

A Brief Manifestation of Nanotechnology

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Abstract Nanotechnology is basically focused on the fabrication of nanomaterials based on the manipulation, control, and integration of atoms and molecules at nanometer scale, due to which there develops sudden change in the size-dependent properties and functions. We have to integrate chemistry, physics and biology to form materials, structures, components, devices, and systems at the nanoscale level. In the metric system, prefix “nano-” refers to one-billionth ($0.000\ 000\ 001 = 10^{-9}$) of the base unit. In the nanoscale, at least one of the particle’s dimensions (height, width, or depth) should be at less than 100 nm. At this level, the chemical reactivity changes dramatically due to the reduction of particle size. This change occurs as a function of the structure and the density of electrons in the outermost electronic energy levels. Along with the physical properties such as optical, electrical, and thermal properties, magnetic characteristics may also change which in-turn depend on the distribution of electrons in the outermost energy levels, leads to the novel optical, electrical, magnetic behaviors and changes in the surface dependent properties. Because of the increase in the surface-to-volume ratio at the nanoscale level the properties of the material become strongly dependent (controllable) on the surface of the materials. The nanomaterials may be classified in number of ways, viz., based on: (i) dimensionality (ii) surface morphology (iii) crystalline forms (iv) chemical nature (v) chemical composition (vi) magnetic behavior (vii) functionalization or (viii) applications. But none of these classifications can be considered as absolute one. They are usually composites or hybrid in nature because in majority of cases organic compounds are used to stabilize them through capping or functionalization during synthesis. Magnetic nanomaterials have giant spins, which

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may be described as a single magnetic domain having uniaxial anisotropy, their EMR signals can be exploited for various biomedical and many other applications. Number of biomedical applications of nanoparticles is becoming possible because of their specific physicochemical properties and controllable dimensions which range from a few nanometers to nearly tens of nanometer, due to which they come in the size range smaller than that of a plant or animal cells having submicron size domain.

Keywords Nanomaterials • Classification • Dimensionality • Surface morphology • Chemical nature

1 Introduction

It will not be an exaggeration to call Nobel Prize winner physicist of the year 1965, Sir Richard Feynman as “Father of nanotechnology,” as he came up with his historical thought of nano by uttering these words, “there is plenty of room at the bottom” in his historic lecture at a conference held by American Physical Society in 1959, though the term nanotechnology was first given by Norio Taniguchi [1] at the University of Tokyo in 1974. Feynman introduced the idea of manipulating the very small, even down to the level of individual atoms for technological purposes. Within the span of a half century nanotechnology industry has taken over. Nanotechnology generally means building things from the bottom level, with atomic precision. Today, nanotechnology is meant for the science of making, synthesizing, designing, producing things which have at least at one dimensions of 100 nm or less and using it for various devices. It means that purposeful engineering of matter by manipulation, control, and integration of atoms and molecules at scales of 100 nm or less forms the basis of nanotechnology to achieve size-dependent properties and functions. This integrates chemistry, physics and biology to form materials, structures, components, devices, and systems to play at nanoscale level especially for industrial and commercial objectives.

Due to their peculiar size and physicochemical properties, nanomaterials offers major advantages. The development of unique nanoscale structures has revolutionized the industry. In the realm of nanotechnology the scientists, chemists, physicist and engineers have started working at the molecular and cellular levels to make important advances (Fig. 1) in various fields such as fabrication, modeling, life sciences, medicine, magnets and healthcare, electronics, smart materials and sensors, nanoscale biostructures, energy capture and storage devices, and consumer products.

