PROJECT FINAL REPORT

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Project acronym: NANOMAGMA

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Funding Scheme: COLLABORATIVE PROJECT

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[1] Usually the contact person of the coordinator as specified in Art. 8.1. of the Grant Agreement.

4.1 Final publishable summary report

This section must be of suitable quality to enable direct publication by the Commission and should preferably not exceed 40 pages. This report should address a wide audience, including the general public.

The publishable summary has to include **5 distinct parts** described below:

- An executive summary (not exceeding 1 page).
- A summary description of project context and objectives (not exceeding 4 pages).
- A description of the main S&T results/foregrounds (not exceeding 25 pages),
- The potential impact (including the socio-economic impact and the wider societal implications of the project so far) and the main dissemination activities and exploitation of results (not exceeding 10 pages).
- The address of the project public website, if applicable as well as relevant contact details.

Furthermore, project logo, diagrams or photographs illustrating and promoting the work of the project (including videos, etc…), as well as the list of all beneficiaries with the corresponding contact names can be submitted without any restriction.

Executive summary

The goal of this project has been the study, development and application of a **novel concept of nanostructured materials formed by the combination of components with plasmonic and magneto-optic (MO) activity.** This combination produces **"magneto-plasmonic" nanomaterials tailored on the nanoscale**, in which the application of an external magnetic field allows controlling the plasmonic properties of the system, and the excitation of Plasmon resonances gives rise to enhanced magneto-optical performances. Thanks to these facts, magneto-plasmonic nanostructures will become **key active material elements in future tunable nano-optical devices and in biosensors with enhanced sensitivity** (in particular, in novel surface magneto-plasmon resonance (SMPR) sensors). In addition, the **identification of relevant applications of magneto-plasmonic materials for microelectronics and information technology** has also been carried out.

In short the S&T objectives can be regarded as four:

(a) Development of nanomaterials that combine plasmons and magnetic properties (films, nanoparticles, core-shell structures).

(b) Investigate the correlation between the optical, magnetic, magneto-optical and magneto-plasmonic properties.

(c) Carry out theoretical calculations of the optical response considering the magneto-optical contribution.

(d) Perform proof of concepts based in the magneto-plasmonic activity and testing for specific applications in the field of chemical sensors and biosensors. Identification of applications for microelectronics and information technology.

The objectives of this project have been realized by a coordinated action involving theoretical calculations, nanofabrication and characterization, achieving as a consequence magnetoplasmonic systems whose properties have been designed, tested, and optimized, with proven outstanding performance. The main S&T results are:

- Development of theoretical tools for magnetoplasmonic modeling.
- Development of a Near-field Scanning Optical Microscope to be able to operate under the application of external magnetic fields.
- Fabrication of magnetoplasmonic trilayered structures with a 200 enhancement factor of the MO activity upon excitation of Plasmon resonance.
- Identification of interface roughness as key parameter for enhanced MO performance and surface Plasmon wavevector modulation.
- Use of a ferromagnetic layer as a probe for the electromagnetic field distribution within a resonant nanostructure, allowing the identification of the optimum position of the ferromagnetic layer in the nanostructure for maximum MO performance.
- Proof of concept of the sensing potential of magnetoplasmonic nanodisks.
- Development of novel mangetoplasmonic nanostructures by chemical routes.
- Development of two surface magneto-plasmon resonance (SMPR) platforms with demonstrated enhanced gas sensing and biosensing sensitivity and potential combination with impedimetric measurements.
- Identification of non-reciprocal components for photonic integrated circuits at 1.55 µm wavelength as a potential application of magneto-plasmonic (MP) materials

Summary description and objectives

The goal of this project is the study, development and application of a **novel concept of nanostructured materials formed by the combination of components with plasmonic and magneto-optic (MO) activity.** This smart combination allows producing **“magneto-plasmonic” nanomaterials tailored on the nanoscale.** While noble metals exhibiting plasmon resonances have no magneto-optical activity and ferromagnetic materials suffer from strong plasmon damping, metallic heterostructures made of noble metals and ferromagnetic materials may sustain surface plasmons and have at the same time magneto-optical activity. The nanoscale here is crucial since the base is the interaction between the magneto-optically active material and the electromagnetic field of the plasmon, whose extension is precisely on the nm scale. In addition, the nanoscale is be needed to effectively excite the localized plasmon resonances, either in *continuous materials with corrugations or topographical features* of nm dimensions that will exhibit resonances associated to propagating plasmons, and *nanoparticles*, i.e. isolated nanostructures that will exhibit localized plasmons. The ferromagnetic material broadens the plasmon resonance of the structure, but it introduces a magneto-optical activity in the system, absent in pure noble metal layers. This way, to achieve the control of light transmission and guiding with subwavelength elements[2] and sensing applications[3] that plasmonic materials make possible, we propose that in magneto-plasmonic materials the action of an external magnetic field will allow controlling externally these guiding properties and enhancing the sensitivity of plasmonic sensors by magnetic field modulation[4]. Therefore, these materials will be applicable in a broad spectrum of research and industrial areas. In particular, we believe that they could become **key elements in future tunable nano-optical devices and in biosensors with enhanced sensitivity**. The novel magneto-plasmonic materials offer the unique ability to control their properties in more than one way, since the magneto-optical activity is affected by the alteration of the plasmonic characteristics and the optical response depends on the magnetic ones[5]. The latter puts an additional advantage over conventional materials, since the optical response can be *actively* tuned by means of an external agent: a magnetic field.

The project has two main goals; the first is to **prepare active magneto-plasmonic materials with tailored properties in the nanoscale** and understanding the interactions of the magnetic properties with the plasmonic and optical ones, linked to electric charge oscillations.

The second goal is to **propose devices for applications** that can benefit of this coupling. Since the optical properties of these materials can be driven by using a magnetic field, this allows designing and developing novel magneto-plasmonic devices. In particular, we have performed a proof concept of a new kind of surface plasmon resonance (SPR) sensor with MO elements, i.e. a surface magneto-plasmon resonance (SMPR) sensor, comparing its performance against standard sensors.

The project also includes prospective tasks for silicon-oriented uses. This part includes the **identification of relevant applications of magneto-plasmonic materials for microelectronics and information technology**. Depending on the materials properties several application routes may be proposed in either opto-electronic, spin-tronic, spin-photonic domains, with the corresponding electromagnetic simulation and integration analysis being performed. Preliminary manufacturing flows are proposed based on 200-to-300mm silicon standards for microelectronic (CMOS) and microsystem (System On Chip SOC) uses.

In short the S&T objectives can be regarded as four, in which we consider both bottom-up and top-down approaches to obtain the desired magneto-plasmonic materials:

(e) *Development of nanomaterials that combine plasmons and magnetic properties (films, nanoparticles, core-shell structures).*
(f) *Investigate the correlation between the optical, magnetic, magneto-optical and magneto-plasmonic properties.*

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[2] T. W. Ebbesen et al., Nature **391**, 667 (1998) ; S. Bozhevoli, et al., Nature **440,** 7083 (2006).
[3] A. G. Brolo, R. Gordon, B. Leathem, and K.L. Kavanagh et al. Langmuir **20**, 4813 (2004)
[4] B. Sepulveda, A. Calle, L. M. Lechuga, and G. Armelles, Opt. Lett. **31**, 1085 (2006)
[5] C. Herman et al., Phys. Rev. B **64,** 235422(2001), J.B. Gonzalez-Diaz et al., Phys. Rev. B *in press* (2007)

(g) *Carry out theoretical calculations of the optical response considering the magneto-optical contribution.*
(h) *Perform proof of concepts based in the magneto-plasmonic activity and testing for specific applications in the field of chemical sensors and biosensors. Identification of applications for microelectronics and information technology.*

Therefore we design novel active (thus “smart”) materials tailored in the nanoscale, in particular we will use nanostructures such as alternate layers of noble metal/MO material (a ferromagnet in this case), magnetic nanoparticles as well as core-shell structures and heterodimer structures; **the materials will find a space for enhanced and innovative applications (in the areas of photonics and sensors)**. The final target is to apply the concept to obtain chemical sensors and biosensors with enhanced sensitivity, but to that end it is necessary to investigate thoroughly the magnetic behavior of the material in the nanoscale and the interaction with the optical response. Results from these developments help defining the other applications in the information technologies area.

Along these lines, in the NANOMAGMA project we want to explore a **novel magneto-plasmonic sensing concept** by using as transducers the sensing MO layers developed within the project and use as detection parameter **not only the optical** properties of the system **but also the magneto-optical properties** of a nanostructured layer or of the nanoparticles. This novel sensing concept has been already tested in continuous MO films[4] showing an improvement of the sensitivity of standard SPR biosensor. The use of **nanostructured material and optimized layer geometries should further increase this sensitivity** with respect to the already obtained ones. In the case of chemical gas sensor we want to test how the interaction mechanism taking place between chemical species in vapor phase (oxidizing or reducing gases and alcohol molecules of different steric hindrance), can be modified and amplified by the presence of a thin and well calibrated layer of nanoparticles with MO properties deposited by different physical and chemical deposition methods onto the calibrated substrate responsible of the SPR phenomena.
Moreover, taking into account that,(a) impedance/electrochemical assays are established detection avenues due to automation, real time measurements, sensitivity, and suitable for miniaturization, and (b) the combination of SPR with electrochemical measurements has been demonstrated as a powerful technique for the simultaneous characterization and manipulation of electrode/electrolyte interfaces, a novel approach proposed within NANOMAGMA consists in the achievement of high performance detection device by combining SMPR and Impedance in an unitary analytical platform with micro flow injection capabilities to address novel magneto-optical surfaces.

Our proposed approach progresses the current state of the art in that it combines the capabilities of the two powerful techniques in a differential, multichannel module with simultaneous SMPR and impedance assessment of the same sensing surface with integrated microfluidics and improved design of the measurement channel(s) to:
- Provide inner control; to test consistency of the two recordings, SMPR and electric, in order to check and to eliminate false positive/negative results; to demonstrate a prerequisite for a future “in field” system.
- Extend the range of addressable sensing platforms, i.e cellular or “cell-like”, where SPR and in principle SMPR alone lacks the necessary sensitivity enabling development and addressing of cellular or “cell like” sensing platforms (e.g. lipid sensors with embedded receptors).
- Ensure a controlled environment and efficient mass transfer of the target analyte towards the sensing surface: Improved mass transfer coefficients are achieved through optimal micro flow cell design and operational flow rate.

On the other hand, identifying relevant applications being silicon-compatible is challenging and it is an important issue in terms of industrial prospects. Indeed, mobile phone and particularly CMOS sensor drive an important part of the semiconductor industry. This very competitive field could benefit from technology that can **increase the optical functionalities or performance of the chip**. Other industrial issues may concern on chip photonic devices, ultra high density data storage where plasmonic, near field magneto-optic and spin photonics are emerging technologies. However, it is not straightforward defining such applications, especially as it strongly depends on the materials properties that are a scientific target of the project. An important goal of this project is to identify potential applications in these fields and investigate the benefit of magnetoplasmonic structures numerically (using electromagnetic simulation tools). Basic research on the magneto plasmonic properties done during the project has been used as an input for this prospective work.

Main S&T Results

The four main objectives described above have been pursued along the project as four work packages as established in the Grant Agreement: WP2 is linked to objective (c) deals with the theoretical developments needed to describe the physics in magnetoplasmonic systems and thus be able not only to model the response but also to predict it; WP3 is related to objective (a) and therefore targets the fabrication of the different nanostructures, aiming to find the best routes to obtain them, as well as to explore the parameter range in which the best response is expected. In WP4, covering objective (b), the focus is on the understanding on the optical and magneto-optical response, so that the subtle interplay between the plasmonic and magneto-optical properties can be unravelled and thus used in the last work package. This is WP5 that aims at the use of the knowledge previously obtained, and so covers objective (d), to envisage applications, both in the area of gas sensing and bio sensing as well as in information technologies.
According to this clasification, in what follows the results will be presented in blocks corresponding to WP's, though due to the nature of the project the results of each WP are of relevance and often interrelated with those of other WPs.

WP2.

From the theoretical point of view, one main aspect has been the development of new tools for the modelling of the magneto-plasmonic response. The developments have been based on two methodologies: scattering matrix method (SMM) and discrete dipole approximation (DDA). The first one is intended to deal with extended, in-plane-periodic structures while the second is more suited to describe isolated structures. In both cases the magneto-optical effect has been introduced, and in the case of the DDA we have found that radiative corrections play a fundamental role in describing correctly the magneto-optical effect of non-absorbing systems. As a final tool we have combined the two methodologies to give rise to a more efficient tool for magneto-plasmonic modelling.
The main activities where these methodologies have been employed are:

(1) ***Design of efficient nanostructures for plasmon control***

The main idea is to analyze both the MO activity as well as the modulation of propagating surface plasmon polariton wavevector in noble metal/ferromagnet/noble metal trilayers by an external magnetic field, as well as in MO nanostructured systems, to optimize and design different experimental setups.
Besides evaluating the best geometries for planar systems in terms of sensitivity we would like to mention the controlled excitation of surface plasmons using a MO nanoparticle.

We have performed an analysis of the interaction between a MO nanoparticle and a flat surface. This approach has allowed us to identify a configuration suitable for an efficient local excitation of a surface-plasmon polariton (SPP) in the presence of an external magnetic field (LMOKE configuration). A quantitative numerical study of that configuration, using the coupled-dipole method extended to account for MO materials (as said a numerical tool developed and validated for this type of systems) shows that, in the presence of a modulated external magnetic field, in the LMOKE configuration, an efficient <u>local</u> and <u>directional</u> excitation of a modulated SPP is possible (see Fig.1). More precisely, we have defined a SPP-LMOKE signal (Fig. 1, right panel) that corresponds to the modulated part of the surface plasmon intensity (that has been excited through the magneto-optical interaction mediated by the nanoparticle).

