Nanochemistry and self-assembly routes to metamaterials for visible light

Reporting

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Final Report Summary - METACHEM (Nanochemistry and self-assembly routes to metamaterials for visible light)
Executive Summary:

Meta-materials form a new class of artificial materials with extraordinary electromagnetic properties, unknown to natural materials or previously developed technologies. Since the first realization of a meta-material in the microwave regime in 2000, the field has been growing exponentially, bringing about some of the most fascinating results in fundamental science of the recent years and opening up new horizons for optics and electromagnetism, telecommunications and information technology.

The novel and outstanding properties are induced by an appropriate structuration of the medium at scales much smaller than the wavelength of the radiation propagating through them. Applications in the microwave regime are in a pre-commercial stage. For visible light, the “effective medium” requirement implies typical sizes of the artificial structures around a few tens of nanometers or less, which constitute a serious fabrication challenge. This is the reason why the call “NMP-2008-2.2-2 Nanostructured meta-materials” has been launched by the European Commission in the 7th Framework Program (Cooperation scheme).

Up to now, the powerful but costly techniques of nanolithography have been successfully used to manufacture nanostructured surfaces and demonstrate the validity of the concept of meta-materials at the frontiers of the visible light domain.

The objective of the METACHEM project has been to use the extreme versatility of nano-chemistry to design and manufacture bulk meta-materials at a much lower cost. The targeted nano-scale patterns are typically around 50 nm in size or less.

Our strategy has consisted in designing and synthesizing ad-hoc nano particles as optical plasmonic nano-resonators and organising them through self-assembly methods in 2 or 3 dimensional networks in order to produce dense highly ordered structures at a nano-scale level. Several subprojects corresponding to different routes have been efficiently pursued, all of them based on existing state-of-the-art chemical and self assembly methods. In addition, the important issue of losses inherent to the plasmonic response of the nano-objects has been addressed in an original way by the adjunction of loss-compensating active gain media.

The input of theorists of electromagnetism has been of crucial importance for the design of the targeted nanostructures. In addition, a special effort has been made on the difficult measurement of the non conventional meta-properties as they constitute the first demonstration of the validity of the concept. A study of technological and industrial aspects has been carried out towards efficient, cost-effective and industrially feasible metamaterials.

The key point of the METACHEM project joining 9 partners from 7 European states has been to bring together for the first time European experts of three complementary fields namely nanochemistry, self-assembly methods and metamaterials science. The majority of the partners were members of FP7 virtual institutes related to these fields, i.e. respectively EMMI, SOFTCOMP and METAMORPHOSE II.
Project Context and Objectives:

Metamaterials are artificial composite materials whose extraordinary electromagnetic properties are induced by an appropriate structuring of the medium at scales much smaller than the operational wavelength. For visible light, this “effective medium” requirement implies typical sizes of the artificial structures around a few tens of nanometers or less, hence setting the framework for the present project.

The fabrication of actual MTMs has always been the core issue of the field. The successful design “split-ring resonator” (SRR) scheme proposed by John Pendry enabled the fabrication of the first MTM operating in the gigahertz range. With the powerful, modern techniques of micro- and nano-lithography, the operating frequencies have risen up until now stepping into the visible domain.

Huge fabrication challenges remain, especially for the most important case of three-dimensional devices. Manufacturing a millimeter-size MTM sample out of individual resonators (with an average density of one to ten resonators per wavelength in the visible) means assembling $10^9$ to $10^{12}$ nano-resonators together. The individual, direct manipulation of such a huge number of nano-objects seems unrealistic for large-scale applications. The combination of nano-chemistry, which is able to finely engineer and synthesize the required resonant nano-objects, with self-assembly techniques, appears as a solution to this daunting task. Self-assembly is actually a highly efficient process, well known in soft condensed matter physics, whereby individual objects spontaneously organize under the effect of complex pair interactions into highly organized two-dimensional (2D) or three-dimensional (3D) structures of various symmetries.

Microscopic designs for the specific target structures, that shall be implemented, should of course be provided by theoretical and numerical studies, so that a successful approach of self-assembled metamaterials should combine the simultaneous inputs of theoreticians, nano-chemists and soft condensed matter physicists.

The goal of our METACHEM research project is precisely to fabricate a new generation of metamaterials at infrared and optical frequencies, based on the use of nano-chemistry and self-assembly of materials.

The implementation of the project relies on the strategic conjunction of four complementary disciplines:

- Nano-scale chemistry which offers today a tremendous versatility in terms of constituent materials, morphologies, sizes and surface functions of achievable nano-particles that will constitute the fundamental building blocks of the nano-structured composites.
- Self-assembly methods (either spontaneous or directed), capable of organizing matter into vastly varied structures at scales ranging from nanometers to hundreds of microns. Combination with the aforementioned synthetic nano-objects opens the way to a quasi unlimited set of achievable nano-structured artificial materials, far beyond the limited number of existing models.
- Theory and EM analysis methods are intended to play a decisive role, by providing chemists with realisable models of metamaterials with targeted EM properties.
- Characterization of the EM meta-properties via advanced optical techniques and the non-trivial development of associated models for data analysis.
We follow three major fabrication routes corresponding to three separate workpackages of our work plan (WP1 to 3).

The first route (WP1) consists in fabricating 3D isotropic metamaterials made of an assembly of new subwavelength resonators, namely nanoparticle clusters whose precisely defined internal architecture is able to generate meta-responses (both magnetic and electric). The second route (WP2) will aim at obtaining metamaterials by incorporating suitable nanoparticles into pre-existing, self-organised soft matter templates, which will order them into subwavelength spatial structures (2D or 3D). The third route (WP3) will focus on metamaterials obtained from dense stackings of nanoparticles which, under the natural action of (appropriately tuned) interparticle forces, directly self-organise into elaborate 3D-structures (e.g. super-lattices and colloidal crystals).

Besides these fabrication-oriented research routes, METACHEM will also include specific research on the development of novel loss-compensation schemes in metamaterials (WP4), as well as research to improve and develop new optical measurements techniques able to demonstrate the reality of the targeted EM-meta properties (WP5). Finally, since the ultimate goal of the research in METACHEM is to open the way new, scalable, low-cost fabrication processes applicable in industry, a specific work towards industrial needs will be implemented (WP6).

Each of these workpackages is described in more detailed below.

a) Workpackage 1: 3D-isotropic metamaterials based on nanoclusters

The concept of this workpackage is the fabrication of a new 3D-isotropic metamaterial based on a very original theoretical scheme from Alù et al. and its further extension by Simovski et al (from TKK in our consortium). We propose to fabricate magnetic nanoclusters by arranging gold or silver nanoparticles onto a central dielectric particle, or a dielectric shell-metal core particle.

The design called MNC (magnetic nanoclusters) and MENC (magneto-electric nanoclusters) consists of an ensemble of core-shell nanoparticles (25-30 nm size range), composed of a gold or silver core coated by a silica shell, which are located around a single central particle (40-60 nm size range) which can be dielectric (for MNC) or metallic (MENC). The silica shell around each of the exterior nanoparticle has two goals: first, to electrically insulate the metal cores by preventing direct contact, and second, to allow a precise adjustment of the interparticle distances.

Such a MNC possesses a magnetic resonance, for which the plasmons within the surrounding nanoparticles couple through the silica shell. This is expected to create a negative permeability in a certain frequency range within the optical spectrum.

On the basis of the MNC concept, our objectives follow a logical progression, leading to the final metamaterial:

1) Optimize by theory the design of MTMs based on magnetic nanoclusters
2) Synthesize the nanoclusters following two strategies: (i) clustering of preformed spherical nanoparticles onto the central particle and (ii) nucleation-growth in situ of nanoparticles around the central particle from seeds deposited at its surface.

3) Fabricate real, dense metamaterial from these building blocks by concentration and assembly of the MNCs and MENCs.

b) Workpackage 2: Template-assisted assembly of metamaterials

The general objective of WP 2 is to fabricate metamaterials using templating organic matrices made of block copolymers. These materials present spontaneous molecular organization in the bulk or in contact with a surface, with long-range order and with characteristic sizes of a few 10 nm. We use these ‘optically neutral’ templates to spatially organize ‘active’ entities, as metals, in order to fabricate ordered anisotropic metal/dielectric hybrid nanocomposites, which can be used towards high-gain optical radiators, sub-wavelength guiding device like nanowire lenses or subwavelength, periodically perforated metal thin films (fishnets) with extreme properties like extraordinary optical transmission due to surface plasmon polaritons. Two classes of templating approaches are considered:

(i) 3D metamaterials assembled from solid ordered phases of diblock copolymers
(ii) 2D metamaterials assembled from water dispersions of amphiphilic diblock copolymers

The objectives of WP2 are thus the following:

- predict the EM properties for the geometries accessible to the chemistry groups and provide guidelines on which structures can be used for the expected applications.
- fabricate metamaterials using block copolymers 3D templates.
- fabricate nano-perforated thin films of noble metal

c) Workpackage 3: Interaction-driven self-assembly of metamaterials

In contrast with WP2, the concept here is to have the nano-objects of interest self-assemble directly, driven by interparticle forces. The end result is the fabrication of dense 2D or 3D structures (colloidal crystals and “superlattices”) presenting a degree of order, which can extend over tens or hundreds of particle radii. These dense materials can then be shaped into real, sizeable samples.

To assemble the materials, we exploit highly successful techniques developed within the consortium. Three directions are followed:

• Spontaneous 3D self-ordering of nanoparticles by using physical chemical routes, such as the solvent evaporation approach.

