INTRODUCTION

❑ *NANO* in NANOMATERIALS

➢ The prefix ‘nano’ means 10^{-9} : it denotes *one billionth* of the base unit.

✓ 1 Nanosecond= 10^{-9} second. **1 Nanometer** = 10^{-9} m (10 angstrom, Å).

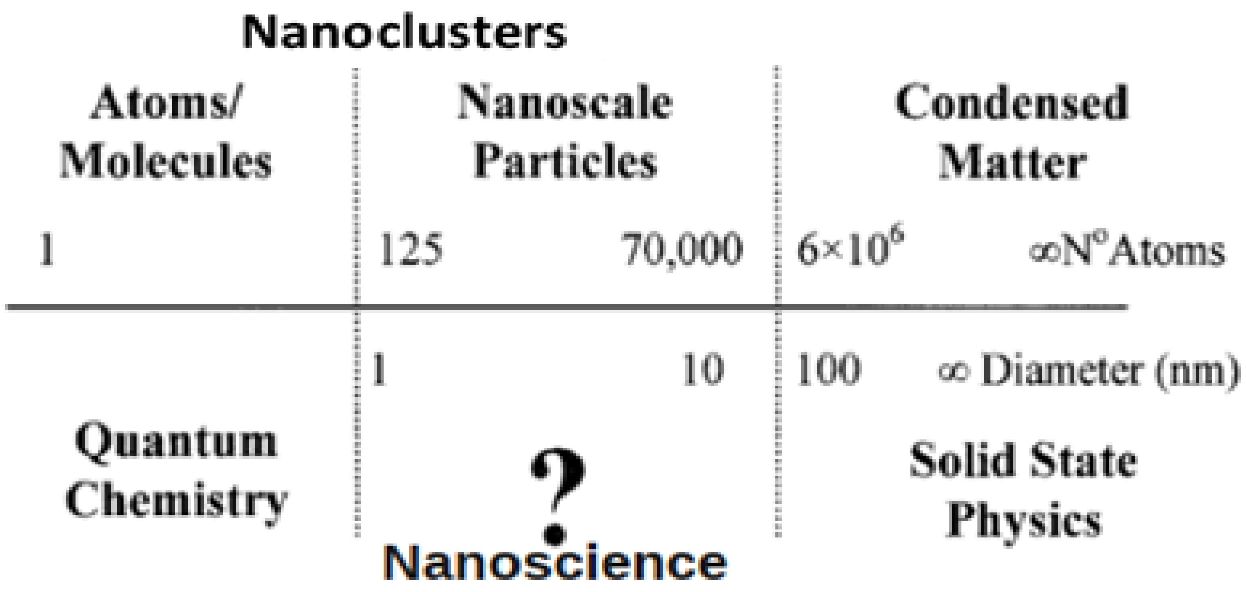
Table 1.1 The world of small dimensions

Number	Name	Symbol
0.1	deci	d
0.01	centi	c
0.001	milli	m
0.000 001	micro	μ
0.000 000 001	nano	n
0.000 000 000 001	pico	p
0.000 000 000 000 001	femto	f
0.000 000 000 000 000 001	atto	a
0.000 000 000 000 000 000 001	zepto	z
0.000 000 000 000 000 000 000 001	yocto	y

NANOMATERIALS

- **Nanomaterials**—are under intense investigation in research laboratories around the world.
- ✓ It turns out that the properties of semiconductors and metals in this size range differ substantially from their bulk.
- A ***nanomaterial*** is taken to be a solid material that exists over the scale of ~1 to ~100 nm and exhibits novel properties that are related to its scale.
- **Nanoscience** is the study of the properties of matter that have length scales between ~1 and 100 nm.
- ✓ When people speak of "**nanotechnology**," they usually mean making devices that are on the ~1–100 nm scale.
- **Nanotechnology** is the collection of procedures for manipulating matter on this scale in order to build nanosized entities for useful purposes.

Size relationships of chemistry, ‘nanoscience’, and condensed matter physics



SIZE COMPARISONS

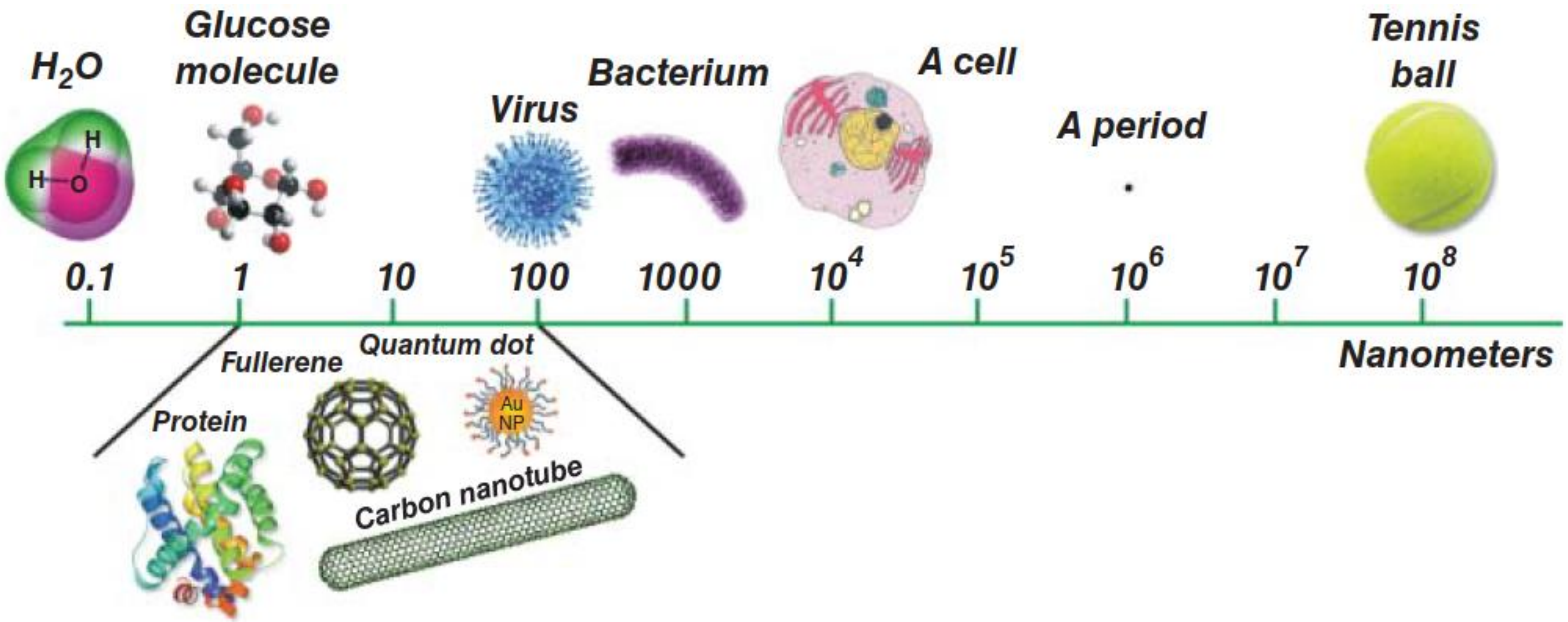


Figure 1.1 Size comparisons of objects, nanomaterials, and biomolecules.

THE NANOWORLD

- Approx. how many gold atoms are there in a 1 nm linear chain?

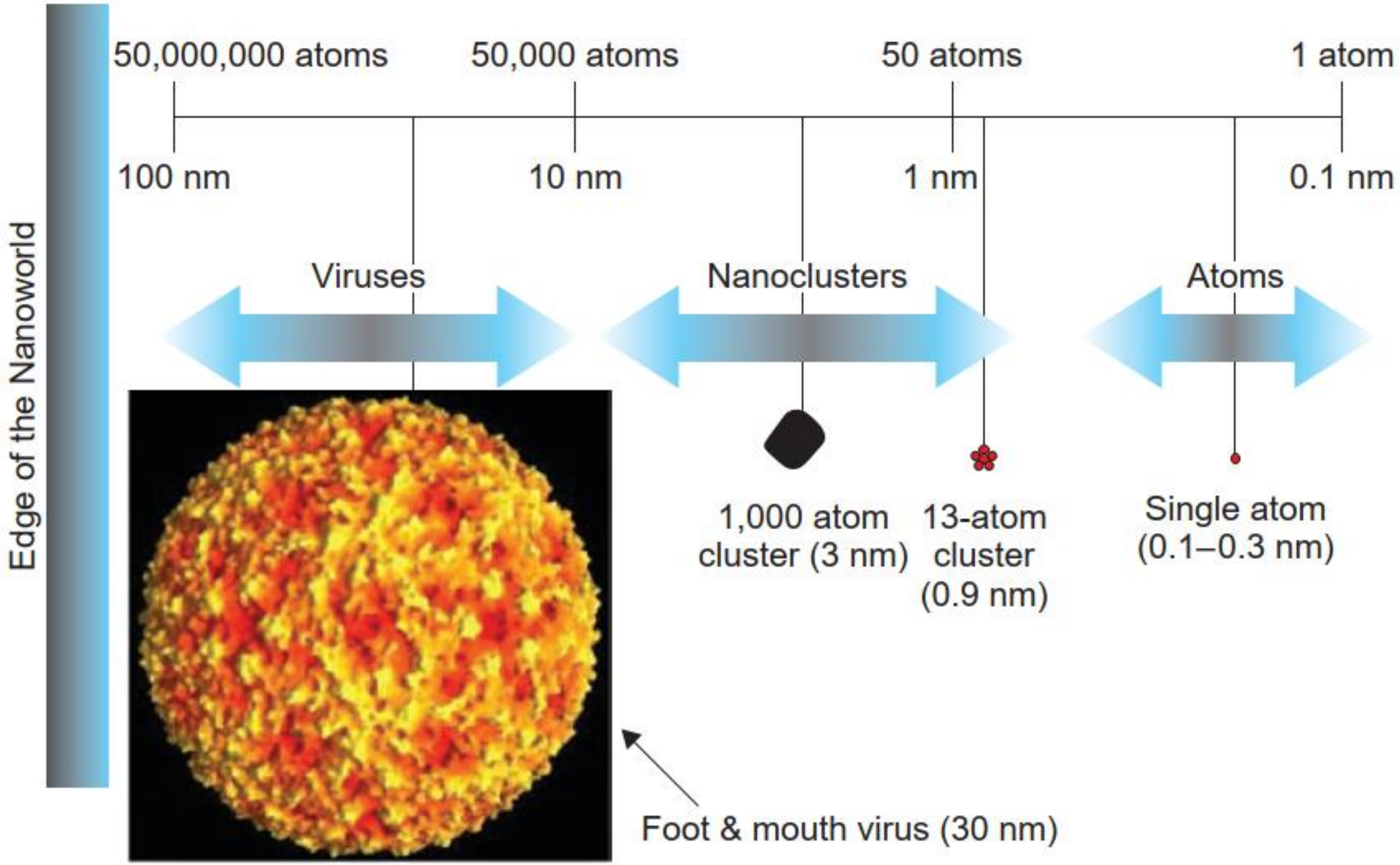
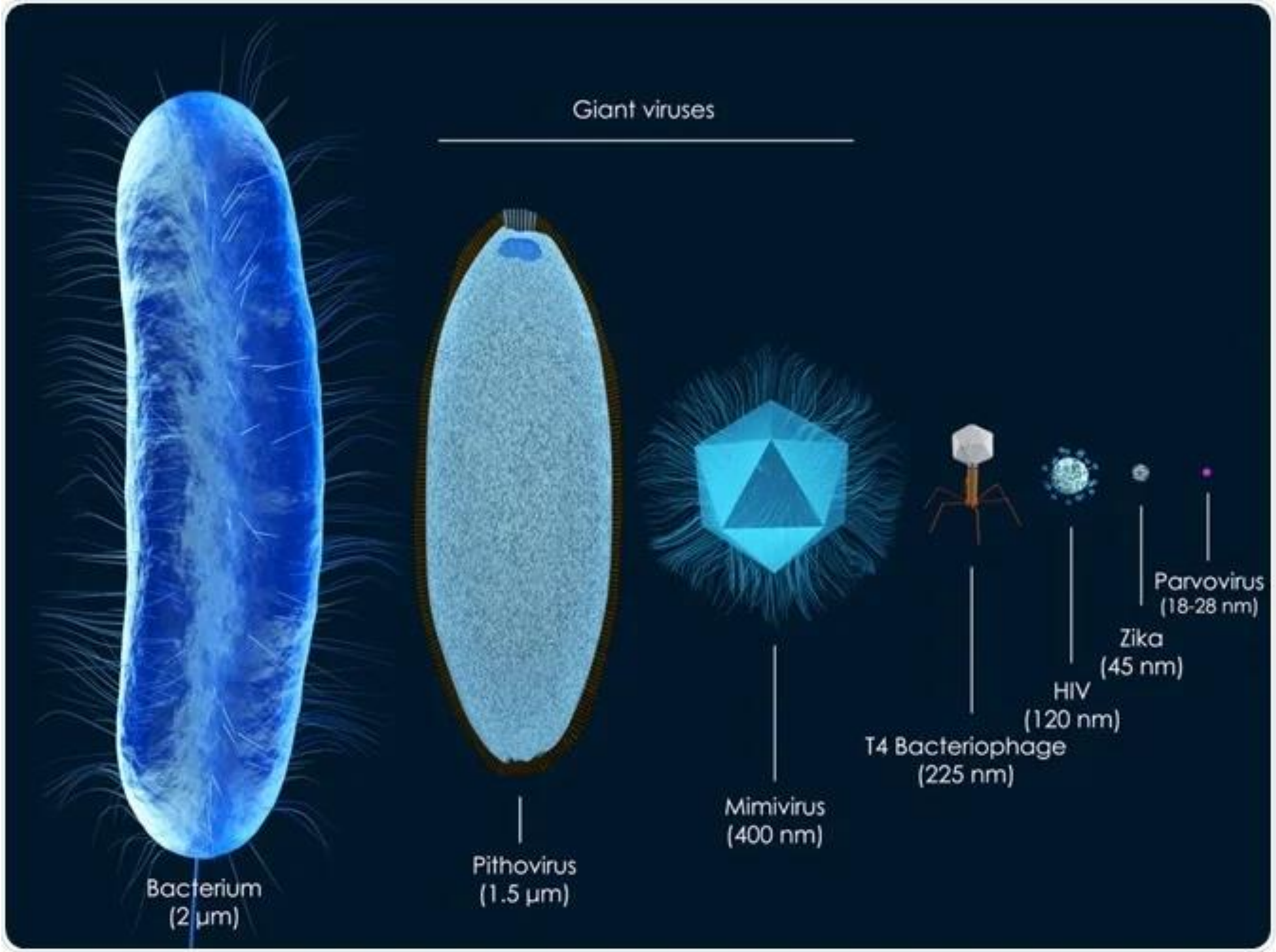
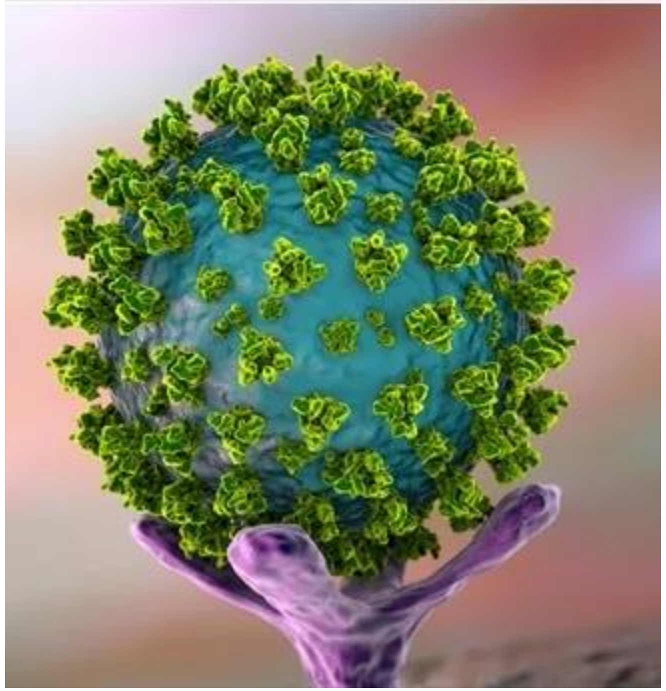


Fig. 1.2 The size range of interest in nanotechnology and some representative objects.