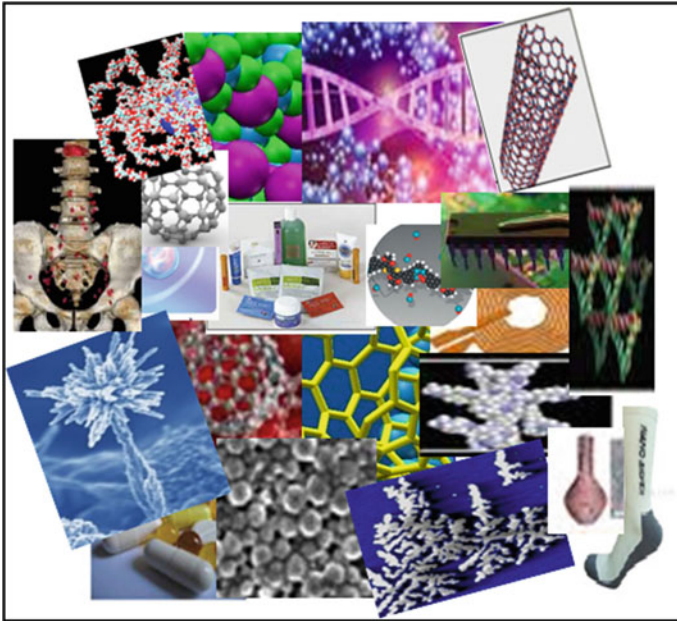


Fig. 1 Materials with nanotechnology

2 Classification

Each and every material is made up of peculiar arrangement of particular atoms in a specific way which defines its properties and behavior. Nanomaterials can be prepared by cutting, chipping, pounding, extruding, ball milling, precipitating and many more top-down and bottom-up methods. The main difference in the structure of nanomaterials arises on how they are prepared. Their formation requires knowledge of new types of synthetic methods and new understanding of the formation of materials at nanoscale. In the case of nanomaterials, the atoms align themselves in space in such a different way which is not found in the bulk form of the same material and there is significant variation in their properties also. According to the difference in certain criteria, nanomaterials may be classified in number of ways. Classifications based on some important criterions are given below

2.1 Classification Based on Dimensionality

Nanomaterials can be created with various modulation dimensionalities. Siegel [2] classified these nanostructured materials accordingly into four categories based on their dimensionality as

- (i) Zero dimensional (0D)—Having three dimensions in the nanometric range (by a dimensionality limited to 50 nm), e.g., atomic clusters, filaments and cluster assemblies, fullerenes, etc.
- (ii) One dimensional (1D)—Having two dimensions in the nanometric range, e.g., multilayers, nanotubes, nanorodes, nanowires, nanofibers manifest more advanced and promising properties as being the 1D quantum wires nanoscopic in diameter but microscopic in length.
- (iii) Two dimensional (2D)—These have one dimension in nanometric range, e.g., ultrafine-grained over-layers or buried layers, heterostructures, and nanodisks.
- (iv) Three dimensional (3D)—Such nanophase materials which consist of equiaxed nanometer sized grains. For example, thin films with atomic-scale porosity, colloidal and different nanoparticles having various structures and morphologies.

Classification based on dimensionality is pictorially represented in Fig. 2.

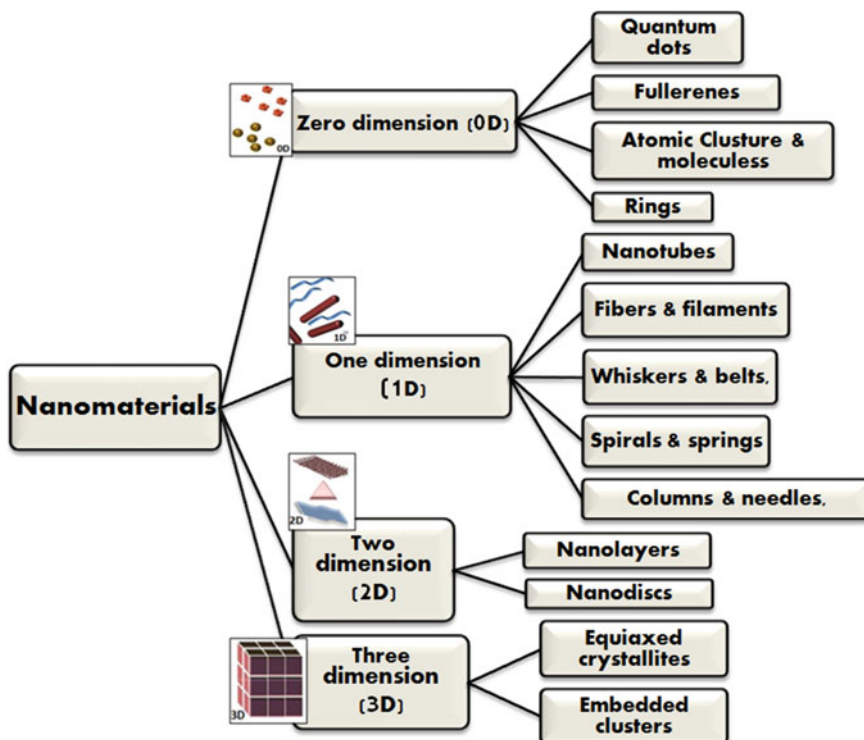


Fig. 2 Classification of nanomaterials based on dimensionality

2.2 Classification Based on *Surface Morphology*

As a reflection of templation or mode of synthesis different types of morphologies or shapes arise spontaneously. The properties and usage of a particular nanoparticles depends on its morphology provides the basic key for their mode of utilization in several advancing technologies. There are nanospheres that are spherical, nanoreefs, nanoboxes, nanoclusters, nanotubes, nanoflowers, etc. They may be classified on the basis of morphology considering their flatness, sphericity and aspect ratio. Aspect ratio is attributed to the proportional relationship between the widths of a structure with its height. Nanoparticles can be classified according to their aspect ratios also as

