1st INTERNATIONAL WORKSHOP ON

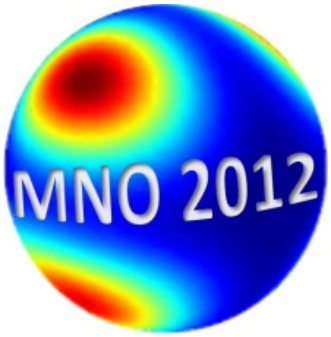
METALLIC NANO-OBJECTS:

FROM FUNDAMENTALS TO APPLICATIONS

elaboration, characterization, properties and applications

University Jean Monnet, Campus Carnot

15th-16th November 2012, Saint-Etienne, France



Book of abstracts

http://mno2012.univ-st-etienne.fr/

Organizers :
Nathalie Destouches, Aziz Boukenter, Laboratoire Hubert Curien, CNRS/Université Jean Monnet, Saint-Etienne, France
Laurence Bois, LMI, CNRS/ Université Lyon 1, France
Mohamed Bouazaoui, PhLAM, CNRS/ Université Lille 1, France
Guy Vitrant, IMEP-LAHC, Minatec, CNRS/Grenoble-INP, France

Table des matières

1. General information

Introduction

This workshop aims to provide an overview on recent advances and challenges in the development of nano-objects and their applications in materials science. Academic and industrial scientists, technologists and students from various national and international universities, institutes or companies are expected to participate in the workshop. This workshop will include a number of talks by key experts and well known speakers on the elaboration, assembly, manipulation, modeling and characterization of metallic nano-objects as well as on their applications.

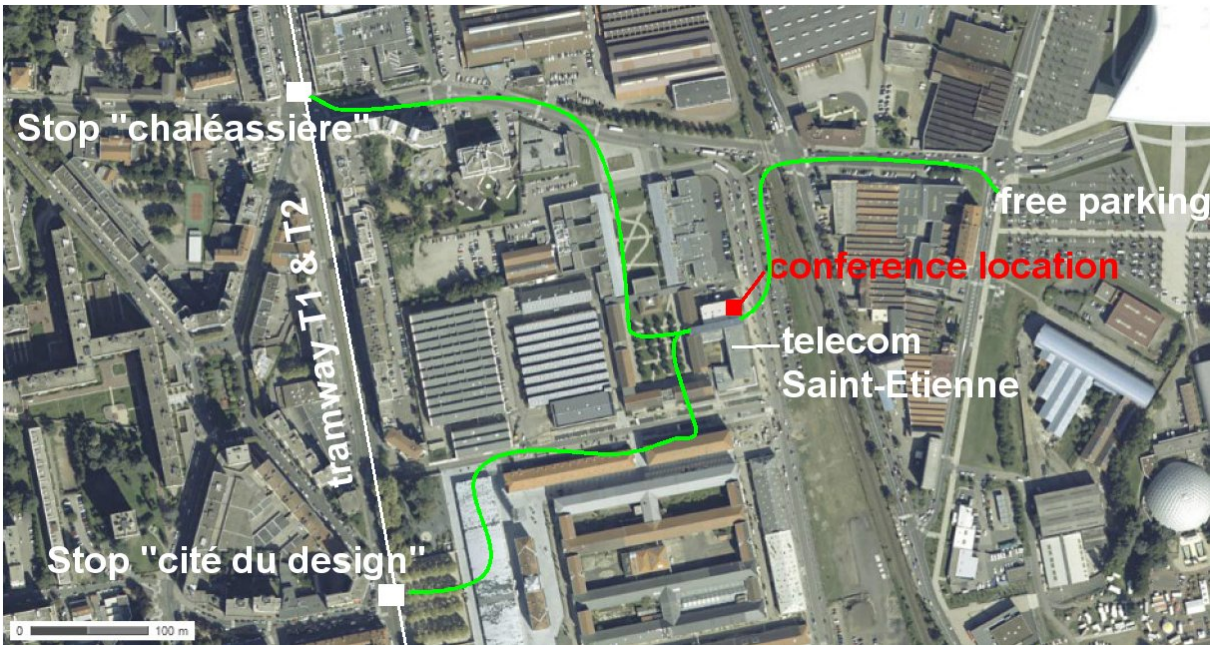
Topics

The topics of the workshop will be organised around the following themes:

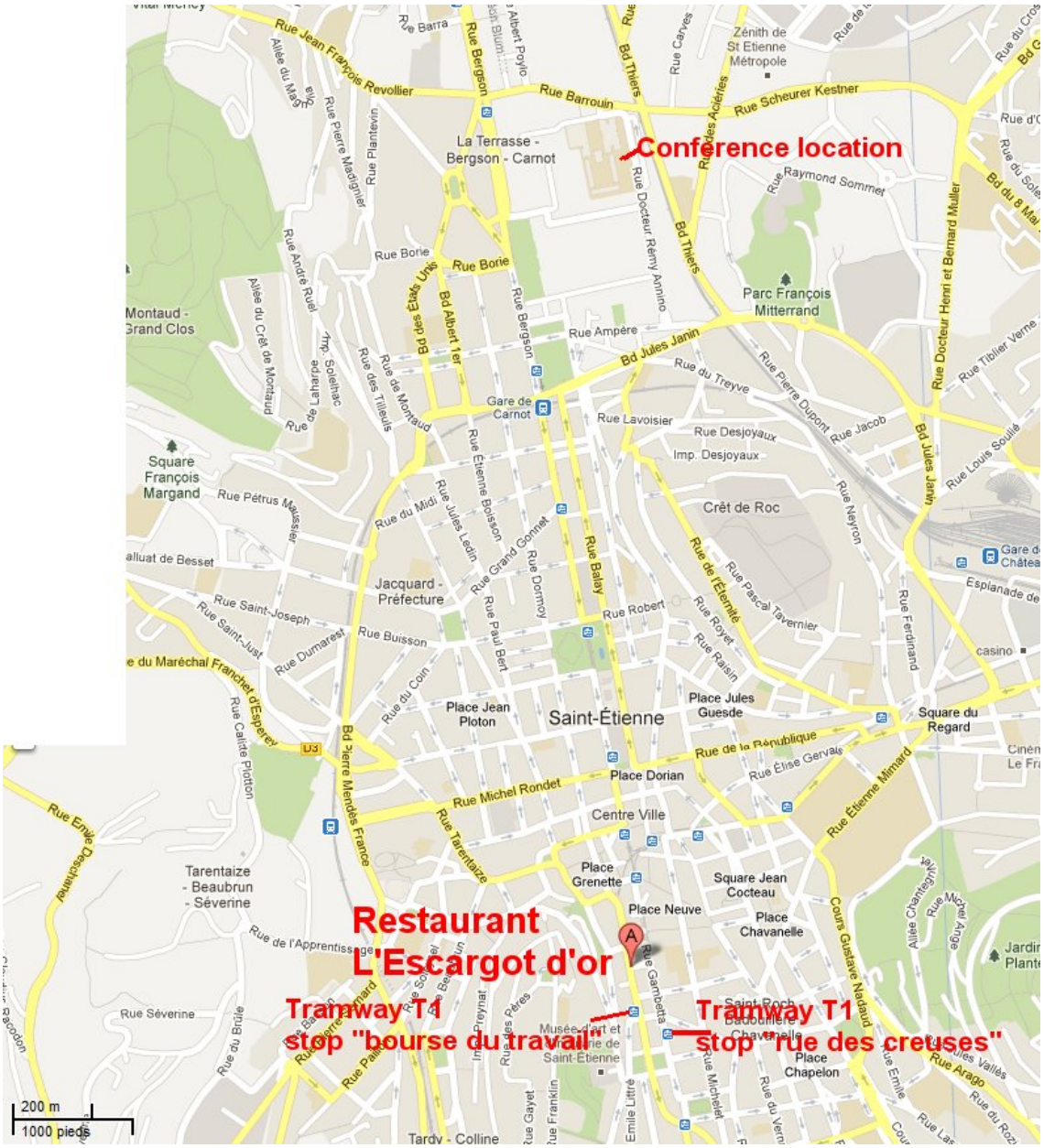
- Plasmonics and nanophotonics, non linear optics, nano-thermal effects
- Growth, reshaping and organization techniques of metallic nanoparticles and nanostructures
- Characterization and modeling of the optical properties, single metallic nano-objects, interparticle coupling
- Applications in art, catalysis, photovoltaic, nanolaser, data storage, cryptography, biology, ...

2. Practical information

18 rue Pr. Benoit Lauras 42000 Saint-Etienne



Conference room: Amphiteater J020 building TELECOM Saint-Etienne
Room for poster, lunch and coffee breaks: D03 in Building D



Dinner Thursday 15 at 8.00 pm : at L'Escargot d'Or - Restaurant Brasserie - 5 cours Victor Hugo- 42000 Saint-Etienne.

3. Programme

Thursday, November 15

1:00 Welcome

1:20 Introduction : Nathalie Destouches, Mohamed Bouazoui

First session: Optical characterization of metal nanoparticles ensembles, chairman: Mohamed Bouazaoui	
1:30	**Invited plenary conference**: Frank Hubenthal, "Noble metal nanoparticles: From fundamentals to applications"
2:10	**Invited speaker**: Pierre-François Brevet, "Second harmonic generation of metallic particles"
2:30	X. Wang, "Plasmon coupling effects on the stationary and transient optical responses of gold nanoparticle arrays"
2 :50	Anthony Aghedu, "Kinetics of anisotropic self-assembling of gold nanorods"

3:10 COFFEE BREAK

Second session: Laser-induced nanoparticles, chairman: Patrice Baldeck	
3:40	**Invited plenary conference**: Gerhard Seifert, "Femtosecond laser reshaping of metallic nanoparticles in glass - mechanisms and application potential"
4:20	**Invited speaker**: Guy Vitrant,"Metallic nanostructures for diffractive micro-optics"
4:40	Bruno Capoen, "Building nanoparticles in a matrix with a laser: several examples"
5:00	Nathalie Destouches, "Dichroic coloring of surfaces by laser-induced self-organization of silver nanoparticles"

5:20 APERITIF

Third session: Plasmonic devices, chairman: Maurizio Ferrari	
6:00	**Invited plenary conference**: Gregory Wurtz, "Active nanodevices: the next challenge for plasmonics"
6:40	**Invited speaker**: Etienne Quesnel, "Plasmonics in PV solar cells: which cell architecture for what benefit ?"
7:00	J. Bellessa, "Tamm surface plasmon laser"

8:00 DINNER

Friday, November 16

Fourth session: Metal nanoparticles in thin films, chairman: Bruno Capoen	
8:40	**Invited plenary conference**: Tetsu Tatsuma, "Plasmon-Induced Charge Separation of Metal Nanoparticles"
9:20	Lionel Simonot, "*In situ* optical monitoring during silver nanoparticle oxidation or/and reshaping"
9:40	V. Lysenko, "Nano-Ag/SiNx plasmonic substrates: fabrication, optical properties and application for cell imaging"
10:00	A. Chiappini, "Colloidal plasmonic photonic crystals"

