METACHEM

Nanochemistry and self-assembly routes to metamaterials for visible light

A specific targeted research project supported by the European objective FP7-NMP-2008-SMALL-2
Contract No 228762 Sept 2009 – Sept 2013

Demonstators to prove scientific results achieved

Objective of Metachem project is the development of particles and nanostructures that show metamaterials effects due to their plasmonic properties. Underlying simulation and modelling which were developed in Metachem Project supported the syntheses, assembly strategies and Understanding of the electromagnetic behavior of produced nanoparticles. The project was focused on properties of the produced layers, particles and structures in the visible regime.

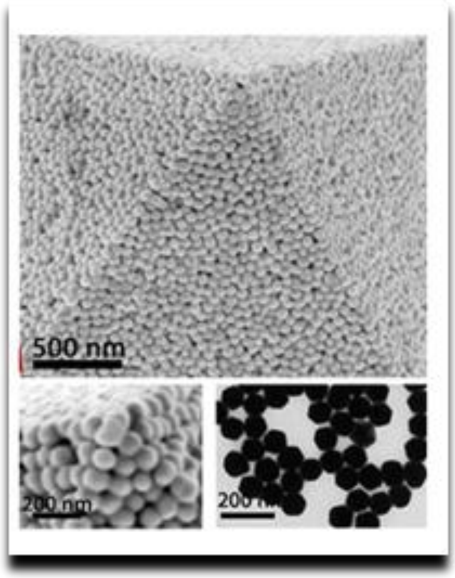
In this survey, most interesting exploitable results are composed and Explained. Relevant information of these demonstrated results can be found in references attached to each example.

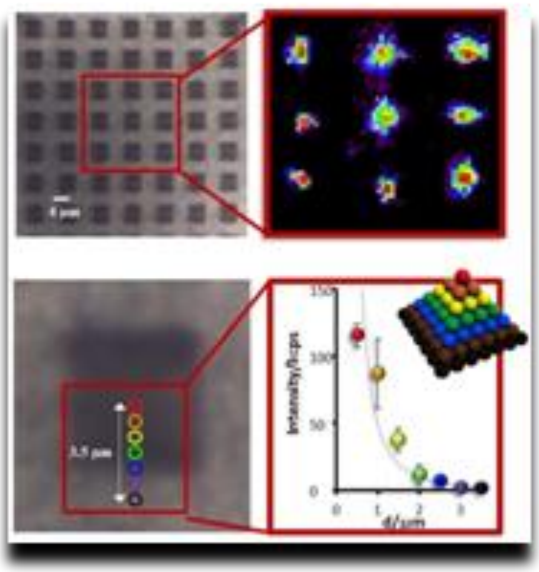
Table of Content

SERS Biosensors

Surface Enhanced Raman Spectroscopy

Controlled assembly of organized colloidal plasmonic nanostructures leads to extraordinary optical properties, as a result of the near electric field propagation from the pyramid to the surfaces and especially to the apexes. As a proof of concept of their potential, we have design an inexpensive, portable, reversible, rapid and ultrasensitive SERS biosensor mimic for CO.





Further information:
Maria Alba, et al. Angew. Chem. 2013, 52, 6459–6463

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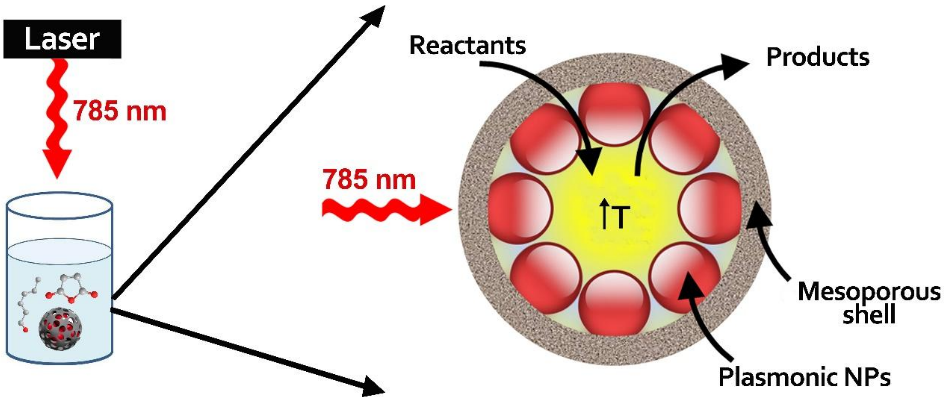
Plasmonic Nanoreactors