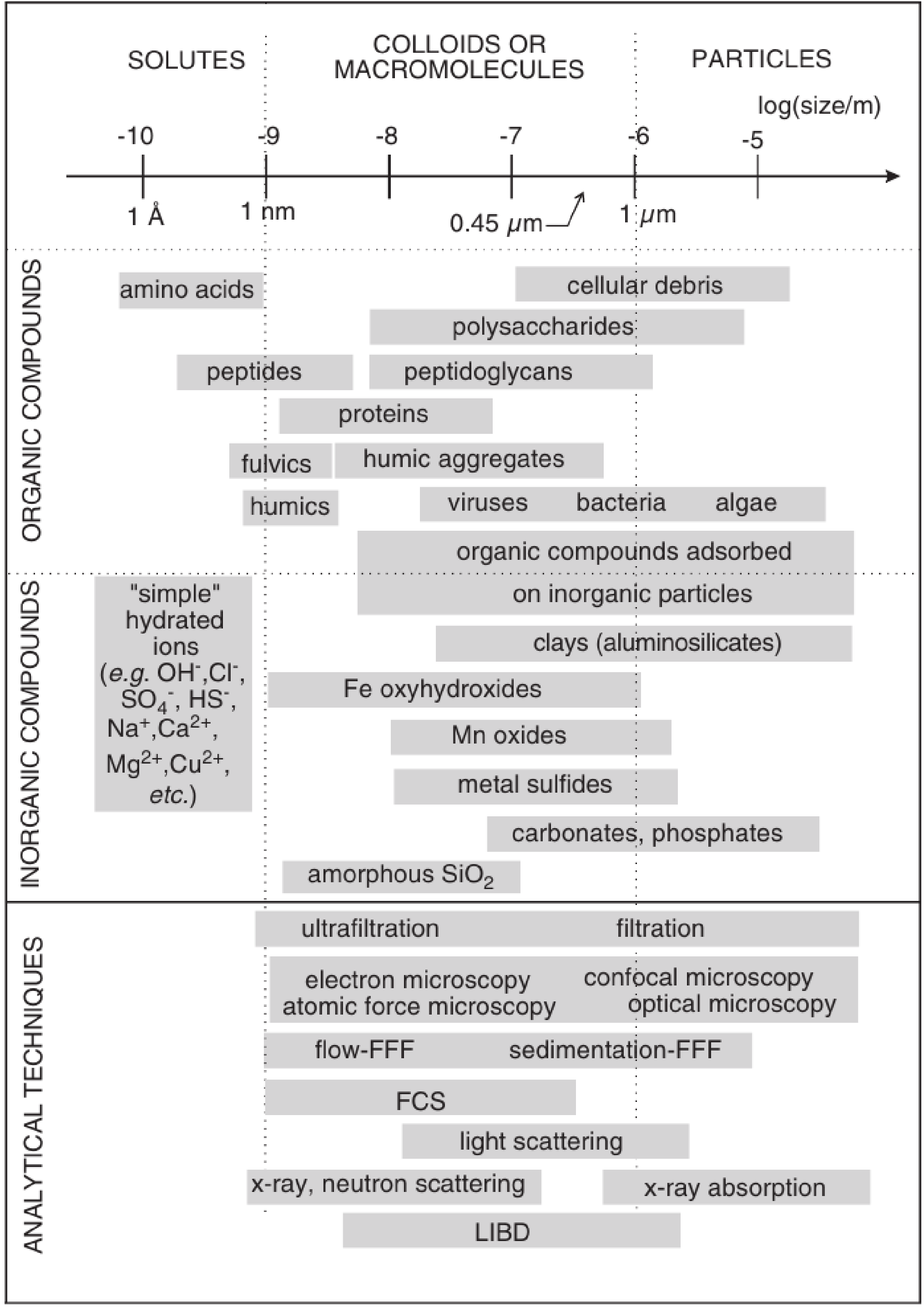




- ➢ Diameter of the SARS-CoV-2 virus ranges between 50 nm to 140 nm.

- ✓ The length of the size tumors surrounding the outermost surface of SARS-CoV-2 can vary in length from 9 to 12 nm.

- Important inorganic and organic naturally occurring nanoparticles and larger solid phases and important separation and analytical techniques used to characterize them.



- As shown in the above Fig., viruses are small enough to be inhabitants of the nanoworld whereas bacteria are much larger, being typically over 10 μm (10,000 nm) in size, *though they are packed with "machinery" that falls into the size range of the nanoworld*.

- Going down in size, the figure shows typical sizes of metal particles, containing ~1000 atoms that can be used to produce advanced materials.

✓ *The properties of these (per atom) deviate significantly from the bulk material*, and so assembling these into macroscopic chunks produces materials with novel behavior.

- Finally, the lower edge of the nanoworld is defined by the size of single atoms, whose diameters vary from 0.1 nm (hydrogen atom) to about 0.4 nm (uranium atom).

- We cannot build materials or devices with building blocks smaller than atoms, and so these represent the smallest structures that can be used in nanotechnology.

UNIQUENESS OF THE NANOSCALE

- **Why should we study 'nanoscience and nanotechnology'?**
- **Why should a fundamental branch of science – *one that is applicable to all sciences* – be named using the *nano* prefix?**
- ***What is so special about this length scale?***

✓ The ***answer lies in the properties*** of any substance ***that is this small (~1 to ~100 nm at least in one dimension)***.

Let’s consider the melting point of gold.

Gold’s melting point is listed at exactly **1,064°C** (1,947°F) in any reference book for metals.

What do you expect if one melts a tiny nugget that is only

a few nanometers in diameter?

The ***melting temperature in this second case is only 427°C*** (800°F).

Have we made a mistake? No!

In the nanosize range, the smaller the particle, the lower the melting temperature.

DEFINITIONS, TERMS and CLASSIFICATION OF NANOMATERIALS

- **Nanomaterials**: A material with *any external dimension* in the nanoscale (the length ranging from approximately 1 nm to 100 nm) or *having internal structure or surface structure* in the nanoscale — *International Organization for Standardization (ISO)*

- It may be that a unique **definition of nanomaterials** is impossible, but it seems that **a good definition needs to *refer to the nanoscale*** (either a **nano-object** – ***a material confined in one, two, or three dimensions at the nanoscale*** (the size typically range between 1 nm and 100 nm) or a **nano-structured** material – ***having an internal or surface structure at the nanoscale***); to the fact that **it has unique properties as a consequence of the scale**; and **whether it is natural or manmade.**

- Though the dimension is taken as less than approximately 100 nm, some organizations in some areas such as ***environment, health, and consumer protection*** favor ***a larger size range*** from ***0.3 to 300 nm to define nanomaterials***. This larger size range allows more research and a better understanding of all nanomaterials and allows to know whether any particular nanomaterial shows concerns for human health or not and in what size range.

DEFINITIONS, TERMS and CLASSIFICATION OF NANOMATERIALS

- Nanomaterials can be metals, ceramics, polymers or composites.
- Nanomaterials can be ***nanoscale in one dimension*** (e.g., surface films) ***two dimensions*** (e.g., strands or fibers) or ***three dimensions*** (e.g., precipitates, colloids).
- ✓ They can exist in *single, fused, aggregated, or agglomerated forms with spherical, tubular, and irregular shapes*.
- Nanocarbons such as fullerenes, carbon nanotubes, and graphene are excellent examples of nanomaterials.
- Siegel ***classified*** nanostructured materials into four categories according to their **dimensionality**: **0D**: nanoclusters or quantum dots, **1D**: nanotubes, nanowires, **2D**: nanograined layers and **3D**: equiaxed bulk solids (with *nanopores/structures*).
- Gleiter further classified nanostructured materials according to the **composition** (metals, semiconductors, polymers or composites**)**, **morphology** (rod, disc) and **distribution of the nanocrystalline component**. This classification includes many possible permutations of materials and is quite broad.

- **Nano-object**: Material confined in one, two, or three dimensions at the nanoscale. This includes *nanoparticles* (all three dimensions in the nanoscale), *nanofiber* (two dimensions in the nanoscale), and *nanoplates* (one dimension in the nanoscale).

- ✓ Nanofiber are further divided into *nanotubes* (hollow nanofiber) *nanorods* (solid nanofiber) and *nanowire* (electrically conducting or semiconducting nanofiber) However, the term nano-object is *not* very popular.

- **Nanostructures:** Materials ***having an internal or surface structure at the nanoscale*.** They are the ordered system of one, two, or three dimensions of nanomaterials, assembled with nanometer scale in certain pattern that includes nanosphere, nanotubes, nanorod, nanowire, and nanobelt.

- ✓ Nanostructured materials are classified as zero-, one-, two-, and three-dimensional nanostructures, showing typical examples with varied dimensionality in nanomaterials as in Figure 1.10 (a–i).

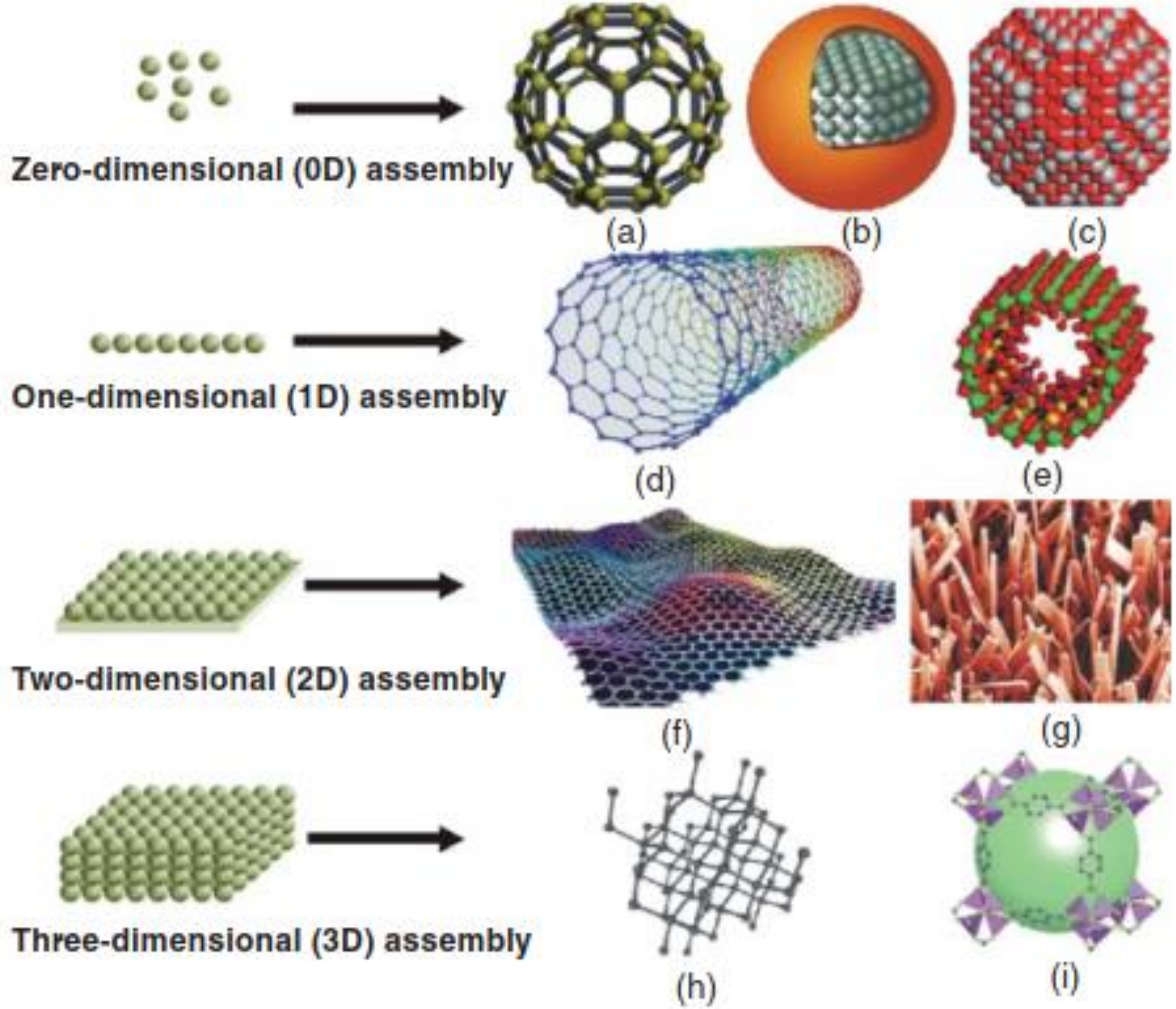
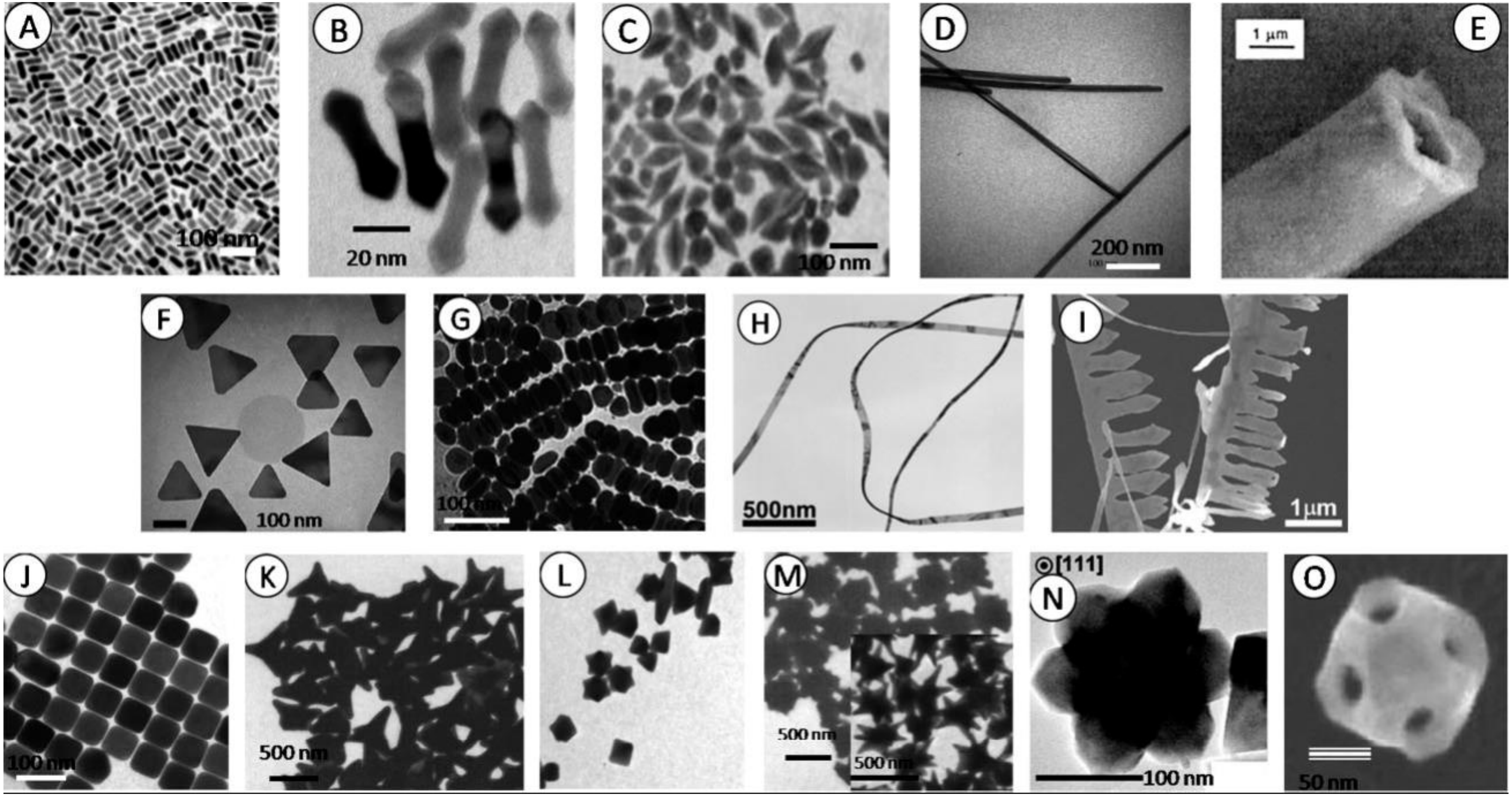


