Chapter 3
Nanomaterials and Their Properties

Abstract The melange of definitions of nanomaterials is discussed. Terminology laid down by the International Organization for Standardization (ISO) and European Commission (EC) concerning nanomaterials is described. Ultrafine grained materials with grain size in nanoscale range show unusually higher mechanical strength than coarse-grained materials. Two vital characterizing parameters representing the degree of dominance of surface effects in materials are dispersion and coordination number. Due to predominance of surface effects, nanoparticles are efficient catalytic agents. Melting points of these particles are lower than those of the bulk material, and phase transitions are hazily defined. The onset of quantum size effect in nanomaterials depends on the dimension of the nanomaterial compared to exciton Bohr radius. Due to quantum confinement, the bandgap of a semiconductor nanocrystal is wider than that of the bulk semiconductor. Dependence of bandgap on nanocrystal size leads to emission of light of different wavelengths from these quantum dots. In metals, interaction of light with surface plasmons leads to resonance oscillations at particular frequencies, thereby producing different color effects. Notable magnetic properties of nanomaterials include the display of superparamagnetic behavior, the exhibition of magnetism in materials that are generally believed to be nonmagnetic, and the giant magnetoresistance effect.

3.1 Bewilderment from a Multitude of Nanomaterial Definitions

A clear-cut definition of “nanomaterial” cannot be introduced straightforward. A multiplicity of definitions can be found in the literature. Each definition is valid within the limited parlance of a particular sector or organization. Hence, each definition forestalls the power and strength of any other definition. An internationally harmonized scenario cannot be seen.

Many modern consumer end products utilizing nanomaterials have originated from existing products by incorporating nanomaterials into solid, viscous, or liquid matrices. So, a variety of prevailing definitions leads to the circumstances that the

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same substance is agreed to be a nanomaterial under the legislation of a governing body but excluded by another body. Such conflicting situations have led to the great puzzlement of consumers, industries, and law enforcing agencies. Integrity of the market has to be assured. Bogus claims must be thwarted. It is therefore essential that a universal definition should be framed, which is acceptable not only nationally but in global market.

3.2 ISO (International Organization for Standardization) Definitions

3.2.1 Nanomaterial

It is a generic term [1]. It includes nano-object and nanostructured material. It applies to a material either having any external dimension in the nanoscale or having its internal structure/surface structure in that scale. A nano-object can be nanostructured.

3.2.2 Nanoscale

This is the scale stretching over the size range from circa 1 to 100 nm. In this size range, the material typically but not wholly, displays such properties, which are not clearly evident and deduced from the properties exhibited by it in a larger size. The size limits are considered approximate for appearance of such properties. Further, the lower limit in this definition ($\sim$1 nm) is purposefully laid out. It is meant to keep away from designation of single and small groups of atoms as nano-objects or elements of nanostructures. These possibilities exist in the absence of a lower limit.

3.2.3 Nano-object

A generic term applicable to all discrete nanoscale objects, it indicates a material possessing one, two or three external dimensions in the nanoscale.

An established general definition for particles is related to nano-objects.

3.2.3.1 Particle

A particle is a minute portion of matter. This portion must have defined physical boundaries. An interface is also considered to be a physical boundary. A particle can move as a complete unit in itself. This generalized definition of particle is valid for nano-objects.

For particles, which are clustered together in agglomerates and as aggregates, the definitions are:

3.2.3.2 Agglomerate

The agglomerate is a collection of particles, which are loosely bound to each other. It may also be a blending of particles and aggregates (defined below). The mixture must conform to the condition that the external surface area of the agglomerate = the sum of the surface areas of the separate components.

3.2.3.3 Aggregate

An aggregate signifies a particle containing firmly attached or merged particles. The interparticle binding takes place in such a manner that the following condition is satisfied: external surface area of the aggregate is significantly < the sum of calculated surface areas of the individual components.

Agglomerates and aggregates are treated as "secondary" particles. This is done to tell them apart from the original individual particles, which are labeled as "primary" particles.

The vocabulary dealing with a few types of nano-objects is familiarized. It includes six distinct shapes together with a supplementary specific case of the quantum dot. Nanomaterials of different dimensions are illustrated in Fig. 3.1.

