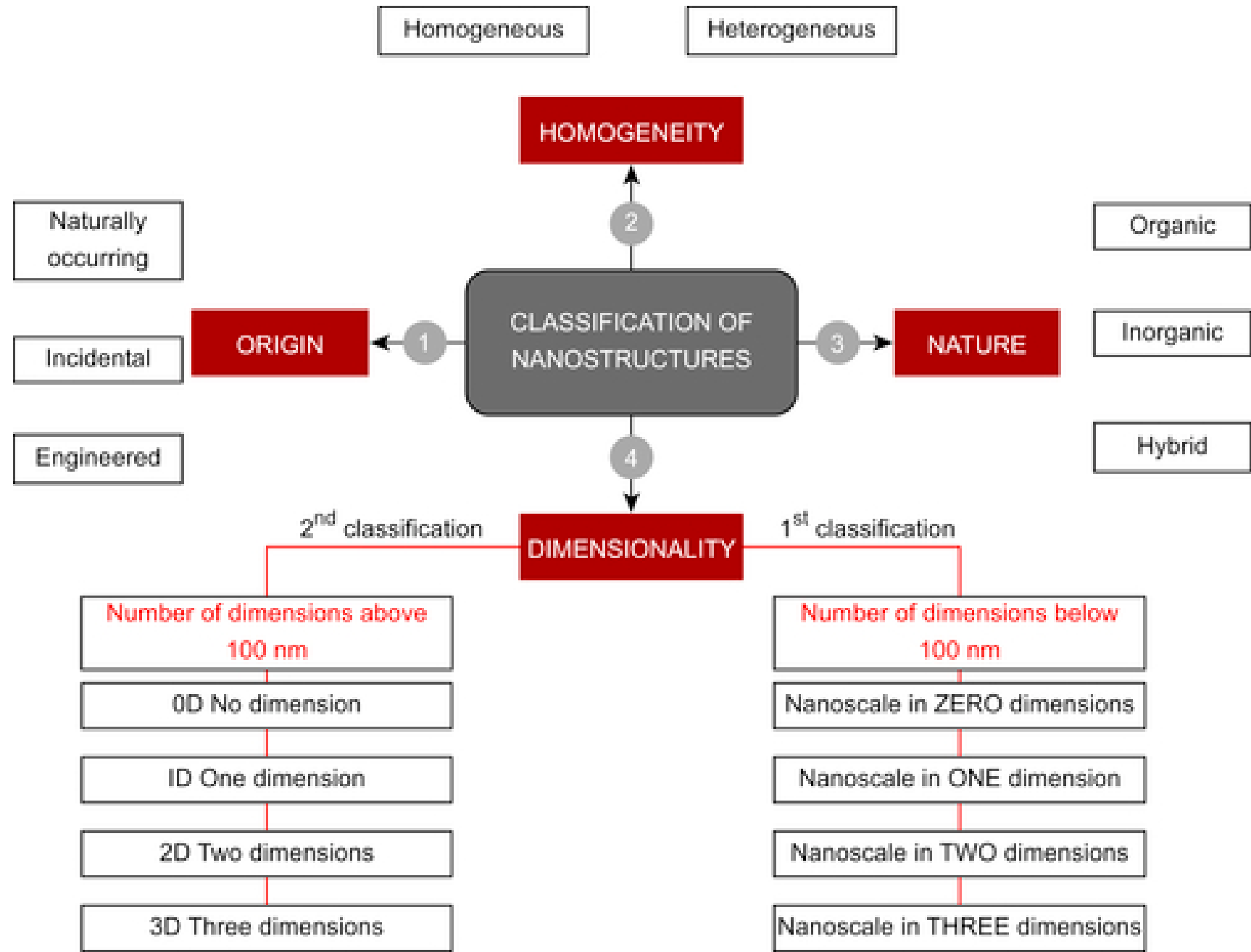


A Few Classes of Nanomaterials

- There are wide varieties of nanostructures which have been **classified in multiple ways** in the literature.
- Adjoining Figure shows the most relevant types of nanostructures in nanoscience and nanotechnology, classified according to four nonexclusive criteria.



Types of Nanoparticles (contd.)

- ❑ Nanoparticles can be classified as *natural*, *anthropogenic* (incidental), or *engineered* in **origin**.
- From a practical point of view, it is important to know the **homogeneity** of the nanostructured materials both for scientific studies as well as for industrial applications.
- **Homogeneity** can be referred to in terms of **chemical composition** or **dimensionality**.
- *Identical nanoparticles are those with the same chemical composition and dimensions.*
- On the contrary, *nanoparticles with the same chemical composition but different dimensions* usually present **different properties**.