Photothermal Heating and Monitoring of Confined Chemical Reactions

These systems allow specifically activating the confined volume while avoiding temperature alterations within the bulk solution. Furthermore, since the thermal effect is induced by the excitation of the localized surface plasmon resonance inside the reactors, the electromagnetic field generated has been exploited for the *in situ* surface enhanced Raman spectroscopy monitoring of the process.



This could be of special relevance in applications involving biological environments. Additionally, these reactors can be used for the real time monitoring of the process providing an alternative to collect real-time information of the course of chemical reactions, critical indeed for the improvement of relevant chemical processes.

Further information
Vázquez-Vázquez, C. J. Am. Chem. Soc. 2013, in press

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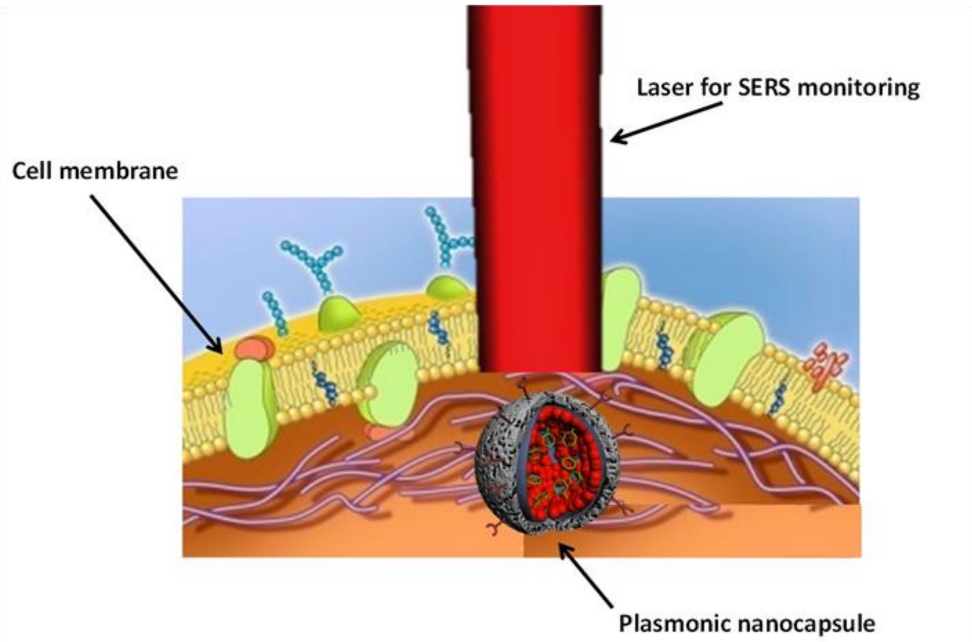
Plasmonic Nanoreactors

Intracellular real time optical monitoring of relevant analytes

Such approaches so far are mainly limited to the fluorescence detection of pH. Many fluorophores sensitive to other analytes such as K+ or Na+ have crosstalk with pH, which makes a quantitative detection complicated, as the origin of their fluorescence response is not clear. In addition fluorophores tend to photobleach, which also make quantitative intracellular detection of analytes complicated. In our case the detection signal is based on SERS, which is more stable in time compare to fluorescence read-out. Moreover, in our case acidic pH favors detection of NO and excludes crosstalk with sensors which have not been internalized by cells. Also multiplexed detection can be envisaged, as due to the sharp bands of SERS emission signals originating from different analyte-sensitive molecules can be spectrally resolved.