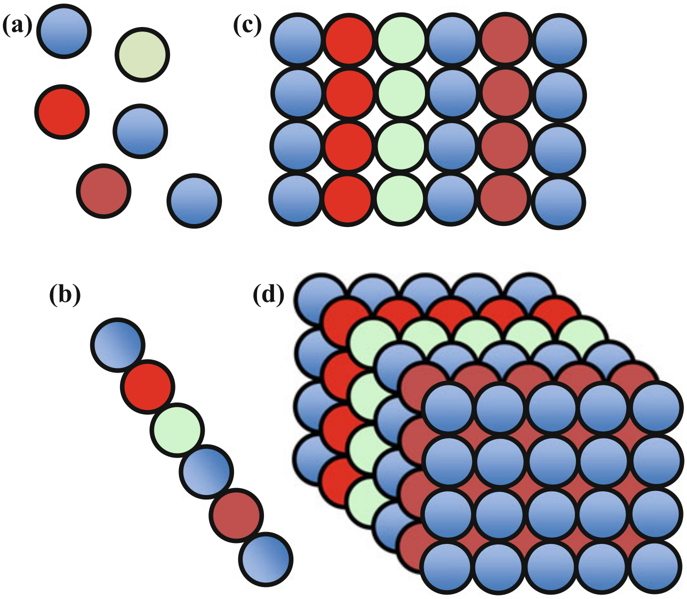

Fig. 3.1 Nanomaterials of different dimensionalities: **a** 0D, **b** 1D, **c** 2D, and **d** 3D

3.2.3.4 Nanoparticle

A nanoparticle is a nano-object. This nano-object has all three external dimensions in the nanoscale. In other words, a nanoparticle is a discrete nano-object. All three Cartesian dimensions of this nano-object are <100 nm.

3.2.3.5 Nanoplate

A nanoplate is a type of nano-object. It has one external dimension in the nanoscale. Its other two external dimensions are much larger. It is correct to refer to a nanoplate as a two-dimensional nano-object.

3.2.3.6 Nanofibre

A nanofibre is a kind of nano-object. It has two similar external dimensions in the nanoscale. Its third dimension is much larger. Nanofibre may be treated as a one-dimensional nano-object.

3.2.3.7 Nanotube

A nanotube is essentially a hollow nanofibre.

3.2.3.8 Nanorod

A nanorod is basically a solid nanofibre.

3.2.3.9 Nanowire

A nanowire is a nanofibre. It may be either electrically conducting or semiconducting.

The three nano entities, namely, nanotube, nanorod, and nanowire are all one-dimensional nano-objects.

3.2.3.10 Quantum Dot

It is a crystalline nanoparticle of a semiconductor material, i.e., a semiconductor nanocrystal. Often, the definition is relaxed to include nanocrystals of conductors such as aluminum. Its size-dependent properties arise from quantum confinement effects on the electronic states. To explain quantum confinement, let us note that:

When the size of the particle becomes comparable to the wavelength of the electron, the random motion of the electron is confined to discrete energy levels instead of energy bands. This effect of confinement or restriction of electron motion is called quantum confinement. The result of the discreteness of energy levels is that the forbidden energy gap is widened. Hence the energy bandgap increases.

Briefly, nanoparticles are materials that are nanoscale in all three dimensions. Thus quantum dots are nanoparticles. So are the colloidal solutions containing finely dispersed particles with linear dimensions <100 nm. Nanowires and nanotubes are materials that are nanoscale in two dimensions. But they are extended in the third dimension. Nanolayers, such as a thin films or surface coatings are materials that have one dimension in the nanoscale. But they are extended in the other two dimensions. Some of the geometrical features seen on computer chips belong to this class.

3.3 EC (European Commission) Definitions

3.3.1 Nanomaterial

There are two subclauses in the article containing the principal recommendation of the commission [2, 3]: (i) “Nanomaterial” means a naturally occurring material, or a parenthetically formed material or a material manufactured by some process. It contains particles, which are either present in an unbound state or as an aggregate or in the form of an agglomerate. One or more external dimensions of these constituent particles must be in the size range 1–100 nm for 50% or greater proportion of their total number with regard to distribution of sizes. (ii) In dealing with situations where safety, environment, health, or competition is of primary interest, the 50% threshold is superseded by a number x satisfying the inequality $1 \geq x \geq 50$.

It is further clarified that by exemption from subclause (i), fullerenes, graphene flakes, and single-walled carbon nanotubes, which have one or more external dimensions <1 nm, i.e., lower than the 1 nm limit, are to be considered as nanomaterials. For explanation of subclause (i), following definitions are laid down:

3.3.2 Particle

It is a minute chunk of matter whose boundaries are precisely and unerringly specified.

3.3.3 Agglomerate

It is a gathering of particles, which are either weakly bound or aggregates. The resulting surface area of these particles equals the sum of the surface areas of the independent components.

3.3.4 Aggregate

It comprises particles that are strongly bound or merged together.

Every time it is scientifically possible and whenever entreated in legislature, obedience of subclause (i) is evaluated from specific area per unit volume. This parameter should be $>60\ \text{m}^2\ \text{cm}^{-3}$. Nonetheless, if a material is judged to be a nanomaterial from subclause (i), it is a nanomaterial. This is acceptable even if its surface area per unit volume is $<60\ \text{m}^2\ \text{cm}^{-3}$.

