Michael Quinten

WILEY-VCH

Optical Properties of Nanoparticle Systems

Mie and Beyond

Michael Quinten

Optical Properties of Nanoparticle Systems

Mie and Beyond

WILEY-VCH

WILEY-VCH Verlag GmbH & Co. KGaA

The Author

Dr. Michael Quinten
Mauritiusstr. 7
52457 Aldenhoven
ulmi.quinten@t-online.de

Cover

Lycurgus Cup, a dichroic glass cup with a mythological scene; Late Roman, 4th century AD; probably made in Rome. The illustration on the right shows the same glass cup when held up to the light. © Trustees of the British Museum.

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

Composition Toppan Best-set Premedia Limited, Hong Kong
Printing and Binding Fabulous Printers Pte. Ltd., Singapore
Cover Design Adam Design, Weinheim

Printed in Singapore
Printed on acid-free paper

ISBN: 978-3-527-41043-9

Michael Quinten

Optical Properties of Nanoparticle Systems

Related Titles

Schmid, G. (ed.)

Nanoparticles

From Theory to Application

2010

ISBN: 978-3-527-32589-4

Gubin, S. P. (ed.)

Magnetic Nanoparticles

2009

ISBN: 978-3-527-40790-3

Fendler, J. H. (ed.)

Nanoparticles and Nanostructured Films

Preparation, Characterization and Applications

1998

ISBN: 978-3-527-29443-5

Bohren, C. F., Huffman, D. R.

Absorption and Scattering of Light by Small Particles

1998

ISBN: 978-0-471-29340-8

To Ulrike, Eva and Christoph

Preface

The optical response of heterogeneous matter consisting of nanoparticles in a surrounding matrix material is often easy to measure, but rather difficult to describe, yet it is almost impossible to give a complete description.

I met this problem first when I joined Professor Kreibig's group in Saarbrücken, Germany, in 1983. I soon learned that classical electrodynamics is helpful, but solid-state physics is also indispensable when dealing with the optical properties of nanoparticles and nanoparticle systems. In my subsequent studies in Saarbrücken and Aachen electrodynamics became dominant, without losing sight of solid-state physics. This was enabled by the long-lasting cooperation with Uwe Kreibig, who is still engaged in the physics of interfaces and surfaces of very small particles.

During the long period of research on the optical properties of nanoparticle matter from 1983 to 2000 at the Universities of Saarbrücken, Aachen, Graz, Chemnitz, and Bochum, I became acquainted with several aspects of light scattering and absorption by small particles in combination with solid-state physics. I learned that a great variety of scientific and engineering disciplines have significant interest in the optical properties of such inhomogeneous nanoparticle matter. Even today, after ten successful years in industry, inhomogeneous nanoparticle matter hits me again via optical metrology solutions for photovoltaics, thin films, organic LEDs, and some further applications of nanoparticle systems. Hence the most important motivation for this book came from applications of nanoparticle matter.

The purpose of this book is to give first an overview of analytical and numerical models for the optical response of nanoparticles and nanoparticle systems. It may, therefore, appear to have a more theoretical character, but many experimental results complement the various calculations. Second, and in the main, this book provides many calculations on the *spectral behavior* of light scattering and absorption by nanoparticles and nanoparticle systems. Here, electrodynamics again meets solid-state physics. The initial interaction of light with matter, expressed by the frequency-dependent dielectric function of the particle material, enters the electrodynamic scattering model and yields characteristic spectra that are determined by the material-specific properties, the particle-specific topological properties and statistics.

Optical Properties of Nanoparticle Systems: Mie and Beyond. Michael Quinten

ISBN: 978-3-527-41043-9

To write this book required reading and evaluating of many monographs and an even larger number of other publications on this subject. However, the amount of published work is too immense to consider them all in such a book. I hope to have included the most relevant and up-to-date literature, and apologize for all the contributions not considered here.

Last but not least, I want to acknowledge all the inspiration and encouragement from many people during the writing of this book. Special thanks are due to Uwe Kreibig for his continuous interest and so many fruitful discussions on several aspects of nanoparticles and nanoparticle matter. In addition, I want to thank all the people who gave me the chance to increase and to improve my knowledge on this subject with a stay in their groups: A. Heilmann (Halle), R. Wannemacher (Leipzig), F. R. Aussenegg and A. Leitner (Graz), R. Hempelmann (Saarbrücken), Th. Henning (Jena), and G. Schweiger (Bochum). I also gratefully acknowledge all the people who supported me by providing relevant data, namely U. Kreibig, H. Eckstein, G. Reuter, M. Gartz, K.-J. Berg, J. Porstendorfer, H. Hofmeister, W. Hoheisel, H. Mutschke, H. Amekura, Y. Takeda, L. M. Liz-Marzan, G. C. Schatz, R. Jin, and R. M. Magruder III. Finally, many thanks go to my family for their support and patience with me during the writing of this book.