- (i) Nanoparticles in which diameter varies with length have generally high aspect ratio. For example, nanotubes, nanorods, and nanowires having various shapes as helices, zigzags, nanobelts, etc.
- (ii) Collections of many particles that exist as powders, suspension, or colloids have generally small-aspect ratio. For example, nanoparticles having that spherical-, oval-, cubic-, prism-, helical-, or pillar-shaped morphologies.

2.3 Classification Based on *Crystalline Forms*

The basic difference between crystalline nanostructures and amorphous nanoparticles lies in the way how the atoms are arranged around each other in the nanocrystalline systems besides their size. Thus on the basis of crystallinity, solids generally appear in three forms (Fig. 3)

- (i) Amorphous—It does not have long range order, e.g., as glasses. They have some short range order at the atomic length scale depending on the nature of chemical bonding.
- (ii) Polycrystalline—They have multiple domains of varying size and orientation. Their orientation may not have any preferred directions. Therefore, they may say to have random texture. These crystallite domains are sometime also referred to as grains.
- (iii) Crystalline—A single extended domain have high long range order, properly arranged domains.

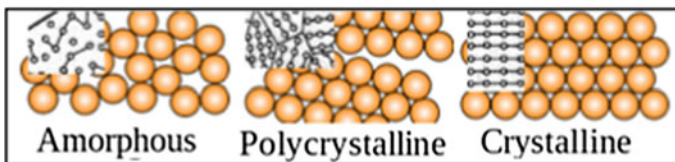


Fig. 3 Different types of crystalline forms

2.4 Classification Based on *Chemical Nature*

We know that all the materials are basically formed with the chemicals which may be inorganic, organic, or mixture of these two. Classification of nanomaterials based on the chemical nature is pictorially depicted in Fig. 4.

2.5 Classification Based on *Chemical Composition*

Chemical composition can be referred to the type of arrangement of atoms according to the ratio of the size of atoms in molecules of a particular material. Upon the addition and subtraction of chemical reagents, chemical composition of the particular substance changes. The properties of a substance are established according to its chemical composition.

According to Gleiter [3] the one-, two-, or three-dimensional nanostructures may be further classified on the basis of their chemical composition too, into four families (Fig. 5).

- (i) First family—In the most simple case in which all the constituents are distributed homogenously through out the region having same chemical composition, e.g., semicrystalline polymers or multilayers of thin film crystallites which are separated by an amorphous layer, etc. [4]