The definition verbalized by EC is more specific and less ambiguous than that prescribed by ISO. This is because it is formulated for legal purposes. Several methods can be applied for measuring the sizes of nanoparticles: (i) Ensemble methods: These methods measure large numbers of particles simultaneously. Dynamic light scattering, small-angle X-ray scattering, and X-ray diffraction are three such methods. (ii) Counting methods: One such method is particle tracking analysis. Imaging techniques, e.g., electron and atomic force microscopies also fall in this class. (iii) Fractionation methods: These include centrifugal liquid sedimentation, field-flow fractionation, size exclusion chromatography, etc.

In applying these methods, three difficulties are faced: First, measurements on the constituent particles inside aggregates are complicated. Second, the experimentally measured signals cannot be straightforwardly correlated with number size distributions. Third, it is not easy to detect and count particles of <10 nm size. None of the present methods can ascertain the fulfillment of the criteria for being a nanomaterial when all the kinds of potential nanomaterials are taken into account.

Thus far, the focus in this chapter has been towards laying down clear-cut definitions on nanomaterials. From the next section onwards, let us divert our attention to seek the underlying causes for the divergence in behavior of nanomaterials from matter in bulk state.

3.4 Mechanical Strength of Nanomaterials

Bulk materials have a grainy structure. Randomly oriented grains are interconnected by grain boundaries. Dislocations are line defects in the material where the atoms are abnormally placed in the crystal. They are either of the two types: edge and screw dislocation. When a stress is applied to the material, the dislocations move resulting in plastic deformation. Therefore, in order to produce a strong material, the motion of dislocations must be opposed. Hindrance to dislocation movement is offered by grain boundaries. They try to block the motion of dislocations. This implies that a material containing more grain boundaries will be more capable of impeding the dislocations. Such a material is one containing more grains. To produce more grains in the same material, one must reduce the grain size. Hence, smaller is the grain size, more is the resistance to dislocation movement and as a result, stronger is the material. For bulk materials, dependence of the yield stress σ_{y} on the grain diameter d is expressed by the Hall-Petch equation

$$\sigma_{y=}\sigma_0 + k_y/\sqrt{d} \tag{3.1}$$

where σ_0 and k_y are constants for the material. The constant k_y is called the strengthening coefficient. Theoretically, one would expect that the yield stress will become infinite as the grain size approaches zero. But this does not happen. The yield stress attains a maximum value at a grain size of ~10 nm. Grains of size <10 nm are prone to another mechanism known as grain boundary sliding.

3.5 Characterizing Parameters for the Influence of Surface Effects on Material Properties

In materials science, two parameters are of paramount importance to get an idea about the extent or degree of surface effects in controlling the properties of the material. These parameters are dispersion and coordination number. Dispersion of a material is the fraction of atoms exposed to the surface. In other words, it is the ratio of surface to bulk atoms expressed as the number N_{S} of atoms located on the surface divided by the total number N_{V} of atoms present in the given volume of the material. Hence, dispersion D is given by

$$D = N_S/N_V \tag{3.2}$$

D is written in terms of the surface area S and the volume V of the material as

$$D = S/V \tag{3.3}$$

In case a spherical particle of radius r is under consideration, the dispersion D_{sphere} is obtained as

$$D_{\mathrm{sphere}} = \frac{4\pi R^2}{(4/3)\pi R^3} = \frac{3}{R} \tag{3.4}$$

As the radius of the particle decreases, the dispersion increases. Hence, the surface effects begin dominating.

Coordination number $\langle N_C \rangle$ of an atom in a molecule, ion, or crystal is the total number of its neighboring atoms. It is obtained by counting the bonds of an atom with neighboring atoms. Surface coordination number $\langle SN_C \rangle$ refers to the number of atoms associated with an atom located at the surface. Bulk coordination number $\langle VN_C \rangle$ signifies the number of atoms adjoining an atom situated in the interior of the material. Needless to say that surface coordination number is smaller than the bulk coordination number because an atom at the surface is surrounded by atoms on three sides only: left, right, and bottom whereas an atom inside the material is surrounded by atoms on all four sides: left, right, top, and bottom, by other atoms.

On decreasing the size of particles, their dispersion, i.e., the fraction of surface atoms increases. As these surface atoms have smaller coordination number than bulk atoms, surface phenomena dominate over bulk phenomena in these small size particles.

