# NANOPHOTONICS

PARAS N. PRASAD



A JOHN WILEY & SONS, INC., PUBLICATION

## NANOPHOTONICS

# NANOPHOTONICS

PARAS N. PRASAD



A JOHN WILEY & SONS, INC., PUBLICATION

Copyright © 2004 by John Wiley & Sons, Inc. All rights reserved.

Published by John Wiley & Sons, Inc., Hoboken, New Jersey. Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 646-8600, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representation or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services please contact our Customer Care Department within the U.S. at 877-762-2974, outside the U.S. at 317-572-3993 or fax 317-572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print, however, may not be available in electronic format.

#### Library of Congress Cataloging-in-Publication Data:

Prasad, Paras N. Nanophotonics / Paras N. Prasad. p. cm. Includes bibliographical references and index. ISBN 0-471-64988-0 (cloth) 1. Photonics. 2. Nonotechnology. I. Title. TA1520.P73 2004 621.36—dc22 2004001186

Printed in the United States of America.

 $10 \ 9 \ 8 \ 7 \ 6 \ 5 \ 4 \ 3 \ 2 \ 1$ 

## Summary of Contents

- 1. Introduction
- 2. Foundations for Nanophotonics
- 3. Near-Field Interaction and Microscopy
- 4. Quantum-Confined Materials
- 5. Plasmonics
- 6. Nanocontrol of Excitation Dynamics
- 7. Growth and Characterization of Nanomaterials
- 8. Nanostructured Molecular Architectures
- 9. Photonic Crystals
- 10. Nanocomposites
- 11. Nanolithography
- 12. Biomaterials and Nanophotonics
- 13. Nanophotonics for Biotechnology and Nanomedicine
- 14. Nanophotonics and the Marketplace

## **Contents**

Preface		xiii	
Acknow	ledgments	XV	
1. Intr	oduction	1	
1.1	Nanophotonics—An Exciting Frontier in Nanotechnology	1	
1.2	2 Nanophotonics at a Glance		
1.3	Multidisciplinary Education, Training, and Research	3	
1.4.	Rationale for this Book	4	
1.5	1.5 Opportunities for Basic Research and Development of		
	New Technologies		
1.6	Scope of this Book	6	
	References	8	
2. Fou	ndations for Nanophotonics	9	
2.1	Photons and Electrons: Similarities and Differences	10	
	2.1.1 Free-Space Propagation	12	
	2.1.2 Confinement of Photons and Electrons	14	
	2.1.3 Propagation Through a Classically Forbidden Zone:	19	
	1 unitering	21	
	2.1.4 Localization Under a Periodic Potential: Bandgap	21	
2.2	2.1.5 Cooperative Effects for Filotons and Electrons	24	
2.2	2.2.1 Axial Nanoscopic Localization	20	
	2.2.1 Axial Nanoscopic Localization	29	
23	Nanoscale Confinement of Electronic Interactions	32	
2.5	2.3.1 Quantum Confinement Effects	34	
	2.3.1 Quantum Commentent Effects	34	
	2.3.2 New Cooperative Transitions	34	
	2.3.5 New Cooperative Transitions 2.3.4 Nanoscale Electronic Energy Transfer	35	
	2.3.5 Cooperative Emission	36	
2.4	Highlights of the Chapter	37	
2.1	References	38	

3.	Nea	r-Field Interaction and Microscopy	41
	3.1	Near-Field Optics	42
	3.2	Theoretical Modeling of Near-Field Nanoscopic Interactions	44
	3.3	Near-Field Microscopy	48
	3.4	Examples of Near-Field Studies	51
		3.4.1 Study of Quantum Dots	51
		3.4.2 Single-Molecule Spectroscopy	53
		3.4.3 Study of Nonlinear Optical Processes	55
	3.5	Apertureless Near-Field Spectroscopy and Microscopy	62
	3.6	Nanoscale Enhancement of Optical Interactions	65
	3.7	Time- and Space-Resolved Studies of Nanoscale Dynamics	69
	3.8	Commercially Available Sources for Near-Field Microscope	73
	3.9	Highlights of the Chapter	73
		References	75
4.	Qua	ntum-Confined Materials	79
	4.1	Inorganic Semiconductors	80
		4.1.1 Quantum Wells	81
		4.1.2 Quantum Wires	85
		4.1.3 Quantum Dots	86
		4.1.4 Quantum Rings	88
	4.2	Manifestations of Quantum Confinement	88
		4.2.1 Optical Properties	88
		4.2.2 Examples	91
		4.2.3 Nonlinear Optical Properties	95
		4.2.4 Quantum-Confined Stark Effect	96
	4.3	Dielectric Confinement Effect	99
	4.4	Superlattices	100
	4.5	Core-Shell Quantum Dols and Quantum Dol-Quantum Wells	104
	4.0	Quantum-Confined Structures as Lasing Media	100
	4./	Highlights of the Chapter	113
	4.0	References	120
_	Dlas		120
э.	Plas	monics	129
	5.1	Metallic Nanoparticles and Nanorods	130
	5.2	Metallic Nanoshells	135
	5.3	Local Field Enhancement	137
	5.4	Subwavelength Aperture Plasmonics	138
	5.5	Plasmonic Wave Guiding	139
	5.6	Applications of Metallic Nanostructures	141
	5./	Kadialive Decay Engineering	142
	5.8	References	14/
			149