The sensors as proposed here thus have the future capacity to reside inside cells are intracellular reporters for multiplexed on-line detection of multiple analytes.

Further information
Pilar Rivera_Gil, et al. Angew. Chem. Int. Ed. 2013, in press.

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Sensors

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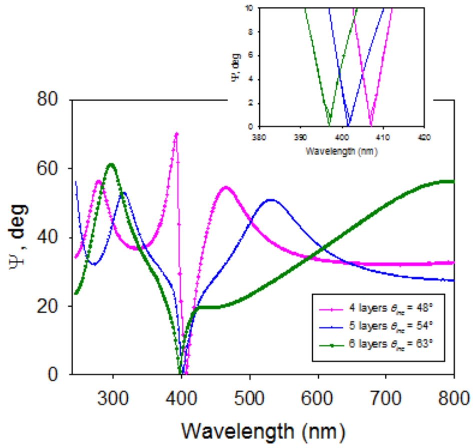
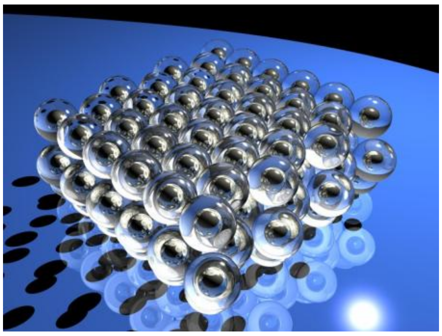
Ultra-sensitive optical sensing:

Optical Absorbers - topological darkness

By the non-conventional values of the dispersion curves (n(λ), k(λ)) of the engineered materials, it is possible to completely extinct the TM reflected wave (i.e. real and imaginary part of TM reflected amplitude are exactly zero). This behavior can be applied for ultra-sensitive sensing. The amplitude and phase of the ellipsometric signal exhibit sharp variations around extinction and, thus, extremely weak variations of the optical conditions can be detected.





The demanded property (zero reflection) could be demonstrated and fully interpreted in optical models with assemblies of silver@silica core-shell nanoparticles. Due to oxidation of silver, the lifetime of the devices is short (~days). Future devices should be made with gold@silica nanoparticles. Modeling has been done but was not demonstrated so far. Next step is the characterization of Sensing performances

Further information

Kravets V. G, *et. al*. Nature Materials, 2013, doi:10.1038/nmat3537
Malassis L, *et. al*, Advanced Materials, 2013, doi: 10.1002/adma.201303426

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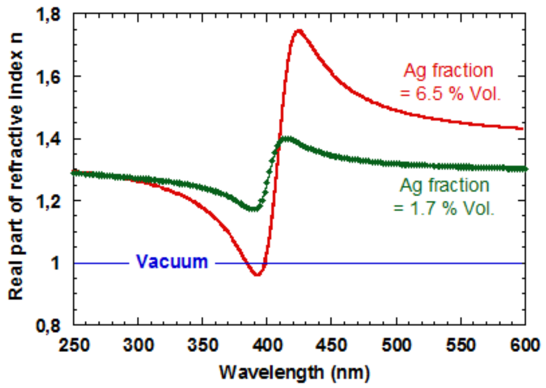
Philippe Barois

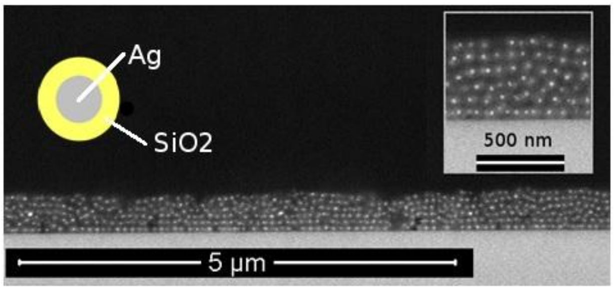
Alexander Grigorenko

Non natural refractive index

Refractive index lower than 1 in self-assembled 2D and 3D plasmonic metamaterials

