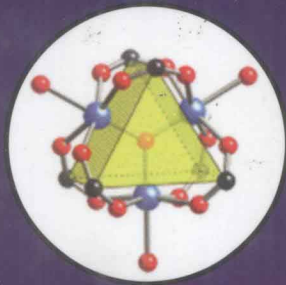
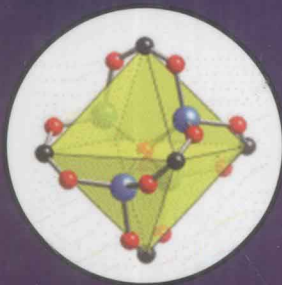
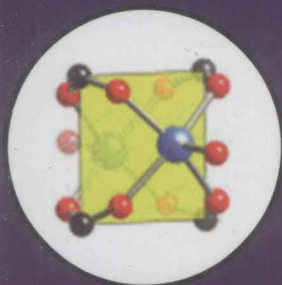


NANOSCALE MATERIALS IN CHEMISTRY

SECOND EDITION



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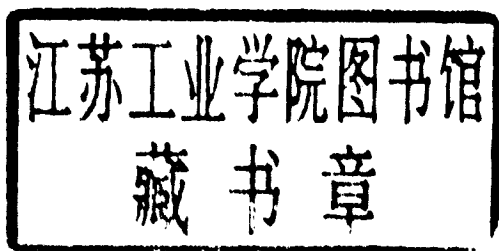
KENNETH J. KLABUNDE RYAN M. RICHARDS

NANOSCALE MATERIALS IN CHEMISTRY

Second Edition

Edited by

Kenneth J. Klabunde and Ryan M. Richards



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NANOSCALE MATERIALS IN CHEMISTRY

*To Sarah, Sydney, Maya, Erik,
and Tyler*

CONTRIBUTORS

Ken-Ichi Aika, The Open University of Japan, Setagaya-ku, Tokyo, Japan

Masakazu Anpo, Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, Osaka 599-8531, Japan

Ehud Banin, The Institute for Advanced Materials and Nanotechnology, Bar-Ilan University, Ramat-Gan 52900, Israel

Matthew T. Basel, Kansas State University, Department of Chemistry and Terry C. Johnson Center for Basic Cancer Research, Manhattan, Kansas

Stefan H. Bossmann, Kansas State University, Department of Chemistry and Terry C. Johnson Center for Basic Cancer Research, Manhattan, Kansas

Stephanie L. Brock, Department of Chemistry, Wayne State University, Detroit, Michigan

K. Dhakal, Comparative Toxicology Laboratories, Department of Diagnostic Medicine/Pathobiology, Kansas State University, Manhattan, Kansas

Winnie Dong, Chemical and Materials Engineering, California State Polytechnic University, Pomona, California

Bruce Dunn, Department of Materials Science and Engineering, University of California, Los Angeles, Los Angeles, California

Sherrie Elzey, Department of Chemical and Biochemical Engineering, University of Iowa, Iowa City, Iowa

L.E. Erickson, Department of Chemical Engineering, Kansas State University, Manhattan, Kansas

Warren T. Ford, Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma

Aharon Gedanken, Department of Chemistry, Kanbar Laboratory for Nanomaterials, Nanotechnology Research Center, Bar-Ilan University, Ramat-Gan 52900, Israel

Anirban Ghosh, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, Texas

Vicki H. Grassian, Departments of Chemical and Biochemical Engineering and Chemistry and the Nanoscience and Nanotechnology Institute at the University of Iowa, Iowa City, Iowa

Courtney Howe, Department of Nanoscience and Nanotechnology Institute at the University of Iowa, Iowa City, Iowa

Taeghwan Hyeon, National Creative Research Initiative Center for Oxide Nanocrystalline Materials, and School of Chemical and Biological Engineering, Seoul National University, Seoul 151-744, Korea

Angela Iseli, NanoScale Corporation, Manhattan, Kansas

David S. Jacob, Department of Chemistry, Kanbar Laboratory for Nanomaterials, Nanotechnology Research Center, Bar-Ilan University, Ramat-Gan 52900, Israel

Katharine Janik, Kansas State University, Department of Chemistry and Terry C. Johnson Center for Basic Cancer Research, Manhattan, Kansas

P. Jeevanandam, Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee-247667, India

Edgar Jordan, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, Texas

Mausam Kalita, Kansas State University, Department of Chemistry and Terry C. Johnson Center for Basic Cancer Research, Manhattan, Kansas

Stefan Kaskel, Institute of Inorganic Chemistry, Technical University of Dresden, Dresden, Germany

Kenneth J. Klabunde, Department of Chemistry, Kansas State University, Manhattan, Kansas

Freddy Kleitz, Canada Research Chair on Functional Nanostructured Materials, Department of Chemistry, Laval University, Québec, Canada

Piot Krawiec, Instituto de Tecnología Química, UPV-CSIC, Valencia, Spain

HaiDoo Kwen, NanoScale Corporation, Manhattan, Kansas

Soon Gu Kwon, National Creative Research Initiative Center for Oxide Nanocrystalline Materials, and School of Chemical and Biological Engineering, Seoul National University, Seoul 151-744, Korea

