# 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



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

Topics in fluorescence spectroscopy/edited by Joseph R. Lakowicz.	
<ul> <li>p. cm.</li> <li>Includes bibliographical references and index.</li> <li>Contents: v. 1. Techniques</li> <li>1. Fluorescence spectroscopy. I. Lakowicz, Joseph R.</li> </ul>	
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

#### Contributors

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 nonradiative 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 ( $\Gamma$ ). These changes occur due to modifications of the photonic mode density (PMD) near the particle in  $\Gamma$ . 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

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

1.	Introductio	)n	1
2.	Preparation	n of Noble Metal Colloids	2
	2.1. Spheri	ical 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. Spheri	ical 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. Nanor	ods 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. Nanor	ods 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 Coll	oid Structures through Layer-by-Layer Assembly	13
	3.1. Layer-	by-Layer Assembly	13
	3.2. Assem	ibly of Au@SiO <sub>2</sub>	13
	3.3. Assem	bly of Au Nanoprisms	15
4.	Conclusion	18	17
5.	Acknowled	Igements	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. Intro	oduction	25
2. Scar	nning Near-Field Fret Microscopy	27
3. Nan	ometric Biosensors and Bioprobes	31
4. App	blied Voltage Combined with NSOM for Structure/Dynamic Measurements	34

5. 6	Interferometric NSOM Measurements	36
0.	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

Distand D	V	
Richard P.	van Duvne	
	· ···· ··· ··· ··· ··· ··· ··· ··· ···	

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

xii

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

xiii

5.	<b>Bioanalytical Sensing Using Noble Meal Colloids</b> 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	1/9
	3.2. Resonance Enhanced Fluorescence (REF)	180
	3.2.1. Physical Principles	180
	3.2.2. Applications	182
	3.2.3. REF IN MICTOTITIET-Plates	104
	3.2.4. Cluster-Layer Enhanced Fluorescence DNA Chip Setup	104
	3.2.5. Clusters Layer Fabrication Methods	100
	3.3. Surface-Ennanced Infrared Absorption (SEIRA)	180
	2.5. Surface Enhanced Demon Sectioning (SEDS)	18/
	3.5. Surface-Ennanced Raman Scattering (SERS)	100
	3.0. Cluster-Quenched Fluorescence	100
4	S. /. Clusici-Elliission Devices (CED)	192
4. 5	Deferences	102
э.		173

6.

	Joel I. Gersten	
1.	Introduction	197
2.	Theory	199
3.	Appendix A	216
4.	References	220

Theory of Fluorophore-Metallic Surface Interactions

#### 7. Surface-Enhancement of Fluorescence Near Noble Metal Nanostructures Paul J.G. Goulet and Ricardo F. Aroca

1.	Introduction	223
2.	Electromagnetic Enhancement	225
3.	Enhanced Absorption	229
4.	Radiationless Energy Transfer and Distance Dependence	230
5.	Coverage Dependence	233
6.	Temperature Dependence	234
7.	Quantum Efficiency and Enhancement	235
8.	Enhancing Substrates	236
9.	SEF of Langmuir-Blodgett Films	239
10.	Summary and Outlook	243
11.	Acknowledgements	244
12.	References	244

#### 8. Time-Resolved Fluorescence Measurements of Fluorophores Close to Metal Nanoparticles Thomas A. Klar, Eric Dulkeith, and Jochen Feldman

4.	Time Resolved Spectroscopy of Fluorophores Bound to Metal Nanoparticles	257
5.	Biophysical Applications	266
6.	Acknowledgements	269
7.	References	269

9.	Copper Coated Self-Assembled Monolayers: Alkanethiols and Prospective Molecular Wires Paula E. Colavita, Paul Miney, Lindsay Taylor, Michael Doescher, Annabelle Molliet, John Reddic, Jing Zhou, Darren Pearson, Donna Chen, and Michael L. Myrick	
1.	Introduction	275
2.	Copper Overlayers on Alkanethiol Self-Assembled Monolayers	278
	2.1. General Factors Affecting the Behavior of Metals Deposited	
	onto Self-Assembled Monolayers	278
	2.2. RAIRS Spectra of Alkanethiol SAMs in the C-H Stretching Region	280
	2.3. Copper on Dodecanethiol and Octadecanethiol [30]	283
3.	Copper on Conjugated Oligomers	293
4.	Acknowledgments	300
5.	References	300

### 10. Principles and Applications of Surface-Plasmon Field-Enhanced Fluorescence Techniques Wolfgang Knoll, Fang Yu, Thomas Neumann, Lifang Niu, and Evelyne L. Schmid

1.	Introduction	305
2.	Surface Plasmons as Interfacial Light	307
3.	Chromophores Near Metal Surfaces	313
4.	Recording Fluorescence from Chromophores Excited by Surface	
	Plasmon Waves	316
5.	Surface Hybridization Studies	321
6.	Protein Binding Studies — the Limit of Detection in SPFS	326
7.	Surface Plasmon Fluorescence Microscopy	329
8.	Conclusions	329
9.	Acknowledgements	331
10.	References	331

11.	<ol> <li>Optically Detectable Colloidal Metal Labels: Properties, Methods, and Biomedical Applications</li> </ol>	
	Steven J. Oldenburg and David A. Schultz	
1.	Introduction	333
2.	Plasmon Resonance	334
	2.1. Experimental and Theoretical Considerations	334
	2.2. Particle Fabrication	337
	2.2.1. Spherical Particles	337
	2.2.2. Anisotropic, Elliptical or Rod Shaped Particles	338
	2.2.3. Core: Shell Particles	339
	2.3. Particle Characterization	339

