet printed MEA chips which can be produced at a fraction of the costs of current commercial versions. We demonstrate the capabilities of the acquisition system by employing it to i) characterize commercial MEA devices by means of electrical impedance measurements ii) record activity from cultures of HL-1 cells extracellularly, and iii) electroporate HL-1 cells through nanostructured MEAs and record intracellular signals. We demonstrate the feasibility of fabricating PEDOT:PSS-based flexible MEAs compatible with the acquisition system using inkjet printing technology. We demonstrated that the chips are capable of acquiring extracellular action potentials from cultures of cardiomyocyte-like cells (HL-1), obtaining signals entirely comparable to those acquired using commercial acquisition systems and silicon-based chips.

References

[1] L. D. Garma *et al.*, "Cost-effective and multifunctional acquisition system for in vitro electrophysiological investigations with multi-electrode arrays," *PLOS ONE*, vol. 14, no. 3, p. e0214017, Mar. 2019.

Control of Coherences and Optical Responses of Pigment−Protein Complexes by Plasmonic Nanoantennae

Ciro A. Guido[1], Stefano Caprasecca[2] and Benedetta Mennucci [2]
[1]Dip. Scienze Chimiche, Università di Padova, via F. Marzolo 1, I-35131 Padova, Italy.
ciro.guido@unipd.it
[2] Dip. Chimica e Chimica Industriale, Università di Pisa, via G. Moruzzi 13, I-56124 Pisa, Italy

Keywords: Plasmonic and dielectric nanoantennas, Plasmon-exciton polaritons, Spectroscopy and nano-imaging.

The key for light-harvesting in pigment-protein complexes are molecular excitons, delocalized excited states comprising a superposition of excitations at different molecular sites [1]. There is experimental evidence that the optical response due to such excitons can be largely affected by plasmonic nanoantennae [2]. In this contribution, I will give an overview of a recent study [3], were we employed a multiscale approach combining time-dependent density functional theory and polarizable classical models [4-6] to study the optical behavior of the LH2 complex present in bacteria when interacting with a gold nanorod. The simulation not only reproduces the experiments [7] but also explains their molecular origin [8]. By tuning the chromophoric unit and selectively switching on/off the excitonic interactions, as well as by exploring different setups, we clearly show that the dramatic enhancement in the optical response, unexpectedly, is not accompanied by changes in the coherences. Instead polarization effects are dominant. These results can be used to design an optimal control of the light-harvesting process through plasmonic nanoantennae [3,8].

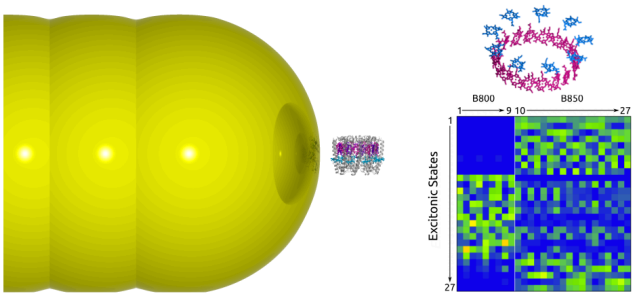


Figure 1: Schematic representation of the LH2-NR assembly and the relative excitonic matrix.

References

[1] G. D. Scholes, G. Rumbles, Nat. Mater. 5, 683-696. (2006).
[2] S.Mackowski, S. Wormke, A. J. Maier, T. H. P: Brotosudarmo, H. Harutyunyan, A. Hartschuh, A. O. Govorov, H. Scheer and C. Brauchle, Nano Lett. 8, 558−564 (2008).
[3] S. Caprasecca, C. A. Guido and B. Mennucci, J. Chem. Phys. Lett. 7, 2189−2196 (2016).
[4] C. Curutchet, A. Muñoz-Losa, S. Monti, J. Kongsted, G. D. Scholes, B. Mennucci, J. Chem. Theory Comput. 5, 1838-1848 (2009).
[5] O. Andreussi, S. Corni, B. Mennucci, J. Tomasi, J. Chem. Phys. 121, 10190 (2004).
[6] C. A. Guido and S. Caprasecca, Int J Quantum Chem. e25711 (2018).
[7] E. Wientjes, J. Renger, A. G. Curto, R. Cogdell, N. F. van Hulst, Phys. Chem. Chem. Phys.16, 24739-24746 (2014).
[8] O. Andreussi, S. Caprasecca, L.Cupellini, I. Guarnetti-Prandi, C.A. Guido, S. Jurinovich, L. Viani, and B. Mennucci J. Phys. Chem. A 119, 5197-5206 (2015).

Remotely Generated Hot-Electron using Surface Plasmon Polaritons

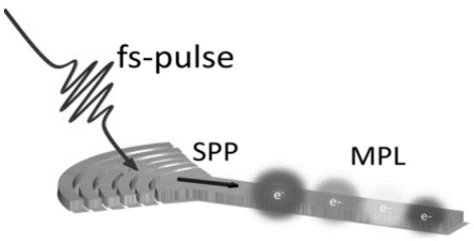
Romain Hernandez[1], *Renato Juliano Martins*[2], *Adrian Agreda*[2], *Marlene Petit*[2],
Jean-Claude Weeber[2], *Alexandre Bouhelier*[2], *Benoit Cluzel*[2], and *Olivier Demichel*[2],
[1]*Laboratoire Interdisciplinaire Carnot de Bourgogne (ICB), Dijon, France, romain.hernandez@u-bourgogne.fr*
[2]*Laboratoire Interdisciplinaire Carnot de Bourgogne (ICB), Dijon, France*

Keywords: Nonlinear plasmonics, Nanophotonics and Hybrid Plasmonics, Spectroscopy and nano-imaging.

Hot-electrons within metallic devices are quite promising to set off tremendous physico-chemical reactions and photocaltalysis [1]. Indeed, the high energy of hot-carriers remaining within nanostructures yields high local temperature at their boundaries. For this purpose, controlling their generation at the nanoscale and their dynamics within plasmonic devices is a key for the future development of hybrid hot-electrons technologies [2]. However, the efficiency of hot-electrons generation is quite low and Surface Plasmons Polaritons (SPPs) are generally used to enhance it through a mechanism called plasmon-induced hot-electron generation. Indeed, nanoantennas, which allow for localized SPP resonances, are known to produce efficiently hot-electrons under femtosecond laser pulse excitation in the near IR [3, 4].

Here we present the first remote generation of hot-electrons assisted by propagative SPPs. For that a plasmonic waveguide efficiently launch SPPs thanks to a grating coupler (Figure 1). Surface plasmons carry enough energy to generate hot-carriers at distance up to 10 microns. More precisely, surface plasmons loose energy towards the medium leading to hot-electrons generation which relaxe emitting a multi-photon photoluminescence (MPPL). MPPL is then used to investigate both hot-electrons generation and dynamics. The spatial distribution of plasmon-assisted hot-electrons is achieved by recording the MPPL signal by hyperspectral near-field microscopy techniques (Figure 2) [5]. We find that their spatial distribution is mapping by the surface plasmon field intensity and that such hot-carriers do not diffuse on distance higher than few nanometers. Moreover, a narrowing of the spectrum along SPP propagation is observed which is related to a decrease of the hot-electron cloud temperature because of SPP damping. We demonstrate that the energy distribution of hot-carriers is correlated to the electromagnetic field intensity of the surface plasmon that decays along the waveguide.

This work opens the way to management at distance of hot-carriers within more complex architecture at the nanoscale and of their dynamics in the picosecond domain.



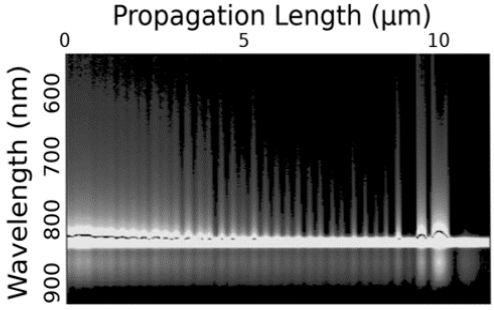


Figure 1 (left): Plasmonic waveguide with grating coupler showing SPP propagation and hot-electrons relaxing emitting MPPL. Figure 2 (right) : Hyperspectral near-field measurement showing the spectral variation of MPPL along the propagation of SPP

References

[1] Mark L. Brongersma, Naomi J. Halas, and Peter Nordlander. Plasmon-induced hot carrier science and technology. Nature Nanotechnology 10, 25 34 (2015).
[2] Wei Li and Jason G. Valentine. Harvesting the loss: surface plasmon-based hot electron photodetection. Nanophotonics 2017, 6(1):177 191.
[3] Regis Mejard, Anthonin Verdy, Marlene Petit, Alexandre Bouhelier, Benoit Cluzel, and Olivier Demichel. Energy-resolved hot-carrier relaxation dynamics in monocrystalline plasmonic nanoantennas. ACS Photonics, 2016, 3(8), pp. 1482 1488.
[4] Paolo Biagioni, Daniele Brida, Jer-Shing Huang, Johannes Kern, Lamberto Duo, Bert Hecht, Marco Finazzi, and Giulio Cerullo. Dynamics of Four-Photon Photoluminescence in Gold Nanoantennas. Nano Letters, 2012, 12(6), pp. 2941 2947.
[5] Jean Dellinger, K. Van Do, Xavier Le Roux, Frederique de Fornel, Eric Cassan, and Benoit Cluzel. Hyperspectral optical near-field imaging: Looking graded photonic crystals and photonic metamaterials in color. Applied Physics Letters, 101(14):141108, 2012.

Plasmonic Enhanced Fluorescence as an Effective Biosensing Platform: Detection of Immunoglobulins in Urine for POC Applications

Bartolomeo Della Ventura[1,2], Monica Gelzo[3], Edmondo Battista[4], Alessandro Alabastri[5], Andrea Schirato[2], Giuseppe Castaldo[3], Gaetano Corso[6], Francesco Gentile[7], and Raffaele Velotta[1]

[1]*Dip. di Fisica E. Pancini, Università di Napoli Federico II, Napoli, Italy, dellaventura@fisica.unina.it*

[2]*Dipartimento di Fisica, Politecnico di Milano.Milano, Italy*

[3]*Dip. di Medicina Molec. e Biotec. Mediche, Università di Napoli Federico II and CEINGE, Napoli, Italy*

[4]*Centro di Ricerca Interdip. sui Biomateriali, Università degli Studi di Napoli Federico II, Napoli, Italy*

[5]*Electrical and Computer Engineering Department, Rice University, Houston, United States*

[6]*Dipartimento di Medicina Clinica e Sperimentale, Università di Foggia, Foggia, Italy*

[7]*Dip. di Ingegneria Elettrica e Tecn. dell'Informazione, Università di Napoli Federico II, Napoli, Italy*

Keywords: Sensor and Biosensors, Devices and Applications

Metallic surfaces can strongly confine electromagnetic field through its coupling to the surface plasmons. This interaction allows a large enhancement of the electromagnetic field intensity, which provides an increase of excitation rate, a raise of quantum yield and an amplification of fluorescence signal by several orders of magnitude. The coupling of metallic nanostructures with specific bio-elements, as the antibodies, make them a powerful biosensors that can be effective in Point-Of-Care (POC) applications. Here, we report the behavior of an analytical device in detecting immunoglobulins in real urine samples that shows a limit of detection of approximately 8 µg/L and a linear range of 10−100 µg/L well below the detection limit of nephelometric method, which is the reference method for this analysis. The principle of detection of IgG and the resulting dose−response curve are reported in Figure 1. The antibodies (antihuman IgG) are tethered covalently to the nanostructured surface by means of a novel photochemical technique developed in our group, which leads to upright orientation (Figure 1a) [1]. The human IgG in urine is recognized and captured by the primary Ab, so that a secondary fluorescent Ab (antihuman IgG tagged with FITC) is able to bind the Ab-antigen complex forming a sandwich structure. In view of the linear dimensions of the antibody, the distance between the fluorophore and the surface is expected to be 10−30 nm well within the effective distance leading to the Plasmonic Enhanced Fluorescenec, the latter being easily detected by examining the substrate under a standard fluorescence microscope (Figure 1b). The fluorescence intensity measured at several human IgG concentrations is reported in Figure 1(c) with the best fit of the experimental data [2].

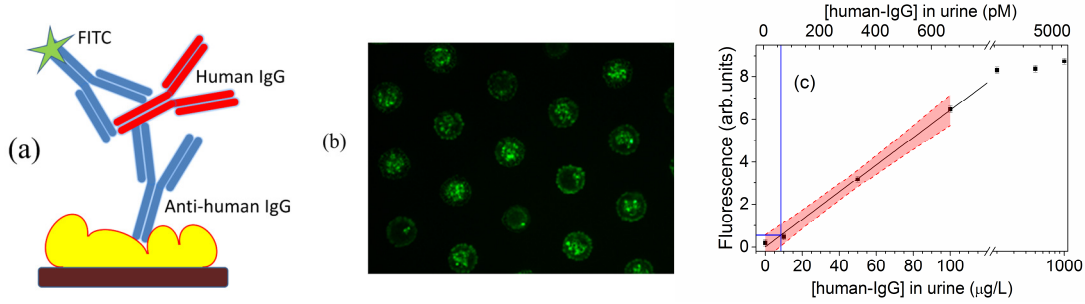


Figure 1: Caption (a) Detection scheme: Antibodies tethered to the substrate by PIT recognize the antigen (human IgG). Secondary antibodies are tagged by FITC and bind the human IgG in a sandwich configuration. (b) Image of the substrate collected at [human IgG] = 200 µg/L with an integration time of 2 s and a magnification 50×. The lamp of the fluorescence microscope excites the FITC at 488 nm and the emitted light in the range 515−545 nm is collected. (c) Fluorescence intensity vs human IgG concentration. The area between the confidence bands at 95% level is highlighted in red.

Our approach, which is inherently extendable to multiplexing analysis, has been successfully validated on serum samples by comparing IgG concentrations values obtained by the biosensor with those provided by a nephelometer.

References

[1] B. Della Ventura *et al*. "Light assisted antibody immobilization for bio-sensing". Biomed. Opt. Express **2**, 3223-3231 (2011).

[2] B. Della Ventura *et al*. "Biosensor for Point-of-Care Analysis of Immunoglobulins in Urine by Metal Enhanced Fluorescence from Gold Nanoparticles". ACS Applied Materials & Interfaces **11**, 3753-3762 (2019).

Study of the Fluorescence Emission at the Surface of 1D-Photonic Crystal Biochips

E. Sepe[1], A. Sinibaldi[1], N. Danz[2], P. Munzert[2], F. Michelotti[1]
[1]Department of Basic and Applied Science for Engineering, SAPIENZA University of Rome, Via Antonio Scarpa 16, 00161 Rome, Italy
[2]Fraunhofer Institute for Applied Optics and Precision Engineering IOF, Albert-Einstein-Str. 7, 07745 Jena, Germany

Keywords: Sensor and Biosensors, Nanophotonic and Hybrid Plasmonics

Nowadays, photonic crystals are widely used in several areas of biosensing applications due to their great versatility [1]. In particular, with the increase of the cancer incidence rate per year, they can be used as a tool for the detection of the disease at its early stage. Herein, we present disposable one-dimensional photonic crystal biochips (1DPC) that are used for cancer biomarkers detection. Such 1DPC, under proper illumination conditions, sustains Bloch surface waves (BSW) that are strongly confined at the surface due to total internal reflection and to the photonic bandgap. Such field confinement can be translated in a strong field enhancement at the surface, which is of particular interest in biosensing.
To demonstrate the presence of a cancer biomarker in several biological matrices, we made use of a read-out platform that can work in both label-free and fluorescence detection modes. In the label-free operation mode, the BSW excitation appears as a dip in the angular reflectance spectrum. According to the interactions that take place at the surface, the angular position of such a dip shifts as a function of refractive index change at the interface. Moreover, by adding directly fluorophores or molecules labelled with fluorescent tags, it is also possible to work in the fluorescence mode, in which fluorescence angular spectra are acquired. Furthermore, the BSW emission matches the fluorophores emission leading to a strong directional fluorescence emission [2]. Despite the great sensitivity offered by the fluorescence detection mode, the measurements are affected by a phenomenon that cannot be neglected when quantitative information is needed: photobleaching. Photobleaching denotes the irreversible loss of fluorescence emitted energy of a dye that dramatically changes its absorption and emission properties. The rate of such a fluorescence decay is affected by several factors such as the power of the illumination beam, the exposure time, and the photonic crystal structure itself. In addition, it is also influenced by the molecule's dipolar moment. In particular, fluorophores having a dipolar moment oriented parallel to excitation polarized light will be excited preferentially. As a consequence, the fluorescence emission will be polarized and the fluorophores distribution anisotropic. This effect is more or less significant depending on how the fluorophores are strongly or weakly bound to the surface [3].
In this work, we present, for the first time, how photobleaching affects a biosensing assay for cancer biomarker detection. Figure 1 describes the role played by photobleaching. In fluorescence mode, in order to collect the fluorescence angular spectra is needed to record more than one scan (minimum 8, average duration of each scan 30 sec). As the number of scans increases, fluorophores are gradually switched off losing their ability to emit light. The exponential decay is well described in the inset, where the integrated fluorescence signal is plotted as a function of scans. In order to manage photobleaching effects, from the fitting curve (dashed black line) one could extrapolate the maximum value as the photobleaching has not already occurred (scan number 0). This approach will permit to precisely quantify cancer biomarker concentrations in complex biological matrices by taking into account the photobleaching issues.

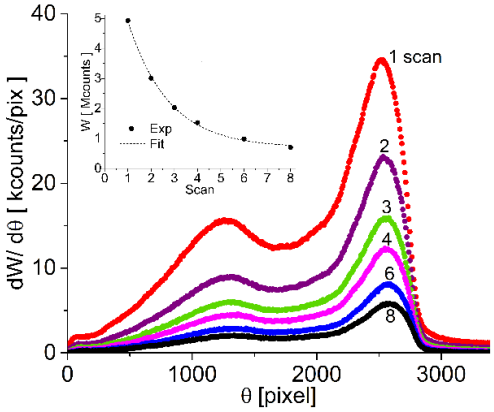


Figure 1: Fluorescence angular spectra acquired after successive scans.
(in the inset: the integrated fluorescence signals over the scans).

References

[1] B. T. Cunningham *et al.*"Recent Advances in Biosensing With Photonic Crystal Surfaces: A Review," *IEEE Sensors*, vol. 16, no. 10, pp. 3349–3366, 2017.
[2] A. Sinibaldi *et al.*, "Detection of soluble ERBB2 in breast cancer cell lysates using a combined label-free/fluorescence platform based on Bloch surface waves," *Biosens. Bioelectron.*, vol. 92, no. February, pp. 125–130, 2017.
[3] M. Sauer, J. Hofkens, and J. Enderlein, *Handbook of fluorescence spectroscopy and imaging*. Wiley-VCH, Weinheim, 2011.

SERS/SEIRA

Surface-Enhanced Raman and Fluorescence Spectroscopy with an All-Dielectric Metasurface

Silvia Romano,[1] *Stefano Managó*,[2] *Giuseppe Calafiore*,[3] *Erika Penzo*,[3] *Stefano Cabrini*,[3] *Anna Chiara De Luca*,[2] *Vito Mocella*[1] *and Gianluigi Zito*[*2]

[1]*National Research Council IMM, Via Pietro Castellino, Naples, 80131, Italy*
[2]*National Research Council IBP, Via Pietro Castellino, Naples, 80131, Italy.* * *Email: g.zito@ibp.cnr.it*
[3]*Lawrence Berkeley National Laboratory, Molecular Foundry, Berkeley, CA 94720, USA*

Keywords: Dielectric metasurfaces, surface-enhanced Raman scattering, bound states in the continuum

Plasmonic nanostructures play a crucial role for confining electromagnetic fields on the nanoscale and amplifying light matter interaction. Indeed, engineered plasmonic nano-architectures have been widely exploited in surface-enhanced fluorescence (SEF) and surface-enhanced Raman scattering (SERS) spectroscopies. Unfortunately, large absorption at optical frequencies induces local heating in metals. In addition, in SEF plasmonic substrates, spacer layers are necessary to minimize undesired fluorescence quenching due to non-radiative decay. Dielectric resonances, mimicking surface-plasmon resonances in terms of spatial localization, high-field intensity and dispersion characteristics, can avoid metallic losses, thus dielectric nanoantennas are of great interest for many applications.
In our work, we discuss the application of bound states in the continuum (BICs), observed in engineered transparent dielectric metasurfaces, for achieving simulatenuos fluorescence amplification and Raman scattering enhancement in standard microscopy at visible wavelengths [1]. BICs in open dielectric resonators provide a different approach for local field amplification which exploits confinement along the normal direction imposed by symmetry protection or topology, whereas the field remains completely delocalized in the resonator plane. This can be useful for versatile real-world applications which require large area substrates and samples. Far field enhancements of $\sim 10^3$ fold of fluorescence emission and Raman scattering intensities of molecules dispersed on the metasurface were observed in our experiments. Furthermore, conventional SERS intensity from gold nanoparticles was increased of more than one order of magnitude by resonant matching of the localized surface plasmon resonance with the BIC field. We foresee the possibility of translating the BIC-based surface amplification here discussed to other fluorescence techniques and cellular Raman imaging.

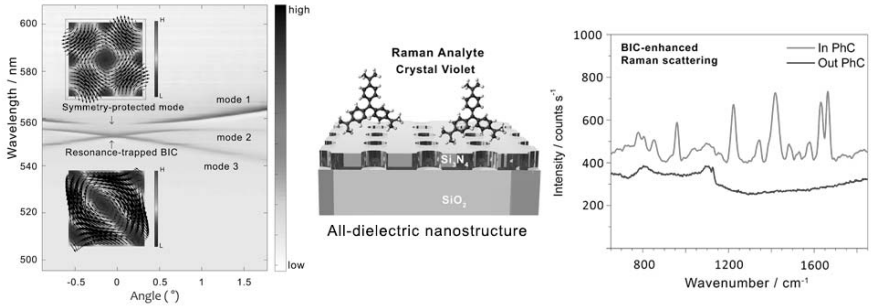


Figure 1: The dispersion diagram of the measurface (left) reveals the existence of normal-incidence BICs, used to amplify the local optical field in proximity to the surface (center) for Raman scattering enhancement (right).

References

[1] S. Romano *et al.*, J. Phys. Chem. C **122**, 19738-19745 (2018).

SERS spectroscopy as a high-performance technique to monitor the DNA melting profile

Debora Caprara[1], *Francesca Ripanti*[1], *Angela Capocefalo*[1] and *Paolo Postorino*[1]
[1]*Sapienza University, Rome, Italy, debora.caprara@uniroma1.it*

Keywords: DNA-nanoparticle systems, SERS spectroscopy, hybridisation, melting profile.

In the last years, the outstanding molecular recognition ability of DNA [1] and the rapid progress of cutting edge techniques, such as DNA origami, have contributed to unique scientific advancements in the area of structural DNA nanotechnology [2].
More recently, the combination of the binding selectivity of DNA bases (A-T, C-G) and the plasmonic properties of metallic nanoparticles (NPs), has opened an intriguing branch of research focused on the implementation of hybrid nanoscaled systems with peculiar plasmonic and optical properties.
The ability to control and engineer the hybridisation process, i.e. the formation of a double-stranded DNA structure from two complementary single-stranded sequences, have led to develop a wide collection of DNA structures of diverse shapes and dimensions as well as complex 2D and 3D supermolecular architectures [3].
In particular, the possibility to find a robust approach that can identify the pairing process of complementary strands constitutes a very sensitive issue for the vast implications in multiplexed biosensing analysis. To this aim, several spectroscopic techniques have been developed to precisely characterise the DNA fingerprint and, among them, Raman spectroscopy has revealed one of the most promising. Many experiments have been carried out to precisely distinguish the proper DNA signature of both pre-hybridised and hybridised sequences, but many of them make use of fluorescent labels [4] which do not allow to extrapolate the direct signal coming from DNA.
We experimentally show how the potentiality of Surface-Enhanced Raman Spectroscopy (SERS) [5] can be exploited to distinguish the signal of single- and double-stranded DNA species by adopting a direct and label-free experimental procedure [6]. Furthermore, we present how it is possible to reconstruct the typical melting profile of complementary DNA strands by precisely monitoring the temperature behavior of the investigated system [6]. Specifically, we start from an easy experimental procedure which allows the synthesis of silver (Ag) NPs and provides for the realisation of micrometer-sized DNA-NP compounds in which the DNA species electrostatically interact with the NP surface. First, we separately characterise the SERS spectrum of three complementary and purposely designed single-stranded DNA filaments at submicromolar concentrations. Following, we mix up equimolar quantities of the single-stranded components, allowing them to hybridise one another; we thus acquire the relative SERS spectrum of the bonded system at the same conditions. We have been able to observe several spectroscopic differences between the spectra of hybridised and non-hybridised samples, proving that these differences occur on both solute and dried samples. These unique spectral marks witness the presence of intrinsic modifications that survive even after the drying process. We highlight that the adopted experimental procedure benefits from the absence of any fluorescent labels and allows to characterise the DNA relevant peaks, providing a clear and precise spectral characterisation.
Finally, we demonstrate that SERS spectroscopy can be adopted to closely monitor the pairing process of complementary bases and to reproduce the melting profile of the investigated sequences.
Hence, the efficacy of the implemented protocol and the capability of collecting signals at very low concentrations combined with the possibility to control the hybridisation profile with a spectroscopic technique, open up an interesting scenario of possible applications in gene detection, nanomedicine and biotechnology.

References

[1] Seeman N. C., Nature, 421-427 (2003).
[2] Condon A., Nat. Rev. Genet., 565-575 (2006).
[3] Wei B., Dai M. and Yin P., Nature, 623-626 (2012).
[4] S.-J. Park, T. A. Taton, C. A. Mirkin, Science, 1503-1506 (2002).
[5] P. L. Stiles, J. A. Dieringer, N. C. Shah, R. P. Van Duyne, Annu. Rev. Anal. Chem., 601-626 (2008).
[6] D. Caprara, F. Ripanti, A. Capocefalo and P. Postorino, *in preparation*.

In situ growth of silver nanoparticles on PDMS membranes for multi-wavelength SERS biosensing platforms

Chiara Novara[1], Alessandro Chiadò[1], Giuliano Caruso[1], Roberta Calmo[1], Niccolò Paccotti[1], Francesco Geobaldo[1], Paola Rivolo[1], Massimo Bertoldi[2], Paola Puppo[2], Fabrizio Giorgis[1]
[1]*Dept. of Applied Science and Technology, Politecnico di Torino, Torino, Italy, chiara.novara@polito.it*
[2]*FLUODY S.r.l., Villanova Mondovì (CN), Italy*

Keywords: Surface Enhanced Raman Scattering, Polydimethylsiloxane, Ag nanoparticles, tunability, Raman reporters

Polydimethylsiloxane (PDMS) was demonstrated to be a functional platform for the development of Surface Enhanced Raman Scattering (SERS) point of care and wearable sensing devices, thanks to its flexibility, transparency and ease of integration in microfluidics [1]. To this aim, noble metal nanoparticles (NPs) were previously deposited on PDMS through physical methods, such as d.c. sputtering [2]. However, the fabricated metal-elastomer nanostructures presented a very poor stability in buffer solutions needed in biological assays [3], thus hindering their application in the biomedical field.

In this work, a new approach based on the *in situ* synthesis of Ag NPs on PDMS membranes is described and optimized to produce stably anchored nanostructures with tunable plasmonic resonances in a wide wavelength range. The reactivity of the residual curing agent used for the PDMS crosslinking was exploited to reduce Ag^+ in aqueous silver nitrate solutions. Several synthesis parameters were analyzed, such as the prepolymer to curing agent ratio, the process time, the membrane thickness, the concentration of the Ag precursors, the temperature and the solvent used for the PDMS incubation. Moreover, the effect of the functionalization of the elastomeric membrane with organosilanes (e.g. APTES (3-aminopropyltriethoxysilane) or MPTMS (3-mercaptopropyltrimethoxysilane) prior to the NPs growth was carefully studied. All the samples were characterized by FESEM (Field Emission Scanning Electron Microscopy) and UV-Vis spectroscopy to assess the synthesis conditions-morphology relationships and to analyze the far-field optical response of the plasmonic nanostructures. The best performing substrates (Fig. 1 a and b) in terms of SERS enhancement efficiency and uniformity were identified through their systematic analysis by Raman mapping of 4-mercaptobenzoic acid (4-MBA) performed with excitation at 532 and 785 nm. These SERS substrates were finally employed for the screening of newly synthesized Raman reporters belonging to cyanine structural class. The dyes have been modified in order to provide a resonant Raman regime with a moderate fluorescence background intensity, in view of their use as labels for SERS-based bioassays. Both NIR (λ_{abs} ~ 750-760 nm) and green absorbing cyanines (λ_{abs} ~ 500-550 nm) were characterized by Raman spectroscopy (Fig. 1c). The results demonstrate that the multiple plasmonic resonances and the hot-spot rich morphology of the Ag-PDMS substrates together with the unconventional features of dyes specifically designed for Raman applications represent a powerful combination for the development of SERS-based ultrasensitive biosensing platforms.

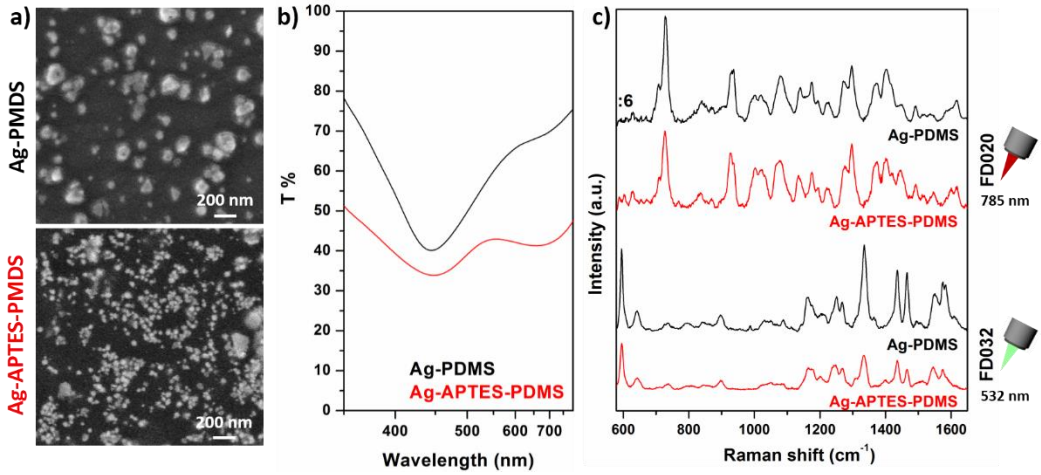


Figure 1: a) FESEM images, b) UV-Vis-NIR transmission spectra and c) SERS spectra of NIR and green cyanines dyes (FD020 and FD032, FLUODY S.r.l.) (10^{-5} M, resonantly excited at 532 and 785 nm, respectively) obtained from the best performing Ag-PDMS substrates (40 °C, 24 h in 100 mM $AgNO_3$).

References

[1] C. Novara, A. Lamberti, A. Chiadò, A. Virga, P. Rivolo, F. Geobaldo, F. Giorgis, RSC Adv. **6**, 21865–21870 (2016).
[2] A. Lamberti, A. Virga, P. Rivolo, A. Angelini, and F. Giorgis, J. Phys. Chem. B **119,** 8194−8200 (2015).
[3] A. Chiadò, C. Novara, A. Lamberti, F. Geobaldo, F. Giorgis, P. Rivolo, Anal. Chem. **88,** 9554–9563 (2016).

Plasmon engineering in self-organized metasurfaces for broadband Surface Enhanced Infrared Absorption (SEIRA) spectroscopy

M.C. Giordano[1], M. Barelli[1], J. Vogt[2], M. Tzschoppe[2], A. Mazzanti[3], G. DelleValle[3], A. Pucci[2], F. Buatier de Mongeot[1]

[1]Dipartimento di Fisica, Università di Genova, Via Dodecaneso, 33 - 16146 Genova- ITALY
[2] Kirchhoff Institute for Physics, University of Heidelberg, Im Neuenheimer Feld 227 D -69120 Heidelberg –GERMANY
[3] Dipartimento di Fisica and IFN-CNR, Politecnico di Milano, Piazza Leonardo da Vinci, 32 I-20133 Milano, ITALY

Keywords: Mid-IR nanoantennas, self-organized metasurfaces, SEIRA.

Infrared (IR) molecular sensing has recently attracted increasing attention due the possibility to probe vibrational modes of a broad range of molecular species in a non-destructive way in solids, polymers and biological tissues. Despite the great advantage given by the low-energy excitation, the small cross section of molecules in the IR spectral range still practically limits the sensitivity of the conventional spectroscopic techniques (e.g. Fourier Transform-IR and IR reflection-absorption spectroscopy) when the concentration is reduced to few layers. A strong improvement of the detection sensitivity up to several orders of magnitude can be achieved by exploiting strong light-matter interaction at the nanoscale in Surface Enhanced Infrared Absorption (SEIRA) Spectroscopy [1]. In this case the enhanced local field at the surface of plasmonic nanoantennas or atomic two-dimensional (2D) materials supporting IR plasmon polaritons selectively enhances the emission of resonantly excited IR-active molecules. So far, highly reproducible SEIRA activity has been observed in lithographically designed nanoantennas over limited areas, while large-area isotropic metal films showed poor reproducibility and gains.

Here we demonstrate broadband, polarization-sensitive SEIRA activity promoted by self-organized (SO) plasmonic nanorod arrays extending over large cm^2 areas [2]. Aligned nanorod-antennas are confined on anisotropic nanopatterned glass templates by maskless glancing angle metal evaporation [3]. The controlled tuning of localized plasmon resonances from the Visible to the Near- and Mid-IR spectrum has been achieved by tailoring the nanorod shape and/or the light polarization. For longitudinal polarization of the excittion we thus demonstrate a broadband Mid-IR plasmon resonance which enables highly homogenous SEIRA activity from self-assembled monolayers of IR-active molecules, with enhancement factors comparable with the state of the art lithographic templates [2].

In parallel, plasmon hybridization with subradiant near-field enhancement and color routing functionalities are demonstrated in the Near-IR spectrum, for transversal excitation of vertically stacked SO nanostripe dimers [4].

References

[1] F. Neubrech et al. Phys. Rev. Lett. 101.15, 157403 (2008).
[2] M.C. Giordano et al. Self-organized nanoantennas for broadband SEIRA, in preparation.
[3] M.C. Giordano et al. Adv. Mater. 26,1801840 (2018).
[4] M.C. Giordano et al., Nano Research 11, 3943-3956 (2018).

Thursday June 20

Alternative Plasmonic Materials and Dielectrics Resonators

Nanoengineered TiO_2 and Ta:TiO_2 films with enhanced optical/electrical properties for advanced photoconversion and plasmonics

Andrea Li Bassi[1,2], Piero Mazzolini[1,2], Luca Ornago[1], Matteo Ghidelli[1], Valeria Russo[1,2], Carlo S. Casari[1,2], Beatrice R. Bricchi[1]

1. *Department of Energy, Politecnico di Milano, via Ponzio 34/3, Milano, Italy*
2. *Center for Nanoscience and Technology – IIT@Polimi, via Pascoli 70/3, 20133, Milano, Italy*

Keywords: scattering; devices and applications.

Transparent conductive oxides (TCOs) have recently demonstrated plasmonic properties that can be tuned, by doping or engineering oxygen stoichiometry, from the visible to the mid-IR range [1], potentially overcoming issues typical of metal nanostructures in which the application range and tunability are limited. This can have an impact e.g. in the fields of photoconversion, sensing, optoelectronics. Ta-doped TiO_2 (Ta:TiO_2) is a performing TCO, with the advantages of TiO_2, such as photoactivity, low-cost, non-toxicity and stability [2]. Ta:TiO_2 in form of ultrathin films or nanoparticles (NPs) is thus a promising material for IR plasmonics, in particular for active electrical modulation of the plasmonic response.

In this work, Pulsed Laser Deposition (PLD) and vacuum annealing of Ta:TiO_2 thin films enable a fine control of thickness and nanostructure, while permitting a systematic investigation of the effect of Ta content (5–10% at.) and O stoichiometry on the material defect chemistry, electrical properties and optical/plasmonic behavior in the UV/Vis/NIR range. We show that this approach enables to control of carrier density (or carrier density gradient) over one order of magnitude (~10^{20}-10^{21} cm^{-3}) in polycrystalline transparent electrodes. The synthesis of Ta:TiO_2 nanostructures and ultrathin films is then discussed together with their potential development as novel mid-IR, tunable plasmonic materials. Specifically, conductive ultrathin films have been successfully obtained down to less than 20 nm (Fig.1), which represents an attractive size for the realization of plasmonic metamaterials or active-modulated TCO-based plasmonic devices.

By increasing the deposition pressure, it is also possible to grow hierarchical TiO_2 or Ta:TiO_2 nanoparticle assemblies, characterized by multiscale porosity, large surface area, strong haze in the solar spectral region combined with efficient electron transport, reporting beneficial effects when employed as photoanodes for photoelectrochemical solar cells or photocatalytic applications [3]. Finally, a single-step co-deposition strategy allows to integrate in the nanoporous oxide morphology Au NP with tunable visible localized surface plasmon resonance (LSPR) response [4], enabling to realize surfaces with plasmonic functionality of potential interest for photocatalytic degradation of organic molecules or Surface Enhanced Raman Scattering (SERS).

