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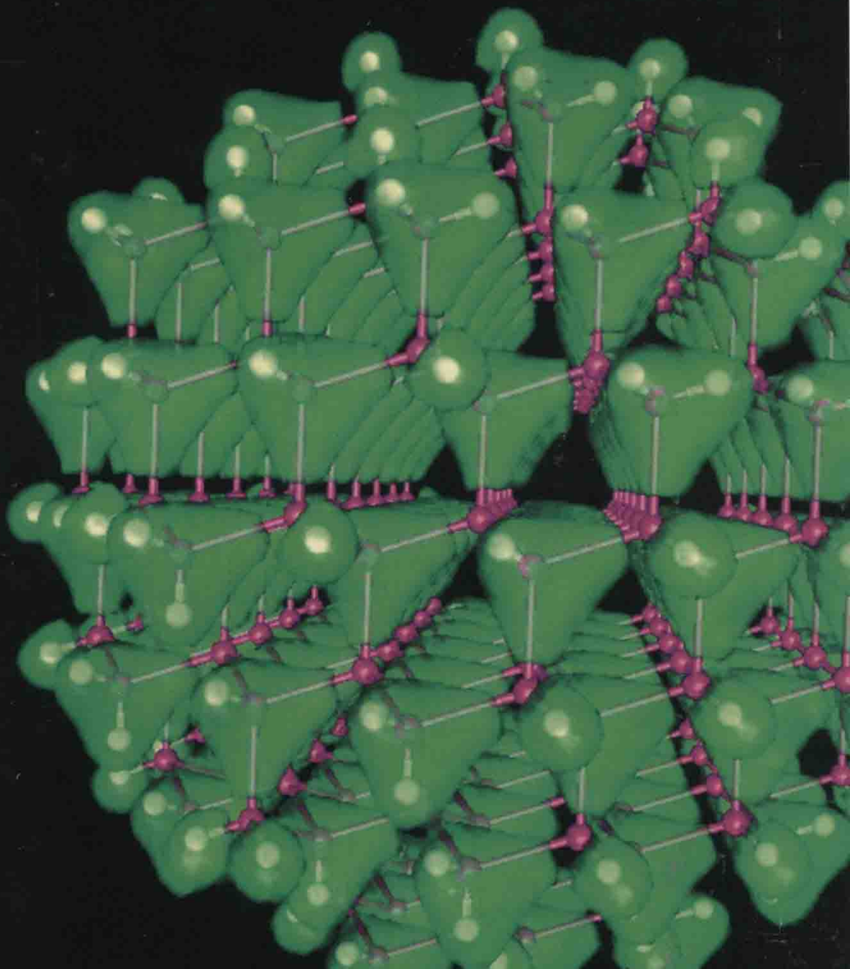

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Nanoparticles

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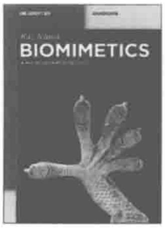

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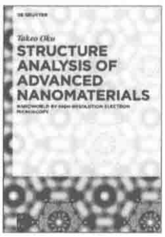

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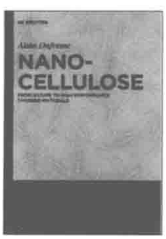

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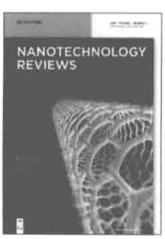

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Preface

Like many researchers who "came of age" (scientifically speaking) during the early days of the nanotechnology "revolution" in the late 1980s and 1990s, I have been fascinated by the new horizons this field entailed. Perhaps the most dramatic manifestation of nanotechnology has been the proliferation of "nanoparticles" – atomic aggregates displaying a variety of compositions and shapes. This "new frontier" of scientific imagination, creativity, and synthetic acumen has yielded a remarkable variety of nanostructures (spheres, cubes, rods, stars, and many others), and physical properties and phenomena associated with the structural features of these nanometer-scale particles. Admittedly, an incentive to write this book has been my desire to acquire a comprehensive understanding of this multidisciplinary field – the types of nanoparticles, their compositions and how the relationship between the atomic constituents affects their properties, as well as potential practical applications of nanoparticles. Indeed, the enormous scope of nanoparticle science and technology became even more apparent to me on researching material for this book and during the writing process. Moreover, the explosive growth of this field, which continues unabated to this day, has meant that I came across many new discoveries and interesting reports on nanoparticles as the book progressed; deciding which systems to include and which to leave out has been especially difficult. My hope is that the final product will endow the reader with a sound knowledge base and new perspectives on nanoparticles, and encourage further exploration of this exciting field.