• 3D self-ordering of nanoparticles controlled by microfluidic evaporation techniques
• Layer-by-layer fabrication of nanostructured 3D structures by using the Langmuir-Blodgett deposition technique

Finally, this workpackage comprises a specific theoretical work to understand how and to what extent the
The presence of various types of disorder affects the meta-properties.

d) Workpackage 4: Loss compensation in metamaterials

The main goal of this workpackage is to address and solve the fundamental problem of optical losses in engineered metallic nanostructures. In fact, these materials suffer from rather strong damping of the plasmon fields, which can become obstructive for most optical and photonic applications. Therefore, eliminating losses in optical metamaterials (MTMs) is critical for enabling their numerous potential applications. The absorptive losses must be compensated with inclusion of active gain media, able to transfer energy to propagating surface-plasmon polaritons (SPPs) and to localized surface plasmons in metal nanostructures using stimulated emission. When dealing with structures of order lambda/10, the emission properties of dyes and quantum dots (QD) are influenced by the presence of other emitters and acceptors which are at distances shorter than the wavelength. Therefore most of the energy is transferred to surface plasmon polaritons through non-radiative processes (Forster transfer). The challenge is to maximize this energy transfer in order to create a stable gain. The crucial point here is to place the gain materials in proper positions with respect to lossy elements and regions of intense field, via advanced design.

The routes that we follow act at different spatial scales, from nano to macro:

- at the nano-scale (10-50nm): by creating “smart nanoparticles” which combine in the same geometrically optimised nano-element a plasmonic (lossy) component generating the desired EM “meta-properties” (e.g. permeability resonance) and gain elements to compensate losses.
- at the meso-scale (20-200nm): by using periodically alternated self-assembled structures (e.g. diblock copolymers), or ternary systems which intercalate sheets of lossy “meta-elements” and optical gain elements. This generally relies on the use of external host-matrices as templates for the alternated structures.
- at the macroscopic scale (1µm and beyond): by infiltration and/or submersion and/or surface coating of macroscopic metamaterial structures with concentrated dye solutions.

Nano- and material chemists in the consortium are working in close integration with theoreticians and EM specialists in charge of performance measurements to offer a picture of the strength and limitations of each of these routes, so as to be able to progressively implement the explored techniques into the MTM structures fabricated in parallel within the other workpackages.

e) Concepts and objectives for Workpackage 5: Demonstration of meta-EM properties

The EM characterization of the materials and samples fabricated in WPs 1 to 4 is organized according to a two-level scheme.

First-level experiments include standard measurement techniques present in the chemistry/fabrication groups, like normal incidence absorption and reflection spectra by spectroscopic techniques, or standard ellipsometry, and are done within each of the WPs. These initial measurements are completed by more advanced measurements and extraction of optical constants by spectroscopic ellipsometry and on the
theoretical side, by the development (and assessment) of models capable of reliably analyzing optical data and extracting the relevant material parameters.

f) Concepts and objectives for Workpackage 6: Industrial needs and processing

In addition to the fabrication of nanostructured metamaterials and the demonstration of their EM properties in the visible range, METACHEM intends to prepare the way to the technological development of future industrial applications.

A “horizontal” work package WP6 is then implemented with three objectives:

1) Define the specifications from an industrial point of view. This implies the evaluation of parameters relevant to industry such as toxicity (in relation with REACH) and rheological (for processing), thermal (for soldering), mechanical (for handling) properties, in addition to the needed physical EM parameters.
2) Start to evaluate the feasibility of further industrial processing and synthesis. This implies the capacity to upscale (i) the chemical syntheses of the nanoparticles and (ii) the assembly methods from academic laboratories to industry (with technical, economical and environmental aspects)
3) Define and propose demonstrators. As the challenging approach of METACHEM is not close to applications, this means essentially realizing “function” demonstrators aimed at demonstrating that the targeted EM properties can be obtained and integrated into components or devices.

An Industrial Advisory Board is created in METACHEM to advise and help in these application-oriented tasks and to give the whole project a somewhat application oriented focus.

Project Results:

WP1 - 3D-ISOTROPIC METAMATERIALS BASED ON NANOCLOUDS

Participants: CNRS-Bordeaux, UVIGO, Aalto, UCL, UNISI

WP1 SUMMARY

The main objective of WP1 deals with the fabrication of metamaterials based on a collection of isotropic resonators made of nanoclusters. The nanocluster morphology is based on an original two-dimensional design by Alù et al. (A. Alù, A. Salandrino, N. Engheta, Opt. Express 14,1557, 2006) generalized by Simovski and Tretyakov (C.R. Simovski, S.A. Tretyakov, Phys. Rev. B 79, 045111 (2009)) as shown in Figure WP1.0. In such a system the magnetic resonance is produced by the effective ring of particles in the outer shell (MNC clusters), whereas the additional dielectric resonance arises from the core particle of larger size (MENC). The core-shell morphology of the plasmonic particles with a metal core and a dielectric shell enables a fine control over the interparticle distance.

The main achievements of the work performed in this work package are summarized as follows:

i) The theoretical scientists have acquired a deep understanding of the interaction of light with NCs by
developing ad-hoc tools for the numerical modelling of the optical response of MNCs, hence overcoming the limitations of general purpose commercial modelling tools. The synergy of theory and numerical modelling allowed the design of optimized MNCs, which have been then realized by experimental teams, and the correct interpretation of measurements of realized samples demonstrating the magnetic nature of the NC response.

ii) High quality MNC and MENC have been synthesized in large enough quantities for subsequent self-assembly via different synthetic approaches. Optical experiments carried out on single objects agree remarkably well with theoretical and numerical studies, hence supporting the presence of a magnetic response of the MNCs. 3D assembly into a bulk material remains to be done. Our first studies show that controlled evaporation in microfluidics devices is the most promising route.

iii) Additionally, as a consequence of the different synthetic strategies developed during the project, other highly interesting results have been obtained, namely:

- in response to theoretical refinements, a novel synthetic approach based on the use of “patchy particles” was developed in which nanosized satellites are attached on specific sites of the core. This will open the way to the controlled attachment of triangular satellite, for enhanced magnetic response.
- hollow plasmonic nanocapsules have been created and used as plasmonic nano chemical reactors (allowing photothermal heating and monitoring of confined chemical reactions), as well as biological nanoprobes (for intracellular real time optical monitoring of relevant analytes).
- plasmonic nano-pyramids have been fabricated and used as demonstrators of inexpensive, portable, reversible, rapid and ultrasensitive SERS biosensors.

LIST OF ACHIEVEMENTS

1 – Theoretical studies:

The magnetic response of Magnetic nano clusters (MNC and MENC) was investigated by theory in order to provide guidance to nanochemists.

- Results available from the literature, which claim the negative permeability for metamaterials based on magnetic nano-clusters in the visible region, are not trustful.
- Using plasmonic dimers we obtained the needed result for magnetic nanorings. This opens the door for plasmonic tripods for MNC.
- However in this way:

1) we can have acceptable results only in the near IR
2) the designs with touching or intersecting nanospheres are very sensitive to the geometric parameters (strict tolerances)

- We have provided multiple-scattering based Macro Basis Functions to provide a reduced-order modeling of an integral equation approach based on the Method-of-Moments for the electromagnetic analysis of arbitrarily shaped 3-D dielectric structures.
- The design with triangular nanoprisms is not so sensitive and allows the magnetic resonance in the visible with large resonance magnitude.
• The size at the magnetic resonance is as small as wavelength/5
• The theoretical models have addressed realistic disordered binary systems.

2 - Chemical synthesis:

• We have successful synthesized MENCs composed of 15-nm Au satellite NPs surrounding a central 60-nm Au NP.
• MNCs of both types SiO₂@Au NPs and SiO₂@Ag NPs were successfully synthesized.
• Films made with MENCs were obtained following two different strategies, self-drying and microfluidic-based process.
• The MNCs has been successfully prepared, which allows the production of thin films in large areas.
• MNCs of SiO₂@Ag triangles have been also obtained in enough quantities for the preparation of films.
• A strategy for the preparation of arrays made with tridimensional structures composed of nanoparticles has been successfully developed.
• Patchy particles were successfully used for the development of a new kind of MNCs.
• A new strategy based on the formation of hollow silica capsules with Au NPs placed in their inner cavities has been developed for the fabrication of MNCs that can be used as plasmonic nanoreactors and bio-nanosensors.

GENERAL CONCLUSIONS

The MENCs failed on the fabrication of metamaterials for visible light. However, those structures were shown to possess highly interesting optical properties, useful for example for the development of SERS-based sensing applications. The synthetic efforts were hence focused on the preparation of MNCs. Those were also successfully synthesized and their first evaluation makes us to propose them as best prototype MNCs for the fabrication of metamaterials for visible light.

Therefore, we focused the synthetic efforts on:

i) the development of both types, SiO₂@Ag and SiO₂@Au MNCs in enough quantities. These structures were successfully synthesized and the fabrication of films made with those particles is an ongoing work. Measurements of the extinction in solution and of the optical response of single isolated MNC are consistent with the presence of a magnetic mode, in agreement with numerical simulations.
ii) the search for novel strategies that enable to fabricate different and unique MNCs that were successfully used for loss compensation studies in WP4. In this manner, hollow plasmonic nanocapsules have been produced which appear as a promising material for the simultaneous performance and optical monitoring of thermal-activated reactions, as well as nanoprobes for intracellular optical monitoring of relevant analytes.