3.6 Catalytic Effects of Nanomaterials

From the coordination number viewpoint, considering a cubic crystal, the atoms at the corners of the cube have the lowest coordination number. Therefore these atoms have unsatisfied bonds. The atoms with unsaturated bonds show the greatest tendency to combine with adsorbate molecules. After the corner atoms come the atoms at the edges of the cube. Their coordination number is higher than that of the corner atoms whereby they are less active in adsorption activities as compared to the corner atoms. At the last place are the atoms on the plane faces of the cube, which are least active due to their high coordination number than previous two classes of atoms. These phenomena indicate that smaller the coordination number, more active is the material in surface exchanges and hence catalytic activity. The small coordination number of nanoparticles considerably improves their catalytic behavior. Gold nanoparticles of size ~2–3 nm are good catalytic agents, losing their noble behavior which has prompted its widespread use as a non-tarnishable metal. Work function of a single platinum atom is 9 eV while that of bulk platinum is 5.3 eV. Acceptance or donation of charges depends on these values. Thus by changing the size of a congregation of particles, their chemical properties are favorably tuned.

3.7 Thermal Properties of Nanomaterials

3.7.1 *Melting Point Depression*

Due to the lower coordination numbers, the strength of stabilization of atoms on nanoparticle surfaces is drastically reduced. Hence, a lower temperature suffices to liberate the molecules from their bonds resulting in fall in melting points. A 2.5 nm

Au nanoparticle has a melting point of 930 K $\ll$ the melting point of bulk gold (1336 K). The melting point T_m of a collection of particles, each having a radius r, is related to the melting point T_M of the bulk material having the latent heat of fusion ΔH, by Gibbs–Thomson equation [4]

$$(T_\mathrm{m} - T_\mathrm{M})/T_\mathrm{M} = -2V\gamma/(r\Delta H) \tag{3.5}$$

where V denotes the volume occupied by 1 mole of the liquid, i.e., its molar volume, and γ stands for the tension existing at the boundary between the solid and liquid, viz., the interfacial tension. Besides lowering of melting point, another conspicuous effect is that the phase transition in a collection of a smaller number of particles loses sharpness. It is rather ill defined. Some portion of the collection is solid while the remaining portion is liquefied.

3.7.2 *Negative Thermal Capacity*

An interesting phenomenon that occurs with such small groups of atoms is negative thermal capacity. Negative thermal capacity arises from the fact that temperature is an indicator of kinetic energy whereas thermal capacity is related to total energy. When a portion of kinetic energy is converted into potential energy, a decrease in temperature is observed. This may be understood with reference to S8 ring and S8 linear chain structures. On application of heat to S8 ring, vibrational and rotational motions increase in amplitude and temperature rises. But when heat is localized to break a bond to convert a hot S8 ring to the cold S8 linear chain, the temperature falls.

3.8 Exciton Bohr Radius: A Characteristic Length for Quantum Confinement

The occurrence of the quantum size effect begins as soon as the size of the nanostructure becomes smaller than a characteristic length called the exciton Bohr radius. The exciton is a quasi-particle defined as a localized, electrically neutral bound state of an electron–hole pair. This pair is held together through attraction by Coulomb electrostatic force. Bohr radius a_H is the average radius of an electron orbiting around the nucleus of a hydrogen atom in its lowest energy level. It is based on the Bohr model of the atom, and is given by

$$a_\mathrm{H} = \hbar/(m_0 c\alpha) \tag{3.6}$$

where $\hbar$ is reduced Planck's constant = 1.05×10^{-34} J s, m_0 is the rest mass of the electron = 9.11×10^{-31} kg, c is the velocity of light = 3×10^{8} m/s and α is fine structure constant = 7.3×10^{-3}, giving $a_H = 0.053$ nm. The exciton Bohr radius a_{exciton} is the distance between the electron and the hole in an exciton. It is expressed as a function of a_H as

$$a_{\text{exciton}} = a_H \varepsilon_r m_0 / \mu \tag{3.7}$$

where ε_r is the relative permittivity of the material and

$$\mu = m_e^* m_h^* / \left(m_e^* + m_h^*\right) \tag{3.8}$$

In this equation, m_e* is the effective mass of the electron and m_h* is the effective mass of the hole. For common semiconductors,

$$50\,\text{nm} \leq a_{\text{exciton}} \leq 2\,\text{nm} \tag{3.9}$$

This means that quantum size effect is likely to take place in these materials in the distance range ~2–50 nm. From the viewpoint of dimensions, there are three kinds of confined structures, namely, (i) a quantum well in which the size of the material is reduced in one direction only so that the exciton can move freely in the other two directions; (ii) a quantum wire in which the material size is decreased in two directions so that free exciton movement is possible in only one direction; and (iii) a quantum dot in which the material is squeezed in all the three directions whereby there is no direction of free movement and the exciton's motion is restricted in all the directions. None of these restrictions applies in an infinite or bulk material.