❑ The other **classification of nanomaterials is based on dimensionality criteria.**

- As shown in the figure above, two classifications may be done, taking into account both the strict dimensions (in the nanoscale) of the nanostructure that give rise to those exceptional properties and the dimensions of the material where nanostructures are present.
- Many **authors have classified nanomaterials depending on the number of dimensions that exceed 100 nm**, being above the nanoscale, nanostructures being thus categorized as 0D, 1D, 2D, or 3D.
- A **0D nanostructure or nanoobject** is a material with all its dimensions comprised in the nanometric scale *with respect to a given length* (e.g., metallic nanoparticles, quantum dots, etc.).
- **1D nanostructures**, which have one dimension of micro/macrometric size (e.g., nanowires or nanorods, carbon nanotubes).
- **2D nanostructures** have two dimensions above nanoscale while one of them is below 100 nm. That is the case of surface nanocoatings or thin films of molecular monolayers.
- **3D nanostructures** are those whose three dimensions escape from the *nanoscale*, but the material *is comprised of a set of nanoparticles* forming a block of micro/macrometric size (e.g., nanoporous materials, powders).

Types of Nanoparticles (contd.)

- ❑ The Royal Society of Chemistry and the Royal Academy of Engineering classified **nanostructures in function of the number of dimensions in the nanoscale** (below 100 nm), distinguishing three types of nanostructures:
 - (1) nanoscale in one dimension, such as surfaces with nanometric thickness (e.g., graphene sheets);
 - (2) nanoscale in two dimensions, such as carbon nanotubes, inorganic nanotubes, nanowires, etc.;
 - (3) nanoscale in three dimensions, which includes metallic nanoparticles and their oxides, quantum dots, fullerenes, and dendrimers.
 - Classification of nanoscale at zero dimension can also be added, such as materials composed of dispersed nanoparticles.

A Few Special Classes of Nanomaterials

Concerning the nature or chemical composition of nanostructures, those are often classified according to their nature as *inorganic*, *organic*, or *hybrid*.

1. Inorganic Nanomaterials

- A) Semiconductor nanocrystals or Quantum dots
- B) Elemental metal nanoparticles
- C) Nanocarbons
- D) Magnetic nanomaterials
- E) Core-shell nanoparticles and so on....

2. Organic Nanomaterials (dendrimers, liposomes, molecular imprinted polymers, etc.)

3. Hybrid/Mixed Nanomaterials (well-organized nanomaterials consisting of two or more types of individual nanocomponents; e.g., gold nanoparticles modified with calixarenes, carbon nanotubes functionalized with ferrocene, etc.).

4. Nanocomposites, Metal-Organic Framework (FOM), and so on.....

A Few Special Classes of Nanomaterials

Nanomaterials particles are often classified according to their nature as *inorganic*, *organic*, or *hybrid*.

1. Inorganic Nanomaterials: *Inorganic nanoparticles* are engineered nanoparticles *made from inorganic sources*. Inorganic nanoparticles cover a broad range of substances: *semiconductor nanocrystals, elemental metals, metal oxides*, metal salts, and so on.....

- A) Semiconductor nanocrystals or Quantum dots** (Group II–VI (e.g., CdSe, CdTe, CdS, and ZnSe), III–V (e.g., InP and InAs), or IV–VI (e.g., PbSe), etc.)
- B) Elemental metal nanoparticles** (Plasmonic (e.g., Ag, Au, etc) nanoparticles; Pd nanoparticles, etc.)
- C) Nanocarbons** (Carbon nanoparticles, carbon nanotubes (CNTs), graphene, etc.)
- D) Magnetic nanoparticles** (Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$, pure metals, such as Fe and Co, and spinel-type ferromagnets, as well as alloys)
- E) Hybrid/Core-shell nanoparticles** (silica core-gold nanoshell)

➤ Moreover, there are other nano-size inorganic *metal oxides*, **silica (SiO_2)**, metal salts, **zeolite**, **clays**, **ceramics** and so on have been prepared and proposed for various applications.

A Few Special Classes of Nanomaterials

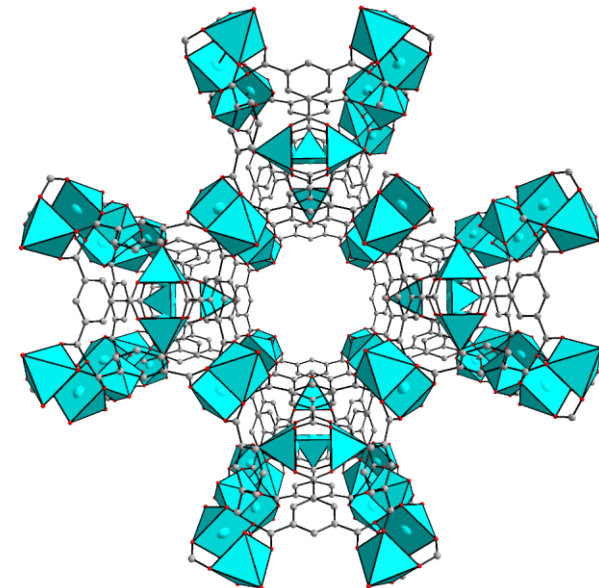
2. Organic Nanomaterials (e.g., DNA, RNA, polymers, polymeric micelles, liposomes, or nanoparticles prepared from polymers or lipids; Virus-based nanostructures,...)