Concerning the formation of films through the assembly of MNCs, the self-drying approach although successful did not allow to extract reliable optical parameters. The non-homogenous thickness of the films obtained through this approach was probably the reason. Thus, the efforts for the preparation of the films were oriented towards the microfluidic approach developed in WP3. Although quite successful for the self-assembly of spherical nanoparticles into dense bulk materials, this method could not assemble bulk...
magnetic materials before the end of the project.

The simple and scalable colloid approach developed in this study opens avenues for the development of advanced materials. In the future, it will allow to fabricate building blocks made of more complex metallic components such as dimer or trimers, nanostars onto dielectric or magnetic beads. It will also allow the development of building blocks made of a controlled number of metallic nanocrystals well-positioned in relation to each other onto a central dielectric core. This is of strong interest, in particular in the case of nanoclusters made of silver nanoprisms. By substituting the conventional silica beads by silica beads bearing “sticky patches” it will allow to develop novel structure and new building units. Such approach allows producing large quantities of colloidal entities made of a central silica core surrounded by a precise number of polystyrene nodules. These multipod-like structures could be used as precursors for the synthesis of spherical particles with a precise number of well-located patches at their surface, which is based on the use of the PS nodules as protective masks. The further adsorption of satellite particles on the “inter-patches” or “patches” areas should provide the next generation of raspberry-like nanoclusters. Their 3D assembly into complex ordered materials will provide unique chances for original functional structures and open the development to a novel domain of “bottom-up” chemistry with enough potential to compete with the “top-down” approaches of nanolithography.

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WP2 – TEMPLATE-ASSISTED ASSEMBLY OF METAMATERIALS

Participants: CNRS-Bordeaux, CNRS-Paris, UCL, UNISI

WP2 SUMMARY:

WP2 deals with the fabrication of anisotropic metal/dielectric hybrid nanocomposites with characteristic size 10-100 nm using the self-assembly of template polymer structures. The objectives are the theoretical prediction of the optical properties of structures (Task 2.1); the fabrication and structural study (Task 2.2) and first-level optical characterization (Task 2.3).

The UNISI and UCL groups have used approaches of infinite-array for the theoretical description of EM properties of anisotropic metal-dielectric hybrid nanocomposites. The UNISI group has developed some techniques to analytically model plasmonic spherical/spheroidal nanostructures. The UCL group has developed a full-wave integral-equation approach which presents unknown electric and magnetic current densities only on the interfaces between piecewise homogeneous media and imposes no other approximations than those related to the geometric discretization of the structure.

Properties have been determined in detail and designs of materials have been suggested for 1/ nano-wire structures presenting interesting properties for sub-wavelength image formation at optical frequencies, 2/ nanolamellar composites of alternating dielectric and metallic layers for sub-wavelength image formation at optical frequencies and 3/ plasmonic metamaterials based on nanostructured metallic films and porous metals (fishnets).

The CNRS Paris partner was in charge of metamaterial fishnets and structured substrates. Commercial
wafer were patterned using an advanced technique for anisotropic miniaturization (patented during the course of the project). The patterned substrate was then filled with a plasmonic resonator, generating a material with strong optical sensitivities to the refractive index of the surrounding media due to the excitation of surface plasmon polaritons. Film synthesis and processing techniques were extended to new systems, testing the limits of bottom-up chemistry.

The CNRS Bordeaux partner was in charge of anisotropic metal-dielectric nanocomposite obtained by templating block copolymer matrices. Lamellar structure were chosen for the system to be focused on. Thin (200 - 600nm) films of lamellar nanocomposites were produced with the layered structure aligned parallel to the substrate surface, and with varying concentration of 10-nm gold nanoparticles in the alternate layers. The optical properties of the films were studied by spectroscopic ellipsometry. The analysis suggests the existence of a strong anisotropy of the dielectric permittivity, with the parallel and perpendicular components having opposite signs in a limited range of wavelength, which corresponds to a hyperbolic metamaterial.

The general objective of WP 2 is to fabricate metamaterials using templating organic matrices made of self-assembling block copolymers. These materials present spontaneous molecular organization in the bulk or in contact with a surface, with long-range order and with characteristic sizes of a few 10 nm, of particular interest for the fabrication of metamaterials in the visible wavelength range. We propose to use these 'optically neutral' templates to spatially organize 'optically efficient' entities, such as metallic nanostructures, in order to fabricate ordered anisotropic metal/dielectric hybrid nanocomposites, which can be used towards high-gain optical radiators, sub-wavelength guiding device like nanowire lenses, or subwavelength periodically perforated metal thin films (fishnets) with extreme properties like extraordinary optical transmission due to surface plasmon polaritons, or negative refractive indices. To achieve these structures, two classes of templating approaches have been considered:

(i) 2D metamaterials assembled from aqueous dispersions of amphiphilic diblock copolymers - Diblock copolymers are macromolecular chains made of two blocks of distinct chemical nature. Amphiphilic diblock copolymers, with one hydrophilic (soluble in water) block and one hydrophobic (of low or zero solubility in water) block form, in dilute aqueous dispersions, self-assembled objects called micelles. Patterned surfaces, with periods of a few 10 nm, can be obtained when such micelles are deposited onto substrates. Our strategy (CNRS-Paris) consists of using such amphiphilic copolymer micelles to form metal nanopatterns on a surface.

(ii) 3D metamaterials assembled from solid ordered phases of diblock copolymers - Diblock copolymers present spontaneous molecular organization in the solid state with symmetries including hexagonally packed cylinders and periodically stacked lamellae and with typical periods an order of magnitude smaller than the wavelengths of visible light. Our strategy (CNRS-Bordeaux) consists of inserting and organizing plasmonic nanoparticles within these types of matrices.

DESCRIPTION OF WORK

The work of WP2 has been: the theoretical prediction of optical properties of structures (Task 2.1); the fabrication and structural study on three main classes of templates and their first-level optical characterization (Task 2.2 / Task 2.3).
Task 2.1: Numerical predictions
The theory groups have used approaches of infinite-array for the theoretical description of EM properties of anisotropic metal-dielectric hybrid nanocomposites. They have developed numerical techniques to analytically model plasmonic spherical/spheroidal nanostructures. A full-wave integral-equation approach has also been developed which considers unknown electric and magnetic current densities only on the interfaces between piecewise homogeneous media and imposes no other approximations than those related to the geometric discretization of the structure.

Task 2.2 / Task 2.3: Fabrication and structural analysis of the nanocomposites; optical study of the nanocomposites

T.2.2.1: Nanopatterned surfaces:

The global goal is the fabrication of periodically nanoperforated metallo-dielectric thin layers.

The synthetic strategy presented here has aimed at creating metallo-dielectric nanopatterned surfaces using bottom-up chemistry. The method employed has proceeded via three steps:

- Step 1/. Liquid deposition of periodically organized inorganic nanopatterns (INP) on substrates: crystalline silicon, ITO and silica substrates
- Step 2/. Dry etching (by reactive ion etching)
- Step 3/. Filling the channels of the etched substrate with Au

Advanced optical characterization demonstrated the potential of gold columns grown within wells in a silica matrix as optical sensors in, for example, medical and biological applications. This potential stems from the fact that the optical properties of the material are susceptible to the refractive index of surrounding media thanks to the excitation of surface plasmon polaritons of the discrete assembly of gold columns. The optical properties were highly anisotropic due to the designed morphology of the material. Different aspect ratios could now be tailored to study the effects on optical waveguide properties.

The synthesis strategy relied mostly on bottom-up fabrication, thus large, homogenous areas of material can be prepared. The organization was not of the same quality as strictly top-down methods, however the preparation method is commercializable due to the low intensity of labor and scalability of the techniques.

- T2.2.2: Lamellar films:

Several synthetic routes were investigated for the preparation of thin ordered films of nanocomposites of polymers and gold nanoparticles. The most efficient is the in-situ reduction of gold salts introduced in the pre-aligned lamellar copolymer thin films. Aligned films of thickness 200-600 nm with a lamellar metallo-dielectric nanostructure were successfully produced.

The optical properties of the films were determined by variable angle spectroscopic ellipsometry. The optical data are consistent with a hyperbolic behaviour (i.e. permittivity has a different sign along two
directions of space) over a limited wavelength range close to the plasmon resonance of the nanoparticles.

In conclusion of this part, the work progress followed well the route which was initially planned concerning the lamellar nanocomposites, and there was some delay but no significant deviations from the initial plans. The work towards producing cylindrical nanocomposites should have followed the successful fabrication methods developed for lamellar systems, but we have decided to focus our efforts on optimizing the lamellar systems rather than working on both morphologies.

GENERAL CONCLUSION

The theoretical and numerical works confirmed the collimation effects from periodic arrays of plasmonic nanorods. It also provided an efficient simulation software based on full-wave integral-equation approach to be used for the electromagnetic analysis of finite and infinite periodic metamaterials at optical frequencies, and more generally of finite and infinite arrays of any arbitrarily-shaped piecewise homogeneous structures.

The bottom-up fabrication of discrete assemblies of gold nanocolumns, presenting specific properties of surface plasmon polaritons has been successfully achieved. Their optical properties are highly anisotropic due and different aspect ratios can now be tailored to study the effects on optical waveguide properties.

The bottom-up fabrication of lamellar plasmonic nanocomposites presenting a strong optical anisotropy has been achieved. Their properties of hyperbolic material over a limited wavelength range has been demonstrated. They need to be further studied and utilized.

