# CHAPTER - 1

Introduction

1.1. Materials Science

Materials science and engineering is an interdisciplinary field dealing with the discovery and design of new materials. This is a new scientific field involves the studies of materials through the materials paradigm (synthesis, structure, properties and performance). It incorporates elements of physics, chemistry and the forefront of nanoscience and nanotechnology research. In recent years, materials science has become more widely known as a specific field of science and engineering. A material is defined as a substance most frequently a solid, but other condensed phases can be included that is intended to be used for certain applications. There are many materials around us–they can be found in anything from buildings to spacecrafts. Solid materials can generally be divided into two classes: crystalline and non-crystalline. The traditional examples of materials are metals, ceramics and polymers. New and advanced materials that are being developed include semiconductors, nanomaterials, biomaterials etc. The field has since broadened to include every class of materials like ceramics, polymers, semiconductors, magnetic materials, medical implant materials, biological materials and nanomaterials. Materials are so important in the development of civilization that we associate ages with them. In the origin of human life on earth, the Stone Age, people used only natural materials like stone, clay, skins and wood. Therefore, materials science is one of the most important multidisciplinary fields in science and engineering which is applied and utilizable science in day-to-day life.

- **Nanoscience**: The study of all kind of nanostructures, involving their properties and the processes that happen at nanometer scale (1 nm = 10^{-9} m).

- **Nanotechnology**: The search of the different applications of the studied nanostructures by trying to control and manipulate them.

1.2. Classifications of nanostructured materials (low dimensional systems)

In nanotechnology, the nanostructured materials are divided into different categories. The important method to classify nanostructured materials is their dimensionality. On the basis of the reduced dimensions to the nanoscale range (< 100 nm), the nanostructured materials classified in the following categories as shown in Figure 1.1

- Zero dimensional (0-D) systems – In zero dimensional systems, all three dimensions (length, breadth and height) are in nanoscale level. In these systems, the charge carriers like electrons or holes are restricted in entire three dimensions and cannot move freely in any spatial direction. Zero dimensional systems include single crystal, polycrystalline and amorphous particles with all viable morphology similar to spheres, cubes and platelets. Example – Quantum dot.

- One dimensional (1-D) systems – In these systems, one dimension is in macroscale and other two dimensions are at nanoscale. The electrons or holes are free to move in one dimension and confined in other two dimensions. Example – Quantum wire.

- Two dimensional (2-D) systems – In these systems, two dimensions are in macroscale and one dimension is in nanoscale. The charge carriers are confined in one dimension and are free to move in two dimensions. Example – Quantum well.

- Three dimensional (3-D) systems – In these systems, all three dimensions are in macroscale and no dimensions are in nanoscale. In 3-D systems, charge carriers are free to move in every three dimensions. Example – Bulk material.
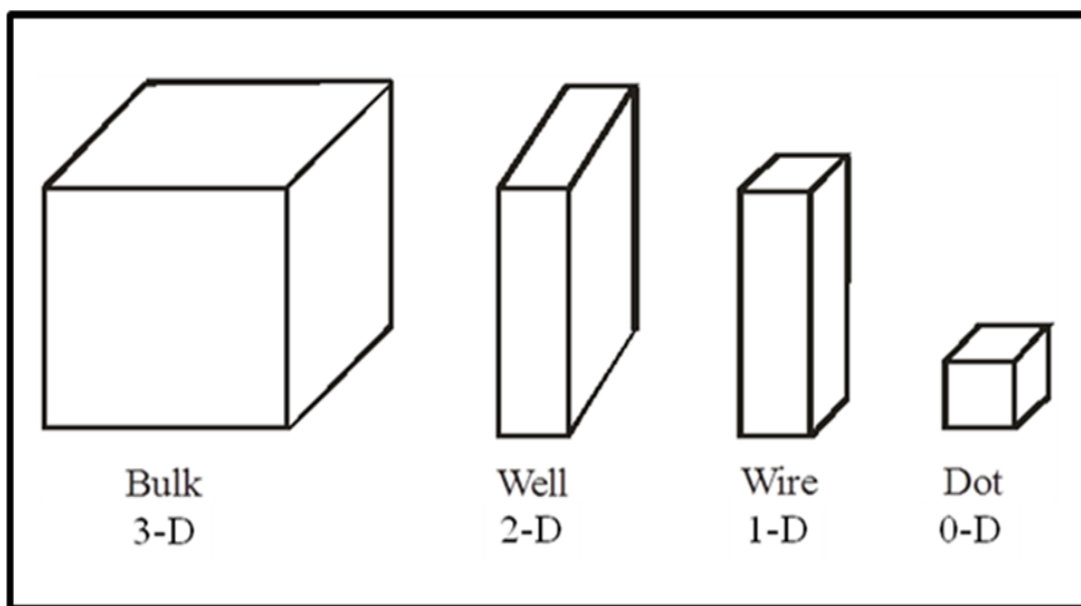
Figure 1.1. Schematic presentation of reduced-dimensional systems.