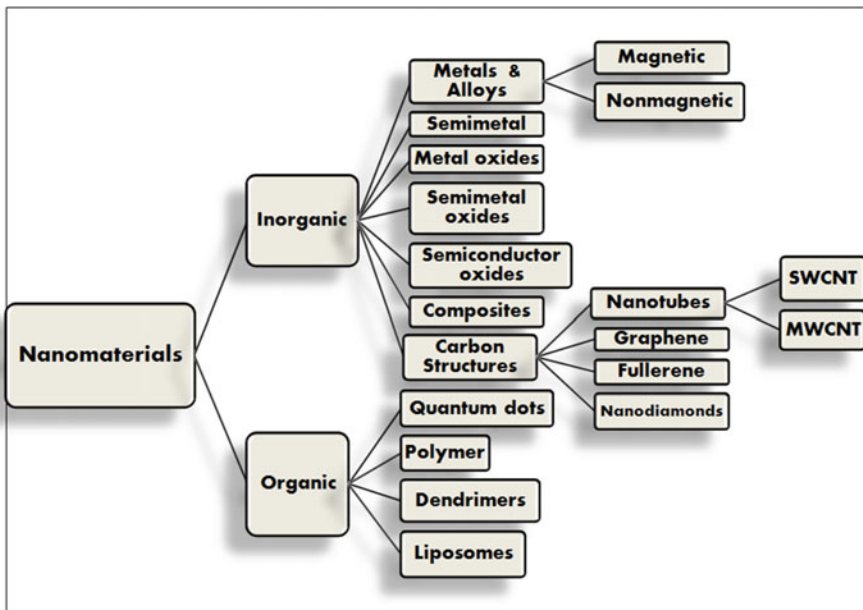


Fig. 4 Classification of nanomaterials based on chemical nature

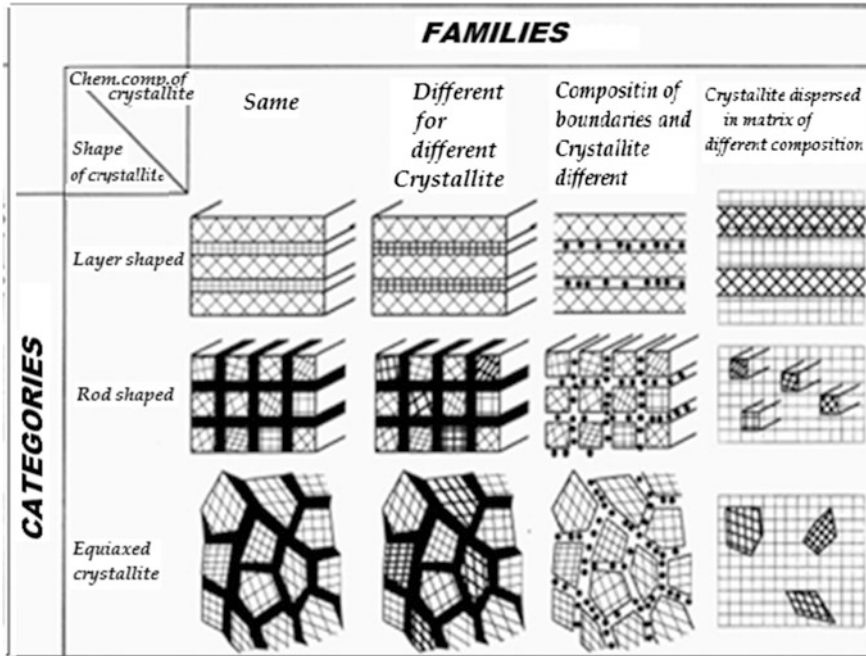


Fig. 5 Classification of nanomaterials based on chemical composition [3]

- (ii) Second family—Those substances in which materials have different chemical composition of constituents, e.g., quantum well structures.
- (iii) Third family—Those materials in which they a different chemical composition or having materials of mixed component system, e.g., alumina ceramic with Ga in its interface [5].
- (iv) The fourth family—All those nanomaterials which are formed by nanometer-sized particles (layers, rods or equiaxed crystallites) dispersed in such a matrix having different chemical composition, e.g., hardened alloys precipitation.

2.6 Classification Based on Magnetic Behavior

All the materials do not respond similarly with the externally applied magnetic field. Thus, on the basis of their response to any externally applied magnetic field, nanoparticles may be classified into five categories, namely, diamagnetic, paramagnetic, ferromagnetic, antiferromagnetic, and ferrimagnetic [6]. Orientations of the magnetic moments in a material place them in the above categories accordingly. At nanolevel also, the particles exhibits magnetic properties only in the presence of an

external magnet and changes to a nonmagnetic state again when the external magnetic field is removed. At this state, many factors play their role in determining the magnetic properties of nanomaterial, such as the, particle size, shape, morphology, their chemical composition and interaction with the surrounding matrix and the neighboring particles. The magnetic behavior of any material can be controlled by altering any of these factors to a certain limiting extent. For example, spontaneous magnetisation occurs below T_C when the particle size is $\geq 1 \mu\text{m}$. For single-domain magnetic particles with particle size equal to 1–30 nm, at $T_b < T_C$, the orientation of the magnetic moment of a particle remains same in space, but the particle ensemble shows a magnetic hysteresis. At higher temperature above to T_b , the particle attains superparamagnetic state. Usual paramagnetic properties are retained by a single atom (ion) with particle size equal to $\sim 0.2 \text{ nm}$. At the range of the quantum dots, high field irreversibility type of new phenomena, superparamagnetism or extra anisotropy contributions, are observed by the magnetic nanoparticles. The magnetic behavior of individual nanoparticles develops such phenomena due to its small and finite-size and surface effects [7]. In a superparamagnetic material, spins are substituted by small ferromagnetic domains. Generally, when the particle comes in a state of uniform magnetization at any field, it should have only a single magnetic domain. As a result of magnetic anisotropy, such type of superparamagnetism arises. It means that the spins are aligned along a preferred crystallographic direction at this state [8]. In the presence of an external magnetic field, the aligned domains generate a strong attractive interaction. Once the external magnetic field is removed, thermal agitation cancels residual magnetization.

