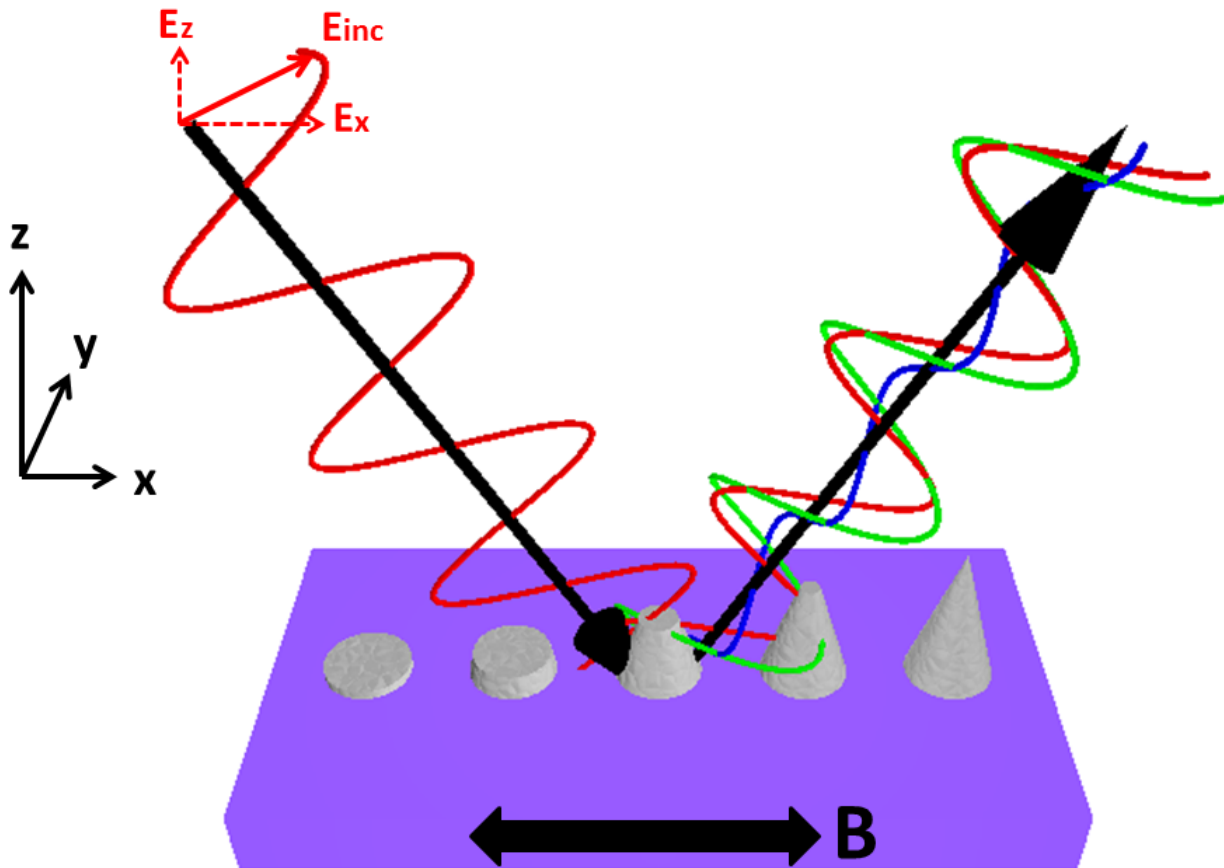




Anisotropy Engineering in 3D Magnetoplasmonic Nanoantennas

*Thesis for Erasmus Mundus Master of Science in Nanoscience &
Nanotechnology*

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Gothenburg, Sweden
June, 2014

Thesis for the degree of Erasmus Mundus Master of Science in
Nanoscience and Nanotechnology

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Cover: Illustration of longitudinal magneto-optic Kerr effect (MOKE). The plane of polarization of the incident light is rotated upon reflection from nanostructures. Nanostructures of increasing heights: 2D nanodisks and nanoellipses (left) to 3D nanocones (right) were considered in this thesis.

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Abstract

The interaction between light and ferromagnetic nanostructures is investigated in this thesis. Studying the influence of magnetic field on the surface plasmon properties and the associated enhancement of the magneto-optical (MO) response is becoming increasingly interesting due to advancements in nanofabrication and characterization [1]. Magnetoplasmonic devices find applications in sensing and telecommunication.

In ferromagnetic materials the off-diagonal terms of the dielectric tensor can be activated (i.e., made non-zero) by the external magnetic field. These terms play a key role in the interaction of ferromagnets with light, producing interesting phenomena like Kerr and Faraday effects [2]. Ferromagnetic nanostructures of varying size, shape and thickness were fabricated in this work on glass substrates using hole mask colloidal lithography [3]. The optical and magnetic properties of these nanostructures can be controlled by these parameters. At the same time, their magneto-optical response can be effectively tuned by the localized plasmon excitations.

Circular and elliptical nickel 2D nanostructures were investigated, followed by the increase in their height towards truly 3D magnetoplasmonic nanoantennas. The nanostructures were characterized by absorption spectroscopy and by the spectroscopic magneto-optical Kerr effect (MOKE). Anisotropy in the particles played a key role in the tunability of the resulting Kerr polarization rotation. Different plasmon resonances (along x , y and z) of the nanostructures were engineered individually to achieve large enhancements in Kerr rotation. The out-of-plane plasmon resonance (along z) is shown to become more and more dominant in the definition of MO response as the structures grew in height,. This ultimately leads to a strong enhancement of MO response in these systems.

Keywords: Magnetoplasmonics, MOKE, nanoantenna

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Contents

1	Introduction	1
1.1	A brief History of Plasmonics	1
1.2	Surface Plasmons (SP)	2
1.2.1	Surface Plasmon Polaritons (SPP)	2
1.2.2	Localized Surface Plasmons (LSP)	3
1.3	Thesis Outline	4
2	Magnetoplasmonics	6
2.1	Origin	6
2.2	Faraday and Kerr Effects	7
2.3	Anisotropy	8
2.4	Engineering Resonances	10
2.5	Theoretical Model	11
3	Experimental Methods	14
3.1	Sample Fabrication	14
3.2	Experimental Setup	18
3.2.1	Absorption Spectroscopy	18
3.2.2	Spectroscopic MOKE	18
4	Results	22
4.1	Optical Spectroscopy	22
4.2	Kerr Spectroscopy	24
4.3	Tuning Plasmon Resonances	29
4.4	Future and upcoming samples	34
5	Conclusion	35
	Bibliography	40

1

Introduction

Plasmonics deals with the study of interaction between light and matter. Surface plasmon polaritons (SPPs), or surface plasmons (SP) are the collective oscillation of the electrons found at the interface of a metal and dielectric [4]. Strictly speaking, they exist at the interface between any two materials where the real part of dielectric function changes sign across the interface. In this interaction, the free electrons respond collectively by oscillating with the frequency of the light wave. Combining plasmonic systems with magneto-optical systems is interesting since SPPs are capable of enhancing the magneto-optic (MO) activity due to localized electromagnetic field enhancement [5]. In this chapter, a brief history of the origin followed by a background knowledge on plasmonics is provided. Finally the theory behind magnetoplasmonics is given followed by a description of the theoretical model used to support the experimental findings of this thesis.

1.1 A brief History of Plasmonics

The interest in plasmons is not new. Their unique properties were utilized by artisans to generate vibrant colours in cups and stained glass windows in churches. Probably, the oldest example of such an application is the Lycurgus cup [6] originating from the Roman Empire dating back to the 4th century AD. The cup shown in the figure below, contained silver and gold nanoclusters which give rise to the colourful appearance. When illuminated from the outside, the cup gives a green/yellow appearance but when illuminated from inside it gives a red appearance. The glass contains very small amounts of nanoparticles of gold and silver that have a mean diameter of about 70nm [7]. Since this size is close to that of visible wavelengths, it gives rise to visually appealing colours shown by the cup [8].



Figure 1.1: Lycurgus cup from 4th century AD [6] displaying different colours when illuminated from outside (Left) and from inside (Right)

Though plasmons were used to create colours from the 4th century AD, the first experimental evidence came only in the early 20th century. In 1902, Prof. Wood reported anomalies when optical intensity drops on reflection from metal gratings. Only in 1956, David Pines theoretically described the energy losses experienced when light waves travel through metal and attributed this effect to the excitation of SPs. He gave the name “plasmons” to these oscillations of free electrons and the year after Robert Fano coined the term “polariton” to account for the combined quasiparticle of light and electrons. A major advancement in this field came about in 1968 when Andreas Otto and co-workers presented methods for optical excitation of SPs on metal gratings. This made experiments on SPs more accessible to scientists and the interest in the field has been growing ever since.

1.2 Surface Plasmons (SP)

The term “plasmon” refers to any type of plasma-like oscillation of electrons. There are bulk plasmons where the oscillation of electrons occur in the bulk of the material. On the other hand, there are surface plasmons where the oscillation of electrons occur at the surface of a material (i.e. require an interface). There are two types of SPs: propagating surface plasmon polaritons (SPP) and the localized surface plasmons (LSP). SPs were first predicted by Ritchie in 1957 [9] and later confirmed experimentally by many scientists: Turbadar [10], Kretschmann [11] and Otto [12] in the 1960’s and by Agarwal in 1980’s [13].

1.2.1 Surface Plasmon Polaritons (SPP)

SPPs are electromagnetic waves that travel along the interface of metal and a dielectric. The name signifies that it involves components from both metal and dielectric: surface plasmon referring to local oscillation of free electrons in metal and polariton referring to waves in air or dielectric [14]. A schematic overview is given in Figure 1.2

It can be seen from the figure that, SPP have components of their field penetrating

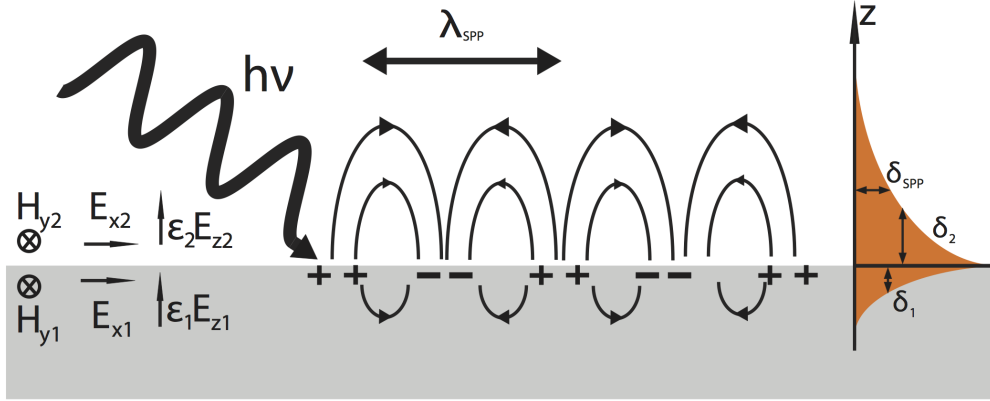


Figure 1.2: Figure showing the oscillation of electron at the surface on excitation with electromagnetic waves [15]. The combined oscillation of the surface electrons moves along the interface where their field penetration decays exponentially into both the medium. Metal layer is shown in gray and dielectric white.

into both metal and dielectric. In metals, the field decay is larger than in dielectrics owing to their smaller skin depth values [14]. In other words, $\delta_1 < \delta_2$ while δ_{SPP} depends on the materials under consideration as it related to the losses incurred during propagation. It is important to note that the wavelength of SPP is much smaller than the wavelength of the light that excites it. This leads to very strong confinement of electromagnetic fields. SPPs continue to propagate along the interface until the energy they contain is lost due to ohmic loss or through scattering events. It is worth mentioning that SPPs cannot be directly excited by light as their dispersion lies to the right of the light line [4]. A change in momentum is also required along with energy to excite SPPs. This can be achieved through various coupling mechanisms like Kretschmann [11] and Otto configuration [12], gratings or surface corrugations.

1.2.2 Localized Surface Plasmons (LSP)

When a particle being excited by light is smaller or equal in size to the wavelength of the light, then it leads to confinement of SPs causing enhancement in the near field [16]. This enhancement decays off exponentially away from the surface of the particle. This confinement of electric fields leads to collective oscillation of surface electrons in the particle resulting in what is called surface plasmon resonance. When this resonance is excited in nanometer scale it is called localized surface plasmon resonance [17]. Due to the high sensitivity to changes in the refractive index of their surroundings, LSPRs are often used in nanoscale sensing applications, where the shift of the resonance frequency is monitored upon changes in the surrounding medium.