In Metachem, Metamaterials were processed as 2D and 3D films of large area (> cm²) by which values of effective permittivity could be controlled by adjusting the volume fraction of metal. The core-shell structure of the meta-atoms enables a fine control of electromagnetic coupling. Values of the refractive index equal or lower than 1 (i.e. vacuum) and epsilons near zero were demonstrated by the developed materials. Amongst others, these materials can be used for waveguide coupling and for ultra sensitive sensing by adjustment and exploitation of dispersion curves.





The used Langmuir-Blodgett technique has to be replaced by a more efficient coating method in order to speed-up the process time

Further information

Malassis L., et al., Langmuir 2013, **29**, 1551s

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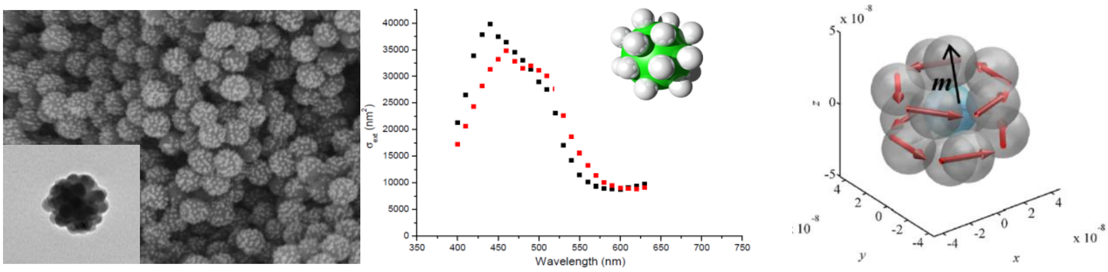
Opto-magnetism

Fabrication of nanocluster(s) with electric and magnetic response in the visible light region

Strong electric and magnetic response for isotropic plasmonic resonator(s) with a raspberry-like architecture was evidenced by single and collective optical measurements. The magnetic resonance is produced by the effective ring of coupled plasmonic metallic particles. With nanoresonator of size of a few tens of nanometers, the magnetic resonance can be distinguished from the electric ones and can be achieved in the visible range wavelengths. This opens up the way to the fabrication of 3D-metamaterial of highest importance to many applications (photonics, lens, waveguides,…).



TEM image of nanoresonators made of a dielectric core and silver satellites nanoparticles (overall diameter -120 nm-) (left) **optical properties of a single nanocluster** (middle) **numerical simulation** of electric and magnetic modes for a nanocluster (right).

Further information:
Ph-D thesis of A.Le Beulze (2013)

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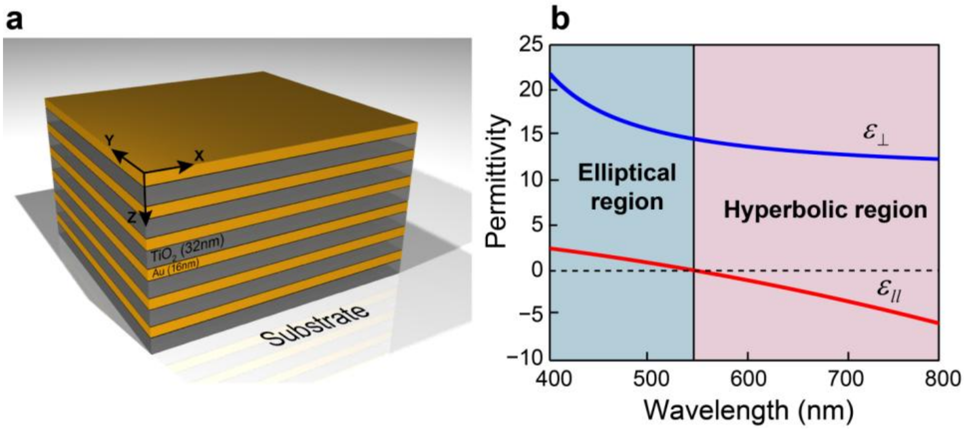
Plasmonic Biosensors

Hypergrating based on hyperbolic metamaterials to enhance sensitivity of biosensors

Hyperbolic metamaterials (HMMs) represent a novel class of fascinating anisotropic plasmonic materials, supporting highly confined bulk plasmon polaritons (BPPs) in addition to the surface plasmon polaritons (SPPs).

