Program and Abstracts booklet
Welcome to Troyes

Places to visit in Troyes here
Unwind after the conference here
MNO will organize guided city tour, a visit to the ”cité du vitrail” museum and a visite to the museum of modern art. You will be asked to choose one of these tours on the check-in day. To help you choose, here are brief descriptions of the places on offer:

**Guided city tour**

Troyes is renowned for its rich historical heritage, dating back to Gallo-Roman times, and for its medieval architecture characterized by colorful half-timbered houses. Take a stroll through Troyes and you’ll be amazed by the many historic monuments to be found here. The majestic Saint-Pierre-et-Saint-Paul cathedral, a true masterpiece of Gothic architecture, and medieval churches such as Sainte-Madeleine, with its exceptional stained-glass windows, are among the treasures to be discovered. A stroll through the narrow streets of Troyes will also allow you to admire the charming half-timbered houses that give the city its medieval atmosphere, as well as emblematic landmarks such as the Maison du Boulanger and the curious Ruelle des Chats.

![Guided city tour images](image1.jpg)

**Modern art museum**

The modern art museum of Troyes was created thanks to generous donations. Located in the former episcopal palace, it was inaugurated in 1982. The museum houses remarkable collections of modern art from the second half of the 19th century to the first half of the 20th century. These collections trace the history of French art, focusing on figuration and the question of modernity in harmony with classical tradition. Significant representations of major artistic currents such as Realism, Fauvism, Cubism, the First School of Paris, the art of the inter-war years and the Second School of Paris are represented by renowned works. In addition to masterpieces, these collections also include artists of singular character, as well as a collection of African and Oceanic art that bears witness to the artistic exchanges between these cultures and Western artists of the 20th century.

![Modern art museum images](image2.jpg)
Cité du vitrail

The “Cité du Vitrail” in Troyes, located in the former Hôtel-Dieu-le-Compte, features a permanent exhibition of over 60 original stained glass works, spanning a period from the Middle Ages to the present day. This museum space allows visitors to plunge into the heart of the art of stained glass, while providing the keys needed to understand and appreciate this art in all its dimensions. In addition to the art of stained glass, the museum houses a remarkable apothecary, considered to be one of the finest in France. The building once served as a hospital, then a pharmacy until 1962, visitors can explore the “grande salle”, where products and plants for making remedies were kept, and the adjacent “laboratoire”, where medicines were prepared. An exceptional collection of earthenware pots and painted wooden pharmaceutical boxes from the 18th and 19th centuries is also housed here, offering a fascinating insight into the history of medicine and pharmacy at the time.
To reach UTT from the train station:
Bus: line 6 (Gare jardin)

To reach city center from UTT:
Bus: line 6 (Technopole), line 8 (UTT)

To reach UTT from city center:
Bus: line 8 (Langevin, Halle)

Bus timetable:
For the bus timetable, please click here
Ps: Select the stop, then the bus line and finally the direction. You’ll get the bus timetable.
Please note: the last passage of lines 6 and 8 through the stops serving university is at 8.30pm. In case you miss these buses, a line 10 that passes both stops (Technopole and UTT) will still be running until 11pm.

Other means of transport:
Taxi Troyes: +33 325783030
For the taxi please use this two adresses:
• 12, rue Marie Curie - 10000 TROYES
• Rue Fernand Sastre - 10430 ROSIERE-PRES-TROYES

UTT contact:
Adresse: 12 rue Marie Curie CS 42060 10004 TROYES CEDEX, FRANCE Phone: +33 3 25 71 11 00

UTT WiFi:
ID : MNO2023
Password : nKz9V77Tn8
Rooms to remember:

Conferences: M500 amphitheater
Cocktails & Lunch: M104
Sponsors
# Program

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**Speaker:** Anne-Laure BAUDRION |
| **Session 1** | Novel materials, synthesis and technologies for Plasmonics  
**Chair:** Nathalie DESTOUCHES |
| **9.05 – 9.50** | Magnesium Nanoplasmonics  
Emilie RINGE – Cambridge University (GB) |
| **9.50 – 10.10** | Direct creation of gold nanoparticles inside a  
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Pham Quang Truong |
| **10.10 – 10.30** | Tunable Photoemission and Photocatalytic Activity  
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Suzanna AKIL |
| **10.30 – 10.50** | Semiconductor Nanoparticles with Metallic Properties  
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**Sensors and bio-plasmonics**  
*Chair: Monika FLEISCHER*

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– UMR CNRS 6226 (FR) |
| 16.40 – 17.00 | Applications of ultra-compact, phase-sensitive SPR device  
Aurélien BRUYANT |
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Claudia Corti |
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Mathieu EDELY |
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### Wednesday 20th September 2023

**Metasurfaces, structural colors and nanophotonics**  
*Chair: Anne-Laure Baudrion*

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Nanoresonator Arrays  
Tal ELLENBOGEN  
Center for Light-Matter Interaction, Tel-Aviv University (IL) |
| 9.45 - 10.05  | Controlling nanostructuration in 2D surfaces to tailor color, matte finish and iridescence  
Glenna DRISKO |
| 10.05 - 10.25 | On the road for sustainable based structural colors based on Bismuth plasmonics: nanostructured metasurfaces vs Fabry-Perot cavities  
Fernando CHACON SANCHEZ |
| 10.25 - 10.45 | Exploring the Temperature-Dependent Optical Properties of VO2 Thin Films for Metasurface Applications  
Benedict MORRIS |
| 10.45-11.05   | Coffee break (M building’s hall) |

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Oumaima HAIDAR |
| 11.25 - 11.45 | Specular reflection and transmission of electromagnetic waves by disordered metasurfaces  
Miao CHEN |
| 11.45 - 12.05 | Hyper Rayleigh Scattering: magnetic field influence on gold nanoparticles with linear and elliptical light polarization  
Michalina SLEMP |
| 12.05 - 12.25 | Molecular adsorption driven atomic migration and electron transfer in plasmonic nanoparticles  
Aimeric OUVRARD |
| 12.25 - 13.30 | Lunch (M104 room) |
| 13.30 - 14.15 | Session 5                                                                 |
|           | Enhanced light-matter interactions at the nanoscale 1                      |
|           | Chair: Céline Fiorini                                                     |
| 13.30 - 14.15 | Subwavelength imaging of chiral nanostructures with photopolymers  
Davy GERARD |
| 14.15 - 14.35 | Creating chiral plasmonic nanostructures using chiral and linearly polarized light: The near-field and hot-electron routes  
Artur MOVSESYAN |
| 14.35 - 14.55 | Hybrid bright and directional single photon sources  
Monika FLEISCHER |
| 14.55 - 15.15 | A single photon source on an ion-exchanged glass waveguide  
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| 15.15 - 15.35 | Plasmon-mediated energy transfer between two systems out of equilibrium  
Camilo PEREZ DE LA VEGA |
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| 18.30 - 20.00 | Poster session - Cocktail soupe champenoise – (M104 room) |</p>
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Invited Speakers
Tal ELLENBOGEN  
Laboratory for Nanoscale Electro-Optics  
Tel-Aviv University, Israel

Prof. Ellenbogen is the Head of the Laboratory for Nanoscale Electro-Optics at Tel-Aviv University. He obtained his bachelor’s degree in Physics and Computers in 2002, his Master’s degree in Physics in 2005, and his PhD in Nonlinear Optics in 2010, all from Tel-Aviv University. He was a Fulbright Postdoctoral Fellow at Harvard University where he worked on nanoplasmonics and excitonics. In addition he was also a member of The Center for Excitonics in MIT. In October 2012 he establish The Laboratory for Nanoscale Electro Optics at Tel-Aviv University. Since then he received several career awards and competitive research grants for contributions to the field of linear and nonlinear metamaterials, including the Kadar Family Award for Outstanding Research, Schmidt Futures, Momentum fund, ERC-STG and ERC-COG grants. He was also appointed as the Head of Tel-Aviv University Excellence Center for Optical Metamaterials. His research interests include nanoscale light-matter interaction, nonlinear and ultrafast optics, and optical metamaterials.
Céline FIORINI
Laboratoire d’Electronique et nanoPhotonique Organique
CEA Saclay, France

After graduating from Institut d’Optique Graduate School, Céline Fiorini obtained her PhD in Physics, (Optics and Photonics, Paris XI Orsay), in 1995. Since then, she has been working as a scientist in CEA Paris Saclay, going from the applied to the fundamental research division. She is currently part of the condensed matter laboratory, her main research topic being devoted to nanophotonics. More particularly, her studies mainly involve optical nano-antennas and molecular plasmonics, organic nonlinear optics and light emission (time-resolved fluorescence spectroscopy, frequency conversion), photochromism, molecular self-organisation, photoinduced ordering and mass transport . . . She has authored or co-authored more than 110 papers. In addition to her research activities, Céline Florini is coordinating a so-called laboratory of Excellence of Paris Saclay University, aiming at promoting synergies between interdisciplinary scientists of different research fields, from nano(spin)electronics to nanophotonics, nanomedicine and nanochemistry.
Davy GERARD  
L2n laboratory  
Université de Technologie de Troyes, France

Davy Gérard is an associate professor at the laboratory Light, nanomaterials, nanotechnologies (L2n) in Troyes, France. After a PhD at the University of Dijon (2004) on near-field imaging of photonic structures, his research interests moved to plasmonics and plasmon-enhanced fluorescence. His current research focuses on light-matter interaction at the nanoscale, including the use of aluminum as a new plasmonic material (in particular for UV-plasmonics), collective resonances in arrays of nanoparticles for light emission, nanoscale imaging, and chiral plasmonics.
Nicolò MACCAFERRI  
Ultrafast Nanophotonics and Advanced Functional  
Materials Group  
Umea University, Sweden

Nicolò holds a tenure-track professorship and is the head of the ‘Ultrafast Nanophotonics and Advanced Functional Materials’ Group at the Department of Physics, Umeå University (Sweden) supported by the Swedish Research Council, the European Innovation Council, the Faculty of Science and Technology, the Kempe and Wenner-Gren Foundations. Currently, he is also a visiting group leader at the Department of Physics and Materials Science, University of Luxembourg. Nicolò performed his PhD research at CIC nanoGUNE (Spain) and got his PhD in Physics of Nanostructures and Advanced Materials from the University of the Basque Country in 2016. In 2015, he received the “Piero Brovetto” Award from the Italian Physical Society for “his contributions in the fields of nanomagnetism and nano-optics and the study of the physical properties of magnetoplasmonic nanoantennas and their application in bio-sensing”. Until now, he was able to collect more than 2.5 M€ to fund his own research. In 2022, he became a Fellow of the Young Academy of Europe, a pan-European initiative of young scientists for networking, scientific exchange and science policy. Nicolò’s research span a broad range of fundamental and applied aspects of natural sciences, with a special focus on both the fundamental and applied aspects of light-matter interactions in advanced and multifunctional nano- and meta-materials for opto-electronics and information processing, photochemistry and biotechnology.
Valérie MARCHI
Institut des sciences chimiques de Rennes
France

Valérie Marchi, graduated from ESPCI (1994) obtained her PhD at the University of Pierre et Marie Curie (Paris 6) and worked on supramolecular chemistry applied to vesicle fusion and adhesion at College de France (1998-2003) as well as Technische Universität München during her postdoc. She moved to Rennes University in 2004 to develop a research group in synthesis, surface chemistry and characterization as well as self-assembling of nanoparticles. Her work is oriented toward Biology-Nanoscience interface and dedicated to bioimaging using protein-quantum dots hybrids with a controlled stoichiometry (Nanolett. 2009, JACS 2009, Nanolett. 2011), self-assemblies of nanoparticles driven by synthetic complementary proteins (ACS Nano 2016, Nanoscale 2020) and the optical properties of these nanostructured materials (Langmuir 2015, Nanoscale 2020 and Nanomaterials 2021) and more recently biolabeling and biosensing with gold nanoclusters. Her group also investigated gold nanorods or quantum rods structured assemblies obtained with short peptidic ligands by SAXS and SEM (ACS Nano 2012 and Small 2014). Recently her research focuses on the original synthesis of bioactivated gold nanoclusters for biomedical applications and applications in medicinal diagnostic, drug delivery system and biosensor (J. Phys Chem Lett 2022, Nanomaterials 2022).
Emilie RINGE
Optical nanomaterials group
University of Cambridge, UK

