

Optical and electrical measurements at the nanoscale

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To uncover more about the world and ourselves

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Declaration of Authorship

I, Alberto Lauri, declare that this thesis entitled "Optical and electrical measurements at the nanoscale" and the work presented in it are my own. I confirm that:

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Abstract

Plasmonics modes, or photon states coupled to the collective oscillations of electrons in metallic structures, are very attractive for applications where small size and strong intensity of light are required, as for bio and chemical sensors, solar cells and photodetectors. The efficient use of plasmonic structures in these fields is due to their advantageous properties such as broadly tunable optical behaviour coupled with catalytically active surfaces and high efficiency of trapping and concentrating of light. Indeed, as the optical properties of these plasmonic materials are highly tunable (by varying size and shape) across the entire visible spectrum they provide an extremely efficient platform for light absorption and collection. Nevertheless, such strong light confinement in plasmonic systems requires the storage of part of the energy in the motion of free-electrons, which are excited out of equilibrium and subject to ohmic losses. These out of equilibrium carrier are highly energetic and if extracted can be used as catalyzer of chemical reaction at the surface of the plasmonic structure with extremely precise control.

In this work a combination of optical and electrical measurements is used to further explore the understanding of the underlying physics at the base of plasmon enhancement and hot carrier production. By probing electrical and optical properties, we try to disclose a tighter link between oscillation of the electromagnetic field and the generation of energetic electron that once out of equilibrium with the oscillation of the field can be harvested with different purpose. After realizing that the acceptor of these energetic carries needs to be placed in the vicinity of the plasmonic structure and spatially localised in the region of highest field of the structure under exam, so to increase the probability of extraction of such energetic carriers from the structure, as well to maximize their energy. I first investigate new manipulation techniques capable of driving a target object to the sphere of action of a plasmonic structure, and then explore the possible way to extract such energetic carriers at two different possible interfaces the metallic/semiconductor one and the metallic/molecular one.

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Publications

Papers

- **A. Lauri**, L. Velleman, X. Xiao, E. Cortes, J. B. Edel, V. Giannini, A. Rakovich, S. A. Maier, 3D Confocal Raman Tomography to Probe Field Enhancements inside Supercluster Metamaterials, ACS Photonics, 2017, 4 (8), pp 20702077
- N. A. Gsken¹, **A. Lauri**¹, Y. Li, T. Matsui, B. Doiron, R. Bower, A. Regoutz, A. P. Mihai, P. K. Petrov, R. F. Oulton, L. F. Cohen, S. A. Maier,^(1 equal contribution) TiO₂-x enhanced Si compatible sub-bandgap photodetection via TiN thin films (*submitted*)
- M. Grell, C. Dincer, T. Le, **A. Lauri**, E. N. Bajo, M. Kasimatis, G. Barandun, S. A. Maier, T. Cass, F. Gder, Autocatalytic Deposition of Metals in Fabrics using Si Ink (*submitted*)
- E. Pensa , **A. Lauri**, J. Gargiulo, E. Cortes and S. A. Maier, Gating hot carriers with electrochemistry(*submitted*)
- S. Simoncelli, E. L. Pensa, T. Brick, J. Gargiulo, **A. Lauri**, J. Cambiasso, Y. Li, S. A. Maier, E. Cortes, Monitoring plasmonic hot-carrier chemical reactions at the single particle level (*submitted*)

Conference Presentations

- **A. Lauri**, E. Cortes, E. Pensa, A. Barik, A. Rakovich, S. Oh, S. A. Maier, Dielectro-Plasmonic tweezers for scalable trapping and hot electrons applications. SPIE Photonics Europe (EPE18), Strasbourg. Proceedings Volume 10671, Nanophotonics VII (2018). Poster presentation.
- **A. Lauri**, L. Velleman, X. Xiao, E. Cortes, J. B. Edel, V. Giannini, A. Rakovich, S. A. Maier, 3D Confocal Raman Tomography to Probe Field Enhancements inside Supercluster Metamaterials, SPIE Photonics Europe (EPE18),Strasbourg. Proceedings Volume 10671, Metamaterials XI; 106711O (2018). Oral presentation.
- **A. Lauri**, E. Cortes, E. Pensa, A. Barik, A. Rakovich, S. Oh, S. A. Maier, Optical and Electrical Signal at the nanoscale, Imperial College Postgraduate Symposium, London (UK); (2017). Oral presentation.
- **A. Lauri**, E. Cortes, E. Pensa, A. Barik, A. Rakovich, S. Oh, S. A. Maier, Dielectro-Plasmonic tweezers for scalable trapping and hot electrons applications. London Plasmonics Forum, London (UK); (2017). Poster presentation.

- **A. Lauri**, L. Velleman, X. Xiao, E. Cortes, J. B. Edel, V. Giannini, A. Rakovich, S. A. Maier, 3D Confocal Raman Tomography , ICSS - San Sebastian (2017). Invited talk.
- **A. Lauri**, L. Velleman, X. Xiao, E. Cortes, J. B. Edel, V. Giannini, A. Rakovich, S. A. Maier, 3D Confocal Raman Tomography. Imperial College Postgraduate Symposium, London (UK); (2016). Poster presentation.
- **A. Lauri**, E. Cortes, E. Pensa, A. Barik, A. Rakovich, S. Oh, S. A. Maier, Dielectro-Plasmonic tweezers . London Plasmonics Forum, London (UK); (2016). Poster presentation.
- **A. Lauri**, E. Cortes, E. Pensa, A. Barik, A. Rakovich, S. Oh, S. A. Maier, Dielectrophoretic tweezers on top of plasmonic antennas for hot electrons applications. London Plasmonics Forum, London (UK); (2015). Poster presentation.

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Chapter 1

Introduction

The way the world is perceived is influenced by how the materials and the object around us interact with light. Indeed, if you look around you, you would notice that silver is a shiny metal used for centuries in coins and tableware. Silicon is a crystalline semiconductor, opaque at visible wavelength and the material of choice for the modern electronic industry. Salt is a transparent insulator, necessary for life. If we had ultraviolet eyes, however, we would see these materials in a complete different way. The shiny silver, would become almost transparent (its reflectance trails to zero towards shorter and shorter wavelengths). The opaque Silicon would become more and more like a mirror. While the boring salt would remain the same.

And what about one of the most abundant optical materials on earth like glass? This simple material (a combination of Silicon and Oxygen) is a key component in windows, computer chips, optical fibers, the sand at the beach, optical gain telescopes, and a vast number of other applications. Glass can be described as a supercooled liquid frozen at room temperature. The fact that it's flowing (slowly) is evident by looking at old church windows: they are actually thicker at the bottom than at the top. The optical property of glass can be easily modified from transparent to opaque, due to scattering of light from small

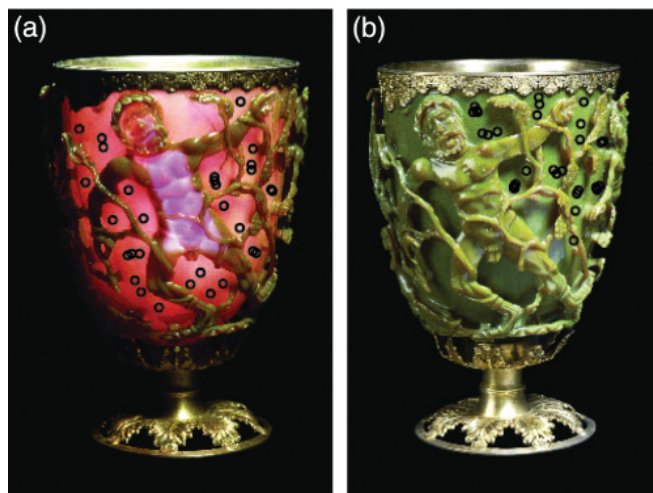


Figure 1.1: *a) The Lycurgus cup is illuminated from the inside and only the transmitted red light is observed. b) The cup is illuminated from the outside, so only the reflected green light is observed.*

air bubbles or particles trapped inside. The most famous example of particles being introduced into glass is the Lycurgus Cup. In this glass, produced in the 4th century A.D. in the great Roman Empire (Figure 1.1), the scattering of metal nanoparticles is at the origin of different colours. As we can see in Figure 1.1, the glass appears red when illuminated from the inside of the cup, and green when illuminated from the outside. The gold-silver nanoparticles inside the glass reflect the green portion of the visible spectrum and transmit the red one. This type of scattering process was explained in mathematical terms only in 1908 by Gustav Mie[1], more than 2000 years later[1,2].

The study of these phenomena was the goal of photonics in the past and, as objects get smaller and smaller, of nanophotonics now. One of the most interesting phenomena in the field of light-matter interaction physics is plasmonics. The field of Plasmonics has been studied since the beginning of the 20th century, however it has only taken off in the last 20 years. Sommerfeld and Zenneck studied radio waves propagation on conductor surfaces at the beginning of the 20th century [2]. Ritchie studied the behaviour of electrons on metal surface using electron loss spectroscopy and the interaction of light with metallic gratings,

in 1957 and 1968 respectively [3]. A method for prism-coupling free-space light into surface plasmon was presented by Otto, Kretschmann and Raether in 1960's [4, 5]. And from then, thousands of paper have been published on the field of plasmonics and its interesting nature of coupled electron and Electro-magnetic (EM) field oscillations [2].

1.1 Overview

Plasmonics modes, or photon states coupled to the collective oscillations of electrons in metallic structures (an in-depth theoretical background is introduced in Chapter 2), are very attractive for applications where small size and strong intensity of light are required, as for bio and chemical sensors, solar cells and photodetectors. The efficient use of plasmonic structures in these fields is due to their advantageous properties such as broadly tunable optical behaviour coupled with catalytically active surfaces and high efficiency of trapping and concentrating of light. These properties opened up the way for a wide range of application in the last decades for the fields mentioned above.

As the optical properties of these plasmonic materials are highly tunable (by varying size and shape) across the entire visible spectrum they provide an extremely efficient platform for light absorption and collection. Thus, incorporating plasmonic metal nanoparticles into photocatalytic systems holds great promise for improving the efficiency of sunlight absorption and solar energy conversion. In addition, plasmon excitation has been widely used for spectroscopic applications, in particular for surface-enhanced Raman spectroscopy (SERS) as we are going to see in Chapter 3.

However in order for the plasmonic system to show extremely high efficiency in spectroscopy applications or photocatalysis, it becomes of great relevance that the target molecule involved in the chemical reaction or sensed must be allowed

to enter the limited sphere of action of the plasmon (which is only in the range of tens of nanometers). Most recent spectroscopy or photocatalysis applications rely, just, on the brownian diffusion of the target object towards the plasmon system [6], however such process is highly inefficient and requires high concentration of the target molecule which is not realistic for most real-life applications [7]. Moreover in order to achieve chemical reaction and hot electron transfer from the plasmonic system, the target molecule must be placed correctly in the region of highest field and in close vicinity to the plasmonic structure as to increase the probability of tunnelling through the vacuum energy [8,9]. In order to overcome such a problem, the study of efficient trapping of nano-scale object, which cannot be achieved by common diffraction-limited optical tweezers has become a wide area of research [7,10,11].

One of the main issues is how to deliver a single particle in a fast and reliable way towards a given plasmonic system, where we want it to be then stably trapped for further experiment or applications. The two fundamental approaches primarily employed, so far, for the trapping of nanoparticles with plasmonic nanoantennas are illuminating periodic arrays of closely spaced plasmonic nanoantennas [12] or illumination of a single plasmonic nanostructure [13]. One approach uses a combination of thermal forces and optical forces, however long calculation and careful design of all the forces involved complicates the design and individual nanoparticle targeting is hardly achievable. On the other hand the second approach exploits only optical forces to create a strong attractive force with a smaller range (diffusion becomes the limiting factor in this case) but with a simpler design process. However, such an approach addresses individual nanoparticles at the cost of reduced control, leaving no room for low-concentration and high-speed applications [7]. The most ideal design would possess the ability to rapidly deliver individual nano-objects to a given il-

luminated nanoantenna on-demand and achieve high-resolution trapping of such objects, without creating persistent perturbing forces (Chapter 3 is dedicated at the investigation of novel manipulation techniques).

As we find a way to manipulate target nanoparticles at the scale of the plasmonic system we can take advantage of the possible interactions arising from the vicinity of the plasmonic structure and of such nanoparticles. One of the possibilities is the extraction of energetic hot carriers that can participate in photochemical reaction by the excitation of surface plasmon resonances (SPR) on our plasmonic system. Indeed, upon SPR excitation, the oscillation of free electrons quickly dephases and leads to the generation of energetic hot electrons and holes on extremely fast time scale ranging from 1 to 100 fs [14]. It has been shown that the plasmon-generated hot electrons can then directly interact with molecules adsorbed on the metal surface, opening up the field of plasmon photocatalysis (as we are going to see in Chapter 6). Another possibility lies in the transfer of hot electrons to an adjacent semi-conductor support via a plasmon-mediated electron-transfer (PMET) pathway. In the plasmonic metal/semiconductor systems, the SPR excitation significantly increases the yield of hot electrons with high potential energy on the plasmonic metals and induces fast and efficient transfer of hot electrons to the semiconductors. The Schottky barrier at the metal/semiconductor interface helps to trap the transferred hot electrons in the conduction band (CB) of semiconductors by delaying them from traveling back to the plasmonic metals and avoiding recombination (Chapter 5).

However the underlying physics of the plasmon enhancement mechanisms leading to SERS, field enhancement and hot electron formation/extraction are intimately related, and indeed often they stem from the same origin. To better develop these types of applications, then it becomes critical to understand the fundamental processes involved in the excitation and decay of plasmons and in

the interactions of the plasmons with molecules or semiconductors.

1.2 Motivation and aim

In this work a combination of optical and electrical measurements is used to further understand and explore the underlying physics at the base of plasmon enhancement and hot carrier production. By probing optical and electrical properties, I try to disclose a tighter link between oscillation of the electromagnetic field and the generation of energetic electron that can be harvested with different energy conversion purpose.

With such an objective in mind, the work in this thesis first aims to create novel manipulation ability to drive a target object to the sphere of action of a plasmonic structure, and then explore the possible way to extract such energetic carriers at metal/semiconductor or metal/molecule interface.

Firstly, two different approach for manipulation are proposed: an approach based on porous material; and one based on dielectro-plasmonic tweezers. In case of porous supercluster material the work presented deepens our theoretical understanding of collective mode inside cluster-based metamaterials by experimentally measuring their behaviour in the visible and near IR (InfraRed). Moreover a study of their ability to harvest and host molecule in their structure is carried out, providing proof of their efficiency as a platform for ultra-sensitive molecular spectroscopy. On the other hand, in the context of active manipulation the design of a novel and innovative type of nanotweezer capable of exploiting two different type of forces is presented. Such a novel design allows for the creation of a nanotweezers capable of addressing a series of extremely valuable issues that current nanomanipulation techniques are facing as briefly explained in the previous section. Reliable and extremely fast and stable trapping by exploiting the new nanotweezer designed is presented. Such techniques represent this work

contribution in the field of manipulation of nano-object, in order to enhance the performance of energetic carrier extraction in plasmonic system.

Building on such new techniques for bringing target object in the vicinity of plasmonic system, in this thesis I start to study the different possible interfaces involved in the transfer of energetic carriers. The first contribution in such field is the study of hot-electron transfer at metal/semiconductor interfaces. Si-compatible sub-bandgap photodetection at zero bias is presented for a backside illuminated 50 nm TiN thin film on a p-type Si substrate, exhibiting a photoresponsivity of 1 mA/W at 1250nm. Moreover, an amorphous TiO_{2-x} interlayer between the pSi and the TiN is shown to be at the origin of a distinct photoresponse which significantly differs from the one of an oxide free pSi/Au comparison sample. Additionally, the photoresponsivity of metal/semiconductor interfaces can be enhanced by an order of magnitude thanks to such interlayer, allowing for the design and fabrication of more efficient hot-carrier extraction Schottky barrier.

The second contribution made by this work is the study of metal/molecule interface. Here by combining electrochemistry and dark-field spectroscopy the study of the role of a single photoexcited Au nanoparticle (AuNP) in the electro-oxidation of aniline to polyaniline is carried on. The findings show how extraction of energetic carriers from the metallic nanoparticle can be effectively used as a photocatalyzer. Furthermore, the energy of hot carriers for triggering the electropolymerization reaction was determined along the plasmon absorption, showing that even if the absorbed initial energy is the same, the hot hole generation efficiency follows the plasmon absorption spectrum, with energy ranging from 24 meV to 240 meV.

To summarize in this work I present:

- The use of porous metamaterials for passive manipulation and efficient

spectroscopy applications;

- The design of a novel nano-tweezers capable of harnessing two different type of trapping forces, and addressing some of the current challenges in manipulation at the nanoscale;
- The use of TiO_{2-x} thin interlayer in metal/semiconductor junction for high efficient transfer of energetic carriers in the IR wavelength regime;
- The use of plasmonic nanoparticles as photocatalyzers in chemical reactions, and a measurement of the energy available for the energetic carriers extracted from such systems.

1.3 Thesis Organisation

This introductory chapter was aimed at providing a general overview of why the underlying physics of the plasmonic enhancement still has venues to be explored, especially in the context of extracting and harvesting energetic hot electron. The first part of this thesis is dedicated to the understanding of collective oscillations of charge in metals and how they can be used to modify the interactions of light with matter. Chapter 2 first introduces the main properties used to describe the interaction of light with matter both in the macroscopic world and the microscopic one. Then the concept of surface plasmon polariton in bound media and localised surface plasmon polariton is presented. A brief introduction to the optical nanoantennas and how to characterise them is also provided. Moreover, a description of the interaction between electrons and light is sketched under the umbrella of what are hot electron and how we can harvest them, which gives rise to the further investigation carried out in the three subsequent experimental chapters. Chapter 3 and 4 build on this and describes our efforts towards novel manipulation techniques at the nanoscale, by exploiting both nano-antennas

(Chapter 4) and metamaterials (Chapter 3). In this chapter, I introduce the ability of plasmonic system to affect the environment around and their ability to modify the motion or properties of object in their field of action. Chapter 4 is dedicated to the harvesting of hot electrons at plasmonic metal/semiconductor interfaces. First the study of new plasmonic material where extraction of hot electron can be more efficient is presented. Then the use of an initial Silicon-Titanium dioxide junction that is capable of introducing controlled tunneling channel for hot-holes collection is studied as a novel solution for Si-sub bandgap photodetection. Chapter 5 is then dedicated to the harvesting of hot electron at plasmonic-metal/molecule interfaces, for plasmon-driven catalysis. Here I introduce the efforts towards the understanding of the energy available after the extraction of hot electron from the metal surface. In this case, single nanoparticle optical and electrochemical measurement are able to shine light on our ability to collect energetic electrons.

Part one, therefore, serves as a theoretical background for the understanding of plasmonics and novel hot electron processes. Part two, instead, introduces the experimental work done in order to have a better understanding of the link between electron in plasmonic system and their extraction.

Part I

Plasmons and Hot electrons

Chapter 2

Theoretical background

An introduction of the theoretical background for the plasmonic field and an overview of its current challenges is provided in this chapter. The link between microscopic (polarizability and permittivity) and macroscopic (refractive index) optical properties is described and the Drude model, one of the earliest and most effective models to relate the optical constants of metals to their electronics properties is introduced. Furthermore, plasmon polaritons and Localised Surface Plasmonic Resonances (LSPR) in metallic structure are discussed as an interesting pathway for the generation of excited carriers as well as for sensing application. Finally, an overview of excited carrier in a metallic structure due to the excitation of plasmonic resonance, called hot electron, is presented.

2.1 Light-matter interaction: Maxwell equation's

As always is the case when approaching a rigorous discussion of light-matter interactions, this chapter starts with Maxwell's equations for macroscopic electromagnetism. Under the hypothesis of presence of charges, we can write [15,16]:

$$\nabla \cdot \vec{D} = \rho_{ext} \quad (2.1)$$

$$\nabla \cdot \vec{B} = 0 \quad (2.2)$$

$$\nabla \times \vec{E} = -\frac{d\vec{B}}{dt} \quad (2.3)$$

$$\nabla \times \vec{H} = \vec{J}_{ext} + \frac{d\vec{D}}{dt} \quad (2.4)$$

with ∇ being the gradient operator (more precisely, the gradient is a vector field which points in the direction of the greatest rate of increase of a function, and its magnitude is the slope of the function in that direction). This set of equations is widely known for linking the four macroscopic fields: $\mathbf{D}$ (dielectric displacement), $\mathbf{E}$ (electric field), $\mathbf{H}$ (magnetic field strength), $\mathbf{B}$ (magnetic field). In particular, Gauss's law (Eq.2.1 and Eq.2.2) implies the generation of electric field due to free charges, as well as the absence of magnetic monopoles. On the other hand, Faraday's (Eq. 2.3) and Ampere's (Eq. 2.4) laws describe how the magnetic field generates an electromotive force, and the electric field generates a magnetic induction. Concerning the charge and current density involved in the Maxwell's equations, there exist a distinction between the external ($\rho_{ext}, \mathbf{J}_{ext}$) and the internal ($\rho, \mathbf{J}$) densities, so that in total $\rho_{tot} = \rho_{ext} + \rho$ and $\mathbf{J}_{tot} = \mathbf{J}_{ext} + \mathbf{J}$. According to such distinction, the external set drives the system (the one that sustains the EM wave in the medium), while the internal set responds to the external stimuli (the polarization or the response of the material when excited by an EM wave) [16].

The four macroscopic fields can be further linked with the following set of equations [15]:

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} \quad (2.5)$$

$$\mathbf{H} = \frac{1}{\mu_0} \mathbf{B} - \mathbf{M} \quad (2.6)$$

with ϵ_0 and μ_0 being the electric permittivity and the magnetic permeability in vacuum respectively. $\mathbf{P}$ describes the electric dipole moment per unit volume that is generated in the material by the alignment of microscopic dipoles with the electric field. Specifically, it is related to the internal charge density by

$$\nabla \cdot \mathbf{P} = -\rho. \quad (2.7)$$

At the same time $\mathbf{M}$, the magnetization in the medium, is defined by the internal current density and its contribution can be identified by

$$\mathbf{J} = \nabla \times \mathbf{M} + \frac{\delta}{\delta t} \mathbf{P} \quad (2.8)$$

Such formulation, then allows us to relate the macroscopic electric field to the overall polarization effect inside a material (both internal and external)

$$\nabla \cdot \mathbf{E} = \frac{\rho_{tot}}{\epsilon_0} \quad (2.9)$$

If we go back to Maxwell's equation 2.3 and apply the vector identity

$$\nabla \times (\nabla \times \mathbf{E}) = \nabla(\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E} \quad (2.10)$$

to Faraday's law, we can write [15]

$$\begin{aligned} \nabla \times (\nabla \times \mathbf{E}) &= -\frac{\delta}{\delta t} (\nabla \times \mathbf{B}) = -\frac{\delta}{\delta t} \nabla \times (\mu_0 \mathbf{H} + \mu_0 \mathbf{M}) \\ &= -\mu_0 \frac{\delta}{\delta t} \mathbf{J} - \mu_0 \frac{\delta^2}{\delta t^2} (\epsilon_0 \mathbf{E} + \mathbf{P}) \end{aligned} \quad (2.11)$$

$$\begin{aligned}\nabla(\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E} &= -\mu_0 \epsilon_0 \frac{\delta^2}{\delta t^2} \mathbf{E} - \mu_0 \frac{\delta}{\delta t} \mathbf{J} - \mu_0 \frac{\delta^2}{\delta t^2} \mathbf{P} \\ \nabla^2 \mathbf{E} - \mu_0 \epsilon_0 \frac{\delta^2}{\delta t^2} \mathbf{E} &= \mu_0 \frac{\delta}{\delta t} \mathbf{J} + \mu_0 \frac{\delta^2}{\delta t^2} \mathbf{P}\end{aligned}\tag{2.12}$$

The last equation (Eq. 2.12) describes how an "internal" current or the polarization of a material create electromagnetic waves, that interfere with the original incoming wave. Moreover, a non-linear polarization of the material creates additional waves at frequency $N \times \omega_0$ (with ω_0 being the center frequency of the propagating wave) in the case of vacuum. In absence of the source term (right side of Eq. 2.12), that describes the variations of the electric ($\mathbf{E}$) and magnetic ($\mathbf{B}$) field due to the presence of charges (static, $\mathbf{P}$, or dynamic, $\mathbf{J}$), we obtain the wave equation of d'Alembert

$$\nabla^2 \mathbf{E} - \frac{1}{c^2} \frac{\delta^2}{\delta t^2} \mathbf{E} = 0\tag{2.13}$$

where we have used the identity $c^2 = 1/\epsilon_0 \mu_0$, with c being the speed of light. Indeed any radiation that travels in vacuum, irrespective of its frequency, travels at the speed of light (c). The simplest solutions to this equation is provided by a harmonic dependence of the type that describes a plane wave in space :

$$\begin{aligned}\mathbf{E}(\mathbf{r}, t) &= \mathbf{E}_0 \cos(\omega t - \mathbf{k} \cdot \mathbf{r}) = \Re\{\mathbf{E}_0 \exp i(\omega t - \mathbf{k} \cdot \mathbf{r})\} \\ \mathbf{H}(\mathbf{r}, t) &= \mathbf{H}_0 \cos(\omega t - \mathbf{k} \cdot \mathbf{r}) = \Re\{\mathbf{H}_0 \exp i(\omega t - \mathbf{k} \cdot \mathbf{r})\}\end{aligned}\tag{2.14}$$

With $\mathbf{k}$ being the wavevector and λ being the wavelength. Such solution to the wave equation are called transverse electromagnetic waves (TEM), as the magnetic and electric fields are perpendicular to the wavevector $\mathbf{k}$ and to each other. In a more general problem, where a monochromatic wave is propagating in a media with a slowly varying permittivity, the wave's propagation can be

described with the Helmolzt equation

$$\nabla^2 \mathbf{E}(r) + k_0^2 \epsilon(r) \mathbf{E}(r) = 0 \quad (2.15)$$

with the different wave parameters linked by the folowing set of relations

$$\begin{aligned} \omega &= 2\pi\nu \\ \lambda &= 2\pi k \\ \omega &= k_0 c \\ \lambda_0 &= c/\nu \end{aligned} \quad (2.16)$$

Another important parameter that needs to be defined in order to characterize an electromagnetic wave is the energy that it carries. Changes in the electromagnetic energy density are caused by flow and dissipation according to the energy conservation law:

$$\delta_t u + \nabla \cdot \mathbf{S} = -\mathbf{J} \cdot \mathbf{E} \quad (2.17)$$

with $\mathbf{S}$ being the Poynting vector and u , the energy density in a lossless and non-dispersive material being

$$u = \frac{1}{2}(\mathbf{E} \cdot \mathbf{D} + \mathbf{B} \cdot \mathbf{H}) \quad (2.18)$$

The Poynting vector $\mathbf{S} = \mathbf{E} \times \mathbf{H}$, is the quantity that represents the flow of energy in the conservation equation (Eq. 2.17) and is parallel to direction of the electromagnetic wave wavevector. As the main topic of this thesis is the "focusing" of light beyond the diffraction limit and the use of the strong optical forces generated in such conditions, it is helpful to introduce an effective energy density u_{eff} describing the ammount of field localization in terms of the

electromagnetic energy distribution. Under the assumption of a material being described by a free-electron-type dielectric function ($\epsilon = \epsilon_1 + i\epsilon_2$), we can write [16]:

$$u_{eff} = \frac{\epsilon_0}{4} \left(\epsilon_1 + \frac{2\omega\epsilon_2}{\gamma} \right) |\mathbf{E}|^2 \quad (2.19)$$

2.2 Optical Properties of Materials

2.2.1 Polarizability

When talking about polarizability, we are, in general, talking about the molecular response to light. If a molecule is excited by an electromagnetic wave with a frequency far from any of its resonances, non-resonant or elastic scattering will be the dominant process of the interaction. In this case, the electric field variation drives the electron cloud out of equilibrium, inducing a dipole in the molecule. The dipole then behaves as a source of radiation at the same frequency as that of the incident wave, until the molecule returns to equilibrium. At any given time the molecule remains in its ground state.

When the frequency of the incoming electromagnetic wave is close to a molecular resonance, resonant absorption occurs: in this case a transition from a ground state to an excited state of the molecule is driven by the EM field. The type and energy of the transition is defined by the frequency and energy of the incoming wave. As the molecule is excited, one of the way to reduce its energy is by collisions: exchanging the photon energy into thermal energy and coming back to its ground state.

The parameter that accounts for the interaction of a molecule with light is its polarizability α . It describes the ability of a molecule to acquire a dipole moment μ in the EM electric field, and its expression can be linked to the sum of all the possible transitions that may occur in the following way [15] (limiting

ourself to an excitation in the z direction):

$$\alpha_{zz} = \frac{2}{\hbar} \sum_n \frac{\omega_{n0} \mu_{z,0n} \mu_{z,n0}}{\omega_{n0}^2 - \omega^2} \quad (2.20)$$

with the terms $\mu_{z,if}$ being the transition dipole matrix elements in the z-direction. From the previous equation, the total dipole moment is therefore the sum of any permanent dipoles, and the dipoles caused by the field and described by the polarizability.

