

## **PART I**

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# **INTRODUCTION TO NANOMATERIALS**

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# 1

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## INTRODUCTION TO NANOSCALE MATERIALS IN CHEMISTRY, EDITION II

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- 1.1 Introduction, 4
- 1.2 Systems with Delocalized Electrons, 4
- 1.3 Systems with Localized Electrons, 6
- 1.4 Instrumentation Introduction, 8
- 1.5 Conclusion, 9
- Problems, 9
- Answers, 10

*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](http://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.

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*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.

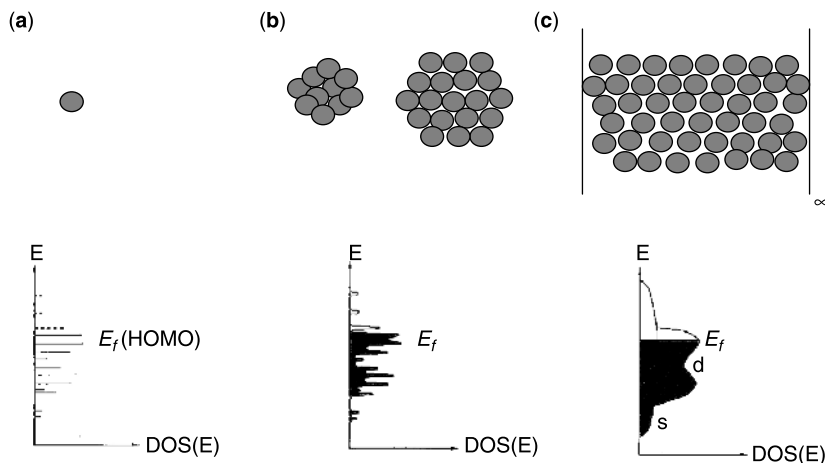
## 1.1 INTRODUCTION

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 (C<sub>60</sub> 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  $\lambda_f =$  wavelength of an electron with  $E_f$ . The wave character of the electron is assumed here, including that the allowed values for the wavelength  $\lambda$  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  $\lambda =$  electronic wavelength,  $h =$  Planck's constant,  $m =$  mass of electron, and  $v =$  speed of electron.

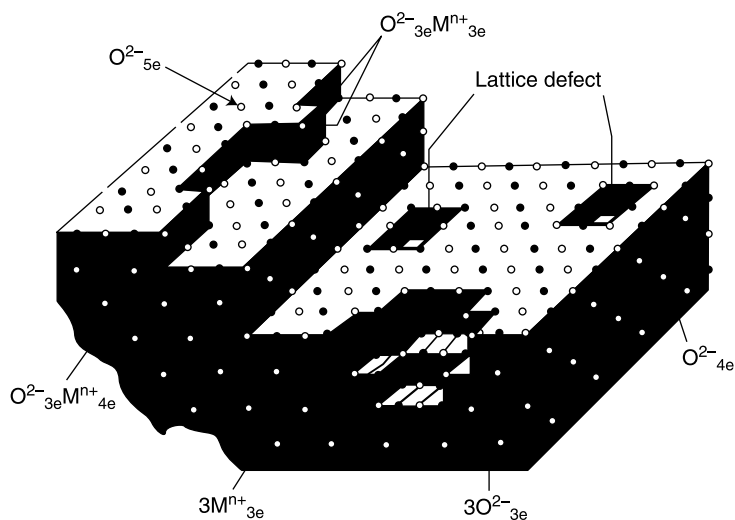
Delocalization of electrons in the conductivity band of a metal is possible as long as the dimension of the metal particle is a multiple of the DeBroglie wavelength. Thus, the smallest metal particles must have a dimension on the order of  $\lambda$ . Smaller

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.