Emilie Ringe obtained her B.A./M.S. (summa cum laude) and Ph.D. at Northwestern University under the supervision of Laurence Marks and Richard Van Duyne. She then took up a Gott Research Fellowship at Trinity Hall as well as a Newton International Research Fellowship (Royal Society) in University of Cambridge, UK. A year later, she was hired as an assistant professor at Rice University, where she established the Electron Microscopy Center and received funding from the Air Force Office of Scientific Research (YIP), NSF, ACS-PRF, 3M, and the US/Israel Binational Science Foundation. In 2018, she moved back to the University of Cambridge, joint between the Department of Materials Science and Metallurgy and the Department of Earth Sciences; she was promoted to professor in 2022. She received an ERC Starting grant and a EPSRC grant to pursue her studies of Earth-abundant plasmonics, for which she has been named one of the 2021 C&EN’s “Talented 12” and recipient of the 2021 The Journal of Physical Chemistry C and ACS PHYS lectureship.
Guillaume VIAU
LPCNO
INSA Toulouse, France

Guillaume Viau is Professor at INSA Toulouse and Director of Laboratoire de Physique et Chimie des Nano-Objets (LPCNO) joint research unit INSA Toulouse-CNRS-Université Toulouse 3. He obtained a PhD Thesis in Materials Science, Université Paris Diderot, in 1995. Since then, his research focusses on liquid phase synthesis of metallic nanoparticles and elucidation of nucleation and growth mechanism thanks to in situ and time-resolved techniques (SAXS, XAS, XRD …). He has developed the synthesis of anisotropic metallic in solution (magnetic nanorods and gold nanowires). He has been involved in several ANR projects Magafil (2008-2010), Tanopol (2016-2019), Pomade (2019-2022), NIMRod (2021-2024) and EU joint projects Refreepermag FP7 (2012-2015), Swimmot H2020 (2020-2024) with researchers working in different fields (magnetism, catalysis, biology). Recently, he has developed and patented a bottom-up approach for permanent magnets fabrication based of 3D assemblies of cobalt nanorods assembly and their integration into microelectronic devices.
Peter WIECHA  
LAAS-CNRS  
France

Peter Wiecha’s research focuses on the interaction of light with subwavelength small structures, and on applications of artificial intelligence in nano-optics and photonics. After studying physics at the Technical University of Munich in Germany he obtained a PhD in 2016 from the Université Paul Sabatier Toulouse, followed by post-docs in Toulouse and at the University of Southampton. Since 2020 he is a permanent CNRS researcher at LAAS-CNRS in Toulouse.
Invited Speakers-Abstracts
This talk will review the progress made over the past five years on the production, understanding, and utilization of colloidally synthesized plasmonic magnesium nanoparticles. Magnesium has emerged as one of the new and exciting plasmonic materials thanks to its many advantages, namely biocompatibility, earth abundance, and good quality factor (better than aluminum) across the UV, visible, and near-IR. The Optical Nanomaterials Group has developed colloidal approaches leading to monodisperse, size- and shape-controlled Mg nanoparticles. The various synthetic strategies employed will be discussed, followed by an overview of the shapes obtained. Then, our extensive studies of the stability in air, water, and at elevated temperatures of these metallic magnesium nanoparticles will be reviewed, followed by the newest results on the utilization of magnesium in catalysis and sensing.
Nucleation and growth of ultrasmall gold particles: the role of pre-nucleation clusters

Raj Kumar Ramamoorthy, Ezgi Yildirim, Lise-Marie Lacroix, Guillaume Viau*

Laboratoire de Physique et Chimie des Nano-Objets, Université de Toulouse, INSA, 135 av de Rangueil 31077 Toulouse Cedex 4
gviau@insa-toulouse.fr

During the last two decades wet-chemistry methods have accomplished considerable progress in the synthesis of metal nanoparticles (NPs) with controlled crystalline structure, shape and surface chemistry for applications in different fields such as catalysis, plasmonics, electronics or magnetism. This is the case of the seed-mediated growth syntheses that are developed to produce a wide variety of shapes, nanorods [1], ultrathin nanoplatelets [2] and bimetallic magnetic-plasmonic particles. For these approaches the control of the heterogenous nucleation at the surface of the metal seeds is of paramount importance.

For the synthesis involving a homogeneous nucleation, several examples of the literature established that nucleation of metal particles in solution follow the classical nucleation theory (CNT). However, recent studies have shown that the association of metal salts and surfactants in organic solvents forms nano-objects, called pre-nucleation clusters (PNCs), that are involved in the metal particle nucleation [3] questioning the CNT. The role of these PNCs in the nucleation step has been studied more precisely in the case of the crystallization of ultrasmall Au particles and ultrathin Au nanowires by reduction of Au(III) salts with silanes in the presence of oleylamine. Such chemical reaction produces particles that crystallize with a structure different from the fcc Au bulk, icosahedral Au particles [4] and tetrahedrally close-packed (tcp) Au nanowires [5].

In collaboration with LGC Toulouse, Small Angle X-ray Scattering (SAXS) and X-ray Absorption Spectroscopy (XAS) have been coupled to microfluidic devices to get in situ and time resolved data with a very good resolution at very short times. These techniques allowed us to evidence the effect of confinement in the PNCs on the nucleation stage and establish an Eley–Rideal mechanism for the growth stage, giving a full description of the crystallization of ultrasmall Au particles in presence of oleylamine. This study has been recently extended to Ag particles with the same observations on the formation of PNCs as precursors and on the unusual structure of the final particles.

Ultrafast control of light-matter interactions is fundamental to mark new technological frontiers, for instance in light-driven information processing and nanoscale photochemistry [1]. In this context, we have explored the possibility to use metal-dielectric nanocavities to achieve all-optical modulation of light reflectance. Without the need of driving higher order effects, our system is based on linear absorption, provides large relative modulation exceeding 100% and switching bandwidths of few hundred GHz at moderate excitation fluence [2]. This archetypical system becomes even more interesting if the dielectric inclusion is not just a “passive” insulator material but an inorganic van der Waals bonded semiconductor, like a transition metal dichalcogenide (TMD). TMDs are subject of intense research due to their electronic and optical properties which are promising for next-generation opto-electronic devices. In this context, understanding ultrafast carrier dynamics, as well as charge and energy transfer at the interface between metals and semiconductors, is crucial and yet quite unexplored. By employing a pump-push-probe scheme, we experimentally study how optically-induced thermionic charge carrier injection affects the exciton formation dynamics in bulk WS2 [3], disclosing excellent opportunities also in nano-chemistry. In fact, if an electronic transition (e.g., exciton or more simply a singlet) strongly interacts with the optical modes of a resonator, we can tailor the energetics and the morphology of a molecular state. By combining quantum mechanical modelling and pump-probe spectroscopy, we shed light on the ultrafast dynamics of a hybrid system composed of photo-switchable dye molecules coupled to optically anisotropic plasmonic nanoantennas, which allow us to selectively switch between two regimes where the light-matter interaction is either weak or strong [4]. Our synergistic approach is thus instrumental to devise new strategies for tailoring electronic states by using plasmons for applications in polaritonic chemistry on femtosecond timescales.

References
Peptidic bioactivable AuNCs for bio-imaging and sensing

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Gold nanoclusters (AuNCs) appear as a recent class of non-toxic fluorophores. Their brightness, their ultrasmall size (< 2 nm), their good biocompatibility and their large window of fluorescence lifetime (1ns – 1μs) make them an attractive alternative as fluorescent probes for biological imaging and biosensing. The synthesis of original aqueous bioactivatable AuNC were performed by using synthetic short peptides. This chemical plateform provides various charged AuNC with potential sensitivity to the environment. By adjusting the surface chemistry, these luminescent probes are easily internalized into cells and in plants. We demonstrated their in vivo targeting ability because of specific recognition groups and possible biosensing because of their sensitivity to microenvironment.

Extracellular vesicles (EVs) are well-known membrane-limited particles that are secreted by healthy and cancerous cells. EVs are involved in cell-cell communication and are considered as biomarkers for early cancer diagnosis. The analysis of their content and its labeling with easily detectable nanoparticles could enable the development of a powerful tool for the early diagnosis of specific diseases. In this view we present an overview of the interaction between such ultra-small luminescent gold nanoclusters and EVs and compare to model liposomes. Contrary to larger plasmonic gold nanoparticles, the smaller size of AuNCs not only prevents the deformation of biological membranes but also allows labeling with higher spatial resolution. In addition their small size make Au NCs attractive to encapsulate them into liposomes without damaging the compartment integrity and then to deliver them into the extracellular vesicles. Cell-like-sized vesicles (GUVs) encapsulating red or blue Au NCs and Exosome-like-sized vesicles (LUVs) containing Au NCs were successfully obtained. Finally the composition of the liposome membrane was optimized with ionizable lipids to induce their fusion with EVs and delivery of AuNC into the lumen of EVs.

References

Active, Nonlinear and Anomalous Optical Dynamics in Nanoresonator Arrays

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Recent focus on phenomena related to collective interactions on 2D lattices has unveiled intriguing and promising optical dynamics, such as Bose-Einstein condensation [1], low threshold up-conversion lasing [2], ultrahigh-Q plasmonic response [3], enhanced generation of classical light [4] and even quantum light [5], just to give a few examples. These emphasize the importance of collectivity in the construction of lattice based optical metamaterials.

In this talk we will present new developments and properties related to collective interactions on metasurfaces and metamaterials composed out of arrays of nanoresonators. We will demonstrate the development of active nonlinear nonlocal metasurfaces, based on hybrid metasurface-liquid-crystal platform. This platform can be used to switch the nonlocal nonlinear signal from the metasurface with modulation amplitude larger than 25dB, both electrically and all-optically. We will also unveil new types of volume collective modes in 3D plasmonic nanoresonator arrays, that exhibit extraordinary, and highly attractive optical characteristics, including vanishing absorption and engineered transmission or reflection approaching unity. We will show that the collective mode distributes the excitation equally along all the constituent nanoparticles within the volume of the metamaterial, regardless of the metamaterial size. This is manifested by a new phenomenon of spectral locking that exhibits an exceptionally high Q-factor, compared to the localized surface plasmon Q-factor of the individual meta-atoms. Finally, we will also present the manifestation of collective-like effects in a system constructed from a single nano resonator in a cavity.

References

Chirality is ubiquitous in nature and plays an important role in many biological processes. In particular, a significant fraction of drugs are chiral molecules, whose two enantiomers can exhibit dramatically different properties. As chiral molecules interacts differently with the left- and right-handed components of circularly polarized light, optical spectroscopies are a method of choice for enantiomer identification. Unfortunately, chiroptical interactions are generally weak, and located in the UV range. A way to both enhance chiroptical interactions and to shift them into other spectral ranges is take advantage of the electromagnetic near-fields around resonant nanostructures, especially metallic ones [1].

In this talk, I present a subwavelength imaging technique based on a azobenzene-containing photosensitive polymer. With the help of this technique, I show that both chiral [2] and achiral [3] plasmonic nanostructures can exhibit a handedness-dependent response in their near-field. In particular, the presence of chiral hot spots is experimentally evidenced in chiral coupled gold nanorods.

References

Artificial intelligence and in particular deep learning (DL) has proven in recent years to provide powerful numerical methods for various fields of research. DL is particularly interesting for inverse design tasks which mostly cannot be solved with analytical or direct approaches [1]. A particularly interesting property of artificial neural networks is their differentiability. It can be exploited for solving inverse problems [4,5] by using a forward network as a fast differentiable surrogate. The speed of DL models allows to optimize many random geometries concurrently via gradient descent. It has been shown, that such iterative approach consistently outperforms one-shot neural networks in terms of solution optimality [2].