2.2.2 Susceptibility

In the case of dense and non-magnetic materials (μ is neglected), the optical response of the material is fully described by its dielectric function, or permittivity. The permittivity of a material has been introduced in the previous section, where the displacement field was expressed as a function of the electric field, following:

$$\mathbf{D} = \epsilon \mathbf{E} \quad (2.21)$$

which can be expanded by separating the electric field itself and the polarization of the medium in terms of its relative permittivity (ϵ_r) and vacuum permittivity (ϵ):

$$\mathbf{D} = \epsilon_0 \epsilon_r \mathbf{E} = \epsilon_0 (1 + \chi) \mathbf{E} = \epsilon_0 \mathbf{E} + \mathbf{P} \quad (2.22)$$

where $\chi = \mathbf{P}/\epsilon_0 \mathbf{E}$ is the electric field susceptibility (ratio between internal and external charges). If we consider the local electric field (Lorentz local field approximation) [15]:

$$\mathbf{E} = \mathbf{E} * \left(1 - \frac{\alpha N}{3\epsilon_0}\right) \quad (2.23)$$

Table 2.1: *main relationships between permittivity and refractive index [15]*

Permittivity	Refractive Index
$\epsilon = \epsilon_1 + i\epsilon_2$	$\bar{n} = n + ik$
$\epsilon = 1 + \chi = \bar{n}^2$	$\bar{n} = \sqrt{\epsilon}$
$\epsilon_1 = n^2 - k^2$	$2n^2 = \sqrt{\epsilon_1^2 + \epsilon_2^2} + \epsilon_1$
$\epsilon_2 = 2nk$	$2k^2 = \sqrt{\epsilon_1^2 + \epsilon_2^2} - \epsilon_1$

we can then link the macroscopic polarization to the molecular polarizability (Eq. 2.20)

$$\mathbf{P} = \alpha N \mathbf{E} \quad (2.24)$$

thus obtaining

$$\chi = \frac{\alpha N / \epsilon_0}{1 - \alpha N / 3\epsilon_0} \quad \epsilon_r = \frac{1 + 2\alpha N / 3\epsilon_0}{1 - \alpha N / 3\epsilon_0} \quad (2.25)$$

The permittivity in Eq. 2.25 can then be rewritten as a sum of all the possible transitions capable of creating a dipole moment μ (as we have seen in the case of the polarizability) at different frequency [15]:

$$\epsilon_r = 1 + \frac{2N}{3\hbar\epsilon_0} \sum_n \frac{\omega_{n0} |\mu_{n0}|^2}{\omega_{n0}^2 - \omega^2} \quad (2.26)$$

From Fig. 2.1 we can see that when the frequency of the driving field matches the resonance of a transition capable of creating a dipole moment, we have a peak in the absorption spectrum (ϵ''). Note that at very low frequency all charged species contribute to the material polarizability, while as the field frequency increases only the fastest polarization mechanism continue to react.

2.2.3 Permittivity and refractive index

The effect of the permittivity of a medium on the propagation of an EM wave, can be seen by getting back to Eq. 2.12 (while dropping the source term) and

using the definition of susceptibility $\chi = \mathbf{P}/\epsilon_0\mathbf{E}$ [15]:

$$\begin{aligned}\nabla^2\mathbf{E} - \mu_0\epsilon_0\frac{\delta^2}{\delta t^2}\mathbf{E} &= \mu_0\frac{\delta^2}{\delta t^2}\mathbf{P} \\ \nabla^2\mathbf{E} - \mu_0\epsilon_0(1 + \chi)\frac{\delta^2}{\delta t^2}\mathbf{E} &= 0 \\ \nabla^2\mathbf{E} - \frac{\bar{n}^2}{c^2}\frac{\delta^2}{\delta t^2}\mathbf{E} &= 0\end{aligned}\tag{2.27}$$

where we have used the definition $\epsilon = 1 + \chi = \bar{n}^2$, with $\bar{n}$ being the complex refractive index. The main relationships between the refractive index and the permittivity are outlined in Table 2.1 [15]. How the refractive index represents the macroscopic description of the optical behaviour of a solid is not clearly pointed out from the previous series of relations. However, if we take note of Equation 2.27 where the propagation of a wave in a material is described (Eq. 2.13 was in vacuum), the phase velocity of the wave is reduced to $v = c/n$. Thus the microscopic polarization effect inside the material is described in the macroscopic picture of the wave by the refractive index as a change in the phase velocity.

Moreover as the refractive index is complex, absorption of energy is taking place in the material. The intensity of the wave will thus be reduced along its propagation direction following the Beer-Lambert's relation:

$$I(x) = I_0e^{-\alpha x}\tag{2.28}$$

with $\alpha = \frac{4\pi k}{\lambda}$ being the absorption coefficient and k being the imaginary part of the refractive index (also referred to as extinction coefficient). In general terms, the refractive index describes the change in properties that the EM wave experiences as it traverse the medium, while the permittivity describes the microscopic response of the electron to the driving field. The real part of the permittivity is related to how much energy is stored and its imaginary part relates to how much

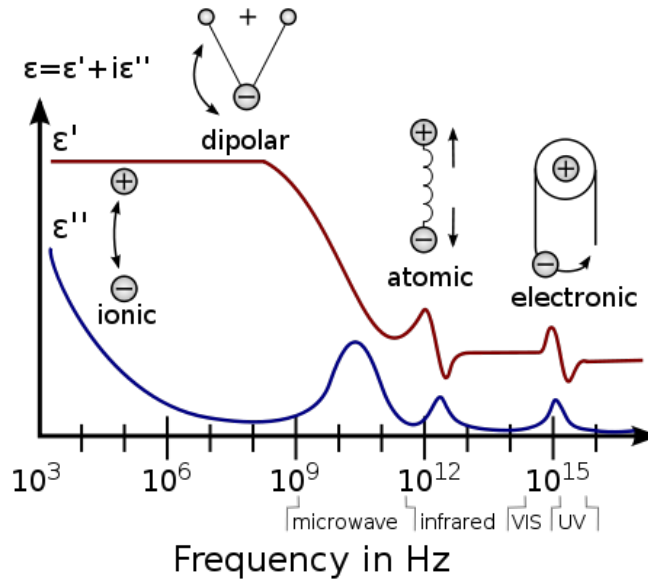


Figure 2.1: The different transitions that can create a dipole μ , are outlined as a function of frequency in the absorption spectrum of the complex permittivity[15].

energy is dissipated[2, 15–17].

2.2.4 The free-electron Drude model

The Drude model is one of the earliest and most effective models used and it relates the optical constants of metals to their electronics properties. Its objective is to describe the behaviour of the dielectric function through the free carrier contribution [18]. The Drude model approach is purely classical, and it relates the polarization of a solid to the displacement of its "free carriers" (usually electrons) due to an incoming EM field [15]. The equation of motion that is derived under such classical assumption is:

$$m\ddot{\mathbf{x}} + m\gamma\dot{\mathbf{x}} = -e\mathbf{E} \quad (2.29)$$

With γ being the "dumping" that the electron cloud experiences, due to the material ions, when displaced by the incoming EM wave. In case of a harmonic

time dependence (as we have also assumed during the derivation of polarizability), the incoming wave can be written as $\mathbf{E}(t) = \mathbf{E}_0 \exp -i\omega t$ for the driving field [16], and the electrons oscillations are described by the particular solution:

$$\mathbf{x}(t) = \frac{e}{m(\omega^2 + i\gamma\omega)} \mathbf{E}(t) \quad (2.30)$$

with the complex amplitude in front of the harmonic field, incorporating all the phase shift of the system. This model is also called the "Plasma model", as it describes the oscillation, driven by an external field, of a free electron gas with respect to a fixed background of positive ions [16]. The macroscopic polarization contribution from the displaced electrons can be written in terms of the electrons' motion as:

$$\mathbf{P} = -\frac{ne^2}{m(\omega^2 + i\gamma\omega)} \mathbf{E} \quad (2.31)$$

which bring us to:

$$\mathbf{D} = \epsilon_0 \left(1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}\right) \mathbf{E} \quad (2.32)$$

where we have introduced $\omega_p^2 = \frac{ne^2}{\epsilon_0 m}$, the plasma frequency of the free electron gas [16]. Thus we can derive easily the dielectric function of a material to which the free electrons gas model is applicable (pricipally metals) as [16]:

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \quad (2.33)$$

It is interesting to consider Eq. 2.33 in the two limiting cases: high and low frequency regimes. In the low frequency regime ($\omega\tau \ll 1$, with $\tau = 1/\gamma$), Eq. 2.33 can be written as:

$$\begin{aligned} \epsilon(\omega) &= 1 - \frac{ne^2\tau}{\epsilon_0 m(\omega^2 + i\omega\tau)} \\ \epsilon &\simeq 1 - \frac{ne^2\tau}{m\omega} \end{aligned} \quad (2.34)$$

given that in the limits of $\omega \rightarrow 0$ the $1/\omega$ term dominates [18]. Moreover as $1/\omega$ dominates, from Eq. 2.34 we can derive that $\epsilon_2 \gg \epsilon_1$ with ϵ_2 being the complex part of the dielectric function and ϵ_1 the real one. In this limit we can also write :

$$\sqrt{\epsilon} \simeq \sqrt{\frac{ne^2\tau}{m\omega}}\sqrt{i} = \bar{n} + i\bar{k} \quad (2.35)$$

with the identity:

$$\sqrt{i} = \frac{1+i}{\sqrt{2}} \quad (2.36)$$

implying $\bar{n} \simeq \bar{k}$, components of the complex refractive index [18]. Indeed we can derive [16]:

$$\bar{n} \simeq \bar{k} = \sqrt{\frac{\tau\omega_p^2}{2\omega}} \quad (2.37)$$

and calculate the Frenel coefficient of reflection, which would yields a value close to 1 [18]. The Drude theory thus states that, at low frequency, a metal (material with a large concentration of free carriers) is a perfect reflector. This is also in line with a large immaginary part of the refractive index (k , to prohibit any evanescent tunneling of light through the material) and a small penetration of the EM radiation inside the material to avoid absorption. Indeed, the absorption of light from a material (metal in this case) is described by the absorption coefficient, defined as[16]:

$$\alpha = \left(\frac{2\omega_p^2\tau\omega}{c^2}\right)^{1/2} \quad (2.38)$$

and is related to the skin depth (material penetration) by [16]:

$$\delta = \frac{2}{\alpha} = \sqrt{\frac{2}{\sigma_0\omega\mu_0}} \quad (2.39)$$

On the other hand, in the high frequency limit ($\omega\tau \gg 1$) Eq. 2.33 can be approximated as:

$$\epsilon \simeq 1 - \frac{en^2}{m\omega^2} \quad (2.40)$$

As the frequency becomes large, the $1/\omega^2$ dependence guarantees that the free carrier effects are less and less important and other processes become dominant [18]. Specifically these other processes are the interband transition, which are not taken into consideration by the purely classical Drude model. In such limit the dielectric function is predominantly real, leading to negligible damping [16]:

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \quad (2.41)$$

This can be read, as the dielectric function of the undamped free electron plasma. Thus, as the Drude contribution becomes unimportant the behaviour of the material is that of a dielectric.

Previously, as well as in Eq. 2.32, a quantity called *plasma frequency* was introduced. In general terms, the plasma frequency can be thought of as the characteristic frequency at which the material changes its behaviour from metallic to dielectric. In other words, the frequency at which the real part of the dielectric function vanishes $\epsilon_1(\omega_p) = 0$. In the real part of the dielectric function the free carrier term makes a negative contribution:

$$\epsilon_1(\omega) = 1 - \frac{ne^2\tau^2}{m\epsilon_0(1 + \omega^2\tau^2)} \quad (2.42)$$

Indeed, we can think of the transition of a material from dielectric to metallic as the transition from a behaviour dominated by the free carrier term to a behaviour dominated by the core ion background.

2.2.5 Dispersion in a free electron gas and interband transition

As the photon energy increases and becomes comparable to the energy gap, other type of absorption processes take place [18]. The interband transition process represents the excitation of an electron from the valence band to an unoccupied state of the conduction band. This process describes the absorption of a photon, the formation of an excited electronic state and an hole left behind in the valence band. The Drude model describes well the optical response of a material, but only for photon energy below the band gap; the interband transition were not considered in the previous formulation (only intraband ones were). However the generalization of the Drude model to include interband transitions is also possible. Specifically we can rewrite the equation of motion for an electron in the following way [16]:

$$m\ddot{\mathbf{x}} + m\gamma\dot{\mathbf{x}} + m\omega_0^2\mathbf{x} = -e\mathbf{E} \quad (2.43)$$

In this case, the interband transitions are treated using the classical picture of a bound electron with a resonance frequency defined by ω_0 (energy of the incoming photon). Indeed the last term of Eq. 2.43 ($m\omega_0^2\mathbf{x}$) describes a resonant excitation of the electron, as in the case of photon absorption and interband transition. In the solution to the equation of motion each possible transition will be described by such a resonant excitation term, extending the validity of the Drude model.

Turning back to the description of the transparency regime or equivalently the regime of possible optical propagation inside a material ($\omega > \omega_p$). If we take Eq. 2.13 in the Fourier domain and we use it together with Eq. 2.41, we can

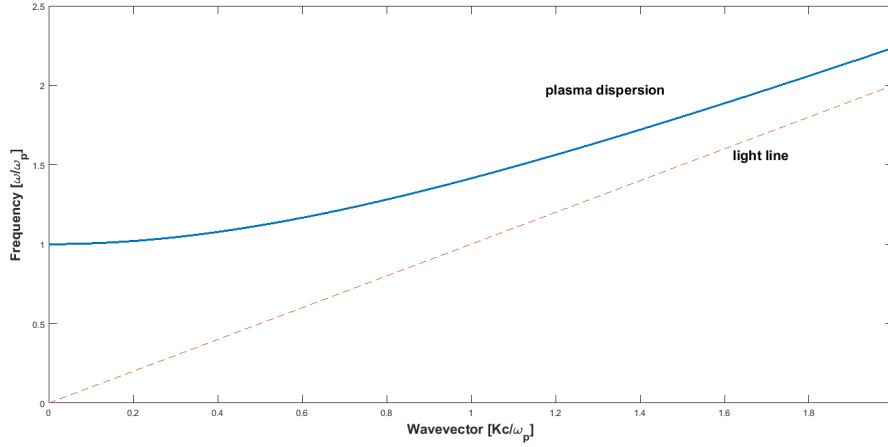


Figure 2.2: Dispersion relation in the case of EM propagating in a metal (plasma dispersion) or in vacuum (light line)

obtain the dispersion relation of waves travelling in a material [16]:

$$\omega^2 = \omega_p^2 + \mathbf{K}^2 c^2 \quad (2.44)$$

This relation is plotted in the Fig 2.2 for the case of a generic metal conductor [16]. From the plot it can be noticed that when the frequency of the incoming wave is smaller than ω_p , then the propagation inside the material is not possible. However, for $\omega > \omega_p$ the "electron plasma" can support transverse waves with a group velocity of $v_g = d\omega/d\mathbf{K} < c$. Moreover we could notice that at the plasma frequency we have $\epsilon(\omega_p) = 0$, and so we can write [16]:

$$\mathbf{D} = 0 = \epsilon_0 \mathbf{E} + \mathbf{P} \quad (2.45)$$

Implying a pure depolarization field (due to the electron plasma oscillation) of intensity $\mathbf{E} = -\frac{\mathbf{P}}{\epsilon_0}$. In other terms, we can recognize that the plasma frequency represents the natural frequency of the electron sea free oscillation. The quanta of such charge oscillation are called *volume plasmons*. Due to their purely longitudinal nature, volume plasmons cannot be coupled to transverse electromagnetic

waves and they usually decay via an energy transfer mechanism called Landau damping [18].

2.3 Localised Surface Plasmon

In the previous section the idea of volume plasmon as the quanta of charge oscillation inside the bulk of a material was introduced. Surface plasmon polaritons are a limit case of such oscillations. Surface plasmon polaritons or SPPs are generally defined as an evanescently confined electromagnetic excitation propagating at an interface between a dielectric and a conductor [19]. The reason they can be seen as a limit case of the volume plasmon, is that these electromagnetic surface waves exist thanks to their coupling to electron oscillation on the conductor side. The property of such highly confined waves depends strongly on both the metal (dielectric function, roughness) and the dielectric properties (refractive index) [19]. To establish confinement in two or three dimensions we need to consider a different type of system. In general, plasmonic oscillation can come in two forms: (1) surface plasmon polaritons (SPPs, that we are not going to treat in this work) and (2) localized surface plasmon resonance (LSPRs). SPPs are propagating modes that travel along a metal dielectric interface and decay evanescently away from the surface. Thus, SPPs require specific illumination conditions such as prism or grating in order to provide phase matching between the mode and the excitation field [4, 20, 21]. On the other hand, LSPRs are related to the near-field modes of metallic nanostructures where confinement in 3D is possible, and contain intrinsic longitudinal field components allowing for direct excitation via far field illumination. In this thesis only LSPRs are going to be taken into consideration. Qualitatively, LSPRs are generated by the perturbation of the free-electron gas in a metallic particle by an incident electric field E_0 . For particles sizes $d \ll \lambda$, the incident field of wavelength λ fully penetrates the

nanoparticle and causes a uniform displacement of the negative electron cloud from the positive core, thus establishing a dipole moment in the particle. As E_0 is reduced, the restoring force will cause the electron cloud to overshoot the equilibrium position and thus decay due to resistive ohmic losses [21].

The quantitative origin of LSPRs can be understood by examining the scattering of light (light reflected with angles different from the propagation one) by a particle with $d \ll \lambda$. In this case, the phase of the incident field is relatively constant over the surface of the particle, and thus the scattering problem reduces to a spherical particle in an electrostatic field. This quasi-static approximation is generally valid under such condition [21,22]. In this case, the Helmholtz equation (2.15) reduces to the Laplace equation:

$$\nabla^2 \phi = 0 \quad (2.46)$$

for some potential ϕ , from which the electric field distribution in the vicinity of the scatterer can be determined via $E = \nabla \phi$ [21]. For a spherical particle of radius a illuminated by a plane wave polarized along the x-axis, the total electric field (incident + scattered) outside the sphere can be described by:

$$\mathbf{E} = E_0(\cos\theta \mathbf{n}_r - \sin\theta \mathbf{n}_\theta + \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \frac{a^3}{r^3} E_0(2\cos\theta \mathbf{n}_r + \sin\theta \mathbf{n}_\theta)) \quad (2.47)$$

where E_0 is the incident electric field amplitude, $\mathbf{n}_{r,\theta}$ is a unit vector in the $\mathbf{r}$ and θ spherical coordinate directions, respectively, and $\epsilon(\epsilon_m)$ is the complex dielectric constant of the particle (medium) [23]. The key feature of Eq. 2.47 is that the scattered field is identical to that of a dipole located at the origin, with a dipole moment $p = \epsilon_0 \epsilon_m \alpha E_0$, so that in analogy to Eq 2.20 we can write the

polarizability of a gold spherical nanoparticles as:

$$\alpha(\omega) = 4\pi a^3 \frac{\epsilon\epsilon_m}{\epsilon + 2\epsilon_m} \quad (2.48)$$

Evidently, the polarizability determines not only the near-field spatial distribution of E , but also implies the condition for the localized dipole resonance:

$$\text{Re}[\epsilon] = -2\epsilon_m \quad (2.49)$$

which, when satisfied, leads to resonant enhancement of the near field due to the divergence of $\alpha(\omega)$. This derivation is only applicable to spheres and provides useful insight into how the polarizability influences the LSPR. However, in current designs, more complicated antennas geometries, including coupled nanorods (dipole antennas) and coupled triangles (bowtie antennas, the one that are going to be widely used in this thesis) with sizes $d \approx \lambda$, are commonly used [21, 24–26]. In general, the resonance wavelength and the near-field enhancement are intimately tied to the geometry of the nanoparticle, however a more shape dependant derivation can be generalized by the Eq 2.48.

2.4 Antennas and Cross Sections

Antennas are structure that enhances the local light-matter interaction. Optical nanoantennas mediate the information and energy transfer between the free radiation field and a localized receiver or transmitter. The degree of localisation and the magnitude of a transduced energy indicates how efficient an antennas is. We can thus define an antennas as a device designed to efficiently convert free-propagating optical radiation to localised energy, and vice versa. [27]

Antenna theory that has been developed for the radio-frequency and the mi-

microwave range of the electromagnetic spectrum, holds great promise for inspiring new concepts in the optical frequency range. Advances in nano-optics and plasmonics have enabled the creation of nanoscale antennas (Figure 2.3) that work at optical frequencies, with the aim to create analogous devices to those that work at larger wavelengths. One of the main difficulties to scale established concept of antenna theory is that at optical frequencies the incident radiation penetrates into the metal and is not perfectly rejected. This gives rise to coherent oscillations of the free-electron gas, i.e. to a plasmon resonance (Section 2.4). Thus the response of a metal at optical frequencies is, therefore, very different from that of a perfect conductor, as is assumed in microwave antenna theory. In order to obtain meaningful results at optical frequencies, it is then necessary to take into account the dielectric function of the metal. For example in the case of rod nanoantennas, an effective wavelength picture has been derived, in which the optical antenna no longer responds to the external wavelength, but to a shorter effective wavelength λ_{eff} , which depends on the material properties via a linear relationship $\lambda_{eff} = n_1 + n_2[\lambda/\lambda_p]$, where λ_p is the plasma wavelength and n_1 and n_2 are coefficients that depend on the properties of the antenna and the surrounding medium [28]. In general, however, no solutions are available for complex geometries. Electromagnetic simulation methods such as Finite Difference - Time Domain (FDTD) or Finite Element Method (FEM) are then generally used to calculate the properties of nanoantennas, as it will also be done in the experimental section of these thesis (Part II).

When using electromagnetic simulation methods, the experimental quantity that is studied and calculate is the cross section of the object. In particular the interaction between light and a particle/nanoantenna can be described by the scattering (ω_{scat}), absorption (ω_{abs}) and extinction (ω_{ext}) cross sections. With the scattering cross section describing the amount of light re-radiated by the

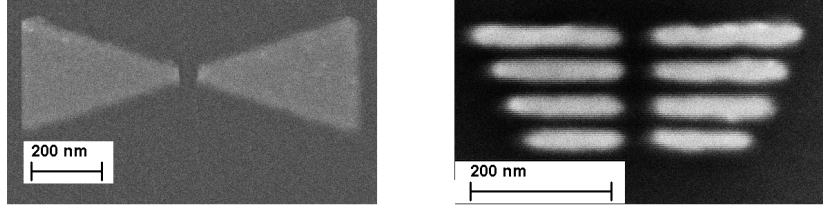


Figure 2.3: *Electron beam lithography fabrication allows for the patterning of extremely complex and small structure with different kind of materials. Here two possible complex antennas design are presented.*

particle and the absorption cross section being how much of it is dissipated, and the extinction being the sum of the two previous quantity. In other words the extinction is the rate of energy removal from an incident electric field by a nanoantenna: $W_{ext} = W_{scat} + W_{abs}$ with W being the a measure of power given by:

$$W_{abs} = - \iint_{\delta V} \text{Re}[\mathbf{E}_{tot} * \mathbf{H}_{tot}^*] \cdot d\mathbf{s} \quad (2.50)$$

where Re indicates the real part, $*$ the complex conjugate, $\mathbf{E}_{tot}(\mathbf{H}_{tot})$ is the total electric (magnetic) field in the vicinity of the nanoantenna. The integration is performed over a surface $\mathbf{s}$ that completely encloses the nanoantenna. The absorption cross section can then be related to Eq 2.50 as:

$$\omega_{abs} = \frac{W_{abs}}{I_0} \quad (2.51)$$

with $I_0 = |\mathbf{E}_{inc}|^2 (2\eta_0)^{-1}$ being the incident optical intensity and $\eta_0 = \sqrt{\mu_0/\epsilon_0}$ the free-space impedance. A similar deduction can be done also for the scattering cross section by taking into account the scattered electric(magnetic) field ($\mathbf{E}_{scat} = \mathbf{E}_{tot} - \mathbf{E}_{inc}$).

2.5 Hot Electrons

Another interesting phenomena that can be excited through the absorption of light with the excitation of plasmon in metallic structures, is hot electron generation. This section aims to provide an overview of the possible mechanisms by which hot electrons can be generated, and also discusses some applications and uses of such energetic electrons in the latest years.

2.5.1 Plasmons and hot electrons

Plasmonics modes, or photon states coupled to the collective oscillations of electrons in metallic structures (as was demonstrated in the previous chapter), are very attractive for applications that require small mode sizes and high field enhancements such, as bio and chemical sensors, solar cells and photodetectors. The high efficiency of trapping and concentrating of light by surface plasmons has opened up the way for a wide range of application. Numerous reviews of the field, in recent past, attest to this fact [29–31]. Localized surface plasmon (LSPR), a “standing wave” variation of the surface plasmon polaritons, can occur in carefully designed nanostructures. The large freedom possible in the design of such nanostructures, thanks to advanced fabrication methods like electron beam lithography (EBL), is another reason of the rapid and wide development of this field [14, 32–35].

More recently, new interest has been directed towards the generation and behaviour of “*hot electrons*” inside plasmonic nanostructures. Hot electrons are electrons that have been photoexcited, and thus have energy higher than the one a thermal excitation at ambient temperature can provide. Indeed, following the absorption of photons and the excitation of the LSPR in the nanostructure, the electromagnetic decay can either proceed through the re-emission of photons

(scattering process) [36] or non-radiatively, by energy transfer to the electronic cloud [14]. Different theories have been developed to describe this process and new possibilities for reaction-driven plasmonic applications are being investigated. In general, photoexcited hot electrons can stimulate a variety of possible thermal, electrical, mechanical and chemical processes (Figure 2.4 [37]). The photoemission process is the most known and studied process involving hot electrons (Figure 1a), since it can provide very useful information about the energy level distribution inside a material and its surface properties. Only a small number of the photoexcited hot electrons are actually extracted from the material, since such extraction processes compete with the faster carrier relaxation ones. Indeed, the extremely fast relaxation processes that convert carrier energy into heat (Figure 1b) are the limiting factor in the use of hot electrons for chemical or physical processes at the metal surface. The energy of a hot electron can be defined as positive or negative accordingly to its energy with respect to the vacuum level. In case of negative hot electron energy, the electron is bound to the nanostructure as the acquired energy is not high enough for extraction, however this is an electron with energy higher than one arising from a simple thermal excitation. Such electrons are of particular interest in chemical and charge transfer applications, since they can fill unoccupied levels of acceptor molecules adjacent to the metal surface or induce a photochemical transformation (Figure 1c - 1d).

Some of the advantages in generating these hot electrons with plasmons, are their ability to tailor the carrier energy distribution as well as the ability to localize the carrier generation spatially. High degree of control can be achieved over their generation, and thus over the photo-excited process that can take place [38]. A wide range of studies are tackling the microscopic mechanism of plasmon decay [38], describing it in classical term (as was done in the previous chapter with the Drude model), or by introducing quantum effects, since plasmons

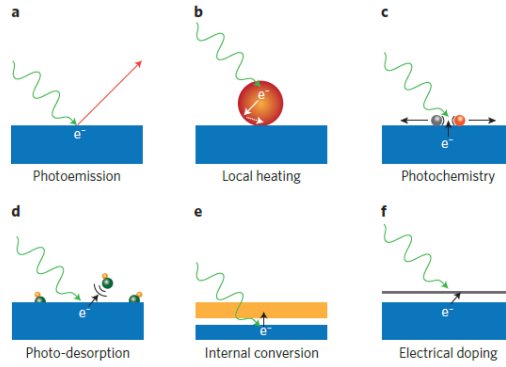


Figure 2.4: *Variety of processes that hot electrons can stimulate.*[37].

can be considered to be fundamentally quantum mechanical [39–41]. However, only *ab-initio* calculations that take into consideration the whole electronic band structure are able to capture effects beyond the free electron limit [38]. Moreover, as the time scales of the excitation processes are quite different, as are the sizes of the devices and the constituent plasmonic elements, it is very difficult to find a unifying theory. In Fig. 2.4 it can be observed where different theoretical approaches become useful at different stages of the energy transfer process. The following subsection outlines the main concepts behind each step, providing an overview of the current understanding of the hot carrier processes.

2.5.2 Hot carrier generation

As photons and surface plasmons are characterized by small momenta, compared to those of electrons, the decay of a plasmon is able to generate only electron-hole pairs with zero net crystal momentum, and only above a certain interband transition energy [38] (direct absorption process). At lower interband energy, absorption and emission of phonons allows the plasmon decay to conserve the momentum and excite different electronic states (indirect absorption process). Something else to consider is the localization of electronic states in a nanoscale system due to plasmon excitation. According to the Heisenberg principle this

localization in space imposes an uncertainty on the momentum eigenstates. Such quantum mechanical effects allow a finite probability for a direct plasmon decay, with the generation of an electron-hole pair of finite momentum and energy lower than the interband threshold. This process is called geometry-assisted intraband transition [38, 42] and the momentum difference for the transition is provided by the nanostructure. From previous observations, it becomes clear that a complete understanding of the processes involved in hot carrier generation, requires accounting for material properties, energy bands and geometry effects [38, 43].

Different theoretical approaches are usually used to describe the different contributions to hot carrier generation, and an understanding of the different parameters involved is necessary for a more complete and descriptive model. In general, the geometry effect is usually treated in quantum mechanical terms. The free electron/ jellium model is the most widely used and its approximation is based on solving the Schrödinger equation for the electronic states in the geometry and then use the golden rule of Fermi to calculate the transition rate between these states [44]. On the other hand, material effects are related to the band structure. Indeed, direct transitions are very sensitive to the band structure due to Fermi's selection rule. Energy effects define, with respect to the structure taken into consideration, which kind of process is dominant in the excitation of hot carriers. For example, direct transition dominates above the interband threshold even for small particles (~ 10 nm) [38]. Whereas phonon-assisted and geometry-assisted intraband transition compete below such threshold [38]. We can conclude that a combination of *ab-initio* calculations and free electron/jellium calculations are needed to understand the different contributions involved to the process of plasmon decay.

2.5.3 Hot carrier transport

The generation of hot carriers happens, with finite probability, according to a precise distribution of initial momenta and in any possible spatial location in the plasmonic material. After being generated, these carriers will travel through the material and experience scattering by electrons, phonons and crystalline defects. Such events will thermalize the carriers, and their energy distribution will condense around the Fermi level of the metal. However, practical applications of hot carrier require energies far from the Fermi level as more energetic carriers are able to more efficiently drive reactions in molecules or cross Schottky barriers towards semiconductors [38, 45] (as further study in Chapter 5 will outline). In these cases, collecting the carriers before scattering processes reduce their energy becomes the challenge for plasmonic hot carrier applications.

Carrier transport in a material is usually studied in one of two possible regimes: ballistic and diffusive. Ballistic transport describes a situation where a carrier is rarely scattered within the characteristic dimension of the nanostructure [38]. Diffusive transport, on the other hand, uses small perturbation from the Fermi-Dirac distribution to describe the spatial variation in the carrier's energy. Common plasmonic structures are in an intermediate regime between the two. Such regime is usually treated using Boltzmann equation with a spatial dependence [38].