Jonathan Lellouche, Department of Chemistry, Kanbar Laboratory for Nanomaterials, Nanotechnology Research Center, Bar-Ilan University, Ramat-Gan 52900, Israel

Russell G. Larsen, Departments of Chemistry and the Nanoscience and Nanotechnology Institute at the University of Iowa, Iowa City, Iowa

Jae-Seung Lee, Massachusetts Institute of Technology, Cambridge, Massachusetts

Abigail K. R. Lytton-Jean, Massachusetts Institute of Technology, Cambridge, Massachusetts

Igor N. Martyanov, Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada

Masaya Matsuoka, Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, Osaka, 599-8531, Japan

Keith P. McKenna, London Centre for Nanotechnology and University College London, London, UK

John A. Pickrell, Comparative Toxicology Laboratories, Department of Diagnostic Medicine/Pathobiology, Kansas State University, Manhattan, Kansas

Shyamala Rajagopalan, NanoScale Corporation, Manhattan, Kansas

Daniel E. Resasco, School of Chemical, Biological, and Materials Engineering, University of Oklahoma, Norman, Oklahoma

Ryan M. Richards, Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado

Shalini Rodrigues, Macungie, Pennsylvania

Daniel F. Shantz, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, Texas

C. M. Sorensen, Department of Physics, Kansas State University, Manhattan, Kansas

Masato Takeuchi, Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, Osaka, 599-8531, Japan

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PART I

INTRODUCTION TO NANOMATERIALS

1

INTRODUCTION TO NANOSCALE MATERIALS IN CHEMISTRY, EDITION II

RYAN M. RICHARDS

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Nanoscale Materials in Chemistry covers a broad area of science and engineering at the core of future technological development. In particular, the challenges of energy and sustainability are certain to be interrelated with breakthroughs in this area. Among current buzz words (i.e. green, bio-, eco-), “nano” has been used (and abused) to describe an amazingly broad spectrum of systems that has led to frustration for many scientists. The National Nanotechnology Initiative has defined nanotechnology as “working at the atomic, molecular and supramolecular levels, in the length scale of approximately 1–100 nm range, in order to understand and create materials, devices and systems with fundamentally new properties and functions because of their small structure” (www.nano.gov). Naturally, this broadly defined area of science and engineering has a significant “chemistry” component. This book aims to explore the chemistry, both traditional and emerging, that is associated with nanoscale materials.

Nanoscale Materials in Chemistry, Second Edition. Edited by K. J. Klabunde and R. M. Richards
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This book is intended to function as both a teaching text for upper-level undergraduate or graduate courses and a reference text, and both fundamental and applied aspects of this field are covered in the chapters. It is intended that each chapter be able to stand on its own to allow instructors to select those topics most appropriate for their course. Additionally, each chapter contains several problems designed by the authors to challenge students and enhance their comprehension of the material.

In this short introduction, we introduce the field of nanoscience in a very general sense and provide background that may be useful to readers not familiar with this area. More in-depth discussions of each topic are provided in the individual chapters, but we have found that an initial superficial introduction to the most common phenomena and instrumentation, followed by the problems provided at the end of the chapter, helps students to understand the broader picture and begin to explore the literature.

1.1 INTRODUCTION

Nanoscience is the natural progression of science exploring the nature of matter between atoms and molecules (defined by quantum mechanics) and condensed matter (defined by solid state chemistry/physics). Thus, one of the central questions in nanoscience is “at what point in diminishing the size of a material does it begin to act more like an atom or molecule?” or, conversely, “how many atoms (in a cluster) does it take to begin observing bulk-like (solid state) behavior?”

With regard to nanoscale materials, there are three general classifications that can be used (at least for inorganics): (1) materials with delocalized electrons (metals or conductors), (2) materials with localized electrons (insulators) and (3) materials with new structures (usually atomically defined) and properties (or new forms of matter) due to their nanostructure (C60 or carbon nanotubes). Semiconductors fall somewhere in between classifications 1 and 2 depending on their band gap. Although these classes of materials will be discussed in detail in the chapters of this book, a quick review of general materials properties and the effects of reducing size is provided here to give readers and students an opportunity to begin thinking about nanoscience in terms of atoms/molecules (i.e. chemistry).

1.2 SYSTEMS WITH DELOCALIZED ELECTRONS

One of the principal concepts influencing the chemistry and physical properties of nanoscale materials with delocalized electrons is the quantum confinement effect. A metal can be thought of as a regular lattice of charged metal ions in a sea of quasi-delocalized electrons. The most important property of metals is their ability to transport electrons. Electrons can become mobile only if the energy band they are associated with is not fully occupied. If molecular orbital theory is used to generate

