Introduction to Nanoscience

Study Guide

Chapter 3 - Characterization Methods

Chapter 3, Characterization Methods, is designed to be "catalogous" in nature. It provides a review of numerous characterization methods and focuses on those that are particularly "nano-relevant. The chapter is somewhat "science-intensive" and most definitely should be included in the curriculum.

Before students study nanotechnology (and nanoscience), they should have some level of familiarity with characterization methods. The compelling reason for this is that characterization methods are referred to often throughout the text. Why not get into the comfort zone early on in the text?

Objectives:

- Understand the bases of analysis in general: why perturb a system to understand it; what is the perturbing agent; what are you expecting to measure; how will you measure the "signal"; and how do you transduce that signal into recorded (e.g. 1° electrons → 2° electrons → detector → signal → image)
- Get a feel for the implications of wavelength and the object that you are trying to resolve– e.g. the de Broglie equation in particular
- Group all the kinds of analytical tools into categories and define each category and its method of operation
- Review spectroscopic analytical techniques and understand principles of operation
- Review thermodynamic analytical techniques and understand principles of operation
- Review and study electron probe methods and understand principles of operation
- Review and study scanning probe methods and understand principles of operation
- Spend special time on SERS. Understand how nanomaterials make the SERS technique possible.
- Surface plasmons are critical to SERS analysis. Understand the nature of the surface plasmon of conducting metals.

- Special attention must be paid to BET analysis. BET is mentioned in every research paper that reports on surface area, porosity, pore volume, etc.

- QCM is an often applied technique that is able analyze film thickness down to nm dimensions

3.0 Characterization of nanomaterials proceeds in most ways like characterization of any material. In other words, techniques based on spectroscopy are able to unravel properties and phenomena of nanomaterials just like for liquids, powders, solids, gases and other forms of matter. Nanoscale materials are after all part of the "material continuum".

Think back to your general and organic chemistry classes. How many kinds of analytical tools (wet or dry) did you apply? If you come from a materials science background, what analytical techniques did you apply to extract information from stubborn substrates? Are you a physicist? A biologist? The table in this section summarize many, certainly not all, analytical techniques. We broke them down into six basic categories (once again, drawing boundaries for the sake of convenience).

- Optical probes based on visible light as the primary probe

- Electron probe methods that utilize the electron and its wave properties to probe nanomaterials. Transmission and electron microscopy in particular are magnificent tools of the nano-trade.

- Scanning probe methods based on the stylus mechanism– a method that opened the gates to the nanoworld proper

- Photon spectroscopies– tried and true methods that exploit the relationships between electromagnetic radiation and matter

- Ion / particle probes are based on matter beams or streams

- Thermodynamic methods– for lack of a better name– are based on input and/or output of a thermodynamic parameter, usually heat or adsorption

- Testing procedures typical of engineering were not covered in this science-based chapter and are reserved for the follow up sister volume, *Fundamentals of Nanotechnology*. Engineering related evaluation include testing for electrical conductivity and resistivity, surface tension, mechanical properties such as Young's and other modulii, tensile strength, hardness, stiffness, strength, toughness, thermal conduction, thermal expansion, fracture toughness, scratch resistance and many more.

Discussion Topic: Have we missed anything? Please delve into more kinds of analytical tools. For example, where would you place HPLC (high pressure liquid chromatography)? The various gas chromatographies? Gel electrophoresis? Pycnometry? Sedimentation techniques? Acoustic methods? Anything else?

Resolution is an important aspect of imaging. Nobody cares for a blurry photograph nor should we settle for a blurry image of a gold-55 quantum dot. How do we maximize the resolving power of an analytical probe?

Discussion Topic: Breakdown the structure of the rods and cones? What nanostructure is apparent in their structure?