This book has benefited from significant help and support of several people. First and foremost I want to thank my family for their patience with me spending many hours working on the book through the nights and over weekends ... I am also grateful to my graduate student Alex Trachtenberg for his help and efforts putting together many of the figures in the book. Special thanks to the Y Café in the Nachlaot neighborhood, Jerusalem, and the Austrian Hospice Café in the Old City of Jerusalem for the hospitality, many hours of inspiration, great coffee and beer that contributed to the realization of this book.

Contents

1 Introduction

For a young scientific discipline which burst on to the stage less than 30 years ago, *nanotechnology* has had a tremendous impact on both fundamental research and development of technology. *Nanoparticles* (NPs) have been among the most visible facets of nanotechnology research. The essence of this field is the realization that the properties of matter are often significantly altered as one ventures into the nanoscale. Indeed, the unique properties of NPs are due in large part to their *nanometer* (10^{-9} meter) dimensions. The interest and activity in this field have led to dramatic contributions in diverse fields of science and technology – chemistry, physics, biology, electronics, and others. In fact, NPs can be considered both products and promoters of the "nanotechnology revolution", as attested by the huge body of work on the subject.

Although the precise definition of NPs may be somewhat fluid, this book focuses on atomic and molecular aggregates which are generally smaller than *tens of nanometers*. While the term "nanoparticle" often evokes an image of a small *spherical* particle, this book is not limited to spherical NP configurations. The discussion rather spans the diverse structural universe of nanoparticles, including *(nano)wires, rods, stars, cubes* and various other morphologies enabled by nature, our imagination, and synthetic acumen. This book is designed to be an introductory textbook to the rapidly evolving field of nanoparticle science and technology. As such, the book aims to present different facets of nanoparticle research to readers who are not necessarily active or experts in this discipline. A scientific knowledge base, however, is quite essential for grasping many of the subjects discussed. Overall, this book aims to endow the reader with a methodical summary of the field – how concepts, synthesis schemes, and applications of NPs have been developed and implemented.

Discussion of the broad and diverse array of systems and experimental strategies is carried out primarily through presentation and analysis of studies published in the scientific literature. Starting from a historical perspective, the book has several underlying themes, including *synthetic routes* for preparing NPs; different NP *structures* and the way the structural and morphological features of the particles affect *functionalities;* novel *constructs* and *devices* utilizing NPs; and the use of NPs *beyond the nanoscale – as* building blocks in higher-order materials. Specific emphasis is placed upon the interface and relationships between NPs and *biological systems*, as important developments of biomedical applications underscore both the potential and risks associated with increased applications of NPs as therapeutic and diagnostic tools. While unique physical phenomena are intrinsic to the properties and applications of NPs, detailed analyses of the *physics* aspects of NPs are beyond the scope of this book.

Naturally it is difficult to cover all pertinent topics and aspects in a single textbook. Accordingly, this textbook will hopefully serve as a "starting point" for nanoparticle science and technologies; the reader is accordingly referred to many excellent comprehensive reviews and scientific publications, outlined in the "Further reading" section at the end of the book. Importantly, the focus here is on nanoparticles and not "nanoscale materials" as a whole. Accordingly, discussion in the text is focused mostly on "stand-alone" *synthetic* NPs self-assembled in *solutions*, rather than nanostructures produced via techniques such as lithography which can technically be perceived as parts of larger entities (e.g. surface). This book also excludes the huge field of "carbon nanomaterials"; carbon nanoparticle allotropes, such as fullerenes and carbon nanotubes, exhibit distinct properties related to the organization and binding of carbon atoms and deserve an independent textbook.