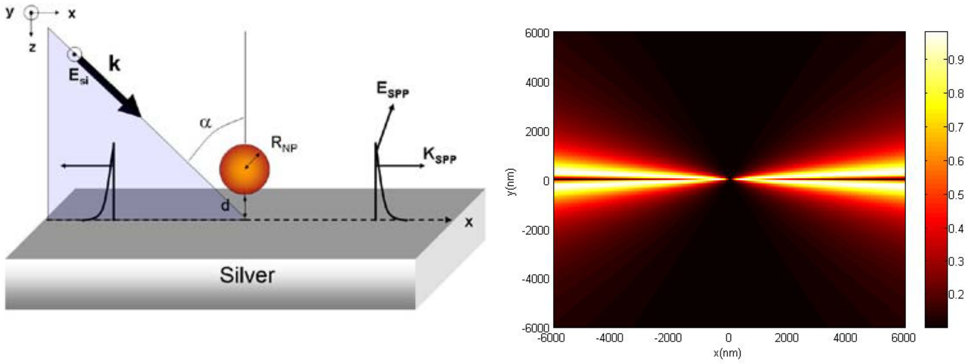


Figure 1: (Left) Scheme for the local excitation of a SPP by a MO nanoparticle (iron) on a flat metallic substrate (silver). The magnetic field is oriented along the x-axis (LMOKE configuration). The excitation wavelength is λ=800 nm. (Right) Top view of the modulated SPP field (modulated LMOKE signal) on the silver surface.

This result confirms the possibility of controlling both the excitation and the directivity of a SPP, taking advantage of a magneto-optical interaction in a realistic configuration.

(2) ***Theoretical study of field enhancements generated by magneto-plasmonic structures***

This is fundamentally oriented to analyze the enhancement and control of molecular fluorescence signal for sensing applications. Potential geometries include periodic gratings, isolated nanoparticles and disordered arrangements of nanoparticles.

2a. Field enhancement on periodic structures

One objective was to study the possibility of enhancing and modulating a fluorescence signal of molecules adsorbed on a substrate with a MO response for sensing applications. Previous works had shown that periodic arrays of dielectric nanorods can produce very large local field enhancements at specific resonant conditions. We have studied theoretically and numerically the possibility of observing similar resonances on periodic gratings made of materials with a non-negligible MO response, and to use them to act on the fluorescence signal (in the linear regime used in sensing applications, the fluorescence signal is directly proportional to the local excitation intensity experienced by the molecules). The grating presents resonances near the Rayleigh condition (the so-called Wood anomalies) for both s- and p-polarizations of the incoming beam. We have computed the field enhancement factor (ratio of the amplitude of the local field and of the incident field). We have found that when the external magnetic field is oriented along the nanorod axis, the enhanced fluorescence signal of molecules adsorbed on a MO nanorod (with their transition dipole oriented along the normal of the grating plane) can be modulated by the MO signal. There is a strong MO modulation of the field enhancement factor for p-polarized incident waves and a TMOKE configuration (see Fig .2). The MO coupling remains negligible for s- polarized waves.

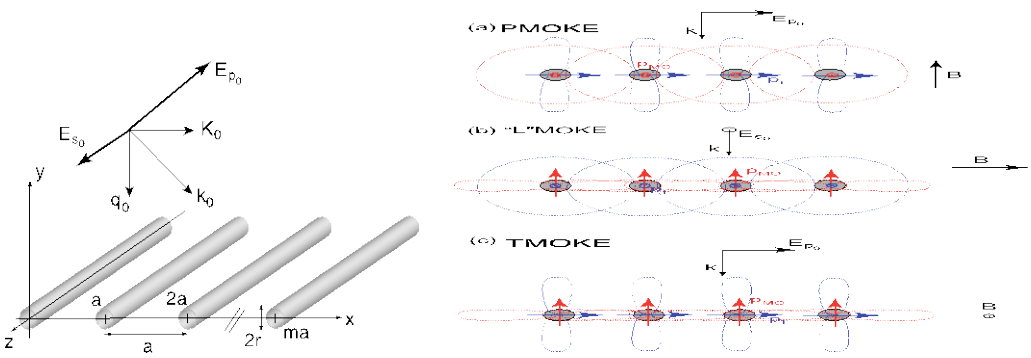


Figure 2: (Left) Geometry of a periodic grating made of infinitely long rods with a section much smaller than the wavelength. The plane of incidence is perpendicular to the rods. (Right) Front view of the interaction process in a TMOKE configuration, under normal incidence with a p-polarized wave. The induced MO dipoles lead to long-range interactions and geometrical resonances.

This study shows that magneto-optics can provide a new way to actively modulate field enhancements (and fluorescence signals) using the external magnetic field as a control parameter. This would open new perspectives in sensing applications.

2b. Control of molecular fluorescence energy transfer

Another objective was to study the potential of magneto-plasmonic structures for the control of molecular fluorescence (enhancement and quenching of the fluorescence signal), and to take advantage of the anisotropic response to get sensitivity or to probe the orientation of the molecular transition dipole. Several simple geometries were *a priori* of potential practical interest, in particular plane substrates and nanoparticles. We have analysed several geometries, involving either a metallic slab or a metallic nanoparticle in interaction with one or two fluorescent molecules, using theoretical and numerical tools (perturbation and coupled-dipole method). The results were not promising in terms of orders of magnitudes, since the change in the fluorescence intensity induced by the MO effect remained very weak. Nevertheless, we found that the magneto-optical response could be particularly interesting for the control of fluorescence resonant energy transfer (or Förster resonant energy transfer, known as FRET) between two molecules. FRET is widely used for the detection of molecules in complex environments (including *in vivo* measurements). The quantitative theoretical and numerical study of FRET mediated by a MO interaction has shown that FRET can be enhanced and/or modulated through the interaction with a magneto-optical nanoparticle. We have introduced a general theoretical framework to study FRET between two fluorescent molecules in the presence of a nanoparticle with an anisotropic magneto-optical response. We have introduced a generalized FRET rate and discussed the orders of magnitude. The main result is that the distance dependence, the FRET efficiency, and the sensitivity to the orientation of the transition dipoles orientation differ from standard FRET and can be controlled using the static magnetic field as an external parameter. We have even shown that two molecules with orthogonal transition dipoles (for which the standard FRET signal would vanish) can be coupled in the presence of an external magnetic field using the MO response of the nanoparticle (see Fig. 3).

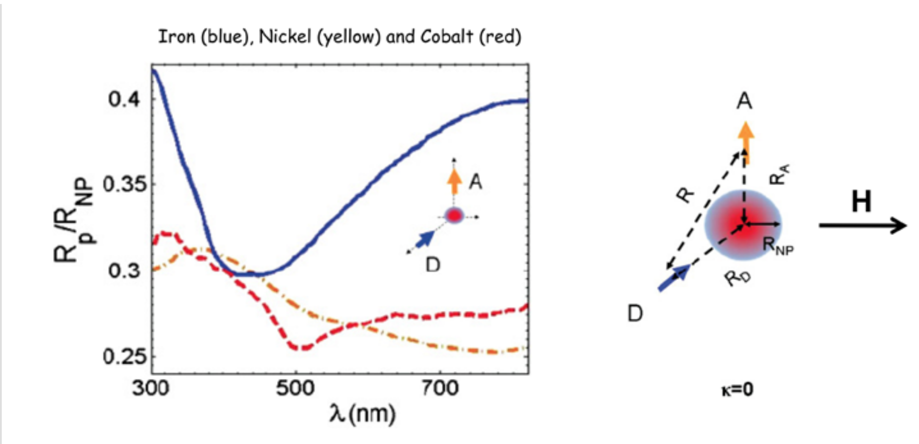


Figure 3: Variation of the MO FRET signal of two molecules (donor and acceptor) coupled through a MO nanoparticle, versus the emission wavelength of the donor. Different materials have been studied (Fe, Co, Ni). The right panel shows the configuration, with the location of the two molecules (D and A) and the orientation of their transition dipoles. The orientation of the external magnetic field H is also indicated.

This work makes a proof of concept, and future work should focus on enhancing the magneto-optical FRET signal, e.g., by designing specific nanoparticles (core-shell structures are potential candidates).

(3) ***Modelling of near-field plasmonic and magneto-optical images***

The main focus is the modelling of near-field optical images, allowing thus quantitative comparison between numerical simulations and SNOM experiments.

The localization of the electromagnetic field in isolated nanostructures has been calculated to be compared with that experimentally obtained (see below in WP4). Since the fluorescent particle is sensitive to all the electromagnetic field components, and since the emitted fluorescence varies with the square of the excitation, we calculated the square of the total field intensity $||E_{tot}||^4$. To take into account the fluorescent particle size, we integrated the signal over a volume V. The measured signal can then be represented by the quantity:

$$S = \int_V \|E_{tot}\|^4 dV$$

A good agreement is obtained between the simulations and the experiments when the particle is considered as a $160\times160\times160 nm^3$ large cube. Such dimensions correspond roughly to the size of the fluorescent particle we usually use for our experiments (between 100nm and 300nm). As for the experimental SNOM image, the pattern is composed of two lobes located between the disks, and whose relative orientation depends on the incident polarization direction. Note that the effect of averaging over a finite volume V only broadens the size of the lobes, but does not change the shape of the pattern.

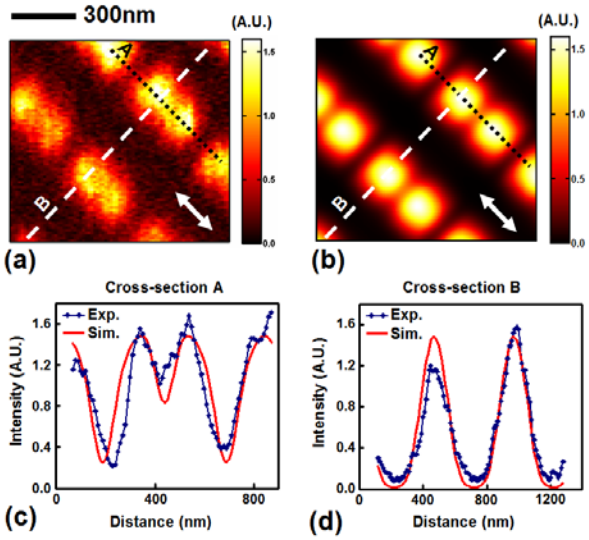


Figure 4: Experimental (a) and simulated (b) SNOM images of the array of nanodisks. The cross-sections parallel (direction A) and perpendicular (direction B) to the incident polarization are given in (c) and (d) respectively.

A quantitative comparison is shown in the high resolution images of Fig. 4. The intensity of the simulated image has been normalized to allow the comparison with the experimental one. A good quantitative agreement is observed in terms of relative intensities. The cross-sections parallel to the incident polarization (cross-section A) exhibit a very similar shape and contrast. From cross-sections B, one can also see that the intensity of the light drops almost to zero between two disks in the direction perpendicular to the incident polarization. All the light is concentrated between the disks in the direction of the incident polarization.

(4) ***Numerical works for defining optoelectronics uses designing the nanostructures to anticipate material-compatibility, integration and manufacturing constraints***

The aim is to evaluate the potential of magneto-plasmonic materials for applications in optoelectronics. This will be described in detail in the applications section, but the bulk research for integrated photonic circuits at telecom wavelength has been theoretical.

WP3

From the fabrication point of view, the aim of WP3 is devoted to the fabrication of nanomaterials that combine plasmons and magnetic properties in a number of schemes, including thin films, nanoparticles, core-shell structures, corrugated structures self assembled onto continuous films etc….

To reach this objective, a multitechnique approach, including physical and chemical routes has been considered, starting with a variety of methods to obtain the desired structures. The first 24 months have been devoted to the exploration and study of the materials and its nanostructuration, while during the remaining time the work focused mostly on the most convenient approaches selected, based on the experience acquired in the first half part of the project.

Along the project we have used the following approaches for the fabrication of the nanostructures:

1. Physical vapour deposition techniques
2. Electrochemical and atomic layer deposition combination
3. Colloidal chemistry synthesis.

1. Physical vapour deposition techniques approach

Thermal evaporation and magnetron sputtering have been used to deposit continuous layers as well as nanostructures. Different lithography techniques (electron beam, laser interference and colloidal lithography) have been explored for the fabrication of the nanostructures. Au, Ag, Fe and Co have been noble metal and ferromagnetic materials utilized. On the other hand, two other approaches, to obtain nanostructures based on the direct deposition on bare substrates by self assembly, have been studied, namely glancing angle deposition and deposition through stencil masks.

1.a. Continuous layers

Continuous Au/Co/Au and Ag/Co/Ag trilayers on BK7 and SF10 substrates have been grown by magnetron sputtering to carry out studies related to the optimization (using the theoretical modelling as guidelines) of the structures and selection of materials to obtain maximum magneto-optical signal and/or variations of the signal in response to variations of the environment refractive index. A number of these structures have been used in sensing experiments.

1.b. Nanostructured systems

Nanostructures with different sizes and shapes have been obtained by e-beam lithography (EBL) (continuous layer growth plus lithography and etching or lithography plus deposition and lift off).

We have analyzed the role that size and shape of Au/Co/Au nanostructures as well as the position of the Co layer within the trilayer play on their magnetoplasmonic response. For far field characterization, a minimum array size of 1 mm x 1 mm is needed. For near field characterization large patterned areas are not required. Figure 5 shows an example of the obtained structures.

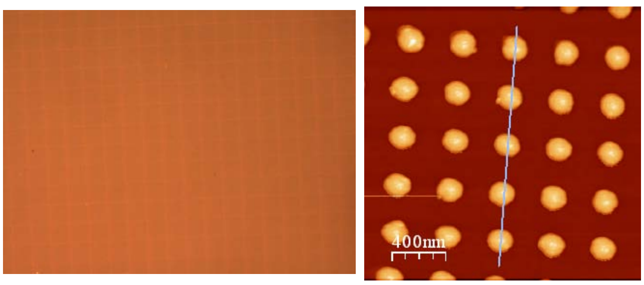


Figure 5: Bright field image of patterned area constituted by multiple 15 μm x 15 μm writing fields (left) and detail (AFM image) of 150 nm diameter discs (right) obtained by EBL negative resist.

Bars (lengths comprised between 200 nm and 1.5 μm and widths varying from 60 to 180 nm) and rings (200 nm and 250 nm external diameter and internal diameter between 90 nm and 140 nm) have also been fabricated (Figure 6). Opening of the holes for the smaller rings is not possible with our available facilities due to resolution limitations. To solve this problem, a new ionLiNE system from RAITH GmbH has been used.