#### viii

6.	Nano	ocontrol of Excitation Dynamics	153
	6.1	Nanostructure and Excited States	154
	6.2	Rare-Earth Doped Nanostructures	158
	6.3	Up-Converting Nanophores	161
	6.4	Photon Avalanche	165
	6.5	Quantum Cutting	166
	6.6	Site Isolating Nanoparticles	171
	6.7	Highlights of the Chapter	171
		References	173
7.	Grov	wth and Characterization of Nanomaterials	177
	7.1	Growth Methods for Nanomaterials	178
		7.1.1 Epitaxial Growth	179
		7.1.2 Laser-Assisted Vapor Deposition (LAVD)	183
		7.1.3 Nanochemistry	185
	7.2	Characterization of Nanomaterials	189
		7.2.1 X-Ray Characterization	190
		7.2.1.1 X-Ray Diffraction	190
		7.2.1.2 X-Ray Photoelectron Spectroscopy	192
		7.2.2 Electron Microscopy	194
		7.2.2.1 Transmission Electron Microscopy (TEM)	195
		7.2.2.2 Scanning Electron Microscopy (SEM)	195
		7.2.3 Other Electron Beam Techniques	197
		7.2.4 Scanning Probe Microscopy (SPM)	199
	7.3	Highlights of the Chapter	204
		References	206
8.	Nan	ostructured Molecular Architectures	209
	8.1	Noncovalent Interactions	210
	8.2	Nanostructured Polymeric Media	212
	8.3	Molecular Machines	215
	8.4	Dendrimers	217
	8.5	Supramolecular Structures	225
	8.6	Monolayer and Multilayer Molecular Assemblies	229
	8.7	Highlights of the Chapter	233
		References	235
9.	Photonic Crystals		239
	9.1	Basics Concepts	240
	9.2	Theoretical Modeling of Photonic Crystals	242
	9.3	Features of Photonic Crystals	246
	9.4	Methods of Fabrication	252
	9.5	Photonic Crystal Optical Circuitry	259

#### X CONTENTS

	9.6	Nonlinear Photonic Crystals	260
	9.7	Photonic Crystal Fibers (PCF)	264
	9.8	Photonic Crystals and Optical Communications	266
	9.9	Photonic Crystal Sensors	267
	9.10	Highlights of the Chapter	270
		References	272
10.	Nano	ocomposites	277
	10.1	Nanocomposites as Photonic Media	278
	10.2	Nanocomposite Waveguides	280
	10.3	Random Lasers: Laser Paints	283
	10.4	Local Field Enhancement	284
	10.5	Multiphasic Nanocomposites	286
	10.6	Nanocomposites for Optoelectronics	290
	10.7	Polymer-Dispersed Liquid Crystals (PDLC)	297
	10.8	Nanocomposite Metamaterials	301
	10.9	Highlights of the Chapter	302
		References	304
11.	Nano	olithography	309
	11.1	Two-Photon Lithography	311
	11.2	Near-Field Lithography	317
	11.3	Near-Field Phase-Mask Soft Lithography	322
	11.4	Plasmon Printing	324
	11.5	Nanosphere Lithography	325
	11.6	Dip-Pen Nanolithography	328
	11.7	Nanoimprint Lithography	330
	11.8	Photonically Aligned Nanoarrays	331
	11.9	Highlights of the Chapter	332
		References	334
12.	Bion	naterials and Nanophotonics	337
	12.1	Bioderived Materials	338
	12.2	Bioinspired Materials	344
	12.3	Biotemplates	346
	12.4	Bacteria as Biosynthesizers	347
	12.5	Highlights of the Chapter	350
		References	350
13.	Nano	pphotonics for Biotechnology and Nanomedicine	355
	13.1	Near-Field Bioimaging	356
	13.2	Nanoparticles for Optical Diagnostics and Targeted Therapy	357
	13.3	Semiconductor Quantum Dots for Bioimaging	358

13.4	Up-Converting Nanophores for Bioimaging	359
13.5	Biosensing	
13.6	Nanoclinics for Optical Diagnostics and Targeted Therapy	
13.7	Nanoclinic Gene Delivery	367
13.8	Nanoclinics for Photodynamic Therapy	371
13.9	13.9 Highlights of the Chapter	
	References	376
14. Nano	ophotonics and the Marketplace	381
14.1	Nanotechnology, Lasers, and Photonics	382
	14.1.1 Nanonetchnology	382
	14.1.2 Worldwide Laser Sales	383
	14.1.3 Photonics	383
	14.1.4 Nanophotonics	386
14.2	Optical Nanomaterials	386
	14.2.1 Nanoparticle Coatings	387
	14.2.2 Sunscreen Nanoparticles	389
	14.2.3 Self-Cleaning Glass	389
	14.2.4 Fluorescent Quantum Dots	390
	14.2.5 Nanobarcodes	391
	14.2.6 Photonic Crystals	391
	14.2.7 Photonic Crystal Fibers	391
14.3	Quantum-Confined Lasers	392
14.4 Near-Field Microscopy		392
14.5	14.5 Nanolithography	
14.6	Future Outlook for Nanophotonics	394
	14.6.1 Power Generation and Conversion	394
	14.6.2 Information Technology	395
	14.6.3 Sensor Technology	395
	14.6.4 Nanomedicine	395
14.7	Highlights of the Chapter	396
	References	397

#### Index

399

### Preface

Nanophotonics, defined by the fusion of nanotechnology and photonics, is an emerging frontier providing challenges for fundamental research and opportunities for new technologies. Nanophotonics has already made its impact in the marketplace. It is a multidisciplinary field, creating opportunities in physics, chemistry, applied sciences, engineering, and biology, as well as in biomedical technology.