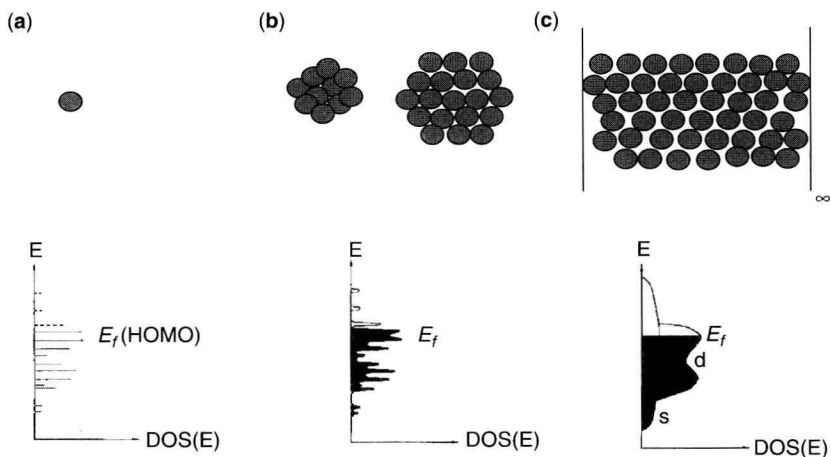


Figure 1.1 Development of the band structure of a metal: (a) molecular state, (b) nanocluster, and (c) bulk with s and d bands. (From Schmid, G. *Nanoscale Materials in Chemistry*, ed. K. J. Klabunde. New York: Wiley, 2001.)

the band structures, bulk metal possesses an indefinitely extended molecular orbital. The relationship between the molecular orbital of a finite molecular system and the indefinite situation in a bulk metal is that the highest occupied molecular orbital (HOMO) becomes the Fermi energy E_f of the free electron (Fig. 1.1). The Fermi energy depends only on the density of the electrons. If we assume that all levels up to the E_f are occupied with a total of N electrons, it can be estimated that the average level spacing is $\delta \sim E_f/N$ and therefore is inversely proportional to the volume $V = L^3$ (L = side length of particle) or $\delta \propto E_f(\lambda_f/L)^3$ where λ_f = wavelength of an electron with E_f . The wave character of the electron is assumed here, including that the allowed values for the wavelength λ are quantized (i.e. for an electron in a box of side L , only discrete values for the energy are allowed). The properties generally associated with bulk metals require a minimum number of electronic levels or a band.

The electrons in a three-dimensional metal spread as waves of various wavelengths usually called the DeBroglie wavelength.

$$\lambda = h/mv$$

where λ = electronic wavelength, h = Planck's constant, m = mass of electron, and v = speed of electron.

Delocalization of electrons in the conductivity band of a metal is possible as long as the dimension of the metal particle is a multiple of the DeBroglie wavelength. Thus, the smallest metal particles must have a dimension on the order of λ . Smaller

particles have electrons localized between atomic nuclei and behave more like molecules. The transition between these two situations is gradual. Thus, for metals or systems with delocalized electrons, upon decreasing size we ultimately reach a size where the band structure disappears and discrete energy levels occur and we have to apply quantum mechanics; this is commonly referred to as the phenomenon of quantum confinement. The quantization effect represents one of the most exciting areas of modern science and has already found numerous applications in fields ranging from electronics to biomedicine.

Quantization refers to the restriction of quasi-freely mobile electrons in a piece of bulk metal and can be accomplished not only by reduction of the volume of a bulk material but also by reducing the dimensionality. A quantum well refers to the situation in which one dimension of the bulk material has been reduced to restrict the free travel of electrons to only two dimensions. Restricting an additional dimension then only allows the electrons to travel freely in one dimension and is called a quantum wire, while restricting all three dimensions results in a quantum dot.

1.3 SYSTEMS WITH LOCALIZED ELECTRONS

The effects of reducing size are very different for materials with localized electrons where defects are the most significant contributor to their properties. Naturally, due to the localization of electrons, the surface contains defects due to edges, corners, “f” centers, and other surface imperfections (Fig. 1.2). Defects can arise from a variety

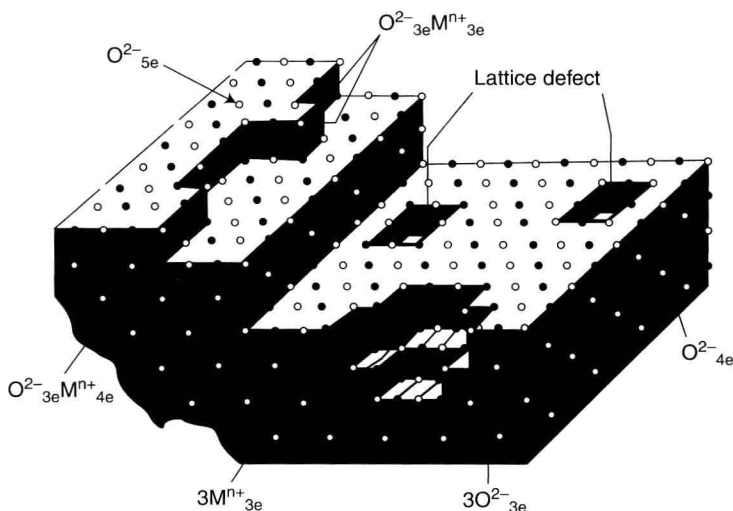


Figure 1.2 A representation of the various defects present on metal oxides. (From Dyrek, K. and Che, M. *Chem. Rev.* 1997, 305–331. With permission.)