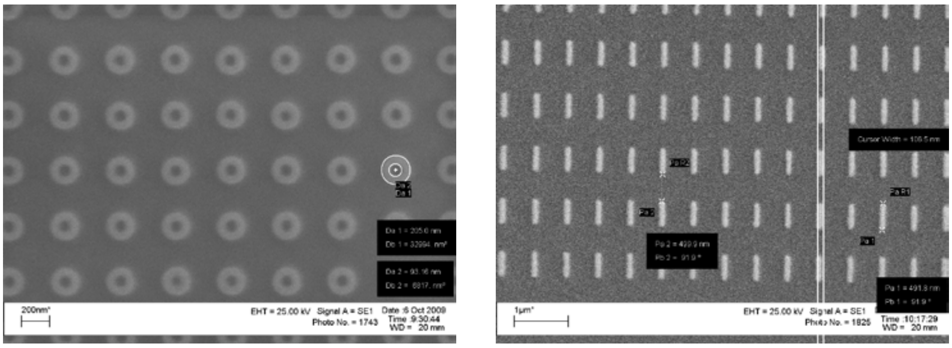


Figure 6: Standard rings (left) and bars (right) obtained by EBL

Additionally, to explore electromagnetic field enhancement effects, dimmer structures have been fabricated on Au (Figure 7).

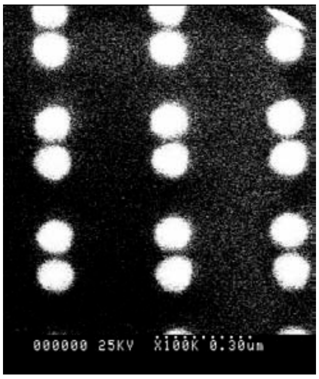


Figure 7: SEM image of Au dimers (110 nm diameter, 15 nm gap)

1.c. Nanostructures obtained by Colloidal lithography (CL).

One of the drawbacks of EBL is that it is a time consuming technique and that obtaining good uniformity over large areas is in the end not a straightforward matter. To circumvent this problem, CL has been implemented as a technique to obtain magnetoplasmonic nanostructures. The deposition of solutions with polystyrene spheres of submicrometric dimensions allows facing the patterning of structures over large (1 cm x 1 cm) areas. The procedure has been fully optimized and currently it is possible to fabricate large areas of Au/Co/Au discs.

As an example, in figure 8, a set of atomic force microscopy images and profiles of a standard Au/Co/Au nanodisk system is shown, with excellent spatial and size homogeneity.

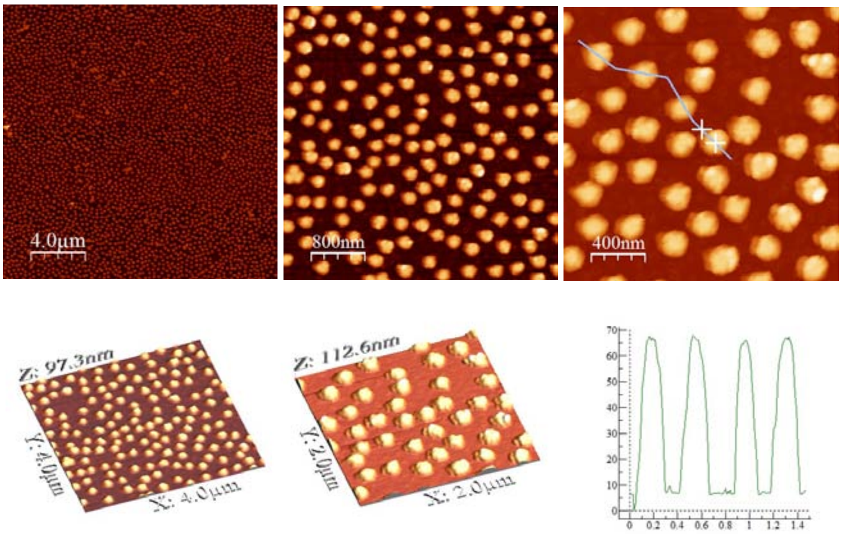


Figure 8: AFM image of Au/Co/Au nanodisc fabricated by colloidal lithography on BK7

1.d. Nanostructures obtained by Laser Interference Lithography (LIL) (lift off).

One of the aims was the fabrication of perfectly ordered arrays of magnetoplasmonic nanostructures in a large area. Laser interference lithography in combination with thermal evaporation was attempted. Unfortunately, due to structure deterioration during template removal process made it not possible to routinely use this approach.

Two other approaches, based on the direct deposition on bare substrates have also been studied:

1.e. Glancing angle deposition by magnetron sputtering and thermal evaporation:

We have carried out deposition of Au on Si substrates and on Au/Co continuous layers grown on Si by magnetron sputtering at 85º off surface normal. Depending on deposition conditions it is possible to tailor the morphology of the deposited material. For example, deposition without substrate rotation about its surface normal produces columnar structures inclined towards the Au flux, while substrate rotation during deposition yields pseudo columnar structures that grow perpendicular to the surface. In Figure 9 below we show SEM images (top views above and cross section views below) of 30 minutes deposits with (right) and without (left) rotation.

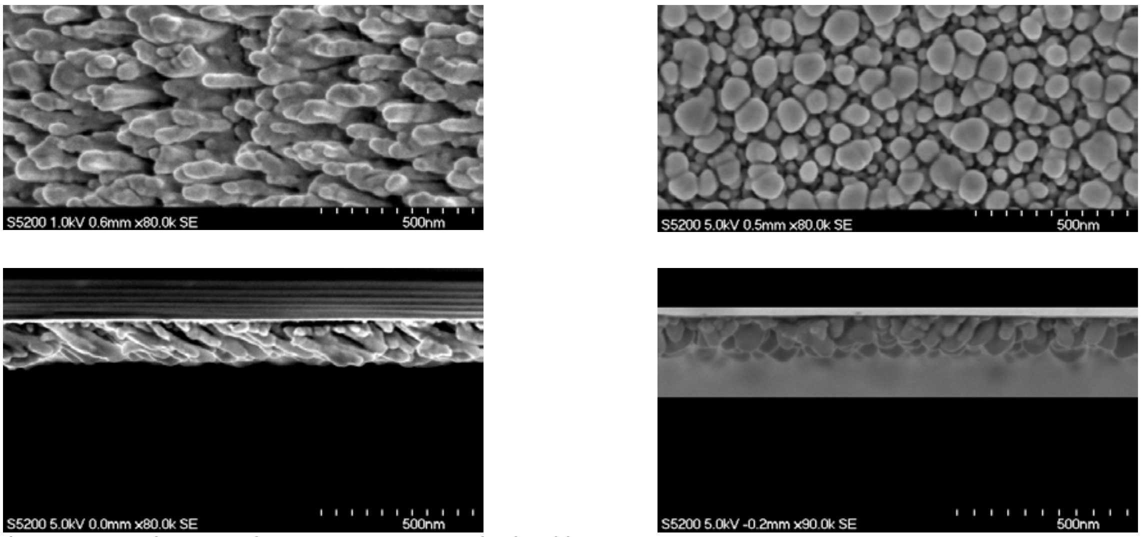


Figure 9: SEM images of Au nanostructures obtained by GLAD.

In addition, columnar-corrugated TiO_2 structures have also been deposited by GLAD on Au/Co/Au trilayers and, after optical and magnetooptical characterization have successfully been used for gas sensing performance due to the porous nature of the TiO_2 layer grown by this technique.

2. Electrochemical and atomic layer deposition combination approach

In this case we have fabricated two kinds of structures by electrochemical methods; one is intended to develop one-dimensional systems within alumina templates, whereas the other is targeted to obtain 2D-0D systems. The fabricated systems can in turn be catalogued in purely metallic systems and metal-dielectric systems. For purely metallic systems Au and Ni are respectively the noble metal and ferromagnetic materials used, whereas for metal-dielectric Ni_xFe_yO and Co_xFe_yO play the role of the MO material instead of Ni.

The work related to the synthesis of one-dimensional magnetoplasmonic nanostructures deposited in porous anodic alumina has been focused on the development of multisegmented Au/Ni nanowires, core-shell Au-Ni or Ni-Au nanowires, and Ni wires with embedded Au nanoparticles on its surface. The first structure has been obtained by alternating nickel and gold electrodeposition. The Ni-Au core-shell has been developed by combination of NiO atomic layer deposition to form the nickel shell and electrodeposition to form the gold core. The generation of the core-shell structure has been successful and a post-thermal treatment has been applied to reduce nickel oxide to metallic nickel.

With respect to the 1D metal-dielectric core-shell systems, electrodeposition and ALD have been used in a combined way to fill the pores of a porous anodic alumina template previously defined, leading to the formation of coaxial core-shell Au-ferrite wires of nanometer diameter dimensions and micrometric lengths. SEM images of the cross and top view of the obtained nanowires is shown in figures 10 and 11.

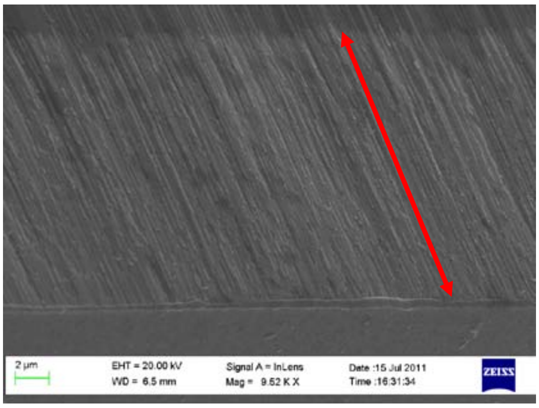


Figure 10: SEM image of a nanowires network cross view

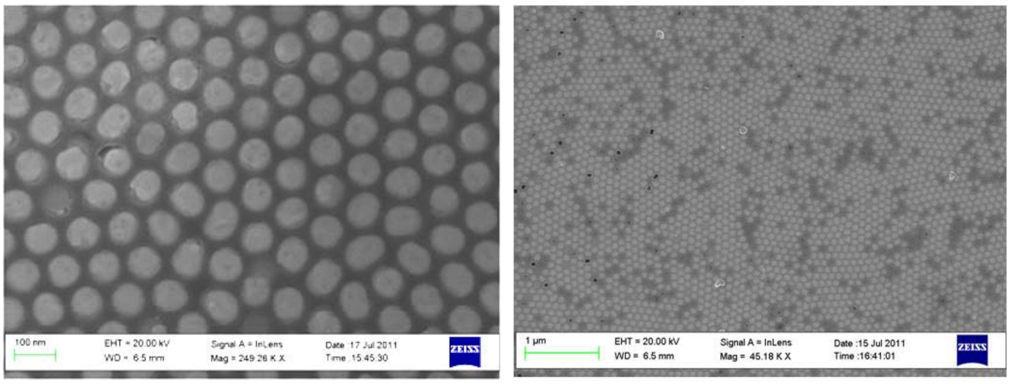


Figure 11: SEM top view of the obtained nanowires

Additionally, the fabrication of 2D-0D magneto-plasmonic nanostructures combining Co and Ni ferrites deposited by ALD and Au nanodisks and nanowires obtained by colloidal lithography and electrodeposition respectively has been carried out.

In the first, 2D-0D case, Atomic Layer Deposition (ALD) is used to produce thin films of $M_xFe_{3-x}O_4$: $Co_xFe_{3-x}O_4$ (hard magnetic) and $Ni_xFe_{3-x}O_4$ (soft magnetic). The tunable parameters of thin films have been thickness (determined by the total number of pulses) and composition (determined by the ratio of Fe to M pulses). On the other hand, colloidal lithography (CL) has been used to produce arrays of gold nanodiscs, in which disk diameter and height can be varied. Deposition of the ferrites on top of the Au nanodisks leads to a core-shell like structure with Au core and ferrite shells.

In figure 12 SEM images of a set of Au nanodisks covered with $CoFe_2O_4$ show the uniformity and homogeneity of the obtained systems.

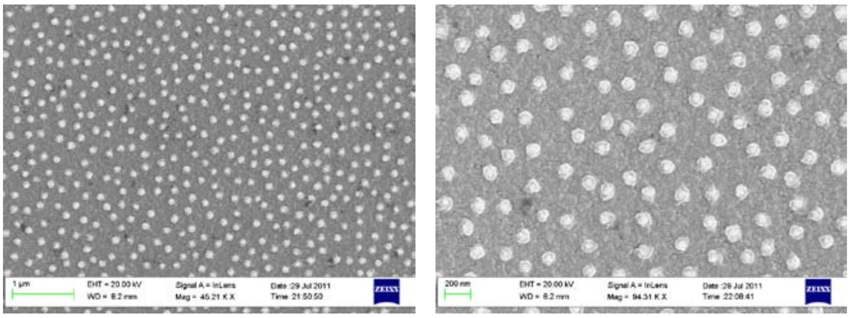


Figure 12: SEM images of Au nanodisks covered with Co ferrite.

Additionally, the AFM images shown in Figure 13, correspond to a set of Au nanodisks before and after deposition of a conformal $NiFe_2O_4$ layer.

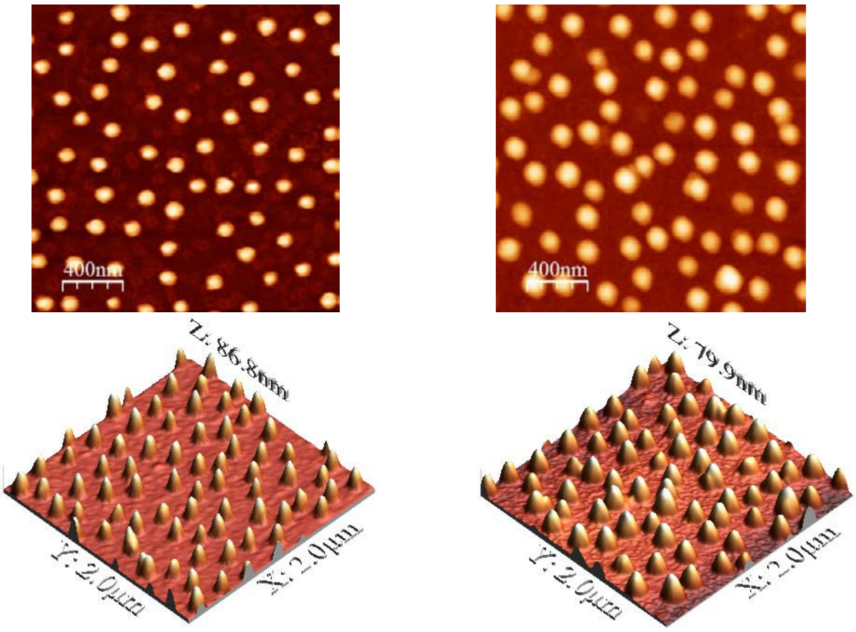


Figure 13: AFM images of Au nanodisks before (left) and after (right) covering with Ni ferrite.