3. Nanocomposites (polymer-nanoparticle composites)

Composites of different material systems can combine the advantages of both and sometimes more than that. Therefore, a variety of composite materials have been developed.

4. Metal-Organic Framework (FOM) and so on.....

Metal-organic frameworks are compounds of metal ions and organic molecules that form structured frameworks. These advanced materials can be compared with sponges with unique abilities – being able to take up, hold and release molecules from their pores. Therefore, metal-organic frameworks (MOFs) are the fastest-growing class of materials in chemistry today. By far, more than 20 000 MOFs have been found in the last 20 years.



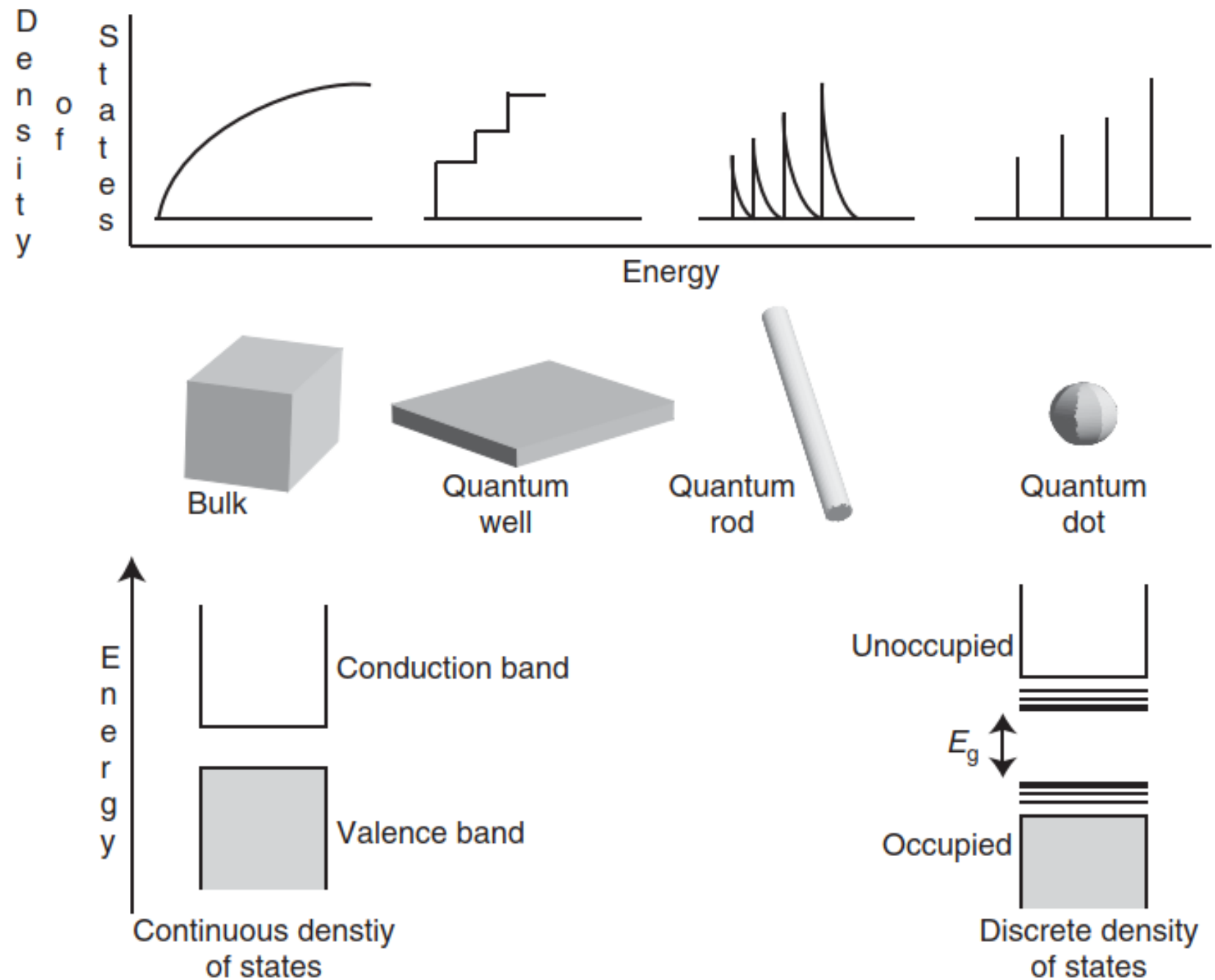
With a highly-ordered framework of pores, metal-organic frameworks exhibit the largest surface areas per gram known to man – one gram of MOF can have a surface area comparable to a FIFA soccer field. That is up to 7 000 sqm surface per 1 gram of MOF material. The large surface area offers more space for chemical reactions and adsorption of molecules. But this is not the only reason for the growing engagement of industries and academia towards metal-organic frameworks.