Figure 1.10 Typical examples showing varied dimensionality in nanomaterials: (a) fullerene; (b) quantum dot; (c) metal cluster; (d) carbon nanotube; (e) metal oxide nanotube; (f) graphene; (g) metal oxide nanobelts; (h) nanodiamond; (i) metal organic frameworks (MOFs).



Figure…. showing examples of various shapes of nanoparticles.

According to the shape of the crystallites, three categories of **nanostructured materials** are distinguished

- Rod-shaped crystallites (with layer thickness or rod diameter of the order of a few nanometres)
- Layer-shaped crystallites
- Nanostructures composed of equiaxed nanometer-sized crystallites.

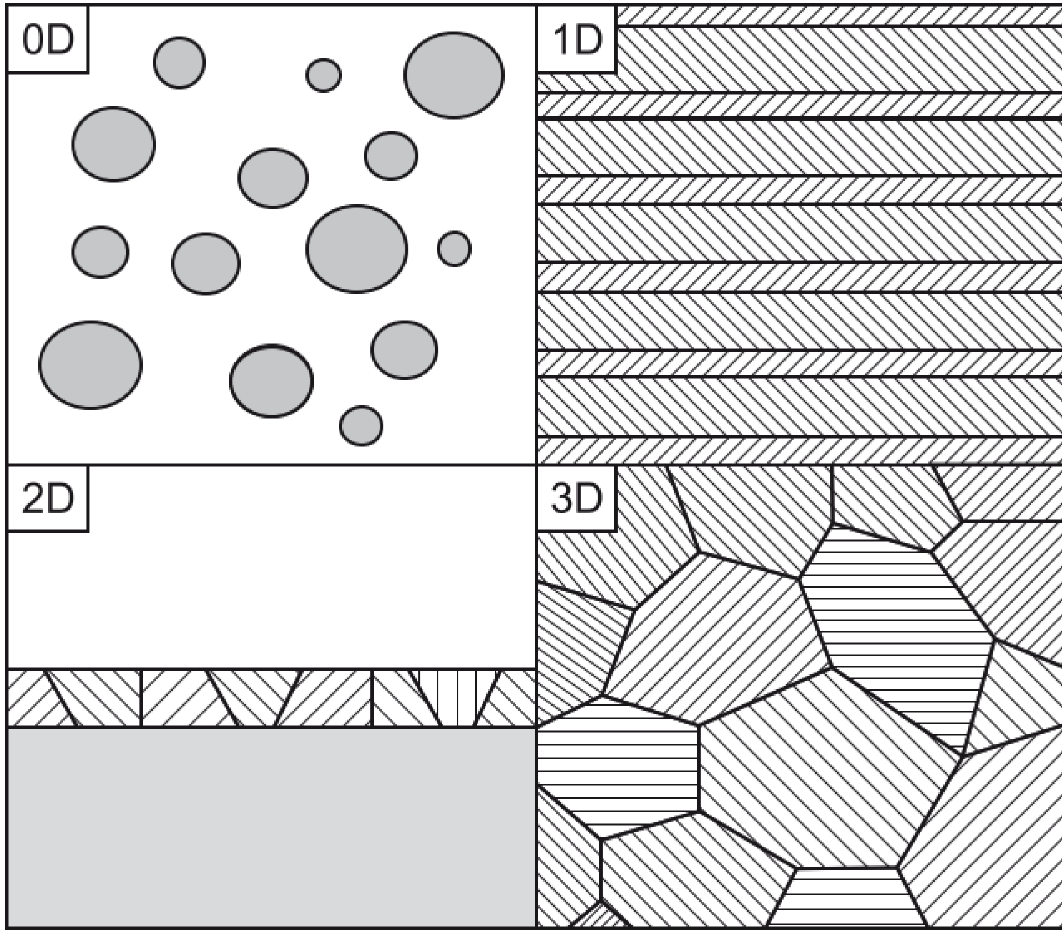


Fig. 1.13 Classification of nanomaterials.
(The boundary regions of the first and second family are indicated in black to emphasize the different atomic arrangements in the crystallites and boundaries).

A **nanocrystallite** is generally understood to possess ***crystalline order*** *in addition to nanoscale size*.

If **one dimension** of the 3D nanostructure is ***quantum confined***, then it is called a **Quantum Well**. If **two dimensions** of the 3D nanostructure are ***quantum confined***, then it is called a **Quantum Wire**.

If all the ***three dimensions*** of the nanostructure are ***quantum confined***, then it is called a **Quantum Dot**.

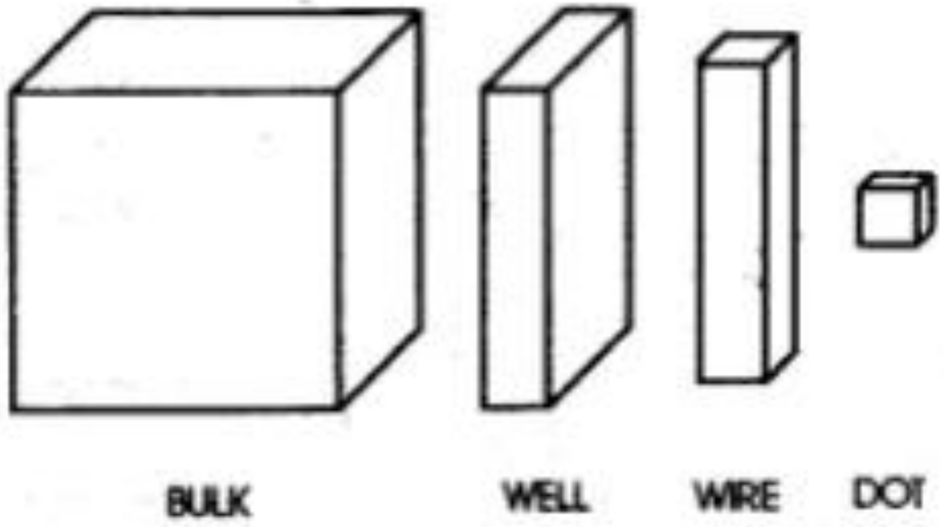


Figure 9.1. Progressive generation of rectangular nanostructures.

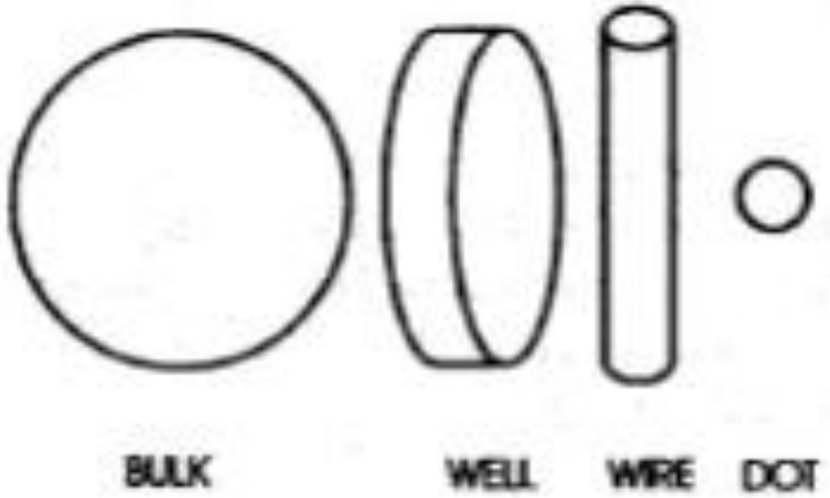
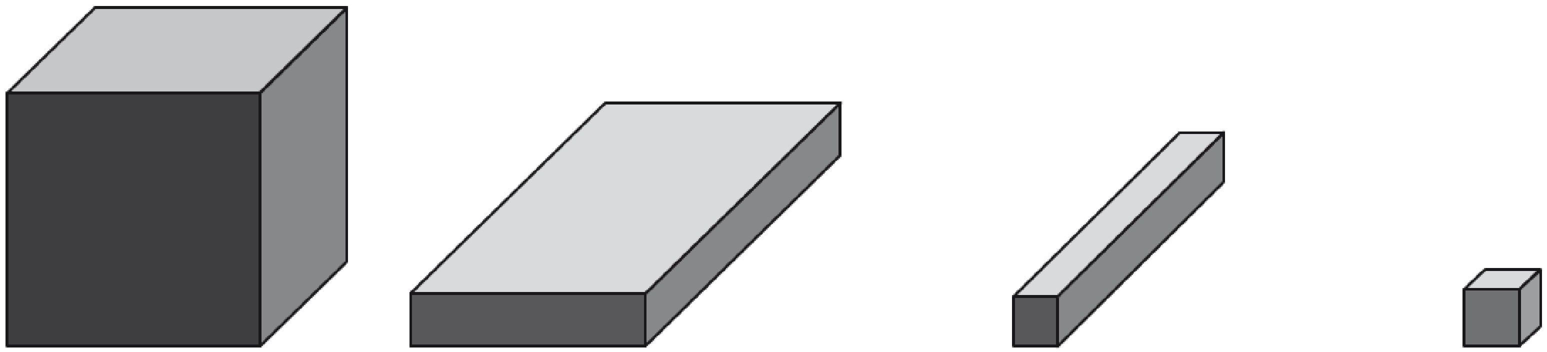


Figure 9.2. Progressive generation of curvilinear nanostructures.

- **Name** the following based on their quantum confinement



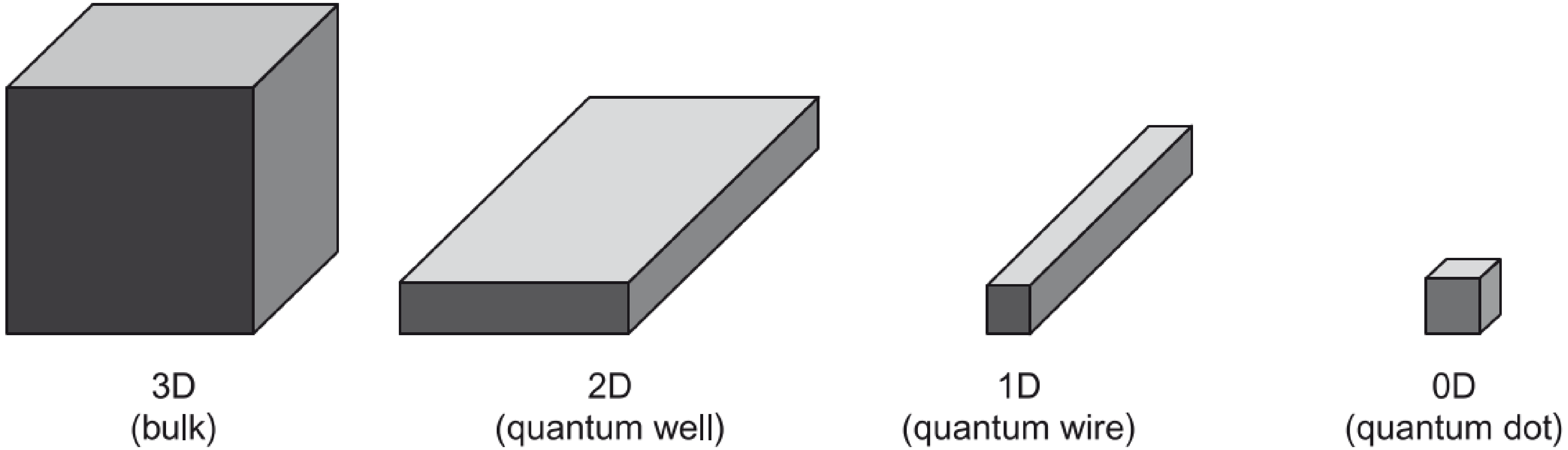


Fig. 1.12 Schematic diagram of quantum confinement in quantum well, quantum wire and quantum dot.

Particle: It is a minute piece of matter with defined physical boundaries. A particle can move as a unit. This general particle definition applies to *nano-objects*.