1.3. Nanoparticles

Nanoparticles are defined as the particles that have at least one dimension in nano range (1 to 100 nm). These particles have high surface area and surface charge density which make them highly reactive. Nanoparticles act as a bridge between bulk materials and atomic or molecular structures [Schmid (2004)]. The difference between these two types of materials lies in the truth that bulk materials have constant physical properties regardless of its size, while nanostructures have size-dependent physical properties [Hsieh and Hsieh (2011), Grassian (2008)]. For this reason, the properties of nanoparticles change as their size decreases and as the percentage of atoms at the surface of a material increases [Grassian (2008)].

1.4. Metal oxides and mixed metal oxides nanoparticles

Among the various types of materials, metal oxides and mixed metal oxides are known for their different kinds of applications in human life. Metal oxides play a very important role in various areas of chemistry, physics, biology and materials science because of their interesting properties [Noguera (1996), Kung (1989), Henrich and Cox (1994), Wells (1987), Rodriguez and Garcia (2007), Garcia *et al.* (2004)]. The metal elements are able

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to form a large diversity of oxide compounds by employing various synthesis methods [Wyckoff (1964)]. These can adopt an enormous number of structural geometries with an electronic structure that can exhibit metallic, semiconductor or insulator character. When two or more metal oxides are mixed together either by physical or by chemical methods to fabricate mixed metal oxide nanoparticles, a novel set of physical and chemical properties may be obtained that would be completely different from that of the individual constituents [Nakka *et al.* (2009), Rodriguez and Stacchiola (2010)]. The distinct properties of nanomaterials arise from quantum size effects [Goldstein *et al.* (1992)], quantum tunneling effects [Reed *et al.* (1989)] and surface effects [Ball and Garwin (1992)]. The confinement of carriers like electrons or holes in low dimensional systems or nanostructured materials could lead to a remarkable change in their physical and chemical properties due to the appearance of quantum size effects [Zhang (1997)]. The confinement or quantum size result becomes important when at least one dimension of the material is comparable to the de Broglie wavelength of the particle [Raimondi *et al.* (2005)]. Physical properties of the materials at nanoscale size are predicted in expressions of quantum mechanics by Schrödinger wave equation which gives a quantitative understanding of different properties of nanostructured materials or low dimensional systems [Tannoudji *et al.* (1991)]. A low dimensional or confined system is any quantum system in which the charge carriers are free to move in one, two, or zero dimensions. In these systems, the spatial dimensions are of the order of the de Broglie wavelength of the carriers and thus the carrier energy states and density of states become quantized. Therefore the electrical, electronics, chemical, magnetic, and optical behavior of the carriers are governed by quantum-mechanical laws. These principles states that all matter at the nanoscale level behaves as both waves and particles [Kerker (1985)]. The complete information about a physical entity like electron, hole and photon or even a physical

system such as an atom is explain by a wave function and is sufficient to show a particle or system of particles.