Nanophotonics has meant different things to different people, in each case being defined with a narrow focus. Several books and reviews exist that cover selective aspects of nanophotonics. However, there is a need for an up-to-date monograph that provides a unified synthesis of this subject. This book fills this need by providing a unifying, multifaceted description of nanophotonics to benefit a multidisciplinary readership. The objective is to provide a basic knowledge of a broad range of topics so that individuals in all disciplines can rapidly acquire the minimal necessary background for research and development in nanophotonics. The author intends this book to serve both as a textbook for education and training as well as a reference book that aids research and development in those areas integrating light, photonics, and nanotechnology. Another aim of the book is to stimulate the interest of researchers, industries, and businesses to foster collaboration through multidisciplinary programs in this frontier science, leading to development and transition of the resulting technology.

This book encompasses the fundamentals and various applications involving the integration of nanotechnology, photonics, and biology. Each chapter begins with an introduction describing what a reader will find in that chapter. Each chapter ends with highlights that are basically the take-home message and may serve as a review of the materials presented.

In writing this book, which covers a very broad range of topics, I received help from a large number of individuals at the Institute for Lasers, Photonics, and Biophotonics at the State University of New York–Buffalo and from elsewhere. This help has consisted of furnishing technical information, creating illustrations, providing critiques, and preparing the manuscript. A separate Acknowledgement recognizes these individuals. Here I would like to acknowledge the individuals whose broad-based support has been of paramount value in completing the book. I owe a great deal of sincere gratitude to my wife, Nadia Shahram. She has been a constant source of inspiration, providing support and encouragement for this writing, in spite of her own very busy professional schedule. I am also indebted to our daughters and our princesses, Melanie and Natasha, for showing their love and understanding by sacrificing their quality time with me.

I express my sincere appreciation to my colleague, Professor Stanley Bruckenstein, for his endless support and encouragement. I thank Dr. Marek Samoc, Professor Joseph Haus, and Dr. Andrey Kuzmin for their valuable general support and technical help. I owe thanks to my administrative assistant, Ms. Margie Weber, for assuming responsibility for many of the noncritical administrative issues at the Institute. Finally, I thank Ms. Theresa Skurzewski and Ms. Barbara Raff, whose clerical help in manuscript preparation was invaluable.

### Acknowledgments

#### Technical Contents:

Mr. Martin Casstevens, Professor Joseph Haus, Dr. Andrey Kuzmin, Dr. Paul Markowicz, Dr. Tymish Ohulchanskyy, Dr. Yudhisthira Sahoo, Dr. Marek Samoc, Professor Wieslaw Strek, Professor Albert Titus

#### Technical Illustrations and References:

Dr. E. James Bergey, Professor Jean M.J. Frechet, Mr. Christopher Friend, Dr. Madalina Furis, Professor Bing Gong, Dr. James Grote, Dr. Aliaksandr Kachynski, Professor Raoul Kopelman, Professor Charles Lieber, Dr. Tzu Chau Lin, Dr. Derrick Lucey, Professor Hong Luo, Professor Tobin J. Marks, Professor Chad Mirkin, Dr. Haridas Pudavar, Dr. Kaushik RoyChoudhury, Dr. Yudhisthira Sahoo, Dr. Yuzchen Shen, Mr. Hanifi Tiryaki, Dr. Richard Vaia, Mr. QingDong Zheng

#### Chapter Critiques:

Dr. E. James Bergey, Dr. Jeet Bhatia, Professor Robert W. Boyd, Professor Stanley Bruckenstein, Dr. Timothy Bunning, Professor Alexander N. Cartwright, Professor Cid de Araújo, Dr. Edward Furlani, Professor Sergey Gaponenko, Dr. Kathleen Havelka, Professor Alex Jen, Professor Iam Choon Khoo, Professor Kwang-Sup Lee, Dr. Nick Lepinski, Professor Hong Luo, Dr. Glauco Maciel, Professor Seth Marder, Professor Bruce McCombe, Professor Vladimir Mitin, Dr. Robert Nelson, Professor Lucas Novotny, Dr. Amitava Patra, Professor Andre Persoons, Dr. Corey Radloff, Professor George Schatz, Professor George Stegeman, Dr. Richard Vaia

#### Manuscript Preparation:

Michelle Murray, Barbara Raff, Theresa Skurzewski, Marjorie Weber

### Introduction

#### 1.1 NANOPHOTONICS—AN EXCITING FRONTIER IN NANOTECHNOLOGY

Nanophotonics is an exciting new frontier that has captured the imaginations of people worldwide. It deals with the interaction of light with matter on a nanometer size scale. By adding a new dimension to nanoscale science and technology, nanophotonics provides challenges for fundamental research and creates opportunities for new technologies. The interest in nanoscience is a realization of a famous statement by Feynman that "There's Plenty of Room at the Bottom" (Feynman, 1961). He was pointing out that if one takes a length scale of one micrometer and divides it in nanometer segments, which are a billionth of a meter, one can imagine how many segments and compartments become available to manipulate.