Ultrafast pump-probe measurements of plasmonic nanostructures [38] can provide a picture of how the energy distribution of excited carriers evolves as function of time. Typically, these kind of studies are characterized by a fast initial rise (10-100 fs) of the pump-probe signal due to electron-electron scattering that converts the few high-energy carriers into a larger number of lower energy ones [38, 46]. The next step is a slower decay (100 fs to 1 ps) that is attributed to electron-phonon scattering events (energy exchange in the case of

electron-phonon scattering is very low due to the Debay energy of the ions). This behaviour is described by a "two temperature model" [38,46], where different temperatures are assigned to the electron, T_e , and the lattice, T_l . According to such model, the collision probability in the phase space describing the position/momenta of the electron increases quadratically with the energy difference from the Fermi level (E_f), and the lifetime drops accordingly as $(E - E_f)^{-2}$ [38,46]. The two-temperature model can be used to extract phenomenological estimates of electron and phonon coupling strengths and relaxation times. However, such information is related to the already thermalized electron distribution, not providing information on how to use such hot carriers. The full analysis of the transport of plasmonic hot carriers that can describe the generation of hot carriers and their distribution, requires solving the Boltzmann equation in spatial term [47]. *Ab-initio* calculations show that the energy is distributed uniformly between zero and the Fermi level [47] after excitation. Thus, electrons excited through collisions can be considered energetic as well and need to be treated as hot carriers. As Direct transitions create low energy electrons and high energy holes, scattering processes thermalize them to equilibrium in quite short distances (100 nm [38]). As more energetic carriers can drive more easily reactions, considerations on how hot carriers diffuse and lose energy inside the plasmonic structure are needed. Indeed, by understanding the transport mechanism, the distance at which the extraction of the energetic carriers must occur can be designed. A more in depth study, introduced by *Cortes et al.* [48], phenomenologically investigates the hot carrier extraction with respect to the plasmon excitation by monitoring a chemical reaction. In this paper the experimental demonstration of how high energetic carriers' extraction is facilitated by the geometrical factor of the nanostructure is presented.

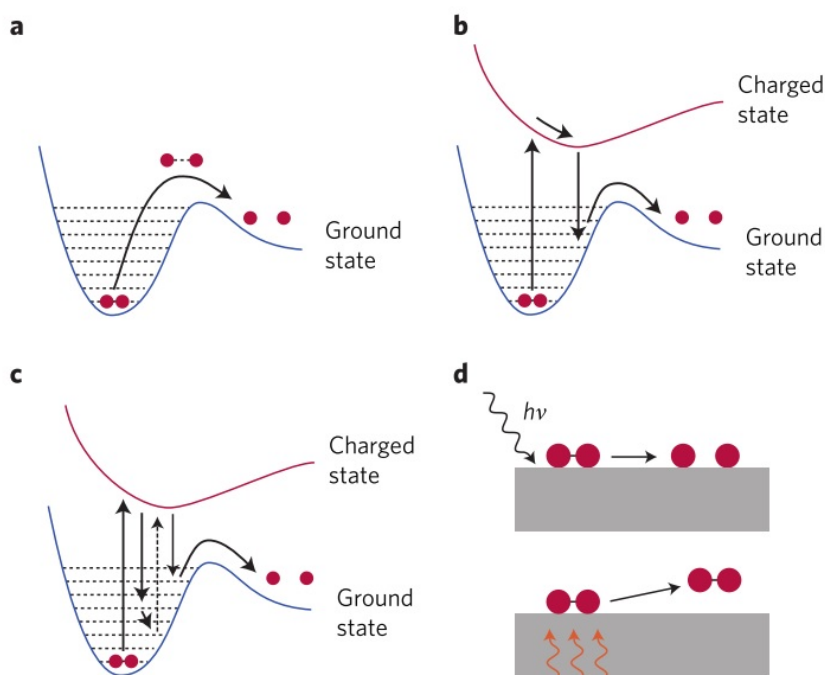


Figure 2.5: *a) Thermal activation for the dissociation of a diatomic molecule. The diatomic molecule remains on the ground-state potential energy surface (PES) for all points along the reaction coordinate. b) Electron-driven dissociation of a diatomic molecule. Injection of an excited electron promotes the molecule to a new PES, thereby inducing nuclear motion. This charged state then decays, which drops the molecule back down to the ground state while populating a higher vibrational mode. c) At high photon flux, subsequent electron injections can occur before the molecular vibration has fully dissipated, thus leading to additional vibrational excitation and a superlinear dependence of the rate of reaction on light intensity. d) Electron-driven reactions (top), for example on plasmonic metal nanoparticles, can potentially target certain chemical reaction pathways that are otherwise unselective in purely thermal reactions (bottom).^[46]*

2.5.4 Hot carriers collection

While talking about the collection and use of these energetic charge carriers, the focus is on their use for photochemical transformation, or, more generally, on chemistry-oriented applications. Indeed, the high field from a plasmon can yield a great number of energetic charge-carriers, which can induce a photochemical reaction either through localized heating or by injection of energetic charges into the adsorbed reactants [46].

The quantum processes usually involved in chemical reactions can be linked to two main "trigger" mechanism: One related to the phonons present in the nanoparticle and one related to the energetic carriers generated in the nanoparticle [46]. Chemical reactions, such as ammonia synthesis, hydrocarbon reforming and the oxidation and hydrogenation reactions are generally triggered by the thermal heating of catalyst nanoparticles [46]. In this process the phonon modes of the nanoparticles, excited by scattering processes (Landau damping) of the energetic carriers, couple with the vibrational modes of the adsorbates. Such coupling, followed by a transfer of energy, allows the evolution of the adsorbate from the reactant to the product state while maintaining the system in the ground state (Fig 2.5) [46]. This type of reactions are completely controlled by the ground state free energy, and the temperature of the nanoparticle. The other kind of "trigger" mechanism exploits the excited charge carriers on the metal surface, as such carriers are able to temporarily populate otherwise unpopulated electronic states. They form transient ions centred on the adsorbate molecule, that forces a transition of the adsorbate from the ground to an excited state. As a results, forces are induced on the different atoms (Fig 2.5) and these forces can bring about nuclear motion allowing a chemical transformation to take place [46]. This mechanism is known as Desorption Induced by Electronic Transitions (DIET). At the heart of this mechanism is the coupling between the excited carrier state and the vibrational state of the adsorbate. In fact, the energy of the charge carrier is converted into kinetic energy of the molecule. Moreover, in contrast to the case of phonon-driven reactions, charge carrier-driven ones are able to pump energy selectively into a specific vibrational mode of the adsorbate. This allows for a selective increase of the adsorbate temperature with respect to the phonon temperature of the nanoparticle and of other adsorbate vibrational modes [46, 49] (Fig. 2.5). However the requirement for high-intensity light on

bulk metal surfaces has made charge-driven chemical reactions on metals difficult for practical applications. The case of a nanoparticle differs thanks to the possibility of plasmon excitation and high yield of carrier generation. *Christopher et al.* [50, 51] suggested that charge carrier conversion is fundamental in activating the oxidation reaction on the surface of a cluster of small Ag nanocubes. These studies outline the fact that all oxidation reactions are controlled by the overall rate of dissociation of molecular oxygen. They postulated that the rate is enhanced by the creation of a transient negative ion, thanks to energetic electron generation. Other studies have also reported charge driven reactions, like the case of the reduction of nitroaromatic compounds absorbed on 6 nm Au nanoparticles illuminated by UVvis light [46]. Moreover bimetallic nanoparticles, comprised of a core of plasmonic material (Ag and Au have been used) with a shell of a more chemically reactive metal (for example, Pt and Pd), can also induce charge-carrier reactions [46, 52].

Of note are also the two possible mechanisms through which the transfer of the excited carrier can take place: direct and indirect. In the case of the indirect charge transfer mechanism, the energetic charge is first formed on the surface of the nanoparticle and then transferred to the adsorbate [53]. As we have seen previously, the energetic carriers are subject to very fast relaxation processes, and thus thermalize to energy close to the Fermi level in hundreds of femtoseconds. The lifetime of such thermalized carriers is longer, making their transfer to the orbitals around the Fermi level of the material more probable.

The direct charge transfer mechanism [53] is often called the chemical interface damping. In this case, the absorption of the photon is linked to the coupling of the plasmon to the available level of the adsorbate, and thus the scattering of the charge carriers through the adsorbate state [46].

The dynamics of these charge-carrier driven transformations are still full of

unresolved questions about the mechanism of the attachment of charges to the adsorbates on the surface of excited nanoparticles, and there is a need for more basic research aimed at the development of models fully describing such processes [54–57].

Part II

Nanomanipulation at the nanoscale

Chapter 3

Porous Supercluster metamaterials

Here, porous supercluster metamaterials are introduced as a design capable of reducing diffusion time of the target molecule towards the nanoantenna. This novel design tackles the diffusion problem with its porous nature, introducing what can be called a passive nanomanipulation concept. Indeed, Self-Assembly of complex plasmonics structure can represent an alternative to classical optical tweezers by offering thousand of hotspots and a porous structure capable of allowing molecular diffusion inside. Controlled manipulation of the target molecule/particle is not possible in this system, however a straightforward fabrication procedure and plasmonic properties spanning over the spectral region typical of molecule and adsorbate attract interest towards this type of system. In this section the optical properties of supercluster metamaterials are studied and a technique to image and exploit the complex porous structure is presented. Moreover the ability of the system to host molecules is studied as well as its use for extremely efficient Surface Enhanced Raman Spectroscopy (SERS) measurement.

3.1 Nanomanipulation

As Maxwell's equations predict that a light field has the ability to carry momentum, it can then apply a force on objects by interacting with it. However, the relatively small momenta of which the field is capable at non-damaging optical powers imply the generation of forces negligible in most situations. For example, a mirror in vacuum will experience an optical force of $F_{\text{optical}} = 2 * P/c$ when reflecting a normally-incident laser beam of power P by 100% (c being the light speed in vacuum). The magnitude of such force is in the pico-Newton range for a beam power of 1 mW [58]. While such a magnitude is unimportant for most applications, this is not the case for the nanoworld, where forces in the pico-Newton range are extremely suitable [6, 59]. The field of optical trapping and manipulation was founded and pioneered by Arthur Ashkin in the early 1970s. He was the one that invented the now widely used method of optical tweezers, in which a highly focused laser beam is used to trap small objects at its focus in all three dimensions [58, 60]. Thanks to the non-invasive nature and high spatial confinement nature of such a technique, optical tweezers have proved themselves to be powerful tools for several applications, such as single molecule force spectroscopy, particle sorting and for driving microscale motors [61–64].

Optical trapping based on far-fields, e.g. traditional optical tweezers, faces performance limitations due to the diffraction limit [65, 66]. This makes it difficult to trap and position objects, and has led to an increased interest in near-field-based optical-trapping methods. Satoshi Kawata et al. demonstrated the optical trapping and propulsion of particles by evanescent fields generated by total internal reflection [66]. Optical manipulation has been performed using a wide range of structures capable to enhance optical performance [67–70]. Moreover these structures present the opportunity for large-scale integration with opti-

cal silicon-based technologies or biological lab-on-a-chip. Compared to photonic structures based on dielectric materials, surface plasmon resonance structures permit light to be strongly localized at sub-wavelength scales. Surface plasmon structures offer additional advantages for their use in integrated optical manipulation chips. Their resonances are broad, fabrication does not require many steps, and the devices are extremely small. The concept of nanometric plasmonic tweezers was proposed by *Novotny et al.* [71] and many efforts have been made in this field since then. However, the heating associated with the Ohmic loss accompanying plasmon excitation can have substantial effects, making tight and stable plasmonic trapping difficult.[72, 73]. In some cases, the illumination of a plasmon structure with a laser beam of moderate power can even result in boiling the water, in which the optical trapping is performed [58] This motivates the development of thermal management approaches for plasmonic optical traps or the development of novel strategies capable of circumventing the problem. Herein, in this chapter, building on the optical trapping theory introduced previously, we discuss novel design consideration for plasmonic trapping taking into consideration two fundamental parameter: heating and diffusion.

Indeed, in order to exploit the strong field enhancements for sensing or trapping applications, what becomes critical is the diffusion of the molecules/adsorbates towards the surface of the metal and thermal management to avoid unwanted temperature related forces to appear. The challenge of guiding nanoparticles towards specific locations has been tackled with a wide range of different techniques, most of which use highly confined optical fields. However, such techniques are often limited by the time that the particle takes to diffuse towards the strong and localized field of the trap. Here, a possible solution to this problem is introduced. The design and study of the optical properties of a porous supercluster metamaterials are performed. In such systems the diffusion problem is avoided

by the porous nature of the structure itself, as it allows for molecular diffusion inside the small gap of its structure. Moreover as the system is characterized by large volume with respect to the excitation region, it allows for fast dissipation of the heat generated by plasmonic losses.

3.2 Self-Assembled supercluster

Self-assembly of nanoscale building blocks into hierarchical superstructures is quickly becoming one of the most pursued topics in nanomaterials science [74–76]. The possibilities obtainable when individual components arrange themselves into an ordered assembly are limitless and of great interest, as some biological self-assembled structures such as DNA, opals and proteins have demonstrated [77–79]. An extensive amount of literature exists on different strategies for the synthesis of self-assembled structures [80,81], however complications arise when a high degree of control is sought over the process. For example, controlled 3D self-assembly of nanoparticles (NPs) is possible utilizing templates with specificity to certain types of particles, such as those achieved by DNA-origami techniques, amongst others [82–85]. However, advanced techniques such as these restrict the surface functionalization of the NPs, thereby negating one of the most important benefits that these structures offer – the ability to control the functionality of the building blocks [86]. Moreover, such particle-by-particle self-assembly methods limit the amount of constituents forming the superstructures to only a few of them, i.e in the range of 10s. Recently, the generation of spherical colloidal crystals with functionalizable building blocks has been demonstrated using a novel self-assembly process based on emulsion formation in the nanoparticles solution [86]. The introduction of plasmonic materials as building blocks of a spherical colloidal cluster is easily achievable, making possible the engineering of materials with complex optical properties and opening up exciting new directions

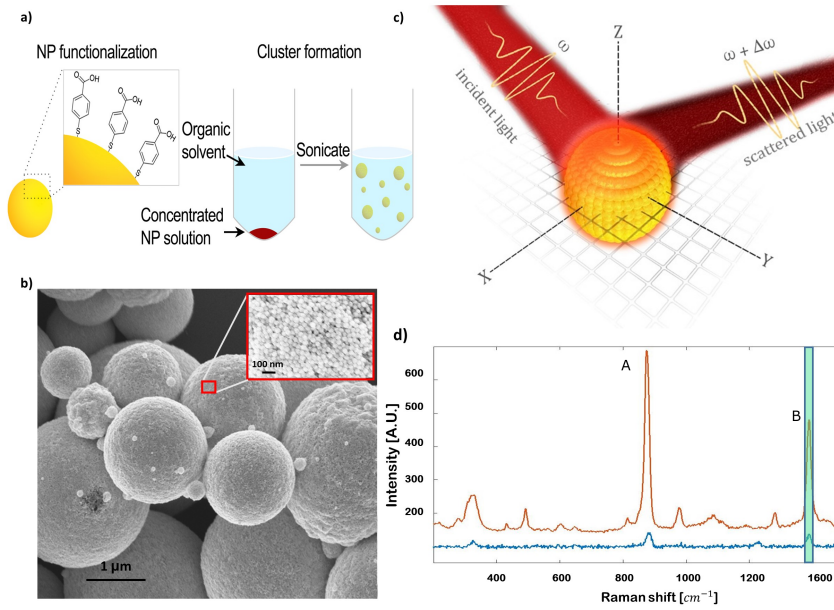


Figure 3.1: *a)* Schematic representation of the functionalization and self-assembly of metallic nanoparticles into superclusters. *b)* SEM image of the superclusters and typical size dispersion observable after drop-casting. The inset shows a zoomed area of one supercluster, with the small gold NPs tightly packed and separated by a distance dictated by the size of the ligands on NPs surfaces. *c)* Schematic representation of 3D mapping of the plasmonic mode using the SERS signal from the 4-MBA Raman marker. The spherical supercluster is excited from the top at different wavelengths, and the signal from a specific XY plane is recorded using a confocal microscope set-up. A series of equally spaced 2D XY planes in the Z direction is used to completely map the plasmonic mode of the cluster. *d)* SERS signal for the 4-MBA Raman marker measured on semi-isolated 40 nm gold nanoparticle (blue line) and on 40nm gold particles assembled into a spherical supercluster of 770 nm of diameter (red line). The signal of the 4-MBA Raman marker is characterized by peaks at 1100cm^{-1} (**A**) and at 1590cm^{-1} (**B**) [90].

in sensing, manipulation and metamaterials research[87–89].

Spherical colloidal clusters, built from plasmonic building blocks, have been proposed to possess remarkable collective supermodes with large local field enhancements [31, 86, 91, 92] and a spectral response extending from the near-infrared to deep into the mid-infrared region [86]. As such, these superstructures hold great promise as a sensing platform that is capable of addressing the whole spectral domain of vibrational molecular fingerprints [93, 94], while simul-

taneously exploiting the advantages of their plasmonic constituents and of their porous structure. Previously, dark-field spectra of plasmonic superclusters [86] indicated an existence of collective plasmonic modes in these structures, however, no direct experimental verification has been obtained to date. This ability to access thousands of hot-spots upon the excitation of a collective mode inside the supercluster metamaterials enables high signal-to-noise ratios - something that is of great significance in sensing and nanomanipulation applications.

3.3 3D Raman Tomography

Different techniques have been employed in the past to visualize the near fields of simple plasmonic structures [95–97], however obtaining similar field maps of complex three-dimensional (3D) plasmonic materials [98–100] still remains very challenging. One possibility that has been exploited in the past is photoluminescence microscopy [101, 102], which relies on detecting the fluorescence of dye molecules next to plasmonic structures. However, in the case of colloidal plasmonic superclusters, the compactness of the array of nanoparticles would result in a strongly quenched fluorescence of the dye molecules [86, 103, 104]. Other techniques utilized for this purpose are Electron Energy Loss Spectroscopy (EELS) [105], cathodoluminescence [106] and Near-field scanning optical microscopy (SNOM) [107–109]. However, these methods are limited to the surface of the plasmonic structures, making it difficult to inspect collective modes inside the superclusters. In contrast, techniques relying on surface-enhanced scattering, such as SERS (Surface Enhanced Raman Spectroscopy) [110–112] and Surface-Enhanced Infrared Spectroscopy [113, 114], are an alternative to 3D inspection of electric field distribution inside complex structures. Indeed, SERS signal gives a direct and extremely sensitive measure of the near-field intensity enhancement [115–118], due to forth power dependency on the (local) electric field. Further-

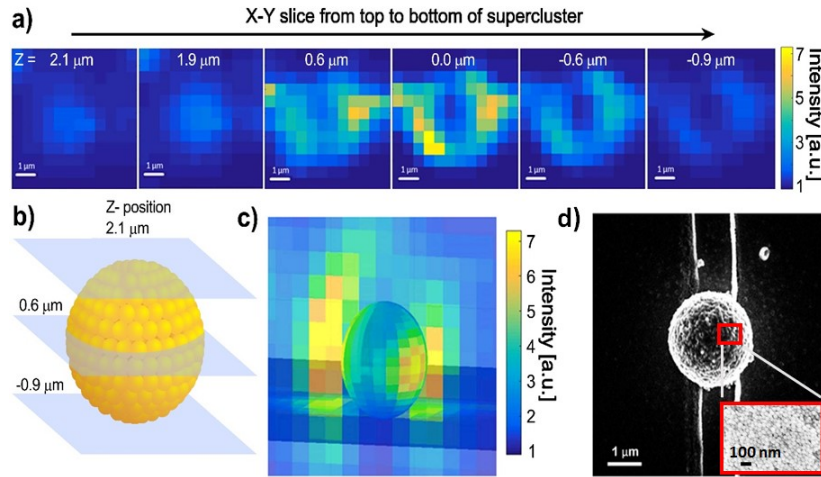


Figure 3.2: *a)* XY Raman maps following the intensity of the B peak of the 4-MBA molecular probe, when excited with a 785 nm CW laser and circular polarization. The 2D planes are taken at different Z values, with Z being the axis along the height of the spherical cluster and $Z = 0$ being slightly lower than the expected center of the supercluster. *b)* 3D reconstruction of the plasmonic mode excited in the spherical supercluster by staking all the 2D Raman map along the Z axis. *c)* Scanning Electron Microscope (SEM) image of the spherical supercluster ($1.61\mu\text{m}$ of diameter).

more, Raman scattering is an optical property that is not afflicted by quenching issues, and thus easily adaptable to 3D inspection of complex structures.

Here an approach to perform 3D tomography of near-field intensity inside a supercluster by exploiting the SERS signal of a molecular probe (4-Mercaptobenzoic acid, 4-MBA) is presented. Specifically, plane-by-plane intensity maps of the local plasmonic near-field are extracted by measuring the Raman spectra of the probe molecule with a confocal microscope. In this way, collective modes are mapped inside supercluster structures of various dimensions providing experimental proof of their existence. The spherical colloidal superclusters were fabricated by self-assembly following the procedure outlined by V. Turek et al. [86]. Firstly, an ultra-concentrated solution of gold nanoparticles was obtained by centrifuging 1 mL of the gold nanoparticles with $100\mu\text{L}$ of an immiscible solvent, dichloroethane, in a 2 mL polypropylene centrifuge tube. The gold nanoparticles pass into the dichloroethane (DCE) phase during centrifugation, resulting in a

small aqueous pellet of ultra-concentrated nanoparticles sitting at the bottom of the centrifuge tube. The aqueous phase is pipetted off to leave the dichloroethane and the ultra-concentrated nanoparticle pellet which is then sonicated for 10 s. The sonication forms a microemulsion, grouping the nanoparticles into solid spherical clusters. The clusters were pipetted onto glass substrates and allowed to dry. The dried substrates were then soaked for a minimum of 24 hours in a fresh solution of DCE to remove residual contaminants which arose from the contact of DCE with the polypropylene centrifuge tube. After soaking, the substrates were dried under nitrogen and stored for later analysis. The only difference from this previously proved workflow was the pre-functionalization of the 40 nm ultra- concentrated gold nanoparticles with the 4-MBA molecular probe prior to assembly process (Figure 3.1 a).

4-MBA was chosen as it is one of the most widely used Raman probes for evaluating SERS in plasmonic structures over a large range of wavelengths [119]. Its popularity is based on an easy and uniform self-assembly on Ag and Au surfaces (thanks to its thiol group), ensuring the presence of the Raman probe inside the extremely small gaps of superclusters. Furthermore, it has high Raman cross-section in the IR and mid-IR [120, 121], i.e. in the spectral regions where the superclusters are expected to have optical resonances. The presence of 4-MBA post-functionalization was confirmed by measuring Raman scattering from a layer of nanoparticles drop-casted on a glass substrate. The blue curve in Figure 3.1d shows a Raman spectrum typical for the 4-MBA, characterized by two strong distinctive peaks at $1100\text{cm}^{(-1)}$ (peak **A**) and at $1590\text{cm}^{(-1)}$ (peak **B**), corresponding to the ν_{12} and ν_{8a} aromatic ring vibrations respectively [122–124]. Next, the pre-functionalized building blocks were self-assembled into spherical colloidal clusters using the previously mentioned methods. A large drop containing clusters with sizes between $0.5\mu\text{m}$ and $3\mu\text{m}$ was then drop-casted onto a glass

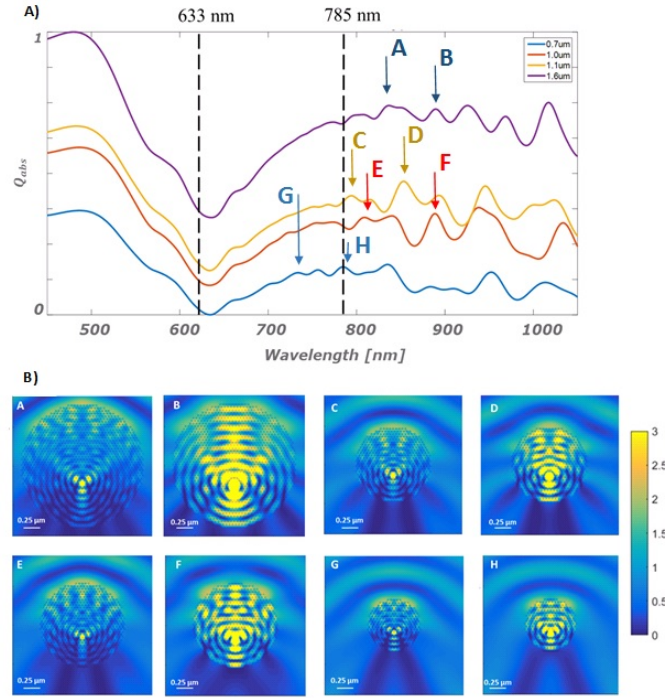


Figure 3.3: *a)* 2D FDTD simulations of the optical response of superclusters of different diameters. Supercluster is simulated as infinite cylinder in 2D to reduce computational weight. A) High variability in the absorption cross-section is observed with small diameter changes that reflect the appearance and disappearance of a plasmonic modes in the near IR. *b)* H/H_0 , normalized magnetic field enhancement for the different peak outlined in the absorption cross section. We can observed that collective mode for cluster larger than $1\mu\text{m}$ can only be excited only further out in the infrared.

slide, patterned with a grid to aid their localization throughout the characterization process. The red curve in Figure 3.1 d shows a representative SERS spectra from an assembled superstructure, exhibiting no changes in spectral features with respect to the non-assembled particles. It should be noted that, although the SERS intensity in the case of supercluster is higher, no direct comparison of the enhancement values can be made, as the number of gold nanoparticle in the focal volumes for the two cases is different (due to the three-dimensionality of the cluster).

Plasmonic near-fields of single superclusters were mapped as shown diagram-

matically in Figure 3.1 c. By scanning the laser focus in the X-Y plane and then repeating these measurements at different Z-position across the height of the cluster, Raman scattering spectra from the entire structure were acquired. The resolution in the X, Y and Z direction was diffraction limited as for an optimized confocal set-up (280nm for 633nm excitation wavelength and 340nm for 785nm excitation wavelength). 2D Raman intensity maps were then extracted from the scattering spectra by integrating the SERS signal across peak B of 4-MBA, using a digital filter extending from 1561 to 1621 $cm^{(-1)}$ (as shown in green in Figure 3.1 d). Figure 3.2 a, shows some of the resulting maps obtained for a $1.6\mu m$ supercluster at 785nm excitation. These series of 2D maps were then joined using Matlab to create a 3D tomographic image of the enhanced SERS signal (Figure 3.2 b) for this cluster. The diameter ($1.6\mu m$) and, more importantly, the position of the cluster were confirmed by SEM (Figure 3.2 c), with the latter being used to correct for any drifts of the scanner during data acquisition. As the Raman process for a molecule next to a plasmonic structure benefits from both the emission and excitation enhancements [125], the intensity of a SERS process can be approximated by $SignalDetected \approx |E|_{Exc}^2 * |E|_{Em}^2 \approx |E|_{SERS}^4$. This 4th power dependency outlines that the intensity of SERS (i.e. a molecule in a plasmonic environment) is a very sensitive parameter of the strength of the local field. Given this relation between SERS signal and plasmonic enhancements [111,126–128], the 3D tomography is a reliable representation of the plasmonic mode excited in the spherical cluster.

Figure 3.2 a-b outline the enhancement of the Raman signal in the $1.6\mu m$ supercluster at 785 nm excitation. The strongest signal is present on the edges and on the top of the cluster, while only a weak signal is present inside. This suggests that, at 785 nm, a cluster of this dimension is mainly scattering light and not absorbing it, resulting in a shallow excitation of the electric field inside

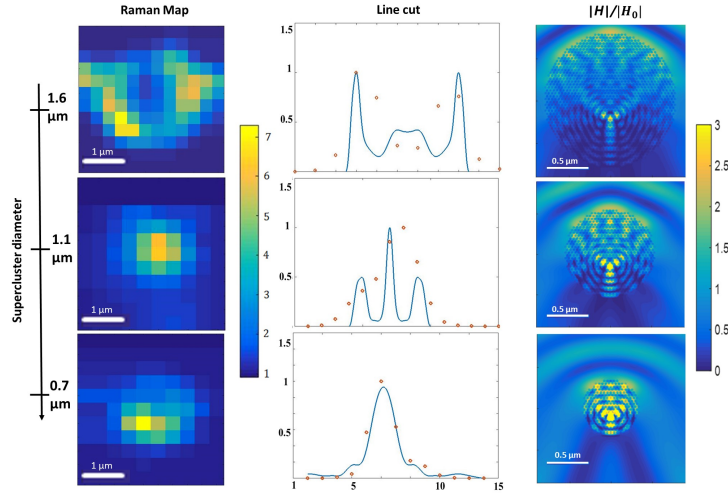


Figure 3.4: *a) Generation of a mode inside a spherical supercluster as the size of the particle is reduced from 1.6 μm to 0.77 μm . In the first column, experimental XY Raman maps are presented for different supercluster sizes (1.61 μm , 1.11 μm and 0.77 μm). Raman maps were obtained by following the intensity of the B peak of the 4-MBA when excited with a 785 nm CW laser and through the center of each cluster. The last column shows the corresponding XZ maps obtained from FDTD simulations of the magnetic field enhancements. The middle column compares the experimental (scatter points) and theoretical (solid lines) cross-sections of the electric field enhancement maps through the center and along the X-direction of the clusters.*

the structure and an enhanced signal present only on the surface. In order to investigate the preliminary results obtained by SERS mapping, finite-difference time domain simulations were performed [129], allowing to assess both the spectral and near-field properties of the structures. The numerical simulations substantiated the experimental results obtained in Figure 3.2b where no collective mode was observed in the infrared for a supercluster with a diameter of 1.6 μm (Figure 3.3).