The best way to visualize (no play on words intended) resolution is to consider the human eye. There is a lens, an aperture (the iris [diaphragm]-pupil [aperture] assembly), a receptor (cones, rods [photosensors] at the retinal region [the screen]) and a means of transmitting a signal to the brain (optic nerve). There are ca. 125 million rods and ca. 7 million cones. There are three types of photosensors in cones– each sensitive to a particular band of wavelength (red from 564-580-nm; green from 534-545-nm- and blue from 420-440-nm). Rod cells are smaller and interact best with blue lights (and not at all with red lights).

Are cones nanostructured materials? Cones 40 - 50 μm in length but 400 to 500-nm in diameter. What is interesting about the diameter?

For an excellent discussion about visual acuity and resolution of the human eye, go immediately to ClarkVision.com at
www.clarkvision.com/imagedetail/eye-resolution.html

Resolution Games One thing to become familiar with is the components of a wavelength-based system that affect resolution. There are a few: aperture dimension (the larger, the better resolution); refractive index of the connecting medium (vacuum = 1, anything else gives you better resolution), and the wavelength of impinging light (the shorter the λ, the better the resolution). Anything else?

For SEM and TEM, resolution is simply a function of the "optics" of the system and the wavelength of the electron beam.

Resolution for AFM and STM instruments is usually dependent on the sharpness of the tip and the sensitivity of the detectors (photo or electronic).

3.1 There are a few major points concerning electron probe methods in this section:

- Electrons behave as particles
- Electrons behave as waves
- At velocity approaching the speed of light, electrons assume relativistic behavior

- Electrons can be diffracted by regular crystalline structures

- Electrons can be scattered elastically or inelastically. Both ways reveal information about the material

- Resolution highly dependent on wavelength of electron beam

The electron as a primary probe, although extremely useful, presents some technological challenges. For one, electrons interact in so many ways with solid materials. By understanding how electrons react with matter, we are able to extract information about matter. Please review **Figure 3.5** and **Tables 3.7** and **3.8** in the text.

Discussion Topic: Review the workings of a scanning electron microscope and discuss the significance of each major component.

3.2 Scanning probe methods are a nanotechnologists dream. They are:

- Affordable (E-beam methods are extremely expensive due to the requirement of ultrahigh vacuum conditions, power demand, expensive filaments and high maintenance).

- A stylus-based probe is able to resolve atomic structure of a material

- Atomic force microscopes are essentially based on a mechanical principle– force applied up or down (or laterally), or tip height at constant force is able to map the three-dimensional topographic features of a surface! The detector is a simple position sensitive photo-detector

- STMs are able to extract information concerning the electronic states of materials by just sitting over an atom (or a small region) and varying the input bias– a process called scanning tunneling spectroscopy

- Materials and systems are designed to isolate the AFM or STM to prevent interference from vibration sources. Cooling to near absolute zero reduces the number of vibrational states in the material (e.g. carbon nanotubes)

3.3 There are many kinds of spectroscopic methods that exploit the entire EM-spectrum: from extremely long wavelength sources such as radio and microwaves down to ultraviolet continuing to 1-nm or less x-rays. Gamma rays are not typically used in analytical techniques for obvious reasons.

Photons interact with matter in a few major ways: light is reflected, absorbed, diffracted or transmitted from or through a material. Elastic scattering is considered as reflection off extremely small particles, molecules or atoms.

Absorption occurs by several types of mechanisms, all due to interactions with electrons and/or atomic structure. Depending on the wavelength of the light and the size of the particle, light is absorbed via energy states that correspond to electronic transitions (including surface plasmons), rotations, diffraction or vibrations (and phonons for larger materials). Emission occurs following decay of excited states back to the ground state. In quantum dots, this emission (fluorescence) is size dependent. Heat is often released following absorption of light. **Figure 3.19** depicts three kinds of interactions with light depending on the size of the particle.

3.4 Nonradiative (as in electromagnetic) methods are abundant. Particle methods, particularly mass spectrometry, have demonstrated great utility over the years in unraveling nanoparticles. Fullerenes were discovered by Richard Smalley et al. from a diagnostic C-60 MS signature.