#### xvi

3.	Particle Surface Modification to Produce Biological Labels	340
	3.1. Particle Surface Modification	340
4.	Dark Field Optical Microscope Designs for Plasmon Resonant	
	Particle (PRP) Detection	341
	4.1. Microscope Configuration	341
	4.2. Illumination Light Sources	343
	4.3. Apparatus for Individual Plasmon Resonant Particle	
	Spectral Determination	344
	4.4. Single Particle Counting	344
5.	Biological Applications	345
	5.1. Individual PRP Detection and Counting in a Protein or DNA	
	Microarray Format	346
	5.2. Individual PRP Detection of Immuno-Labeled Tissue	348
	5.3. Plasmon Resonant Particles and Other Nanoparticles as Labels	
	for Biomedical Applications	349
6.	References	349

# 12. Noble Metal Nanoparticle Biosensors Nidhi Nath and Ashutosh Chilkoti

1.	Introduction	353
2.	Noble Metal Nanoparticle	355
	2.1. Optical Properties of Noble Metal Nanoparticles	355
	2.2. Noble Metal Nanoparticles: Historical Perspective	357
3.	Nanoparticle SPR Biosensor	360
	3.1. Noble Metal Nanoparticles: Synthesis	361
	3.2. Self-Assembly of Noble Metal Nanoparticles on Substrate	362
	3.3. Optical Properties of self-Assembled Gold Nanoparticle on Glass	365
	3.3.1. Refractive Index Response of Metal Nanoparticles	365
	3.3.2. Spatial Sensitivity of Immobilized Gold Nanoparticles on Glass	368
	3.4. Biosensing Using Noble Metal Nanoparticles	370
	3.4.1. Receptor Presentation	371
	3.4.2. Biomolecular Binding	373
4.	Future Directions	376
5.	Acknowledgements	376
6.	References	377

#### 13. Surface Plasmon-Coupled Emission: A New Method for Sensitive **Fluorescence Detection** Ignacy Gryczynski, Joanna Malicka, Zygmunt Gryczynski and Joseph R. Lalowicz

1.	Introduction	381
2.	Surface Plasmon Resonance Analysis	381

3.	Surface Plasmon-Coupled Emission	386
	3.1. Properties of SPCE with Reverse Kretschmann Excitation	386
	3.2. Properties of SPCE with Kretschmann Excitation	394
	3.3. Background Rejection with SPCE	396
	3.4. DNA Hybridization Using SPCE	398
4.	Discussion	401
5.	Acknowledgment	401
6.	References	401
6.	References	401

14. Radiative Decay Engineering (RDE) Chris D. Geddes, Kadir Aslan, Ignacy Gryczynski, Joanna Malicka and Joseph R. Lakowicz

1.	Introduction	405
2.	Enhanced Emission from Low and High Quantum Yield Species	
	Using Silver Island Films (SiFs)	411
3.	Enhanced Intrinsic Fluorescence Using SiFs	415
4.	Distance Dependence of Enhanced Fluorescence Using SiFs	417
5.	Release of Self-Quenching Using SiFs	419
6.	Other Metal-Nanostructures for MEF Using Indocyanine Green (ICG)	422
	6.1. Silver Island Films (SiFs)	424
	6.2. Immobilized Silver Colloids	425
	6.3. Photo-Deposition of Silver onto Glass	426
	6.4. Electoplating of Silver on Substrates	434
	6.5. Roughened Silver Electrodes	435
	6.6. Silver Fractal-like Structures on Glass	439
	6.7. Silver Nanorods	443
7.	Closing Remarks	445
8.	Acknowledgments	446
9.	References	446

#### xviii

### PREPARATION OF NOBLE METAL COLLOIDS AND SELECTED STRUCTURES

#### Isabel Pastoriza-Santos, Jorge Pérez-Juste, and Luis M. Liz-Marzán<sup>\*</sup>

#### **1. INTRODUCTION**

Metal colloids have been around for centuries because of their striking optical properties. A typical example of ancient colloidal metal nanoparticles is the famous Lycurgus cup, which dates back to the fourth century AD. The cup is still at the British Museum<sup>1</sup> and possesses the unique feature of changing color, since it is green when viewed in reflected light, but it appears red when a light is shone from inside and is transmitted through the glass. Analysis of the glass reveals that it contains a very small amount of tiny (ca. 70 nm) crystals of metal containing silver and gold in an approximate molar ratio or 14:1. It is the presence of these nanocrystals which imparts Lycurgus cup with its special color display. After such early origins, metal colloids, and particularly colloidal gold, were known and used in the Middle Ages by the alchemists for their health restorative properties, which are still popular nowadays.<sup>2</sup> Although the discovery that glass could be colored red by adding a small amount of gold powder is often credited to Johann Kunckel, a German glassmaker in the late seventeenth century,<sup>1</sup> it was not until 1857 that Michael Faraday performed a systematic study on the synthesis and color of colloidal gold.<sup>3</sup> Since that pioneering work, thousands of scientific papers have been published on the synthesis, modification, properties, and assembly of metal nanoparticles, using a large variety of solvents and other substrates. All this has led not only to reliable procedures for the preparation of metal nanoparticles of basically any size and shape, but also to a deep understanding of many of the physico-chemical features that determine the special behavior of these systems.

One of the very interesting aspects of metal colloids is that their optical properties strongly depend on particle size and shape. Bulk gold for instance has a high absorbance along the whole visible range, except for a slight dip around 400-500 nm, which makes Au thin films look blue in transmission. As particle size is reduced from say 500 nm down to ca. 3 nm, the color changes gradually to orange, through several tones of purple and red. These effects are due to changes in the so-called surface plasmon resonance,<sup>4</sup>

Isabel Pastoriza-Santos, Jorge Pérez-Juste, and Luis M. Liz-Marzán, Departamento de Química Física, Universidade de Vigo, 36200, Vigo, Spain.