The chapters in the book are devoted to different nanoparticle *compositions* and *types*: *semiconductor NPs* (Chapter 2), of which "quantum dots" occupy a prominent position; *metal NPs* (Chapter 3), including the highly diverse applications of *gold, silver*, and *transition metal NPs; metal-oxide NPs* (Chapter 4) employed in varied technologies such as solar energy harvesting and biomedical imaging; *biological and polymer NPs* (Chapter 5), in which organic building blocks have been used to construct nanoparticles; *hybrid NPs* (Chapter 6), comprising more than one component and displaying intriguing configurations – from *core-shell NPs*, all the way to more exotic species, such as "nanostars", "nanodumbbells", nanocages, and others. A specific chapter is devoted to the effects of nanoparticles on biological entities – cells, proteins, and DNA (Chapter 7); and the last chapter focuses on the use of NPs as building blocks for larger and more complex materials (Chapter 8). A certain overlap naturally exists between topics. Thus, for example, *NP assemblies* are discussed both in a dedicated chapter (Chapter 8), as well as in individual chapters (such as solar cells comprising of *titanium oxide NPs*). Similarly, the interface between NPs and the biological world is a vast and recurring theme in several chapters; the significance of this topic is also reflected in a thorough discussion in a specific chapter (Chapter 7).

Nanoparticles have inspired the scientific and technological communities for several decades now, and the sheer activity in this field promises to continue generating new discoveries, revolutionary products, and novel physical phenomena. The remarkable progress in our understanding of NPs and the ability to control and modulate their properties will undoubtedly further expand the frontiers of chemistry, physics, material sciences, and biomedicine.

1.1 Historical context and early work

"Pornography is a matter of geography" as the saying goes; this aphorism might seem relevant to many scientific disciplines in which long-known phenomena are explained using new physical and chemical tools and new terminology. This has also been partly the case with nanoparticles. Indeed, NPs have been produced since mankind learned to manipulate materials, although the actual term (and hype...) of "nanoparticles" was coined much more recently. One of the earliest and most famous examples of the use of NPs for everyday objects was the "Lycurgus Cup" (Fig. 1.1). Manufactured by a

Fig. 1.1: The Lycurgus Cup. Image provided by the British Museum.

Roman craftsman almost 2000 years ago from special glass speckled with "gold and silver dust", this extraordinary object changes its color depending on the position of the incident light. When illuminated from the outside, the cup appears green, however when the light source is placed inside the cup it shines red. This rather unusual property is directly related to the interplay between reflection and scattering of the light beam from metal nanoparticles embedded within the glass. The Romans did not of course know they were working with NPs, and in fact the unique mechanism responsible for the optical properties of the Lycurgus Cup was deciphered not that long ago. However, the Lycurgus Cup illustrates a notable facet of NP science and technology – that varied chemical and physical phenomena associated with NPs have, in fact, been known for quite a long time. Indeed, part of early NP research was aimed at providing a solid physical/chemical understanding of known processes and materials.

In a historical context, NP research emanated in large part from a convergence of two distinct scientific disciplines – the study of *atomic clusters*, and *colloids* research (Fig. 1.2). Clusters are loosely defined as aggregates of relatively small numbers of atoms, held together by both noncovalent and covalent bonds (Fig. 1.3). Importantly, it has been determined that clusters possess different physical properties, both compared to individual molecules, as well as in relation to the bulk material. In particular, scientists concluded that the unique characteristics of atomic clusters can be largely traced to the significantly high ratio between atoms at the surface of a cluster and its inner core. Indeed, this (high) ratio is a major determinant distinguishing clusters (and nanoparticles) from their bulk counterparts.

Colloid research is the other major preceding field which led to the emergence of nanoparticle science. Colloidal systems are defined as molecular aggregates which are usually dispersed within a more abundant substance (such as a solvent. Milk is a prime example of an aqueous colloidal suspension). Indeed, colloid dispersions are

