1 Nanomaterials

Principles and Properties

1.1 Bionanotechnology: Concept and History

1.2 Nanomaterials in Bionanotechnology

1.3 Nanosized vs Bulk Materials

1.4 The Ratio of Surface Atoms to Volume

1.5 Surface Energy

1.6 Strategies to Reduce Surface Energy

1.7 Principles of Nanomaterial Synthesis

1.8 Nano(crystal) Growth

1.9 Ostwald Ripening and Coalescence

1.10 Nuclei Formation and the Control of the Nanoparticle Shape

1.1 Bionanotechnology: Concept and History

Bionanotechnology is an interdisciplinary field at the intersection of nanotechnology and biology. Whereas nanotechnology provides tools and
platforms for exploration and transformation of biological systems, biology is a source of inspiration and building blocks, all with the aim to design new materials and devices.

Historically, it is believed that the emergence of nanotechnology was hinted in the lecture of Richard Feynman (1918–1988) at Caltech in 1959 and in an article published in 1960 entitled ‘There’s plenty of room at the bottom’ (Feynman, 1960; 25 years later he gave an updated talk ‘Tiny machines’ available online at https://youtu.be/4eRCygdW--c). Although his lecture and article give a vivid description of science that can enable manipulation of matter at the atomic and molecular level, the word nano (from Greek for dwarf) is not mentioned nor is there any description of the technology that will enable this manipulation. Nanotechnology was touched upon more in Feynman’s lecture ‘Infinitesimal machinery’ given in 1983 and published as an article in 1993, in which he discusses design of silicon micromotors and touches upon many topics including potential application of such tiny machines in computing (Feynman, 1993). The term nanotechnology was independently coined by Norio Taniguchi (1912–1999) in 1974, and then again by Eric Drexler in the late 1970s. Drexler’s paper published in 1981 entitled ‘Molecular engineering’ talks about design of protein machines by precise positioning of reactive groups on atomic level, and use of such technology for computing and manipulation of biological materials (Drexler, 1981). This sounds much like the bionanotechnology of today.

There were several discoveries in the 1980s to mid 1990s, which marked the beginning of bionanotechnology as a separate field. One was the exploitation of DNA as a structural element for a design of programmed nanostructures predicted in 1981 and then demonstrated in 1983 by Ned Seeman, a pioneer of DNA nanotechnology (Seeman, 1981; Kallenbach et al., 1983; see also Chapter 6). A few years later, in the mid 1990s, a method was patented that demonstrated DNA sequencing with the help of protein nanopore (Dreamer, 2016), and Chad Mirkin and his coworkers described DNA biosensors based on DNA-modified gold nanoparticles (Mirkin et al., 1996; Chapter 6). Around the same time Doxil, a liposomal formulation of powerful chemotherapeutic doxorubicin was approved by the US Food and Drug Administration (FDA), making it a first nanoformulated drug in use and on the market. This ultimately led to development of nanomedicine, which is closely linked to bionanotechnology and will be explored in Chapters 8 and 9.

1.2 Nanomaterials in Bionanotechnology

It is important to remember that rules are different down at the bottom. Properties of materials change as the size and the scale decrease and as we
approach the molecular and atomic world. Surfaces become larger, surface energy bigger, electrons get confined in small spaces. In the past decades, the number of different nanomaterials has grown, but they can be grouped into a few main classes, all of which have found use in bionanotechnology (Table 1.1). These are metallic nanomaterials, mainly nanoparticles (NPs) and nanorods made of noble metals (Au, Ag, Pt, Cu), metal oxides such as magnetic nanomaterials based on iron oxide (Fe₃O₄), or titanium oxide (TiO₂), semiconducting nanomaterials such as quantum dots (note that the definition of quantum dots in physics will differ from the one we use in nanotechnology), carbon nanomaterials (graphene, carbon nanotubes and nanodiamonds) and (bio)polymeric/organic nanoparticles made either from man-made or natural polymers such as polysaccharides and organic molecules such as lipids or peptides.