3. Colloidal chemistry synthesis approach.

Here we cover the fabrication of nanoparticles and heterodimer by chemical synthesis, with five main activities:

a.Optimisation of transition metal based magnetic colloidal materials, with particular attention to magnetite and cobalt ferrite nanospheres.

The variety of systems prepared can be rationalised as a continuous series of materials ranging from magnetite (Fe_3O_4) to cobalt ferrite ($CoFe_2O_4$), obtained through an increasing substitution of Fe^{2+} ions in magnetite with Co^{2+} ions. As a function of cobalt content, ferrites exhibit a variation in their magnetic properties (blocking temperature and coercivity increase with Co^{2+} molar fraction, as a result of the high single ion anisotropy of Co^{2+}). In a similar way, spectroscopic MCD features vary significantly.
A particular effort was made to control both size distribution and shape of the nanocrystals, in order to obtain a starting material that is at the same time highly performing and easy to model. The synthesis of such systems was carried out using procedures based on the high temperature decomposition of organometallic precursors, the route that at the moment is known to yield nanocrystals of the best quality. In addition to TEM, SQUID and MCD studies, the magnetic systems were characterised by ICP, in order to assess the Fe/Co ratio and by x-ray diffraction to check crystal size and quality. Finally, an EXAFS study has been performed to gain information on the distribution of Co^{2+} ions between octahedral and tetrahedral sites, which has a strong influence on the magnetic properties of the materials.

b. Preparation of plasmonic gold based metallic nanoparticles of different sizes, with varying plasmon resonance frequencies.

Gold nanospheres ranging from very small (2 nm) thiol protected to large (10 nm) amine capped units were synthesised and characterised by means of TEM, visible spectroscopy and MCD spectroscopy. These systems were used both as starting materials to prepare magnetoplasmonic hybrid systems, and as independent plasmonic units to model plasmon MCD response, as well as to prepare, along with the ferrite particles described above, mixed systems of non interacting magnetic and plasmonic moieties.

c. Experiments in the synthesis of enhanced MO response materials based on rare earth-doped ferrites.

MO response is strongly related to spin-orbit coupling, since photon helicity and electron spin are not related in dipole-governed transitions such as those involved in the visible electronic spectrum. Thus, coupling of the angular moment of the polarised photon to spin occurs through the electron orbital moment. While transition metals (TM) like Fe and Co exhibit relatively high spin-orbit coupling, in rare earth (RE) ions the coupling is extremely strong, making them in principle ideal candidates for MCD studies. In addition, RE ions like Dy^{3+} possess very high single ion anisotropy. If one is able to dope ferrites with RE ions then, being able to make the ions couple magnetically, a significant increase in the MO response of the material is to be expected, as well as an increased magnetic anisotropy of the system.
An exploratory synthesis of Dy doped magnetite has been carried out. However, magnetic properties seem not to diverge much from those of magnetite.

d. Synthesis of hybrid magnetic-plasmonic materials with heterodimer and core@shell geometries based on transition metal oxides and gold.

Hybrid colloidal nanomaterials have been synthesised in two geometries: TM oxide-gold heterodimers and gold core @ TM oxide shell/hollow shell concentric systems. Two other geometries have been attempted without success, namely TM oxide-gold-TM oxide dumbbell structures and TM-oxide core @ gold shell particles.
The synthesised systems feature a gradual increase in the degree of interaction between the magnetic and the plasmonic moieties, ranging from the very strong interaction found in core@shell

systems to a weaker regime typical of heterodimer structures, to finish with simple mixtures of the two components, in which no direct interaction is present.

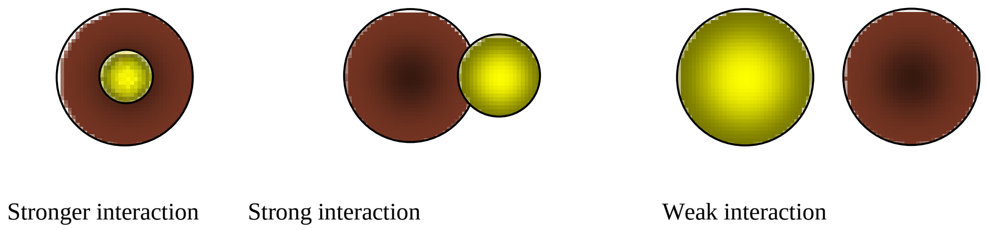


Figure 14: Sketch of the desired structures.

The synthesis is based on the heterogeneous nucleation of the TM oxide on the surface of Au particle seeds. Au seeds can be either preformed or prepared *in situ* before the TM oxide nucleation step. Gold surface acts as a catalyst to oxide nucleation, significantly lowering the activation energy of this process; thus, homogeneous nucleation is very efficiently prevented in favour of heterogeneous nucleation. Lattice mismatch between the two lattices (Au and ferrites) is within a few percents of integer values, so the oxide can grow epitaxially on Au faces; whether the growth takes place on a single face or on multiple faces, leading to heterodimers or core@shell structures, respectively, is related to the polarity of the solvent used as reaction medium, and the effect is believed to depend on the ability of the solvent to shield more or less efficiently the surface charges that build up on the gold surface as nucleation takes place on it.

Using this general method, several combinations have been obtained, ranging from systems with very small gold cores (3 nm), in which the plasmon resonance is strongly damped by the oxide layer, to big gold cores (8 nm), surrounded by a thin layer of magnetite (1 nm). As mentioned above, not only Au-Magnetite core@shell systems were obtained, but also more complex systems, namely Au@CoFe@CoFeO onion systems and Au-core@CoFeO-hollow shell systems.

In all cases, a strong shift in the plasmon resonance peak position was observed with respect to the corresponding unconjugated Au particle due to the difference in the dielectric constant between the organic capping layer and that of the TM oxide.

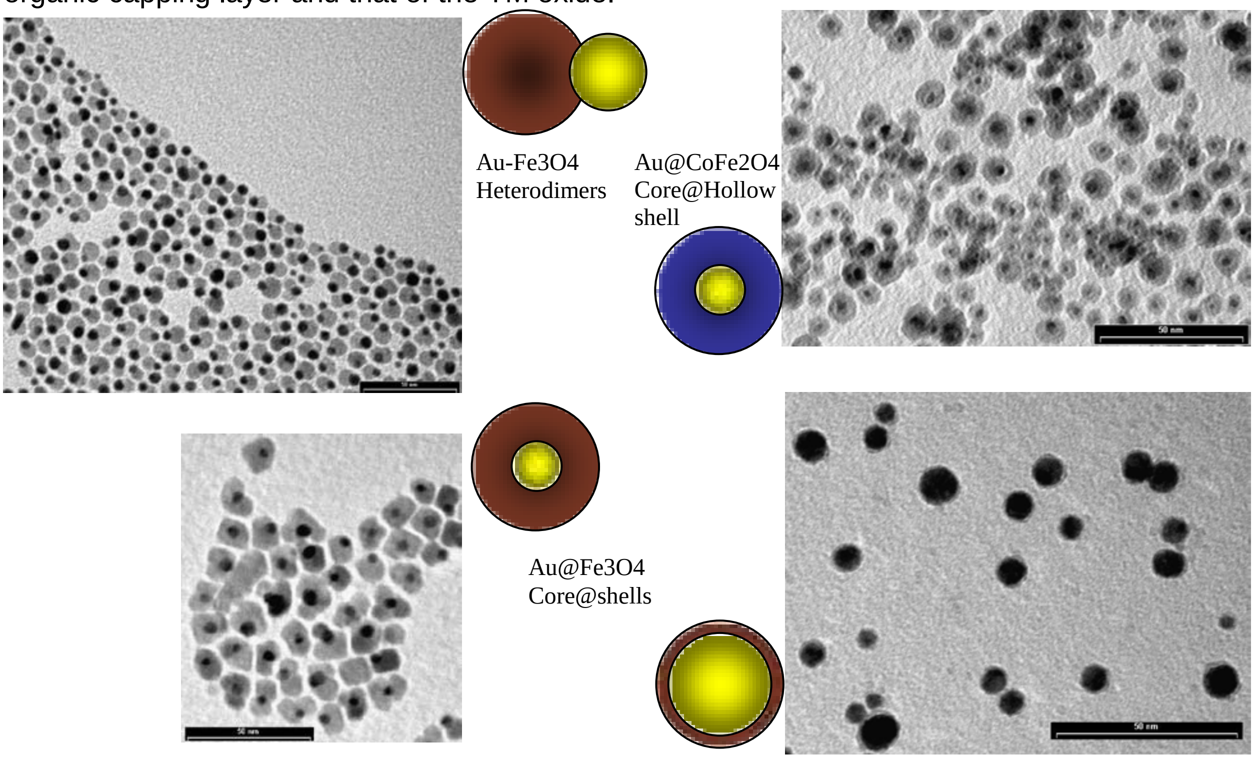


Figure 15: Electron micrographs of the obtained structures with a cartoon detailing their internal architecture.

e. Preparation of polymer matrix-embedded nanosystems based on the materials described above, both in the shape of optically addressable free-standing thick films and supported thin films.

Polystyrene embedded nanoparticles were prepared as thick, self-supported films by drop casting and as silicon, quartz, glass and gold supported thin films by spin coating. Through careful control of spinning time and speed, as well as initial viscosity of the polymer-nanoparticle solution, reproducible control over film thickness in the hundreds of nanometers range can be achieved.
On the other hand, additional studies have been carried out to obtain patterned films of particles embedded in silicon oxide thin layers on silicon. Finally, nanosystems exhibiting free-standing gold surfaces (gold particles and heterodimers) could be organised as monolayers on surfaces using sulphur chemistry; preliminary tests are being carried out in this direction.

WP4

The magnetoplasmonic response as well as the physical mechanisms that govern it have been the main driving force in this part of the project, since mastering this knowledge favours fruitful implementations in application oriented areas. At the same time a predictive capability has been developed, that allows finding directions to enhance the performance of the systems in the specific aspects that are required depending of the intended use.

One aspect that is important in this field is the near field distribution of the electromagnetic field. Therefore one of the main tasks was to develop a Near-field Scanning Optical Microscope to be able to operate under the application of external magnetic fields. The apparatus has been successfully built and shows good stability when the magnetic field is applied. A photograph of the experimental set-up is given in Figure 16. Coils have been integrated to the system. An AC magnetic field of ~20 mT can be applied to the sample at a frequency of 40 to 500Hz. A DC magnetic field of ~ 50 mT can also be applied to the sample by approaching a magnet to the tip/sample region. The scanning area is 100µm x 100µm. The SNOM works in contact and non-contact modes and can scan at different distances of the sample surface. Such features allow measuring 2D and 3D maps of the electromagnetic field distribution.

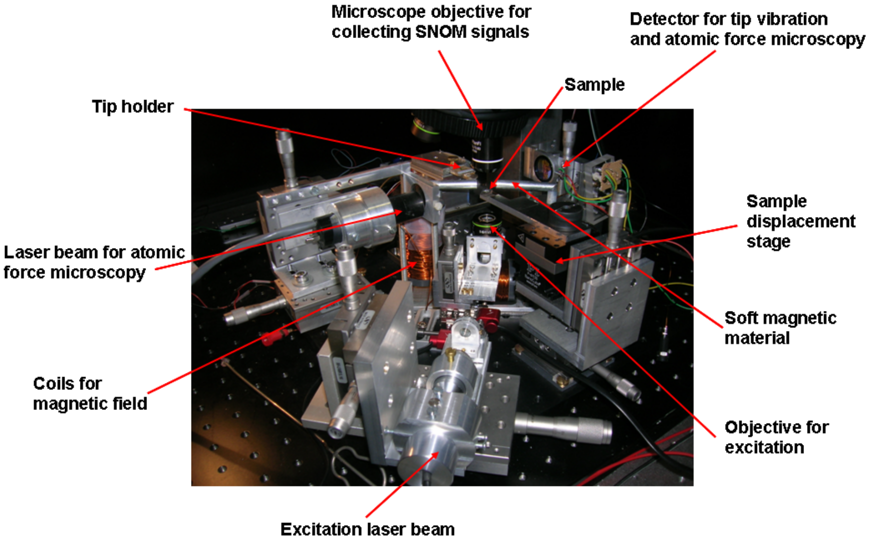
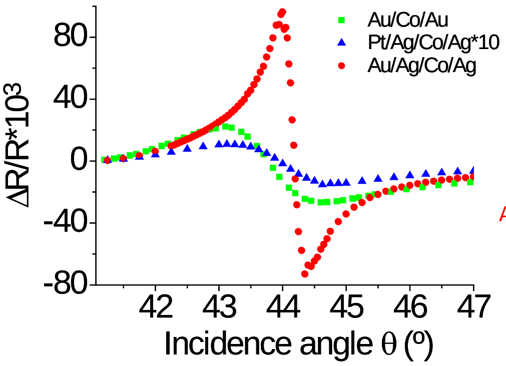


Figure 16: the experimental set-up developed during the period.

The predictive capabilities for the nanostructures response mentioned above have been gained by taking into account the relationships between nanostructural and magnetic, magneto-optical and near/far-field plasmonic properties. Below we present a summary of the main findings.

1) Firstly, it has been found a close relationship between the excitation of plasmonic resonances (propagating ones for continuous multilayers and localized ones for nanostructures, the so called SPPs-Surface Plamon Polaritons and LSPs-Localized Surface Plasmons, respectively) and the enhancement of the magneto-optical activity in the same spectral region. In fact, even pure gold nanostructures, such as nanodisks and nanoparticles, can exhibit magneto-optical activity at low magnetic field values due to the excitation of plasmonic resonances. But in general, in order to observe magnetoplasmonic effects two different kinds of materials have to be combined: those exhibiting high magneto-optical (MO) activity (as the ferromagnetic transition metals: Fe, Co and Ni) and those exhibiting intense and narrow plasmonic resonances (typically the noble metals: Ag and Au). Provided that the dimensions of the different constituents are tailored to exhibit plasmon resonances in the nIR-V-nUV spectral range, such combination produces two main benefits: on the one hand, the localization of the electromagnetic field when the plasmon resonances are excited leads to an enhancement (*up to two orders of magnitude* as seen in Fig. 17) on the magneto-optical response; on the other hand, by applying a magnetic field some plasmonic properties can be tuned, in particular the wavevector of the SPPs in magnetoplasmonic multilayers.



	TMOKE	$TMOKE_{SPP-ON}/TMOKE_{SPP-OFF}$
Au/Co/Au	$2.2*10^{-2}$	40
Pt/Ag/Co/Ag	$1.1*10^{-3}$	4
Au/Ag/Co/Ag	$9.6*10^{-2}$	210

Figure 17: TMOKE signal as a function of the incidence angle for three different multilayered systems. The table shows the absolute values of the signal and the enhancement obtained upon plasmon excitation.