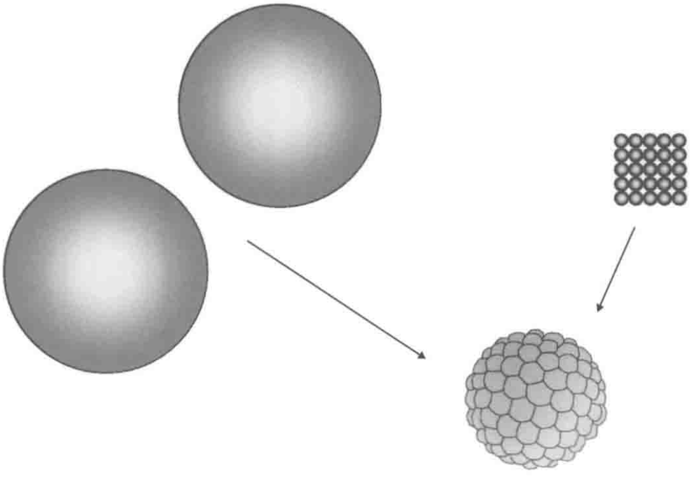

Fig. 1.2: Nanoparticle research emerged from the convergence of colloids research (*top left*) and the study of atomic clusters (*top right*).

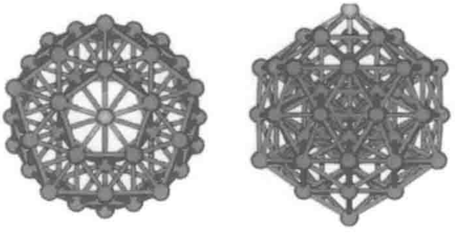

Fig. 1.3: Scheme of a metal cluster. Top view (left) and side view (right) of a Cu_{55}^- cluster. Reprinted with permission from Rapps T. et al., *Angew. Chem.* **52** (2013), 6102–6105, © John Wiley and Sons.

among the bedrocks of metallurgy and materials science in general. While colloids have been prepared routinely for millennia, the advent of science and technology has brought about the realization that the properties of colloids, particularly particle size, have intimate relationships with the overall functions and macroscopic characteristics of colloid assemblies. This link between the size of colloids and their overall material properties is one of the most important aspects of NP research, and is a fundamental phenomenon manifested in different NP systems presented throughout this book. Milk, in fact, is a case in point highlighting the significance of nanoparticles in determining material properties. The white, opaque appearance of milk is due to its composition as an *emulsion* of small colloids comprising of fats, proteins, and calcium. Moreover, it has been found in recent years that some of these colloidal species are tiny protein nanoparticles which are easily digested and contribute to the important nutritional properties of milk (Fig. 1.4).

The microscopy image in Figure 1.4 highlights another important aspect of the explosive growth of NP research – visualization. Indeed – "seeing is believing", and the advent of microscopy techniques, particularly variations of electron microscopy

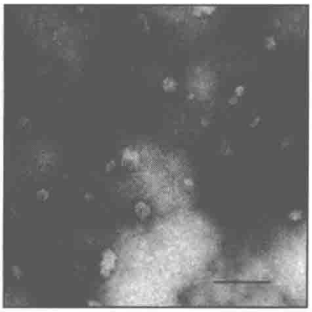

Fig. 1.4: Protein nanoparticles in milk. Transmission electron microscopy image of nanoparticles comprising casein, a major protein in milk. Scale bar corresponds to 100 nm.

and scanning probe microscopy have been pivotal to the expansion of NP science and technology. Indeed, as discussed below in detail, obtaining microscopic insights into the fine structural features of NPs, their crystallinity and atomic organization, have been among the main aspects shaping the field to this day. The development and refinement of NP synthesis schemes have been another powerful driving force. While progress in metallurgy and gold chemistry has occurred over hundreds (or thousands) of years providing tools for manipulating metallic materials, the much more recent and dramatic proliferation of NP studies and technological applications is linked to the rapidly evolving synthetic universe involving inorganic materials, semiconducting assemblies, rare earth metals, biological molecules, and others.

While it is hard to “pinpoint” the exact birth of nanoparticles as a distinct scientific discipline, the onset of research on *nanocrystals (NCs)*, particularly *semiconducting NCs*, in the 1980s, is considered (partly in retrospect . . .) a prominent marker. The great interest in NCs arose from the observation that they exhibited unique physical properties remarkably different from macroscopic crystalline aggregates (e.g. the “bulk” state of the material). Indeed, NC *size* has been shown to be a fundamental parameter affecting a variety of physical features. *Quantum confinement* (Fig. 1.5), in particular, has been one of the most central experimental observations contributing to burgeoning NC research.

