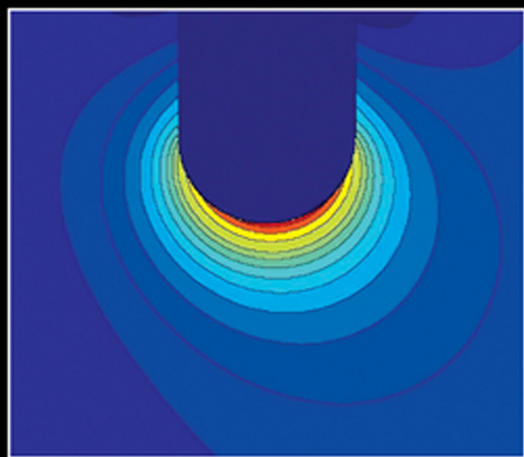


A Wiley – ScienceWise Publishing Co-Publication

Introduction to Metal-Nanoparticle Plasmonics



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Cover design: John Wiley & Sons, Inc.
Cover illustration: Courtesy of Garnett Bryant

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Published simultaneously in Canada.

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Library of Congress Cataloging-in-Publication Data:

Pelton, Matthew, 1975–

Introduction to metal-nanoparticle plasmonics/ Matthew Pelton, Garnett Bryant.

pages cm

Includes bibliographical references and index.

ISBN 978-1-118-06040-7 (cloth)

1. Plasmons (Physics) 2. Metal powders—Optical properties. 3. Nanoparticles—Electric properties. I. Bryant, Garnett W. II. Title.

QC176.8.P55P450 2013

560.4'4—dc23

2012039993

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

To Éva,
for all her support
and to
Virginia, Sean, and Eric
for their patience,
understanding, and
encouragement

Contents

Acknowledgments	ix
Introduction	xi
I.1 Why All the Excitement?	xi
I.2 Historical Perspective	xiv
I.3 Book Outline	xvii
 1 Modeling: Understanding Metal-Nanoparticle Plasmons	 1
1.1 Classical Picture: Solutions of Maxwell’s Equations	2
1.2 Discrete Plasmon Resonances in Particles	13
1.3 Overview of Numerical Methods	25
1.4 A Model System: Gold Nanorods	31
1.5 Size-Dependent Effects in Small Particles	39
References	46
 2 Making: Synthesis and Fabrication of Metal Nanoparticles	 51
2.1 Top-Down: Lithography	52
2.2 Bottom-Up: Colloidal Synthesis	67
2.3 Self-Assembly and Hybrid Methods	76
2.4 Chemical Assembly	86
References	92

3	Measuring: Characterization of Plasmons in Metal Nanoparticles	97
3.1	Ensemble Optical Measurements	97
3.2	Single-Particle Optical Measurements	102
3.3	Electron Microscopy	125
	References	132
4	Coupled Plasmons in Metal Nanoparticles	135
4.1	Pairs of Metal Nanoparticles	136
4.2	Understanding Complex Nanostructures Using Coupled Plasmons	149
	References	161
5	Nonlinear Optical Response of Metal Nanoparticles	165
5.1	Review of Optical Nonlinearities	166
5.2	Time-Resolved Spectroscopy	170
5.3	Harmonic Generation	187
	References	191
6	Coupling Plasmons in Metal Nanoparticles to Emitters	193
6.1	Plasmon-Modified Emission	193
6.2	Plasmon–Emitter Interactions Beyond Emission Enhancement	210
	References	225
7	Some Potential Applications of Plasmonic Metal Nanoparticles	229
7.1	Refractive-Index Sensing and Molecular Detection	229
7.2	Surface-Enhanced Raman Scattering	233
7.3	Near-Field Microscopy, Photolithography, and Data Storage	239
7.4	Photodetectors and Solar Cells	242
7.5	Optical Tweezers	249
7.6	Optical Metamaterials	254
	References	266
	Index	271

Acknowledgments

In 2008, we published an article, titled “Metal-Nanoparticle Plasmonics,” in what was then a rather new journal, *Laser & Photonics Reviews*. This book is, in many ways, built around that review article. We are therefore deeply indebted to Javier Aizpurua, our coauthor for the article. We are also grateful to Dennis Couwenberg for recruiting us to write both that article and this book, and for making sure that we got them both done. We would also like to thank all of our colleagues at Argonne National Laboratory, at the National Institute of Standards and Technology, and around the world who have given us the encouragement and insight needed to put the book together.

M.P.
G.B.

Introduction

I.1 WHY ALL THE EXCITEMENT?

The interaction between light and matter is central to life and to science. Sunlight is the primary source of all useful energy on the Earth. Most of us know what is in the world around us because of light that passes into our eyes. Our scientific understanding of the world has, for a large part, been based on extending our vision using optical instruments, from telescopes to see the very large to microscopes to see the very small. Our information economy is enabled by optical signals that travel down glass fibers. But there are limits on our ability to put light to use. For a long time, it was thought that a fundamental limit was set by the wavelength of light itself. Propagating waves, whether they are light waves, radio waves, sound waves, or any other kind of wave, cannot be focused down to a spot smaller than about half their wavelength. For visible light, wavelengths range from about 400 to about 750 nm. This would seem to keep optics, at best, on the outskirts of nanoscience and nanotechnology.

However, it has recently come to be understood that this is not always the case—that “nano-optics” is not necessarily a contradiction. Central to this understanding is the realization that light is not restricted to freely propagating waves. Electromagnetic fields oscillating at optical frequencies can also exist in the form of evanescent waves, bound to the surfaces of objects. These evanescent fields rapidly decay away from the objects, rather than carrying energy away into space. They are therefore referred to as the “near field” of the object, as opposed to the “far field” that propagates away. Near-field radiation is not subject to the same diffraction limit as far-field radiation, and can be confined to dimensions as small as the atomic scale. The trick

behind nano-optics is thus to find a way to efficiently direct optical energy into evanescent waves.