Table 1.1 Most widely used nanomaterials in bionanotechnology and their characteristic properties

<table>
<thead>
<tr>
<th>Nanomaterials</th>
<th>Typical representatives</th>
<th>Characteristic property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Noble metal nanoparticles</td>
<td>Au, Ag, Cu, Pt</td>
<td>Surface plasmon</td>
</tr>
<tr>
<td>Metal oxides</td>
<td>SiO₂, TiO₂, Fe₃O₄</td>
<td>Superparamagnetism, photocatalysis</td>
</tr>
<tr>
<td>Quantum dots</td>
<td>CdS, CdSe, CdSe–ZnS,</td>
<td>Fluorescence, photocatalysis</td>
</tr>
<tr>
<td>Carbon nanomaterials</td>
<td>Nanotubes, graphene, nanodiamonds</td>
<td>Biocompatibility conductivity</td>
</tr>
<tr>
<td>(Bio)polymer-based nanoparticles</td>
<td>Polysaccharides (chitosan, cellulose), man-made polymers</td>
<td>Adaptability, soft materials, biocompatibility</td>
</tr>
<tr>
<td>Others i.e. supramolecular structures, porous materials</td>
<td>Metal organic frameworks, mesoporous silica</td>
<td>Porosity, loading capacity, large surface area</td>
</tr>
</tbody>
</table>

In this chapter we will explore characteristic properties of these materials such as their high surface area and surface energy, their interaction with light and size-dependent fluorescence, and have a look at why they differ from their bulk counterparts.
1.3 Nanosized vs Bulk Materials

As a result of their small size, materials at the nanoscale behave more like molecules than a bulk material. Surface effects and quantum confinement determine physical and chemical properties, including increased catalytic activity, tunable fluorescence, surface plasmons and change in magnetic properties and conductivity.

Atoms at the surfaces of nanomaterials have fewer neighbours than their bulk counterparts and their unsatisfied, dangling bonds make the system more unstable. The smaller the particle, the larger the number of atoms on its surface and the larger the binding energy per atom. Such a system will have a high affinity to bind other species or to engage in various interactions that can minimise the surface energy, making nanosized systems excellent catalysts (materials that speed up chemical reactions).

As we approach the world of atoms, quantum size effects start to play an important role. In metals and semiconductors the electronic wave functions of conduction electrons are delocalised over the entire system; these electrons can be described as ‘particles in a box’. The density of state (DOS) and the energies of the particles depend on the size of this box. As the box becomes smaller, properties such as light absorption, light emission, ionisation potential, and the number of electrons available for bond formation change.

What happens at the small scales and within small spaces? If we consider a reaction between two molecules in a dilute solution, we know that the reaction will be governed by the concentration of these molecules and the reaction rate constant. But when reacting species are confined within a small space, electrostatic or hydrophobic interactions become more intense easing the intramolecular interactions and product formation. Chemists often say that the effective molarity of the system increases. This effect is particularly important in biological systems; molecules concentrated in a particular cell compartment will react much faster than when they are dispersed throughout the entire cell interior. In fact, we know that the reactions that rarely occur in bulk may be driven by an increased effective molarity when they are packed within structures such as nanowells or nanopores. Design of nano-reactors and artificial compartments has already made an impact in the field of catalysis. Confining reagents within nanostructures often leads to an increase of reaction rates and yields. A perfect example of such a system are proteins, in particular catalytic proteins (enzymes), which accelerate a myriad of reactions within the cell by confining reagents within the small volume of their reactive pocket.
What about the quantum effects at the nanoscale? How do they affect the properties of the materials? We will try to illustrate this without getting into the complexity of the quantum mechanics (see Further Reading at the end of this chapter for more details). Let us consider a spherical metal nanoparticle with a radius of 2 nm. Depending on the material, this nanoparticle might contain tens or thousands of atoms (see In Numbers 1.1 for a calculation).