Nanomaterials containing metal oxides and mixed metal oxides nanoparticles have been synthesized in different morphologies, such as nanorods [Hassan *et al.* (2013), Eskandari *et al.* (2011)], nanowires [Li *et al.* (2006), Wang *et al.* (2010)], nanospheres [Park *et al.* (2009), Sun *et al.* (2014)], nanosheets [Wang *et al.* (2003)], nanoplates [Zhao *et al.* (2012), Li *et al.* (2012)], nanocubes [Xu *et al.* (2003)], nanofibers [Hassan *et al.* (2012)], flower-like [Huang *et al.* (2013), Xie *et al.* (2013), Srivastava *et al.* (2011), Tao *et al.* (2012)], hexagonal nanogranules [Pudukudy and Yaakob (2014a)], hierarchical nanostructures [Dedova *et al.* (2013)], nanoribbons [Ke *et al.* (2009)], nanoflakes [Wei *et al.* (2014)] and nanotubes [Pang *et al.* (2009)]. The physico-chemical properties of nanomaterials depend on the composition, particle size, surface area, shape, structure, crystallinity, homogeneity and synthetic methods [Henglein (1989), Alivisatos (1996), Burda *et al.* (2005)]. The morphology of few metal oxide and mixed metal oxide are shown in Figure 1.2–1.6. Morphology of nanofibers (Figure 1.2), nanorings (Figure 1.3), nanotubes (Figure 1.4) and flower-like (Figure 1.5) were reported for Ce_2O_3–TiO_2 [Hassan *et al.* (2012)], ZnO [Hughes *et al.* (2004)], NiO [Pang *et al.* (2009)] and CuO [Yang *et al.* (2011)] respectively. Bright field TEM image of γ-Fe_2O_3 (Figure 1.6) shows nanosphere particles [Hyeon *et al.* (2001)].
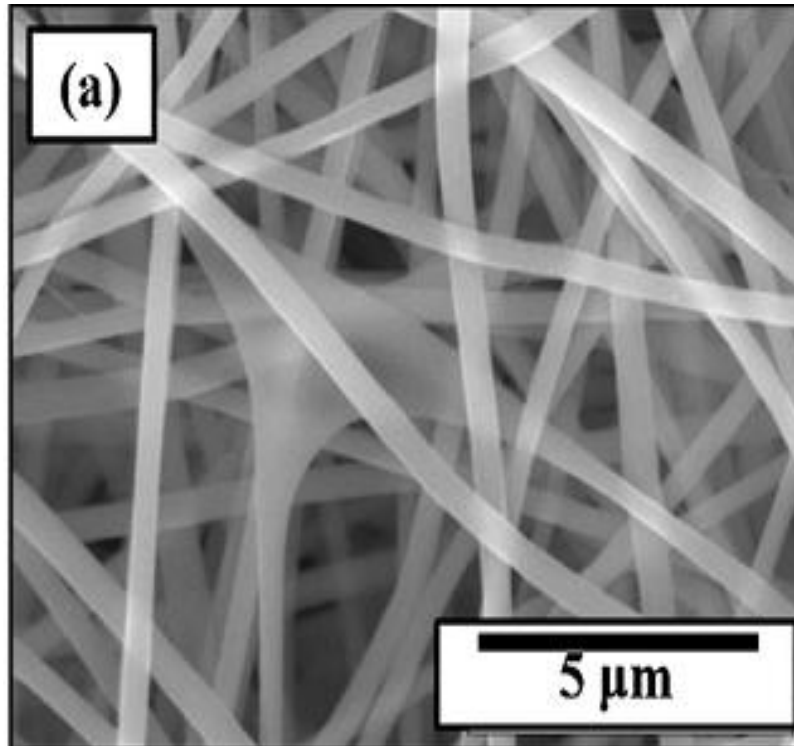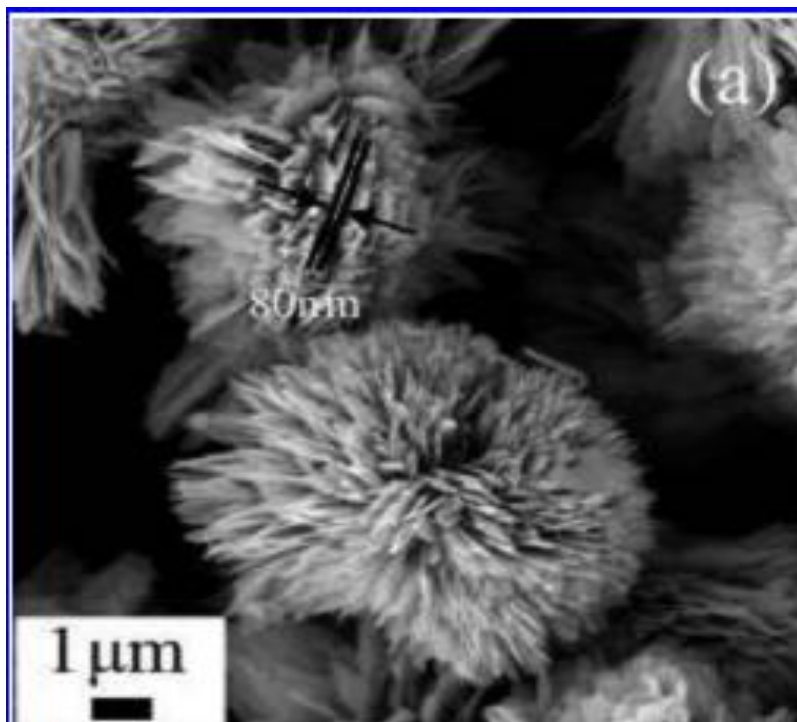
Figure 1.2. SEM image of the Ce_2O_3–TiO_2 composite nanofibers [Hassan *et al.* (2012)].
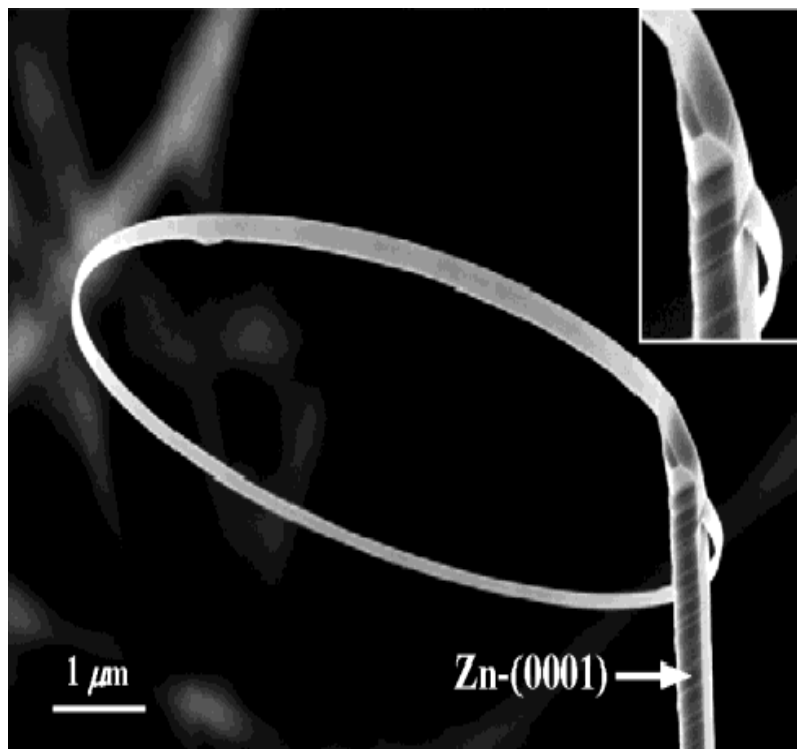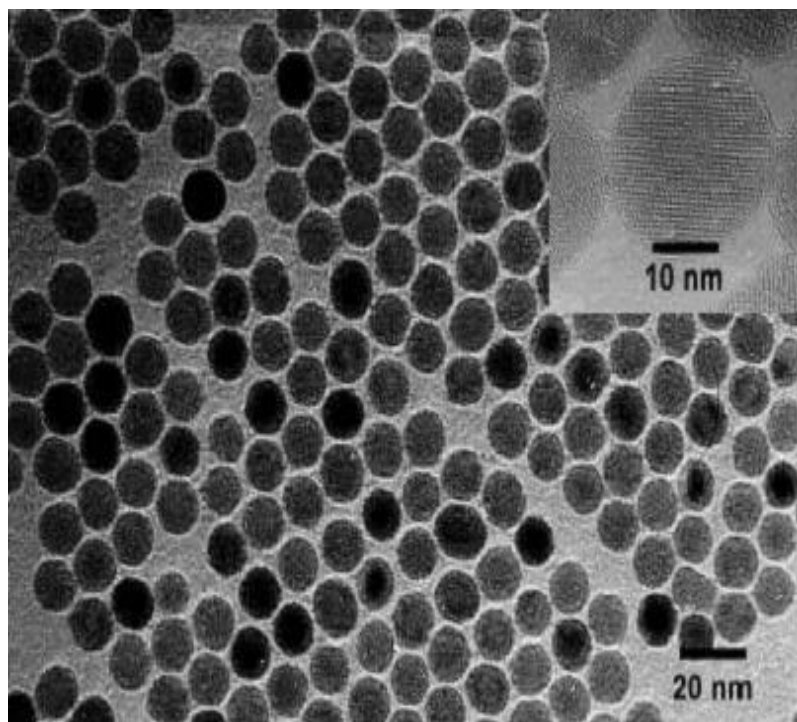