- ❖ **Nanoparticle**: It is a nano-object with ***all three external dimensions in the nanoscale***.
- ✓ Nanoparticles constitute of several tens or hundreds of atoms or molecules and can have a variety of sizes and morphologies (amorphous, crystalline, spherical, needles, etc.).
- ✓ Nanoparticles surfaces can act as carriers for liquid droplets or gases.
- ✓ Nanoparticles of different material classes, for example, metals, semiconductors, carbon, etc. have been prepared by means of several production techniques.
- ✓ *Industrial scale production of nanoparticulate materials* such as carbon black, polymer dispersions, or micronized drugs has been established for a long time.
- ✓ Another important class of nanoparticulate materials is ***metal oxide* nanopowder** that includes silica (SiO_2), titania (TiO_2), alumina (Al_2O_3), or iron oxide (Fe_3O_4, Fe_2O_3); *compound semiconductors* (e.g., cadmium telluride, CdTe or gallium arsenide, GaAs), *metals* (especially precious metals such as Ag, Au), and *alloys* are also included in this category that are being commercialized.
- ❖ **Nanoparticulate matter**: It refers to a ***collection of nanoparticles***, emphasizing their collective behavior.

FASCINATING NANOMATERIALS

- Nanomaterials may occur in ***several different geometric configurations*** *including wires, tubes, rods, horns, shells, pores, etc*. They possess unique properties and are being developed for specific applications. Some of these interesting and emerging trends in nanostructures are described below.

- **Linear nanostructures** such as **nanorods, nanotubes, or nanowires** can be generated from different material classes, for example, metals, semiconductors, or carbon, by means of several production techniques.

- **Nanorods: *Nanorods have typical aspect ratios* (=Length/Width) of *3–5***. *This means that unlike nanowires with an unconstrained dimension along the longitude,* ***nanorods have all their dimensions in the range 1–100 nm*** *and hence are* ***3D nanostructures***. They may be synthesized from a variety of materials and can find diverse applications ranging from display technologies (the reflectivity of the rods can be changed by changing their orientation with an applied electric field) to micromechanical switches.

❖ **Nanotubes:** These are **tubes with diameters in the nanoscale**. Although nanotubes of various other materials have been reported, carbon nanotubes are by far the most important group.

➢ **Carbon nanotubes (CNTs)** can occur in a variety of modification (e.g., single-, or multiwalled, filled or surface modified) At present, carbon nanotubes can be produced by CVD methods on a several tons per year scale.

➢ A ***single-walled carbon nanotube*** (SWCNT) is obtained by rolling a sheet of graphite (a hexagonal lattice of carbon) into a cylinder.

✓ Typical diameters of SWCNTs are in the range of 0.7–1.4 nm and their length can be several micrometres.

➢ ***Multi-walled carbon nanotubes*** (MWCNTs) can be regarded as a coaxial assembly of SWCNTs.

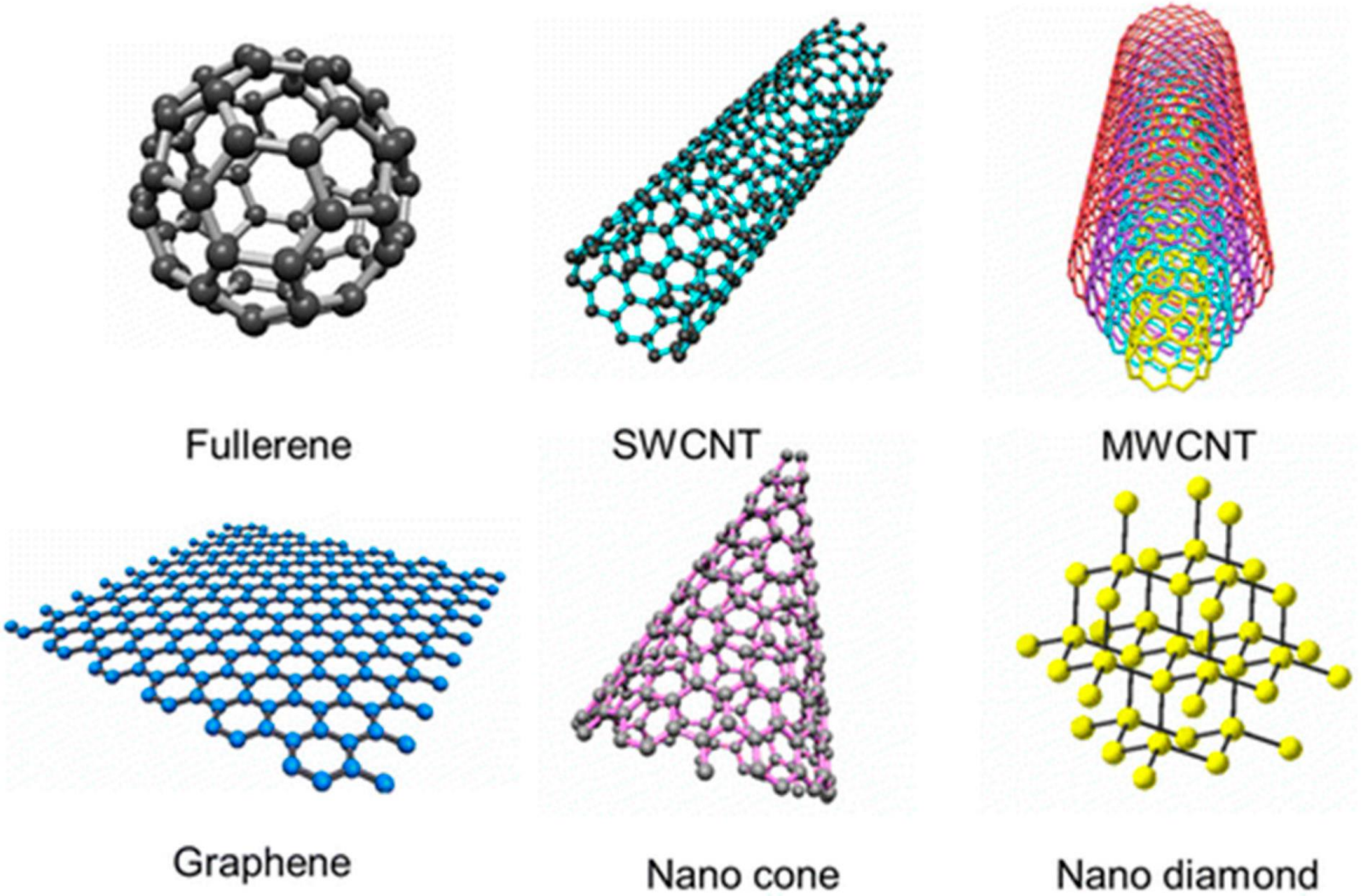
✓ MWCNTs have their diameters in the range of 5–50 nm.

✓ Carbon nanotubes are unique nanostructures with remarkable electronic and mechanical properties, some of which are due to the close relation between the carbon nanotubes and graphite, and some from their one-dimensional aspects.

✓ Carbon nanotubes also exhibit good nano-mechanical properties due to their high Young's modulus (a record of 1210 GPa by single-walled and of 1260 Gpa by multi-walled CNTs).

✓ In comparison, metallic wires such as copper and steel have a modulus of only 110 and 200 GPa, respectively.

Nanocarbons



- **Nanowires:** These can be defined as 1D nanostructures with nanometric width dimensions and exhibiting **aspect ratios** (***the ratio between length and width***) **of 1000 or more** (Fig. 1.16).

- ✓ *Nanowires exhibit interesting properties deviating from bulk behavior, due to quantum confinement in the lateral dimension*.
- ✓ Nanowires are also, therefore, frequently referred to as '***quantum wires***'.
- ✓ So far, nanowires of several metals (Au, Ni, Pt), semiconductors (InP, Si, GaN) and insulators (SiO_2, TiO_2) have been fabricated.
- ✓ Nanowires can find interesting applications in the field of electronic, opto-electronic and nano-electromechanical sensors and devices.
- ✓ They are also used as metallic interconnects in quantum devices and for toughening advanced composites.
- ✓ It is possible to alter the growth parameters of nanowires so that they grow in a ***helical formation***. Such nanowires are referred to as ***nanosprings***. Nanosprings could have many applications as mechanical components with miniaturization of devices.

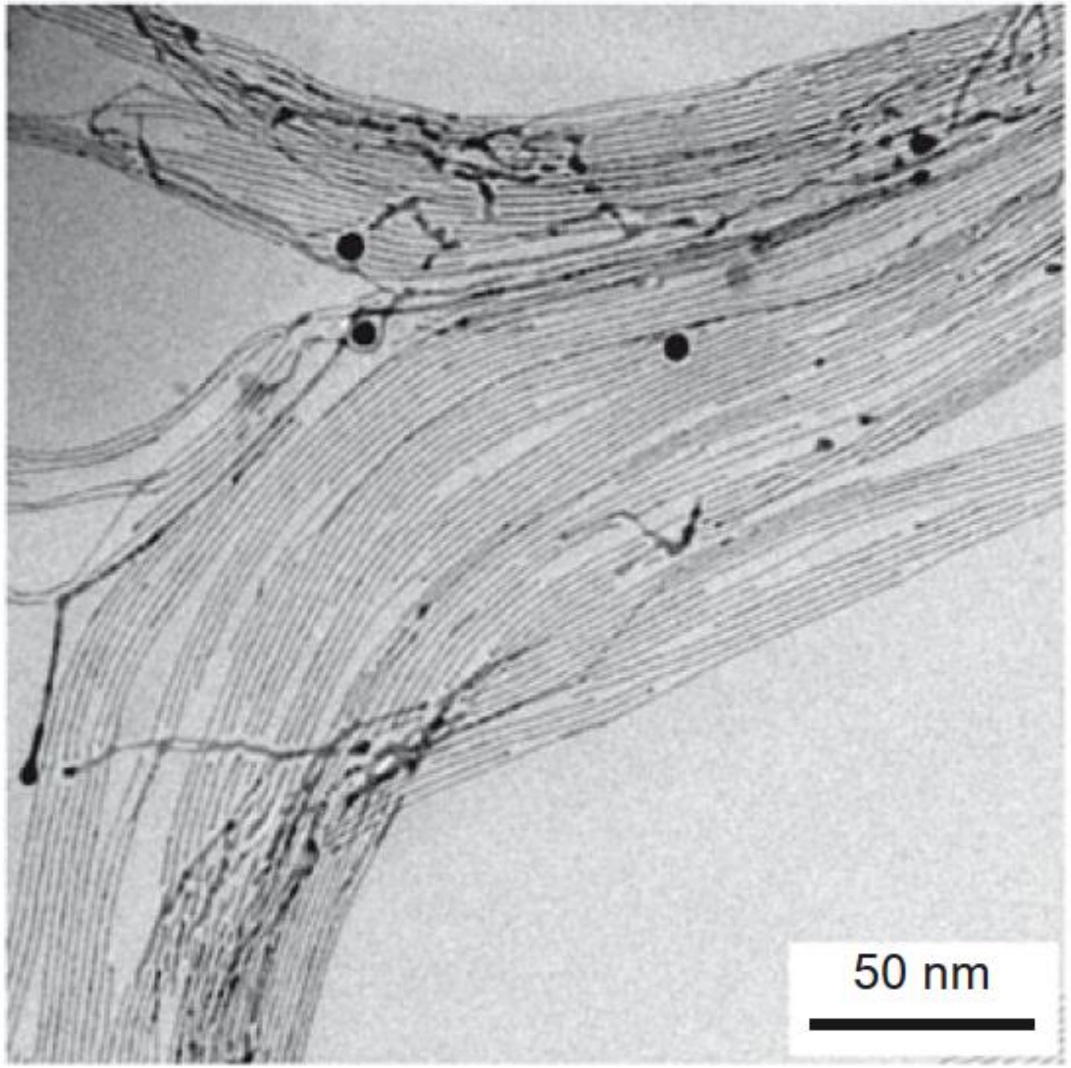


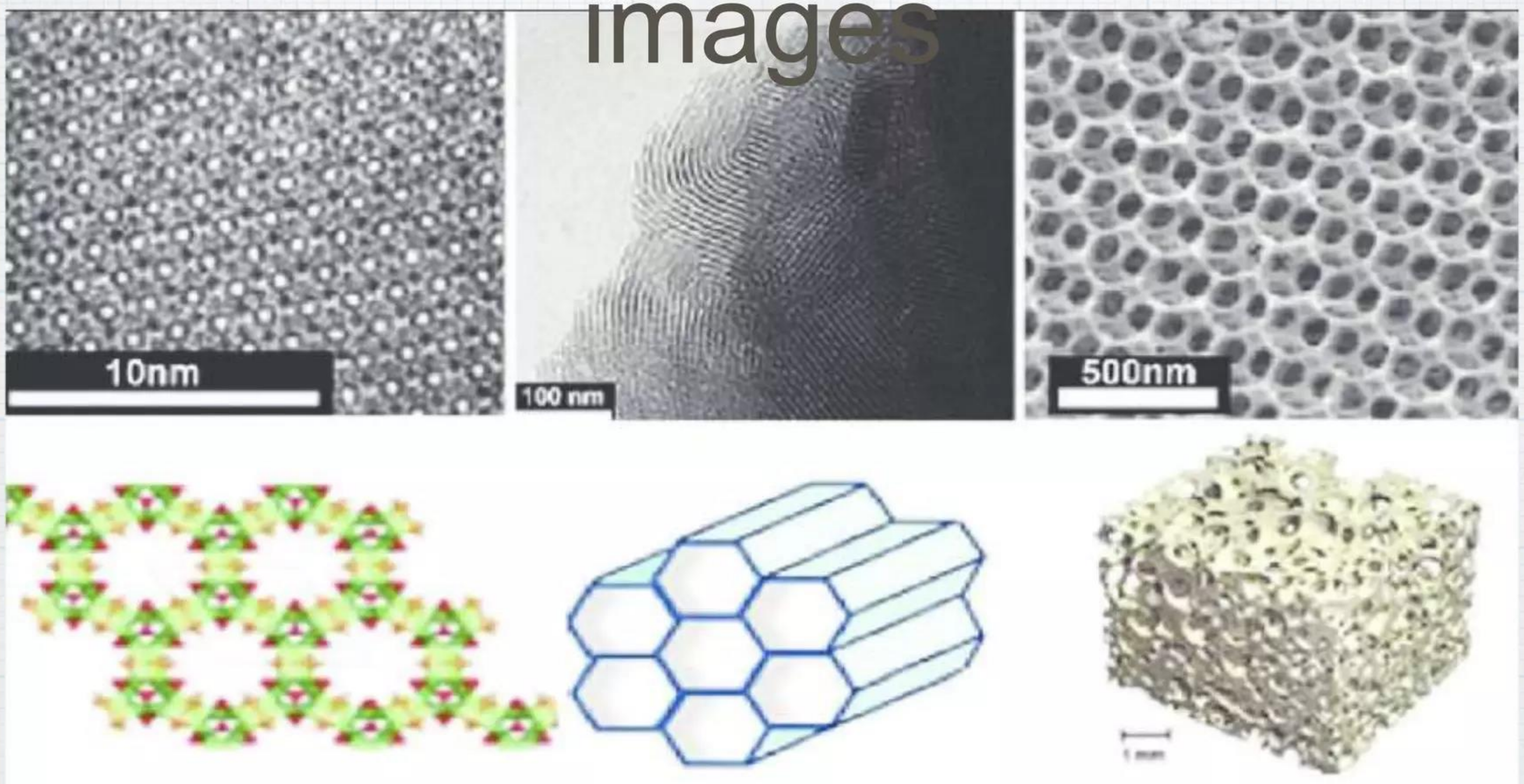
Fig. 1.16 Molecular scale Au nanowires (< 2 nm diameter) produced by wet chemical synthesis. The wires are formed by oriented attachment of amine-capped Au nanoparticles in a toluene medium. (Courtesy: N. Ravisankar, IISc, Bangalore).