WP3 - SELF-ASSEMBLED METAMATERIALS

Participants: CNRS, CNR IPCF, UCL, UNISI, Rhodia LOF

WP3 SUMMARY:

The general objective of WP3 is to obtain metamaterials by controlled stacking and self-assembly of nanoparticles under the sole effect of interparticle forces, resulting in dense 2D or 3D “superlattices”.

WP3 has a twofold theoretical and technological challenge: designs based on electromagnetic simulations and theoretical analysis point out the expected EM properties and connect them to the actual structures. Fabrication was planned along three main routes:

- Direct ordering (2D self assembly +1D directed) by using Langmuir Blodgett and layer by layer methods to fabricate nanostructured materials
- Spontaneous 3D self organization by physical chemical routes, such as solvent evaporation
- Assembly of NPs by microfluidics techniques

The main achievements planned for the project duration have been reached:
Detailed specifications of the design rules for fabrication to obtain defined EM properties for the class of metamaterial envisaged in WP3. The main objective of the theoretical developments of the theory groups in UNISI and UCL has been to model the interaction of electromagnetic fields with bulk metamaterials by means of effective parameters capable of taking into account their inherent qualities and complex nature. We have first explored the applicability of classical homogenization theories for 3D array of spherical inclusions both in the long wavelength (static) limit and their quasi-static extension. Then, in order to account for spatial dispersivity, we have applied the generalized Lorentz-Lorenz (GLL) method for the homogenization of metamaterials which is capable of providing a comprehensive description of both spatial and frequency dispersion phenomena. By combining the GLL approach and the Single/Dual dipole approximation model with a 3D periodic Green’s function for infinite crystals, we have been able to calculate modal propagation and retrieve effective parameters for various plasmonic metamaterials of interest. The GLL method has been also extended to the case of binary metamaterials.

Full-wave simulation of analysis of multi-layered metamaterials with complex inclusions has been performed, with an integral-equation method with complexity proportional to the number of layers.

Accurate integral-equation analysis of scattering by non-periodic metamaterials and study of localized field enhancement in such arrangements has been carried out.

Synthesis and production of nanoparticles required for all the assembly routes in WP3. The main challenge has been to achieve a precise control on the size distribution of the NPs and their surface functionalization both in aqueous and organic solvents. Synthetic strategies to obtain highly monodisperse plasmonic nanostructures, both Au NPs and Au@SiO2 NPs, have been successfully combined with appropriate size sorting procedures implemented at CNR IPCF-Bari. In addition, a range of other more complex plasmonic nanostructures like multicore Au@SiO2 NPs, Au@SiO2 NPs decorated with Au NPs, core-shell metal@dielectric NPs of various sizes and shell thickness have been synthesized with silver and gold core, and core-shell Silica shells doped with fluorescent dyes are have been produced at CNRS Bordeaux and delivered to CNR IPCF Cosenza.

Production of nanostructured materials by using the physical chemistry routes and microfluidics evaporation techniques. Several series of materials have been produced: (a) monolayer and multilayer assemblies of plasmonic core-shell silver@silica nanoparticles have been fabricated by CNRS Bordeaux. The expected modulation of the dielectric permittivity has been demonstrated on samples of large area, leading to original materials that enable ultra-sensitive sensing applications. Packing disorder does not affect the effective electromagnetic properties if metallic resonators are encapsulated in dielectric shells that controls the separation (and hence the coupling) between the plasmonic cores. The effective material parameters of nanometric silver are different from values reported in bulk silver. (b) microfluidic evaporation based materials have been fabricated by a microfluidic assembling of metal-based nanoparticles (NPs). Upon engineering and optimization of the microfluidic device, kinetic regimes especially favorable for growing materials out of dilute dispersions of functional NPs have been found and quantified. In these regimes, 3D materials with a high degree of bulkiness, very flat faces, and made of various types of NPs have been grown. Optical characterization using microspot ellipsometry permitted us to evidence that when NPs are very concentrated (about 40% volume fraction), the materials display an extremely large refractive index in the near infra-red regime with potential application for telecom.
Macroscopic superlattices of self-assembled core-shell gold@silica with incorporated fluorescent dyes have been synthesized by Rhodia-LOF and delivered to CNR-Cosenza for loss compensation tests.

-iv- The formation of 2D superlattices based on highly monodisperse Au NPs (11 nm) obtained by the combined size sorting approach has been demonstrated with a highly controlled geometry and extending over µm2 when drop cast onto a suitably functionalized silicon substrate. The assembly procedure over mm at CNR IPCF Bari. The role of monodispersity, solvent composition and substrate functionalization has been found crucial to accomplish the result.

Sets of superlattices have been delivered to UNIMAN for a EM characterization. Ellipsometric investigations on self-assembled Au NPs has shown that the sample surface results homogeneous and uniform and a strong reflected signal, characterized by a reduced noise has been recorded and a good agreement between experimental and fitting Psi data has been found.

DESCRIPTION OF WORK

Task 3.1 Theoretical assessment of the EM properties of the fabricated structures

The theoretical work has resulted in the production of design rules by theory for materials fabrication.

In particular the work done can be classified in terms of (i) development of theoretical tools, and (ii) calculation of optical properties of some metamaterials that can be built within the consortium.

(i) Theoretical tools developed: software able to determine transmission and reflection by arrays of plasmonic nanoparticles, using the single dipole approximation (SDA). Software able to determine propagation characteristics in layers or 3D lattices of nanoparticles. Application and development of previously existing approximate methods to determine the homogenized properties of metamaterials. Software able to evaluate fields from nanoparticles, interaction among nanoparticles, response of arranged nanoparticles to an external beam, using a full wave spherical wave expansion. Software and theory to evaluate interface effects, between air (or solvent) and a metamaterial made by arrayed nanospheres.

(ii) Properties of arrays (2D and 3D lattices) of plasmonics nanospheres and nanoshells (metal-dielectric, where metal is either Gold or Silver). Properties of 3D lattices of voids (of air or silica) in a bulk metal. The properties examined are low permittivity or refractive index, high permittivity, backward propagation. Mode propagation in 3D lattices, in terms of transverse polarization (in this case the metamaterial can be homogenized in most of the cases) and longitudinal polarization. This last one is present in some frequency ranges, and cannot be described in terms of homogenization theory. Properties of 3D lattices of binary composites like CuCl and Silver (CuCl is an excitonic substance) that are able to provide a negative refractive index. We have examined also the case of a metamaterial with CuCl at the center of the nanoshells. Some examples are given next.

(iii) Characterization of composite materials made of 3D periodic arrays of spheres. Composite materials made of three dimensional (3D) periodic arrays of spheres have been studied to understand the propagation of modes with complex wavenumber excitable in such composite materials, and the interesting properties achievable, such as epsilon-near-zero materials (ENZ), and artificial magnetism. Below we show an example of ENZ material.
(iv) Multilayer for subwavelength resolution. A multilayered structure for subwavelength imaging applications has been studied. The purpose was to understand the design process of a layered medium which can transfer both the propagating and most of the evanescent part of the spectrum of a source through the multilayer. Such a device will create a replica of the original source at the image point with a higher level of detail than that of conventional optical lenses.

(v) Full-wave simulation of analysis of multi-layered metamaterials with complex inclusions, with an integral-equation method with complexity proportional to the number of layers.

(vi) Accurate integral-equation analysis of scattering by non-periodic metamaterials and study of localized field enhancement in such arrangements.

Task 3.2 Nanochemistry routes for obtaining NPs to self assembly

At CNR-IPCF synthesis of colloidal metal particle, Au NPs, dielectric SiO2 NPs, and metal-dielectric core-shell particles, Au@SiO2 have been set up in order to achieve NPs in a tuneable size regime and with a low size polydispersity. The colloidal nanoparticle synthesis is indeed the starting step towards metamaterial fabrication, as it provides the functional building blocks with tailored size- and shape-characteristics able to ultimately define the final geometry of the resulting superstructures, and, accordingly, their collective electro-magnetic properties.

Synthesis of different types of NPs has been designed in order to produce convenient building blocks to be assemble in dense materials.

A precise control on the size distribution of the NPs and their surface functionalization both in aqueous and organic solvents has been achieve.

Synthetic strategies to obtain highly monodisperse plasmonic nanostructures have been implemented.

The following types of plasmonic NPs have been prepared by combining suitable surface reatment with carefully defined synthetic protocols and appropriate size sorting procedures, including density gradient centrifucagion and size sorting precipitation:

- Au NPs with controlled size in the range between 7 and 17 nm
- Au@SiO2 NPs
  -- SiO2@Au nanoshells

In addition, a range of other more complex plasmonic nanostructures including SiO2@Au nanoshell, multi core Au@SiO2 NPs, core-shell Au@SiO2 NPs decorated with Au NPs,core-shell metal@dielectric nanoparticles of various sizes and shell thickness have been synthesized with silver and gold core,

The proposed strategies are able to offer a way to control NP dispersity and to specifically define the final nanostructures by a careful adjustment of the synthetic parameters and use of suitable post preparative procedures. The described approach can thus effectively provide a versatile tool to prepare plasmonic materials with specific morphology and optical properties, to be used as building blocks suitable to design and fabricate metamaterials by self assembly procedures.
Task 3.3 Physical chemistry and microfluidic based strategy to assembly NPs

Two systems have been investigated:

A - Nanoparticles for implementation of the Langmuir-Blodgett technique

The Langmuir-Blodgett technique consists of three steps: (i) spreading on water surface of a suspension of nanoparticles (NPs) in a volatile organic solvent (ii) compression of the surface film to form a compact Langmuir monolayer and (iii) transfer of the Langmuir monolayer on a solid substrate. Multilayer samples are obtained by successive transfers.

