

# Preface

The field of plasmonics is built on the resonant interaction of light with the free electrons of a noble metal. The polarizability of the free electron cloud allows particles much smaller than the incoming wavelength to couple efficiently with incoming light. The first application of this wavelength-specific interaction dates back to the Roman Empire with the use of metal particles in coloured glass. Resonant light/matter interactions are however abundant in optical sciences with dielectric spheres and cavities as well as atomic gases; so why has plasmonics triggered so much interest in the last 30 years? If plasmon resonances do not exhibit the highest oscillator strengths, they could exhibit quality factors in the range of interest for many applications and arise in solid-state materials that offer robust chemical and mechanical properties. Furthermore, the negative dielectric permittivity of noble metals at optical frequencies induces a drastic increase of the incoming electromagnetic field in the vicinity of the metal structure. This enhanced light/matter interaction, which occurs at the nanometer scale, sparked a growing interest in metallic nanostructures with the discoveries in 1976 of full-light absorption and in 1977 of surface-enhanced Raman scattering. The development, in the following decade, of surface-enhanced spectroscopy and plasmon-based biosensing has attracted the attention of a broad scientific community ranging from physicists to biochemists. Technical breakthroughs in nanofabrication, electromagnetic modelling and near-field optics added a new momentum to the field of plasmonics at the end of the 1990s with groundbreaking experiments in surface plasmon sub-wavelength optics; in particular, extraordinary optical transmission, plasmon polariton waveguiding and near-field enhancement imaging. During the last decade, the study of plasmon resonances has brought together an eclectic array of research fields ranging from quantum electrodynamics to electrical engineering for the understanding of light/matter interactions and from solar energy to pharmacology as potential applications. The recent development of metamaterials, optical antennas, nanosensing as well as photothermal cancer therapy make plasmonics one of the most dynamic and exciting research fields of this new millennium.

As the scientific community involved in plasmonics exponentially grows, exhaustive reference textbooks become crucial. The objective of this book is to thoroughly describe the physics of surface plasmons before addressing the most important and promising applications. The number of chapters has been deliberately restricted to offer authors the opportunity to develop their arguments and to detail their subjects while preserving the didacticism of their chapter. It is divided into three parts. Part I addresses surface plasmons polaritons propagating on metallic surfaces. Part II is dedicated to surface plasmons localized on metallic particles together with their applications in spectroscopy, energy production and biophotonics. Part III is devoted to the imaging and nanofabrication of metallic nanostructures.

## Part I

The first two chapters are written by Daniel Maystre who discovered in 1976 with Hutley the phenomenon of full-light absorption by a nanostructured metal. In [Chap. 1](#), Daniel Maystre describes the major advances of the twentieth century on plasmon surface polaritons propagating on metal surfaces. [Chapter 2](#) is devoted to the Wood anomalies and the total absorption of light. These two discoveries made at intervals of 74 years have strongly impacted the discipline in the twentieth century. How can such a reflective metal absorb light when its surface is structured at a scale around one-tenth of the illuminating wavelength? Daniel Maystre explains in detail the phenomenon from an electromagnetic point of view. After defining the surface plasmon polariton as the complex pole of the scattering operator, he studies the trajectory of this pole in the complex plane as a function of the grating depth.

The publication in 1998 of the unexpected light transmission through a metal film perforated with nanoholes offered a new dynamism to the research on plasmon resonances. The need for convincing explanations of this so-called ‘extraordinary’ transmission has greatly advanced the knowledge of surface plasmon properties on nanostructured metals. Theoretical works that were carried out throughout the twentieth century by Rayleigh, Fano, Hessel and Oliner were needed to explain the famous Wood’s anomalies. Philippe Lalanne and Haitao Liu show in [Chap. 3](#) the interest of these works in the more modern context of the extraordinary light transmission. They discuss the concept of surface wave and define in particular quasi-cylindrical waves. They detail the subtle differences between these surface waves and surface plasmons, before presenting their microscopic theory that was able in 2008 to predict the phenomenon.

[Chapter 4](#) written by Jean-Jacques Greffet is devoted to the theory of surface plasmons. The strength of this chapter is to describe the plasmon dispersion formulas in solid-state physics and electromagnetism formalisms. In the first case, the surface plasmon is described as a collective oscillation of free electrons while, in the second case, the microscopic properties of the metal are ‘hidden’ in the

permittivity of the metal. The surface plasmon is then defined as a pole of the scattering operator and described as a surface wave propagating at a metal/dielectric interface. Jean-Jacques Greffet explains the term ‘polariton’ that describes the coupling between an electromagnetic wave and the free electrons. An analysis of the dispersion curves shows the different regimes of propagation between the frequencies ranging from microwave to optical frequencies. He explains the physical content of the dispersion relations for lossy metals. In particular, the divergence of the local density of states and the resolution limit are discussed.