2) Secondly, the influence of the choice for the different materials involved has been understood:

- The noble metal: gold exhibits higher optical absorption than silver in the studied range and therefore its plasmon resonances are not so sharp. As a result, Ag-based systems give better performance than Au-based ones, although a capping layer is mandatory since Ag deteriorates easily in ambient conditions. The best results are then obtained using Ag-based systems with Au capping as can be seen in Fig.17.

- The ferromagnet: since Fe and Co exhibit MO constants of the same order of magnitude, the MO activity obtained in Fe-based systems is similar than that of Co-based systems. When iron or cobalt oxides are used instead, the MO activity is smaller, but such oxides (ferrites, magnetite, etc) can be useful when dealing with liquid environments.

3) Thirdly, the dependence on the structure and morphology has been clarified:

- Shape: From the point of view of applications, it is important to achieve a soft magnetic behaviour, i. e. that the structures can be saturated using a weak external magnetic field. As a rule of thumb, this is obtained in systems in which the shape anisotropy dominates, such as thin films and nanodisks.

- Interfaces and crystal structure: The magnetic-field induced SPP wavevector modulation in epitaxial multilayers is higher (up to three times) than that obtained in equivalent polycrystalline multilayers. However, crystallinity itself does not play an important role. What is really relevant is the quality of the interfaces and the surface flatness: systems with rough interfaces can be optically considered as an effective medium composed by a mixture of noble metals and ferromagnets, therefore exhibiting effective MO constants lower than those of bulk ferromagnets. Epitaxial structures possess sharper interfaces than polycrystalline ones and as a consequence they exhibit higher SPP wavevector modulation.

- Position of the Ferromagnet: When plasmon resonances are excited, there is an intensification and confinement of the electromagnetic near field. The MO response is proportional to the electromagnetic field in the MO active material, i.e. the ferromagnet. In the case of the continuous films, the intensity gradually decreases as the ferromagnetic layer is placed further from the upper interface, so the closer to the surface the ferromagnet is, the higher the MO activity. However, in the case of nanodisks, the intensity of the electromagnetic field distribution associated to the LSP excitation shows a U-like shape with maximum values at the upper (air/metal) and bottom (metal/substrate) interfaces, and as a result the MO activity increases when the ferromagnetic layer is near the surface or the substrate and reaches lower values when is located at intermediate positions.

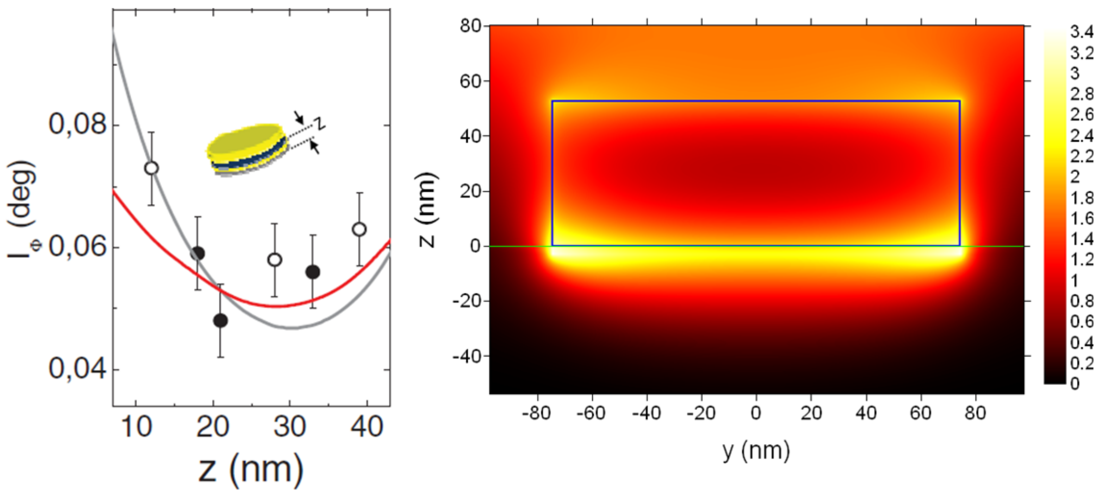


Figure 18: Magneto-optical activity of 75nm radius disks (left) and theoretically calculated electromagnetic field distribution (right) showing the high correlation between the field and the MO activity.

- Dielectric environment: As plasmon resonances are highly sensitive to the metal/dielectric interfaces, the dielectric environment also plays an important role in the magnetoplasmonic properties. In the case of magnetoplasmonic multilayers, the magnetic-field induced SPP wavevector modulation depends on the refractive index of the dielectric layer on top: higher index leads to a higher magnetic modulation of the wavevector. In the case of nanostructures exhibiting LSPs, the wavelength at which such resonances take place, and therefore the spectral location of the region with enhanced MO activity, can be tuned by changing the dielectric environment. For instance, in ferromagnetic membranes there is a redshift of the region with enhanced MO Kerr rotation when the refractive index of the material inside the pores increases.

4) Finally, some specific issues related to magnetoplasmonic nanostructures made by chemical routes have been also understood:

- Alloy based nanoparticles: if the amount of ferromagnetic layer is large, there is a chemical damping of the LSP resonances. So, only for low concentration of ferromagnetic material (which can be considered as doping noble metals nanoparticles with ferromagnets) LSP resonances and MO activity can be simultaneously obtained.

- Core-shell nanoparticles: only plasmonic core with magnetic shell have been obtained by chemical routes. Provided that the thickness of the shell is large enough to give rise to ferromagnetic behaviour, in the MO signal two separate contributions appear: one associated with a diamagnetic component from the core and another ascribed to the ferromagnetic shell.

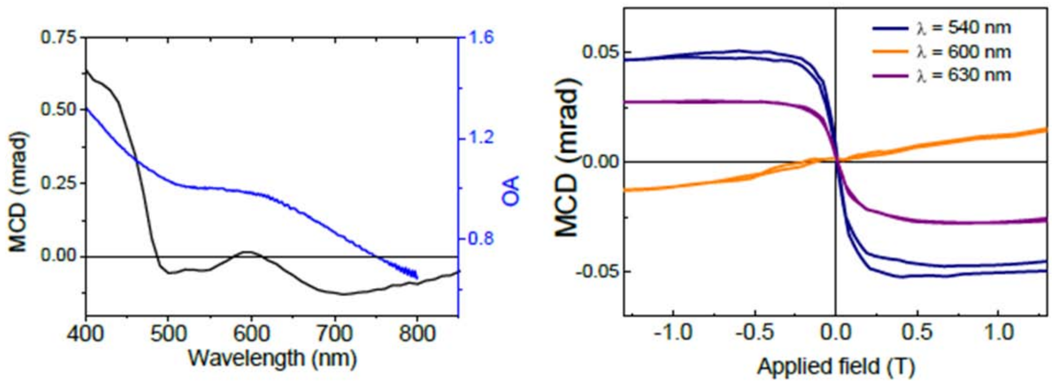


Figure 19: MO and OA spectra and MO loops measured with light of different wavelengths of 4nm Au@ 3 nm Fe oxide NPs, evidencing the ferromagnetic (540nm and 630nm) and diamagnetic (600nm) character of the MO response.

WP5

From the applications side we have in mind two different areas where we think the developed materials can play a relevant role in the near future: sensing and telecom applications. In the case of sensing applications the use would be in the so-called label-free (i.e. not using complex marking with fluorescent or other developer entities) sensors framework, and in the case of telecom applications the idea is to use the materials as the base ones for optical isolators and non-reciprocal waveguides.

1. Sensing applications

In the case of sensing applications we have performed experiments in gas sensing and bio sensing. In both cases we have obtained an increase in the sensing performance using the developed devices based on the new generation of magneto-optical materials.

For that task we have developed two different set-ups, one is a work-bench based device able to obtain simultaneously standard plasmonic (SPR) and magneto-plasmonic (SMPR) measurements in liquid and gas phase, the second is a combined SMPR and Electrochemical Impedance Sensing platform based on commercial Spreeta sensing platform.

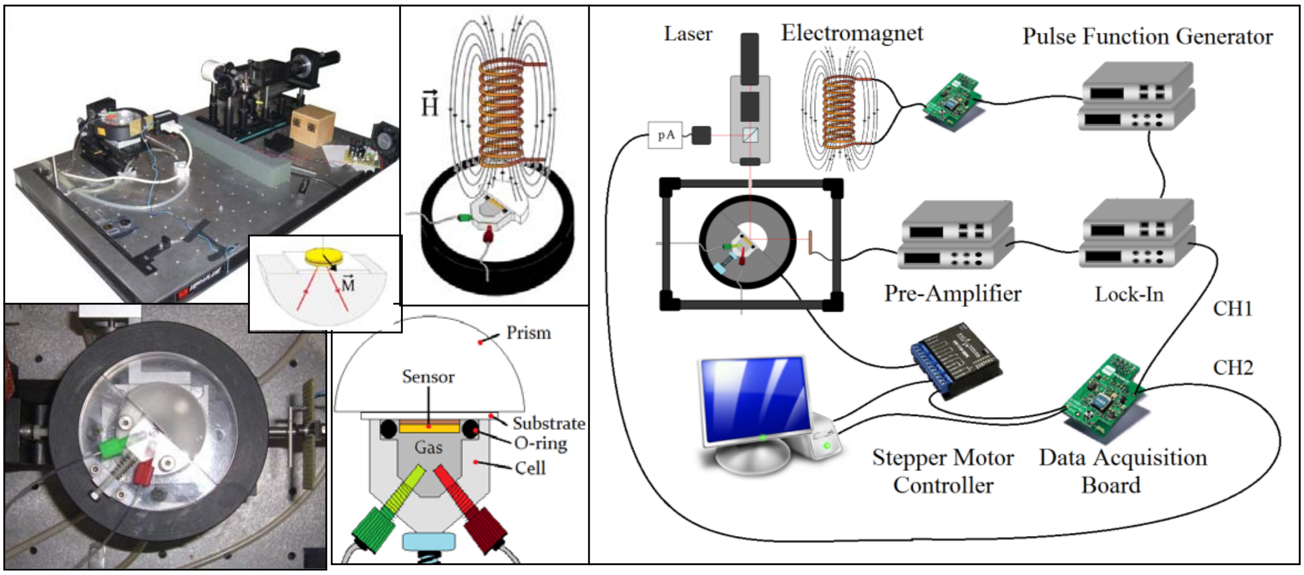


Figure 20: Photograph and scheme of the data acquisition system used in the realized MO-SPR setup

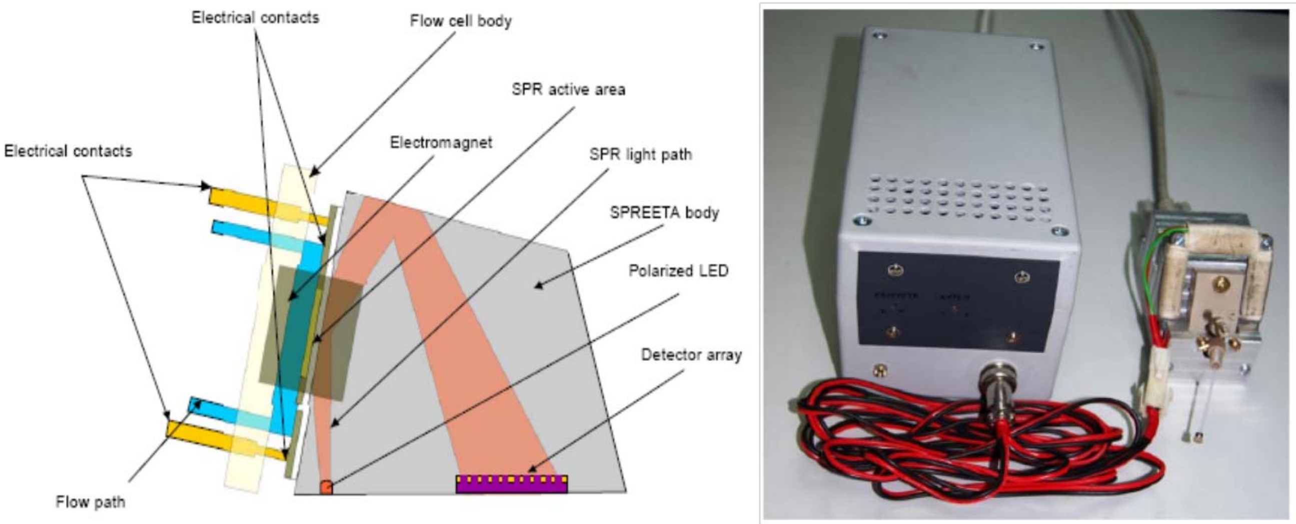


Figure 21: Left: Schematics of the integrated platform – side view. Right: The combined SMPR and Impedance / electrochemical sensing platform.

Regarding the experimental results, we can say that we have obtained both an increase in the sensing performance for both gas sensors and biosensors implemented devices realized by the use of the new generation of magneto-optical materials. Below some results can be found.

Let us first point to some results concerning gas sensing characterization by using the novel magneto-plasmonic materials and the novel MOSPR technology, using different "sensing layers" and different deposition techniques.
For gas-sensing we have used two different TiO2 sensing layers, one deposited by Glancing angle deposition (GLAD), the other nanocrystalline TiO2 prepared by colloidal routes (brookite TiO2 nanorods, capped with an organic shell of oleate/oleyl amine surfactants), deposited by using the Matrix-Assisted Pulsed-Laser Deposition (MAPLE) technique.
Porous TiO2 layer deposited by GLAD have reported the best sensing performance with respect to colloidal TiO2 nanocrystal layers. In fact the porous nature of the sensing layer makes it more sensitive to local refractive index changes at the Au/air interface.

As an example we are presenting the calibration curves (Fig. 22) where the sensor response is reported with respect to the concentration of the tested analytes, particularly by the slope of the curve, in its linear part, which gives important information about the sensitivity.