Figure 1.3 shows a good example of LSPR of silver platelets. By increasing the size of the platelets, a clear red-shift in the extinction peak can be seen. The width of

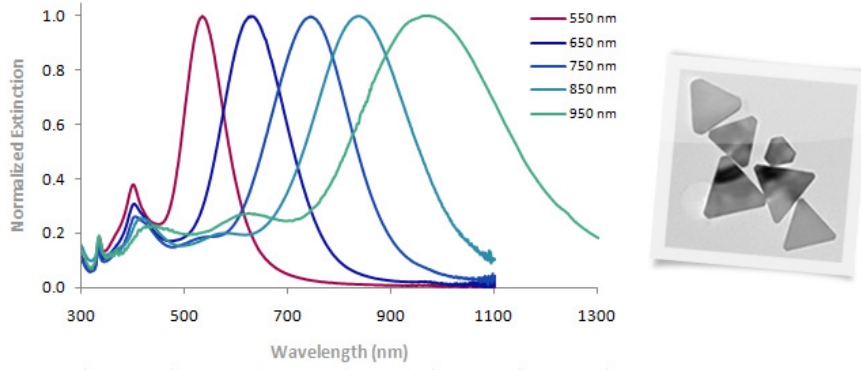


Figure 1.3: Illustration of LSPR: The graph on the left shows the change in the extinction spectra with changing size of the nanoparticle. With increasing size, the plasmon resonances become broader and shift to longer wavelengths (red-shift). On the right is SEM of silver platelet nanoparticles

the plasmon resonance also broadens with size. The reason for this is that, as size of particles increases, coherent oscillations of electrons become increasingly difficult leading to increased scattering effects. This results in shorter plasmon lifetimes and hence broader resonance (spectral bandwidth of LSPR is inversely proportional to plasmon lifetime [18]). In general, LSPR can be tuned by means of size (resonance frequency), shape (anisotropic behaviour), particle material (shape of absorption spectra) and the surroundings (refractive index).

1.3 Thesis Outline

This thesis consists of five chapters:

Chapter2 : This chapter is divided into two sections. In the first, a description of magnetoplasmonic theory is provided which is required to understand the results discussed in this thesis. The second summarizes a theoretical model used to calculate the MO behaviour of the nanostructures used in this project. The calculations were provided by the Nanomagnetism group from CIC-Nanogune, San-Sebastian, Spain.

Chapter3 : This chapter is devoted to the description of the fabrication methodology used and the experimental setup utilized to characterize the samples optically and magneto-optically.

Chapter4 : This chapter is divided into two sections. The first details the results obtained from various designs of plasmonic nanostructures. A comparative study is given using calculated data from the theoretical model. At the end of this section, various techniques used to tune the plasmonic properties are described. The second section describes the ideas behind the design of a new batch of nanostructures and how it can lead

to even larger enhancements in MO activity.

Chapter5 : The final chapter provides a summary of the work done in which it is shown that the MO activity can be significantly enhanced by effectively engineering the plasmon resonances along all the three symmetry axes of the nanostructures. A conclusion is drawn from the findings and an outlook is provided for further research and possible applications.

2

Magnetoplasmonics

With advancements in plasmonics technology, the next logical step is to develop useful active components like modulators, sensors, switches etc. But in order to build such devices a mechanism to actively alter the plasmonic properties is required. Much of the work done in plasmonics is passive: the properties are fixed once fabricated. Work has been done towards active plasmonic devices by controlling the properties using temperature [19], voltage [20] and photons [21]. This thesis deals with magnetic control of plasmonic properties.

2.1 Origin

Magnetism induced change in optical properties was first discovered by Faraday in 1845 [22] and John Kerr in 1875 [23]. Years later, magneto-optic (MO) response of plasmonic structures was found to be enhanced as a result of coupling with the enhanced near fields [24]. Designing plasmonic resonances will hence play an important role in enhancing the MO activity. This brought about increased interest in MO devices. Enhanced MO activity is now sought out in optical devices like modulators, sensors and optical isolators.

For noble metals, the MO activity is described pretty well by the Drude model [26]. According to the model, the frequency dependent MO constant is represented by:

$$\epsilon_{mo} = i \frac{\omega_c (\omega_p \tau)^2}{\omega [(1 - i\omega\tau)^2 + (\omega_c \tau)^2]} \quad (2.1)$$

where $\omega_c = eH/m^*$ is the cyclotron frequency, τ is the electron relaxation time, $\omega_p = \sqrt{Ne^2/m^*\epsilon_0}$ is the plasma frequency. For noble metals under moderate magnetic fields, $\omega_c \ll \omega_p$ and as a consequence, their MO activity is low. Since their magnetic remanance is intrinsically very low or even non-existent, this also results in lower MO

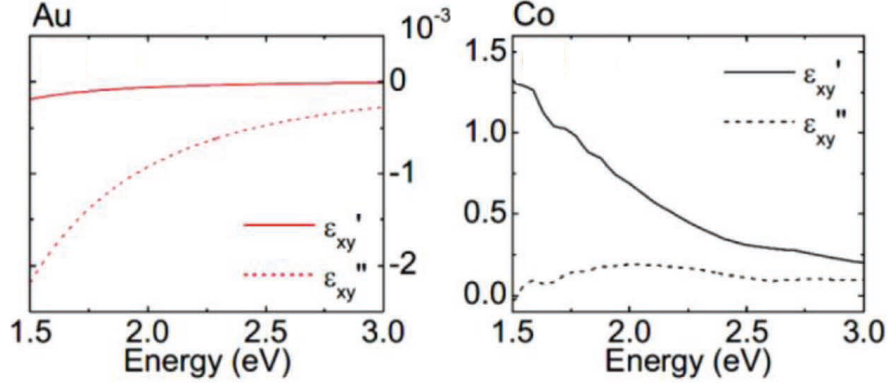


Figure 2.1: Illustration of contrasting MO constants of metals (left: Au) and ferromagnetic materials (right: Co) [25]. The real part of the MO constant is shown in dark line and the imaginary part in dashed line. MO constant of Co is three orders of magnitude larger than Au.

activity. But for ferromagnetic materials, their MO constant depends on spin-orbit coupling, exchange frequency and band structure [1]. As an example from ref.[25], the real and imaginary parts of MO constant are shown in Figure2.1. It can be seen that the MO constant for Cobalt is much higher than that of gold. Engineering the individual plasmon resonances along all three dimensions (3D nanostructures) in ferromagnetic nanostructures is shown to lead to enhanced MO activity (specifically Kerr rotation). These structures are also called as magnetoplasmonic nanostructures.

2.2 Faraday and Kerr Effects

For isotropic materials under the absence of magnetic field, the dielectric tensor has only the diagonal elements non-zero. But under the presence of an external magnetic field, the tensor adopts the form:

$$\epsilon = \begin{pmatrix} \epsilon & a\Pi_z & a\Pi_y \\ -a\Pi_z & \epsilon & -a\Pi_x \\ -a\Pi_y & a\Pi_x & \epsilon \end{pmatrix} \quad (2.2)$$

where $a\Pi_i = \pm i\epsilon_i Q m_i$ represents the MO constant of the material, $Q(\omega)$ is the frequency dependent magnetic factor and m_i the magnetization of the material ($i=x,y,z$) [1]. From the tensor, it can be seen that, the effect of an external magnetic field depends predominantly on the alignment of the field with respect to the material. For example, if the field is applied along x and is aligned parallel to the sample plane, the tensor modifies to the form:

$$\epsilon = \begin{pmatrix} \epsilon & 0 & 0 \\ 0 & \epsilon & -a\Pi_x \\ 0 & a\Pi_x & \epsilon \end{pmatrix} \quad (2.3)$$

These off-diagonal terms are the reason for MO phenomena such as Faraday and Kerr Effects. When light of certain polarization is incident on a sample and an external magnetic field is applied, then due to nanoscale interaction of light, magnetism and matter, the light undergoes a change in its polarization upon transmission (Faraday) or reflection (Kerr). There are mainly 3 types of Kerr effect identified depending on the relative orientation of the polarization of incident light and that of the field [27]. For example, when the polarization of incident light is parallel to the applied magnetic field (magnetic field in plane of sample) as shown in Figure 2.2.B, it is called longitudinal Kerr effect. The other two types are Transversal and Polar as shown in the figure. In this thesis, the focus is on designing plasmonic nanostructures to demonstrate enhanced longitudinal Kerr effect.

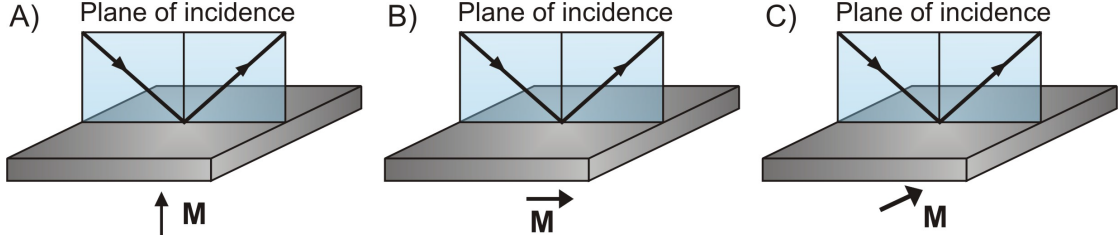


Figure 2.2: Illustration of various types of MOKE [27]: a) polar MOKE (the magnetization is perpendicular to the sample plane and parallel to the plane of incidence.) b) longitudinal MOKE (magnetization is parallel to both sample plane and plane of incidence) and c) transversal MOKE (magnetization is parallel to the sample plane and perpendicular to the plane of incidence.)

2.3 Anisotropy

As described in the previous section, the dielectric tensor changes form depending on the orientation of the applied field and its relative orientation with respect to the incident light's polarization. In order to be able to tune the plasmonic response of nanostructures, it is important to include anisotropy in the design. The theory used to formulate the design principles is given below.

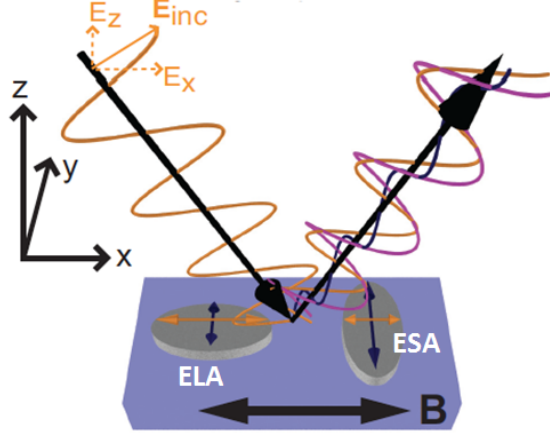


Figure 2.3: Illustration of the relative orientations of the incident light and the applied magnetization. In the L-MOKE setup shown here, both the polarization of the incident linearly-polarized light and magnetization is along x -axis. The light has a small electric field component along z -axis too. Upon reflection, the p -polarized light acquires a small s component and hence becomes elliptically polarized. In the ellipse on the left, the polarization and the magnetic field are aligned (as shown in orange) along the long axis. We call this configuration Elliptical Long Axis (**ELA**). While on the other ellipse, they are aligned with the short axis (**ESA**). An incident angle of 25° (normal to sample plane) was used in this thesis. If the angle approaches the normal, then it results in reduction of Kerr signals [28]. This angle allows us to couple to both the x and z modes directly.

Plasmonic Anisotropy

The dielectric tensor for anisotropic materials takes the form:

$$\epsilon = \begin{pmatrix} \epsilon_{xx} & a\Pi_z & a\Pi_y \\ -a\Pi_z & \epsilon_{yy} & -a\Pi_x \\ -a\Pi_y & a\Pi_x & \epsilon_{zz} \end{pmatrix} \quad (2.4)$$

It can be seen that the polarizability is different along different material axes. This means that incident light with a particular polarization can induce different plasmon resonances along different symmetry directions. For example, in the Figure2.3, when light with polarization along x (shown in brown) is incident on a sample with anisotropic structures (ellipses), the electric dipole along x (i.e. plasmon resonance along x) is directly excited. The possibility of the dipole perpendicular (along y) to be excited depends on the spin-orbit coupling (shown in blue in the figure) strength between the two axes. This spin-orbit coupling is amplified at LSPR and hence plays a key role in enhancing MO activity. This type of anisotropy is called “plasmonic anisotropy” and is shown in Figure2.4.