3.9 Electronic and Optical Properties of Nanomaterials

3.9.1 Bandgap Broadening of a Spherical Semiconductor Nanocrystal: The Quantum Dot

In a bulk semiconductor crystal, the motion of electrons in a periodic crystal lattice is described by the Bloch wave function $\psi_{\text{Bloch, bulk}}(x)$. The Bloch wave function at a position x is given by

$$\psi_{\text{Bloch, bulk}}(x) = \exp(ikx) u_k(x) \tag{3.10}$$

where k is the wave vector of the crystal. The function u_k in the Bloch wave function is a periodic function. This function has the same periodicity as the crystal. Hence, we can write

$$u_{\mathrm{k}}(x) = u_{\mathrm{k}}(x + a) \tag{3.11}$$

The symbol a represents the lattice constant. Physically, the Bloch wave function $\psi_{\text{Bloch, bulk}}$ (x) is a plane wave exp (ikx). This plane wave is modulated by a periodic function $u_{\mathrm{k}}(x)$.

In a semiconductor nanocrystal or quantum dot, the Bloch wave function is corrected for the spatial confinement of the charge carriers and the exciton. This correction is done by multiplying the Bloch wave function $\psi_{\text{Bloch, bulk}}$ (x) by the envelope function ϕ_{env} (x) to account for the confinement effects. Hence, the Bloch wave function in the nanocrystal $\psi_{\text{Bloch, nano}}$ (x) becomes

$$\psi_{\text{Bloch, nano}}(x) = \psi_{\text{Bloch, bulk}}(x) \times \phi_{\text{env}}(x) \tag{3.12}$$

The envelope is a solution of the Schrodinger equation for the problem of particle in a three-dimensional box. If the confinement is identical in all the directions, the nanocrystal is a spherical box representing a quantum dot. The solutions are

$$\phi_{\text{env}}(\theta, \phi, r) = Y_l^m(\theta, \phi)R(r) \tag{3.13}$$

where $Y(\theta, \phi)$ are spherical harmonics and R (r) are Bessel functions. The solutions exhibit a striking similarity to the wave functions of the hydrogen atom. But in a hydrogen atom, the electron is constrained by the attractive force due to the positively charged nucleus containing a single proton. In a spherical nanocrystal, the electron is confined within the spherical potential well of diameter D. Substitution of Eq. (3.13) into the Schrodinger equation yields the solutions for the discrete energy levels of the electron restricted within the spherical potential well as

$$E_{n,l}^{\text{Conf}}(D) = 2\hbar^2\chi_{n,l}^2/\left(m^* D^2\right) \tag{3.14}$$

where m^* is effective mass of charge carriers (electrons or holes) and $\chi_{n,l}$ are the roots of the Bessel function, which are absolute values increasing with principal quantum number $n = 1, 2, 3, \ldots$ and secondary quantum number $l = 0, 1, 2, 3, \ldots$. The first energy level has the quantum numbers $n = 1$, $l = 0$. The second energy level has the quantum numbers $n = 1$, $l = 1$. Quantum numbers of the third energy level are $n = 1$, $l = 2$. Note that the restriction $l \leq (n - 1)$ for a hydrogen atom is inapplicable to the nanocrystal because of the difference in potential functions for the two cases.

The total bandgap of the nanocrystal = the fundamental bandgap of bulk semiconductor + the confinement energy of electrons + the confinement energy of holes, which is expressed as

$$E_{\mathrm{g}}^{\mathrm{total}} = E_{\mathrm{g}}^{\mathrm{bulk}} + 2\hbar^2\chi_{n,l}^2/\left(m_{\mathrm{e}}^*D^2\right) + 2\hbar^2\chi_{n,l}^2/\left(m_{\mathrm{h}}^*D^2\right) \tag{3.15}$$

Since the electron and hole are treated independently, it is implicitly assumed that the Coulomb interaction between them is inadequate for the formation of a bound exciton. This assumption is valid only when the radius a of the nanocrystal is $\ll$ exciton Bohr radius a_{exciton}. This is called the strong confinement regime. In this regime, the Coulomb energy is $\ll$ the confinement energy of the carriers. The kinetic energy of the charge carriers is $\gg$ Coulomb electrostatic energy. Hence, they are uncorrelated and independent. However, when $a > a_{\mathrm{exciton}}$, the confinement energy originates from the quantization of motion of the center of mass of the exciton. Instead of the electron in spherical potential, one has to consider an exciton in a spherical potential well. The discrete energy levels for the exciton are given by an equation similar to that for the electron. The solitary differentiating aspect of this circumstance is that the effective mass of charge carriers (electrons or holes) is replaced by the effective mass of the exciton. The confinement energy for a nanocrystal of radius a is given by [5]

$$E_{n,l}^{\mathrm{Conf}}(a) = \left\{\hbar^2\pi^2/\left(2a^2\right)\right\}\left\{\left(1/m_{\mathrm{e}}^*\right) + \left(1/m_{\mathrm{h}}^*\right)\right\} = \hbar^2\pi^2/\left(2\mu a^2\right) \tag{3.16}$$

