



edited by
Christian von Borczyskowski
Eduard Zenkevich

Tuning Semiconducting and Metallic Quantum Dots

Spectroscopy and Dynamics





Tuning Semiconducting and Metallic Quantum Dots

Tuning Semiconducting and Metallic Quantum Dots

Spectroscopy and Dynamics

edited by

Christian von Borczyskowski

Eduard Zenkevich

PAN STANFORD  PUBLISHING

Published by

Pan Stanford Publishing Pte. Ltd.
Penthouse Level, Suntec Tower 3
8 Temasek Boulevard
Singapore 038988

Email: editorial@panstanford.com

Web: www.panstanford.com

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

**Tuning Semiconducting and Metallic Quantum Dots:
Spectroscopy and Dynamics**

Copyright © 2017 by Pan Stanford Publishing Pte. Ltd.

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the publisher.

For photocopying of material in this volume, please pay a copying fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. In this case permission to photocopy is not required from the publisher.

ISBN 978-981-4745-24-6 (Hardcover)

ISBN 978-981-4745-25-3 (eBook)

Printed in the USA

For Sabine and Tamara

Contents

<i>Preface</i>	xiii
<i>Acknowledgments</i>	xvii
1. Size Matters: Optical Properties of Nanoparticles	1
<i>Christian von Borczyskowski and Eduard Zenkevich</i>	
1.1 Introduction	1
1.2 Quantum Confinement	3
1.2.1 Basic Concepts	3
1.2.2 Wavefunction Tunneling	7
1.2.3 Density Functional Theory	10
1.3 Optical Transitions	13
1.3.1 Assignment of Optical Transitions	13
1.3.2 Relaxation of Excited Quantum Dots	14
1.3.3 Surface and Trap States	15
1.3.4 Multiexcitons and Charged Quantum Dots	17
1.4 Synthesis, Crystal Structure, and Ligands	21
1.5 Metal Nanoparticles	24
1.5.1 Plasmonic Nanoparticles	25
1.5.2 Metal Clusters	28
1.6 Conclusion	32
2. New Insights: Photophysics of CdSe Quantum Dots (Temperature-Related Approach)	41
<i>Eduard Zenkevich, Alexandre Stupak, and Christian von Borczyskowski</i>	
2.1 Introduction	42
2.2 Experiments	44
2.3 Results	45
2.3.1 Absorption Spectra	46
2.3.2 Photoluminescence Properties	50
2.3.2.1 Photoluminescence spectra	50
2.3.2.2 Time-resolved photoluminescence	53

	2.3.2.3	Photoluminescence excitation spectra	58
	2.3.3	Summary of Experimental Findings	61
2.4		Discussion	62
	2.4.1	Temperature-Dependent Stokes Shift and Fine Structure	67
	2.4.2	Temperature Dependence of Spectral Properties	71
	2.4.2.1	Spectral width and oscillator strength	71
	2.4.2.2	Absorption and photoluminescence energies	75
	2.4.3	Ligand-Induced Phase Transition	76
	2.4.4	Correlation of Kinetics and Spectra of CdSe/ZnS Photoluminescence	78
	2.4.5	Near-Band-Edge and Deep-Level Trap States	83
2.5		Conclusion	90
3. Temperature-Dependent Exciton–Phonon Coupling in Quantum Dots			103
<i>Eduard Zenkevich, Alexandre Stupak, and Christian von Borczyskowski</i>			
3.1		Introduction	103
3.2		Results	107
	3.2.1	Temperature-Dependent Optical Absorption	107
	3.2.2	Temperature-Dependent Photoluminescence	110
3.3		Discussion	115
	3.3.1	Temperature Dependence of Absorption Properties	116
	3.3.2	Temperature Dependence of Photoluminescence Energy and FWHM	122
	3.3.3	Temperature-Dependent Photoluminescence Intensities	126
3.4		Temperature Dependence of Stokes Shifts	129
3.5		Exciton–Phonon Coupling in AM-Type QDs	132
3.6		Conclusion	135