We propose an optical hyperbolic metamaterial based on Au/TiO_2 multilayers (6 bilayers), confirming the hyperbolic dispersion and the presence of high-k modes through Effective Medium Theory (EMT) and ellipsometric measurements to validate the negative behavior of $\square_{||}$.



Characterization of hyperbolic metamaterial (a) Schematic diagram of fabricated hyperbolic metamaterial, which consists of 6 bilayers of Au/TiO_2, (b) Real parts of effective permittivity of HMM determined with effective media theory. The permittivity tensor component in the parallel direction (XY plane) is determined and fitted using spectroscopic ellipsometry

We experimentally demonstrate the excitation of both surface and bulk plasmon polaritons in the HMM through a grating coupling technique of plasmon excitation that makes use a hypergrating, which is a combined structure of metallic diffraction grating and HMM. We performed spectroscopic ellipsometry reflection measurements as a function of incident angle and excitation wavelength, showing the existence of BPPs and SPPs inside the hypergrating.

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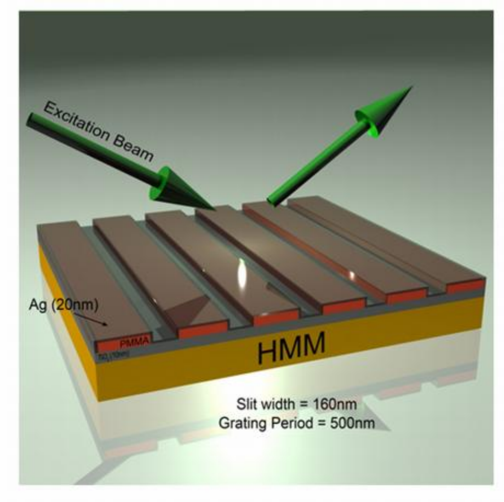
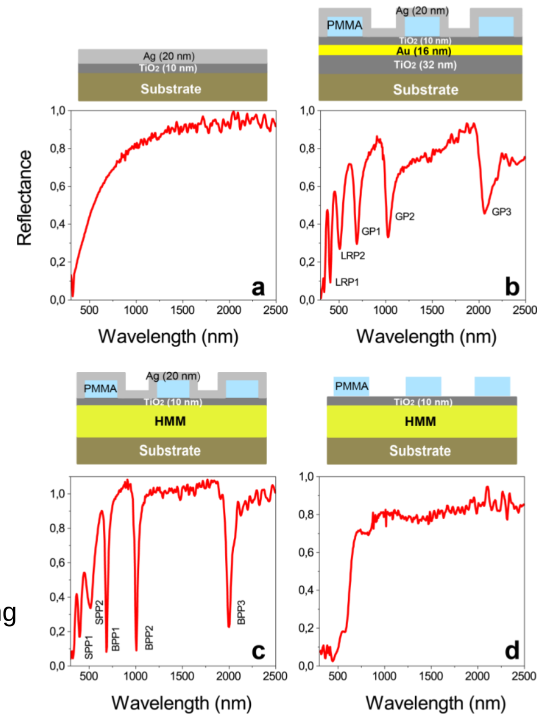
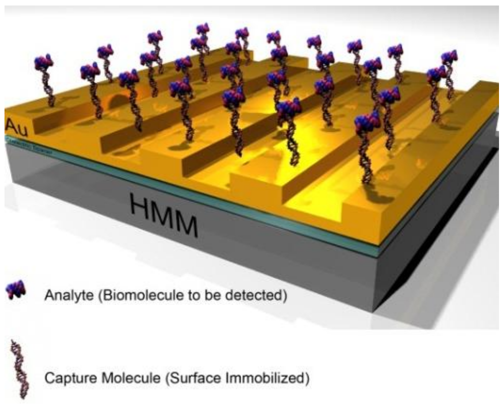