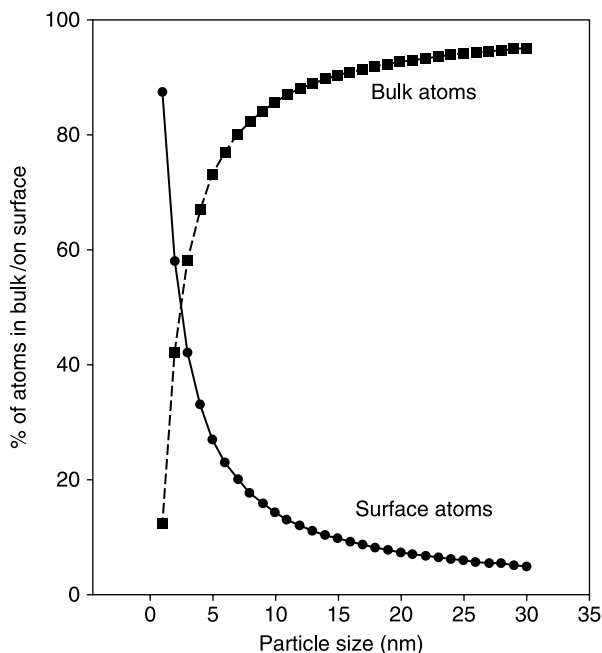
Quantization refers to the restriction of quasi-freely mobile electrons in a piece of bulk metal and can be accomplished not only by reduction of the volume of a bulk material but also by reducing the dimensionality. A quantum well refers to the situation in which one dimension of the bulk material has 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



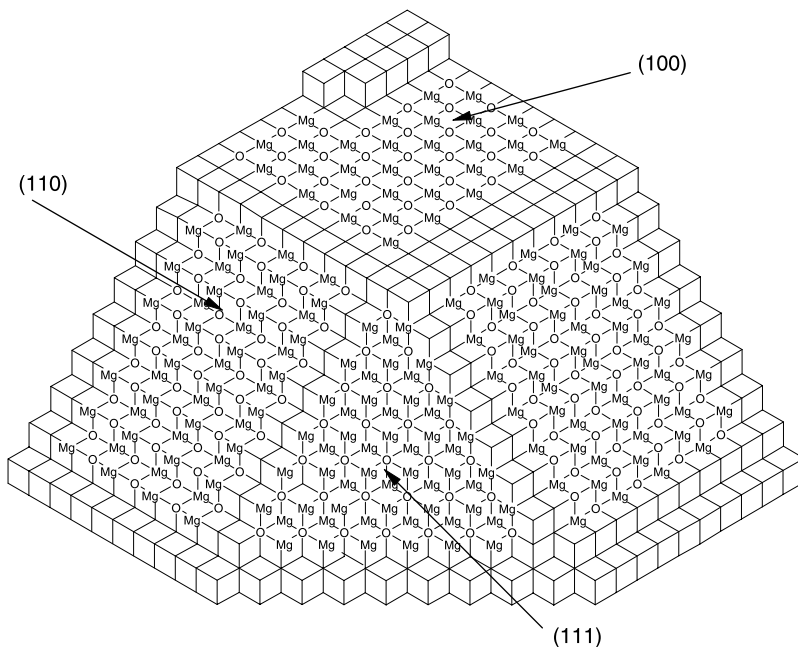
**Figure 1.2** A representation of the various defects present on metal oxides. (From Dyrek, K. and Che, M. *Chem. Rev.* 1997, 305–331. With permission.)



**Figure 1.3** Calculated surface to bulk atomic ratio (for Fe). (From K. J. Klabunde et al. *J. Phys. Chem.* 1996, 100: 12142–12153. With permission.)

of causes: they may be thermally generated, or may arise in the course of fabrication of the solid, incorporated either unintentionally or deliberately. Defects are important because they are much more abundant at surfaces than in bulk, and in nanoscale materials they become predominant due to the large surface area (Fig. 1.3). Because of the number of atoms at the surface and the limited number of atoms within the lattice, the chemistry and bonding of nanoparticles is greatly affected by the defect sites present.

The defects that occur in the solids with localized electrons are grouped into the following classes: point, linear, planar, and volumetric defects. Point defects are a result of the absence of one of the constituent atoms (or ions) on the lattice sites, or their presence in interstitial positions. The most common defects are coordinatively unsaturated sites, for example, materials with a rock salt structure prefer to be bound to six neighbors, so those atoms on the surface are five-coordinate, on edges four-coordinate, and corners three-coordinate. Thus, using MgO as an example, the coordinatively unsaturated sites possess Lewis base character. Further, the crystallographic facet on the surface (as given by Miller indices) can also dramatically influence the properties of the system. For example, the (100) facet of MgO consists of alternating Mg cations and O anions and is thermodynamically favored, however, the (111) facet consisting of alternating layers of cations and anions has a polar surface and therefore different physical and chemical properties (Fig. 1.4).