Semiconductor nanocrystals or Quantum dots (QDots or QDs)

- ❑ Semiconducting nanoparticles have been investigated intensively for their optical properties.
- ❑ These particles are often called **quantum dots (QD)** because quantum effects become important in *these three-dimensionally confined particles (dots)*.
- We know that in atoms and small molecules, electrons occupy discrete atomic/molecular orbitals, whereas in macroscale solids the electrons occupy delocalized bands.
- ❑ Semiconductors have valence and conduction bands separated by a band gap, E_g .
- ❑ For semiconductors, both theory and experiment tell us that when **the semiconductor particle size is roughly at 1 to 10 nm (about 10–100 atoms across) or below, the semiconductors show discrete energy states like molecules or atoms**. The exact number depends on the specific semiconductor material.
- The equations of quantum mechanics that were used for electrons in atoms can be applied to electrons (and holes) in semiconductors to estimate the size where materials undergo a crossover from molecular orbitals to bands.
- ❑ Because *these effects become important at ~1 to 10 nm, semiconductor particles with diameters in this size range are called quantum dots (or artificial atoms)*.

FIGURE 10.1 Diagrams illustrating the fundamental principles of quantum confinement and size-dependent properties of semiconductor quantum dots.

- As the dimensionality decreases, the energy levels become less continuous and more discrete. In zero-dimensional structures such as quantum dots, the energy levels appear as sharp, quantized lines.
- The QD bandgap energy is the function of particle size, which allows continuous tuning of the emission wavelength.



Metals on the Nanoscale

- Metals also show unusual properties on the $\sim 1\text{--}100\text{-nm}$ length scale.
- Fundamentally, this is because the *mean free path of an electron in metal at room temperature is typically about $1\text{--}100\text{ nm}$* . So, when the particle size of metal is $\sim 100\text{ nm}$ or less, one might expect unusual effects because the “sea of electrons” encounters a “shore” (the surface of the particle).
- Both the *physical and chemical properties of metallic nanoparticles may be different from the properties of the bulk materials*.
- ✓ Gold particles less than 20 nm in diameter melt at a far lower temperature than bulk gold, for instance, and when the particles are between $2\text{ and }3\text{ nm}$ in diameter, gold is *no longer a “noble,”* unreactive metal; in this size range, it becomes chemically reactive.
- ✓ At nanoscale dimensions, silver has properties analogous to those of gold in its beautiful colors, although it is more reactive than gold.

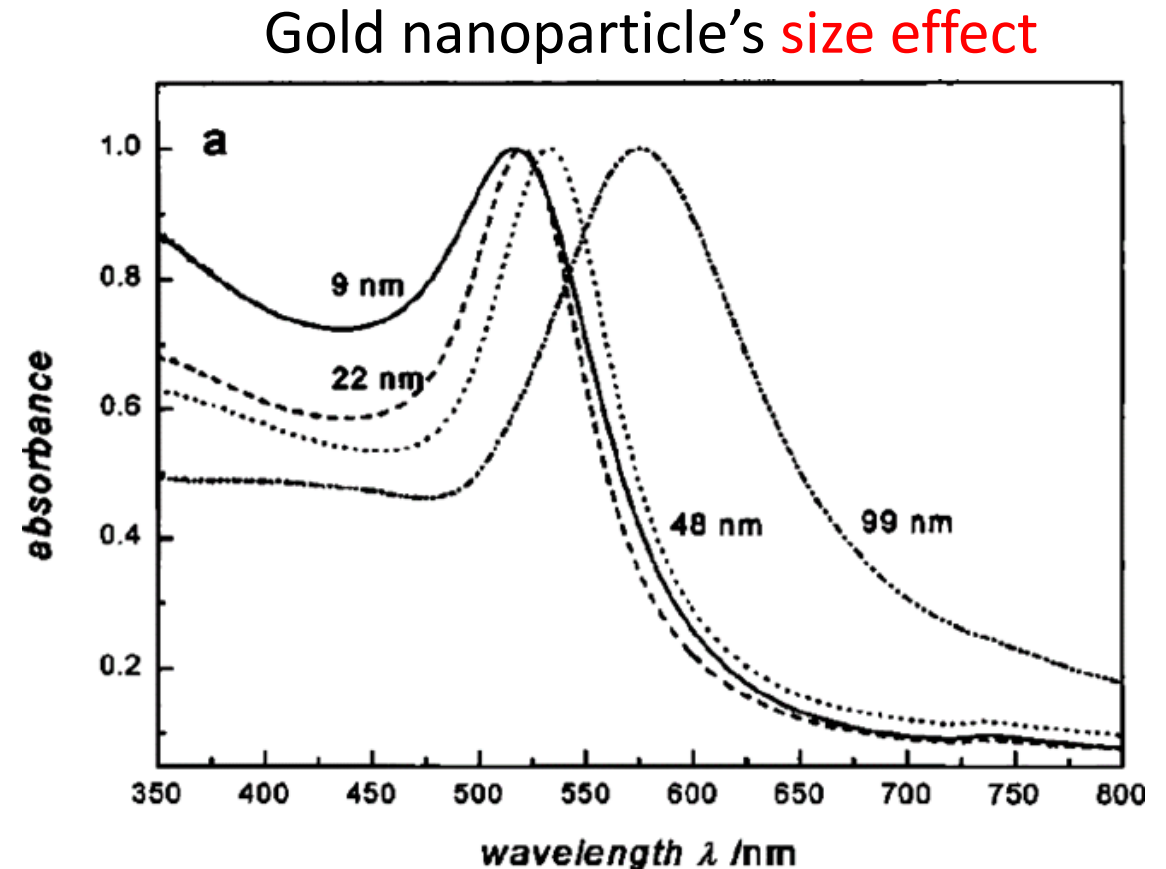
Metals on the Nanoscale: Optical Properties