Despite of the great importance of the morphology of nanoparticles, in magnetic devices for storing or processing information, where well-defined magnetization axes and switching fields are required, and the alignment of domains play its important role.

2.7 Classification Based on Functionalization

With the advancement in the nanomaterial-based applications, the development of functionalized nanoparticles gained specific recognition especially in the field of biomedical and life sciences. Clinical results have shown that functionalized nanoparticles with different functional groups or can say multifunctional nanoparticles yielded enhanced efficacy with minimal side effects [9]. For stabilization purposes and to avoid agglomeration, nanoparticles surface modification/coating is done by some capping or functionalizing agents. Thus, the on the basis of coating/functionalization, nanoparticles can also be classified as

- (i) Bare nanoparticles—without any coating
- (ii) Capped Nanoparticles—to avoid agglomeration

- (iii) Functionalized nanoparticles—to perform certain specific task. Functionalization may be of two types
- Post Functionalization—When the functionalization of nanoparticle is done by capping or grafting organic groups onto the active surface of nanomaterials after the synthesis is known as post functionalization [10].
 - In situ* Functionalization—When during the synthetic process only functionalization and modification of nanomaterials is carried by organic compounds, then it is said to be *in situ* functionalization [11, 12]

2.8 Classification Based on Applications

Jack et al. have well said in their book “The Next Big Thing Is Really Small” [13] that how the future of our business will be changed by nanotechnology, i.e., nanotechnology has a wide horizon of its applicatory attributes. Perhaps not a single sphere of application is left without nanotechnology. Its broad applicatory scenario may be broadly classified as mentioned in Fig. 6.

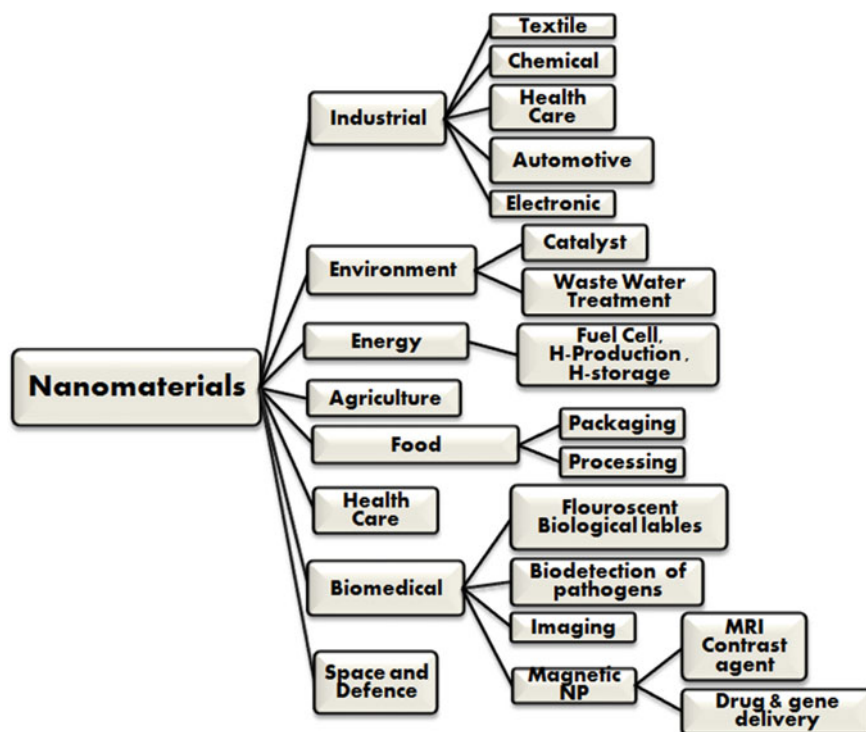


Fig. 6 Classification of nanomaterials based on applications

3 Reason for the Peculiarity in the Properties

As the sizes of a substance begins to move towards the nanoscale, its properties become unique and dramatically different from the same substances in the bulk form. For doing nanotechnology, scientists work at the nanoscale level to enable them to utilize this unique different properties, viz., physical, chemical, mechanical, and optical properties of materials that naturally occur at this scale. Properties such as melting point, fluorescence, electrical conductivity, magnetic permeability, chemical reactivity, etc., changes as a function of the size of the particle. The reason for the dramatic change in the properties of nanomaterials can be attributed to the following two facts.