Following this finding, the theoretical studies were expanded in order to understand when the excitation of a collective mode inside the supercluster was possible. In Figure 3.3a the normalized absorption cross-section is shown as the diameter of the cluster is varied between 1.6 μm and 0.7 μm . It was found that, in the mid-IR, the absorption of the cluster varies strongly with the diameter

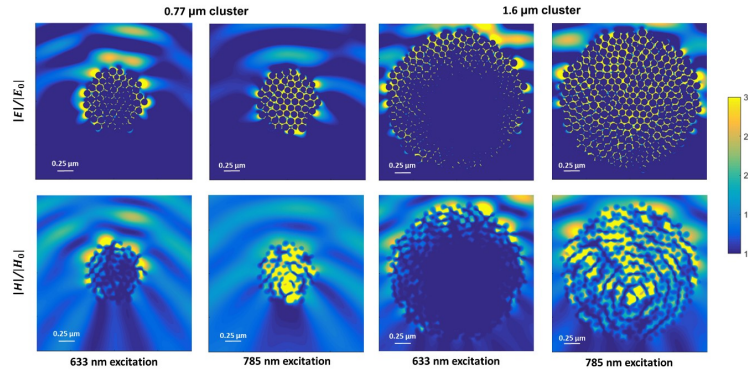


Figure 3.5: *2D FDTD simulation of Supercluster metamaterials with 2nm inter-particles distance and nanoparticle diameter distribution centred at 40nm and with a standard deviation of 3.5 nm to study crystalline defects effects on collective resonance. Missing nanoparticles in the overall structure have been also randomly introduced.*

and coherent collective modes appear at 785 nm only when the diameter of the cluster is less than $1\mu m$. This suggests that, as the diameter of the supercluster is reduced, the excited collective mode starts to internalize and, as the size is reduced further, this process becomes more efficient. This stipulation was supported by the results of FDTD simulations of the near-field intensities inside superclusters of varying diameters ($1.6\mu m$, $1.1\mu m$ and $0.7\mu m$), excited at 785 nm (see last column of Figure 3.4). It should be noted that the simulations of the near-field intensities hold also when the structure simulated is not perfectly crystalline as shown in 3.5, when different possible defects were introduced inside the supercluster structure. To confirm these theoretical expectations, Raman tomography was performed on similarly-sized superclusters. The first row of Figure 3.4 presents large area 2D Raman scans of the three different superclusters excited at 785 nm, taken exactly through the vertical center of each.

From the SERS map it can clearly observed that as the diameter size of the cluster is reduced, an internal collective mode start to be excited. This can be seen in the second row of Figure 3.4, where the integrated Raman intensity of the B peak of 4-MBA is plotted across the supercluster center. As the cluster

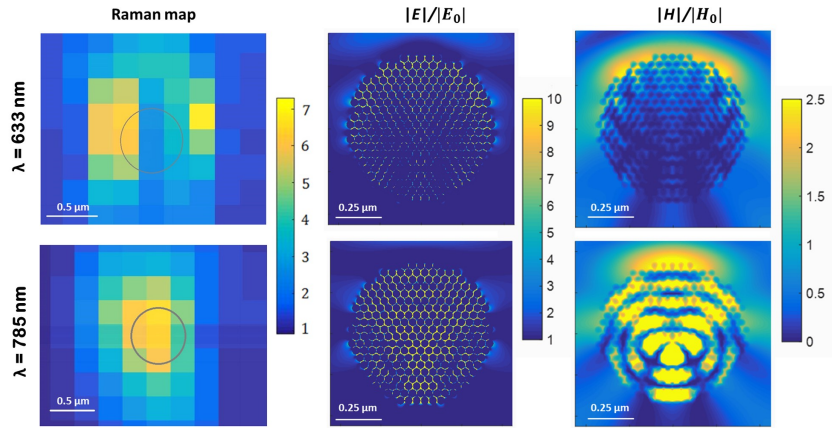


Figure 3.6: *a) Top and bottom rows correspond to 633 nm and 786 nm excitation respectively. The first column shows the experimentally-obtained Raman maps in the XZ plane. The other two columns compare these results to FDTD simulations: the calculated electric field enhancements (E/E_0) and magnetic field enhancements (H/H_0) are shown in second and third columns respectively.*

dimension reaches $1.1\mu\text{m}$ in diameter, an internal collective mode is excited, and all the pixels across the center of the particle show a coherent field enhancement. Moreover, as the size of the supercluster is reduced even further (to $0.77\mu\text{m}$), the field enhancement from the central pixel of the spherical cluster likewise increases further. Such behaviour is consistent with the simulations presented in the last row of the same figure, where similar observations can be made about the magnetic field distribution inside the different clusters. Finally, the near-field distributions for the smallest spherical cluster was evaluated ($0.77\mu\text{m}$) for different excitation wavelengths. In particular, in Figure 3.6, the mapping by SERS and the Finite-Difference Time Domain (FDTD) simulations were compared for a cluster with a diameter of $0.77\mu\text{m}$ and excited at 632 nm and a 785 nm. The first row of Figure 3.6, presents the two SERS maps of the plasmonic mode visualized on the X-Z plane at the center of the cluster, as extrapolated by the 3D reconstruction.

The dark grey circle represents the expected position of the particle with

respect to the grid structure around it, as determined from SEM microscopy. From the SERS maps it can be seen that when the spherical cluster is excited at 632 nm, the electric field enhancement is present only on the edges of the particles with no seepage inside and a signal enhancement spatially defined only by our laser penetration depth (similar to what observed in supercrystal system with normal SERS measurements [130]). This is corroborated by the electric field FDTD simulations presented in the second row of Figure 3.6. Indeed, from the calculations, it can be seen that the field is scattered from the spherical cluster towards the excitation direction and electric field enhancement is present only on the outer layer of particles forming the cluster. On the other hand, when the excitation wavelength is switched to 785 nm, a completely different profile is obtained. From the Raman maps the presence of field enhancement over the entirety of the cluster is observed, especially with a stronger field localized at the center - in other terms, the collective plasmonic mode is excited inside the cluster. The presence of an internal collective mode can also be seen from the field enhancement simulations, where for the 785nm strong field enhancements in almost all the inside gaps of the spherical cluster is present. This observation can become even clearer by looking at the magnetic field distribution whose variations are less abrupt. In the third row of Figure 3.6 the magnetic field distributions inside the $0.7\mu m$ cluster are shown for the two excitation wavelengths. While at 633 nm the magnetic field distribution clearly shows that no plasmonic collective mode is excited inside the supercluster, at 785 nm the field distribution of a mode similar to what can be found in a transparent cylinder can be observed [86, 129] as well as the beginning of an internal collective mode. Indeed, if not for the presence of a collective mode, the internal excitation of the structure would not be possible as the LSPR of the single nanoparticles is centered at 530 nm with negligible extinction contribution at 785 nm. This internalization of a mode was

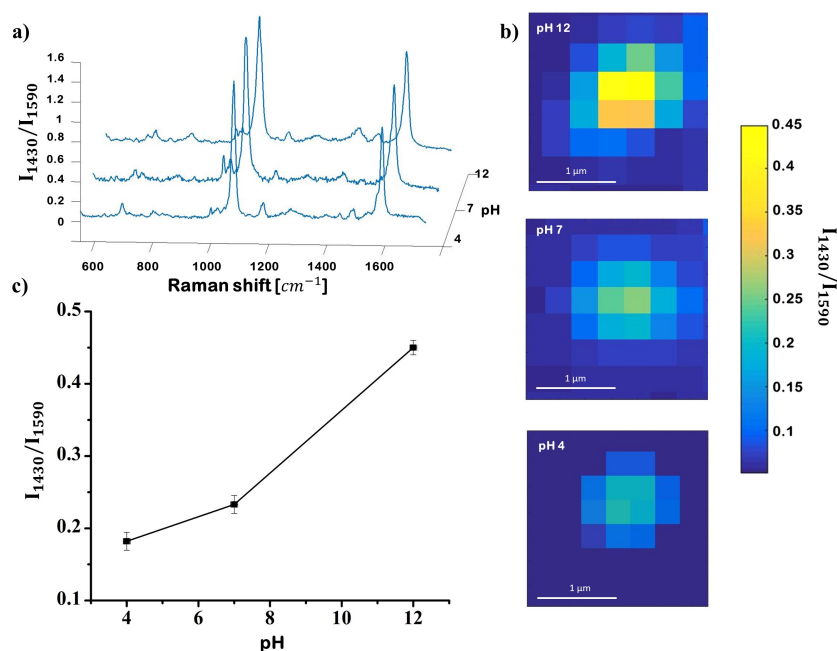


Figure 3.7: *pH sensing with a single supercluster excited at 785 nm.*) Panel a) presents the spectra for clusters exposed to solutions of three different pH values. As pH was increased, a peak at 1430cm⁻¹ appeared, corresponding to the stretching mode of MBA after deprotonation of its carboxyl group. b) 2D Raman maps on the same supercluster for the different pH values show that signal from the stretching mode is originating from the entirety of the supercluster. c) The increase of the intensity of the pH-sensitive stretching mode of MBA relative to the pH-insensitive mode at 1590cm⁻¹, when exposing the supercluster to progressively higher pH values.

found to be consistent for clusters of comparable sizes, despite small variations in clusters geometry due to different sizes and different packing imperfections (Figure 3.5).

These optical modes can be extremely useful as the field enhancements are localized in each gap between the NPs. This is relevant to spectroscopy because large hot spots densities lead to larger interactions with the field and therefore improved detection [130]. Furthermore, the porous structure of the supercluster outlines its ability to uptake and host a huge number of molecules and exploit this large hotspot density [131]. To prove such characteristic of the superclusters pH sensing measurements were performed, taking advantage of the previously

characterized collective mode at 785nm. The pH sensitivity in the measurement comes from the changes in the Raman spectrum of 4-MBA due to protonation/deprotonation [132] of its carboxylic acid end group. Indeed, as previously reported [133], when 4-MBA is deprotonated (i.e. when $pH > pK_a$) a new vibrational mode appears at 1430cm^{-1} , representing the stretching of deprotonated ν_{8a} group (COO^-). This can be clearly observed in Figure 3.7 b, where three Raman spectra are presented for the same cluster that has been exposed to three different pH solutions: as the pH value is increased, the appearance of the new vibrational mode at 1430cm^{-1} becomes clearer. In order to confirm that the Raman signal from the new vibrational mode originated from the entirety of the supercluster structure, we also obtained 2D Raman maps (Figure 3.7 c) for clusters exposed to different pH values. Tracking the ν_{8a} (COO^-) mode progressively confirmed the diffusion of the protons inside the clusters, since the signal was coming from the very center of the supercluster and its distribution was consistent with the previously reported mode at 785 nm. This experiment as well as the observation of coherent collective modes inside of a cluster functionalized with 4-MBA after the process of self-assembly (Figure 3.4), proves the ability of this system to host small molecules in its porous structure. Finally, the response of the supercluster to pH was measured by quantitatively evaluate the ratio of intensities of the pH-dependent ν_{8a} (COO^-) peak at 1430cm^{-1} and the internal standard vibrational mode at 1590cm^{-1} . Figure 3.7a shows that, unlike the previously reported measurements involving single gold nanoparticles [133], the deviation of the pH sensing measurements was statistically insignificant compared to the change in the qualitative response of clusters. Thus, superclusters are capable of increasing the pH sensitivity of the constituent gold nanoparticles by presenting a coherent ensemble of hot-spots, and thus representing a valuable resource for high-sensitivity SERS measurements. Moreover, by being capable

of hosting large concentration of molecules inside their porous structure they present themselves as an interesting alternative to more common manipulation techniques.

3.4 Conclusion

In conclusion, superclusters plasmonic resonance have been studied in the visible and near infra-Red range by 3D Raman tomography. As the intensity of the SERS signal is strongly related to the field enhancement typical of a plasmonic resonance, collective modes inside Supercluster metamaterials have been experimentally analysed and reported for the first time thanks to this technique. The strong cumulative signal coming from the reported collective modes and the wide range of frequency over which they are available, outlines the Superclusters as a valuable resource for high-sensitivity SERS measurements and molecular spectroscopy. Moreover, given thier ability to host large concentration of molecules inside their porous structure they present themselves as an interesting alternative to more common manipulation techniques. Indeed, thanks to the large number of hot spots available that cover all the possible route inside the pouros matrix of the supercluster metamaterials, manipulation and sensing of molecules infiltrated inside their structure is an extremely interesting possibility.

Chapter 4

Dielectro-plasmonic tweezers

In the previous chapter a porous material was presented as an interesting solution in order to avoid the need of driving the target object close to the hotspot as well as to avoid unwanted thermal forces thanks to the large volumes involved and by compensating the need for high power by exploiting a large number of hotspot as a cumulative signal. However, the degree of freedom with which the target nanoparticle can be controlled are minimal and no flexibility is allowed. In this section instead, a solution capable of actively manipulate the target object is proposed by exploiting both electrical and optical forces. First the basic principle of Dielectrophoresis and optical forces are going to be introduced. Following that, a novel design of nanotweezer capable of merging electrical and optical forces in a seamless design is presented.

4.1 Nanomanipulation

As Maxwell's equations predict that a light fields has the ability to carry momentum, it can then apply a force on objects by interacting with it. However, the relatively small momenta of which the field is capable at non-damaging optical powers imply the generation of forces negligible in most situations. For example,

a mirror in vacuum will experience an optical force of $F_{\text{optical}} = 2 * P/c$ when reflecting a normally-incident laser beam of power P by 100% (c being the light speed in vacuum). The magnitude of such force is in the pico-Newton range for a beam power of 1 mW [58]. While such a magnitude is unimportant for most applications, this is not the case for the nanoworld, where forces in the pico-Newton range are extremely suitable [6, 59]. The field of optical trapping and manipulation was founded and pioneered by Arthur Ashkin in the early 1970s. He was the one that invented the now widely used method of optical tweezers, in which a highly focused laser beam is used to trap small objects at its focus in all three dimensions [58, 60]. Thanks to the non-invasive nature and high spatial confinement nature of such a technique, optical tweezers have proved themselves to be powerful tools for several applications, such as single molecule force spectroscopy, particle sorting and for driving microscale motors [61–64].

Optical trapping based on far-fields, e.g. traditional optical tweezers, faces performance limitations due to the diffraction limit [65, 66]. This makes it difficult to trap and position objects, and has led to an increased interest in near-field-based optical-trapping methods. Satoshi Kawata et al. demonstrated the optical trapping and propulsion of particles by evanescent fields generated by total internal reflection [66]. Optical manipulation has been performed using a wide range of structures capable to enhance optical performance [67–70]. Moreover these structures present the opportunity for large-scale integration with optical silicon-based technologies or biological lab-on-a-chip. Compared to photonic structures based on dielectric materials, surface plasmon resonance structures permit light to be strongly localized at sub-wavelength scales. Surface plasmon structures offer additional advantages for their use in integrated optical manipulation chips. Their resonances are broad-band, fabrication does not require many steps, and the devices are extremely small. The concept of nanometric plasmonic

tweezers was proposed by *Novotny et al.* [71] and many efforts have been made in this field since then. However, the heating associated with the Ohmic loss accompanying plasmon excitation can have substantial effects, making tight and stable plasmonic trapping difficult.[72, 73]. In some cases, the illumination of a plasmon structure with a laser beam of moderate power can even result in boiling the water, in which the optical trapping is performed [58] This motivates the development of thermal management approaches for plasmonic optical traps or the development of novel strategies capable of circumventing the problem. Herein, in this chapter, building on the optical trapping theory introduced previously, we discuss novel design consideration for plasmonic trapping taking into consideration two fundamental parameter: heating and diffusion.

Indeed, in order to exploit the strong field enhancements for sensing or trapping applications, what becomes critical is the diffusion of the molecules/adsorbates towards the surface of the metal and thermal management to avoid unwanted temperature related forces to appear. The challenge of guiding nanoparticles towards specific locations has been tackled with a wide range of different techniques, most of which use highly confined optical fields. However, such techniques are often limited by the time that the particle takes to diffuse towards the strong and localized field of the trap. Here another possible solution tackling this problem is introduced. A novel type of nanotweezer is designed by optimizing the coupling of two different driving forces: optical field and AC electric field. Such novel integration of two profound different approaches allow us to influence the target object at long distances reducing the diffusion time and increasing the efficiency of the trap. Moreover as the system is characterized by large volume with respect to the excitation region, it allows for fast dissipation of the heat generated by plasmonic losses and the elimination of unwanted thermal forces capable of disrupting the trap efficiency.

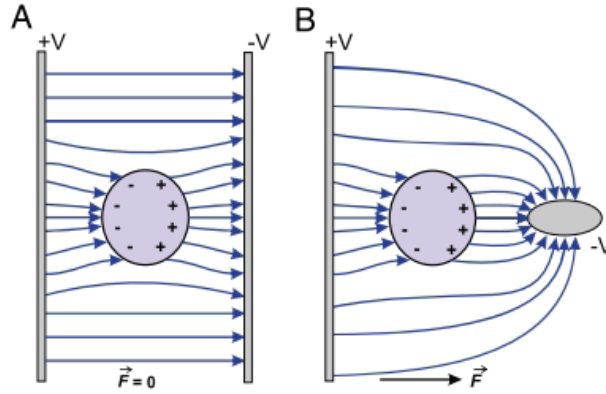


Figure 4.1: *Dielectrophoresis force [140]. Two different cases: Dielectrophoretic forces when the particle is placed in a uniform electric field (left); Dielectrophoretic forces when the field around the particle is not uniform anymore and the field gradient induces a net force on the particle (right).*

4.2 Dielectrophoretic Trapping

An interesting alternative to electromagnetic pressure is the use of dielectrophoretic forces [134–137]. Dielectrophoretic (DEP) forces have a series of interesting advantages such as: they act effectively on a wide range of dielectric particles; they use gradients of electric fields as trapping forces (like those provided by the sharp features of plasmonic nanoantennas). It is a well-established technique in a liquid environment [138, 139] and it can be easily implemented. Moreover, rapid development of lithography techniques have made feasible the fabrication of metal and/or insulator structures that can generate electric field gradients strong enough to manipulate and trap particles to areas as small as a few nanometres [140].

The theory of dielectrophoretic forces has been widely studied [134, 141, 142]. In general, the term DEP can be described as a phenomenon in which a force is exerted on a polarizable object by a non-uniform electric field. If a polarizable object is placed in an electric field, there will be an induced positive charge on one side of the object and an induced negative charge (of the same magnitude as the

induced positive charge) on the other side. The positive charge will experience a pulling force; the negative charge will experience a pushing force. In a uniform field, as depicted in Fig. 4.1 , the pulling force will cancel the pushing force, and the net force will be zero. However, in a non-uniform field, as depicted in Fig. 4.1, the electric field will be stronger on one side of the object and weaker on the other side of the object. Thus, there is now a net non-zero force acting on the object [134]. Note that both the medium and the particle can be polarized by the electric field, and so DEP is almost always a two-body system. Given different polarizability and different frequency dependence for the two bodies, two classes of DEP are possible: positive and negative [134]. If the particle polarizability is higher than that of the surrounding medium, then the DEP force pushes the particle toward the higher electric field region. This case is called positive dielectrophoresis [134]. In the opposite case, when the medium polarizability is higher than the particle one, the particle is pushed towards region of weaker electric field. This is called negative dielectrophoresis.

If we consider the previously mentioned dielectric particle in an electric field $\mathbf{E}$, it will behave as a dipole with moment proportional to the electric field $\mathbf{p} \propto \mathbf{E}$. Taking into account the relationship between momenta and electric field for a spherical particle ([138]) the force acting on a particle can be written as

$$\mathbf{F}_{DEP} = 2\pi V \epsilon_m \alpha_r \nabla(\mathbf{E}_{RMS}^2) \quad (4.1)$$

With V being the volume of the particle, $\mathbf{E}_{RSM}$ is the average value of the AC electric field and α_r is the real part of the Clausius-Mossotti factor which describes the dielectric property of particle and medium by

$$\alpha_r = \Re\left(\frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m}\right) \quad (4.2)$$

As the Clausius–Mossotti factor can vary between -0.5 and $+1$, it is possible to have positive and negative forces applied to the particle. Indeed when it is positive, the particles move in the direction of higher electric field regions (positive dielectrophoresis). While when it is negative, the particles move towards smaller electric field regions (negative dielectrophoresis) [134]. From Eq. 4.1 a series of conclusion can be made. Firstly, it can be noticed that the force has an strong dependence on volume, as we have also previously seen in the case of optical tweezers. Secondly, quantum effect have not been taken into consideration, while at the molecular level they might become dominant. Thirdly, the frequency dependence of the dielectric constants of medium and the particle give rise to different forces at different frequencies - this is often exploited in micro-manipulation and cell-sorting based on DEP [134, 143]. Finally, equation 4.1 is valid both for DC and AC electric field. The dielectrophoretic force does not differentiate between the two type of fields, however there are some advantages to employing AC, such as selectivity (due to the frequency dependence of the dielectric constants of solvent and analyte) [134] and lower power requirements [134].

Another effect that can be obtained by applying an AC electric field on a polarizable object is to orient that object with respect to an electric field. Specifically, the induced dipole moment of an object interacts with the electric field and, if not aligned, it will experience a torque given by:

$$\mathbf{T} = \mathbf{p} \times \mathbf{E} \tag{4.3}$$

This effect has been used to orient DNA and nanotubes in solution, and also nanotubes during growth in gas or vacuum. It can also be used to orient cells and other micron-sized objects [134]. Electrorotation occurs when the direction of the applied electric field is itself rotating as a function of time. This can be

achieved by using four electrodes surrounding a central region, where the phases of the AC voltages applied to each electrode are properly phase shifted. More sophisticated geometries can also allow a particle to be moved. For example, a set of electrodes with AC voltages adjusted in such a way as to generate a traveling wave electric field, can instigate motion of a particle in the direction of the traveling wave [134].

From Eq. 4.1, a typical dielectrophoretic force acting on a particle of size 100 nm is expected to be roughly 1 fN. This is of the same order of magnitude as the force exerted by optical tweezers [144]. In fact, both optical tweezers and dielectrophoresis are based on the same principles [134]. The primary difference between optical tweezers and electronic tweezers is that optical tweezers also affect particles whose size is comparable to the (optical) wavelength, of order of μm , the so-called Mie limit. The analogy with electronic tweezers is more appropriate in the limit where the particle size is smaller than the optical wavelength, the so-called Rayleigh limit. For optical tweezers in the Rayleigh limit (particle size $\gg \lambda$), the force is proportional to the volume of the particle, as it is for DEP [134]. For optical tweezers in the Mie limit (particle size $\ll \lambda$), the force is independent of the particle size but it can nullify as the field gradient felt by the particle becomes more and more uniform. A similarity between optical tweezing and DEP exist when they are applied to particles in solution. Both must strive to overcome the random forces due to Brownian motion. Hence, it makes sense that the induced forces for both optical and electronic tweezers exert comparable forces [134]. One clear advantage that DEP has over optical tweezers is scalability: millions or even billions of electrodes can be easily and economically integrated onto a silicon chip for low-cost lab-on-a-chip systems. Additionally, the electronic trap can, in principle, hold a particle indefinitely, while the optical tweezers, in some cases, only last for a few seconds due to laser-induced damage

[134].

Technology

DEP techniques have advanced considerably in the latest years. Besides having now the term DEP widely accepted as a manipulation technique for biological cells and dielectric beads, there have been great advances in electrode design, DEP test chambers and also monitoring techniques for particle trapping. One of the problems which often affected earlier systems, was the appearance of a thermal effect as high voltages were applied to the system. However the miniaturization of electrode design has allowed the use of smaller voltages in DEP measurement (reduction of electrode spacing produces higher gradient for lower voltages). Indeed with a reduction of the electrode size by 1000-fold, the same DEP force on a particle can be achieved with a 100-fold smaller applied voltage [142]. The use of smaller and smaller gap, possible thanks to the advancement of nanofabrication techniques (Electron Beam Lithography), allows the generation of the same dielectrophoretic force intensity by the application of smaller voltages thanks to the increase in gradient intensity due to reduction in size. This is of great interest for the DEP techniques, as smaller voltages imply: Reduced generation of unwanted effects (as electro-osmosis induced convection in the liquid); Reduced risk of electron-migration and breakdown of the capacitive structure due to high voltage applied; Reduced size of the DEP trap and smaller target possible. In fact, following these reflections what becomes critical in the future development of DEP techniques is the advancement in fabrication technique that will allow for the creation of smaller and smaller gap filled with material capable of preventing the capacitor breakdown. And that is the current aim of the field.

One of the most widely used electrode configurations is the interdigitated or castellated configuration. Such configuration [145, 146] was chosen for its ability

to provide high electric field gradient, with small voltage applied. As described by [146], such configuration can be used to observe both types of dielectrophoretic forces (negative and positive) just by tuning the frequency of the applied signal. The cells experiencing negative DEP are elevated above the electrode plane, into the fluid medium. This have been often used for DEP separation and isolation of different cell type [147, 148].

In the original castellated electrode design particles were aggregating in triangular shaped clusters around the electrodes when low enough frequency was applied. This effect represents one of the limitations that DEP presents. At low enough frequency (upper limit in the range of 100 KHz), effect of hydrodynamic flow, induced by electro-osmotic stress arising from the interaction of the electric field and the electrical double layer, can become dominant [149]. Such anomalous frequency effect is especially significant in high conductivity fluids, and as such, it is the main limitation of the DEP application in biological and medical fields.

It is worth noting that, a number of interesting designs capable of exploiting this low-frequency effect, have also been presented in recent years. One possible design is the so-called "zipper" electrode [150, 151], which exploits the electro-osmotic flow for movement and DEP for focusing of particle.

Another electrode design that has found a wide range of application is the quadrupole one. Geometries with a wide range of electrode separation (from few microns to hundreds) have been extensively used for both DEP and electrorotation experiments. For example Kuo and Hsieh have described [142] a method for performing single-bead-based biochemical assays on a quadrupole chip. The quadrupole design has proved its great reliability as a negative DEP trap in highly conductive fluids.

The trapping recording has also evolved from the simple photographic one, to a wider range culminating in a variety of available methods used today. Plasmon-

enhanced Raman signal, changes in the optical scattering due to the suspension of the particle, computerized image analysis of particle motion and changes in the electron impedance are just a few example of the most newly-proved detection methods [142]. More recently, fluorescence spectroscopy has been used to measure the DEP collection of submicron particles [152,153].

Usually DEP trapping is carried out using metal electrodes that can provide high field gradients. However in such configuration, measurement below 1 KHz are usually limited because of water electrolysis or electro-osmotic flow (as was outlined previously in the literature review). A possible solution to such a problem was presented in the form of electrodeless DEP [154]. This configuration exploits constrictions or channels in an insulating material to squeeze the electric field in a conducting solution, thereby creating high field gradient maxima [155]. The advantages of this electrodeless form of DEP are that no metal evaporation is required during the fabrication process, it is mechanically robust and chemically inert, and very high fields can be applied without gas evolution due to electrolysis at metal electrodes. *Chou et al.* [155] demonstrated that this electrodeless form of DEP can be used to concentrate and pattern both single-strand and double-strand DNA, at far lower frequencies than those feasible with metallic trapping structures. This technology brings DEP down to the molecular level: an exciting development that is already being directed toward rapid DNA hybridization assays. Another possible application of electrodeless DEP presented by *Chou et al.* [135], was the molecular dam lab-on-a-chip. In such design, insulating constriction were able to generate such strong negative DEP forces that fast accumulation and enrichment of the analyte solution was possible in mere seconds.

Another alternative DEP electrode approach, in which some electrodes are energized while others are electrostatically floating, has been recently presented

by *Golan et al.* [156,157]. They demonstrate that floating electrodes can produce effective DEP forces, with the advantage being that they do not require a connection to an external signal. This greatly simplifies the situation where nanoelectrodes are to be used, and is envisaged as a potential bottom-up DEP fabrication tool where nanoparticles need to be manipulated with nanometer spatial resolution.

A concept of four-dimensional manipulation using DEP forces has been introduced by *Honegger et al.* [158] using Janus particles. Janus particles are dissymmetric systems with two faces that possess two different physical/chemical properties. In this microfluidic experiment, Honegger demonstrated that not only precise 3D localization of these particles is possible, but also that their rotation can be controlled by the gradient of the applied electrical field.

However in the majority of these experiments, no optical component or plasmon-enhanced mechanism appears. The link between plasmonics and electronic tweezers (DEP) is indeed an interesting and exciting new avenue to explore.

4.2.1 Optical forces

As outlined before, the idea that light can be used as an universal palette capable of manipulating physical object was put on mathematical terms by James C. Maxwell, who described what is called radiation pressure. Radiation pressure is a form of mechanical force that light can exert on a body: light "reflecting" on a surface produces a force on that surface. And this mechanical force, can be applied with such precision and with such control that it has created a prosperous field of research in the last 40 years [159]. Applications, have been the driving motor of optical tweezers research in the latest years.

While a growing number of experiments have been done in areas such as

colloidal dynamics, statistical mechanics, hydrodynamics, Brownian motion and nanomanipulation, the biggest range of applications for optical tweezers lies in the field of biology [159]. Shortly after Ashkin [60] demonstrated the concept of optical tweezers, he made use of his new tool to make measurements on cells. This has inspired a huge subfield of work that looks at both cellular and molecular properties [159]. Some of the most interesting experiments, have been aimed at understanding the functionality of single molecules. In the context of molecular motor, measurements of base pair stepping by RNA polymerase (RNAP), in which an RNAP molecule moves along a DNA molecule, have been achieved [61–64]. This measurement is incredibly accurate: each displacement is on the order of the size of a hydrogen atom. This demonstrates what kind of insight such manipulation tool can provide at the molecular level.

Another interesting direction of research is aimed at evaluating the properties of blood cells, as these are relatively easy to trap, as well as bacteria by performing spectroscopy. With the straightforward combination of optical tweezers and any spectroscopic technique, sophisticated analysis of extremely sensitive and small biological objects can be achieved. Raman spectroscopy, which is often limited by the long integration times in unstable environments, is of great interest in the field of optical traps. Indeed, as cells are trapped, it becomes easier to probe sub-cellular structures and specific sites of the cell membrane otherwise not possible without a proper manipulation technique. Another interesting development has been the optical stretcher [159, 160]. In this experiment the deformations of cells are studied. This is of great interest as the health of a cell can be often linked to the properties of its cytoskeleton [160]. As an example, for cancerous cells their membrane becomes more squishy as to facilitate regeneration [160]. The alterations in the cytoskeleton can be detected by the optical stretch, and with such a technique no molecular markers are needed, just a mechanical measurement.

The work of Arthur Ashkin was the base for the development of optical tweezers in the widely used tool of today. He was the first one to address the thermal problem using a new light source called the laser. With it, Ashkin realized that he could use particles that were transparent and therefore non-absorbing at the wavelength of the light source [159]. This de-coupling of optical and thermal forces paved the way for a number of significant breakthroughs [60]. In 1970s, Ashkin and his collaborators performed a series of experiments aimed at showing the capabilities of this new tool. An important landmark in such research was the demonstration of trapping by using a vertically propagating beam and using gravity to balance out the radiation pressure force [60]. Much of Ashkin's early work was aimed at improving the stability of this manipulation tool. And it wasn't until 1986, that Ashkin demonstrated a single-beam gradient trap and a more powerful technique was born [161]. The genius intuition was to focus the beam so tightly to produce a gradient force in the propagation direction that was able to counteract any scattering force. That was the moment that modern optical tweezers were born.