We are living in an age of "nano-mania." Everything nano is considered to be exciting and worthwhile. Many countries have started Nanotechnology Initiatives. A detailed report for the U.S. National Nanotechnology Initiative has been published by the National Research Council (NRC Report, 2002). While nanotechnology can't claim to provide a better solution for every problem, nanophotonics does create exciting opportunities and enables new technologies. The key fact is that nanophotonics deals with interactions between light and matter at a scale shorter than the wavelength of light itself. This book covers interactions and materials that constitute nanophotonics, and it also describes their applications. Its goal is to present nanophotonics in a way to entice one into this new and exciting area. Purely for the sake of convenience, the examples presented are selected wherever possible from the work conducted at our Institute for Lasers, Photonics, and Biophotonics, which has a comprehensive program in nanophotonics.

As a supplemental reference, a CD-ROM of the author's SPIE short course on nanophotonics, produced by SPIE, is recommended. This CD-ROM (CDV 497) provides numerous technical illustrations in color in the PowerPoint format.

#### **1.2 NANOPHOTONICS AT A GLANCE**

Nanophotonics can conceptually be divided into three parts as shown in Table 1.1 (Shen et al., 2000). One way to induce interactions between light and matter on a



Table 1.1. Nanophotonics

nanometer size scale is to confine light to nanoscale dimensions that are much smaller than the wavelength of light. The second approach is to confine matter to nanoscale dimensions, thereby limiting interactions between light and matter to nanoscopic dimensions. This defines the field of nanomaterials. The last way is nanoscale confinement of a photoprocess where we induce photochemistry or a light-induced phase change. This approach provides methods for nanofabrication of photonic structures and functional units.

Let's look at nanoscale confinement of radiation. There are a number of ways in which one can confine the light to a nanometer size scale. One of them is using near-field optical propagation, which we discuss in detail in Chapter 3 of this book. One example is light squeezed through a metal-coated and tapered optical fiber where the light emanates through a tip opening that is much smaller than the wavelength of light.

The nanoscale confinement of matter to make nanomaterials for photonics involves various ways of confining the dimensions of matter to produce nanostructures. For example, one can utilize nanoparticles that exhibit unique electronic and photonic properties. It is gratifying to find that these nanoparticles are already being used for various applications of nanophotonics such as UV absorbers in sunscreen lotions. Nanoparticles can be made of either inorganic or organic materials. Nanomers, which are nanometer size oligomers (a small number of repeat units) of monomeric organic structures, are organic analogues of nanoparticles. In contrast, polymers are long chain structures involving a large number of repeat units. These nanomers exhibit size-dependent optical properties. Metallic nanoparticles exhibit unique optical response and enhanced electromagnetic field and constitute the area of "plasmonics." Then there are nanoparticles which up-convert two absorbed IR photons into a photon in the visible UV range; conversely, there are nanoparticles, called quantum cutters, that down-convert an absorbed vacuum UV photon to two photons in the visible range. A hot area of nanomaterials is a photonic crystal that represents a periodic dielectric structure with a repeat unit of the order of wavelength of light. Nanocomposites comprise nanodomains of two or more dissimilar materials that are phase-separated on a nanometer size scale. Each nanodomain in the nanocomposite can impart a particular optical property to the bulk media. Flow of optical energy by energy transfer (optical communications) between different domains can also be controlled.

Nanoscale photoprocesses can be used for nanolithography to fabricate nanostructures. These nanostructures can be used to form nanoscale sensors and actuators. A nanoscale optical memory is one of exciting concepts of nanofabrication. An important feature of nanofabrication is that the photoprocesses can be confined to well-defined nanoregions so that structures can be fabricated in a precise geometry and arrangement.

#### 1.3 MULTIDISCIPLINARY EDUCATION, TRAINING, AND RESEARCH

We live in a complex world where revolutionary progress has been and continues to be made in communications, computer memory, and data processing. There is a growing need for new technologies that rapidly detect and treat diseases at an early stage or even pre-stage. As we get accustomed to these advances, our expectations will demand more compact, energy-efficient, rapidly responding, and environmentally safe technologies. Photonic-based technology, coupled with nanotechnology, can meet many of these challenges. In the medical area, new modes of photonic diagnostics, which are noninvasive and molecular-based, may recognize the prestages and onset of a disease such as cancer and thus provide a major leap (Prasad, 2003). Nanomedicine, combined with light-guided and activated therapy, will advance individualized therapy that is based on molecular recognition and thus have minimal side effects.

The past several decades have witnessed major technological breakthroughs produced by fusion of different disciplines. This trend is even more likely in this millenium. Nanophotonics in its broader vision offers opportunities for interactions among many traditionally disparate disciplines of science, technology, and medicine. As shall be illustrated in this book, nanophotonics is an interdisciplinary field that comprises physics, chemistry, applied sciences and engineering, biology, and biomedical technology.

A significant multidisciplinary challenge lies ahead for the broader nanophotonics visions to become reality. These challenges require a significant increase in the number of knowledgeable researchers and trained personnel in this field. This need can be met by providing a multidisciplinary training for a future generation of researchers at both undergraduate and graduate levels, worldwide. A worldwide recognition of this vital need is evident from the growing number of conferences and workshops being held on this topic, as well as from the education and training programs being offered or contemplated at various institutions. For example, the author has offered a multidisciplinary course in nanophotonics at Buffalo as well as a short course in this subject at the SPIE professional society meetings. Much of the material covered in this book was developed during the teaching of these courses and was refined by valuable feedback from these course participants.

#### 4 INTRODUCTION

It is hoped that this book will serve both as an education and training text and as a reference book for research and development. Also, this book should be of value to industries and businesses, because the last chapter attempts to provide a critical evaluation of the current status of nanophotonic-based technologies.

