



Vol — Topics in —
8 Fluorescence
Spectroscopy

Radiative
Decay Engineering

Joseph R. Lakowicz
Chris D. Geddes



Vol — Topics in —
8 Fluorescence
Spectroscopy

Radiative
Decay Engineering

Joseph R. Lakowicz
Chris D. Geddes

Topics in Fluorescence Spectroscopy

Volume 8

Radiative Decay Engineering

Topics in Fluorescence Spectroscopy

Edited by JOSEPH R. LAKOWICZ and CHRIS D. GEDDES

Volume 1: Techniques

Volume 2: Principles

Volume 3: Biochemical Applications

Volume 4: Probe Design and Chemical Sensing

Volume 5: Nonlinear and Two-Photon-Induced Fluorescence

Volume 6: Protein Fluorescence

Volume 7: DNA Technology

Volume 8: Radiative Decay Engineering

Topics in Fluorescence Spectroscopy

Volume 8
Radiative Decay Engineering

Edited by

CHRIS D. GEDDES

*The Institute of Fluorescence
Medical Biotechnology Center
University of Maryland Biotechnology Institute
Baltimore, Maryland*

and

JOSEPH R. LAKOWICZ

*Center for Fluorescence Spectroscopy and
Department of Biochemistry and Molecular Biology
University of Maryland School of Medicine
Baltimore, Maryland*

 Springer

The Library of Congress cataloged the first volume of this title as follows:

Topics in fluorescence spectroscopy/edited by Joseph R. Lakowicz.

p. cm.

Includes bibliographical references and index.

Contents: v. 1. Techniques

1. Fluorescence spectroscopy. I. Lakowicz, Joseph R.

QD96.F56T66 1991
543'.0858—dc20

91-32671
CIP

Front cover—Surface Plasmon Coupled Emission (SPCE). See *Journal of Fluorescence* 14(1), 119–123, 2004, and chapter within

ISSN: 1574-1036

ISBN 0-387-22662-1 (HB)

Printed on acid-free paper

©2005 Springer Science+Business Media, Inc.

All rights reserved. This work may not be translated or copied in whole or in part without the written permission of the publisher (Springer Science+Business Media, Inc., 233 Spring Street, New York, NY 10013, USA), except for brief excerpts in connection with reviews or scholarly analysis. Use in connection with any form of information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed is forbidden.

The use in this publication of trade names, trademarks, service marks and similar terms, even if they are not identified as such, is not to be taken as an expression of opinion as to whether or not they are subject to proprietary rights.

Printed in the United States of America

9 8 7 6 5 4 3 2 1 SPIN 11306818

springeronline.com

Contributors

Ricardo F. Aroca • Materials & Surface Science Group, Department of Chemistry and Biochemistry, University of Windsor, N9B 3P4, Windsor, Ontario, Canada

Kadir Aslan • Institute of Fluorescence, University of Maryland Biotechnology Institute 725 West Lombard Street, Baltimore, Maryland 21201

Donna Chen • Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, South Carolina 29208

Ashutosh Chilkoti • Department of Biomedical Engineering, Duke University, Durham, North Carolina 27708

Paula E. Colavita • Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, South Carolina 29208

Michael Doescher • Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, South Carolina 29208

Eric Dulkeith • Photonics and Optoelectronics Group, Physics Department and Center for NanoScience, Ludwig-Maximilians-Universität München, Amalienstraße 54, 80799 München, Germany

Robert C. Dunn • Department of Chemistry, University of Kansas, Lawrence, Kansas, 66045

Jochen Feldmann • Photonics and Optoelectronics Group, Physics Department and Center for NanoScience, Ludwig-Maximilians-Universität München, Amalienstraße 54, 80799 München, Germany

Chris D. Geddes • Institute of Fluorescence, University of Maryland Biotechnology Institute, and Center for Fluorescence Spectroscopy, 725 West Lombard Street, Baltimore, Maryland 21201

Joel I. Gersten • Department of Physics, City College of the City University of New York, New York, New York 10031

Paul J.G. Goulet • Materials & Surface Science Group, Department of Chemistry and Biochemistry, University of Windsor, N9B 3P4, Windsor, Ontario, Canada

Ignacy Gryczynski • Center for Fluorescence Spectroscopy, University of Maryland, School of Medicine, 725 West Lombard Street, Baltimore, Maryland 21201

Zygmunt Gryczynski • Center for Fluorescence Spectroscopy, University of Maryland, School of Medicine, 725 West Lombard Street, Baltimore, Maryland 21201

Amanda J. Haes • Northwestern University, Department of Chemistry, 2145 Sheridan Road, Evanston, Illinois 60208-3113

Christy L. Haynes • Northwestern University, Department of Chemistry, 2145 Sheridan Road, Evanston, Illinois 60208-3113