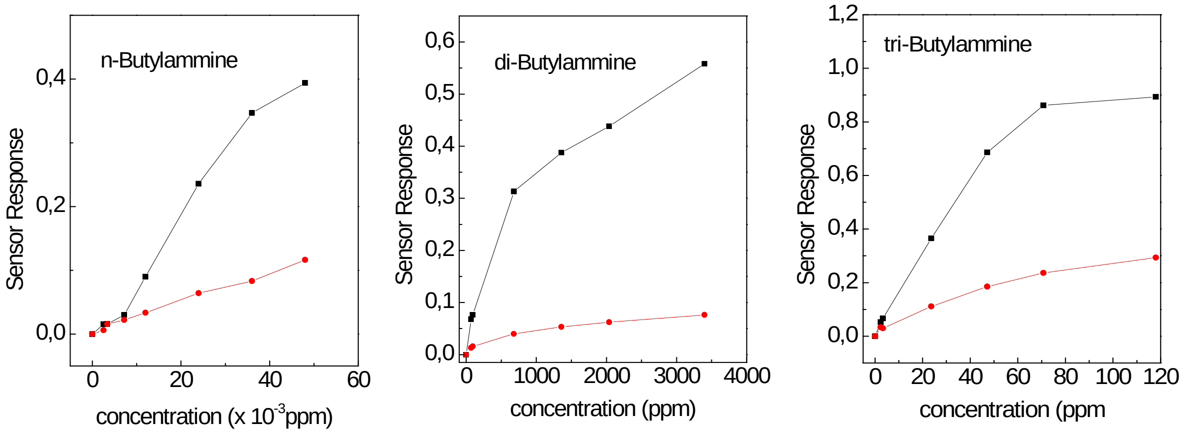


Figure 22: Comparison of SPR (red) and MOSPR (Black) Sensor response relative to of ethane-bridged Zinc porphyrins dimmers deposited onto Au/Co/Au substrates towards different ammine vapours

Regarding biosensors analysis, synthetic BSA-antiBSA tests were performed to demonstrate the increasing in the sensitivity of MOSPR measurements respect to SPR. To that end a special immobilization protocol is established, as follows:

Gold-coated SPR or MOSPR chips were immersed for at least 48 hours in 150 mM solution of 11-MUA in glycerol/ethanol 1:1(v/v). Afterwards chips were rinsed with ethanol 95%, again with ultra pure water before placing in SPR or MOSPR chamber. Then freshly 11-MUA-modified chip was placed in the test chamber and conditioned in ethanol 95%, followed ultra pure water. After conditioning, when stable readout was achieved, the carboxyl groups of 11-MUA SAM were activated by treating with 50 mM NHS in water/ethanol (10:1 v/v) for 5 minutes followed by 30 mM EDAC in water/ethanol (10:1 v/v) followed by a mixture of NHS/EDAC at the same concentration for 30 minutes. Subsequently the chip was washed with 10% ethanol followed by ultra pure water until stable readout was obtained. Then BSA (100 ppm) was diluted with ultra pure water and was injected in the test chamber for at least 45 minutes. After this step a water solution was injected in the sensor cell to move away the unbound BSA until a stable readout is obtained.

The improved sensing performance reached by MOSPR setup with respect to SPR configurations is clearly evidenced in Fig 23 where the calibration curves relative to the interaction BSA protein and anti-BSA antibody is reported for different concentration of the selected antibodies.

A great increase of the sensor response can be recognized in the MOSPR configuration besides the improved sensitivity which can be extracted from the slope of the linear part of the calibration curve.

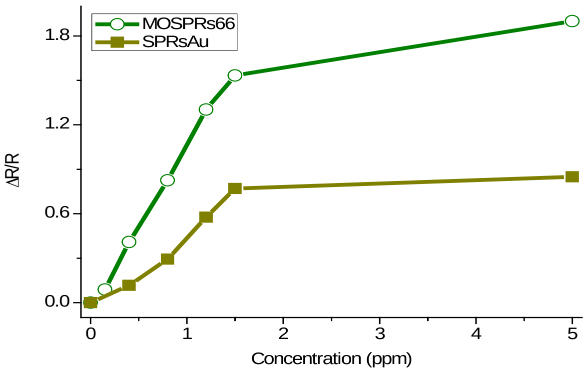


Figure 23: Calibration curves relative to MOSPR and SPR configuration for the BSA-antiBSA biological assay

In order to take into consideration the stability of the sensor signal during time, the MOSPR signal has been monitored after two days in water conditions. The Au/Co/Au deposited on glass transducing layers have demonstrated a very good stability, reporting the same signal even after two or more days without any signal of ageing.

The last example involves cell detection capabilities of combined EIS/SPR sensing platforms based on novel magneto-optical materials. This is based on series of assays aiming to detect target analyte using sensing platforms involving novel magneto-optical materials and selected antibodies. Appropriate fluidics, analytic instrumentation and measuring protocols were developed for this purpose.

The promising biosensing results provided by SMPR and EIS instrumentation and sensing protocols advanced were hampered by lack of stability exhibited by some sensing surfaces (chips) during SMPR as well as EIS measurements, especially in saline solutions (required by biosensing assays). Several corrective approaches are considered for improving the chip stability:
(1) advancing multilayered SMPR chips comprising Au and Co based magnetic layers (e.g. alloys Co with Fe); (2) use of protective matrices (via functionalization of the top Au layer) for minimizing interaction with running saline solutions under microfluidic regime; (3) decreasing the time length of the measurement by relating the specific response of the sensor, both for SMPR and EIS assays, to the electro-optic behavior of the sample when applying magnetic actuation (related to TMOKE).

One example is given by the calibration curves for Escherichia coli detection obtained with SMPR and EIS simultaneous measurements are presented in Fig. 24. Classical SPR measurements obtained by measurements at a fixed angle (monitoring the reflectance from a single pixel) are also showed.

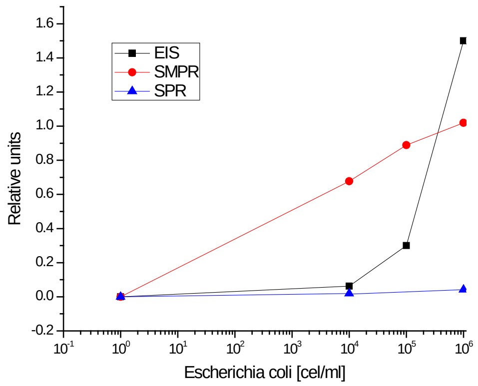


Figure 24: Calibration curves for Escherichia coli detection. Left - simultaneous EIS, SPR and SMPR detection on titanium/gold/thiol covered chips. EIS measurements were made using a continuous active electrode and a platinum counter electrode. Right - SPR and SMPR same as left but EIS measurements performed using coplanar electrodes.

Although not as drastic as in other structures, the titanium protected ones also presented signs of degradation after several analyses (Fig. 25). This showed that a thicker protective layer could be required but adding a thicker absorbent layer will also decrease the useful magneto-plasmonic effect.

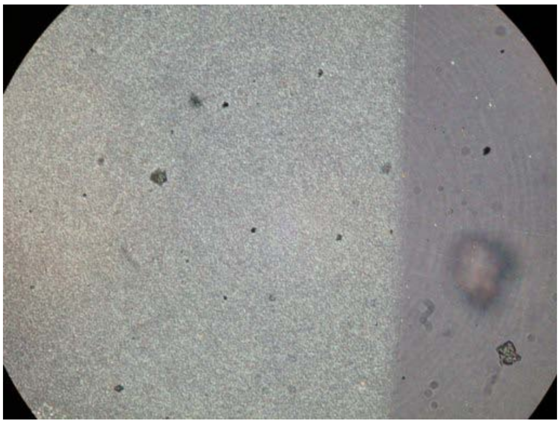


Figure 25: Surface of corroded titanium/gold/thiol coated chip following SMPR assays (the dark side was not exposed to saline flow)

In conclusion, using the methods and the instrumentation developed during the project, we assessed the detection capabilities of combined EIS/SPR sensing platforms based on novel magneto-optical materials. The issue of chip stability was also addressed and several structures with protective layers allowed for relevant combined SMPR and EIS biosensing measurements. These experiments enabled comparison between behavior SMPR and EIS measurement methods. It is worth emphasizing that high sensitivity of SMPR assays when compared to EIS in the case of titanium/gold/thiol covered chips when EIS set-up consisted in a continuous active electrode and a platinum counter electrode on top of the flow through measurement chamber. Where possible (i.e. in the cases of titanium protected chips) the SPR data acquired in the same conditions (simultaneously) showed a lower sensitivity as compared to either SMPR or EIS methods.

2. Telecom applications

We have identified non-reciprocal components for photonic integrated circuits at 1.55 µm wavelength as a potential application of magneto-plasmonic (MP) materials. We have evaluated this approach with respect to other ways to achieve non-reciprocity proposed in the literature. The objective is to identify the main issues for the design and fabrication of optical isolators and to evaluate the best target for magneto-plasmonic materials. We also report on simulation results showing the interest of using magneto-plasmonic materials to create non-reciprocal integrated waveguides.

We propose a generic non-reciprocal waveguide configuration shown in Fig. 26. It is based on a standard silicon waveguide with a magneto-plasmonic cladding on top. The magneto-plasmonic stack used has to be compatible with standard microelectronics CMOS fabrication techniques.

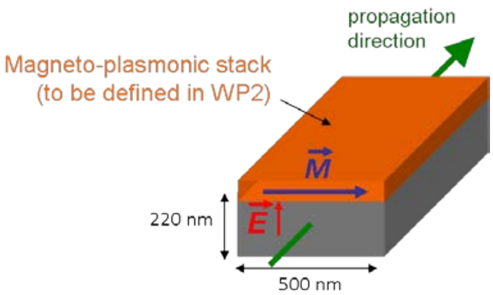


Figure 26: Schematic of magneto-plasmonic waveguide structure

The more appropriate magneto-plasmonic metal can be typically an alloy of FeCo which can be easily deposited by PVD (Physical Vapour Deposition). The equiatomic composition leads to the best compromise between magneto-optical activity and absorption losses.

FeCo is a magneto-plasmonic material as it combines both magneto-optical (as a ferromagnetic material) and plasmonic properties (as a metal with relatively high conductivity). The waveguide is operated in the Kerr configuration with transverse magnetization with respect to the propagation direction and to the electric field in order to maintain the same polarization along the waveguide. As FeCo is spontaneously magnetized in the layer plane, TM guided modes will be used. However, if needed, TE guided modes could also be used with other MO materials like TbFeCo with preferential magnetization in the direction perpendicular to the layer. TbFeCo is a well-known material which has been widely used in magneto-optical data storage a few years ago.

The objectives of these simulations are:

- to maximize the non-reciprocity of the waveguide and to assess the performances in terms of non-reciprocity (or equivalently isolation ratio), transmission in the forward direction (or equivalently insertion losses). The key parameter will be the FeCo cladding thickness.
- to understand whether the plasmonic properties of this material, provided that they are smartly used, can enhance its magneto-optical properties.

Once optimized, the non-reciprocal waveguide sections can be inserted in interferometric structures, like a Mach-Zehnder interferometer as illustrated in Fig. 27, or like a resonant ring side-coupled to a waveguide.

The Mach-Zehnder length necessary to achieve isolation is given by:

- $L_{MZ} = \lambda / (8\pi \Delta n_{eff})$ if the two arms of the Mach-Zehnder comprise non-reciprocal waveguide sections with opposite magnetization
- $L_{MZ} = \lambda / (4\pi \Delta n_{eff})$ if only one arm of the Mach-Zehnder comprises a non-reciprocal waveguide section

Alternatively, optical isolation can be achieved in a simple non-reciprocal waveguide section by using the non-reciprocal absorption.

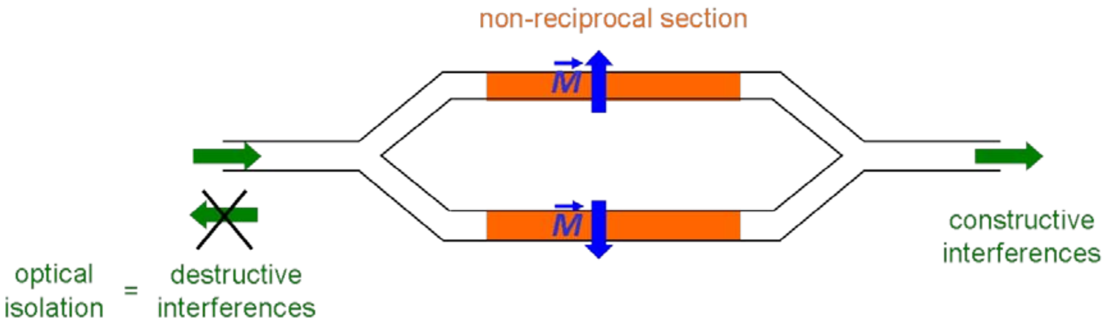


Figure 27: Example of integrated optical isolator structure consisting of a Mach-Zehnder interferometer. Each arm of the interferometer comprises a non-reciprocal waveguide section. The sections are magnetized with opposite directions**.**

The important elements to investigate are the guided modes supported by the magneto-plasmonic waveguide. For each guided mode of interest, we study the effective index n_{eff} and the propagation losses α. Then we define several figures of merit to guide the optimization:

- the non-reciprocity of the effective index of the guided mode in the forward and backward directions or equivalently the non-reciprocity for opposite magnetization directions

$$NR_{phase\ shift} = \frac{n_{eff}^{forward} - n_{eff}^{backward}}{n_{eff}(M=0)} = \frac{n_{eff}(+M) - n_{eff}(-M)}{n_{eff}(M=0)}$$

- the non-reciprocity of the propagation losses of the guided mode in the forward and backward directions

$$NR_{losses} = \frac{\alpha_{eff}^{forward} - \alpha_{eff}^{backward}}{\alpha_{eff}(M=0)} = \frac{\alpha_{eff}(+M) - \alpha_{eff}(-M)}{\alpha_{eff}(M=0)}$$

- the product $\alpha \times L_{MZ}$ where $L_{MZ} = \lambda_0 / 4\left(n_{eff}(+M) - n_{eff}(-M)\right)$ is the Mach-Zehnder length required to achieve optical isolation. The minimization of this figure of merit allows minimizing simultaneously the propagation losses and the length of the isolator device.

The non-reciprocal effective index variations are plotted in Fig. 28 for the three guided modes (photonic TE mode, photonic TM mode and plasmonic TM mode). For each mode, the magnetization is applied in the Kerr configuration, i.e. perpendicular to the electric field (in the *y* direction for the TE mode and in the *x* direction for the TM photonic and plasmonic modes).