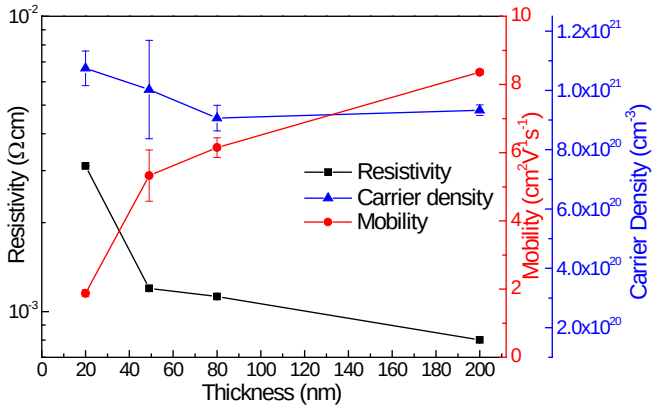


Fig.1: Carrier density, mobility and resistivity of PLD Ta:TiO_2 films as a function of film thickness (5% at. Ta content, 1 Pa O_2 deposition pressure).

References

[1] Naik et al, Adv Mater 25, 3264 (2013).
[2] Mazzolini et al, J Phys Chem C 119, 6988 (2015)
[3] L. Passoni et al., ACS Nano 7, 10023 (2013);
[4] B.R. Bricchi et al., Mater.&Design 156, 311 (2018)

Surface Plasmon Waveguides in the THz range for photoluminescent and nonlinear emitters based on Ge/SiGe Quantum Wells

Chiara Ciano[1], Michele Montanari[1], Luca Persichetti[1], Luciana Di Gaspare[1], Giovanni Capellini[1,2], Alexej Pashkin[3], Manfred Helm[3], Michele Virgilio[4], Giovanni Isella[5], Jacopo Frigerio[5], Andrea Ballabio[5], Jonas Allerbeck[6], Joel Kuttruff[6], Daniele Brida[6,7], Andrea Mancini[8], Leonetta Baldassarre[8], Michele Ortolani[8], and Monica De Seta[1]

[1] *University of Roma Tre, Rome, 00154 Italy*
[2] *IHP-Leibniz-Institut für innovative Mikroelektronik, Frankfurt (Oder), 15236, Germany*
[3] *Helmholtz-Zentrum Dresden-Rossendorf, Dresden, 01328 Germany*
[4] *Dipartimento di Fisica "E. Fermi", Università di Pisa, 56127 Pisa, Italy*
[5] *Politecnico di Milano, Polo Territoriale di Como - L-NESS Lab, 22100 Como, Italy*
[6] *Department of Physics and Center for Applied Photonics, Univ. of Konstanz, 78457 Konstanz, Germany*
[7] *Physics and Materials Science Research Unit, Univ. of Luxembourg, 1511 Luxembourg, Luxembourg*
[8] *Sapienza University of Rome, Rome, 00185 Italy*

Keywords: Non-linear Plasmonics, Terahertz

Semiconductor quantum devices, composed of semiconductor quantum wells and heterostructures, are becoming ubiquitous in our daily lives as devices for optoelectronics [1]. The operation of quantum well (QW) optical devices is based on the optical transitions between the discrete states that arise from the electron/hole confinement. The ease of engineering the electronic subbands, thanks to the modern growth techniques, makes them therefore very attractive for optoelectronic applications. It is well established [2] that in QW structures embedded in surface plasmon waveguides, the light is highly confined thanks to the double excitation of the plasmons at the metal/semiconductor and semiconductor/highly-doped semiconductor interfaces. Thus, to increase the efficiency of the device a plasmon on top of the QWs can be used.

Here, we present two possible QW designs, to which correspond different applications, of Ge/SiGe quantum well emitters grown by means of chemical vapor deposition. In the first experiment n-type strained asymmetric coupled QWs (ACQWs) designed as three-level systems have been pumped with high-power pulses from FELBE free electron laser around 10 THz (0→2 intersubband transition) searching for optically induced photoluminescence (PL) emission from level 2. The second experiment consists of the generation of second harmonic emission (SHG) from p-type asymmetric QWs with optical pumping at 29 THz either by continuous wave quantum cascade laser or a pulsed nonlinear optical parametric amplifier (OPA). Samples have been shaped in a 70° surface plasmon waveguide to favor the intersubband transitions [3] and exploit the plasmon arising at the surface between metal (Au) and SiGe to enhance the emitted signal.

The first experiment is part of a project that has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 766719

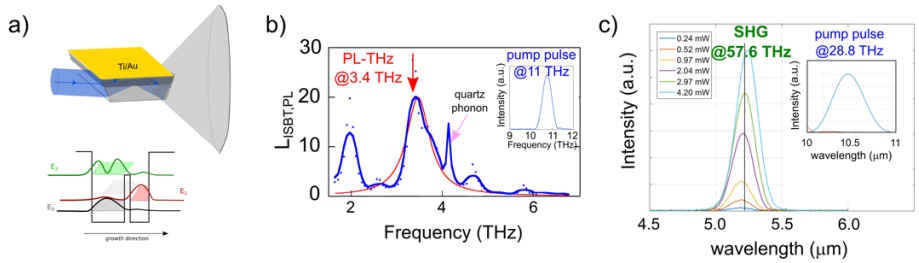


Figure 1: a) Sketch of the 70° surface plasmon waveguide configuration used for both the PL experiment performed on n-doped ACQWs and the SHG experiment on p-doped ACQWs. A PL spectrum and a SHG spectrum are also reported in panel (b) and (c), with the FEL pump pulse and the OPA pump pulse as insets, respectively.

References

[1] Vitiello M. S., *et al.*, *Optics Express* **23**, 2015
[2] Kohler R., *et al.*, *Nature* **417**, 2002
[3] Helm M., Intersubband transitions in quantum wells, in Semiconductors and Semimetals, edited by H. C. Liu and F. Capasso (Academic Press, New York, 2000), pp. 1−99.

Plasmon-Assisted Phenomena in Gold-Carbon Nanotubes Hybrids

Mareen Glaeske, Stephanie Reich, *Antonio Setaro*[1],
[1]*Freie Universität Berlin, Berlin, Germany, setaro@physik.fu-berlin.de*

Keywords: Nanophotonics and Hybrid Plasmonics.

The plasmonic near-fields localize around the surface of metallic systems and markedly alter the local character of the electromagnetic radiation. Their squeezing in space and enhancement in intensity pushes spectroscopy to sensitivities unachievable by the standard techniques, leading e.g. to SERS, TERS, and so on.

Carbon nanotubes (SWNTs) have excitation energies spanning over the whole energy range of gold colloidal nanosystems. Placing them in the close proximity of gold nanoparticles (Fig. 1) enables various plasmon-assisted phenomena. Thanks to the near-field pumping, we reported enhancement of the luminescence from gold-SWNT hybrids [1–3]. SWNTs can optically readout the peculiar electromagnetic environment around metallic surfaces and, through their emission, provide unique information about the nature of the near fields. Resonant plasmonic studies point at the interplay between exciton and plasmon leading to exciton-polariton formation.

Beyond the ability of interacting with elementary excitation in solids, plasmons moreover enable physico-chemical processes which wouldn't be allowed, for example acting as catalysts for otherwise unattainable chemical reactions. We showed that plasmon help overriding the limitations provided by the Förster energy transfer framework, allowing energy capture from molecules active in the solar-energy-capture region but unable to transfer their excitation onto the SWNTs [4].

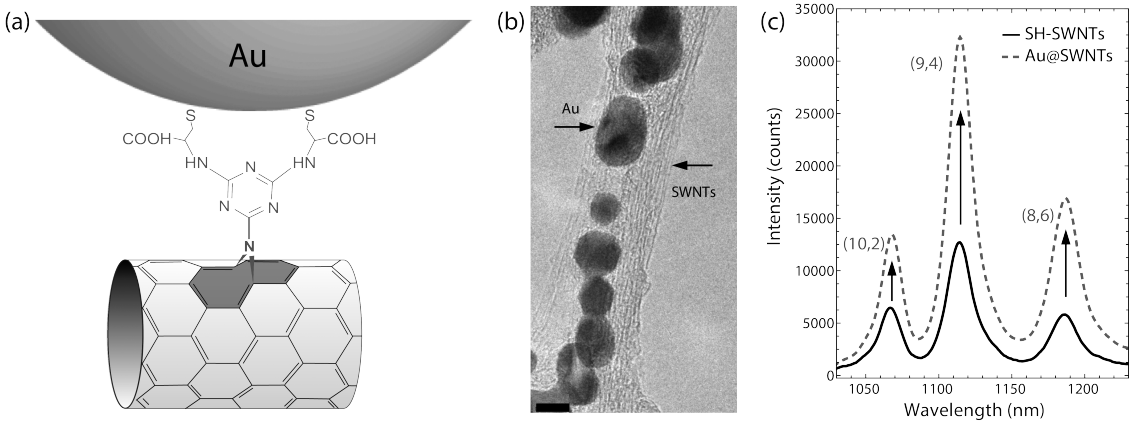


Figure 1: (a) Molecular sketch of AuNPs covalently anchored to thiol-functionalized SWNTs. (b) TEM micrograph of Au@SWNTs hybrids. Scale bar, 5 nm. A few-SWNTs bundle can be observed as well as AuNPs assembled along the tubes. (c) Enhancement of the luminescence emission of SWNTs after covalent attachment of AuNPs onto their surface: Comparison of the emission of the Au@SWNT hybrids (dotted curve) with the one of SH-SWNT (black curve). Picture adapted from [2].

References

[1] M. Glaeske and A. Setaro, Nano Res. **6**, 593 (2013).
[2] A. Setaro M. Adeli, M. Glaeske, D. Przyrembel, T. Bisswanger, G. Gordeev, F. Maschietto, A. Faghani, B. Paulus, M. Weinelt, R. Arenal, R. Haag, and S. Reich, Nat. Comm. **8**, 14281 (2017).
[3] M. Glaeske, M Kumar, T Bisswanger, S Vaitiekenas1, C Soci, R Narula, A Bruno, and A Setaro, Nanotech. **28**, 255202 (2017).
[4] M. Glaeske, S. Juergensen, L. Gabrielli, E. Menna, F. Mancin, T. Gatti, and A. Setaro, Phys. Stat. Sol. RRL **12**, 1800508 (2018).

THz technology for imaging: from Time Domain Spectroscopy (TDS) to THz Quantum Cascade Laser (THz QCL) Imaging

Francesco M. Vitucci [1]
[1]*Crisel Instruments srl, Rome, Italy, vitucci@crisel-instruemnts.it*

Keywords: THz, THz imaging, Time domain spectroscopy, THz Quantum Cascade Laser THz QCL.

Introduction

TeraHertz imaging has attracted more and more attention from the technological and scientific point of view in the last decades but for the lack of reliable devices (like sources, detector and suitable optics) this field had very slow development. In the last very few years the availability of innovative technologies had led to a new era of THz wave development. In this work we will focus on the imaging capabilities of this new and powerful field of investigation

From THz TDS to frequency domain Spectroscopy through THz QCLs

THz waves are constituted by non-ionising long wavelength radiation. This means that it is not dangerous for the health and – at the same time - it can penetrate many materials like plastics, ceramics, woods, fabrics or composites (generally un-polar, dry or non-metallic, as microwaves). THz waves also can achieve spectroscopic information (as infrared spectroscopy). This combination of properties make THz radiation unique and promising for many applications: nondestructive testing (NDT), biomedical imaging, security screening. In particular, imaging using THz radiation has gained increasing attention, as it promises penetrating, contactless and submillimeter diffraction-limited imaging [1]. Until recently, the majority of THz imaging systems reported have been based on the principles of time-domain spectroscopy (TDS) [2], this approach suffers from many limitation: low spectral resolution, very low THz powers (~ nW) and long acquisition time. The availability of THz Quantum Cascade laser in the THz region has led the development of frequency domain spectroscopy.

THz Quantum cascade Laser THz-QCL

The main advantage of these new THz-QCL sources is that they are extremely efficient. Following remarkable development over the past decade, QCL devices have now been demonstrated with emission frequencies throughout the range 1.2–5.2 THz [3]. Peak powers have recently been reported to exceed 1 W in pulsed mode and 100 mW in CW operation [4]. Such performances offer huge benefits in terms of imaging capability compared to the TDS sources. By using a THz confocal microscope based on a QCL source, moreover, lateral and axial resolutions have been demonstrated to be better than 70 μm and 400 μm respectively [5].

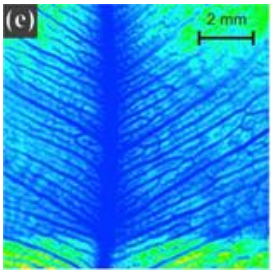


Fig. 1 High-resolution THz images acquired with a 50 μm step size [5].

Conclusions

THz frequency QCL is now established as a reliable high power, compact, spectrally pure source, particularly suited for THz imaging across a wide range of disciplines as biomedicine, security controls, industrial inspection, non-destructive analysis and spectroscopic mapping of materials.

References

[1] Gellie P, Breakthrough for Real-Time THz Imaging - Photonics Spectra 2016
[2] Davies A.G. et al. 2008 Mater. Today 11 18–26 [3] F. Ladouceur and J. D. Love, (Chapman & Hall, 1995), Chap. 8.
[3] Scalari G et al. 2008, Laser Photon. Rev. 3 45–66
[4] Li L, Chen L et al. Electron. Lett. 50 309–11
[5] de Cumis U.S. et al. Opt. Express 20 21924–31

Cavities and Resonators

Dielectric nanocavities for enhanced Purcell effect and strong directionality

Riccardo Sapienza, The Blackett Laboratory, Department of Physics, Imperial College London, London, SW7 2AZ, UK

In this talk I will discuss our experiments with dielectric nanocavities for single photon manipulation.

I will report parabolic antennas surrounding an individual quantum dot as a source of collimated single photons, which can then be easily extracted and manipulated. These are fabricated by direct laser writing over a single quantum dot localised by confocal microscopy. The parabolic antenna provides one of the largest reported experimental directivities (D = 106) and the lowest beam divergences ($\Theta 1/2 = 13.5°$) and a broadband operation over all of the visible and near-infrared range together with extraction efficiency of more than 96\%, offering a practical advantage for quantum technological applications.

Moreover, I will discuss a design concept for tailoring the local density of optical states (LDOS) in dielectric nanostructures, based on the phase distribution of the scattered optical fields induced by point-like emitters. I will report dielectric Mie resonators with up to 1000 Purcell enhancements. The coherent design provides a powerful tool for high-performance dielectric resonators, and affords fundamental insights into light-matter coupling at the nanoscale.

[1] A metal-dielectric parabolic antenna to direct single photons, S Morozov, M Gaio, SA Maier, R Sapienza, Nano Letters 18, 3068 (2018) [2] Nanoscale design of the local density of optical states, Sandro Mignuzzi, Stefano Vezzoli, Simon A. R. Horsley, William L. Barnes, Stefan A. Maier, Riccardo Sapienza Nano Letters 19, 1613—1617 (2019)

Near-field spectroscopy of Phonon Polariton resonators

Andrea Mancini[1], Yi Li[1], Rodrigo Berté[1], Christopher R. Gubbin[2], Simone De Liberato[2], Alberto Politi[2] and Stefan A. Maier[1]

[1] *Chair in Hybrid Nanosystems, Nanoinstitute Munich, Faculty of Physics, Ludwig-Maximilians-Universität München, 80799 München, Germany A.Mancini@lmu.de*

[2]*School of Physics and Astronomy, University of Southampton, Southampton, SO17 1BJ, UK*

Keywords: Spectroscopy and nano-imaging, Plasmonic and dielectric nanoantennas

Surface plasmon polaritons (SPP) and localized surface plasmon resonances (LSPR) of metal nanostructures have been extensively investigated for many different applications in the visible and near infrared ranges, ranging from molecular sensing to control and enhancement of light-matter interactions at the nanoscale. However, due to the intrinsic high losses of metals at optical frequencies, potential applications requiring long propagation of SPP or high quality factor of LSPR are hindered.

To overcome these limitations, there has been a renewed interest in polar dielectrics displaying negative permittivity between a transverse and a longitudinal optical phonon, in the so called *Reststrahlen* band, where surface phonon polaritons (SPhP) can be excited [1]. Moreover, while lifetimes of SPP in metals are of the order of tens of femtoseconds, SPhP decay much more slowly on a picosecond timescale due to higher order phonon-phonon scattering processes. This favors propagating and localized SPhP resonances to have much higher quality factors than what can be achieved with their plasmonic counterparts.

Silicon carbide (SiC) is a polar dielectric having the *Reststrahlen* band at high energy in the mid-IR, between around 10 and 12 μm depending on the specific SiC polytype. Arrays of SiC pillars have been previously investigated both from an experimental [2] and theoretical [3] point of view. It has been shown that the modes of such system can be explained in terms of the coupling of the modes of an isolated pillar to the surface resonance of the bare SiC surface, while at the same time the array structure leads to the back-folding of the SPhP dispersion.

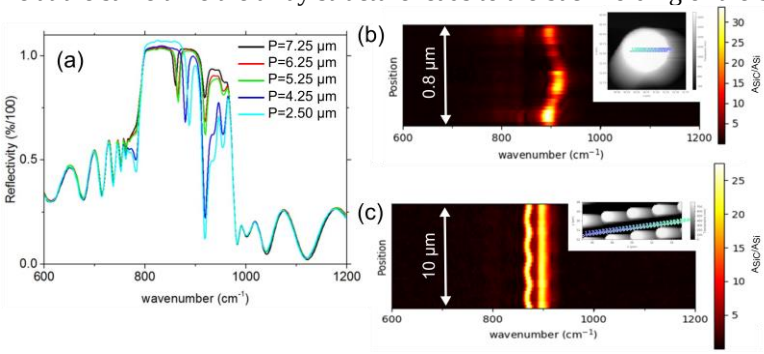


Figure 1: (a) Far field reflectivity spectra of SiC pillar arrays with different array pitches *P*. Near-field signal on a line along the top of a pillar (b) and along the SiC surface between pillars (c), showing frequency modulations that are otherwise obscured by far-field averaging.

However, an experimental investigation of the detailed near field response of such system was still lacking. In order to understand the nanoscale behavior of SPhP we use nano-FTIR [4], a technique based on the same principle of far-field FTIR, but in which one of the two optical paths of the interferometer is focused on the sample and coupled to an AFM tip working in tapping mode. The e.m. field back-scattered by the tip is then collected, isolating the contribution from a region of tens of nanometers below the tip. In this way we are able to investigate the detailed nanoscale properties of SPhP resonators, which are otherwise concealed by far-field averaging. In particular, we detect interesting spatial modulations of the modes of the array, both on top of single pillars and on the SiC surface between pillars. The knowledge of the nanoscale field distribution in SPhP resonators will be important for their possible applications as a platform for enhanced molecular sensing [5] or as optical sources in the mid-IR [1].

References

[1] Caldwell, Joshua D., et al. Nanophotonics **4.1,** 44-68 (2015).
[2] Chen, Yiguo, et al. ACS Photonics **1.8**, 718-724 (2014).
[3] Gubbin, C. R., Maier, S. A., & De Liberato, S. Physical Review B, **95(3)**, 035313 (2017).
[4] Hillenbrand, R., T. Taubner, and F. Keilmann. Nature **418.6894**, 159 (2002).
[5] Berte, Rodrigo, et al. ACS Photonics **5.7**, 2807-2815 (2018).

A Semi-Classical view on the Occurrence and Hybridization of Resonant Tunnelling Epsilon-Near-Zero Modes in Metal/Insulator Nanocavities

Vincenzo Caligiuri[1], *Milan Palei*[1], *Giulia Biffi*[1,2], *Sergey Artyukhin*[1], *Muhammad Imran*[1,2], *Liberato Manna*[1] *and Roman Krahne*[1].

[1] *Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy*

[2]*Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, Via Dodecaneso, 31, 16146 Genova, Italy*

Keywords: Metamaterials, Sensor and Biosensors, Devices and Applications

Epsilon-Near-Zero (ENZ) dielectric response is an exotic propagation regime lying at the basis of important technological achievements. [1–3] One example of natural ENZ permittivity is the Ferrell-Berreman mode in Ag subwavelength layers, occurring only at 327 nm and exclusively under p-polarized excitation. [4] Here, we outline a way to engineer ENZ resonances in Metal/Insulator/Metal (MIM) nano-cavities in a broad range, for both p- and s-polarized excitation. Spectroscopic Ellipsometry, corroborated by a homogenization of the MIM's dielectric permittivity, elucidates the low-loss ENZ nature of the MIM's resonances. The group velocity of the light trapped in the cavity slows down to zero allowing the mode to propagate for several microns in the MIM waveguide. [5,6] The dispersion relation of MIM structures is calculated in a quantum framework, individuating the MIM as the photonic analog of the finite square well for electrons. This new look allows to identify the dielectric permittivity as the optical potential. We found out that MIM's resonances are suppressed in the spectral range where the ratio n/κ between the real and imaginary part of the refractive index of the metal exceeds a certain threshold, above which non-Hermitian processes are non-negligible. [5] The quantum approach leads to an intuitive interpretation of these modes as the *resonant tunneling* frequencies of the MIM, lifting from the need of momentum matching techniques. [5] As two noticeable applications, we propose a MIM superabsorber and a MIM *resonant tunneling* refractive index sensor. [5] We extend the quantum approach to double MIMIM cavities exploring both experimentally and theoretically the hybridization of the ENZ modes as the equivalent of the coupled double quantum well. Its dual resonant response is exploited to enhance the photophysical response of a fluorophore placed on the top of the MIMIM double ENZ cavity whose high and low energy resonances are tuned respectively to the absorbance and emission of the selected fluorophore. [7] In the end, we show how to engineer an ultra-broad ENZ response via multiple cavity systems.

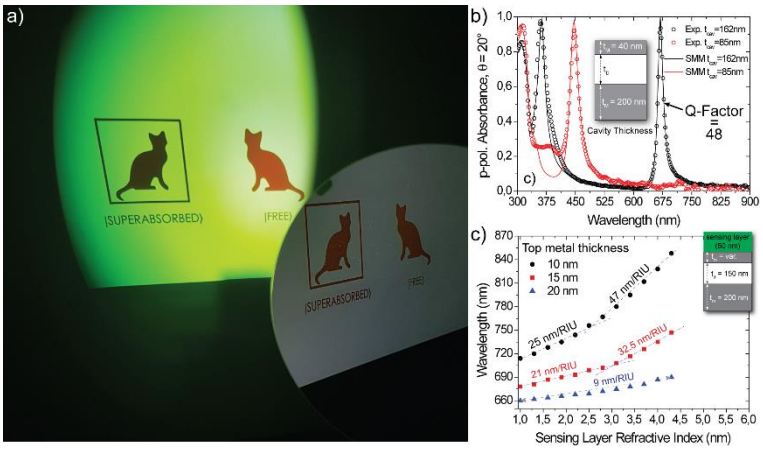


Figure 1: (a) Colour change of the p-polarized image of a cat in a box that turns black on the screen due to the superabsorption of its original red colour, in contrast to the non-polarized one that remains black. (b) MIM based superabsorber and (c) refractive index sensor.

References

[1] N. Engheta, Science. **340**, 286 (2013).
[2] S. Savoia, G. Castaldi, V. Galdi, A. Alù, and N. Engheta, Phys. Rev. B - Condens. Matter Mater. Phys. **91**, (2015).
[3] K. V. Sreekanth, Y. Alapan, M. El Kabbash, E. Ilker, M. Hinczewski, U. A. Gurkan, A. De Luca, and G. Strangi, Nat. Mater. **15**, 621 (2016).
[4] W. Newman, C. L. Cortes, J. Atkinson, S. Pramanik, R. G. DeCorby, and Z. Jacob, ACS Photonics **2**, 2 (2014).
[5] V. Caligiuri, M. Palei, G. Biffi, S. Artyukhin, and R. Krahne, Nano Lett. (2019), DOI: 10.1021/acs.nanolett.9b00564.
[6] A. Ciattoni, A. Marini, C. Rizza, M. Scalora, and F. Biancalana, Phys. Rev. A - At. Mol. Opt. Phys. **87**, 053853 (2013).
[7] V. Caligiuri, M. Palei, M. Imran, L. Manna, and R. Krahne, ACS Photonics **5**, 2287 (2018).

Enhanced single molecule detection using Plasmonic Nanochannels and Zero-Mode Waveguides

Xavier Zambrana-Puyalto[1], *Paolo Ponzellini*[1], *Francesco De Angelis*[1], *Denis Garoli*[1]
[1]*Istituto Italiano di Tecnologia, Via Morego 30, 16136 Genova, Italy*

Keywords: lifetime, FRET, FCS.

In this presentation, we will summarize our last works in single molecule spectroscopy. In particular, we have thoroughly studied two different families of structures: Zero-Mode Waveguides (ZMWs) and Plasmonic Nanochannels (PNs).

We have fabricated different typologies of ZMWs and have characterized their optical properties to be used for single molecule detection. The optical characterizations are based on Fluorescence Correlation Spectroscopy (FCS) and lifetime measurements (see Figure 1). We have fabricated i) standard circular 50nm ZMWs made in Al; ii) 60x130nm^2 nanoslots made of Au-Al; iii) 40x100nm^2 nanoslots made of Au; iv) 40x100nm^2 hybrid nanoslots made of Au-Si. We have observed that the nanoslots of the kind ii) greatly enhance the single molecule efficiency with respect to the standard ZMWs[1]. Then, we have studied the spectral properties of iii) and iv). We have seen that the ZMW behavior of the structure can be lost by a blue-shift of 40nm. Furthermore, we have observed that the addition of a semiconductor layer made of Si can greatly enhance the emission of single molecules [2].

We have also fabricated PNs and tested their optical properties for different configurations. The PNs can be easily integrated into microfluidic chips and they have a great field enhancement at the tip of the channel. Moreover, their resonant behavior can be controlled by changing the inner and outer diameter of the tip. We have fabricated and characterized these devices with the aim of using them for optical DNA sequencing. We plan to detect the passage of molecules through the PNs using FRET. For that reason, we have functionalized the nanopores with a dye. We have seen the effect that different PNs have on the emission of the dye [3]. Then, the other dye of the donor/acceptor has been diffused through the tip of the PNs and their FRET interaction has been recorded [4].

To wrap up the presentation, we will discuss the challenges that we face when we want to compare the experimental results with electromagnetic simulations. Namely, we will comment on the influence of using plane waves or tightly focused beam for the simulations [2].

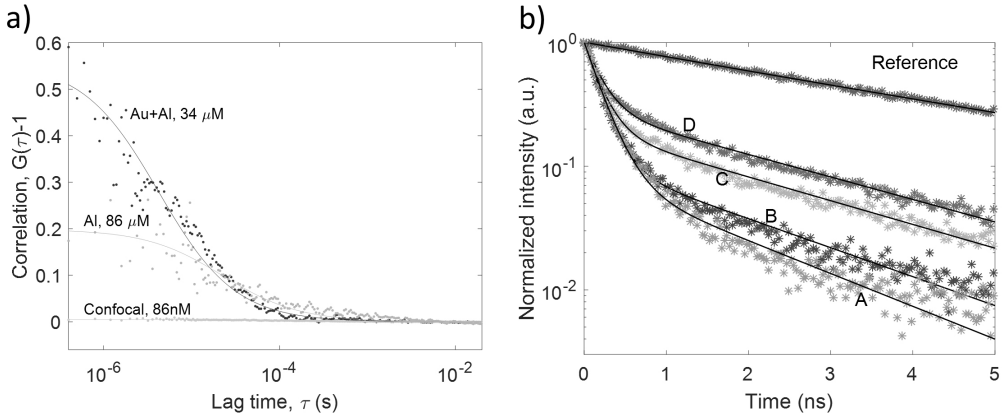


Figure 1: a) FCS measurements using ZMWs. b) Lifetime measurements using PNs.

References

[1] P. Ponzellini, X. Zambrana-Puyalto, N. Maccaferri, L. Lanzanò, F. De Angelis and D. Garoli, Nanoscale **10**, 17362-17369 (2018).
[2] X. Zambrana-Puyalto, P. Ponzellini, E. Tessarolo, M.G. Pelizzo, W. Zhang, G. Barbillon, G. Lu, F. De Angelis and D. Garoli *in preparation*.
[3] X. Zambrana-Puyalto, N. Maccaferri, P. Ponzellini, G. Giovannini, F. De Angelis and D. Garoli, arXiv:1811.03309 (2019).
[4] X. Zambrana-Puyalto, *et al., in preparation*.

Two-dimensional nanostructure arrays for plasmonic nanolaser devices

Diego Piccotti[1], *G. Pirruccio*[2], *N. Michieli*[1], *B. Kalinic*[1], *C. Scian*[1], *T. Cesca*[1] *and Giovanni Mattei*[1]
[1]*Physics and Astronomy Department, University of Padova, via Marzolo 8, I-35131 Padova, Italy*
[2]*Solid State Department of the Physics Institute, UNAM, Apartado Postal 20-364, México D.F. 01000, México*

diego.piccotti@phd.unipd.it

Keywords: Plasmonic and dielectric nanoantennas, Nanophotonics and Hybrid Plasmonics, Devices and Applications.

The need to reduce the size of laser devices to nanometer dimensions has to deal with several problems, such as the diffraction limit imposed on the most common optical cavities. Plasmonic nanolasers can potentially overcome these limitations and replace the current light source technology in many fields as photonic integrated circuits, optical communications and high performance biosensors [1,2].

In a plasmonic nanolaser the standard laser cavity can be replaced by a two-dimensional lattice of plasmonic nanostructures, whose resonant scattering and field-enhancement properties can provide a sufficient feedback to turn on the lasing action [2,3]. These properties arise from lattice periodicity and plasmon resonances of the nanostructured material. In order to maximize the efficiency and throughput of a nanolaser, the match between the fluorescent emission of the selected gain medium and the plasmonic resonance of the nanostructure is needed [3,4].

The aim of this work is to synthesize two-dimensional plasmonic nanostructure arrays for plasmonic nanolaser devices working in the visible and NIR spectral region. Two shapes are taken into account: nanodomes (Fig.1**a**) and nanodisks. The fabrication of these plasmonic nanoarrays is made by NanoSphere Lithography which, to date, is one of the highest-throughput and most cost-effective techniques to nanofabricate high quality ordered nanoparticle arrays. The nanoarrays are coupled with laser dye molecules embedded in a solid or liquid matrix. The emission is studied as a function of the pump intensity and on a broad angular range by a collection system placed on a rotating arm, showing a non-normal high directionality of the amplified emission and with a narrow angular divergence.

In particular, we have compared the behavior of plasmonic nanoarrays with pure dielectric nanostructure arrays (Figure 1**b**). This study shows that the geometrical behavior of the emitted beam, directionality and angular divergence, is related to pure lattice effects; whereas, the low threshold and in-phase emission can be related to the plasmonic properties of the nanostructures. The band-structure of the nanoarrays was characterized by transmittance measurements at different incidence angles reconstructing an extinction map (Figure 1**c**). In this way, the photonic and plasmonic properties of the nanoarray are analyzed, showing also a hybridization region where the best coupling with the active medium can be obtained.

Furthermore, in order to confirm the stimulated emission nature of the amplified emission, we performed interference measurements. By a Michelson interferometer with inclined mirrors, we collected interference patterns from which we can estimate the coherence length related to the temporal coherence of the emitted beam.

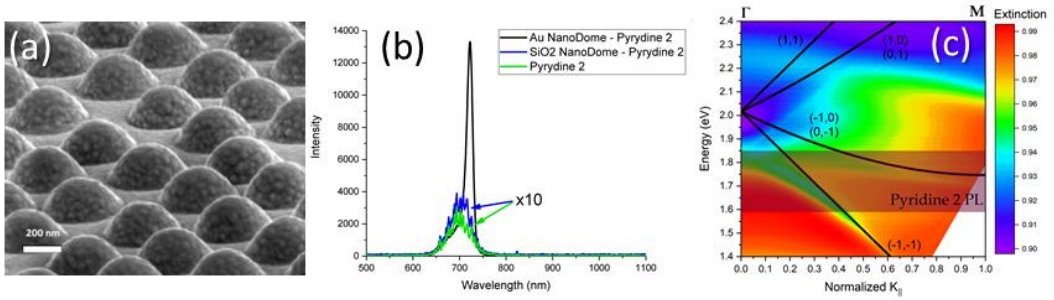


Fig.1: plasmonic nanolaser: (a) nanodome array; (b) PL emission comparison and (c) extinction map.

References

[1] Gaio, M. et al. A nanophotonic laser on a graph. Nature Communications 10, 226 (2019).
[2] Chou, Y.-H. et al. Ultracompact Pseudowedge Plasmonic Lasers and Laser Arrays. Nano Lett. 18, 747–753 (2018).
[3] Zhou, Wei, et al. Lasing action in strongly coupled plasmonic nanocavity arrays. Nature nanotechnology 8, 506 (2013).
[4] Deeb, C. et al. Correlating Nanoscopic Energy Transfer and Far-Field Emission to Unravel Lasing Dynamics in Plasmonic Nanocavity Arrays. Nano Lett. 18, 1454–1459 (2018).

Multiphysics systems

Coupling Plasmonics with Magnetism in Magnetoplasmonic Hybrid Nanoalloys

Alessio Gabbani [1], *Elvira Fantechi* [1,2], *Andrea Caneschi*[2,3], *Claudio Sangregorio*[4], *Francesco Pineider* [1,2]

[1] *Department of Chemistry and Industrial Chemistry, University of Pisa, Pisa, Italy,*
alessio.gabbani@dcci.unipi.it
[2] *INSTM, Florence, Italy*
[3] *Department of Chemistry "Ugo Schiff", University of Florence, Sesto Fiorentino, Italy*
[4] *CNR-ICCOM, Florence, Italy*

Keywords: Magneto-Plasmonics

The active control of the optical response of plasmonic nanoparticles (NPs) by means of an applied magnetic field, i.e. magnetoplasmonics, can improve the performances of plasmonic devices, such as optical switches, modulators or more efficient refractometric sensors [1]. In a previous work we proved the ability of Magnetic Circular Dichroism (MCD) to detect small magnetic field-induced energy shifts of the plasmonic modes in simple Au NPs [2]. Nevertheless, the MCD signal of Au NPs is too small for applications in devices. The enhancement of the magneto-optical signal of surface plasmons is a challenging goal in magnetoplasmonics. Some examples of nanostructures have been already proposed in the literature: nickel nanodisks [3] and Au-Co-Au sandwich nanostructures [4] showed the most promising results.

In this work we propose an alternative approach which is based on the hybridization of plasmonic and magnetic properties in a single NP, a nanoalloy made of a magnetic and a plasmonic metal. Colloidal chemistry was used as an alternative nanofabrication tool with respect to the more widely employed lithographic methods, exploiting the possibility to control the size and the composition of the NPs, as well as the low cost and mild conditions needed. In these hybridized magnetoplasmonic NPs, the interaction between the conduction electrons of Au and *d* electrons of the magnetic metal can lead to an increase of the magnetic modulation.

We prepared AuFePt nanoalloys, where the presence of Pt helps to overcome the miscibility gap between Au and Fe, allowing us to tune the Au-to-Fe ratio in a range where the NPs have both magnetic and plasmonic properties. The formation of an homogeneous alloy was confirmed by X-ray Powder Diffraction, while Transmission Electron Microscopy revealed spherical NPs of about 9 nm. We then investigated the interplay between magnetic and plasmonic properties in AuFePt nanoalloys of different metal ratios (Figure 1) through MCD at room temperature. The experiments revealed that with low amount of Fe (7%), the typical plasmonic derivative-like shape of the MCD signal is observed, centered at the extinction peak, and the magnetic hysteresis loops are linear. On the other hand, if we increase the iron content up to 35%, the MCD signal is dominated by the magnetic part and the presence of the plasmonic contribution is very weak. With 11% of iron we also observed a derivative-like shape in correspondence to the extinction maximum, but with an increase of the peak to peak signal with respect to what expected for pure Au NPs [2], suggesting an enhancement of the plasmonic contribution to the magneto-optical signal due to an interaction between Au and the magnetic atoms.

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

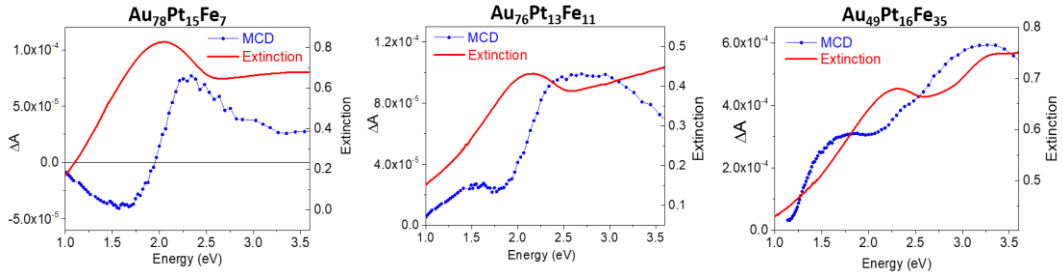


Fig. 1 : MCD spectra (blue) at 1.4 Tesla, and extinction spectra (red) of three AuFePt nanoalloys with different composition, dispersed in a polymer film.

References

[1] G. Armelles *et al.*, Advanced Optical Materials **1**, 10-35 (2013).
[2] F. Pineider *et al.*, Nano letters **13**, 4785–4789 (2013).
[3] N. Maccaferri *et al.*, Nat. Commun. **6**, 6150 (2015).
[4] V. V. Temnov *et al.*, Nat. Photonics **4**, 107–111 (2010).

Chiral optical forces and optical trapping of optically active particles

Francesco Patti[1,2], *R. Saija*[1,2], *P. Denti*[1], *G. Pellegrini*[3], *P. Biagioni*[3], *M.A. Iatì*[2], *O. M. Maragò*[2]
[1] *MIFT, Università di Messina, I-98156 Messina, Italy*
[2] *CNR-IPCF, Istituto per i Processi Chimico-Fisici, I-98158 Messina, Italy*
[3] *Dipartimento di Fisica, Politecnico di Milano, I-20133, Milano, Italy*

Keywords: Scattering, Sensor and Biosensors, Devices and Applications.