The third plasmonic dipole, along the z -axis (normal to sample plane) is excited by the small field component along z . The MO enhancement due to excitation of this

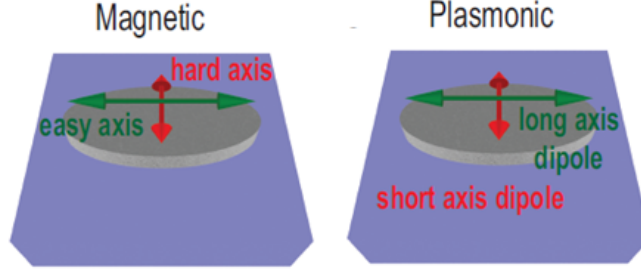


Figure 2.4: Left: Magnetic anisotropy: Easy and Hard axis. Right: Plasmonic Anisotropy. The plasmonic mode (dipole) along long-axis can be excited by light of longer wavelengths while the short-axis dipole by shorter wavelengths.

dipole is the main focus of this thesis. It is expected that, with increasing height of the nanostructures, the role of this out-of-(sample)plane resonance will lead to increasing enhancements. The anisotropy induced symmetry breaking is expected to play a key role in tuning the plasmonic resonances leading to large enhancements in MO activity.

Magnetic Anisotropy

The second type of anisotropy involved is related to the ferromagnetic properties of the material, in our case nickel. Ferromagnetic materials develop easy and hard axis depending on the dimensions of the sample [29] and hence in the case of elliptical nanostructures, the easy axis is along the long axis and hard axis is along the short axis of the ellipse. Since, in this thesis, all samples were measured at magnetic saturation, much attention is not devoted to engineering this type of anisotropy.

2.4 Engineering Resonances

When the samples are excited with p-polarized light (Figure 2.3) with the polarization parallel to the in-plane x -axis and traveling in z -direction, the plasmon dipoles along x and z are excited. In other words, $p_x = \alpha_{xx}E_x$ and $p_z = \alpha_{zz}E_z$ where, p_i and E_i are the induced polarization and field components along the direction $i = x, y$ or z . α_{xx} and α_{zz} are the diagonal elements in the polarizability tensor α . The dipole along the second in-plane axis y can also be excited due the spin-orbit coupling between the z and y axes. Or,

$$p_y = \alpha_{yz}E_z = \frac{\epsilon_{yz}\alpha_{yy}\alpha_{zz}}{(\epsilon - \epsilon_m)^2}E_z = \alpha_{so}\alpha_{yy}\alpha_{zz}E_z \quad (2.5)$$

where, ϵ and ϵ_{yz} are the diagonal and off-diagonal terms in the dielectric function respectively. ϵ_m is the dielectric function of the surrounding medium and $\alpha_{so} = \frac{\epsilon_{yz}}{(\epsilon - \epsilon_m)^2}$ is the spin-orbit-coupling induced off-diagonal term in the polarizability tensor α . The spin-orbit term is intrinsic to a ferromagnetic material, in this case, nickel. It can be seen that the polarizability of the particle along y depends on the off-diagonal term α_{yz}

which in turn depends on the dimensions of the sample and most importantly also on the refractive index of the surrounding medium. The ratio between p_y and p_x is proportional to the longitudinal Kerr rotation and can be calculated from the above equation as:

$$\frac{p_y}{p_x} = \frac{\alpha_{yy}}{\alpha_{xx}} \alpha_{so} \alpha_{zz} \frac{E_z}{E_x} \quad (2.6)$$

It can be seen from equation.2.6 that, assuming the ratio of field strengths remain same for all samples, the amplitude of net Kerr rotation is proportional to the polarizability of the particle along y and along z and inversely to that along x . This means that if the dimensions of particle are designed in such a way that, the dipole resonances along y and z come close spectrally, it will lead to large enhancements in the rotation amplitude. Futher, when the resonance along x is made to go far away from the other resonances spectrally (i.e, off resonance) then the rotation amplitude can further be enhanced. Thus, directly from the model it can be seen that the rotation amplitude can be boosted simply by tuning the plasmon resonances along all symmetry axes of the particle. Furthermore, the phase contributions from different components can be extracted in the following form:

$$\phi \left(\frac{p_y}{p_x} \right) = [\phi_{yy} - \phi_{xx}] + \phi_{so} + \phi_{zz} \quad (2.7)$$

It can be seen from equation.2.7 that the total phase contribution to the longitudinal Kerr effect depends on the difference in the phases of the two in-plane modes (x and y), the intrinsic spin-orbit (SO) term and finally the contribution from the out-of-plane mode (z). When the nanostructures are small in height compared to the in-plane dimensions, the contribution from ϕ_{zz} is negligible. The contribution from the SO interaction is fixed for a given material. The tunability of the Kerr response in this case relies entirely on the in-plane resonances. As the structures become taller, the contribution from out-of-plane increases and affects the net phase contribution dramatically. Hence, the nanostructures should be designed in such a way that the out-of-plane and in-plane resonances are very close spectrally. This in turn induces very strong coupling between the modes leading to strong enhancements in MO activity. It is important to note that, the formalism provided is general. Similar effects can be expected for any MOKE configuration.

2.5 Theoretical Model

Theoretical modeling for the samples was provided by Nanomagnetism group from CIC-Nanogune, Spain. The samples are modeled as generalized nano-ellipsoids with semi-axes a_x , a_y and a_z embedded in a matrix of a uniform refractive index [30] as illustrated in Figure2.5.

The model includes two dielectric functions: one for the ellipsoid itself ($\tilde{\epsilon}_2$) and one for the surrounding medium ($\tilde{\epsilon}_1$). For each of the different directions (x , y or z), the incident light is modeled as an electromagnetic wave traveling with electric field $\mathbf{E}_1$ when it is outside the ellipsoid and with the induced field $\mathbf{E}_2$ inside the nanoparticle. Calculation

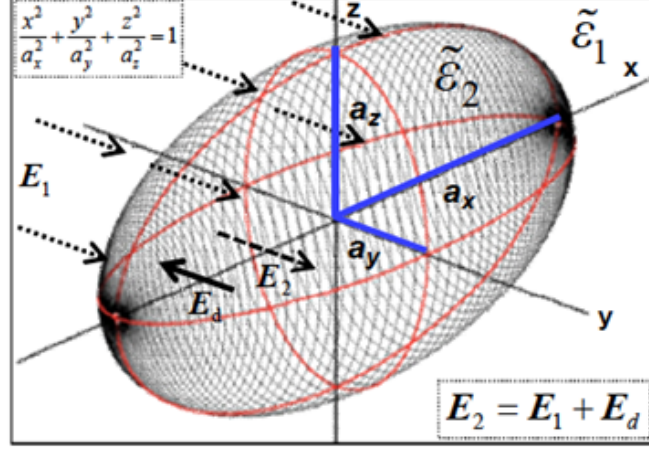


Figure 2.5: The circular and elliptical disks are modeled as generalized nano-ellipsoids embedded in a uniform matrix of a fixed refractive index.

is done for all 3 major axes of the nanoparticle, resulting in the full polarizability matrix, including off-diagonal terms. Due to the dielectric characteristics of the ellipsoid, the incident electric field induces polarization. In order to completely model the plasmonic behaviour, the depolarization field $\mathbf{E}_d$ is also considered. Hence, $\mathbf{E}_1 = \mathbf{E}_2 + \mathbf{E}_d$. These components are depicted in the figure.

The model starts by describing the dielectric tensor for the particle when exposed to an external magnetic field. This tensor is similar to the one described here in chapter.2:

$$\epsilon_2 = \begin{pmatrix} \epsilon_{xx} & a\Pi_z & a\Pi_y \\ -a\Pi_z & \epsilon_{yy} & -a\Pi_x \\ -a\Pi_y & a\Pi_x & \epsilon_{zz} \end{pmatrix} \quad (2.8)$$

Then the induced polarization of the particle is given by:

$$\mathbf{P} = (\tilde{\epsilon}_2 - \tilde{\epsilon}_1)\mathbf{E}_2 = (\tilde{\epsilon}_2 - \tilde{\epsilon}_1)\mathbf{E}_1 + \mathbf{E}_d = \tilde{\alpha}\mathbf{E}_1 \quad (2.9)$$

where $\tilde{\alpha}$ is the polarizability of the particle. This polarizability was calculated using the above equation by modeling the depolarization field. The components of the dielectric tensor for the surrounding medium and the particle are fixed by the choice of materials and the strength and orientation of the magnetic field. In the calculations, based on the material, the value of saturation magnetization m_x is used which defines the field dependent off-diagonal terms. m_x depends only on the amount of magnetic material used. The electric field components except $\mathbf{E}_d$ are fixed by the orientation and wavelength of incident light used. The layer containing the uniform ensemble of the nanostructures (disks) is modeled by approximating that the particle is embedded in a uniform medium of a fixed refractive index - called Maxwell Garnet Effective Medium approximation (EMA).

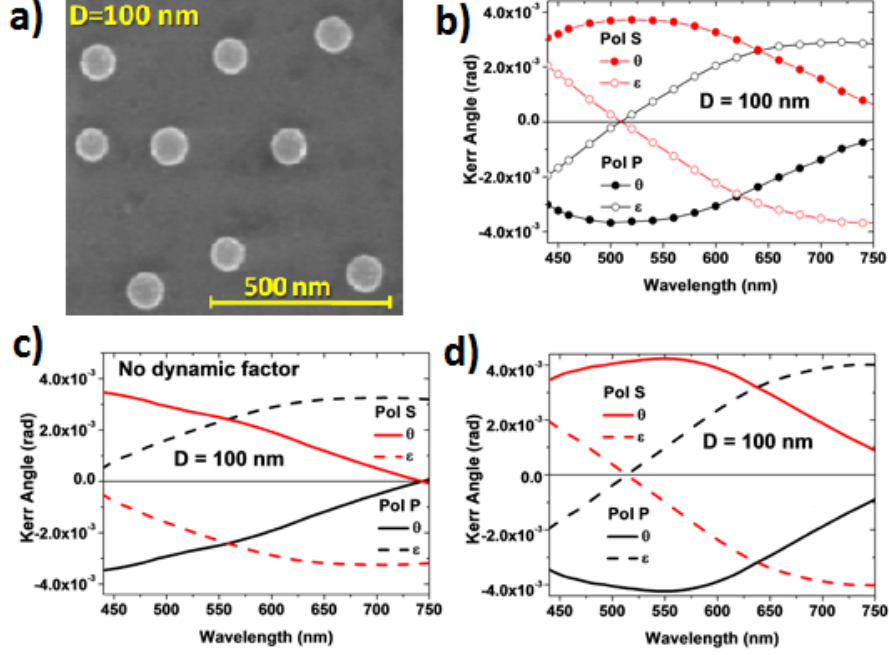


Figure 2.6: Comparison of simulated data with experimental results for circular disks of 100 nm base diameter and thickness of 30 nm [30]. a) SEM picture of the disks, b) Experimental L-MOKE spectra, c) Calculated spectra for the sample without depolarization field E_d . d) With depolarization field taken into account. It can be seen that when the depolarization field is taken into account, the results from the theoretical calculation matches well with the experimentally observed data. *Results for both p and s-polarized incident light are shown.*

Since in reality, the nanostructures are fabricated on glass ($n=1.5$) and are surrounded by air ($n=1$), a mean refractive index of $n = 1.15$ was chosen for the uniform medium in this approximation. Substrate effects are included in the model using Transfer Matrix Method (TMM) formalism. TMM is important as it gives the Fresnel coefficients required to calculate the far-field response of the nanostructures. The incident angle is finally included after using the EMA and TMM formalism, where basically the incident angle defines the amplitude ratio between E_x and E_z and thus the coupling strength to the different plasmonic modes. Now, the transmission and reflection properties can be calculated from the TMM in which the polarizability of the EMA layer has been modeled (taking into account particle densities and polarizability of an individual nanoparticle).

The Figure 2.6.b shows the calculated Kerr spectra for the 100 nm circular disks of height 30 nm. It is important to note that, though the P-MOKE calculations were done using incidence angle of only 2.5° , there is a good match between the theoretical model and the experimental data. This is also demonstrated in the case of 2-dimensional nanostructures in ref.[31].

3

Experimental Methods

3.1 Sample Fabrication

With the advent of nanofabrication tools and technology exotic nanostructures can now be made with ease. Electron Beam Lithography (EBL) is an advanced lithography technique providing resolution well below the diffraction limit of light. These structures would require very advanced design and alignment techniques with standard photolithography tools. On the other hand, processing larger substrates (cm^2) takes a very long time with EBL. Colloidal lithography is a suitable alternative. It exploits self-assembly of tiny particles dispersed in solution (colloids) to define templates for patterning surfaces [32]. Various nanostructures have been fabricated using derivatives of colloidal lithography, namely, nanosphere colloidal lithography and sparse colloidal lithography [33, 34, 35]. Hole mask Colloidal Lithography (HCL) was later developed to address the drawbacks of these techniques [3]. It is a special type of colloidal lithography that uses nanoholes in thin film as a mask for deposition. .

Substrate Preparation

The process is started with cleaning $15 \times 15 \text{ mm}^2$ glass substrates in an ultrasonic bath at full power for 5min each, first in Acetone followed by Isopropanol (IPA) and finally deionized water. The substrates were then dried and then a 200 nm sacrificial layer of PolyMethylMethacrylate (PMMA) is spin coated. The samples were then baked at 180°C for 10min in order to allow PMMA to reflow and form a uniform layer. The PMMA layer is then etched in an oxygen plasma at a power of 50W for 3s to make the top layer of PMMA hydrophilic. This step is required to be able to form self-assembled layers on top.

