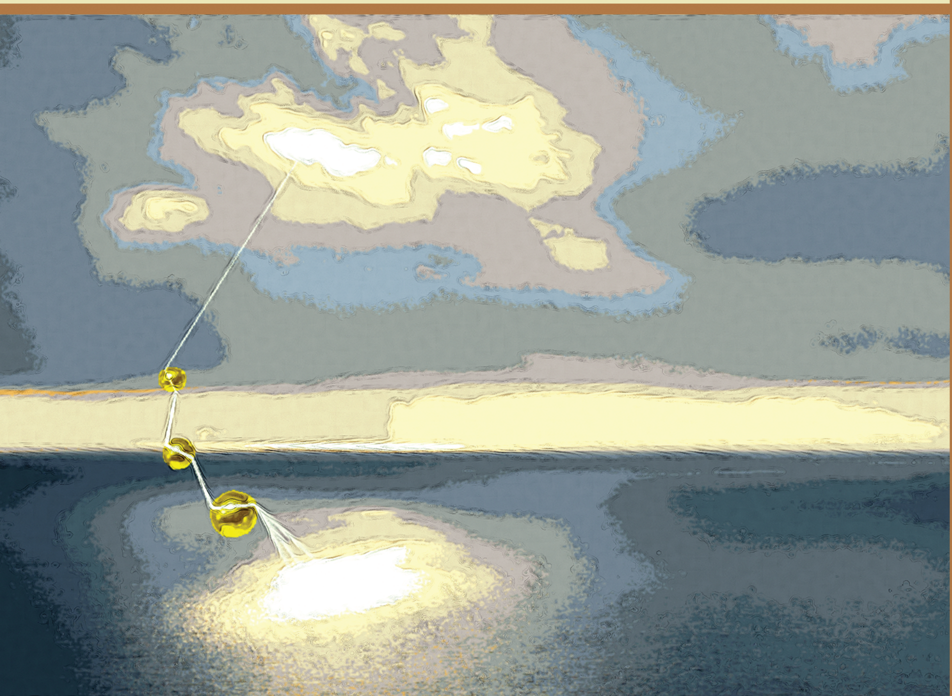
Introduction to Plasmonics

Advances and Applications

edited by

Sabine Szunerits

Rabah Boukherroub



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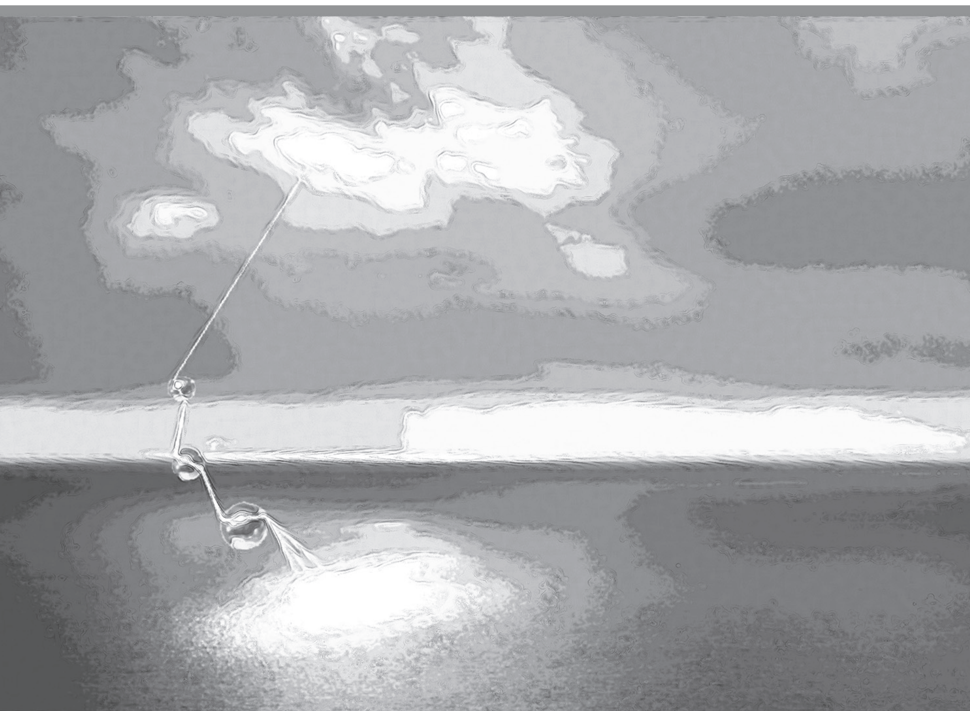