This is where metal nanoparticles enter the picture. When light is incident on a metal nanoparticle, its electric field pushes the electrons in the particle toward one side of the particle. This means that the negative charges of the electrons accumulate on that side, leaving behind a positive charge on the opposite side. These negative and positive charges attract one another; if the negative charge were suddenly released, then, it would oscillate back and forth with a certain frequency, like a mass on a spring. If the frequency of the incident light matches this natural resonance frequency, it will produce large oscillations of all of the free electrons in the metal. Because so many electrons are oscillating back and forth together, large electric fields are produced in the immediate vicinity of the particle; these fields themselves act on the electrons, reinforcing the oscillations. This coupled excitation, consisting of oscillating charges inside the particle and oscillating electromagnetic fields immediately outside the particle, is known as a plasmon resonance (or, often, as a localized surface plasmon or a particle plasmon).

These plasmon resonances are a genuinely nano-optical phenomenon. Although analogies are often drawn to much larger metal antennas and waveguides that are designed to broadcast, receive, and transmit radio waves and microwaves, the response of metal nanoparticles to light is qualitatively different. Conduction electrons move extremely quickly when an electric field is applied to a metal, on the order of femtoseconds. This is essentially instantaneous compared to the periods of microwaves and radio waves, so that the metals can be treated as perfect conductors. At near-infrared and optical frequencies, by contrast, the response time becomes comparable to the period of the electromagnetic wave; this matching of time scales leads to the strong coupling between electromagnetic fields and electron motion that we refer to as plasmons. Plasmons move across metal surfaces with phase velocities that can be very different from those of freely propagating light waves. In extended metal objects, whose dimensions are comparable to or larger than the optical wavelength, this phase mismatch means that incident light does not naturally excite plasmons with high efficiency. In nanoscale objects, whose dimensions are small compared to the optical wavelength, this restriction is overcome, and the coupling between light and plasmon resonances can be very strong.

Metal nanoparticles thus have the capability of pushing optics fully into the nanometer size regime, allowing ordinary light fields to produce strong evanescent waves that are confined on the nanoscale. This means that the dimensions of optical components can be reduced down to size scales that are comparable to those of electronic components. The prospect of integrating optics and electronics into systems with densities comparable to those of integrated circuits has inspired a tremendous amount of research dedicated to the generation, control, manipulation, and transmission of plasmons in metal nanostructures. This research field has been given its own name, “plasmonics,” and has grown to the point where it is beyond the scope of an introductory book such as this. Plasmons in extended metal structures—flat surfaces, thin films, patterned or structured films, strip waveguides, and the like—have

been covered in other recent monographs. This book is therefore dedicated solely to plasmons in metal nanoparticles.

More specifically, it is dedicated to plasmons in gold and silver nanoparticles. These materials have been the nearly exclusive subject of plasmonics research because they support high quality plasmon resonances at optical frequencies. This is, in part, due to the high density of conduction electrons in these materials: the more electrons involved in a plasmon oscillation, the greater the electrostatic restoring force, and thus the greater the resonance frequency. Just as importantly, losses in silver and gold are relatively low, at least compared to other metals. Copper, for example, can also support plasmon resonances at optical frequencies, but these resonances are weak because the plasmons are rapidly dissipated by losses in the metal. Silver, in fact, has the lowest losses, and thus the strongest plasmon resonances, of all known materials. Gold, though, is more stable, chemically and physically, than silver, so it is often used instead. Other materials can produce plasmon resonances in other frequency ranges—aluminum, for example, supports plasmons at ultraviolet frequencies, and highly doped semiconductors and oxides support plasmons at infrared frequencies—but we will limit ourselves here to plasmons at optical and near-optical frequencies.

Within this spectral range, gold and silver nanoparticles can be designed to produce resonances at any desired frequency. The electric fields around the metal nanoparticles that produce the plasmon oscillations depend on the shape of the nanoparticles. Sharp points and high aspect ratios result in the concentration of fields; this, in turn, results in lower restoring forces and thus lower resonance frequencies. Similarly, plasmons in separate nanoparticles couple together when the particles are brought close to one another, leading to further shifts of the resonance to lower frequencies and further concentration of fields to small volumes. Design of nanoparticle assemblies thus allows plasmon resonances to be tuned to match a given optical frequency, and makes it possible to confine optical fields on three dimensions to length scales of only a few nanometers.

This nanoscale confinement of light does far more than simply reduce the size of optical components: it dramatically increases the interaction between light and matter. In a sense, metal nanoparticles can focus light down to spots hundreds or thousands of times smaller than any ordinary lens; the light will thus interact with material in that spot thousands or millions of times more strongly than it otherwise would. Effects that would previously be observable only with specialized, high power lasers can now be reached with more ordinary light sources.

This new, nanoscale control over light opens up unprecedented technological opportunities. To cite just a few examples, plasmon resonances in metal nanoparticles allow for highly sensitive chemical sensing and identification, down to the level of single molecules. Luminescence from molecules or semiconductor nanostructures can be enhanced by nearby metal nanoparticles, potentially enabling a new generation of light-emitting devices. The ability of metal nanoparticles to squeeze light down to nanoscale volumes provides unprecedented resolution for near-field optical microscopy, optical patterning, and optically assisted data storage. Metal nanoparticles can reduce the size, and thus increase the performance, of photodetectors,