However, neural-network based gradient optimization has several shortcomings. Major challenges are convergence to local minima and failed extrapolation [3]. We discuss how to overcome these limitations with other techniques from artificial intelligence [6]. Finally, we will critically review deep learning methods in general and briefly discuss areas of applications where – in our point of view – using DL can make sense but also in which cases conventional methods are probably better suited.

References

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What can we learn from the two-photon luminescence of gold nanoparticles?

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Often referred to as plasmonic fluorophores, gold nanoparticles have been widely studied either for their nanoantenna properties or their intrinsic luminescence, with their size and shape playing a key role. In our group, we have mainly been focusing on elongated particles such as nanorods or nano-bipyramids since they can quite easily be adjusted to exhibit two plasmonic resonances, in the visible and IR, which happens to be particularly important for the development of nonlinear labels for in-depth imaging in biology.¹ During this talk, I will more particularly present a phenomenological model enabling to describe quantitatively the two-photon luminescence (TPL) properties of nanorods (NRs) taking into account the different processes involved in plasmonic TPL from local field enhancement effects at the NRs longitudinal and transverse plasmon resonances, to hot electrons relaxation.²,³ As a direct consequence, I will show that TPL happen to be a very accurate tool to evidence photo-induced morphological changes that happen to be hardly impossible to determine using common imaging methods such as AFM or SEM.⁴ I will finally discuss the interest of TPL for the characterization of nanoantennas aimed at enhancing the frequency conversion properties of dielectric nanocrystals. Next step will now consist in studying how TPL can be taken into profit to probe any changes in the particle surroundings. Indeed, resonantly excited plasmonic nanoparticles (NP) are also known to activate chemical transformations directly in their surroundings, from energy conversion to photocatalysis, phototherapy or nanofabrication⁵. In this respect, monitoring plasmon mediated chemical activity at the nanometer scale is of primary importance.

References

Enhanced Light Matter interactions
Metallic nanoparticles in perovskite solar cells: plasmonic effects or others?

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Numerous experiments have demonstrated improvements on the efficiency of perovskite solar cells, one of the most promising materials for next-generation photovoltaics, by introducing plasmonic nanoparticles. However, the underlying mechanisms are still unclear: the particles may enhance light absorption and scattering, as well as charge separation and transfer, or the perovskite’s crystalline quality. In a recent paper [1], we showed for instance that a small addition of gold nanoparticles modified the growth mechanism of the perovskite MAPbI\textsubscript{3} layer and led to better crystalline quality and reduced grain boundaries. This translated into improved light absorption in the red spectral range and increased photovoltaic efficiency by a relative 10\% enhancement.

Eventually, it can still be debated whether unambiguous plasmonic increase of light absorption has indeed been achieved. In this report [2], we employ various optical models to provide a physical understanding of the relevant parameters in plasmonic perovskite cells and the conditions under which light absorption may be enhanced by plasmonic mechanisms. By applying the recent generalized Mie theory to gold nanospheres in perovskite, we show that their plasmon resonance is conveniently located in the 650-800 nm wavelength range, where absorption enhancement is most needed. We evaluate for which active layer thickness and nanoparticle concentration a significant enhancement can be expected. We then analyze the experimental literature on plasmonic perovskite solar cells in light of our theoretical description. We estimate that only a small portion of these reports can be associated with light absorption and point out the importance of reporting the perovskite thickness and nanoparticle concentration in order to assess the presence of plasmonic effects.

References

Control of the emission directionality and intensity of quantum emitters is crucial for single-photon sources and integrated photonics. In the last two decades, surface plasmon polaritons (SPPs) found numerous applications in optical elements (SPP-waveplates, mirrors, lenses, beam-splitters), and are a promising tool for controlled surface plasmon coupled emission. Although previous studies focused on the modification of the photoluminescence of emitters inside the plasmonic gratings, here, we report on the unidirectional emission at controlled angle from emitters positioned outside a plasmonic array on a gold film.

In this case, the emitters photoluminescence is coupled to the plasmonic array through the excitation and propagation of SPPs on the smooth underlying gold film. Using spatial filtering and Fourier space imaging techniques, we extract the angle-resolved emission diagram (k-space map) only from the plasmonic array area and filtered the main emission spot. In this case the emission outcoupling is totally governed by the grating properties and, consequently, its polarization and outcoupling angle are directly controllable. In opposition to emitters positioned inside the array, here the emission is not symmetrical, due to the selective interaction with the array SPP Bloch modes in only one direction. The directional emission intensity depends on the distance between the excitation spot and array edge. Although the intensity falls exponentially, the emission angle stays unaltered for the distances up to 30 microns. The angle-resolved photoluminescence maps had an indication of the interference pattern, in particular small oscillations in intensity and line-shape. Theoretical analysis revealed that this effect originates from the interaction between the light scattered by the edge of the array and the light transmitted inside and decoupled by the grating.

In conclusion, we demonstrate unidirectional photoluminescence decoupling from a plasmonic array while the emission source is placed outside the grating at a distance from 1 to 30 microns, which is of interest for novel optoelectronic integration strategies, directional single photon sources and sensing applications.
Creating chiral plasmonic nanostructures using chiral and linearly polarized light: The near-field and hot-electron routes

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In this work, we present a computational study of the induction of chiral patterns on initially achiral NC geometries using the near-field and hot-electron mechanisms. First, we formulate the fundamental principles to form chiral patterns of field and local hot-electron generation using both circularly and linearly polarized light (CPL and LPL) excitations. For the substrate (Fig. 1a) and solution (Fig. 1b) settings, those principles can be very different. We start with the model of plasmonic NCs on a photoactive polymer film (Figure 1a).[1] Our results show that both CPL and LPL illuminations can create chiral electromagnetic energy patterns on the photoactive substrate [2].

Then, we describe the formation of chiral patterns of the hot-electron generation utilizing various settings and geometries. One crucial observation coming from our study is that the photoinduced chirality in 3D (Fig. 1d) is fundamentally weaker than that for the 2D substrate setting (Fig. 1c). Finally, our work provides a summary of chiral photoinduced geometries and settings [2].

Figure 1. (a) and (b), settings used in the study. (c) and (d), 2D and 3D chirality.

References

We investigate photoconductance of colloidal PbS quantum dot layers in nanoscale gold electrode gaps [1] and find a consistent power law dependence of the photocurrent on the light intensity with an exponent slightly below 0.7. The gap sizes are varied between 25 and 800 nm and by scanning photocurrent microscopy we evidence the strong localization and high reproducibility of photocurrent generation. Different flat-faced and pointed electrodes are compared and practically identical photocurrent response for a wide range of gap sizes and geometries are found. Interestingly, plasmonic effects related to optical near field enhancements seem to play a minor role.

Scanning photocurrent microscopy image of QDs in bow tie nanogaps overlayed to a SEM image of the same sample region including (a) three gaps and (b) one gap in higher magnification. (c) Photocurrent profile extracted along the blue line in (a). The scale bar in (a) is 2 µm and in (b) 500 nm.

References

Hybrid bright and directional single photon sources

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The deterministic generation of single photons can amongst others be realized by semiconductor quantum dots. For efficient single-photon sources parameters such as the brightness, photon rates, directionality, room-temperature stability, etc. need to be optimized. Here, a design that enables bright room-temperature emission by coupling individual quantum dots to nano-antennas is shown.

The directionality of the quantum-dot-based single photon sources is enhanced by positioning single nanocrystals at the center of concentric Bragg antennas [1,2]. Their emission rates are increased via coupling to nano-cone antennas, which leads to a reduction of the lifetime and consequently to a brightness enhancement [3,4]. As sketched in the Figure, we combine both approaches in a hybrid design [5]. The devices are numerically optimized for strong collimation effect, allowing for high collection efficiencies in systems with low numerical apertures. The geometry is illustrated by scanning electron microscopy images, and the optical performance is evaluated in terms of the projected photon rates.

Schematic of hybrid nano-cone/bullseye antenna with quantum dot emitter [L. Lüder]

References

A single photon source on an ion-exchanged glass waveguide.

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Introduction

For quantum photonics, it is essential to be able to efficiently couple quantum emitters with photonic structures such as waveguides [1], interferometers [2] and optical cavities [3] in order to be able to scale for all practical purposes. Several quantum photonics platforms are currently being explored such as epitaxial quantum dots [4] where the source and the photonic parts are separated, using diamond [5] or silicon carbide [6] color centers where the photonic structures are directly produced in the material such as in the form of photonic crystals [7]. Until now, it has proven difficult to bring together quantum emitters of nanoscale objects and photonics-ready platforms.

In this work, we aim to explore a new way to connect the "nano" world to the "macro" world by optically connecting a nanosource of light with a conventional optical waveguide. Our method paves the way for scaling up to multiple quantum emitters by tackling the interfacing of strong light matter between photons and nanosources of light on a single optical platform. The ability to scale is at the heart of quantum networks [8] and small-scale quantum photonic simulators [9]. This differs from the usual approach of obtaining the greatest light extraction from nanostructures on a substrate [10]. The substrate is used here as the active element of the device which can be seen as an optical bus.

Experimental and results

In order to realize our integrated single photon source working at room temperature as a first proof of principle, it is necessary to look for an emitter that emits single photons reliably and which do not require low temperatures. In the literature, only few emitters are relevant as single photon emitters, such as nanodiamonds (NDs), single molecules or nanocrystals (NCs). We use NCs as almost 90% of them are single photon emitters and these core/shell CdSe/ZnS NCs are synthesized in house.

The hybrid structure consists of a titanium dioxide (TiO₂) slab waveguide placed on top of an IEW in glass manufactured by the company Teem Photonics. For deposited CdSe/ZnS nano-crystals (NCs) on the IEW with TiO₂ structure, the functionalization
was used. For that, the sample was placed on a silane solution to make the connection between the surface and emitters. Figure 1 shows the diagram representing the single photon source. A dedicated setup was used to characterize it. To detect the position of the CdSe/ZnS NCs (emission at 610 nm), a scan is performed with a 532 nm CW laser. A measurement of the second-order autocorrelation function $g^{(2)}(\tau)$ is measured and presented via the black curve in Figure 1. On the second-order autocorrelation functions, the value of $g^{(2)}(\tau = 0)$ is less than 0.5. The NC is therefore unique. The sample was then pigtailed with optical fiber by the company Teem Photonics. The red curve in Figure 1 represents the NC emission at the fiber output at 610 nm. The NC emission couples well with the IEW thanks to the TiO$_2$ structure. We have therefore produced a single fibered photon emitter device.
Conclusion

In this work, we have presented a fibered single photon source based on a hybrid photonic structure. The use of the IEW makes it possible to have a fibered source emitting a single photon. The addition of the high index structure of TiO$_2$ to the emitter allows better coupling into the waveguide. In the future, we would like to switch to IR emitters to switch to the telecommunications field, by replacing the emitters with SiV NDs.
Acknowledgments

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References
Plasmon-Mediated Energy Transfer between Two Systems out of Equilibrium

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The development of plasmonic nanostructured samples consisting of organic and inorganic emitters, has opened up new avenues for energy harvesting and the creation of optoelectronic devices. However, comprehending the interactions between the distinct elements in these complex configurations remains challenging. This work explores the energy transfer dynamics between inorganic quantum dots (QDs) and an organic dye (J-aggregated TDBC), mediated by surface plasmon polaritons. The emitters are deposited on top of a silver film in which microstructuration of the organic layer allows probing the electromagnetic environment resulting from the hybridization of J-aggregates emission and the SPP mode with QDs. We introduce a theoretical model of the photoluminescence of the system to quantify the energy transfer between the two species through the chemical potential of photons. The excellent agreement between the simulations and experiments shows that our method enables a comprehensive characterization of photoluminescence and energy transfer within systems where thermalized materials with different chemical potential couple within structures supporting plasmonic modes.