#### I. PASTORIZA-SANTOS et al.

which is the frequency at which conduction electrons oscillate as a response to the alternating electric field of an incoming electromagnetic wave. Below 3 nm, the color changes to brownish and eventually colorless, which is mainly due to quantum effects.<sup>5</sup> Shape effects are even stronger, and slight deviations from the spherical geometry can lead to quite impressive color changes.

The plasmon resonance is one of the most characteristic properties of some noble metal colloids, and can be predicted using classical calculations of the scattering by small particles, which is usually known as Mie theory.<sup>6</sup> Although UV-visible spectra for all metals can be calculated from such theory,<sup>7</sup> only metals with free electrons (basically Au, Ag, Cu, and the alkali metals) possess plasmon resonances in the visible that provide them with intense colors. Elongated nanoparticles (ellipsoids and nanorods) display two distinct plasmon bands related to transversal and longitudinal electron oscillations, being the longitudinal one very sensitive to the aspect ratio of the particles.<sup>8</sup> Apart from single particle properties, also the environment in which the metal particles are dispersed is of relevance to the optical properties.<sup>9</sup> The refractive index of the dispersing medium<sup>10</sup> as well as the average distance between neighboring metal nanoparticles<sup>11</sup> have been shown to influence the spectral features, which has been exploited for applications such as DNA detection.<sup>12</sup>

Metal nanoparticles also have important applications in catalysis,<sup>13,14</sup> mainly because of their extremely large surface to volume ratio, which allows a more effective utilization of expensive transition metals, and additionally, since the metal nanoparticles can be either supported onto solid substrates or dispersed in a solvent, they can be used for both heterogeneous and homogeneous catalysis. We are not going to describe in detail the catalytic properties of metal colloids here.

In this chapter, we intend to introduce to the reader some of the most popular preparation methods of noble metal colloids, but do not intend by any means to thoroughly review the scientific literature on metal colloid synthesis. We have chosen examples of synthesis in aqueous and organic solvents, and differentiate between spherical and anisotropic nanoparticles (nanorods and nanoprisms). Additionally, in section 3 we shall describe one of the most popular recent procedures to assemble metal colloids into nanostructured materials (layer-by-layer assembly), as well as the properties of the resulting structures.

#### 2. PREPARATION OF NOBLE METAL COLLOIDS

#### 2.1. Spherical Nanoparticles in Water

#### 2.1.1. Citrate Reduction

Probably the most popular method to prepare Au nanospheres dispersed in water is the reduction with sodium citrate at high temperature. This method was first introduced by Turkevich and co-workers back in the fifties,<sup>15</sup> and further studied and modified in a number of later papers.<sup>16-19</sup> This preparation is basically performed by heating a dilute (typically 1-5 x 10<sup>-4</sup> M) aqueous solution of HAuCl<sub>4</sub> to its boiling point and then rapid addition of sodium citrate solution. The formation of the gold colloid is then rather slow, with a spectacular color change from light yellow (due to HAuCl<sub>4</sub>) to colorless, then to gray, blue, purple, and finally (after some 10 minutes) deep wine red, revealing the

#### NOBLE METAL COLLOIDS.

formation of very uniform (standard deviation of ca. 10%) Au nanoparticles. Frens<sup>17</sup> demonstrated that the average particle diameter can be tuned over quite a wide range (ca. 10-100 nm) just by varying the concentration ratio between gold salt and sodium citrate. However, for particles larger than 30 nm, deviations from the spherical shape are observed, as well as a larger polydispersity. Lower temperatures can also be used, by which the reduction process is notably slower, and thus allowed to study the nucleation and growth mechanism.<sup>19</sup> Such studies revealed the presence of large and irregular aggregates of gold nuclei during the initial stages (these are responsible for the intermediate gray color) which eventually peptize to form the final monodisperse colloid. Examples of the initial aggregates and the final nanoparticles are shown in Figure 1.

The same procedure can be used to reduce a silver salt, but results in the formation of larger, non-uniform particles, with a rather high polydispersity. Using mixtures of Au and Ag salts, alloy nanoparticle colloids can be obtained, with surface plasmon bands centered at wavelengths intermediate between those for pure silver (400 nm) and pure gold (520 nm).<sup>20,21</sup> Citrate reduction has also been applied to the production of Pt colloids of much smaller particle sizes (2-4 nm), which could be further grown by hydrogen treatment.<sup>22,23</sup>

#### 2.1.2. Borohydride Reduction

Sodium borohydride is quite a strong reducing agent and therefore it has been often used for the reduction of metal salts to produce small metal particles in solution. Klabunde and co-workers performed a large amount of work on the synthesis of magnetic particles based on iron and cobalt<sup>24</sup> using borohydride reduction. For these metals however, some complications can arise if the stoichiometry is not carefully adjusted, since otherwise one can easily end up with the corresponding metal borides.<sup>25</sup> Borohydride has also been applied for the reduction of noble metals, both in aqueous and in non-aqueous solution. We restrict ourselves in this section to reactions in aqueous media, while borohydride production of nonaqueous colloids is discussed in Section 2.2.1.



Figure 1. Typical TEM micrographs of aggregates form at the initial stages and the final Au nanoparticles prepared using the sodium citrate reduction method.

#### I. PASTORIZA-SANTOS et al.

The formation of metallic platinum by borohydride was first reported by Brown and Brown<sup>26</sup> related to the study of hydrogenation reactions. These authors did not use any stabilizing agent, and therefore obtained what they termed "finely-divided black precipitates". A more detailed and systematic study using polyvinylpyrrolidone (PVP) as a protective agent (this was the traditional term for polymers, surfactants or other molecules used to stabilize colloids, and which has nowadays been replaced by other terms such as stabilizer or capping agent) and comparing borohydride with other reducing agents, was performed by Van Rheenen et al.<sup>27</sup>

Gold and silver, as well as bimetallic nanoparticles can also be easily formed using borohydride as a reductant, and suitable stabilizers. Liz-Marzán and Philipse<sup>28</sup> studied all possible combinations of Ag, Au and Pt, using clay fibers as supporting colloids. Optical analysis of the obtained colloids suggested that core-shell morphologies were obtained in some cases. Rather monodisperse silver nanoparticles can also be prepared by borohydride reduction in the presence of poly(acrylic acid),<sup>29</sup> and stabilization with citrate ions leads to small (ca. 3 nm) and rather uniform Au nanoparticles, which have been used as seeds for growth of larger spheres,<sup>30</sup> nanoshells,<sup>31</sup> and nanorods,<sup>32</sup> as detailed below.