❑ **Nanoporous Materials:** Materials with ***defined pore sizes in the nanometer range*** are of special interest for a broad range of commercial applications because of their outstanding properties with regard to ***thermal insulation, controllable material separation and release***, and their ***applicability as templates or fillers for chemistry and catalysis***.

➢ They have very large pore volume (up to 70%) and very high surface area (>700 m^2/g)

✓ One example of nanoporous material is **aerogel (pore volume ~99% and surface area > 1000 m^2/g and has a porous solid network with 99.9% air in its pockets)**, which is produced by sol–gel chemistry. A broad range of potential applications of these materials include catalysis, thermal insulation, electrode materials, environmental filters and membranes as well as controlled release of drug carriers.

Nanoporous materials examples and their TEM images

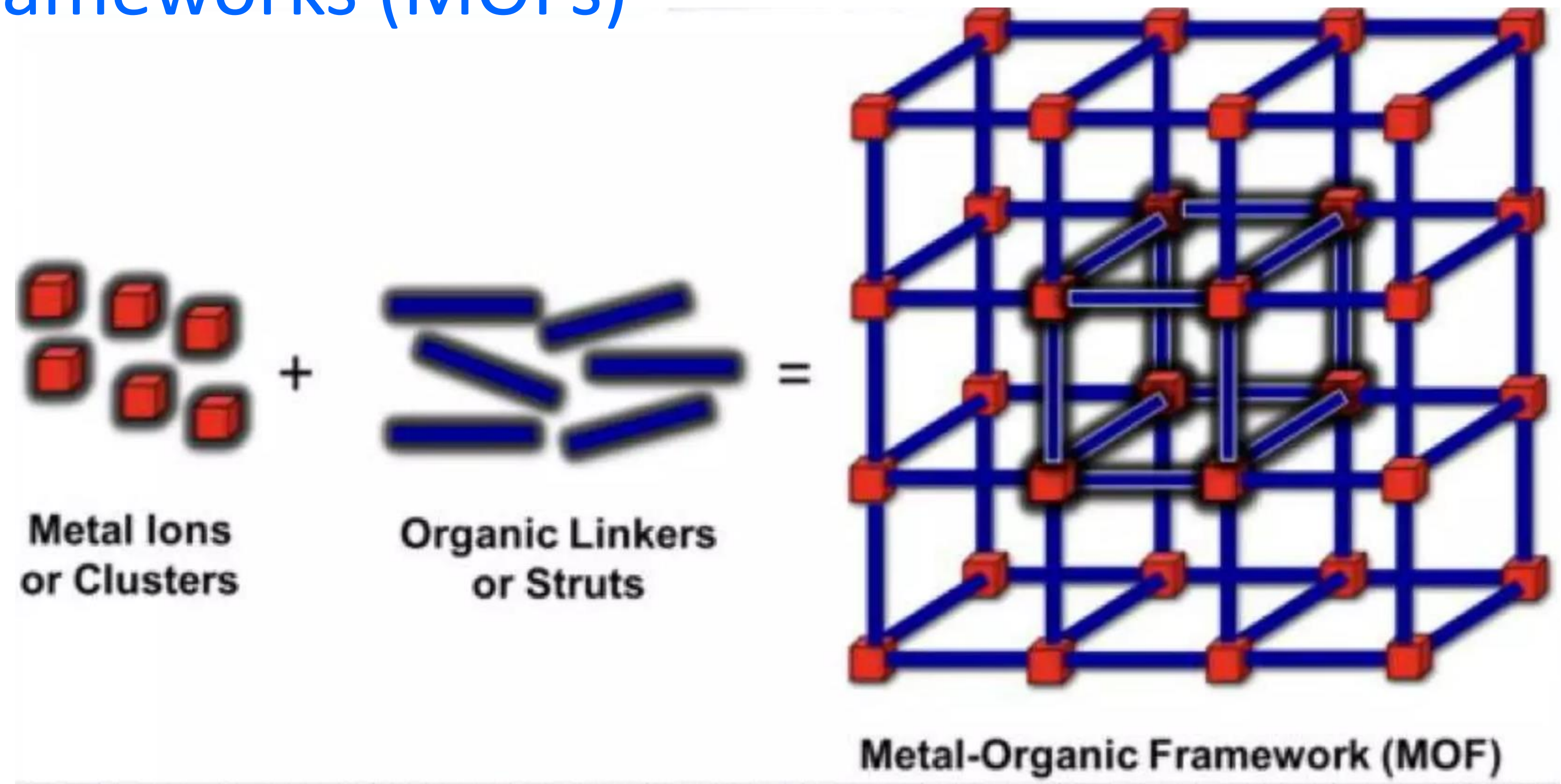


Microporous
Less than 2 nm
(Zeolites)

Mesoporous
2-50 nm
(Mesoporous silicates)

Macroporous
Greater than 50 nm
(Ceramics)

Metal Organic Frameworks (MOFs)



- Metal-organic frameworks are compounds of metal ions or metal clusters 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.

- **Pore Size:** 0.5-3 nm and **Surface area: ~**6000 m^2/g.
- 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.

- **Applications**

- Gas Adsorption, Separation & Purification
- Gas Storage
- Catalysis
- Sensing

❑ **Nanocluster**: Nanoclusters refer to aggregates of atoms or molecules that consist of anywhere from a few to thousands of atoms (viz., Au_xL_y where x number of atoms of gold make an entity binding with y number of L, ligand molecules, typically thiolate). They are typically in the ***size range of 1–2 nm*** size

➢ These entities bridge the gap between individual atoms or molecules and bulk materials, exhibiting unique physical, chemical, and optical properties that are not found in their isolated or bulk counterparts.

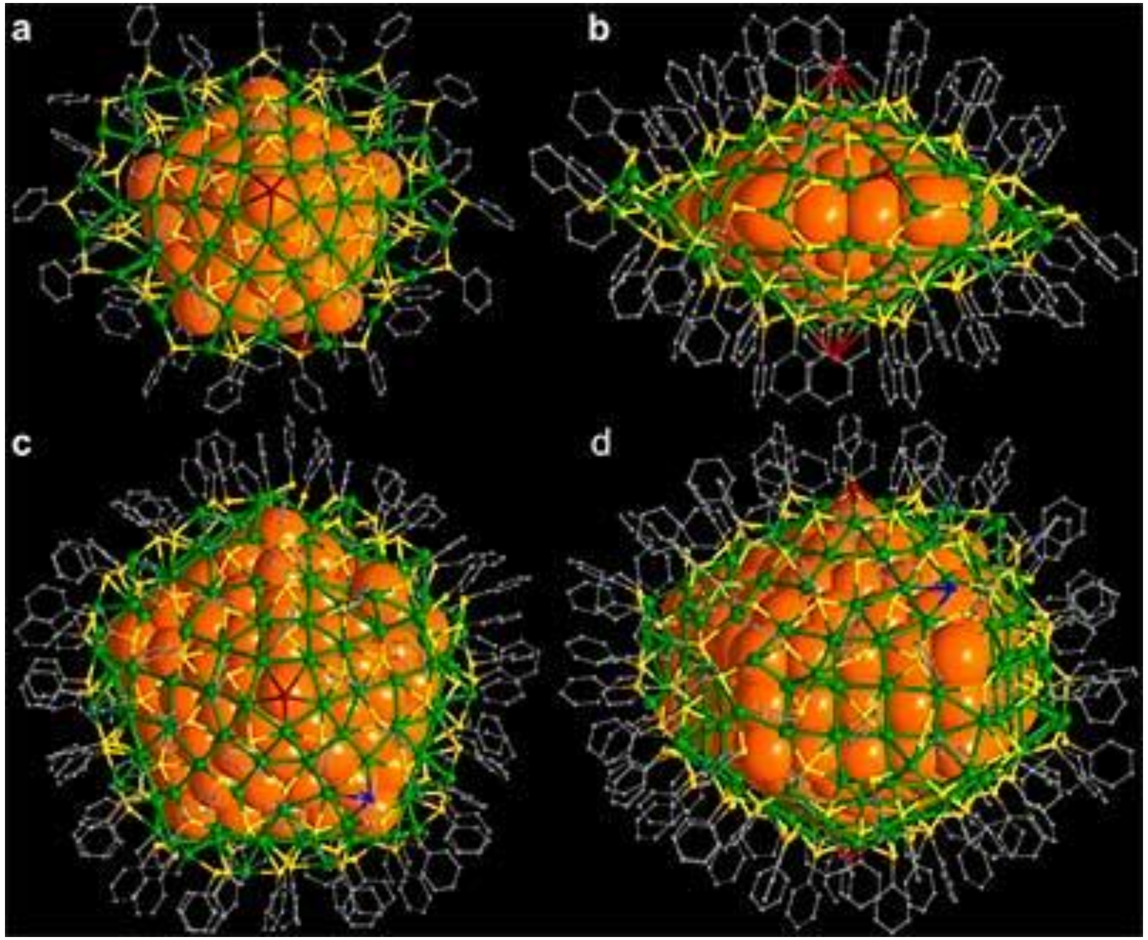
➢ Nanoclusters play a pivotal role in various applications, including catalysis, electronics, and biomedicine, due to their size-dependent properties.

➢ **Key Features and Benefits:** Nanoclusters are distinguished by several key features:

•**Size-Dependent Properties**: The physical and chemical properties of nanoclusters can be finely tuned by controlling their size, composition, and surface modification.

•**High Surface-to-Volume Ratio**: Nanoclusters possess a high surface-to-volume ratio, making them highly reactive and suitable for catalysis and sensor applications.

•**Quantum Effects**: At the nanoscale, quantum size effects become significant, leading to unique optical and electronic properties that are exploited in quantum computing and photovoltaics.



Upper row: (a) top and (b) side view of the 136-atom silver nanocluster.
Lower row: (c) top and (d) side view of the 374-atom silver nanocluster.

- *The metal cores of these clusters have a diameter of 2 and 3 nm, respectively. Silver atoms in the metal core are denoted by large orange sphere. The core is protected by a silver-thiol layer (green: silver; yellow: sulfur; carbon: gray). (Image: Nanfeng Zheng, Xiamen)*

➢ Applications of Nanoclusters

The unique properties of nanoclusters find applications in several fields:

•**Catalysis:** Nanoclusters can serve as highly efficient and selective catalysts for various chemical reactions due to their high surface area and tailored electronic properties.

•**Optoelectronics and Sensing:** The size-dependent optical properties of nanoclusters make them attractive for applications in light-emitting diodes, solar cells, and optical sensors.

•**Biomedicine:** Nanoclusters can be functionalized with biomolecules, making them suitable for applications such as targeted drug delivery, bioimaging, and biosensing.

•**Energy Storage:** Nanoclusters have been explored for use in electrochemical energy storage devices, such as batteries and supercapacitors, due to their high surface area and unique redox properties.

Nanolayers/Nanocoatings/Hybrid Nanomaterials:

- Nanolayers are one of the most important topics within the range of nanotechnology. Through nanoscale engineering of surfaces and layers, a vast range of functionalities and new physical effects (e.g., magnetoelectronic or optical) can be achieved. Furthermore, a nanoscale design of surfaces and layers is often necessary to optimize the interfaces between different material classes (e.g., semiconductor compound on silicon wafers) and to obtain the desired special properties.

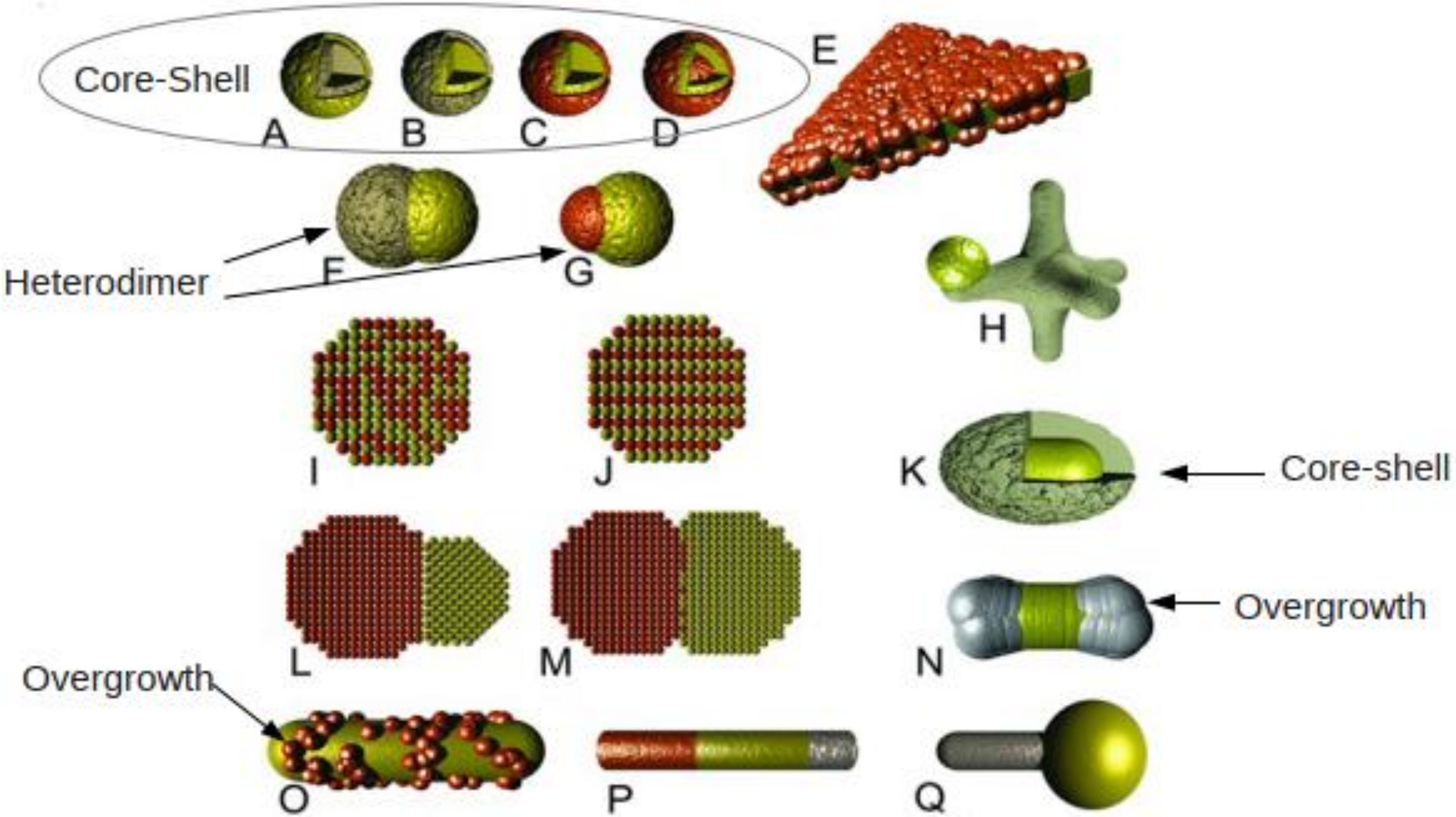


Figure 1. …. showing examples of hybrid nanoparticles (see next slide for descriptions)

(Source: Michael B. Cortie and Andrew M. McDonagh, *Chem. Rev.* 2011, 111, 3713–3735).