Modeling optical tweezers in the T-matrix formalism has been of key importance for accurate and efficient calculations of optical forces and their comparison with experiments [1]. Here we extend this formalism to the modeling of chiral optomechanics and optical tweezers where chiral light is used for optical manipulation and trapping of optically active particles. We show analytically that all the observables (cross sections, asymmetry parameters) are split into a helicity dependent and independent part and study a practical example of a complex resin particle with inner copper-coated stainless steel helices. Then, we apply this chiral T-matrix framework to optical tweezers where a tightly focused chiral field is used to trap an optically active spherical particle, calculate the chiral behaviour of optical trapping stiffnesses and their size scaling, and extend calculations to chiral nanowires and clusters of astrophysical interest.

Chiral Optomechanics A chiral object is affected by the lack of symmetry under reflection [2]. Both radiation and material objects may have this property. The two chiral versions of an object are referred to as *enantiomers*. A great number of organic molecules, such as proteins and sugars, are characterized by optical activity, in fact gyrotropic studies possess a wealth of information, which has caused Barron to claim that "optical activity provides a peephole into the fabric of universe "[3]. Also the electromagnetic radiation can be considered a chiral field, expecially when we refer to left (LCP) and right (RCP) circular polarization. Its degree of chirality is measured through *optical chirality* C:

$$C = \frac{\varepsilon_0}{2}\vec{E}\cdot\vec{\nabla}\times\vec{E} + \frac{1}{2\mu_0}\vec{B}\cdot\vec{\nabla}\times\vec{B}$$

Introduced by Lipkin in the eary sixties [4]. The main feature of the interaction between a chiral media and a chiral radiation is that depends on the chirality version involved. The goal of this work is to calculate the dynamics of the interaction between a chiral nanoparticles (e.g. a drop of water-sugar) and a chiral radiation (e.g. circular polarization), both when it is a plane wave and in the case of optical tweezers configuration [5].

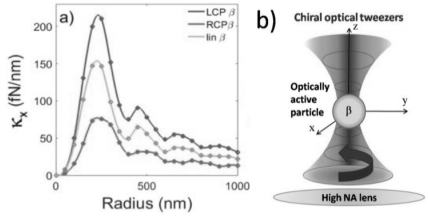


Figure 1: a) Transverse optical trapping stiffnesses as a function of the particle radius for 10 mW incident power. Different polarization states result in different optical trapping forces: for linear polarization optical trapping stiffnesses lie in between the circular polarization results. b) A chiral Gaussian beam is tightly focused through a high numerical aperture lens (chiral optical tweezers) and the optical trapping behaviour of an optically active particle is investigated.

References

[1] P. POLIMENO, A. MAGAZZÙ, M. A. IATÌ, F. PATTI, R. SAIJA, C. DEGLI ESPOSTI BOSCHI, M. G. DONATO, P. G. GUCCIARDI, P. H.JONES, G. VOLPE, O. M.MARAGÒ: *Optical tweezers and their applications* Journal of Quantitative Spectroscopy and Radiative Transfer, Volume 218, October 2018, Pages 131-150
[2] LAKHTAKIA, A., VARADAN, V., VARADAN, V.: *Time-Harmonic Electromagnetic Fields in Chiral Media.* . Springer, 1989
[3] BARRON, L. D.: *Molecular light scattering and optical activity.* Cambridge University Press, 2004
[4] LIPKIN, D. M.: *Existence of a new conservation law in electromagnetic theory.* Journal of Mathematical Physics 5, 696-700, 1964
[5] F. PATTI, R. SAIJA, P. DENTI, G. PELLEGRINI, P. BIAGIONI, M. A. IATÌ, O. M. MARAGÒ : *Chiral optical tweezers for optically active particles in the T-matrix formalism* Scientific Reportsvolume 9, Article number: 29 (2019)

Difference nanospectroscopy of Proteins in Cell Membranes Located in a 10-nanometer wide Plasmonic Nanogap

Raffaella Polito[1], Valeria Giliberti[2], Eglof Ritter[3], Matthias Broser[3], Peter Hegemann[3], Ljiljana Puskar[4], Ulrich Schade[4], Laura Zanetti-Polzi[5], Isabella Daidone[5], Stefano Corni[6,7], Francesco Rusconi[8], Paolo Biagioni[8], Leonetta Baldassarre[1] and Michele Ortolani[1,2]

[1] *Department of Physics, Sapienza University of Rome, Italy, raffaella.polito@uniroma1.it*

[2] *Istituto Italiano di Tecnologia, Center for Life NanoScience, Roma, Italy*

[3] *Humboldt-Universität zu Berlin, Institut für Biologie, Berlin, Germany*

[4] *Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany*

[5] *Department of Physical and Chemical Sciences, University of L'Aquila, L'Aquila, Italy*

[6] *Department of Chemical Sciences, University of Padova, Italy*

[7] *CNR Institute of Nanoscience, Modena, Italy*

[8] *Dipartimento di Fisica, Politecnico di Milano, Milano, Italy*

Keywords: Spectroscopy and nano-imaging, Sensor and Biosensors

Transmembrane proteins (TMPs) are fundamental cell receptors that can act as ion pumps and channels through the cell membrane. TMPs perform their function through a series of conformational changes triggered by external stimuli, including visible light as for example in Bacteriorhodopsin (BR). Fourier Transform InfraRed (FTIR) difference-spectroscopy can provide a valuable insight into changes of secondary structures of proteins, but requires large amounts of purified proteins [1]. In order to study the more biologically interesting case of proteins embedded in natural cell membranes, which are intrinsically heterogeneous, IR difference spectroscopy has to be performed at the nanoscale exploiting plasmonic approaches, such as in the tip-enhanced IR nanospectroscopy (also referred as AFM-IR, because it is based on an atomic force microscope illuminated by a IR quantum cascade laser, detecting photothermal expansions under the tip).

Our samples consist of thin dried cell membrane patches of approximately 1 micron in diameter (well below the diffraction limit for IR spectroscopy) containing BR, deposited on ultraflat gold substrates. The use of a gold-coated AFM tip produces a plasmonic nanogap whose width is defined by the cell membrane thickness itself. In the present case of double cell membrane stacks, this is 10 nanometers. The field enhancement in the gap is of the order of 50 (see Fig. 1a). The radiation field in the nanogap is vertically polarized, as demonstrated by the normalized AFM-IR absorbance in Fig. 1b of membrane stacks of different thickness. Therein, the intensity of amide II band at 1540 cm^{-1} (mainly due to in-plane N-H vibrations) is reduced with decreasing thickness, while the intensity of amide I band at 1660 cm^{-1} (mainly due to out-of-plane C=O vibrations) remains constant, and its signal-to-noise ratio even improves thanks to plasmonic electric-field enhancement.

Difference AFM-IR spectra were acquired for the first time on a protein system under visible light illumination [3] (Fig. 1c). As a control experiment, we measured by standard diffraction-limited micro-FTIR the difference absorption spectra in the region of amide I band of two sample regions of thickness 500 and 100 nm and compared them with vibrational calculations performed in a hybrid quantum-classical approach (Fig. 1d). The minor differences are attributed to changes in orientation of dipole moments during the BR photocycle in the case of the two different electric field orientations.

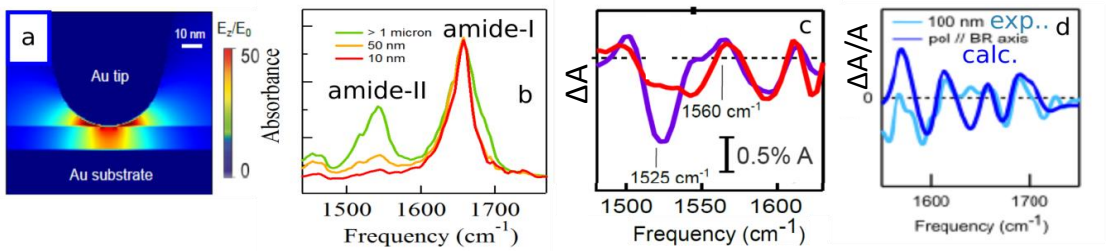


Figure 1: (a) Simulation of field enhancement in the 10-nm wide plasmonic nanogap. (b) AFM-IR absorption spectra of BR. (c) Difference AFM-IR ΔA under visible light stimuli on a 1 micron thick film (purple) and on the 10-nm thick membrane stack in the nanogap (red). (d) ΔA/A comparison with theory.

References

[1] E. Ritter et al., *Front Mol Biosci*. 2, (2015)

[2] V. Giliberti et al., *Small*, 13, 1701181 (2017)

[3] V. Giliberti et al, accepted for publication on *Nano Letters*, 2019

Plasmonics of Au Nanoparticles in a Variable-Temperature Thermodynamic Bath

Marzia Ferrera[1], Michele Magnozzi[1,2], Francesco Bisio[3], Maurizio Canepa[1]
[1]*OptMatLab, Dipartimento di Fisica, Università degli Studi di Genova, via Dodecaneso 33, 16146 Genova, Italy, ferrera@fisica.unige.it*
[2]*Istituto Nazionale di Fisica Nucleare, via Dodecaneso 33, 16146 Genova, Italy*
[3]*CNR-SPIN, corso Perrone 24, 16152 Genova, Italy*

Keywords: Thermo-Plasmonics.

Electromagnetically-heated metal nanoparticles can be exploited as efficient heat sources at the nanoscale [1]. The assessment of their temperature is, however, often performed indirectly by modelling their temperature-dependent dielectric response. Direct measurements of the optical properties of metallic nanoparticles in equilibrium with a thermodynamic bath provide a calibration of their thermo-optical response, to be exploited for refining current thermo-plasmonic models or whenever direct temperature assessments are practically unfeasible. We investigated the plasmonic response of supported Au nanoparticles in a variable-temperature thermodynamic bath from room temperature to 350 °C by means of in-situ spectroscopic ellipsometry. The experiments were performed within a roll-on/roll-off high-vacuum chamber equipped with a heating stage, placed between the arms of a spectroscopic ellipsometer (J.A Woollam M-2000) [2].

A model explicitly including the temperature-dependent bulk dielectric function of the metal and finite-size corrections to the nanoparticles' permittivity correctly reproduced the experimental data for temperatures up to 75 °C (Figure 1a). In absence of any further assumption, the model accuracy gradually faded for higher temperatures, underestimating the plasmon damping. Introducing a temperature-dependent correction term in the permittivity of the nanoparticles that effectively mimics an electronic surface-scattering-like source of damping restored good agreement with the experimental data (Figure 1b). A finite-size thermodynamic effect such as surface premelting is invoked to account for this effect [3].

We show that finite-size thermodynamic effects do play a role in the thermo-plasmonic response of nanosystems and need to be explicitly included in theoretical models for thermo-plasmonics.

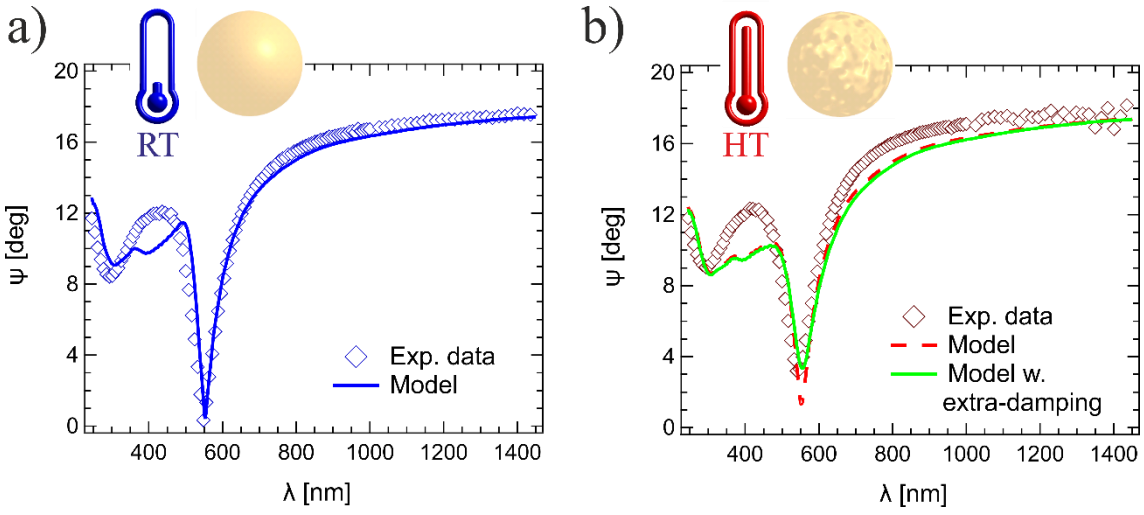


Figure 1: Experimental ellipsometric spectra (markers) and calculated curves (lines) at a) room temperature (RT) and b) high temperature (HT). Agreement at HT is improved by considering an extra-damping contribution in the model (green curve).

References

[1] G. Baffou and R. Quidant, Laser Photonics Rev., **7** (2), 171-187 (2013).
[2] M. Magnozzi et al., Appl. Surf. Sci., **421**, 651-655 (2017).
[3] M. Magnozzi et al., Nanoscale, **11**, 1140-1146 (2019).

Polarization-dependent thermoplasmonic response of anisotropic metal nanoparticles

R. Gillibert,[1] *F. Colas,*[2] *M. Lamy de La Chapelle,*[3] *M. G. Donato,*[1] *O. M. Maragò*[1] *and P. G. Gucciardi.*[1]

[1] *CNR-IPCF, Viale F. Stagno D'Alcontres 37, 98168 Messina, Italy*
[2] *IFREMER LDCM, Centre Bretagne, CS 10070, 29280 Plouzané, France*
[3] *IMMM, Le Mans Université, Av. O. Messiaen, 72085 Le Mans, France*

Keywords: Thermoplasmonic, bubbling threshold, polarization.

Heat generation is enhanced whenever metal nanoparticles are excited resonantly with their localized surface plasmons (LSP).[1] Anisotropic nanoparticles, such as gold nanorods, feature spectrally distinct LSPs that can be selectively excited by varying the wavelength and the polarization of the incident light. Theoretical simulations suggest that heat generation in anisotropic nanoparticles is polarization-dependent.[2]

Here we show this effect experimentally, by measuring the power necessary to induce bubbling on gold nanorods immersed in water, varying polarization and wavelength of the excitation field.[3] A strongly anisotropic polarization-dependence of the bubbling threshold is observed when the laser is resonant with any of the nanorods' LSPRs. The heating efficiency is observed to change proportionally to the square of the projection of the incident field on the nanorods' principal axis. This effect is observed also for the transverse plasmon, but only when its oscillator strength is enough to overcome the dissipation induced by the longitudinal plasmon. At shorter wavelengths (e.g. 488nm), when the interband transitions are excited, the thermal response of the samples is observed to be isotropic.

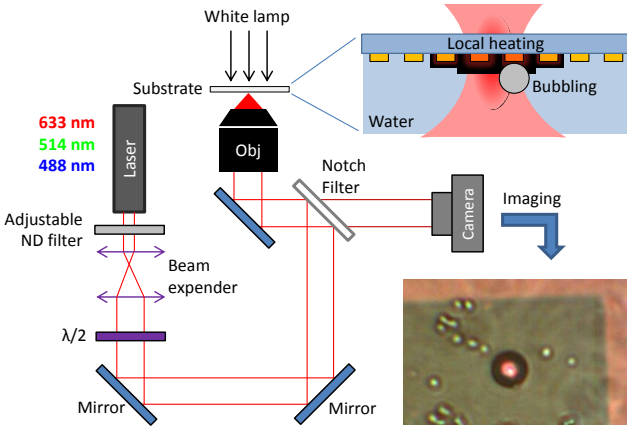


Figure 1: Experimental setup used to excite plasmons and visualise induced bubbling.

References

[1] Baffou, G.; Quidant, R. Laser Photonics Rev. 2013, 7, 171–187..
[2] Girard, C.; et al. J. Opt. 2018, 20, 075004.
[3] Gilliber et al. 2019, submitted.

Second Harmonic Scattering from Hybrid Gold – Dielectric Nanoparticles

Zacharie Behel[1], Rachael Taitt[2], Virginie Monnier[2], Yann Chevolot[2], Melissa Maldonado[4], Renato E. de Araujo[3], Anderson S.L. Gomes[4], Ch. Jonin[1], P.F. Brevet[1]

[1]Institut Lumière Matière, ILM UMR CNRS 5306, Université Claude Bernard Lyon 1, Université de Lyon, Villeurbanne France, zacharie.Behel@univ-lyon1.fr
[2]Institut des Nanotechnologies de Lyon INL UMR CNRS 5270, Ecole Centrale de Lyon, Université de Lyon, Ecully, France;
[3]Departmento de Eletronica e Sistemas, Universidade Federal de Pernambuco, Recife, Brazil ;
[4]Departamento de Física, Universidade Federal de Pernambuco, Recife, Brazil;

Keywords: Scattering, Nonlinear Plasmonics, Plasmonic and dielectric nanoantennas

.

Second harmonic scattering (SHG) is an ideal method to characterize gold nanoparticles dispersed in solutions in the absence of substrates. SHG is indeed a nonlinear optical phenomenon where symmetry is critical in determining these properties. Hence, performing this characterization in absence of substrate removes the possible problems related to the supporting substrates.
Whole metallic nanoparticles of different size and shape have been investigated in the past, especially those with a centrosymmetric shape like nanospheres, nanorods or nanocubes. Understanding the origin of the response has been at the center of the attention in order to design nanoparticles with the best cross-section, also known as first hyperpolarizability, for the SHG process and therefore applications like sensing. However, besides size and shape, the morphology is also an interesting route that has been recently explored.
In this work, we present our recent results where we have investigated hybrid gold – dielectric nanoparticles. In particular, for a better insight into the key parameters driving the response, we have explored two routes. The first one is that of gold nanoshells where the inner dielectric core, silica, is amorphous and therefore not SHG efficient. The second entails the replacement of the inefficient inner core material silica by the efficient SHG material lithium niobate. We report the first hyperpolarizabilities as well as depolarization ratios and size effect parameters for these hybrid systems and compare them to pure gold nanospheres (see Figure 1) to provide a comprehensive view of the problem.

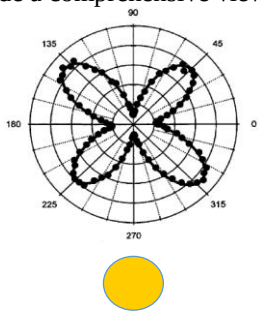


Figure 1 : Polar plot of the Second Harmonic Scattering intensity polarized perpendicularly to the plane of scattering recorded for an aqueous suspension of dispersed 150 nm gold nanospheres.

References

[1] J. Butet, P.F. Brevet, O.J.F. Martin, Optical Second Harmonic Generation in Plasmonic Nanostructures: From Fundamental Principles to Advanced Applications, *ACS Nano,* **9** (2015) 10545
[2] J. Butet, A. Maurice, E. Bergmann, G. Bachelier, I. Russier-Antoine, C. Ray, O. Bonhomme, Ch. Jonin, E. Benichou, P.-F. Brevet, Second Harmonic Generation with Metallic Nanoparticles, in Metal Nanostructures for Photonics, Elsevier, Amsterdam, 2018
[3] I. Russier-Antoine, E. Benichou, G. Bachelier, Ch. Jonin, P.F. Brevet, Multipolar Contributions of the Second Harmonic Generation from Silver and Gold Nanoparticles, *J. Phys. Chem. C*, **111** (2007) 9044

Probing and Imaging

Probing resonant modes in hyperbolic metamaterial nanostructures with electron energy loss spectroscopy

Tommi Isoniemi[1], Nicolò Maccaferri[1,2], Quentin M. Ramasse[3], Rosaria Brescia[1], Giuseppe Strangi[4,5], Francesco De Angelis[1]

[1] *Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy*

[2]*University of Luxembourg, 162a avenue de la Faïencerie, L-1511 Luxembourg, Luxembourg*

[3] *SuperSTEM Laboratory, STFC Daresbury, Keckwick Lane, Daresbury, WA4 4AD, UK*

[4]*Department of Physics, Case Western Reserve University, 10600 Euclid Avenue, Cleveland, Ohio 44106, USA*

[5]*CNR-NANOTEC Istituto di Nanotecnologia and Department of Physics, University of Calabria, 87036, Italy*

Keywords: Metamaterials, Plasmonic and dielectric nanoantennas, Spectroscopy and nano-imaging

Layered metal/dielectric hyperbolic metamaterials (HMMs) [1] support a rich landscape of plasmon polariton excitations. In addition to surface plasmon polaritons, coupled Bloch-like gap-plasmon polaritons with a high modal confinement inside the layered structure can be excited. Photons can excite only a subset of these polaritonic modes, and typically with a limited energy and momentum range, with respect to the wide set of high-k modes supported by hyperbolic dispersion media. Strikingly, electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM) allows to excite and map the spatial distribution of both bright and dark modes using nm-scale local excitation, [2] including low energy phonons.

Herein, the full range of these modes is observed using an aloof electron beam adjacent to the HMM nanostructures, and the nature of the modes is confirmed with corresponding simulations of EEL spectra and optical near-field intensities. HMM slots provide subwavelength scale waveguides useful for photonic nanocircuitry, and display prominent standing waves at resonant energies (Fig. 1). Localized Bloch plasmon polariton modes are seen in HMM pillar resonators, which can be applied to produce spectrally separate optical scattering and absorption channels. [3] We report experimental evidence of the spatial distribution of plasmon polaritons in a multilayered type II HMM, paving the way towards a full control of radiative and nonradiative mechanisms in hyperbolic dispersion materials.

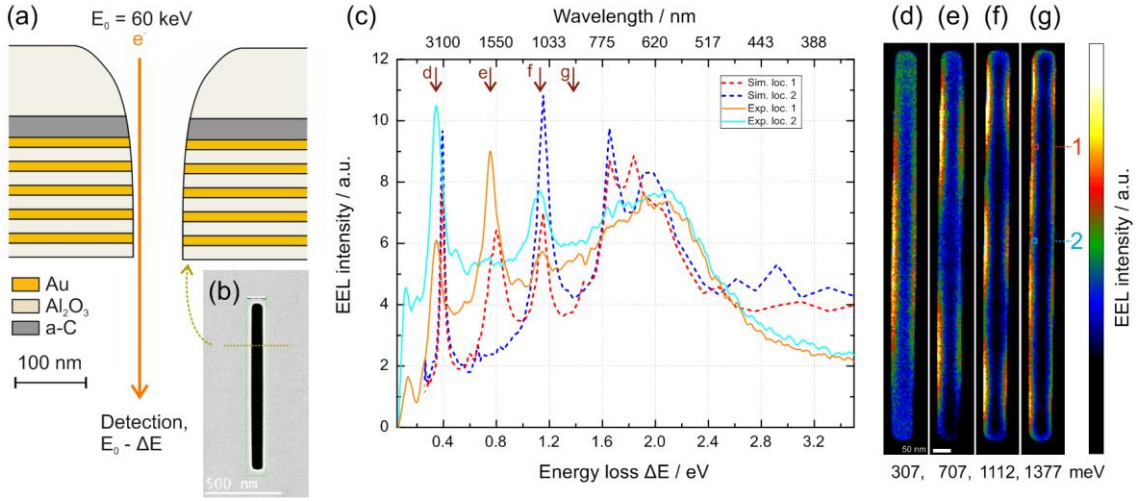


Figure 1: HMM slot resonator, length 1 µm. a) Cross-section schematic of the measurement. b) High-angle annular dark field STEM image of the slot. c) Simulated and experimental EELS spectra at two positions marked in g) with resonant peaks marked and the zero-loss peak substracted. d-g) Experimental EELS intensity maps of the same slot at the marked energy losses.

References

[1] A.N. Poddubny, I. Iorsh, P. Belov, Y. Kivshar. Nat. Photonics **7**, 948–957 (2013).

[2] S. Raza, M. Esfandyarpour, A.L. Koh, N.A. Mortensen, M.L. Brongersma, S.I. Bozhevolnyi. Nat. Commun. **7**, 13790 (2016).

[3] N. Maccaferri, Y. Zhao, T. Isoniemi, M. Iarossi, A. Parracino, G. Strangi, F. De Angelis. Nano Lett., **19**(3), 1851-1859 (2019).

Near-field imaging of surface-plasmon vortex-modes around a single elliptical nanohole in a gold film.

Claudia Triolo[1*], Salvatore Savasta [1], Alessio Settineri[1], Sebastiano Trusso[2], Rosalba Saija[1], Nisha Rani Agarwal[3], Salvatore Patanè[1]

[1] *Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra, University of Messina, Messina, Italy.* *trioloc@unime.it

[2] *CNR-IPCF, Istituto per i Processi Chimico-Fisici del CNR, Messina, Italy*

[3] *Faculty of Science, University of Ontario Institute of Technology, Oshawa, ON Canada*

Keywords: Spin-Momentum Locking, Plasmon-Vortex, Scanning Near-field Optical Microscopy.

Light carries both spin and momentum. Spin−orbit interactions (SOIs) of light come into play at the subwavelength scale of nano-optics and nanophotonics, where they allow to control the spatial degrees of freedom of light selecting the spin states of incident photons. However, due to the small momentum carried by photons, the SOIs of light are exceedingly small and their experimental observation is challenging. In order to explore such weak processes, plasmonic metamaterials (nanoparticles or nanostructured thin films that support plasmon resonances) are largely used, thanks to the flexibility of their structural design and the enhanced subwavelength local field. In this context, we discuss about the SOIs effects generated in near-field region by means the excitation of surface plasmon polaritons (SPPs) around a single elliptical nanohole in a gold thin film. The optical setup is a Near-field Scanning Optical Microscope (SNOM) working in transmission mode. Exploiting the rotational symmetry breaking due to the elongated shape of the nanohole, a plasmonic vortex mode is generated by illuminating the hole with an incident light beam without a spin state (linearly polarized beam) able to excite SPPs and localized plasmon resonances. SNOM technique allows to obtain information on both the amplitude and phase of the electromagnetic near-field distribution and, thanks to this feature, a direct observation of the vortex mode is possible. Interestingly, the rotation direction of the vortex (right- or left-hand rotation) depends on the angle that the linear polarization direction forms with the major axis of the nanohole ($\pm 45°$, respectively). This behaviour can be considered as a counterpart of the photonic spin Hall effect generated in absence of the spin state of the light and caused by the rotational symmetry breaking of the elliptical nanostructure. Results are supported by Finite Element Method (FEM) simulations, which reproduce the plasmonic vortex mode of the scattered field around the nanohole at 2 nm from the sample surface. Due to the geometrical anisotropy of the nanohole, both number and the distribution of the phase singularities change. Especially, when the linear polarization direction of incident field and the symmetry axes are tilted, phase singularity points are odd and the system acquires a topological charge ± 1, which generates a spiral-like flow of the optical momentum vector around the nanohole and, hence, of the scattered field.

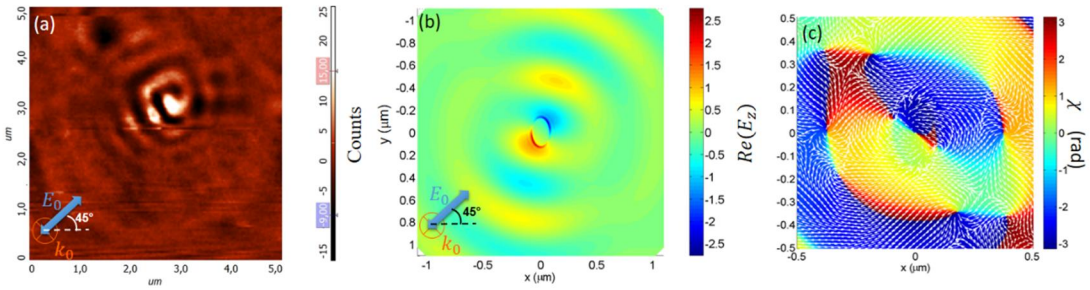


Figure: (a) SNOM image (scan area 5μm×5μm) performed using an incident beam at $\lambda_{exc} = 632$ nm with normal incidence and linear polarization at 45° on an elliptical nanohole in a thin gold film. In order to mainly detect the scattered contribution, a second linear polarizer, crossed to the first one, is placed in the collect optical path. (b) Near-field intensity distribution of $Re(E_z)$ around the elliptical nanohole illuminated by a plane wave at $\lambda_{exc} = 632$ nm, at 2 nm from the metal surface. Simulations are performed by FEM simulation. Size of nanohole: major axis a=130 nm, minor axis b=80 nm. (c) Spatial distribution (1μm × 1μm) of the phase variation of the z-component of the total field calculated by FEM simulations at 2 nm from the Au surface for an incident polarization direction at 45°. White arrows are the optical momentum vectors that evidence the formation of optical vortices around the phase singularities.

References

[1] C. Triolo, S. Savasta, A. Settineri, S. Trusso, R. Saija, N. R. Agarwal, S. Patanè, "Near-field imaging of surface-plasmon vortex-modes around a single elliptical nanohole in a gold film", to appear on *Scientific Reports*.

Quantitative measurement of the optical cross-sections of single nano-objects

Attilio Zilli[1,†], *Lukas Payne*[1], *Yisu Wang*[1], *Zoltan Sztranyovszky*[2], *Wolfgang Langbein*[2], *Paola Borri*[1]

[1] *Cardiff University, School of Biosciences, Museum Avenue, CF10 3AX Cardiff, UK*

[2] *Cardiff University, School of Physics and Astronomy, The Parade, CF24 3AA Cardiff, UK*

[†] *Present address: Politecnico di Milano, Physics Department, Piazza L. Da Vinci 32, 20133 Milano, Italy*

e-mail: attilio.zilli@polimi.it

Keywords: Plasmonic and dielectric nanoantennas, Spectroscopy and nano-imaging, Scattering

The linear optical properties of a nano-object are described by its cross-sections for scattering (σ_{sca}) and absorption (σ_{abs}) of light. The presently available experimental techniques capable of measuring the cross-section magnitude — namely, the strength of the interaction between the object and the electromagnetic field — require costly equipment and complicated analyses, and are often unable to accurately quantify σ_{sca}. In contrast, we have developed a simple method to measure quantitatively both σ_{sca} and σ_{abs} which can be implemented on a commercial optical microscope equipped with a camera or a spectrometer [1].

In my presentation, I will first introduce the rationale of our method, and compare its advantages and limitations with respect to the main alternative experimental tools. I will then display results obtained on a variety of relevant nanoparticle systems, including silver cubes (see Fig. 1), gold spheres, gold rods, and dielectric spheres. Comparison of quantitative cross-section measurements with numerical simulations — which must carefully reproduce the illumination and detection conditions of high numerical aperture microscopy experiments [1, 2] — can bring about an accurate estimate of some unknown parameter of the system, such as for instance a geometric dimension (so-called *optical sizing*). Additionally, correlating measurements of the same object in different environments can offer more robust estimates, especially in systems with multiple unknown parameters. Fig. 1 provides a simple example of such analysis.

Our group has been developing a widefield image analysis technique which is capable of measuring >100 objects per image with a sub-nm^2 noise level in the extinction cross-section [3]. I will show that this technique as well can be accurately quantitative and, in conjunction with the optical sizing procedure described above, offer a high-throughput optical characterization of colloidal samples [4] which outperforms widespread diffusion-based techniques (such as dynamic light scattering) in a range of relevant scenarios.

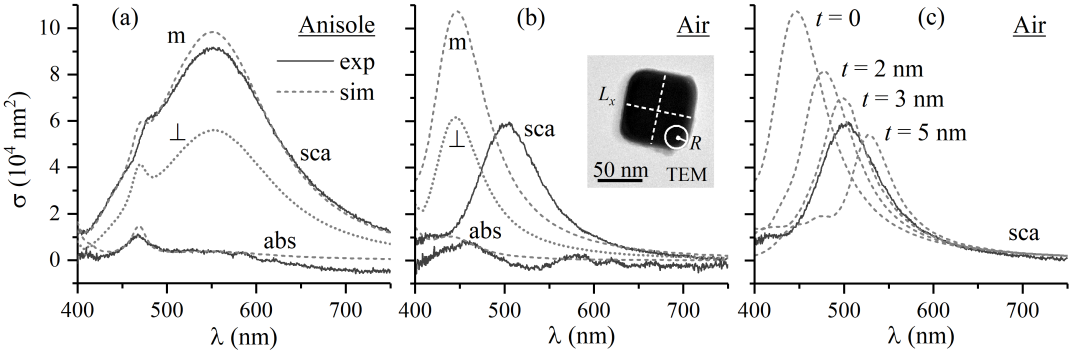


Figure 1: Measured (solid line) and simulated (dashed/dotted line) cross-section (σ) spectra of the silver cube shown in the transmission electron microscopy (TEM) inset of panel (b). The cube is deposited on a 40 nm silica TEM grid and surrounded by (a) anisole ($n = 1.52$) and (b) air. In anisole, the simulation indicated by m (dashed) includes an accurate description of the high numerical aperture illumination of experiments, and brings about a better agreement to the experiment than the simulation indicated by $\perp$ (dotted), where the excitation is modeled as a plane wave impinging normally onto the substrate. In air, the dipolar plasmonic resonance of $\sigma_{sca}(\lambda)$ is red-shifted by 60 nm with respect to the numerical prediction. As shown in (c), this can be explained as due to the oxidation of a $t \simeq 4$ nm thick superficial layer (whereas adhesion of contaminants would red-shift the simulated peak but at the same time increase its amplitude).

References

[1] A. Zilli, W. Langbein, and P. Borri, "Lights and shadows at the nanoscale", *under review*.

[2] L. Payne, A. Zilli, Y. Wang, W. Langbein, and P. Borri, Proc. SPIE **10892**, 108920J (2019).

[3] L. Payne, W. Langbein, and P. Borri, Phys. Rev. Appl. **9**, 034006 (2018).

[4] W. Langbein, P. Borri, L. Payne and A. Zilli, British pat. req. GB1,711,886.0 (Jul 2017).

Scattering Assisted Imaging

Marco Leonetti[1, 2, 3], Alfonso Grimaldi[1], Silvia Ghirga[3], Giancarlo Ruocco[1,2] & Giuseppe Antonacci[4]
[1]*Center for Life Nano science @ Sapienza, IIT, Viale Regina Elena, 291,00161, Roma,Italy.*
[2]*CNR NANOTEC Institute of Nanotechnology, Via Monteroni, 73100, Lecce, Italy.*
[3]*Dipartimento di Fisica,Universitá "La Sapienza", Piazzale Aldo Moro, 5, I-00185, Roma, Italy.*
[4]*Photonics Group, Ghent University - imec, Technologiepark Zwijnaarde 15, 9052, Ghent, Belgium.*

Keywords: Microscopy, Scattering, Super Resolution.

Standard imaging systems provide a spatial resolution that is ultimately dictated by the numerical aperture (NA) of the illumination and collection optics. In biological tissues, the resolution is strongly affected by scattering, which limits the penetration depth to a few tenths of microns. In a recently published paper [1], we exploit the properties of speckle patterns embedded into a strongly scattering matrix to illuminate the sample at high spatial frequency content. Combining adaptive optics with a custom deconvolution algorithm, we obtain an increase in the transverse spatial resolution by a factor of 2.5 with respect to the natural diffraction limit. Our Scattering Assisted Imaging (SAI) provides an effective solution to increase the resolution when long working distance optics are needed, potentially paving the way to bulk imaging in turbid tissues.

When illuminated with coherent light, turbid media generate speckle patterns, macular light structures arising from the interference of the scattered or transmitted electromagnetic waves[2]. In the bulk of a scattering system, these "embedded speckles" show peculiar properties because they typically exhibit a smaller dimension than the illumination point spread function (PSF) of an imaging system [3] . An embedded speckle can indeed reach a size that is independent on the system NA and given by $\lambda/2n$, with n being the refractive index of the medium and λ the wavelength [4].

By embedding a fluorescent sample into a custom, opaque mounting medium, (the gelatinous material fixing a biological sample or a cell culture), it is possible to produce embedded speckles which are much smaller than the PSF of the collection optics. Then, we exploit a custom de-convolution algorithm, which includes the priors of the known size of the speckles patterns and PSF of the collection optics to obtain a super resolved image of a biological, fluorescent sample (see Fig. 1 below).

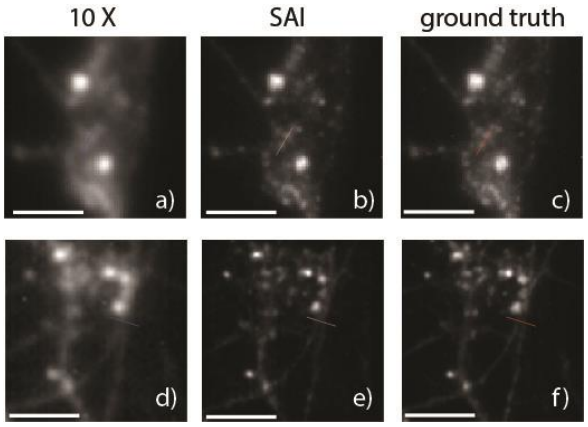


Figure 1 a-d: Images obtained of a cortical neuron taken with a low numerical aperture objective (NA=0.25) . b-e: Super resolution images obtained with the same objective (NA=0.25) and Scattering Assisted Imaging deconvolution. c-f: Ground truth obtained with a high resolution objective (NA=0.75).

References

[1] Leonetti M. et al.: Sci. Rep. 9, 4591 (2019).
[2] . Goodman, J. W. Speckle phenomena in optics: theory and applications (Roberts and Company Publishers, 2007).
[3] Rayleigh, L. J. Royal Microsc. Soc. 23, 474–482 (1903).
[4] Roarke H. et al. ; Nat. Photon. 9, 563 (2015).

Friday June 21

Plasmonic metamaterials

Andrea Alù
Photonics Initiative, Advanced Science Research Center, City University of New York
Physics Program, Graduate Center, City University of New York
Department of Electrical and Computer Engineering, City College of New York
85 St. Nicholas Terrace, New York, NY 10031, U.S.A.