3.1 Discreteness of Energy Level

When we go from the macroscopic to the microscopic to nanoscopic to atomic dimension, we move from classical mechanics to quantum mechanics. Quantum mechanics gives a complete version to the world of nanometric scale, which is absolutely different from the classical Newtonian mechanics, which governs operations of everyday objects involving properties that are size-dependent. But quantum mechanics governs the interactions of very small things that range from micro-molecules to nano to atomic and subatomic particles. Nobel laureate Max Planck (won Prize for Physics in 1918), show in his famous quantum mechanics, that the particle of energy that is exchanged between matter and radiation is called quanta, a discontinuous quantity. E. Schrödinger and P. Dirac (Nobel Prize winners for Physics in 1933) have developed wave mechanical concept by incorporating physicist Louis de Broglie's matter wave concept and quantum mechanics which has driven a "revolution" in this field. Wolfgang Pauli's exclusion principle designated the states of particles, which has given highest degree of accuracy in the atomic world though this world resides on probabilities and uncertainties. A molecule is formed by the overlapping of atomic orbitals (the space where the probability of finding electron is highest), i.e., representation of electrons at discrete energy levels, can only be attained as a simulation.

The electron's energy levels in quatum dots are discrete and quantified as in an atom or in a molecule and not as in the case of an ordinary semi-conductor where electrons are spread out in energy bands (Fig. 7). The distribution of energy on these levels occurs according to the particle size of the crystal.

Thus, in nanocrystals, the electronic energy levels are discrete having finite density of states, because of the confinement of the electronic wave function to the physical dimensions of the particles and not continuous band as in the bulk. This phenomenon is known as Quantum confinement. Due to the quantum confinement, there occurs change in electrical properties of the material. Some materials that show conductivity in the bulk form may become semiconductors or poor

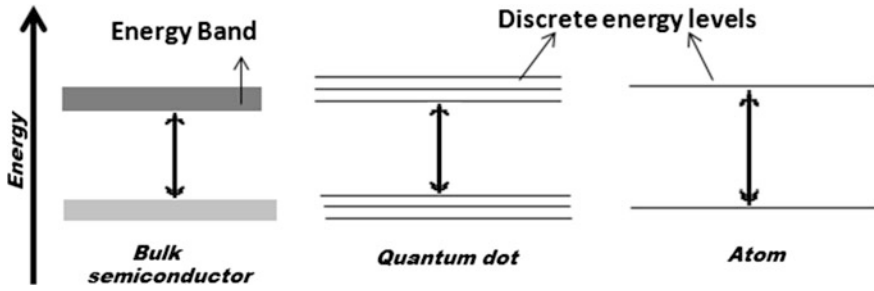


Fig. 7 Representation of the comparison of band gap energy between bulk, nano, and atom

conductors at the stage of nanometer level. Some materials that were semiconductors may become conductors or superconductors. However, the atoms at the surface experience different surrounding than those present at the center of the particle because of the presence of unsatisfied free electrons or dangling bonds. The presence of dangling bonds onto the surface of a material can change its conducting properties.

Optical properties are also size-dependent at the nanoscale level. As said above, confinement leads to a transition from continuous to discrete energy levels (Fig. 7). Due to the discreteness of energy levels, the excitonic band gap increases which restrict the movement of electrons. It cannot move about as freely. Therefore, the quantum confinement of the electrons changes the optical properties of a substance, i.e., it reacts differently to light. As the band gap increases, those substances which are usually opaque in bulk becomes transparent to light at nanolevel. For example, at the macro scale gold appears yellow in bulk but the color changes to red at nanosized scale. Similarly, large-sized zinc oxide particles are used for sun screen because it scatters visible light and appear white but at nanolevel zinc oxide particles do not scatter visible light and becomes transparent to sunlight. With the decreasing particle size, quantum dots changes the appearance of a substance by creating different phosphor and fluorescent colors.

It was found that magnetic nanoparticle can often be described as a single magnetic domain with the uniaxial anisotropy (which comes from the shape of the particle and effect of surface spins) even in materials with other type of anisotropy (such as cubic). The orientation of its magnetic moment points may be either up or down in the absence of magnetic field. During the synthesis of a crystal, there may develop several types of defects on the surface as well as in the core, such as atomic vacancies, changes in the atomic coordination, dangling bonds or lattice disorder. Due to these defects some electronic spins remain uncompensated which leads to the surface magnetization (ferromagnetism or antiferromagnetism) and again, it depends on the size of the particle and on the extent degree of disorder at the surface [14, 15]. Small particles can have very high magnetic susceptibility with permanent magnetic dipole. Small clusters consisting of a single ferromagnetic domain that follow the applied field freely are placed in the category of super

paramagnetism. The magnetic susceptibility of superparamagnetic particles is in orders of magnitude larger than bulk paramagnetic materials.