#### 1.4 RATIONALE FOR THIS BOOK

Naturally, for a hot area such as nanophotonics, many excellent reviews and edited books exist. Nanophotonics has meant different things to different people. Some have considered near-field interactions and near-field microscopy as the major thrust of nanophotonics, while others have considered it to be focused in photonic crystals. Another major direction has been nanomaterials, particularly the ones exhibiting size dependence of their optical properties; these are the quantum-confined structures. For engineers, nanoscale optical devices and nanolithography are the most relevant aspects of nanophotonics.

In terms of optical materials, the scientific community is often divided in two traditional groups: inorganic and organic, with very little cross-fertilization. The physics community focuses on inorganic semiconductors and metals, while shying away from complex organic structures. The chemical community, on the other hand, deals traditionally with organic structures and biomaterials and feels less comfortable with inorganic semiconductors, particularly with concepts defining their electronic and optical properties. Importantly, a new generation of hybrid nanomaterials, which involve different levels of integration of organic and inorganic structures, holds considerable promise for new fundamental science and novel technologies. For example, novel chemical routes can be utilized to prepare inorganic semiconductor nanostructures for nanophotonics. Engineers, who could exploit these new materials' flexibility for fabrication of components with diverse functionalities and their heterogeneous integration, often lack experience in dealing with these materials. Biologists have a great deal to offer by providing biomaterials for nanophotonics. At the same time, biological and biomedical researchers can utilize nanophotonics to study cellular processes and use nano-optical probes for diagnosis and to effect light-guided and activated therapy.

Often, a major hurdle is the lack of a common language to foster effective communication across disciplines. Therefore, much is to be gained by creating an environment that includes these disciplines and facilitates their interactions.

This book will address all these issues. It proposes to fill the existing void by providing the following features:

- A unifying, multifaceted description of nanophotonics that includes near-field interactions, nanomaterials, photonic crystals, and nanofabrication
- A focus on nanoscale optical interactions, nanostructured optical materials and applications of nanophotonics
- A coverage of inorganic, organic materials, and biomaterials as well as their hybrids

- A broad view of nanolithography for nanofabrication
- A coverage of nanophotonics for biomedical research and nanomedicine
- A critical assessment of nanophotonics in the market place, with future forecasts

## 1.5 OPPORTUNITIES FOR BASIC RESEARCH AND DEVELOPMENT OF NEW TECHNOLOGIES

Nanophotonics integrates a number of major technology thrust areas: lasers, photonics, photovoltaics, nanotechnology, and biotechnology. Each of these technologies either already generates or shows the potential to generate over \$100 billion per year of sales revenue. Nanophotonics also offers numerous opportunities for multidisciplinary research. Provided below is a glimpse of these opportunities, categorized by disciplines.

#### **Chemists and Chemical Engineers**

- Novel synthetic routes and processing of nanomaterials
- New types of molecular nanostructures and supramolecular assemblies with varied nanoarchitectures
- Self-assembled periodic and aperiodic nanostructures to induce multifunctionality and cooperative effects
- Chemistry for surface modifications to produce nanotemplates
- One-pot syntheses that do not require changing reaction vessels
- Scalable production to make large quantities economically

#### Physicists

- Quantum electrodynamics to study novel optical phenomena in nanocavities
- Single photon source for quantum information processing
- Nanoscale nonlinear optical processes
- Nanocontrol of interactions between electrons, phonons and photons
- Time-resolved and spectrally resolved studies of nanoscopic excitation dynamics

#### **Device Engineers**

- Nanolithography for nanofabrication of emitters, detectors, and couplers
- Nanoscale integration of emitters, transmission channels, signal processors, and detectors, coupled with power generators
- Photonic crystal circuits and microcavity-based devices
- Combination of photonic crystals and plasmonics to enhance various linear and nonlinear optical functions
- Quantum dot and quantum wire lasers

#### 6 INTRODUCTION

- Highly efficient broadband and lightweight solar panels that can be packaged as rolls
- Quantum cutters to split vacuum UV photons into two visible photons for new-generation fluorescent lamps and lighting

#### **Biologists**

- Genetic manipulation of biomaterials for photonics
- Biological principles to guide development of bio-inspired photonic materials
- Novel biocolloids and biotemplates for photonic structures
- Bacterial synthesis of photonic materials

#### **Biomedical Researchers**

- Novel optical nanoprobes for diagnostics
- Targeted therapy using light-guided nanomedicine
- New modalities of light-activated therapy using nanoparticles
- Nanotechnology for biosensors

#### 1.6 SCOPE OF THIS BOOK

This book is written for a multidisciplinary readership with the goal to provide introduction to a wide range of topics encompassing nanophotonics. A major emphasis is placed on elucidating concepts with minimal mathematical details; examples are provided to illustrate principles and applications. The book can readily enable a newcomer to this field to acquire the minimum necessary background to undertake research and development.

A major challenge for researchers working in a multidisciplinary area is the need to learn relevant concepts outside of their expertise. This may require searching through a vast amount of literature, often leading to frustrations of not being able to extract pertinent information quickly. By providing a multifaceted description of nanophotonics, it is hoped that the book will mitigate this problem and serve as a reference source.