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Foreword

The phenomenon of surface plasmon polaritons (or surface plasmons for short) propagating as a bound electromagnetic wave, as surface light, along an interface between a (noble) metal and a dielectric medium has been known for a long time. Already in 1902, R. W. Wood, while monitoring the spectrum of (white) light after reflection by an optical (metallic) diffraction grating, noticed, "I was astounded to find that under certain conditions, the drop from maximum illumination to minimum, a drop certainly of from 10 to 1, occurred within a range of wavelengths not greater than the distance between the sodium lines" (taken from: "On a remarkable case of uneven distribution of light in a diffraction grating spectrum" *Philos. Mag.* **4**: 396). Later, this observation was understood as the first example for the optical excitation of a surface plasmon mode by light, i.e., by plane waves, reflected off the surface of a metallic grating. Various other coupling schemes using prisms to fulfill the required matching conditions between energy and momentum of surface plasmons and plane waves demonstrated a broad range of experimental configurations that allowed for the excitation of this surface light. The wavelength-dispersed direct observation of surface plasmons, excited by white light upon reflection at the metallized base of a right-angle prism as first reported by J. D. Swalen et al. ("Plasmon surface polariton dispersion by direct optical observation," *Am. J. Phys*. (1980) **48:** 670)) is shown in Figure 1. The dark curve—the "Black Rainbow"—demonstrates directly the dispersion of surface plasmons, i.e., their momentum given as the angle of resonance as a function of the excitation wavelength.

These and other experiments marked the early days of surface plasmon research aiming at elucidating the basics and potential applications, e.g., in biosensing, of these evanescent waves propagating at the interface between a mere dielectric medium and a metal that shows collective excitations of its conduction electron cloud, the plasmons. This surface light interacts with spatial (refractive index) heterogeneities at the interface in much the same way as plane waves do, thus giving rise to the full set of optical features known from normal photons interacting with refractive index variations, like refraction, diffraction, or scattering (elastic and inelastic), and can be used for imaging purposes or for the excitation of fluorescence emission provided the chromophores are located near the interface, i.e., within the decay length of the evanescent field. Many of these aspects of surface plasmons are described in the first chapters of this book dealing with propagating surface plasmon modes.

Figure 1 The Black Rainbow.

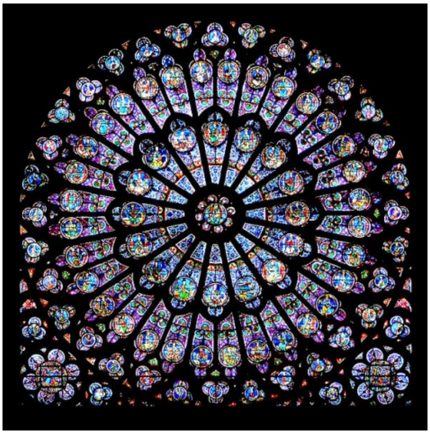

Figure 2 Gothic stained glass rose window of Notre-Dame de Paris. The colors originate from localized surface plasmons, excited in Au colloids, nanoparticles, that are embedded in the glass matrix.

More recently, another very old form of matter, i.e., colloidal gold, reinvented and renamed "Au nanoparticles," attracted a lot of interest in the context of (localized) surface plasmon excitation. Although used in stained glass for centuries (cf., e.g., the colored glass window of the cathedral Notre-Dame in Paris, shown in Figure 2) it was not until the discovery of their enormous enhancement factors seen in Raman spectroscopy or in non-linear optical spectroscopy that these nanoscopic objects became so prominent in the emerging communities of nano-scientists and nano-engineers. The obtainable optical field enhancements are well-understood as given by the resonant excitation of localized surface plasmons in particles, shells, rods, triangles, cubes, beau-ties, and a dozen other shapes of the corresponding nanoscopic resonators made from different (noble) metals. Together with a smart surface functionalization optimized for specific chemical or biological sensing platforms, this allowed for the development of spectroscopic tools, e.g., for the vibrational characterization of even single molecules or for the ultra-sensitive detection of bio-molecules from an analyte solution with an unprecedented limit of detection.