The deciding factor of the properties of materials such as conductivity, magnetism, and reactivity is the electrons possessed by the materials. Electromagnetic force is unaffected by mass, as it is a function of charge and distance. This becomes even more stronger at the nanosize level. Since electromagnetic forces operate between protons and electrons, therefore as the distance between these charged particles decreases, they experience stronger electromagnetic attraction between them and vice versa. The forces that act on atoms can be attractive or be repulsive. It means that it is these columbic attractive forces that helps an atom in giving its shape and size which in-turn reflects the ability of an atom to form chemical bonds that depends on the attractive forces acting on the outermost valence electronic energy level of an atom. An atom that has incomplete outer energy level attains stability by the rearrangement of valence shell electrons by transfer or sharing of electrons with any other atom. During these rearrangements, potential energy for a chemical bond develops which is responsible for the interactions between atoms and molecules. Therefore, it is very important for the development of nanotechnology. Covalent and ionic bonds are much stronger than hydrogen bond and van der Waals forces. At the nanoscale, van der Waals forces become very prominent. Due to which materials become sticky. That is why nanofibre can be very effective in attracting and trapping small particles. This makes nanofibres excellent materials for use in filtration.

3.1.1 Increased Surface-to-Volume Ratio

We know that as the size of particle decreases, the surface area and therefore, surface-to-volume ratio also increases. This increased surface area of nanoparticles is responsible for the development of peculiar properties of a substance at the nanoscale level (Fig. 8). Due to large surface area there occurs change in the reaction time of a substance. As the particle size decreases, the percentage of atoms on their surface increases [16]. This accounts for the increase in the surface-to-volume ratio. The higher surface-to-volume ratio increase the rate of reaction due to the drastic increase in the amount of exposed surface area at the nanoscale level causing the increase in the reaction rate for a chemical reaction. Nanomaterials are inherently unstable due to high surface energy. Atoms exist at the surface or interface are different from the same atoms exist in the interior of a material. At surface due to free dangling bonds nanomaterial acquires high surface energy which make them highly unstable causing agglomeration.

The properties such as melting point, rate of reaction, capillarity and adhesion, etc., are controlled by their surface area. For example, Gold at the macro scale, has melting point of 1064 °C [18]. Its melting point radically drops about 100 °C as its particle size reduces from 100 to 10 nm diameter. On the further size reduction to

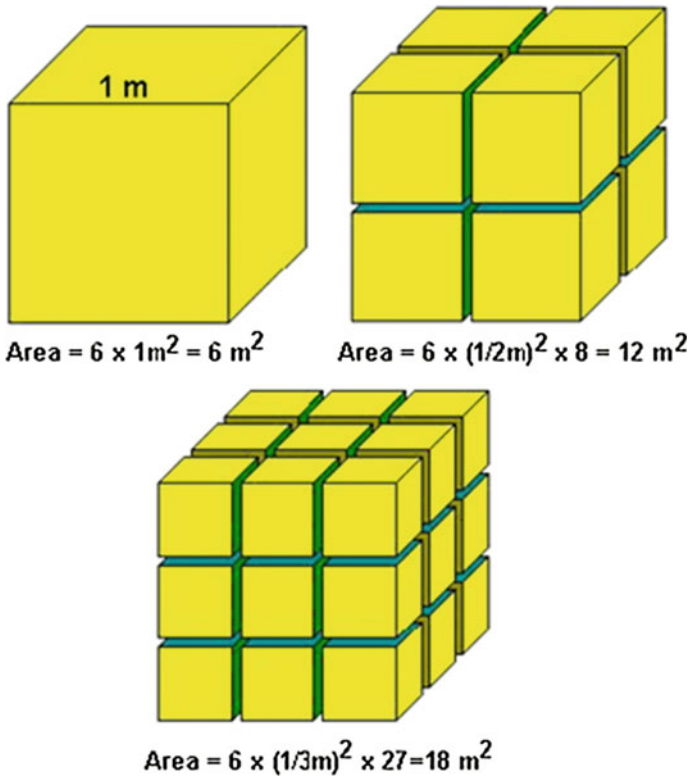


Fig. 8 Representation of increasing area as the particle size decreases [17]

about 2 nm the melting temperature reduces to about half of the melting temperature at the macro scales level. At this level gold will no longer be able to conduct electricity.