In this talk, I discuss our recent effort in the context of hybrid metasurfaces formed through nanophotonic engineering metasurfaces and 2D materials, reporting our recent theoretical and experimental results in the context of hyperbolic plasmon propagation, topological polaritonics and embedded eigenstates. I will also discuss our recent efforts in the context of plasmonic cloaking, and its impact from radio-waves to nano-optics. During the talk, I will discuss their highly unusual light-matter interactions and potential opportunities of these ideas for nanophotonic devices.

Modes & Topology

Full-Wave Mode Hybridization in Nanoparticle Dimers

Mariano Pascale[1], *Giovanni Miano*[1], *Roberto Tricarico*[1,2], *Carlo Forestiere*[1]

[1] *Department of Electrical Engineering and Infromation Technology, Università degli Studi di Napoli "Federico II", via Claudio 21, 80125, Naples, Italy, mariano.pascale@unina.it*

[2] *ICFO Institut de Ciències Fotòniques, The Barcelona Institute of Science and Technology, 08860 Castelldefels, Barcelona, Spain*

Keywords: Plasmonic and Dielectric Nanoantennas; Scattering; Nanophotonics and Hybrid Plasmonics.

The plasmon hybridization theory is based on the quasi-electrostatic approximation of the Maxwell equations. It neglects magnetic interactions, retardation effects, and radiation losses. As a consequence, the magnetic modes, which play a dominant role in the scattering from dielectric nanoparticles, are completely disregarded. We propose a hybridization theory for non-hermitian composite systems, based on the full-Maxwell equations that overcomes all these limitations. It unlocks the description of dielectric dimers and refines the understanding of metal dimers. When applied to deep subwavelength metal dimers, it returns the well-known plasmon hybridization model.

We investigate the modes and resonances of the electromagnetic scattering by a dimer of spheres by using the concept of material-independent-modes (MIM) [1, 2] in the full-Maxwell regime. Specifically, each dimer mode is naturally expanded in terms of the hybridization of the modes of the two constituent spheres (assumed to be isolated), and we provide the quantitative expressions of the hybridization weights. The scattered field is then represented by an expansion in terms of the dimer-modes, where the contributions of the geometry and of the material are disentangled. By using this theoretical framework, we investigate the resonant scattering from metallic and dielectric dimers under different excitation conditions. We rigorously identify the dimer-modes behind each peak of the scattered power spectra. Then, we quantitatively provide the corresponding hybridization weights. For instance, in Fig. 1 (left), we decompose the scattering

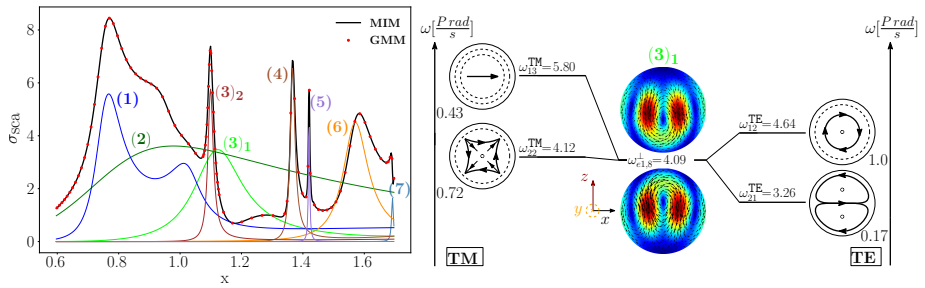


Figure 1: Scattering efficiency of a Si-spheres homodimer as a function of the size parameter $x = 2\pi R/\lambda$ of the constituent spheres, obtained via MIM expansion (black line) and by direct-calculation (red dots). The radius of each sphere is R=100nm, the edge-edge distance 25nm. The dimer is excited by a plane wave propagating orthogonally to the dimer and polarized along the dimer axis. Partial scattering efficiency (in color) of eight dominant dimer modes are shown. A hybridization diagram of the mode responsible for the third peak is displayed on the right.

efficiency of a Si-sphere homodimer in terms of its dominant dimer-modes. Then, on the right, we decompose the mode responsible for the third peak (3) in terms of the isolated sphere modes, showing below the hybridization weights. This is an extension of the hybridization diagrams by Prodan et al. [3] to the full-Maxwell case, which illustrates the hybridization of the electric and magnetic modes of an isolated-sphere into the dimer-modes and the corresponding frequency levels.

To the best of our knowledge this study represents the first full-retarded theory of hybridization in Si dimers, and it also constitutes a refinement of the plasmon-mode hybridization in a full-retarded scenario.

References

[1] C Forestiere, G Miano, Material-independent modes for electromagnetic scattering, Physical Review B 94 (20), 201406 (2016).

[2] C Forestiere, G Miano, On the nanoparticle resonances in the full-retarded regime, Journal of Optics 19 (7), 075601

[3] E Prodan, C Radloff, NJ Halas, P Nordlander, A hybridization model for the plasmon response of complex nanostructures Science 302 (5644), 419-422

Dipolar sources for directional and selective excitation of guided modes

Michela F. Picardi[1], *Martin Neugebauer*[2,3], *Jörg S. Eismann*[2,3], *Peter Banzer*[2,3], *Gerd Leuchs*[2,3], *Anatoly V. Zayats*[1] and *Francisco J. Rodríguez-Fortuño*[1]

[1]*Department of Physics, King's College London, Strand, London, WC2R 2LS, United Kingdom*

michela.picardi@kcl.ac.uk

[2]*Max Planck Institute for the Science of Light, Staudtstr. 2, D-91058 Erlangen, Germany*

[3]*Institute of Optics, Information and Photonics, University Erlangen-Nuremberg, Erlangen, Germany*

Keywords: Plasmonic and dielectric nanoantennas, Nanophotonics.

Dipolar sources have proven to be very suitable candidates for exciting modes in waveguides of any geometry, owing to the ease of realising them by illuminating individual nanostructures. Scattering from high-index dielectric nanoparticles, for example, is accurately described by a superposition of electric and magnetic dipoles when the illumination is in the visible range. Amplitudes and phases of the two dipolar excitations can be controlled tuning the illumination wavelength and polarisation [1, 2]. The interference between these electric and magnetic dipoles can give rise to interesting near-field directionalities, the most fascinating of which is arguably that of the Janus dipole. This source comprised of two orthogonal linear electric and magnetic dipoles oscillating 90° out-of-phase earns its name from its dual face behaviour. In fact, it will excite a guided mode in a waveguide if facing it from one side, while showing a complete absence of coupling when facing it from the opposite side [3], as can be seen in Fig. 1 (a) and (b), respectively. In this work, we show the first experimental realization of such a source, and introduce its spinning version, enabling omnidirectional coupling and noncoupling [4].

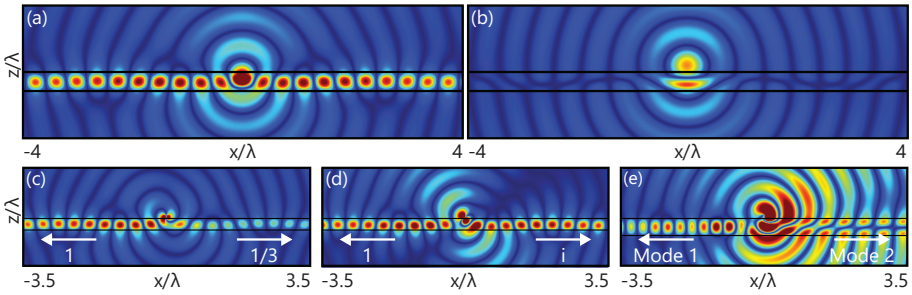


Figure 1: Magnetic field of a coupling (a) and noncoupling (b) Janus dipole placed near a single mode waveguide. In (c), (d) and (e), a multimode waveguide is excited in opposite directions with three different dipolar sources, which (c) couple to the same mode with different amplitudes, (d) couple to the same mode with opposite phases and (d) couple to two different modes.

The noncoupling Janus dipole is one of the three fundamental dipolar sources that show destructive interference (i.e., no propagation) of a specific guided mode in at least one direction. The other two are the circularly polarised and the Huygens dipoles [3]. This, however, can be extended to multimode waveguides, so that we can design dipolar sources, superpositions of electric and magnetic dipoles, that will selectively excite only one mode, or more than one, each with tunable amplitude and phase. This is seen in the lowermost panels of Fig. 1. In Fig. 1 (c), the same mode is excited in different directions with different amplitudes, in (d) the same mode is excited in different directions with the same amplitude but 90° out-of-phase. In (e), two different modes are excited at the same time, each propagating in one defined direction only. Once the waveguide's dispersion relation is known, design and optimization of the aforementioned examples of dipolar sources can be performed analytically [5]. The fascinating scenario of deciding which mode to excite in multimode waveguides, with a full control over amplitudes and phases by simply tuning the components of electric and magnetic dipoles, can lead to signigicant advancements in subwavelength light routing, information processing, and all-optical nanophotonic circuitry.

References

[1] M. Neugebauer et al, Polarization Controlled Directional Scattering for Nanoscopic Position Sensing, Nat. Comm. **7**, 11286 (2016)

[2] J. Eismann, M. Neugebauer, P. Banzer, Exciting a chiral dipole moment in an achiral nanostructure, OPTICA **5** 954-959 (2018)

[3] M. F. Picardi, A. V. Zayats and F. J. Rodríguez-Fortuño, Janus and Huygens Dipoles: Near-Field Directionality Beyond Spin-Momentum Locking, Phys. Rev. Lett. **120**, 117402 (2018).

[4] M. F. Picardi et al, Experimental demonstration of linear and spinning Janus dipoles for polarisation and wavelength selective near-field coupling, Accepted for publication Light: Science and Applications (2019). Preprint arXiv:1901.07236

[5] M. F. Picardi, A. V. Zayats and F. J. Rodríguez-Fortuño, Engineering dipolar far and near-fields for selective excitation and full amplitude and phase control of guided modes, In preparation.

Topological photonics: Mistaken paradigms and new opportunities

A. Garcia-Etxarri[1,2,], M. Blanco de Paz[1], M. Garcia-Vergniory[1,2], D. Bercioux[1,2] and B. Bradlyn[3]*

[1] Donostia International Physics Center, 20018 Donostia-San Sebastian, Spain
[2] IKERBASQUE, Basque Foundation for Science, Maria Diaz de Haro 3, 48013 Bilbao, Spain
[3] Department of Physics and Institute for Condensed Matter Theory, University of Illinois at Urbana-Champaign, Urbana, IL, 61801-3080, USA

Keywords: Topological photonics, Photonic Crystals, light-matter interaction

Topological states of matter were first discovered in the field of solid-state physics but recent contributions are proving their existence in diverse fields of science. To mention a few, topological surface states have been recently identified in the fields of optics [1], acoustics [2] and in excitonic and polaritonic materials [3].

Most of these cross-disciplinary designs have been directly inherited from concepts previously discovered in electronic materials. Nevertheless, these different physical mechanisms, should lead to distinct effects with interesting properties of their own. Unfortunately those assets will remain hindered if the research on topological effects in these fields continues to be exclusively based on analogies with solid-state systems.

A recent article unveiled a new method, named Topological Quantum Chemistry (TQC) [4], which allows predicting the emergence of topological phases on matter based exclusively on Elementary Band Representations, a mathematical tool very well known in the field of crystallography. Applying TQC to electronic, photonic, excitonic and acoustic systems could unveil the emergence of novel and distinct topological states pivoted by the unique characteristics of the distinct physical excitations in each system.

In this work, we applied TQC to Photonic crystals; surprisingly, we discovered that certain paradigms in the design of Photonic Topological insulators are not strictly truthful. Moreover, the versatility of the method allowed us to design novel topological photonic systems with unprecedented physical properties.

References

[1] Lu, L., et. al. Nature Photonics, 8(11), 821 (2014)

[2] He, Cheng, et. al. Nature Physics, vol. 12, no 12, p. 1124 (2016)

[3] S. Klemb et. al. Nature 562, 552–556 (2018)

[4] Barry Bradlyn et. Al. Nature 547 (7663), 298 (2017)

Metamaterial Simulation with ANSYS

F. Calvano[1]

(1) Ansys

Metamaterials are rapidly becoming a key research topic in today's leading academic and commercial laboratories. Applications ranging from cloaking to miniaturization have necessitated new analysis and design approaches to these electromagnetically complex materials. Full-wave 3D electromagnetic tools, such as ANSYS HFSS, are frequently used to test theory, extract effective material properties, and predict real-world effects.

Non Linear Effects

Nonlinear Light Generation in Disordered Micro-Balls

Romolo Savo[1], *Andrea Morandi*[1], *Fabian Kaufmann*[1], *Flavia Timpu*[1], *Marc Reig Escalé, Michele Zanini*[2], *Lucio Isa*[2] *and Rachel Grange*[1]

[1] *Optical Nanomaterial Group, Institute for Quantum Electronics, Department of Physics, ETH Zürich, Auguste-Piccard- Hof 1, 8093 Zürich, Switzerland*

[2] *Laboratory for Interfaces, Soft Matter, and Assembly, Department of Materials, ETH Zürich, Vladimir-Prelog- Weg 5, 8093 Zürich, Switzerland*

Keywords: Plasmonic and dielectric nanoantennas, Nonlinear plasmonics, Metamaterials.

Disordered photonic materials offers original strategies to overcome phase-matching limitations in nonlinear optical generation. In particular, polycrystalline structures with random distribution of the crystalline domains can produce a globally incoherent nonlinear light generation with relaxed phase-matching conditions. This effect is known as random quasi-phase matching (RQPM) and its distinctive feature is the linear scaling of the nonlinear light intensity with the number of domains [1-2]. RQPM has been exclusively investigated in transparent polycrystalline films generating a second-harmonic signal, with domains size of the order of the coherence length (few tens of microns). However, RQPM is expected for any size of the crystal domains [3], down to the nano-scale, but no evidence has been produced so far, because of material and fabrication limitations.

Here, we employ bottom-up assembly of noncentrosymmetric metal-oxide nanoparticles to realize disordered micro-spheres that generate random quasi-phase matched second harmonic. Despite the intrinsic inhomogeneity (40% porosity) the micro-spheres are surprisingly transparent in the visible range and can also sustain Mie resonances. Under near infrared femtosecond laser illumination, the second harmonic generation appears as a speckle pattern, confirming the random nature of the nonlinear generation. We investigated several tens of structures of growing size and observe a robust linear scaling of the generated second harmonic with their volume, remarkably over three orders of magnitude. As far as we know, this is the first evidence of random quasi-phase matching in nanostructured systems. Very interestingly, on top of the pure volume dependence, we observe highly peaked second harmonic signal for some specific sphere sizes, suggesting resonant effects stemming from the outer geometry.

References

[1] Baudrier-Raybaut, M., et al. *Nature* 432.7015 (2004): 374.
[2] Skipetrov Sergey E. *Nature* 432.7015 (2004): 285-286.
[3] Vidal Xavier and Jordi Martorell, *Physical review letters* 97.1 (2006): 013902.

Efficient Second Harmonic Generation in Dielectric Nanoantennas with Epsilon-Near-Zero Substrate

Davide Rocco[1,2], Costantino De Angelis[1,2], Domenico De Ceglia[3], Luca Carletti[1,3], Maria Antonietta Vincenti[1,2].

[1]*Department of Information Engineering, University of Brescia, Via Branze 38, 25123 Brescia, Italy*

[2]*National Institute of Optics (INO), Via Branze 45, 25123 Brescia, Italy*

[3]*Department of Information Engineering, University of Padova, Via G. Gradenigo, 6/B, Padova, Italy*

Keywords: Scattering, Plasmonic and dielectric nanoantennas.

Dielectric nanoantennas have recently gained increasing interest for many applications [1,2]. Recently, a nanoscale system based on AlGaAs nanodisks placed over an AlO_x substrate pumped in the telecom range has been theoretically and experimentally proposed as an efficient approach to enhance second-order nonlinear effects in nanoscale optics with a conversion efficiency up to 10^{-5} [3,4].

Nonetheless, the generated nonlinear signal tends to remain more confined in the substrate since it typically has a greater refractive index than the upper surrounding air. To overcome this drawback a promising possibility is the use of epsilon near zero (ENZ) substrates. Here we demonstrate how one can exploit the peculiar ability of ENZ substrates to re-direct the electromagnetic radiation to increase the efficiency of nonlinear processes generated in high-refractive index nanoantennas. We consider an AlGaAs nanodisk with optimized radius *r* equal to 232 nm and height *h* of 400 nm. The dispersion of the ENZ substrate is modelled with a single Lorentz oscillator with the epsilon near zero condition around λ = 775 nm, i.e. the second harmonic wavelength. Figure 1(a) shows the electric field distribution for the designed nanoantenna when the substrate is the ENZ material with a plane wave excitation. It can be seen how the electric field inside the cylinder reached an enhancement factor equal to 35. The field distribution at the interface between the substrate and the cylinder can be attributed to the excitation of surface plasmon polaritons of the underlying ENZ material by the dielectric nanoparticle on top. Figures 1(b) and (c) also report the corresponding SH electric field enhancement and the SH far field, respectively. We calculate a second harmonic conversion efficiency up to 3×10^{-3} for a plane wave pump with amplitude E_0 and corresponding intensity I_0 equal to 1.6 GW/cm^2 at a fundamental wavelength of 1550 nm.

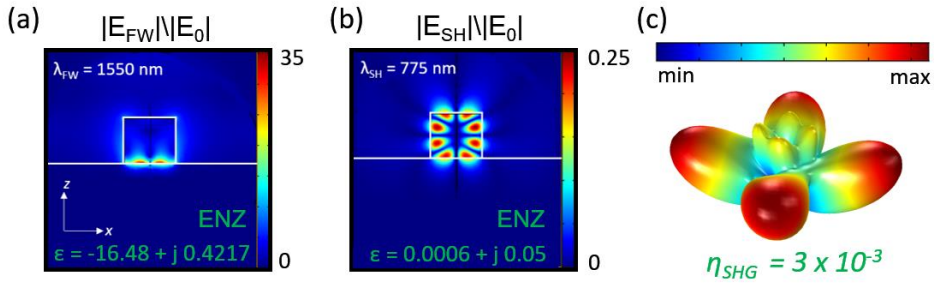


Figure 1: Electric field enhancement at the Fundamental Wavelength (FW) [(a)] and Second Harmonic (SH) [(b)] in the case of nanocylinder with radius *r* and height *h* placed over the ENZ. The permittivity of the ENZ substrate is also indicated. (c) The SH Far Field.

We also verify that the presence of the ENZ can improve the scattered SH signal up to three orders of magnitude with respect to a dielectric substrate and up to two orders of magnitude with respect to a metallic one when placing the same AlGaAs nanoantenna over the different materials. Thus, in this work, we demonstrate how it is possible to enhance the second harmonic efficiency and directivity by exploiting simultaneously the strong electric field enhancement induced inside the structure at the FW and the ENZ condition at the SH wavelength.

References

[1] A.I. Kuznetsov, A.E. Miroshnichenko, M.L. Brongersma, Y.S. Kivshar, B. Lukyanchuk, B. Science, **354** (2016).

[2] D. Smirnova, Y. S. Kivshar. Optica **3**, 1241-1255 (2016).

[3] V.F. Gili, L. Carletti, A. Locatelli, D. Rocco, M. Finazzi, L. Ghirardini, I. Favero, C. Gomez, A. Lemaître, M. Celebrano, C. De Angelis, G. Leo. Optics Express, **24,** 15965-15971 (2016).

[4] D. Rocco, V.F. Gili, L. Ghirardini, L. Carletti, I. Favero, A. Locatelli, G. Marino, D.N. Neshev, M. Celebrano, M. Finazzi, G. Leo, C. De Angelis. Photonics Research, **6**, B6-B12 (2018).

Parameter-free Hydrodynamic treatment of Difference-frequency Generation in plasmonic nanostructures

Federico De Luca[1,2], *Cristian Ciracì*[1]
[1]*Center for Biomolecular Nanotechnologies, Istituto Italiano di Tecnologia, via Barsanti 14, 73010 Arnesano (LE), Italy*
[2]*Dipartimento di Matematica e Fisica, Università del Salento, via Arnesano, 73100 Lecce, Italy*
email: federico.deluca@iit.it

Keywords: Nonlinear plasmonics

The efficiency enhancement of nonlinear optical processes in extremely confined volumes ($\sim$100 nm^3) is a great challenge in the field of nanophotonics, but it may lead to new applications in different areas, including optical parametric amplification, holography and parametric down-conversion for quantum cryptography and computing applications [1]. In this context, the opacity and the large absorption of metals are usually considered a hindrance for high efficiency in traditional photonic systems. However, light interaction with metal nanoparticles, i.e. plasmonics, gives unmatched possibilities of both confinement and electromagnetic field enhancement. These properties, together with the large intrinsic nonlinear susceptibilities of metallic systems, make plasmonic systems ideal candidates for nonlinear optics applications, as already demonstrated for second-harmonic generation (SHG) [2]. Here, we present a theoretical model for the numerical analysis of the optical properties of a plasmonic nanostructure for efficient difference-frequency generation (DFG). We analyze the nonlinear characteristics of the system using a hydrodynamic approach to describe the electron dynamics inside the metal, and we derive the equations for the nonlinear polarization in the case of DFG, the undepleted pump approximation being assumed. A key element for the implementation of these equations is to write the nonlocal contributions as purely surface current terms [3]. This may be done by exploiting the particular mathematical form of the nonlinear surface terms, which, turns out to be approximated as a function of the bulk and external values of the electric field. As a result we obtained a parameter-free model for DFG in plasmonic systems. Finally, as an application of our method, we have designed the doubly-resonant gold nanostructure shown in Figure 1, estimating an effective second-order nonlinear susceptibility $\chi^{(2)}_{eff} \approx 1$ nm/V.

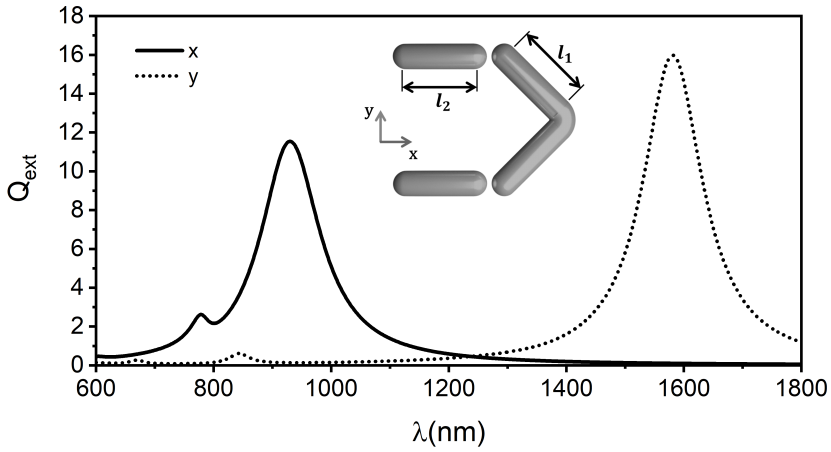


Figure 1: Scattering spectrum of the plasmonic nanostructure: straight and dot lines represent the linear extinction efficiencies of the coupled antenna, calculated using FEM method, when illuminated with light polarization parallel (x-axis) and orthogonal (y-axis), respectively, to the nanorods. Inset: doubly-resonant gold nanostructure designed for efficient DFG.

References

[1] A.V. Krasavin, P. Ginzburg and A. V. Zayats, Laser Photon. Rev. 12, 1700082 (2018)..
[2] M. Celebrano, X. Wu, M. Baselli, S. Großmann, P. Biagioni, A. Locatelli, C. De Angelis, G. Cerullo, R. Osellame, B. Hecht, L. Duò, F. Ciccacci and M. Finazzi, Nat. Nanotech. 10, 412 (2015).
[3] C. Ciracì, E. Poutrina, M. Scalora and D. R. Smith, Phys. Rev. B 86, 115451 (2012).

Quantum Effects

Field Quantization in Arbitrarily-Shaped Metal Nanoparticles

Roberto Tricarico[1,2], *Carlo Forestiere*[1], *Giovanni Miano*[1], *Mariano Pascale*[1]
[1] *Department of Electrical Engineering and Infromation Technology, Università degli Studi di Napoli "Federico II", via Claudio 21, 80125, Naples, Italy, roberto.tricarico@unina.it*
[2] *ICFO Institut de Ciències Fotòniques, The Barcelona Institute of Science and Technology, 08860 Castelldefels, Barcelona, Spain*

Keywords: Quantum Plasmonics.

In the last few decades, plasmon nanoparticles (NP) have been proposed as a suitable platform to control and enhance the light-matter interaction. Nowadays, modern technologies are pushing this interaction to the extreme: single quantum emitters can be isolated, few-nanometer particles can be fabricated, single-photon state can be measured. For a complete analysis of the coupling phenomena involving plasmon nanoparticles, a proper quantum description is needed.

In a large part of the scientific literature, the quantization of the plasmon modes has been carried out using a quasi-electrostatic (Q-ES) approximation for the electromagnetic field and assuming regular NP geometries, such as a sphere (e.g. [1, 2]). However, when the dimension of the nanoparticle increases, the Q-ES approximation breaks down and the retardation effects have to be included in the description. Indeed, the plasmon resonance frequencies shift and, due to the radiated power toward infinity, the plasmon modes decay in time. The quantum counterparts of these retardation phenomena are the energy shifts and the finite lifetimes of the plasmon excitations, respectively. A proper quantum description of the spherical nanoparticle in the full-wave regime has been recently introduced (e.g. [3, 4]).

A complete description of plasmon quantization in an arbitrarily shaped particle is still missing. This is very important for the applications, because NP shape can be used as a design parameter to engineer the NP electromagnetic response. In this paper, we develop a quantum theory for arbitrary shape plasmon nanoparticles. We consider a fluid description of the electrons gas within the nanoparticle, expanding the corresponding electron displacement field into a set of oscillating modes. By quantizing the interaction between the electron displacement field and the electromagnetic field, we derive the plasmon-photon quantum Hamiltonian. Then, by applying the equations of motion method, we compute the retarded Green's function and the self-energy of each plasmon mode. Eventually, we show the radiative lifetime and the plasmon energy shift for NP of different geometries and sizes.

References

[1] E. Waks and D. Sridharan, Cavity qed treatment of interactions between a metal nanoparticle and a dipole emitter, Phys. Rev. A, vol. 82, p. 043845, Oct 2010.
[2] E. Andrianov, A. Pukhov, A. Vinogradov, A. Dorofeenko, and A. Lisyansky, Spontaneous radiation of a two-level atom into multipole modes of a plasmonic nanoparticle, Photonics and Nanostructures - Fundamentals and Applications, vol. 12, no. 5, pp. 387-397, 2014.
[3] F. Alpeggiani and L. C. Andreani, Quantum theory of surface plasmon polaritons: Planar and spherical geometries, Plasmonics, vol. 9, pp. 965-978, Aug 2014.
[4] V. Y. Shishkov, E. S. Andrianov, A. A. Pukhov, and A. P. Vinogradov, Hermitian description of localized plasmons in dispersive dissipative subwavelength spherical nanostructures, Phys. Rev. B, vol. 94, p. 235443, Dec 2016.

Molecular Switches interacting with Localized Surface Plasmons: a Density Functional Theory Approach

Giulia Giannone[1,2], *Fabio Della Sala*[1,3], *and Stefania D'Agostino*[1]
[1]*Center for Biomolecular Nanotechnologies-IIT, Arnesano, Italy, giulia.giannone@iit.it*
[2]*Department of Mathematics and Physics "E. De Giorgi", University of Salento, Lecce, Italy*
[3]*CNR Institute for Microelectronics and Microsystems, Lecce, Italy*

Keywords: Quantum Plasmonics, Nanophotonics and Hybrid Plasmonics.

Time-Dependent Density Functional Theory (TD-DFT) [1] represents nowadays the most accurate approach for the study of the electrodynamic coupling at sub-nanometer scales between molecular emitters and nanoantennas, able to consider all the quantum effects (charge transfer, chemical bonding, ect.) emerging at these scales and, thus, to overcome the limits imposed by a classical description.
In the framework of TD-DFT, we investigated the interactions between a localized surface plasmon excitable in a silver tetrahedral cluster of Ag_{20} and a molecular exciton. The molecular counterpart, *trans-trans*-1,4-diphenyl-1,3-butadiene (*t,t*-DPB), belongs to the class of photo-switches and is optically active in the same energy range of the metallic cluster. As the graph reported in Figure 1 shows, the absorption spectrum for the system in an ultra-near-field regime of interaction is characterized by the presence of two well distinguishable peaks, which can be explained in terms of a plasmon-exciton electromagnetic interaction model, as the sketch in the inset of Figure 1 explains.

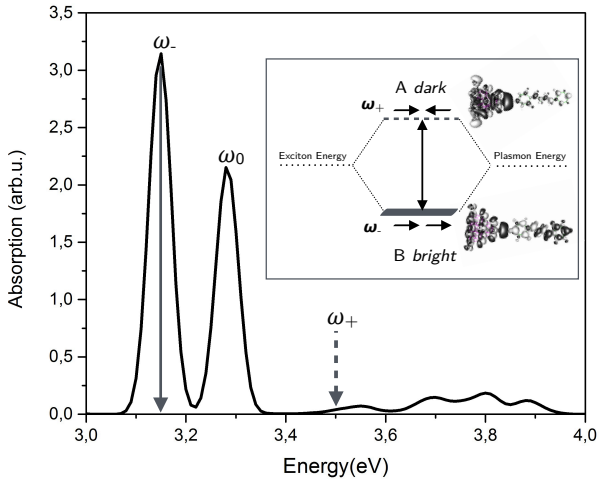


Figure 1: TD-DFT absorption spectrum of the whole system for the metal-molecule distance of 2 Å. In the inset, a pictorial scheme of the coupling between a plasmon and an exciton. All the calculations have been performed with TURBOMOLE code [2].

In fact, when the two counterparts are sufficiently close to allow a coupling between their transition dipole moments, two possible states, *B* (bonding) at energy ω_- and *A* (anti-bonding) at energy ω_+, are possible, corresponding to a parallel (*A* state) or anti-parallel (*B* state) alignment of the two transition dipoles along the z axis. The *A* state is optically active or bright, differently from the *B* state, which is characterized by a small total transition dipole and it results to be optically inactive or dark. Between the states *A* and *B*, there is the plasmonic peak of the cluster at energy ω_0 which does not interact with the molecule. Moreover, from the analysis of the transition densities, which we reported in the inset of Figure 1 for the *A* and *B* states, we found out that both the excitations at energy ω_- and ω_+ are hybrid, while, the excitation at energy ω_0 is localized on the cluster, this confirming the above interaction scheme. This fully atomistic approach here presented represents, thus, a complete theoretical scheme able to consider both the electronic and optical effects taking part to the interaction of a plasmonic system with a molecular switch.

References

[1] M. A. L. Marques and E. K. U. Gross, Annu. Rev. Phys. Chem. **55**, 427-455 (2004).
[2] Information available at www.turbomole.com.

Ab initio Plasmonics of Externally Doped Silicon Nanocrystals

F. Della Sala[1,2], M. Pezzolla[2], S. D'Agostino[2] and E. Fabiano[1,2]
[1] *Institute for Microelectronic and Microsystems (CNR-IMM), Lecce, Italy*
[2] *CBN@UNILE, Istituto Italiano di Tecnologia (IIT), Arnesano, Italy*
email: fabio.dellasala@unisalento.it
Keywords: Quantum plasmonics, plasmonic and dielectric nanoantennas

Heavily-doped semiconductor nanocrystals represent a new class of plasmonic nanosystems with applications in different fields. [1]. In these systems the localized surface plasmon resonance (LSPR) frequency is directly related to the electron density which can be tuned (by doping) over a wide interval, including the near-infrared region (NIR). In case of dynamical doping, external electrons are added to the NCs via reversible capacitive effect [2]. To date the modeling of the plasmonics properties of heavily-doped semiconductors NCs has been mostly limited to simple classical models [1], with few exceptions.[3, 4] In this work, we report atomistic first-principles calculations Time-dependent Density Functional Theory (TD-DFT) of the externally doped silicon semiconductor NCs [5], see Fig. 1a. Silicon has been chosen as a model semiconductor due to recent investigations in which silicon has been proposed for plasmonics.[6]

We provide results for silicon NCs with different sizes (up to 2.4 nm) and number of excess electrons (up to 30) including or not the interaction with the valence electrons. TD-DFT predicts a peak at low energy (about 1-1.5 eV) strongly dependent on the number of excess electrons. Using the Generalized-Plasmonicity-Index(GPI) [7], we show that the plasmon peak is strongly screened by the valence electrons, see Fig. 1b. A comparison with classical results shows that the latter can be applied only for NCs with a diameter larger than 2 nm.

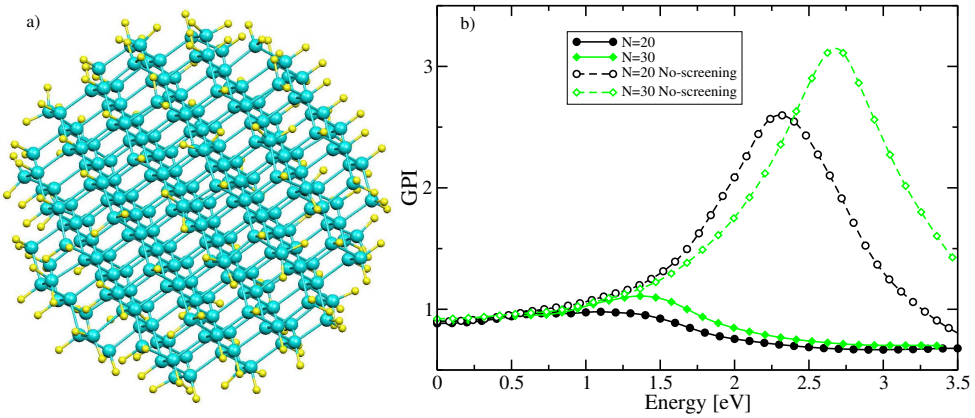


Figure 1: a) Atomic structure of one of the considered silicon NC. The surface atoms have been passivated with hydrogen atoms. b) GPI for a NC with different number (N) of excess electrons: the GPI increases (and blu-shifts) with N and it is much larger (and blue-shifts) when the interaction with the valence electron is switched off (no screening).

References

[1] A. Agrawal et al., *Localized Surface Plasmon Resonance in Semiconductor Nanocrystals*, Chem. Rev. 118:3121-3207, 2018.
[2] G. Garcia et al., *Dynamically Modulating the Surface Plasmon Resonance of Doped Semiconductor Nanocrystals*, Nano Lett. 11:4415-4420, 2011.
[3] H. Zhang et al., *Theory of Quantum Plasmon Resonances in Doped Semiconductor Nanocrystals*, J. Phys. Chem. C 118:16035-16042, 2014.
[4] A. Schimpf et al., *Charge-Tunable Quantum Plasmons in Colloidal Semiconductor Nanocrystals*, ACS-Nano 8:1065-1072, 2014.
[5] F. Della Sala, M. Pezzolla, S. D Agostino, and E. Fabiano, *Ab-initio Plasmonics of Externally doped silcon Nanocrystals*, ACS Photonics 2019.
[6] H. Zhang et al., *Doped Silicon Nanocrystal Plasmonics*, ACS Photonics 4:963-970,2017.
[7] R. Zhang et al., *How To Identify Plasmons from the Optical Response of Nanostructures*, ACS Nano 11:7321-7335, 2017.

The Role of Quantum Mechanical Effects in Metal-Molecule Interactions

Stefania D'Agostino[1], *Giulia Giannone*[1,2] *and Fabio Della Sala*[1,3]

[1]*Center for Biomolecular Nanotechnologies@ UNILE-Istituto Italiano di Tecnologia, Arnesano, Italy*

stefania.dagostino@iit.it

[2]*Department of Mathematics and Physics E. De Giorgi, University of Salento, Lecce, Italy*

[3]*CNR Institute for Microelectronics and Microsystems, SP Lecce-Monteroni, Lecce, Italy*

Keywords: Nanophotonics and Hybrid Plasmonics, Plasmon-exciton polaritons, Quantum plasmonics.

In the last few years, the development of fabrication and characterization techniques and their capabilities to manage light-matter interaction at the sub-nanometer scale have spreaded the interest toward the quantum nature of matter among the scientific communities dealing with nanophotonics and plasmonics. In this work the absorption properties of an hybrid system consisting of a molecular emitter, i.e. trans,trans-1,4- diphenyl-1,3-butadiene (t,t-DPB), interacting with a tetrahedral cluster of Ag20 are investigated by considering four levels of approximations: (i) the Time-Dependent Density Functional Theory (TDDFT) [1], (ii) the subsystem formulation of time-dependent density functional theory within the the frozen-density Embedding (FDE) framework [2], the Finite Element Method (FEM) [3] and (iv) the Dipole-Dipole Model. For metal-molecule distances smaller than 0.45 nm, each absorption spectrum is characterized by the presence of two peaks. Reasoning in terms of two-coupled dipoles model, these two peaks are explained as the bonding dipole due to the hybridization of the z- components of the surface charge of the two oscillators, i.e. molecule and cluster, and the uncoupled x- and y- modes of the three-fold degenerate plasmon. In more details, the molecule transition dipole moment oriented along the z-direction interacts only with the z component of the cluster transition dipole and creates two hybrid states, one of which is not visible or dark. In Fig.1 the effects of the metal-molecule distance on the spectral position of the lower-energy peak are reported. Even if the dipole-dipole interaction model seems to work well in terms of trend for distance larger that 0.5 nm, the effects of the quantum electron density distribution appear to be crucial in order to faithfully describe the electro-optical interaction among the two nanosystems in close contact (almost touching). The differences among the Embedding TDDFT approach and the standard TDDFT one, then, shed light on the effects of charge transfer among the molecular and the metallic counterparts, this contributing to faithfully control the role of the different the quantum mechanical effects not considered by classical approaches.