(Figure 1. Examples of hybrid nanoparticles:

(A) dielectric@metal core-shell,

(B) metal@dielectric core-shell,

(C) metal@metal coreshell,

(D) metal@metal@metal core-shell,

(E) metallic nanotriangle with **overcoat** of second metal,

(F) heterodimer composed of dielectric and metal parts,

(G) heterodimer composed of two different metal parts,

(H) semiconductor crystal with attached metal nanosphere,

(I) cross section through **alloyed** metal nanoparticle showing disordered nature of atomic occupancies,

(J) cross section through nanoparticle composed of **an intermetallic compound** showing ordered atomic occupancy,

(K) metal nanorods coated in a thick shell of dielectric,

(L) dimer with incoherent crystalline interface between the parts,

(M) dimer with coherent interface between the parts,

(N) nanorods with overgrowth of another metal at the rod ends,

(O) nanorods with a sparse overgrowth of a second metal,

(P) segmented nanowires or nanowire composed of two or more elements, and

(Q) “nanotadpole”.

- ***Core-shell Nanoparticles:* Nanoshells.** These are those structures where the nanocrystalline particles are coated with a ***thin layer of a different material with thickness in nanometric dimensions***.

- ✓ Figure 1 shows a schematic diagram of a variety of core shell particles. Surface of the core particle can be modified using bifunctional molecules and then small particles can be anchored on it (Figure 1 *a*).
- ✓ Nanoparticles grow around the core particle and form a complete shell (Figure 1 *b*). In some cases, a smooth layer of shell material can be deposited directly on the core by co-precipitation method (Figure 1 *c*).
- ✓ Small core particles such as gold or silver (10–50 nm) can be uniformly encapsulated with silica (Figure 1 *d*).
- ✓ Also a number of colloidal particles can be encapsulated inside a single particle (Figure 1 *e*).
- ✓ ***Core particles can be removed*** either by calcination or by dissolving them in a proper solvent. This gives rise to ***hollow particles*** also known as ***quantum bubbles*** (Figure 1 *f*).
- ✓ Concentric shells also can be grown on core particles to form a novel structure known as ***multishell*** or ***nanomatryushka*** (named after the Russian doll; Figure 1 *g*).

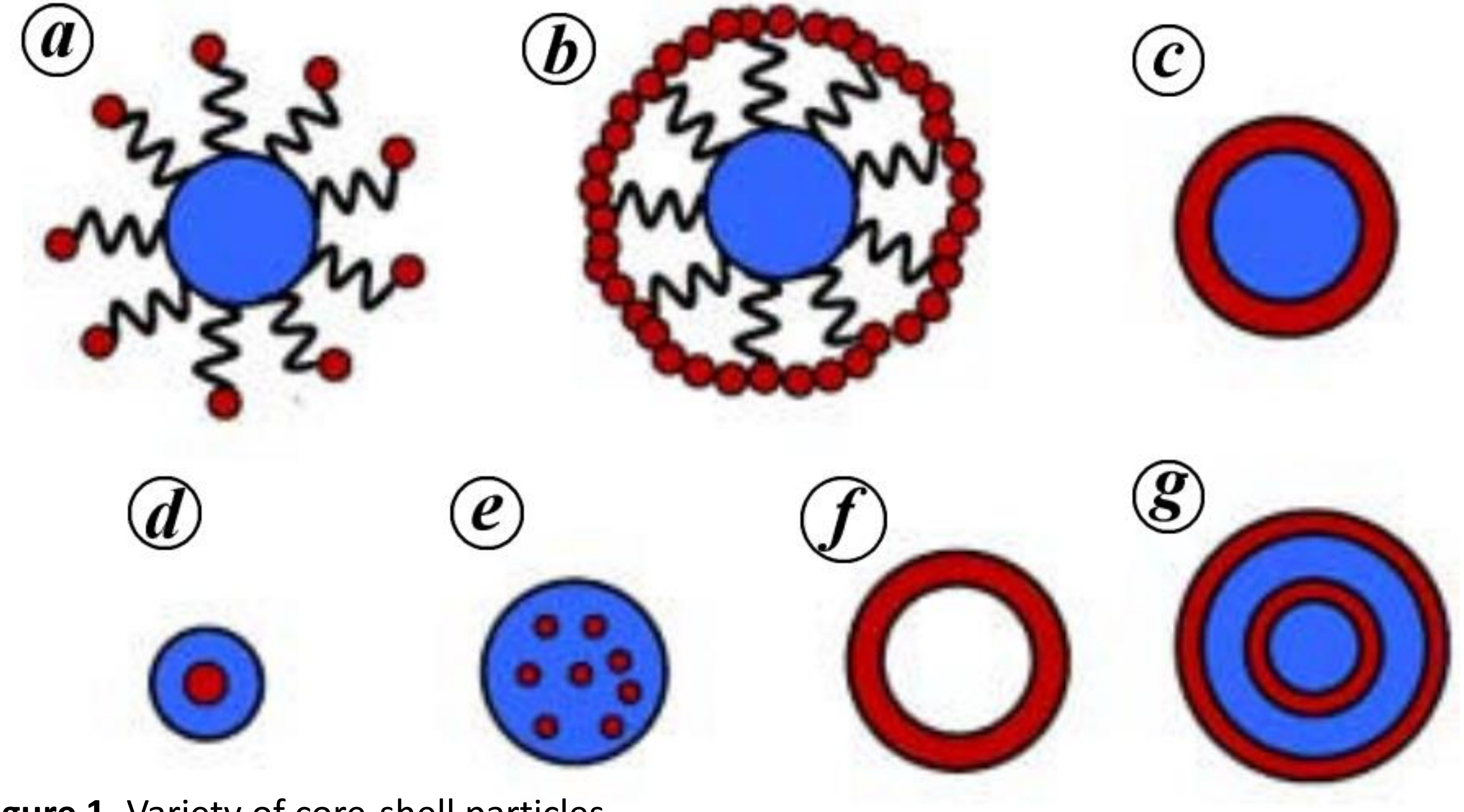


Figure 1. Variety of core-shell particles.
a, Surface-modified core particles anchored with shell particles.
b, More shell particles reduced onto core to form a complete shell.
c, Smooth coating of dielectric core with shell.
d, Encapsulation of very small particles with dielectric material.
e, Embedding number of small particles inside a single dielectric particle.
f Quantum bubble.
g, Multishell particle (***nanomatryushka***).

- Due to ***their nanometric width and size, nanoshells can exhibit interesting quantum confinement effects***. Nanoshells possess highly ***favorable optical and chemical properties for biomedical imaging and therapeutic applications***. For example, ***gold nanoshells coated on dielectric silica nanoparticles*** have been widely studied in *drug research*. It is possible to vary the light absorption and emission characteristics of gold nanoshells by controlling the thickness and size of the nanoparticles (particularly as they approach the wavelength dimensions of the light medium used). Study of **plasmon resonance wavelength shift** as a function of nanoshell composition for the case of a gold/silica nanoshell with a 100-nm core, demonstrates the ability to tune the optical resonance of nanoshells to a desired wavelength. This property is critical in nano-drug delivery for in vivo therapeutic applications. Laser light is not strongly absorbed generally by human tissues and blood. However, due to resonance effects, it is possible for nanoshells to absorb significant amounts of incident laser light, resulting in intensive localized energy absorption. By attaching certain antibodies to such nanostructures, it is possible to provide site specificity, for example, for ***selective segregation of such nanoparticles in cancerous or tumour cells***. Subsequently, as the body is ***irradiated with laser light, there will be selective heating of nanoshells concentrated at cancerous cells, leading to selective burn out of such deleterious cells***. Nanoshells can also find application in nano-medical diagnostic tools, for example, in thermal imaging.

- **Agglomerate**: It is a group of ***particles held together by weak forces*** such as van der Waals forces, some electrostatic forces, and surface tension. It should be noted that agglomerate will ***usually keep*** a high ***surface-to-volume ratio***.
- **Aggregate**: It is a group of ***particles held together by strong forces*** such as those associated with *covalent or metallic bonds*. It should be noted that an aggregate ***may keep*** a high ***surface-to-volume ratio***.
- **Nanofluids:** These are fluids (e.g. water, ethylene glycol, lubricants) with dispersions of nano-sized particles (e.g. carbon, metals, metal oxides, etc.).

✓ The nanofluids are characterized by unique properties and have several applications.

✓ The most popular nanofluids are ***magnetic nanofluids*** (ferrofluids) and ***thermal nanofluids***.

✓ In case of thermal nanofluids, *improvements in energy efficiency and convective heat transfer have been demonstrated* by many investigators and thermal conductivity of the fluids has been enhanced to as high as 150% with the dispersion of minute quantities of nanoparticles.

✓ A number of applications such as drug delivery, magnetic storage media, refrigerant chillers, electronic manufacturing, cosmetics, pharmaceuticals, power generation, air-conditioning, etc. are envisaged for nanofluids.

TABLE 1.3 Characteristics of Nanomaterial and Their Importance

Characteristic	Importance
Size	Key defining criterion for a nanomaterial.
Shape	Carbon nanosheets with a flat geodesic (hexagonal) structure show improved performance in epoxy composites versus carbon fiber.
Surface charge	Surface charge is as important as the size or shape. It can impact adhesion to surfaces and agglomeration characteristics. Nanoparticles are often coated or “capped” with agents such as polymers (PEG) or surfactants to manage the surface charge issues.
Surface area	This is a critical parameter as the surface-to-volume (mass) ratio for nanomaterials is huge. For example, 1 g of an 8-nm-diameter nanoparticle has a surface area of 32 m^2. Nanoparticles may have occlusions and cavities on the surface.
Surface porosity	Many nanomaterials are characterized with zeolite-type porous surfaces. These engineered surfaces are designed for maximum adsorption of a specific coating or to accommodate other molecules with a specific size.
Composition	The chemical composition of nanomaterials is critical to ensure the correct stoichiometry being achieved. The purity of nanomaterials, impact of different catalysts used in the synthesis, and presence of possible contaminants need to be assessed along with possible coatings that may have been applied.
Structure	Knowledge of the structure at the nanoscale level is important. Many nanomaterials are heterogeneous, and information concerning crystal structure and grain boundaries is required.

The above examples allow us to easily and precisely *define nanoscience and nanotechnology*.

- **Nanoscience is the field of science that measures and explains the changes of the properties of substances as a function of the nanodimension.**

- ✓ Like the melting of gold, the properties of any substance will remain constant as its size gets smaller and smaller—that is, until the size is reduced to the nanoscale (***depending on the substance and the property being measured, roughly 10–100 nm***).

- ✓ *In the dimensional nanoscale, any physical property measured will continuously change with size, and often dramatically so.*

- ***Nanotechnology*** **is the *application of property modifications* that happen at the nanoscale to some beneficial endeavor**—and what a warehouse of beneficial endeavors there are!

- In other words, **nanotechnology** is the study and the manipulation of matter at length scales of the order of a few nanometers (100 atoms or so) to produce useful materials and devices.

- This still leaves a lot of room for maneuver.

- A nanotechnologist working on suspensions of particles might tell you that it is achieving ***better control of tiny particles a few nanometers across*** (nanoparticles) so that ***face creams can penetrate the epidermis*** (outer skin layer).
- A scientist working at the so-called "life sciences interface" would say that it is finding ways of ***attaching antibodies to magnetic nanoparticles to develop revolutionary cancer treatments***.
- A researcher working on "***molecular electronics***" will tell you that it is creating ***self-ordered assemblies of nanoparticles to produce electronic circuits in which the active components are a thousand times smaller than a single transistor on a Pentium IV chip***.
- Some nanotechnologists (a small minority) would tell you that it is finding ways to ***build tiny robots whose components are the size of molecules (nanobots)***.

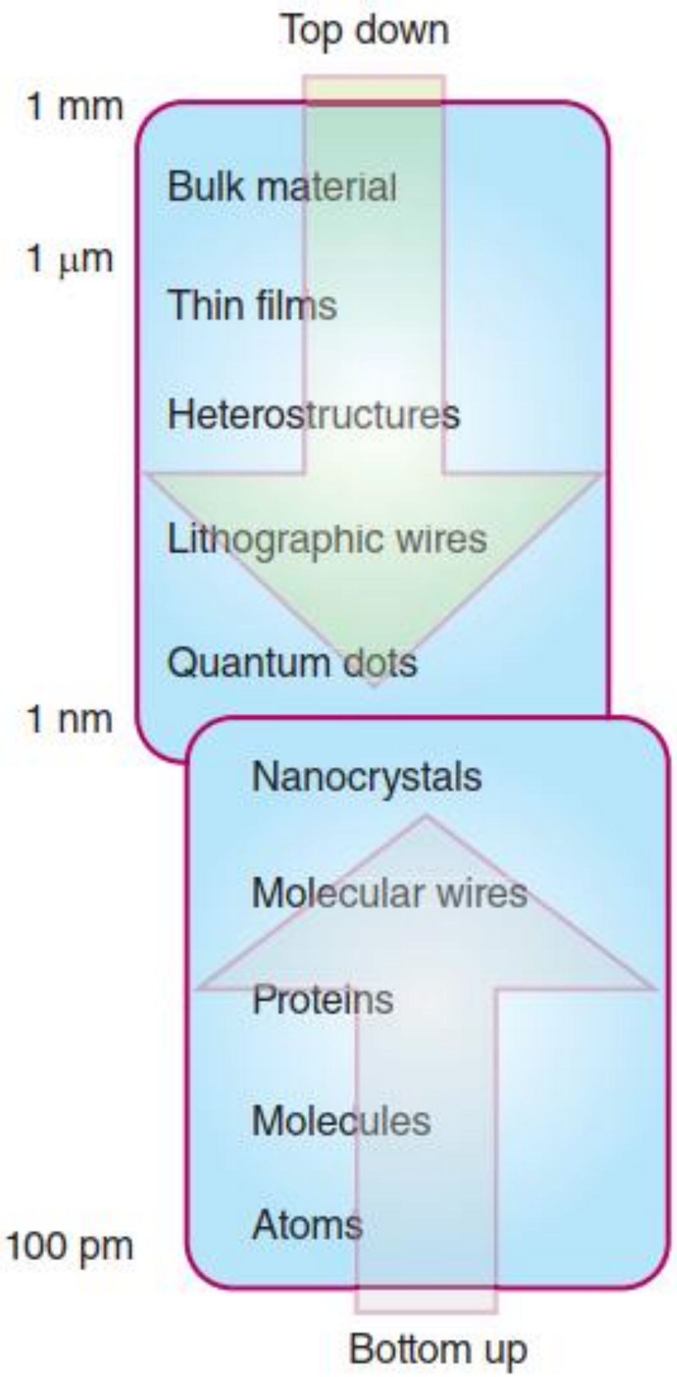
➢ **The promise of nanoscience is so great and the application of nanotechnology so vast that they are projected to change our world,** similar to the current biological revolution occurring in genomics or the AI-ML in computer science.