Then the total bandgap of the nanocrystal reduces to the form

$$E_{\mathrm{g}}^{\mathrm{total}} = E_{\mathrm{g}}^{\mathrm{bulk}} + \hbar^2\pi^2/\left(2\mu a^2\right) \tag{3.17}$$

According to this equation, if the radius a of the nanocrystal decreases, i.e., for a smaller size nanocrystal, the second term increases and hence the bandgap of the nanocrystal is larger than the bandgap of the bulk semiconductor. Absorption spectra studies have shown that the energy of the exciton in the nanocrystal is shifted towards the blue color with respect to the bulk value resulting in the so-called “blue shift”. This is because the blue color corresponds to higher frequency and hence larger energy.

Theoretical calculation based on effective mass approximation was presented by Brus who gave the equation [6]

$$E_{\mathrm{g}}^{\mathrm{total}} = E_{\mathrm{g}}^{\mathrm{bulk}} + \hbar^2\pi^2/\left(2\mu a^2\right) - 1.786q^2/\left(\varepsilon_0\varepsilon_{\mathrm{r}}a^2\right) \tag{3.18}$$

where the second negative term arises from the Coulomb attraction between the electron and the hole having charges $\pm q$. The numerical factor derives from the computations of overlap integrals of the wavefunction. Its value differs marginally for different materials due to variation of dielectric constant ε_{r}.

Another effect, which has been overlooked so far, is the electron–hole spatial correlation effect. Kayanuma treated this effect [7]. Its inclusion resulted in the equation

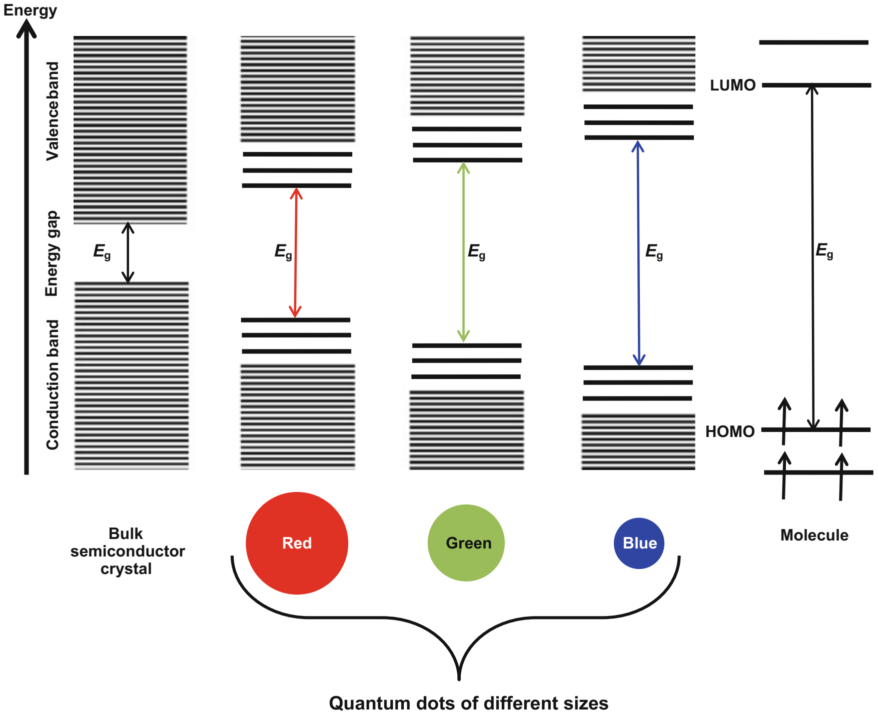

Fig. 3.2 Energy level splitting and bandgap widening with decreasing size of semiconductor crystal due to quantum confinement

$$E_g^{\text{total}} = E_g^{\text{bulk}} + \hbar^2\pi^2/\left(2\mu a^2\right) - 1.786q^2/\left(\varepsilon_0\varepsilon_r a^2\right) - 0.248E_{Ry}^* \qquad (3.19)$$

where E_{Ry}^* is the exciton Rydberg energy. The last subtractive term is consequential only for semiconductors having a small dielectric constant.

Figure 3.2 shows the effect of decrease in size of a semiconductor crystal on its energy band diagram.