Figure 1.3. SEM image of ZnO nanorings [Hughes *et al.* (2004)].
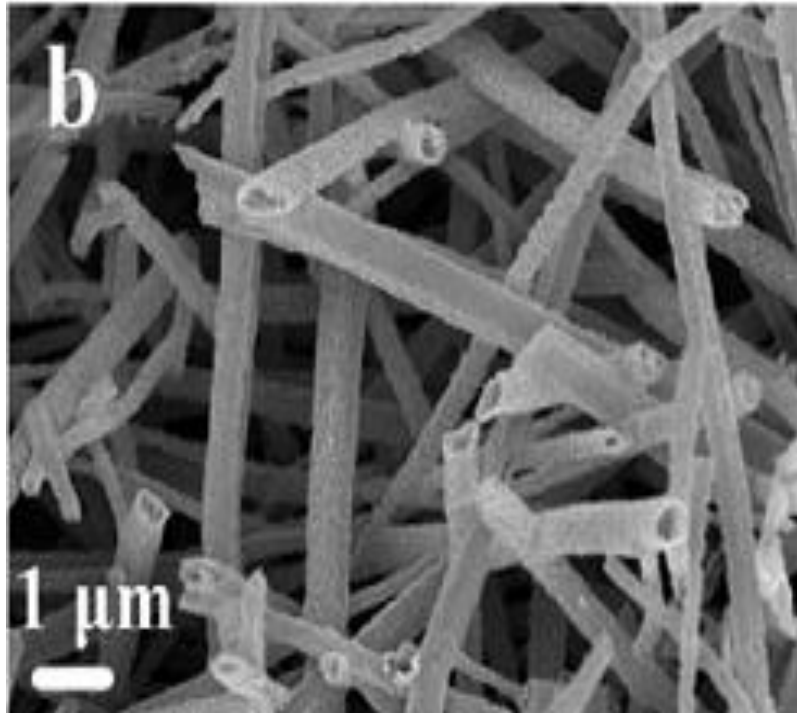
Figure 1.4. SEM image of NiO nanotubes [Pang *et al.* (2009)].