References


Metasurfaces, Structural colors and nanophotonics
Hyper-Rayleigh scattering (HRS) is a technique for measuring second harmonic light from liquid media. With this technique, not only second-order non-linear optical polarizability (hyperpolarizability $\beta$) can be measured, but also the role of the size and shape of the nanoparticles as well as the macroscopic origin of the response. [1-2].

In this work, we analyse the behaviour of magnetic nanoparticles: AuNPs, AuFeNPs and AuCoNPs obtained using laser ablation. It should be noted that this technique “freezes” the instable state of AuFe and AuCo creating nanoparticles otherwise not present in nature [3-4]. Furthermore, the novel experiment involving quarter waveplate allows for deep understanding of interactions between matter and elliptically polarized light. We discuss the theory behind elliptically polarized light and gold NPs interactions.

Additionally, a magnetic field is being applied to the samples in search for new interaction modes in HRS signal. We present the influence of the field on both linear and elliptically polarized light polarization and compare it to the acquired dependence without magnetic field.

This work paves the way for sensing applications, as well as selective imaging or in-situ targeting tumors and blood knots in the human body.

References

Controlling nanostructuration in 2D surfaces to tailor color, matte finish and iridescence

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Appearance in 2D surfaces can be designed by controlling the morphology, composition and spatial arrangement of resonant particles and layers, creating new optical effects, such as diffuse iridescence and diffuse halos.¹ For example, stratified surfaces decorated with silver nanoparticles can be particularly interesting for scattering light in the visible range, yielding angle-dependent coloration. The plasmonic resonance of these particles can hybridize with the Fabry-Perot resonances of the thin films, creating vivid and unique color transitions, as well as a resilience to polydispersity defects.² Thus, robust optical effects are achieved on a large scale. The color of the substrate, at relatively low silver nanoparticle densities, depends solely upon Fabry-Perot resonances. The matte/glossy appearance can be tuned independently of the color by varying the density of plasmonic resonators on the surface.

Correlation in disordered surfaces provides an additional means for tuning optical appearance. We can create perforated silica surfaces with correlated disorder.³ The perforation diameter and the density of these resonant cavities can be tuned by varying the experimental parameters. We are currently experimenting with the chemical nature, and thus the refractive index, of an intermediate layer between the perforations and the substrate, as well as with curved surfaces. The optical results for these materials emphasize how material design can be exploited to manipulate multiple aspects of a surface's appearance.

References

Specular reflection and transmission of electromagnetic waves by disordered metasurfaces

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Metasurfaces composed of disordered monolayers of resonant nanoparticles have many degrees of freedom. Recently, it has been evidenced that a wide range of appearance attributes, including color, matte/glossy effects, and iridescence, can be tailored with unprecedented versatility compared to traditional materials$^{1,2}$. In the ERC project, UNSEEN$^3$, we aim to explore new visual appearances and functionalities of disordered metasurfaces. Understanding the complex light-matter interactions in such systems requires accurate models that consider both near- and far-field interactions. Furthermore, numerical methods that go beyond the Rayleigh hypothesis are essential to enable the design of metasurfaces without constraints on particle shape, inter-particle distances, and particle-interface distances, all while minimizing computational loads.

In this talk, our focus is on the specular reflection and transmission of disordered metasurfaces. We fabricate silicon nano-cubes on a glass substrate with varying density, packing fraction, and particle size using EBL. We analyze the observed changes in amplitude and frequency shifts in the measured spectra of these samples using a state-of-the-art multiple-scattering model$^4$. Additionally, we employ full-wave numerical calculations using the recently developed concept of the global polarizability matrix (GPM)$^5$ to compare with experimental data and model outputs. Our findings are expected to inspire and drive further advancements in metasurface design, particularly in the creation of visually complex and captivating appearances.

We acknowledge our colleagues from ICMCB (Glenna Drisko, Mona Treguer-Delapierre) and Inria (Romain Pacanowski), in Bordeaux, for fruitful discussions. Technological realizations were partly supported by the French RENATECH network.

References

Molecular adsorption driven atomic migration and electron transfer in plasmonic nanoparticles

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Understanding the strong coupling between molecules and plasmonic nanoparticles (NP) exhibiting is of great relevance for photo-catalyze chemical reactions or enhanced charge transfer in optoelectronic devices. NP electronic structures and surface plasmon resonance (SPR) can be modified by adjusting their size, composition or by anchoring molecules at their surface. However, probing these objects down a single molecule or NP is challenging due to size/shape dispersion, instrumental sensitivity or surrounding environment. To overcome these limitations, we have elaborated by physical vapor deposition in ultra-high vacuum, dense arrays of plasmonic NP, on an Al₂O₃ bilayer on Ni₃Al(111) [1]. The impact of molecular adsorption on NP structure [2], molecular optical response and SPR are investigated [3]. For that, we combined STM microscopy to reveal surface topography at nanoscale, UV/Vis optical reflectance spectroscopy to follow SPR (supported by finite element analysis) and molecular absorption changes as well as ultrafast non-linear vibrational spectroscopy to probe adsorbed molecules (sites, orientation and dynamics). We present two hybrid systems where electronic/optical couplings of molecules with LSPR are evidenced: (i) CO/Pd-Au NP where the SPR is controlled by the migration of Pd to the shell induced by CO adsorption and NP temperature (Fig. 1a). (ii) C₆₀/Pd-Ag NP where we monitor with a sensitivity of one C₆₀/NP, how the LPRS and molecular response, evidencing charge transfer to the plasmonic NP (Fig. 1b).

Figure: UV/Vis reflectivity change showing: (a) the impact of Pd migration at the Au shell surface on NP SPR and (b) charge transfer from NP to C₆₀ and SPR changes.

References
On the road for sustainable based structural colors based on Bismuth plasmonics: nanostructured metasurfaces vs Fabry-Pérot cavities

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Bismuth (Bi)-based materials are attractive for their use in a diverse range of sustainable energy and environmental applications due to their low toxicity and eco-friendliness [1]. In the field of nanophotonics, Bi has been recently demonstrated as a non-conventional plasmonic material exhibiting negative permitivities in the ultraviolet and visible spectral regimes, promoted by intense interband transitions in the near infrared [2-4]. In addition, Bi exhibits a relatively low melting temperature (~270 °C), with its solid-to-liquid phase transition being accompanied by significant changes in its optical response. Taking advantage of this property, in previous works we have demonstrated the optical switching of Bi-nanocomposite films both by hot-plate annealing (phase light switching) and by ns-laser irradiation (ultrafast response) [5-6]. In this work, we have designed and experimentally validated two different approaches for the realization of pure macroscopic colors. Both approaches are based on Al/oxide/Bi structures. One relies on the use of gap-plasmon metasurfaces where the top, 10 nm-thick Bi layer is structured in the form of nanodisks arranged in a square lattice and supporting localized dipolar resonances. The second approach consists of more conventional Fabry-Pérot cavities based on continuous 10 nm-thick Bi films lying on an oxide/aluminum thin film configuration. Both designs have been successfully fabricated employing e-beam lithography and pulsed laser deposition (PLD) techniques for the case of structured devices, and PLD-only for the Fabry-Pérot cavities. Characterization of each structure was carried out via angularly resolved reflectance measurements, showing excellent agreement with r simulations. We will discuss peculiarities, pros and cons of each approach in terms of color purity, fabricability and specific advantages for different applications.

Effect of the porous layer on the detection of the Tamm state in a nanostructured metal lattice and a Bragg reflector

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Tamm modes are highly confined modes appearing in the photonic bandgap \cite{1}. These modes have a high quality factor, making them highly advantageous for detection. We are working on Tamm plasmons generated by a nanostructured gold grating deposited on a SiO\textsubscript{2}/Si\textsubscript{3}N\textsubscript{4} distributed Bragg reflector (DBR) (figure 1(a)) \cite{2}. Our idea is to use a porous layer beneath a nanostructured gold grating to allow the analyte to penetrate the porous layer and fill its pores. Indeed, the effective index of the porous layer changes as a function of the analyte refractive index, shifting the Tamm resonance.

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure1.png}
\caption{(a) Schematic representation of the Tamm plasmon structure constituted by double period Tamm structure with porous silicon. (b) Reflection spectra as a function of wavelength of structure a for a refractive index variation of 1\%. With a porous silicon layer, porosity P = 55\%.

A single porous layer improved the sensitivity of the structure (without porous silicon) by 4 times $s=94$nm/RIU with a quality factor of $Q=2255$.

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\end{itemize}
\end{figure}
Exploring the Temperature-Dependent Optical Properties of VO$_2$ Thin Films for Metasurface Applications

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Localised Surface Plasmon Resonance (LSPR) in metal nanoparticles gives rise to resonant absorption dependent, amongst other parameters, on the environment of the nanoparticles. Vanadium dioxide (VO$_2$), a phase transition material, displays modulation not only of its optical properties but also of its electrical and crystalline behaviour [1]. The phase transition occurs at the temperature $T_{MIT}=68$ °C for pure VO$_2$, and $T_{MIT}=25$ °C for VO$_2$ doped with tungsten ($W_{2\%}V_{98\%}O_2$) [2].

By coupling nanoparticles with a material that experiences changes in its properties with temperature, it becomes possible to create metasurfaces that can be precisely controlled [3]. This necessitates a thorough understanding of the optical properties of the surrounding medium, namely VO$_2$. However, a complete understanding of VO$_2$’s optical properties is lacking, despite extensive studies. A clear and generic method for studying the complex and inhomogeneous VO$_2$ thin films has not yet been documented.

In this study, we investigated the temperature and thickness-dependent optical properties of VO$_2$ thin films using spectroscopic ellipsometry. The results were analysed alongside structural and electronic characterisations to elucidate the underlying physical origin of VO$_2$’s distinctive properties. Subsequently, our findings were utilised to simulate the optical response of innovative metasurfaces for smart window applications, employing first gold nanoparticles coupled with a VO$_2$ thin film then VO$_2$ nanoparticles.

Through this research, we aim to contribute to a deeper understanding of VO$_2$’s optical behaviour and provide valuable insights into the design and development of metasurfaces utilising VO$_2$ for advanced smart window technologies.

References

Novel materials, synthesis and technologies for Plasmonics
Synthetic approaches to colloidal Mg nanoparticles

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Alternatives to well-established plasmonic metals, Au and Ag, have proliferated in the past decades, including earth-abundant Cu and Al. Recently, earth-abundant and biocompatible magnesium has attracted attention due to its plasmonic response across the ultraviolet, visible and near-infrared wavelength range [1]. Mg’s hexagonal lattice leads to nanoparticle (NP) shapes different from those of all other common plasmonic metals [2]. Protected by a thin native oxide layer, Mg NPs are stable both in inorganic solvents and in air. In air, Mg resists degradation up to 350\degree C. Excellent stability, the broad resonant range and variety of unique shapes destine Mg for applications in sensing, cancer therapy, and photocatalysis. However, as for any other plasmonic metals, the efficient utilization of plasmonic properties of Mg relies on tuning the LSP frequency, usually achieved by synthetic control of the NP’s size and shape.

We will discuss the different synthetic approaches to colloidal Mg NPs including single step syntheses, seed-mediated approaches, and continuous flow syntheses. In single step syntheses, a Mg metal organic precursor is reduced with arene (naphthalene, biphenyl, phenanthrene) radical anions and dianions to obtain metallic, plasmonic Mg NPs. We demonstrate that their size and shape depend on the ratio of dianion to radical anion, which in turn determines the reduction potential of the reaction medium. Recently developed one-pot, seed-mediated growth approach [3,4] utilizes Li dianion to induce the nucleation of single crystalline seeds followed by rapid \textit{in-situ} conversion of dianion into radical anion by addition of arene to the reaction mixture. Such modification of the reduction potential shifts nucleation to predominantly growth. This novel approach for Mg NPs synthesis yields tunable size and high monodispersity, as required for plasmonic application. Finally, we report our recent advances in Mg NPs synthesis in a glass helix reactor in continuous flow regime. We demonstrate that rapid mixing, precise control over mean residence time, and scalability enabled by continuous flow synthesis makes it a promising alternative to a batch approach.