This novel class of surface plasmons in nanostructures is in the focus of the second set of chapters of the current book.

Enjoy the reading of this state-of-the-art summary of the basics and some applications of surface plasmon optics.

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Preface

It was in the autumn of 2002, working at the CEA (commissariat à l'énergie atomique) in Grenoble, when I became familiar with surface plasmon resonance (SPR). I had no idea that this topic would fascinate me to a point that it would become one of several common research activities with Rabah Boukherroub and finally result in the acceptance to co-edit a book on this interdisciplinary topic. The fascination around the field of plasmonics is that this topic is continuously changing and many researchers and scientists from different fields have joined the field in one way or the other.

This book presents the most widely employed plasmonic approaches and the numerous applications associated with these optical readouts. It seems that several elements underlie plasmonics research today. Advances made in nanoscience and nanotechnology have made the fabrication of plasmonic nanostructures, deposition of thin films, and development of highly sensitive optical characterization techniques possible. The different approaches to nanostructuring metals has led to a wealth of interesting optical properties and functionality via the manipulation of the plasmon modes that such structures support. The sensitivity of plasmonic structures to changes in their local dielectric environment has led to the development of new sensing strategies and systems for chemical analysis and identification.

The first part of the book deals with propagating surface plasmon resonance. Chapter 1 (by Shalabney) explores the properties, excitation, and some applications of surface plasmon polaritons on smooth and planar surfaces. Since SPR biosensors combine two building blocks, the SPR interface where the plasmonic wave is generated and an appropriate surface functionalization, it is clear that the overall performance of an SPR biosensor depends on both the intrinsic optical performance of the SPR sensor and the characteristics of the surface functionalization. Chapter 2 (by

Szunerits and Boukherroub) reviews several approaches used to impart biofunctionality to SPR interfaces and structures and hence transforming them into biosensors; a special focus was put on glycan-functionalized SPR interfaces. More recently, a third advantage was brought by the SPR imaging (SPRi) performances, which permit to follow multiple interactions in parallel. Chapter 3 (by Buhot, Pingel, Fiche, Calemczuk, and Livache) presents the SPRi apparatus and its interests for the DNA sensing and analysis.

Plasmon waveguide resonance (PWR) spectroscopy, a relatively new plasmonics-based biophysical method is presented in Chapter 4 (by Alves). Its use for the study of supported proteolipid membranes and interaction of membrane active peptides with lipid membranes is presented. Chapter 5 (by Knoll, Kasry, Huang, Wang, and Dostalek) gives an excellent insight into the race for the most sensitive platforms for biosensing applications. The chapter, entitled "Surface-Wave Enhanced Biosensing," discusses surface-plasmon field-enhanced fluorescence, long-range surface plasmon fluorescence spectroscopy, and optical waveguide fluorescence spectroscopy. This first part will be concluded by Chapter 6 (by Franzen, Losego, Kang, Sachet, and Maria) on infrared surface plasmon resonance. The state of the art of mid-infrared instrumentation and materials is discussed.

The second part of the book considers the interest of localized surface plasmons. Chapter 7 (Akjouj and Lévêque) summarizes the physical concept behind localized surface plasmon resonance. Chapter 8 (by Maurer) outlines, in a systematic manner, the different fabrication methods employed to generate plasmonic nanostructures. The use of metallic nanostructures in solution for colorimetric sensing is presented in Chapter 9 (by Aili and Sepulveda). Chapter 10 (by dos Santos, Temperini, and Brolo) follows up and describes surface-enhanced Raman scattering as means to obtain chemical information and as high sensitive detection tool. Chapter 11 (by Kocabas , Balci, and Polat) is focused on a rather novel aspect of plasmonics, graphene plasmonics. The last chapter, Chapter 12 (by Larroulet), entitled "SPR: An Industrial Point of View," rounds up the book and gives an overall conclusion.

The authors and editors of this book hope that the content will be of interest for researchers, students, and anybody interested in the diverse aspects of plasmonics. We wish you a good time reading the chapters.

Sabine Szunerits
Rabah Boukherroub