Scattering and gradient forces

The description of optical forces can be done by examining three distinct size regimes: (1) the Rayleigh regime, where the particle diameter is $d < \lambda$, (2) the Mie regime, where $d \approx \lambda$, and (3) the intermediate regime where $d > \lambda$. The two primary forces in these regimes are the scattering (radiation pressure) force $\mathbf{F}_{scat}$, which is directed parallel to the local Poynting vector $\mathbf{S} = 1/2\text{Re}[\mathbf{E}\mathbf{H}^*]$, and the gradient force $\mathbf{F}_{grad}$, which is generated by local inhomogeneities in the optical intensity distribution [21, 161]. We can understand the optical scattering force as a result of reflection of rays from the particle, while the optical gradient force as a result from refraction of rays at the particle surface (so having transverse and

axial components) [21]. The competition between these two forces is the basis of optical trapping and is the motivation behind the study of techniques to increase $\mathbf{F}_{grad}$ over $\mathbf{F}_{scat}$ [21].

For the scope of this thesis I am going to focus to the Reyleigh and intermediate regime. In the Reighley regime, a particle can be treated as a point dipole that oscillates in phase with the incoming electromagnetic field, acquiring a dipole moment $\mathbf{p}(\mathbf{r})$ and thus an induced polarization current $\mathbf{P}(\omega)$. The oscillation of $\mathbf{P}(\omega)$ produces then a secondary radiative field (scattered field) that changes the magnitude and direction of the energy flux of the incoming electromagnetic wave, and creates a momentum transfer to the particle [162]. This process gives rise to the optical forces acting on the particle, which can be written in terms of the Lorentz force acting on the oscillating dipole [21]:

$$\mathbf{F}_L = [\mathbf{p} \cdot \nabla] \mathbf{E} + i\omega \mathbf{p} \times \mathbf{B} \quad (4.4)$$

By taking into consideration Eq.2.20 and the vector identity $(\mathbf{A} \cdot \nabla) = 1/2 \nabla | \mathbf{A}^2 | - \mathbf{A} \times \nabla \times \mathbf{A}$, we can rewrite the previous equation as:

$$\mathbf{F}_L = \mathbf{F}_{grad} + \mathbf{F}_{scat} = \frac{\alpha}{2} \nabla I(\mathbf{r}) + \frac{\sigma_{ext}}{c_m} I(\mathbf{r}) \mathbf{n}_S \quad (4.5)$$

where $I(\mathbf{r})$ is the local intensity distribution, $c_m = c_0/n$ is the speed of light in the medium, and $\mathbf{n}_S$ is a unit vector parallel to the Poynting vector [21]. Here, $\nabla \mathbf{E} \approx 0$ follows from the quasi-static approximation, in which the extinction cross section is given by $\sigma_{ext} = kIm[\alpha]$. From this, some fundamental features about optical forces at the nanoscale can be inferred:

- The gradient force is proportional to the local gradient in optical intensity, $\nabla I(\mathbf{r})$, and will direct particles with $n > n_m$ (refractive index of the particle higher than the one of the medium) towards the region characterised by

high field intensity.

- The scattering force is proportional to the intensity, $I(\mathbf{r})$, and will direct particles in the direction of the energy flux of the electromagnetic wave (same direction as the Poynting vector).

In the case of the particle size being comparable to the input wavelength, the scattering problem becomes too complicated to be solved analytically for a random object, and the use of ray optics is invalid. Calculation of optical forces in this regime requires the use of the Maxwell stress tensor (MST), $\mathbf{T}$. The stress tensor describes the conservation of linear momentum in an optical field, and by its integration the optical force $\mathbf{F}$ on an arbitrary object in an arbitrary electromagnetic field can be retrieved:

$$\langle \mathbf{F} \rangle = \left\langle \iint_{\delta V} [\epsilon_m \mathbf{E} \mathbf{E} - \mu_0 \mathbf{H} \mathbf{H} - \frac{1}{2}(\epsilon_m E^2 + \mu_0 H^2) \mathbf{I}] \cdot \mathbf{n} ds \right\rangle \quad (4.6)$$

where $\mathbf{n}$ is the unit normal to surface, $\mathbf{A} \mathbf{A}$ represents the outer product of vector $\mathbf{A}$, $\langle \rangle$ represents the time average, and $\mathbf{I}$ is the unit matrix. Thus in order to calculate the optical force on an arbitrary object, it is enough to know the values of $\mathbf{E}$ and $\mathbf{H}$ on any surface surrounding the object and the electromagnetic field environment.

Plasmonic tweezers

Conventional optical trapping and manipulation makes use of high-NA optics to tightly focus a Gaussian laser beam to a diffraction-limited focal spot in order to create the strong gradients needed as we outlined before. This strong gradient forces, are sufficient to overcome the scattering force and enable 3-dimensional manipulation of objects ranging from 50 nm to $> 10 \mu m$ in diameter in the focal volume [21, 163–165]. These optical tweezers are then usually employed for

handling particles smaller than $\approx 5\mu m$ suspended in an aqueous medium, where the optical forces are strongest (thanks to the refractive index difference between the particle and the medium) [21, 161, 166]. Given the small particle dimensions, Brownian motion becomes significantly into trapped particle dynamics. Brownian motion is a result of random thermal perturbations to the particle and is characterized by a diffusion coefficient $D = k_B T / (6\pi\mu a)$ ¹ where k_B is Boltzmann's constant, T is the temperature, and μ is the fluid viscosity [21]. The optical force can also be obtained via $\mathbf{F}_{grad} = \nabla U(\mathbf{r})$ where $U(\mathbf{r}) = \mathbf{p} \cdot \mathbf{E}$ is the potential energy landscape formed by the local intensity distribution [21, 167]. Consequently, a stable optical trap depends on the optical potential energy landscape $U(\mathbf{r})$ formed by the focused beam to be sufficiently deep so as to prevent ejection of the particle by large, random Brownian fluctuations [21, 161]. A deep potential well thus generates optical forces that are strong enough to prevent thermal destabilization of the trap [21].

The use of plasmonic nanostructures for optical manipulation is then motivated by the optical diffraction limit, which sets an upper bound on the achievable gradient forces in conventional optical tweezers [21]. In such system progressively large input powers are thus required to manipulate objects of smaller and smaller size, owing to the a^3 dependence of the gradient force [21]. This size effect becomes especially problematic for manipulation of biological species, which can be damaged by high optical powers [21, 168]. On the other end, the ability of focusing the electromagnetic radiation to sub-diffraction limit offered by plasmonic antennas provides higher field gradients, capable of compensating the size reduction without the need of an input power increase. Indeed, the utilization of the plasmonic structure for optical trapping is able to offer the following advantages:

- The highly confined evanescent fields significantly reduce the trapping volume;

- The large field gradients result in a larger trapping force;
- The field enhancement allows the reduction of illumination power and radiation damages to the sample [71].

As a result, a wide variety of nanostructure geometries have been investigated for optical manipulation since the first demonstration of plasmonic trapping in 2007 by Righini et al. [13]. Examples include nanodots [169], nanopillars [170], nanoblocks [11], and dipole nanoantennas [13, 21].

To date, however, such structures have been employed in isolation for optical trapping, that is, in arrays and exploiting only the strong local optical field generated thanks to the plasmonic resonance of the structure [21]. There remains significant room to improve such structures by designing them also to harvest dielectrophoretic forces. Thus this chapter of the dissertation will focus on how one can increase the performance of plasmonic optical trapping by coupling it with dielectrophoretic trapping as well.

4.3 A new dielectro-plasmonic design

The use of plasmons in the context of optical trapping has become an increasingly interesting direction of research, with new and interesting applications being continuously discovered. *Volpe et al.* [171] tried to understand surface plasmon radiation forces, while working on plasmon propagating on a gold film. *Novotny et al.* focused on the use of plasmon for particle trapping at the end of AFM tips [71]. Quidant and Van Dorpe researched the use of plasmon cavity resonance as a way to trap particles [172, 173]. Their approach, called SIBA, exploits the plasmon resonance dependency on to the refractive index of the environment a self-mechanism for trapping single particles in nano-slots. *Yin et al.* [174] recently discussed the force and torque generated by a cap-shaped Ag nanopar-

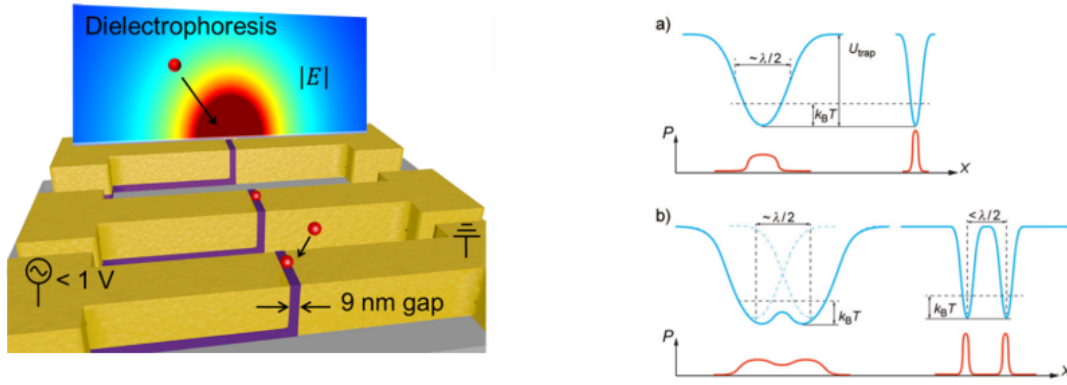


Figure 4.2: *a) Dielectrophoretic forces wide range in electrode like configuration with small gaps [175] b) Plasmonic tweezers trapping potential with respect to optical tweezers trapping potential. [58]*

ticle. They proposed the possibility of manipulating in 2D the beads that were trapped by the plasmon resonance of a metal nanoparticle. A similar work was presented by *Boltasseva et al.* [7], where two beads were trapped in the hot-spot of a plasmon micro-pillar. They also demonstrated that the manipulation of the trapped beads in the trapping plane was possible by the rotating the polarization of the excitation light.

All these approaches exploited the strong optical forces that a plasmon generates in the near-field regime in order to trap nanometer-sized particles. However, such forces are very limited in space (the plasmon field is very highly localized) and can be generated only in the limited area defined by the focus of the excitation source (excitation signal cannot be applied to the whole array like in the case of DEP electrodes). Moreover the sensing ability and capability of the excited energetic charges of the plasmon is completely ignored in favour of its ability to generate localized high electric fields. Only recently, some work has been done on combining the use of plasmonics with other trapping techniques. One of the choices have been the use of dielectrophoresis as trapping mechanism and of as plasmonics a detection mechanism. *Oh et al.* [71,176–178] were one of the first in trying to combine plasmonics effects and dielectrophoresis forces in an

efficient way. They have demonstrated the ability of the dielectrophoresis force to trap particles as small as 20 nm (as well as some proteins) and the ability to detect their small concentration thanks to the use of the plasmons excited in a nanoholes array [179]. More recently, the integration of dielectrophoresis and surface plasmonic was used for improving the detection ability of fluorescent events [180].

If we aim to design a new type of nanotweezers a series of reflection about the type of structure that we are aiming to design are needed. The first thing to consider in this regard is what are the main aspect of the nanotweezers that will affect the direction of the design. A highly efficient nanotweezer, would be a structure capable of:

- Stably trap nanoscale object at addressable plasmonic hotspot;
- Rapidly deliver target nano-object to the plasmonic hotspot;
- Trap the nano-object with high spatial resolution;
- Dynamically control the nano-object;

With these observation into account for the design, we can reflect on the plasmonic tweezers and dielectrophoretic one that were outlined in the previous section. The use of plasmonic tweezer can allow for high spatial localization of the trapped particle, thanks to a strong gradient of the evanescent field that is created only at the hotspot region [58]. Moreover, due to this strong gradient, plasmonic tweezers allow for a highly stable trap, since a deeper trapping potential is available (as can be derived from the gradient force Eq. 4.5)[58].

On the other hand, dielectrophoretic tweezers can start to affect particles at a large distance due to the stray field away from capacitor like electrodes [175]. Furthermore, given the frequency dependent behaviour of dielectrophoretic

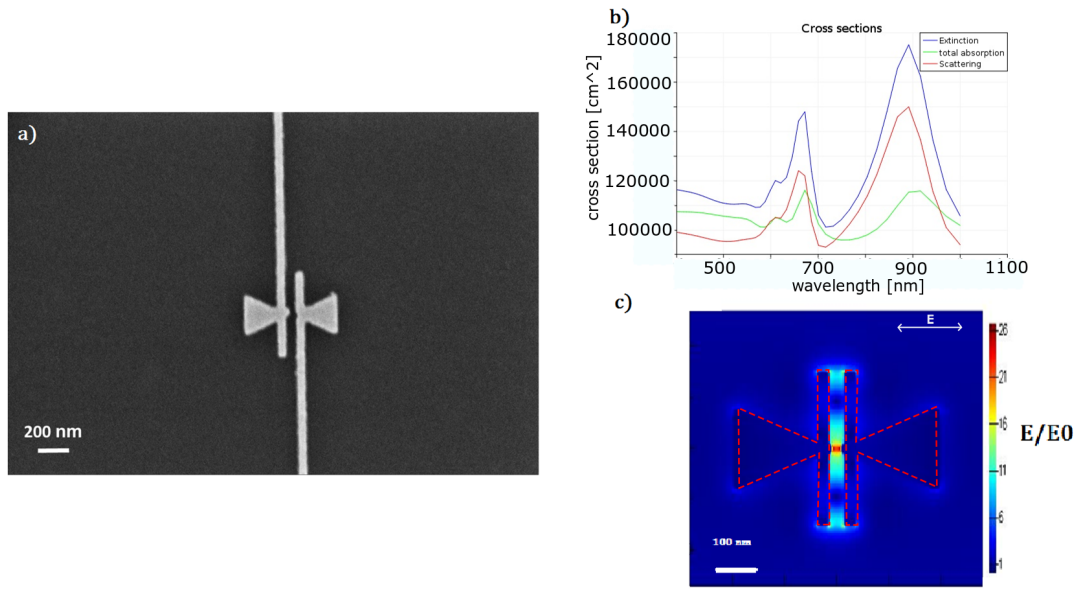


Figure 4.3: *a)* SEM image of the new Au antenna fabricated on SiO₂ substrate. *b)* Scattering, absorption and extinction cross section calculated by FDTD simulation for the new antenna design; *c)* Field enhancement (E/E_0 , with E_0 being the intensity of the source field) profile 5nm on top of the new antenna design at 900nm excitation wavelength.

forces (Eq. 4.1) a larger dynamic range is introduced. This means, the ability of switching the sign of the force from attractive to repulsive, allowing for a greater range of possible particle manipulation with respect to the static trapping potential that plasmonic tweezers alone can give access to.

Indeed, such a design capable of integrating the use of plasmonic resonance with an electrically wired structure capable of supporting high frequency AC electric field, should be able to merge dielectrophoretic and plasmonic optical forces providing the way for an highly efficient and novel nanotweezers.

The design that we propose, capable of integrating dielectrophoretic and optical forces, is the one presented in Fig 4.3.

This design integrates a bowtie type of nanoantenna [181], known for holding high field focusing in the nanogap at the centre of the structure and widely used for optical trapping experiments [58, 181–185], and a parallel plate capacitor. The design makes use of the electrical contacts needed to bringing the AC

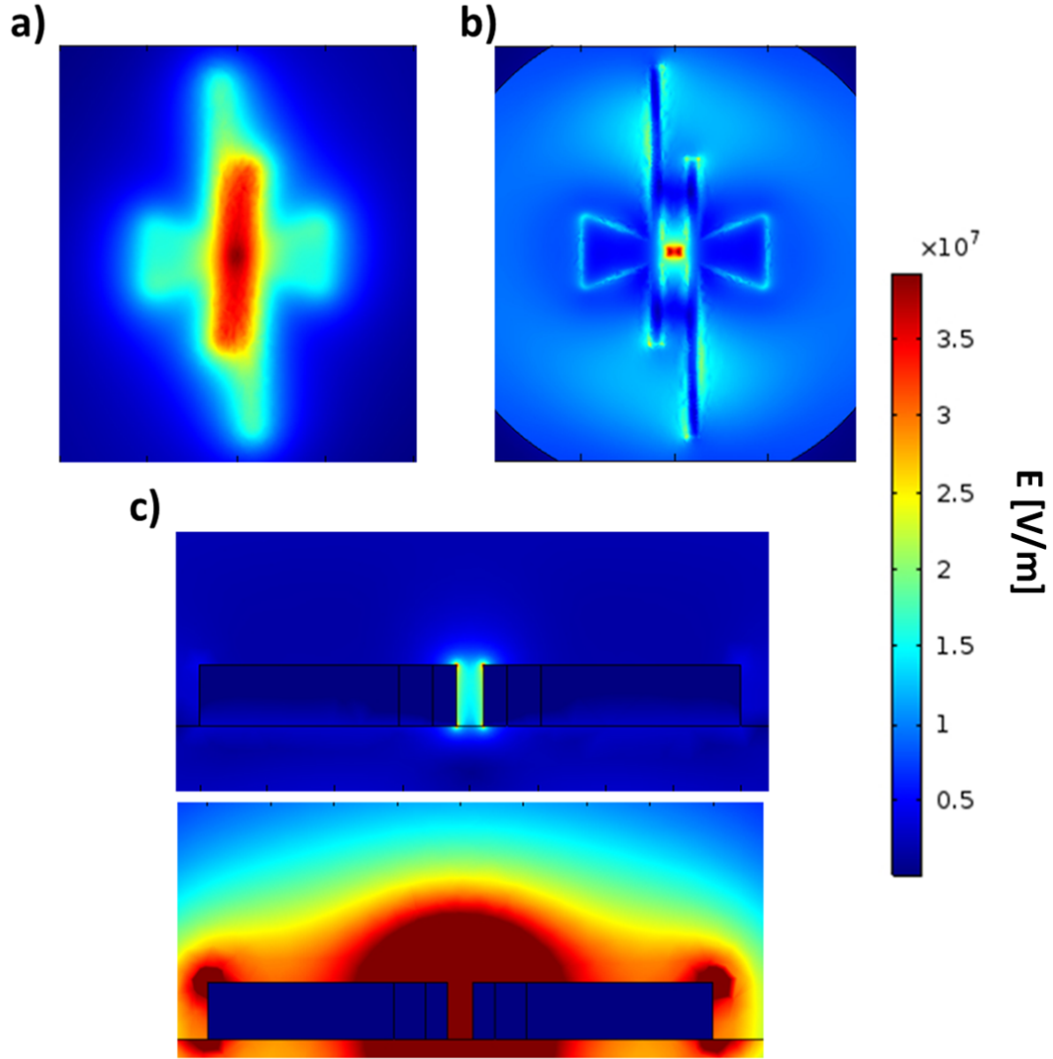


Figure 4.4: *a) plane-cut 35nm above the antenna of the E field profile generated by an AC signal applied; b) field profile due to plane wave excitation of the plasmonic antenna; c) Top - field enhancement plane cut due to plasmon excitation on the antenna; Bottom - field enhancement plane cut due to the AC electric signal applied.*

electric field to the two different side of the nanoantenna to introduce a wide capacitor on top of the plasmonic antenna. This allows the exploitation of the extremely small gap of the plasmonic bowtie and of the metallic connection to generate a parallel plate capacitor characterized by high electric field gradient. When designing such a structure, of great importance becomes the position at which the metallic connections are placed with respect to the bowtie antenna. Indeed, in order to not affect the plasmonic nature of the plasmonic bowties (e.g. the free electron oscillation inside the metallic structure that give rise to a plasmonic resonance due to geometrical factor), the metal connection must be of negligible thickness with respect to the main part of the antenna, as well as being placed after the tip of the triangular bowtie structure (Figure 4.3(a)). A wide number of FDTD simulation were performed in order to optimize the position of the metal connection with respect to the bowtie antenna (Figure 4.3(b-c)). The gap size, the metal connections' width and their position were optimized to achieve high field enhancement at the center of the structure, as well as to have a plasmonic resonance as close as possible to the visible spectrum. Indeed, given the large metallic connections, such a structure tends to have plasmonic resonance towards the IR. In our case, the plasmonic resonance was optimized for the 785 nm wavelength. After optimization of the structure in terms of plasmonic resonance and field profile at 785 nm, Comsol simulation of the antenna were performed (Figure 4.4). The FEM simulations, where performed in two different environments, AC electric field and Electromagnetic wave, in order to calculate optical and dielectrophoretic forces and their overlap in the final antenna design. In Figure 4.3(a) the electric field profile of generated by AC field of 1 Vpp is observed. From the simulation it becomes clear that the use of the metal interconnection in a parallel plate design delivers a wide range of action, capable of trapping a nanoparticle all over the area of the nanoantenna. On the

other hand in Figure 4.3(b) we can see the electric field profile generated on top of the antennas when excited at 785nm with a power of $2mW/\mu m$. In this case the region of high field and strong gradient is highly spatially confined at the very centre of the nanoantenna structure. By comparing the two field profiles on top of the nanoantenna, it can be observed how the field gradient proportional to the dielectrophoretic forces generates a large trapping area and it can affect the particle motion from a couple of μm away from the plasmonic nanoantenna. On the other hand the field profile generated by the plasmonic resonance 4.3(b), is highly localized and it affects a very restricted volume. The working principle of the antenna can then be outlined as: first the AC electric field is applied so that a large number of particles is accumulated on top of the nanoantenna in the large region of maximum gradient; Second the laser excitation is turned on and optical forces come also into action, adding a stronger gradient at the very centre of the antenna; This created a stable trap of small volume (one particle max) precisely at the hotspot; After the frequency of the AC electric field is changed, bringing a change in sign of dielectrophoretic forces and releasing all the particles besides the one still trapped by the optical forces at the very centre. Such a procedure not only allows for reduced trapping time but also for a dynamic behaviour of the trap not seen before. A final consideration is that the sharp features of the DEP-bowtie antenna, where the trapping of molecules is designed to occur, is also where the plasmon enhancement sensing scheme is designed to happen, allowing the localization of the particles in the most sensitive region.

4.3.1 Antennas fabrication

Bowties-capacitor nano-antennas were fabricated following a one-step electron beam patterning procedure. In Figure 4.5 the basic protocol at each step of the fabrication can be observed. A quartz substrate is cleaned in de-ionized water,

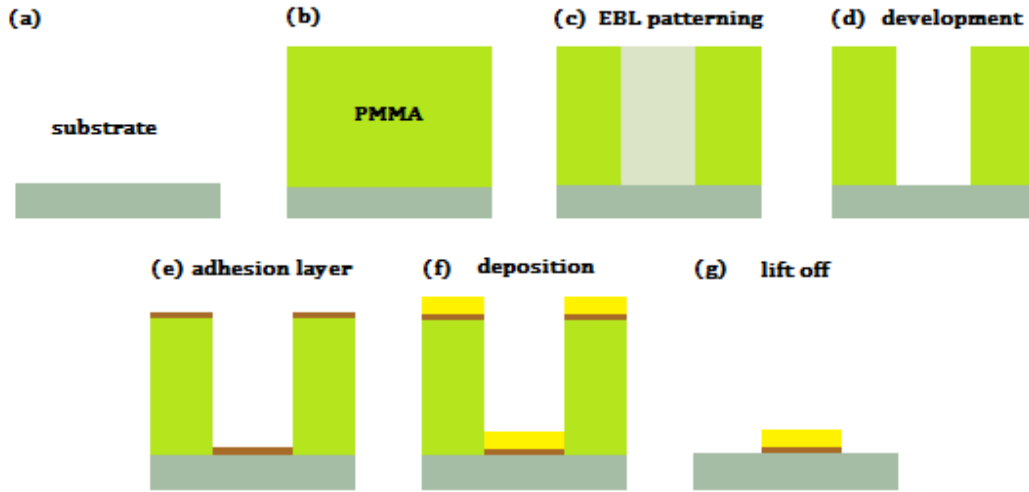


Figure 4.5: *Different steps involved in a one step EBL writing*

acetone and isopropyl alcohol (IPA) by immersing in each solution for 3 min and sonicating at high power. Poly(methyl methacrylate) (PMMA) is then spin-coated on the sample at 3500 rpm for 1 min, after which it is baked for 3 min in a hot plate at 180°C . The baking step is of great importance to ensure the homogeneity of the deposited PMMA film. The final thickness of the PMMA 950k A4 spin-coated under this conditions is of 180 nm.

To finish preparing the sample for the patterning, a thin layer of 2 nm of a conductive polymer (Showa Denko's ESpacer 300Z) is deposited to prevent charging effects during electron beam exposure [186]. Figure 4.5(b) shows a scheme of the layer of PMMA on top of the quartz substrate. The PMMA is then patterned with a 20 kV, $10\ \mu\text{m}$ aperture, 10 mm working distance electron beam, as outlined in figure 4.5(c). After exposure, the sample is developed in a solution of 3:1 methyl isobutyl ketone:IPA for 30 s and cleaned for 30 s in IPA to make sure of the stopping of the development process, which would reduce further the thickness of the negative PMMA layer. Figure 4.5(d) shows the patterned PMMA after the development step. In order to ensure good adhesion of gold to the quartz substrate a series of possible adhesion layers can be deposited.

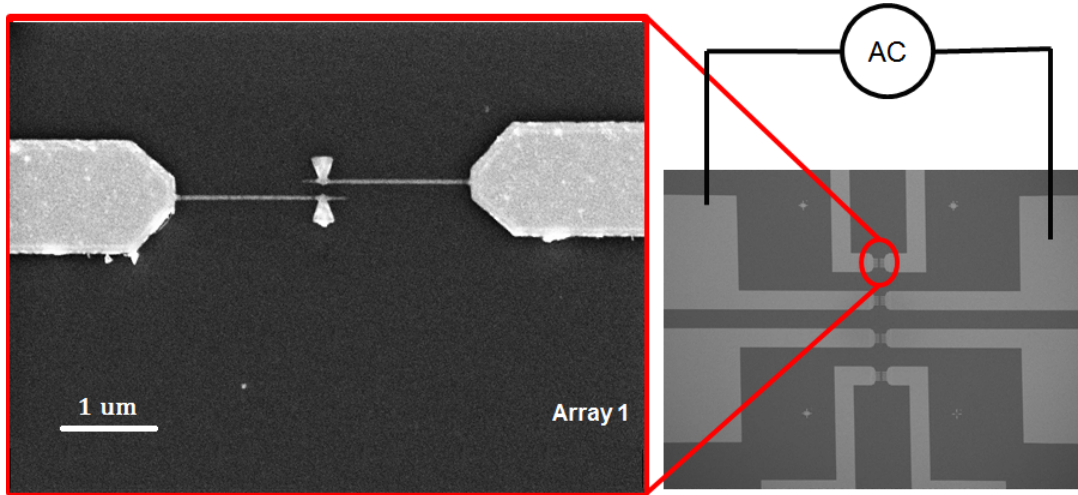


Figure 4.6: *a) SEM images of the new Au antenna design fabricated by Electron Beam Lithography (EBL) with an overview of the DEP trapping chip.*

In order to not affect strongly the plasmonic resonance usually a self-assembled monolayer is deposited prior to the evaporation of the metal. However, given the requirement of high conductivity and heat capacitance for trapping purpose, an adhesion layer of 2 nm of Cr (Chromium) was deposited instead. Figure 4.5(e) shows a scheme of Cr adhesion layer, which is deposited by thermal evaporation at a rate of $0.2 \text{ \AA/s}^{-1}$ at low chamber pressure. Following this, a layer of gold is also thermally evaporated in the same chamber at a rate of $2 \text{ \AA/s}^{-1}$ to a final thickness of 45 nm at 10^{-6} Torr. This recipe produces highly homogeneous golden films [187].

The evaporated golden layer can be observed in Figure 4.5(f). Finally, the sample is lifted-off by immersing in acetone for 24 h and rinsing at the end with acetone and IPA to eliminate any remaining debris of PMMA. Figure 4.6 shows scanning electron images of the bowtie-capacitor antennas fabricated along with their scattering, absorption and extinction spectra as calculated by FDTD methods. The SEM show homogeneity in fabrication in terms of small gaps fabrications as well as gold connections. From Figure 4.6 we can see both the single nanonantenna as well as the wider electrical connection designed to bring the

high frequency AC electrical signal to the capacitor bowtie antenna. The large interconnections were fabricated with an EBL step prior to the single antenna fabrication process described in this section. The fabrication of the large metallic interconnections followed the same fabrication procedure, except for the choice of the aperture size used for the EBL exposure. Given the large size and the low requirement in terms of resolution, needed for the large contact a $60\mu m$ aperture was used instead of the $10\mu m$ one. The large pad of the metal interconnection were then wire bonded to a chip older designed with the help of David Bower from the mechanical workshop of Imperial college. Some more consideration must be given to the design of the overall chip used for trapping. Each antenna array was reduced to a small number of antennas in parallel in order to lower as much as possible the RC constant of the circuit, allowing for efficient driving of the electrical circuit. Moreover the lowering of the antenna number reduced the risk of short-circuiting due to fabrication non-uniformity. A last consideration must be given to the overall structure. Such large interconnection as the ones used here, also play a role as heat sink when the antennas are under laser excitation. This allows for a strong temperature reduction and minimization of unwanted thermal effect that can cause trapping instability.