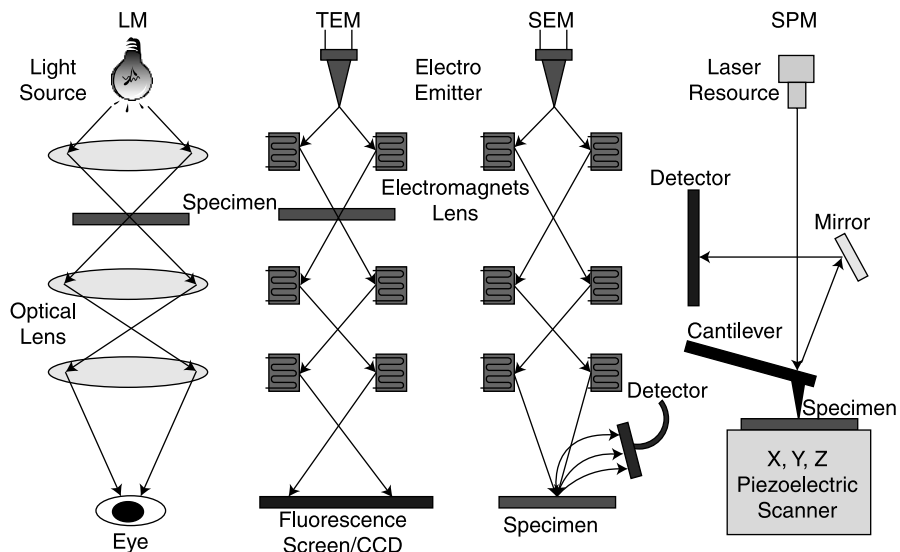


**Figure 1.4** Schematic depiction of the (100), (110), and (111) facets of MgO.

## 1.4 INSTRUMENTATION INTRODUCTION

Developments in instrumentation, in particular microscopy, have allowed scientists to observe materials and phenomena with angstrom-level resolution, leading to a much deeper understanding of nanostructured materials. The two types of electron microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM), utilize an electron beam rather than light to resolve images (Fig. 1.5). In general, a TEM can be envisioned as a process similar to a film projector in which a beam passes through a sample and projects an image onto a screen. Conversely, an SEM is more comparable to shining a flashlight around a room and gaining a sense of the topography. With this technique resolution limits are generally on the nanometer length scale but the advantage lies in the topographical information gained. A great deal of caution should be taken when assessing the data provided by these techniques because they are operator biased in that they only show a small portion of the overall sample. While electron microscopy images provide valuable information regarding size, shape, composition, etc., they should be corroborated by a “bulk” technique such as powder x-ray diffraction (XRD) to demonstrate that the information in the microscopy image is representative of the whole sample.

In addition to electron microscopy techniques, developments in scanning probe microscopies have also allowed visualization and even the ability to manipulate matter at a new level. This class of microscopies acquires data by using a physical



**Figure 1.5** Schematic depiction of traditional light microscopy, transmission electron microscopy, scanning electron microscopy, and scanning probe microscopy.

probe to scan the surface (Fig. 1.5). Generally, the probe is moved mechanically across the surface in a raster scan, providing line by line data of the probe location and the interaction with the surface. There are now countless types of scanning probe microscopies, with the two most common being atomic force microscopy (AFM) and scanning tunneling microscopy (STM).

## 1.5 CONCLUSION

Hopefully, this short introduction instigates some class discussion about nanoscale materials in chemistry and facilitates an entry into the topics covered in this book and the literature. The editors have attempted to gather chapters covering a breadth of topics both fundamental and applied to provide the reader with an understanding of this important area of science and engineering. The contributors have been selected for their expertise in the subject area and have all done an excellent job of sharing their knowledge and making their topic accessible to a broad readership.