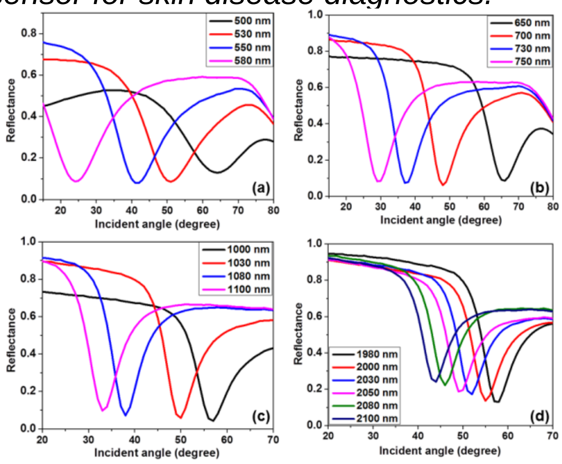
Above: Hypergrating geometry
Schematic diagram of fabricated hypergrating structure in reflection geometry, obtained by combining a Ag based grating with the HMM structure



Right: Reflectance spectra as a function of excitation wavelengths: Studied structure is shown above each graph: (a) Uniform Ag layer of 20 nm thickness on a TiO2/glass substrate, (b) Control sample (Ag grating on a 1bilayer of Au/TiO2), (c) Hypergrating (Ag grating on a 6 bilayer of Au/TiO2), and (d) hypergrating without Ag layer on top of the grating. (a)- (d) Incident grazing angle is taken to be 50°.

The proposed configuration is expected to find potential applications in bio-chemical sensors, integrated optics and optical sub-wavelength imaging.
Just as an example, we can show the idea related to a possible application in the field of *hypergrating-based plasmonic biosensor for skin disease diagnostics.*





Proposed plasmonic biosensor on a plastic substrate, used to achieve high sensitivity in bio-molecule detection

Further information

Sreekanth, K. V. et al.“Experimental demonstration of surface and bulk plasmon polaritons in hypergratings,” Sci. Rep. (Nature) (Under revision)

Partner in charge

CNR-IPCF Cosenza
A. De Luca, K. V. Sreekanth, G. Strangi in collaboration with NanoPlasm Laboratory – Case Western Reserve University (OH – USA)