4 Magnetization Dynamics of Nanomaterials

In order to study magnetic properties and magnetization dynamics, electron magnetic resonance (EMR) or electron spin resonance (ESR) spectroscopy is preferred. Earlier a conventional ferromagnetic approach, where dynamics of the magnetization was defined as ferromagnetic resonance (FMR) with the help of Landau-Lifshits equation, considering strong thermal fluctuations have been used to study EMR of nanoparticles [19, 20]. The behavior of nanomagnetic objects lie at the boundary line between quantum dynamics and classical thermodynamics. Considering magnetic nanoparticle as a giant spin, Noginova et al. [21] have assumed that the EMR signals are resulted as a collective contributions of quantum

transitions that occurred between energy levels developed due to the projections of the giant spin onto the direction of the magnetic field. Such nanoparticles gives peculiar features in EMR signals that are common in quantum systems, as the variations in narrow spectral component and multiple-quantum transitions with temperature. As the particle size increases, the relative intensity of such EMR signals decreases significantly. This suggests a route of a gradual transition from a purely quantum system applied to sub atomic state to a classical behavior of comparatively large systems, where such effects diminishes. Noginova and co-workers [22] have also explored the effects of the particle size and magnetization dynamics, with EMR studies of magnetic nanoparticles to determine their potential to use them as building blocks for tunable microwave metamaterials.

5 Biological Importance

Molecular or cellular parts of biological systems lie in the submicron size domain, As the size of the nanoparticles lie within these dimensions, they viable to have number of biomedical applications, such as they can be exploited as a very small probes to spy within the cellular machinery without disturbing or interfering their working conditions. They can be easily capped with biological molecules, such as DNA, RNA, proteins or carbohydrates, to enable them to interact with or bind to a biological moieties, i.e., by “tagging” or “addressing” they can provide a controllable means of delivering drug of in diagnostic applications. By changing gradient of external magnetic field, magnetic nanoparticles can be taken and assembled to the desired target. Since human tissues have intrinsic penetrability to the magnetic fields, with such type of external control mechanism operating from an optimum distance, opens up many applications which involves transportation and immobilization of these magnetic nanoparticles, or magnetically tagged biological species. In such cases, the external magnetic field assists the injected magnetic nanoparticles along with the tagged drug to the desired site within the body acting as a site-specific drug delivery busses. Magnetic nanoparticles such as gadolinium may be used as contrast agents in magnetic resonance imaging (MRI). On subjecting to an external magnetic AC field, the temperature around the effected sites can be raised up to 40 °C as a hyperthermic cancer treatment destroying the cancerous tissues and tumors [23].

Since magnetic nanocomposites have shown to have fluorescent, radio-opaque and paramagnetic properties, they may be utilized in confining and concentrating the target analytes in a very small minute volume for in situ optical detections. Therefore, magnetic nano particles functionalized or tagged with biomolecules such as DNA, proteins, peptides or antibodies significantly improves the selectivity and sensitivity of the system serving as bio- and chemo-sensors [24, 25]. Corr et al. have utilized electrostatic interactions to develop new fluorescent-magnetic nanocomposites. They have prepared fluorescent magnetite-porphyrin nanocomposites by interacting core nanoparticle, the spacer group and the fluorophore. Intracellular

fragmentation of the above said nanocomposite have shown their utility as subcellular imaging contrast agents and in targeted drug delivery systems [26].

Magnetic iron oxide nanoparticles have thus shown a very wide spectrum of applications in various clinical, diagnostics and therapeutic fields such as, cancer, cardiovascular, neurological disorders, hyperthermia, magnetic separation of cells, proteins, DNA/RNA, and in other biomolecular probes. Although they have been found to be very useful in various biomedical and in vitro applications but because of the agglomeration and necessity of fast detection via immune cells in physiological medium, their clinical use are mired [27–31]. In order to use nanoparticles in biological systems, its water-dispersibility in bio-systems is very important and it should be bio-compatible. The colloidal stability of nanoparticle suspension should also be maintained in the bio-physiological conditions, with a wide range of pH [9].

6 Conclusion

Physicist Richard Feynman ignited the torch of revolution called nanotechnology and it has illuminated the minds all over the world. Now it has developed number of tentacles. Nanomaterials accordingly classified in number of ways and its applications in many fields are discussed. At the nanoscale level, quantum mechanics plays very important role in determining the properties and characteristics of a material which leads to change in its optical, electrical and magnetic behaviors. The properties of the material become more or less surface dependent. Due to the increase in the surface-to-volume ratio at the nanoscale many surface-dependent properties show changes in many folds. When nanomaterials are engineered in the right way, they not only become electrifying in terms of applications, but also become very significant in current and fast growing field of nanotechnology.

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