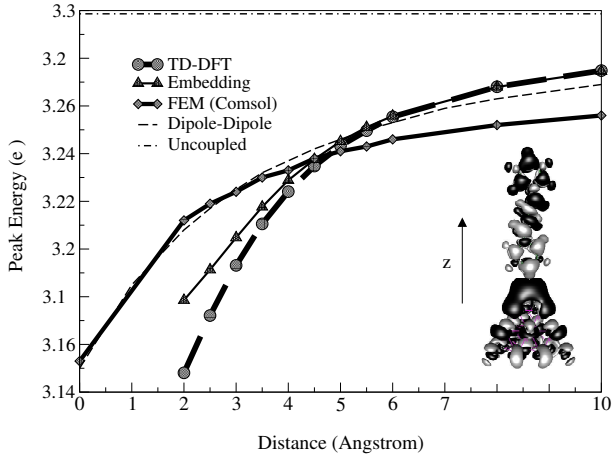


Figure 1: Bonding mode energy *vs* metal-molecule distance for the four applied methods. Inset: transition density at the bonding mode resonance for d = 2 Å.

References

[1] TURBOMOLE available at www.turbomole.com.

[2] J. Neugebauer, J. Chem. Phys. **126**, 134116 (2007).

[3] Comsol Multiphysics available at https://www.comsol.com/.

Metasurfaces

Large-area nanostripe gratings for flexible NIR plasmonics and optoelectronics

Debasree Chowdhury, C. Mennucci, R. Chittofrati, G. Manzato, M. Barelli, M.C.Giordano and F. Buatier de Mongeot
Dipartimento di Fisica, Università di Genova, Via Dodecaneso 33, I-16146 Genova, Italy
**Corresponding author, e-mail: debu.sinp@gmail.com*

Keywords: Plasmonic and dielectric nanoantennas, Metamaterials, Nanophotonics and Hybrid Plasmonics

Periodic arrays of metal and metallo-dielectric structures are targeted for the development of optoelectronic components or biosensors [1, 2] and emerging photovoltaics for their unique properties and functionality based on localized surface plasmon resonance (LSPR). Current top-down approaches to nanoscale fabrication like electron beam lithography or scanning probe lithography are excellent in control of size and shape but suffer serious drawbacks of small area coverage and time consumption. On the other hand, bottom-up approaches like defocused ion beam sputtering (IBS) [3] represent an inexpensive and time-saving way to fabricate large-area arrays of self-organized nanopatterns which feature broadband and tunable plasmonic functionalities [4] but possess less control on array periodicity and ordering. In many applications like e.g, in plasmon enhanced sensing, sharper and tunable plasmon resonances are highly desired.

In this work, we demonstrate the fabrication, via laser interference lithography (LIL), of mono-dispersed arrays of one-dimensional Au nanostripes which extend over cm^2 areas and exhibit tailored dipolar and multipolar plasmon resonances. The arrays can be supported both on flat dielectric substrates as well as on flexible polymer films [5]. By vertically stacking the nanostripes with a dielectric spacer, we obtain dimer structures featuring plasmon hybridization engineering from the VIS to the NIR range. The metasurfaces, exhibit magnetic dipole resonances in the near infrared part of spectrum associated to strong subradiant near-field enhancement up to a factor of 12. We compare the results with similar self-organized plasmonic nanostructures synthesized by IBS, demonstrating the role of lateral order in the response of such plasmonic metasurfaces: the extremely sharp spectral features observed in the case of monodisperse arrays are due to the hybridization of the grating lattice resonances with the LSP of the individual nanostripes.

The results thus enable large area plasmon enhanced applications in nanospectroscopies like e.g. Surface Enhanced Raman Scattering as well as in non-linear and index-sensing applications. Moreover, since the nanostripe arrays are also endowed with remarkably low sheet resistance values in the 10 Ohm/sq range, they represent a natural platform for multifunctional flexible electro-optic applications.

References

[1] A. Sobhani et. al., Nat. Comm. **4**, 1643 (2013).
[2] A. G. Brolo et. al., Nat. Photonics **6**, 709–713 (2012).
[3] M. C. Giordano and F. B. de Mongeot, Adv. Mat., **30**, 1801840, (2018).
[4] M.C. Giordano et. al., Nano Res. **11**, 3943 (2018).
[5] C. Mennucci, D. Chowdhury, M. Barelli, G. Manzato, F. Buatier de Mongeot, Under submission.

Anomalous effective permittivity of Vogel spiral metamaterials.

Franco Marabelli[1, 2], Lucia Fornasari[2], Francesco Floris[1], Luca Dal Negro[3]
[1]Physics Departement University of Pavia, Pavia, Italy, franco.marabelli@unipv.it
2Plasmore S.r.l., Pavia, Italy
[3]Department of Electrical and Computer Engineering & Photonics Center, Boston University,
8 Saint Mary's Street, Boston, MA 02215, USA

Keywords: Plasmonic and dielectric nanoantennas; Nanophotonics and Hybrid Plasmonics, Metamaterials.

In recent years plasmonic and photonic structures attracted the attention of the scientific community due to their ability to manipulate and modify the electromagnetic field.

In this work we present the optical characterization of a quasi-ordered hybrid plasmonic-photonic crystal, constituted by nano-sized Silicon cylinders with a gold disk on top arranged in a Vogel spiral distribution. Depending on the divergence angle of the Spiral, different geometries can be obtained, leading to different wave localization regimes [1-3].

We have characterized the optical response of such structures through Reflectance measurements in the NIR-VIS range, with light linearly and circularly polarized and through spectral ellipsometric measurement in the range 400-2300 nm. The Reflectance spectra highlight the presence of the plasmonic resonances which resonates in the gold caps. These resonances are slightly dispersive and are not very sensitive to variations in the spiral shape.

An unexpected result appears from ellipsometric measurement (see Figure 1). As evident in Figure 1(b) the imaginary part of the effective permittivity ε_2 (pseudo-function) assumes negative values in the range between 800 nm and 1500 nm for angles between 25° and 45°. This is in correspondence with an ellipsometric phase difference exceeding 180° (see Figure 1(c)). An analogous behavior has been observed also for other Vogel spiral distribution.

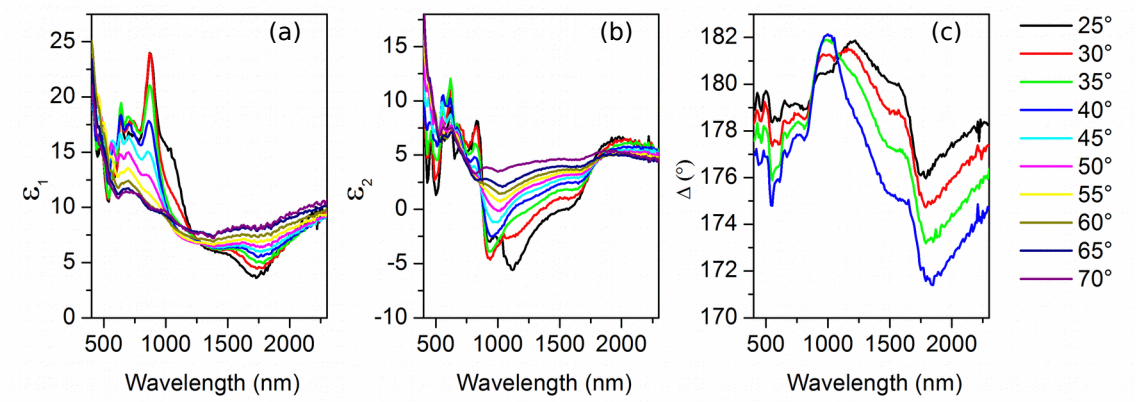


Figure 1: (a) ε_1- and (b) ε_2- pseudo-functions and (c) Δ measured for a Golden Angle Vogel spiral distribution of gold capped Silicon cylinders.

Then, the effect seems to be due to a peculiar correlated behavior of the active modes along the two polarization directions parallel and perpendicular to the plane of incidence. We have developed a model of the samples based on a kind of birefringent structure. It makes possible to fit the whole set of experimental data and allows to interpret the physical behavior of these structures. Minor effects of angle dependent dispersion of modes can be observed.

References

[1] J. Trevino, H. Cao, L. Dal Negro, *Circularly-symmetric light scattering from nanoplasmonic spirals,* Nano Letters **11**, 2008–2016 (2011)

[2] J. Trevino, S.F. Liew, H. Noh, H. Cao, L. Dal Negro *Geometrical structure, multifractal spectra and localized optical modes of aperiodic Vogel spirals*, Optics Express, 20, 3015 (2012);

[3] F. Sgrignuoli, R. Wang, F. A. Pinheiro, and L. Dal Negro, *Localization of scattering resonances in aperiodic Vogel spirals,* Phys. Rev. B, 99, 104202 (2019)

Mid-infrared Bloch Surface Waves for Sensing Biomolecules by their Fingerprints

Michele Ortolani[1,2], Marialilia Pea[3], Agostino Occhicone[1], Valeria Giliberti[2], Alberto Sinibaldi[1], Francesco Mattioli[3], Sara Cibella[3], Raffaella Polito[1], Alessandro Nucara[1], Leonetta Baldassarre[1] and Francesco Michelotti[1]

[1]Sapienza University of Rome, Rome, 00185 Italy

[2]Center for Life Nanosciences – Istituto Italiano di Tecnologia, Rome, 00161 Italy

[3]CNR – Institute for Photonics and Nanotechnologies, Rome, 00154 Italy

Keywords: Plasmon-exciton polaritons, Sensors and Biosensors.

Surface Waves (BSWs) are a kind of electromagnetic surface waves existing at the interface between a continuous medium (e.g. air or water) and a periodic thin-film structure with alternating high/low refractive indices. The latter is designed to operate as a 1D photonic crystal (1DPC) with a forbidden frequency gap of light propagation, and it is located on top of a prism. BSWs have found application in the visible and near-IR range as low-loss alternatives to surface plasmon polaritons (SPPs) in biosensors [1]. BSWs are also exploited for fluorescence enhancement and for photonic circuits [2]. Recently, the first realization of a BSW-supporting structure in the mid-IR and guided-mode excitation with a quantum cascade laser have been reported [3], but broadband spectroscopic evidence for BSWs is still lacking.

We developed a thermal evaporation process for deposition of ZnS/CaF_2 multilayers directly on CaF_2 prisms (index 2.2/1.4, calculated thickness for 1DPC operation 0.8/2.1 μm). A "defect" layer of thickness 170 nm is also located at the 1DPC-continuous medium interface to pin the BSW mode to a specific linear dispersion relation. The latter was probed with a custom variable internal-reflection angle setup built into a FTIR spectrometer. In Fig. 1 spectroscopic evidence of BSWs in the 3.5-5.5 μm range is presented and compared to calculations. The expected operating range of our structures encompasses the mid-IR fingerprint range 3 to 10 μm, and the coupling efficiency at target wavelength can be engineered by selecting the defect layer thickness.

In summary, we envisage SPP-like biosensing applications, in which the mid-IR fingerprints of thin samples located at the interface are detected with high sensitivity by BSWs.

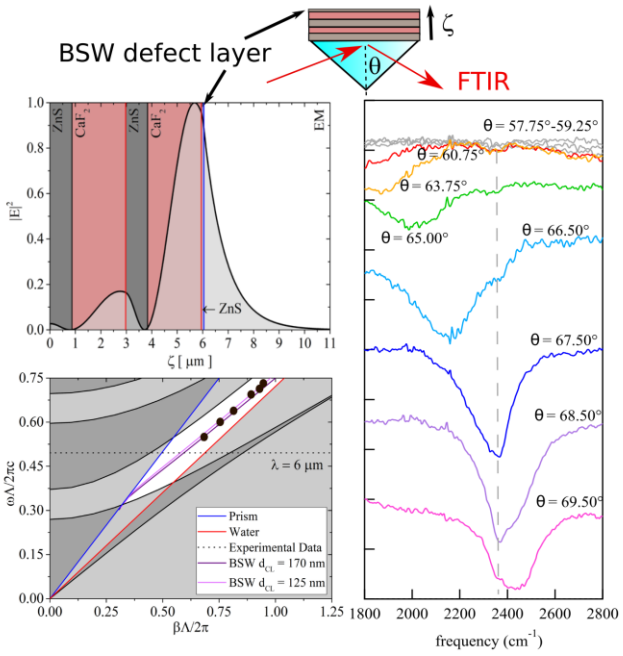


Figure 1. Top-left: Calculated electric field profile of the BSW along ζ with characteristic evanescent tails on both sides of the interface (ζ ~ 6 μm) between the 1DPC (red/grey stripes) and the dielectric medium (white). The ZnS defect layer is located at the interface. Right: Spectroscopic evidence of BSWs in our structure obtained by FTIR spectroscopy at variable internal reflection angle θ: the depth of the narrow dips at specific TIR-angle-dependent frequencies is related to BSW excitation efficiency and to BSW losses. Electric field polarization was in-plane (TE). Bottom-left: Calculated dispersion relations of the guided modes of the 1DPC-prism structure plotted as reduced frequencies and wavevectors (Λ is the 1DPC periodicity). Purple lines are the BSW dispersion relations. Black dots represent the experimental data and fall on the calculated BSW dispersion.

References

[1] E. Descrovi, T. Sfez, M. Quaglio, D. Brunazzo, L. Dominici, F. Michelotti, H.P. Herzig, O. Martin, and F. Giorgis. "Guided Bloch Surface Waves on Ultrathin Polymeric Ridges" *Nano Lett.* 10, 2087–2091 (2010).

[2]. L. Yu, E. Barakat, T. Sfez, L. Hvozdara, J. Di Francesco and H. P. Herzig "Manipulating Bloch surface waves in 2D: a platform concept-based flat lens" *Light: Science & Applications* 3, e124 (2014).

[3]. G. M. Smolik, N. Descharmes, and H. P. Herzig "Toward Bloch Surface Wave-Assisted Spectroscopy in the Mid-Infrared Region" *ACS Photonics* 5, 1164−1170 (2018).

Sensing using Surface Plasmon Polaritons in THz metagrids

Gian Paolo Papari[1,2], Can Koral[3], Antonello Andreone [1,2,3].
[1] *Dipartimento di Fisica, Università di Napoli "Federico II," Piazzale Tecchio 80, I-80125 Naples, Italy*
[2] *CNR-SPIN, UOS Napoli, via Cinthia, I-80126 Naples, Italy*
[3] *INFN Naples Unit, via Cinthia, I-80126, Naples, Italy*

Keywords: Terahertz, Metamaterials, Sensor and Biosensors.

There is a growing interest in the use of surface plasmon polaritons (SPP) as a probe for accurate sensing. We present here, in the frequency range 0.1-1 THz, the transmission properties of two different grid-shaped metasurfaces (metagrids, MG) [1]. In such artificial structures SPPs can be activated at frequency as low as in the THz range by "diluting" the metal. The first metasurface has a metallic (copper) layer 30 μm thick patterned as a grid (GR) with uniform wires, whereas the second one is shaped as a chessboard (CB) with single metallic square patches (see fig. 1(a) and (b) respectively). A unit cell filling factor *F* defines the amount of metal within each "meta-atom" and controls the threshold between the plasmonic and the dielectric behavior of the GMs. In this way the signal transmission can be ruled by a "transition frequency" ω_t that can be as low as tenths of THz. When a MG is irradiated at a frequency $\omega < \omega_t$, spoof SPPs (SSPPs) modes are activated, whereas for $\omega > \omega_t$, high order SPPs (HOSPPs) resonant modes are triggered. HOSPPs are responsible for enhanced transmission phenomena and can be fruitfully used for high accuracy label-free sensing since their (evanescent) electric field extension is larger than the MG thickness. Therefore, MGs can detect a substance deposited on their surface exploiting the dependence of resonating HOSPP modes on the dielectric environment, in the same fashion "classical" metasurfaces, consisting of arrays of individual resonators, do. Using full wave electromagnetic simulations we can study the evolution of the dielectric function ε with respect to *F*. A simple lumped element model is proposed to describe the relation between *F* and the transition frequency that in our case can be tuned of about a factor 10 passing from 0.1 to about 1 THz. Time domain spectroscopy measurements are carried out to retrieve information on the dielectric function (ε) of the two MGs. In Fig.1, a sketch of the respective unit cells and the transmissions characteristics of the two MGs are reported.

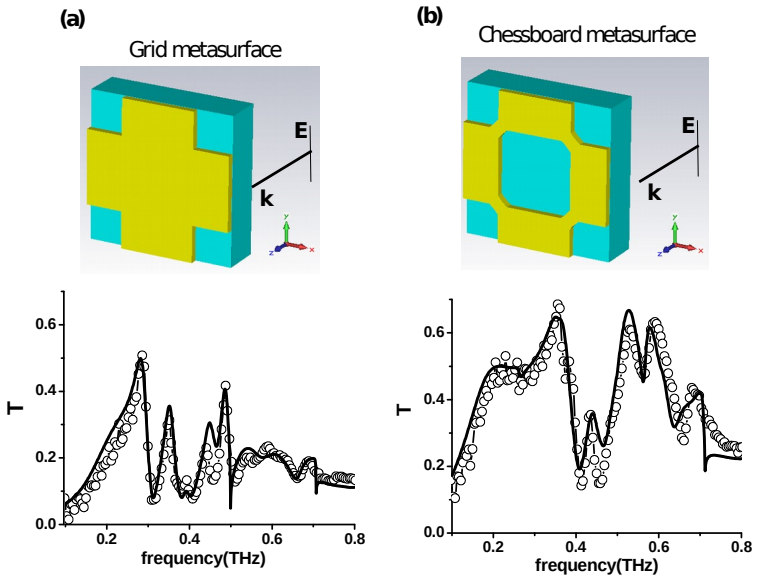


Figure 1: geometrical sketch of the unit cell and transmission properties of a GR (a) and a CB (b) metasurface. Open circles describe the experimental results whereas black continuous lines represent full wave electromagnetic simulations.

References

[1] G. P. Papari, C. Koral, and A. Andreone, "Geometrical Dependence on the Onset of Surface Plasmon Polaritons in THz

Posters

Pauli-Gaussian kinetic energy functionals for quantum hydrodynamic theory

Henrikh Baghramyan[1], *Fabio Della Sala*[1,2], *Cristian Ciracì*[1],
[1]*Center for Biomolecular Nanotechnologies, Istituto Italiano di Tecnologia,*
Via Barsanti 14, 73010 Arnesano (LE), Italy, cristian.ciraci@iit.it
[2]*Institute for Microelectronics and Microsystems (CNR-IMM), Via Monteroni,*
Campus Unisalento, 73100 Lecce, Italy

Keywords: Plasmonics, Surface Plasmons.

Quantum hydrodynamic theory (QHT) includes nonlocal contributions of kinetic energy (KE) functional and can accurately describe plasmon resonance, the spill-out, and retardation effects [1]. The nonlocal kinetic energy originates from the spatial dependence of the electron density that can be considered via the von Weizsäcker (vW) term [2]. Here we consider QHT approach with nonlocal contributions via more general Pauli-Gaussian (PG) kinetic energy functionals [3]:

$$T_s[n] = T_s^{\mathrm{W}} + \int \tau^{\mathrm{TF}} F_{\mathrm{s}}^{\mathrm{p}}(s)\,\mathrm{d}^3\mathbf{r}, \tag{1}$$

where $\tau^{\mathrm{TF}} = (3/10)k_{\mathrm{F}}^2 n$ is the Tomas-Fermi (TF) KE density, with n being the electron density, $k_{\mathrm{F}} = \left(3\pi^2 n\right)^{1/3}$ is the Fermi wave vector, $s = |\nabla n|/(2k_{\mathrm{F}}n)$ is the reduced gradient, $T_{\mathrm{s}}^{\mathrm{W}} = \int \tau^{\mathrm{TF}}\left(5s^2/3\right)\mathrm{d}^3\mathbf{r}$ is the vW KE and $F_{\mathrm{s}}^{\mathrm{p}} = \mathrm{e}^{-\mu s^2}$ is the Pauli KE enhancement factor.

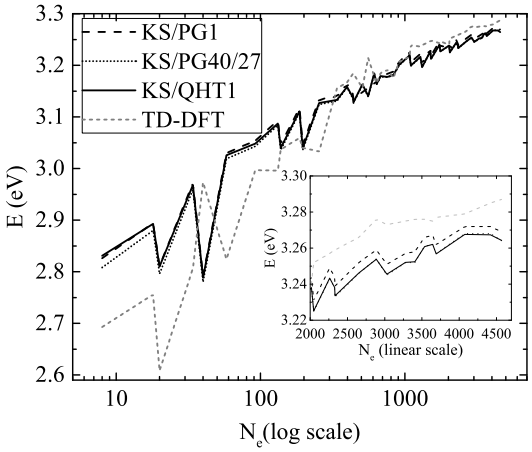


Figure 1: Plasmon resonance of the linear response calculations for jellium nanospheres as a function of $\mathrm{N_e}$ number of electrons. The behavior for large particles is shown in the inset. Wigner-Seitz radius $r_s = 4$ a.u. is considered which represents sodium.

In Fig. 1 two values of μ coefficient for $F_{\mathrm{s}}^{\mathrm{p}} = \mathrm{e}^{-\mu s^2}$ are considered: $\mu = 1$ and $\mu = 40/27$ referring to PG1 and PG40/27 correspondingly. They are plotted against the results of time-dependent density functional theory (TD-DFT) and QTH1 cases taken from the reference [1]. The ground-state densities are from Kohn-Sham (KS) DFT calculations [1] and the system is excited by a plane-wave. QHT1 refers to the case when KE functional is a sum of TF and vW terms (in fact, that is the case with $\mu = 0$). Exchange-correlation energy is considered as well. The inset shows that PG40/27 energies almost overlap with QTH1 results for bigger particles. In addition, as expected, all the results are approaching to value from Mie theory $\hbar\omega_{\mathrm{Mie}} = 3.4$ eV. Thus, the performance of QHT with PG functionals is justified for the description of plasmon resonances and opens the way for the further optimizations via inclusion of higher-order terms of KE functional expansion of electron density [3].

References

[1] C. Ciracì and F. Della Sala, Phys. Rev. B **93**, 205405 (2016).
[2] C. F. von Weizsäcker, Eur. Phys. J. A **96**, 431 (1935).
[3] L. A. Constantin, E. Fabiano and F. Della Sala, J. Phys. Chem. Lett. **9**, 4385 (2018).

Time-resolved THz spectroscopy of Ge/SiGe multi-quantum wells

Leonetta Baldassarre[1], Chiara Ciano[2], Luca Persichetti[2], Michele Virgilio[3], Luigi Bagolini[3], Michele Montanari[2], Luciana Di Gaspare[2], Marvin Zoellner[4], Oliver Skibitzki[4], David Stark[5], Giacomo Scalari[5], Jerome Faist[5], Kirsty Rew[6], Douglas. J. Paul[6], Thomas Grange[7], Stefan Birner[7], Alexej Pashkin[8], Manfred Helm[8], Michele Ortolani[1], Giovanni Capellini[2, 4] and Monica De Seta[2]

[1] *Dipartimento di Fisica, Università di Roma La Sapienza, Roma, 00185, Italy*
[2] *Dipartimento di Scienze, Università di Roma Tre, Rome, 00146, Italy*
[3] *Dipartimento di Fisica, Università di Pisa, Pisa, 56127, Italy*
[4] *IHP-Leibniz-Institut für innovative Mikroelektronik, Frankfurt (Oder), 15236, Germany*
[5] *Institute of Quantum Electronics, ETH Zurich, Zurich, 8093, Switzerland*
[6] *School of Engineering, University of Glasgow, G12 8LT, United Kingdom*
[7] *nextnano GmbH, Garching b. München, 85748, Germany*
[8] *Helmholtz-Zentrum Dresden-Rossendorf, 01328 Dresden, Germany*

Keywords: THz

The FET-Open project FLASH aims at developing a far-infrared quantum cascade laser (QCL) with silicon foundry-compatible group-IV semiconductor heterostructures exploiting the conduction band of n-doped Ge multi-quantum wells with SiGe barriers grown on Si substrate. The use of SiGe structures could lead to a broader wavelength range of emission towards the far-infrared, if compared with current QCLs based on III-V compounds, due to the non-polar nature of the materials [1].

We study asymmetric-coupled Ge/SiGe quantum wells [2] grown by Chemical Vapour Deposition. Samples are shaped into a single-plasmon waveguide, that allows to have a TM polarized electromagnetic field in the active region (see Fig.1a). Single-color pump-probe measurements are being performed at FELBE Free-Electron Laser (FEL) in Dresden, by tuning the photon energy to the E01 subband transition. Comparing the time relaxation measured experimentally with modeling, we aim at disentangling the relative role of optical phonon, acoustic phonon, electron-electron and interface roughness scattering channels as a function of temperature, subband energy separation and pump power. The power-dependence of the sample transmittance is also studied, in order to verify the presence of saturable absorption providing an estimation of the population induced by FEL pumping in the upper levels of the subbands (see Fig.1b-d).

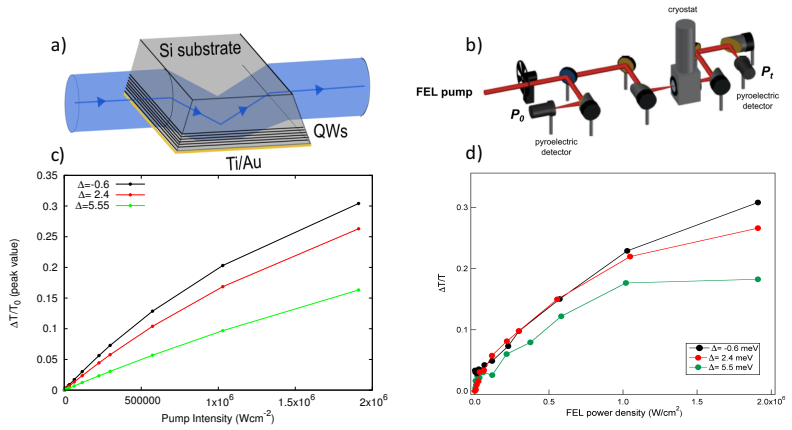


Figure 1: a) Single plasmon waveguide geometry for measuring in transmission the Ge/SiGe structures. The metal layer ensures a TM polarization of the electromagnetic field in the active region, enabling the study of intersubband transitions. b) Sketch of the experimental geometry used to measure the saturable absorption of the samples in order to provide an estimate of the percentage of photo-excited carriers. c) Experimental and d) theoretical $\Delta T/T_0$ for different values of FEL pump detuning Δ with respect the the intersubband resonance energy.

References

[1] D. J. Paul, Laser Photon. Rev. **4**, 610 (2010).

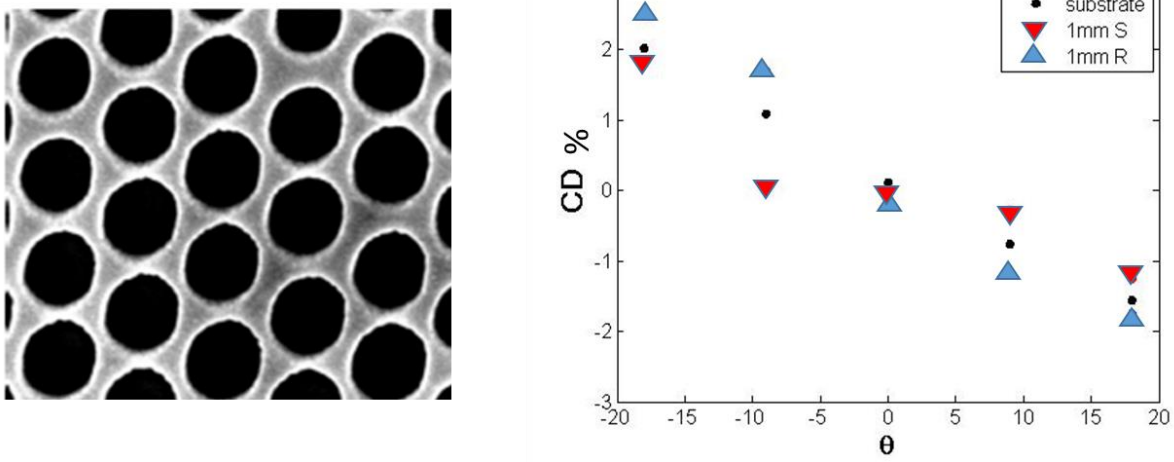
[2] C. Ciano et al., Phys. Rev. Appl. **11**, 014003 (2019).

Circular dichroism of chiral molecules on asymmetric hole array

Alessandro Belardini[1], Emilija Petronijevic[1], Nikola Zaric[1], Grigore Leahu[1], Tiziana Cesca[2], Carlo Scian[2], Fabiana Pandolfi[1], Giovanni Mattei[2], Leonardo Mattiello[1], Concita Sibilia[1]
[1]Universita'di Roma La Sapienza, Dipartimento SBAI, Roma, Italy alessandro.belardini@uniroma1.it
[2]Università di Padova, Dipartimento di Fisica e Astronomia, Padova, Italy

In order to enhance the optical enantioselectivity of chiral molecules suitable substrates must be adopted. Self-assembled approach allows realizing plasmonic metasurfaces with a low cost reliable procedure. By using self-organized polystyrene spheres deposited on glass substrate, it is possible to produce an hole array on a metal thin film. In our case the spheres (518 nm in diameter) where reduced by selective reactive ion etching and then covered by gold, that is evaporated at a glancing angle. After the removing of the spheres an elliptical-hole array is produced forming a circular-dichroic substrate.

In fig.1 we show the realized substrate and the circular dichroic behavior as a function of the incidence angle when shined by 633 nm circular polarized light.



(a) (b)

Figure 1: (a) SEM image of the realized sample. (b) circular dichroism as a function of incidence angle of the bare substrate (black circles), right-handed molecules on the substrate (blue triangles), left-handed molecules on the substrate (red reversed triangles).

The coupling with the hole array changes the circular dichroic response of the molecules as a function of the intrinsic (zero deg.) and extrinsic chirality of the substrate.

Two new enantiomers (right-handed and left-handed molecules) have been synthesized in order to present a wide band CD in the visible domain.

References

[1] E. Petronijević , G. Leahu, R. Li Voti , A. Belardini , C. Scian, N. Michieli , T. Cesca , G. Mattei , and C. Sibilia. "Photo-acoustic detection of chirality in metal-polystyrene metasurfaces," Appl. Phys. Lett. 114, 053101 (2019).

Slit arrays for plasmon-enhanced vibrational circular dichroism

F. Mattioli,[1] G. Mazzeo,[2] G. Longhi,[2] S. Abbate,[2] G. Pellegrini,[3] F. Rusconi,[3] M. Celebrano,[3] M. Finazzi,[3] L. Duò,[3] C. Zanchi,[4] M. Tommasini,[4] M. Pea,[1] S. Cibella,[1] F. Sciortino,[5] L. Baldassarre,[5] A. Nucara,[5] M. Ortolani,[5] P. Biagioni[3]

[1]Istituto di Fotonica e Nanotecnologie (IFN), CNR, Roma IT

[2]Dipartimento di Medicina Molecolare e Traslazionale, Univ. di Brescia, Brescia IT

[3]Dipartimento di Fisica, Politecnico di Milano, Milano IT

[4]Dip. di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano, Milano IT

[5]Dipartimento di Fisica, Sapienza Università di Roma, Roma IT

Keywords: Plasmonics, superchirality, vibrational circular dichroism

Recently, novel 'superchiral' approaches have been proposed to enhance the circular dichroism (CD) signal by tailoring the properties of the electromagnetic field through the control of the associated optical chirality [1]. In this framework, plasmonic chiral sensing holds exciting perspectives [2-4] but several challenges have also been discussed [5-7]. The mid-infrared spectral range is especially promising for plasmon-enhanced vibrational circular dichroism [8]. We report recent results exploiting resonant arrays of chiral plasmonic slits to generate sharp and intense features associated with their chiroptical activity. We also observe a dramatic change in the plasmonic CD spectrum when the slits are covered with dimethyl D-tartrate (DDT). All spectra are checked for artifacts by measuring both plasmonic enantiomers, rotating the sample around the surface normal, and flipping the sample with respect to the light propagation direction. Numerical electromagnetic modelling complements the analysis.

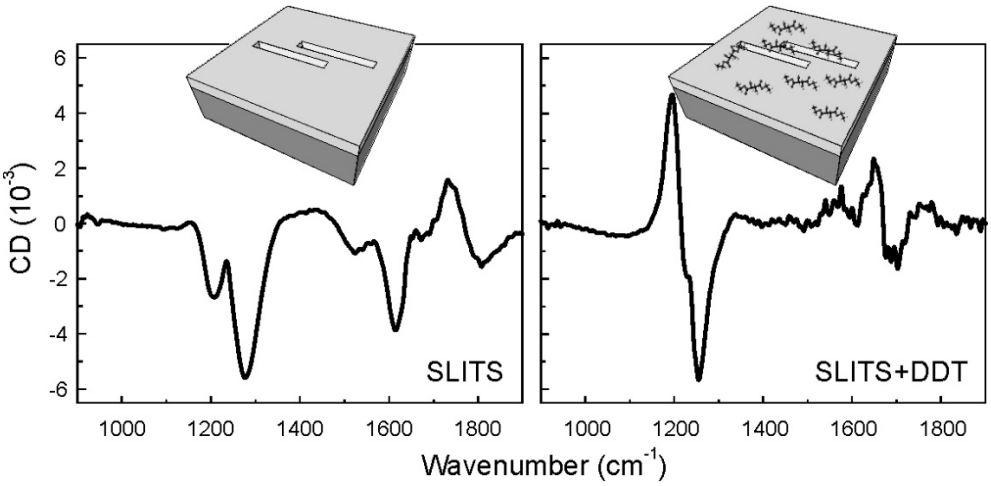


Figure 1: Representative CD spectra from clean slits (left) and slits covered with DDT (right).

We acknowledge funding from MIUR, PRIN 2015 program (project No. 2015FSHNCB).

References

[1] Tang, Y.; Cohen, A.E. Phys. Rev. Lett. **2010**, 104, 163901.
[2] Hendry, E. et al. Nature Nanotech. **2010**, 5, 783.
[3] Zhao, Y.; Askarpour, A.N.; Sun, L.; Shi, J.; Li, X.; Alù, A. Nature Comm. **2017**, 8, 14180.
[4] García-Guirado, J.; Svedendahl, M.; Puigdollers, J.; Quidant, R. Nano Lett. **2018**, 18, 6279.
[5] Schäferling, M.; Dregely, D.; Hentschel, M.; Giessen, H. Phys. Rev. X **2012**, 2, 031010.
[6] García-Etxarri A.; Dionne, J. Phys. Rev. B **2013**, 87, 235409.
[7] Finazzi, M.; Biagioni, P.; Celebrano, M.; Duò, L. Phys. Rev. B **2015**, 91, 195427.
[8] Knipper, R. et al. ACS Photonics **2018**, 5, 3238.

Plasmon-enhanced Ge-based Metal-Semiconductor-Metal photodetector at near-IR wavelengths

M. Bollani,[1,2] M. Lodari,[1,3] M. Ortolani,[4] L. Baldassarre,[4] G. Isella,[1,2] P. Biagioni,[1,3]
[1]IFN-CNR, p.zza Leonardo da Vinci 32, 20133 Milano, Italy,
[2]L-NESS, Dipartimento di Fisica, Politecnico di Milano, Polo di Como, Como, Italy
[3]Dipartimento di Fisica, Politecnico di Milano, p.zza Leoardo da Vinci 32, 20133,Milano, Italy
[4] Dipartimento di Fisica, Sapienza Università di Roma, P.le A.Moro 2, 00185 Roma, Italy

Keywords: metal-semiconductor photodetector; plasmonic grating; nano-lithography

Localized and/or propagating surface plasmon polaritons (SPPs) have been already successfully used to enhance the performance of photodetectors. In particular, photo-detection for sensing applications is one of the election fields for the exploitation of plasmonic effects [1-3].
In this work, we report on the use of plasmonic effects to boost the near-infrared sensitivity of metal-semiconductor-metal detectors. Plasmon-enhanced photodetection is achieved by properly optimizing Au interdigitated electrodes, micro-fabricated on Ge, a semiconductor that features a strong near-IR absorption. Specifically, the metallic fingers are used to couple the light with the collective electron oscillations in the contact structure at a specific incident wavelength $\bar{\lambda}$. To be effective, the incident electric field must be orthogonal to the longitudinal direction of the interdigitated fingers, and the grating periodicity has to be suitably designed to achieve plasmonic enhancement at a given $\bar{\lambda}$ as reported in Figure 1. Finite-difference time-domain simulations, photocurrent experiments and Fourier-transform IR spectroscopy are performed to validate how a relatively simple tuning of the contact geometry allows for an enhancement of the response of the device, adapting it to the specific detection needs. A 2-fold gain factor in the Ge absorption characteristic is experimentally demonstrated at 1.4 μm, highlighting the potential of this approach for optoelectronic and sensing applications.