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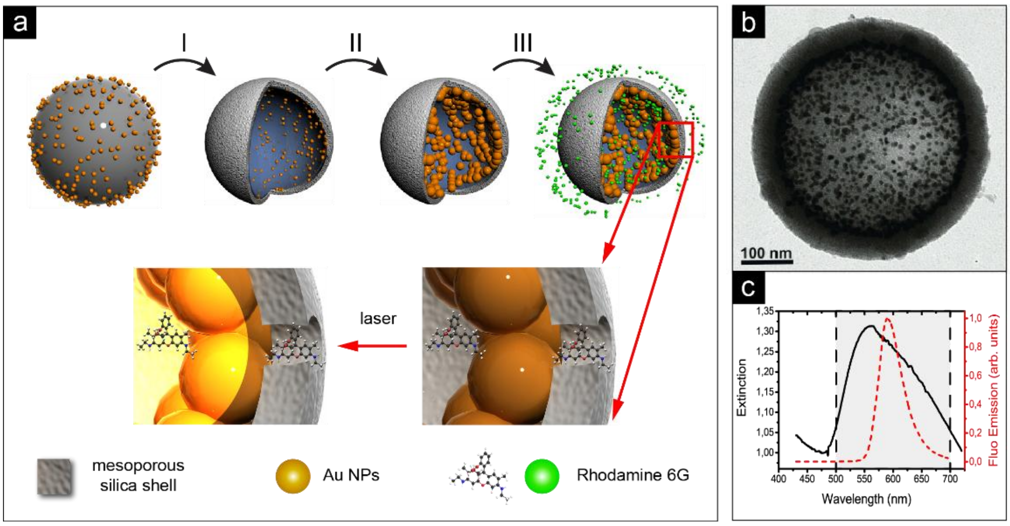
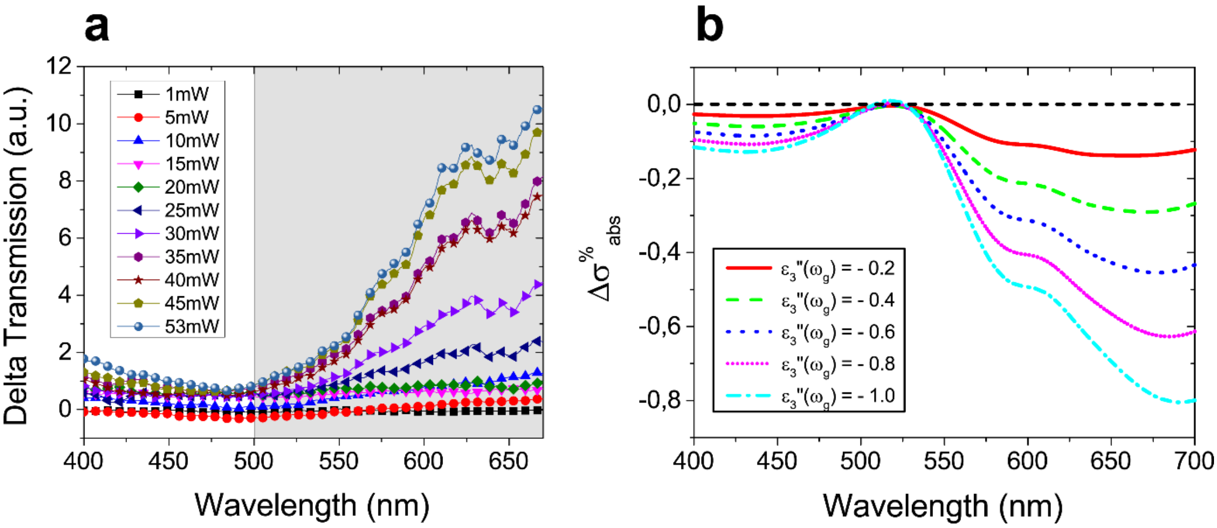
Gain-assisted plasmonic mesocapsules for low-loss collective resonances

Broadband loss compensation in hollow plasmonic mesocapsules by means of infiltration of gain medium

We demonstrate that hollow mesoporous capsules fabricated at a scale intermediate between the single plasmonic nanostructure and real materials show remarkable form-function relations. At this scale, in fact, the plasmon-gain interplay is dominated by the donor-acceptor separation as well as the position of the gain medium with respect to the distribution of the local field. In particular, the hollow spherical cavities of these structures allow regions of uniform plasmonic field where the energy transfer occurring between chromophoric donors and the surrounding plasmonic acceptors, giving rise to a broadband induced transparency, confirmed by a theoretical model.



(a) Sketch the mesocapsules growth process and infiltration of gain material (III) **(b) TEM image** of a single mesocapsule. **(c) Broadband plasmon resonance** of a solution on mesocapsules (blackline) and fluorescence curve of R6G dye solution (dashed red line)



(a) Experimental evidence of broadband loss compensation at the mesoscale range through an overall increase of Delta of transmission as a function of wavelength. (b) Theoretical model showing the behavior for $\Delta \sigma^{\%}_{abs}$ for different values levels of gain from -0.2 to -1.0. Gain elements are assumed to be both outside and in the core of mesocapsules.