Figure 1.5. SEM image of flower-like CuO [Yang *et al.* (2011)].

Figure 1.6. TEM image of γ-Fe$_2$O$_3$ spherical nanoparticles [Hyeon *et al.* (2001)].

1.5. Applications of metal oxides and mixed metal oxides nanoparticles

Metal oxides and mixed metal oxides nanoparticles have received extensive interest due to their potential uses in different applications, such as catalysis [Srivastava *et al.* (2011), Rodriguez and Stacchiola (2010)], photocatalysis [Pudukudy and Yaakob (2014a), Sathishkumar *et al.* (2011)], sensors [Li *et al.* (2012), Huang *et al.* (2013), Sharma *et al.* (2012), Verma and Gupta (2012)], antimicrobial activity [Hassan *et al.* (2012), Christy *et al.* (2013), Gordon *et al.* (2011)], biomedical [Perez *et al.* (2008), Tarnuzzer *et al.* (2005)], electronics [Sieradzka *et al.* (2012)], optics [Tharsika *et al.* (2014), Kernazhitsky *et al.* (2010)], magnetic materials [Agulhon *et al.* (2012), Oliva *et al.* (2012)], medicines [Sierra *et al.* (2008), Raj *et al.* (2015)], adsorbents [Mahdavi *et al.* (2013), Venkatesh *et al.* (2012)], UV-blockers and filters [Hassan *et al.* (2012), Zhang *et al.* (2011)], fuels cells [Wu and Saito (2000), Suh *et al.* (2000)], solar cells [Maruyama (1998), Snaith and Mende (2007)], waste water treatment [Zanoni *et al.* (2004), Hoffmann *et al.* (1995),

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Yang *et al.* (2005), Xie *et al.* (2006)] and ceramic materials [Ge *et al.* (2013)] (Figure 1.7).

- Metal oxides and mixed metal oxides nanoparticles have important applications in biological and medical sciences such as cancer treatments, drug delivery, fluorescent imaging, bio labeling and bio tagging [Hernandez-Sierra *et al.* (2008)].

- Gordon et al. have reported antibacterial activity of $ZnO-Fe_2O_3$ nanoparticles against *Escherichia coli* and *Staphylococcus aureus* [Gordon *et al.* (2011)].

- SnO_2-MgO nanoparticles perform as catalyst in different organic reactions, e.g. Baeyer–Villiger oxidation of cyclohexanone to caprolactone and oxidation of dimethyl ether to hydrocarbons [Li *et al.* (2008), Yu *et al.* (2007)].

- $CuO-ZnO$ mixed oxide nanoparticles are active catalysts for CO oxidation at ambient temperature [Agrell *et al.* (2003)].

- Nanocrystalline MgO is used as an efficient adsorbent for many toxic chemicals (e. g. organophosphorous compounds) and acid gases [Salomao *et al.* (2011), Carnes *et al.* (2002)].

- SiO_2-NiO nanoparticles are considered as the best catalysts for the hydrogenation of benzene [Zhang *et al.* (2010)].