10:20 COFFEE BREAK

Fifth session: Nanocharacterization, chairman: Guy Vitrant	
10:40	**Invited plenary conference**: Javier García de Abajo, "Graphene plasmonics"
11:20	**Invited speaker**: Florent Tournus, "Study of *small* nanoparticles by advanced TEM imaging techniques"
11:40	Zackaria Mahfoud, "Nanooptical study of structural defects of lithographed plasmonic antennas"
12:00	S.C. Laza, "Cold welding of colloidal gold nanorods"

12:20 BUFFET AND POSTER SESSION

Sixth session: Applications of metal nanoparticles, chairwoman: Nathalie Destouches	
14:00	**Invited plenary conference**: Philippe Colomban, "Light-metal nanoparticle interaction, a way to master the colour of glass and glaze since millennia"
14:40	**Invited speaker**: Laurent Dubost, "Silver nanoparticles embedded in SiOCH matrix for transparent antibacterial coating"
15:00	Christophe Lavenn, "Atomically defined thiolate gold nanoclusters for heterogeneous catalysis"
15:20	D. Vouagner, "Characterization of SERS substrates for the amplification of amorphous matrix Raman signals"
15:40	Patrice Baldeck, "Hybrid Gold nanoparticles for fluorescent imaging and photodynamic therapy"

16:00 Conclusion

Poster session

Said Bakhti, "Plasmon resonance on a single metallic axis-symmetric particle: general properties and accurate near-field extraction"

Audrey Berrier, "Optical investigation of mettalic nanoparticles at the percolation threshold"

Soma Biswas, "Reversible growth of silver nanoparticles using a biased tip of atomic force microscope"

Jean-Philippe Blondeau, "Nano second Laser or annealing precipitation and modification of silver nanoparticles monitored by on-line extinction measurements"

Nicolas Crespo-Monteiro, "Optical and structural characterization of laser-induced changes in mesoporous TiO2-Ag films"

Odile Cristini-Robbe, "First sol-gel-derived optical fibre preforms with copper and silver nanoparticles precipitated under reducing environment"

Stéphane Mottin, "Homogenization for Periodic Media & Complex Nanostructures (in Biophotonics)"

Robert Ossig, "Detecting low concentrations of pollutant chemicals in water by SERS: Combining optimised nanoparticle ensembles and SERDS"

Cherif Sow, "Calculation of temperature distribution induced by ultraviolet continuous wave laser exposure of silver-exchanged glass"

M. Tonelli, "New precursors to form gold nanoparticles in silica monoliths by direct laser-irradiation"

E. Vandenhecke, "Subwavelength arrays of silver nanoparticles for SERS applications"

A. S. Voloshko, "Modeling of nanoparticle formation in plasma discharges"

Xiaoli Wang, "Large ultrafast optical modulation by a nanoplasmonic photonic crystal cavity"

Benjamin Vial, "Engineering eigenmodes in open microstructured resonators for far infrared filtering applications"

4. List of participants

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5. Abstracts of oral presentations in the order of appearance

NOBLE METAL NANOPARTICLES: FROM FUNDAMENTALS TO APPLICATIONS

F. Hubenthal

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KEYWORDS

Plasmons, SERS, surface structuring field enhancement, local field, ablation, laser tailoring

ABSTRACT

After a general introduction in the unique optical properties of noble metal nanoparticles, I explain nanoparticle generation on substrates by Volmer-Weber growth. I demonstrate how the morphology of the nanoparticles can be precisely tailored with laser light and how this technique is exploited to optimise the nanoparticles for applications based on the local field enhancement as well as to extract the fundamental damping parameter, which has to be included in the size dependent dielectric function. In particular the latter measurements lead to a fundamentally new understanding of plasmon resonances. On the other hand, tailored nanoparticle ensembles have a wide range of applications, for example in biosensing, confocal microscopy, or for surface enhanced spectroscopy techniques. Exemplarily, I demonstrate that noble metal nanoparticles prepared by laser tailoring are suitable SERS substrates for routine trace detection of toxic PAH molecules in water [1,2].
Afterwards experiments aiming at a parallel generation of sub-diffraction sized nanostructures in fused silica will be presented. The key point of these experiments is the electromagnetic near field in the vicinity of highly ordered triangular nanoparticles on substrates, prepared by nanosphere lithography. The near field is exploited to overcome locally the ablation threshold of the fused silica substrate. For this purpose, supported triangular gold nanoparticle arrays have been irradiated with one or two 35 fs pulses of a Ti:sapphire multipass amplifier. Depending on the laser fluence and polarisation direction, sub-diffraction sized nanostructures with extraordinary shape have been generated [3,4]. Finally, first studies will be presented, in which two time-delayed pulses with orthogonal polarisation directions are applied. This strategy allows the generation of more complex predetermined nanostructures and to monitor the ablation process of the triangular nanoparticles by investigating the nanostructure evolution as a function of the time delay between the two pulses.

[1] F. Hubenthal, D. Blázquez Sánchez, N. Borg, H. Schmidt, H.-D. Kronfeldt, F. Träger; Appl. Phys. B **95**, 351 (2009).
[2] Y. H. Kwon, R. Ossig, F. Hubenthal, H.-D. Kronfeldt; J. Raman Spec., DOI 10.1002/jrs.4093 (2012)
[3] F. Hubenthal, R. Morarescu, L. Englert, L. Haag, T. Baumert, F. Träger; Appl. Phys. Lett. **95**, 063101 (2009)
[4] A. A. Jamali, B. Witzigmann, R. Morarescu, T. Baumert, F. Träger, F. Hubenthal; Appl. Phys. A, DOI: 10.1007/s00339-012-7135-8

SECOND HARMONIC GENERATION OF METALLIC PARTICLES

J. Butet, E. Benichou, N. Lascoux, C. Jonin, I. Russier-Antoine and P.F. Brevet

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KEYWORDS

Metallic Nanoparticles, Second Harmonic Generation, Field Multipoles, Nonlinear Polarization

ABSTRACT

Gold and Silver metallic nanoparticles have received a large interest over the recent years owing to their optical properties in the visible spectrum. These properties largely stem from the collective excitation of their conduction band electrons, also known as surface Plasmon (SP) resonances. The large field enhancements associated with these resonances have also triggered an interest for the nonlinear optical processes. In this context, we have investigated the different sources and separated the different multipoles contributing to the nonlinear response.

Recently, we have been able to perform studies at the level of a single gold metallic nanoparticles, performing a 3D mapping of the particle distribution in a transparent polymer matrix. Single particles and aggregates were clearly distinguished in particular with a light polarization analysis. All these studies have led us to the demonstration of sensitive plasmonic sensors making use of the quadrupolar SP resonance.

REFERENCES

[1] J. Butet *et al.*, *Phys. Rev. Lett.*, 2010, 105, 077401
[2] G. Bachelier et al., Phys. Rev. B, 2010, 82, 235403
[3] J. Butet et al., Nano Lett., 2012, 12, 1697
[4] J. Butet *et al.*, *Nano Lett.*, 2010, 10, 1717

Plasmon coupling effects on the stationary and transient optical responses of gold nanoparticle arrays

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KEYWORDS
Plasmon coupling, nanoparticle arrays, near field, far field, ultrafast optical response

ABSTRACT
Noble metals nanoparticles (NPs) exhibit the well known localized Surface Plasmon Resonance associated with the local electromagnetic field enhancement in the NPs. The electromagnetic coupling between NPs plays an important role in the spectral characteristics of the resonance, so as NP assemblies with controllable dimensions and spatial ordering have raised great interest.[1,2] We have studied experimentally and theoretically plasmon coupling effects in the stationary optical properties of ordered 50-nm gold NP 2D arrays with different interparticle distances (Fig., a, b). This study reveals the role played by electromagnetic near- and far-field coupling between neighbouring NPs as well as retardation effects. A very good agreement is found between simulation and experiment results. Furthermore, we have investigated the ultrafast transient optical response of the arrays. The simulated ultrafast transient response exhibits a global similar behaviour for all the arrays. Nevertheless, some discrepancies are observed, stemming from the interparticle electromagnetic coupling. Pump-probe spectroscopy experiments (Fig. c) confirm these predictions.

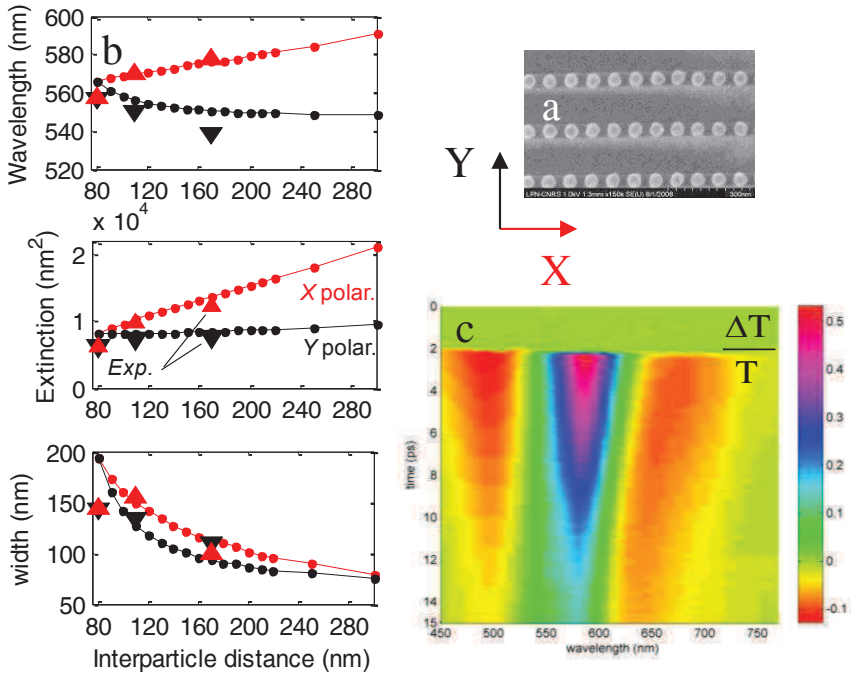

Fig. (a): SEM image of one Au-NP array. (b) Characteristics of the plasmon band (spectral location, width, amplitude) as a function of the interparticle distance in y direction (the distance is x direction is fixed at 80 nm). Triangles are experimental data. (c): Dynamics of the pump-induced relative transmission change of an array, as obtained by pump-probe spectroscopy.

REFERENCES
[1] K.-H. Su, Q.-H. Wei, and X. Zhang, Nano Lett. 3 (8), 1087-1090 (2003).
[2] P. K. Jain and M. A. El-Sayed, Chem. Phys. Lett. 487 (4-6), 153-164 (2010).