References

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Semiconductor Nanoparticles with Metallic Properties

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Metal chalcogenide nanoparticles, belonging to a semiconductor family of compounds, in many cases can exhibit typical metallic properties, such as localized surface plasmon resonance (LSPR) and high electric conductivity. This behavior rather unusual for semiconductors stems from their composition tuneability. The latter in turn can be chemically controlled either directly during their colloidal synthesis or by applying a post-synthetic modification, providing an efficient toolbox to achieve desired properties.

One of the members of the metal chalcogenide family is copper chalcogenide (in particular, copper sulfide and copper selenide) nanocrystals (NCs), which will be in the focus of this presentation. Their wet-chemical synthesis is facile and straightforward yet very versatile, providing a range of compounds with tunable composition, various crystal phases, tunable surface capping, etc. Figure 1 demonstrates how changing reaction conditions influences the composition, sizes, and shapes of Cu$_{2-x}$Se NCs.

Figure 1. Scheme of the synthesis of Cu$_{2-x}$Se NCs with different compositions, sizes, and shapes, which depend on reaction conditions. Transmission electron microscopy images overview their shape and absorption spectra of the NCs show their LSPR.

References

Tunable Photoemission and Photocatalytic Activity of Au-ZnO Nanostructures

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Hybrid nanostructures based on the interaction of a luminescent nanosemiconductor with metallic nanostructures have become one of the attractive subjects in research areas due to their unique size and shape-dependent properties.¹,² The resulting exciton-plasmon coupling is considered of great interest due to the improvement of the system functional features, by which the metal generated plasmons can enhance the charge separation, light absorption as well as luminescence of the semiconductor, making them suitable and desirable for applications in energy conversion and production, light-emitting diodes (LED), optoelectronic devices, nanosensors, biomedical detection, and photocatalysis.³,⁴ In this work, we focus on the fabrication of pure ZnO nanostructures by hydrothermal method and their coupling to gold nanoparticles (AuNP) in different synthesis conditions. The role of AuNP plasmonic properties on tuning the photoemission of ZnO nanostructures was investigated.⁵ In addition, the hybrid system photocatalytic activity was examined through the ability to degrade the methylene blue (MB) dye before and after decorating ZnO with AuNP.

References

Direct Laser-Induced Gold Printing of 2D Structures and Electronic Devices

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Novel flexible manufacturing technologies are the key for the fabrication of future integrated electronic and optoelectronic devices. Direct laser induced writing (DIW) has the potential for highly flexible and low-cost rapid prototyping or producing of metal micro structures and adaptable electronics. We have recently introduced an improved DIW method for electrical gold wiring of 2D van-der-Waals sheets or the fabrication of photo switches and field effect transistors on various rigid and elastic materials with interspacing resolution down to 100 nm. The key is a novel light sensitive ink consisting of a metalloid (Au32-nanoclusters) that allows for low-power cw-laser exposure without further post-treatment. The unexposed ink can be removed with a simple lift-off procedure, leaving the bare device behind. We have characterized the optical, structural and the electronic properties of the structures with photoluminescence (PL) spectroscopy, Energy Dispersive X-ray Spectroscopy (EDX), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and (temperature-dependent) conductivity measurements. Our technique realizes ultrafast, high resolution and high precision production of integrated electronics and may pave the way the fabrication of novel prototype circuits on variable surfaces.

Figure: Gold Luminescence image of a micro-reproduction of Banksy’s Street Art interpretation “The Girl with the Pearl Earring” (J. Vermeer), depicted in greyscale. Scale bar: 10 μm. Source image from Flickr published under a CC BY NC license.[1]

References

Direct creation of gold nanoparticles inside a polymer matrix

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The ability to manipulate the optical response of a photonic device by incorporating metallic nanoparticles within a polymer matrix has opened up new possibilities for achieving unique optical characteristics [1]. Recently, we showed that gold nanoparticles (Au NPs) can be directly created within a polymer matrix using a thermal treatment method [2]. This allowed obtaining Au NPs in large area of polymer matrices. For some applications, it requires a control of Au NPs distribution at sub-\(\lambda\) scale. We then demonstrate a novel and cost-effective technique called low one-photon absorption (LOPA) direct laser writing with optically induced thermal effect to realize desired structures containing Au NPs inside a photoresist thin film. By using a continuous-wave (CW) laser to locally excite a hybrid metal/photoresist material, we achieve simultaneous photoreduction of metallic ions and an optically assisted thermal effect, resulting in the direct creation of Au NPs inside a polymer medium. This approach offers significant advantages over conventional methods as it eliminates the need for polymeric templates and complex lift-off processes, simplifying the fabrication of metallic nanoparticles in a polymeric host. The simplicity, low cost, and high efficiency of this technique make it highly promising for a wide range of applications in various fields.

References


Figure 1. (a) Transmission electron microscopy (TEM) image of Au NPs created by a thermal treatment method. (b) Optical microscope image of polymeric/Au NPs letters fabricated by LOPA direct laser writing technique.
Sensors and bio-plasmonics
Surface-enhanced Raman spectroscopy (SERS) has demonstrated its ability as a powerful tool that can provide us information about the structure and the conformation of biomolecules such as DNA. One can probe the interaction between two biomolecules and extract some evidences of the conformation changes induced by the interaction. It is of primary importance to understand such interaction to improve the performances of sensors that are based on the capture of analyte by a bioreceptor. In addition, molecular interactions are the basis of many biological mechanisms. It is therefore important to have a better understanding of these phenomena and to be able to answer to specific questions as: how does the interaction take place? is it dynamic or static? is there any specific conformation for the interaction?

In this work, we focus on the interaction between two DNA complementary strands as well as strands containing mismatch in their sequences. To do this, we study the interaction between a DNA sequence consisting of 20 Bases of poly-Thymine (PolyT) with its complementary poly-Adenine (PolyA). The PolyA strand is grafted at the surface of the gold nanostructured surface (Hamamatsu commercial SERS substrate [1]) using a thiol group at the 5' extremity of the DNA strand. We assume that we form a monolayer of PolyA. Some solutions of PolyT with different concentrations (10^{-7}, 10^{-6}, 10^{-5} and 10^{-4} M) are successively deposited on the SERS substrate. We performed Raman mapping on the surface and we recorded 400 spectra using a 633 nm excitation wavelength. One can observe the 735 cm^{-1} band assigned to the ring breathing mode of the PolyA and some variations of its intensity depending on the position on the map. By changing the concentration, we observe a decrease of the average SERS intensity of this band as well as a decrease of the standard deviation of the intensity of this band. We interpret this intensity change by some modification of the orientation and flexibility of the PolyA DNA strands interacting with the PolyT [2]. The increase of the concentration of Poly-T induced a loss of flexibility of the PolyT/PolyA molecular complex. We performed similar experiments by introducing a mismatch inside the PolyA sequence. A C base is inserted at different positions in the sequence of polyA and we can observe some modification of the interaction between the PolyA and the PolyT strands. This study provides a new approach for the reliable quantification and structural analysis of biological molecules.

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References
Hybrid gold-DNA origami nanostructures for colorimetric sensing

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To develop a colorimetric sensing platform compatible with single-molecule detection, we assemble gold-nanosphere dimers on a 3D Y-shaped DNA origami that acts as a nanoscale actuator (Fig. 1-a). DNA origamis are a flexible platform to produce nanostructures that shift their morphology when interacting with specific targets, such as DNA/RNA strands, proteins, or specific cations [1]. To translate such conformational changes in colorimetric information, we exploit the nanoscale dependence of plasmon coupling between two gold nanospheres. We demonstrated that dark-field microscopy allows the far-field monitoring of nanoscale distance changes in single gold dimers on a simple color camera [2,3]. The scaffold of our DNA origami features an active site with a conformation that can be tuned by hybridizing specific DNA single strands (Fig. 1-b). The morphology of the hybrid nanostructure is governed by the geometry of the DNA origami but also by steric and electrostatic repulsions between the nanospheres. We observed that the difference in conformation of the active site is only visible in the optical response for high ionic strength, when these steric and electrostatic repulsions are reduced. One-step colorimetric sensing of DNA single strands is achieved at high ionic strength using a strand displacement reaction. These measurements are carried out both by performing single-nanostructure scattering spectroscopy (Fig. 1-c) and by monitoring the hue of single dimers in dark-field images (Fig. 1-d), obtaining similar statistical responses. These results open exciting perspectives for the colorimetric sensing of individual DNA strands on a color camera.

Figure 1: (a) EM images of 40nm-gold-spheres dimers assembled with DNA origami (b) Different conformations of the active site (c) Distributions of resonance wavelength (top) of single-nanostructure scattering spectra (bottom) (d) Distributions of maximum hue value of single-nanostructures (top), retrieved from dark-field color-camera images (bottom).

References
Surface plasmon resonance (SPR) technology utilizes plasmonic effects to detect changes in the refractive index on the surface of a biochip, allowing for sensitive and label-free analysis of target substances. By monitoring shifts in plasmonic resonance, SPR provides real-time and quantitative measurements, making it valuable in fields like biosensing, drug discovery, and environmental monitoring. However, the widespread adoption of this technology is limited by its cost and system size. In this presentation, we introduce an ultra-compact SPR system powered by USB. This versatile system offers sensitive phase measurement, improving sensitivity and also providing the additional benefit of ellipsometric measurements.

Herein, we will highlight the unique capabilities of this device and explore potential applications, notably for research, teaching and point-of-care testing (POCT). Examples include monitoring of oxidation of plasmonic layer, pesticide detection with DNA probes, and more.

**References**


Theoretical and numerical studies
Enhancing Fano resonances through coupling of dark modes in a dual-ring nanostructure

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A Fano resonance occurs by the interference of a bright plasmonic mode, which can be directly excited by light, with a dark plasmonic mode, which cannot. Fano resonances are highly tunable and sensitive to changes in the environment, making them interesting for chemical or biological sensing applications. Previous papers have already investigated plasmonic Fano resonances of many different device geometries, with each resonance being caused by a coupling between a single bright and a single dark mode [1]. To enable an additional coupling between dark modes, we propose a nanostructure that consists of two nanodiscs and two nanorings [2]. The nanodiscs provide the bright mode for the Fano resonances while the nanorings each provide narrow dark modes. Placing the two nanorings in a concentric arrangement allows for a coupling between the dark modes of the inner and the outer nanoring. This coupling mechanism occurs in addition to the coupling between bright and dark modes, thus changing the properties of the Fano resonances.

![Dual-ring nanostructure](image1)

**Figure 1:** a) Dual-ring nanostructure. b) Electric near-field enhancement at a Fano resonance of this nanostructure. c) Simulated scattering cross-section of the nanostructure.

To investigate the changes that are caused by this coupling, we use numerical simulations to calculate the scattering cross-section and the electric near-field of this nanostructure. We also investigate the isolated Fano resonances of the inner and the outer nanoring to get a frame of reference of the uncoupled system. The results of these simulations are then used to model this system with a set of coupled harmonic oscillators, confirming the coupling between dark modes. The additional coupling between dark modes modifies the scattering cross-section of the nanostructure and increases the sensitivity of the nanostructure to changes of the refractive index, which improves the performance of a plasmonic nanostructure as a chemical or biological sensor.

Graph Neural Networks (GNNs) are specifically designed to work on data structured as graphs. A graph is made up of nodes connected with edges [1]. Datasets in fields like social networks or molecular systems can be easiest represented by such graphs. Here, we use graphs to represent thin film layer stacks and their optical scattering matrices [2], as depicted in figure 1 below. A GNN is then used to predict the reflectivity of a physical structure with known refractive indices and thicknesses, no matter the number of layers.