Aldenhoven, October 2010 *Michael Quinten*

Contents

Optical Properties of Nanoparticle Systems: Mie and Beyond. Michael Quinten

ISBN: 978-3-527-41043-9

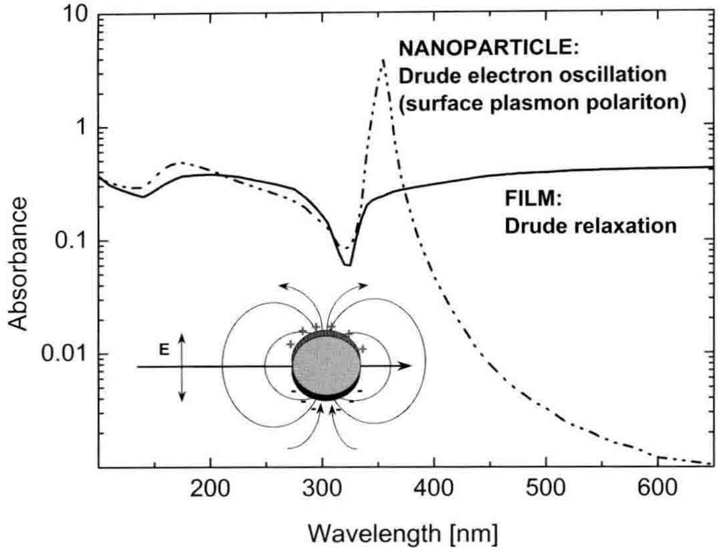

Figure 1.1 The conduction electron oscillator in a silver nanoparticle compared with the conduction electron relaxator in a silver film.

not realize it, nanoparticles belong to our everyday life: cosmetics, medicines, alternative energy, communication, and displays are examples which benefit from the basic science of nanotechnology. As in various applications the magic threshold of 100 nm is exceeded, this book also treats nanoparticles up to 999 nm in size so as to include these cases.

A reduction in size down to a few nanometers often leads to size- or material-specific peculiarities which can be used in new applications of the materials. These peculiarities cannot be observed with macroscopic pieces of the same material. For example, nanoparticulate matter exhibits increased hardness, fracture strength, additional electronic states, increased chemical selectivity, and increased surface energy. One of the most interesting peculiarities is the resonant absorption of light by nanometer-sized gold or silver particles. Unlike in bulk gold and silver, the collective excitation of the conduction electrons by an external electromagnetic field does not result in a relaxator but is transformed into an oscillator type of behavior with a distinct resonance, called surface plasmon polariton. Figure 1.1 illustrates this behavior for a silver nanoparticle (oscillator) compared with a bulk silver film (relaxator).

Hence metal nanoparticles play a particularly pronounced role in nanomaterial science. Nature even seems to have a preference for metals. More than two-thirds of all elements are metals. When looking at the optical properties of nanoparticles, not all metals exhibit such striking properties as gold and silver, nor do most of the metal particles remain unchanged under ambient conditions. Rather, oxides, sulfides, nitrides, and so on are formed with their own specific peculiarities. Therefore, this book considers also the optical properties of nonmetallic nanoparticles and provides many examples of various nanoparticle systems of metallic, semiconducting, carbonaceous, and dielectric particles.

During the last 40 years, a huge number of papers, reviews, and books have appeared which are concerned with nanotechnology, nanoelectronics, nanoopto-electronics, information technology with nanomaterials, self-assembly, nanostructured magnetic materials, nanocomposites, nanowires, and nanobelts. They mainly cover mechanical, electronic, quantum mechanical, and medical aspects, with little attention to optical properties. The most perceptible to humans, however, are the optical properties, for example, the color of paintings and the colors due to interference.

Optical properties of nanomaterials include elastic light scattering, absorption, reflectance and transmittance, second harmonic generation, third-order nonlinear optical properties, surface-enhanced Raman scattering, and others. This book concentrates on the *linear* optical properties: elastic light scattering and absorption of single nanoparticles and on reflectance and transmittance of nanoparticle matter.

Elastic light scattering has turned out to be a powerful tool for examination of the properties of small particles. Scientists and engineers from a large variety of disciplines – physics, electrical engineering, meteorology, chemistry, biophysics, and astronomy – are concerned with this field.