The book is structured so that it can also be of value to educators teaching undergraduate and graduate courses in multiple departments. For them, it will serve as a textbook that elucidates basic principles and multidisciplinary approaches. Most chapters are essentially independent of each other, providing flexibility in choice of topics to be covered. Thus, the book can also readily be adopted for training and tutorial short courses at universities as well as at various professional society meetings.

Each chapter begins with an introduction describing its contents. This introduction also provides a guide to what may be omitted by a reader familiar with the specific content or by someone who is less inclined to go through details. Each chapter ends with highlights of the content covered in it. The highlights provide the takehome message from the chapter and serve to review the materials learned. Also, for researchers interested in a cursory glimpse of a chapter, the highlights provide an overview of topics covered. For an instructor, the highlights may also be useful in the preparation of lecture notes or PowerPoint presentations.

Chapter 2 provides an introduction to the foundations of nanophotonics. The nanoscale interactions are defined by discussing similarities and differences between photons and electrons. Spatial confinement effects on photons and electrons are presented. Other topics covered are photon and electron tunneling, effect of a periodic potential in producing a bandgap, and cooperative effects. Ways to localize optical interactions axially and laterally on a nanoscale are described.

Chapter 3 defines near-field interactions and describes near-field microscopy. A brief theoretical description of near-field interactions and the various experimental geometries used to effect them are introduced. The theoretical section may be skipped by those more experimentally oriented. Various optical and higher-order nonlinear optical interactions in nanoscopic domains are described. Applications to the highly active field of single molecule spectroscopy is described.

Chapter 4 covers quantum-confined materials whose optical properties are sizedependent. Described here are semiconductor quantum wells, quantum wires, quantum dots, and their organic analogues. A succinct description of manifestations of quantum confinement effects presented in this chapter should be of significant value to those (e.g., some chemists and life scientists) encountering this topic for the first time. The applications of these materials in semiconductor lasers, described here, exemplify the technological significance of this class of materials.

Chapter 5 covers the topic of metallic nanostructures, now with a new buzzword "plasmonics" describing the subject. Relevant concepts together with potential applications are introduced. Guiding of light through dimensions smaller than the wavelength of light by using plasmonic guiding is described. The applications of metallic nanostructures to chemical and biological sensing is presented.

Chapter 6 deals with nanoscale materials and nanoparticles, for which the electronic energy gap does not change with a change in size. However, the excitation dynamics—that is, emission properties, energy transfer, and cooperative optical transitions in these nanoparticles—are dependent on their nanostructures. Thus nanocontrol of excitation dynamics is introduced. Important processes described are (i) energy up-conversion acting as an optical transformer to convert two IR photons to a visible photon and (ii) quantum cutting, which causes the down-conversion of a vacuum UV photon to two visible photons.

Chapter 7 describes various methods of fabrications and characterization of nanomaterials. In addition to the traditional semiconductor processing methods such as molecular beam epitaxy (MBE) and metal–organic chemical vapor deposition (MOCVD), the use of nanochemistry, which utilizes wet chemical synthesis approach, is also described. Some characterization techniques introduced are specific to nanomaterials.

Chapter 8 introduces nanostructured molecular architectures that include a rich class of nanomaterials often unfamiliar to physicists and engineers. These nanostructures involve organic and inorganic–organic hybrid structures. They are stabilized in a three-dimensional architecture by both covalent bonds (chemical) and noncovalent interactions (e.g., hydrogen bond). This topic is presented with a mini-

mum amount of chemical details so that nonchemists are not overburdened. Nanomaterials covered in this chapter are block copolymers, molecular motors, dendrimers, supramolecules, Langmuir–Blogdett films, and self-assembled structures.

Chapter 9 presents the subject of photonic crystals, which is another major thrust of nanophotonics that is receiving a great deal of worldwide attention. Photonic crystals are periodic nanostructures. The chapter covers concepts, methods of fabrication, theoretical methods to calculate their band structure, and applications of photonic crystals. One can easily omit the theory section and still appreciate the novel features of photonic crystals, which are clearly and concisely described.

Chapter 10 covers nanocomposites. A significant emphasis is placed on the nanocomposite materials that incorporate nanodomains of highly dissimilar materials such as inorganic semiconductors or inorganic glasses and plastics. Merits of nanocomposites are discussed together with illustrative examples of applications, such as to energy-efficient broadband solar cells and other optoelectric devices.

Chapter 11 introduces nanolithography, broadly defined, that is used to fabricate nanoscale optical structures. Both optical and nonoptical methods are described, and some illustrative examples of applications are presented. The use of direct two-photon absorption, a nonlinear optical process, provides improved resolution leading to smaller photoproduced nanostructures compared to those produced by linear absorption.

Chapter 12 deals with biomaterials that are emerging as an important class of materials for nanophotonic applications. Bioderived and bioinspired materials are described together with bioassemblies that can be used as templates. Applications discussed are energy-harvesting, low-threshold lasing, and high-density data storage.

Chapter 13 introduces the application of nanophotonics for optical diagnostics, as well as for light-guided and light-activated therapy. Use of nanoparticles for bioimaging and sensing, as well as for targeted drug delivery in the form of nanomedicine, is discussed.

Chapter 14 provides a critical assessment of the current status of nanophotonics in the marketplace. Current applications of near-field microscopy, nanomaterials, quantum-confined lasers, photonic crystals, and nanolithography are analyzed. The chapter concludes with future outlook for nanophotonics.