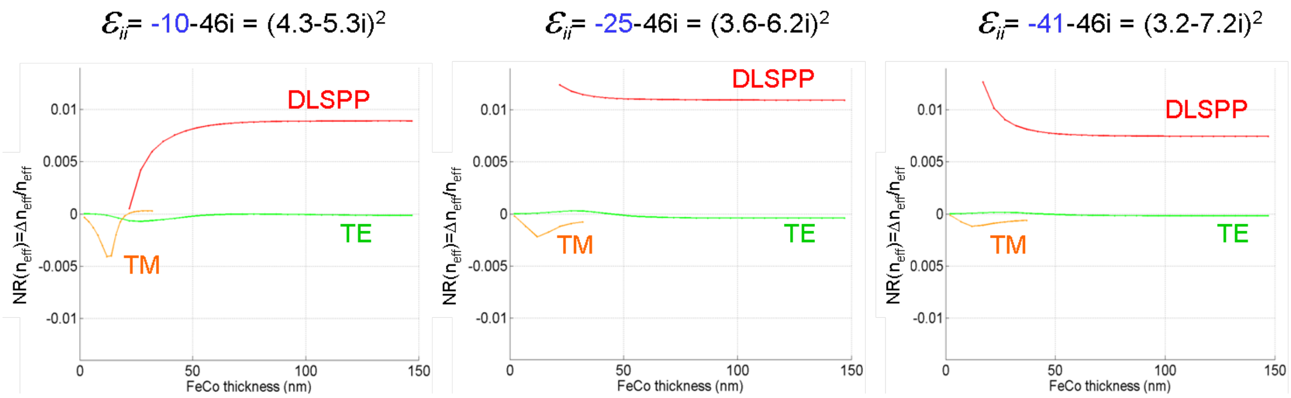


Figure 28: Evolution of the non-reciprocity of propagation for the guided TE, TM and DLSPP modes of the Si/MP waveguide as a function of the MP material thickness, for different values of the complex refractive index of the MP material.

The first observation is that non-reciprocity is much larger for the plasmonic mode than for the photonic modes.

The optimal value of non-reciprocity is obtained for a MP material refractive index close to Si and large value of MP material thickness (above 60-70 nm). Typically, the non-reciprocal phase shift is in the range $7\text{x}10^{-3}$ – $1.1\text{x}10^{-2}$ whatever the value of the refractive index of the MP material. It is higher by a factor of 2 to 3 with respect to the plasmonic mode.

The non-reciprocal variations of losses are plotted in Fig. 29. This figure of merit is also interesting to compute, because if non-reciprocity is large enough, a simple non-reciprocal waveguide section can be enough to achieve optical isolation with a significant isolation ratio.

Again, the non-reciprocity of propagation losses NR(α) is larger for the plasmonic modes than for the photonic modes whatever the MP material thickness and whatever the refractive index of this material with respect to Si. For the plasmonic mode, the value of non-reciprocity is in the range 1 – $5\text{x}10^{-2}$. The evolution of NR(α) greatly depends on n_{MP}. There is an inversion of non-reciprocity, depending on the value of n_{MP} with respect to n_{Si}. When $n_{FeCo}>n_{Si}$, NR(α)>0 and when $n_{MP}<n_{Si}$,. NR(α)<0.

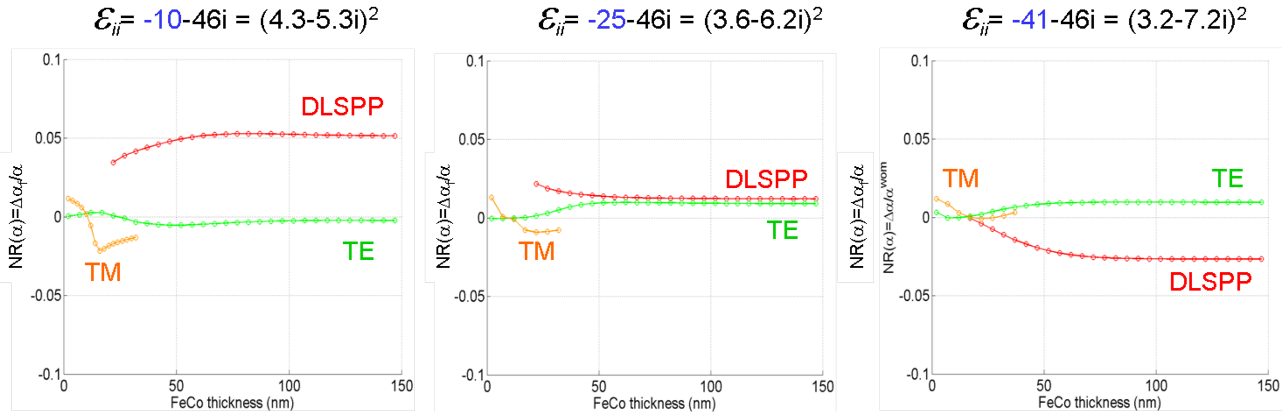


Figure 29: Evolution of the non-reciprocity of propagation losses for the guided TE, TM and DLSPP modes of the Si/MP waveguide as a function of the MP material thickness, for different values of the complex refractive index of the MP material.

As stated above, the product $\alpha \times L_{MZ}$ has to be minimized to achieve the best performances of Mach-Zehnder based isolator devices. Indeed, minimizing this product ensures the more compact devices with the maximum transmitted power in the forward direction.

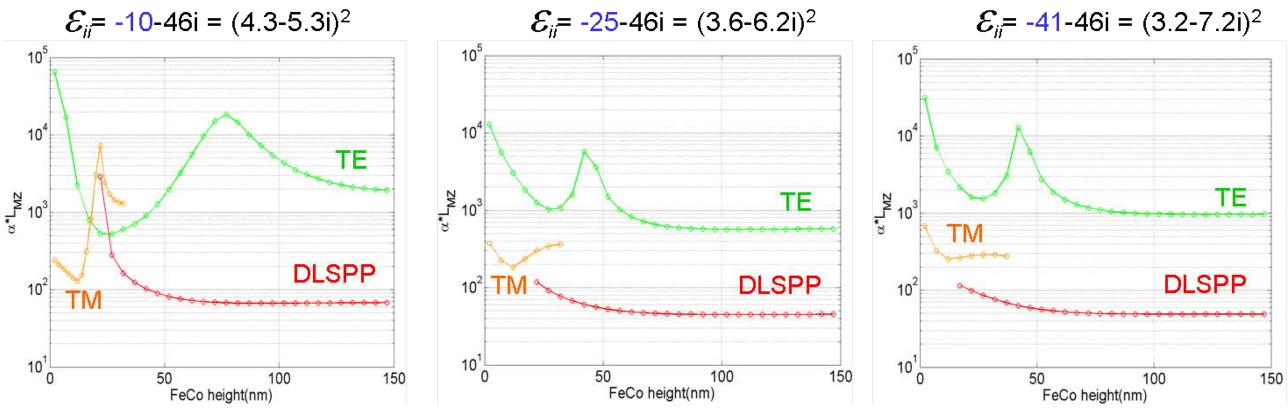


Figure 30: Evolution of the product $\alpha \times L_{MZI}$ of the guided TE, TM and DLSPP modes of the Si/MP waveguide as a function of the MP material thickness, for different values of the complex refractive index of the MP material.

For the photonic modes there is a local optimum of MP material thickness to minimize the product $\alpha \times L_{MZ}$: 27 nm for TE and 12 nm for TM for $\varepsilon_{ii} = -10 - 46i$. The corresponding Mach-Zehnder lengths defined by $L_{MZ} = \lambda / (4\pi \Delta n_{eff})$ are 247µm for TE mode and 55µm for TM mode.

For the plasmonic mode, the product $\alpha \times L_{MZ}$ decreases when the MP material thickness increases. Thus it is preferable to have a thickness above 60 nm. This product is smaller than for photonic modes whatever n_{MP}. The optimum is achieved for n_{MP} close to n_{Si} In this case, the Mach-Zehnder length is the shortest with only 11µm.

For all three kinds of modes, the best performances are achieved for n_{MP} larger than n_{Si}.

In conclusion, better isolation performances are achieved when using the plasmonic TM mode of the Si/MP waveguide instead of the standard photonic modes. Propagation losses are larger for the plasmonic modes but non-reciprocity is much larger, leading to a smaller global product $\alpha \times L_{MZ}$. This means that the larger non-reciprocity leads to a significant reduction of the required device length which more than compensates the larger propagation losses.

We have studied non-reciprocal waveguides based on a classical silicon ridge waveguide with a ferromagnetic cladding showing magneto-plasmonic properties like FeCo. Such waveguides support TE and TM photonic guided modes and a TM plasmonic mode. **We have found that the largest non-reciprocity of the propagation is obtained by using the plasmonic mode**. **Although associated propagation losses are larger, the plasmonic mode allows in the end to achieve the best compromise between losses and compactness.** The best performances are achieved for FeCo thickness in the range 60-100 nm. The typical length is 10 µm, i.e. about five times shorter than for the classical TM photonic mode and more than one order of magnitude shorter than for the TE photonic mode.

<u>Potential impact (including the socio-economic impact and the wider societal implications of the project so far) and the main dissemination activities and exploitation of results</u>

Impact

The proposed materials and prototypes requires downscaling to the tens of nanometer scale which means the use of less active material, with the associated reduction in the environmental impact and, possibly, in the energy consumption. This will also contribute to a reduced recycling need at the end of a potential product life. Preservation of resources is inherent to a specific envisaged application, namely source tagging for recycling purposes.
In terms of the sensing devices the benefits are twofold. The first one is related to the fact that the most sensitive label-free sensor is based on the Mach-Zehnder interferometer. Therefore it is a Silicon based device whose fabrication is somehow complex and requires expensive clean room facilities. The measurement process is also not straight-forward. On the other hand the SMPR is based on metal deposition (easy, requires only vacuum conditions) plus a microfluidic system (as well as the MZ). This means that the actual cost of a high sensitive device can be severely reduced. The main difference is that the MZ sensitivity is between two or three orders of magnitude better than the conventional SPR. However, using the nanostructures to be developed in our project we expected the sensitivity of the SMPR to be enhanced so that this device would compete with the MZ in sensitivity, requiring less complexity both in fabrication and measurement and being considerably cheaper. A direct consequence of the cost reduction is the possibility of **massive on-site quality control of pollutants, bacteria concentration, etc**, that will efficiently help preventing the appearance and proliferation of diseases. The second is related to the signal modulation capabilities, which will allow the reduction of the signal-to-noise ratio in opto-electronic devices using a simple approach. Therefore high-quality reception will not necessarily involve increasing the signal intensity, decreasing in this way the electromagnetic pollution in dense population areas.

On the first topic, based on the **two patent applications** mentioned in **Template B1**, the partner issuing them aims to develop portable, stand-alone systems for in field, quality control testing of **1) raw materials used in food industry** (e.g. in milk, honey) such as: biological load, presence of: toxins, pharmaceutical residues, pesticides, and herbicides and **2) environment (water, aquatic media in lakes, or rivers**). This approach is expected to be further developed via research projects in a range of ~ 2-3 years

The commercial exploitation of R & D results is expected to have a major impact in the following areas: Food Safety & Health - the possibility to assess in field, rapidly, accurate and cost effectively the quality of raw materials using automatic systems, user friendly, without the need of qualified personnel. The new portable system will be easily implemented in public alimentation units where the healthy food is a must e.g. hospitals (also in point of care units) and schools. Also, it is envisaged to be used in fighting bioterrorism

The economic impact relies on the technical results generated, promoting newly developed technologies and improving the performance of quality detection procedures. The expected accessible price and the user friendly manner of using it will place the product as a prime option for the customers willing to test the quality of food and water.

The economic impact will be reflected by the producers increased income. The portable system can be used by public authorities, for example testing Laboratories and Qualitative Analysis, Food Control Authorities and also by food producers and retailers; moreover, it will be useful for the analytical and diagnosis instrumentation manufacturing companies.

Noteworthy, the system is expected to provide a cost effective, local (*in field*) alternative for testing raw materials instead of sending them to distant certified laboratories. The integration of “the know-how” in EU companies, private or public authorities, will have an immediate result in creating new approaches on food quality testing.

On the second topic, the work carried out in the project has led to the design of different configurations of non-reciprocal waveguide structures for integrated optical isolators at telecom wavelength (see Deliverable D5.10 for details). The non-reciprocal waveguides proposed by the responsible of D5.10 are based on the appropriate combination of ferromagnetic FeCo material and Cu plasmonic metal in order to enhance the non-reciprocal properties and to build more compact devices. Compactness is indeed a strong requirement for integrated photonic circuits, in particular with the expected convergence between photonics and CMOS microelectronics in the next years.

The foreground might be of interest for Alcatel. Namely, Alcatel have carried out a work on integrated amplifying optical waveguide isolator at 1.3 µm wavelength in the last 5 years. In 2006, they have demonstrated a device based on AlGaInAs/InP for the active material and FeCo for the magneto-optical material. The device is based on non-reciprocal modal absorption in an InP-based semiconductor optical amplifier. Non-reciprocity is provided by the ferromagnetic FeCo material which is also used as electrode to contact the device. Current injection in the active structure compensates for the propagation losses in the forward direction.

Some designs proposed within the NANOMAGMA project can be considered as an improvement of the Alcatel device toward better isolation performances for a given length or better compactness of the device for a given isolation ratio. Some other designs proposed, like the plasmonic slot waveguide, can be considered as alternative waveguide designs. The foreground gained could therefore be exploited to design optical isolators to be integrated with laser sources either on InP or on SOI substrates.

Discussions have been started between CEA and Alcatel to inform them about the designs proposed. As Leti has joined Alcatel-Thales III-V Lab in 2011, there is no confidentiality issue, although the patent is not yet deposited. Semiconductor optical amplifiers at 1.3 µm will be considered first, but the relevance of designs adapted to the so-called C-band around 1.55 µm wavelength will also be discussed.

Further research will be necessary before launching the fabrication of prototypes. Firstly, additional FeCo developments should be carried out in order to optimize the magneto-optical properties and to improve the reproducibility of the material. Secondly, the work within the NANOMAGMA project has focused on the design of the core non-reciprocal waveguide. Additional simulation/design work should be conducted to design out-couplers to standard InP or SOI waveguides, depending on the material platform chosen for applications. Specific out-couplers should be designed both for the magneto-plasmonic slot waveguide configuration and for the so-called dielectric-loaded waveguide configuration (DL-SPP).