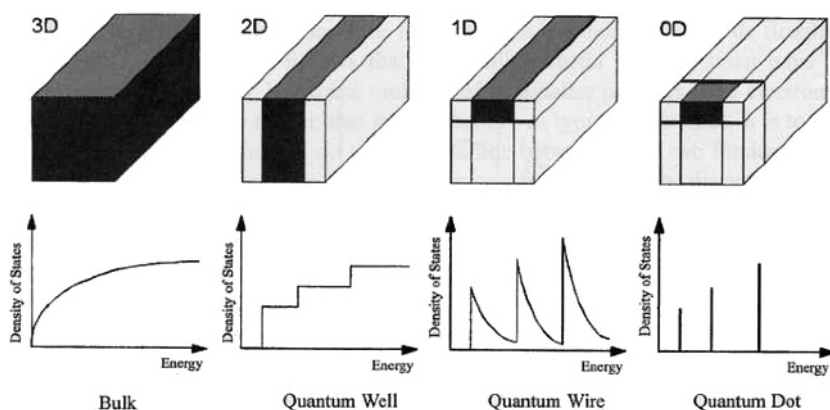
## PROBLEMS

1. Draw figures illustrating the relationship of the density of states versus energy for (a) bulk, (b) quantum well, (c) quantum wire, and (d) quantum dots.
2. For a 2.1 nm cube of MgO (100) calculate the number of five-, four-, and three-coordinate sites.

3. Use the magic numbers equation  $\Sigma(10n^2 + 2)$  to show the number of atoms in clusters with one, two, and three shells and calculate the number of surface atoms in each.
4. List five types of scanning probe microscopies and give a brief description of each.
5. Find the 12 principles of Green Chemistry and discuss how nanotechnology might have an impact on these areas.
6. Investigate the following analytical techniques and provide a brief description of each, including the information provided and limitations: TEM, SEM, powder XRD, XPS, EXAFS, XANES, nitrogen physisorption.
7. Explain what happens to the melting point and specific heat of metals as the size changes from the bulk to the nanoscale.
8. Provide MO diagrams for  $\text{Li}_2$ ,  $\text{Li}_{20}$ , and bulk Li.
9. Describe what is meant by “bottom up” and “top down” preparations of nanoscale materials.
10. Describe the two paradigms of colloidal stabilization, steric and electrostatic, and provide an example of each.

## ANSWERS

1. From K. J. Klabunde, editor. *Nanoscale Materials in Chemistry*, 1st edn. New York: Wiley Interscience, 2001, p. 22.



2. For MgO 100, d spacing is  $\sim 2.1 \text{ \AA}$ , thus a 2.1 nm cube is  $\sim 10 \times 10 \times 10$  units or 1000 MgO that break down as follows:  
5 coordinate = faces =  $8 \times 8 \times 6$  (# faces)

4 coordinate = edges =  $8 \times 12$  (# edges)

3 coordinate = corners = 8

leaving a core of  $8 \times 8 \times 8$

Note: some students have an easier time starting with corners, then edges and faces. Also, this is a simplified exercise, in reality the highly unsaturated sites are often hydroxylated and the overall charge of the molecule is balanced.

3. 1 shell = 13 atoms (12 on surface)  
2 shells = 55 atoms (42 on surface)  
3 shells = 147 atoms (92 on surface)
4. Any of the following surface probe microscopies are possible:
  - AFM, atomic force microscopy
    - Contact AFM
    - Non-contact AFM
    - Dynamic contact AFM
    - Tapping AFM
  - BEEM, ballistic electron emission microscopy
  - EFM, electrostatic force microscope
  - ESTM, electrochemical scanning tunneling microscope
  - FMM, force modulation microscopy
  - KPFM, kelvin probe force microscopy
  - MFM, magnetic force microscopy
  - MRFM, magnetic resonance force microscopy
  - NSOM, near-field scanning optical microscopy (or SNOM, scanning near-field optical microscopy)
  - PFM, piezo force microscopy
  - PSTM, photon scanning tunneling microscopy
  - PTMS, photothermal microspectroscopy/microscopy
  - SAP, scanning atom probe
  - SECM, scanning electrochemical microscopy
  - SCM, scanning capacitance microscopy
  - SGM, scanning gate microscopy
  - SICM, scanning ion-conductance microscopy
  - SPSM, spin polarized scanning tunneling microscopy
  - SThM, scanning thermal microscopy
  - STM, scanning tunneling microscopy
  - SVM, scanning voltage microscopy
  - SHPM, scanning Hall probe microscopy

Of these techniques AFM and STM are the most commonly used followed by MFM and SNOM/NSOM.

### 5. The 12 principles of Green Chemistry:

This is a rapidly developing area of science and instructors may find it helpful to use recent literature reports to illustrate these points.