Self Organization

A thin monolayer of Poly-(diallyl dimethyl ammonium chloride) (PDDA) is applied from a solution of 0.2 vol% PDDA for 30s. The sample is then rinsed with de-ionized water and blow dried with nitrogen gas. Then the sample is covered with solution of 0.2 wt% Polystyrene beads (PS) of 100 or 170 nm average diameter for about 2min. The positively charged PDDA layer improves the adhesion of the negatively charged PS beads to the PMMA layer. Electrostatic repulsion between the beads and attraction between the beads and the PDDA layer defines short-range ordered pattern resulting in a random but uniform array of PS nanoparticles. The samples were then rinsed and dried carefully so that the self-organized pattern is not destroyed. This is the most critical step in the process and needs to be carried out carefully. The uniformity of the nanoparticles pattern was checked using a dark-field microscope. Larger particles scatter strongly and give a strong bluish background but for smaller particles only a gray shine could be seen. For smaller particles, it requires other techniques (like SEM) to verify the uniformity of the pattern.

Mask Layer Deposition

The samples were then loaded into a material deposition chamber which is pumped to pressures below 5×10^{-7} mbar. Thermionically emitted electrons accelerated by a high voltage (e-beam evaporation) are focused towards the source material by magnetic fields which causes material to vaporize. The vaporized source material undergo very few collisions in the vacuum chamber and as a result travel in straight lines and deposit on the substrate. A thin metal film (usually of chromium (Cr)) was thus deposited which acts as the mask. The PS beads block part of the deposition which leaves circular nanoholes in the metal layer. The mask can alternatively be deposited at an angle to the sample plane. The PS beads block part of the beam of metal ions leaving a shadow behind them. The angle of deposition used determines the length of this shadow. For example, a mask deposited at an angle of 45° to the sample plane gives elliptical holes in the metal layer with aspect ratio of 1:1.4. The PS beads were removed by tape-stripping and the sample is then etched for 3-5min in an Oxygen plasma. This step drills through the PMMA layer forming undercuts below the nanoholes. It is important to tune this step such that the PMMA below the holes is etched until the glass is reached. This is essential because, the final ferromagnetic material deposition will be adhered directly on glass. It is desirable to etch for a slightly longer time in order to facilitate lift-off. If the etch time is short and incomplete, the final lift-off will fail leading to removal of all nanostructures leaving behind only the glass substrate. Also, very long etch times might result in a drop of the mask (due to the removal of supporting PMMA underneath) making lift-off impossible.

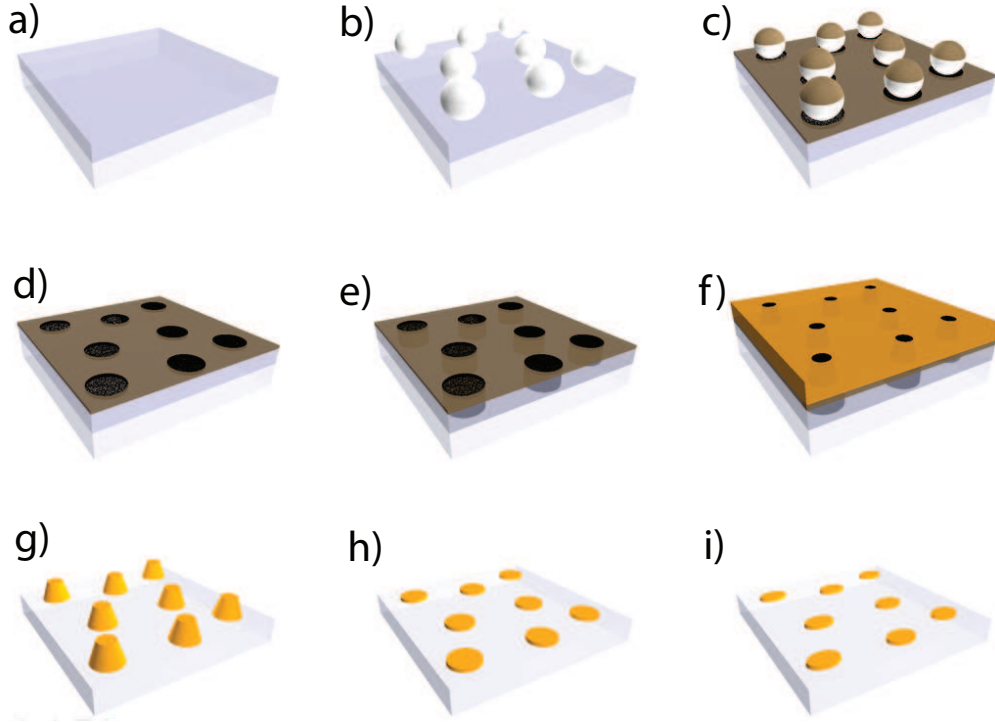


Figure 3.1: The process steps of HCL Technique: a) Glass substrate ($15 \times 15 \text{ mm}^2$) is spin coated with PMMA and then baked. A 220 nm uniform layer of PMMA is formed. b) Charged Polystyrene beads of various sizes (100, 170, 124, 150 nm) were self organized. They mutually repel each other eventually forming a uniform distribution. c) Mask deposition: Thin layer of desired metal (usually chromium) is evaporated. Angle deposition leads to anisotropic nanostructures. d) Tape stripping of beads e) Oxygen plasma etch of PMMA through the nanoholes made in the mask layer. Slight over-etch forms undercut thus facilitating lift-off. f) Metal Deposition: Desired thickness of metal (Nickel) is evaporated. g) Lift off in acetone leaves behind nanostructures standing on glass substrate. h) Circular nanodisks resulting from perpendicular mask evaporation and i) Elliptical disks (nanoellipses) from angle evaporation.

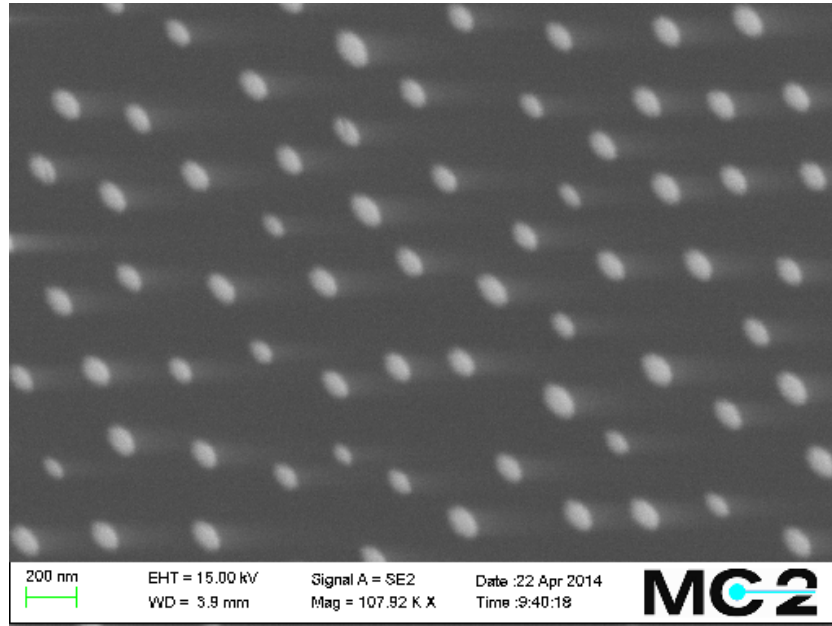


Figure 3.2: 150 nm tall elliptical disks with a base diameter of 100 nm along short axis and 140 nm along long axis. The aspect ratio can be clearly seen in the image. The particles assume a uniform distribution over the entire substrate.

Final Deposition

Once the etching is complete, the samples were loaded into the evaporation chamber and pumped to reach high vacuum conditions (pressures below 5×10^{-7} mbar). This was done to ensure low contamination in the chamber and to ensure stable deposition rates resulting in uniform films. Nickel film of varying thicknesses ranging from 60 nm till 180 nm were evaporated once the desired chamber pressure is reached.

Lift-Off

Once the deposition is complete, the PMMA is removed through lift-off in acetone (sonication was used when needed). The entire metal deposition on top of the PMMA is removed leaving behind the nanostructures on glass (Figure 3.2).

Nanostructures

For small metal layer thickness, the nanostructures were circular and elliptical disks. As the thickness of the metal increases, the metal starts to deposit on the side walls of the nanoholes in the mask and as a result the holes start closing. Instead of ellipsoids, the nanostructures were either truncated or full cones depending on the thickness of the metal deposited. The maximum height of cone possible depends on the dimensions of the nanoholes (determined by the diameter of PS beads), and also the thickness of

the PMMA and mask layer. Larger PS bead diameters allow a much taller cone than smaller ones because the side wall angle remains the same regardless of the nanoparticle underneath.

3.2 Experimental Setup

3.2.1 Absorption Spectroscopy

The samples were characterized optically using Varian Cary 5000 (UV-Vis-NIR) Spectrophotometer. The system is capable of spectroscopic measurements in the range 175-3300 nm. It uses a white light source and with a multiple grating monochromator and filters to select particular wavelengths [36].

The spectrophotometer has an isolated sample mount which reduces noise in the measurements. It also has a large sample compartment that has railings to mount samples in various orientations and also has the enough space to add additional components like beam shaper, polarizer, etc. in the path of the beam. The system is controlled by Varian software which supports variety of measurements like absorption, colour, concentration, etc. All samples were measured with the light beam incident perpendicular to the sample plane.

3.2.2 Spectroscopic MOKE

MO activity of the samples was determined by measuring the Kerr polarization rotation. This was done using a spectroscopic longitudinal magneto optic Kerr setup (L-MOKE). A detailed schematic is shown in Figure 3.3. This type of setup is used to measure wavelength dependence of the MO activity (Kerr effect). Following subsections detail the important components of the setup. All components are controlled using LabVIEWTM software from National Instruments Pvt. Ltd.

Summary of the setup

The setup used in this thesis is based on the experimental setup described in ref.[37]. Light from a supercontinuum laser source is filtered to single out a wavelength and then collimated. The light then trasmits through a polarizer set at 0 or 90° to choose between p or s polarization. The light then is focussed onto the sample mounted on a special holder placed between the coils of a strong electromagnet. The magnet is calibrated using a hall probe sensor (Keithley 2400) and controlled using a Bipolar Junction Amplifier based controller. The reflected light from the sample passes through a Photo Elastic Modulator (PEM-90, Hinds Instruments) which modulates the light at 50kHz by inducing retardation between the fast and slow axes. The output of the PEM is taken as a reference signal for the lock-in amplifier (Stanford Research Systems, SR830

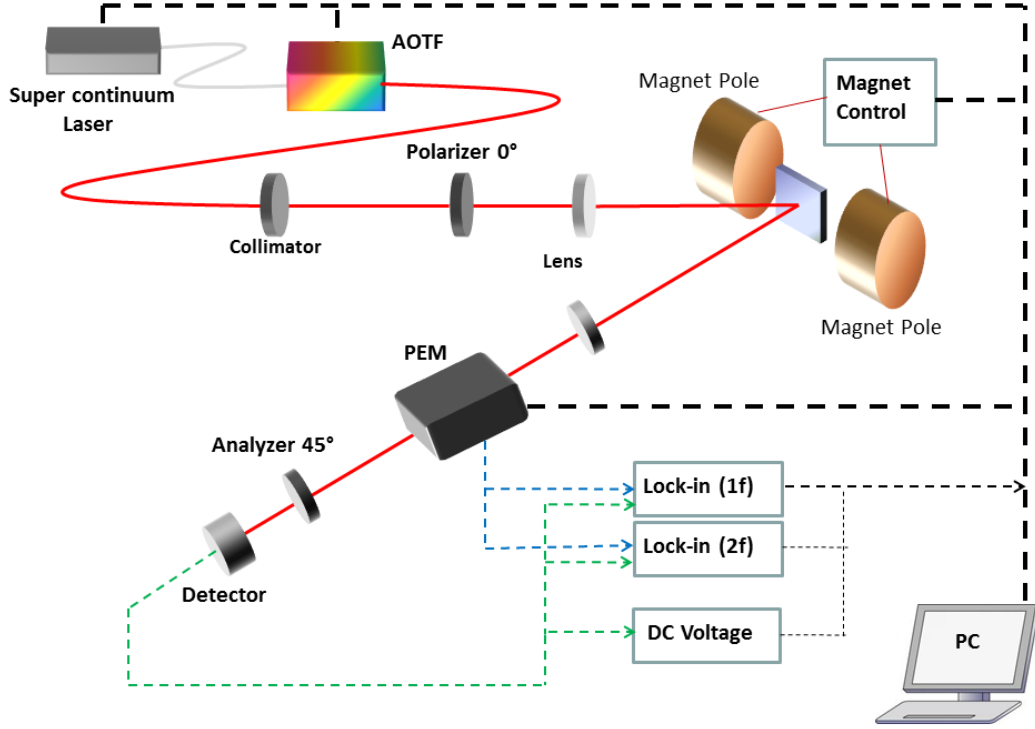


Figure 3.3: Schematic depicting the spectroscopic longitudinal-MOKE setup. Laser beam is represented by the red line. PEM generates reference signals at 1f and 2f which are sent to lock-ins (blue-line). Detector sends signals which are fed to lock-ins and voltmeter which are controlled by a computer. The computer control lines are indicated by black strip lines.