BOTTOM-UP/TOP-DOWN NANOTECHNOLOGY

It is worth mentioning here the way of categorizing nanotechnology, that is, **bottom-up** and **top-down** approaches.

- In a **bottom-up approach**, the building block (nanoparticle, molecular machine component, etc.) is identified and produced naturally and then assembled to produce the material or device required.

- In the **top-down approach**, you start with a block of some material and machine a device or structure out of it. This is akin to conventional engineering using lathes and millers to machine a shape out of a solid block. The modern tools of nanotechnology, however, are able to machine structures with sizes of a few nanometers, so the size of components made with a top-down approach is not much different from the building blocks of the bottom-up approach.



The flexibility of top-down tools—in particular, *focused ion beam systems* (FIBs)—is further enhanced by their ability to deposit material to produce nanoscale features as well as to remove it. This is beautifully illustrated in Fig. 0.4, which shows an example of a “wine-glass” with a cup diameter 20 times smaller than the width of a human hair produced by depositing carbon. Although this is a rather big structure on the scale of nanometers, the smallest feature size that can be produced by a modern FIB is less than 100 nm.

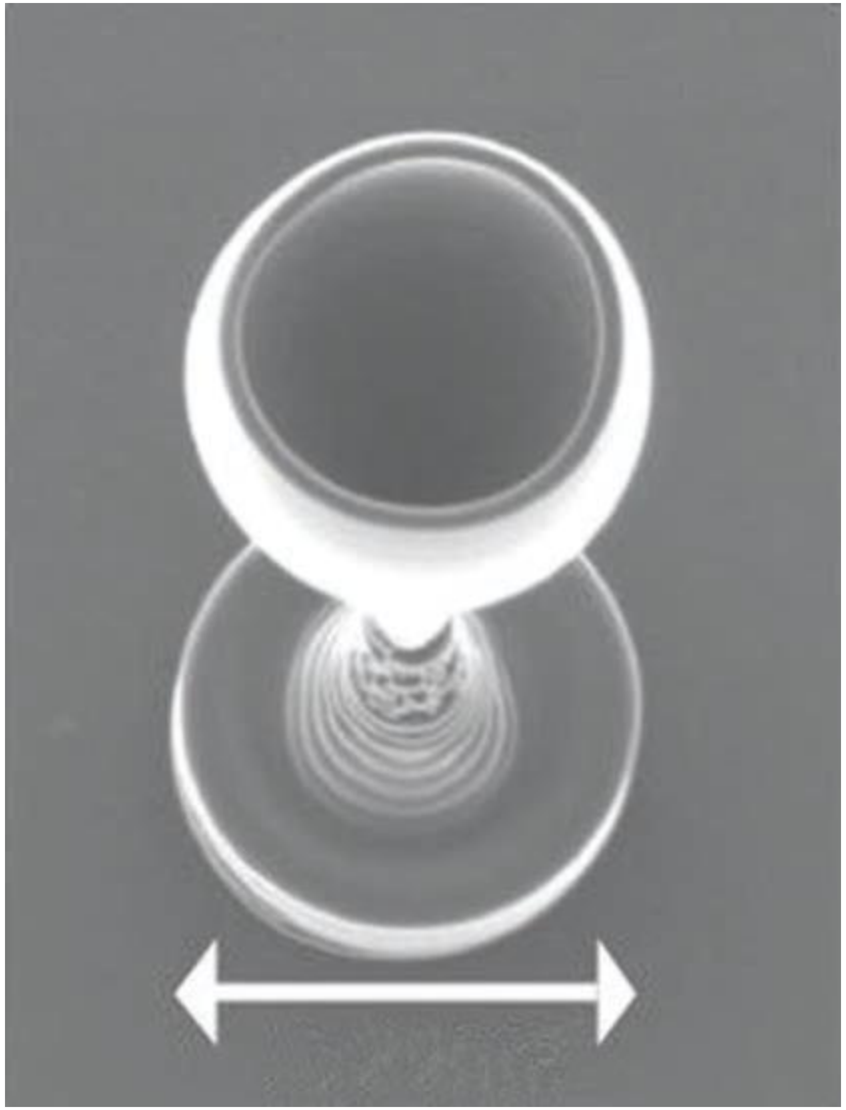


Fig. 0.4 The smallest wineglass in the world (authorized by Guinness World Records). Wine glass whose cup diameter is 20 times smaller than the width of a human hair produced by deposition of carbon using a focused ion beam (FIB) machine. The structure arose from a Joint development by SII NanoTechnology, NEC, and the University of Hyogo, Japan. Although this is a rather big structure on the scale of nanometers, the smallest feature size that can be produced by a modern FIB is less than 100 nanometers

- The two approaches (top-down and bottom-up) are complementary, and some of the most exciting research arises out of combining them. For example, if one wants to measure the electrical or magnetic properties of an individual nanoparticle, the fantastic precision of a modern top-down tool enables the production of electrodes that can attach to it.

History

- ***Humans have, in fact, practiced nanotechnology for centuries, although it was more of an art than a science or engineering discipline.*** It is only recently that the chemistry of nanosized particles has engendered such high levels of interest and research funding.
- For example, *gold and silver compounds have been used to produce red and yellow stained glass, respectively,* for centuries.
- In stained glass, *the gold and silver metal atoms exist as nanoparticles (known previously as 'colloidal particles') with optical properties that depend strongly on their size.*
- Metallic nanopigments are now becoming a focal point of biomedical nanotechnology because they can be used to tag DNA and other active nanoparticles.
- Other classical examples of nanotechnology include the photosensitive nanosized particles in silver halide emulsions used in photography, nanoparticulate TiO_2 pigments, and the nanosized carbon granules in the 'carbon black' used for reinforcing tyres and in printer's ink.

Figure 1.8 (a) Lycurgus cups. When viewed in ***reflected light***, as in this flash photograph, the cup's dichroic glass is ***green*** in colour, whereas when viewed in *transmitted light*, the glass appears *red*. [Courtesy of Trustees of the British Museum. © The Trustees of the British Museum]

(b) ancient Maya fresco painting. © 2005. With permission of The Royal Society of Chemistry.

Actually, some aspects of nanotechnology can be considered to date back to the ancients. For example, the invention of Indian ink, probably in China around 2700 B.C., relies on producing carbon nanoparticles in water. Also, medieval potters in Europe knew how to produce a lustre on pots by coating them with copper and silver nanoparticles, a process that can be traced back to 9th century A.D. Mesopotamia.

Figure 0.2 shows an electron microscope image of the glaze of a 16th-century Italian pot, whose luster derives from the coating by 5-nm-diameter copper particles.

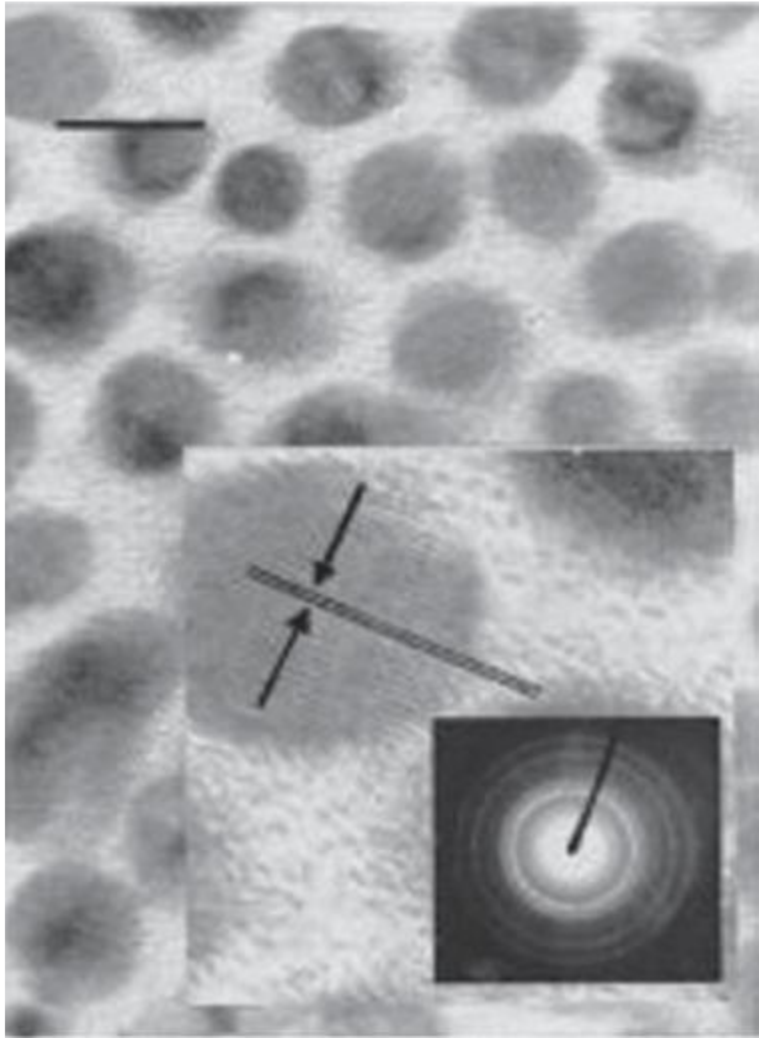


Fig. 0.2 Ancient Incremental Nanotechnology. Copper nanocrystals on a 10th century pot of about 10 nm diameter used to produce a surface luster. The inset shows an increased magnification image of a single 7 nm diameter particle with atomic planes visible revealing its crystallinity.
Reproduced with the permission of Elsevier Science from I. Borgia et al.

- Most modern nanotechnologists would be proud of the size control of the particles in the above picture. Whereas these days a process that involved nanoparticles such as this would be proudly claimed to be nanotechnology and thus open the door to research funding, spin-off companies, and so on, the ancients were developing processes that did something invisible to the materials but nevertheless allowed them to achieve certain results. In this sense, a lot of nanotechnology can sometimes be considered to be a re-branding of other, more traditional lines of research such as materials science and chemistry. The nanotechnology title is still useful, however, since nanotechnology is, by its nature, multidisciplinary and it encourages cross-disciplinary communication between researchers.
- The aspect of nanotechnology that has really changed in the modern world is the development of instruments that can probe at the nanoscale and image the particles within materials or devices. Researchers can actually observe what is happening to the particles or grains in response to changes in processing. This not only makes development of new processes more efficient but also leads to the discovery of completely new structures that were not known to exist and hence new applications. Nature is full of surprises when one studies sufficiently small pieces of matter, as will become clear throughout this book.

- The modern beginnings of nanoscale science and technology happened in 1959, the year that Richard Feynman, a quantum physicist and one of the 20th-century's greatest scientists, gave a speech to the American Physical Society entitled "***There's Plenty of Room at the Bottom***." Feynman was fascinated by the notion of scaling, and in this speech, he imagined that a single bit of information could be stored in a nanospace (specifically a 125-atom cluster), an exceptionally bold prediction at that time. At that scale of miniaturization, he estimated that all the text ever written in books in the history of the world could be stored within a cube 0.2 mm on a side (thus his lecture title).
- Feynman's genius was his realization that *all things do not simply scale down in proportion*, which is now considered the *cornerstone of nanoscience*. He was predicting that when **materials were scaled down to the nanometer size range, they would behave differently**, which could be turned into an advantage.
- The science and engineering of nanotechnology began to take shape in the latter half of the twentieth century. One significant leap forward in nanotechnology occurred when Gerd Binnig and Heinrich Rohrer developed the **scanning tunneling microscope**, which was the forerunner to all other forms of scanning probe microscopy. Later, a *scanning probe tip* was used to rearrange atoms on a surface to spell out words, so demonstrating an ability to manipulate and characterize nanoscale structures. Work in the areas of nanoscience and nanotechnology has thus been multidisciplinary as well as diverse in scope.

NANOTECHNOLOGY IN NATURE

- ✓ The original version of nanotechnology occurred in nature, where organisms developed an ability to manipulate light and matter on an atomic scale to build devices that perform specific functions, such as storing information, reproducing themselves, and moving about.
- ✓ In this sense, ***DNA is the ultimate nanomaterial***, as it stores information as the sequence of base pairs that are spaced about 0.3 nm apart. *Folded DNA molecules have an information density of more than about 1 Tb cm^{-2} (1 Tb = 10^{12} bits)*.
- ✓ Indeed, several natural structures including proteins and the DNA diameter of around 2.5 nm, viruses (10–60 nm), and bacteria (30 nm to 10 µm) find the above definition of nanomaterial, while others are of mineral or environmental origin.
- ✓ Photosynthesis is another example of biological nanotechnology in which nanostructures are exploited to absorb light, separate electric charge, shuttle protons around, and ultimately convert solar energy into biologically useful chemical energy.
- ✓ Our quest to harness solar energy has also turned to the nanoscale, where nanocatalysts are improving our ability to convert light to electrical energy by using photovoltaic materials.

- Figure 1.4a shows an electron microscopic image of *a sensory patch in amphibian ears*, which consists of a single bundle of *stereo cilia projecting from the epithelium of the papilla* and acts **as a nanomechanical cantilevers that measure deflection as small as 3 nm because of sound waves**.