A great advantage of GNNs is their independence of the graph size, hence GNNs can deal with larger graphs than used during training. While such extrapolation is generally difficult, we find that providing all scattering matrices (S in figure 1) to the GNN during training, significantly increases the accuracy of extrapolation to thin film stacks with more layers than used in training.

Graph representation of thin film stacks

Figure 1: Two examples of thin film stacks and their graph representations in the training dataset. Scattering matrices are used only for training, they are set to zero during inference.

References
A magnetic monopole nanoantenna
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Magnetic monopoles are hypothetical particles which, similarly to the electric monopoles that generate electric fields, are at the origin of magnetic fields. Despite many efforts, to date, these theoretical particles have yet to be observed. Nevertheless, many systems or physical phenomena mimic the behavior of magnetic monopoles. Here, we propose a new type of photonic nanoantenna behaving as a radiating magnetic monopole. We demonstrate that a half-nanoslit in a semi-infinite gold layer generates a single pole of an enhanced magnetic field at the nanoscale and that this single pole radiates efficiently in the far field (Figure 1). We also introduce an effective magnetic charge using Gauss’s law of magnetism, in analogy to the electric charge, which further highlights the monopolar behavior of this new antenna. Finally, we show that different plasmonic and metallic materials can provide magnetic monopole antennas covering the visible to near infrared range, and even down to GHz frequencies. This original antenna concept opens the way to a new model system to study magnetic monopoles and a new optical magnetic field source to study the “magnetic light-matter coupling”. Furthermore, it opens potential applications at lower frequencies, such as in magnetic resonance imaging.

Figure 1. Illustration of a magnetic monopole nanoantenna made in a semi-infinite gold layer.
Ultrafast and nonlinear plasmonics
Disentangling the ultrafast optical response of Titanium Nitride: from films to nanoantennas

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During the past decade, Titanium nitride (TiN) has attracted notable interest in the search for plasmonic materials alternative to noble metals [1]. In particular, for what concerns the ultrafast optical response, TiN boasts a hot-carrier relaxation time of tens of fs only, i.e. ~100 times shorter than gold [2]. Given the growing interest towards TiN, a comprehensive, broadband description of the origin of TiN ultrafast optical behavior is demanded. In this work, we first calculate the increase of carrier and lattice temperatures following ultrafast photoexcitation, by means of a rate-equation model. Then, we evaluate the photoinduced modulation of TiN permittivity, disentangling the interband and the intraband contributions on a broad spectral range. We start our study from the simplest structure, i.e. a 200-nm TiN film on glass. The model is validated by ultrafast pump-probe spectroscopy experiments, using an ultrashort pump (at 500 nm) and a broadband probe (320-550 nm), with ~100 fs temporal resolution [3]. The numerical model is then extended to study TiN nanoantennas. Exploiting experimental results from the literature [4,5] we are able to fully disentangle the ultrafast optical response of TiN nanodisks and nanospheres with 200 nm and 50 nm diameter, respectively. We find that the interband permittivity modulation plays a key role in generating the ultrafast features (< 150 fs) in TiN’s transient optical response observed experimentally. Our work paves the way for the design of new, ultrafast, TiN-based devices for the all-optical modulation of light.

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References
Ultrafast plasmonics for the generation of reactive oxygen species in biomedical applications

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Gold nanoparticles in a biological medium can produce reactive oxygen species (ROS) under ultrashort pulsed light [1]. This ROS generation is tightly linked with the multiphotonic emission of electrons [2,3] and the energy transfer in the plasmonic near-field. While beneficial for photodynamic therapy, it is prohibitive for other biomedical applications such as imaging or targeted gene/drug delivery by plasmonic photothermal conversion.

In this communication, gold nanorods (AuNRs) are synthesized and coated, either with silica, or with PEG. ROS are produced by sub-ps laser pulse irradiation and detected by fluorescence spectroscopy. We demonstrate the involvement of electron emission and near-field properties in the generation of ROS. In addition, we assess the link between the nonlinearity of the near-field enhancement and the laser intensity dependence of the ROS production. We evidence that a dense silica shell added onto AuNRs hinders the formation of \(^1\)O\(_2\) and •OH efficiently [4]. Further, we investigate in vivo the therapeutic efficiency of AuNR irradiation as a cancer treatment. Irradiation of patient-derived tumor xenografts in mice with ultrashort laser pulses in the presence of AuNRs makes it possible to induce major tumor necrosis from 48 hours as well as all cell death types, with a disappearance of ROS products. Our results suggest a combined effect of hyperthermia and photodynamic therapy with preferential death of cells with initially elevated ROS levels. This preclinical study provides valuable insights into the underlying mechanisms of cell death triggered by ROS and offers promising outlooks for the use of AuNRs as ROS-based cancer therapeutic agents.

References

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

Here, we report on a periodic, plasmonic metasurface whose pitch can be optimized to allow maximal extraction of the second-harmonic generation (SHG) emitted by the individual meta-atom, i.e. an L-shaped gold nanoantenna. In particular, we found that the SHG from the first horizontal diffraction order can be enhanced by a factor of 2 after optimizing the metasurface pitch (Figure 1a). We confirmed this by experimentally reconstructing the SHG radiation pattern of a single nanoantenna from different diffraction orders (Figure 1b) through angular-resolved excitation.

Finally, considering the thin angular width of the emission lobe (Figure 1c), and its dependence on the surrounding refraction index, the archived overlap opens an avenue for sensing purposes.

Figure 1: (a) SH power emitted at 775 nm by the metasurface in the (+1;0) diffraction order, as a function of the pitch in the x axis. Inset: SEM image of the metasurface. (b) Simulated and reconstructed emission pattern in the horizontal axis of the BFP. (c) Simulated emission pattern as function of superstrate refractive index.

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

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The present drive towards the miniaturization of nonlinear optics is motivated by the number of functionalities it could bring about in integrated devices, such as frequency conversion, sensing, and active control of optical signals. The exploitation of localized electromagnetic resonances supported by nanoantennas can boost the efficiency of the nonlinear processes, which is typically low due to the small volume of matter involved. We recently explored a wave-mixing process excited by a pulse of angular frequency $\omega$ (corresponding to the telecom wavelength $\lambda = 1550 \text{ nm}$) and its second-harmonic replica pulse at $2\omega$. When the two pulses are temporally and spatially overlapped, sum-frequency generation (SFG) is observed at $3\omega = \omega + 2\omega$ (Figure 1) [1,2]. This output is coherent and frequency-degenerate with the third-harmonic generation (THG) at $3\omega = \omega + \omega + \omega$ seeded by the pump at $\omega$ alone. Here we focus on a gold dimer constituted by a V-shaped nanoantenna coupled to a rod [2]. The lack of axial symmetry of the resonant modes involved unlocks the coherent crosstalk between THG and SFG, resulting into interference. By varying the delay $\tau$ between the input pulses (see inset in Figure 1) the total signal at $3\omega$ exhibits a power modulation up to a factor of 2. Moreover, modulation amplitude is controlled by the relative phase of the two pumps. This effect is a proof of concept implementing an all-optical coherent (i.e. phase based) control of the up-converted signal.

References

Posters
Local and deterministic integration of plasmonic and luminescent nanoparticles

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The prospect advances in quantum applications have made the fabrication and manipulation of single photon sources a recurrent subject of study during the last years. In this context, the integration of single photons through low loss photonic integrated circuits (PICs) is a challenge that faces several difficulties concerning the stability, simplicity, robustness, and efficiency of the used integration technique. In this work, we demonstrate a new approach of patterning individual nanoparticles using two-photon polymerization (TPP) coupled to surface functionalization and colloidal deposition [1]. First, the surface is chemically patterned by fabricating ultrathin single polymer dots through one shot direct laser writing in a pre-functionalized photopolymer [2]. After developpement, the sample is immersed in a colloidal solution of negatively charged nanoparticles. These later will be selectively trapped on the positively charged surface of polymer dots. This approach makes it possible to achieve local and deterministic integration of single nanoparticles. Thanks to a deep photochemical study concerning the threshold polymerization energy of the pre-functionalized photopolymer, we identified a diffusional regime allowing to adjust the competition between polymerization and inhibition and thus to tune the polymer thickness of polymer dots. This in turn allowed us to control the number of trapped NPs. We have succeeded in immobilizing single gold NPs, fluorescent Nitrogen Vacancy center nanodiamonds (N-V NDs) and CdSe/CdS/ZnS single quantum dots (QDs). This approach was used to successfully integrate single QDs at the vicinity of a plasmonic nano-antenna that, based on our FDTD simulations, will efficiently couple the single photon emission through a TiO2 ridge which by turn will couple this emission through a low loss Ion Exchange Waveguide (IEW). The single photon emission was confirmed by g2 measurements and the local integration precision was confirmed using photoluminescence (PL) mapping.

References

Photochemical imaging of near-field in chiral nanostructures


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Chiral nanostructures interact differently with right and left circularly polarized light. Moreover, they exhibit enhanced electric and magnetic near-fields leading to the so-called superchirality. This effect can be used for the detection of chiral biological objects with high enantio-sensitivity. Indeed, the optical chirality C is correlated with the rate of excitation of the chiral molecule [1], so that increasing the optical chirality at the location of the molecule can significantly improve its detection [2]. We present here a subwavelength imaging approach that is based on the interaction between the highly exalted near-field of chiral nanoparticles and an azobenzene molecule (DR1, disperse red 1) grafted to a polymeric chain (i.e., PMMA). Under illumination, the azobenzene molecules (DR1) undergo photoisomerization cycles, which induce a displacement of matter inducing measurable topographical modifications that can be tracked using atomic force microscopy. Therefore, we obtain in the polymer a map of the near-field of the chiral nanostructures [3]. We recently demonstrated that chiral effects and field dissymmetry in plasmonic nanostructures can be imaged with this technique [4]. Here, we apply photochemical imaging to chiral metallic nanostructures composed of two coupled gold nanorods. Each rod has a length of 140 nm, a width of 70 nm and a height of 50 nm. They are separated by a 40 nm wide gap and are shifted with respect to each other by a distance ‘$S$’ along their long axis. We show that the near-field chiral response can be imprinted in the photopolymer. It is shown that it is possible to experimentally map the near-field dissymmetry factor [5], which is the contrast in the local near-field response of the object under RCP and LCP excitation.

References

Photothermal therapy (PTT) is a technique used for cancer treatment that exploits the thermoplasmonic properties of gold nanoparticles (AuNPs). In fact, AuNPs convert electromagnetic radiation into heat due to the excitation of the plasmon. Such property can be used for the thermal ablation of tumor cells. AuNPs of specific sizes and shapes are able to convert visible or near-IR radiation into heat [1]. The aim of this project is to study the thermoplasmonic properties of AuNPs in the visible to near-IR area, by observing and analyzing temperature variations. The first part of this study consists of synthesizing different shapes and sizes of AuNPs to exploit their physico-chemical properties. The AuNPs are characterised by UV-Visible to determine the position of the localized surface plasmon resonance (LSPR). In a second part, we focus on the thermoplasmonic study of AuNPs alone and after functionalization with a PEG molecule. Using a thermal camera, we measure the temperature rise induced by laser excitation on colloidal solutions at different wavelengths. We determine the direct influence of several experimental conditions: size, shape and environment of the AuNPs, on the temperature variation. One can observe a correlation between the plasmon resonance of the AuNP and the heat of the solution as well as an influence of the PEG layer on the temperature increase.

Reference

Sensitizing Silicon Carbide for Enhanced Photocatalytic Applications Using Platinum Nanoparticles

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Silicon carbide (SiC) has emerged as a promising material for various applications due to its exceptional physical and chemical properties. In recent years, the integration of SiC with noble metal nanoparticles has gained significant attention for enhancing its photocatalytic performance. This study focuses on sensitizing SiC with platinum nanoparticles (Pt NPs) to harness their catalytic properties and improve the photocatalytic efficiency of SiC-based systems.