- (1) *Prevention*: It is better to prevent waste than to treat or clean up waste after it has been created. (Catalysis by nanoscale particles.)
- (2) *Atom Economy*: Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product. (Optimizing the number of surface atoms and their activity comes from making nanoscale materials.)
- (3) *Less Hazardous Chemical Syntheses*: Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment. (There have been several reports of nanoscale catalysts that have allowed processes to become more green, using water as solvent or no solvents, eliminate by products, etc.)
- (4) *Designing Safer Chemicals*: Chemical products should be designed to effect their desired function while minimizing their toxicity. (Nanotoxicity and nanoparticle lifecycle in the environment needs to be closely studied.)
- (5) *Safer Solvents and Auxiliaries*: The use of auxiliary substances when used.
- (6) *Design for Energy Efficiency*: Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure. (Nanocatalysis.)
- (7) *Use of Renewable Feedstocks*: A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
- (8) *Reduce Derivatives*: Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
- (9) *Catalysis*: Catalytic reagents (as selective as possible) are superior to stoichiometric reagents. (Many nanoscale catalysts exhibit improved selectivity and/or activity as compared to bulk systems.)
- (10) *Design for Degradation*: Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
- (11) *Real-time Analysis for Pollution Prevention*: Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
- (12) *Inherently Safer Chemistry for Accident Prevention*: Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

From P. T. Anastas, J. C. Warner. *Green Chemistry: Theory and Practice*. New York: Oxford University Press, 1998, p. 30. By permission of Oxford University Press.

6. TEM: Under vacuum conditions focuses an electron beam through a sample dispersed on a grid. The resulting image can provide Å level resolution including lattice fringes. Most useful for determining particle size, size distribution and shape. Can also provide a great deal of additional information from diffraction techniques.

SEM: Provides more topography information than TEM but resolution is generally limited to nm scale.

Powder XRD: Provides information regarding unit cell, long range order, bonding and lattice. Can be helpful to determine the phase of a material (for example anatase vs rutile for  $\text{TiO}_2$ ) and Scherrer eqn can be applied to estimate particle size.

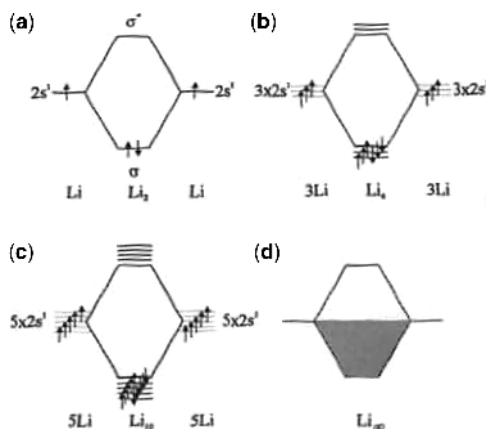
XPS, X-ray photoelectron spectroscopy: Can be used to study first few layers of surface and provide the energies of the orbitals. This information can then be used to determine oxidation state of the element.

EXAFS and XANES are generally performed at a synchrotron facility and provide information about neighboring atoms of the atom under investigation.

Nitrogen physisorption: Used to determine surface area, pore size, pore volume, pore size distribution and further textural properties through analysis of adsorption/desorption isotherms.

7. Students are directed to Chapter 8 in the first edition for comprehensive discussion. (See K. J. Klabunde, editor. *Nanoscale Materials in Chemistry*, 1st edn. New York: Wiley Interscience, 2001, pp. 263–277). In general, for free nanoparticles the melting point is always lower than the bulk value. Specific heats are generally enhanced as compared to the bulk.

8. From K. J. Klabunde, editor. *Nanoscale Materials in Chemistry*, 1st edn. New York: Wiley Interscience, 2001, p. 16.



9. “Top down” approaches to nano refer to those in which larger systems are broken down until they reach they nanoscale while “bottom up” involves building nanoscale materials by putting together atoms or molecules.
10. The two general modes of colloidal stabilization are electrostatic (left) and steric (right). In the electrostatic mode there is a bilayer of anions (often halides) and a second layer of cations (for example tetra alkylammonium). In the steric stabilization there is a single bulky molecule attached to the surface (usually a P, N, or S donor, alkyl thiols are common).