- ZnO nanoparticles exhibit strong antifungal activity against *Botrytis cinerea* and *Penicillium expansum* [He *et al.* (2011)].

- TiO_2-ZnO mixed oxides are reported [Perez-Larios *et al.* (2012)] as photocatalysts for hydrogen production from water splitting.

- NiO nanoparticles have a suitable adsorption capacity for the removal of heavy metals from aqueous solutions because of their high surface area, low production cost and natural porosity [Mahmood *et al.* (2011), Song *et al.* (2009)].

- Zinc oxide and titanium dioxide nanoparticles now appear on the ingredients list of general household products as various as cosmetics, toothpaste, sunscreens, food coloring, paint and coatings for vitamin supplements [Yu *et al.* (2011)].

- NiO/SrBi$_2$O$_4$ is used as photocatalytic disinfection of pathogenic bacteria *Escherichia coli* and *Staphylococcus aureus* in water under visible light irradiation [Hu *et al.* (2006)].

- CuO–NiO nanoparticles have been used in humidity sensing [Jeseentharani *et al.* (2010)].

- Hierarchical flower-like Co–Cu mixed metal oxide microspheres used as highly efficient catalysts for selective oxidation of ethylbenzene [Xie *et al.* (2016)].

- Fe$_2$O$_3$/SiO$_2$ nanoparticles are used in magneto optical sensors.

- Nanostructures materials used in medicine, e.g. Active agents in cancer therapy and drug delivery, tissue engineering, fluorescent biological labels, fast test for medical diagnosis, detection of proteins, tumor destruction, separation and purification of biological molecules and cells.

- Nanostructures materials also used in cosmetics, e.g. Antiseptic cream, UV light protection creams and tooth paste.

These applications have resulted in a fast expansion of research in these kinds of structures. There is an enormous attention in the development of synthetic procedures in order to control shape, morphology, size and crystallinity of nanoparticles.
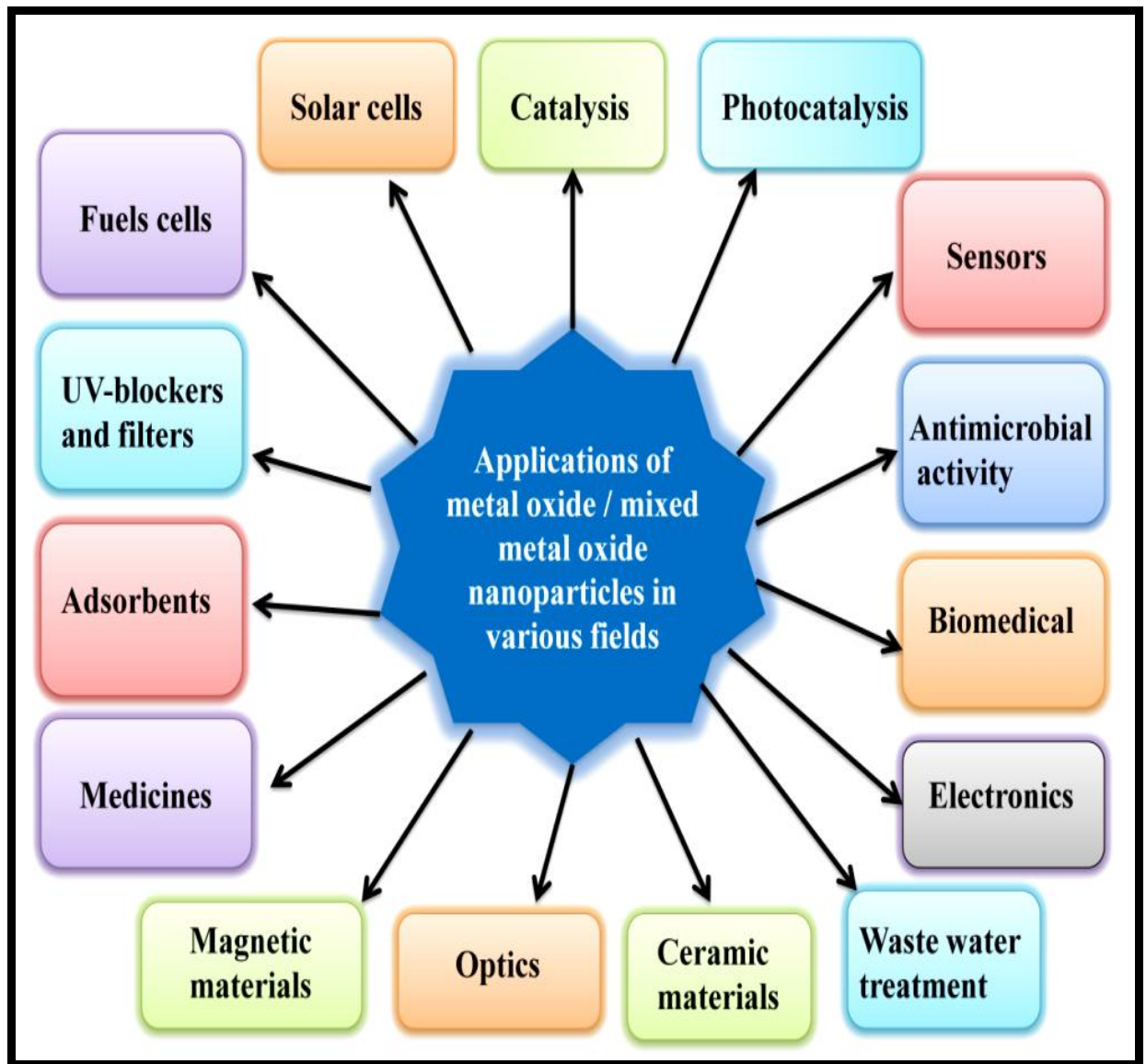
Figure 1.7. Application of metal oxides and mixed metal oxides nanoparticles in various fields.

