Fundamentals of nanomaterials

Lecture 5

OUTLINE

- What can nanomaterials be?
- What is a dimension?
- Does size mean a lot?
- What is a potential well?
Classification

- Classification is based on the number of dimensions, which are not confined to the nanoscale range (<100 nm).
- (1) zero-dimensional (0-D),
- (2) one-dimensional (1-D),
- (3) two-dimensional (2-D), and
- (4) three-dimensional (3-D).
Zero-dimensional nanomaterials

- Materials wherein all the dimensions are measured within the nanoscale (no dimensions, or 0-D, are larger than 100 nm).
- The most common representation of zero-dimensional nanomaterials are **nanoparticles**.
  - **Nanoparticles** can:
    - Be amorphous or crystalline
    - Be single crystalline or polycrystalline
    - Be composed of single or multi-chemical elements
    - Exhibit various shapes and forms
    - Exist individually or incorporated in a matrix
    - Be metallic, ceramic, or polymeric
One-dimensional nanomaterials

- One dimension that is outside the nanoscale.
- This leads to needle like-shaped nanomaterials.
- 1-D materials include **nanotubes, nanorods, and nanowires**.
  - **1-D nanomaterials** can be
  - Amorphous or crystalline
  - Single crystalline or polycrystalline
  - Chemically pure or impure
  - Standalone materials or embedded in within another medium
  - Metallic, ceramic, or polymeric
Two-dimensional nanomaterials

- Two of the dimensions are not confined to the nanoscale.
- 2-D nanomaterials exhibit plate-like shapes.
- Two-dimensional nanomaterials include **nanofilms**, **nanolayers**, and **nanocoatings**.
  - **2-D nanomaterials** can be:
    - Amorphous or crystalline
    - Made up of various chemical compositions
    - Used as a single layer or as multilayer structures
    - Deposited on a substrate
    - Integrated in a surrounding matrix material
    - Metallic, ceramic, or polymeric
Three-dimensional nanomaterials

- **Bulk** nanomaterials are materials that are not confined to the nanoscale in any dimension. These materials are thus characterized by having three arbitrarily dimensions above 100 nm.
- Materials possess a nanocrystalline structure or involve the presence of features at the nanoscale.
- In terms of nanocrystalline structure, bulk nanomaterials can be composed of a multiple *arrangement of nanosize crystals*, most typically in different orientations.
- With respect to the presence of features at the nanoscale, 3-D **nanomaterials** can contain dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multiananolayers.
Three-dimensional space showing the relationships among 0-D, 1-D, 2-D, and 3-D nanomaterials.

- **0-D**: All dimensions at the nanoscale
- **1-D**: Two dimensions at the nanoscale, one dimension at the macroscale
- **2-D**: One dimension at the nanoscale, two dimensions at the macroscale
- **3-D**: No dimensions at the nanoscale, all dimensions at the macroscale
Summary of 2-D and 3-D crystalline structures
Matrix-reinforced and layered nanocomposites

These materials are formed of two or more materials with very distinctive properties that act synergistically to create properties that cannot be achieved by each single material alone. The matrix of the nanocomposite, which can be polymeric, metallic, or ceramic, has dimensions larger than the nanoscale, whereas the reinforcing phase is commonly at the nanoscale.
Carbon

- Carbon is a basic element of life
- Carbon is special because of its ability to bond to many elements in many different ways
- It is the sixth most abundant element in the universe
- The most known types of carbon materials: diamond; graphite; fullerenes; and carbon nanotubes
Diamond and graphite are **two allotropes** of carbon: pure forms of the same element that differ in structure.

2s and 2p electrons available for bonding

**Diamond**

\[ sp^3 \ (3D) \ 1332 \ \text{cm}^{-1} \]

\[ a_0 = 0.357 \ \text{nm} \]

**Graphite**

\[ sp^2 \ (2D) \ 1582 \ \text{cm}^{-1} \]

**Chain**

\[ sp^1 \ (1D) \ 1855 \ \text{cm}^{-1} \]
DIAMOND

- chemical bonding is purely covalent
- highly symmetrical unit cell
- extremely hard
- low electrical conductivity
- high thermal conductivity (superior)
- optically transparent
- used as gemstones and industrial grinding, machining and cutting
GRAPHITE

- Layered structure with strong bonding within the planar layers and weak, van der Waals bonding between layers
- Easy interplanar cleavage, applications as a lubricant and for writing (pencils)
- Good electrical conductor
- Chemically stable even at high temperatures
- Excellent thermal shock resistance

Applications:
Commonly used as heating elements (in non-oxidizing atmospheres), metallurgical crucibles, casting molds, electrical contacts, brushes and resistors, high temperature refractories, welding electrodes, air purification systems, etc.
Graphite is a layered compound. In each layer, the carbon atoms are arranged in a hexagonal lattice with separation of 0.142 nm, and the distance between planes is 0.335 nm.

The acoustic and thermal properties of graphite are highly anisotropic, since phonons propagate very quickly along the tightly-bound planes, but are slower to travel from one plane to another.

http://en.wikipedia.org/wiki/Graphite
Graphene

Graphene is an one-atom-thick planar sheet of $sp^2$-bonded carbon atoms that are densely packed in a honeycomb crystal lattice. It can be viewed as an atomic-scale chicken wire made of carbon atoms and their bonds.