The sensitization of SiC was achieved through a facile and scalable method involving the synthesis and deposition of Pt NPs onto the SiC surface. Initially, Pt NPs were synthesized using a controlled reduction method, followed by their immobilization onto the SiC substrate using various techniques, such as drop-casting, spin-coating, or electrochemical deposition. The choice of deposition method and optimization of experimental parameters influenced the coverage, distribution, and stability of the Pt NPs on the SiC surface.

The sensitized SiC samples were characterized using various techniques, including scanning electron microscopy (SEM) and X-ray diffraction (XRD), to investigate the morphology, size and distribution of the Pt NPs. Additionally, spectroscopic techniques, such as UV-Vis absorption spectroscopy and photoluminescence spectroscopy, were employed to evaluate the optical properties and charge carrier dynamics of the sensitized SiC samples.

The photocatalytic activity of the sensitized SiC samples was evaluated through the generation of hydrogen through water splitting under visible light irradiation. The performance of the sensitized SiC photocatalysts was compared to the SiC without Pt NPs to assess the catalytic enhancements achieved through sensitization. The results demonstrate that the integration of Pt NPs onto SiC surfaces effectively enhances the photocatalytic activity of SiC. The sensitized SiC samples exhibited improved absorption of light in the visible range, increased charge separation, and enhanced catalytic efficiency compared to pristine SiC. This study highlights the potential of sensitizing SiC with Pt NPs for advanced photocatalytic applications.
Magnesium nanoparticles (Mg NPs) have recently attracted attention for plasmonic applications owing to Mg’s broad plasmonic response (UV to IR), its biocompatibility and abundance in Earth’s crust, as well as its HCP crystal structure that gives rise to a variety of NP shapes. While much work has been done on characterising Mg’s optical response, Mg NPs’ performance in enhanced spectroscopies, such as in surface enhanced Raman spectroscopy (SERS) and metal enhanced fluorescence (MEF), is yet to be revealed. Mg is appealing for MEF as its wide working wavelength range leads to a large operating range for matching with fluorophore absorption/emission energies, including in the UV.

In this work, we present the fluorescent properties of Mg NPs, naturally surrounded by a thin MgO layer, coated with a silica spacer of varying thickness and a fluorescent dye. Our preliminary results show fluorescence emission from fluorescein supported on Mg, both in bulk and single particle level, and a clear indication of fluorescence intensity decrease upon oxidation of the metallic Mg core. To support experimental results, we have also performed numerical studies investigating the effects of MgO, silica coating and tip rounding on the electric field enhancement of various Mg NP shapes present in the sample.

References

MoS$_2$-based Nanoantennas for Nanophotonic Applications

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Light manipulation at the nanoscale is a priority research avenue in photonics. It has been shown in many laboratories around the world that the electric and magnetic components of optical waves can be controlled on the nanoscale by using resonant nanostructures, which form the basis of modern nanophotonics and are known as optical nanoantennas. Generally, nanoantennas can be separated into several types depending on the material they are made from and on the corresponding operation principles: metallic (often referred to as plasmonic) and dielectric. The plasmonic nanoantennas are characterized by a strong localization of the exciting electromagnetic field at the nanometer scale but suffer from dissipative losses, that can be overcome by using dielectric nanoantennas. These latter are fabricated from materials with a high refractive index and the lowest possible absorption coefficient in the optical range. Recently, transition metal dichalcogenides (TMDCs) nanoantennas, in the form of nanodisks, demonstrated distinct Mie resonances [1]. In the present study we present an in-depth study of the sulfurization of monocrystalline $\alpha$-MoO$_3$ thin films [2], pre-deposited on a substrate by atomic layer deposition (ALD), by means of annealing at a temperature around 700 °C in the presence of gaseous hydrogen sulfide (H$_2$S) as sulfur source. Advanced characterization techniques, including Raman spectroscopy, X-ray diffraction (XRD) and photoluminescence spectroscopy were used to understand the fundamental properties of the achieved MoS$_2$ thin films. Additionally, we delved deeper into the spatial distribution (nanometer scale) of luminescent properties across the surface of MoS$_2$ thin films (by using the cathodoluminescence technique, CL), revealing information about the excellent homogeneity and quality of the films. Finally, we show the fabrication process and CL characterization of MoS$_2$ nanoantennas by combining electron beam lithography and reactive ion etching techniques.

References
Biocompatible fluorescent carbon dots nanoparticles for security markings

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For many years, cultural property in general and archaeological artefacts have been liable to be stolen during and after the excavation process in order to be introduced to the black market. Globally, it is commonly estimated that the illicit trafficking of cultural heritage ranks among the biggest illicit trade in the world, grossing several billion dollars¹.

The challenge of the project is to be able to implement a safe technical solution which makes it possible to mark archaeological artefacts in a unique way. Carbon dots are a 0D nanomaterial made of a hybrid structure with a graphene like core of sp² carbon and an outer shell of amorphous sp³ carbon. Since they are composed mainly of carbon, they constitute a safer alternative to heavy metals quantum dots and allow us to avoid trace contamination before analysis. Moreover, carbon black which is the basis of the black inks used, are chemically identical to C-dots. We integrated carbon dots synthetized using a protocol from Yan et al² into a protective coating used for marking cultural artefacts. The coating produces orange photoluminescence under UV but also green light excitation, constituting a new kind of security marking.

Figure 1. Carbon dots in solution under green laser excitation;
Figure 2. Clear nail polish for classic marking (left) and carbon dots incorporated to clear nail polish for marking (right) under visible and UV light.

References

Correlation between DNA bases and the intensity of the Raman bands with SERS

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Raman spectroscopy has become a popular tool for analyzing biological samples such as DNA. It allows us to access to the vibrational levels of molecules and thus to identify the chemical composition and to observe the structure of molecular systems. [1]

In this work, we recorded the SERS spectra of DNA strands with different sequences and grafted at the surface of gold nanoparticles. Our objective is to study the correlation between the DNA sequences and its base composition and the intensity of Raman bands observed in SERS.

To reach a high density of DNA on the surface of the gold nanoparticles, the DNA strands include a thiol group (SH) at their 5’ end and are conjugated to gold nanoparticles using the freeze-thaw cycle method.

SERS measurements are performed on dried drops deposited on a glass slide. We recorded 5 spectra for each sample using a 785nm excitation wavelength. We observed several bands that can be assigned to the different bases and to the phosphate backbone. For instance, the bands of ring breathing mode of adenine and the carbonic skeleton of the DNA are observable at 733cm⁻¹ and 1029cm⁻¹ respectively. [2]

We then compare the relative intensity of the different bands such as the 733cm⁻¹ or 1029cm⁻¹ ones. We found that the relative intensity of the 733cm⁻¹ band is correlated with the amount of adenine in the DNA sequence. This study provides a new approach for reliable quantification and analysis of genetic information associated with DNA molecule sequencing.

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References


Immobilization of gold nanoparticles by DNA hybridization to code information

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DNA is a large and complex molecule which contains genetic information that determines the physical and biological characteristics of a living organism¹,². However, the use of DNA is no longer limited to genetic. Nowadays, DNA is also used to encode information³,⁴, as it can store large quantities of data in a nanoscale space. This use of DNA as a data storage offers many advantages, such as durability and storage density, and can be used in many different fields.

The challenge of the project is to develop a technique to encode information in a nanoparticle-based ink and to be able to collect and read the coded information once deposited on a surface. We use DNA hybridization to ensure the selectivity of the recognition technique. In fact, by hybridizing nanoparticles on a surface using DNA coding (Figure 1) and by collecting the spectral response of the nanoparticles, it is possible to detect and recognize the code.

First, we verified our hybridization protocol by hybridizing DNA strands with fluorophores at their ends. Then, we immobilized gold nanoparticles and Qdots on a glass substrate by DNA hybridization. Finally, we explored the potential use of the analysis principles of Antigen Covid tests or ELISA tests.

References

More and more structural colors successfully replace pigment-based ones. Most of the proposed solutions relies on plasmonic architectures, that is subdiffractive structures, demanding rather complicated and expensive techniques. Reproducible, cost-effective, large scale fabrication methods remain challenging. We report on the design of sub-micronic metasurface (cylinders of given depth or height) allowing for control of spatial distribution of the scattered light as well as management of the ratio between specular and diffusely reflected light. Interferometric control is here provided thanks to quasi Fabry-Perot cavities of given depth, diameter, spatial distribution and density.

References


White light interferometry applied to local spectroscopy of oriented assemblies of silver nanowires

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Oriented assemblies of silver nanowires (AgNW) have the remarkable ability to manipulate light, and in particular the polarization of light. These anisotropic materials created by bottom-up technology are prepared using a simple and versatile method called “Grazing Incidence Spraying” (GIS) allowing to control the in-plane orientation of anisometric nano-objects like AgNWs.[1] The latter can be combined with the layer-by-layer (LbL) approach to prepare anisotropic multilayer films with unprecedent complexity. Their optical properties are determined not only by the properties of the individual elements, but also by how they interact with each other, probably through coupling effects. The main challenge of this work is to study how light interacts with these nanostructures on a microscopic scale and to control their optical behavior on a macroscopic scale. White light interferometric microscopy can be used to obtain a two-dimensional spectral map with micrometric or submicrometric resolution. We have developed new local spectroscopy methods using white light interferometry [2]. One of the main advantages of our optical configuration is the ability to perform local spectroscopy measurements (pixel by pixel or by area), in addition to topography measurements [3]. With just one measurement, we have access to topographic and spectral information at exactly the same location. In parallel we have also developed a super-resolution local spectroscopy technique using the microsphere technique [4] allowing a lateral resolution of up to 100 nm, with the advantages of being marker-free and providing multimodal acquisitions. The measurement set-up has been improved to include TE and TM polarization measurements of the samples. Here we will show some preliminary results from samples deposited on glass slides or silicon wafers using combined GIS/LbL technology and studied by local spectroscopy.

References

Optical Tamm states in 2D nanostructured magnetophotonic structures

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Optical Tamm modes are highly confined electromagnetic modes appearing at the interface between a metal layer and a Bragg mirror. Here, the metal is patterned to form a grating, and a magnetic layer is added between the metal and the Bragg mirror. The use of a grating allows for the creation of additional modes \cite{1} and a direct access to the last layer of the Bragg mirror where the energy of the Tamm mode is concentrated.

We numerically explore in this work the Transverse Magneto-Optic Kerr effect (TMOKE) signal in this 2D nanostructured magnetophotonic structure. The simulated TMOKE signals reach values that are comparable to conventional magnetoplasmonic structures. Using different angles and planes of incidence as well as different polarizations, several Tamm modes supported this structure are also investigated. These modes provide high energy confinement in between the metal stripes, paving the way for higher sensitivities in bio- and chemical sensing applications.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Figure1.png}
\caption{Magnetophotonic structure}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Figure2.png}
\caption{Reflectivity and TMOKE signal}
\end{figure}

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Plasmonic Nanotweezers for Enantiomer Separation

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Enantiomer separation is a critical step in the synthesis of many compounds, as a chirality change can lead to many undesirable effects – up to turning medicine into poison [1]. While many chemical methods rely on bulk separation, isolation of specific compounds in small quantities with high precision remains insufficient, Optical tweezers have been demonstrated to be a tool of growing interest for contactless manipulation on single objects down to the molecular scale especially for enantiomer separation. By combining with plasmonic structures, they are optimized to allow manipulation at the sub-wavelength scale [2].

Plasmonic structures are of great interest due to their large tunability and panel of parameters – material used, shapes, size, etc. While achiral structures can be overlooked due to their non-chiral nature, they can in fact exhibit local chirality change under correct conditions. [3] In this communication, we exemplify the principles of chiral optical forces nearby plasmonic structures. Using numerical simulations, we show a local chirality enhancement even for achiral shapes, leading to chiral optical force generation.