#### 2.1.3. YRadiolysis

When speaking about metal nanoparticles and their properties, Prof. Arnim Henglein's name should always be borne in mind. Henglein's pioneering contribution to understanding the special properties, not only of metal nanoparticles and clusters,<sup>33</sup> but also of semiconductor quantum dots<sup>34</sup> has inspired much of the work subsequently performed, as revealed in a recent festschrift issue in The Journal of Physical Chemistry.<sup>35</sup> One of these outstanding contributions has been the development of a very useful technique for the production of metal nanoparticles of controlled size, based on the formation of hydrated electrons and organic radicals in solution through  $\gamma$ -radiolysis, which then acted as reducing agents for metal ions, yielding metal atoms which subsequently coalesce to form larger particles.<sup>33</sup>

Henglein and co-workers were pioneers in the application of radiation chemistry to synthesize very small metal nanoparticles,<sup>36-38</sup> as well as to study their photochemistry<sup>39</sup> and reactivity.<sup>40-43</sup> They also synthesized larger metal particles of Au<sup>44,45</sup> and Ag<sup>50</sup> with narrow size distributions by enlarging Au and Ag seeds, respectively, which in the case of Au constituted a useful material to study fast electronic processes.<sup>46</sup> Additionally, the same group applied radiation chemistry techniques to produce core-shell bimetallic particles. In the presence of suitable stabilizers, shells of different metals and various thickness could be grown around chemically performed seeds by varying the type and concentration of the metal ions in solution. Thus, high quality metal particles such as, Au@Pb,<sup>47,48</sup> Au@Pb@Cd,<sup>47</sup> Ag@Au,<sup>49</sup> Pt@Ag,<sup>50</sup> Au@Hg,<sup>51</sup> Pt@Au<sup>52,53</sup> and Pd@Au<sup>48,54</sup> were produced to study their optical and chemical properties.

Other groups like those of Belloni<sup>55-57</sup> or Doudna<sup>58,59</sup> also applied  $\gamma$ -radiolysis to reduce metals. Most of the systems reported by these groups were metallic alloys with catalytic applications. Recently, Doudna et al.<sup>60</sup> reported a method based on radiolytic reduction to generate filament-like nanostructures of Ag@Pt.

#### NOBLE METAL COLLOIDS.

#### 2.1.4. Growth on Preformed Nanoparticles

There are many synthetic methods to produce metal nanoparticles with sizes typically below 20 nm, but only a few methods produce particles of uniform size. To obtain larger particles, the difficulty in controlling the nucleation and growth steps occurring at intermediate stages results in a broad particle size distribution.<sup>61</sup> A common approach for controlling the size of nanoparticles is seeding growth.<sup>45,62-65</sup> In seeding growth methods, small metal particles are prepared first and later used as seeds (nucleation centers) for the preparation of particles with larger size. Providing a controlled number of preformed seeds and growth conditions that inhibit any secondary nucleation, the particle size can be controlled simply by varying the ratio between seed and metal salt concentrations. The main difficulty is to find suitable growth conditions to avoid that a new nucleation process takes place during the growth stages, which strongly limits the application of these methods.<sup>66</sup> Henglein employed radiolytic reduction for seeded growth of gold and silver particles, since the flux of  $\gamma$ -rays can be conveniently controlled to vary the amount of metal atoms produced.<sup>45,67</sup> Natan and co-workers used a reducing agent (hydroxylamine) that is too weak to reduce the gold metal salt without the presence of seeds, since these act as catalysts.<sup>30</sup> Similarly, Murphy and co-workers used ascorbic acid as the reducing agent and added cetyltrimethyl ammonium bromide in the growth solution to complex the gold salt and prevent its reduction in the absence of seeds.<sup>65</sup> The growth mechanism consists of an electron transfer from the reducing agent to the metal particles, followed by the reduction of the gold salt on the surface of the seed, so that the growth process follows electrochemical mixed current theory.<sup>68,69</sup> Schematically,

$$M_n^{(x+1)-} + AuCl_4^- \rightarrow Au_{(n+1)}^{x-} + 4Cl^-$$
(1)

where  $M_n^{(x+1)}$  is a metal particle that has already accumulated x electrons.

To avoid additional nucleation, a step-by-step particle enlargement method is more useful, allowing a large metal to salt ratio to be maintained throughout successive growth steps.<sup>66</sup> A limitation of the seeded growth method is the lack of availability of smaller seeds with a narrow size distribution. The seeding growth method has been also used for the preparation of different metallic core-shell particles; Au@Ag,<sup>70</sup> Ag@Au,<sup>71</sup> Pt@Au and Au@Pt.<sup>52</sup>

#### 2.1.5. Growth of Silica Shells on Metal Nanoparticles

Among the various surface modification processes developed for metal (and other) colloids, the growth of silica shells with tailored thickness has recently gathered great attention. One of the major reasons for silica coating is the anomalously high stability of silica colloids, especially in aqueous media, but other reasons are the easy control on the deposition process, its processibility, chemical inertness, controllable porosity, and optical transparency. All these properties make of silica an ideal material to modulate surface properties, while maintaining the physical properties of the underlying cores.