- Light impinging on metallic particles causes optical excitation of their electrons. The principal type of optical excitation that occurs is the collective oscillation of electrons in the valence band of the metal. Such coherent oscillations occur at the interface of a metal with a dielectric medium and are called **surface plasmons**. At a certain frequency of the incident light there is a **resonance** at which there is *a maximum **absorption** or **scattering** of energy from the incident light wave and a peak is observed* in the absorption/scattering spectra. This peak is called the “**surface plasmon resonance (SPR)**” peak.
- *Quantized coherent oscillations of free electrons at the surface of the metal nanoparticles (and dielectric interface) are called the **Surface Plasmon Resonance (SPR)**.*
- In nanoparticles, the **surface plasmons are localized** and plasmon excitation occurs with high intensity.
- ✓ *The SPR in nanoscale particles is known as **Localized Surface Plasmon Resonance (LSPR)**.*
- ✓ **Plasmonic Nanoparticles:** *The nanoparticles that show **LSPR**.*
- The peak intensity of the **surface plasmon absorption for gold and silver occurs in the optical region of the spectrum**, and so these **metallic nanoparticles are useful as pigments**.

Metals on the Nanoscale: Optical Properties

- ❖ The characteristics (viz., spectral *bandwidth*, *peak height*, and the *peak wavelength* of *plasmon absorption* depend on the nanoparticle's chemical *composition*, *size*, *geometrical shape*, *surface charge*, *surface-adsorbed species*, *interparticle interactions*, and the *dielectric property* of the surrounding environment.

Fig. 5.4. Experimental extinction spectra of gold nanoparticles of *diameters 9, 22, 48 and 99 nm*. (reprinted with permission from American Chemical Society).



MAGNETIC NANOPARTICLES

- Different magnetic nanocrystals were prepared from metals, Fe, Co, Ni, FePt, etc. and metal oxides Fe_3O_4 , Fe_2O_3 , MnO, CoO, MnFe_2O_4 , and CoFe_2O_4 .
- The size of the nanocrystals can be as small *as five nanometers*. Furthermore, recent studies have demonstrated the ability to form a *single crystalline 30 nm* magnetite (Fe_3O_4) nanotube.
- Some research is focused on the coating of magnetic nanoparticles with various organic materials. One example is the use of lipid coating with results in water-soluble magnetic nanoparticles.
- In addition to electronic conductivity, *magnetism is another unique property*.
- Several *characteristic length scales* in the nanometer range exist in magnetism. An important length scale for the magnetic phenomena at nanoscale is the **domain size** in ferromagnetic crystals. Typically, *the domain size is in the range 10-200 nm*.
- ✓ One of the important (size) effects that is observed as a result of this is the phenomenon of **superparamagnetism** in nanometer-sized ferromagnetic crystals.

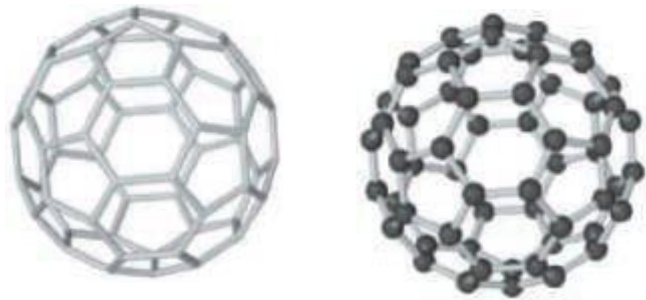
- Another very important application of magnetic nanoparticles is their use as **contrast agents in magnetic nuclear imaging (MRI)**.
- The phenomenon of ***giant magnetic resistance*** arises due to the spin of the electrons and is observed in a stack of alternating, nanometer thick, magnetic and nonmagnetic layers. ***The ability to control and manipulate the spins of electrons, has given rise to a whole new field of spin-based electronics or spintronics*** where the electron carries not only the ***charge*** but also information in the form of its ***spin***.
- *High-density data storage needs magnetic particles.*
- Magnetic nanoparticles are very useful both as the media for **storage** as well as part of nanoscale **reading heads**.