References


On the orientation mechanism of non-polar dyes in light-emitting guest-host systems

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After many years of development, OLEDs have continuously been optimized to reach higher efficiency, for which the horizontal orientation of the emitter molecules is one of the dominant factors [1]. For the purpose of studying intrinsic orientation without electrostatic interaction, our work considers non-polar dyes, namely TTPA, BSBCz, DIP and DBP. While the emitter orientation has been studied in neat film as a basic approach, their behavior in guest-host systems has not been studied widely. In this work we focus on the correlation between emitter concentration and its orientation. With the results from experimental and simulation study, we also discuss the possible orientation mechanism of emitter molecules on the substrate surface in terms of molecular structure, possibility to form crystallites and the effective glass transition temperature (T_g) of the guest-host system. We observe that isotropic structure of the emitter as well as the crystallized and aggregated molecules are not favorable for horizontal orientation. However, molecules having a rod-like structure have the tendency to arrange horizontally to the substrate. These results contribute to a further understanding of orientation of non-polar emitter molecules.

References

Surface plasmon resonance (SPR) biosensors detect changes in the refractive index (RI) of a biochip surface which is coated with a plasmonic film. These changes indicate the presence of a specific target substance and can be measured by observing the shift in the angular or spectral plasmonic resonance. In a real detection system, plasmonic resonance undergoes both an angular shift and slight deformation in the response curves. Neglecting this deformation can affect measurement precision. Recent studies [1-2] have utilized a phase and intensity-based SPR sensor to improve accuracy and obtain more information about the sample. This research demonstrates how considering both phase and intensity measurements, even at a single measurement angle, significantly enhances the precision of RI measurement. The measured data is projected onto a complex space using the reflectivity expression $R = |\text{Re}(r) + i \text{Im}(r)|^2$, where $r$ represents the experimental complex reflectivity. Fast angular scans are performed at different time points during the experiment to enable offline correction, through an evaluation in the complex space (cf. figure 1 below). By considering the distinct behaviors of the intensity and phase components in response to SPR deformations, this technique provides a more accurate measurement of the effective RI. This study contributes to a broader understanding of the behavior of SPR responses in the complex space.

Figure 1: SPR angular scans and sensorgram projection in the complex space.

References

Symbolic Regression for the retrieval of the effective refractive index of a dilute system with spherical metallic nanoparticles

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Symbolic Regression (SR) is an extensively used tool that has proven to be very effective in theoretical studies within different research fields [1]. It provides a closed-form expression that describes the problem studied, without requiring information about its algebraic form [2]. Recently, we have successfully used SR to model the optical properties of transparent and absorbing dielectrics [3]. This motivated us to extend the applicability of SR to problems with turbid media. Dilute systems of Mie metallic particles have been previously studied [4]. In this approach, the system is replaced by an homogeneous medium described by an effective refractive index. We make use of Symbolic Regression to retrieve, from spectral information, a closed-form expression that represents the effective refractive index of a dilute system formed by spherical Cu nanoparticles, with a double dependency on the radius of the particle and the incident wavelength. Although we considered a simple case, there are no evident restrictions to extend this approach to more complex configurations.

\[ n_{\text{eff}} = 1 + \frac{0.377 \frac{\lambda}{a} - 0.203 + i 0.264}{-2.045 \frac{\lambda}{a} + 2.194 + 0.151 \frac{a}{\lambda}} \]

References

Magnesium Plasmonic Array Fabrication with Nanosphere Lithography

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Nanosphere lithography (NSL) is a common and successful approach to fabricating high quality, large-area plasmonic arrays. Using conventional plasmonic materials (Ag, Au, Cu), such arrays of nanotriangles or nanoholes have been employed in refractive index sensing and surface-enhanced Raman spectroscopy. Here, we use this well-established technique to fabricate magnesium (Mg) arrays, show the potential of Mg as a plasmonic device material, and address challenges in the fabrication processes. Specifically, we used monodispersed polystyrene nanospheres to form a self-assembled hexagonally packed monolayer on a water-air interface. The monolayers were then used as a mask for Mg deposition, performed in ultra-high vacuum with a thermal evaporator placed in an argon-filled glovebox. We first found that the quality of the arrays varied greatly with deposition rate. Once optimized, this deposition was performed with 3 different nanosphere diameters as masks (350, 500, and 750 nm). The absorbance profiles of the arrays vary with nanosphere diameter as expected and as predicted from numerical simulations with FDTD.

Furthermore, to show the potential use of Mg arrays in sensing applications, we coated a thin layer of alumina as a protective layer with atomic layer deposition. This layer was demonstrated to prevent oxide and hydroxide formation in aqueous environments, with thicker layers providing better resistance. The optical response of the array redshifted with increasing alumina thickness, as expected. These results show that Mg, an unconventional but cheap, abundant, and biocompatible metal, can be used as a sensor array.
Gold nanoparticle networks in topological defects of smectic liquid crystal

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A liquid crystal (LC) is a mesophase where the molecules are free to move as in a fluid, but show a certain degree of order as in a crystal lattice. Under specific conditions, a thin film of LC can form a pattern of flattened hemicylinders called “oily streaks” that present different kinds of topological defects (1D and 2D defects) able to trap and orient nanoparticles [1]. When using gold nanoparticles, this composite can activate interesting plasmonic properties coming from the interaction of the nanoparticle networks. Previous results from our group show the coexistence of chains and hexagonal networks of gold nanospheres oriented along the hemicylinder direction, confirmed also by X-ray diffraction experiments [1]. We are currently interested in using gold nanorods functionalized with thiol-ended polystyrene. Absorption measurements reveal that these rods can form chains in the 1D defect and ribbons in the 2D defect. The defects being strictly oriented in the LC pattern, we obtain these two assemblies with a unique orientation, allowing activation of the plasmonic properties by light polarization. The chains present an end-to-end configuration of the rods, leading to the formation of aligned plasmonic cavities of giant exaltation between the rods. In contrast the ribbons correspond to a side-to-side assembly. The side-by-side assembly is perpendicular to what was previously observed for nanorods functionalized with alkyl chains, making us believe that the ligands monitor the orientation of nanorods with respect to the 2D defects. Controlling nanorod concentration we control the coexistence of the two kinds of assembly, allowing activation of light absorption from the composite.

References

Controlling the polymerization pattern of diazonium salts through heat and hot electron generation in gold nanoparticles

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Aryl diazonium salts (DS) have been known for over a century and became important building blocks in organic synthesis due to their ability to covalently couple with a wide variety of compounds. Recently, DS have been undergoing a Renaissance driven by the possibility of their grafting on a surface. This grafting can be induced by electron transfer and followed by aryl radical formation together with the elimination of a nitrogen molecule.[1] Simultaneously, the spontaneous grafting is also possible caused by the thermodynamic instability of DS, which accelerates upon heating. Since gold nanoparticles are able to generate both hot carriers and heat under illumination [2], we can distinguish grafting mechanisms of DS and control their polymerization pattern on gold nanoparticle surface. We demonstrate that choosing the excitation wavelength that match interband transition, where the most of energy transforms into heat, we obtain a uniform growth of the polymer on the gold nanoparticle surface (Fig. 1). While the excitation of the plasmon resonance leads to the polarization-dependent pattern, corresponding to plasmonic hot spots (Fig. 1).

Fig. 1 Scheme of DS polymerization on a gold nanocube with experimental SEM images

References

Broadband optical properties of MXene nanoparticles

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MXenes, two-dimensional titanium carbides and nitrides have metallic properties, high conductivity and are considered one of the most promising materials for energy storage in batteries and supercapacitors [1-2]. At the same time, the possibility of using MXenes in photonics is much less well studied, although a number of papers suggest their use in surface-enhanced Raman spectroscopy [3], phototherapy of cancer [4], broadband absorbers [5] and plasmonic devices [6].

To investigate the optical response of Ti₃C₂, precise ellipsometric measurements of the dielectric function of a titanium carbide crystal over a wide range from 300 to 3300 nm on a thin film fabricated by vacuum filtration were performed in this work. A good agreement between the measured and simulated transmittance spectra of Ti₃C₂ films of different thicknesses was demonstrated and the band structure of titanium carbide was calculated to confirm the validity of the results. These studies have shown that Ti₃C₂ exhibits a dual dielectric-plasmonic response over a wide spectral range.

Inspired by recent success in fabricating transition metal dichalcogenide nanospheres that retain the crystalline structure and optical response of its bulk counterpart [7], in this work we proposed the use of Ti₃C₂ nanoparticles as theranostic agents for cancer therapy. It was found that Ti₃C₂ nanospheres can simultaneously absorb radiation resonantly in two important biomedical therapeutic spectral windows. In the first window (700 - 980 nm), Ti₃C₂ outperforms gold, silicon and competes with titanium nitride. Meanwhile, in the second window (1100 - 1700 nm), which has greater potential for cancer therapy, Ti₃C₂ outperforms all other materials by a wide margin due to localized plasmon resonance.

References

Analysis of bias-stress effect on S-DNTT-10-based OTFTs via SERS

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Organic thin-film transistors (OTFTs) features low cost, large-area fabrication, and high flexibility compared with inorganic transistors. The electric performance was affected by organic semiconductor (OSC).

S-DNTT-10 (as one OSC material) was utilized into the OTFTs and performed well electric performance.

Our study aimed to further explore the electric characteristics of top-contact-OTFTs fabricated by the PVD method through Raman technique. High mobilities exceeding 5.5 cm2.V-1.s-1 are consistently obtained in the lab using PVD.

We have done the related tasks: (i) Performed a DFT simulation to identify the nature of molecular vibration in the measured Raman spectrum of S-DNTT-10 thin-films as shown Fig.1 (a), (ii) Achieved SERS (Surface-enhanced Raman spectroscopy) maps on the 10 nm thick Au nanostructures forming the OTFT electrodes as illustrated Fig.1 (a). (iii) Studied the changes in the OTFT performances and molecular characteristics under the electrodes after bias stress for 40 minutes using an electric measurement setup colocalized with the Raman system (Fig.1 (b)).

Firstly, we confirmed S-DNTT-10 molecular vibrational modes and we enhanced the weak Raman signal using SERS. Secondly, we measured the SERS signal on the electrodes before and after bias stress. The results show changes in the sum intensities (counts) for both the 1108-1140 cm⁻¹ band (the C-H band) and the 1325-1400 cm⁻¹ band (C=C and C-S bands). This suggests an influence of the electric field on inner and peripheral molecular bonds. Other measurements suggest that the effect could be related to the electric field strength. The stress also reduces the effective mobility, suggesting a pi-electron overlapping degradation. This could demonstrate that the degraded performance of OTFTs due to bias stress is correlated with a change of the molecular organization.

Additional comparison of SERS measurements at the source and drain electrodes will be discussed to support field strength influence.

References
Large scale self assembly of silicon Mie resonators for optical metasurfaces

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We presented a microfluidic platform to produce a pattern with particular size design within a microchannel, based on sequential capillarity-assisted Si nanoparticles assembly. The NPs assembly result is shown in Fig.1, the SEM micrograph of a randomly selected assembly area 1 and area 2 showing the deposition of single NPs is presented. The filling rate is almost 100%, and the Si NPs arrays stays well organized on the substrate after removing PMMA. This is also confirmed by AFM image shown in Fig.1 (f inset). First transmission optical measurement has been obtained and presented in Fig.1 (f) and shows an optical resonance in NIR. Other optical measurements on a larger range are in progress and will be presented.

![Fig. 1 NP assembly. SEM micrograph of a randomly selected assembly area 1 showing the deposition of single NPs (a) with PMMA matrix and (b) after removing the mask. (c) Dark field optical image of a randomly selected assembly area after removing PMMA mask. SEM micrograph of a randomly selected assembly area 2 showing the deposition of single NPs (d) with PMMA matrix and (e) after removing PMMA. (f) Extinction spectrum of area 2 assembled by SmartForce after removing PMMA. The inset picture is the corresponding AFM image for this area.](image)

References