Silica coating of metal colloids presents the difficulty of a chemical mismatch between the core and the shell materials. Liz-Marzán and Philipse<sup>72</sup> first approached the synthesis of Au@SiO<sub>2</sub> particles through borohydride reduction of AuCl<sub>4</sub><sup>-</sup> in the presence

of small silica spheres, followed by extensive silica growth in ethanol of the resulting heteroaggregates. Although coated gold nanoparticles were obtained, these were mixed with pure silica spheres, which were difficult to separate.

A method that has provided substantially better results was later designed by Liz-Marzán et al.<sup>73,74</sup> using silane coupling agents as primers to deposit a first monolayer of silanol groups on the surface, which would then be receptive toward deposition of thin silica layers from sodium silicate solution. Subsequent shell growth could be carried out in ethanol using the so-called Stöber method.<sup>75</sup> Monodisperse colloids can be obtained using this procedure with nearly perfect core-shell structures. Examples of such particles are shown in Figure 5 below. This system has proved extremely useful for instance for systematic studies of optical properties, both in solution<sup>74,76,77</sup> and within nanostructures.<sup>11,78,79</sup> A similar strategy can be applied to the coating of silver colloids,<sup>29</sup> with the additional difficulty that dissolution of the Ag cores was observed when concentrated ammonia was added to increase the thickness of the silica shell, leading to formation of hollow silica shells.<sup>80</sup>

Other methods have been devised for the preparation of  $Ag@SiO_2$ , such as consecutive reactions within microemulsion droplets,<sup>81</sup> or the reduction of  $Ag^+$  by *N*,*N*-dimethylformamide (DMF) in the presence of an amino-silane.<sup>82</sup> However, none of these methods have been used for systematic studies until now.

#### 2.2. Spherical Nanoparticles in Organic Solvents

#### 2.2.1. Two-Phase Reduction

One of the currently most used methods for the preparation of gold nanoparticles has been developed by Brust et al.<sup>83,84</sup> in 1994. This method combines borohydride reduction with the use of thio- or amino-derivatives as steric stabilizers, by means of a two-phase reaction. Basically, HAuCl<sub>4</sub> is dissolved in water and subsequently transported into toluene by means of tetraoctylammonium bromide, which acts as a phase transfer agent. The toluene solution is then mixed and thoroughly stirred together with an aqueous solution of sodium borohydride, in the presence of thio-alkanes or amino-alkanes, which readily bind to the formed Au nanoparticles. Depending on the ratio between Au salt and capping agent (thiol/amine), the particle size can be tuned between ca. 1 and 10 nm. Several refinements of the preparative procedure including the development of analogous methods for the preparation of silver particles have been reported.<sup>85,86</sup> Murrav and coworkers also contributed to enhance the method's popularity by offering an interesting and elegant alternative to the two-phase reduction method which has opened a new field of preparative chemistry. They explored routes to functionalized monolayer protected clusters by ligand place exchange reactions.<sup>87-91</sup> Simple alkane thiol ligands can be completely or partially exchanged by a variety of functional groups, which can be for instance electrochemically active<sup>87,89,90</sup> or photoluminiscent,<sup>90</sup> allowing the chemical modification of their ligand shell.

#### 2.2.2. Reduction by the Solvent

Several examples exist on the reduction of metallic salts by organic solvents. Probably the most popular one has been ethanol, which was long used by Toshima and co-workers for the preparation of metal nanoparticles such as Pt, Pd, Au or Rh (suitable

#### NOBLE METAL COLLOIDS.

for catalytic applications) in the presence of a protecting polymer.<sup>92-94</sup> Another interesting example is found in Figlarz's polyol method, which was initially developed for the formation of larger colloidal particles,<sup>95,96</sup> though later was also adapted and improved for the production of silver nanoparticles.<sup>97</sup> Propanol was also used by Mills and coworkers for the preparation of silver colloids in basic conditions.<sup>98</sup> Related to these processes we can also mention the reduction of noble metal salts by non-ionic surfactants, and more specifically by those with a large number of ethoxy groups, to which the reducing ability has been assigned.<sup>99,100</sup>

N,N-dimethylformamide (DMF) is also one of the usual organic solvents for numerous processes, and it has been shown to behave as an active reducing agent under suitable conditions. Pastoriza-Santos et al. reported the ability of DMF to reduce  $Ag^+$  ions to the zero-valent metal, even at room temperature and in the absence of any external reducing agent.<sup>101,102</sup> Stable spherical silver nanoparticles were synthesized in DMF, using poly(vinyl pyrrolidone) as a stabilizer,<sup>103</sup> but additionally silica-<sup>82</sup> and titania-<sup>104</sup> coated nanoparticles were produced by the same method, in the presence of aminopropyl-trimethoxysilane and titanium tetrabutoxide, respectively. It was also shown that formamide<sup>105</sup> can act as a powerful reductant for silver or gold salts in the absence of oxygen. More recently, Diaz and coworkers reported the preparation of silver nanoparticles by the spontaneous reduction of silver 2-ethylhexanoate in dimethyl sulfoxide (DMSO) at room temperature.<sup>106</sup>

#### 2.2.3. Reduction within Microemulsions

Microemulsions have been used as confined reaction media during the past two decades, since, due to the very small size of the droplets, they can act as microreactors capable to control the size of the particles and at the same time to inhibit the aggregation by adsorption of the surfactants on the particle surface when the particle size approaches that of the microreactor droplet. The synthesis of nanoparticles using reactions in microemulsions was first described by Boutonnet and coworkers<sup>107</sup> They synthesized monodispersed metal particles of Pt, Pd, Rh and Ir by reduction of metal salts with hydrogen or hydrazine in water in oil (w/o) microemulsions. Since then, many different types of materials have been prepared using microemulsions, including metal carbonates,<sup>108</sup> metal oxides,<sup>109,110</sup> metal chalcogenides,<sup>111-113</sup> polymers,<sup>114</sup> etc.