Arnim Henglein • Hahn-Meitner Institut, 14109 Berlin, Germany

Thomas A. Klar • Photonics and Optoelectronics Group, Physics Department and Center for NanoScience, Ludwig-Maximilians-Universität München, Amalienstraße 54, 80799 München, Germany

Wolfgang Knoll • Max-Planck-Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Joseph R. Lakowicz • Center for Fluorescence Spectroscopy, University of Maryland, School of Medicine, 725 West Lombard Street, Baltimore, Maryland 21201

Luis M. Liz-Marzán • Departamento de Química Física, Universidade de Vigo, 36200, Vigo, Spain

Joanna Malicka • Center for Fluorescence Spectroscopy, University of Maryland, School of Medicine, 725 West Lombard Street, Baltimore, Maryland 21201

C. Mayer • Analytical Biotechnology, Technical University of Delft, Julianalaan 67, 2628 BC Delft, The Netherlands

Adam D. McFarland • Northwestern University, Department of Chemistry, 2145 Sheridan Road, Evanston, Illinois 60208-3113

Paul Miney • Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, South Carolina 29208

Annabelle Molliet • Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, South Carolina 29208

David S. Moore-Nichols • Department of Chemistry, University of Kansas, Lawrence, Kansas, 66045

Michael L. Myrick • Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, South Carolina 29208

Nidhi Nath • Department of Biomedical Engineering, Duke University, Durham, North Carolina 27708

Thomas Neumann • Max-Planck-Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Lifang Niu • Departments of Chemistry and of Materials Science, National University of Singapore, 10 Science Drive 4, Singapore 11754

Steven J. Oldenburg • Seashell Technology, La Jolla, California 92037

Isabel Pastoriza-Santos • Departamento de Química Física, Universidade de Vigo, 36200, Vigo, Spain

Darren Pearson • Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, South Carolina 29208

Jorge Pérez-Juste • Departamento de Química Física, Universidade de Vigo, 36200, Vigo, Spain

John Reddic • Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, South Carolina 29208

Th. Schalkhammer • Nanobioengineering, Vienna Biocenter, Universität Wien Dr. Bohrgasse 9, 1030 Wien, Austria. *Current address:* Schalkhammer KG, Klausenstrasse 129, 2534 Alland, Austria

David A. Schultz • David A. Schultz, University of California, San Diego, La Jolla, California 92093-0319

Evelyne L. Schmid • Departments of Chemistry and of Materials Science, National University of Singapore, 10 Science Drive 4, Singapore 11754

Lindsay Taylor • Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, South Carolina 29208

Richard P. Van Duyne • Northwestern University, Department of Chemistry, 2145 Sheridan Road, Evanston, Illinois 60208-3113

Fang Yu • Max-Planck-Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Jing Zhou • Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, South Carolina 29208

Preface

Spatial control of photonic mode density is changing the practice of fluorescence spectroscopy. This laboratory has been active in fluorescence spectroscopy for nearly 30 years. During that time we have investigated many phenomena in fluorescence, including quenching, energy transfer and anisotropy, to name a few. Until recently we relied completely on the free-space emission properties of fluorophores observed in transparent media. The free-space quantities in fluorescence are determined by the values of the radiative and non-radiative properties of excited fluorophores. The observed changes in fluorescence intensities, lifetimes, etc. are due almost completely to changes in the non-radiative decay rates such as quenching. The rate of radiative decay is determined by the extinction coefficient or oscillator strength of the transition. This rate is essentially constant in most media.

In about 2000 we began to examine the effects of silver metallic particles on fluorescence. Examination of the literature revealed that proximity to silver particles could have dramatic effects on fluorescence quantum yields and lifetimes. Such changes are typically due to changes in the non-radiative decay rates. In contrast, the metal particles changed the radiative decay rate (Γ). These changes occur due to modifications of the photonic mode density (PMD) near the particle in Γ . This was the first time in 30 years that we saw an opportunity to modify this fundamental rate. Numerous opportunities became apparent as we considered the effects of PMD, including increased quantum yields, increased photostability and changes in resonance energy transfer. Additionally, we saw the opportunity to obtain directional rather than isotropic emission based on local changes in the PMD. We described these phenomena as radiative decay engineering (RDE) because we could engineer changes in the emission based on the fluorophore-metal particle geometries.

During these three years our enthusiasm for RDE has continually increased. Many of the early predictions have been confirmed experimentally. As one example we recently observed directional emission based on fluorophores located near a thin metal film, a phenomenon we call surface plasmon coupled emission (SPCE). We see numerous applications for RDE in biotechnology, clinical assays and analytical chemistry. The technology needed to implement RDE is straightforward and easily adapted by most laboratories. The procedures for making noble metal particles and surfaces are simple and inexpensive. The surface chemistry is well developed, and the noble metals are easily tolerated by biochemistry systems.