The carbon-carbon bond length in graphene is about 0.142 nm. Graphene is the basic structural element of some carbon allotropes including graphite, carbon nanotubes and fullerenes.
Allotropes of carbon

- a) diamond
- b) graphite
- c) lonsdaleite (hexagonal diamond)
- d) fullerenes (C60, C540, C70);
- e) amorphous carbon
- f) carbon nanotube

Wikipedia
Graphene (below, top), a plane of carbon atoms that resembles chicken wire, is the basic building block of all the “graphitic” materials depicted below. Graphite (bottom row at left), the main component of pencil “lead,” is a crumby substance that resembles a layer cake of weakly bonded graphene sheets. When graphene is wrapped into rounded forms, fullerenes result. They include honeycombed cylinders known as carbon nanotubes (bottom row at center) and soccer ball–shaped molecules called buckyballs (bottom row at right), as well as various shapes that combine the two forms.
If there's a rock star in the world of materials, it's graphene: single-atom-thick sheets of carbon prized for its off-the-charts ability to conduct electrons and for being all but transparent.

Those qualities make graphene a tantalizing alternative for use as a transparent conductor, the sort now found in everything from computer displays and flat panel TVs to ATM touch screens and solar cells.

But the material has been tough to manufacture in anything larger than flakes a few centimeters across.

Now researchers have managed to create rectangular sheets of graphene 76 centimeters in the diagonal direction and even use them to create a working touch-screen display.
Quantum effects

• The overall behavior of bulk crystalline materials changes when the dimensions are reduced to the nanoscale.
• For 0-D nanomaterials, where all the dimensions are at the nanoscale, an electron is confined in 3-D space. No electron delocalization (freedom to move) occurs.
• For 1-D nanomaterials, electron confinement occurs in 2-D, whereas delocalization takes place along the long axis of the nanowire/rod/tube.
• In the case of 2-D nanomaterials, the conduction electrons will be confined across the thickness but delocalized in the plane of the sheet.
Electrons confinement

- For **0-D nanomaterials** the electrons are fully confined.
- For **3-D nanomaterials** the electrons are fully delocalized.
- In **1-D and 2-D nanomaterials**, electron confinement and delocalization coexist.

The effect of confinement on the resulting energy states can be calculated by quantum mechanics, as the "**particle in the box**" problem. An electron is considered to exist inside of an infinitely deep **potential well** (region of negative energies), from which it cannot escape and is confined by the dimensions of the nanostructure.
where \( \hbar \equiv h/2\pi \), \( h \) is Planck’s constant, \( m \) is the mass of the electron, \( L \) is the width (confinement) of the infinitely deep potential well, and \( n_x, n_y, \) and \( n_z \) are the principal quantum numbers in the three dimensions \( x, y, \) and \( z \).

**The smaller** the dimensions of the nanostructure (smaller \( L \)), the **wider** is the separation between the energy levels, leading to a spectrum of discreet energies.
What’s different at the nanoscale?

Each of the different sized arrangement of gold atoms absorbs and reflects light differently based on its energy levels, which are determined by size and bonding arrangement. This is true for many materials when the particles have a size that is less than 100 nanometers in at least one dimension.
Energy levels in infinite quantum well

\[ \psi_4(x) = A \sin \left( \frac{4\pi x}{L} \right) \quad E_4 = \frac{\hbar^2}{2m} \frac{16\pi^2}{L^2} \]

\[ \psi_3(x) = A \sin \left( \frac{3\pi x}{L} \right) \quad E_3 = \frac{\hbar^2}{2m} \frac{9\pi^2}{L^2} \]

\[ \psi_2(x) = A \sin \left( \frac{2\pi x}{L} \right) \quad E_2 = \frac{\hbar^2}{2m} \frac{4\pi^2}{L^2} \]

\[ \psi_1(x) = A \sin \left( \frac{\pi x}{L} \right) \quad E_1 = \frac{\hbar^2}{2m} \frac{\pi^2}{L^2} \]
The finite potential well

For the finite potential well, the solution to the Schrodinger equation gives a wavefunction with an exponentially decaying penetration into the classically forbidden region.

Confining a particle to a smaller space requires a larger confinement energy. Since the wavefunction penetration effectively "enlarges the box", the finite well energy levels are lower than those for the infinite well.

The solution for \(-L/2 < x < L/2\) and elsewhere must satisfy the equation

\[
-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x)}{\partial x^2} = (E - U_0)\Psi(x)
\]

With the substitution

\[
\alpha = \sqrt{\frac{2m(U_0 - E)}{\hbar^2}} = \sqrt{\beta^2 - k^2}
\]

\[
\frac{\partial^2 \Psi(x)}{\partial x^2} = \alpha^2 \Psi(x)
\]

with general solution of form:

\[
\Psi(x) = Ce^{\alpha x} + De^{-\alpha x}
\]
The finite potential well

\[ V(x) = 0 \text{ for } -L/2 \leq x \leq L/2 \]
\[ V(x) = V_0 \text{ otherwise} \]

Notice that \( E = KE + PE \), thus
\[ KE(x) = E - PE = E - V(x) \]

“classically”
forbidden: \( KE < 0 \)

“classically”
allowed: \( KE > 0 \)

“classically”
forbidden: \( KE < 0 \)
Comparison of Infinite and Finite Potential Wells

Eigenstates with \( E < V_0 \) are bound or localized.

Eigenstates with \( E > V_0 \) are unbound or delocalized.
Electron energy density

The behavior of electrons in solids depends upon the distribution of energy among the electrons:

\[ n(E)\Delta E = g(E)f(E)\Delta E \]

This distribution determines the probability that a given energy state will be occupied, but must be multiplied by the density of states function to weight the probability by the number of states available at a given energy.

Density of states in (a) metal, (b) semimetal (e.g. graphite).