DSP) which measures both 1st and 2nd harmonic of the detected signal. The modulated light then passes through an analyzer and is focused onto an ultrafast response Si or InGaAs photodetector for detection. The signal from the detector serves as the input for the lock-in amplifiers. The 1st harmonic is proportional to the ellipticity while 2nd to the Kerr rotation of the reflected signal (explained later).

Laser Source and Filters

A supercontinuum white light laser supplied by Fianium Ltd. is used as the light source. It is a high power fiber laser generating ultra broadband supercontinuum radiation. The system mainly consists of three parts: a passively mode-locked low-power fiber laser (main source), a high-power cladding pumped fiber amplifier and finally a high non-linearity supercontinuum generator. The output of the laser is fed through an alignment tuning module and finally through a highly non-linear optical fiber. The light from the end of this fiber is fed to a collimator which also acts as the emitter.

The laser system supplies a maximum output power of about 5W and produces

broadband radiation ranging from 450 nm to about $2\mu\text{m}$. In order to filter out a particular wavelength from the supercontinuum spectrum, a dual Acoustic-Optic Tunable Filter (AOTF) system is used. This system comes with two photonic crystals: one configured to work in the visible 450-690 nm range and other for vis-NIR 600-1100 nm range. The RF to crystals is set at 30% in order to have optimal power output, maintaining reasonable line-width. Both AOTF modules can be controlled simultaneously using the software provided.

Polarizer and Analyzer

The polarizer allows only one linear polarization of the light to pass through. In order to test the MO activity of our samples, the polarization is set to be perpendicular to the plane of the sample i.e p (0°) or s (90°). The analyzer is placed on the detection side at an angle of 45° with respect to the polarizer. The alignment was optimized by selecting a wavelength of 750 nm (where the laser power is maximum), switching off the magnetic field and then rotating the Polarizer carefully until the V_{2f} signal is minimized ($< .1\mu\text{V}$). As a result, the dynamic range of the lock-in amplifiers were minimized in order to improve the Signal to Noise (S/R) ratio.

Photoelastic Modulation

The PEM module modulates the light at 50kHz and generates 2 reference square wave signals (0-5V peak) that are fed into the lock-in amplifiers. The first reference signal is at the frequency of the PEM i.e. 50kHz which serves as a reference for the V_{1f} harmonic measurement. The second reference signal is modulated at 100kHz in order to facilitate V_{2f} harmonic measurement. Lock-in amplifiers provide large Signal-to-Noise ratios (SNR) which facilitates measurement of very weak signals (Kerr rotation signals in nanostructures are weak [38]). In order to use lock-ins, the signal needs to be modulated with a known reference frequency. Hence, the PEM module combined with lock-in amplifiers eliminates noise.

Signal Detection

Ultrafast response photodetectors (Si and InGaAs) were used to detect the reflected signal from the sample. The Si detector provides good response for wavelengths below 800 nm. Beyond this, the AC response of the detector is slow leading to parasitic effects. To overcome this issue, InGaAs photodetector was used which provides more accurate data in this wavelength range. It is important not to change the alignment of any component in the setup to ensure a smooth transition between both spectral ranges.

LabVIEW Programs

Two main programs were used LabVIEW for performing MOKE measurements. The first one automates Kerr hysteresis measurements for a given wavelength. The magnetic field is swept in steps between the given values and has the option to perform desired

number of averaging steps in case the measured signals are noisy. The second program performs spectroscopic Kerr measurements. The program performs two loops of measurements where in the first the magnetic field is set to a positive value (corresponding to the saturation field measured using the first program) and performs spectroscopic measurement of the Kerr rotation for each wavelength. The second loop is a similar measurement, but with the negative saturation field. The software finally plots the difference in the Kerr rotation values for every wavelength. All programs have options to set laser power, lock-in integration time and lock-in sensitivities.

Operation Principle

Operation of MOKE can be understood from Mueller series and Fourier series expansions. Using Mueller matrix analysis of the stokes vector of light arriving at detector, its intensity can be written as [27]:

$$I(t) = I_o[1 + 2\theta\cos(A_o\omega t) - 2\epsilon_k\sin(A_o\omega t)] \quad (3.1)$$

where I_o represents the DC intensity, A_o the retardation amplitude of the PEM and $\omega = 2\pi f$ is the angular frequency of the PEM oscillations. The above equation can be now expanded using fourier series into,

$$I(t) \cong I_o[1 + 2\theta_k J_o(A_o) - 4\epsilon_k J_1(A_o)\sin(\omega t) + 4\theta_k J_2(A_o)\cos(2\omega t) + \dots] \quad (3.2)$$

where, θ_k is the Kerr rotation angle and ϵ_k the ellipticity of the reflected light. The second term is part of the DC intensity and is usually neglected in order to concentrate on the AC terms. Hence retardation of PEM is chosen to be $A_o = 2.405\text{rad}$ (hence, $J_o = 0$). This choice makes the amplitudes J_1 and J_2 come close to 0.5 such that similar sensitivities are obtained for both ellipticity and rotation measurements. In the experiment, three voltages are measured: V_{DC} , V_{1f} and V_{2f} . The lock-in signals are normalized with the DV signal which corrects for fluctuations in light intensity and varying sensitivities of the detector for different wavelengths. Mathematically, this is done by normalizing the AC term in the above equation by the DC term to arrive at:

$$\theta_k = \frac{\sqrt{2}}{4J_2} \frac{V_{2f}}{V_{DC}} \quad (3.3)$$

$$\epsilon_k = \frac{\sqrt{2}}{4J_1} \frac{V_{1f}}{V_{DC}} \quad (3.4)$$

Since, the terms J_1 and J_2 are similar in amplitude, the Kerr rotation angle of the reflected light is proportional to the 2^{nd} harmonic voltage while the ellipticity to 1^{st} harmonic voltage.

4

Results

The samples were first characterized using optical spectroscopy which revealed the spectral position of various plasmon resonances. Since our goal was to engineer the plasmon resonances along all three sample axes, it was important to characterize the samples spectrally and to understand the nature of the resonances. When the plasmonic nanostructures are engineered in such a way that the plasmon resonances along different axes are spectrally close, the mutual coupling between them would presumably lead to strongly enhanced MO activity.

4.1 Optical Spectroscopy

The circular nanodisks and nano-ellipses of varying height (60-180 nm) were first characterized. The nanodisks have nominal diameter of 100 nm while the nanoellipses have a short/long axes of 100/140 nm. Figure 4.1 shows how Ni particles have very broad dipolar LSPR. This is intrinsic to nickel and results from the large imaginary part in the dielectric function. In the case of nanodisks, the resonance positions spectrally are same for both in-plane modes (x and y). But in the case of nanoellipses, the two in-plane dipole modes are close spectrally, which results in a broader resonance - a combination of the two modes. In both nanodisks and ellipses, the out-of-plane resonance (along z) is situated in the UV and could not be resolved in the measurement window.

In the case of 60 nm tall nanodisks, only a single resonance was observed. But as the height is increased to 90 nm and beyond, the tail of a second resonance peak can be seen at shorter wavelengths. This resonance is due to the out-of-plane dipole mode (situated along z). The strength and spectral position of this resonance depends on the height of the nanostructures as well as on the refractive index of the surrounding medium. It can be seen that the out-of-plane resonance red-shifts to longer wavelengths with increasing height of the particles as expected.

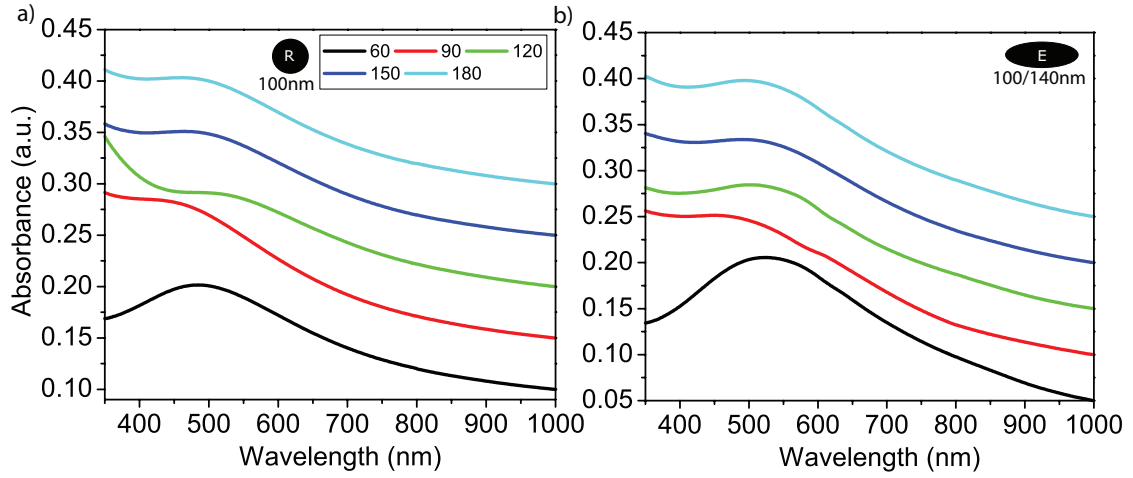


Figure 4.1: Absorption spectra displaying the plasmon resonances. a) Spectra for circular nanodisks. b) Spectra for nano-ellipses. The spectra are shifted vertically relative to each other for better viewing. *Inset: schematic of the sample. The height is varied while the base dimensions are kept.*

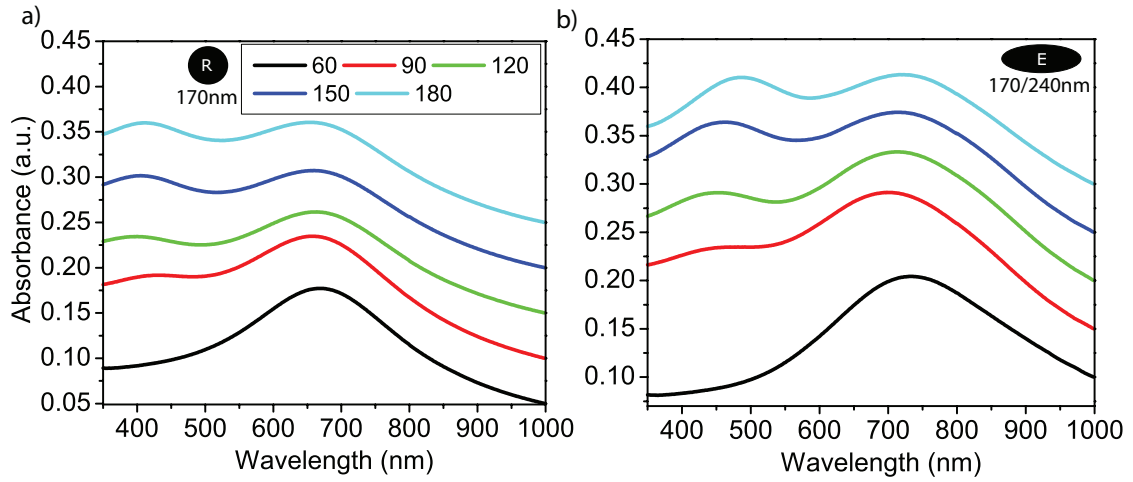


Figure 4.2: Absorption spectra displaying the plasmon resonances a. Spectra for nanodisks. Two broad peaks are observed in the absorption spectra. The one situated close to 700 nm is the result of the merge between two in-plane modes and the second one is the out-of-plane resonance. *Inset: schematic of the sample. The height is varied while the base dimensions are kept.*

In order to push this out-of-plane resonance into the measurement window (vis), larger diameter particles were fabricated. In this second set of samples, the nanodisks have a nominal diameter of 170 nm while the nano-ellipses have short/long axes of 170/240 nm. Figure 4.2 shows the spectra for these samples. The out-of-plane resonance becomes more pronounced and shows similar absorbance as the in-plane modes. This is expected to lead to larger enhancements in the MO activity. Similar to the case of 100 nm diameter particles, the out-of-plane resonance seems to be activated only for heights above 90 nm. The resonances in the nano-ellipses are broader than the nanodisks owing to the spectral overlap of the two broad in-plane dipole modes.