While implementation of RDE is relatively simple, understanding the principles of RDE is difficult. The concepts are widely distributed in the optics and chemical physics literature, often described in terms difficult to understand by biophysical scientists. In this volume we have presented chapters from the experts who have studied metal particle optics and fluorophore-metal interactions. We believe this collection describes the fundamental principles for the widespread use of radiative decay engineering in the biological sciences and nanotechnology.

Joseph R. Lakowicz and Chris D. Geddes
Center for Fluorescence Spectroscopy
Baltimore, Maryland
August 13, 2003

Contents

1. Preparation of Noble Metal Colloids and Selected Structures Isabel Pastoriza-Santos, Jorge Pérez-Juste and Luis M. Liz-Marzán

1. Introduction.....	1
2. Preparation of Noble Metal Colloids	2
2.1. Spherical Nanoparticles in Water	2
2.1.1. Citrate Reduction.....	2
2.1.2. Borohydride Reduction	3
2.1.3. γ -Radiolysis	4
2.1.4. Growth on Preformed Nanoparticles.....	5
2.1.5. Growth of Silica Shells on Metal Nanoparticles	5
2.2. Spherical Nanoparticles in Organic Solvents.....	6
2.2.1. Two-Phase Reduction.....	6
2.2.2. Reduction by the Solvent	6
2.2.3. Reduction within Microemulsions	7
2.3. Nanorods and Nanoprisms in Water	8
2.3.1. Synthesis of Nanorods within Porous Membranes.....	8
2.3.2. Nanorods from Wet Synthesis in Solution	8
2.3.3. Synthesis of Nanoprisms in Water	10
2.4. Nanorods and Nanoprisms in Organic Solvents	11
2.4.1. Reduction within Microemulsions	11
2.4.2. Reduction by the Solvent	11
2.4.3. Shape Control Using DMF.....	11
3. Metal Colloid Structures through Layer-by-Layer Assembly.....	13
3.1. Layer-by-Layer Assembly	13
3.2. Assembly of Au@SiO ₂	13
3.3. Assembly of Au Nanoprisms	15
4. Conclusions.....	17
5. Acknowledgements.....	17
6. References	17

2. Near-Field Scanning Optical Microscopy: Alternative Modes of Use for NSOM Probes

David S. Moore-Nichols and Robert C. Dunn

1. Introduction.....	25
2. Scanning Near-Field Fret Microscopy	27
3. Nanometric Biosensors and Bioprobes	31
4. Applied Voltage Combined with NSOM for Structure/Dynamic Measurements..	34

5. Interferometric NSOM Measurements.....	36
6. Fluorescence, Topography and Compliance Measurements Using Tapping-Mode NSOM.....	40
7. Conclusions.....	43
8. Acknowledgments	44
9. References.....	44
3. Nanoparticles with Tunable Localized Surface Plasmon Resonances: Topics in Fluorescence Spectroscopy Christy L. Haynes, Amanda J. Haes, Adam D. McFarland, and Richard P. Van Duyne	
1. Introduction.....	47
1.1. General Overview	47
1.2. Fabrication of Nanostructures with Tunable Optical Properties.....	48
1.3. Fundamental Studies of Tunable Optical Properties.....	52
1.3.1. Defining the Fundamental Characteristics of the Localized Surface Plasmon Resonance	52
1.3.2. Controlling the Localized Surface Plasmon Resonance	53
1.3.3. Implications for Related Phenomena.....	55
1.4. Applications of Tunable Optical Properties.....	57
1.5. Goals and Organizations	59
2. Tunable Localized Surface Plasmon Resonance.....	59
2.1. Introduction to Colloidal Nanoparticles.....	59
2.2. Colloidal Nanoparticle Experimental Section.....	60
2.2.1. Fabrication of Surfactant-Modified Silver Nanoparticles	60
2.2.2. Fabrication of Core-Shell Nanoparticles	60
2.2.3. Transmission Electron Microscopy Characterization.....	61
2.3. Structural and Optical Properties of Colloidal Nanoparticles.....	61
2.4. Study of Electromagnetic Coupling Using Electron Beam Lithography Substrates	64
2.5. Experimental Methods.....	66
2.5.1. Sample Fabrication.....	66
2.5.2. Optical Characterization of Nanoparticle Arrays	67
2.5.3. Structural Characterization of Nanoparticle Arrays	68
2.6. Optical Properties of Electron Beam Lithography-Fabricated Nanoparticle Arrays.....	69
2.7. Tunable Localized Surface Plasmon Resonance Using Nanosphere Lithography.....	70
2.7.1. Effect of Nanoparticle Material on the LSPR	70
2.7.2. Effect of Nanoparticle size on the Ag LSPR.....	70
2.7.3. Effect of Nanoparticle Shape on the Ag LSPR	71
2.7.4. Effect of the External Dielectric Medium on the Ag LSPR.....	73
2.7.5. Effect of Thin Film Dielectric Overlayers on the LSPR	74
2.7.6. Effect of the Substrate Dielectric Constant on the LSPR	75