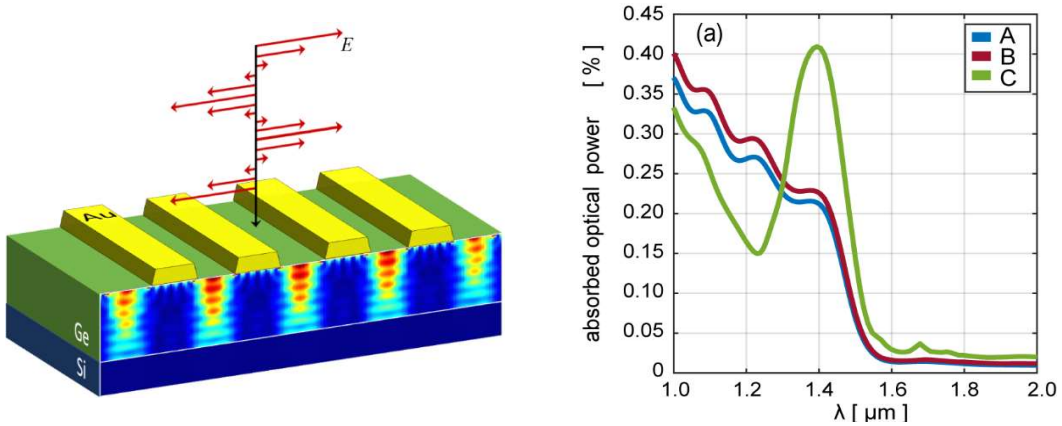


Figure 1: Left: Cartoon of a metallic grating. Au and Ge layers are depicted in yellow and green, respectively. Normal illumination and an electric field polarization orthogonal to the metal grating elements are taken into account. The color map reports the simulated absorption. Right: The simulated absorption spectra vs. λ of the resonant (C) and not resonant (A and B) MSM photodetectors.

References

[1] Cao, L.; Park, J.-S.; Fan, P.; Clemens, B.; Brongersma, M. L. "Resonant Germanium Nanoantenna Photodetectors", *Nano Lett.* 2010, 10, 1229–1233.
[2] Yu, Z.; Veronis, G.; Fan, S.; Brongersma, M. L. "Design of Mid Infrared Photodetectors Enhanced by Surface Plasmons on Grating Structures", *Appl. Phys. Lett.* 2006, 89, 151116.
[3] Tagliabue G.; Jermyn A.S.; Sundararaman R.; Welch A.J.; DuChene J.S.; Pala R.; Davoyan A.R.; Narang P.; Atwater H.A. "Quantifying the role of surface plasmon excitationand hot carrier transport in plasmonic devices", *Nat. Commun.* 2018, 9, 339.

Scattering of single photons on a single nanoparticle

Łukasz Bujak[1], Andreas Schell [2], Marek Piliarik[1]
[1] *Institute of Photonics and Electronics of the AS CR, v. v. i., Prague, Czech Republic*
[2] *CEITEC—Central European Institute of Technology, Masaryk University, Brno, Czech Republic*

Keywords: scattering, devices and applications, spectroscopy and nano-imaging

Recent developments in fluorescence-based super-resolution microscopy and nanoscopic tracking techniques helped to reach a spatial resolution in length scales reaching below 10 nm[1,2]. These advances rely on the efficient collection of fluorescence at single-molecule level. However, complex photo physics, saturation and bleaching of fluorescent labels limit the temporal resolution down to millisecond timescales. To overcome the spatiotemporal limitations of fluorescent-based techniques it is possible to employ scattering techniques, like dark-field microscopy[3] or interferometric scattering microscopy (iSCAT)[4].

Measurements of delicate specimens that are sensitive to light need to be done with a limited number of photons not to damage it. Low photon flux, however, limits the localization precision proportionally to the inverse square root of the number of detected photons (i.e. derived from the shot-noise limit), for both fluorescence and scattering-based microscopy. This fundamental limit has been theoretically and practically tested over the last decades[5], and recent realizations of efficient light-matter interactions on the quantum level, between single nanoparticle plasmons and single photons, shows that it is possible to accomplish measurements of light extinction with an accuracy exceeding that of the shot-noise limit[6].

Here, we show that scattering labels can be imaged and localized with a nanometer precision realized with iSCAT and low light conditions. We investigate theoretical and experimental limits of sub-shot-noise detection of gold nanoparticles (GNP) and identify pitfalls and limits of imaging for which the localization fidelity drops rapidly due to fluctuations of the detected number of photons in the low light regime. Our work paves the way to microscopy of nano-objects with sub-shot-noise detection.

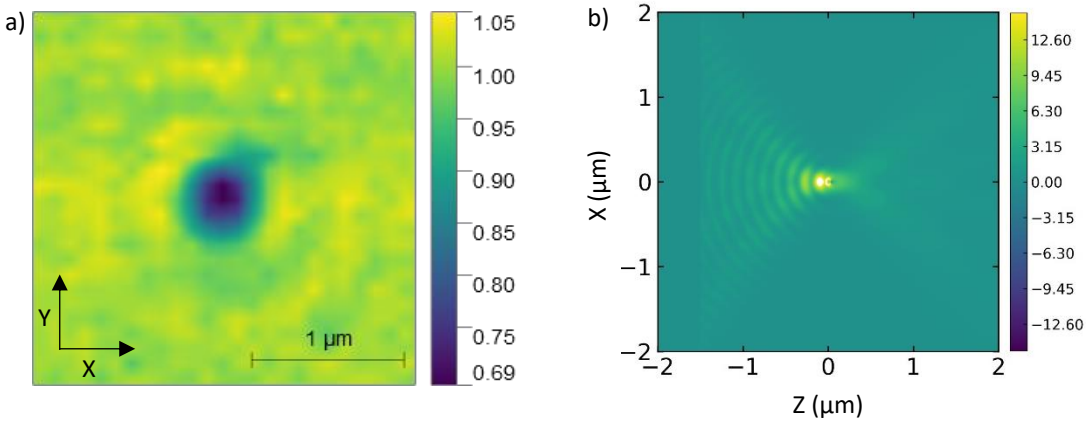


Figure 1: a) Raw iSCAT image of a 60 nm GNP immobilized on functionalized glass. Colour scale represents iSCAT contrast. b) Simulation of distribution of $|E|^2$ electric field injected at Z = -1.5 µm and focused on GNP.

References

[1] E. Betzig, G.H. Patterson, R. Sougrat, O.W. Lindwasser, S. Olenych, J.S. Bonifacino, M.W. Davidson, J. Lippincott-Schwartz, H.F. Hess, Science 313 (2006) 1642–1645.
[2] M.J. Rust, M. Bates, X. Zhuang, Nat Meth 3 (2006) 793–796.
[3] H. Ueno, S. Nishikawa, R. Iino, K.V. Tabata, S. Sakakihara, T. Yanagida, H. Noji, Biophys. J. 98 (2010) 2014–2023.
[4] M. Piliarik, V. Sandoghdar, Nature Communications 5 (2014) 4495.
[5] M. Xiao, L.-A. Wu, H.J. Kimble, Phys. Rev. Lett. 59 (1987) 278–281.
[6] M. Celebrano, R. Lettow, P. Kukura, M. Agio, A. Renn, S. Götzinger, V. Sandoghdar, Opt. Express, OE 18 (2010) 13829–13835.

Acknowledgements

This work was funded by the Ministry of Education Youth and Sports of the Czech Republic [LL1602].

Fabrication of Silver NPs-Coated AFM Probes for Tip-Enhanced Raman Spectroscopy by Solid-State Dewetting

Angela Capaccio[1,2], Giulia Rusciano[2], Antonio Sasso[2].
[1]*University of Naples "Federico II", Naples, Italy, angela.capaccio@unina.it*
[2]*University of Naples "Federico II", Naples, Italy*

Keywords: TERS, Raman Spectroscopy, Nanofabrication, Dewetting

In last decades, the interest in Tip-Enhanced Raman Spectroscopy (TERS) has been greatly increased thanks to its capability to brings Raman Spectroscopy at nanoscale resolution. The technique combines the chemical selectivity of Raman Spectroscopy, the high sensitivity of Surface Enhanced Raman Spectroscopy (SERS) and the lateral resolution (~20-50 nm) of AFM technology which overcomes the diffraction limit of the light [1,2]. The main challenge, however, involves the development of AFM tips covered with proper metallic nanostructures that act as optical antennas capable to enhance the scattered light. Indeed, recent simulations have demonstrated how plasmonic enhancement strongly depends on the separation and number of metallic nanoparticles on the surface of tips [3].

Our study is focused on the implementation of a simple procedure to produce silver NPs-coated tips with a high detection efficiency. The strategy is based on the fabrication of tips with a core-shell nanostructures. Firstly, in order to tune plasmon resonance to the excitation wavelength, we proceed with the oxidation of a commercial silicon tip which modifies the refractive index [4]. After that, a thin silver layer is deposited on the surface of tip by sputtering. The formation of silver nanoparticle is then achieved by inducing solid-state dewetting of this layer thanks to a plasma and/or thermal treatment. This procedure has already been pre-tested on silicon wafer and the obtained morphology is shown in Fig. 1. The performances of such probes are evaluated by using Single Walled Carbon Nano Tubes (SWCNT) samples, used in both standard and gap-TERS modes.

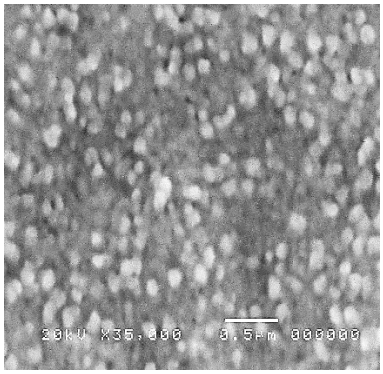


Figure 1: Dewetting of an Ag layer @60 nm deposited on a silicon wafer after oxidation, induced by 2:30 minutes of plasma treatment. The bar scale corresponds to 0.5 μm.

References

[1] Z. Zhang et al., Anal. Chem. **88(19)** , 9328-9346 (2016).
[2] G. Rusciano et al., ACS Nano **8**, 12300-12309 (2014).
[3] A. Taguchi, Nanoscale **7**, 17424-17433 (2015).
[4] N. Hayazawa et al, J. Raman Spectrosc. **43**, 1177-1182 (2012).

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

L. Ghirardini[1], L. Carletti[2], C. Gigli[3], G. Marino[3], V. Gili[3,4], A. Zilli[1], G. Pellegrini[1], L. Duò[1], 1 M. Finazzi[1],1 D. Rocco[2], A. Locatelli[2], I. Favero[3], I. Roland[3], A. Lemaître[5], D. Neshev[6], A. V. Zayats[7], C. De Angelis[2], G. Leo[3], M. Celebrano[1]

[1] Department of Physics, Politecnico di Milano, 20133 Milano, Italy
Corresponding author: michele.celebrano@polimi.it
[2] Department of Information Engineering, University of Brescia, 25123 Brescia, Italy
[3] Matériaux et Phénomènes Quantiques, Université Paris Diderot - Sorbonne Paris Cité, 75013 Paris, France
[4] "Institute of Applied Physics, Friedrich Schiller University Jena, 07745 Jena, Germany".
[5] Centre de Nanosciences et de Nanotechnologies, CNRS-UMR9001, 91460 Marcoussis, France
[6] Nonlinear Photonic Center, Australian National University, 2601 ACT Canberra, Australia
[7] Department of Physics, King's College London, Strand, London WC2R 2LS, United Kingdom

Keywords: Nanophotonics, Nonlinear Optics, Second Harmonic Generation, Semiconductors

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

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

We experimentally investigated the nonlinear properties of our sample with an ultrafast Erbium-doped fiber laser centered at 1554 nm (150 fs pulses, 80 MHz repetition rate), in a nonlinear confocal microscopy setup. We measured a conversion efficiency up to 10^{-5} for a 1.6 GW/cm^2 pump and a well-defined polarization dependence on the resonator geometry, in excellent agreement with the theoretical prediction [4,5]. Despite being among the most efficient SHG platforms, these nanoantennas suffer from unfavorable angular distribution of the emitted SHG [6], which prevents the efficient collection with standard optics. For this reason, we have recently devised a number of approaches to enable the active reshape and control of the nonlinear emission of the nanopillars. The first is based on asymmetric gratings that reshape the SHG emitted by the pillar [7]. The second is realized by pumping the nanoantenna with a tilted angle. This approach enables the emission of SHG in the forward direction, which is maximized for a pump angle of about 45° [8] as predicted by the selection rules imposed by the SHG in the nanopillar [6]. We also developed a hybrid nanoantenna based on a AlGaAs pillar working at the anapole condition and surrounded by a plasmonic ring, which enhances both the SHG as well as the Third Harmonic Generation thanks to an optimized in- and out-coupling of light to the anapole [9].

The high conversion efficiency and radiation control achieved show the potential of these platforms in the nonlinear manipulation of light at the nanoscale, paving the way to the design of efficient integrated nonlinear nanophotonics active components.

References

[1] A. I. Kuznetsov, et al., Sci. Rep. **2**, 1 (2012).
[2] A. B. Evlyukhin, et al., Nano Lett. **12**, 3749 (2012).
[3] S. Person, et al., Nano Lett. **13**, 1806 (2013).
[4] V. F. Gili, et al., Opt. Expr. **24**, 15965 (2016).
[5] L. Ghirardini, et al., Opt. Lett. **42**, 559-562 (2017).
[6] L. Carletti, et al., ACS Photonics **3**, 1500 (2016).
[7] L. Ghirardini, et al. Nano Lett. **18**, 6750-6755 (2018).
[8] L. Carletti, et al. ACS Photonics **5**, 4386-4392 (2018).
[9] V. F. Gili et al. B. J. Of Nanotech. **9**, 2306-2314 (2018).

Long-and short-range ordered gold nanoholes as large-area optical tunable transducers for sensing applications

Adriano Colombelli [1], Daniela Lospinoso[1,2], Maura Cesaria[1], Antonietta Taurino[1], Roberto Rella[1] , Maria Grazia Manera[1]

[1]*Institute for Microelectronics and Microsystems IMM-CNR, Campus Ecotekne, 73100 Lecce, Italy*
[2]*University of Salento, Campus Ecotekne, via Monteroni, 73100 Lecce, Italy;*
**Correspondence: adriano.colombelli@le.imm.cnr.it*

Keywords: Metamaterials, nanoplasmonics, refractometric sensing.

Nanosphere lithography (NSL) [1,2] and colloidal lithography (CL) [3,4] are two low cost, simple and alternatives to the top-down techniques, fabrication methods of large-areas nano-optical devices.

These approaches use self-assembly processes of polymer (silica, latex or polystyrene) colloids at a liquid-liquid or liquid-solid interface starting with a suspension of commercial monodispersed colloids [5,6].

In this work, both NSL and CL are implemented to fabricate two-dimensional distributions of gold nanoholes (NHs) arrays, which have being widely studied for basic understanding and optimization of their optical properties as well as applications in several fields (for instance, sub-wavelength photolithography [7], nonlinear optics (interferometric plasmonic sensing) [8], surface-enhanced Raman scattering (SERS) [9], surface enhanced fluorescence spectroscopy [10] and especially chemical sensors and biosensors [11-13].

In the case of NSL, highly ordered arrays of gold NHs distributed in hexagonal lattice were fabricated. In parallel CL was implemented to produce short-range ordered gold NH arrays.

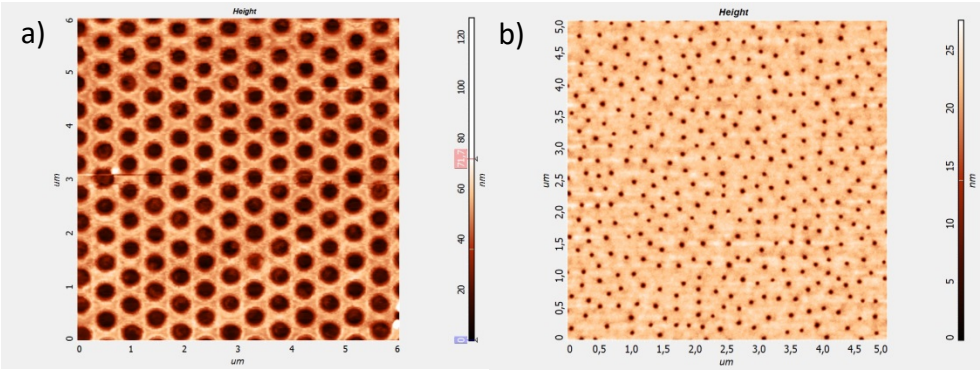


Figure 1: AFM topography of long-range (a) and short-range (b) ordered NH.

For both nanofabrication techniques, the choice of proper experimental conditions for the mask assembly for the resulting long-and short-range ordered NH distributions is crucial. Here such conditions are discussed and correlated to the NH array optical properties, namely to the excitation and spectral identification of propagating and localized Surface Plasmon modes.

For all the fabricated NH arrays, transmittance and/or reflectance spectra were recorded in air, exhibiting interesting optical features in the Vis-NIR spectral range.

Functional characterization related to the detection of refractive index changes in liquid environment is reported, thus paving the way for future perspectives in the biosensing field.

References

[1] Haynes, C.L.; Van Duyne, R.P. *J. Phys. Chem. B* **2001,** *105*, 5599-5611.
[2] Duval Malinsky, M.; Kelly, K.L.; Schatz, G.C.; Van Duyne, R.P. *J. Phys. Chem. B* **2001**, *105*, 2343–2350.
[3] Prikulis, J.; Hanarp, P.; Olofsson, L.; Sutherland, D.; Käll, M. Nano Lett. 2004, 4, 1003–1007.
[4] Hanarp, P.; Sutherland, D.S.; Gold, J.; Kasemo, B. Colloids Surfaces A Physicochem. Eng. Asp. 2003, 214, 23–36.
[5] Xia, Y.; Gates, B.; Yin, Y.; Lu, Y. Adv. Mater. 2000, 12, 693-713.
[6] Burmeister, F.; Schäfle, C.; Keilhofer, B.; Bechinger, C.; Boneberg, J.; Leiderer, P. Adv. Mater. 1998, 10, 495–497.
[7] Luo, X.; Ishihara, T. Opt. Express 2004, 12, 3055–3065.
[8] Gong, Y.; Joly, A.G.; El-Khoury, P.Z.; Hess, W.P. J. Phys. Chem. Lett. 2014, 5, 4243–4248.
[9] Anderson, D.J.; Moskovits, M.J. Phys. Chem. B 2006, 110, 13722–13727.
[10] Liu, Y.; Blair, S. Opt. Lett. 2003, 28, 507–509.
[11] Blanchard-Dionne, A.-P.; Meunier, M. Adv. Opt. Photon. 2017, 9, 891–940.
[12] Gordon, R.; Sinton, D.; Kavanagh, K.L.; Brolo, A.G. Acc. Chem. Res. 2008, 41, 1049–1057.
[13] Brolo, A.G.; Gordon, R.; Leathem, B.; Kavanagh, K.L. Langmuir 2004, 20, 4813–4815.

A robust ellipsometric analysis of nanoscale layered structures

Antonio De Luca [1], Giuseppe Emanuele Lio[1], Giovanna Palermo[1], Roberto Caputo[1]
[1] *Dipartimento di Fisica and CNR-Nanotec, Rende, Italy, Antonio.deluca@unical.it*

Keywords: numerical ellipsometry, nanoscale multi-layered systems

A simple and robust method able to calculate and predict, with high accuracy, the optical properties of single and multi-layer materials by exploiting a Comsol Multiphysics simulation platform is presented. For each considered material, it is possible to extract physical quantities of interest like reflectance, transmittance and Brewster angle, for different incident polarizations. In order to validate the predictive capabilities of the method, four real cases with nanoscale features have been considered: i) a single thin layer (20 nm) of Ag deposited on a glass substrate; ii) a metamaterial composed of five bi-layers of Ag/ITO (Indium Tin Oxide), with a thickness of 20 nm each; iii) a metamaterial composed of three tri-layers, AZO/ITO/Ag slabs without thickness periodicity (AZO stands for Al2O3/Zinc Oxide). The fourth case represents a study on a special configuration of a metal/insulator/metal configuration. Numerical results have been compared with experimental data provided by real ellipsometric measurements performed on nanostructures that respect the structural constraints mentioned above. Within the experimental uncertainty, the obtained agreement is excellent, suggesting this research as a valid design approach to realize multi band metamaterials able to work in a wide/broad spectrum range.

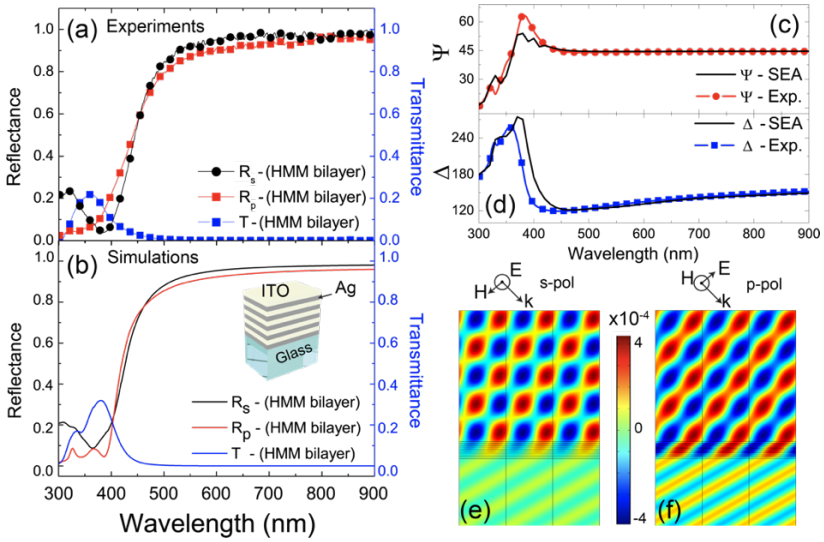


Figure 1: Reflectances (*Rp*, *Rs* red and black lines with symbols) and Transmittance (*T* blue lines with squares) measured (a) and calculated (solid) by a FEM model based on Comsol Multyphysics (b) for a five bilayers Ag/ITO HMM (b), sketched in the inset. Comparison of experimental (colored with symols) and numerical (solid) Ψ (c) and Δ (d), for the same sample. (e-f) Electric field maps distribution for TE (s-pol) and TM (p-pol) waves, respectively, extracted for an impinging wavelength of 390nm.

Preliminary attempts implementing a numerical ellipsometric analysis by means of finite element method (FEM) simulation in different spectral ranges have been reported in literature,[1–3] mainly proposing an ideal starting point like the solution of single layer materials with functionalities in the NIR-VIS range. However, in these cases the approach is limited to a scattered field study instead of a full field analysis. Here, we report a novel attempt, based on the COMSOL commercial platform,[4] providing a comprehensive ellipsometric analysis of general multi-layer systems with extreme freedom of design in terms of thickness and composition of the single layer as well as their number.

References

[1] Rana, G.; Deshmukh, P.; Duttagupta, S.; Prabhu, S. Design of a Simple and Robust Asymmetric Ellipsometer for Terahertz (THz) using COMSOL Ray Optics Module.
[2] Wiklund, H.; Arwin, H.; Järrendahl, K. A FEM-based application for numerical calculations of ellipsometric data. physica status solidi (a) 2008, 205, 945–948.
[3] Gross, H.; Model, R.; Baer, M.; Wurm, M.; Bodermann, B.; Rathsfeld, A. Mathematical modelling of indirect measurements in scatterometry. Measurement 2006, 39, 782–794
[4] Zimmerman,W. B. Multiphysics modeling with finite element methods;World Scientific Publishing Company, 2006; Vol. 18.

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

M. Celebrano,[1] A. Locatelli,[2] L. Ghirardini,[1] G. Pellegrini,[1] P. Biagioni,[1] X. Wu,[3,4] S. Grossmann,[3,4] L. Carletti,[2] C. De Angelis,[2] L. Duò,[1] B. Hecht,[3,4] M. Finazzi.[1]

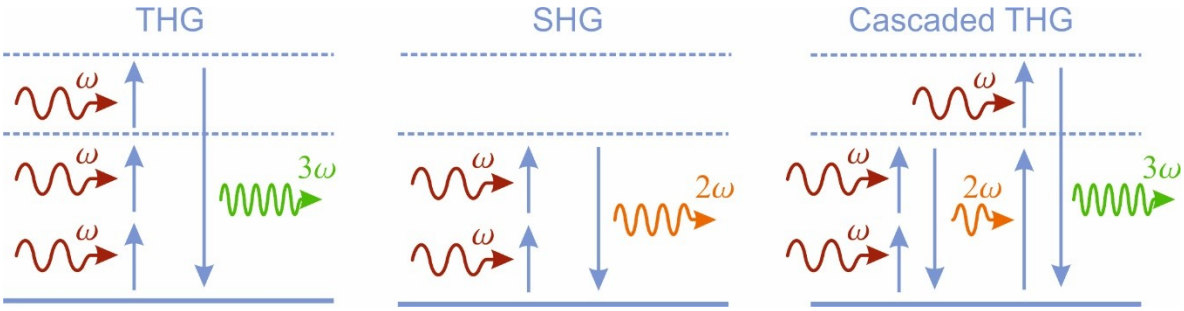
[1] *Physics Department, Politecnico di Milano, Piazza Leonardo Da Vinci 32, 20133 Milano, Italy. Corresponding author: marco.finazzi@polimi.it*
[2] *Department of Information Engineering, University of Brescia, Via Branze 38, 25123 Brescia, Italy.*
[3] *Nano-Optics & Biophotonics Group - Department of Physics - Experimental Physics 5, University of Würzburg, Am Hubland, 97074 Würzburg, Germany.*
[4] *Röntgen Research Center for Complex Material Systems (RCCM), Am Hubland, 97074 Würzburg, Germany.*

Keywords: Nanophotonics, Plasmonics, Nonlinear Optics, Second Harmonic Generation, ThirdHarmonic Generation

The optimization of nonlinear optical processes at the nanoscale is a crucial step for the development of nanoscale photon sources for quantum-optical networks. Designing innovative plasmonic nanoantennas and hybrid nanostructures able to enhance optical nonlinearities in very small volumes represents one of the most promising routes. In such systems, the upconversion of photons can be achieved with high efficiencies via third-order processes, such as third harmonic generation (THG), thanks to the resonantly-enhanced volume currents[1-5].

Conversely, second-order processes, such as second harmonic generation (SHG), are often inhibited by the symmetry of metal lattices and of common nanoantenna geometries. SHG and THG processes in plasmonic nanostructures are generally treated independently, since they typically represent small perturbations in the light-matter interaction mechanisms.

In this work, we demonstrate that this paradigm does not hold for plasmon-enhanced nonlinear optics, by providing evidence of a cascaded process in THG, which is seeded by SHG and sizably contributes to the overall yield. We address this mechanism by unveiling a characteristic fingerprint in the polarization state of the nonlinear emission from non-centrosymmetric gold nanoantennas and point out that such cascaded processes may also appear for structures that exhibit only moderate SHG yields. The presence of this peculiar mechanism in THG from plasmonic nanoantennas at telecommunication wavelengths allows gaining further insight on the physics of plasmon-enhanced nonlinear optical processes. This could be crucial in the realization of nanoscale elements for photon conversion and manipulation operating at room-temperature.



References

[1] T. Hanke et al., *Phys. Rev. Lett.* **2009** 103, 257404.
[2] M. Danckwerts et al., *Phys. Rev. Lett.* **2007**, 98, 026104.
[3] H. Harutyunyan et al., *Phys. Rev. Lett.* **2012**, 108, 217403.
[4] G. Sartorello et al., *ACS Photon.* **2016**, 3, 1517−1522.
[5] M. Hentschel et al, *Nano Lett.* **2012**, 12, 3778−3782.

Real-time dynamics of plasmonic resonances in nanoparticles described by a general dielectric function

Gabriel Gil[1,†] and *Stefano Corni*[1,2]
[1] *Dipartimento di Scienze Chimiche, Università degli studi Padova, Italy.*
[2] *S3, Istituto di Nanoscienze, CNR, Modena, Italy.*
[†] *gabrieljose.gilperez@unipd.it*

Keywords: plasmon resonances, electric field enhancement, nanoparticles, polarizable continuum model

Plasmon resonances of noble metal nanoparticles allows to focus the electromagnetic radiation within the nanoscale. The localized field enhancement they provide gives rise to interesting phenomena such as surface enhanced Raman scattering, surface enhanced infrared absorption, and metal enhanced fluorescence. Furthermore, when coupled to ultrafast lasers, plasmonic nanoparticles might be key to disclose, probe and manipulate a host of other photochemical phenomena at a single-molecule level, such as excited state dynamics, high-harmonic generation and photosynthetic energy-transfer pathways. Time-dependent Polarizable Continuum Model (TDPCM) [1, 2], formally a time dependent boundary element method, is a suitable framework to account for the real-time electric field enhancement in the long-wavelength limit for any nanoparticle shape [3]. Until now, the computational strategy tackling TDPCM has been accessible only for materials described by either Debye or Drude-Lorentz dielectric functions [2–4]. Albeit adequate, the latter models do not describe fatithfully the dielectric properties of realistic nanoparticle media. In this contribution, we lay down an extension of the TDPCM approach to obtain the real-time electric field enhancement for a light pulse impinging on a plasmonic nanoparticle that is characterized by a dielectric function that depends in a generic way on the frequency. It is sufficient to know (e.g., from measurements or ab initio calculations) such frequency-dependent complex dielectric function only on a discrete set of frequencies. Based on these values, we can build up an equation of motion for the time-dependent polarization charges of the nanoparticle due to the external field, generalizing the achivement of Ref. [3]. To show the potential of our technique, we perform real-time simulations on prototypical nanoparticles subjects to various pulses. In particular, we compute the absorption spectrum of the nanoparticle out of the Fourier transform of the time-dependent polarization dipole, and we compare it with the result of a frequency-domain calculation. Moreover, we discuss the time dependent polarization charges and field dynamics when the nanoparticle interacts with an external laser pulse.

References

[1] J. Tomasi, B. Mennucci, R. Cammi, Chem. Rev., 2005, 105 (8), pp 2999–3094.
[2] M. Caricato, F. Ingrosso, B. Mennucci, and J. Tomasi, J. Chem. Phys., 2005, 122, 154501.
[3] S. Corni, S. Pipolo, J. Phys. Chem. C, 2016,120 (50), pp 28774–28781.
[4] S. Corni, S. Pipolo, R. Cammi, J. Phys. Chem. A, 2015, 119 (21), pp 5405–5416.

Investigating hot-electrons with metal-semiconductor-metal slit arrays

R. Hernandez,[1,2] O. Demichel,[1] M. Lodari,[3,4] M. Celebrano,[2] M. Finazzi,[2] L. Duò,[2]
G. Isella,[3,4] A. Bouhelier,[1] M. Bollani,[3,4] P. Biagioni,[2,4] and B. Cluzel[1]

[1]Laboratoire Interdisciplinaire Carnot de Bourgogne, Dijon, France
[2]Dipartimento di Fisica, Politecnico di Milano, Milano, Italy
[3]L-NESS, Dipartimento di Fisica, Politecnico di Milano, Polo di Como, Como, Italy
[4]IFN-CNR, Milano, Italy

Keywords: Plasmonics, hot electrons, photodetector

Hybrid devices based on metallic plasmonic nanostructures and semiconductors are promising for future ultrafast applications such as photodetection [1]. Hot-carriers can be produced within Au gratings and the generation efficiency can be enhanced by localized plasmons [2]. It has been shown that when these nanostrips of Au are coupled with a semiconductor, hot-carriers generated within the metal can overcome the Schottky barrier and yield a photocurrent [2]. This internal photoemission mechanism allows one to detect photons with energy just above the Schottky barrier, i.e. below the energy band gap of the semiconductor. Furthermore, the relaxation time of hot-electrons is in the ps range [3]. Harvesting such hot-electrons before they thermalize is a key challenge to ultrafast photodetection, since it allows one in perspective to emit/receive information at THz rates.

We aim at studying the dynamics of hot-electrons in a metal-semiconductor-metal device. FDTD simulations demonstrate that Au gratings on SOI (silicon on insulator) wafers, with specific filling factor and periodicity, can resonantly enhance the absorption of light within the Au grating at 1.55 μm wavelength (Figure 1). This device is being employed to study the generation of hot-carriers, their transfer efficiency towards the semiconductor and the speed of this process. Two-pulse photocurrent correlation techniques [4] are also employed to assess the dynamics of the device.

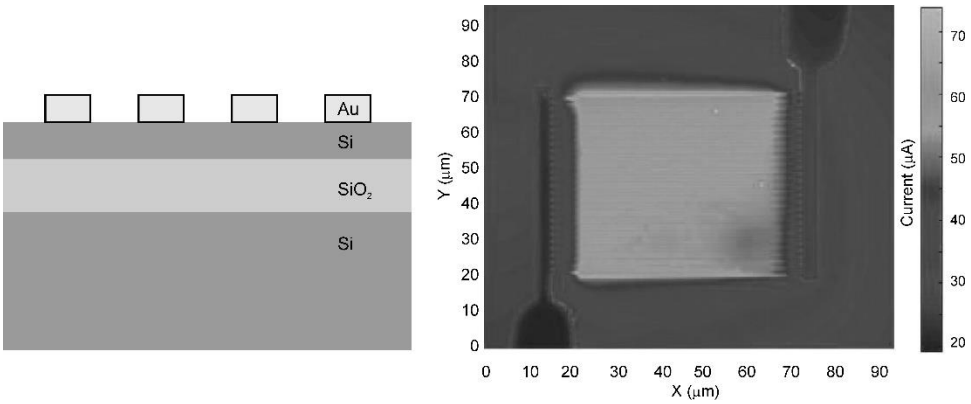


Figure 1: Sketch of the investigated device (left) and preliminary photocurrent mapping at 790 nm wavelength with 3 mW power and 0.5 V bias (right).

We acknowledge funding from MIUR, PRIN 2015 program (project No. 2015FSHNCB).

References

[1] M. L. Brongersma, N. J. Halas and P. Nordlander. Plasmon-induced hot carrier science and technology. Nature Nanotechnology, 2015.

[2] A. Sobhani, M. W. Knight, Y. Wang, B. Zheng, N. S. King, L. V. Brown, Z. Fang, P. Nordlander, and N. J. Halas. Narrowband photodetection in the near-infrared with a plasmon-iduced hot-electron device. Nature Communications, 2012.

[3] O. Demichel, M. Petit, S. Viarbitskaya, R. Méjard, F. de Fornel, E. Hertz, F. Billard, A. Bouhelier, and B. Cluzel. Dynamics, Efficiency, and Energy Distribution of Nonlinear Plasmon-Assisted Generation of Hot Carriers. ACS Photonics, 2016.

[4] H. Wang, C. Zhang, W. Chan, S. Tiwari, and F. Rana. Ultrafast response of molybdenum disulfide photodetectors. Nature Communications, 2015.

Spectral control of disorder photonic modes

Francesca Intonti[1,2], Dario Balestri[1,2], Maurangelo Petruzzella[3], Simona Checcucci[2], Niccolò Caselli[1,2], Fabrizio Sgrignuoli[1], Frank W. M. van Otten[3], Andrea Fiore[3], and Massimo Gurioli[1,2]

[1]*European Laboratory for Nonlinear Spectroscopy, 50019 Sesto Fiorentino, Italy*

[2]*Department of Physics and Astronomy, University of Florence, 50019 Sesto Fiorentino, Italy*

[3]*Department of Applied Physics, Eindhoven University of Technology, 5600, The Netherlands*

Keywords: Spectroscopy and nano-imaging, Nanophotonics and Hybrid Plasmonics,

Optical localization in strongly disordered photonic media is an attractive topic for proposing novel cavity-like structures [1,2]. In fact, disordered photonic materials are less sensitive to fabrication errors or defects, offering a more robust design platform [3]. Moreover, for optoelectronics and quantum sources the large density of photonics modes in these systems represents an important advantage since it weakens the constraint of spatial matching with randomly distributed emitters. However, due to fact that the spatial and spectral positions of random modes is unpredictable, the ability to fine-tuning the spectral resonance of random modes without affecting their spatial intensity distribution is of the utmost relevance for cavity-like quantum electrodynamics experiments.

We investigated two-dimensional disordered photonic systems made either by a single GaAs membrane or by two parallel GaAs membranes. Both systems are patterned with randomly distributed circular air scattering centers. We pursued two different approach to spectrally control the random modes. By applying a post-fabrication method based on laser assisted nano-oxidation of the single GaAs membrane system, performed by near-field illumination, the resonance of a given random mode can be gently blue-shifted to a desired target wavelength [4]. In order to develop a reversible tuning method, we exploited the double membrane system [5]: by mechanically varying the air distance between the two membranes, controlling the force exerted by the near-field tip on the upper membrane, we induce either red or blue shift, depending on the spatial parity of the modes [6] (Fig. 1). We reached a spectral shift larger than 40 nm without affecting the spatial distribution of the modes. Our results allow to efficiently tailor the light-matter interaction in disordered systems, facilitating the exploitation of random localization both for the development of new optoelectronic devices and for quantum electrodynamics experiments.

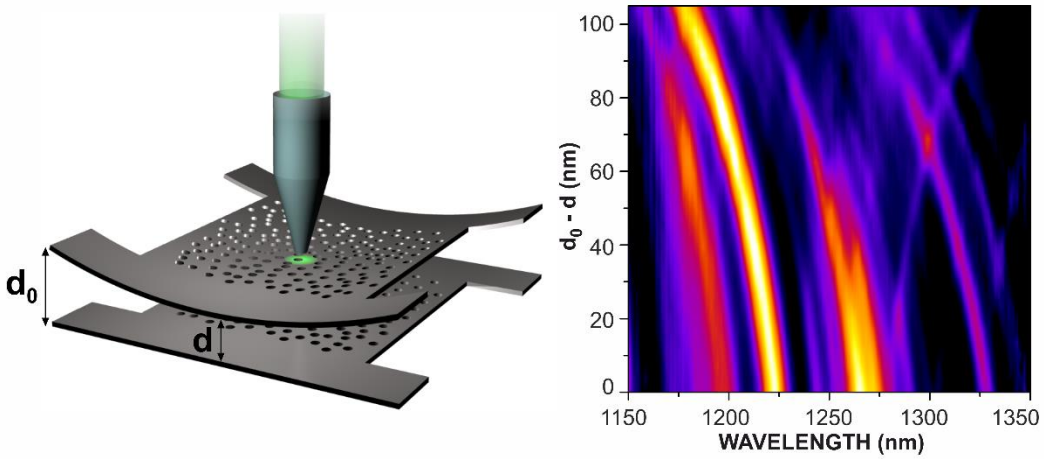


Figure 1: Sketch of the double membrane tip compression, where we exaggerated the bending for sake of illustration. Typical spectra (with many modes), reported in a color map, at different double membrane compression. Note the dominance of asymmetric modes, but also the presence of one symmetric mode on the long-wavelength side.