The method has been improved by us to enable the transfer of defect-free monolayers of nanoparticles.

- The Langmuir-Blodgett assembling method has been successfully implemented and adapted to obtain the targeted metamaterials, namely dense films of meta-atoms of optical quality over large areas.
- The structural characterization of the films has been achieved, as planned in the work programme, mostly by electron microscopy.
- The first-level optical characterization of the films has been achieved after synthesis.
- The best samples have been delivered to the relevant partners for advanced optical studies as planned in the work programme.
- The extraction of effective electromagnetic parameters has been successfully achieved. Several important results have been obtained:

  a. the sharp resonance of the dielectric permittivity leading to high or low values of the refractive index has been demonstrated.
  b. the packing disorder, inevitably associated with self-assembly, does not affect the effective electromagnetic properties if metallic resonators are encapsulated in dielectric shells that controls the separation (and hence the coupling) between the plasmonic cores.
  c. the effective material parameters of nanometric silver are different from values reported in bulk silver. Losses are consequently higher than expected, but still lower than for Au.

- The dispersion properties \( (n(\omega), k(\omega)) \) of the composite materials can be tuned to reach the "topological darkness" condition (i.e. identically zero reflection coefficient). This property opens the way to the fabrication of highly sensitive sensors.

B - Metal-dielectric multilayers. Model structures of A-B-A-B type (Task 3.3)

Metal-dielectric multilayer materials are known to exhibit non conventional electromagnetic behaviour. In particular, the permittivity can have different signs along different directions (so-called hyperbolic materials). Sub-wavelength imaging by such materials has been demonstrated by Fang et al. in Science 308 534 (2005). Hyperbolic materials can be produced by top down evaporation techniques. Two different ways are investigated in METACHEM, namely templating by diblock-copolymers (in WP2) and a combination of vapour deposition and spin-coating in this task.
Despite a successful fabrication of multilayer demonstrators, the method was finally abandoned after M36 when it appeared that it could not compete with other approaches (including WP2 copolymer template).

- thermal cross-linking of the successive spin-coated polymer layers strongly damaged the underlying structure of the previously deposited layers. As a result, stacking more than 4 layers was not possible.
- thicker multilayers of high structural quality could be produced if thermal cross-linking was not performed, but the polymer layers were then fragile and did not protect silver from fast oxidation.

Several polymers were used in this study (polystyrene, poly-vinyl-alcohol, Ormocer resin supplied by partner Fraunhofer), with increasing performance, but still not sufficient to compete with other techniques.

The decision was hence made to focus efforts on LB assembly.

C - Self-assembly by evaporation of solvent in microfluidic channels

The goal is to assemble NPs in small solid structures by means of a recently developed microfluidic technique that enables the manipulation of very small quantities of solution of NPs (~ µL) in order to concentrate the nanocolloids by controlled extraction of the solvent. In the first step, PDMS microchips, which are permeable to water and other solvents but not to NPs, have been used to selectively extract the solvent. As a result, more and more NPs get accumulated in the microchannel and their concentration increases with time, in a manner which is easily predictable for ideal solutions and calculable for interacting species.

In this way, it is possible to concentrate species, including colloids and nanoparticles, starting from a very dilute solution possibly up to a dense state. It is crucial to work with stable NP dispersions in order to prevent colloidal aggregation. For this purpose, different types of NPs solutions have been extensively studied in order to define a model system. The robot-assisted preparation of the samples enabled a fast screening of a large range of different chemical physical conditions. A set of complementary techniques was used to characterize the aggregation status within the solutions (i.e. UV-visible spectroscopy, colorimetry, and dynamic light scattering).

Microfluidic evaporation has been used at Rhodia LOF to assemble metal-based NPs. Upon engineering and optimization of the microfluidic device, kinetic regimes that are especially favorable for growing materials out of dilute dispersions of functional NPs have been found and quantified. In these regimes, 3D materials have been grown with a high degree of bulkiness, very flat faces, and made of various types of NPs (including unary and binary dispersions, anisotropic particles, composites, etc.). Optical characterization using microspot ellipsometry permitted us to evidence that when NPs are very concentrated (about 40% volume fraction), the materials display an extremely large refractive index in the near infra-red regime with potential application for telecom.

It is possible to concentrate functional NPs designed to be very stable at high concentration, from a dilute state up to very concentrated, dense states within a dedicated microfluidic device and thus to grow 3D arrays of densely packed NPs.
The material can be obtained directly molded into the microfluidic geometry, and thus replicates its shape. The faces of the materials are actually very flat, which enable optical characterization. Bulk materials were grown from monodisperse or anisotropic NPs and binary materials. We performed optical characterization (microspot ellipsometry) with partners of the project and found that the refractive index of the materials depends largely on the amount of metal present in the structure. The most promising materials are obtained with high loads of metal (up to 40% volume fraction of metal with NPs with a size ~ 20 nm) for which the plasmonic response is significantly red-shifted and which display a huge refractive index in the near infra-red region of the spectrum, and with moderate losses. These materials are promising candidates for optical components working in the telecom band.

D - Self assembly of colloidal NPs by solvent evaporation:

Superlattices have been fabricated by exploiting a solvent evaporation approach. Several types of NPS of interest for the project have been assembled, including Au nanospheres, Au-silica core-shell NPs and monodisperse and bi-disperse populations of PbS NPs, which have been synthesized by using a colloidal chemistry route, based on the use of a non coordinating solvent and a mixture of surfactants. Organic coated PbS NPs characterized by a monomodal and a bimodal size distribution, respectively, have been obtained and self assembled.

The influence of the nature of the solvent, of the substrate, of the size distribution and of the surface function of the NPs have been investigated in order to optimize the organization of the colloidal lattice.

The results of the microscopic, morphological and structural investigation, achieved by TEM, SEM and XRD techniques, at small and high angle on self assembly obtained by solvent evaporation for the model systems based on bimodal population of PbS NPs have been used for implement reliable procedure for the fabrication of binary metal dielectric superlattices, with defined geometry by suitably controlling the experimental parameters.

Oleylamine capped Au NPs have been deposited onto both TEM grids and silicon after a size focusing procedure carried out by means size selective precipitation.

Thermal treatment performed onto Au NP toluene solution cast samples and dipping from NP toluene solution have demonstrated to provide high range order NP self assembled structures.

Assembly of SiO2 NPs and core shell Au@SiO2 NPs have been also performed and the critical factors for achieving a successful long range assembly, represented by size distribution, solvent, and NP surface chemistry, pointed out.

The here presented results highlight that:

- size selected Au NPs assembled in higher ordered structure with respect to the as prepared NP, both on TEM grid and silicon substrate. In this latter case irrespectively on the deposition strategy monolayer as
well as with multilayer structure can be observed.
- The thermal treatment during the solvent evaporation improves the extent of order in the NP assembly
- Choosing the deposition strategy and particle concentration of ODTMS functionalized silica NP and silica coated Au NPs suspension allows to tune particle assembly from multilayer to monolayer structure.

Irrespectively of the type of tested NPs, being Au or silica or silica-coated Au NPs with a hydrophobic surface, the observed reduced substrate coverage suggest that a substrate pre-treatment (alkyl terminated SAM, CFX plasma treatments, etc.) could be necessary towards an improvement of the particle-to-substrate interaction during the assembly process.

WP4 – LOSS COMPENSATION IN METAMATERIALS

Participants: CNR-Cosenza, CNR-Bari, CNRS-Bordeaux, UCL, UNISI, UVIGO, Rhodia-LOF

WP4 SUMMARY:

WP4 objective was to face the fundamental problem of optical loss in nano-engineered plasmonic structures. We proposed a multi-scale complementary approach to introduce optically active components right at the heart of the engineered meta-materials (dyes, quantum dots, semiconductor nanocrystals) by promoting effective energy transfer from gain media to plasmonic building blocks.

For compensating absorptive losses we used the versatility of nano-chemistry by introducing optically active components right at the heart of the engineered meta-materials. In particular three classes of materials have been considered, namely metallic nanoparticles, luminescent quantum dots, and organic dye based nanoparticles. For this purpose also protocols and materials developed in WP1, WP2 and WP3 have been mutated and used. Theoretical studies were performed via multiscale approaches to drive nanochemists towards the design and synthesis of appropriate gain functionalized nano-objects as well as to gain further understanding about EM properties arising by experimental investigations. Further step was to create adequate chemical and physical conditions to embed gain doped plasmonic nanoparticles in transparent matrices to create bulk materials. A multipronged approach has been followed based on different host systems (Bulk PDMS, Liquid crystals, microfluidic PDMS chip).

Optical spectroscopy as well as photo-physical investigations performed on these systems showed that plasmon mediated resonant energy transfer processes, between gain materials and plasmonic nanostructures, are behind the striking metal enhancement effects. Fluorescence quenching is accompanied by a remarkable Raleigh scattering and transmission enhancements within the compensation band. Whereas, according to Kramers-Kronig integral relations an increase of extinction coefficient is measured at the higher energy neighbor band. These results clearly demonstrate that optical loss can be moderated in plasmonic nanostructures either by functionalizing single elements with proper gain units placed in close proximity and by assisting larger scale nanostructures surrounded by effective gain materials.