**In Numbers 1.1 How Many Atoms Are There in a Nanoparticle?**

Taking 166 pm as the atomic radius of gold, calculate the number of gold atoms in a spherical 2 nm gold nanoparticle.

**Solution**

Assuming that both nanoparticle and atom are spheres, we can calculate the volumes (keeping in mind that 2 nm refers to the diameter of the nanoparticle):

\[
V = \frac{4}{3} \pi r^3
\]

\[
V_{\text{nanoparticle}} = 4.19 \times 10^{-27} \text{m}^3
\]

\[
V_{\text{gold atom}} = 1.92 \times 10^{-29} \text{m}^3
\]

The number of gold atoms is therefore:

\[
N_{\text{atoms}} = \frac{V_{\text{nanoparticle}}}{V_{\text{gold atom}}} = 2194.
\]

This is an approximation, as atoms will be packed within the nanoparticle following the rules of crystal packing, which means there will be some empty space between them.

Interacting atoms result in distribution of a large number of energy levels that form energy bands. In a single atom, two energy levels will be separated by a significant energy gap. Two interacting atoms produce two new energy levels (four all together), four atoms eight (Figure 1.1). With each new atom added, levels become closer in energy, resulting in densely packed bands and energy gaps which are easier to cross. After a certain number of atoms is packed together, the bands will overlap and the electrons will be able to move freely among the atoms.
The overlap and the gap between energy bands will differ for metals, semiconductors and insulators (Figure 1.2). An important concept to introduce at this point is the Fermi level, which describes the top filled electron energy level in a given material at absolute zero. It is a hypothetical concept also used to describe work needed to be done to add one electron to a given system.

Insulators are characterised by a Fermi level, which lies between two bands of different energy, in a large band gap that prevents electrons from transitioning from one band to another. In metals, the Fermi level lies within the highest occupied band, which means there is no energy gap to overcome and the electrons can move freely between the bands. Note that only those electrons very close to the Fermi energy are excited above it.
The average spacing between the energy states $\Delta E$ is given by

$$\Delta E = \frac{4E_F}{3N},$$

(1.1)

where $E_F$ is the Fermi energy and $N$ is the total number of valence electrons.

We can see that for a bulk metal with a large number of valence electrons, the spacing is small, and ultimately a continuous band is formed. As dimensions decrease and fewer atoms are present within a given volume, there are fewer valence electrons and the spacing between energy states increases. In short, energy levels become discrete and a small volume of materials starts to resemble the electronic structure of an atom. This is known as quantum confinement.

To achieve quantum confinement, at least one of the dimensions needs to be less than 100 nm. As the volume decreases, the density of state function $D_s$ – a mathematical model that explains how the number of available electron energy states vary with unit volume and energy – becomes more discrete (see Back to Basics 1.1).

For metals in which the Fermi level lies within the bands, discrete density of states exist further away from the Fermi level (Figure 1.3) and as a result, quantum confinement can be achieved only when the size is significantly decreased (to a few nm) and there is a small number of atoms within the given volume (see In Numbers 1.2).
The total number of energy states $N_s$ with energy up to $E$ (material will have a certain amount of energy, which is distributed among free electrons) is:

$$N_s = \left( \frac{8\pi}{3} \right) \left( \frac{2m_e E}{\hbar^2} \right)^{3/2} D^3,$$

where $m_e$ is the mass of the electron, $D^3$ is volume and $\hbar$ is Planck’s constant.