## Part II

In [Chap. 5](#), Javier Aizpurua and Rainer Hillenbrand introduce surface plasmons localized on metallic particles before presenting their interest in surface-enhanced Raman spectroscopy. The interaction of light with nanoparticles much smaller than the wavelength can be described in the quasistatic approximation. The authors introduce the analytical expressions of the scattering and absorption cross-sections of a dipolar nanoparticle. They describe the higher multipolar modes and the impact of retardation effects before introducing the very important concept of coupled dipoles. The last part of their chapter is devoted to the use of nanoparticles to probe vibrational states of molecules (Surface-Enhanced Raman Spectroscopy and Surface-Enhanced Infrared Absorption). The discovery of the surface-enhanced Raman scattering dates back to 1977 and it initiated the creation of the very active discipline of ‘molecular plasmonics’. The authors therefore present the basics of Raman spectroscopy and show the importance of enhancing the optical near field in the vicinity of metal nanoparticles for increasing the Raman signal.

The use of nanoparticles in dielectric materials has been known since antiquity, but it recently experienced a renewed interest with the use of metallic particles in solar cells. Predicting the optical properties of a large ensemble of nanoparticles in a homogeneous medium can be performed by considering the material as homogeneous. The techniques of homogenization of Maxwell-Garnett and Bruggeman are described in [Chap. 6](#), written by Ross McPhedran. These methods were developed in the late nineteenth and early twentieth centuries by renowned scientists such as Clausius, Mossotti, Maxwell, Rayleigh, Lorenz, Lorentz and Maxwell-Garnett. This chapter contains technical sections, but Ross McPhedran carefully highlights the main results and unveils the physics behind the formulas. He shows in particular the resonant character of the effective dielectric permittivity calculated when the metal particles are considered as inclusions in a glass matrix, which proves that the Maxwell-Garnett formulation is able to take into account plasmonic resonances supported by metallic particles. The usefulness of the homogeneization technique is illustrated in the context of photovoltaic and photo-thermal energy production. Ross McPhedran then discusses cloaking and spasers, two very modern advances that should appear in this book.

Medical diagnosis is the first industrial application of surface plasmons. [Chapter 7](#) written by Romain Quidant is devoted to the promising role of plasmonics in health. He emphasizes the use of metallic particles for the development of light and heat sources for light trapping, biosensing and photothermal cancer therapy. Romain Quidant first shows the importance of the shape of the nanoparticle on the heat power emission spectra calculated numerically using the dyadic Green's function. The maps of heat density are interesting since they differ largely from that of light intensities. He then describes a technique of microscopy capable of measuring the temperature around the nanoparticles. [Chapter 5](#) describes the ability of nanoparticles to focus incident light into tiny volumes, while this chapter uses this property for the optical sensing of proteins or the light trapping of cells and viruses. Combining biosensing and trapping techniques could lead to the design of cost-effective biochips capable of quickly analysing liquid samples. Romain Quidant concludes his chapter with a description of a new therapy against certain cancers based on the heating of metal nanoparticles.

## Part III

The first seven chapters of this book described the theory of surface plasmons and showed their interest in the enhancement of light/matter interactions, with important applications in nanophotonics and biophotonics. These breakthroughs were made possible by advances in imaging techniques and nanofabrication.

The first direct observation of surface plasmons performed in the mid-1990s is now considered as a key moment in plasmonics history. Alexandre Bouhelier, Gérard Colas des Francs and Jonathan Grandidier write a very detailed chapter on the different techniques of surface plasmon imaging. They distinguish three techniques: near-field optical imaging, far-field optical imaging and electron microscopies. The authors introduce in this chapter the fundamental concept of spatial resolution, and explain the difference between near and far fields before extending these concepts to the temporal resolution needed to observe the dynamics of surface plasmons. Besides these three main techniques of microscopy, the authors present fluorescence microscopy, dark-field microscopy and photochemical imaging. This chapter contains many coloured surface plasmon images which will help the reader understand the nature of surface plasmons.

Plasmonics is at the crossroads of optics and nanotechnology. Electromagnetism modelling and transformational optics lead to original designs of metallic nanostructures that will push the boundaries of nanotechnology. The huge industrial markets of microelectronics have led to massive investments in technological platforms in order to increase the precision of surface patterning. The plasmonics community greatly benefits from the recent progress of nanotechnology, and the last chapter of this book written by Gilles Léron del, Sergei Kostcheev and Jérôme Plain addresses the different techniques of nanofabrication. They describe in detail the techniques of electron beam lithography, ion beam

lithography as well as optical lithography. The authors nicely emphasize the growing role that will be played by chemical self-assembly and surface functionalization techniques.

We gratefully thank the authors for their participation in this book. We particularly appreciated the scientific discussions that emerged during this project. Our careful editing of these comprehensive chapters has increased our knowledge and understanding of plasmon resonances. We hope our readers will have the same exciting journey in the field of plasmonics and that it will help them launch novel research ventures.

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Plasmonics

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