1.6. Important properties of nanostructured materials

Two most important factors are responsible for the unique physico-chemical properties of nanostructured materials than that of their bulk counterparts:

(i) Quantum confinement or size effects: The nanostructured materials have a reduced dimension at least in one dimension between approximately 1 and 100 nanometers (nm). Quantum confinement effect restricts the motion of electrons in that particular direction and resulting different properties [Link *et al.* (2003)]. In nanostructured materials, the electronic energy levels are not continuous as in the bulk but are discrete in nature.

(ii) Large surface area to volume ratio: The nanostructured materials have a relatively greater surface area compared to the same volume or mass of the materials formed in a bulk. As a result, the number of atoms on the surface increases which finally causes to increase surface energy. This makes nanostructured materials more chemically reactive.

1.6.1. Magnetic properties

The result of reducing the physical size of materials is of great significance from both fundamental considerations and recent practice. As the particle size decreases below 100 nm, a large fraction of the constituting atoms are found on the surface of the nanocrystals; hence inducing important changes in the magnetic structure and properties of the materials at nanoscale regime as compared to their bulk counterparts. The magnetic properties of nanoparticles are determined by several factors including the chemical composition, the type and the degree of defectiveness of the crystal lattice, the particle size and shape, the morphology, the interaction of the particle with the surrounding matrix and the neighbouring particles.

(a) Origin of magnetism

Magnetism arises from electron motions, the spin of an electron, clockwise or anticlockwise and the motion of the electron around the nucleus (orbital angular momentum) (Figure 1.8) [Jiles (1990), McCurrie (1999)]. In orbitals with two electrons of opposite spin the magnetic moments cancel, although orbitals with an unpaired electron have a magnetic moment.
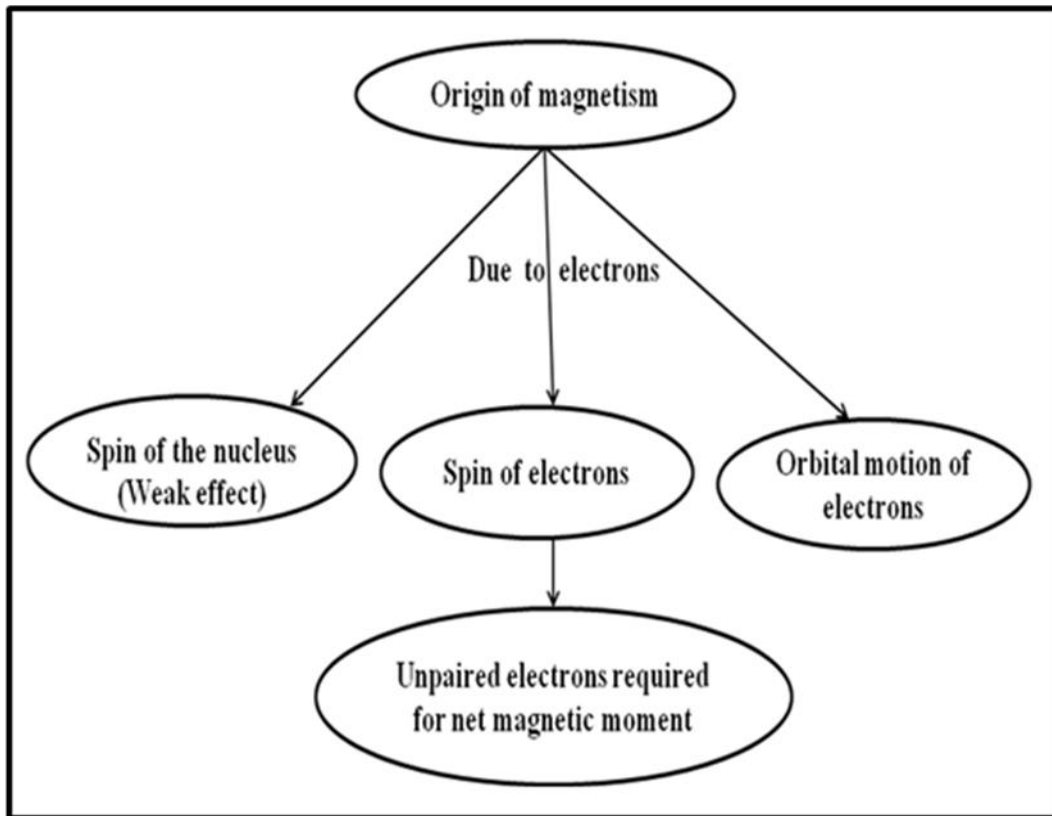
Figure 1.8. Origin of magnetism.