References

[1] L. Sapienza, H. Thyrrestrup, S. Stobbe, P.D. Garcia, S. Smolka, P. Lodahl, Science **327**, 1352 (2010)

[2] F. Riboli, N. Caselli, S. Vignolini, F. Intonti, K. Vynck, P. Barthelemy, A. Gerardino, et al., Nature Materials **13**, 720 (2014)

[3] D. S. Wiersma, Nat. Photonics **7**, 188 (2013).

[4] N. Caselli, F. Riboli, F. Intonti, F. La China, F. Biccari, A. Gerardino, M. Gurioli APL Photonics **1**, 041301 (2016)

[5] M. Petruzzella, T. Xia, F. Pagliano, S. Birindelli, L. Midolo, Z. Zobenica, L.H. Li, E.H. Linfield, A. Fiore1 APL **107**, 141109 (2015)

[6] D. Balestri, M. Petruzzella, S. Checcucci , F. Intonti, N. Caselli, F. Sgrignuoli, Frank W. M. van Otten, A. Fiore, M. Gurioli, Adv. Mater. **31**, 1807274 (2019)

Novel plasmonic nanocavities for optical trapping-assisted sensing applications

Alemayehu Nana Koya †, Remo Proietti Zaccaria
Cixi Institute of Biomedical Engineering, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, 315201 China
†*E-mail: alulanana@gmail.com*

Keywords: Plasimonic nanocavity, plasmonic nanotweezers, biosensing with nanotweezers

Properly designed plasmonic nanocavities provide deep potential energy well and huge local field intensity [1 - 3], implying their potentials for trapping and sensing of nanosized objects with low laser power. In our recent in-depth review [4], we have explored the fundamentals and functionalities of various geometries of plasmonic nanocavities for such applications as optical trapping, sensing, and Raman enhancement of single particles and small molecules. Here, we show recent developments of optical trapping and sensing of nanoparticles in plasmonic nanocavities. Nanoparticle trapping-induced resonance shift of plasmonic nanocavity can be related to the trapping potential of the nanosystem via the intercavity field intensity (Figure 1). This analytical expression is experimentally validated by demonstrating optical trapping and sensing of single nanoparticles and small molecules with plasmonic nanotweezers. We also show the possibility of merging optical tweezers with Raman spectroscopy to develop optical trapping-assisted Raman biosensors that can simultaneously trap and detect nanoparticles at the single molecule level [5]. To realize such a novel biosensing device, we found that plasmonic nanocavities as ideal candidates.

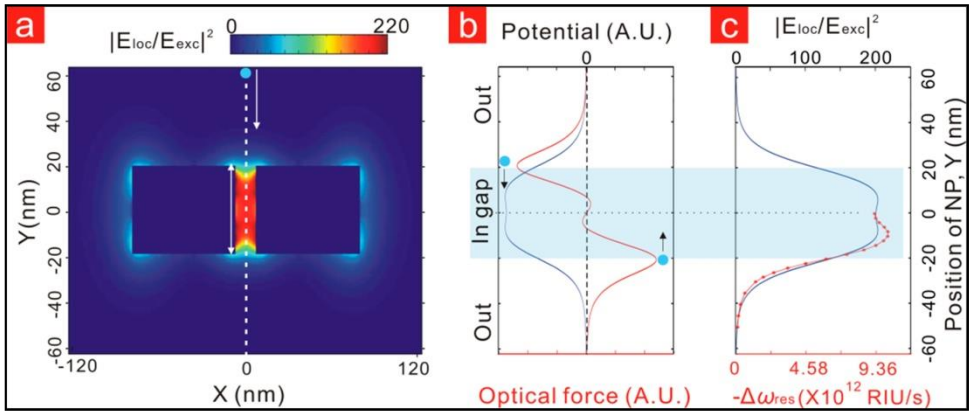


Figure 1: (a) Local field intensity plasmonic dimer nanocavity. (b) Optical force and trapping potential of the nanocavity. (c) Relationship between trapping-induced resonance frequency shift (red) and associated potential energy (blue) of the nanocavity upon trapping of small nanoparticle [3].

References

[1] M.-K. Kim et.al., Nano Lett. **15**, 4102−4107 (2015).
[2] Y. Lu, et. al., Sci. Rep**. 6**, 32675 (2016).
[3] W. Zhang, O. J. F. Martin, ACS Photonics **2**, 144−150 (2015).
[4] A. N. Koya, et. al., (under review).
[5] R. Gordon, Opt. Laser Technol. **109**, 328–335 (2019).

Nanoscale Numerical Behavior of Flexible Plasmonic Materials

G.E. Lio, G. Palermo, R. Caputo and A. De Luca

[1] Department of Physics and CNR-Nanotec, University of Calabria,
Via P. Bucci, 87036 Rende (CS), Italy

Research interest on materials and methods to control the nanoscale response of resonant nanostructures is relevant for the potential application in tunable and reconfigurable devices. Typical approaches promote the interplay between external macroscale stimuli (mechanic, thermal, acoustic, electric, and chemical) and plasmonic systems to achieve nanoscale effects. In plasmo-mechanics, an external mechanic strain applied to a flexible substrate is employed to induce plasmonic coupling between neighbouring Au particles. In this contribution, we report on a comprehensive numerical study able to predict strain-related phenomena in a plasmonic system made of different uniform distributions of metallic nanoparticles immobilized on a flexible elastomeric tape. Results evidence how the plasmo-mechanic control of the system depends on external parameters like incident light polarization, nanoparticle distance, and distribution arrangement.

[1] G.E. Lio, G. Palermo, R. Caputo and A. De Luca, Opto-mechanical control of flexible plasmonic materials, J. App. Phys 2019 (doi: 10.1063/1.5055370).

3D biosensing interfaces mediated by artificial lipid bilayers

Claudia Lubrano, Giuseppina Polino, Giuseppe Ciccone, Laura Matino, Francesca Santoro
Istituto Italiano di Tecnologia, Center for Advanced Biomaterials for Healthcare (CABHC), Naples, Italy, claudia.lubrano@iit.it

Keywords: 3D, bionsensors, supported lipid bilayers.

Supported lipid bilayers (SLBs) are well known as models of cell membranes with potential bio-technological applications [1]. As reported in literature, SLBs can be a perfect platform for cell culture, but the hardest challenge is represented by the integration of membrane proteins, which could give the proper rigidity to the bilayer and make them perfectly resembling the cell membrane [2]. In this work, we aim to develop supported lipid bilayers as cells-material bioelectronic interface in order to enhance cells adhesion on planar and 3D organic devices. In particular, planar and 3D substrates have been realized with PEDOT:PSS, an organic conductive polymers which has been identified as the most advanced conductive polymer due to a good trade-off between conductivity, stability, transparency and biocompatibility [3]. 3D structures have been realized through Reactive Ion Etching technique. In this work, we synthesized a bilayer using cells blebs, *i.e.* a bilayer made with cell membrane components; the idea is that in this way we could "seal" cells on the substrate underneath. First, we have collected blebs from HEK-293 cells (human embryonic kidney cells) and added POPC vesicles to form the bilayer. Then, we have characterized the adhesion of HL-1 cells and fibroblasts to analyze cells morphology. Finally, we were also able to engineer a fibronectin-functionalized synthetic bilayer with a higher fluidity in order to increase cells adhesion on the substrate underneath. This kind of platforms can have several applications, providing a better cell-material coupling even, for instance, on nanopatterned gold surfaces [4]: the possibility of incorporating trans-membrane proteins inside the bilayer could offer the chance of having a very efficient communication between plasmonic substrates and cells.

References

[1] R. P. Richter, R. Bérat, and A. R. Brisson, "Formation of Solid-Supported Lipid Bilayers: An Integrated View," *Langmuir*, vol. 22, no. 8, pp. 3497–3505, Apr. 2006.
[2] M. J. Richards *et al.*, "Membrane Protein Mobility and Orientation Preserved in Supported Bilayers Created Directly from Cell Plasma Membrane Blebs," *Langmuir*, vol. 32, no. 12, pp. 2963–2974, Mar. 2016.
[3] M. Sessolo *et al.*, "Easy-to-Fabricate Conducting Polymer Microelectrode Arrays," *Adv. Mater.*, vol. 25, no. 15, pp. 2135–2139, Apr. 2013.
[4] R. G. Moulick, G. Panaitov, L. Du, D. Mayer, and A. Offenhäusser, "Neuronal adhesion and growth on nanopatterned EA5-POPC synthetic membranes," *Nanoscale*, vol. 10, no. 11, pp. 5295–5301, Mar. 2018.

Hybrid organic-inorganic nanosystems: assessing a boundary element method approach to optical properties of gold bipyramidal nanoparticles

Jacopo Marcheselli[1], *Stefano Corni*[2], *Ivan Rivalta*[3−4], *Marco Garavelli*[3], *Stefano Baroni*[1]
[1]*International School for Advanced Studies (SISSA), Trieste, Italy, jmarches@sissa.it*
[2]*Dipartimento di Scienze Chimiche, Università di Padova, Padova, Italy*
[3]*Dipartimento di Chimica Industriale, Università degli Studi di Bologna, Bologna, Italy*
[4]*Laboratoire de Chimie, Ecole Normale Supérieure de Lyon, Lyon, France*

Keywords: Nanophotonics and Hybrid Plasmonics, Plasmonic and dielectric nanoantennas, Scattering

Hybrid organic-inorganic Nanoparticles (HNPs) are very interesting and widely studied materials, for their versatile applications in biotechnology and medicine, with high potential in biomedical imaging, gene and drug delivery, and photothermal cancer therapy [1, 2], making them one of the most promising materials for early and accurate cancer diagnosis and effective cancer therapy. However, computing their physico-chemical properties in details proves to be a challenge. While the nature of the organic component of the HNPs necessitates a full quantum chemical treatment, the size of the inorganic component renders this treatment computationally too expensive to be assessed with an homogeneous technique.

For this reason hybrid models have been developed combining a QM level treatment and a classical electromagnetism approach, respectively, for molecules and the inorganic nano-structures upon which they are adsorbed [3]. In particular, the inorganic component, usually a metal, is considered as a classical continuous body, characterized by its own frequency dependent dielectric function, for which the Maxwell equations are solved using the Boundary Element Method (BEM), while excitation energies due to the energy transfer from the molecule to the metal is evaluated exploiting Time Dependent Density Functional Theory (TDDFT).

The first step towards a correct application of this model is to prove that the polarization charges distribution that shape the surface of the metallic objects, introduced by BEM, well describes the optical properties of bare inorganic NPs. With this scope in mind, we reproduced experimental spectra [4, 5] of bare gold NPs using the aforementioned BEM tools implemented in the code SCUFF-EM [6] to compute Mie scattering and absorption of Gold Nano-bipyramids with different sizes and aspect ratios, having TEM data as only input. The plasmonic bands have been correctly reproduced in all cases, staying within an error of 0.05 eV from the actual experimental values, mostly as a result of the uncertainty introduced by the resolution of TEM images.

References

[1] R. Jiang, B. Li, C. Fang, and J. Wang, Adv. Mater. **26**, 5274-5309 (2014).
[2] U. Banin, Y. Ben-Shahar, and K. Vinokurov, Chem. Mater. **26**, 97-110, (2014).
[3] O. Andreussi, S. Corni, B. Mennucci, J. Tomasi, J. of Chem. Phys. **121**, 10190 (2004).
[4] Chateau et al., Nanoscale **7**, 1934 (2015).
[5] Sánchez-Iglesias et al., J. Am. Chem. Soc. **139**, 107-110, (2017)
[6] M. T. Homer Reid et al., *ArXiv e-prints*, **2013**, arXiv:1307.2966.

Pancharatnam-Berry transformation optics for total angular momentum sorting

Michele Massari[1, 2], Gianluca Ruffato[2,3], Pietro Capaldo[1], Alessia Mezzadrelli[2,4], Alessandro Pozzato[4], Erfan Mafakheri[2], Filippo Romanato[1,2,3,4]

[1]*CNR-IOM National Laboratory, Basovizza (TS), Italy, massari@iom.cnr.it*

[2]*LaNN – Laboratory for Nanofabrication of Nanodevices, EcamRicert Srl, Padova, Italy*

[3]*University of Padova, Department of Physics and Astronomy 'G. Galilei', Padova, Italy*

[4]*ThunderNIL Srl, Padova, Italy*

Keywords: metamaterials, devices and applications, nano-optics.

Orbital Angular Momentum (OAM) states of light have been recently considered for disruptive applications in a wide range of fields, from biology to microscopy, from holography to telecommunications. While the polarization state is described in a two-dimensional basis, the OAM degree of freedom opens to an unbounded state space, in which light beams carrying different integer OAM values are orthogonal to each other, propagating at the same frequency with no interference. This has aroused particular attention in the telecom field, which is constantly pursued by the worldwide restless demand for increasing bandwidth.

The pivotal part of a communication system based on OAM-MDM (Mode Division Multiplexing) is represented by the so-called multiplexer, i.e. a device allowing to generate a bunch of collimated and superimposed orthogonal beams. One of the most effective methods is represented by transformation optics, which perform a conformal mapping between angular and linear momentum states.

Paramount importance and interest has recently acquired parallel sorting of orbital angular momentum and polarization: due to their inherently polarization-sensitive optical response, optical elements acting on the geometric phase has proven to be useful for processing structured light beams with orthogonal polarization states by means of a single optical platform.

In this work, we present the design, fabrication and test of two optical devices: a 3D optical element fabricated as 256-level phase-only diffractive optics, for the sorting of OAM beams with unprecedented levels of miniaturization and OAM resolution [1], and a 2D Pancharatnam-Berry optical element (PBOE), realized in the form of continuously-variant subwavelength gratings, for the fabrication of an OAM sorter based on the conformal mapping between angular and linear momentum states [2,3]. With respect to 3D bulk and diffractive optics, acting on the dynamic phase of light, Pancharatnam-Berry optical elements transfer a phase which is geometric in nature by locally manipulating the polarization state of the incident beam (Figure 1). Furthermore, a hybrid device has been fabricated, assembling the metasurface for the geometric phase control with multi-level diffractive optics for the polarization-independent manipulation of the dynamic phase [3].

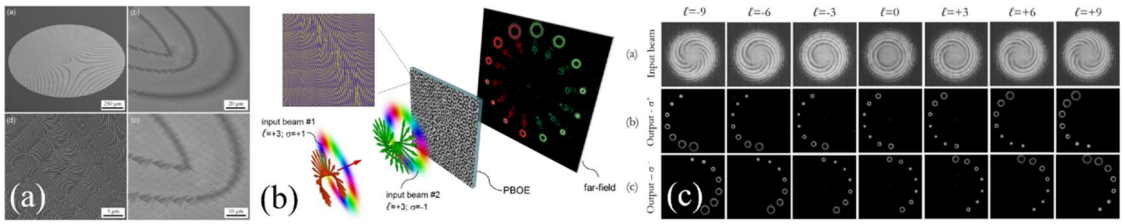


Figure 1: (a) SEM inspection of the metasurface fabricated in the form of continuously variant sub-wavelength gratings on a silicon substrate: it is worth appreciating the continuity of the grating-vector rotation angle at the meta-pixel boundaries. Inside each pixel, the grating vector varies continuously and the duty-cycle changes accordingly. (b) Scheme of the Pancharatnam-Berry optics working principle for OAM-beam sorting with the method of optical beam projection. When a circularly-polarized OAM beam illuminates the optical element, a bright spot appears in the far-field, at a position depending on the carried OAM and on the polarization handedness. (c) Interference patterns of the OAM beams exploited for the sorter characterization. The number and handedness of the spirals denotes the carried OAM.

References

[1] G. Ruffato, M. Girardi, M. Massari, E. Mafakheri, B. Sephton, P. Capaldo, A. Forbes, and F. Romanato, Sci. Rep. **8(1)**, 10248 (2018).

[2] P. Capaldo, A. Mezzadrelli, A. Pozzato, G. Ruffato, M. Massari, and F. Romanato, Opt. Mat. Express **9(3)**, 1015-1032 (2019).

[3] G. Ruffato, P. Capaldo, M. Massari, E. Mafakheri, and F. Romanato, submitted to Opt. Express (in press) (2019). Arxiv: https://arxiv.org/abs/1902.01325.

Full Resolution of Cell-Biosensor Interface *Via* Scanning Electron Microscopy/Focused Ion Beam

Laura Matino[1,2], *Francesca Santoro*[1]

[1] *Center for Advanced Biomaterials for Healthcare, Italian Institute of Technology, 80125, Naples, Italy*, laura.matino@iit.it , francesca.santoro@iit.it

[2] *Department of Chemical Materials and Industrial Production Engineering, University of Naples Federico II, Naples, Italy*

Keywords: interface, scanning electron microscopy, focused ion beam, high resolution imaging

Biosensors are conceived to be coupled with cells or tissues, to monitor their electrical activity or promote reaction to electrical stimulation. At cellular level, the interplay with the devices is crucial to determine the effectiveness and the success of the coupling. Therefore, during the last years, researchers have been motivated to engineer the interface, introducing pseudo-3D micro and nanostructures protruding from the substrate to foster a more intimate contact between cells and substrate underneath. To achieve a detailed characterization of cell-material crosstalk, many attempts have been carried out. However major limitations have been presented in respect to resolution in case of optical microscopy and artefacts in case of electron microscopy. Here, we present an advanced microscopy method (scanning electron microscopy/focused ion beam) based on ultra-thin resin plasticization which uniquely allows the visualization of the interface between cells and materials with 5-10 nm resolution [1-3].

This technique paves the way to a broader investigation of cell-material interactions including in the case of plasmonic devices.

References

[1] Santoro, F., et al., Revealing the Cell–Material Interface with Nanometer Resolution by Focused Ion Beam/Scanning Electron Microscopy. ACS Nano, 2017

[2] Li, X., et al., A Nanostructure Platform For Live Cell Manipulation of Membrane Curvature, Nature Protocol, 2019.

[3] Dipalo, M., et al., Cell Adhering to 3D Vertical Nanostructures: Cell Membrane Reshaping without Stable Internalization, Nano Letters, 2018.

Polarization switch between parallel and orthogonal collective resonances in aluminum arrays

Alina Muravitskaya[1], Artur Movsesyan[2], Pierre-Michel Adam[2]
[1]*B. I. Stepanov Institute of Physics, National Academy of Sciences of Belarus, Minsk, Belarus*
alina.muravitskaya@gmail.com
[2]*Université de Technologie de Troyes, Troyes Cedex, France*

Keywords: plasmonic and dielectric nanoantennas.

Optical properties of periodic arrays of metal nanoparticles differ from those of the isolated nanoparticles, due to the appearance of the lattice plasmon (LP) resonances resulting from the diffraction mediation of the radiative coupling between the nanoparticles. These collective resonances feature high quality factors, high enhancement of the near-field, field delocalization and tunability which makes them an attractive platform for optical sensors and nanolasing [1, 2, 3].

The lattice plasmon resonances appear as a propagating wave usually in the direction perpendicular to the external electric field [4]. In some publications a homogeneous refractive index is regarded as an important condition for the effective diffraction coupling [4, 5]. However, few publications showed the possibility of the parallel coupling in the nanoparticles arrays on the interface of media with mismatching refractive indexes [5, 6]. In this case the diffraction waves travel in the direction of the polarization vector of the incident field. Parallel coupling is promising for the number of application due to the high electric field delocalization in the superstrate and tolerance to the refractive index difference [5].

In this work we discuss the excitation of orthogonal and parallel collective resonances in arrays of aluminium nanoparticles. In the rectangular array under consideration (Fig. 1) the polarization change does not affect the direction of the diffractive waves propagation, but only switches from orthogonal to parallel coupling. It allows us to vary the plasmonic resonance position from 420 nm to 630 nm with the use of polarization. We study the difference of the far-field interactions in the array for the both a homogeneous and heterogeneous refractive index environment and show that in the latter case the effective coupling exists in both directions. We also examine the excitation of the neighboring nanoparticles by the scattered field. The incident plane wave excites the dipolar mode of the nanocylinders in the array and the redistributed field additionally excites the in-plane quadrupolar mode in the neighboring nanoparticles. The rate of this excitation depends on the interparticle distance and allows us to control the intensity of the coupled lattice mode.

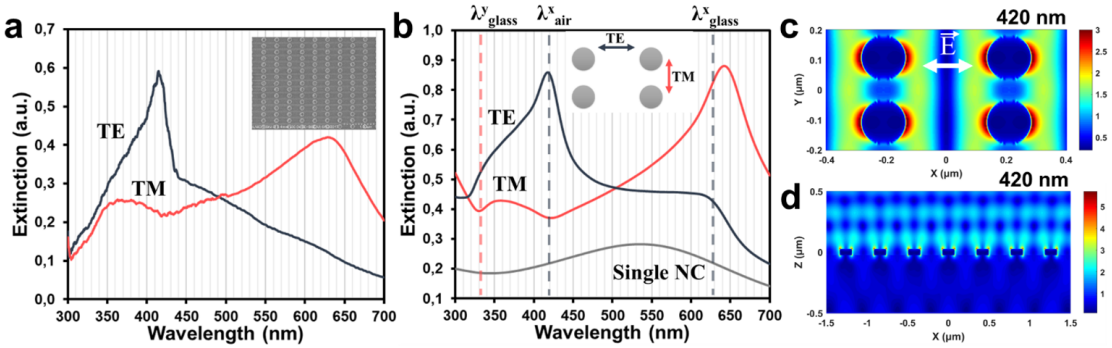


Figure 1: Experimental (a) and simulated (b) extinction spectra of the Al nanoparticles array (lattice 420x216 nm) for two orthogonal polarizations. Calculated extinction spectrum of the single Al nanocylinder on glass (d=150 nm, h=50 nm) (b). Electric field maps for the polarization along the X axis at the resonance wavelength (420 nm) in XY (c) and XZ (d) cuts.

References

[1] V. G. Kravets, A. V. Kabashin, W. L. Barnes, and A. N. Grigorenko, Chem. Rev. **118**, 5912–5951 (2018).
[2] M. Ross, C. Mirkin, and G. Schatz, J. Phys. Chem. C, **120**, 816–830 (2016).
[3] D. Khlopin, F. Laux, W.P. Wardley, J. Martin, G.A. Wurtz, J. Plain, N. Bonod, A.V. Zayats, W. Dickson, D. Gérard, JOSA B, **34**, 691-700 (2017).
[4] R. Guo, T. K. Hakala, and P. Törmä, Phys. Rev. B, **95**, pp. 1–11 (2017).
[5] A. Vitrey, L. Aigouy, P. Prieto, J. M. García-Martín, and M. U. González, Nano Lett., **14**, 2079–2085 (2014).
[6] L. Lin and Y. Yi, "Orthogonal and parallel lattice plasmon resonance in core-shell SiO2/Au nanocylinder arrays," Opt. Express, **23**, p. 130-142 (2015).

Nanoscale Surface Thermal Gradients in Mid-infrared Vertical Antenna Arrays

Andrea Mancini[1,2], Valeria Giliberti[3], Alessandro Alabastri[4], Eugenio Calandrini[5], Francesco De Angelis[6], Denis Garoli[6] and Michele Ortolani[1,3]
[1]*Sapienza Università di Roma, Dipartimento di Fisica, Rome, Italy*
[2]*Ludwig Maximilian University, Munich, Germany*
3 Istituto Italiano di Tecnologia – Center for Life Nanoscience, Rome Italy
4 Rice University - Department of Electrical and Computer Engineering, Houston, United States
5 Synchrotron SOLEIL, Sacaly, France
6 Istituto Italiano di Tecnologia – Plasmon nanotechnology Department, Genoa, Italy

Keywords: Thermo-Plasmonics, Plasmonic antennas.

We studied nanoscale heat generation due to enhanced molecular absorption by molecules at the apex of polymer-embedded, gold-coated vertical antennas excited with a quantum cascade laser emitting at mid-infrared wavelengths resonant with the molecule vibrational absorption. Enhanced absorption is based on the surface enhanced infrared absorption (SEIRA) effect. Vertical nanoantenna arrays display narrow plasmonic resonances at specific wavelengths that can be tuned by varying the antenna height and the array pitch [1].

The embedding of vertical nanoantennas protruding from a gold-coated substrate (height 2.2 microns, diameter 250 nm) in a non-IR-absorbing polymer creates thermal isolation between the apical hotspot and the heat sink (support wafer). Vibrational mid-infrared absorption by strongly-IR-absorbing molecules (PMMA) located at the antenna apex generates nanoscale temperature gradients at the surface. We imaged these gradients with a photothermal expansion device based on atomic force microscopy (AFM-IR) [2]

We found gradient values up to 10 K/micron for laser illumination of 20 mW on a diffraction-limited spot size of 100x30 microns (illumination at 70° incidence) [3]. Values up to 1000 K/micron can be foreseen at maximum quantum cascade laser power of 2 W. These gradient intensities are crucially dependent on the resonance condition where the radiation wavelength resonates with both the molecule vibrations and the plasmonic mode of the antennas. The gradient intensity drops by more than one order of magnitude out of resonance (no plasmonic resonance or no molecular absorption present at the illumination wavelength, or both). The presented embedded nanoantenna arrays therefore provide a promising substance-selective and wavelength-selective thermoplasmonic platform for antenna-assisted thermophoresis and resonant mid-infrared photocatalysis.

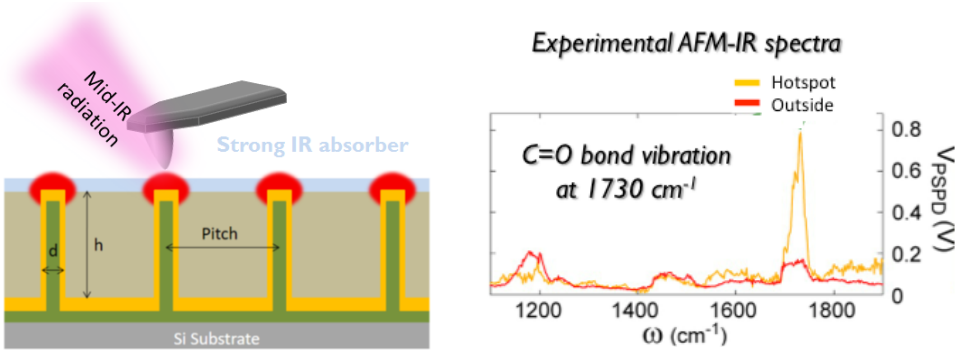


Figure 1: Left: scheme of the experimental setup for detection of the local photothermal expansion (Anasys NanoIR2 with MIRcat Quamtum Cascade Laser). Right: AFM-IR spectra demonstrating the vibrational absorption enhancement for the C=O bond of PMMA resonant with the antennas.

References

[1] M. Malerba et al., Sci. Rep., 5, 16436 (2015)
[2] F. Lu et al., Nat. Photonics 8, 307-312 (2014)
[3] A. Mancini et al., J. Phys. Chem. C 122, 13072−13081 (2018)

T-matrix calculations of spin-dependent optical forces in optically trapped nanowires

P. Polimeno[1,2], *M. A. Iatì*[2], *R. Saija*[1], *O. M. Maragò*[2],
[1]*Dip. di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra, Università degli Studi di Messina, Italy, polimenop@unime.it*
[2]*CNR-IPCF, Istituto per I Processi Chimico-Fisici, Messina, Italy*

Keywords: Scattering.

Our work is based on the use of the Transition Matrix method (T-matrix) [1] for the calculation of spin-dependent optical forces in optically trapped nanowires at the mesoscale. T-matrix formalism is currently one of the most accurate methods for the calculating of the electromagnetic scattering from non-spherical particles, both isolated and interacting in composite structures [2]. The incident and scattered fields are expanded into vector spherical harmonics so that the respective expansion coefficients are linked to each other through a Transition Matrix. Therefore, this method has proved to be extremely efficient also for the modeling of the optical forces [3, 4].

Subsequently, by breaking the cylindrical symmetry in zinc oxide nanowires, we have shown the evidence of a non-conservative force component linked to the light helicity and proportional to the linear momentum of Belinfante [5]. The effects of this transverse optical force are traditionally considered 'virtual' and they have recently been measured in experiments with evanescent waves [6] and in the trapping of nanowires. After analyzing the scattering force on the nominal focus of the trap, we analyzed how it is distributed over the most trapping region, eventually calculating its curl [Fig. (1)].

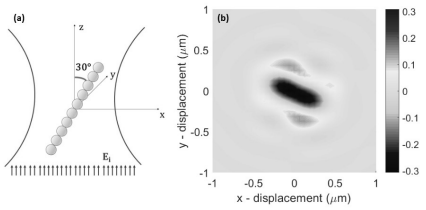


Figure 1: Map in the *xy*-plane near the focus of the difference between curl radiation force in left circular polarization and right one. The nanowire is presented in the configuration at polar angle $\theta = 30^\circ$, sketched in (a). The difference $(\nabla \times \mathbf{F}_{\sigma_+}) - (\nabla \times \mathbf{F}_{\sigma_-})$ is shown in (b). The dark color found in the neighborhood of the focal point demonstrates the remarkable difference in circulation between left- and right-handed polarized incoming radiation. The unit of measure of this quantity is $\mathrm{pN}/(\mathrm{mW{\cdot}nm})$.

References

[1] P. C. Waterman, Phys. Rev. D **3**, 825 (1971).
[2] F. Borghese, P. Denti, and R. Saija, in Scattering from model nonspherical particles: Theory and applications to environmental physics, Springer Science & Business Media (2007).
[3] F. Borghese, P. Denti, R. Saija, and M. A. Iatì, Opt. Express **19**, 11984-11998 (2007).
[4] P. Polimeno, R. Saija, C. Degli Esposti Boschi, O. M. Maragò, M. A. Iatì, AAPP **1**, (2019)
[5] F. J. Belinfante, Physica **5**, 449−474 (1940).
[6] M. Antognozzi, C. R. Bermingham, R. L. Harniman, S. Simpson, J. Senior, R. Hayward, H. Hoerber, M. R. Dennis, A. Y. Bekshaev, K. Y. Bliokh, et al., Opt. Express **8**, 731 (2016).

Calculation of optical forces in optically trapped resonant gain metal/dielectric nanoshell

P. Polimeno[1,2], *J. Sánchez*[3], *M. Infusino*[3], *M. A. Iatì*[2], *R. Saija*[1], *O. M. Maragò*[2], *A. Veltri*[3],
[1]*Dip. di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra, Università degli Studi di Messina, Messina, Italy, polimenop@unime.it*
[2]*CNR-IPCF, Istituto per I Processi Chimico-Fisici, Messina, Italy*
[3]*Colegio de Ciencias e Ingenieria, Universidad San Francisco de Quito, Quito, Ecuador*

Keywords: Scattering, Nanophotonics and Hybrid Plasmonic.

Optical tweezers, highly focused laser beams, are a crucial tool for manipulation and study without mechanical contact of micro- and nanoscopic particles of different nature [1–3]. Among the various applications, the study of optical forces in optically trapped resonant gain metal/dielectric multilayered nanostructures appears to be of particular interest. Resonant gain (RG) phenomena occurs because the presence of plasmonic structures amplify enormously the photons emitted by dye molecules which resonantly interact with the system. Gain molecules in the considered nanoshell structure makes it possible to obtain optical features which can be useful in different application fields [4].

Here, we present a theoretical study of optical forces on resonant gain metal/dielectric nanoshells in the dipole approximation. In particular, we have analyzed the optical trapping of this nanostructure in a single Gaussian beam optical trap [2] and in a counterpropagating configuration [5], eventually studying the trend of trap stiffnesses as a function of wavelength. In the first case, the detrimental effect of the scattering force prevent optical trapping near resonance. However, the trapping spectral region increases with gain. In the second case, the counterpropagating configuration ensures stable trapping even for low numerical aperture and optical trapping is achieved on the red side of the resonance as expected. The behaviour of nanostructures with gain is fully investigated showing the role of resonant amplification on optical trapping.

References

[1] P. H. Jones, O. M. Maragò, G. Volpe, in Optical tweezers: Principles and applications, Cambridge University Press (2015).
[2] P. Polimeno, A. Magazzù, M. A. Iatì, F. Patti, R. Saija, C. Degli Esposti Boschi, M. G. Donato, P. G. Gucciardi, P. H. Jones, G. Volpe, O. M. Maragò, JQSRT **218**, 131-150 (2018).
[3] P. Polimeno, R. Saija, C. Degli Esposti Boschi, O. M. Maragò, M. A. Iatì, AAPP **1**, (2019)
[4] V. Caligiuri, L. Pezzi, A. Veltri, A. De Luca, ACS Nano **11**, 1012-1025 (2017).
[5] M. G. Donato, O. Brzobohatý, S. H. Simpson , A. Irrera, A. A. Leonardi, M. J. Lo Faro, V. Svak, O. M. Maragò, P. Zemánek, Nano Lett. **1**, 342-352 (2019).

Metallic porous Aluminum for UV enhanced spectroscopy

Paolo Ponzellini[1], Giorgia Giovannini[1], Sandro Cattarin[2], Remo Proietti Zaccaria[1], Sergio Marras[1], Andrea Schirato[3], Eugenio Calandrini[1], Francesco De Angelis[1], Wei Yang[4], Jin Haiju[4], Alessandro Alabastri[3], and Denis Garoli[1]

1 Istituto Italiano di Tecnologia, via Morego 30, I-16163, Genova, Italy.

2 CNR , Padova, Italy

3 Rice University, USA

4 Shenyang National Laboraory for Materials Science Institute of Metal Research, Chinese Academy of Sciences 72 Wenhua Road, Shenyang 110016 P.R. China

Keywords: Sensor and Biosensors.

During the last decade, Localized surface plasmon resonances (LSPRs) have been explored extensively for their various technological applications. Up to now, plasmonic applications were mainly focused Ag and Au because of their optical properties in the visible range, but the exploitability of Ag and Au is limited down to 350nm, due to the intrinsic properties of these metals. On the contrary, there is now increasing interest in extending plasmonics down to UV and deep-UV (DUV) wavelengths. For instance, UV and DUV excitations can allow to extend the application of Raman spectroscopy to some biomolecules that have small Raman cross sections in the visible and NIR regions [1]. Aluminum (Al) has recently been suggested as promising plasmonic material in the UV and DUV regions because it has a negative real part of the dielectric function down to a wavelength of ≈100 nm [2]. The excellent optical properties of Al make it an excellent material for UV nanoantennas [3], DUV SERS [1,4], light emission enhancement of wide-bandgap semiconductors [5], and improvement of light harvesting in solar cells [6]. The controllability of LSPR energies is highly required for plasmonic applications. For instance, DUV-SERS of adenine on Al nanostructures requires the resonance peaks to be close to the excitation wavelength to ensure high-electromagnetic nearfield enhancement [1,4]. Al NPs are generally designed through electron beam lithography (EBL) and focused ion beam (FIB) lithography in order to obtain well-controlled structures [3]. However, these approaches are slow and expensive.

Porous metal films have recently attracted increasing interest due to the unique properties related to their very high specific surface area. While several examples of porous metal applications exist in the Vis / Infrared spectral regions, studies in the UV region have not been reported so far.

We are going to present a porous material obtained through a galvanic replacement reaction (GRR) [7]. The GRR reaction can be performed both with Mg and with the Al_{12}-Mg_{17} alloy, as the solid reagent, to obtain two different porous materials. Both the resulting materials are composed by aluminum only. Such a porous metals can be exploited for plasmon enhanced UV spectroscopy, in particular for enhanced fluorescence. The fluorescence enhancement performances of the obtained porous material will be described, along with the fabrication procedure, the optical characterization and the XPS, XRD and EDS analysis.

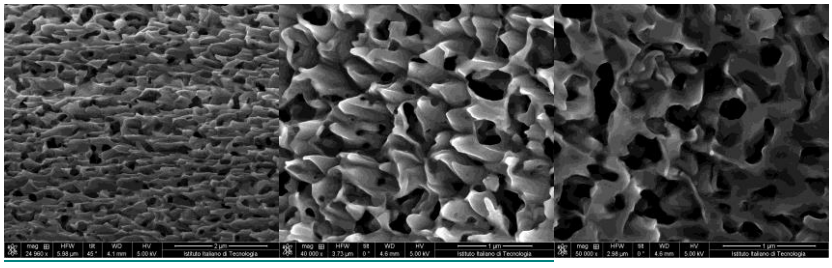


Figure 1: SEM micrographs of the porous aluminum material. Different areas of the same sample.

References

[1] S. K. Jha , Z. Ahmed , M. Agio , Y. Ekinci , J. F. Loffl er , J. Am. Chem. Soc. 2012 , 134 , 1966 .
[2] E. D. Palik , Handbook of Optical Constants of Solids , Academic Press Inc , San Diego, CA 1998 .
[3] M. W. Knight , et al. , Nano Lett. 2012 , 12 , 6000 .
[4] D. O. Sigle , E. Perkins , J. J. Baumberg , S. Mahajan , J. Phys. Chem. Lett. 2013 , 4 , 1449 .
[5] Y. J. Wang , H. P. He , Y. L. Zhang , L. W. Sun , L. Hu , K. W. Wu , J. Y. Huang , Z. Z. Ye , Appl. Phys. Lett. 2012 , 100 , 112103.
[6] Y. N. Zhang , Z. Ouyang , N. Stokes , B. H. Jia , Z. R. Shi , M. Gu , Appl. Phys. Lett. 2012 , 100 , 151101.
[7] Yang, W.; Zheng, X.-G.; Wang, S.-G.; Jin, H.-J., J. Electrochem. Soc. 2018. https://doi.org/10.1149/2.0881809jes.