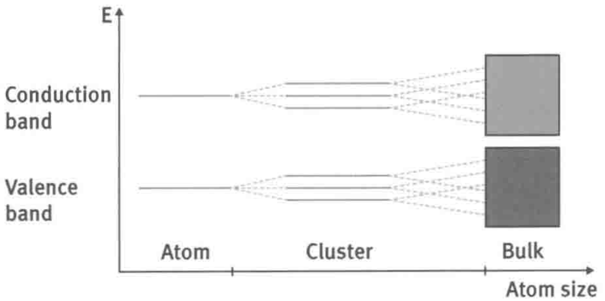

Fig. 1.5: Quantum confinement in semiconductor nanoclusters. The energy level diagram depicts the transformation of energy bandgap between atom-cluster-bulk configurations. Atomic clusters exhibit discreet energy levels.

Quantum confinement encompasses spectroscopic phenomena – essentially light absorption and emission – which directly emanate from the size regime of an NC. Quantum theory heralded the "golden age" of modern physics by predicting the existence of distinct energy levels for atoms and molecules, accurately explaining phenomena such as the discreet light absorption/emission spectral lines observed for gases. It was soon realized that while individual atoms or molecules exhibited energy level separation in larger aggregates (and in bulk materials), the levels essentially "coalesced", forming continuous energy bands. The remarkable phenomenon which came to light in the 1980s was the "intermediate" spectral properties of NCs – between individual atoms on the one hand and bulk materials on the other. Specifically, while NCs are comprised of many atoms, the physical dimensions of the NC still give rise to "quantum effects" – the discreet energy levels predicted by quantum theory. Apart from the fact that NCs provide a fine example of "quantum mechanics in action", quantum confinement has spawned major research efforts towards controlling optical properties of materials through careful tuning of NC sizes, utilization of the various atomic compositions and material classes, and exploration of practical applications and commercial targets. More detailed discussion of the quantum confinement phenomenon and its scientific and technological implications for different NPs is provided in the individual chapters.

2 Semiconductor nanoparticles

Nanoparticles and nanocrystals made of semiconducting materials were among the first to burst onto the world nanotechnology stage in the 1980s. The impact of this family of NPs has been profound, both in terms of the new scientific phenomena as well as their applications in diverse fields including solar energy, biological imaging, photonics and electronics. By common definition, semiconducting materials exhibit electrical conductivity between *metals* and *insulators*. In physics parlance, the *bandgaps* of semiconductors, e.g. energy difference between the *valence energy band*, which in semiconductors is usually fully occupied by electrons, and the empty *conduction band* at a higher energy, generally fall between insulators and conductors (Fig. 2.1).

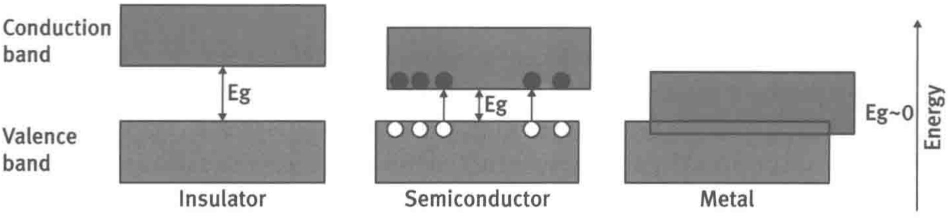

Fig. 2.1: Relative bandgaps (Eg) in insulators, semiconductors, and metals.

Significantly, the magnitude of the bandgap in a semiconductor makes excitation of electrons from the valence band to the conduction band through thermal energy, light irradiation, and other means possible, thereby creating an "electron-hole" pair (e.g. "exciton"). Exciton mobility and electron-hole recombination kinetics constitute the basis for the fundamental optical and electronic phenomena encountered in semiconductors. Another parameter pertaining to the performance and practical applications of semiconducting materials is whether the energy bandgap is *direct* or *indirect* (Fig. 2.2). Generally, indirect bandgap semiconductors exhibit slower and less efficient exciton formation and consequent light emission through electron-hole recombination, thus they exhibit more limited applicability in optoelectronic devices.