Kinetics of anisotropic self-assembling of gold nanorods

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KEYWORDS

Plasmonic nanoparticles, self-assembling, kinetic analysis

ABSTRACT

Self-assembling of nanoparticles (NPs) has become an important research issue in nanotechnologies in the last years.[1] Metal NPs can present a plasmon resonance the characteristics of which are related to their composition, size and shape. It has also been shown that this resonance is sensitive to the electromagnetic interactions between neighbouring NPs, and then to their organisation in the host medium.[2] Thus, the morphology of NP assemblies can be deduced from their optical absorption spectrum. Here we discuss a new method to analyse the kinetics of the self-assembling of gold nanorods (NRs) in aqueous solution using optical spectroscopy along with numerical calculations. Simulations based on the discrete dipole approximation (DDA) are carried out to determine the absorption spectra of different NR assemblies.[3] The method of kinetics analysis supported by numerical tools allows us to get a deep understanding of the preferential morphologic conformations of NRs at different stages of their aggregation.

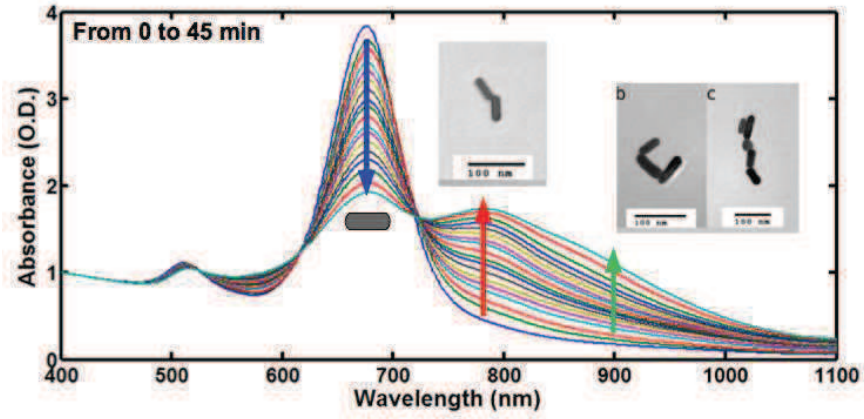

Figure 1. Kinetics of the optical absorption spectrum of 50-nm long gold nanorods over their anisotropic self-assembling

References

1. Nie, Z., Petukhova, A., and Kumacheva, E. (2009). Nature Nanotechnology, 5(1), 15–25.
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3. Draine, B. and Flatau, P. (1994). JOSA A, 11(4), 1491–1499.

FEMTOSECOND LASER RESHAPING OF METALLIC NANOPARTICLES IN GLASS - MECHANISMS AND APPLICATION POTENTIAL

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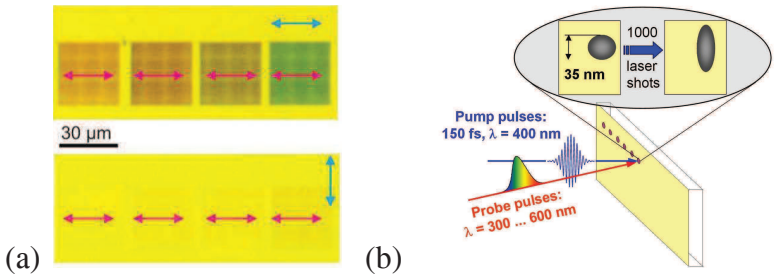
KEYWORDS
Silver nanoparticles, femtosecond laser, dichroism, optical data storage

ABSTRACT
Silver nanoparticles embedded in glasses can be been transformed to non-spherical shapes in a controlled way by successive irradiation with several hundred femtosecond laser pulses. As the orientation of the reshaped particles is defined by the laser polarization, this technique allows us to produce arbitrary dichroic microstructures in such nanocomposites (Fig. 1a). Since the discovery of this effect by our group [1], we have studied in detail the involved physical processes by various techniques including fs pump probe spectroscopy [2, 3] (Fig. 1b). In this talk I will discuss these mechanisms as well as provide an outlook to prospective applications like long-term optical data storage [4].



(a) (b)

Figure 1: (a) 4 dichroic squares obtained via fs laser irradiation, observed with parallel (top) and perpendicular (bottom) polarization of light with respect to laser; (b) schematic sketch of Pump-Probe experiment during reshaping [3]

REFERENCES

[1] M. Kaempfe, T. Rainer, K.-J. Berg, G. Seifert, H. Graener, Ultrashort laser pulse induced deformation of silver nanoparticles in glass, *Appl. Phys. Lett.* 1999, 74, 1200.

[2] A. A. Unal, A. Stalmashonak, G. Seifert, and H. Graener, Ultrafast dynamics of silver nanoparticle shape transformation studied by femtosecond pulse-pair irradiation, *Phys. Rev. B* 2009, 79, 115411.

[3] A. Warth, J. Lange, H. Graener, G. Seifert, Ultrafast Dynamics of Femtosecond Laser Induced Shape Transformation of Silver Nanoparticles Embedded in Glass, *J. Phys. Chem. C* 2011, 115, 23329.

[4] A. Stalmashonak, A. Abdolvand, G. Seifert, Optical storage of information in metal-glass nanocomposites, *Appl. Phys. Lett.* 2011, 99, 201904.

METALLIC NANOSTRUCTURES FOR DIFFRACTIVE MICRO-OPTICS

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KEYWORDS

Photo-induced micro-fabrication, diffractive optics, metallic nanostructures.

ABSTRACT

Two-photon absorption induced microfabrication techniques are routinely used in many laboratories to fabricate 2D and 3D nano-objects of various chemical natures and of almost any shape. Equipment setups are nowadays commercially available. In the last years, we implemented this technique to fabricate metallic nano structures by two-photon induced precipitation of a metallic salt, mainly silver and gold [1]. An example is shown figure 1.
We show in this paper that the high absorption of metals can be used to fabricate micro optics elements [2]. For instance a planar double micro-lines structure is easy to fabricate and is found to exhibit efficient focusing properties (figure 2) in excellent agreement with diffraction theory. This opens new opportunities to fabricate 2D and 3D diffractive optical elements.

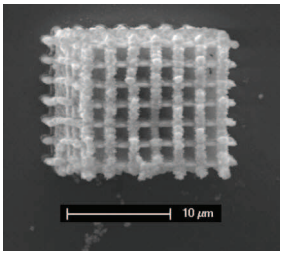

Figure 1: silver 3D "woodpile" structure of micrometer size

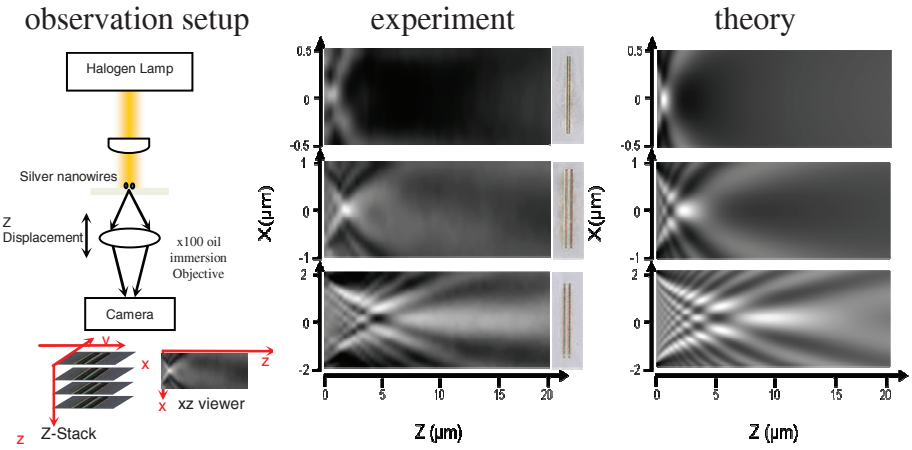

Figure 2: Light focusing by metallic double nano-lines with different separations.

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Building nanoparticles in a matrix with a laser: several examples

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KEYWORDS

Silica bulk xerogels, silicate glass, gold nanoparticles, silver nanoparticles, laser irradiation

ABSTRACT

Structuring the matter has appeared for several decades as an essential step in the quest for more and more efficient optical devices. Particularly, periodic arrangements of different refractive indices in dielectrics or polymers have allowed the arrival of the well-known photonic band gap (PBG) materials. For instance, one-dimensional PBG systems have been exploited for a long time as Bragg gratings in optical waveguides, the concept of which has been recently extended to two or three dimensions: the so-called photonic crystals. In order to improve the contrast or to give a spectral tunability to such PBG materials, it would be interesting to achieve a periodic growth of metal or semiconductor nanostructures in dielectric matrices. Furthermore, the expected nonlinear optical behavior of such nanostructures could be put to good use in all-optical devices based on power-dependent absorption or refraction. Space-structuring of nanoparticles at the micron or sub-micron scale may also have a fundamental interest in studying coupling of collective resonance effects in plasmonic systems.

While self-assembly chemical organizations of nanocrystals remain limited to predefined structures, imposed by the nature of nanoparticles and ligands, the field of photonics devices is rather interested in localized structures embedded in stable oxide matrices, like xerogels and glasses. A solution to achieve this may be found in laser irradiation methods, which allow the local growth of several types of nanocrystals in various kinds of matrices.

Our purpose is to give an overview of laser-assisted growth of metallic nanoparticles (gold or silver) in bulk silicate glasses and xerogels. Depending on the employed laser, the particles are formed near the sample surface (UV, visible light) or deep inside the silica matrix (IR light). In the second case however, ultra-short pulses are required, in order to generate multi-photon absorption since neither particle precursors nor the matrix presents a linear absorption in this wavelength range. All the presented results confirm that, when using femtosecond pulsed laser, the mechanisms of nanoparticle growth are quite different from the ones under continuous-wave conditions, where the laser-induced heat plays a major role.

Dichroic coloring of surfaces by laser-induced self-organization of silver nanoparticles

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KEYWORDS
Self-alignment, metal nanoparticles, continuous wave laser, thin film, titania, permanent color

ABSTRACT

Noble metal nanoparticles have been used since antiquity to stain glasses and create shinning metallic colors on lustered ceramics [1]. Embedded in dense glassy matrix, they have proven to be stable over centuries, and recently, femtosecond lasers have been used to spatially control the optical properties of metal nanoparticles within glasses for perennial data storage [2]. Interesting dichroic properties were obtained but few different hues were reported. Here we demonstrate that transparent coatings of mesoporous titania loaded with silver salt can be the seat of a multicolor permanent laser-induced marking.
Under continuous wave visible laser exposure of high irradiance, self-aligned silver nanoparticles can be grown below a dense titania film that acts as a protective layer as well as an interferometric coating. Nanoparticles spontaneously align along chains periodically spaced with a period that depends on the wavelength, and oriented parallel to the laser polarization. Due to a strong interparticle plasmon coupling along chains, such samples exhibit a strong dichroism whose characteristics depend on the laser exposure conditions. Thin film interferences due to the stack of the silver nanoparticles plane and the TiO_2 film also give rise to shining colors in specular reflection. Color changes and spectral variations with polarization will be characterized under various geometrical configurations. Changes in the film nanostructure and crystal phase occurring during illumination will also be shown. Such colored films appear very stable under high temperature rises or high intensity UV or visible exposures and are good candidates for colored data storage.