3.9.2 Interaction of Light with Metallic Nanoparticles

In contrast to a semiconductor nanocrystal where light is absorbed/emitted according to the bandgap of the material, in a metallic nanoparticle a different phenomenon takes place. When the oscillating electric and magnetic fields in the electromagnetic wave representing the light beam pass near the free electrons of a metallic nanoparticle, they cause an oscillatory motion of the electronic charge resulting in the phenomenon called surface plasmon resonance in which the free electrons of the metallic nanoparticle collectively oscillate in synchronization with the frequency of the incident light. During surface plasmon resonance with 30 nm Au nanoparticles, the blue-green light of wavelength 450 nm is absorbed whereas red light ~700 nm is reflected so that the Au nanoparticles look reddish in color [8]. On increasing the size of Au nanoparticles beyond 30 nm, the red light is absorbed and blue light is reflected. Hence, the Au nanoparticles acquire a pale blue or purple color appearance. On decreasing the Au nanoparticle size to 2–5 nm, a yellow color is perceived. 40 nm Ag nanoparticles are blue while 100 nm Ag nanoparticles are yellow. Thus by varying the size of Au or other nanoparticles, their optical properties can be tailored in the desired manner. Colorimetric sensors based on Au nanoparticles exploit such color changes to assess the quality of food.

3.10 Magnetic Properties of Nanomaterials

3.10.1 Superparamagnetic Nanoparticles

Paramagnetic materials such as Mg, Mo, Ta, etc., are materials which experience a small force in an external magnetic field due to alignment of unpaired spins producing a feeble attraction. They lose their magnetic behavior after withdrawal of the field due to thermal agitation. In contrast, superparamagnetic iron oxide nanoparticles <50 nm in size contain a single ferromagnetic or ferromagnetic domain. These single domain magnets align their magnetic moments in the presence of the external magnetic field creating a strong attractive interaction. This interaction is much stronger than observed in a paramagnetic material. The magnetic susceptibility of nanoparticles is $\gg$ that of paramagnets; hence they are said to be superparamagnetic. On removing the magnetic field, the magnetization of nanoparticles exhibits random flipping under the influence of ambient temperature. Consequently, a net zero magnetic moment and zero residual magnetism are observed. The average time between flips is called Neel relaxation time. Generally, any ferromagnetic or ferrimagnetic material transfers to the paramagnetic state above a temperature known as Neel temperature but supermagnetic nanoparticles do so below the Neel temperature of the material. Thus superparamagnetic nanoparticles bridge ferromagnetism with paramagnetism. They share with ferromagnetism the property of reaching a high magnetization level in a low-intensity magnetic field but do not share with it the property of retention of magnetism after field removal. They share with paramagnetism the property of lose of magnetism after the external field is withdrawn but do not share with it the small magnetization generated in a paramagnetic material in the presence of the field.

3.10.2 Magnetism in Gold Nanoparticles

Bulk gold is a diamagnetic material. But 2 nm size gold nanoparticles coated with dodecanethiol ($C_{12}H_{26}S$) show ferromagnetic behavior. This magnetism is size-dependent. Its strength increases as the nanoparticles of larger diameters are used in the range 0.7–3 nm. The peak value occurs at 3 nm diameter. After 3 nm limit, the magnetism becomes weaker [9], showing properties like bulk gold. Spin-orbit coupling between the thiol compound bound to the surface with the surface atoms of gold nanoparticle is responsible for this magnetism. Magnetic moments produced by the spin polarization of surface atoms of Au nanoparticles are not quenched fully. In opposition, such quenching is achieved in bulk lattice. Thus stabilization of gold nanoparticles with thiols provides a route towards producing ferromagnetic properties.

3.10.3 Giant Magnetoresistance (GMR) Effect

It is a change in electrical resistance between two ferromagnetic materials separated by a thin layer of a nonmagnetic material having thickness in the nanoscale. In the absence of an external magnetic field, the magnetizations of the two magnetic layers are oriented in opposite directions. But on applying a magnetic field, they are aligned in the same direction. When these magnetizations are anti-directional, the resistance is maximum but when they become unidirectional, the resistance decreases to the minimum value. The effect is noticed only when the intervening nonmagnetic layer between the two magnetic layers has thickness in nanometer regime so that coupling between the magnetic layers can take place. The GMR is a quantum-mechanical effect.

3.11 Discussion and Conclusions

Definitions of nanomaterials were clarified. Associated terminology was discussed. Reasons for departure of nanomaterial properties from bulk behavior were described. Mechanical, chemical, thermal, optical, electronic, and magnetic properties of nanomaterials were treated. As nanomaterials differ in properties from the bulk materials, they may be considered as a separate class of materials with novel applications.