In the case of noble metals, several protocols have been described to produce metal nanosized particles by chemical reduction in microemulsions. Pileni and co-workers synthesized metallic particles of Ag,<sup>115</sup> Cu,<sup>116</sup> Co<sup>117</sup> (and other materials) by reduction of the corresponding salts in w/o microemulsions using borohydride or hydrazine as reducing agents. They also showed a correlation between the structure of the mesophase in the surfactant system with the size and shape of the formation of metallic particle.

The wide range of applications (in catalysis, as biological stains, as condensers for electron storage in artificial photosynthesis or as ferrofluids) has also motivated studies by other groups on the formation of colloidal Ag,<sup>118</sup> Au,<sup>119</sup> Ni,<sup>120</sup> Cu,<sup>121</sup> Pd<sup>122</sup> and Co<sup>123</sup> particles. However, there is still a strong controversy on whether the microemulsion droplet size actually controls the final size of the obtained nanoparticles.

In recent years, the use of supercritical solvents has offered a new alternative in the synthesis of nanoparticles in microemulsions which presents several advantages over conventional organic solvents, because their solvation properties can be easily controlled by varying pressure. Colloidal silver<sup>124-126</sup> and copper<sup>126</sup> have been synthesized using microemulsions of water in supercritical  $CO_2$  with fluorinated surfactants.

#### 2.3. Nanorods and Nanoprisms in Water

#### 2.3.1. Synthesis of Nanorods within Porous Membranes

The first procedure reported for the production of metal nanorods is called template synthesis.<sup>127,128</sup> This method entails the preparation or deposition of the desired material within the cylindrical and monodisperse pores of a nanopore membrane. Martin and co-workers used polycarbonate filters, prepared by the track-etch method,<sup>129</sup> and nanopore aluminas prepared electrochemically from Al foil,<sup>130</sup> as template materials. This method allows the preparation of cylindrical nanostructures with monodisperse diameters and lengths, and depending on the nature of the membrane and the synthetic method used, these may be solid nanowires or hollow nanotubes.<sup>131</sup>

The earliest applications of the template method consisted of the preparation of microscopic and macroscopic electrodes prepared by depositing Au within the pores of policarbonate membranes using electrochemical<sup>132</sup> or electroless plating<sup>133</sup> methods. In the electrochemical method, the Au deposition is more uniform and starts at the pore walls creating, at short deposition times, hollow Au nanotubes within the pores.<sup>134</sup> Further deposition results in the formation of Au nanowires. The electroless method comprises the application of a catalyst to all the surfaces of the templating membrane. The membrane is then immersed into the electroless plating bath which contains Au<sup>1</sup> and a chemical reducing agent. Considering that the reduction of Au<sup>1</sup> to metallic Au only occurs in the presence of the catalyst, Au nanotubes are obtained along the pore walls. The thickness of the nanotube walls increases and the inner diameter of the tubes decreases with electroless plating time. At longer plating times, membranes containing nanowires are obtained.

A sequential electrodeposition within a porous template can be used to prepare striped nanowires with tailorable dimensions and composition.<sup>135</sup> Variation in composition along the length of the wire can be used to incorporate electrical functionalities, <sup>136</sup> optical contrast, <sup>137</sup> and the desired surface chemistry.<sup>138</sup>

Although very uniform thickness and controlled length were achieved, the amounts that could be made following this procedure were always very small, but still considerable basic work on the optical properties and alignment of these rods could be achieved.<sup>139-141</sup>

#### 2.3.2. Nanorods from Wet Synthesis in Solution

Wang and co-workers have developed an electrochemical solution phase synthesis of gold nanorods.<sup>142,143</sup> Their synthetic approach is to control the growth by introducing into the electrochemical system appropriate "shape-inducing" cationic surfactants and other additives that were found empirically to favor rod formation and act as both the supporting electrolyte and the stabilizer for the resulting cylindrical Au nanoparticles. In the electrochemical method for Au nanorod formation the micellar system consists of two cationic surfactants: cetyltrimethyl ammonium bromide (CTAB) and the much more hydrophobic surfactant tetradecyl ammonium bromide (TDAB). The ratio between the surfactants controls the average aspect ratio of

#### NOBLE METAL COLLOIDS.

the gold nanorods. The synthesis works in a small scale and is very difficult to carry out on a large scale, but represents a landmark in terms of shape control. The groups of El-Sayed and Hartland have shown that such rods possess quite unique and interesting optical properties. The particles may be selectively melted using laser pulses and show exciting coupling of the electron gas to bending modes.<sup>144,145</sup> Additionally, very strong optical polarization effects have been observed in nanorod polymer films.<sup>146</sup>

Subsequently, Murphy and co-workers discovered reduction conditions that enable the entire synthesis of gold and silver nanorods to be carried out directly in solution,<sup>32,147,148</sup> and their protocols enabled excellent aspect ratio control. In this seed mediated method a preformed silver or gold seed was used to promote gold or silver growth in solution in the presence of CTAB to promote nanorod formation. A mild reducing agent, such as ascorbic acid was used to avoid any extra nucleation, while the addition of different volumes of the seed solution produced gold nanorods with different aspect ratios. In the case of gold nanorods, the reproducibility depends on the presence of adventitious ions such as  $Ag^+$  and stringent seed preparation conditions. A mechanism for rod formation could not be provided.



Figure 2. UV-visible spectra and TEM micrographs of Au nanorods prepared by chemical growth on small seeds (varying seed concentration), in the presence of CTAB and AgNO<sub>3</sub>.