#### REFERENCES

- Feynman, R. P., There's Plenty of Room at the Bottom, in *Miniaturization*, Horace D. Gilbert, ed., Reinhold, New York, 1961, pp. 282–296.
- NRC Report, Small Wonders, Endless Frontiers—A Review of the National Nanotechnology Initiative, National Academy Press, Washington, D.C., 2002.
- Prasad, P. N., Introduction to Biophotonics, Wiley-Interscience, New York, 2003.
- Shen, Y., Friend, C. S., Jiang, Y., Jakubczyk, D., Swiatkiewicz, J., and Prasad, P. N., Nanophotonics: Interactions, Materials, and Applications, J. Phys. Chem. B 140, 7577–7587 (2000).

### Foundations for Nanophotonics

The basic foundation of nanophotonics involves interaction between light and matter. This interaction is for most systems electronic, that is, it involves changes in the properties of the electrons present in the system. Hence, an important starting point is a parallel discussion of the nature of photons and electrons. Section 2.1 begins with a discussion of the similarities and differences between photons and electrons, including the nature of the propagation and interactions. This section is followed by a description of confinement effects. Photon and electron tunneling through a classically energetically forbidden zone are discussed, drawing similarities between them. Localization of photons and electrons in periodic structures—photonic crystals and electronic semiconductor crystals, respectively—is presented.

Cooperative effects dealing with electron–electron, electron–hole, and photon– photon interactions are described. Examples of photon–photon interactions are nonlinear optical effects. Examples of electron–electron interactions are formation of electron pairs in a superconducting medium. Electron–hole interactions produce excitons and biexcitons.

Section 2.2 discusses optical interactions localized on nanometer scale. Methods of evanescent wave and surface plasmon resonance to produce axial localization of electromagnetic field of light are presented. Lateral (in-plane) localization of light can be achieved by using a near-field geometry.

Section 2.3 provides examples of nanometer scale electronic interactions leading to major modifications or new manifestations in the optical properties. Examples given are of new cooperative transitions, nanoscale electronic energy transfer, and the phenomenon of cooperative emission. Other examples, quantum confinement effects and nanoscopic interaction dynamics, are deferred for Chapters 4 and 6.

Finally, Section 2.4 provides highlights of the chapter.

Some parts of the chapter utilize a more rigorous mathematical approach. The less mathematically inclined readers may skip the mathematical details, because they are not crucial for understanding the remainder of the book.

For further reading the suggested materials are:

Joannopoulos, Meade, and Winn (1995): *Photonic Crystals* Kawata, Ohtsu, and Irie, eds. (2002): *Nano-Optics* Saleh and Teich (1991): *Fundamentals of Photonics* 

#### 2.1 PHOTONS AND ELECTRONS: SIMILARITIES AND DIFFERENCES

In the language of physics, both photons and electrons are elementary particles that simultaneously exhibit particle and wave-type behavior (Born and Wolf, 1998; Feynman et al., 1963). Upon first comparing them, photons and electrons may appear to be quite different as described by classical physics, which defines photons as electromagnetic waves transporting energy and electrons as the fundamental charged particle (lowest mass) of matter. A quantum description, on the other hand, reveals that photons and electrons can be treated analogously and exhibit many similar characteristics. Table 2.1 summarizes some similarities in characteristics of photons and electrons. A detailed description of features listed in the table follows.

When both photons and electrons treated as waves, the wavelength associated with their properties is described, according to the famous de Broglie postulate, by

Table 2.1. Similarities in Characteristics of Photons and Electrons

Photons	Electrons			
Wavelen	Wavelength			
$\lambda = \frac{h}{p} = \frac{c}{\nu}$	$\lambda = \frac{h}{p} = \frac{h}{mv}$			
Eigenvalue (Wav	e) Equation			
$\left\{ \nabla \times \frac{1}{\varepsilon(r)} \nabla \times \right\} \mathbf{B}(r) = \left(\frac{\omega}{c}\right)^2 \mathbf{B}(r)$	$\hat{H}\psi(r) = -\frac{\hbar^2}{2m} (\nabla \cdot \nabla + V(r))\psi(r) = E\psi$			
Free-Space Pro	opagation			
Plane wave $\mathbf{E} = (\frac{1}{2})\mathbf{E}^{\circ}(e^{i\mathbf{k}\cdot\mathbf{r}-\omega t} + e^{-i\mathbf{k}\cdot\mathbf{r}+\omega t})$	Plane wave: $\Psi = c(e^{i\mathbf{k}\cdot\mathbf{r}-\omega t} + e^{-i\mathbf{k}\cdot\mathbf{r}+\omega t})$			
$\mathbf{k}$ = wavevector, a real quantity	$\mathbf{k}$ = wavevector, a real quantity			
Interaction Potentia	al in a Medium			
Dielectric constant (refractive index)	Coulomb interactions			
Propagation Through a Clas	ssically Forbidden Zone			
Photon tunneling (evanescent wave) with wavevector, <b>k</b> , imaginary and hence amplitude decaying exponentially in the forbidden zone	Electron-tunneling with the amplitude (probability) decaying exponentially in the forbidden zone			
Localiza	tion			
Strong scattering derived from large variations in dielectric constant (e.g., in photonic crystals)	Strong scattering derived from a large variation in Coulomb interactions (e.g., in electronic semiconductor crystals)			
<b>Cooperative Effects</b>				
Nonlinear optical interactions	Many-body correlation Superconducting Cooper pairs Biexciton formation			