Review Exercises

3.1 Explain the problems arising from the multiplicity of definitions of a nanomaterial.
3.2 What is the range over which the nanoscale extends? What are the reasons for specifying 1 nm as the lower limit of this scale? What will happen if the lower limit is not defined?
3.3 What is a nano-object? Define a particle.
3.4 Distinguish between agglomerate and aggregate.
3.5 Define a nanoparticle. What is a nanoplate? Differentiate between nanotube and nanofibre.
3.6 What are nanorods and nanofibres?
3.7 What is a quantum dot? How does the size of a quantum affect its properties?
3.8 How does the EC definition of a nanomaterial differ from its ISO definition? Explain the subclauses (i) and (ii) in EC definition.
3.9 Name the three materials, which are exempted from subclause (i) in EC definition of nanomaterial.
3.10 What is the guideline regarding specific area per unit volume for classifying a material as a nanomaterial? Explain in what respects the EC definition is more unequivocal than ISO definition?
3.11 Name three methods of measuring the size of nanoparticles.
3.12 Why is a nanomaterial mechanically stronger than bulk material? Write Hall-Petch equation and explain the symbols used.
3.13 Define dispersion of a material. What is meant by coordination number of an atom in a material? How do these parameters help in explaining the surface effects in materials?
3.14 Differentiate the catalytic activity of nanoparticles from that of materials in bulk form.
3.15 Why does a nanomaterial show a lower melting point than a bulk material? Why is phase transition in the nanomaterials not as sharp as for bulk state?
3.16 Write the Gibbs–Thomson equation. What does this equation describe?
3.17 Explain the reason for negative heat capacity of a nanomaterial with an example.
3.18 What is an exciton? Define: (i) Bohr radius and (ii) Exciton Bohr radius. How are they related? What is the typical range of values of the exciton Bohr radius in common semiconductor materials?
3.19 Define: (i) quantum well, (ii) quantum wire, and (iii) quantum dot. How is the exciton motion restricted in these nanostructures?
3.20 Write the equation for the Bloch wave function in a bulk semiconductor and explain the symbols used. How is this equation modified for a nanocrystal?
3.21 How are the solutions of the Schrodinger wave equation for a nanocrystal similar to those for the hydrogen atom? In what ways do they differ? What is the impact of this difference on the restriction of values for the secondary quantum number for the quantum dot?

3.22 What is strong confinement regime for the charge carriers? What happens in the weak confinement regime? Write the equations for the confinement energy of a nanocrystal in both types of confinement. Explain the symbols used.

3.23 Write the Brus equation for the energy bandgap of a nanocrystal and explain the symbols used in this equation. What correction was introduced by Kayanuma in the Brus equation?

3.24 How does light interact with metallic nanoparticles? Why do gold nanoparticles of different sizes have different colors?

3.25 What is superparamgnetism phenomenon observed in nanoparticles? What are the common features between superparamagnetism and paramagnetism, and between superparamagnetism and ferromagnetism?

3.26 Is gold a magnetic material? Explain the origin of magnetic properties in gold nanoparticles coated with thiols.

3.27 What is giant magnetoresistance effect? Why is this effect called a nanoscale phenomenon?

References

1. Lövestam G, Rauscher H, Roebben G et al (2010) JRC reference reports: considerations on a definition of nanomaterial for regulatory purposes. Publications Office of the European Union, Luxembourg, pp 1–36
2. Lidén G (2011) Commentary: the European commission tries to define nanomaterials. Ann Occup Hygiene 55(1):1–5
3. Linsinger TPJ, Roebben G, Gilliland D et al (2012) JRC conference report: requirements on measurements for the implementation of the European commission definition of the term ‘nanomaterial’. Publications Office of the European Union, Luxembourg. ©European Union 2012, pp 1–52
4. Roduner E (2006) Size matters: why nanomaterials are different. Chem Soc Rev 35:583–592
5. Koole R, Groeneveld E, Vanmaekelbergh D, et al (2014) Chapter 2 Size effects on semiconductor nanoparticles. In: de Mello Donega C (ed) Nanoparticles: workhorses of nanoscience. Springer, pp 13–51
6. Brus LE (1984) Electron–electron and electron–hole interactions in small semiconductor crystallites: the size dependence of the lowest excited electronic state. J Chem Phys 80(9):4403
7. Kayanuma Y (1988) Quantum-size effects of interacting electrons and holes in semiconductor microcrystals with spherical shape. Phys Rev B 38(14):9797–9805
8. Gold Nanoparticles: Properties and Applications. http://www.sigmaaldrich.com/materials-science/nanomaterials/gold-nanoparticles.html, Accessed 4 Feb 2016
9. Mujica V, Marquez M, Ratner MA (2007) Size dependence of ferromagnetism in gold nanoparticles: mean field results. Phys Rev B 76:224409-1–224409-6