Thermodynamic methods involve some thermodynamic parameter. This seems to be a catchall category for techniques that are non-photon, non-electron and non-scanning. Thermodynamic techniques revolve around techniques based on phenomena that you would find in a physical chemistry textbook. Scanning calorimetry measures the heats of formation; BET measures surface coverage by physisorptive mechanisms that involve description by isotherms; although not covered explicitly in the text, all chromatography is classified as thermodynamic methods (at least by us) that involve adsorption, flow, pressure, temperature etc.

There are many techniques that cannot neatly be placed in one category or another. Particle sizing, for example, utilizes light scattering but also involves equations describing viscosity diffusion, temperature and the Boltzmann constant, all thermodynamic parameters.

Chapter 3 Summary:

- Without methods to analyze the nanoscale, we are blind to the nanoscale
- There are several major groupings of analytical techniques: spectroscopic techniques (based on EM-radiation) that analyze electronic, magnetic or vibrational transitions; electron probe techniques (based on high energy electron beams), scanning probes (based on sharpened tips– some to points less than 1-nm curvature– forces and currents) that offer atomic resolution and electronic information; particle methods that utilize energetic particles to react with substrates, thermodynamic methods that measure thermodynamic parameters such as pressure, surface tension, adsorption, heat transfer, temperature, flow, etc.; and engineering tests (mechanical, electrical, thermal, etc.)
- The de Broglie equation is fundamental to electron beam analytical techniques
- A relativistic term (γ) is added to the de Broglie relation in order to scale for relativistic effects

- Calculation of the wavelength of the electron beam with regard to accelerating voltage: $\lambda = h/\sqrt{(2m_e eV)}$

- Electron diffraction is based on the Bragg law: $n\lambda = 2d\sin\theta$

- Electron interactions with matter– there are many / 2°, Auger, backscattered, elastically scattered, inelastically scattered, diffracted electrons; heat, cathodoluminescence, Bremsstrahlung x-rays, characteristic x-rays and specimen current.

- Scanning probe methods rely on a finely sharpened tip (curvature < 1-nm to 20-nm to larger). The higher the curvature, the better the resolution of the image

- The STM and SEM have similarities. Both rely on electrons emitted from a source, for STM, however, in the form of a tunneling current.

- Both electrons and x-rays are capable of generating characteristic x-rays or characteristic electrons that help to identify an element in the material

- Absorption and emission (fluorescence) spectroscopic methods are used to identify nanomaterials and are especially effective for quantum dots

- The optical response of metal colloids and clusters greater than 10-nm in size is due to the surface plasmon– the free electron cloud on the surface. As the particle is reduced in size, the plasmon absorption is shifted blue. In quantum dots, the emission is due to size as well, but in this case, the Bohr radius, a function of particle size, affects the position of the absorption/emission.

- Raman spectroscopy is the seminal method to identify single-walled carbon nanotubes. The Raman signal is a function of vibrational signals (symmetric) modulated by a laser light carrier wave.

- Surface enhanced Raman spectroscopy (SERS) is a pure nano method that is effective in detecting molecules at the attomole level. Nanoparticles or nanofacets on a substrate, depending on their shape and orientation, are able to enhance the electric field of the light by several orders of magnitude and hence, the signal of the adsorbed analyte.

- X-ray diffraction is a tried and true method that is useful in deciphering the atomic structure of a crystalline material.

- The thermodynamic method of note to understand is the BET method to determine surface area, porosity and pore volume. N_2 adsorption occurs in phases: the first phase covers the surface with a monolayer of N_2 molecules. The second phase consists of additional layers on top of the previous ground layer until all pores are filled. The forces responsible for this are simple Van der Waals forces (an assumption). The Kelvin effect is also in effect in pore filling physical mechanisms.

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