4.2 Kerr Spectroscopy

The samples were characterized using Kerr Spectroscopy using p -polarized light. This section is divided into two subsections: first one covers the results of the 100 nm diameter particles and second covers the larger 170 nm ones. The Kerr rotation spectra for nanodisks are shown in Figure 4.3.

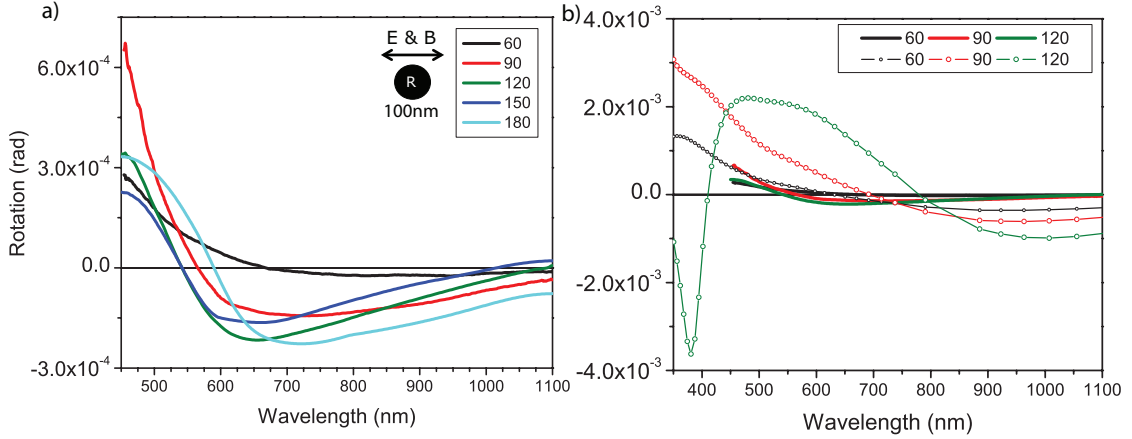


Figure 4.3: a) Kerr spectra for nanodisks of base diameter of 100 nm and varying heights of 60-180 nm. b) Comparison of the experimental data (solid lines) with the calculated ones (dotted lines). Inset: schematic of the sample. The orientation of polarization of the incident light (E) and that of magnetic field (B) is also shown. The height is varied while the base dimensions are kept.

It can be immediately seen that the maximum enhancement in rotation occurs at the edge of the measurement window at 450 nm. From the absorption spectra of the particles (Figure 4.1), we see that this rotation occurs at the tail of the out-of-plane plasmon resonance. The inversion points (wavelength at which the rotation changes sign) shows a blue-shift with increasing particle height. From the comparison figure, it can be seen that the experimental spectra start to diverge from the calculated ones with increasing heights. For heights below 120 nm, apart from the reduced amplitudes, the trends in

the rotation values are comparable. But for heights above 120 nm, the divergence is substantial. This divergence can be understood from the way the particles are modeled in the calculations. As the particles become taller, they feel the dielectric environment progressively more in the z -direction. Since LSPRs are very sensitive to the change in the refractive index of surrounding medium, the out-of-plane dipole resonance is increasingly blue-shifted with increasing heights. The in-plane modes are not that strongly affected since they are influenced mainly by the substrate. As a result, out-of-plane mode moves spectrally away from the in-plane modes. This leads to lower MO activity compared to calculated values. Also, from the calculated data for the 120 nm tall particles, it can be seen that the peak of the rotation occurs at about 500 nm which matches with the resonance of the y mode (see Figure4.1.a). In this particular case, the dimension along y is 100 nm that comes close to the out-of-plane dimension of 120 nm. This leads to strong interaction between the two modes as predicted by equation2.6. This trend can also be seen in the experimental results.

Compared to nanodisks, the nanoellipses exhibit more enhancement in Kerr rotation as shown in Figure4.4a.

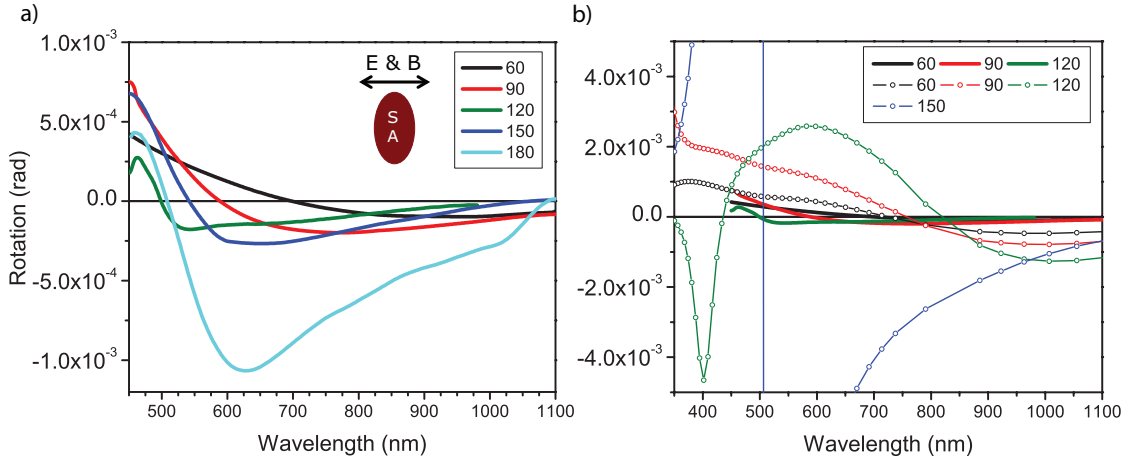


Figure 4.4: a) Kerr spectra for nano-ellipses with short/long axis of 100/140 nm excited along short axis for varying heights. b) Comparison of the experimental data (solid lines) with the calculated ones (dotted lines).

In the ESA configuration, the short axis dipole (x dimension 100 nm) is directly excited by the incident light. It couples through SO to the perpendicular in-plane long axis dipole (y dimension 140 nm). This causes red shift in the Kerr rotation inversion points when compared to nanodisks of same heights. The sample with 180 nm tall particles gives the maximum value in rotation of about 1.2 mrad which corresponds to about 0.07 deg. From the comparison shown in Figure4.4.b, it can be seen that, the divergence trend is similar to nanodisks but for heights above 90 nm it is much more significant. As discussed for nanodisks, the peak value for the rotation in case of 120 nm occurs at the wavelength closer to the resonance of y mode (see Figure4.1.b). But in this

case, the z mode (dimension 120 nm) is not close enough to the SO y mode. As a result, the enhancement in rotation is not very large. But as the height is increased to 150 nm (as shown in dotted blue line), the z mode comes close to y spectrally while the x mode is off-resonance. From equation.2.6, such a condition should give very large enhancements. This rotation enhancement can be very dramatic as shown in the Figure4.5 (simulation results). Also, the shape and sign of the curves are much different in 150 nm case compared to 120 nm. This might be because the z mode spectrally switched with the y mode.

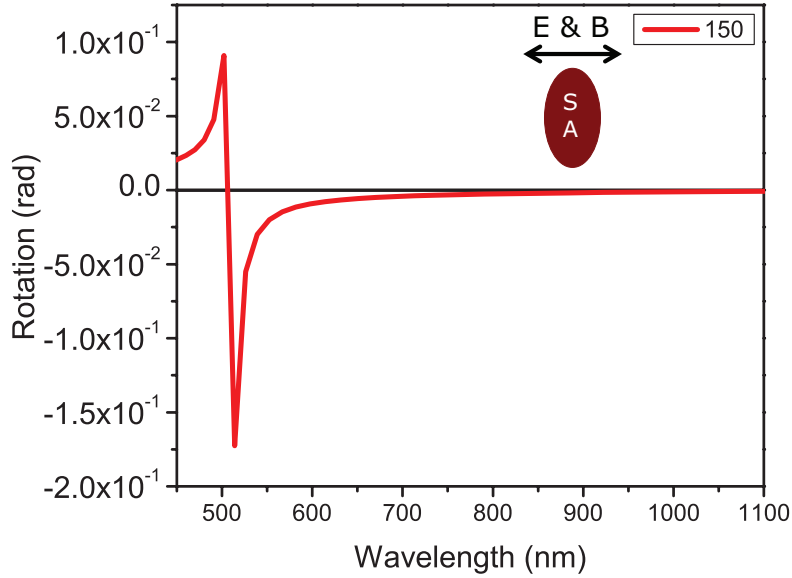


Figure 4.5: Kerr spectra calculation for 150 nm tall nanoellipse (100/140 nm) excited along short axis (ESA).

The model predicts maximum rotation of almost $0.175 \text{ rad} = 10^\circ$ while the actual measured maximum for this particular case of 100 nm base diameter and 150 nm tall nanoellipses is only about 0.04° , roughly two orders of magnitude smaller.

The spectra for the nanoellipses excited along long axis is shown in Figure4.6.

In ELA configuration, the long-axis dipole (x dimension 140 nm) is directly excited by the incident light. This dipole couples through SO to the short-axis dipole (y dimension 100 nm) resonant at shorter wavelength. As a result there is a spectral blue shift in the inversion points when compared to nanodisks. The sample with 150 nm tall particles gives the maximum value in rotation of about 2.1 mrad which corresponds to 0.12° . The same value is obtained for 180 nm tall particles as well. The peak of the rotation occurs at the edge of measurement window (450 nm). This is expected as the resonance of the SO mode y is excited at shorter wavelengths. In this case, the y mode is off resonance with the z mode while the x mode is in resonance. From equation.2.6, this condition should lead to weak coupling and hence less enhancement in rotation. Com-

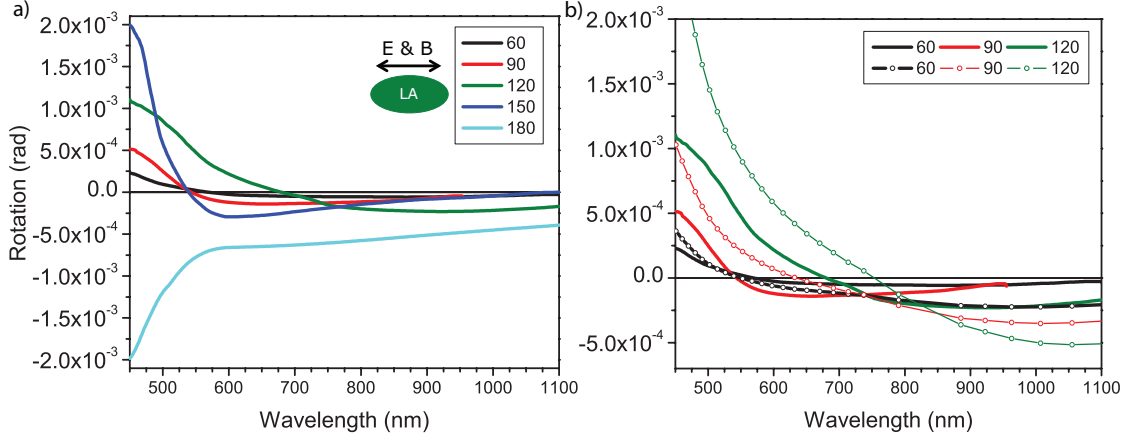


Figure 4.6: Kerr spectra for nanoellipses of short/long axis of 100/140 nm (short/long axes respectively) excited along long axis for varying heights. b) Comparison of the experimental data (solid lines) with the calculated ones (dotted lines).

paring the calculations with the ones for ESA, this is the case. The change in the sign for 180 nm sample in Figure 4.6.a is because of the relative phase contributions from the different modes. From equation 2.7, it is possible that the interplay between the phases of all the components x , y , z and the SO modes might have caused the net phase to go over $\Pi/2$ resulting in a change of the rotation sign. This situation is explained in ref.[31].

The Kerr rotation spectra for the 170 nm base diameter samples are discussed below. The samples were prepared with heights ranging from 60 nm to 180 nm in steps of 30 nm. The Kerr spectra for the nanodisks are shown in Figure 4.7. The spectra for nanoellipses are shown in Figure 4.8 for ESA and in Figure 4.9 for ELA configurations. It can be immediately seen that in all three cases, the rotation values are lower when compared to the 100 nm nanoellipses. From absorption spectra (Figure 4.2), it can be seen that, though the out-of-plane mode is excited and visible in the spectra, it is situated far from the in-plane y mode to induce any sizable enhancements in rotation. From the comparison with the calculations, in nanodisks as well as the ellipses, the trends are similar apart from minor reduction in amplitude in the experimental data.