Nanocarbons

- Almost one-fifth of the weight of the human body is carbon, which is more than any other element except oxygen. Not only most biological entities such as proteins, nucleic acids, and lipids are C-containing organic compounds but much of the common industrial products such as nylon, plastic, Teflon, etc. are made of carbon as a key constituent. Also new materials including hyper-strong but light-weight materials such as KEVLAR® are based on organic entities such as aromatic amides.
- Carbon can be obtained in nature in several forms.
- Until 1985, the known allotropic forms of carbon were ***amorphous, graphite, and diamond***.
- This by itself shed some light of the diversity of carbon organization at the molecular level, as *graphite is one of the softest* materials known in nature while *diamond is of course one of the hardest*. ***That implies that the precise molecular organization of the carbon can dramatically affect its macroscopic properties.***
- The ease with which carbon forms conjugated p electron systems leads to several geometries that can carry electricity, including conducting polymers. Carbon continues to draw our attention more than any other element, as research continues to search for ways to efficiently capitalize on the electronic and structural properties of these novel materials.

Nanocarbons

- We have seen that elemental carbon is quite versatile. In its bulk sp^3 -hybridized solid-state form, it is diamond; in its bulk sp^2 -hybridized solid-state form, it is graphite.
- Over the past four decades, scientists have discovered that sp^2 -hybridized carbon can also form discrete (0D) *molecules*, one-dimensional (1D) *nanoscale tubes*, and two-dimensional (2D) *nanoscale sheets*. Each of these forms of carbon shows very *interesting properties*.



Buckminsterfullerene, C_{60} . The molecule has a highly symmetric structure in which the 60 carbon atoms sit at the vertices of a truncated icosahedron. The bottom view shows only the bonds between carbon atoms.

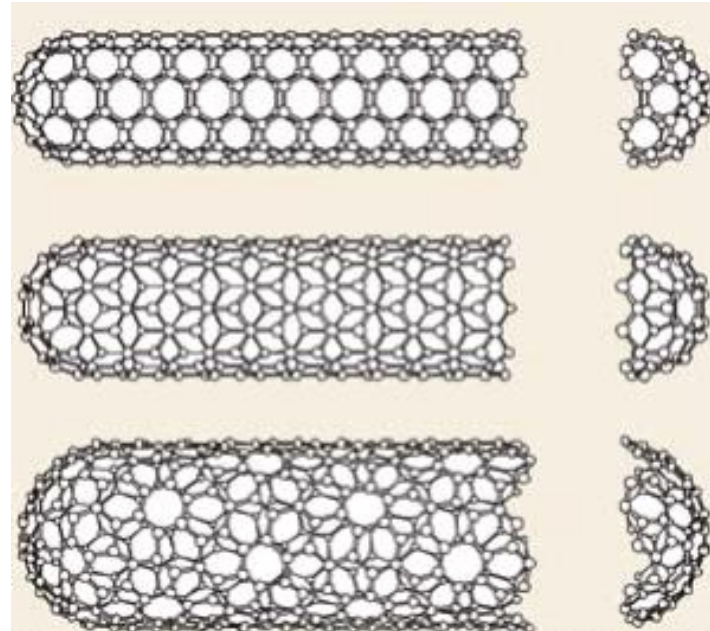


Figure 12.50 Atomic models of **carbon nanotubes (CNTs)**.

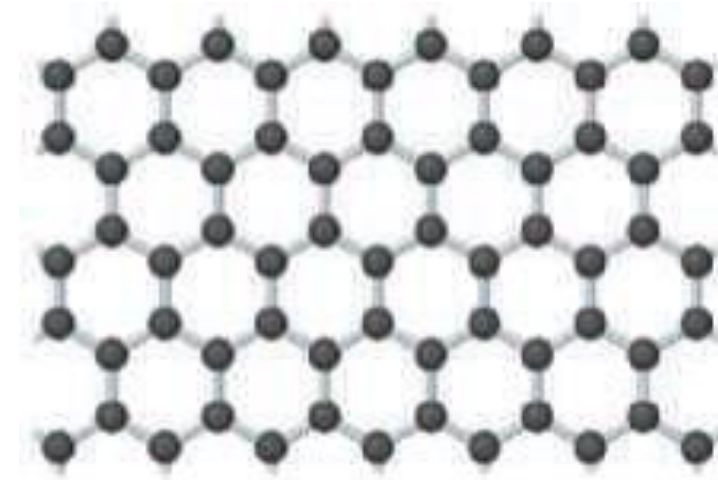


Figure 12.51 A portion of a two-dimensional **graphene** sheet.