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PLASMONICS FOR THE DESIGN OF ACTIVE NANODEVICES

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KEYWORDS

Plasmons, nanorods, metamaterials, plasmonic crystals, non-linear optical properties.

ABSTRACT

Plasmonic nanomaterials show promise to revolutionize nanotechnology, in particular in the area of information technology. Their potential in the design of active nanodevices with the speed of photonic devices and the nanoscale dimension of semiconductor electronics, will open a new technological era not constrained by the limitations in size and speed photonics and electronics devices currently show. [1]

In this presentation we will discuss the potential of complementary plasmonic structures made of assemblies of strongly interacting nanorods[2] as well as plasmonic crystals[3] in providing effective solutions in the development of active nanodevices.

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Plasmonics in PV solar cells: which cell architecture for what benefit?

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KEYWORDS
Photovoltaïc, plasmonics, scattering, thin film solar cells.

ABSTRACT
Despite decades of research and a strong industrial background, the photovoltaic (PV) solar cells produced today are still suffering from limited conversion efficiencies slowing down their massive introduction into the energy production market. It is quite surprising that beyond fundamental limitations inherent to the physics of semiconductors, the lack of efficient sun light absorption inside the solar cells remains one of the major issues. These last years, the light trapping topic has thus attracted much attention in the PV research field showing that Optics, like Optronics, constitutes a key concern in the PV field. So far, most optical studies dedicated to PV dealt with basic AR coatings or cell surface texturing. It was done using simple chemical roughening processes or increasingly sophisticated technologies (fig. 1) for enhanced light scattering inside the solar absorber. Furthermore, the possibility to induce additional light absorption and scattering via plasmonics related effects was considered recently as a possible alternative way [1].
After an introduction on the basic principles of solar cells and their main performance limitations, this talk will review different solar cell architectures that could promote enhanced cell efficiency through plasmonics effects. When available, examples of realisation will be given to illustrate the potential of such development routes. The associated technological issues will be also discussed, keeping in mind that a solar cell is a complex multifunctional device which must absorb light, generate a bias voltage and deliver current at the same time.

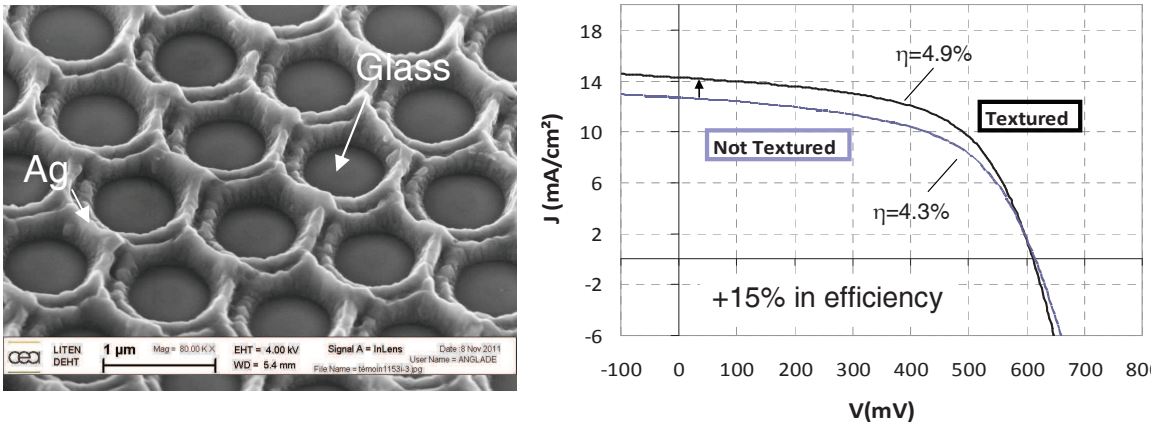

Figure 1: (left) advanced texturing of Ag back reflector on glass and (right) efficiency improvement after integration into an a-SiGe:H thin film solar cell (CEA-Liten).

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Tamm surface plasmon laser

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KEYWORDS

Plasmonics, laser, confined surface modes

ABSTRACT

Plasmonic Tamm states are interface modes formed at the boundary between a photonic structure and a metallic layer. These modes present both the advantages of surface plasmons and of microcavities photonic modes. Tamm plasmons can be spatially confined by structuring the metallic part of the system, thus reducing the size of the mode and allowing various geometries. They are very good candidates for optimizing the emission properties of semiconductor nanostructures. Recently the extraction of single photon emitted by a quantum box has been evidenced [1] in a Tamm plasmon structure. Due to the relatively low damping and the versatility of the Tamm geometries, these modes are also good candidate for new type of lasers.

We will show that lasing can be obtained for InGaAs semiconductor quantum wells embedded in a GaAs/AlAs Bragg mirror covered by silver or gold. For this purpose the sample is optically excited with a pulsed laser. For low excitation power a strong coupling regime is observed, with formation of hybrid Tamm/plasmon exciton states. When the excitation power increases a modification of the emitting diagram appear with a strong emission at k=0 at the energy of the bare Tamm mode. The typical threshold in the emitted power and the modification of the emission diagram is observed [2].

Due to the large variety of geometries of confined lasers which can be obtained with Tamm structures and the compatibility of these types of devices with electrical excitation, the Tamm laser can represent a promising type of new confined lasers.

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Plasmon-Induced Charge Separation of Metal Nanoparticles

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KEYWORDS
Localized surface plasmon resonance, photoelectrochemistry, photochromism, titania

ABSTRACT
Recently we found that photo-induced charge separation is possible at the metal nanoparticle (NP)-semiconductor (*e.g.* TiO_2) interface [1, 2]. The charge separation is caused by electron transfer from resonant Au NPs to TiO_2 (Figure 1) and promoted by plasmonic near field [3]. Various photoelectrochemical reactions can be driven by the separated charges. In the case of Au-TiO_2 systems, Au NPs are so stable that the system can be applied to photocatalysis and photovoltaic cells [2]. If Ag NPs are used, the charge separation results in oxidation of Ag to Ag^+ and reduction of, for instane, O_2. The Ag NPs form again by UV-excitation of TiO_2. The visible light-induced oxidation and UV light-induced reduction of Ag NPs can be applied to photomorphing hydrogels [4]. The process is also applied to multicolor photochromism (Figure 2) [1] and infrared photochromism [5].

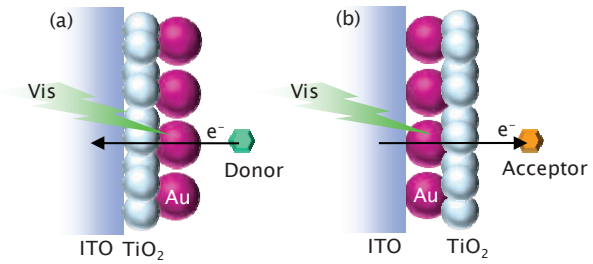

Figure 1: Plasmon-induced charge separation [2 and ChemPhysChem, 2009, 10, 766].

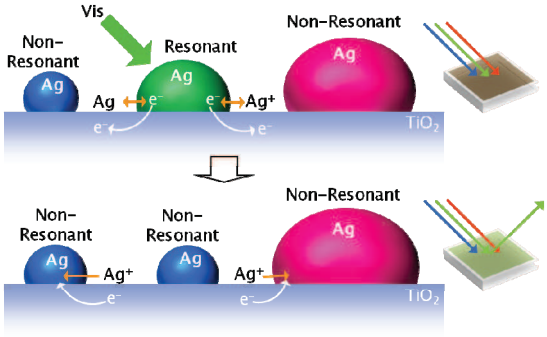

Figure 2: Multicolor photochromism.

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IN SITU OPTICAL MONITORING DURING SILVER NANOPARTICLE OXIDATION OR/AND RESHAPING

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KEYWORDS
Surface plasmon resonance, in situ optical spectroscopy, silver nanoparticles

ABSTRACT
Silver nanoparticles (NPs) synthesized by magnetron sputtering are exposed to partially ionized oxygen or/and to Ar bias plasma. *Post mortem* analyses (transmission electron microscopy, X-ray scattering) enables to access the nanostructures while *in situ* surface differential reflectance spectroscopy allows monitoring the minute changes in surface plasmon resonance (SPR) of the NPs during the treatments [1,2].
Oxygen exposure induces an important increase of both the NP size and the interparticle distance that could be explained by Ostwald ripening or migration and coalescence. The SPR is red-shifted and damped up to its complete disappearance suggesting strong chemical interactions between oxygen species and the Ag NPs as well as broad size and shape distributions. On the contrary, bias plasma treatment induces a decrease of both the NP size and the interparticle distance due to sputtering/redeposition effects along with an increase of the NP aspect ratio (height / in-plane diameter). The SPR is blue-shifted (shape effect) and damped (size effect). Finally, silver NPs are exposed to oxidation/etching cycles (figure 1). The SPR is first completely suppressed under oxygen exposure and then reappears under plasma annealing, suggesting the removal of the oxide species encapsulating pure silver NPs.

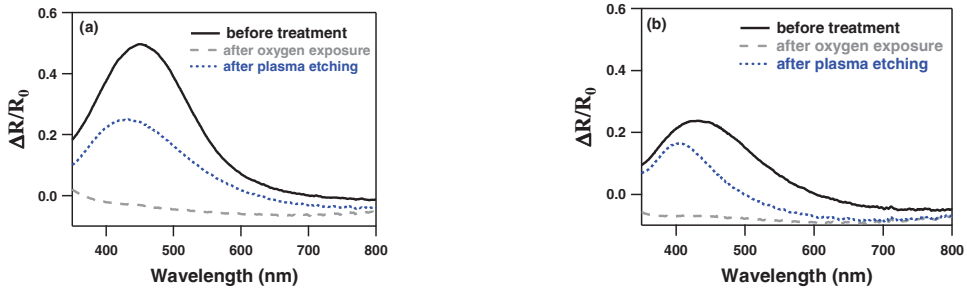

Figure 1: surface differential reflectance during oxidation/etching cycles (a) 1st cycle (b) 2nd cycle

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Nano-Ag/SiNx plasmonic substrates: *fabrication, optical properties and application for cell imaging*

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KEYWORDS

Plasmonic substrates, localized plasmons, plasmon enhanced photoluminescence, biological cell imaging

ABSTRACT

Randomly arranged Ag nano-islands were fabricated on SiNx substrates [1] as shown in Figure 1. Their experimentally studied plasmon induced optical properties are found to be in good agreement with those deduced from 3D FDTD simulations. The nano-Ag/SiNx substrates were used for plasmon enhanced photoluminescence of Si and SiC quantum dots [2, 3] due to precise tuning of their multi-polar plasmon modes to match resonantly excitation and emission bands of the quantum dots. These substrates are reported to be very efficient for significant luminescence enhancement of label-free fibroblast cells and cells labeled with the SiC quantum dots.