From the results of 100 nm and 170 nm diameter particles, it can be seen that the 100 nm particles give more absolute rotation values compared to the larger 170 nm particles. In 170 nm particles, we conclude that the out-of-plane mode is spectrally situated too far from the in-plane modes to induce large enhancements in MO activity. From the absorption spectra of the particles with the L-MOKE spectra, a certain trend in the MO behaviour can be observed. For both 100 and 170 nm case, the most enhancement in rotation spectrally occurs roughly at the saddle point between the combined in-plane resonances (x and y) and the out-of-plane resonance (z). This is because the modes situated along x and z are MO active as they are directly excited by the incident light.

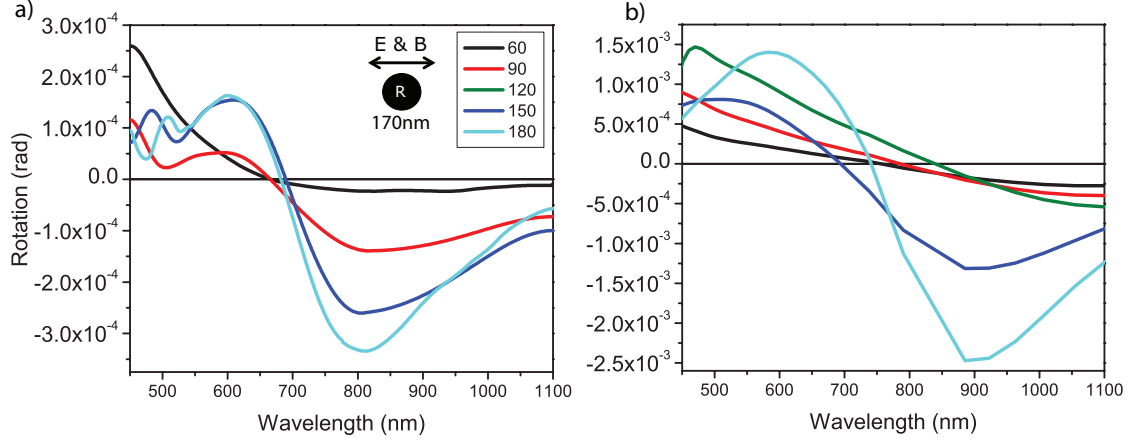


Figure 4.7: a) Kerr spectra for circular nanodisks of base diameter of 170 nm and varying heights of 60-180 nm. The sample with 120 nm tall particles were not measured owing to problems in the experimental setup. b) Calculated spectra for the nanodisks.

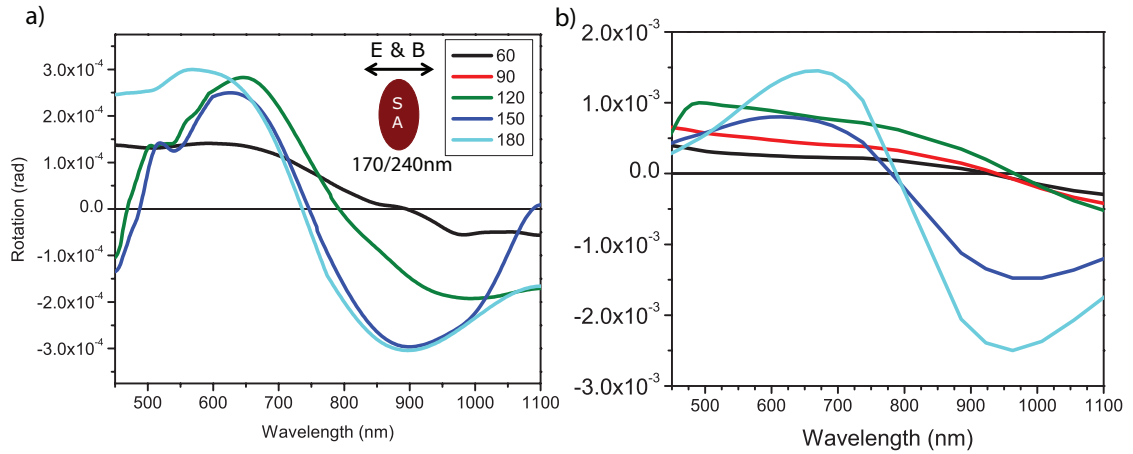


Figure 4.8: a) Kerr spectra for nanoellipses (170/240 nm) excited along short axis for varying heights of 60-180 nm. a) Spectra for ESA b) Spectra for ELA. The rotation amplitudes are lower than those measured with 100 nm diameter particles.

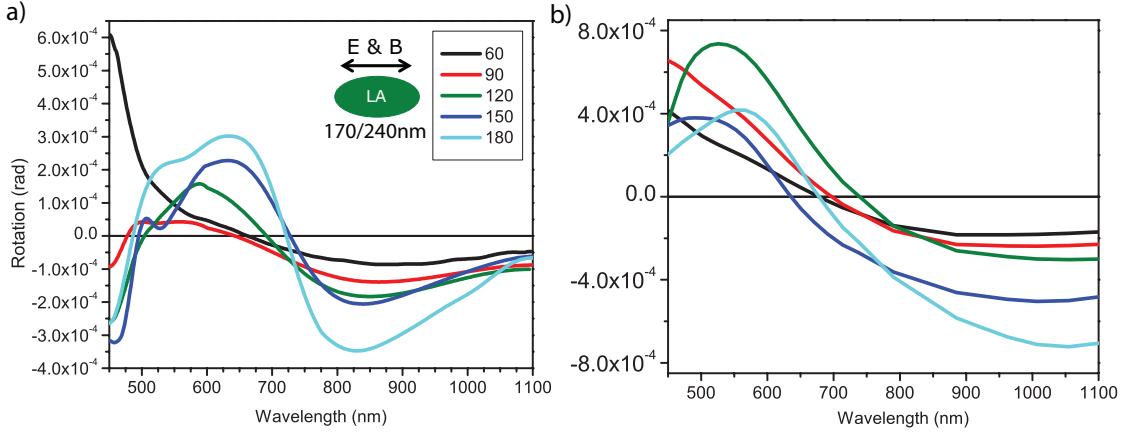


Figure 4.9: Kerr spectra for nanoellipses of 170/240 nm (short/long axes respectively) and varying heights of 60-180 nm. a) Spectra for ESA b) Spectra for ELA. The rotation amplitudes are lower than those measured with 100 nm diameter particles.

The mode along y is activated through SO coupling. When the SO mode is engineered to have resonance close to that of the out-of-plane mode, very large enhancements in MO activity were observed. When the resonances satisfy the requirements of equation.2.6, dramatic enhancements were predicted as discussed for 150 nm tall particles (Figure4.5).

Hence, in order to achieve maximum absolute rotation values, it is required to tune the positions of the individual plasmon resonances. It is important to engineer the resonances in such a way that the y mode (coupled through SO interaction) is positioned spectrally close to the out-of-plane mode while the x mode (that which induces the SO coupling) is off-resonance. To achieve this, first, it is required to red shift all the resonances into the visible spectrum so that they can be resolved completely with the current experimental setup. In case of 100 nm samples, this red shift might push the Kerr spectral features to longer wavelengths and instead of only the tail, the entire rotation peak could be resolved. This might even give large rotation values.

4.3 Tuning Plasmon Resonances

In order to tune the individual plasmon resonances (x , y and z), a number of techniques were used: Index matching oil immersion, oxide growth and PMMA coating. Each of these techniques and their results are discussed below:

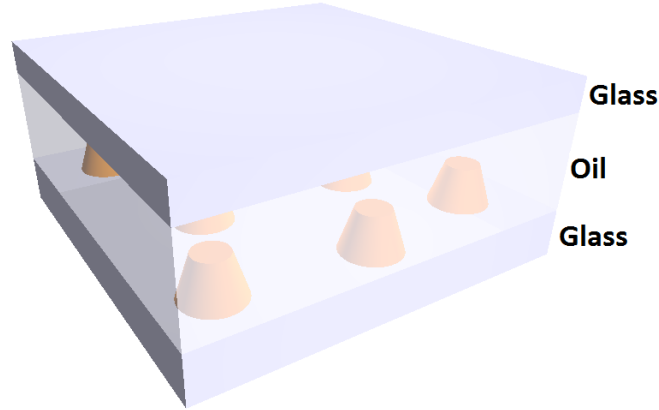


Figure 4.10: Schematic depicting the sample after oil immersion. The nanostructures are completely covered in a uniform layer of immersion oil and sealed with glass cover.

Oil Immersion

In order to red shift the plasmon resonances and bring them into the measurement window (450-1100 nm), it is important to match the refractive index of the surrounding medium with that of the substrate. The substrate (glass) has a refractive index of 1.55. Immersion oil with index $n=1.515$ was drop-coated on the samples and covered with another glass slide in order to make the system rigid. The resulting situation is shown schematically in Figure4.10.

The samples became highly reflective (from top glass and oil) and as a result the signals detected by L-MOKE measurements were very noisy and rotation features could not be resolved properly. Since oil and glass forms a uniform flat layer on top of the nanostructures, the difference in refractive index between oil and glass leads to back scattering. This leads to reduced signal-to-noise (S/N) ratios. To overcome this issue, a technique that forms an uniform index matching medium that follows the topography of the structures was required.

Oxide Growth

RF sputtering of silicon dioxide (SiO_2) was also done on top of the nanostructures. Initially 10 nm SiO_2 was grown and the result is shown in Figure4.11. In a, the original L-MOKE response of the sample is shown (in this case 100 nm diameter and 120 nm tall elliptical disks). The maximum rotation in this case is $1.2\text{mrad} = 0.07\text{deg}$ shown in red curve. Figure4.11.b shows the result after a 10 nm thin layer of SiO_2 was sputtered. About 50 nm of spectral red shift in the Kerr rotation inversion was observed but the peak of the rotation still could not be resolved. From the inversion points (zero crossing of rotation), it is apparent that the in-plane modes were also very sensitive to the oxide. The maximum rotation value was reduced to 0.04deg . The reason for reduced amplitudes

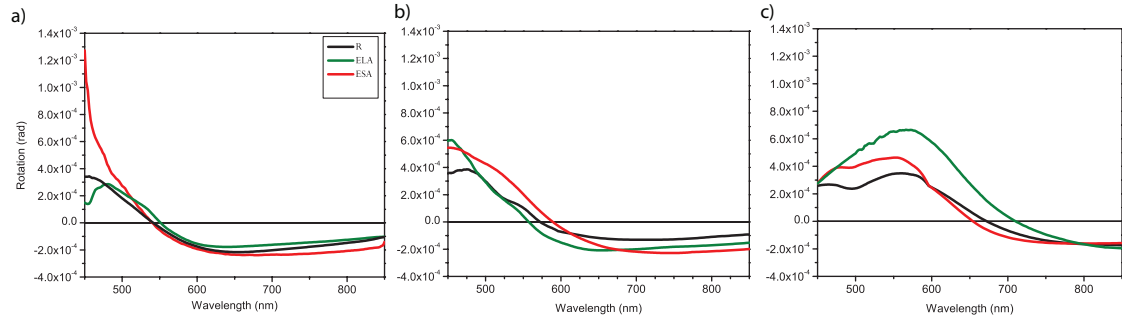


Figure 4.11: Kerr spectra for 120 nm tall 100/140 nm diameter elliptical particles a) Original spectra without oxide b) After growing a 10 nm thin layer of oxide c) after a 50 nm oxide layer. Spectra in black is for circular particles, red for ESA and green for ELA.

might be that, the modes are shifted too far and into the spectral region where nickel intrinsically has weak MO response (large negative imaginary part of dielectric function) In Figure 4.11.c, the graph shows the result after 50 nm layer of SiO_2 was sputtered. There is a significant shift in the curves towards longer wavelength and finally the entire shape of the curve can be seen including the peak.

PMMA coating

To overcome the back scattering issue, a thin layer of PMMA was spin-coated. PMMA has refractive index close to that of glass and hence will help red shift the resonances into the measurement window. To ensure that the nanostructures were completely covered in PMMA, the spin settings were adjusted which resulted in a 220 nm thick layer. The PMMA coated samples were first characterized optically and then by L-MOKE. The results are discussed below.

The Figure 4.12.a shows the result of PMMA coating on 100 nm diameter elliptical samples. Both the in-plane and out-of-plane plasmon resonances are significantly red-shifted into the L-MOKE measurement window. In 150 nm sample, the out-of-plane mode seems to be absorbing as much as the in-plane modes while in 180 nm sample, the out-of-plane resonance starts to dominate. In Figure 4.12.b, the case for 170 nm samples is shown. Here there is a dramatic change in the relative absorption of the in-plane and out-of-plane modes. As the particles are larger at the base compared to their heights, the effect of substrate is more than that of the surrounding medium (PMMA). Hence, the in-plane mode is seen to dominate the out-of-plane resonance. These dramatic changes in the plasmon response demonstrate the sensitivity of the dipole modes to refractive index of the environment.