Organic Nanomaterials

- *Nanoparticles can be considered as objects in-between the compact organic compounds and single molecules.*
- The progress in biochemistry and nanomedicine is determined by the properties of complex organic compounds, which, in addition to carbon and hydrogen, can include atoms of oxygen, sulfur, and halogens, and also by the mechanisms of processes involving these compounds.
- **Organic nanoparticles** (NPs) are templated upon *natural* or *synthetic* organic molecules.
- Nature provides a wide range of examples of organic NPs such as protein aggregates, lipid bodies, milk emulsions, or more complex organized structures such as viruses, to name a few.
- One of the most important features of organic NPs is that they offer relatively simple routes for the encapsulation of materials.
- This together with the fact that the molecules used for the fabrication of the organic NPs can be biodegradable makes organic NPs the most appealing systems for drug delivery and biomedical applications.

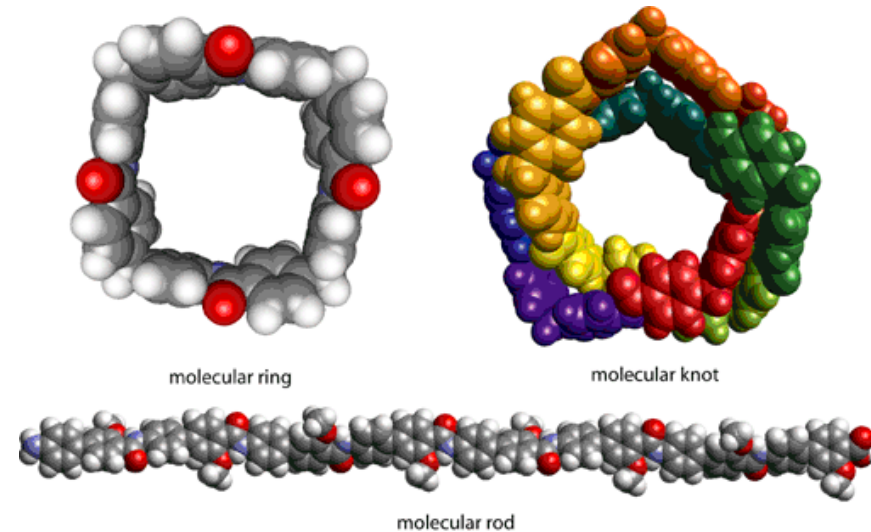
- Organic NPs are part of many *industrial products*, mostly ***food*** and ***cosmetics***.
- Many food products such as creams, chocolate, and cakes present nanoemulsions in their formulation and that is also the case in the cosmetic industry.
- Organic NPs are used in ***pharmaceutical formulations***, that is, liposome vectors, polymersomes, polymer–protein, or polymer–drug conjugates.
- Organic NPs are also used in agriculture.

Polymeric nanoparticles (PNPs)

- Polymeric nanoparticles (PNPs) have attracted considerable interest over the last few years due to their unique properties and behaviors resulting from their small size.
- These nanoparticulate materials show potential for a wide range of applications such as diagnostics and drug delivery.
- Advantages of PNPs as carriers include controlled release, the ability to combine both, therapy and imaging (theranostics), protection of drug molecules and its specific targeting, facilitating improvements in the therapeutic index.

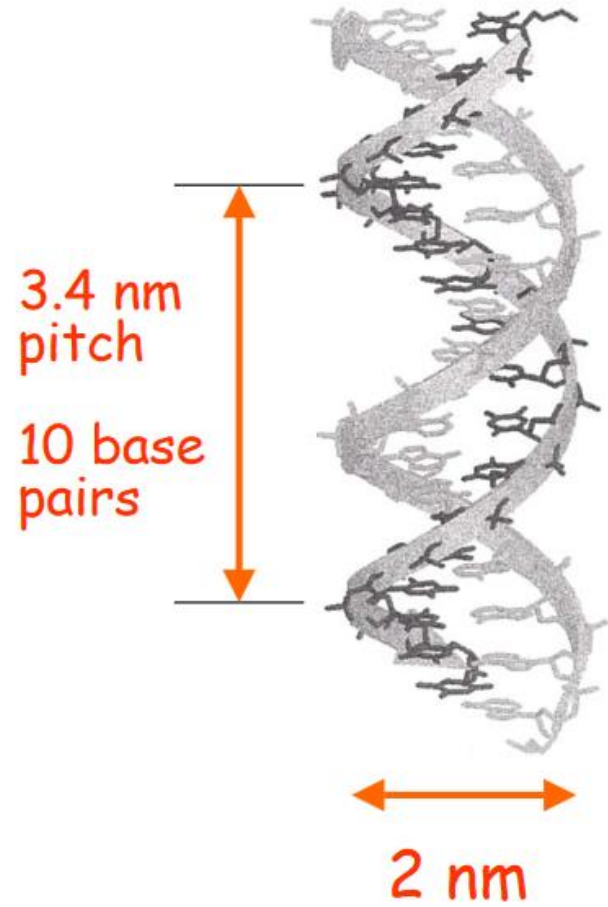
Biomolecular Nanotechnology

- Chaperone structures
- DNA templating
- Synthetic biology
- Synthetic proteins
- Liposomes and novel cellular structures