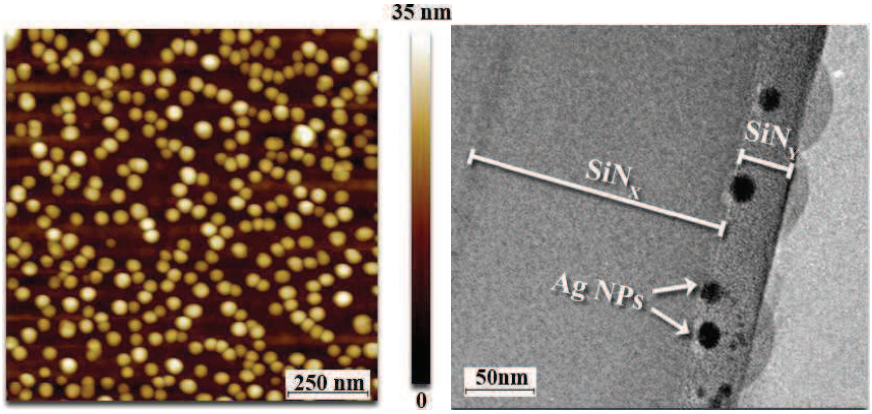

Figure 1: AFM and TEM images of the nano-Ag/SiNx plasmonic substrates

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COLLOIDAL PLASMONIC PHOTONIC CRYSTALS

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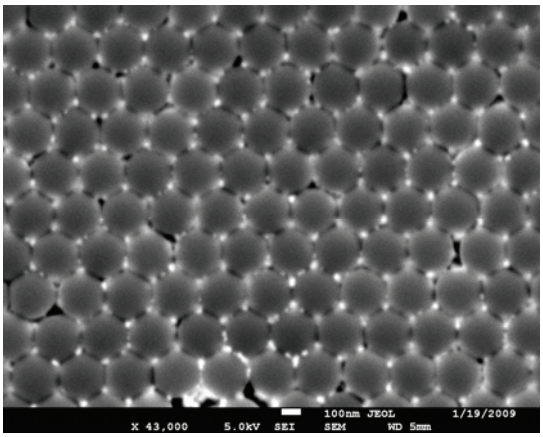
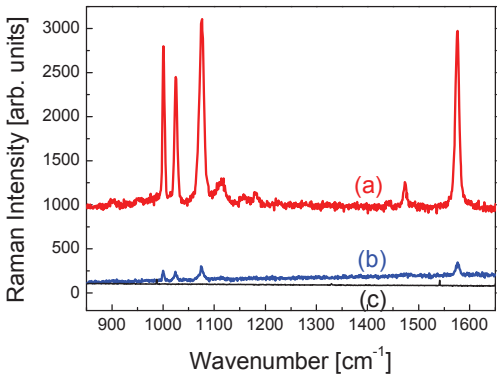
KEYWORDS: Au nanoparticles, colloids, photonic crystals, optical properties

ABSTRACT

Photonic crystals and noble metal nanoparticles are extensively studied because of their attractive properties involving photonic band gap and localized surface plasmon resonance, respectively. One appealing structure is represented by metal nanoparticles-infiltrated composite photonic crystals, which have attracted considerable attention because of their potential applications in photonics, sensing and as SERS substrates. We report on fabrication and optical characterization of colloidal plasmonic photonic crystal systems considering two different structures (i) polystyrene colloidal crystals infiltrated with gold nanoparticles, (ii) metallo-dielectric colloidal structures based on the realization of inverse silica opals and relative attachment of Au nanoparticles on the silica network of the inverse structure.



SEM image of the top surface of a polymeric opal infiltrated with Au nanoparticles



Raman spectra of 5 µl drop benzenethiol adsorbed on a metallo-dielectric colloidal structure (a); on a sputtered gold film (b); on a inverse silica opal.

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GRAPHENE PLASMONICS

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KEYWORDS

Graphene, plasmonics, nanophotonics

ABSTRACT

We will discuss the extraordinary optical properties of highly doped graphene, along with new classical and quantum phenomena involving plasmons in this material. Doped graphene can host low-energy collective plasmon oscillations with unprecedented levels of spatial confinement, large near-field enhancement, and long lifetimes, which facilitate their application to enhanced light-matter interaction, optical detection, sensing, and nonlinear optics. Graphene plasmons only exist when the carbon sheet is electrically charged, as they involve collective motion of the doping charge carriers, and their frequencies, which scale up with the doping density, can be readily controlled through electrostatic gates, thus opening a realistic avenue towards electrical modulation of plasmon-related phenemona. We will start with a tutorial description of graphene plasmons and a critical comparison with conventional noble-metal plasmons. A summary of recent experimental observations will be presented, including spatial mapping of confined graphene plasmons and spectroscopic evidence of plasmon-mediated resonant absorption [1]. Theoretical descriptions of graphene plasmons will be examined, ranging from classical electromagnetic theory to first-principles quantum-mechanical approaches. We will elucidate the conditions under which quantum nonlocality shows up in the optical response of this material. The interaction with quantum emitters (e.g., quantum dots) placed in the vicinity of the carbon sheet will be shown to reach the strong-coupling regime and potentially serve as a robust platform for quantum-optics devices that can achieve temporal control of plasmon blockade, Rabi splitting, super-radiance, and other quantum phenomena via electrostatic doping [2]. Classical devices for infrared spectroscopy, sensing, and light modulation will be also discussed [3]. Prospects to extend these phenomena to the visible and near-infrared regimes will be examined. These advances in graphene constitute a viable realization of strong light-matter interaction, temporal control of quantum phenomena, and ultrafast electro-optical tunability in solid-state environments, thus bringing the expectations raised within the field of plasmonics closer to reality.

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Study of small nanoparticles by advanced TEM imaging techniques

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KEYWORDS

Bimetallic magnetic nanoparticle, CoPt, FePt, corrected TEM, HREM, HAADF-STEM

ABSTRACT

Small nanoparticles (NPs) with sizes less than typically 4-5 nm are fascinating objects with surprising physical, chemical and structural properties. The detailed study of their structure requires high spatial resolution techniques, and Transmission Electron Microscopy (TEM) is then a privileged tool, especially using recent aberration-corrected High Resolution TEM and Scanning TEM (HAADF mode : High Angle Annular Dark Field imaging) instruments. We will focus here on bimetallic magnetic NPs, such as CoPt and FePt f.c.c. alloys, which are potential candidates for ultra-high density magnetic storage devices [1]. It is well established that their crystallographic structure controls their magnetic properties: in particular, the extremely high magnetocrystalline anisotropy of the bulk $L1_0$ tetragonal phase originates from the ordered stacking of pure Co (or Fe) and Pt atomic planes in the [001] direction [2]; the degree of ordering of NPs has then to be characterized precisely [3].
This work will present TEM investigations on annealed CoPt and FePt NPs as small as 2 nm in size, showing the coexistence of different atomic arrangements, some of them being predicted but never observed at this scale (ordered multiple-twinned NPs with five-fold symmetry) or unexpected (i.e. $L1_0$ multi-variants) [4].

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Nanooptical study of structural defects of lithographed plasmonic antennas

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KEYWORDS

Nanooptics, Electron Energy Loss Spectroscopy, Cathodoluminescence, Surface Plasmon Resonance

ABSTRACT

We studied the optical response of gold and silver nanorods antennas made by EBL by electron energy-loss spectroscopy (EELS) and cathodoluminescence spectroscopy (CL) in a scanning transmission electron microscope (STEM) at the nanometre scale. For the sake of benchmarking the nanoantennas performances, we also performed EELS on chemically grown rods.
The first finding is that like chemically grown rods, lithographed ones also have stationary surface plasmon resonances, which depend on their size and aspect ratio. A systematic study on tens of nanoantennas allowed us to derive precise dispersion laws, that exhibit large fluctuations compared to that of chemically grown ones. In particular, we will present results obtained on gap-coupled rods having the same longitudinal coupling behaviour than these chemically grown one, see [2] for an example.
The second finding is a unique behaviour of EBL systems. We show that the intrinsic roughness of EBL nanorods leads to the emergence of structural defects of a few nanometers. These defects can be related to anomalies in the EELS and CL spectra in the form of localised variation of intensity. Such features can be related to the loosely defined “hot spots” that are predicted in the literature and supposed to influence many physical properties (SERS, …).
We will show how these local variations surprisingly appear at different energies but same location and point out the physical significance of the different behaviour of EELS and CL.

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COLD WELDING OF COLLOIDAL GOLD NANORODS

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KEYWORDS
Gold nanorods, nanowire, self-assembly, cold welding, plasmon resonance

ABSTRACT

The increasing interest for the self-assembling of metallic nanoparticles is due to their potential use in the construction of functional nano/micro-systems for sensing, photonics, biomolecular electronics, etc[1]. For these reasons in the last years the self-assembling is a major research theme in nanotechnology. One of the main factors determining the final geometry of the resulting assembly is the nanoparticle's shape. At present, among the anisotropic metallic nanoparticles, there is considerable interest for gold nanorods (GNRs) due to their potential for bidirectional ordering[2].
Here we demonstrate a new, fast and simple way to produce long chains of end-to-end assembled GNRs in water. Moreover, due to its ability to induce cold welding[3] of colloidal GNRs, this assembling strategy has possible applications to the bottom-up production of gold nanowires[4] with micrometric length.

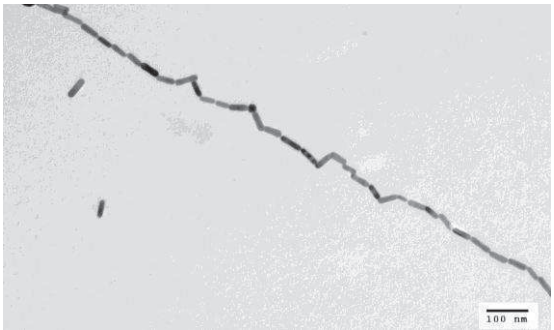
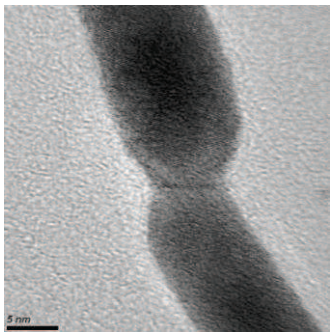
a).  b). 

Figure 1: a).TEM photo of Au nanowire formed by self-assembling of GNRs,b).HRTEM detail of interparticle connection.