Semiconductors by themselves are often poor conductors; their conductivity can generally be enhanced through physical or chemical modifications, such as addition of foreign substances as "impurities" (e.g doping). The most common semiconductor is *silicon*. In the nanoparticle universe, the impact of silicon was smaller than that of *binary semiconductor* materials, such as "II-VI" compounds (i.e. an element from group II in the periodic table, such as cadmium, bonded to an element from group VI, such as selenium) or III-V materials, such as gallium arsenide.

Crystalline semiconductor nanoparticles (NPs) took center stage in the 1980s as striking examples of *quantum effects* – physical phenomena recorded when the di-

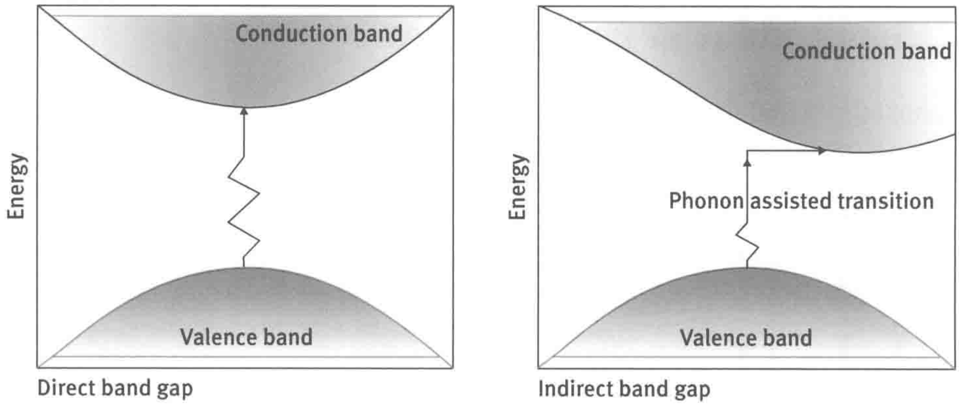

Fig. 2.2: Energy structure of (left) direct and (right) indirect band gap semiconductors.

mensions of the materials are significantly reduced, spanning a few nanometers. One of the most dramatic quantum effects in semiconducting NPs is *quantum confinement*, distinguishing the NP aggregates both from bulk materials as well as from individual molecules. As shown in Figure 2.3, quantum confinement generates discreet bandgap energy levels (and corresponding transitions) which constitute the basis for the remarkable optical and electronic properties associated with semiconducting NPs. Spherical semiconductor NPs, which were among the pioneering nanoparticle assem-

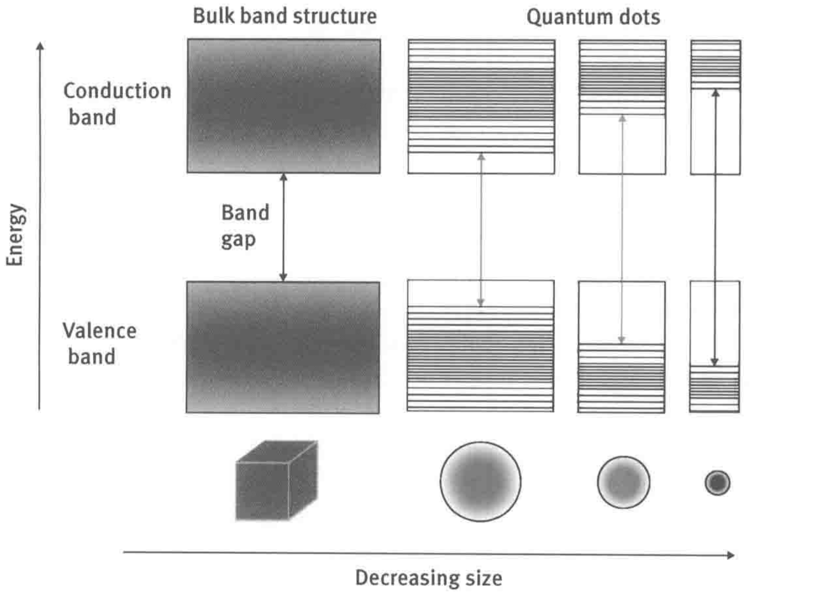

Fig. 2.3: Size-dependence of energy bandgaps in semiconductor nanoparticles (quantum dots).