The main achievements at M48 definitely match the expectations of the initial work program.
DESCRIPTION OF WORK

I: Theory and Modeling.

We aimed towards understanding the response of plasmonic (metallic) nanoparticles put in the presence of a chromophore/fluorophore dye able to couple to the plasmonic resonance, and whether or not this resonance can be compensated in terms of losses, or even amplified to give “nanolaser”-like, spectrally sharp, light emission.

We have approached the problem of the optical response of metallic core-dielectric shell nanoparticles with gain in the shell. In a first approach, the gain medium was described as a macroscopic, continuous medium, and in a second step, a unique microscopic model of the optical response of metallic nanoparticles decorated with gain molecules was developed in which all interactions between dyes molecules and the core are considered within a Green’s function framework.

This model presents a singularity condition where a limited number of modes are amplified and dominate the optical response which becomes extremely sharp and intense, yielding a very high-quality “plasmon”. This is very strongly reminiscent of the spaser and nanolaser effects observed experimentally on similar or different nanoparticle geometries. Therefore this electromagnetic model appears as the first plausible, detailed model for the spaser effect, and also provides deep insight into the amplification mechanisms within the aggregate and the way to amplify plasmons to make them sharp and intense.

Beside the analytical models, the possibility of compensating losses in different types of metamaterial structures by incorporation of active media (dyes) was investigated numerically.

An equivalent constitutive relation was achieved by modelling the gain medium as a generic four-level lasing system. Beyond a critical pumping rate, nonlinearities arise which can be described by iterating the linear model in a harmonic balance scheme, thus predicting gain saturation and harmonic generation effects.

We have studied the optical response of:

- 3D arrays of metallic spheres, of metallic shells with dielectric core
- 2D periodic arrays (layers) of metallic spheres coated with a shell of gain material, or metallic shells with a gain material core.
- collections of magnetic MNC nanoclusters in which the gain material is incorporated in the metamaterial nanostructure by inclusion of a distribution of quantum dots, or fluorescent dyes, and the case when the active optically pumped gain material is used as the host medium. In particular, we have analysed the effects of embedding certain naturally available dye materials, e.g. Coumarin C500 and Rhodamine 6G.

We have shown that the effectiveness of loss compensation essentially relies on the concentration of the dye material, its emission bandwidth and the coupling strength to the external electric field. In fact, increasing the pumping rate can just bring the system to saturation. Compensation of losses can be
potentially achieved around the atomic transition frequency of the dye that should coincide with one of the NC metamaterial resonances (e.g. the magnetic resonance).

With the approach of incorporating the dye material in the coating of the constituent in order to obtain stronger compensation effects, thick active material shell should be used. However, this would significantly change the optical response of the NC moving both the electric and magnetic resonances. Indeed, we found that complete compensation of losses with existing dye materials is rather challenging. Even for high concentration of the Coumarin C500, for example, complete compensation of losses could not be achieved. However, we have shown that loss compensation would be possible provided that a dye material with a smaller emission bandwidth (or a larger coupling strength to the incident field), implying that a larger power spectral density is coupled to the metamaterial in the emission bandwidth.

We showed that incorporating the active gain material as the host medium of the metamaterial lattice, turned out to be somewhat more effective than incorporating the active material into the coating of the constituent particles.

II: Synthesis and Fabrication.

Nanosized building blocks (spherical Au and Au@SiO2 core shell NPs, Au nanorods and luminescent CdS@ZnS core shell QDs) have been synthesized with fine control of size, shape and composition.

The obtained nanostructures have been properly engineered and functionalized in order to conveniently exploit them for the fabrication of metamaterials.

Distinct strategies have been designed and implemented in order to provide flexible solutions able to fulfill the different needs in terms of fabrication and spectroscopic properties.

Several systems incorporating gain elements have been produced:

- QDs coupled to Au NPs embedded in a plastic PDMS matrix
- multilayered structures coupling luminescent QDs and Au@SiO2 core shell NPs onto modified quartz substrates.
- Direct functionalization of QD@SiO2 NPs with Au NPs:
- Core-shell Au@SiO2 NPs functionalized with luminescent QDs:
- dispersions of Au@PEG NPs in water (gold core of 15 nm) and rhodamine 6G (R6G, soluble in water with main absorption at 520 nm, and emission at 560 nm) were assembled in microfluidic evaporators.

III. Experimental Validation Of Optical Losses Compensation.

Opto-Plasmonic Investigations to Demonstrate Optical Loss Reduction in Plasmonic Nanosystems

We investigated experimentally the resonant energy transfer processes from organic gain materials, or semiconductor quantum dots (QDs), to noble metal nanoparticles, properly designed to create optical metamaterials via self-assembling routes. Multiple experimental investigations indicate that losses at
optical frequencies, mainly due to plasmon-radiation field coupling, can be partly compensated. Resonant excitation energy transfer occurs via non-radiative process, by proper overlapping gain and plasmonic spectra and by optimizing size-ratios. From the very beginning, we focused most of the efforts to analyse and manage the parameters main responsible of high efficient energy transfer processes: 1) NPs size; 2) gain-metal interdistance and 3) band overlapping between plasmon resonance and fluorescence curves. A series of correlated experimental investigations were performed to select materials and characterize the optical properties of gain assisted meta-subunits.

We distinguished two different types of dispersions, Gain-assisted and Gain-functionalized, depending on the fact if the gain material is dispersed in solution or embedded in the silica shell. The gain assistance of plasmonic elements through non-radiative processes is emphasized by Fluorescence quenching, enhanced of Scattering Rayleigh as well as Transmission, mitigation of radiation damping and related radiative and non-radiative effects via reduction of decay lifetimes. This is why we performed a multi-pronged experimental approach able to investigate all these elements by means of the same experimental set-up. We implemented two different set-up, depending on the time scale used to perform the experiments. A pump-probe set-up based on a Nd:YAG pulsed laser (repetition rate of 20Hz, 3ns of pulses and second/third harmonic generation, 532 and 355nm, respectively) was used to perform fluorescence measurements, increasing of transmission and scattering of the probe (Xenon lamp with monochromator, He:Ne and DPSS lasers) (see details in deliverable D4.4).

An ultra-fast spectroscopic set-up was used to perform lifetime measurements and broadband probe signal enhancement (super continuum generation). The main result here was the possibility to selectively induce transparency in a particular optical band showing the importance of the band overlapping to induce effective energy transfer processes (in-resonance or off-resonance).

These results are a clear experimental demonstration of the compensation of loss in metal NPs and enhancement of the quality factor of surface Plasmon resonance by optical gain. Different dye molecules have been selected so that their emission curves present a band overlapping with the plasmon bands of the core-shell NPs.

Our experimental studies clearly show that the interplay between metal nanoparticles and luminescent species involves two major phenomena: the enhancement of the local excitation field and the modification of radiative and nonradiative decay rate of fluorophores, inducing a remarkable quenching of fluorescence. Preliminary investigations on dispersions of core/shell nanoparticles at nanoscale confirmed this behaviour.

Then we tried to move towards meso- and macro-scale systems, in which the strong interaction between metal sub-units now plays a decisive role. We obtained quite demonstrative results in three different systems

a) gain-assisted porous meso-capsules.
b) plastic matrices of mixture of gold NPs and QDs and
c) multilayes microstructures.
a) Hollow mesoporous silica capsules of 500nm diameter, in which multiple gold seeds have been grafted on the inner walls of the porous silica shell. By adding R6G dye to the solution and increasing concentration by means of several centrifugation steps, we were able to obtain a functional nanostructures showing a remarkable widening of the plasmon resonance band, covering half of the visible spectrum (500-700 nm), accompanied by a substantial loss compensation effect.

b) Coherent interactions between CdSe@ZnS core–shell quantum dots (QDs) and Au nanoparticles (NPs), simultaneously dispersed in a flexible polymer matrix (PDMS) generate a clear enhancement of the absorption cross-section of the QDs, remarkably modifying the optical response of the entire system. Optical and time resolved spectroscopy studies revealed an active gain-plasmon feedback behind the super-absorbing overall effect.

c) We realized a hyperbolic metamaterial (HMM) alternating 6 bilayers of TiO2 (32nm) and Au (16nm), and verified negative values of ε above 550nm (hyperbolic dispersion). A dye doped polymer film (DCM+PMMA) was spin coated on the top of the structure in order to demonstrate the existence of high-k modes by means of lifetime measurements. Excitation of SPPs and BPPs was performed by ellipsometric spectroscopic measurements in reflection and transmission. Hypergrating coupling technique was used in order to couple light inside the structure and induce the excitation of these modes.

GENERAL CONCLUSION

We eventually demonstrated the possibility to fabricate low-loss metamaterials where gain media can be adequately inserted at different scale levels, ranging from nanoscale to the macroscopic scale. Effective Resonant Energy Transfer (RET) processes are behind the remarkable modifications of the effective dielectric permittivity of the gain functionalized nanostructures. Therefore, these results are of particular importance to move metamaterials from fundamental scientific challenges to applied materials.

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WP5 - CHARACTERIZATION AND DEMONSTRATION OF META-ELECTROMAGNETIC PROPERTIES

Participants: All parties in the consortium

WP5 SUMMARY

The main objective of WP5 was to characterize the materials produced within WPs 1 to 4. In the first year of the research we had to develop and to assess efficient methods of optical analysis of metamaterials with non-trivial refractive index.

The work for the first reporting period contained one main task: T5.1 – Spectroscopic ellipsometry combined with developed EM.