#### I. PASTORIZA-SANTOS et al.

The seed mediated method has been recently improved by El-Sayed and coworkers,<sup>149</sup> resulting in a spectacular increase in the yield of rod formation, similar to the photochemical method but easier to produce. Two modifications were applied to the seed-mediated growth method: (a) replacement of citrate with CTAB molecules in the seed formation step and (b) adjustment of the silver content of the growth solution to grow nanorods with controlled aspect ratios, resulting in the formation of only 0-1% of spheres. Examples of rods formed using this procedure are shown in Figure 2. In the same figure, the corresponding UV-visible spectra were plotted, to show how an increase in aspect ratio leads to a red-shift of the longitudinal plasmon band, while the transversal resonance only slightly varies due to differences in particle thickness.

Other methods that were recently reported include a seedless and surfactantless wet chemical method by Murphy and co-workers, to obtain silver nanowires in the presence of sodium citrate and sodium hydroxide,<sup>150</sup> as well as a photochemical method developed by Yang et al. for the synthesis of gold nanorods.<sup>151</sup> In contrast to the seed mediated mechanism proposed by Murphy, in the photochemical method the addition of a preformed gold seed is not needed. However, different amounts of silver nitrate are added to the growth solution containing CTAB and the gold salt before irradiating the solution with UV light. Again, the role of the Ag<sup>+</sup> in controlling the aspect ratio of the rods could not be determined.

Some work has also been recently carried out on the solution synthesis of bimetallic nanorods, employing gold nanorods as preformed cores. Jang and co-workers synthesized Au@Ag core-shell nanorods using the electrochemical method to obtain the gold nanorods and the seed-mediated mechanism to get the desired core-shell structure.<sup>152</sup> The combination of the different optical resonances from the core and the shell metals leads to a quite spectacular optical spectrum from these composite, anisotropic nanoparticles.

#### 2.3.3. Synthesis of Nanoprisms in Water

Although some triangular and polygonal flat nanoprisms are often obtained during every metal colloid preparation, the synthesis of metal flat nanoprisms with relatively high yield is quite recent. Only in November 2001,<sup>153</sup> Jin et al. reported the conversion of citrate-stabilized silver nanospheres into (truncated) triangular nanoprisms driven by irradiation with a 40-W fluorescent lamp, in the presence of bis(p-sulfonatophenyl) phenylphosphine. Apparently, the initial silver nanoparticles are first fragmented into smaller culsters, and subsequently there is a growth of particles with nanoprism shape, at the cost of the smaller clusters, which is induced by the phosphine present in solution. The optical spectra of the nanoprisms displayed bands for in-plane dipole resonance, as well as for in-plane and out-of-plane quadrupole resonances, while the out-of-plane dipole was only reflected as a small shoulder. Truncated triangles were also obtained by Chen and Carrol<sup>154</sup> using a procedure quite similar to the seeded growth method described for Au nanorod formation. In this case, the reduction was performed using ascorbic acid to reduce silver ions on silver seeds in a basic solution of concentrated CTAB.

Malikova et al.<sup>155</sup> synthesized Au nanoprisms in aqueous solution by reduction of neutralized HAuCl<sub>4</sub> with salicylic acid at 80 °C. Although the yield of nanoprisms was not outstanding, the formation of thin films showed that strong optical coupling occurs when the nanoprisms are close enough to each other (see Section 3.3 below).

#### NOBLE METAL COLLOIDS.

#### 2.4. Nanorods and Nanoprisms in Organic Solvents

#### 2.4.1. Reduction within Microemulsions

While the microemulsion method has been widely applied to the production and stabilization of spherical metal particles with various sizes and compositions, shape control of noble metallic particles using this procedure has only been demonstrated in a handful of studies to date. Pileni and co-workers demonstrated that it is possible to control nanocrystal shape to some extent within microemulsions.<sup>156</sup> Although the shape of the templates plays a role during the growth of the nanocrystals, these authors showed that the particle shape can be controlled even if the microscopic structure of the self-assembled surfactant system used as a template remains unchanged and that addition of salt to the templates can induce drastic changes in the particle shape. Recently, the same group also reported the synthesis of silver nanodisks in reverse micellar solution by reduction of Ag(AOT) with hydrazine, with various sizes that depended on the relative amount of hydrazine, but with constant aspect ratio.<sup>157</sup>

Ni nanorods have been synthesized by reduction of nickel chloride with hydrazine hydrate in w/o microemulsion.<sup>158</sup> Another use of interfaces to drive the synthesis of nanomaterials of variable morphology was introduced very recently by Sanyal and coworkers,<sup>159</sup> who demonstrated that the reduction of aqueous chloroaurate ions by anthracene anions bound to a liquid-liquid interface produced thin nanosheets of gold.

#### 2.4.2. Reduction by the Solvent

Xia and coworkers recently demonstrated that the polyol method<sup>95</sup> can be applied for the production of silver nanowires by reducing silver nitrate with ethylene glycol in the presence of poly(vinyl pyrrolidone)(PVP).<sup>160-162</sup> Silver nanoparticles with high aspect ratios were only formed in the presence of (Pt) seeds formed in situ prior to the addition of the silver salt. In the course of refluxing, These authors claim that Ostwald ripening takes place at the high temperatures used, forming nanoparticles with larger sizes at the expense of smaller ones. It is likely that PVP controls the growth rates of various faces of silver by coordinating to the surface. As a result, silver nanowires with diameters in the range of 30-60nm and lengths up to ~50µm were formed. They could control the dimensions of the silver nanowires by varying the experimental conditions (temperature, seed concentration, ratio between silver salt and PVP, etc...). In a later report,<sup>163</sup> the same group showed that, again through control of the concentrations of silver salt and PVP, silver nanocubes can be produced, which are single crystals, but with slightly truncated corners and edges. Additionally, all these silver particles with different shapes can be converted into hollow nanostructures (nanotubes, nanocubes, etc.) by reacting with salts of Au, Pt or Pd in water at reflux,<sup>164</sup> which opens a new way to exciting morphologies with interesting properties.