Since, with PMMA coating, the resonances were successfully red-shifted in to the experiment window of L-MOKE, more enhancements in rotation could be expected.

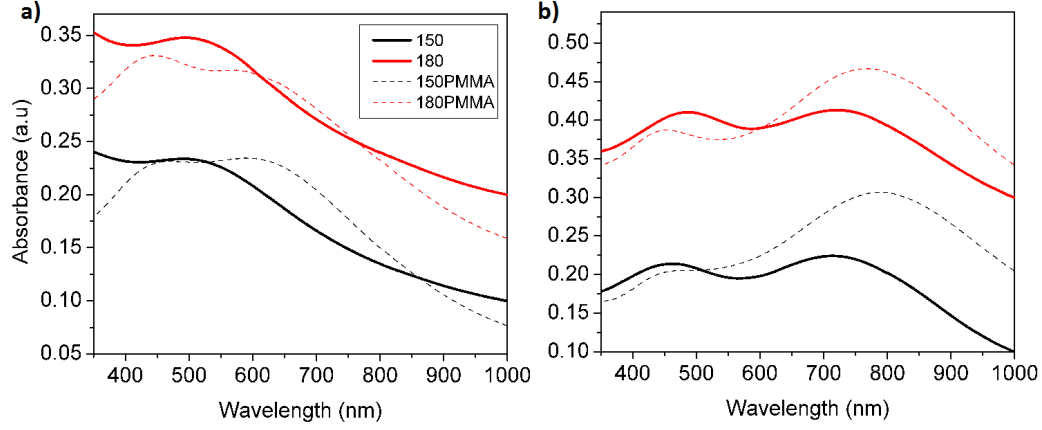


Figure 4.12: Absorption spectra for 150 nm and 180 nm tall particles. a) 100/140 nm diameter particles b) 170/238 nm diameter particles. The curves are shifted relative to each other for better viewing. The scale on the left does not show absolute absorption values. Only elliptical samples are shown for simplicity

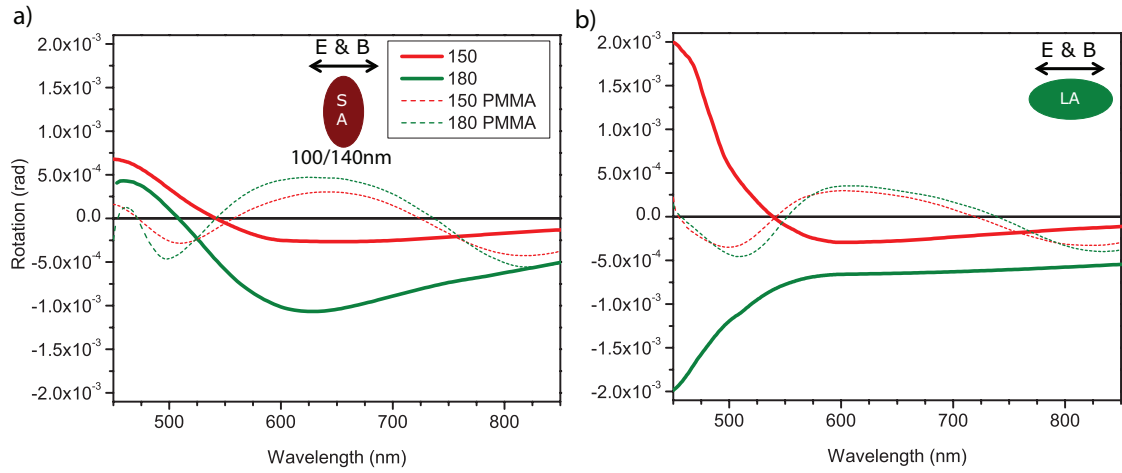


Figure 4.13: Kerr spectra for 150 nm and 180 nm tall 100/140 nm diameter particles. a) Measured along ESA b) along ELA. Dark lines show spectra before PMMA coating and dashed lines show the new spectra after PMMA coating.

Contrary to our expectation, the Kerr rotation values were strongly reduced (as shown in Figure4.13). From Figure4.13.b it can be seen that the 180 nm tall sample where the rotation curve was inverted compared to the 150 nm sample, now follows the same trend as 150 nm sample. By embedding the particles in uniform medium of PMMA, the resonances are red-shifted and now it would appear that the phase contribution from z is similar to that of y while increasing height from 150 to 180 nm. The follow-up calculations were obtained with the particles embedded in uniform medium of index $n = 1.5$. When the PMMA covered sample data is plotted together with the calculations (Figure4.14), it can be seen that the trends for both ESA and ELA are similar except for minor increase in amplitude for the calculations. This might be due to the small difference in refractive index ($n_{PMMA} = 1.419$) [39]. This proves that the refractive index of the medium is playing an important role that might give rise to dramatic rotation values that was predicted by calculations for the ESA configuration.

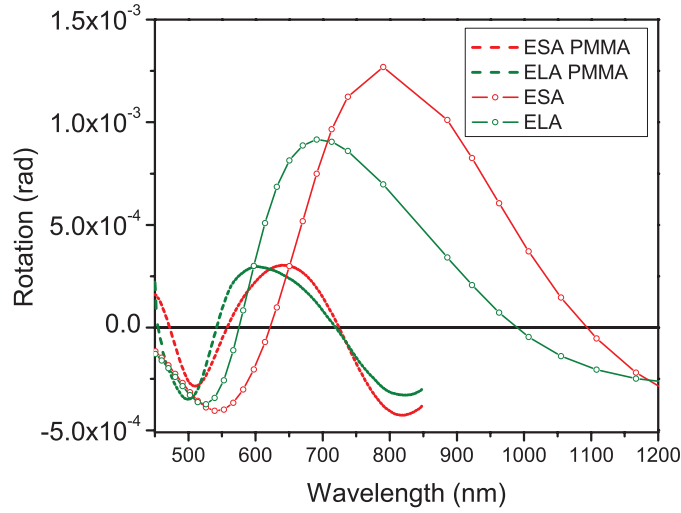


Figure 4.14: Kerr Spectra comparison of experimental PMMA coated samples with re-calculated model data with $n=1.5$ instead of 1.15. PMMA coated experimental data is in dashed lines. Calculated data in dash-dot lines. *all data is for 150 nm tall nanoellipses (100/140 nm).*

The goal of the described approaches was to red-shift the resonances into the L-MOKE measurement window (450-1100 nm) so that the interaction between the individual plasmon modes could be studied. All techniques had some advantages and some disadvantages and were all able to red-shift the resonances successfully. From the results of L-MOKE, it can be seen that the net rotation values are highly reduced as a result. All significant features in rotation again occur at the wavelength corresponding to the saddle point between the in-plane SO y mode combined with the in-plane x mode and the out-of-plane mode z . It can thus be inferred that, it is not only important to red-shift the resonances, but it is equally important to tune the individual spectral positions of the modes and bring the out-of-plane mode spectrally close to the in-plane mode.

4.4 Future and upcoming magnetoplasmonic nanostructures

New samples were fabricated by taking into account the design principles formulated in the previous section. The particles were made slightly bigger (base diameter of 124 nm) compared to 100 nm in order to push the resonances into the measurement window. The height of the particles were tuned such that the two in-plane and out-of-plane resonances come closer spectrally. The samples were first characterized optically followed by L-MOKE. The results are shown in Figure 4.15.a. A very broad resonance was obtained. This could be the result of a combination of all 3 modes.

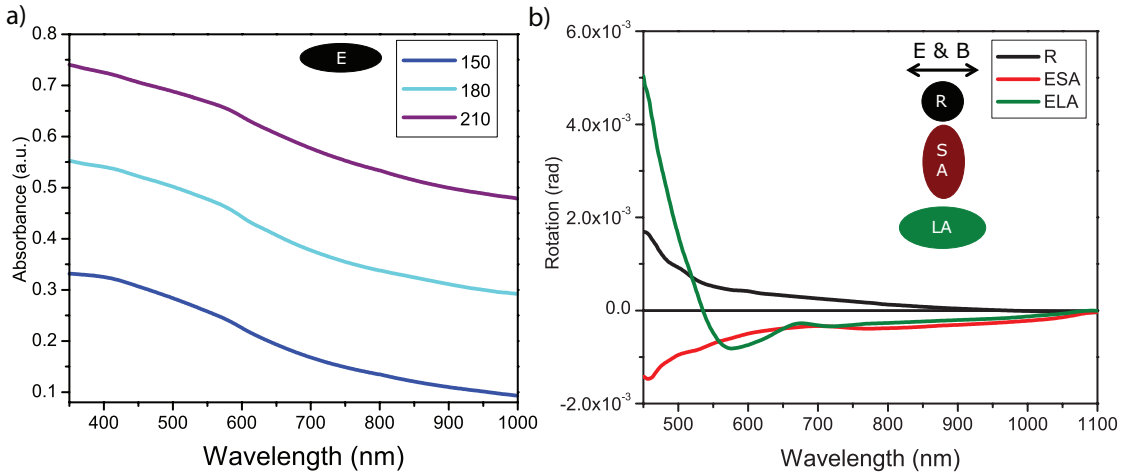


Figure 4.15: Experimental data for the nanoellipses with dimensions 124/174 nm (short/long): a) Absorption spectra for varying heights. b) Kerr spectra for the 180 nm tall nanoellipse (124/174 nm).

The L-MOKE results for samples with 124 nm base diameter and 180 nm high particles are displayed in Figure 4.15.b. As expected, a large increase in maximum rotation values are seen. The maximum rotation when measured along long axis (ELA) amounts to about 0.3° which is already more than twice of what was achieved with 100 nm particles (0.12°). The maximum rotation value measured along short axis as well as on the circular samples also yielded enhanced values proving that the out-of-plane plasmon mode is definitely playing an important role. Just by a marginal increase in the size of the particles, a dramatic increase in the MO activity was achieved. Interplay between the multiple plasmon modes of the particles can thus be tuned by carefully designing the nanostructures.

5

Conclusion

Interaction between light and magnetism at the nanoscale has been investigated in this thesis. Three-dimensional magnetoplasmonic nanostructures made of nickel were fabricated using hole mask colloidal lithography. Nanodisks and nanoellipses of varying heights were characterized spectrally using absorption spectroscopy and L-MOKE.

The absorption spectra revealed that the out-of-plane plasmon becomes more and more dominant with increasing height of the structures. It was also found that, for smaller disks (100 nm), the out-of-plane plasmon is not entirely situated in the experimental window (450-1100 nm) but on the other hand for larger structures (170 nm), it was clearly visible. The absorption spectra of the structures were then used to understand their Kerr spectra. We found that, the most interesting features (in terms of absolute rotation values) occur for wavelengths corresponding to the saddle point between the in-plane SO mode (y) and the out-of-plane mode (z). It was found through calculations that, the absolute rotation values depend on the individual phase contribution from various modes which in turn depends on the relative strength and position of the out-of-plane plasmon mode with respect to the in-plane modes. For the case of smaller disks, the maximum rotation achieved was 0.12° while for the larger disks it was in the order of mdeg. Hence, in order to achieve high enhancements in MO activity and large Kerr rotation values, it is important to not only have dominant out-of-plane mode but also the relative spectral positions of the individual modes is equally so. Moreover, the size of the particles also plays a big role as it determines their spectra. In summary, the resonances of out-of-plane mode and in-plane SO mode need to be brought closer while the other in-plane mode needs to be off-resonance in order to achieve large enhancements in MO activity.

Finally, new batch of circular and elliptical samples were fabricated with dimensions of 124/174 nm at the base and varying heights taking into account the requirements for

high rotation amplitudes. It was found that, in these samples, the spectral positions of the out-of-plane and in-plane modes are very close resulting in a very broad spectrum. As a result, the sample with 180 nm tall elliptical particles gave the highest rotation for a nickel based magnetoplasmonic nanostructure at 0.3° .

To conclude, anisotropy engineering was found to be a powerful tool to modify the magneto-optical response of magnetoplasmonic nanostructures. Out-of-Plane plasmon was found to play a very important role in determining the amount of Kerr rotation enhancement that a structure can produce. Large enhancement in Kerr rotation (12mdeg to 0.3°) was achieved by individually tuning the various plasmon modes. Nickel, though being a poor plasmonic and ferromagnetic material [40] was found to give very strong enhancements in MO activity through engineering of the individual plasmon modes. In a stronger ferromagnetic material like cobalt, which has intrinsically more MO activity than nickel [41], orders of magnitude enhancement in Kerr rotation could be achieved. Supposedly, similar design of nanostructures in cobalt could give about three times more Kerr rotation than nickel. Hence, by continuing this line of research, with help from calculations, nanostructures can be designed to obtain Kerr rotation values in excess of 1° . Then, real applications are possible such as magnetically controlled optical isolators, ultra-fast switches, modulators and so on.

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