4. Optical Detection of Single Quantum Dots	143
<i>Christian von Borczyskowski</i>	
4.1 Introduction	143
4.2 Single Quantum Object Detection: From Holes to Dots	145
4.2.1 Spectral Line Width	146
4.2.2 Optical Sensitivity	150
4.2.3 Specific Nature of Single Quantum Objects	151
4.2.3.1 Photon bunching	151
4.2.3.2 Photon correlation	153
4.2.3.3 Photon antibunching	153
4.2.3.4 Ergodicity	154
4.3 Experimental Concepts	155
4.3.1 Wide-Field Microscopy	158
4.3.2 Confocal Microscopy	160
4.3.3 Data Analysis	162
4.4 Optical Features of Single Quantum Dots	166
4.4.1 Luminescence Intermittency	166
4.4.1.1 Threshold-based analysis	169
4.4.1.2 Change point analysis	175
4.4.1.3 Autocorrelation analysis	180
4.4.1.4 Photoluminescence intensity-lifetime correlation	180
4.4.1.5 Correlation of photoluminescence energy with blinking and photoluminescence decay times	185
4.4.1.6 Suppression of blinking	187
4.4.1.7 Blinking models	187
4.4.2 Spectral Diffusion	215
4.5 Quantum Dot Nanoprobes	220
4.5.1 Influence of Substrates and Interfaces	222
4.5.2 Influence of Dielectric Properties	226
4.6 Influence of External Fields	229
4.6.1 Electric Fields	230
4.6.1.1 Stark effect	230

4.6.1.2	Charging of QDs and electric field-related blinking phenomena	231
4.6.2	Magnetic Fields	240
4.7	Conclusion	240
5.	Optical Spectroscopy of Single Ag Nanoclusters	259
	<i>Stefan Krause</i>	
5.1	Introduction	260
5.2	Single Ag Nanoclusters from Ag ₂ O Films	261
5.3	Colloidal Silver Particles	263
5.4	Dendrimer and DNA-Encapsulated Ag Nanoclusters	265
5.5	Ag Nanoclusters from Zeolite Y Cages	272
5.6	Conclusion	277
6.	Tuning Luminescence Intermittency	283
	<i>Ines Trenkmann, Clemens Göhler, Cornelius Krasselt, and Christian von Borczyskowski</i>	
6.1	Introduction	283
6.2	Identification of Different Types of Blinking	284
6.2.1	Blinking Analysis	284
6.2.1.1	Truncated power-law blinking of CdSe/ZnS	284
6.2.1.2	Anomalous power-law blinking of CdSe/ZnS	293
6.2.1.3	Interrelation of photoluminescence decay time blinking and intensity blinking	299
6.2.1.4	Assignment of three types of intensity blinking	310
6.2.2	Correlation of Intensity Blinking and Energy Jumps of Emitting States	313
6.2.3	Modeling Photoluminescence Intensity and Lifetime Blinking	330
6.3	Excitation Intensity and Energy-Dependent Blinking	340

6.3.1	Influence of Excitation Intensity	340
6.3.2	Influence of Excitation Energy	349
6.3.3	Excitation-Dependent Blinking Model	351
6.4	Influence of Substrate Surfaces and Ligands on Blinking	354
6.4.1	Influence of Substrate Modifications on Blinking	354
6.4.2	Impact of Ligands on Blinking	358
6.5	Conclusion	366
	<i>Index</i>	377

Preface

During the last few decades, nanomaterials have become an intensively growing field of interest, with respect to both applications and fundamental science. These materials, especially from semiconductors and metals, are equally important for applications such as nanoelectronics, sensoric applications, and life sciences. Nowadays, this field can be characterized by several material classes, including the related preparation or manufacturing processes. According to the widely varying features of these materials, scientific approaches in analyzing, understanding, and modeling are inherently interdisciplinary and cover a still growing range of physical, chemical, and biological disciplines. Common to many of these materials is the fact that their properties depend on the dimensions in the nanometer range: size matters! According to the extremely small size, a large surface-to-volume ratio is an inherent property of all these materials. This opens access to both surface and core features. However, this perspective is not merely a linear superposition of the respective properties but constitutes completely new ones. Naturally, interfaces play a central role. Though this is a central aspect of nanomaterials, a detailed understanding and control of inherent properties of surfaces and interfaces, such as structure–function relationships, has to be investigated with respect to the specific class or even subclass of nanomaterials.

Moreover, in an analogy to quantum well structures, dimensions can be further downsized to quantum dots from semiconductors or metals. At a critical dimension, bulk properties (such as optical ones) deviate from those of the bulk and become size dependent. This results in considerably changed features intermediate between both the original solid and its constituting atoms (or molecules). In this respect (optical) properties can be tuned by the dimension of the (nano)material.

In this book, we will concentrate on the optical properties of colloidal semiconductor quantum dots and to some extent also those of metal particles. Since there is already a considerable number of publications reviewing the size dependence of optical properties

of such nanomaterials, we prefer to concentrate on interfaces or surfaces and the perspectives of tuning of the related electronic energies and dynamics.

The experimental approach is based on static and dynamic optical spectroscopy, both on ensembles of quantum dots and on single ones. The latter approach is extremely sensitive and opens a wide field for detailed understanding and sensoric applications in material and life sciences. This has been recently acknowledged by the 2014 Nobel Prize in Chemistry awarded to E. Betzig, S. Hell, and W. E. Moerner for the invention and implementation of super-resolution optical microscopy.

Experimental reports in this book, some of them even unpublished, are based on results obtained in our groups during the last 10 years and especially include luminescence intermittency (blinking dynamics) in single quantum dots. The latter is a fascinating phenomenon, often observed but far from being understood at a microscopic level.

The book is organized in the following way: We have virtually divided it into two parts: “Electronic States of Quantum Dots” (Chapters 1–3) and “Single Quantum Dots” (Chapters 4–6). Each part starts with an introductory chapter followed by several case studies in separate chapters. The introductory parts summarize relevant basic aspects of the related subjects and are to a certain extent a kind of review without being exhaustive in the respect. Correspondingly, the bibliography at the end of each chapter contains some leading papers, recent reviews, and books in which the readers may find some additional specific references relevant to their subjects of interest.

In “Electronic States of Quantum Dots,” we report on several not yet reported spectroscopic features of CdSe excitons or trap states and related temperature-dependent exciton–phonon coupling. Both subjects pay special attention to the influence of the heterogeneous interfaces, including organic ligands on colloidal quantum dots.

The chapters in “Single Quantum Dots,” besides a basic introduction to the related optical properties and detection schemes, concentrate on a review of experiments on single metal (Ag) nanoclusters. The central part is the tuning of photoluminescence intermittency (blinking) and spectral diffusion of CdSe quantum dots with special emphasis on interface-related effects. We present a new model for blinking processes.

Altogether, we aim with this book for a thorough understanding of subtle effects of interfaces and surfaces, which noticeably tune optical properties with respect to both optical energies and (interfacial) dynamics. We feel that we contribute to a deeper understanding of these to a large extent heterogeneous nanostructures. We make as often as possible use of a combination of experiments on ensemble and single nanostructures, an approach which has so far not been intensively used in literature. In the end our contributions might in the case of blinking processes be useful for either suppressing such effects for highly sensitive sensoric applications or even controlling blinking for applications in stochastically based super-resolution microscopy.

Christian von Borczyskowski

Chemnitz, Germany

Eduard Zenkevich

Minsk, Belarus

September 2016

Acknowledgments

All results from our groups in Chemnitz and Minsk have been obtained by graduate students, PhD students, and postdocs. We appreciate all the work which they have contributed to the development of this field during the last 10 years.

The book contains many results which have not yet been published: Ines Trenkmann (parts of Chapter 6), Cornelius Krasselt and Clemens Göhler (parts of Chapters 4 and 6), and Stefan Krause (parts of Chapter 5).

Writing a book like this would not have been possible without many fruitful discussions and help in writing and layout. Especially, we would like to mention Danny Kowerko (experimental part of Chapter 4), Frank Cichos and Michel Orrit (modified version of blinking models in Chapter 4), and Clemens Göhler, Thomas Blaudeck, and Cornelius Krasselt for figure preparations. Stefan Krause prepared the graph of Ag nanoparticles on the cover page, which is gratefully acknowledged.

We would also like to acknowledge and appreciate financial support throughout the years from various institutions: (i) Belarussian State Program for Scientific Research “Convergence 3.2.08: Photophysics of Bioconjugates, Semiconductor and Metallic Nanostructures and Supramolecular Complexes and Their Biomedical Applications” (Chapters 2 and 3); (ii) INTAS Project 03-50-4540, “Optical Active Assemblies of Colloid Quantum Dots and Tetrapyrrole Compounds: Laser Induced Relaxation Processes and Opto-Electronic Functionalities” (Chapters 2 and 3); (iii) DAAD Grant No A/08/08573, “Single Particle Spectroscopy of Individual Nanoobjects Fixed on Heterogeneous Surfaces” (Chapters 1, 2, and 3); (iv) DFG Project GR 2695/8-1, “Optical Probe for Semiconductor Nanoparticles” (Chapters 4 and 6); (v) DFG Research Unit FOR 388, “Laboratory Astrophysics” (Chapter 4); (vi) DFG Graduate College GRK 82, “Accumulation of Single Molecules to Nanostructures (Accumol)” (Chapters 4 and 6); and (vii) DFG Research Unit FOR

877, “From Local Constraints to Macroscopic Transport” (Chapters 1, 2, and 3).

Quantum dot spectroscopy is based on for over more than 25 years on a stimulating and fruitful cooperation between research groups from Minsk (Zenkevich) and Chemnitz (von Borczyskowski). The scientific and personal exchange was strongly supported over these years by the Volkswagen-Foundation, INTAS, DAAD, and especially within the framework of the DFG Research Unit FOR 877.