Optical Fiber SERS Optrodes based on Nanosphere Lithography

Giuseppe Quero[1], Gianluigi Zito[2], Stefano Managò[2], Francesco Galeotti[3], Marco Pisco[1], Antonello Cutolo[1], Anna Chiara De Luca[2*], Andrea Cusano[1*].
[1]*Optoelectronic Division - Engineering Dept., University of Sannio, Benevento, Italy*
[2]*National Research Council, Institute of Protein Biochemistry (IPB-CNR), Napoli, Italy*
[3]*National Research Council, Institute for Macromolecular Studies (ISMAC-CNR), Milano, Italy*
*corresponding author, E-mail: a.cusano@unisannio.it, a.deluca@ibp.cnr.it

Keywords: Optical fiber sensor; SERS; Nanosphere lithography.

In this paper, we report on the engineering of repeatable surface enhanced Raman scattering (SERS) optrodes realized through nanosphere lithography on fiber.

SERS is an analytical technique that allows the detection of molecules at extremely low concentrations and with high specificity [1]. The unique advantages offered by optical fibres, alongside the "Lab on Fiber" technological advancements, make the optical fiber a valuable platform for SERS sensors in biological and biomedical applications. Additionally, the use of self-assembly fabrication approaches to realize reproducible SERS active surfaces on the optical fiber tips can provide a significant technological advancement by granting low fabrication costs and high throughput [2].

The "Lab-on-Fiber" SERS optrode consists of polystyrene nanospheres in close-packed arrays (CPA) configuration covered by a thin film of gold onto the OFT [3-4]. In order to engineer and optimize the SERS probes, we first evaluated and compared the SERS performances in terms of Enhancement Factor (EF) pertaining to different patterns (see Figure 1a,b) with different nanospheres diameters (d) and gold thicknesses (t_{Au}). The analysis allowed us the identification of the most promising SERS platform with d=500 nm and t_{Au}=30 nm, measuring an EF values comparable with state-of-the-art SERS EF achievable with highly performing colloidal gold nanoparticles. As a second important step towards engineering of the SERS optrode, Raman excitation/collection efficiency and related background pertaining to different commercially available optical fibers were investigated using a reference BiPhenylThiol (BPT) solution as benchmark. As a result, we selected the fiber probe with core in pure silica, 200 µm diameter and high numerical aperture (i.e. 0.5) because it offered a favorable trade-off between collection efficiency and background (see Figure 1c) [5]. Following these developments, current activities are devoted to the assessment and exploitation of the investigated sensing platform for human Thyroglobulin detection.

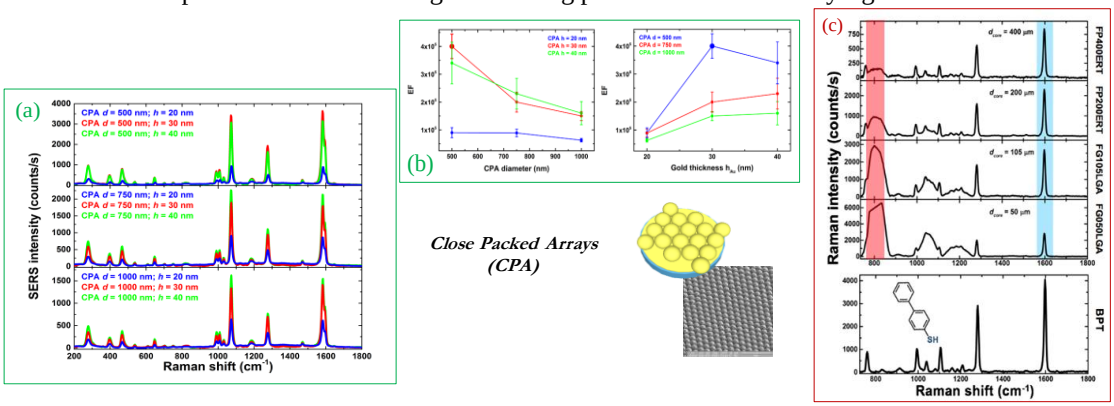


Figure 1: (a) BPT SERS spectra of hexagonally CPA structure with nanospheres diameters, d = 500, 750, 1000 nm and gold film thickness, t_{Au} = 20, 30, 40 nm. (b) EF as function of the CPA diameter and gold thickness, respectively. (c) Raman spectrum from 100 mM BPT solution through different optical fibers and Raman spectrum from the BPT solution with the Raman microscope without the fibers.

References

[1] P.R. Stoddart, D.J. White, Anal. Bioanal. Chem., **394**, 1761-1774 (2009).
[2] F. Galeotti, M. Pisco and A. Cusano, Nanoscale, 10, 22673 (2018).
[3] M. Pisco, F. Galeotti, G. Grisci, G. Quero, A. Cusano, Proc. SPIE 9634, 24th International Conference on Optical Fibre Sensors, 96341N, 2015); doi: 10.1117/12.2193658.
[4] M. Pisco, F. Galeotti, G. Quero, G. Grisci, A. Micco, L.V. Mercaldo, P. Delli Veneri, A. Cutolo, A. Cusano, Light: Science & Applications, **6**, e16229 (2017).
[5] G. Quero, G. Zito, S. Managò, F. Galeotti, M. Pisco, A. C. De Luca, A. Cusano, Sensors, 18, 680 (2018).

SERS-active hybrid plasmonic nanoparticles for intracellular sensing

S. Managò[1], M. Terracciano[2], G. Zito[1], E. Lonardo[3], L. De Stefano[2], A.C. De Luca[1], I. Rea[2]

[1]Institute of Protein Biochemistry, National Research Council, Naples, Italy
[2]Institute for Microelectronics and Microsystems, National Research Council, Naples, Italy
[3]Institute of Genetics and Biophysics, National Research, Naples, Italy

Keywords: Devices and Applications, Sensor and Biosensors.

Porous biosilica nanoparticles obtained from diatomite (DNPs), a fossil material of sedimentary origin, were demonstrated to be non-toxic nanovectors of therapeutic agents in cancer cells [1,2].
In this work, a label-free intracellular sensing system based on SERS (Surface Enhanced Raman Scattering)-active hybrid DNPs was proposed. DNPs were decorated with gold NPs (AuNPs) by one-pot liquid-phase synthesis and, finally, covered by polyethylene glycol (PEG) [3]. Hydrodynamic diameter and surface charge of the nanocomplex PEG-DNPs@AuNPs dispersed in deionized water were investigated by dynamic light scattering (DLS) analysis. An average diameter of about 400 (50) nm and a surface charge of 12 (2) mV were measured. **Figure 1A** reports a TEM image of PEG-DNPs@AuNPs: DNPs, characterized by irregular shape and porous morphology, are covered by AuNPs, mainly nanospheres, with an average size of about 20 nm.
The uptake of the nanocomplex PEG-DNPs@AuNPs was evaluated in colorectal (CRC) cancer cells using the label-free Raman imaging approach [4]. CRC cells were plated on calcium fluoride (CaF_2) coverslips and allowed to attach for 4 h. Afterwards, PEG-DNPs@AuNPs were incubated with CRC cells for 6 h; cells were then washed and fixed with 2% paraformaldehyde. Cell imaging was performed with an inverted confocal Raman microscope (XploRA INV, Horiba Jobin Yvon, Villeneuve d'Ascq, France), equipped with a 785-nm wavelength diode laser. Raman mapping involves raster-scanning the laser spot and collecting the Raman spectra at each location across the sample; the Raman map can then be computationally constructed to produce a pseudo-coloured image shaded according to the relative intensity of the Raman spectra at a given wavelength at each pixel [4].
Figures 1B and 1C show the reconstructed Raman map based on the integration of a group of peaks between 600-1800 cm^{-1} that result from selected vibrations native to cellular components (nucleic acids, protein, lipid etc.). Hybrid NPs internalized in cancer cells can be visualized on the basis of their enhanced Raman signal due to the excitation of gold surface plasmons by the laser probe.

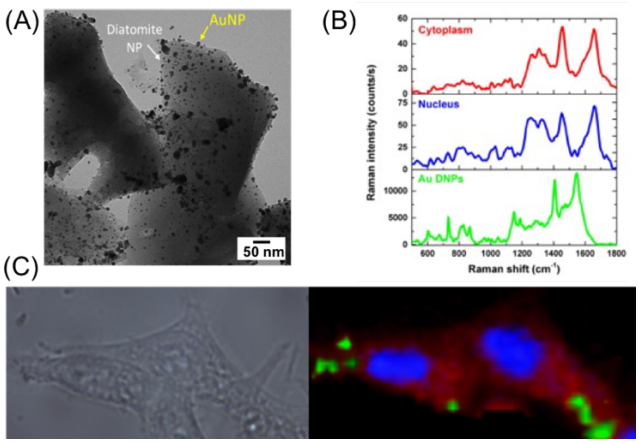


Figure 1: A) TEM of PEG-DNPs@AuNPs. (B) Representative Raman spectra of the cytoplasm (red), nucleus (blue), and PEG-DNPs@AuNPs (green). (C) Bright field and Raman images of PEG-DNPs@AuNPs uptake in CRC cancer cells. SERS signals from hybrid NPs are represented by green color.

References

[1]. I. Rea et al. BBA - General Subjects 1840, 3393-3403 (2014).
[2]. M. Terracciano, M.A. Shahbazi, A. Correia, I. Rea, A. Lamberti, L. De Stefano, H.A. Santos, Nanoscale 7, 20063-20075 (2015).
[3]. M. Terracciano, M. Napolitano, L. De Stefano, A.C. De Luca, I. Rea, Nanotechnology 29, 235601 (2018).
[4]. S. Managò et al. , J Biophoton 11, e201700207 (2018).

Study of interface roughness in doped SiGe Quantum Wells for future Silicon-based THz emitters

Andrea Rossetti[1], Chiara Ciano[2], Michele Montanari[2] , Luca Persichetti[2], Monica De Seta[2], Michele Virgilio[3], Luigi Bagolini[3], Leonetta Baldassarre[1] and Michele Ortolani[1].
[1] *Sapienza University of Rome, Rome, 00185 Italy*
[2] *University of Roma Tre, Rome, 00154 Italy*
[3]*Dipartimento di Fisica "E. Fermi", Università di Pisa, 5612, Pisa, Italy*

Keywords: Terahertz

Quantum Wells(QW)-based semiconductor emitters hold great promise for applications in the THz spectral region in particular for medical diagnostics, food quality control, non-destructive analysis of artwork. Ge/SiGe heterostructures in particular could allow one to emit in a broader range (towards the far-infrared) of frequencies if compared to III-V semiconductor devices, thanks to the nonpolar behaviour of Silicon and Germanium. Moreover, such SiGe material platform allows for straightforward CMOS-compatibility, making these devices in perspective extremely appealing for commercial use.

Intersubband (ISBT) cavity polariton modes have been proposed for THz emission [1] in III-V compounds and also to achieve strong coupling regimes [2]. The study of the same mechanism in SiGe QW could be however hindered by interface roughness due to the high lattice mismatch between Si and Ge, thus broadening or preventing the excitation of the ISBT polaritons.

It has been shown that interface roughness impacts on the intrinsic linewidth of ISBTs as observed in dichroic Fourier Transform IR spectroscopy (FTIR) experiments [3]. Here we study the THz absorption spectrum of several n-type strained Ge/SiGe multi-QW (MQWs), grown on Si (001) substrates, in order to assess the role of the different scattering mechanisms on ISBTs. We measure the ISBT by FTIR spectroscopy of MQWs with different design at 70° surface plasmon waveguide geometry (see Fig. 1a) . From the analysis of the linewidth of the ISB transitions in rectangular, asymmetric-coupled and single-step quantum wells it is possible to investigate how interface roughness affects the behaviour of our system.

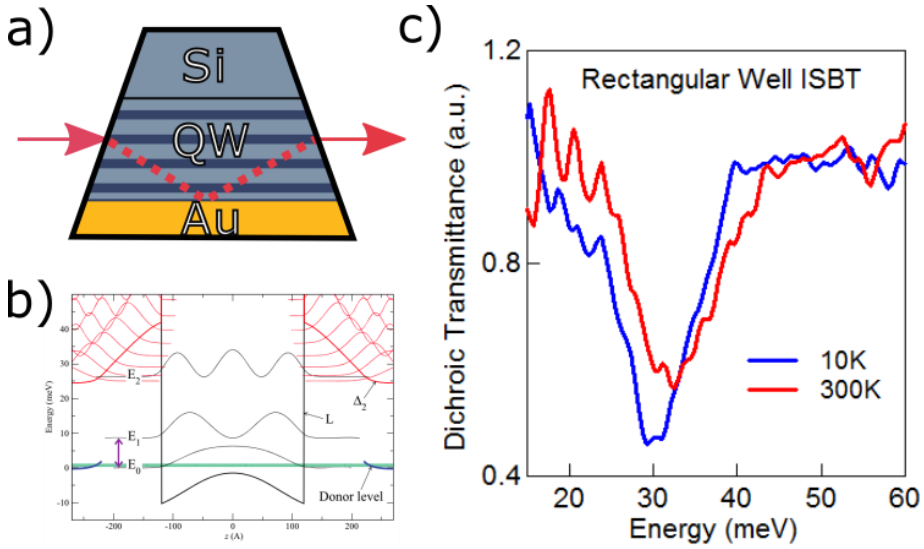


Figure 1: a) Schematic representation of the single-plasmon waveguide geometry used for measurements. Red arrows represent light coming in and out of the sample. b) Square modulus of the wavefunctions and energy levels of a rectangular quantum well. c) ISBT in a rectangular QW measured by Fourier-Transform IR spectroscopy

References

[1] R. Colombelli et al. "Quantum cascade intersubband polariton light emitters" Semicond. Sci. Technol. 20 985–990 (2005)

[2] A. Delteil et al. "Charge-Induced Coherence between Intersubband Plasmons in a Quantum Structure" Phys. Rev. Lett. 109, 246808 (2012)

[3] M. Virgilio et al. "Physical mechanisms of intersubband-absorption linewidth broadening in s-Ge/SiGe quantum wells" Phys. Rev. B 90, 155420 (2014)

A label-free optic SPR biosensor for mechanotransduction and force generation

Maria Salbini[1, 2], T. Stomeo[1], C. Ciracì[1], R. Fiammengo[1], V. Mangini[1], M. Leoncini[3], F. Pisano[1], F. Pisanello[1], T. Verri[2], D. R. Smith[4], M. De Vittorio[1,5].

[1]*Center for Biomolecular Nanotechnologies, Istituto Italiano di Tecnologia, Arnesano (Lecce), Italy;*
[2]*Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, Università del Salento, Lecce, Italy;*
[3]*Istituto Italiano di Tecnologia, Genova, Italy;*
[4]*Center for Metamaterials and Integrated Plasmonics, Duke University, Durham, NC, United States;*
[5]*Dipartimento di ingegneria dell'innovazione, Università Del Salento, Lecce, Italy.*
**corresponding author, E-mail: maria.salbini@iit.it*

Keywords: Plasmonic and dielectric nano antennas, nanophotonics, biosensors

Sensing of force and movement in biology involves the conversion of an external mechanical stimulus into a biochemical signal, a process termed *mechanotransduction*[1,2]. We discuss the possibility of implementing a novel bio-sensing platform based on surface plasmon resonances (SPRs) for investigating this mechanism of force generation by mechanosensory cells and organs. The structure under study is composed by a gold layer deposited on silicon substrate, a polyelectrolyte (PE) dielectric layer with thickness in the range 1÷9nm, which acts as a spacer layer between the top gold nanorods (GNRs) and the gold film. Systems in which GNRs are within a short distance from a gold film are optically very sensitive to any modification occurring in the gap and represent a promising platform for creating next-generation biosensors. We studied this system as a function of gap size and determined modifications of its plasmon modes. GNRs synthesized using seed mediated growth technique (Figure 1) show high surface area, as compared to nanoparticles, what their best characteristics, not present in other nanoparticles. As it is known, SPR strongly depends on the rods size and dielectric properties of the spacer layer[3], making the reflectance properties of the surface easily tunable by slightly changing the gap dimension. Changes in the refractive index (RI) near the GNRs induced a shift in the SPR peak position. Both simulation and experimental results showed that the plasmon resonance of the nanorods blue-shifts with increasing gap size. We also studied the properties of the PE layer composed of PAH/PSS in PBS (pH 7.4). In fact, as our biosensor will be in contact with the cells, it is desirable to be able to control both the swelling level of the PE layer by specific stimulus and the wettability of the surface. To compare PE layers swelling behavior, the films were examined at different time points during an immersion time of about 30 min in PBS. Then, the films were dried to examine whether swelling influences the dry-state thickness and to determine a "molecular memory" caused by previous treatment. Spectra shows a shift of the coupled NR-film SPR during incubation in PBS, suggesting that GNRs are being pushed away from the gold film because of the swelling of the PE layer. After drying, the shift disappears because of the deswelling of the PE layer, showing that no appreciable memory effect is present. The study of the wetting properties of surfaces is currently a cutting-edge research topic as researchers seek to overcome the challenge of making nano-devices and look for feasible solutions[4]. The wetting state of surface can be controlled physically from the highly hydrophobic to hydrophilic states using GNRs by means of contact angle, because the wetting property and wetting process are closely related to the surface morphology and roughness. Measurements show that by increasing the surface coverage of the PE layers using GNRs the contact angle increases to higher values, with a difference of ~20° between the surface not covered and the one covered with nanorods. These results denote that a shift of SPR can be exploited for measuring changes in dielectric layer thickness, which can be applied to produce sensors for estimating forces in cellular mechanotransduction.

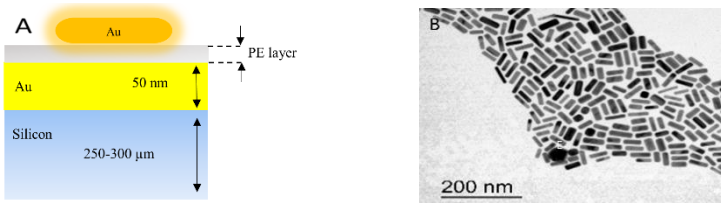


Figure 1: Au nanorods over a Au film (A). TEM images of GNRs as fabricated (B).

References

[1] M. A. Wozniak et al., *Nature Rev. Molecular Cell Biol.*, **2009**, vol. 10, no. 1, pp. 34–43.
[2] C. Hahn and M. A. Schwartz, *Nature Rev. Molecular Cell Biol.*, **2009**, vol. 10, no. 1, pp. 53–62.
[3] M. Morsin et al., *Int. J. of Integrated Eng.*, **2017**, Vol. 9, no 4, pp. 124-128.
[4] A. K. Behera et al., *New J. Chem.*, **2015**, vol. 39, pp 8893-8998.

CaF_2 embedding for nano-imaging of plasmonic vertical nanoresonators in the mid-infrared

F. Sciortino[1], G. C. Messina[2], V. Giliberti[3], M. Pea[4], F. Mattioli[4], S. Cibella[4], M. Malerba[5], R. Colombelli[5], L. Baldassarre[1] and M. Ortolani[1]

[1]Dipartimento di Fisica, Università di Roma La Sapienza, P.le Aldo Moro 5, I-00185 Roma, Italy

[2]CNR-ISC Dipartimento di Fisica, Università di Roma La Sapienza, P.le Aldo Moro 5, I-00185 Roma, Italy

[3]Istituto Italiano di Tecnologia Center for Life NanoScience Viale Regina Elena 291, I-00161 Roma, Italy

[4]Istituto di Fotonica e Nanotecnologie (IFN), CNR, Via Cineto Romano 42, 00156 Roma, Italy

[5]Centre for Nanoscience and Nanotechnology (C2N Orsay), CNRS UMR9001, Univ. Paris Sud, Univ. Paris Saclay, 91405 Orsay, France

Keywords: Vertical antennas, near-field imaging.

Plasmonics is nowadays used for a broad range of applications such as enhanced sensing or heat delivery [1]. Among several possible nanoantenna structures, vertical nanocylinders arrays have displayed strong electromagnetic field confinement at infrared (IR) wavelengths [2], thus allowing for local heat generation, by exploiting the mid-IR surface enhanced absorption effect of molecules placed at the antenna tip [3].

In order to evaluate the intensity and quality of the resonances excited at the single resonator level, near-field characterization techniques, based on the coupling of Atomic Force Microscopes and IR sources can be employed. In the case of vertical nanostructures, the embedment of the entire body of the antennas in a solid medium is necessary to allow their nanoscale investigation with an AFM tip. In this view, several attempts have been made by using weakly absorbing polymers, however this approach strongly limits the range of use of the device due to presence of vibrational features that can overlap and hide the spectral region of interest.

Here we use CaF_2 as embedding material for vertical Au nanoantennas. The CaF_2 was deposited via thermal evaporation, and characterized by means of Fourier Transform Infrared Spectroscopy to assess the material quality. We found that, despite presenting smaller absorbance than polymers, the evaporated material still presents some impurity-activated vibrational modes that could lower the quality factor of the antenna resonances. We use an infrared nanoimaging technique, based on photothermal induced expansion, in order to estimate also the dimension of the hot-spots in the CaF_2 sample and compare them to the same obtained with a polymeric embedment.

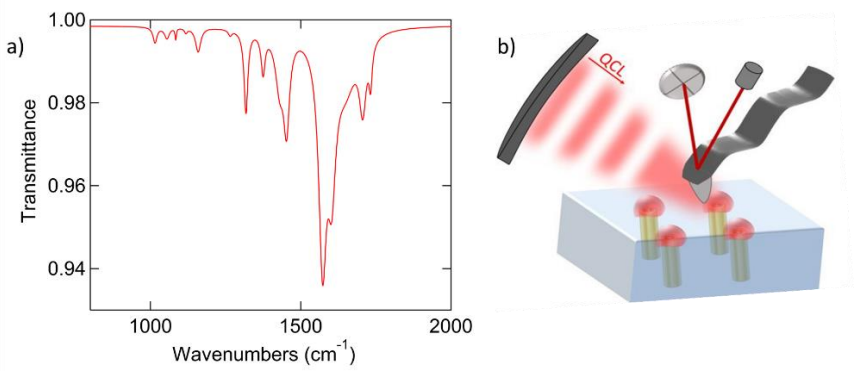


Figure 1: a) Transmittance of 2.2µm-thick evaporated CaF_2 film measured by Fourier Transform InfraRed spectroscopy in the fingerprint region. b) Pictorial sketch of the nanoIR setup used for the measurements.

References

[1] Guillaume Baffou and Romain Quidant, Laser Photonics Rev. **7**, No. 2, 171–187 (2013).

[2] Mario Malerba, Alessandro Alabastri, Ermanno Miele, Pierfrancesco Zilio, Maddalena Patrini, Daniele Bajoni, Gabriele C. Messina, Michele Dipalo, Andrea Toma, Remo Proietti Zaccaria and Francesco De Angelis, Sci. Rep. **5**, 16436 (2015).

[3] Andrea Mancini, Valeria Giliberti, Alessandro Alabastri, Eugenio Calandrini, Francesco De Angelis, Denis Garoli and Michele Ortolani, Appl. Phys. Lett. **114**, 023105 (2019).

Theoretical Study of Mechanical Behavior of Carbon Nanotubes (CNTs), Under Controlled Indentation Force. Applications in Quantum Nano Photonics

Katya Marinova SIMEONOVA

Department of Solid Mechanics/ Institute of Mechanics, Bulgarian Academy of Sciences
Sofia, Bulgaria
Corresponding-author e-mail address: katyas@bas.bg

Carbon nanotubes (CNTs), discovered by Iijima in 1991, [1] makes a revolution in materials science studies especially in nanoscience. (CNTs) possess extraordinary mechanical, optical, electronic, electric, transport, conductivity, chemical, etc. properties, [2]. These nanoscale materials have chirality nanostructure and small nanosizes (about 50-100nm in diameter and some microns in length). These both facts give an opportunity CNTs to find applications in many different areas of technique, engineering, semiconductors, transistors, emitters, environments and space, nanooptics, quantum optics, nano Quantum optics, [3]. Carbon nanotubes play an important role in molecular and cell biology and nanotechnology for cancer as well. Regarding all these facts mentioned above, we could be pointed out that modelling of CNTs, at different loadings is a very perspective and useful one. The aim of the paper, presented could be formulated as follows: to give a modified theoretical model for study of the mechanical behaviour of carbon nanotubes under controlled indentation force. The theoretical model has been developed by assuming the contact area to be ellipse, under a load *F*, described by, and following [4]. Numerical algorithms and numerical Fortran programs, designed by author have been given in the work. Numerical results, obtained have been presented at figures. Comparison between experiments and the author's model, shows a very good agreement.

Key words: Carbon nanotubes (CNTs); chirality nanostructure, quantum optics, controlled indentation force; numerical FORTRAN programs

[1]. S. Iijima, Nature, 395, 1991
[2]. K. Simeonova, G. Milanova, ISCOM2007, Book of Abstracts, poster P123, page 136 (Grant)
[3]. K. Simeonova, Computational Modeling of Carbon Nanotubes' Electronic and Optical Properties, (Grant), XXV Intern. Summer School "Nicolas Cabrera" Miraflores de la Sierra, Spain, Sept. 9-14, 2018
[2]. A .P. Boress and O. M. Sidebottom, *Advanced Mechanics of Materials*, (J. Wiley& Sons, New York), (1985)

Ultrafast vs thermodynamic heating of plasmonic Al nanodisks

Maria Sygletou[1], Patrick O'Keeffe[2], Daniele Catone[2], Andrea Toma[3], Jacopo Stefano Pelli Cresi[2], Maurizio Canepa[1], Francesco Bisio[4]

1. OptMatLab, Dipartimento di Fisica, Università di Genova, via Dodecaneso 33, 16146 Genova, Italy
2. CNR-ISM, Division of Ultrafast Processes in Materials (FLASHit), Rome, Italy
3. Istituto Italiano di Tecnologia, via Morego 30, 16163 Genova, Italy
4. CNR-SPIN, C.so Perrone 24, 16152 Genova, Italy

Keywords: plasmonics, thermoplasmonics, ultrafast dynamics

Electromagnetically-heated metal nanoparticles can be exploited as efficient heat sources at the nanoscale, and find application in different areas such as photocatalysis, nanochemistry or sensing devices. One of the major challenges in this field, especially whenever ultrafast processes are involved, is however to ascertain the actual temperature of these nanosystems, something typically done with the aid of models and assumptions about the T-dependent nanoparticle response.

Here we compare the effects of ultrafast laser heating of aluminium nanodisks (NDs) with their static optical response measured in a variable-temperature thermodynamic bath, following an approach successfully exploited for Au plasmonic nanosystems [1].

The time resolved dynamics of Al nanodisks 120-nm in diameter, excited by ultrashort laser pulses, was measured in pump-probe configuration in order to examine the dynamics of the transient absorbance at the LSPR (540 nm) and interband transition (825 nm). A fs laser beam at tunable wavelengths (275 nm, 550 nm and 800 nm) acted as the pump, while a time-delayed white light beam probed either the transmission or the reflection of the Al nanodisks. The power dependence of the carrier dynamics was also investigated by pumping at 550 nm, in different pump energies.

We compare these results with static transmittance spectroscopy as a function of temperature in vacuum. The plasmonic response of periodic Al nanodisks upon heating, from room temperature to 390 °C, was accordingly investigated, providing a calibration for the temperatures achieved in the system upon ultrafast irradiation.

References

[1] M. Magnozzi et al., Nanoscale 11, 1140 (2019)

Acknowledgments

*This project has received funding from the **European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement Nº799126***

Terahertz Scattering Microscopy for Dermatology Diagnostics

Alfonso Alessandro Tanga[1,2], Maddalena Daniele[3], Francesco Vitucci[2], Vincenzo Ricco[2],
Domenico Vitulano[4], Vittoria Bruni[4,5], Giancarlo Ruocco[1,3], Michele Ortolani[1,3], Valeria Giliberti[3]
[1]*Sapienza University of Rome, Department of Physics, 00185 Rome, Italy*
[2]*Crisel Instruments srl, 00167 Rome, Italy*
[3]*Istituto Italiano di Tecnologia, Center for Life Nano Science IIT@Sapienza, 00161 Rome, Italy*
[4]*Istituto per le Applicazioni del Calcolo 'M.Picone', Consiglio Nazionale delle Ricerche, 00185 Rome, Italy*
[5]*Sapienza University of Rome, Department of Basic and Applied Sciences for Engineering, 00161 Rome, Italy*

Keywords: Devices and Applications, Terahertz, Scattering

Terahertz (THz) radiation can penetrate dielectric materials deeper than visible or infrared radiation. In the case of human skin, the penetration is estimated around 1 mm for frequencies around 0.5 THz [1]. The diagnosis of skin diseases that imply the modification of the texture of tissues 1 mm under the epidermis should be possible. The project MICoTeD (terahertz microscopy for dermatology) is developing a THz scattering microscope for the study "in vivo" of the internal structure of human tissues buried under the epidermis at depths beyond 100 micrometers, which are not accessible to epiluminescence, infrared imaging or optical coherence tomography.

The project aims at measuring and modeling the scattering properties of the different layers of the skin through the observation with a terahertz camera of the focal spot of the reflected terahertz radiation beam. The focal spots of beams reflected by rough or inhomogeneous surfaces appear as deformed Airy disks. The shape of the focal spot is then studied by 2D Fourier transformations and/or by fitting with 2D Gaussian profiles. Our scattering microscopy setup operates at non-normal incidence and at a frequency of 0.6 THz, hence obtaining a diffraction-limited resolution around 1 mm, high enough for e.g. early skin cancer detection, if appropriate imaging contrast exists. The THz radiation source is an amplifier-multiplier chain emitting 2 mW in CW (TS-600, by Lytid Sas). The THz imaging camera is a large-pixel-area (50 μm) microbolometer array (320x240 pixels, TZcam by i2s/CEA-LETI). Off-axis parabolic mirrors are employed to focus and collect the THz radiation.

The image on the left of the figure represents the intensity distribution in the focal spot of the terahertz radiation beam reflected by a skin simulant sample (hydrated collagen gel). The intensity distribution approximately follows a 2D Gaussian function, although diffraction rings are barely visible around the main spot, indicating that the actual distribution is an Airy function. The line profile, cut across the focal spot in the diagonal (45°) direction, is plotted next to the spot image. One can appreciate the good signal-to-noise ratio provided by our imaging setup, considering the estimated sample reflectance below 10% and the integration time of 2 minutes, compatible with dermatology diagnostic practices.

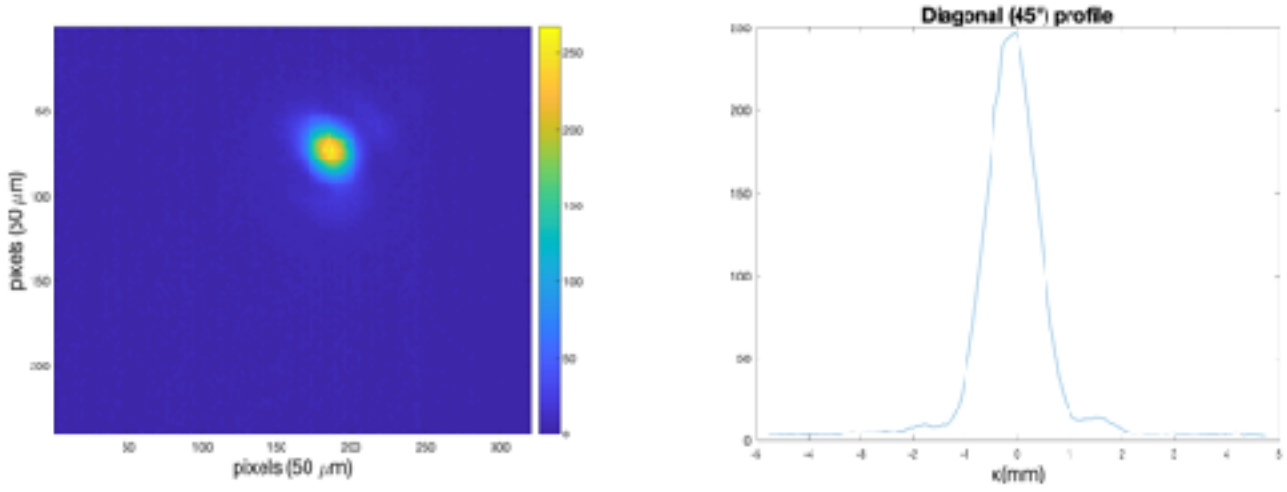


Fig. 1 On the left: focal spot on a terahertz camera of the beam reflected by a skin simulant sample. On the right: the plot shows a line profile along the diagonal (45°) direction. Intensity in ADC counts.

References

[1] Z. Taylor et al., "THz Medical Imaging: in vivo Hydration Sensing" *IEEE Trans. on THz Sci. Technol.* **1** (1), 0034 (2011)

Nanoplastics Detection in Seawater Samples with an Infrared Plasmonic Nanoprobe

Maria Eleonora Temperini[1], *Raffaella Polito*[1], *Valeria Giliberti*[2], *Maria Sighicelli*[3], *Loris Pietrelli*[3], *Leonetta Baldassarre*[2], *Alessandro Nucara*[2] *and Michele Ortolani*[1,2]
[1]*Department of Physics, Sapienza University of Rome, Italy*,
[2]*Center for Life NanoScience, Istituto Italiano di Tecnologia, Rome, Italy*
[3]*ENEA Research Center "Casaccia", Rome, Italy*
email: temperini.1651569@studenti.uniroma1.it; Michele.ortolani@roma1.infn.it

Keywords: sensors and biosensors; spectroscopy and nanoimaging; devices and applications

The challenge of the assessment of the ecological role of nanoplastics requires the identification of the chemical structure of a plastic particle simultaneously with its size, or better, its precise shape. This is essential in order to estimate the fraction of plastic waste at sea to sub-micrometer size particles that have most probably escaped detection up to now. Infrared micro-spectroscopy (microIR) is presently employed for plastic detection on solid filters through which seawater was passed. MicroIR with a focal plane array can provide both the chemical structure and the image (hence the size and the shape) of a plastic particle. However, optics is limited by diffraction, which sets the pixel size (or the smallest possible resolvable object) approximately at the level of the wavelength of the employed light.

An approach to bring optical microspectroscopy beyond the diffraction limit is scanning-probe-assisted nanospectroscopy. Therein, the scanning probe tip of an atomic force microscope (AFM), with a tip apex of few tens of nanometers, serves as the detector of the optical interaction between a laser beam and the sample located below the tip. The detection can be based on electromagnetic effects or on the photothermal expansion. Since light propagation from the sample to a far-field detector is not required any more, the diffraction limit does not hold and nanometer-scale pixel sizes are obtained (typically between 10 and 100 nm).

In our IR nanospectroscopy setup (NanoIR2), the IR quantum cascade laser radiation is absorbed by the nanoscale sample portion under the tip, the sample heats up by a few degrees and then expands in the vertical direction, pushing the tip towards the cantilever, which then starts to oscillate as a spring. This movement is sensitively detected by the AFM instrument, and the amplitude of the cantilever oscillation, being proportional to the absorbed IR energy, is taken as a measure of the sample absorption coefficient in the IR. The plasmonic nanoantenna effect of the gold-coated tip enhances the lateral resolution of the pohotothermal effect by increasing thermal gradients. The NanoIR offers IR absorption spectra and performances similar to those obtained microIR, but on objects (or parts of objects) of dimensions down to 100 nanometers. Additionally, the AFM topography image of the object is also obtained with typical lateral resolution of 20 nm. This is ideal to attempt nanoplastic detection on solid filters with mesh size below 1 micron, much needed for ecological assessment of the role of nanoplastics.

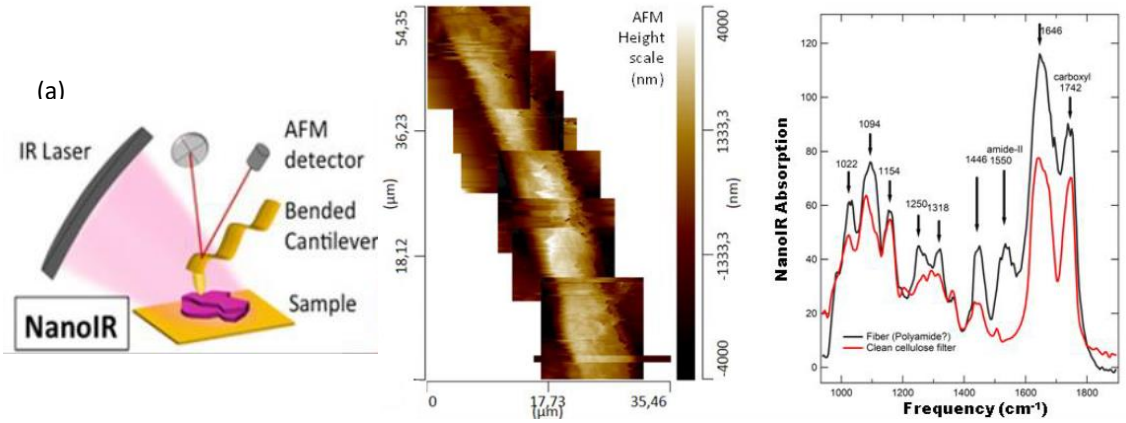


Figure 1: (a) Sketch of the AFM-IR instrument. (b) AFM image in contact-mode of a micro-fiber found on a cellulose filter through which seawater was passed. (c) NanoIR absorbance of the micro-fiber (black line) compared to the absorbance of the clean cellulose filter surface (red line).

References

[1] Cabernard et al., "Comparison of Raman and Fourier Transform Infrared Spectroscopy for the quantification of microplastics in the aquatic envirronmnet", *Environmental Sci. Technol.* 52 (22) (2018)