3.	Recent Applications of the Tunable Localized Surface Plasmon Resonance	75
3.1.	Sensing with Nanoparticle Arrays	75
3.1.1.	Experimental Procedure	76
3.1.2.	Effect of the Alkanethiol Chain Length on the LSPR	76
3.1.3.	Streptavidin Sensing Using LSPR Spectroscopy	78
3.1.4.	Anti-Biotin Sensing Using LSPR Spectroscopy	80
3.1.5.	Monitoring the Specific Binding of Streptavidin to Biotin and Anti-Biotin to Biotin and the LSPR Response as a Function of Analyte Concentration	80
3.2.	Sensing with Single Nanoparticles	82
3.2.1.	Experimental Procedure	84
3.2.2.	Single Nanoparticle Refractive Index Sensitivity.....	84
3.2.3.	Single Nanoparticle Response to Adsorbates.....	85
3.3.	Plasmon-Sampled Surface-Enhanced Raman Excitation Spectroscopy	86
3.3.1.	Experimental Procedure	87
3.3.2.	Varying the Excitation Wavelength in PS-SERES.....	89
3.3.3.	Varying the Molecular Adsorbate in PS-SERES	89
4.	Conclusions.....	92
5.	Acknowledgements.....	93
6.	References.....	93

4. Colloid Surface Chemistry

Arnim Henglein

1.	Introduction.....	101
2.	Radiolytic Methods.....	101
3.	Silver Colloid Preparation.....	103
4.	Pulsed Particle Formation	105
5.	Redox Potential and Particle Size	106
6.	Polymer Stabilized Clusters	109
7.	Electron Donation and Positive Hole Injection.....	109
8.	Photoelectron Emission	111
9.	Nano-Electrochemistry	114
10.	Bimetallic Particles	115
11.	Fermi Level Equilibration in Mixed Colloids	122
12.	Adsorption of Electrophiles	124
13.	Adsorption of Nucleophiles	126
14.	Competitive Adsorption and Displacement Processes.....	130
15.	Final Remarks	131
16.	References.....	131

5. Bioanalytical Sensing Using Noble Metal Colloids	
C. Mayer and Th. Schalkhammer	
1. Bio-Nanotechnology	135
1.1. Metal Colloids	136
1.2. Metal Colloid Devices	140
2. Nano-Cluster Based Technology	141
2.1. Properties	141
2.2. Metal Colloids and Quantum Dots	144
2.2.1. Techniques to Prepare Noble Metal Colloids	145
2.3. Nano-Switches	151
2.4. Cluster-Cluster Aggregates	154
2.5. Coating Clusters with Biomolecules	156
2.6. AFM	158
2.7. Immune Colloidal Techniques	161
2.8. Binding and Assembly of Functionalized Colloids	161
2.9. Bio-Templating	163
2.10. Colloidal Particles and Electrodes	165
2.11. SPR-Transduction	165
2.12. Electroluminescence	166
3. Nano-Cluster and Field Effects	166
3.1. Surface Enhanced Optical Absorption (SEA)	166
3.1.1. Physical Principles	166
3.1.2. Applications	168
3.1.3. Distance Layer and Colloid Layers	169
3.1.4. SEA-Biochips	171
3.1.4.a. The SEA Chip	171
3.1.4.b. Applications and General Requirements	171
3.1.4.c. Setup	172
3.1.4.d. Example and Results	175
3.1.5. Nano-Distance Transduction via SEA Biochips	176
3.1.5.a. How It Works	176
3.1.5.b. Polyvinylpyrrolidone as Distance Layer	177
3.1.5.c. Proteins as Distance Layer	177
3.1.5.d. Spin-Coating of DNA	178
3.1.5.e. Setup of a MICORIS Chip	179
3.2. Resonance Enhanced Fluorescence (REF)	180
3.2.1. Physical Principles	180
3.2.2. Applications	182
3.2.3. REF in Microtiter-Plates	184
3.2.4. Cluster-Layer Enhanced Fluorescence DNA Chip Setup	184
3.2.5. Clusters Layer Fabrication Methods	185
3.3. Surface-Enhanced Infrared Absorption (SEIRA)	186
3.4. Scattered Evanescent Waves (SEW)	187
3.5. Surface-Enhanced Raman Scattering (SERS)	188
3.6. Cluster-Quenched Fluorescence	190
3.7. Cluster-Emission Devices (CED)	192
4. Acknowledgements	193
5. References	193