#### 2.4.3. Shape Control Using DMF

As it is previously shown, N,N-dimethylformamide (DMF) can reduce Ag<sup>+</sup> ions to the zero-valent metal, even at room temperature and in the absence of any external reducing agent,<sup>82</sup> which takes place through the following reaction:

$$HCONMe_2 + 2Ag^{+} + H_2O \rightarrow 2Ag^{0} + Me_2NCOOH + 2H^{+}$$
(2)

A basic difference between this reaction and the reduction by other organic compounds is that it proceeds at a meaningful rate even when performed at room temperature and in the dark. This is readily observed through yellow coloration of the solution, which deepens with time. This reducing ability under mild conditions points toward a larger tendency of this solvent for the reduction of  $Ag^+$  as compared to ethanol or other organic solvents.

Interestingly, the shape (and size) of the obtained nanoparticles depends on several parameters, such as silver salt and stabilizer concentrations, temperature and reaction time. Specifically, when poly(vinyl pyrrolidone) (PVP) is used as a protecting agent, spherical nanoparticles form at low AgNO<sub>3</sub> concentration (0.76 mM), while increasing silver concentration (up to 0.02 M) the formation of anisotropic particles is largely favored, though again the concentration of PVP and the reaction temperature strongly influence the shape of the final particles.

Figure 3 shows examples of nanospheres, nanorods and nanoprisms obtained by reduction of AgNO<sub>3</sub> in DMF, in the presence of PVP. It can be clearly observed that for high Ag concentration, at low PVP content nanorods are mainly formed, but when higher PVP concentrations are used, the formation of nanorods is suppressed, and mainly trianglular and other polygonal nanoplates predominate, which indicates that at low PVP:Ag ratios some crystallographic facets can become more active with respect to nanoparticle growth. In fact, TEM observation shows that initially, small spheres are formed which then assemble into certain shapes, which are determined by the crystallographic structure of the initial nanocrystals, and ultimately a restructuration takes place, which leads to fcc single crystals with well-defined shapes.<sup>165</sup> Additionally, in the case of nanoprisms, it was also observed that they become larger with time, and a wider variety of shapes are found for longer boiling times.

Atomic force microscopy (AFM) measurements demonstrated the flat geometry of the nanoprisms, as shown in Figure 3, indicating an average thickness of ca. 35 nm for lateral dimensions of the order of 200 nm. It can also be observed in this image that most of the nanoprisms are truncated triangles, which sometimes leads to other polygonal shapes.



Figure 3. TEM micrographs showing Ag nanoparticles obtained by reduction in DMF in the presence of PVP: (a) [PVP]=0.76 mM,  $[Ag^+]=0.76 \text{ mM}$ ; (b) [PVP]=0.06 mM,  $[Ag^+]=0.02 \text{ M}$ . (c) AFM image of Ag nanosprisms obtained by reduction in DMF ([PVP]=0.4 mM,  $[Ag^+]=0.02 \text{ M}$ ).

# 3. METAL COLLOID STRUCTURES THROUGH LAYER-BY-LAYER ASSEMBLY

#### 3.1. Layer-by-Layer Assembly

The use of polyelectrolytes for the assembly of nanoparticles was developed only recently,<sup>166</sup> but has experienced a tremendous advance during the last decade. The basis of this, so-called layer-by-layer (LBL) technique is the electrostatic attraction between oppositely charged species.<sup>167</sup> Briefly, a charged substrate is immersed within a solution of an oppositely charged polyelectrolyte, so that the surface charge is reversed, which is known as overcompensation effect. A subsequent immersion in a solution of nanoparticles with the appropriate surface charge leads to the deposition of a homogeneous, compact nanoparticle monolayer on the surface. The process can be repeated in successive cycles to deposit more monolayers and build up a hybrid film. If we compare this process to traditional deposition techniques, such as sputtering and vacuum evaporation, layer-by-layer assembly possesses features that make it specially valuable for the formation of complex nanostructures. Importantly, LBL can be carried out at room temperature and does not require subsequent annealing of the deposited film, so that a wide variety of substrates can be used. Furthermore, the shape and size of the constituting nanoparticles can be selected prior to assembly, which makes possible a careful design of the properties of the film by means of the proper choice of the colloid. With respect to other standard film formation techniques, such as Langmuir-Blodgett deposition, LBL assembly is much simpler to carry out and does not require special equipment such as Langmuir troughs. However, it is also true that Langmuir-Blodgett films show a higher in-plane order.

All these features make LBL an ideal technique for the assembly of core-shell and anisotropic nanoparticles (among others), since the nanoparticles can be completely synthesized prior to the assembly process, and the desired properties can be designed in the first synthetic stage. We only describe here two examples of the versatility of this technique for the assembly of metal nanoparticles, which allows to obtain structures with special optical features.

#### 3.2. Assembly of Au@SiO<sub>2</sub>

The interest of the assembly of silica-coated gold nanoparticles relies on the possibility of controlling the particle volume fraction by means of the variation of the silica shell thickness, provided that the assembled films are close-packed. In close-packing conditions, the separation between metal cores is just twice the thickness of the coating shell, which can be controlled during the synthesis of the colloids. This system has been recently studied in detail by Ung et al.,<sup>11,168</sup> and described here are the main results on the influence of metal nanoparticles volume fraction (through interparticle interactions) on the optical properties of the films.

In refs. 11 and 168, experimental and calculated absorbance and reflectance spectra are compared for thin films with different metal contents (through variation of silica shell thickness). This comparison shows that, as the gold volume fraction increases (the separation between nanoparticles decreases), there is a red-shift of the plasmon resonance, as well as a broadening of the band. This effect originates in the dipole-dipole interactions between neighboring nanoparticles, and a separation of just 15 nm is