To briefly summarize the work done in M1 to M18, we have:
1. upgraded ellipsometry software to study bi-anisotropic metamaterials with arbitrary permittivity and permeability tensors; upgraded interferometry, transmission and reflection kits.

2. checked the installations on optomagnetic metamaterials made with the help of electron beam lithography and studied non-local optical properties of regular arrays of nanoparticles.

3. observed field enhancements in the composite structures of different sizes produced by electron beam lithography and studied samples produced in Fraunhofer and Calabria.

The work in the remaining WP5 contained two parts: T5.1 - Measurements of optical constants of fabricated metamaterials and T5.2 - Impedance matching and improvement of theoretical methods for data analysis.

To summarize the work done in the second period M18 to M36, we have:

1. Measured resistive coupling of regular arrays of plasmonic resonances
2. Combined fabricated structures with graphene to measure field enhancement and to develop extremely sensitive plasmonic sensors. For example, we measured hydrogenation of graphene using non-local response of plasmonic nanoarrays.
3. Developed a new concept of topological optical darkness.
4. Studied the optical properties of silver core-shell nanoparticles fabricated by Bordeaux, WP3. We also extracted optical constants of the structures.
6. Measured optical properties and extracted effective constants of lamellar structures fabricated by CNRS Bordeaux, WP2.
7. Measured optical properties and extracted effective constants of 3D metamaterials produced by evaporation, LOF Rhodia, WP3.

To summarize the work done in the last period of Metachem (M36 to M48), we have

1. Developed new theoretical methods of media homogenization with new extraction methods for effective optical constants.
2. Measured optical properties and extracted effective optical constants of improved anisotropic lamellar structures fabricated by Bordeaux, WP2.
3. Measured optical properties and extracted effective optical constants for micro fluidic bulk metamaterials made from silver and gold core nanoparticles in Bordeaux, WP3.
4. Studied optical properties of core-shell nanoparticles and raspberries fabricated in Univ. Cosenza and Vigo, respectively.
5. Checked fabricated metamaterials on the presence of negative refractive index and negative optical phase.

To summarize the whole work done in WP5, we have not been able to measure negative refractive index in artificial metamaterials made by self-assembly. The reason for that is the difficulty of making "bulk" negative refractive index with metal nanostructures (losses are too high). At the same time, we found several new exciting phenomena: topological darkness in self-assembled metamaterials, resistive coupling of plasmonic resonances, high refractive index in 3D bulk metamaterials, high phase sensitivity to
molecular binding for graphene based plasmonics.

DESCRIPTION OF WORK

1. Upgrade of ellipsometry software.

The main task for the first year was Task 5.1 – spectroscopic ellipsometry combined with developed EM models. To this end we have upgraded the ellipsometry software to include META-6 modeling which allows treatment of bi-anisotropic metamaterials with arbitrary permittivity and permeability tensors. The model also contains 2 gyrotropic tensors in order to describe bi-anisotropy. It has to be noted that there is still debate on validity of using bi-anisotropic models for descriptions of non-local optical media. Some scientists believe that such metamaterials should be described in terms on spatial dispersion. We applied the META-6 model to theoretical negative refractive metamaterial (not bi-anisotropic) and check the model validity (the extraction of the optical constants from the modeled ellipsometry data).

2. Upgrades of interferometry, transmission and reflection kits.

The interferometry kit was upgraded by adding polarization rotation components and blue laser (ordered). The MATLAB software has been developed which allows one to measure the optical path in the metamaterial sample using phase shift of the interferometer fringes. This custom software dramatically improves signal-to-noise ratio of phase extraction (and hence of extraction of the real part of the refractive index of a sample) by producing spatial averaging of the interferometric pattern. The optical kits which measure transmission and reflection from the sample under normal angle of incidence have been upgraded by adding new fiber components and light sources.

3. Trial measurements of double-dot optomagnetic metamaterials.

To check the upgrades and software we have studied optomagnetic metamaterials based on regular arrays of double dots made with the help of electron beam lithography. (Ideally, installations has to be checked on the sample prototypes made in WP1, however, this was impossible due to the theoretical process of choosing the most promising structure for the negative index metamaterial). We have measured reflection, transmission, ellipsometry and interferometry of a whole variety of these samples. Negative optical phase has been observed and we have extracted negative real part of the refractive index, V. G. Kravets et al. Optics Express 18, 9780 (2010), see Figure below. The ellipsometry results are under analysis and preparation for publication. On average all kits worked well proving us with the position of the plasmon resonance peaks and the optical constants of the samples. We also obtained new interesting results on behavior of the phase of the optomagnetic metamaterials as a function of the angle of incidence. These measurements are essential for the checking installation and preparing it for measurements of self-assembled negative index metamaterials.


One of the main obstacles on the route of extracting optical constants of composite metamaterials is the presence of spatial dispersion (non-local response). It has to be said that optomagnetic metamaterials are
inherently spatially dispersive (permeability is just a long wavelength limit of spatial dispersion.) To achieve high values of permeability the concentration of plasmonic resonators has to be high which leads to pronounced spatial dispersion. Recently we have shown that the presence of spatial dispersion can be beneficial, e.g. for obtaining plasmonic resonances with unusual properties, say high quality (V. G. Kravets et. al., Phys. Rev. Lett. 101, 087403 (2008)). We have studied the influence of non-local response on extraction of optical constants (as well as for the sensing properties) and showed that in the presence of the spatial dispersion metamaterial cannot and should not be described with the help of effective media theory (V. G. Kravets et al. Optics Express 18, 9780 (2010)).

5. Field enhancement in composite nanostructures.

It is well known that composite plasmonic nanostructures required by theory for generation of negative index of refraction often produce extremely large electro-magnetic field in near-field region. Using electron beam lithography we checked one of the most prospective nanolenses produced by a set of self-similar nanoparticles, where so-called cascaded enhancement of electromagnetic fields happens. Figure below shows the studied structure (V. G. Kravets et al. Phys. Rev. Lett. 105, 246806 (2010)). We observed about 100 cascaded field enhancement in triple structure and measured Raman and fluorescent maps of the signals in the vicinity of nanostructures.

We also experimentally and theoretically studied the field enhancement in various double and triple structures using Raman spectroscopy and confocal fluorescence.

6. Polymer substrates.

Using spectroscopic ellipsometry we have measured optical properties of polymer substrates (ORMOCER thin films) produced by Fraunhofer-Institut, Germany as a prospective material for self-assembly substrates. We also studied the change of optical properties of the polymer under different thermal treatments. The general conclusion of this investigation is that the polymer could potentially improve some self-assembly procedure.

7. Gain-assisted nanoparticles.

We have prepared to study spectroscopic and transmission spectra of functionalized nanoparticles (core-shell nanoparticles with gain material in the shell) under different illumination condition (with and without pumping) in the presence and in the absence of the additional near-fields. This work is just started and will be done in collaboration with University of Calabria, Italy.

The main objective of WP5 in the third year of the research was to measure the optical constants of the first generation of metamaterials produced by collaboration partners, to analyze the results of measurements and provide feedback to the groups performing fabrications.

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WP6 - INDUSTRIAL NEEDS AND PROCESSING
Participants: Fraunhofer, Rhodia-LOF (now Solvay)

WP6 SUMMARY

The tasks of WP6 were focused on the investigation of technological aspects relevant for the usage of plasmonic Nanoparticles for (optical) components. Additionally, WP6 supported the consortium to meet technological challenges which arise when plasmonic nanoparticles will be applied as layer or bulk materials. In order to get specifications from industry, industrial board member was asked to compose basic information with respect to general specifications for optical components. In order to get a wider view on the interests and requests of companies dealing with metamaterials a web-based survey was performed which was distributed to almost 200 partners from optical industries. According to this survey, interest for the bottom-up approach based on chemically synthesized plasmonic nanoparticles raised up due to the possibility to address large-area applications.

The syntheses developed by partners within the METACHEM project were investigated with respect to the capability to up-scale the synthesis and to transfer it into industrial scale and environment. Result of this investigation is that most of syntheses schemes described by METACHEM partners can be used in industrial scale with few adaptations, in principle. Cost aspects were not investigated in detail since the pricing depends on the application and on the added value created by the metamaterial nanoparticles. Environmental and legally aspects were considered and the availability of suitable / existing supply chains for synthesis up-scaling.

DESCRIPTION OF WORK

In order to use plasmonic nanoparticles as a technological component in a product, it is necessary to scale up the assembly of uniform layers or bulk of NPs. Fraunhofer ISC supported these activities by development of pre-patterned substrate and by creating binding materials to glue the nanoparticles. Investigations for patterned functionalisation were performed. The patterns or patterned functionalisation of substrates is used to direct the self-assembly of nanoparticles or the orientation of block-copolymers. A patterned functionalisation results in a locally changing surface energy, polarity, etc.... To realise these layer, different ORMOCER®s were synthesized and patterned. In addition to that, commercial photo resists, SU-8 and silanes were used for the manufacturing of patterned SAMs (self assembled monolayers). A demonstration of the suitability of these pre-patterned substrates could be performed only partially within the frame of metachem project due to lack of time or resources at partner sites.

The results of the characterization of Nanoparticles resulted in a list of feasible demonstrators based on ideas of the consortium. Industrial input was not requested since the TRL is still too low. No reliable information was expected by the consortium due to incomplete data of nanoparticle performance and, in particular, of assemblies of nanoparticle layers and bulks. The list of demonstrators was composed in a twelve-sided flyer and is linked within the METACHEM web-page.