Biological Length Scales

DNA



Virus (TMV)

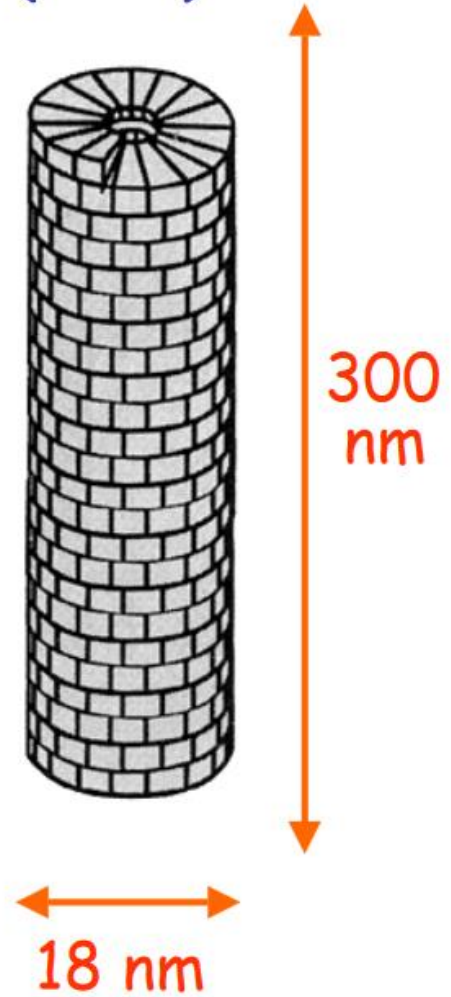
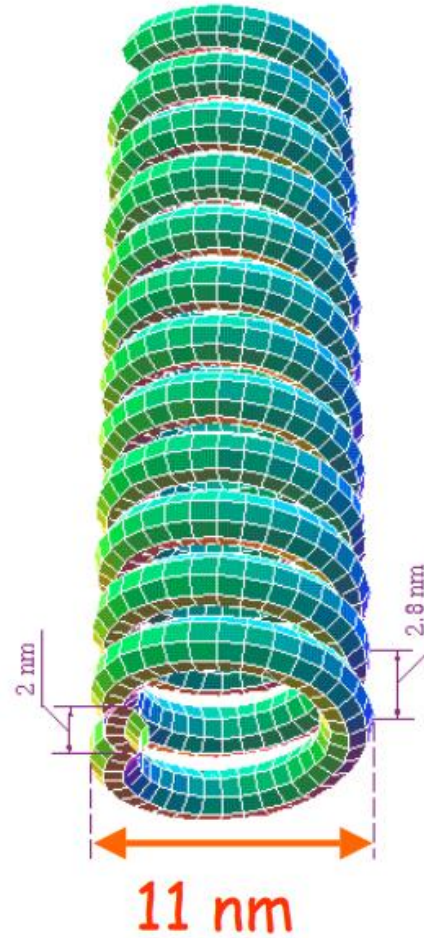


TABLE 4.1 Summary of the Organic NPs Fabricated via “Bottom-Up” Techniques

Nanoparticle Type	Composition	Size	Fabrication Techniques	Applications
Micelles	Amphiphilic molecules	Since 15–20 Å	Self-assembly	Drug delivery
Vesicles and liposomes	Natural and synthetic glycolipids and phospholipids	30–400 nm	Self-assembly, solvent-free techniques and solvent displacement techniques	Nanocarriers for drug delivery, food industry, and cosmetics
Polymersomes	Amphiphilic block copolymers	50–200 nm	Self-assembly, solvent-free techniques and solvent displacement techniques	Nanocarriers for drug delivery, labeling, and tracking and in environmental field to entrap selective toxic molecules
Polymer conjugates	Polymers, proteins, and drugs	5–20 nm	“Grafting to,” “grafting from,” and “grafting through” using ATRP and RAFT	Pharmaceutics as polymer therapeutics
Dendrimers	Polymers	From 10 nm	Divergent and convergent methods	In the biomedical field for <i>in vitro</i> diagnosis, as contrast agents, as drug delivery systems, as therapeutic agents, in gene therapy, and in regenerative medicine. In the industry to improve processes like nanocatalysis or in purification
Nanocapsules	Polymers	From 20 nm	Interfacial polymerization and by direct deposition of preformed polymers	Nanocarriers for drug delivery
Polymeric nanoparticles	Polymers	From 20 nm	Interfacial polymerization and by direct deposition of preformed polymers	Nanocarriers for drug delivery