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LIGHT-METAL NANOPARTICLE INTERACTION, A WAY TO MASTER THE COLOUR OF GLASS AND GLAZE SINCE MILLENNIA

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KEYWORDS

Nanoparticle, silver, copper, gold, history, Raman, resonance

ABSTRACT

High temperature firing under a reducing atmosphere was the first technique to prepare glass and pottery artefacts. Empirically controlled redox reactions allow producing metal nanoparticles that interact with light in a very complex way by two different phenomena: i) the light absorption of isolated particles in a dielectric matrix (e.g. a silicate glass) is strong for the plasmon and for high energy wavelengths leading to yellow to red colour, ii) the Bragg diffraction arising from interference driven by alternation of layers with or without metal nanoparticles; the later phenomenon gives very vivid shining from blue to gold colour but requires a very specific orientation of the observer eyes vs. the artefact and the source of light. The history of lustre pottery and yellow/red coloured glass obtained by controlled dispersion of copper, silver gold metal nanoparticles is reviewed since the Neolithic times. Representative examples of materials, analysed by (High resolution) Transmission Electron (TEM) and Optical (OM) Microscopy are presented. Emphasis is given to the Raman analysis of metal particles containing glassy silicates, especially to the Volume Enhanced Raman Scattering (VERS), a phenomenon rather similar to the Surface Enhanced Raman Scattering (SERS) that permits to detect the Raman signature of molecule traces interacting with a metal nanoparticle.

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Silver nanoparticles embedded in SiOCH matrix for transparent antibacterial coating

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KEYWORDS

Silver nanoparticle, Antibacterial coating, thin film

ABSTRACT

Silver is a well known antibacterial agent used for various applications. However its very strong activity may induce unwanted effects because of its cytotoxicity for example. The way it is used and applied must then be well controlled. The aim of the project Actiprotex was to develop antibacterial textiles to be used in food industry or in medical surroundings like bed sheets for hospitals. HEF worked on vacuum deposited films able to adjust the antibacterial activity against *Listeria innocua* LRGIA 01 without any colour change of the textile and able to sustain industrial cleaning process. Although the specifications associated to the cleaning process at 90°C were not reachable, we have proposed a range of thin films able to exhibit well-controlled antibacterial activity [1, 2].

The thin film materials developed in this study are based on silver nanoparticles imbedded in SiOCH matrix. Several thin films exhibiting different silver nanoparticles densities and SiOCH matrix thicknesses were deposited using PVD magnetron sputtering and capacitive parallel plate PECVD technologies associated in the same vacuum chamber. Thin film materials were deposited simultaneously on textile and glass slides mounted on a rotating substrate holder. The target was to find the relevant quantity of antibacterial agent to obtain an acceptable and stable antibacterial activity against *Listeria innocua* LRGIA 01. ToF-SIMS and XPS tools were used to measure the silver content and density profile in the SiOCH matrix. TEM observations showed different densities and aggregate of particules when the power applied on sputtering cathode was changed.

Encapsulation layers were added on top of the active films to protect it from mechanical abrasion or scratches and reduce chemical reaction during cleaning process. These stacks were tested with the same bacteria but still showed an antibacterial activity although the active layer was buried below dense film up to 1µm thick.

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Atomically Defined Thiolate Gold Nanoclusters for Heterogeneous Catalysis

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KEYWORDS: Thiolate gold nanoclusters, synthesis, absorption, magnetism, catalysis

ABSTRACT

Gold nanoparticles have been demonstrated to exhibit catalytic activity in many chemical processes.[1] However, fundamental investigations on the structure-catalytic activity relationships still lag behind, partly due to the polydispersity issue of gold nanoparticles. Indeed polydisperse particles obscure the interesting size-dependent catalytic activity of nanogold and preclude an in-depth understanding of the origin of this size dependence. Recently, atomically monodisperse, thiolate-capped Au nanoclusters (denoted as $Au_n(SR)_m$) have been successfully isolated and their catalytic properties have been demonstrated.[2] These well-defined gold clusters hold promises as a new generation of catalysts and, more importantly, permit in-depth studies on the subtle correlation of structure and catalytic activity, since these nanoclusters are well defined and their structures start to be solved.[3]

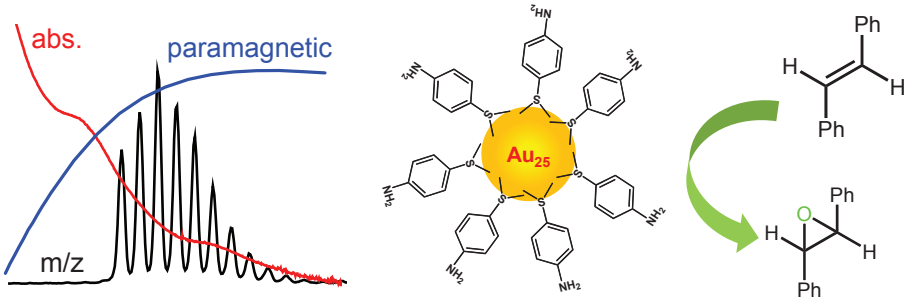

Figure 1: $Au_{25}(SPhNH_2)_{17}$ nanoclusters.

To investigate the influence of the size, the type of ligands at the surface and also the support effect different nanoclusters have been synthesized. Here we present the synthesis of new clusters made of 4-aminothiophenol ($HSPhNH_2$). Among them $Au_{25}(SPhNH_2)_{17}$ have been isolated and fully characterized by mass spectrometry, X-ray diffraction and XPS. Moreover these clusters exhibit absorption bands and a paramagnetic behaviour related to their molecular state. Catalytic activity for oxidation of alkene and alcohol derivatives of these colloidal or supported clusters were investigated and compared to the commonly used $Au_n(SCH_2CH_2Ph)_m$ nanoclusters.

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CHARACTERIZATION OF SERS SUBSTRATES FOR THE AMPLIFICATION OF AMORPHOUS MATRIX RAMAN SIGNALS

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KEYWORDS
Raman scattering, SERS, sol gel TiO_2 films, metallic nanoparticles, klarite substrates

ABSTRACT

Signals in telecommunication optical fibers are attenuated due to the presence of impurities (scattering, absorption…) and need regular amplifications. A widely used technique developed to compensate for these losses is Erbium Doped Fiber Amplifier (EDFA). Raman amplification, based on the stimulated Raman scattering process, is an alternative to rare earth doped fiber amplifier leading to the Raman scattering cross section optimization of the optical fiber material. The surface plasmon effect of noble metallic nanoparticles (NP-Me) can be used to increase the yield of inelastic scattering mechanisms. In fact, the electromagnetic field strengthening of light waves in the vicinity of these NP-Me can enhance the Raman signal of about a 10^6 factor near their surface (Surface Enhanced Raman Scattering or SERS).

This work is based on the characterization of SERS substrates for the amplification of amorphous matrix Raman signals [1-2]. An amorphous film of TiO_2 was deposited by the sol gel process on several nanostructured substrates such as klarite® (commercial substrate) and nanostructured silver films. TiO_2 was chosen because Raman bands were intense and easily recognizable. Results of SERS measurements are discussed in terms of the surface plasmon resonance (SPR) position, excitation wavelength and TiO_2 film thickness (SERS range).

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HYBRID GOLD NANOPARTICLES FOR FLUORESCENT IMAGING AND PHOTODYNAMIC THERAPY

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KEYWORDS
Gold nanoparticles, polymers doped with photoactive molecules, fluorescence, photodynamic therapy

ABSTRACT

We will review our work on hybrid Gold nanoparticles (GNP) that are coated with polymers bearing photoactive molecules optimised for their fluorescence or PDT activity. Our first goal in using GNP is to load a large density of photoactive molecules onto a biocompatible nanoplatform. Our second goal is to optimize the molecule GNP interaction to improve the photoactive properties.
In this project GNP have typical dimensions in the 50-100 nm that are suitable for in vivo imaging and therapy. Their geometrical shapes included spheres, rods, bipyramids and stars. The spherical shape is efficient only when a spacer is used to maintain a minimum distance between the photoactive molecule and the metallic surface. However, more elongated shapes, or tipped shapes can be used for a direct grafting of photoactive molecules if their transition dipole moments are maintained perpendicular to the surface (J-aggregate type of interaction between the GNP and molecules). We will report on optical spectroscopy, fluorescence imaging, cell uptake, cytotoxity, and PDT action of several type of polymers coatings and photoactive dye loading.

6. Abstracts of poster presentations by alphabetical order of first author

Plasmon resonance on a single metallic axis-symmetric particle: general properties and accurate near-field extraction

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KEYWORDS

Plasmon resonance, metallic nanoparticle, null-field method, pole finding algorithm

ABSTRACT

Metallic nanoparticles are known for their specific optical properties, and are widely used in the fields of biological and chemical sensing, nano-photonics and for surface enhanced Raman spectroscopy (SERS). The main interest of these particles relies on their ability to exhibit localized surface plasmon resonances in the visible spectrum in the case of noble metals such as gold and silver. Modeling the nanoparticles optical properties can confirm some experimental results or predict the position of plasmon resonances depending on particle size and shape.
We implement a semi-analytical approach based on Maxwell's equations in order to study the light scattering by non-spherical particles. The null-field method [1] is particularly well suited to axis-symmetric particles and consists to rewrite the scattering problem in a matrix form. Various scattering parameters can then be computed as optical cross-sections and near-field. We propose an original numerical method, based on a previous study [2], to extract accurately the characteristics of plasmon resonances (position and bandwidth as well as the pure plasmon field) directly from a few computations of scattering parameters. This method is first applied to silver spheres, for which we study the evolution of different resonance modes depending on the particle size, and the plasmon near-field distribution for each mode (Fig. 1). We then study the degenerated dipole modes in the case of small spheroids thereby proposing a general physical approach to characterize the plasmon resonances.

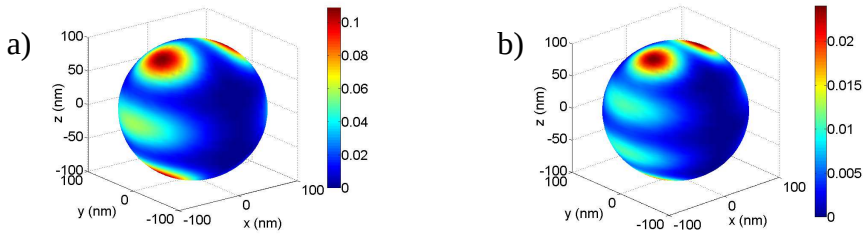

Figure 1: plasmon field norm of the a) third and b) fourth order resonances in the case of a 100 nm radius silver sphere with a z-directed and x-polarized incident plane wave.

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OPTICAL INVESTIGATION OF METALLIC NANOPARTICLES AT THE PERCOLATION THRESHOLD

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KEYWORDS
Metallic nanoparticle, ellipsometry, percolation threshold

ABSTRACT

When a metal is evaporated onto a dielectric surface, the metallic atoms start to cluster, and at first form isolated nanoparticles. When the coverage of the metal on the surface increases, the nanoclusters start to percolate and the surface reaches a finite conductivity value [1]. Eventually the layer becomes complete and reaches the bulk properties of the metal after a certain deposited thickness. Interesting optical properties of the metallo-dielectric composite are observed close to the percolation threshold.