Beyond the general basic specifications given by the industry, it is not trivial to sharpen the request and needs from the industrial point of view. The intrinsic properties of metamaterials as developed in METACHEM leads in principle to a variety of applications. Prerequisite is the development of uniform
layers and bulks using the developed nanoparticles. Thereafter, it is possible to characterize the macroscopic elements and to suggest promising applications and components. This information defines markets and industrial sectors which can take advantage of the proposed components which can be realized. Not till then it is possible to provide a higher level of details and specifications which could be possible for further development in METACHEM.

Three ways to produce macroscopic layers and bulks were assessed as promising taking into account that respective application processes should be reasonably easy to implement.

- Generation of layers by solvent evaporation
- Generation of alternating layers (dielectric, metallic) for hyperbolic media
- Generation of metamaterials nanoparticle bulks by microfluidic approach.

All three methods have shortcomings when they are up-scaled.

- Control of ambient atmosphere, substrate pretreatment
- Vacuum process; series of very thin metal or dielectric layers leads to a high proneness of defects.
- Mechanical stability of the generated bulk materials; possible appearance of gradual density distribution

These findings were underlined by a survey which was performed by Fraunhofer ISC with industrial partners in order to find out the advantages to take a chemical bottom-up approach instead of a physical top-down approach.

This web-based survey was carried out with the participation of 23 respondents, mostly from optical industry. The majority of people investigated the possibility to use metamaterials for optical application, in particular, optical microcomponents. Other fields of application, such as e.g. sensors, displays or functional surfaces was named as well. The participants expressed doubts to use the metamaterials concept due to a lack of maturity, especially when materials and processes are up-scaled. Amongst the respondents there was a clear preference to use top-down processes. Most convincing argument for the chemical approach (bottom-up) was a better suitability for large area substrates and applications.

It was also attempted to get additional information from industry by conversation in the frame of the conference organized together with the NIMNIL and NANOGOLD project in Jena (July 2012).

Result of all these discussions was that a defined list of specifications can only be assembled after components are defined which use reliable, up-scalable layers or bulks exploiting the properties of synthesized nanoparticles.

GENERAL CONCLUSIONS

Finally, METACHEM consortium described promising concepts to use metamaterial nanoparticles and published these concepts as a twelve-sided flyer on the METACHEM web-page. These results are rather on a scientific or conceptual level than on a technological level. It was decided that it is not useful to present these results to interested industry under Non-Disclosure-Agreements since the maturity of these
concepts could not be proven in the framework of METACHEM project.

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WP7 - DISSEMINATION ACTIVITIES

Seven significant actions have been implemented in this WP:

-1- All the METACHEM beneficiaries contributed to the training workshop (TWS) organized in December 2009 in Brussels. This workshop was a good opportunity to meet the partners of other FP7-NMP funded projects, namely NIMNIL, NANOGOLD and MAGNONICS. Moreover, the connexion with the ECONAM project was established as a useful step towards a more unified description and understanding of the experimental extraction of the EM properties.

-2- The METACHEM beneficiaries contributed to the EU brochure entitled “Nanostructured Metamaterials” which describe the current state-of-the art at a general level.

-3- The METACHEM website has been launched. It contains a public and a restricted access area, the latter being used by the beneficiaries for exchanging reports and data. See https://www.metachem-fp7.eu/

-4- The METACHEM teams have presented their results in a series of communications (oral and posters) in International Conferences and in publications.

-5- The METACHEM partner contributed to the common Dissemination Workshop that was held in Jena in July 2012 together with NIMNIL, NANOGOLD and MAGNONICS and a panel of industries.

-6- METACHEM contributed to the EU brochures on exploitable results and on modelling.

-7- The coordinator of METACHEM has organized the last Metamaterials 2013 Conference in Bordeaux in September 2013. This international conference, one of the most significant in the field, has gathered around 350 attendants, and was followed by a doctoral school on the topic of "Self-assembled metamaterials", promoting the avenues of research pursued under METACHEM and other similar projects.

Project management during the period:

The management activities by the coordinator (CNRS-Bordeaux) since the starting date (Sept 15th 2010) included:

- Distribution of funding to the beneficiaries
- Organization of the Kickoff meeting in Bordeaux (October 2009)
- Meeting of the nanochemists in Bordeaux (February 2010)
- Organization of a 6 month meeting of the Governing Board in Manchester (April 2010)
- Organization of the first meeting of the Industrial Advisory Board (Paris April 2010)
- Collection of deliverables, formatting, uploading to the Sesame database.
- Organization of the 12 month meeting in Karlsruhe (Sept 2010).

- Organization of the 18 month meeting of the GB in Siena (March 2011)
- Organization of the 24 month meeting in Barcelona (Oct 2011)
- Organization of the 30 month meeting in Paris (March 2012) with selection, approved by GB, of a shortlist of priority materials for each beneficiary (in deliverable D8.2.2).
- Co-organization of the Dissemination meeting in Jena (July 2012)
Potential Impact:

- Scientific impact:

The METACHEM project aims at the fabrication of nanostructured metamaterials operating at the frequencies of visible light by self-assembly of metallic nano-objects as electromagnetic (EM) resonators. The targeted properties are extraordinary values of the effective electromagnetic parameters such as the dielectric permittivity, the magnetic permeability and the refractive index. The final results can be organized in four major items:

(i) design by theory of the target nanostructures. Theory provided materials scientists with accurate designs of nanostructured metamaterials. It implied the definition of the structures and a calculation (or computation) of the expected properties. Close interaction with materials scientists has been necessary to keep the designs on the tracks of achievable materials.

(ii) fabrication of the nanoresonators as basic building blocks by nanochemistry. The synthesis of metallic nanoparticles exhibiting plasmon resonances is quite common. The achievements of METACHEM have gone well beyond the classical nanoobjects: specific surface functions that enable spontaneous self-assembly and controlled interactions with a host matrix, core-shell nanoparticles in which a plasmonic core is encapsulated in a dielectric shell controlling the strength of the electromagnetic coupling, hybrid nanoclusters targeting an optical magnetic response are the most important nanoobjects which have been produced. In all cases, the size of the nanoresonators must be much smaller than the operating wavelength to justify the concept of effective homogeneous medium.

(iii) self-assembly of these building blocks. Manufacturing a bulk metamaterial operating in visible light requires more than $10^{12}$ resonators per mm$^3$. Self-assembly indeed appears as a realistic way to assemble such a large number. The achievements of METACHEM have been to develop (and compare) several assembling methods, namely template-assisted assembling (in copolymer nanostructures), controlled evaporation (including microfluidics devices) and layer-by-layer Langmuir-Blodgett transfer.

(iv) extraction and characterization of the electromagnetic properties for demonstration and applications. The achievements were to develop and implement appropriate electromagnetic models to extract the obtained electromagnetic properties.

(v) compensation of losses. The objective is to demonstrate and implement the concept of loss compensation by active gain media. Gain is obtained by optical pumping of fluorescent dyes which return their energy to plasmons.

Based on the above achievements, the METACHEM project made significant steps towards the following fundamental scientific breakthroughs:

- the scientific demonstration that efficient metamaterials can be produced by bottom-up methods.
- the creation of non existing metamaterials such as isotropic resonant artificial magnetic media in the
visible frequency range.
- the creation of more efficient metamaterials owing to the improved resonant properties of metamaterial “nanomolecules” and to the compensation of absorptive losses. This point is of particular importance to move metamaterials from fundamental scientific challenges to applied materials.
- the investigation of the novel concept of disordered or random metamaterials, in definite rupture from the lithography approach.
- ultimately the fabrication of self-assembled, large-scale, 3D left-handed materials operating at visible light frequencies.

Technological impact:

METACHEM aims at opening the way to the fabrication of new optical elements for laser optics (perfect lenses, phase plates, hyper lenses) and more generally it has:

- opened the way to new bio-sensors and ultra-sensitive sensors, nano-chemical reactors, novel SERS substrates, new numerical methods.
- stimulated research on new optical devices based upon metamaterials, such as e.g. nanolenses, field concentrators, nanolasers, etc.
- contributed to develop materials with “ideal” electromagnetic response over broad frequency ranges, that can be customized, made active, or made modulable or tunable.
- contributed to the new perspective of optical nano-electronics and circuitry, in which a network of sub-wavelength nanoscale metamaterial structures and nanoparticles may provide a mechanism for tailoring, patterning, and manipulating optical electric fields in a sub-wavelength domain, leading to the possibility of optical information processing at the nanometre scale. In this sense nanoparticle based metamaterials may play the role of nanocircuit elements such as nanoinductors, nanocapacitors, and nanoresistors, analogous to microelectronics components.

In addition, some side results may provide interesting impacts: for example, surfaces decorated with plasmonic clusters have proved to be performing substrates for SERS (Surface Enhanced Raman Scattering). The large-scale production of engineered hybrid nanoparticles has been developed. New software for the analysis of meta-electromagnetic properties has been developed.

- Main dissemination activities:

-1- All the METACHEM beneficiaries contributed to the training workshop (TWS) organized in December 2009 in Brussels. This workshop was a good opportunity to meet the partners of other FP7-NMP funded projects, namely NIMNIL, NANOGOLD and MAGNONICS. Moreover, the connexion with the ECONAM project was established as a useful step towards a more unified description and understanding of the experimental extraction of the EM properties.

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List of Websites:

Public website:

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Related documents

final1-d633-part2-demonstators-to-prove-scientific-results-achieved.pdf

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