The number of energy states per unit volume $n_s$ is then:

$$n_s = \frac{N_s}{D^3} = \left( \frac{8\pi}{3} \right) \left( \frac{2m_e E}{\hbar^2} \right)^{3/2}.$$

The density of state function $D_s$, the derivative of the above equation with respect to energy, refers to the number of available electron energy states per unit volume, per unit energy:

$$D_s = \frac{8\sqrt{2\pi m_e}}{\hbar^3} \sqrt{E}.$$

It is important to remember that $D_s$ is only a mathematical model, and unlike the model, the real density of states function becomes more discrete as the volume changes and dimensions move towards the nanometre scale. In bulk materials, the energy levels are continuous, for 2D materials in which one dimension is on the nanoscale (thin films for example) the energy levels can change stepwise. As we go towards 1D materials (two dimensions on the nanoscale, for example nanowires), the separation is more discrete and finally in 0D materials (three dimensions on the nanometre scale), they will be clearly separated.
In Numbers 1.2 At What Diameter Does a Gold Nanoparticle Achieve Quantum Confinement at 25 °C?

Some electrons can be excited above the Fermi energy and need to have energy larger than $k_B T$. For quantum confinement, the following must be true:

$$\Delta E = \frac{4E_F}{3n_v} > k_B T,$$

where $n_v$ is a number of valence electrons, $k_B$ is Boltzmann’s constant and $E_F$ for gold is 5.53 eV. By rearranging the above equation we get:

$$n_v < \frac{4E_F}{3k_BT}$$

$$n_v < \frac{4(8.86 \times 10^{-19} \text{ J})}{3(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})} = 288.$$

This means that particle needs to have fewer than 288 valence electrons. Gold has a density of 19 320 kg m$^{-3}$ and atomic mass is 79 g mol$^{-1}$. Density of atoms is:

$$\frac{19 320 \text{ kg m}^{-3} \times N_A}{0.079 \text{ kg mol}^{-1}} = \frac{(19 320 \text{ kg m}^{-3})(6.02 \times 10^{23} \text{ atoms m}^{-3})}{0.079 \text{ kg mol}^{-1}} = 1.5 \times 10^{29} \text{ atoms m}^{-3}.$$

The volume of the particle is given by

$$V_p = \frac{288 \text{ atoms}}{1.5 \times 10^{29} \text{ atoms m}^{-3}} = 1.92 \times 10^{-27} \text{ m}^3.$$

If we assume that the nanoparticle is spheric, volume will be defined as

$$V = \frac{4}{3}r^3 \pi$$

and

$$r = \left(\frac{3V}{4\pi}\right)^{1/3} = \left(\frac{3(1.92 \times 10^{-27} \text{ m}^3)}{4\pi}\right)^{1/3} = 7.7 \times 10^{-10} \text{ m}.$$

Taking this into account the gold particle will achieve quantum confinement and behave as non-metal when its diameter is less than 1.4 nm.
However, as the size gets smaller, a significant role in metal nanoparticles is played by the large number of surface atoms and electrons, which results in formation of an electron cloud known as a surface plasmon. Surface plasmon describes the collective excitation of free electrons in metals, which can oscillate when stimulated by an energy source (Back to Basics 1.2). Surface plasmon has been extensively exploited in bionanotechnology, in particular for design of biosensors.

**Back to Basics 1.2**  
**Surface Plasmon**

The early work on surface plasmon (SP) was done by Rufus H. Ritchie (1924–2017) in the 1950s – the impact of his 1957 paper becoming clearer only decades later with the development of nanotechnology (Ritchie, 1957). Understanding surface plasmons opened up the fields of nanoplasmonics and nanophotonics, and resulted in a number of applications in optoelectronics, solar energy conversion and medicine.

A plasmon is a quantum of the collective excitation of free electrons in solids. A surface plasmon is an electromagnetic wave that propagates on the metallic–dielectric interface of metallic thin films. Essentially, surface plasmons are the light waves that are trapped on the metal surface because of their interaction with the free electrons, which respond collectively by oscillating in resonance with the wave of light. A combined excitation consisting of a surface plasmon and the electromagnetic field of light is called a surface plasmon polariton (SPP) at a planar interface, or a localised surface plasmon (LSP) for the closed surface of a metal nanosphere.

By interaction of the incident electromagnetic field of light with the metal nanoparticle, the conduction electrons at the nanoparticle surface oscillate with respect to the nanoparticle lattice due to the Coulomb attraction.