Below this threshold, all the nanoparticles are isolated and support particle plasmons, shifting to lower frequencies as the size of the particles increases. Above the percolation threshold, the metallic layer starts to conduct and a Drude contribution to the permittivity is introduced. The combination of the particle plasmon with the Drude contributions gives rise to a peak in the real part of the permittivity of the metallo-dielectric complex [2]. The maximum value of the permittivity is linked to the sharpness of the plasmonic resonances.

In this work we investigate the optical properties of metallo-dielectric complexes by variable angle spectrometric ellipsometry (VASE). The samples are prepared using gold seeds on a substrate made of silicon with a 200 nm thick layer of SiO_2. The Au seeds are prepared by depositing Au nanoparticles onto the SiO_2 layer. Au or Ag films are subsequently evaporated using an e-beam heated effusion cell. Different evaporation rates and substrate temperature are used. Atomic force microscopy (AFM) measurements characterise the topography of the samples. We report on the evolution of the permittivity as a function of the nominal film thickness.

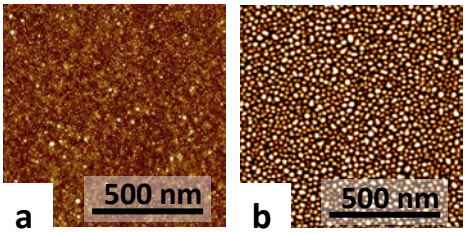

Figure 1:AFM pictures of two samples after deposition of a Silver film.

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REVERSIBLE GROWTH OF SILVER NANOPARTICLES USING A BIASED TIP OF ATOMIC FORCE MICROSCOPE

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KEYWORDS

Thin film, silica, silver nanoparticle, atomic force microscope

ABSTRACT

Metal nanoparticles have a number of potential applications in inorganic catalysis, micro and nano-electronics, opto-electronics devices and biosensors because of its tunable size and shape. For most of the abovementioned technological applications, it is necessary to precisely control the growth and positioning of metal nanoparticles at a desired location on the surface. There are different techniques for controlled nano-patterning such as electron beam lithography, optical lithography but all these processes require development steps, which make these techniques time consuming. In contrast to these lithographic processes, atomic force microscope (AFM) based lithographic technique is a simple one-step process and at the same time the image of the patterned surface can be acquired after the manipulation using the same tip. Among different AFM based lithographic techniques, oxidation lithography using a properly biased AFM tip is commonly used for controlled patterning at nanoscale. Even though AFM-based electrical oxidation of materials is not a new technique, there are only a few reports of the AFM induced controlled reduction of nanoparticles on the surface [1].
In this work we report on a process of AFM-induced (and controlled) reduction of metal ions to metal nanoparticles on mesoporous silica thin films. The process does not involve any ink, but relies on the local reduction of $AgNO_3$ salt already present in mesoporous silica films. The latter have been elaborated by a sol-gel way, dip coated and calcined before being impregnated with the silver salt solution. Silver nanoparticles have been successfully grown using an electrochemical reduction reaction controlled by the applied bias between the AFM tip and the sample. Both positive and negative tip biases have been used. The metallic nanoparticles have been characterized by Kelvin force microscopy (KFM). It has been shown for the first time (to the best of our knowledge) that AFM based lithography can be used for the successive reduction and oxidation of silver nanoparticles leading to the growth, complete removal and regrowth of silver nanoparticles at a specific location on the surface.

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Nano second Laser or annealing precipitation and modification of silver nanoparticles monitored by on-line extinction measurements

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We have investigated the effect of nanosecond laser irradiation at 532 nm or annealing on precipitation of Ag nanoparticles (NPs) in soda lime glasses doped with silver after Ag+-Na^+ ion-exchange process. Formation and subsequent modification of Ag NPs during laser irradiation or annealing were studied by on-line extinction measurements making use of the localized surface plasmon resonance (LSPR). These investigations were further completed using scanning and transmission electron microscopies to examine the average size and distribution of nanoparticles within the sample. It has been shown that formation of NPs, its rate and their size strongly depend on the fluence and the total number of deposited laser pulses or the annealing temperature. It has been found that Ag NPs are formed after some specified number of pulses and they rapidly grow in size and number until some maximal value of extinction has been reached. Further irradiation of such samples only results in destruction of precipitated NPs due to the photo breakup, laser ablation and migration of Ag ions and atoms outside the laser irradiated area. Moreover, due to strong irradiation the Further irradiation of such samples only results in destruction of precipitated NPs due to photobreakup, laser ablation confirmed by strong plasma emission observation. Moreover, due to strong irradiation,the host matrix can also be affected by changing its refractive index which manifests as the blue shift of the LSPR.

Optical and structural characterization of laser-induced changes in mesoporous Ag:TiO_2 films

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KEYWORDS
Photochromism, thin film, titania, silver nanoparticles, color

ABSTRACT

Due to their surface plasmon resonance silver nanoparticles are known to absorb visible light and give glasses various colors. Grown in mesoporous titania films, they give the material a photochromic behavior that can be used to produce rewritable data carriers[1]. On the one hand, UV light initiates the photocatalytic reduction of silver thanks to the release of electrons by titania and leads to the growth of silver nanoparticles. On the other hand, visible light is usually used to change the nanoparticle size distribution via the photoexcitation of electrons on the metallic nanoparticles and their stabilization within the surrounding matrix. In this study, we characterize three distinct behaviors of such Ag:TiO_2 films occurring in different intensity ranges for visible light: a change in the film hue due to a modification in the size distribution of silver nanoparticles, a bleaching caused by the oxidation of nanoparticles and a well-controlled engraving of the film surface due to crystallization of titania submitted to the plasmon-induced nanoparticles heating.

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First sol-gel-derived optical fibre preforms with copper and silver nanoparticles precipitated under reducing environment.

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KEYWORDS

Metal nanoparticles, bulk glass, reduction process, size control

ABSTRACT

From now on, the major efforts in the synthesis of metallic nanoparticles inside a bulk silicate glass are based on the melting process. However, concerning the synthesis of pure silica, the sol-gel route provides a convenient low-temperature method, able to yield bulk matrices for various doping species and especially for nanoparticles. Yet, it is to be noted that the achievement of sol-gel dense silica monoliths without cracks remains a challenge, recently taken up by our team [1]. Furthermore, except for very few works [2], sol-gel glassy samples doped with noble metal nanoparticles have been limited to powders or thin films. We present here, for the first time to our knowledge, a simple method to yield the precipitation of metal NPs inside a bulk silica optical fiber preform.

Ionic copper- or silver-doped dense silica rods have been preliminary prepared by first loading sol-gel porous silica xerogels with ionic precursors and then sintering them up to the dense state. The precipitation of Cu or Ag nanoparticles was achieved by heat-treatment under hydrogen atmosphere followed by annealing under air atmosphere. The surface plasmon resonance bands of copper and silver nanoparticles have been clearly observed in the absorption spectra. The widths or the spectral positions of these bands were found to depend slightly on the particle size, which could be tuned by varying the annealing conditions. To confirm spectroscopy results, transmission electron microscopy showed the formation of spherical copper nanoparticles in the range of 3.3-5.6 nm. On the other hand, in the case of silver, both spherical nanoparticles in the size range 3–6 nm and nano-rods were detected.

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Homogenization for Periodic Media & Complex Nanostructures (*in Biophotonics*)

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KEYWORDS

Nanoparticle, Absorbing Nano-objects, Small Animal Imaging and Spectroscopy, Far-field Optical Tomography, Homogenization, Partial Differential Equation (PDE).

ABSTRACT

The mathematical tools for the up-scaling from nano, micro to macro in “periodic media” are considered in the use of multifaceted nano-objects with a special mention to *in vivo* biophotonics (functional imaging with femtosecond or continuous laser) where biological tissues are highly heterogeneous media at the nanoscopic, microscopic and macroscopic scales.

The light absorption in a tissue with nano-objects could be modeled by the Helmholtz equation :

$$-\Delta u_{\varepsilon,\delta,\omega} + q(x_1/\varepsilon)\, u_{\varepsilon,\delta,\omega} = f \qquad (1)$$

ε and δ (small parameters <1) describe the periodic medium, and ω^{-1} (small parameter <<1, function of the wavelength) is the ratio between the scattering coefficient and the absorption coefficient.

Usually these two constant homogenized parameters [1-3] have been used with the equation 1. This communication discusses the limitations of this approach in the case of this stationary case (elliptic PDE) [1] and also the time-resolved case (parabolic PDE).

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Detecting low concentrations of pollutant chemicals in water by SERS: Combining optimised nanoparticle ensembles and SERDS

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KEYWORDS

SERS, SERDS, silver nanoparticle

ABSTRACT

The detection of molecules is an important task in many fields of modern science. One prominent example is the detection of pollutant chemicals, e.g. trace amounts of molecules in water which are toxic to biota. One large group of pollutant chemicals are polycyclic aromatic hydrocarbons (PAHs). PAHs dissolve in water only in very low concentrations, mainly because of their high octanol/water coefficient. Although the concentrations are very low, the molecules are extremely dangerous due to bioaccumulation in aquatic organisms. For a reliable trace detection of these molecules a technique is desired which is, both, capable to measure small concentrations and easy to apply. For this purpose we have combined shifted excitation difference Raman spectroscopy (SERDS) with surfaced enhance Raman spectroscopy (SERS), exploiting the superior optical properties of supported noble metal nanoparticle ensembles.
The nanoparticle ensembles, which serve as SERS substrates, have been prepared under ultra high vacuum conditions by Volmer-Weber growth. The morphology and thus the optical properties of the nanoparticles have been tuned in situ to perfectly match the excitation wavelength of the used diode laser system.[1] The diode laser is capable to generate two slightly different emission wavelengths ($\Delta\lambda \approx 0{,}5$ nm) each with a spectral width of ≈ 10 pm which is ideal for SERDS. This technique enables the removal of the strong flourescence background common for SERS and, thus, improves the overall signal quality and the signal to noise ratio significantly.
We demonstrate, that SERDS in combination with SERS is an ideal tool for the detection of low pollutant concentrations in water.[2] In addition, we show that for an optimum SERS signal it is essential to tune the optical properties of the metal nanoparticle ensembles in the vicinity of the excitation wavelength. For example, for of-resonance nanoparticle ensembles, the limit of detection (LOD) for pyrene is in the order of several tens of nanomol. In contrast, if the plasmon resonances coincides with the excitation wavelength an LOD of 2 nmol/l is feasible. Experimentally, an concentration of 6 nmol/l for pyrene and 4 nmol/l for flouranthene has been measured.

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J. Raman Spec., DOI 10.1002/jrs.4093 (2012)

Calculation of temperature distribution induced by ultraviolet continuous wave laser exposure of silver-exchanged glass

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KEYWORDS
Silver-exchanged glass, temperature distribution.