the same relation  $\lambda = h/p$ , where *p* is the particle momentum (Atkins and dePaula, 2002). One difference between them is on the length scale: The wavelengths associated with electrons are usually considerably shorter than those of photons. Under most circumstances the electrons will be characterized by relatively larger values of momentum (derived from orders of magnitude larger rest mass of an electron than the relativistic mass of a photon given by  $m = hv/c^2$ ) than photons of similar energies. This is why electron microscopy (in which the electron energy and momentum are controlled by the value of the accelerating high voltage) provides a significantly improved resolution over optical (photon) microscopy, since the ultimate resolution of a microscope is diffraction-limited to the size of the wavelength. The values of momentum, which may be ascribed to electrons bound in atoms or molecules or the conduction electrons propagating in a solid, are also relatively high compared to those of photons, thus the characteristic lengths are shorter than wavelengths of light. An important consequence derived from this feature is that "size" or "confinement" effects for photons take place at larger size scales than those for electrons.

The propagation of photons as waves is described in form of an electromagnetic disturbance in a medium, which involves an electric field **E** (corresponding displacement **D**) and an orthogonal magnetic field **H** (corresponding displacement **B**), both being perpendicular to the direction of propagation in a free space (Born and Wolf, 1998). A set of Maxwell's equations describes these electric and magnetic fields. For any dielectric medium, the propagation of an electromagnetic wave of angular frequency  $\omega$  is described by an eigenvalue equation shown in Table 2.1. An eigenvalue equation describes a mathematical operation  $\hat{\mathbf{O}}$  on a function **F** as

$$\hat{\mathbf{O}}\mathbf{F} = C\mathbf{F} \tag{2.1}$$

to yield a product of a constant *C*, called eigenvalue, and the same function. Functions fulfilling the above condition are called eigenfunctions of the operator  $\hat{\mathbf{O}}$ . In the eigenvalue equation in Table 2.1,  $\varepsilon(r)$  is the dielectric constant of the medium at the frequency  $\omega$  of the electromagnetic wave, which, in the optical region, is equal to  $n^2(\omega)$ , where *n* is the refractive index of the medium at angular frequency  $\omega$ . The dielectric constant, and thereby the refractive index, describes the resistance of a medium to the propagation of an electromagnetic wave through it. Therefore, light propagation speed *c* in a medium is reduced from light propagation speed  $c_0$  in vacuum by the relation

$$c = \frac{c_0}{n} = \frac{c_0}{\varepsilon^{1/2}}$$
(2.2)

The eigenvalue equation in Table 2.1 involves the magnetic displacement vector, **B**. Since the electric field **E** and the magnetic displacement **B** are related by the Maxwell's equations, an equivalent equation can be written in terms of **E**. However, this equation is often solved using **B**, because of its more suitable mathematical character. (The operator for **B** has a desirable character called Hermitian). The eigenvalue *C* in the equations for photon is  $(\omega/c)^2$ , which gives a set of allowed frequencies  $\omega$  (thus energies) of photons in a medium of dielectric constant  $\varepsilon(r)$  and thus refractive index n(r). The dielectric constant may be either constant throughout the medium or dependent on spatial location **r** and the wavevector **k**.

The corresponding wave equation for electrons is the Schrödinger equation, and its time-independent form is often written in the form of an eigenvalue equation shown in Table 2.1 (Levine, 2000; Merzbacher, 1998). Here  $\hat{H}$ , called the *Hamiltonian operator*, consists of the sum of operator forms of the kinetic and the potential energies of an electron and is thus given as

$$\hat{H} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(\mathbf{r}) = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r})$$
(2.3)

The first term (all in the parentheses) is derived from the kinetic energy; the second term,  $V(\mathbf{r})$ , is derived from the potential energy of the electron due to its interaction (Coulomb) with the surrounding medium.

The solution of the Schrödinger equation provides the allowed energy states, eigenvalues *E* of energy, of the electron, while wavefunction  $\psi$  yields a probabilistic description of the electron. The square of this function,  $|\psi(\mathbf{r})|^2$ , describes the probability density for the electron at a position  $\mathbf{r}$ . Thus, the wavefunction  $\psi$  for an electron can be considered an amplitude of the electron wave, the counterpart of the electric field  $\mathbf{E}$  for an electromagnetic wave.

The analogue of the interaction potential for electromagnetic wave propagation in a medium is the spatial variation of the dielectric constant (or refractive index). This variation causes a modification of the propagation characteristics as well as, in some cases, a modification of the allowed energy values for photons. The interaction potential V of Eq. (2.3) describes the Coulomb interactions (such as electrostatic attraction between an electron and a nucleus). This interaction modifies the nature of the electronic wavefunction (thus the probability distribution) as well as the allowed set of energy values E (eigenvalues) obtained by the solution of the Schrödinger equation listed in Table 2.1. Some examples of these wave propagation properties for photons and electrons under different interaction potentials are discussed below.

Despite the similarities described above, electrons and photons also have important differences. The electrons generate a scalar field while the photons are vector fields (light is polarized). Electrons possess spin, and thus their distribution is described by Fermi–Dirac statistics. For this reason, they are also called *fermions*. Photons have no spin, and their distribution is described by Bose–Einstein statistics. For this reason, photons are called *bosons*. Finally, since electrons bear a charge while the charge of photons is zero, there are principal differences in their interactions with external static electric and magnetic fields.

#### 2.1.1 Free-Space Propagation

In a "free-space" propagation, there is no interaction potential or it is constant in space. For photons, it simply implies that no spatial variation of refractive index n