4.4 Trapping test bench and experimental set-up

Scalable trapping of quantum dots or nanodiamonds in the single photon source regime is something that the current state of research has not reached yet. Some possible solutions have been presented in the recent years [182,188,189], however they all fall short either in the scalability of the system or in the coupling of the single photon source to a plasmonic antenna for emission enhancement. With

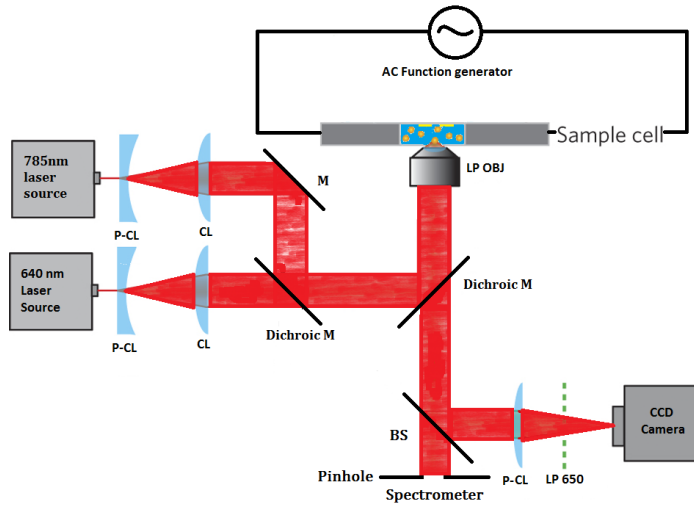


Figure 4.7: *Experimental set-up outline. The laser source goes through a plano-convex lens (P-CL), who focuses the beam from the fiber inside the microscope, a collimator (CL) and a Long working distance objective (LP OBJ). The signal collected from the trapped particles is guided by a system of mirrors (M) to a 650 long pass filter (LP 650), before being focused on the CCD camera by a plano-convex lens (P-CL).*

the dielectro-plasmonic tweezer we could be able to advance further on this way, providing a strong tool for manipulation and coupling of single photon source to plasmonic antennas. The first step was the creation of an experimental set-up for trapping experiment as described in Figure 4.7, with a corresponding test-bench measurement in order to prove the ability to perform simultaneous optical and dielectrophoretic trapping. The test bench used for the experiments are polystyrene beads from Thermofisher (FluoSpheres Polystyrene Microspheres, dark red) of different size ($2\mu m$, $200nm$, $40nm$), which can be excited in the red (645 nm) and that emit further in the red ($680\text{ to }750\text{ nm}$). The set-up built is a normal inverted microscope system, to which a spectrometer and CCD camera have been coupled, in order to record trapping events as well as to retrieve emitted signals from the trapped objects. Moreover two laser line have also been coupled in, a wide beam circumference one at $647nm$ used for exciting emission from the polystyrene beads and a tightly focused one at $785nm$ used for the excitation of the LSPR on top of the capacitor-bowtie antenna.

Before moving to the more complicate capacitor-bowtie antenna, stable and reliable trapping of the 200 nm polystyrene beads was proved on pyramidal antennas [178] fabricated by the group of Prof. Sang-Hyun Oh in Minnesota. In the first series of trapping experiments, an electrode to electrode distance of $40\mu\text{m}$ was used and different peak-to-peak voltage were applied. As we can see from Fig. 4.8 we were able to reliably control the trapping by DEP, with as low as 2 Vpp of signal applied. The switching between trapping and release of the beads was possible by changing the AC signal frequency. This frequency dependence of the trapping behaviour is consistent with DEP being the underlying mechanism of trapping, since varying frequency changes the sign of the dielectrophoretic force, thus switching the system from negative to positive DEP. The luminous spot in Fig. 4.8, represent signal recorded with the CCD camera of the photoemission of the beads. The focal plane is at the top of the pyramidal structure, and it can represent a cluster of beads as well as a single bead. When the frequency is switched to "release", the particles before trapped at the tip of the pyramid are pushed away and we observe them moving away from the pyramid tip and from its plane of focus.

Having proved the ability to perform dielectrophoretic trapping on a known system reported by the literature [178], the next step was to move to the more complex capacitor-bowtie antennas for dielectro-plasmonic trapping.

4.5 Scalable trapping of nanobeads

First step towards scalable trapping of nanobeads was the use of the newly designed capacitor-bowties nanoantenna for dielectrophoresis trapping. In this case, the open voltage as well as the maximum voltage that could be applied to the circuit were measured. By doing a simple IV sweep from 1V up to 7V, it was found out that the circuit was able to sustain without break down up to

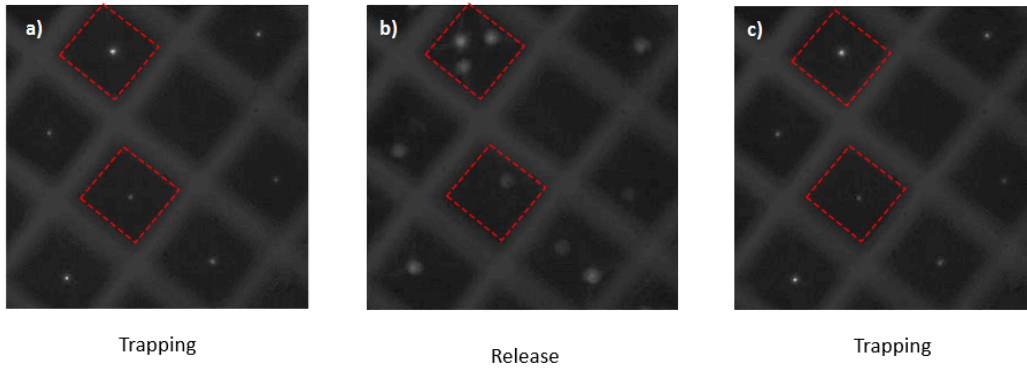


Figure 4.8: *Dielectrophoresis force trapping of 200 nm latex beads from Thermofisher. a) Applying 2 Vpp at 1 MHz, results in stable trapping of multiple beads. b) By switching the frequency of the signal to 1 KHz the particles are released. c) As the signal frequency is back to 1 MHz the particles are trapped again. This series of captions, by showing the typical frequency dependence of DEP trapping, proves the mechanism behind the experiment.*

6V of DC signal. This value was generalised to AC signal, as the RC constant even though negligible, would not allow for such a nominal voltage to be applied to the side of the capacitor. Indeed the circuit was able to sustain signal up to 6Vpp without any sign of break-down. After establishing an upper limit for the maximum signal applicable to the circuit, testing of dielectrophoretic trapping could begin.

A batch of low concentration 200nm polystyrene beads in DI water was drop-casted on top of the dielectro-plasmonic chip. After focusing the 647 nm laser beam on top of the antenna array and checking that randomly moving particles were observed, an AC signal was then applied. Starting from 50 0mV, and in 100 mV steps, higher AC signal were applied to the circuit until a trapping event was not recorded by the CCD camera (see Figure 4.7 for the trapping set-up). With Comsol multiphysics (Figure 4.9) the estimated DEP force generated 30 nm away from the electrode boundary on a 200 nm particle that can be generated from the capacitor-bowtie nanoantenna by applying a voltage of 2 Vpp is approximately of 5 pN. Such a force, in order to stably trap the target nanoparticle in solution

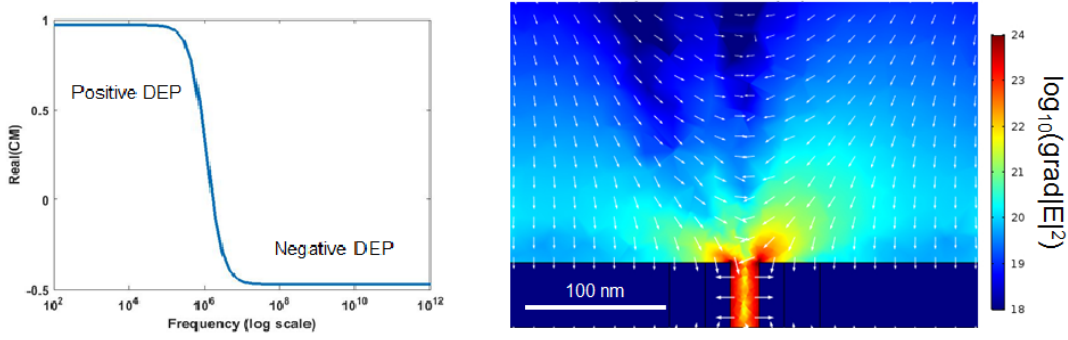


Figure 4.9: *a) Calculation of the Claussius-Mossotti factor for the polysterene beads under study, a frequency cut-off at 2.6 MHz is found. b) DEP trapping forces simulated with Comsol multiphysics. The arrow represent the intensity of the Fz force in logarithmic scale while the color map shows the gradient of the electric field in the x-z plane with respect to the nanoantenna. To notice that a not completely optimized mesh is at the origin of an asymmetrical gradient of the electric field.*

needs to overcome the force due to the thermal motion (F_{th}), which for a particle of radius R is given by:

$$F_{th} = \frac{K_B T_R}{2R} \quad (4.7)$$

where k_B is the Boltzmann constant and T_R is the ambient temperature. Using Eq. 4.7, the maximum thermal force on a 200nm is estimated to be smaller than 1 pN, such that by applying a voltage of around 2 Vpp the bead should be stably trapped on top of our antenna. Moreover by calculating the Claussius-Mosotti factor according Eq.4.2 for polystyrene beads, characterised by $\epsilon_R = 3$, (Figure 4.9) the frequency switching point between positive and negative dielectrophoretic forces was found to be 2.4 MHz. Indeed a stable trapping event was found to occur when an AC signal of 2.5 Vpp and a frequency of 100 kHz was applied as we can observe from Figure 4.10. We can attribute the discrepancy between simulation and experiment on the trapping threshold to the RC constant of the trapping circuit. Indeed, even if small, such a constant lowers the maximum real voltage signal applicable to the system.

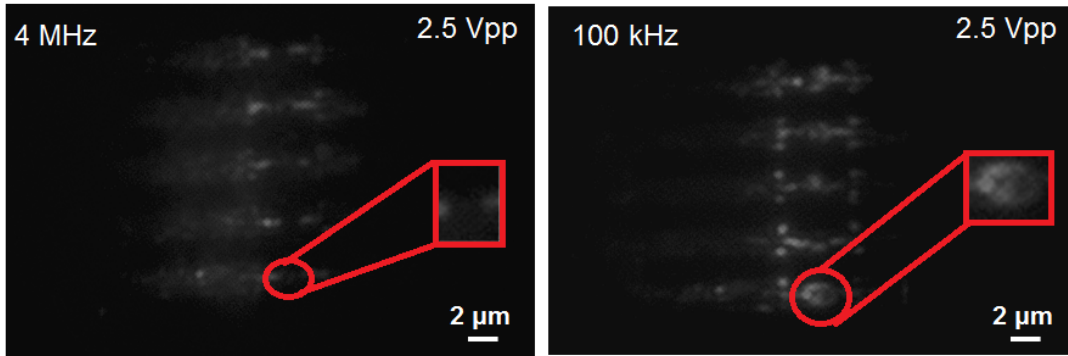


Figure 4.10: *Dielectrophoresis force trapping of 200 nm latex beads from Thermofisher. Trapping and untrapping event related to frequency switching as typical of dielectrophoretic forces.*

Nonetheless by switching the signal frequency between 4 MHz and 100 kHz, dynamic control over the trap was achieved. In fact, as the frequency was switched to the higher frequency spectrum, repulsive DEP forces were pushing away the particles clearing the top of the nanoantenna. Of note in these experiments was first the reproducibility of the trapping events by frequency switching, and second the speed at which the particles were stably trapped. Indeed in just a few seconds after the 2.5 Vpp threshold was reached several particles were trapped. In this case, as we can also observe from Figure 4.3, the DEP trap size is quite wide and indeed allows for more than one particle to be trapped on top of the nanoantenna. Moreover, given the wide area, the particle is not spatially localised but is seen hovering on top of the antenna, circling in the large area of high electric field gradient. To provide a higher degree of spatial control, optical forces need to come into play. As of now, optical trapping was not proved in combination with DEP trapping with the current set-up setting. However, this is due to the power density that we can currently achieve with our focusing. From Comsol multiphysics calculation, in order to achieve the optical forces of the same intensity as the one generated by DEP under a signal of 2 Vpp at 100 kHz, a power density of $2 \text{ mW}/\mu\text{m}^2$ is needed. With our current laser and focusing, we are only able to achieve a power density two order of magnitude lower than

the one needed for stable trapping.

Future steps in this direction, will be the design of a new optical path, allowing for tight focusing of the 785nm laser (responsible for the excitation of the plasmonic resonance and thus the generation of the optical trapping forces) and collimation of the 632nm laser (for particle tracking). In this new configuration a higher power density will be possible, and stable trapping should be achieved. However, a new stage with micron-meter precision will be needed for controlled excitation of the antenna under study. As stable trapping is achieved, reduction of the nanoparticle size will become the new goal. If the system is able to perform scalable and stable trapping of 20-40nm nanoparticle then extremely interesting experimental venue would be opening up. First of all, trapping of quantum dots for single photon emission on arrays of plasmonic antennas. Second, SERS measurement on low concentration of analytes as blood cell or protein components. These experiments, would firmly establish dielectro-plasmonic tweezer as a reliable tool for nanomanipulation and control of colloidal component on top of plasmonic antennas.

4.6 Conclusions

In summary, this study builds on the current available abilities to manipulate target object at the nanoscale. A different approach has been proposed, based on dielectro-plasmonic tweezers. The design of a novel and innovative type of nanotweezer capable of exploiting two different type of forces was presented. This allows for the creation of a novel nanotweezers capable of addressing a series of extremely valuable issue of the current nanomanipulation techniques. Proof of a new design as well as of reliable and extremely fast and stable trapping was presented, although the last step of high spatial localisation was not yet achieved. In general novel avenue for manipulation at the nanoscale were presented and

some of the major issues were addressed by this study.

Part III

Optical/electrical measurements at the nanoscale

Chapter 5

TiN hot holes based Infrared Photodetector

In this chapter we are going to study in deeper details the generation of hot carriers and their extraction in metal-semiconductor-junction. By building on Chapter 2.6.3 we know that hot carriers after being generated, will travel through the material and experience scattering by electrons, phonons and crystalline defects. Such events will thermalize the carriers, and their energy distribution will condense around the Fermi level of the metal. However, practical applications of hot carrier require energies far from the Fermi level as more energetic carriers are able to more efficiently cross Schottky barriers. In this chapter we are going to study how this transport mechanism can be enhanced for carriers close to the Fermi level by placing a thin semiconducting of TiO_{2-x} . First we are going to introduce a new interesting plasmonic material TiN and then we are going to explain how this material can be of interest in IR (InfraRed) photo detectors application. This work was done in collaboration with Nicholas Gusken, PhD student in the EXSS group and co-author of the project.

5.1 IR photodetectors

Efficient charge carrier separation at the nanoscale is the core of solar-to-electricity conversion bearing much promise to become a key future building block in a sustainable power supply [190,191]. In the infrared (IR) this mechanism is of interest in various applications ranging from broad band photodetection, including solar cells and gas detection, to imaging sensors and power monitoring [192]. Here, a silicon based approach is preferred due to existing fabrication schemes and in depth knowledge obtained over the last decades on Si [193]. The harvesting of light in the near IR however, is inherently limited by the Si bandgap energy of about 1.1 eV, impeding the realization of a CMOS compatible and cheap alternative to commercially used Ge and GaAs photo detectors as well as hindering the collection of photons at telecommunication wavelengths. The development of so-called hot carrier Schottky barrier (SB) junctions has been shown to bear much potential to overcome this limitation [193,194]. Such junctions are created when a metal and semiconductor (SC) are brought into contact, so that the difference in the work function of both materials leads to an energy band bending at the surface due to the Fermi energies of both materials aligning. Depending on the type of majority carriers in the SC involved (p- or n-type), as well as bandgap energy and respective work function to the metal, an accumulation layer or a Schottky barrier can be formed at the interface. The resultant potential barrier is smaller than the bandgap energy of the SC and can thus be overcome by excited carriers from the metal at energies below the bandgap.

In this work the use of a homogeneous TiN thin film (thickness $d=50$ nm) as the respective metal absorber in a SC/Metal junction is presented and compared to an Au thin film in the near IR regime. TiN has recently gained much interest in nanophotonics as a material capable of combining a wide range of valuable

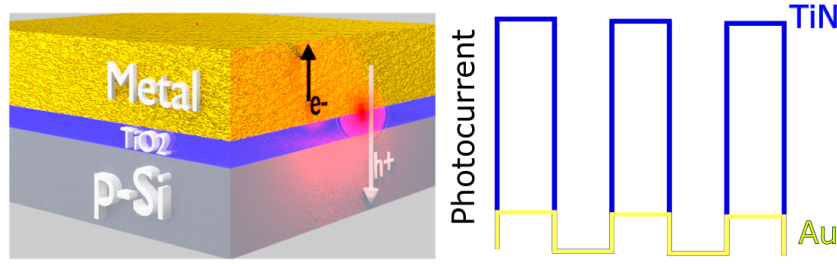


Figure 5.1: *Set-up outline, excitation is coming from the p-type Si side with the laser being focused at the interface between the metal and the TiO_2 interface. Excitation of holes and electron is then separated by the Schottky junction. A strong increase of current is reported in TiN with respect to Au, in the infra-red region of the absorption spectrum.*

characteristics such as mechanical robustness, biocompatibility, strong heat resistance, relatively high electrical conductivity and non-corrosivity [42,191,195,196]. Making it an extremely interesting choice for medical sensors and implants [197, 198] as well as water splitting [191]. TiN has also shown promises for hot carrier excitation in plasmonic nanostructures, where strong fields and losses require a heat robust material over a wide range of frequencies [199]. In the system proposed by this work, strong photo absorption is achieved via backside illumination of metallic thin films ($d/2$, with the incident wavelength in air and d being the film thickness) through Si, as it has been recently demonstrated an efficient solution for hot carrier excitation in thin film junction [200]. Here, absorption as strong as 54% have been achieved in a 50 nm TiN thin film by exploiting backside illumination and absorption enhancement via so-called zeroth order Fabry-Perot resonances [201,202]. This approach bears the advantage that no additional patterning is needed, keeping the fabrication steps to a minimum, contrary to the general case of plasmonic nanostructure such as nanoparticles or gratings. Our findings show that amorphous TiO_2 -x interlayer formed as a TiN surface layer during growth gives rise to a significant deviation of the photo response compared to a pSi/Au junction and can, in conjunction with pSi, be

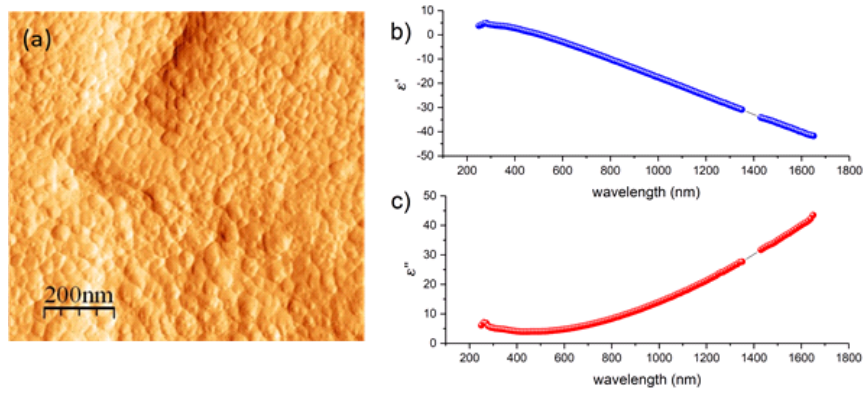


Figure 5.2: *a) AFM image of a 50nm thin TiN film surface with an estimated RMS roughness of 0.7 nm. b),c) Real (ϵ') and imaginary (ϵ'') part of the permittivity extracted from ellipsometry measurements on the TiN film shown in a).*

used as a platform for IR photo current enhancement at zero bias for a range of different metal films.

5.2 TiN and TiO₂ film

RF reactive magnetron sputtering was used to produce a smooth and homogeneous 50 nm TiO_xN_y ($x = 13.5\%$ and $y \approx 40\%$) film with a RMS roughness not exceeding 0.7 nm as determined by AFM measurements, shown in Figure S4 a). The oxygen content in the TiO_xN_y film was estimated XPRD to be about $x = 13.5\%$ which is sufficiently metallic in the IR as shown by the relative permittivity measurements depicted in Figure 5.2 b). Hence, we refer to these films as TiN throughout the report.

All electrical measurements (except the pSi background acquisition) took place on patterned square pads (for all metals) in order to minimize potential parasitic leakage currents and clearly define the contact size making the measurements comparable. The metal thin film pads ($60\mu m \times 60\mu m$) have been patterned with a chromium-based lift-off method. A 300 nm layer of poly(methyl methacrylate) (PMMA) 950 K A4 was coated onto pSi (100) substrates at 3000

rpm for 60 s and then baked for 3 min at 160°C . The square pads were then defined into PMMA by an electron beam exposure at 20 keV (eLINE Plus, Raith GmbH), followed by an MIBK/IPA (1:3)-based development procedure. The pattern was consecutively cleaned by a plasma ash etch step (Femto, Diener Electronic GmbH, 12 s at 40% power). A 120 nm chromium layer was evaporated at $1.5 \text{ \AA/s}$ via thermal evaporation (Amod, Angstrom Engineering Inc.), as the hard mask for a high-temperature sputter process, compatible with a standard acetone lift-off process. In case of TiN, a 50 nm thick TiO_xN_y thin film was deposited by RF reactive magnetron sputtering, from a high-purity Ti target (Pi-kem), using a MANTIS Deposition System at 600°C . The deposition was carried out using a gas mixture of Ar and N_2 with a total constant pressure of 0.2 Pa. A standard chromium etchant containing ceric ammonium nitrate was used to remove the chromium mask and the TiO_xN_y residues on top of the mask. The sample was rinsed with DI water and evaporated with Al on the other side to complete the fabrication process as described above. Ti and Au were deposited via sputtering and thermal evaporation, respectively in an Angstrom vacuum deposition chamber. The TiO_2 thin film pads (60 m x 60 m) for the comparison samples were deposited via sputtering while the patterning process is equal to the one described above. Different TiO_{2-x} films of thickness 5 nm and 30 nm were deposited by DC sputtering from a high-purity Ti target (Pi-kem), using an Angstrom deposition system at room temperature. In order to compare the crystal structure of the $\text{TiO}_2 - x$ surface layer of TiN and the 5 nm sputtered TiO_{2-x} thin film, XRD measurements were performed on both layers shown in Figure 5.3. Here, both films show very similar spectra while no indication of any particular crystal orientation is observed. The weak common peak at around 32.9° can be attributed to forbidden Si (200) reflection coming from the substrate. Thus, both films can be considered to be amorphous and the

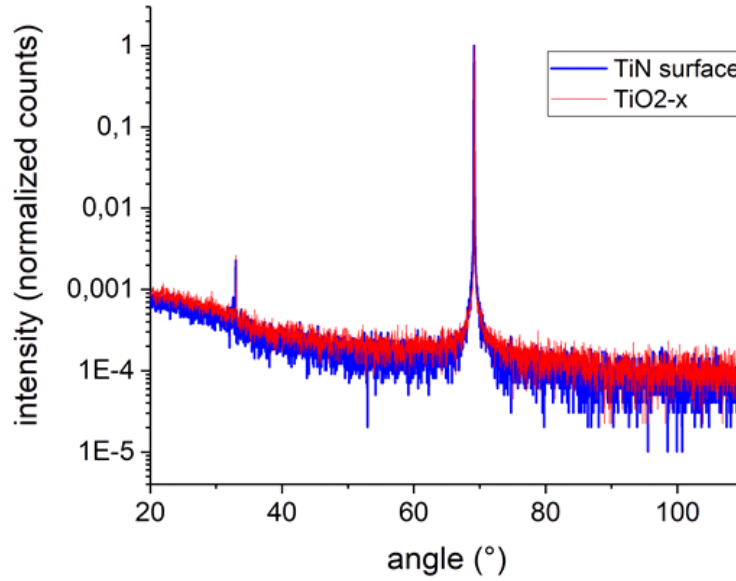


Figure 5.3: XRD spectra of TiN and TiO_{2-x} on pSi. The prominent peak at around 69° stems from the Si substrate and was used for normalization while the weak peak at around 32.9° can be attributed to TiO_{2-x} . Both samples show essentially the same spectra, confirming the similar crystal properties of the films.

absence of any TiN peaks shows that the 50 nm TiN film is amorphous as well.

5.3 Hot holes based TiN photodetectors

The opto-electric setup used for the photo detectors characterization is illustrated in Figure 5.5 a). A supercontinuum quasi CW laser source (Fianium) in conjunction with an acousto-optic tunable filter (AOTF) was used to illuminate the samples in a wavelength regime from 1100 nm to 1600 nm. The laser beam was focused via a near IR optimized 50x objective exhibiting a NA of 0.5 which produces a spot size of $< 3.9\mu\text{m}$. For backside contacting, the corners of a double side polished Si substrate were scratched and covered with Al forming an ohmic contact with the pSi ($500\mu\text{m}$), the Al was in contact (via Ag paste) with a gold metal piece on which a tip Au micro probe metal tip was placed. For frontside

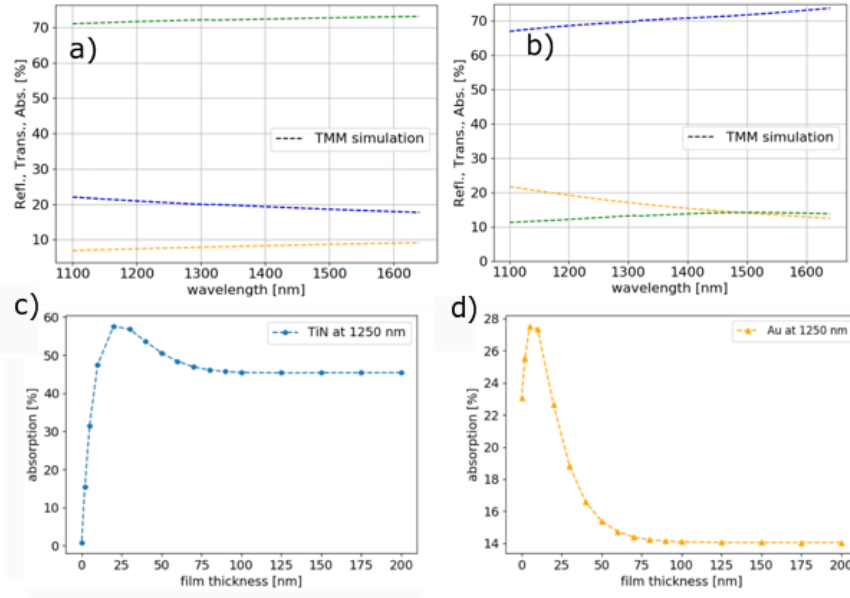


Figure 5.4: *Transfer matrix method (TMM) simulations for backside illuminated a) pSi/TiO_{2-x}/Ti (5nm TiO_{2-x}, 50nm Ti) and b) pSi/TiO_{2-x}/Au (5nm TiO_{2-x}, 19 nm Au). The green line is the absorption, blue the reflection and orange the transmission. TMM calculations of backside illuminated pSi/metal systems at 1250 nm illumination wavelength showing the absorption of c) a TiN thin film and d) a Au thin film on a 2 nm Cr adhesion layer, both in dependence on film thickness. Silicon thickness was taken to be 100 μ m*

contacting, the micro probe was directly placed on the sample. The probes used have a tip size diameter of about 2.5 μ m. The current was measured by 4 contact measurements via a source measurement unit (SMU, Keithley 236) and recorded using a custom-built Python script connected via GPIB and a multifunction I/O device (USB-6343, National Instruments) to the SMU. During the measurement, we maximized the photocurrent while assuring that the laser spot was not closer than 10 μ m to the metal tip in order to exclude any direct influence of the tip onto the photocurrent measurement. Micro probe tips connected to a source measuring unit were placed as electrical back and frontside contacts and a wavelength selective super-continuum light source was used for backside illumination through a double side polished pSi substrate.

The 500 m thick pSi substrate assures hole collection via the backside contact

as indicated in Figure 5.5 a). The setup enables photo current measurements to determine the photo responsivity (PR) which is a main figure of merit for photodetectors and is defined as

$$PR = \frac{I_{photo} - I_{dark}}{P_{in}} \quad (5.1)$$

with I_{photo} being the photo induced current, I_{dark} the dark current and P_{in} the power of the incident laser beam. All measurements were performed in the wavelength regime ranging from 1100 nm to 1600 nm. The metal film thickness of Au (19nm), TiN(50nm) as well as Ti (50nm) were chosen based on analytical solution of the Fresnel equations, by optimizing thickness d under the given conditions (Figure 5.4, TMM simulations). Indeed, by TMM calculations of backside illuminated pSi/metal systems at 1250 nm illumination wavelength we can see perfect absorption of 5.4 a) a TiN thin film and 5.4 b) a Au thin film on a 2 nm Cr adhesion layer, both in dependence on film thickness. Figure 5.5 b) depicts the responsivity under illumination and in the dark (on/off) in dependence on time, comparing a pSi/TiN with a pSi/Au junction.

Although both junctions are expected to exhibit a comparable hole SB at the SC/metal interface of 0.61 eV for Au and 0.58 eV (see SI for Au and [203] for TiN), the pSi/TiN junction provides a stable PR signal of $\approx 1mA/W$ which is in the competitive range with comparable zero-bias photo detection studies [190, 194, 200, 204] and about one order of magnitude higher compared to its pSi/Au counterpart. The PR dispersions of pSi/TiN and pSi/Au shown in Figure 5.5 c) (blue and orange curve) deviate significantly from one another which points towards a different current generation mechanism at play. The measured photo response of hot carrier SB junctions is commonly described [194, 205, 206] by the

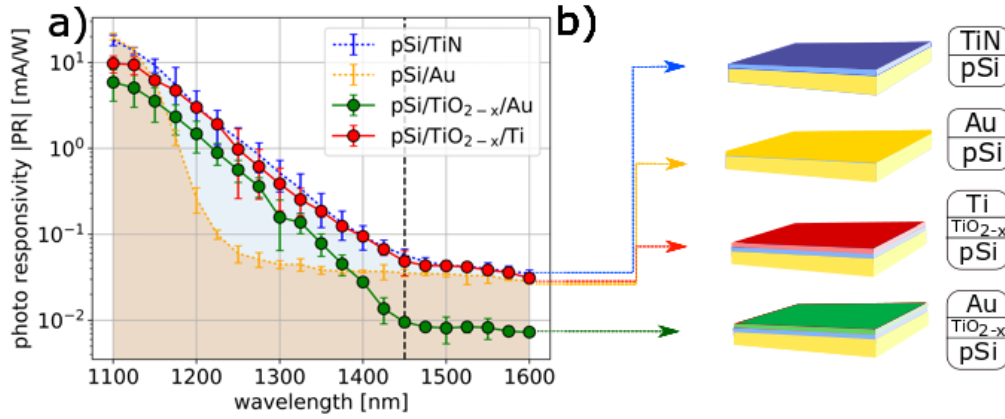


Figure 5.5: a) Absolute PR of the individual material systems illustrated in d). The inset shows a Fowler equation fit (red broken line) to the pSi/Au data obtained with a fit parameter of $C_f = 1.2 \times 10^{-3} / \text{eV at } B = 0.56 \text{ eV}$. b) Schematics of the material stacks investigated with thin film thicknesses of 50 nm (TiN), 50 nm (Ti), 19 nm (Au). When indicated an amorphous 5 nm TiO₂ thin film has been sputtered as interlayer. The pSi/TiN is shown without TiO_{2-x} interlayer as TiO₂ was not additionally deposited but was naturally formed during deposition.

modified Fowler equation [?, ?]:

$$PR_{\text{fowler}} = \frac{qC_f A(\lambda)(hf - \phi_{SB})^2}{hf^2} \quad (5.2)$$

with q being the elementary charge, C_f the Fowler emission coefficient, $A(\lambda)$ the wavelength dependent absorption, hf the energy of the incident photon and ϕ_{SB} the SB potential height at the SC/metal interface. From fitting of the experimental data obtained for pSi/Au shown in the inset of Figure 5.5 c), a barrier height of 0.56 eV can be extracted which agrees well with the barrier height of 0.61 eV estimated via the thermionic emission model and dark IV measurements (Figure 5.7).