The potential of the foreground is for integrated optical isolator components to be commercialized in 5+ years

Dissemination activities

The main dissemination activities during the project lifetime were the following:

• Project WEB site: public and restricted areas online
A notable activity of the NANOMAGMA project consisted in structuring, developing and maintaining a WEB site (Portal) being able mainly to disseminate widely its results, spreading therefore Excellence not only in Europe but also in other countries: www.nanomagma.org. To meet this requirement, the NANOMAGMA portal was coupled with the already existing Phantoms Foundation Nanotechnology platform (*www.phantomsnet.net*) receiving around 10.000 visits a month and hosting up to four other European funded Projects (nanoCODE: FP7-NMP; nanoICT Coordination Action: FP7-ICT/FET; MULT-EU-SIM: FP7-ICT/FET and AtMol Integrated Project: FP7-ICT/FET).

This WEB site therefore fostered a high quality of communication both outside and inside the consortium. The NANOMAGMA Home page presented detailed information on the project: project description (public content), etc. It also proposed online the consortium partner geographical distribution (interactive map) and a detailed description of each partner. A list of events was proposed in order to provide visitors detailed information about the main meetings, sessions or symposia related with NANOMAGMA. A list of publications was proposed in order to provide visitors detailed information about the NANOMAGMA papers (E-nano newsletter contributions) produced by the project Working Groups and NANOMAGMA Consortium publications list, updated accordingly to publications submitted online in CORDIS

General information with databases providing visitors and consortium partners information on conferences/courses, jobs and news…

Intranet restricted area: (database: documents and internal events) for the Management Board (and individuals belonging to the project) was developed to allow secured exchange of confidential documents about the project and to display information on: progress about the project, calendar, plenary meetings, reports, etc.
External Collaborations: nanoICT coordination action (partners database) – allowed to provide detailed info on NANOMAGMA partners core competences, infrastructures, etc.

• General Dissemination activities

Flyers, providing basic information on the project were printed and distributed in order to publicise the project on a worldwide scale. The flyer included significant scientific results (and related publications).
Pdf format available online – Home and publications pages of the NANOMAGMA project


Short facts
- NANOMAGMA — NANOstructured active MAGneto-plasmonic MAterials
- EC contribution — 2.963.156 Euros
- Contract number — FP7-214107-2
- N° of partners — 10
- Coordinator — IMM / CSIC (Spain) / Antonio Garcia-Martin
- Start date — November 01, 2008
- Duration — 36 months
- WEB site — www.nanomagma.com

Nanomagma Objetives

The purpose of this European funded project is the study, development and application of a novel concept of nanostructured materials formed by the combination of components with plasmonic and magneto-optic (MO) activity. This smart combination will produce "magneto-plasmonic" nanomaterials tailored on the nanoscale.

Highlights
- Experimental verification of plasmon wave vector modulation by magnetic fields
- Strong enhancement of the MO response due to localized plasmon excitation
- Development of a versatile numerical tool for the analysis of the optical and MO response of magneto-plasmonic structures of arbitrary shape
- Development of a novel SNOM for near field under magnetic fields (MO-SNOM)
- Development of a novel measurement bench for MO sensing devices, including microfluidics and functionalization protocols

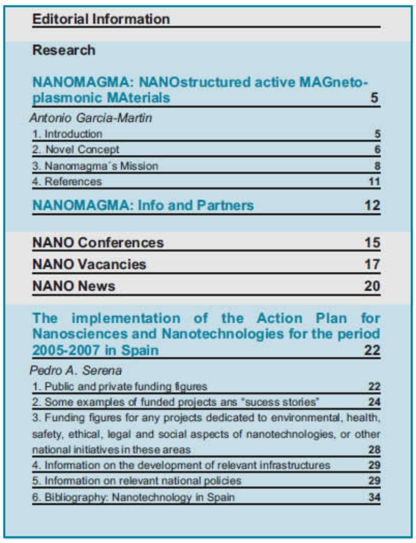
Publications
- V.V. Temnov et al, Nat. Phot. (2010)
- B. Sepulveda et al, Phys. Rev. Lett. (2010)
- S. Albaladejo et al, Opt. Express (2010)
- C. de Julian et al, Nanotechnology (2010)
- C. Vandenbem et al, Journal of optics A: pure and applied optics (2010)
- MG Manera et al, Journal of Optics (2010)
- M Gheorghiu et al, Biosens Bioelectron (2009)

Events

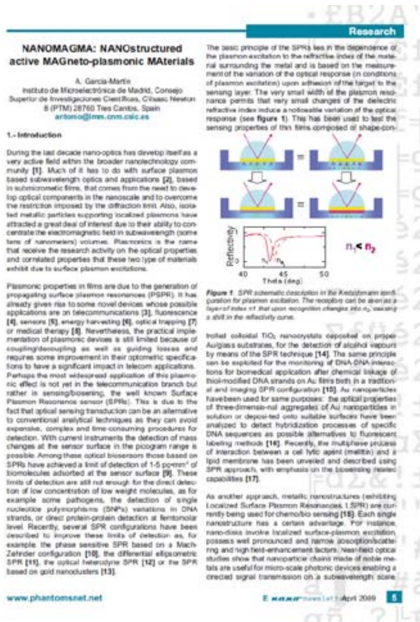
PPM 2011
April 11-14, 2011
Bilbao Exhibition Centre (Spain)
www.imaginenano.com

E-nano Newsletter contributions:

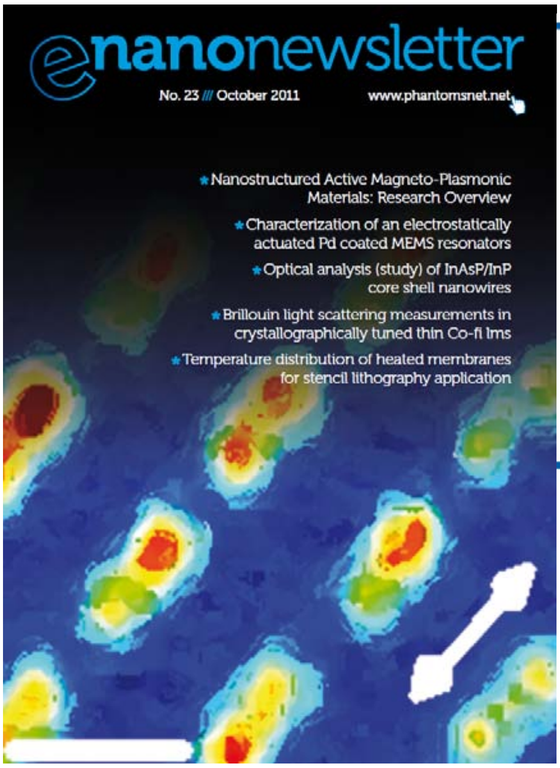
- (Month 9) a review article on the current status of "magneto-plasmonics and applications" and a list of the partners i nvolved in the related EU funded Project NANOMAGMA (NANOstructured active MAGneto-plasmonic MAterials), detailing their activities and core competences


Editorial Information

Research



- (Month 36) Eight extended abstracts from the Nanomagma workshop (D1.9) were published in the E-nano Newsletter (nº 23)



contents

editorial information

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Short facts:

- 1500 printed copies
- Pdf version available online for download
- Other dissemination channels (Slideshare, Issuu, etc.) used to enhance visibility

One short interdisciplinary **training course** (1/2 day duration) was organized by the project partners as well as a NANOMAGMA school and one Industrial / Scientific Workshop in collaboration with the PPM conference.

☛ Short Training Course (in collaboration with the 2nd Spanish NanoPhotonics Conference, CEN2010): Segovia (Spain) - June 15, 2010
Short facts:

- ½ day duration (June 15, 2010)
- Grants available (for PhD students)
- 4 invited speakers (professors)
- 23 participants (including speakers)

☛ NANOMAGMA School 2011: Florence (Italy) - June 08, 2011.The aim of the school was to bring up students and experts in the fields of magnetism and plasmonics to cross to the other side of the river. During this one-day school lectures regarding the main magneto-plasmonic experiments, phenomena and theories were presented. Some lectures also covered applications of magnetic and plasmonic nanomaterials and magneto-optical techniques, as well as novel findings in the field of magneto-plasmonics
Short facts:

- Nanomagma School Florence
- 9 speakers
- 49 participant**s**

NANOMAGMA Workshop

Workshop on “Nanostructured active Magneto-plasmonic Materials”

A one-day NANOMAGMA workshop / industrial session was organized within the PPM 2011 (Photonics, Plasmonics and Magneto-Optics), took place on the 13th of April. This event allowed extended discussions between the different groups involved in the project and therefore fostered cooperation between them. This Workshop was a forum for most of the groups working on this area to present their results through poster or oral presentations. Full presentations were requested from contributors. Industrial participation was enhanced during the Workshop and an industrial day established (contributions from industrial partners), informing the industry about relevant progresses in this R&D emerging area (testing of product-like devices developed by project partners), providing a feedback loop for industrial mid and long-term interests and fostering the merging between academic research, the state-of-the art progress in optical technologies at research lab level, and the (pre)-industrial requirements and environment.

Short facts:

- PPM2011 & NANOMAGMA Workshop – around 120 participants
- 9 speakers (only NANOMAGMA Workshop)
- 7 travel-ship bursaries for consortium PhD students

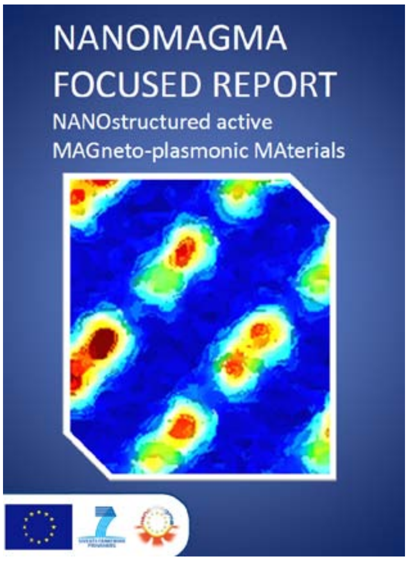
TENTATIVE PROGRAM PPM 2011 - NANOMAGMA SESSION		
Wednesday - April 13, 2011		
Chairman: **Alfonso Cebollada** *(IMM-CNM-CSIC, Spain)*		
11:40-12:20	**Alexei Tchelnokov** *(CEA-Leti, France)*	**(I)**
	Title not available	
12:20-13:00	**Chiraz Frydman** *(HORIBA Scientific, France)*	**(I)**
	"Real time, multiplex and label-free Bio-interaction analysis by Surface Plasmon Resonance imaging"	
13:00-13:40	**Bernard Dieny** *(SPINTEC, France)*	**(I)**
	"Spin transfer RF nano-oscillators for wireless communications and microwave assisted magnetic recording"	
13:40-15:00	**Lunch**	
Chairman: **Antonio Garcia Martin** *(IMM-CNM-CSIC, Spain)*		
15:00-15:40	**Vasily Temnov** *(MIT, USA)*	**(I)**
	"Ultrafast acousto-magneto-plasmonics in hybrid metal-ferromagnet multilayer structures"	
15:40-16:00	**Lionel Aigouy** *(LPEM-ESPCI-CNRS, France)*	**(O)**
	"Light Localization on a Gold Nanodisk Array Probed by Near-Field Optics "	
16:00-16:20	**Juan Jose Saenz** *(UAM, Spain)*	**(O)**
	"Magneto-Optical properties of nanostructured thin films"	
16:20-16:40	**Alfonso Cebollada** *(IMM-CNM-CSIC, Spain)*	**(O)**
	"Internal electromagnetic field distribution and magneto-optical activity of metal and metal-dielectric magnetoplasmonic nanodisks"	
16:40-17:00	**Rémi Vincent** *(Institut Langevin, ESPCI ParisTech, France)*	**(O)**
	"Controlling fluorescence resonant energy transfer with a magneto-optical nanoantenna"	
17:00-17:40	**Harald Giessen** *(University of Stuttgart, Germany)*	**(I)**
	"Three-dimensional optical metamaterials and nanoantennas: Chirality, Coupling, and Sensing"	
17:40-19:30	**Poster Session - Coffee Break**	

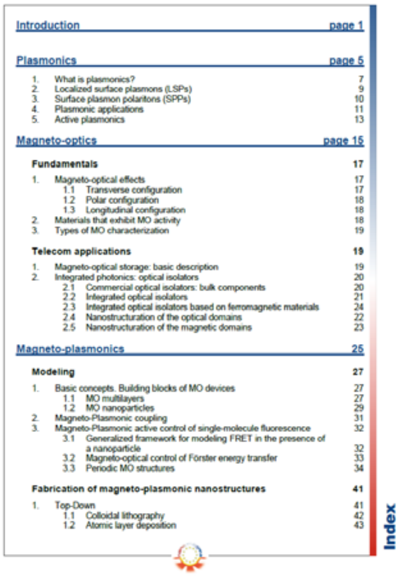
NANOMAGMA Focused report

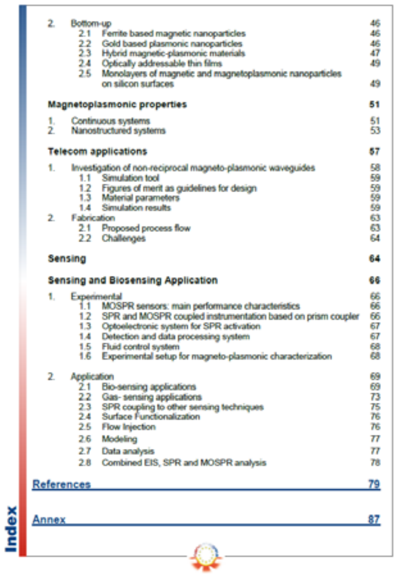
The principal aim of the NANOMAGMA focused report was to predict the main trends in the emerging R&D area of “Nanostructured active Magneto-plasmonic Materials” over the next 10 years. This report provides focus and accelerate progress in identified R&D directions for the NMP program, guide public research institutions keeping Europe at the forefront in research and also provide a valid source of guidance for the related industry. This report summarizes the last decades efforts in the development of a new discipline devoted to benefit from optical excitations in materials where metals are key element (Plasmonics).

Short facts:

- 200 printed copies
- Pdf version available online for download
- Other dissemination channels (Slideshare, Issuu, etc.) used to enhance visibility







- The address of the project public website, if applicable as well as relevant contact details.

www.phantomsnet.net/Nanomagma/indexMagma.php?project=5&f=1 & www.nanomagma.org (during the project lifetime)

Furthermore, project logo, diagrams or photographs illustrating and promoting the work of the project (including videos, etc…), as well as the list of all beneficiaries with the corresponding contact names can be submitted without any restriction.

Project Logo: