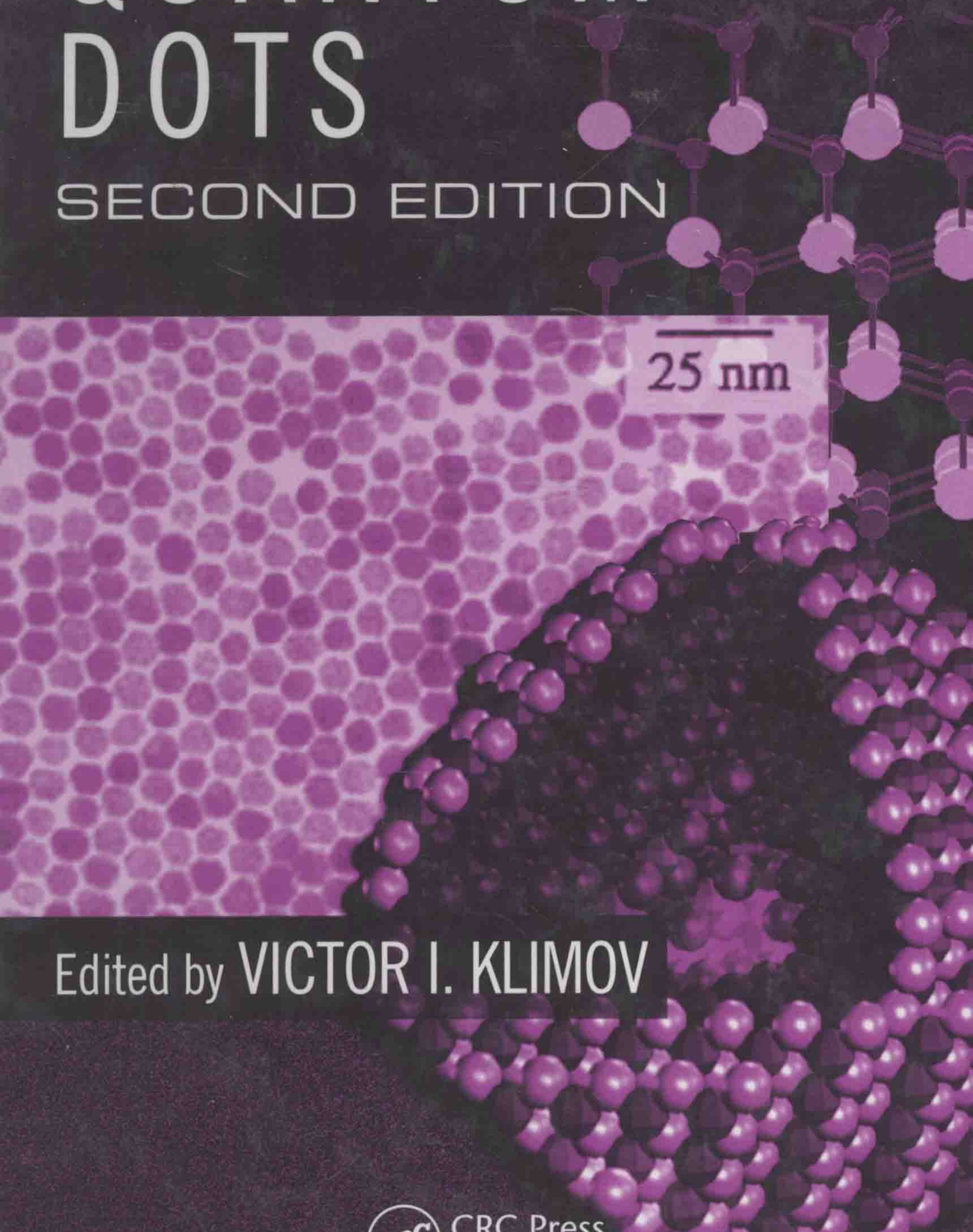
NANOCRYSTAL QUANTUM DOTS

SECOND EDITION



Edited by VICTOR I. KLIMOV

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SECOND EDITION

Preface to the Second Edition

This book is the second edition of *Semiconductor and Metal Nanocrystals: Synthesis and Electronic and Optical Properties*, originally published in 2003. Based on the decision of the book contributors to focus this new edition on semiconductor nanocrystals, the three last chapters of the first edition on metal nanoparticles have been removed from this new edition. This change is reflected in the new title, which reads *Nanocrystal Quantum Dots*. The material on semiconductor nanocrystals has been expanded by including two new chapters that cover the additional topics of biological applications of nanocrystals (Chapter 10) and nanocrystal doping with magnetic impurities (Chapter 11). Further, some of the chapters have been revised to reflect the most recent progress in their respective fields of study.

Specifically, Chapter 1 was updated by Jennifer A. Hollingsworth to include recent insights regarding the underlying mechanisms supporting colloidal nanocrystal growth. Also discussed are new methods for multishell growth, the use of carefully constructed inorganic shells to suppress "blinking," novel core/shell architectures for controlling electronic structure, and new approaches for achieving unprecedented control over nanocrystal shape and self-assembly.

The original version of Chapter 5 focused on processes relevant to lasing applications of colloidal quantum dots. For this new edition, I revised this chapter to provide a more general overview of multiexciton phenomena including spectral and dynamical signatures of multiexcitons in transient absorption and photoluminescence, and nanocrystal-specific features of multiexciton recombination. The revised chapter also reviews the status of the new and still highly controversial field of carrier multiplication. Carrier multiplication is the process in which absorption of a single photon produces multiple excitons. First reported for nanocrystals in 2004 (i.e., after publication of the first edition of this book), this phenomenon has become a subject of much recent experimental and theoretical research as well as intense debates in the literature.

Chapter 7 has also gone through significant revisions. Specifically, Neil C. Greenham expanded the theory section to cover the regime of high charge densities. He also changed the focus of the remainder of the review to more recent work that appeared in the literature after the publication of the first edition.

Chapter 9 was originally written by Arthur J. Nozik and Olga I. Mićić. Unfortunately, Olga passed away in May of 2006, which was a tremendous loss for the whole nanocrystal community. Olga's deep technical insight and continuing contributions to nanocrystal science will be greatly missed, but most importantly, Olga will be missed for her genuineness of heart, her warmth and her strength, and as a selfless mentor for young scientists. The revisions to Chapter 9 were handled by Arthur J. Nozik. He included, in the updated chapter, new results on quantum dots of lead chalcogenides with a focus on his group's studies of carrier multiplication. Nozik also incorporated the most recent results on Schottky junction solar cells based on films of PbSe nanocrystals.

The focus of the newly added Chapter 10, by Hedi Mattoussi, provides an overview of the progress made in biological applications of colloidal nanocrystals. It discusses available techniques for the preparation of biocompatible quantum dots and compares their advantages and limitations. It also describes a few representative examples illustrating applications of nanocrystals in biological labeling, imaging, and diagnostics.

The new Chapter 11, by Rémi Beaulac, Stefan T. Ochsenbein, and Daniel R. Gamelin, summarizes recent developments in the synthesis and understanding of magnetically doped semiconductor nanocrystals, with emphasis on Mn^{2+} and Co^{2+} dopants. It starts with a brief general description of the electronic structures of these two ions in various II-VI semiconductor lattices. Then it provides a detailed discussion of issues related to the synthesis, magneto-optics, and photoluminescence of doped colloidal nanocrystals.

I would like to express again my gratitude to all my colleagues who agreed to participate in this book project. My special thanks to the new contributors to this second edition as well as to the original authors who were able to find time to update their chapters.

Victor I. Klimov
Los Alamos, New Mexico

Preface to the First Edition

This book consists of a collection of review Chapters that summarize the recent progress in the areas of metal and semiconductor nanosized crystals (nanocrystals). The interest in the optical properties of nanoparticles dates back to Faraday's experiments on nanoscale gold. In these experiments, Faraday noticed the remarkable dependence of the color of gold particles on their size. The size dependence of the optical spectra of semiconductor nanocrystals was first discovered much later (in the 1980s) by Ekimov and co-workers in experiments on semiconductor-doped glasses. Nanoscale particles (islands) of semiconductors and metals can be fabricated by a variety of means, including epitaxial techniques, sputtering, ion implantation, precipitation in molten glasses, and chemical synthesis. This book concentrates on nanocrystals fabricated via chemical methods. Using colloidal chemical syntheses, nanocrystals can be prepared with nearly atomic precision having sizes from tens to hundreds of Ångstroms and size dispersions as narrow as 5%. The level of chemical manipulation of colloidal nanocrystals is approaching that for standard molecules. Using suitable surface derivatization, colloidal nanoparticles can be coupled to each other or can be incorporated into different types of inorganic or organic matrices. They can also be assembled into close-packed ordered and disordered arrays that mimic naturally occurring solids. Because of their small dimensions, size-controlled electronic properties, and chemical flexibility, nanocrystals can be viewed as tunable "artificial" atoms with properties that can be engineered to suit either a particular technological application or the needs of a certain experiment designed to address a specific research problem. The large technological potential of these materials, as well as new appealing physics, have led to an explosion in nanocrystal research over the past several years.

This book covers several topics of recent, intense interest in the area of nanocrystals: synthesis and assembly, theory, spectroscopy of interband and intraband optical transitions, single-nanocrystal optical and tunneling spectroscopy, transport properties, and nanocrystal applications. It is written by experts who have contributed pioneering research in the nanocrystal field and whose work has led to numerous, impressive advances in this area over the past several years.

This book is organized into two parts: semiconductor nanocrystals (nanocrystal quantum dots) and metal nanocrystals. The first part begins with a review of progress in the synthesis and manipulation of colloidal semiconductor nanoparticles. The topics covered in this first chapter by J. A. Hollingsworth and V. I. Klimov include size and shape control, surface modification, doping, phase control, and assembly of nanocrystals of such compositions as CdSe, CdS, PbSe, HgTe, etc. The second Chapter, by D. J. Norris, overviews results of spectroscopic studies of the interband (valence-to-conduction band) transitions in semiconductor nanoparticles with a focus on CdSe nanocrystals. Because of a highly developed fabrication technology, these nanocrystals have long been model systems for studies on the effects of three-dimensional quantum confinement in semiconductors. As described in this

Chapter, the analysis of absorption and emission spectra of CdSe nanocrystals led to the discovery of a "dark" exciton, a fine structure of band-edge optical transitions, and the size-dependent mixing of valence band states. This topic of electronic structures and optical transitions in CdSe nanocrystals is continued in Chapter 3 by Al. L. Efros. This chapter focuses on the theoretical description of electronic states in CdSe nanoparticles using the effective mass approach. Specifically, it reviews the "dark/bright" exciton model and its application for explaining the fine structure of resonantly excited photoluminescence, polarization properties of spherical and ellipsoidal nanocrystals, polarization memory effects, and magneto-optical properties of nanocrystals. Chapter 4, by P. Guyot-Sionnest, M. Shim, and C. Wang, reviews studies of intraband optical transitions in nanocrystals performed using methods of infrared spectroscopy. It describes the size-dependent structure and dynamics of these transitions as well as the control of intraband absorption using charge carrier injection. In Chapter 5, V. I. Klimov concentrates on the underlying physics of optical amplification and lasing in semiconductor nanocrystals. The Chapter provides a description of the concept of optical amplification in "ultra-small," sub-10 nanometer particles, discusses the difficulties associated with achieving the optical gain regime, and gives several examples of recently demonstrated lasing devices based on CdSe nanocrystals. Chapter 6, by K. T. Shimizu and M. G. Bawendi, overviews the results of single-nanocrystal (single-dot) emission studies with a focus on CdSe nanoparticles. It discusses such phenomena as spectral diffusion and fluorescence intermittency ("blinking"). The studies of these effects provide important insights into the dynamics of charge carriers in a single nanoparticle and the interactions between the nanocrystal internal and interface states. The focus in Chapter 7, written by D. S. Ginger and N. C. Greenham, switches from spectroscopic to electrical and transport properties of semiconductor nanocrystals. This Chapter overviews studies of carrier injection into nanocrystals and carrier transport in nanocrystal assemblies and between nanocrystals and organic molecules. It also describes the potential applications of these phenomena in electronic and optoelectronic devices. In Chapter 8, U. Banin and O. Millo review the work on tunneling and optical spectroscopy of colloidal InAs nanocrystals. Single electron tunneling experiments discussed in this Chapter provide unique information on electronic states and the spatial distribution of electronic wave functions in a single nanoparticle. These data are further compared with results of more traditional optical spectroscopic studies. A. J. Nozik and O. Micic provide a comprehensive overview of the synthesis, structural, and optical properties of semiconductor nanocrystals of III-V compounds (InP, GaP, GaInP2, GaAs, and GaN) in Chapter 9. This Chapter discusses such unique properties of nanocrystals and nanocrystal assemblies as efficient anti-Stokes photoluminescence, photoluminescence intermittency, anomalies between the absorption and the photoluminescence excitation spectra, and long-range energy transfer. Furthermore, it reviews results on photogenerated carrier dynamics in nanocrystals, including the issues and controversies related to the cooling of hot carriers in "ultra-small" nanoparticles. Finally, it discusses the potential applications of nanocrystals in novel photon conversion devices, such as quantum-dot solar cells and photoelectrochemical systems for fuel production and photocatalysis.

The next three chapters, which comprise Part 2 of this book, examine topics dealing with the chemistry and physics of metal nanoparticles. In Chapter 10, R. C. Doty, M. Sigman, C. Stowell, P. S. Shah, A. Saunders, and B. A. Korgel describe methods for fabricating metal nanocrystals and manipulating them into extended arrays (superlattices). They also discuss microstructural characterization and some physical properties of these metal nanoassemblies, such as electron transport. Chapter 11, by S. Link and M. A. El-Sayed, reviews the size/shape-dependent optical properties of gold nanoparticles with a focus on the physics of the surface plasmons that leads to these interesting properties. In this Chapter, the issues of plasmon relaxation and nanoparticle shape transformation induced by intense laser illumination are also discussed. A review of some recent studies on the ultrafast spectroscopy of mono- and bi-component metal nanocrystals is presented in Chapter 12 by G. V. Hartland. These studies provide important information on time scales and mechanisms for electron-phonon coupling in nanoscale metal particles.

Of course, the collection of Chapters that comprises this book cannot encompass all areas in the rapidly evolving science of nanocrystals. As a result, some exciting topics were not covered here, including silicon-based nanostructures, magnetic nanocrystals, and nanocrystals in biology. Canham's discovery of efficient light emission from porous silicon in 1990 has generated a widespread research effort on silicon nanostructures (including that on silicon nanocrystals). This effort represents a very large field that could not be comprehensively reviewed within the scope of this book. The same reasoning applies to magnetic nanostructures and, specifically, to magnetic nanocrystals. This area has been strongly stimulated by the needs of the magnetic storage industry. It has grown tremendously over the past several years and probably warrants a separate book project. The connection of nanocrystals to biology is relatively new. However, it already shows great promise. Semiconductor and metal nanoparticles have been successfully applied to tagging bio-molecules. On the other hand, bio-templates have been used for assembly of nanoparticles into complex, multi-scale structures. Along these lines, a very interesting topic is bio-inspired assemblies of nanoparticles that efficiently mimic various bio-functions (e.g., light harvesting and photosynthesis). "Nanocrystals in Biology" may represent a fascinating topic for some future review by a group of experts in biology, chemistry, and physics.

I would like to thank all contributors to this book for finding time in their busy schedules to put together their review Chapters. I gratefully acknowledge M. A. Petruska and J. A. Hollingsworth for help in editing this book. I would like to thank my wife, Tatiana, for her patience, tireless support, and encouragement during my research career and specifically during the work on this book.

Victor I. Klimov
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Editor

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Dr. Klimov received his MS (1978), PhD (1981), and DSc (1993) degrees from Moscow State University. He is a fellow of the American Physical Society, a fellow of the Optical Society of America, and a former fellow of the Alexander von Humboldt Foundation. Klimov's research interests include the photophysics of semiconductor and metal nanocrystals, femtosecond spectroscopy, and near-field microscopy.

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Contents

1

"Soft" Chemical Synthesis and Manipulation of Semiconductor Nanocrystals

Jennifer A. Hollingsworth and Victor I. Klimov

CONTENTS

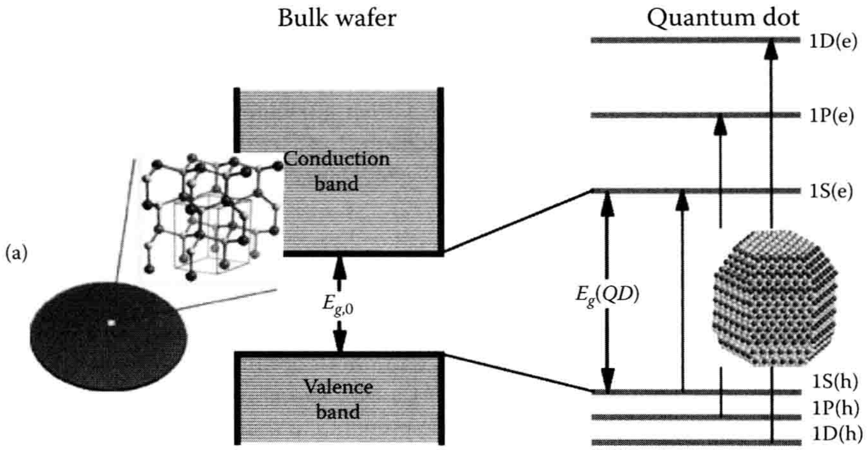
1.1 INTRODUCTION

An important parameter of a semiconductor material is the width of the energy gap that separates the conduction from the valence energy bands (Figure 1.1a, left). In semiconductors of macroscopic sizes, the width of this gap is a fixed parameter, which is determined by the material's identity. However, the situation changes in the case of nanoscale semiconductor particles with sizes less than ~10 nm (Figure 1.1a, right). This size range corresponds to the regime of quantum confinement for which electronic excitations "feel" the presence of the particle boundaries and respond to changes in the particle size by adjusting their energy spectra. This phenomenon is known as the *quantum size effect*, whereas nanoscale particles that exhibit it are often referred to as quantum dots (QDs).

As the QD size decreases, the energy gap increases, leading, in particular, to a blue shift of the emission wavelength. In the first approximation, this effect can be described using a simple "quantum box" model. For a spherical QD with radius R, this model predicts that the size-dependent contribution to the energy gap is simply proportional to $1/R^2$ (Figure 1.1b). In addition to increasing energy gap, quantum confinement leads to a collapse of the continuous energy bands of the bulk material into discrete, "atomic" energy levels. These well-separated QD states can be labeled using atomic-like notations (1S, 1P, 1D, etc.), as illustrated in Figure 1.1a. The discrete structure of energy states leads to the discrete absorption spectrum of QDs (schematically shown by vertical bars in Figure 1.1c), which is in contrast to the continuous absorption spectrum of a bulk semiconductor (Figure 1.1c).

Semiconductor QDs bridge the gap between cluster molecules and bulk materials. The boundaries between molecular, QD, and bulk regimes are not well defined and are strongly material dependent. However, a range from ~100 to ~10,000 atoms per particle can been considered as a crude estimate of sizes for which the nanocrystal regime occurs. The lower limit of this range is determined by the stability of the bulk crystalline structure with respect to isomerization into molecular structures. The upper limit corresponds to sizes for which the energy level spacing is approaching the thermal energy kT, meaning that carriers become mobile inside the QD.

Semiconductor QDs have been prepared by a variety of "physical" and "chemical" methods. Some examples of physical processes, characterized by high energy input, include molecular-beam-epitaxy (MBE) and metalorganic-chemical-vapor-deposition (MOCVD) approaches to QDs,[1,2,3] and vapor-liquid-solid (VLS) approaches to quantum wires.[4,5] High-temperature methods have also been applied to chemical routes, including particle growth in glasses.[6,7] Here, however, the emphasis is on "soft" (low-energy-input) colloidal chemical synthesis of crystalline semiconductor nanoparticles that will be referred to as nanocrystal quantum dots (NQDs). NQDs comprise an inorganic core overcoated with a layer of organic ligand molecules. The organic capping provides electronic and chemical passivation of surface dangling bonds, prevents uncontrolled growth and agglomeration of the nanoparticles, and allows NQDs to be chemically manipulated like large



(b)

$$E_g(QD) \approx E_{g,0} + \frac{\hbar^2\pi^2}{2m_{eh}R^2}$$

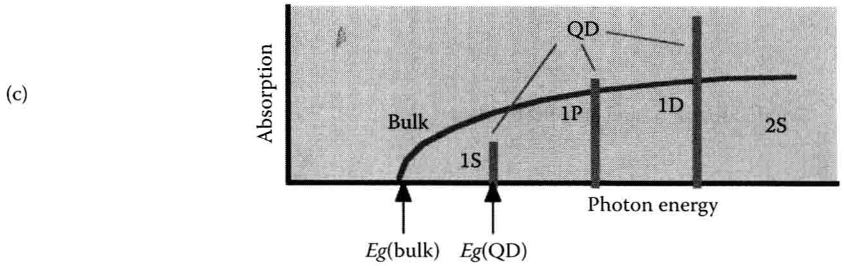


FIGURE 1.1 (a) A bulk semiconductor has continuous conduction and valence energy bands separated by a fixed energy gap, $E_{g,0}$ (left), while a QD is characterized by discrete atomic-like states with energies that are determined by the QD radius R (right). (b) The expression for the size-dependent separation between the lowest electron [1S(e)] and hole [1S(h)] QD states (QD energy gap) obtained using the "quantum box" model [$m_{eh} = m_e m_h/(m_e + m_h)$, where m_e and m_h are effective masses of electrons and holes, respectively]. (c) A schematic representation of the continuous absorption spectrum of a bulk semiconductor (curved line), compared to the discrete absorption spectrum of a QD (vertical bars).

molecules with solubility and reactivity determined by the identity of the surface ligand. In contrast to substrate-bound epitaxial QDs, NQDs are "freestanding." This discussion concentrates on the most successful synthesis methods, where success is determined by high crystallinity, adequate surface passivation, solubility in nonpolar or polar solvents, and good size monodispersity. Size monodispersity permits the study and, ultimately, the use of materials-size-effects to define novel materials properties. Monodispersity in terms of colloidal nanoparticles (1–15 nm size range) requires a sample standard deviation of $\sigma \leq 5\%$, which corresponds to ± one lattice constant.[8] Although colloidal monodispersity in this strict sense is increasingly common, preparations are also included in this chapter that achieve approximately $\sigma \leq 20\%$, in particular where other attributes, such as novel compositions or shape control, are relevant. In addition, "soft" approaches to NQD chemical and structural modification as well as to NQD assembly into artificial solids or artificial molecules are discussed.

1.2 COLLOIDAL NANOSYNTHESIS

The most successful NQD preparations in terms of quality and monodispersity entail pyrolysis of metal-organic precursors in hot coordinating solvents (120°C–360°C). Generally understood in terms of La Mer and Dinegar's studies of colloidal particle nucleation and growth,[8,9] these preparative routes involve a temporally discrete nucleation event followed by relatively rapid growth from solution-phase monomers and finally slower growth by Ostwald ripening (referred to as recrystallization or aging) (Figure 1.2). Nucleation is achieved by quick injection of precursor into the hot coordinating solvents, resulting in thermal decomposition of the precursor reagents and supersaturation of the formed "monomers" that is partially

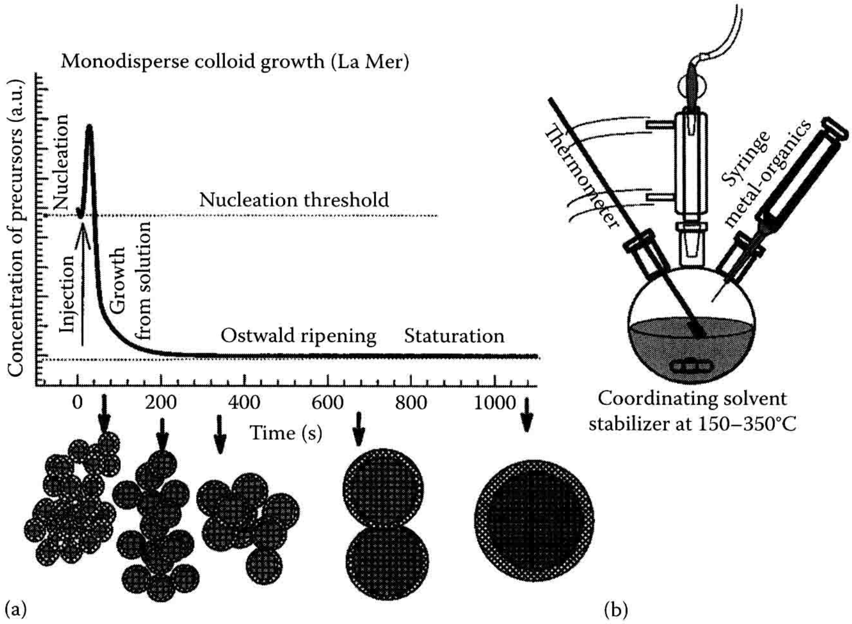


FIGURE 1.2 (a) Schematic illustrating La Mer's model for the stages of nucleation and growth for monodisperse colloidal particles. (b) Representation of the synthetic apparatus employed in the preparation of monodisperse NQDs. (Reprinted with permission from Murray, C. B., C. R. Kagan, and M. G. Bawendi, *Annu. Rev. Mater. Sci.*, 30, 545, 2000.)