The good agreement with the Fowler model matches well with our expectation that the response obtained by illuminating the pSi/Au thin film system can be understood by a hot carrier mechanism as also observed in comparable studies [8,19]. Here, sufficiently energetic intraband transitions ($> \phi_{SB}$) of carriers in the

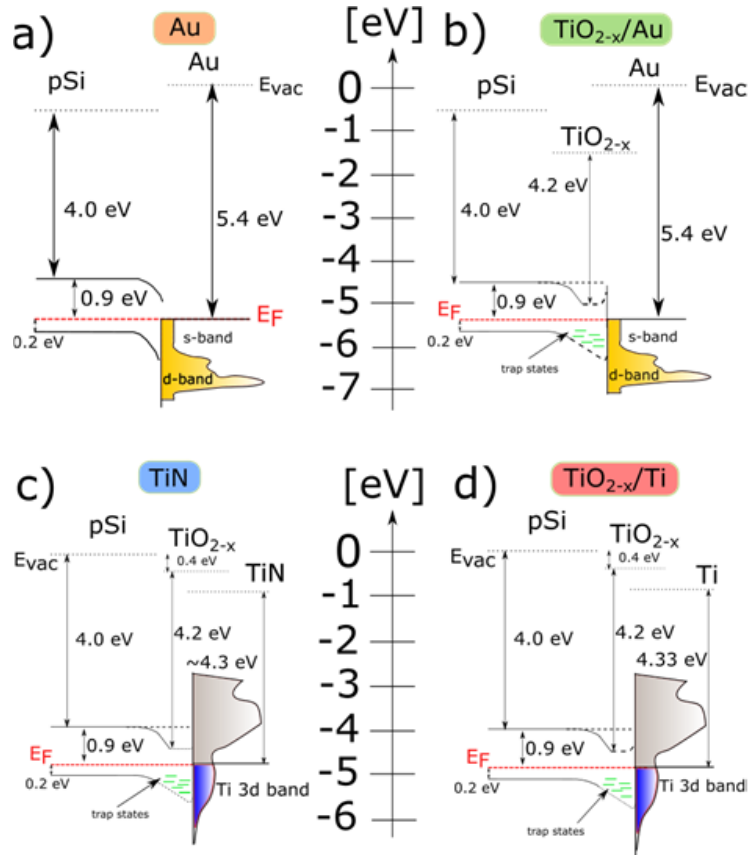


Figure 5.6: Band energy diagrams showing the simplified band alignment of a) Au/pSi b) pSi/TiO_{2-x}/Au c) pSi/TiO_{2-x}/TiN and d) pSi/TiO_{2-x}/Ti. The SB of pSi/Au has been estimated from dark IV curves using the thermionic model, while all other energies were extracted from literature.

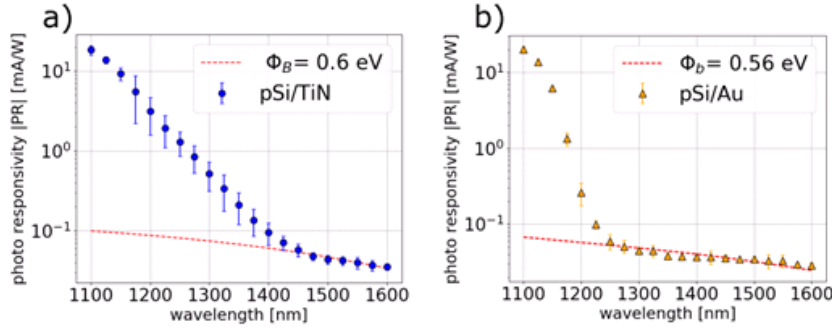


Figure 5.7: Fowler equation fit (red broken line) to a) pSi/TiN data (50 nm TiN thin film on pSi substrate) and b) pSi/Au data (19 nm Au thin film on pSi substrate with a 2 nm Cr adhesion layer) obtained with the fitting parameters of $C_f = 1.0 \times 10^{-3}/\text{eV}$ at $\phi_B = 0.6\text{eV}$ for TiN and $C_f = 1.2 \times 10^{-3}/\text{eV}$ at $\phi_B = 0.56\text{eV}$ for Au, respectively.

gold sp-band give rise to hole transfer over the SB at the pSi/Au interface and consecutive collection in the pSi [?], thus separating the charges as schematically illustrated in Figure 5.6 a).

On the contrary the response of the pSi/TiN sample, shown in Figure 5.5 c), clearly shows a distinct PR from the pSi/Au one and deviates from the expected Fowler equation. Due to such novel behavior the pSi/TiN system exceeds the pSi/Au PR in a range from 1150 nm and 1450 nm by up to one order of magnitude. The dark current was estimated to 10 nA and the open circuit potential is 150 mV at 1250 nm. The high PR of 1mA/W shows that TiN can indeed be used for efficient carrier separation and self-powered photo detection, outperforming commercial Si detectors in the IR regime [200]. Indeed Silicon based photodetectors, usually sharply decline after 900nm and their photocurrent becomes negligible after the 1100nm when the photon energy becomes smaller than the bandgap. However, the system here proposed is still not as efficient as top of the art IR photodetectors based on GaAs or InGaAs quantum well structure.

Typical photoresponses of these structure are one or two order of magnitude higher than the system here proposed. However, low working temperature and extremely complicated fabrication procedures based on molecular beam epitaxy

are needed for the quantum well structure. In this work, instead high photoreponse are achieved in an extremely easy to fabricate system. Here, we claim that an amorphous TiO_{2-x} film of around 5 nm in thickness which forms between the TiN and pSi during growth is at the origin of this deviation, allowing for a facilitated trap state mediated hole transfer in TiO_{2-x} . We support this hypothesis in the following by comparing the response of a TiO_{2-x} free system (pSi/Au) to systems in which amorphous TiO_{2-x} interlayers have been additionally introduced by sputtering, namely pSi/ TiO_{2-x} /Ti, pSi/ TiO_{2-x} /Au and pSi/ TiO_{2-x} as shown in Figure 5.5 d). Further evidence in favor of this argument is found by pump probe as well as XPS measurements on the TiO_2 /TiN interface presented later in the report. We may note that unresolved discrepancies between the measured photo response and the Fowler model in hot carrier junctions containing TiO_{2-x} interfacial layers have been reported by various other studies [207, 208] and this report might contribute to a better understanding of this deviation.

5.3.1 TiO_{2-x} interfaces for novel transport mechanism

Figure 5.5 c) shows the PR of the respective sample systems depicted in Figure 5.5 d). The comparison of the oxide free pSi/Au system (orange curve) and pSi/ TiO_{2-x} /Au (green curve) for which a 5 nm amorphous TiO_{2-x} interlayer has been deposited discloses that the addition of a TiO_{2-x} thin film changes the response drastically, enhancing the response between 1160 nm and 1400 nm. The shape of the pSi/ TiO_2 /Au curve is very similar to the response of pSi/TiN, while exhibiting the same slope cut off value at 1450 nm. Moreover, the same holds true for the PR of a Ti thin film (red curve) deposited on an amorphous 5 nm TiO_2 interlayer. For pSi/ TiO_{2-x} /Au however, the PR for longer wavelength ($> 1400nm$) has dropped by one order of magnitude compared to Au only and TiN. This drop can be attributed to the low absorption, $A(l)$, of

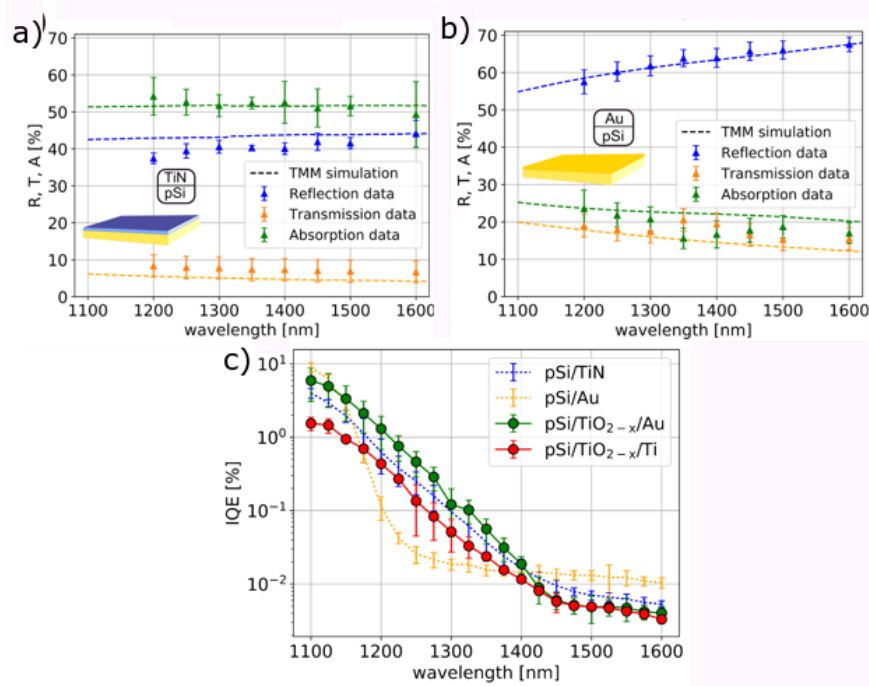


Figure 5.8: Reflection, transmission and absorption measurements compared to transfer matrix method (TMM) simulations for a) Au/pSi and b) TiN/pSi, respectively corresponding to the percentage of incident light which is absorbed, reflected or transmitted. c) IQE of TiN, Au, TiO_{2-x}/Au, TiO_{2-x}/Ti films on pSi.

the pSi/ TiO_2 /Au stack which is merely 11% compared to 52% in pSi/TiN and 25% in pSi/Au as shown from absorption measurements in Figure 5.8 a), b) and transfer matrix method (TMM) simulations (see Figure 5.4). The prominent role of the metal absorption becomes apparent when the internal quantum efficiency (IQE) dispersion defined as [?]:

$$IQE = \frac{PR \cdot hf}{q \cdot A(\lambda)} \quad (5.3)$$

is taken into consideration as shown in Figure 5.8 c). Here, the absorption normalized response shifts the IQE of all TiO_{2-x} containing samples to similar values. The IQE at wavelengths left to the cut off (1450nm) differ slightly. Such behavior can be attributed to the different mean free paths (MFP) of the materials and to unequal band bending at the TiO_2 /metal interface which results in an effectively diminished TiO_2 potential barrier for TiO_2 /Au as illustrated in Figure 5.6 b) d) . The TiO_{2-x} containing samples show an IQE of around 0.2% at 1250 nm. The comparison of oxide free systems (pSi/Au) with TiO_{2-x} containing samples points out that the TiO_{2-x} interlayer is at the core of the deviating PR dispersion observed for pSi/TiN. More importantly, our findings suggest that an amorphous TiO_{2-x} thin film in a pSi/ TiO_{2-x} /metal system enables a significant PR enhancement for various metals compared to an oxide free system in the IR, as here explicitly shown for an Au thin film. The strong metal absorption dependence apparent from the IQE dispersion shown in Figure 5.8 c) implies that the metal predominantly acts as an absorber while the actual TiO_{2-x} /metal interface plays the role of facilitating hole transport in the Sub-bandgap region. This piece of information can also be accessed by IV measurements under illumination shown in this chapter. In order to further clarify the origin of the PR cut off observed for all TiO_{2-x} containing samples, the PR from a 5 nm TiO_{2-x} thin film deposited on pSi (purple curve) as shown in Figure 5.9 was determined.

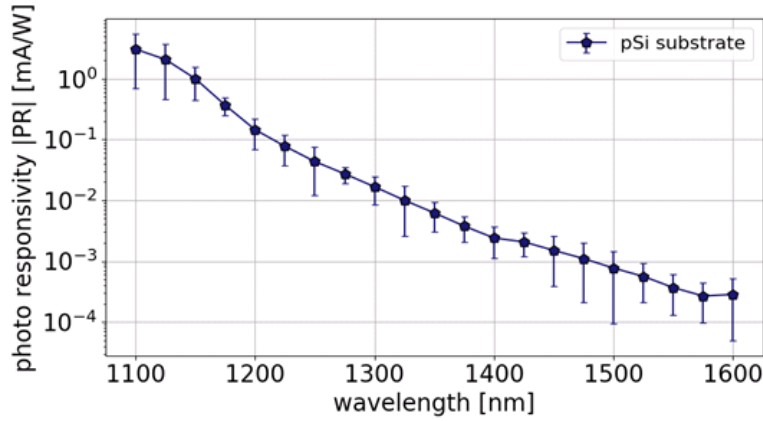


Figure 5.9: Measured (background) photo responsivity of the pSi substrate used throughout the experiment.

The PR is significantly smaller due to the absence of a metal absorber providing carriers. The cut off however can be clearly reproduced and attributed to an altered current response due to the availability or absence of trap states in the TiO_{2-x} providing an effective hole transfer channel. This claim is further confirmed by pump-probe measurements shown in Figure 5.8 d), accessing the trap state response directly via exciting electrons occupying the trap states into the TiO_{2-x} conduction band. The comparison between the TiO_{2-x} free Au/pSi system and the TiO_{2-x} containing systems such as pSi/ TiO_{2-x} /Ti, pSi/ TiO_{2-x} /Au and pSi/ TiO_2 allow three main observations:

- a deviating PR dispersions which points towards different current generation mechanisms at play
- a distinct PR cut off value separating the PR dispersion into two different regimes
- a strong PR increase for TiO_{2-x} containing systems between 1160 nm and 1400 nm.

In order to approach the observations listed above we consider band model diagrams as depicted in Figure 5.6. The band model diagram of a TiO_{2-x} free

pSi/Au system is shown in Figure 5.6 a), illustrating hot hole excitation and transfer over the SB at the pSi/Au interface which can be described by the Fowler model. Figures 5.6 b) d) show the pSi/ TiO_{2-x} /TiN, pSi/ TiO_2 /Au and pSi/ TiO_{2-x} /Ti system, taking a 5 nm thin TiO_2 interlayer into account. Amorphous TiO_{2-x} possess a bandgap energy of about 3.2 eV [209] constituting a hole barrier which is usually too large to be overcome by the excitation energies considered here (1.1 eV – 0.77 eV). However, a $\approx 9nm$ n-type (TiO_{2-x} side) depletion region width at the pSi/ TiO_{2-x} interface estimated via Poisson equations (Eq. S4 and S5) gives rise to a strongly diminished band gap and steep band profile as schematically indicated in Figure 5.6 b)-c). Indeed, the estimated widths of the space charge region at the pSi/ TiO_{2-x} junction interface based on Equation 5.5 and 5.4 which follow from the Poissons equation are:

$$w_{TiO_2} = \left(\frac{2\epsilon_{TiO_2} V_d}{q} \frac{n_A/n_D}{n_A + n_D} \right)^{1/2} \quad (5.4)$$

$$w_{pSi} = \left(\frac{2\epsilon_{Si} V_d}{q} \frac{n_D/n_A}{n_A + n_D} \right)^{(1/2)} \quad (5.5)$$

where q is the elementary charge, ϵ_{Si} the Silicon permittivity, ϵ_{TiO_2} the TiO_2 permittivity, V_d the built in potential for which we use a conservative estimate of $V_d = 0.6V$ assuming a Fermi level position of $\approx 0.2eV$ above the valence band in pSi and 0.3 eV below the conduction band in TiO_{2-x} , n_A and n_D being the carrier densities in the boron doped silicon and the n-type TiO_{2-x} , respectively. Thus, we calculate a conservative estimate for the depletion region width of the n-type TiO_{2-x} region as $w_{TiO_2} = 9nm$ and an approximate pSi space charge region width of $w_{pSi} = 0.9\mu m$. Considering that we used an oxide layer thickness of about 5 nm in our experiments it becomes obvious that the interlayer region is subject to significant band bending due to carrier depletion at the heterojunction interface.

Additionally, inter-bandgap trap states in amorphous TiO_{2-x} introduce trap state assisted transitions [209–211] which are in line with the pump probe and the PR. We propose that the response laying to the left from the cut off is originated in trap state assisted carrier transfer and thus exhibits different dispersion from the hot hole excitation over a SB observed in pSi/Au. The response laying to the right off the cut off might be attributed to conduction through tunneling channels [212] in the few nm oxide thin film. The distinction in carrier transfer mechanisms between the metal and the pSi becomes further clear under reverse bias operation. The PR of the pSi/Au Schottky contact under reverse bias shown in Figure 5.10 a) increases with bias as the carriers can be excited over the SB and consecutively collected due to the external field while the dark current stays at a minimum due to the Schottky barrier blocking potential [193, 206, 213, 214]. On the contrary as shown in Figure 5.10 b), pSi/ TiO_{2-x} /Au exhibits a saturation behaviour in reverse bias which is typical for photo diodes in photoconductive mode and can be equally observed for pSi/TiN. Here, the photo current is created via electron-hole pair generation in the p-n depletion region. The IR excitation energies used in our case however, lead to negligible absorption in the pSi/ TiO_{2-x} depletion region as confirmed by a weak PR from pSi/ TiO_{2-x} alone (cf. Figure 5.5 c)).

Considering that TiO_{2-x} usually acts as a hole blocking layer, the findings suggest that the signal is mainly based on hole transfer via trap states and not over the SB while the carriers are provided by excitations in the metal thin film as illustrated in Figure 5.10 d). Interestingly, the pSi/ TiO_{2-x} /Au PR rises from about 0.8 mA/W at zero bias to 4 mA/W at -0.45 V. The spectral dependence is due to the fact that higher energies are able to excite a wider range of carriers in the metal which are consecutively available for transfer. The observations are in line with the non-Fowler type PR dispersion observed (cf. Figure 5.5 c)) and

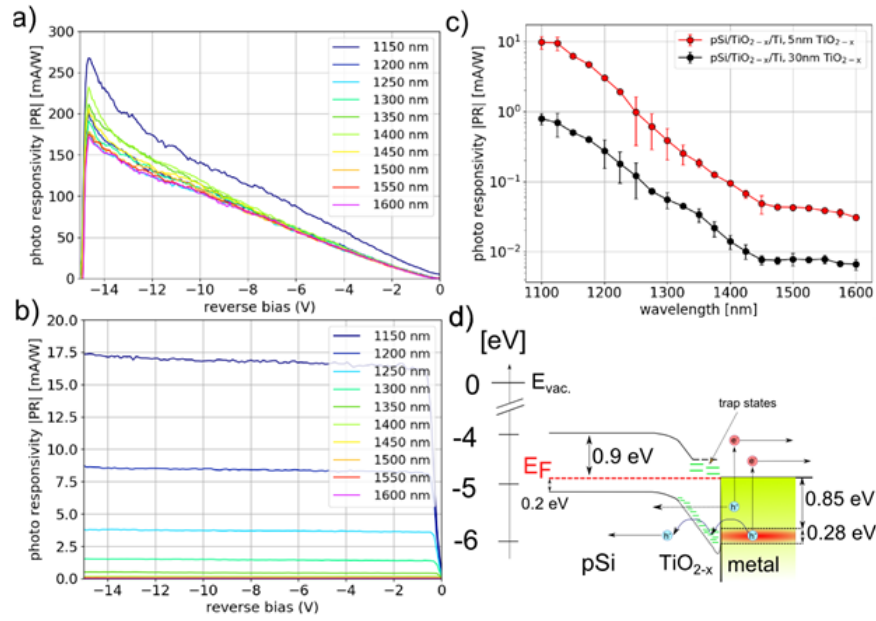


Figure 5.10: Responsivity under reverse bias for a) pSi/Au and b) $pSi/TiO_{2-x}/Au$ at different wavelength. c) Responsivity without bias for $pSi/TiO_{2-x}/Ti$ with different TiO_{2-x} thickness of 5 nm and 30 nm. d) Band energy diagram of the $pSi/TiO_{2-x}/metal$ system under study illustrating the proposed mechanism and the current directions. Here, the energy range and position of the carriers excited in the metal by the incident energy is highlighted by a red ribbon, the holes by blue dots and electrons by red dots.

show that efficient carrier injection supported by a metal absorber via trap states is possible. We further support this hypothesis by comparing different thickness of the TiO_{2-x} interlayer namely 5 nm and 30 nm of the pSi/ TiO_{2-x} /Ti system as shown in Figure 5.10 c). Here, we expect an increase of the TiO_{2-x} effective bandgap as the pSi/ TiO_{2-x} SCR width stays constant thus decreasing the current response due to a larger distance to the metal. Although the absorption in both Ti thin film samples is very similar (see 5.4), the PR drops by over one order of magnitude while the dispersion stays the same. This shows that the vicinity to the metal is crucial for a high PR but does not define the dispersion. A similar observation has been made by Tan et al. [209] for Au on TiO_{2-x} , however a rough Au film gave rise to plasmonic enhancement which is not plausible for the smooth films used here (see 5.3). Based on our observations the transfer illustrated in Figure 5.10 d) is proposed. Here, the metal absorber provides holes which can travel to the pSi/ TiO_{2-x} interface where they participate in the trap state assisted carrier excitation and are consecutively injected into the pSi. With increasing TiO_{2-x} thickness, fewer holes can travel to the pSi/ TiO_{2-x} SCR as they are blocked by the TiO_{2-x} bandgap further proving the trap assisted transport mechanism.

Further work to improve the performance of the photodetector, would be to in the direction of improved absorption in terms of carrier generation efficiency and spectrum. The addition of an ITO interlayer would allow for a broader absorption in the red, further pushing the performance of the photodetector in the red/near-infra-red range. On the other hand the creation of resonant plasmonic structure by patterning of the metallic layer, would be able to push further the efficiency in carrier generation by increasing the absorption of the photodetectors by two or three order of magnitude.

5.4 Conclusions

In conclusion we have demonstrated Si-compatible sub-bandgap photodetection at zero bias for a backside illuminated 50 nm TiN thin film on a p-type Si substrate, exhibiting a photoresponsivity of 1 mA/W at 1250nm. We showed that the amorphous TiO_{2-x} interlayer between the pSi and the TiN is at the origin of a distinct photoresponse which significantly differs from the one of an oxide free pSi/Au comparison sample. Moreover, we disclosed that a 5 nm amorphous TiO_{2-x} interlayer between a pSi substrate and a metal thin film leads to an increase in photoresponsivity at zero bias of about one order of magnitude compared to an oxide free system. The change in dispersion was observed for Ti, Au and TiN and a clear PR enhancement was measured for Au thin films. Our findings suggest that the metal merely acts as an absorber enabling hole transfer via TiO_{2-x} trap states which can consecutively be collected in the pSi. Additionally, the photoresponsivity of pSi/ TiO_{2-x} /Au can be increased from about 0.8 mA/W to 4 mA/W at zero and 0.45V reverse bias, respectively allowing for bias dependent photo switching. We believe that the study conducted is valuable as it shows that pSi/ TiO_{2-x} can be used as a platform for photo current enhancement at zero bias while it combines the extensively studied materials TiO_2 and Si with TiN which constitutes a promising candidate for a wide range of opto-electronic and plasmonic applications. Indeed, the high PR of 1mA/W shows that TiN can indeed be used for efficient carrier separation and self-powered photo detection, outperforming commercial Si detectors in the IR regime [200]. Indeed Silicon based photodetectors, usually sharply decline after 900nm and their photocurrent becomes negligible after the 1100nm when the photon energy becomes smaller than the bandgap. However, the system here proposed is still not as efficient as top of the art IR photodetectors based on GaAs or InGaAs quantum

well structure. Typical photoresponses of these structure are one or two order of magnitude higher than the system here proposed. However, low working temperature and extremely complicated fabrication procedures based on molecular beam epitaxy are needed for the quantum well structure while no power, room temperature and low cost are strong point of the structure here presented.

Chapter 6

Screening the energy of hot carriers

This section is dedicated to the study of hot electron in the context of hot electron driven chemical reaction. When light impinges on a metallic nanoparticle, electrons may be promoted to energies above the Fermi level. As a result of the plasmon decay, Landau damping process can lead to the generation of hot-carriers, that when extracted can be used for triggering external chemical reaction. The aim of this work in collaboration with Dr. Evangelina Pensa is to study the energy and efficiency of hot carriers for triggering the electrochemical polymerization of aniline into polyaniline (PANI).

6.1 Hot electron chemistry

The unique capacity of plasmonic nanostructures to concentrate electromagnetic fields, scatter electromagnetic radiation, or convert the energy of photons into heat makes them suitable for various applications. Plasmonic metals have been used in single-molecule spectroscopy, surface-enhanced Raman spectroscopy, molecular sensing and detection in biological systems, medicinal

heat-induced selective tissue targeting and solar cells [215]. These applications take advantage of either plasmon-amplified light-molecule interactions or laser-induced, plasmon-mediated local heating of nanostructures, which triggers accelerated thermal processes in the neighbourhood of the nanostructure [54]. Similarly plasmonic chemistry aims at manipulating the reactivity of the plasmon-molecule interface. As an example, charge transfer can be induced by plasmonic structures, altering the chemical composition of their surrounding environment [54]. Such a process is the first step for many fundamental physicochemical phenomena with important technological applications, such as catalysis and molecular electronics. However, nanoscale control of these processes is hard to achieve, turning traditional technologies to still prevail over the plasmonic ones [8]. It becomes of great relevance then the study of the plasmonic-molecule interface to maximize efficiencies and ultimately control and externally manipulate these processes. Plasmon excitation in metal nanoparticles decay non-radiatively (see Chapter 2.6) by generating non-equilibrium hot carriers, i.e. electron-hole pairs, which thermalize after electron-electron scattering, increasing the surface temperature of the gold nanoparticle [14, 53, 216, 217]. These two mechanisms (hot-carriers and surface temperature) are at the base of the energy transfer capable of driving chemical reaction at milder conditions compared with respect to the non-excited nanostructures, meaning that illuminated nanoantennas can behave in the same way as photocatalysts. Recently, the photocatalytic effect of excited nanostructures has been successfully demonstrated for different systems ranging from semiconductor to metal nano-antennas [48, 217–219] and either for the reduction or oxidization of different analytes.

It has been found that the reduction of many molecules as H_2O [220], CO_2 [221], thiols [222] can be effectively achieved through the extraction of hot-electrons from the plasmonic nanostructure, while fewer examples can be found

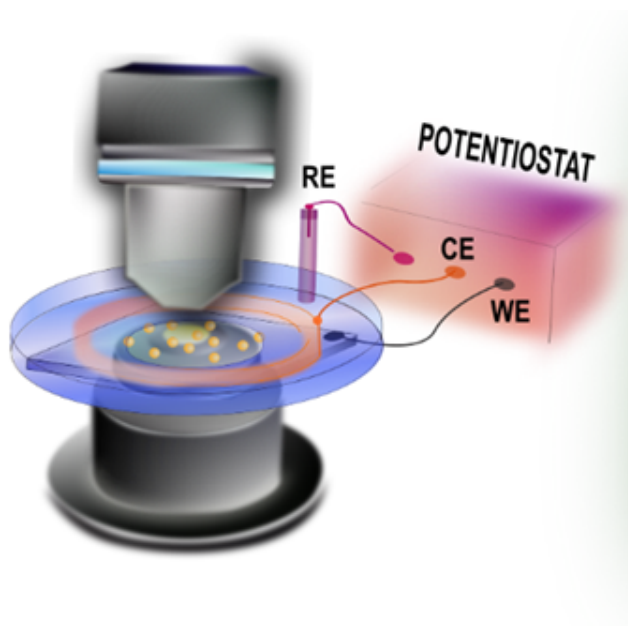


Figure 6.1: *Experimental set-up used for the electrochemistry and dark-field measurements. An electrochemical cell was designed to hold the liquid as well as the electrical contact, while allowing for the immersion of the objective for optical measurements*

for photo-oxidation reactions [223]. Despite a large number of examples showing how hot-carriers can assist chemical reactions, very little knowledge is available about the effective energy of such plasmonic-derived carriers at the metal-molecule interface. However, this knowledge is one of the key aspects for further exploit of plasmonic-driven photochemical reactions and the design of effective plasmonic photocatalysts. To date, the determination of hot-carriers energy has been done by detecting either the increase of the product concentration or the decrease of the reactants by conventional analytical techniques. However, these techniques are limited by the requirement of a critical amount of analyte (products or reactants) in order to achieve a good signal to noise ratio. In these experiments, such limitation was overcome by the use of an assembly of plasmonic nanostructure, and a value for the energy that hot-electrons need to provide for the reduction of ferricyanide anions on Au nanoparticles was reported as 0.24V [224].

In this work, a combination of electrochemistry and dark-field spectroscopy is used to study the role of a single photoexcited Au nanoparticle (AuNP) in the electro-oxidation of aniline to polyaniline (Figure 6.1). Electrochemistry provides a side-way to control the Fermi level of the metal nanoparticle, allowing to measure the hot-holes' energy. Our results show that the reaction can be effectively photocatalyzed by the AuNP when excited at its plasmon resonance. Using wavelength-dependence studies the contribution of each mechanism of the plasmon-decay is disentangled. Furthermore, the energy of hot carriers for triggering the electro-polymerization reaction was determined at different wavelength along the plasmon absorption, showing that even if the absorbed initial energy is the same, the hot hole generation efficiency follows the plasmon absorption spectrum, with energy ranging from 24 meV to 240 meV.