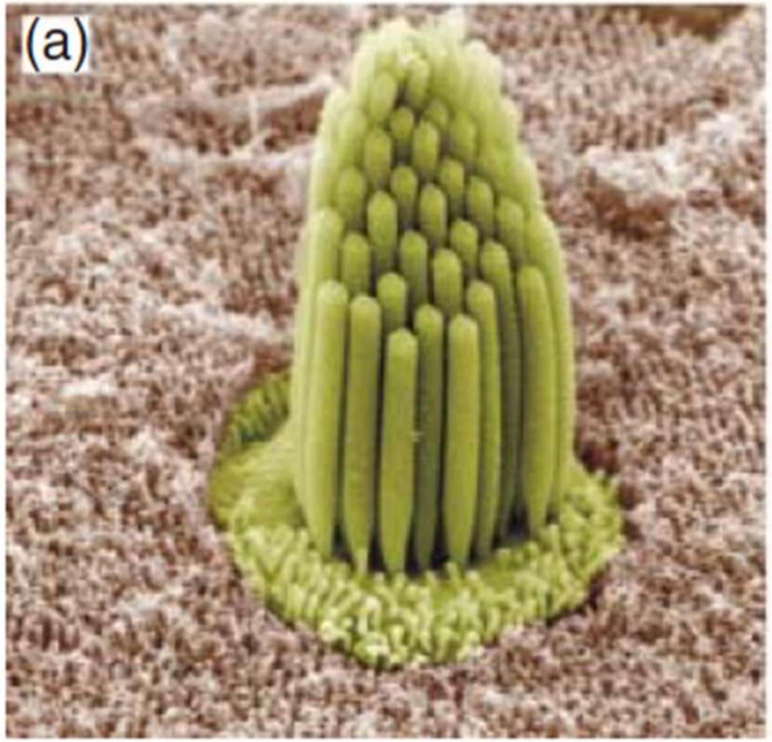


Figure 1.4 Nanotechnology in nature:

(a) electron microscopic image of a sensory patch in amphibian ears. http://scinerds.tumblr.com/post/35542105310/stereocilia-stairsteps;

- Figure 1.4b shows glittering colors of peacock feather where ***barbs project directly from the main feather stem, and barbules (~0.5 mm long) attached to each side of the barb generate the typical "shimmer" of iridescence.*** *Electron microscopy (Figure 1.4c and d) of barbules* ***reveals a highly ordered structure of melanin rods of high refractive index embedded in keratin of lower refractive index with air tube between each square of melanin rods.*** **The whole array of melanin rods, keratin matrix, and air holes comprises a 2D photonic crystal.**

- There is much interest on mimicking these natural wonders with potential applications in optical engineering and communications. ***Less seriously, photonic crystal pigment-free paints would not fade, fabrics might be more vibrant…..***

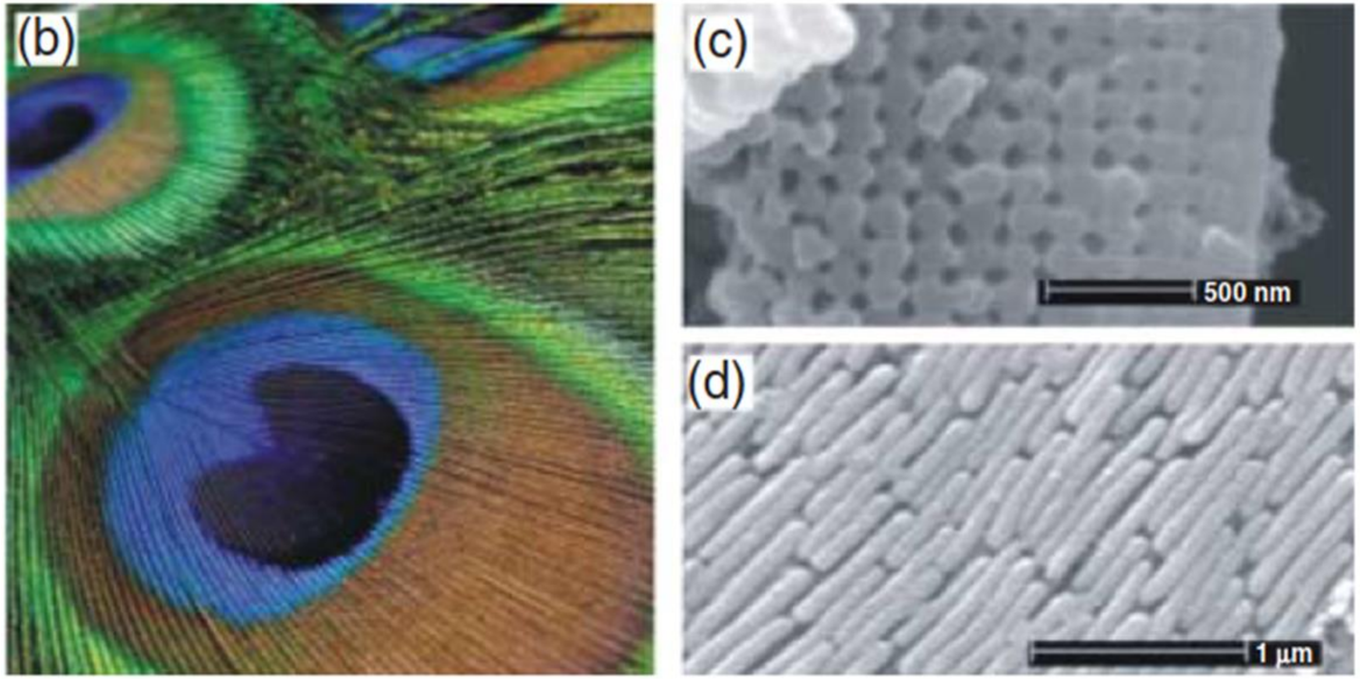


Figure 1.4 Nanotechnology in nature:
(b) peacock feather showing barbules, representing a photonic lattice;
(c and d) electron microscopy image of transverse and longitudinal sections of barbules.

Nanoscience in Action in Biological World: Lotus Effect

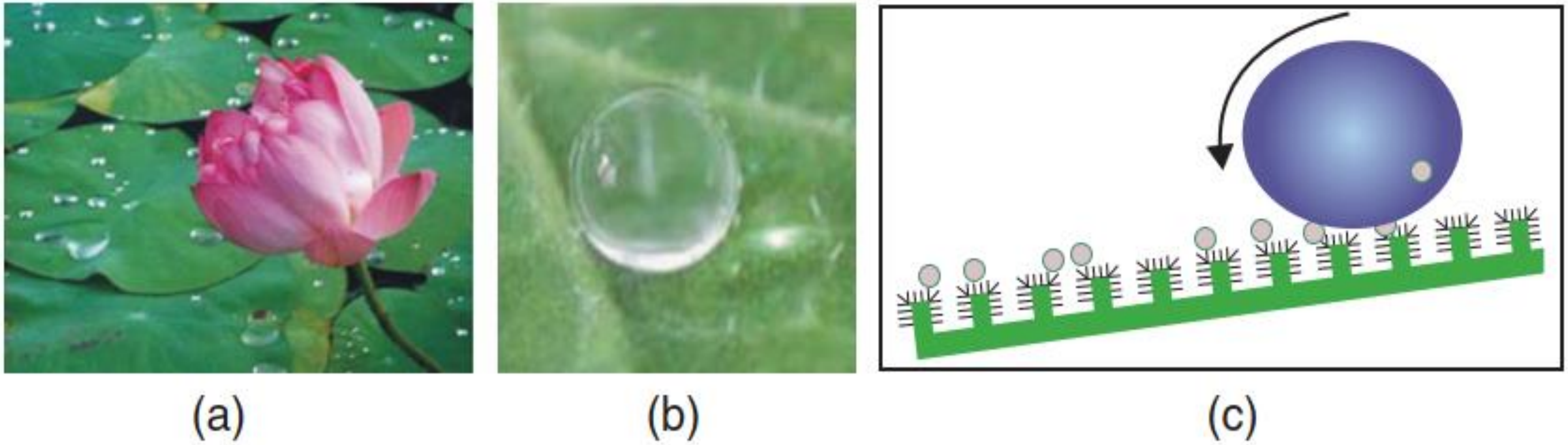


Figure 1.6 (a) Lotus (Nelumbo nucifera) plant;

(b) spherical water droplet on a nonwettable lotus plant leaf. © 2003 Nature Publishing Group;

(c) self-cleaning: a drop picks up the dirt particles as it rolls off the leaf's surface.

- Although the water repellency (nonwettable nature) of lotus leaf had long been recognized, its scientific basis was understood only in 1997 when two botanists Wilhelm Berthelot and Christophe Neinhuis, at the University of Bonn in Germany, examined leaf surfaces of lotus using a scanning electron microscope that resolves structures as small as 1–20 nm (Figure 1.6).
- The self-cleaning property is due to the "**Super hydrophobicity**" of the convex papillae on the surface of leaves, which is coated with wax crystals of nanoscopic dimension of approximately 10–100 nm (Figure 1.6b). Water drop picks up the dirt particles as it rolls off the leaf's surface, showing self-cleaning process (Figure 1.6c).
- The papilla greatly reduces the contact area of water droplets with it. Every epidermal cell forms a micrometer-scale papilla and has a dense layer of epicuticular waxes superimposed on it. Each of the papillae consists of branch-like nanostructures on the surface, for example, of the lotus leaves, the almost spherical water droplets will not come to rest and simply roll off if the surface is tilted even slightly, which is now usually referred to as the "**Lotus effect**." The self-cleaning effects of the surfaces of the lotus flower have been attributed to the combined micro- and nanostructure, which in combination with hydrophobic groups give the surface a water and dirt-repellent behavior.
- Recently, numerous companies have realized products such as paint, glass surface, and ceramic tiles with dirt-repellent properties resembling the surface morphology and chemistry of the lotus leaf.

❖ Nature makes good use of this ***magnetic size effect***. Bacteria, such as the one shown in Fig. 1.5, have evolved, which use strings of magnetic nanoparticles to orient their body along the local magnetic field lines of the Earth. The strain shown in the figure, which is found in northern Germany, lives in water and feeds off sediments at the bottom. For a tiny floating life form such as this, knowing up and down is not trivial. If the local field lines have a large angle to the horizontal, as they do in Northern Europe, then the string of magnetic nanoparticles makes the body point downwards and all the bacterium has to do is to swim knowing that it will eventually find the bottom.

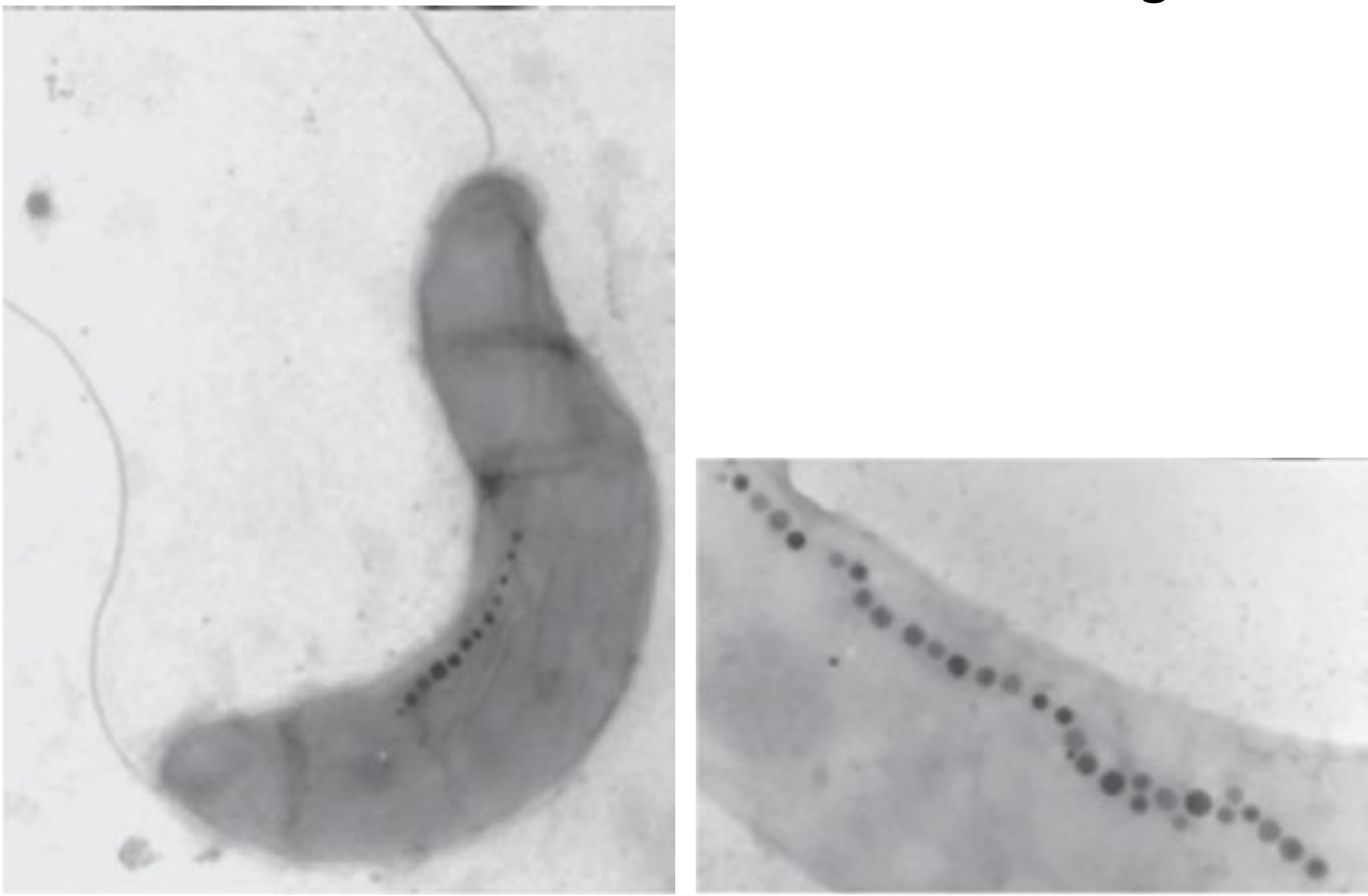


Fig. 1.5 **Magnetic bacterium** using single-domain particles. The Magnetic bacterium (magnetospirillum gryphiswaldense) from **river sediments** in Northern Germany. The lines of (permanently magnetized) ***single-domain*** magnetic nanoparticles, appearing as dark dots, ***align the body of the bacterium along the local direction of the Earth's magnetic field***, which in Germany is *inclined at 55^0 from horizontal*. This means that the ***bacterium will always swim downwards towards the sediments where it feeds***. Reproduced with With kind permission of Springer Science and Business Media from D. Sch¨uler [2].

- The intelligence of evolution is highlighted here. If the particles are single-domain particles, then they will stay magnetized forever, so forming a string of these ensures that the navigation system will naturally work. ***If the bacterium formed a single piece of the material the same size as the chain of particles, then a domain structure would form, and it would become magnetically dead.*** The nanoparticles are composed of magnetite (Fe_3O_4) rather than pure iron, but the argument is the same. There is currently research devoted to persuading the bacteria to modify the composition of the nanoparticles by feeding them with cobalt-containing minerals as a method of high-quality nanoparticle synthesis.

APPLICATIONS and SCOPE OF NANOMATERIALS

- Electronic devices
- Opto-electronic devices
- Quantum computers
- Insulation
- Phosphors
- Cutting tools
- Medicine
- Renewable energy
- Catalysis
- Filtration
- Elimination of pollutants
- Sensors
- Consumer products
- Sports
- Textiles