ABSTRACT

Silver nanoparticles (NPs) embedded in glass matrix have attracted much interest because they confer optical properties to the glass that can be adjusted by varying the size, shape and packing density of the particles. We are previously demonstrated the growth of silver NPs in silver-exchanged soda-lime glasses by ultraviolet (UV) continuous wave (cw) laser irradiation[1]. As reported elsewhere[2-3], this kind of cw irradiation leads to the formation of micro-lenses, due to local melting of the glass. Indeed, due to the locally high absorption of light, the glass is heated to temperatures higher than the glass transition temperature and after cooling, maintains the shape of a liquid droplet, which behaves as a micro-lens.
In this work, we present the calculation of the temperature distribution induced by the irradiation of the glass which explains the shape of the droplet observed in our samples. Two parameters are required to perform the calculation: thermal conductivity and absorption coefficient of the glass. Since the measurement of the absorption coefficient remains tricky, it has been deduced from the calculations and then the temperature profile was optimized. From surface profile measurements, we determine the experimental radius of the micro-lenses for various powers. Finally, we calculate the temperature distribution of our samples for various powers. The maximum temperature, obtained in our case, varies between 1190 K and 1380 K for power from 100 mW to 130 mW, which is suitable for the formation of glass liquid droplets.

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New precursors to form gold nanoparticles in silica monoliths by direct laser-irradiation

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KEYWORDS

Gold precursors, silica xerogels, gold nanoparticles, laser irradiation

ABSTRACT

A solvent-free and laser-assisted growth of gold nanoparticles (Au-NPs) from both Au (III) and Au (I) precursors within a silica monolith is reported. The novelty of the synthetic method lies in that Au-NPs, about 20 nm in diameter and well dispersed in the matrix, were obtained with no need of both reducing and capping agents. Moreover, the described laser-assisted synthetic procedure made it possible to achieve reproducible 2D and 3D patterns of Au-NPs. For this purpose, suitable Au (I) and Au (III) precursors, soluble in dichloromethane, were easily prepared following a well-known procedure.

The mesoporous silica matrix was first loaded with the precursors *via* a simple impregnation and then irradiated using either a continuous laser (λ = 266 or 532 nm) or a pulsed laser (λ = 800 nm; pulse duration: 120 fs; repetition rate: 1 KHz). In all cases, a photothermal gold reduction was observed. The reduction of the precursors was followed *via* Raman spectroscopy and UV-Vis absorption spectroscopy in order to compare the mechanism of Au-NPs formation when different lasers and wavelengths of irradiation are employed. Moreover, the Au-NPs characterization was performed by means of UV-Vis absorption spectroscopy, X-Ray Diffraction and Transmission Electron Microscopy.
Finally it was proved that the excess of gold precursors can be removed after the Au-NPs synthesis by a simple washing of the monolith with a few immersions of this latter in the pure solvent.

The stability of the Au-NPs was further tested by a series of heat-treatments up to 500°C, showing that the silica monolith acts as an effective support to prevent the agglomeration of the nanoparticles.

SUBWAVELENGTH ARRAYS OF SILVER NANOPARTICLES FOR SERS APPLICATIONS

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KEYWORDS
Nanoripples, silver nanoparticles, Surface Enhanced Raman Scattering

ABSTRACT

Planar arrays of metallic nanostructures such as nanoparticles or nanowires periodically aligned on dielectric surfaces are ideal for fundamental studies of coupling and ordering phenomena as well as for applied research. Especially nanoparticles both isolated and near-field coupled which act as nanoantennas, permit the enhancement of the absorption, fluorescence and Raman scattering of molecules via the excitation of localized surface plasmon resonances responsible for the strong enhancement of the local field (and of the Raman scattering in SERS). We present a "bottom-up" technique for the elaboration of large scale arrays of metallic nanoparticles (Figure 1). The process includes the nanopatterning of dielectric surfaces by off-normal ion erosion and the deposition of metallic nanoparticles at glancing incidence. Their optical properties exhibit a strong dependence on the light polarization, which can be interpreted as the consequence of both the in-plane spatial organization of the particles and their shape anisotropy. Preliminary SERS experiments made with randomly oriented bipyridine molecules adsorbed on such organized surface at different excitations wavelengths and for two polarizations (parallel and perpendicular to the particles chains) highlight firstly the strong enhancement of the signal compared to a random distribution of nanoparticles, and secondly the effect of the thickness of the protective matrix that cap the particles.

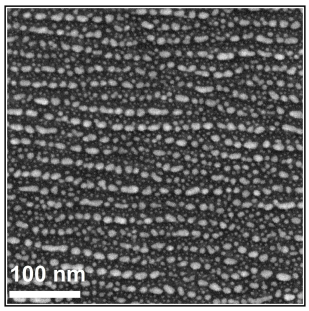

Figure 1: Plane-view HAADF-STEM images of rippled Al_2O_3/Ag/Al_2O_3 trilayers after glancing-angle (5°) Ag deposition.

MODELING OF NANOPARTICLE FORMATION IN PLASMA DISCHARGES

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KEYWORDS

Metal nanoparticles, plasma, modeling

ABSTRACT

Electrodes erosion caused by spark discharge can lead to effective nanoparticles formation. In this work, we present the simulation of the early stage of the discharge formation. In particular, streamer parameters are calculated in 1D and in 2D and compared with the results of previous experiments and models [1-3].

Two infinite parallel-plate electrodes are considered, the initial electron distribution is Gaussian at the anode. Electron's drift and diffusion, Townsend ionization and photo-ionization processes are shown to be dominant factors of positive streamer formation and propagation. An implicit scheme is applied for the calculation of the electric field based on Poisson's equation. The calculation results demonstrate a transition from streamer to spark. In addition, we calculate the power input for the following cathode erosion thus providing initial conditions for nanoparticle formation model (next step).

This work is performed in the frame of the FP7 project "BEOUNAPART-E". The results of the model are under verification by a comparison with the experimental results obtained by other partners.

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Large ultrafast optical modulation by a nanoplasmonic photonic crystal cavity

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KEYWORDS

Gold nanoparticles, plasmon, photonic crystal, ultrafast modulator, switching

ABSTRACT

Metal-dielectric nanocomposites have attracted much attention as promising optical materials based on the surface plasmon resonance. Their optical properties can be modified on an ultrafast time scale by a series of energy conversion and exchanges processes following light pulse absorption. These modifications can be further enhanced by the use of the amplified field localized in the defect of a photonic crystal. The defect mode can thus be ultrafastly modulated or switched. In this work, we introduce gold nanoparticles in the defect layer of a 1D photonic crystal cavity in order to combine the plasmonic and cavity effects. Both the stationary and ultrafast transient optical responses are investigated, allowing optimizing the device characteristics. The challenge is to demonstrate a large modulation effect despite the fact that the resonant cavity is rendered absorbing by the introduction of gold nanoparticles. The ultrafast transient modification of the device transmittance is calculated in the very short time scale by solving Boltzmann equation for the electron distribution in the athermal regime together with the Rosei model for the metal energy band structure and Lindhard's theory of the dielectric function. The transmission spectra are deduced from the transfer matrix method. We show that, under certain conditions, the transient response of the nanocomposite medium can be hugely enhanced by interference effects in the cavity. These simulations are successfully validated by pump-probe spectroscopy experiments on a multilayer device elaborated by Pulsed Laser Deposition (see figure).

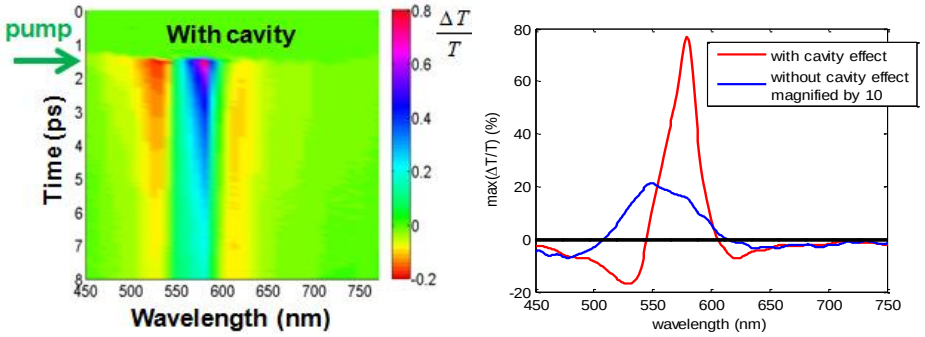

Figure: (Left) Ultrafast transient relative change of the device transmittance after 150-fs pump pulse absorption. (Right) Comparison of the transmittance relative change at maximum with (red) and without (blue) cavity effects. Note that the blue curve is magnified ten times.

ENGINEERING EIGENMODES IN OPEN MICROSTRUCTURED RESONATORS FOR FAR INFRARED FILTERING APPLICATIONS

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KEYWORDS

Eigenmodes, finite element method, diffraction grating

ABSTRACT

Sub-wavelength diffractions gratings can be studied using the finite element method. A recent formulation allows us to solve for the field diffracted by arbitrary bi-periodic gratings embedded in multi-layer stacks, and to compute the related diffraction efficiencies. A more powerful approach presented here consists in finding straightly the resonances of these structures by searching for their complex eigenfrequencies (using PML), with real parts corresponding to resonant frequencies and imaginary parts to damping ratios. We show that the field diffracted by the studied grating can be expanded on the basis of its eigenmodes. This results in a reduced modal representation of the field in the open structures with clear physical insights on the resonant processes at stake. Finally, we apply this technique to the design of polarization and angle insensitive reflexion band stop filters in the far infrared based on metal/insulator/metal grating (cf. Figs 1 and 2).

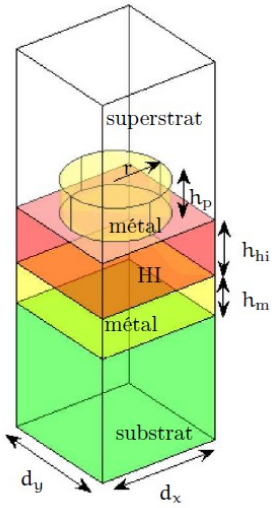

Figure 1 : Unit cell of the studied structure

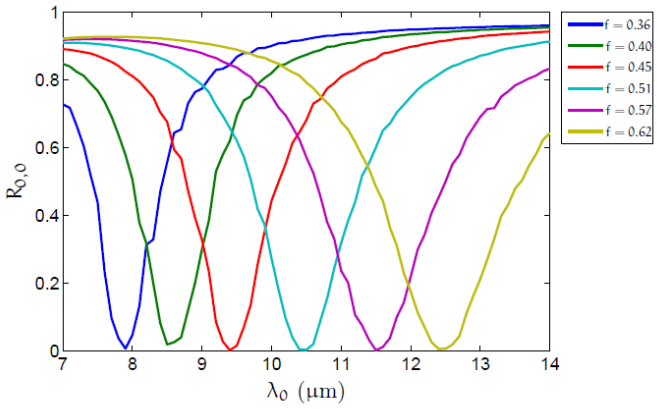

Figure 2 : Reflectivity in the (0,0) order as a function of incident wavelength for different filling factor f=2r/d