Further information

Infusino M. *et al.* “Gain-Assisted plasmonic mesocapsules: a novel strategy for low-loss collective resonances”, Advanced Optical Materials (2013)

Partner in charge

CNR-IPCF Cosenza
Collaboration with Prof. G. Strangi - NanoPlasm Laboratory – Case Western Reserve University (OH – USA)

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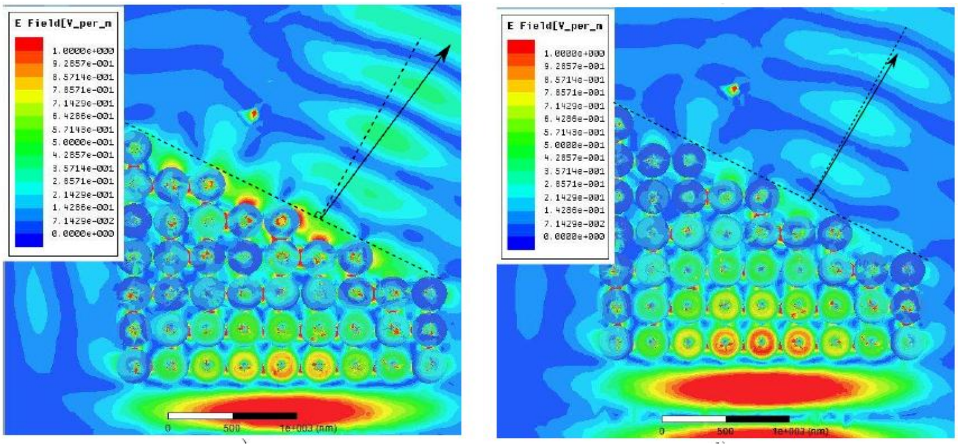
Modelling of electromagnetic behaviour of nanoclusters

Modelling of electromagnetic behavior for negative permeability / permittivity and near zero permeability / refractive index

Application: The layer of the isotropic near-zero permittivity material covering a strip dielectric waveguide can be applied for creating a new type of leaky-wave optical antennas of s-polarized waves operating in the visible range. It can be used also in many other applications suggested in the literature for ENZ materials. The same refers to isotropic near-zero permeability materials with replacement of s-polarized waves by p- polarized waves. The layer of material with isotropic low-loss negative permeability material on an arbitrary substrate can be applied e.g. for creating a new type of surface waves with plasmonic type of the dispersion but with dominating magnetic field – s-polarized surface-plasmon polaritons (s-SPP) that can be used for creating new optical antennas, for broadening the capacities of existing SPP-microscopy, etc. The flat layer of isotropic material with negative refractive index can be applied for creating a frequency-selective aberration-less pseudo-lens .The model of electromagnetic characterization is of prime importance for metamaterial-based devices since it allows the control of optical properties of the metamaterial during its fabrication in situ.

To achieve the practical results as mentioned in the previous section one needs to perform the theoretical and experimental research i.e. to create a theoretical model of suggested devices and experimental prototypes.



Numerical simulation of negative refraction (left) and near-zero (right) refraction due to near-zero permittivity in the array of core-shell Ag - a-Si particles.

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Further information

Simovski,. C. R et. al., Phys. Rev. B, vol. 79, p. 045111, 2009
Simovski,. C. R et al., Phys. Rev. B, Vol. 79, 214303(1-4), 2009
Simovski,. C. R et al., Vol. 107, 726–753, 2009
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Simovski,. C. R et al., Vol. 8, No. 4, 254-263, 2010
Morits, D. K. et al., J. Optics, Vol. 14, 125102, 2012
Morits, D. K. et al.,, Phys. Rev. B, Vol. 82, 165113, 2010
Simovski,. C. R, Journal of Optics, Vol. 13, 013001 (1-22), 2011
Morits, D. K. et al., Metamaterials, Vol. 5, Issue 3, 71-78, 2011
Albooyeh, M. et al., Metamaterials, Vol. 5, Issue 3, 93-111, 2011

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