6.1.1 Dark field set-up for scattering measurement

The oxidation of aniline molecules to generate polyaniline (PANI) on the surface of 80 nm Au Nanoparticles (NPs) was studied in an electrochemical cell mounted on a dark-field microscope with a water immersion objective, as shown in Figure 6.1. This opto-electrochemical set-up allows tuning the Fermi level of Au NPs (by the use of the potentiostat) as well as the illumination and spectroscopic characterization of single NPs through the microscope optical path. The inverted microscope used for dark field spectroscopy measurement is better outlined in Figure 6.2.

In Figure 6.2 the light path through a dark-field microscope is shown:

- Light enters the microscope for illumination of the sample from the bottom path;
- A specially sized disc, the patch stop, blocks some light from the light source, leaving an outer ring of illumination;

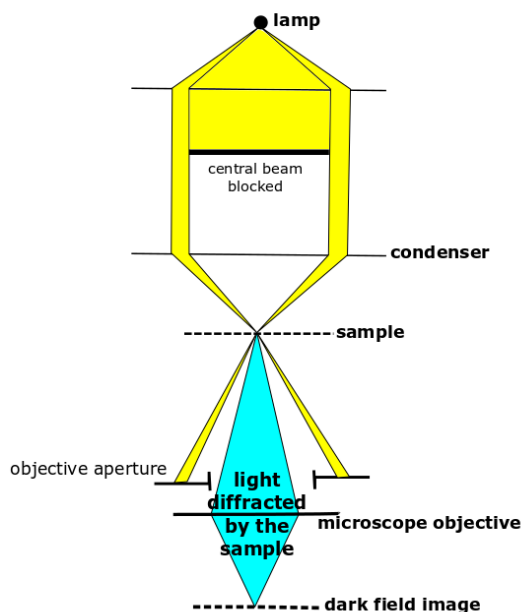


Figure 6.2: *The path of light involved in the dark field configuration used in our experimental set-up.*

- The condenser lens focuses the light towards the sample;
- The light enters the sample: most is directly transmitted, while some is scattered from the sample;
- The scattered light enters the objective lens, while the directly transmitted light simply misses the lens and is not collected due to a direct-illumination block;
- Only the scattered light goes on to produce the image, while the directly transmitted light is omitted;

Dark-field microscopy is a very simple yet effective technique and well suited for uses involving live and unstained biological samples, such as a smear from a tissue culture or individual, water-borne, single-celled organisms. Considering the simplicity of the set-up, the quality of images obtained from this technique is impressive.

The main limitation of dark-field microscopy is the low light levels, however by the use of water immersion objective (capable of high NA values) and powerful white light sources such limitation can be overcome. In the experiment presented, single 80nm Au nanoparticles can be imaged by dark field spectroscopy. Moreover such microscopy technique is almost entirely free of artifacts, due to the nature of the process. While the dark-field image may first appear to be a negative of the bright-field image, different effects are visible in each. In bright-field microscopy, features are visible where either a shadow is cast on the surface by the incident light or a part of the surface is less reflective, possibly by the presence of pits or scratches. Raised features that are too smooth to cast shadows will not appear in bright-field images, but the light that reflects off the sides of such the feature will be visible in the dark-field images. Given the strong absorption and scattering properties of plasmonic nanoparticles (NP), such a technique becomes a powerful tool for their imaging and for the measurement of the scattering cross section (Chapter 2.5) of these structures.

6.2 Aniline polymerization

The electro-polymerization of aniline starts with the oxidation of an aniline molecule to the radical cation at the AuNP surface, as sketched in Figure 6.3 a). Then, these cations react forming the conductive polymer PANI. The formation of PANI is then monitored optically through changes in the scattering spectra of the Au NPs thanks to the plasmon sensitivity towards its surrounding. Single NP spectra were obtained using a Witec spectrometer based on a 180 lines/mm diffraction grating and a cooled CCD device. A halogen lamp and a dark-field condenser were used to achieve dark-field illumination 6.2. When immersed in aniline solution, the NPs present a scattering peak at $561 \pm 3nm$, as shown in Figure 6.3 c) (orange curve). Polymerization of aniline generates a

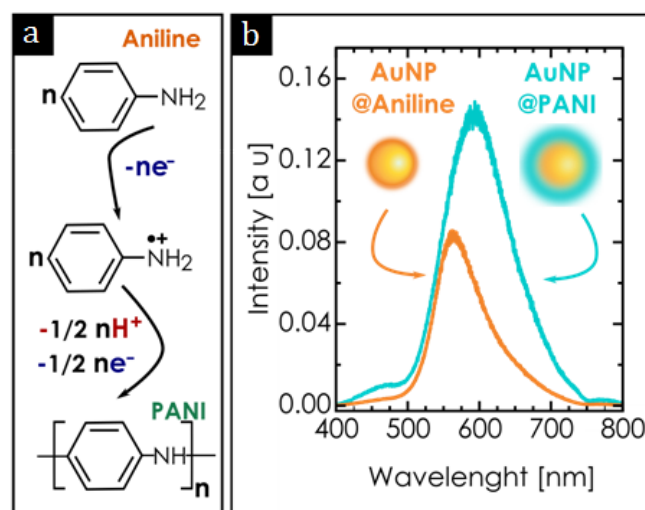


Figure 6.3: *a) The aniline polymerization under study. b) Dark field spectra of the Au nanoparticle with aniline in its surroundings (red curve) or with the PANI polymer (blue curve).*

change in its refractive index, causing a red-shift and an intensity increase in the NPs scattering spectra (Figure 6.3 c) light blue).

The first step carried out was the study of a potentiostatic-polymerization in the absence of light. Electrochemical control was performed by using the three-electrode configuration (see Figure 6.1) and 0.2 M aniline in 0.5 M H_2SO_4 solution as supporting electrolyte. A saturated calomel electrode and a Pt coil served as reference electrode (RE) and counter electrode (CE), respectively. The Au NPs on an ITO substrate act as the working electrode (WE).

Using a potentiostat the potential of the WE (E_w) is varied relative to RE while any potential-induced change on the WE is followed by measuring the current between the WE and CE. With this configuration, it is possible to control the potential of the WE relative to the RE, which is equivalent to controlling the energy of the electrons within the WE (i.e. the Fermi level of the Au NPs on ITO). By imposing a higher positive potential (E_w), the Fermi level can be lowered and vice-versa. In Figure 6.4 b) measured current vs E_w is presented. The exponential increase in the current for high E_w values, indicates the gener-

ation around the Au NP of the conductive PANI layer. By exponential fitting of such a curve, the threshold voltage needed for the reaction to start is found to be at $E_{onset} = 0.679 \pm 0.004V$. Polymer generation is also noticed by observing the measured scattering spectra for different E_w values (before and after the threshold) 6.4 a). The E_w was step-increased by 0.1V from 0.2V up to 0.7V (Figure 6.4 a)). Between every step, the potential was held at -0.2V while the scattering spectra was measured. This was done to avoid any voltage dependence of the refractive index of PANI. Indeed, the scattering spectra measured after the threshold shows a red shift, with respect to the one of a NP in aniline solution. Such a red shift is attributed to the generation of the PANI polymer as we confirmed by a Raman spectroscopy measurement 6.4 c). It is important to note that polymerization takes place onto the entire WE i.e. on both ITO and AuNPs surfaces [225], however the scattering spectra measured only probes the polymerization occurring around the NP in the range of the plasmon evanescent field. Figure 6.4 d)(purple curve) shows how the peak of the scattering spectra maximum shifts versus the applied voltage E_w . A strong shift is observed at voltages higher than the aniline polymerization threshold, indicating the equivalence between the macroscopic current measurement and the single-particle spectroscopic measurement and outlining the strong relationship between these two different measurements.

6.2.1 Hot electron energy measurements

The aniline polymerization under plasmon excitation was then studied. Single NPs were placed under laser illumination at their plasmon resonance with a 561nm CW laser focused to its diffraction-limit spot using a water immersion objective with a 1.0 NA and a magnification of 63X (Figure 6.1). The NP was subject to 30 s of illumination with an irradiance of $2.2 \text{ mW}/\mu\text{m}^2$ and a bias

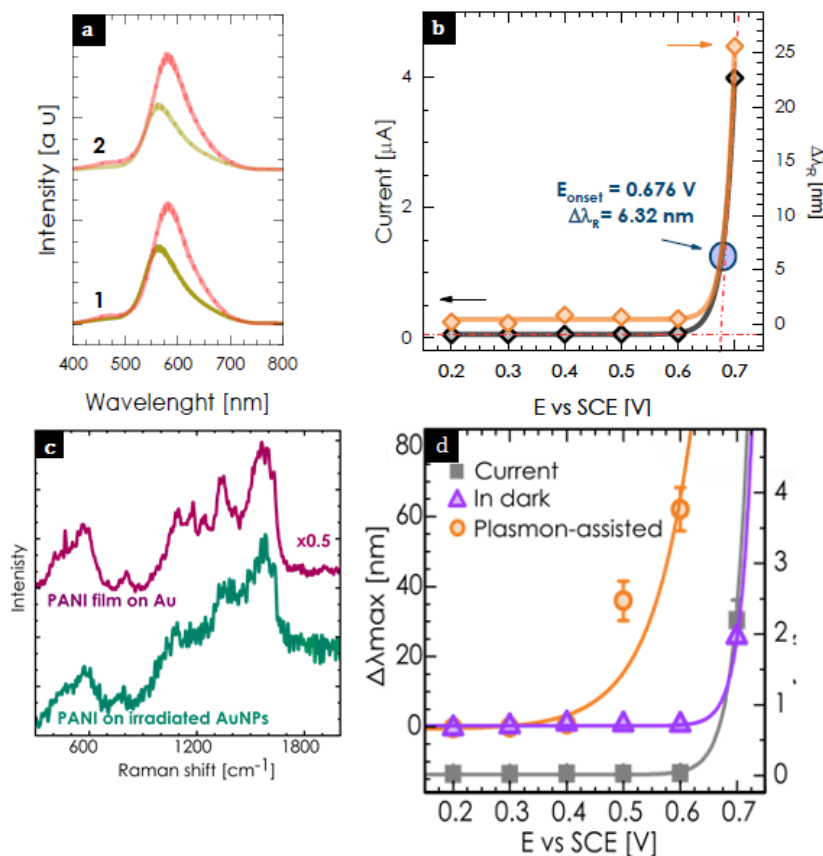


Figure 6.4: *a)* Dark-field spectra taken at two different points: before the threshold (red) and after (green), for two different nanoparticles. *b)* Electrochemical measurements carried on the AuNPs-ITO substrate for the polymerization to occur. *c)* Raman spectra of PANI on (top, orange) AuNPs-ITO substrate and (bottom, green) laser-irradiated AuNPs *d)* Electropolymerization conducted in dark (purple) and under laser-excitation of AuNPs with 561nm CW laser for 30sec at $I = 2.2 \text{ mW m}^{-2}$ (orange). Red-shifts of the maxima scattering wavelength ($\Delta\lambda_{max}$) as function of E_w . In dark, the electropolymerization reaction takes place onto the particles after $E_w = 0.7\text{V}$ is applied. Contrarily, when the polymerization is conducted under AuNPs-irradiation, the irradiated-nanoparticles catalyze the reaction making it occurring at lower voltages, while the non-irradiated one remains inactive until $E_w = 0.7\text{V}$ is applied. The symbols and the error bars correspond to the mean and standard deviation of $\Delta\lambda_{max}$ for more than 5 particles from at least 2 independent samples.

voltage (E_w). The scattering spectrum was then measured with the laser in the off state at $E_w = -0.2V$. Figure 6.4 d) (orange curve) shows the spectral shift of the scattering maximum vs applied voltage E_w . Interestingly, the polymerization threshold is shifted to lower voltage values when the particle is illuminated (0.5V instead of 0.7 V), showing the role of the plasmon as catalyser of the reaction and lowering the energy threshold needed. Moreover given the diffraction limit of the illumination (only a single NP is affected) at 0.5 V, PANI is formed selectively only on the surface of the illuminated NPs, and not on the non-illuminated ones or on the ITO surface as we can observe from Figure 6.5 a). When then the voltage applied reaches the 0.7 V threshold, the polymer is formed onto the entire sample. It is of importance to take notice that if the irradiation is conducted in aniline-free electrolyte, no changes are observed in the scattering spectra of the NPs, confirming the dependence of the spectral shift to the formation of the PANI polymer and not to geometrical changes of the NP due to heating.

Plasmons can play the role of chemical catalyzer with one of the following three mechanism, namely:

- intense electromagnetic fields;
- local heating;
- generation of highly energetic electronhole pairs (hot-carriers);

These three possible mechanisms are addressed in the following section, in order to prove that PANI polymerization is due to plasmon generated hot-holes.

Gold NPs when illuminated upon their plasmon resonance can produce high enhancement of the electromagnetic field close to their surface as we seen in the previous chapter [226]. It has been shown that such an increase in field intensity can be a driving force for chemical reaction by direct excitation of the molecules in the vicinity of the gold NP [227]. However, this cannot occur in the present case

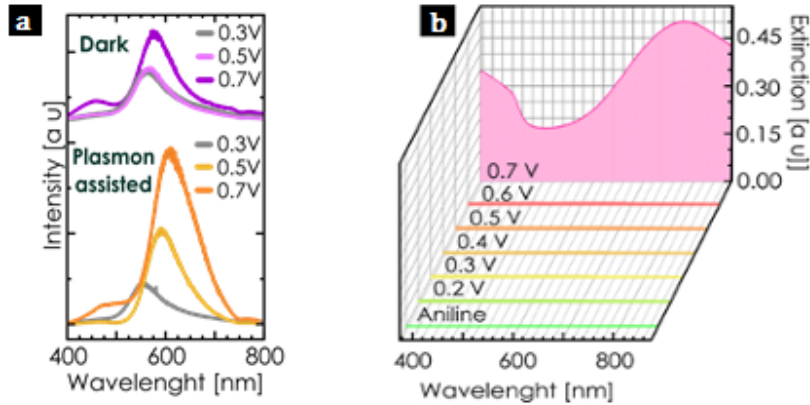


Figure 6.5: *a) Dark field spectra at different E_w both in the dark and under illumination. It can be seen as the spectral shift introduced by the polymerization of aniline appears at earlier voltage when the AuNPs is under illumination. b) UV-Vis spectra of the WE as function of E_w showing that any photo-active species are generated at E_w lower than 0.7V. Aniline spectrum is also included as background.*

because aniline is transparent to the excitation wavelength. Indeed, Figure 6.5 b) shows absorption spectra of aniline on the working electrode at different voltages E_w . No absorption peak is present in the visible range before the formation of PANI. Moreover, if such a process was driven by field enhancement we should have observed the formation of PANI on the illuminated NP at any voltage. Such consideration, rule out the near field as the possible driving mechanism.

Plasmonic structure are known to be efficient converters of light into heat due to their high absorption cross section and highly likely scattering events [228]. Indeed, when plasmonic structure are illuminated, their temperature can increase by tens or even hundreds of degrees. This can lead to thermal catalysis of chemical reaction close to the plasmonic structure. As this process is strongly linked to the generation of hot carriers, disentangling temperature and hot electron extraction catalytic process is quite complex. In order to do so, an experiment was designed where the NPs temperature was kept constant while changing the excitation wavelength. Four different wavelength were used for this

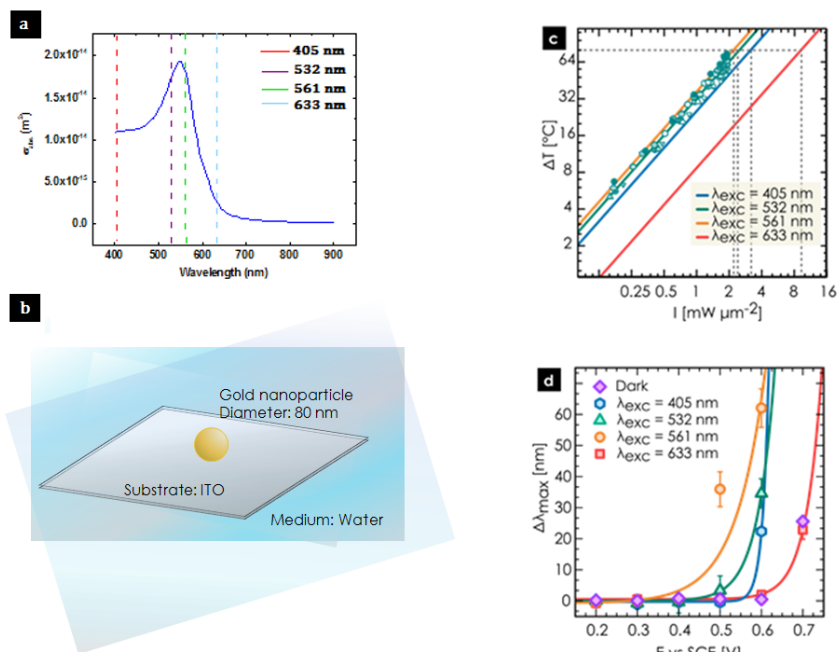


Figure 6.6: a) Simulated absorption spectrum of AuNPs on ITO immersed in aqueous media. Vertical lines show the wavelength of the different employed: 405 nm (blue), 532nm (green), 561 nm (orange) and 633 nm (red). b) Sketch of the simulated system, a AUNP of 80nm of diameter on top of an ITO substrate, immersed in water. c) Increase of the AuNPs surface temperature obtained from simulation (solid lines) and from photoluminescence measurements (dotted symbols) when AuNPs were irradiated with 532nm-cw laser. Note that temperature values from photoluminescence follows the same trend than simulated ones. The different symbols and the error bars correspond to the mean and standard deviation of ∇T for 5 particles. (d) $\Delta\lambda_{\text{max}}$ as a function of the applied potential for different irradiation wavelength compensated by absorption: (blue) 405 nm ($I_{405} = 3.2\text{mW}/\mu\text{m}^{-2}$), (green) 532 nm ($I_{532} = 2.4\text{mW}/\mu\text{m}^{-2}$), (orange) 561nm ($I_{561} = 2.2\text{mW}/\mu\text{m}^{-2}$) and, (red) 633 nm ($I_{633} = 9.3\text{mW}/\mu\text{m}^{-2}$). For comparison, $\Delta\lambda_{\text{max}}$ in-dark is included in violet. Solid lines correspond to the exponential growing fit. The symbols and the error bars correspond to the mean and standard deviation of $\Delta\lambda_{\text{max}}$ for more than 5 particles from at least 2 independent samples.

experiment: 405 nm (blue), 531 nm (green), 561 nm (orange), 633 nm (red). With the different colour representing vertical lines outlining the wavelengths used in the experiments in Figure 6.6 a).

Figure 6.6 a) shows the absorption spectrum of the 80 nm NPs, calculated using Lumerical FDTD Solutions according to the model depicted in Figure 6.6 b). A nanoparticle of 80 nm radius, material Au from *Johnson et al.* [229], was placed on top of a substrate of material ITO (with material properties from *Konig et al.* [230]) The nanoparticle was then surrounded by water. Given that the refractive properties of water are relatively constant and loss-free in the studied wavelength range of 400–1,000 nm, it was modelled as homogeneous wavelength-independent material, with refractive index of 1.33. A mesh step of 1.5nm was used and test were done to assure convergence. Finally, a total-field scattered-field source was used to measure the scattering cross-section outside the source area (with the source being a Gaussian beam). Special attention was given to the system not being perfect: the gold nanoparticle was buried inside the ITO substrate by 2 nm to reproduce a more realistic system.

In order to properly estimate the temperature, a nanothermometry technique based on Photoluminescence mapping was implemented. This technique allows the experimental measurement of temperature increases on individual NPs. The technique is based on the measurement of the photoluminescence spectra of the single gold nanoparticle at different power. By normalizing the spectra at two different power, for the blue part of the spectrum is possible to retrieve a temperature dependence with respect to the phonon distribution inside the material [231,232]

In Figure 6.6 c) (scatter dots) we present temperature increase vs irradiance for eight individual NPs illuminated at 532 nm. Using input from these measurements, a temperature calculation was performed in COMSOL for every

wavelength, lines in Figure 6.6 c). Comsol simulation were performed by creating a 3D model according to the sketch of Figure 6.6 b). Materials properties were extracted from the previous simulation in Lumerical FDTD Solution and imported into COMSOL multiphysics. The module used for the heat calculation was the Heat Transfer in Solids (hf). In the module, besides defining a conductive heat transfer across the whole volume, the nanoparticle was defined as heat source with power Q_0 (W/m^3). Such power was evaluated as $Q_0 = I_\lambda - \sigma_{abs}(\lambda)$, with I_λ being the irradiance used in the experiment at that specific wavelength and $\sigma_{abs}(\lambda)$ being the absorption cross section for that specific wavelength as calculated in Figure 6.6 a). In order to better match the simulation with the experimental data, two thin layer thermal resistances were introduced on the heat conductive path between the nanoparticle and the water/ITO. Such surface thermal resistances arise due to the mismatch between the phononic vibration of the gold nanoparticle and the surrounding material and express a "coupling strength" in terms of heat transfer. The role of NPs illumination in the aniline polymerization was then studied at the four different wavelengths. Irradiance was chosen for each laser so that the temperature increase of the NPs was always $\Delta T = 79.7^\circ$, as shown in the vertical line in Figure 6.6 c). Figure 6.6 d) shows scattering maximum shift $\Delta\lambda_{max}$ as function of E_w . Interestingly, the threshold voltage to start the reaction was different for each wavelength, meaning that temperature is not the key phenomena catalyzing the reaction. Moreover, at 633 nm (blue diamonds in figure 6.6 d)), the threshold voltage is similar as the purely electrochemical experiment, which indicates that local-heating alone cannot start the aniline polymerization and pointing to hot-hole extraction as the main mechanism catalyzing the reaction.

Using the previous wavelength-dependence studies the contribution of each mechanism of the plasmon-decay is disentangled and the hot-hole extraction is

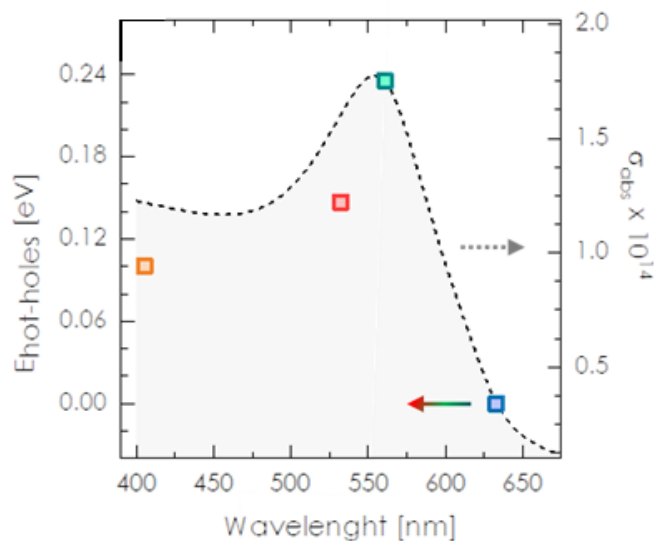


Figure 6.7: *Energy of the hot-holes for the four irradiation wavelength employed in this study. The energy values follow the absorption spectrum of AuNPs (dotted line).*

found to be the main mechanism catalyzing the reaction. Furthermore, by evaluating the different energies of the hot carriers extracted from the Au NP at the different excitation wavelength we can obtain a picture of energetic carriers generation. Indeed in Figure 6.7, we observe the energy of hot carriers for triggering the electro-polymerization reaction as determined at different wavelength along the plasmon absorption spectrum. It is interesting to observe how even if the absorbed initial energy is the same, the hot hole generation efficiency follows the plasmon absorption spectrum, with energy ranging from 24 meV to 240 meV.

6.2.2 Conclusion

In Summary, a combination of electrochemistry and dark-field spectroscopy was used to study the role of a single photoexcited Au nanoparticle (AuNP) in the electro-oxidation of aniline to polyaniline. Electrochemistry provides a side-way to control the Fermi level of the metal nanoparticle, allowing to measure the

hot-holes energy. The results show that the reaction can be effectively photocatalyzed near the AuNP when excited at its plasmon resonance. By the study of wavelength-dependence studies the contribution of each mechanism of the plasmon-decay can be disentangled. Furthermore, the energy of hot carriers for triggering the electro-polymerization reaction was determined along the plasmon absorption, showing that even if the absorbed initial energy is the same, the hot hole generation efficiency follows the plasmon absorption spectrum, with energy ranging from 24 meV to 240 meV.

Chapter 7

Conclusion

In this work a combination of optical and electrical measurements was explored to further our understanding of the underlying physics at the base of plasmon enhancement and hot hole production. By not only probing optical properties, we try to disclose a tighter link between oscillation of the electromagnetic field and the generation of energetic electron that once dephased from the oscillation of the field can be harvested with different purpose. However in order to properly harvest such energetic carries, the acceptor of the energetic carries needs to be placed in the vicinity of the plasmonic structure and spatially localised in the region of highest field of the structure under exam. Such considerations are made, so to increase the probability of extraction of the energetic carriers from the structure, as well as maximizing their energy. With such an objective in mind, the first it becomes of vital importance the creation of manipulation techniques capable of driving a target object to the sphere of action of a plasmonic structure, and then explore the possible way to extract such energetic carriers at metal/semiconductor or metal/molecule interface.

In this regard two different approach for manipulation are introduced: a passive manipulation approach based on porous material; an active manipulation one based on dielectro-plasmonic tweezers. In case of porous supercluster material

the theoretical understanding of collective mode inside cluster-based metamaterials was deepened by experimentally measuring their behaviour in the visible and near IR (InfraRed). The first direct experimental proof of the existence of such collective modes was provided in the visible and near IR. Moreover the ability of such porous system to harvest and host molecule in their structure was studied, providing the basic of an efficient platform for ultra-sensitive molecular spectroscopy. This can open up more venues for the design of plasmonic systems. The use of clustered structure for hosting molecules and exploit the small gap is something of great interest and it can be developed further in the context of lab-on-a-chip. Moreover, having proved the ability to access collective modes inside clustered metamaterials, we can further our understanding of how plasmonic mode behave in complex structures. Indeed, if we can excite the cluster structure and obtain information from the whole system, the increase in terms of sensitivity can outline an extremely interesting direction for the creation of efficient molecular spectroscopy platforms. On the other hand, in the context of active manipulation, the design of a novel and innovative type of nanotweezer capable of exploiting two different type of forces was presented. Such a novel design allows for the creation of a nanotweezers capable of addressing a series of extremely valuable issue of the current nanomanipulation techniques. Proof of a new design as well as of reliable and extremely fast and stable trapping was presented. The use of two different approaches for the manipulation of the target object, not only opens up the venue for the development of a more complex tool capable of more degree of freedom than a plasmonic tweezer. But it also opens up to the idea of integrating techniques already used in the field of biology with more novel optical trapping techniques. This can definitely outline a development route for more complex manipulation tools. In general novel avenue for manipulation at the nanoscale were presented in order to further enhance the

ability of such systems to trap target object and enhance the performance of energetic carrier extraction in plasmonic system.

Building on such new techniques for bringing target object in the vicinity of plasmonic system, the study of the different possible interfaces involved in the transfer of energetic carriers was carried out. The first contribution in such field is the study of hot-electron transfer at metal/semiconductor interfaces. Si-compatible sub-bandgap photodetection at zero bias for a backside illuminated 50 nm TiN thin film on a p-type Si substrate was presented, and it exhibited a photoresponsivity of 1 mA/W at 1250nm. Moreover, the role of amorphous TiO_{2-x} interlayer between the pSi and the TiN was showed to be at the origin of a distinct photoresponse which significantly differs from the one of an oxide free pSi/Au comparison sample. A 5 nm amorphous TiO_{2-x} interlayer between a pSi substrate and a metal thin film was shown to lead to an increase in photoreponsivity at zero bias of about one order of magnitude compared to an oxide free system. The change in dispersion was observed for Ti, Au and TiN and a clear PR enhancement was measured for Au thin films. These findings suggest that the metal merely acts as an absorber enabling hole transfer via TiO_{2-x} trap states which can consecutively be collected in the pSi. Additionally, the photoresponsivity of pSi/ TiO_{2-x} /Au can be increased from about 0.8 mA/W to 4 mA/W at zero and 0.45V reverse bias, respectively allowing for bias dependent photo switching. The study conducted on such interface is highly valuable as it shows that pSi/ TiO_{2-x} can be used as a platform for photo current enhancement at zero bias while it combines the extensively studied materials TiO_2 and Si with TiN which constitutes a promising candidate for a wide range of opto-electronic and plasmonic applications. Further direction in this regard will be to develop techniques for the patterning of TiN, such a novel and interesting plasmonic material. With the creation of a patterned structure we can further improve

the photocurrent generated with the ability of plasmonics system to enhance the near field and thus absorption.

The final contribution of this work was the study of energetic carriers extraction at metal/molecule interface, by combining electrochemistry and dark-field spectroscopy to study the role of a single photoexcited Au nanoparticle (AuNP) in the electro-oxidation of aniline to polyaniline. Electrochemistry provides a side-way to control the Fermi level of the metal nanoparticle, allowing to measure the hot-holes energy. The results show that the reaction can be effectively photocatalyzed near the AuNP when excited at its plasmon resonance. By the study of wavelength-dependence studies the contribution of each mechanism of the plasmon-decay is disentangled. Furthermore, the energy of hot carriers for triggering the electro-polymerization reaction was determined along the plasmon absorption, showing that even if the absorbed initial energy is the same, the hot hole generation efficiency follows the plasmon absorption spectrum, with energy ranging from 24 meV to 240 meV. This results is of extreme interest, as it shows that the energy of the hot carriers can also map the absorption spectrum. In other words we can observe the plasmonic absorption resonance based on the energy of the electron dephased from the plasmonic oscillation. This is an extremely interesting insight, as it shows how such energetic carriers behaves after dephasing from the electromagnetic wave oscillation as well as providing some number to the energy that are exploitable. In this contest it becomes of interest to explore such a reaction but on a more complex structure. If we can perform the same experiment on a bowtie structure, we should be able to observe if geometrical effects (sharp tips, e.g.) can allow for the extraction of more energetic carriers. If that is proved to be true, novel design routes in the context of plasmonic photo-catalysis can be outlined.

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