Hence light scattering and absorption by small particles has already been treated in numerous textbooks [3–5] and monographs [6–16], so it would appear almost unnecessary to write a further book on this topic. However, these monographs either deal mainly with particles larger than 1000 nm that are important in geophysics, planetary science, and astrophysics; nanoparticles appear here almost only for species that are relevant for the Earth's radiation budget and in astrophysics, for example, carbon or silicates; or, they mainly consider in detail the spatial (angular) distribution of scattered light. Only Kreibig and Vollmer [11] have given a comprehensive overview of the optical properties of metallic nanoparticles, clusters, and cluster matter, including a discussion of size and quantum size effects. Their book is restricted to particle sizes less than approximately 100 nm and to metals for which nanoparticles exhibit characteristic resonances in absorption and scattering. It gives a good overview of the developments in nanoparticle science from the beginning in the 1970s until 1995 and includes also an overview of preparation techniques. The present book is intended to fill the gap in the description of the optical properties of small particles with sizes less than 1000 nm and to provide a comprehensive overview of the *spectral behavior* of nanoparticulate matter of metallic, semiconducting, carbonaceous, and dielectric particles.

From the physical point of view, the spectral behavior must be a function of the photon energy $\hbar\omega$. On the other hand, the optical properties of small particles strongly depend on the size compared with the size of the electromagnetic radiation, that is, the wavelength λ. Moreover, in commonly used spectrometers for the ultraviolet, visible, and near-infrared spectral ranges, the output is usually given versus the wavelength. In this respect, the wavelength seems to be the appropriate quantity which permits direct comparison with experimental results, for which I

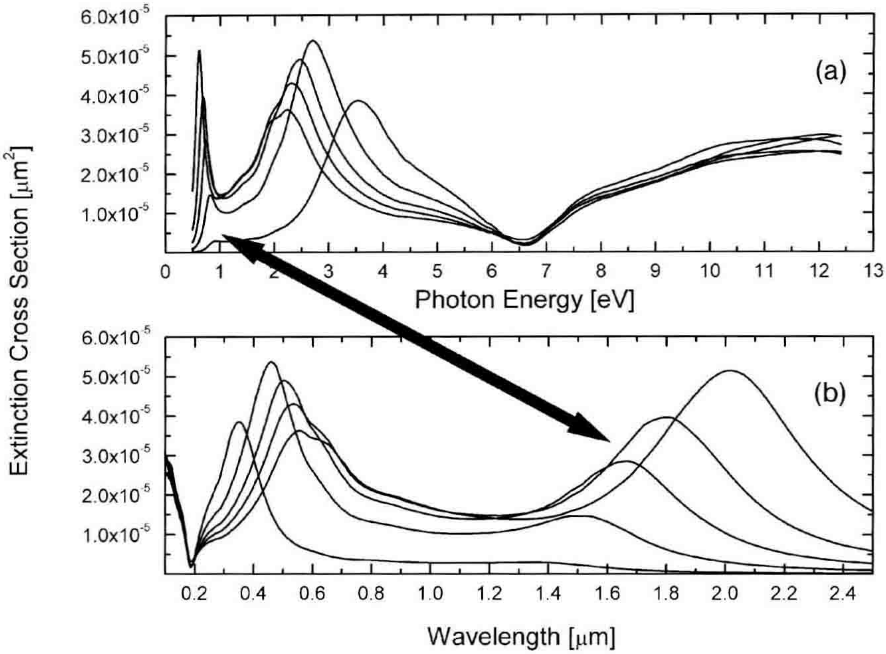

Figure 1.2 The influence of abscissa scaling on the appearance of optical data: extinction cross-section spectra of yttrium nanoparticles (a) versus photon energy and (b) versus wavelength.

preferably use the wavelength as abscissa to allow comparison with measured optical properties. Note that in the mid- and far-infrared regions the wavenumber in cm^{-1} is often used. This quantity is proportional to the energy $\hbar\omega$, but has the advantage of being measured in simple natural numbers instead of floating point numbers. Figure 1.2 demonstrates the difference between wavelength and photon energy as abscissa in the optical absorption spectra of nanoparticles. Using the photon energy, the UV region becomes spread and the IR region squeezed, and vice versa when using the (vacuum) wavelength.

In general, there are two steps on the way to the optical properties of a nanoparticle system. The first step (Figure 1.3) considers the geometry of a single isolated nanoparticle and its intrinsic optical properties, that is, its dielectric function. This information enters a suitable classical electrodynamic model, derived either rigorously or approximately, or formulated as a numerical method. The enormous practical advantage of any electrodynamic scattering model is that it enables one to compute *numerically* the optical response for arbitrary *realistic* particle materials. However, the classical electrodynamics used, being a phenomenological theory to describe light propagation, does not yield information about optical material properties. They enter via the dielectric functions inserted into the Maxwell boundary conditions, which must be taken from elsewhere, for example, from experiments or from quantum solid-state theory model calculations. The results of the first step are the optical properties of a single particle.