The magnetic induction (B) of a material when placed in an applied magnetic field (H) can be expressed by

$$B = H + 4\pi M \tag{1.1}$$

The magnetic moment per unit volume is called intensity of magnetization (M) and is given by

$$M = m/V \tag{1.2}$$

where V is the volume of the substance. The specific magnetization (σ) is given by

$$\sigma = m/W = M/\rho \ (emu/g) \tag{1.3}$$

where W is the mass and ρ is the density of the substance. The magnetic properties of a substance are characterized not only by the magnitude and sign of intensity of magnetization, but also the method in which intensity of magnetization varies magnetic field and temperature (M versus H and M versus T).

The magnetization per unit magnetic field is called the magnetic susceptibility (κ)

$$\kappa = M/H \ (emu/cm^3Oe) \tag{1.4}$$

The ratio of magnetic induction to an applied magnetic field is a material's permeability (P) and given by

$$P = 1+4\pi\chi_{mol} \tag{1.5}$$

where χ_{mol} is a material's molar susceptibility and described as

$$\chi_{mol} = \kappa F/\rho \tag{1.6}$$

F is the formula weight of the material and ρ is its density. Depending on the values and orders of susceptibility, substances are classified into certain categories.

(b) Classification of magnetic materials
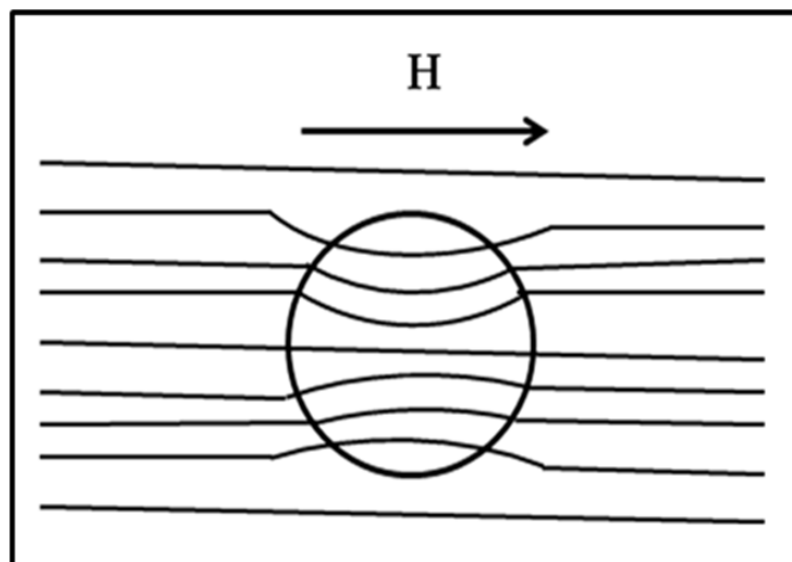
(i) Diamagnetic

The material contains no unpaired electrons and, thus, no net magnetic moment. These types of materials generally have negative magnetic susceptibilities (10^{-6}–10^{-5}) and a permeability value less than one. A diamagnet is expelled from a strong applied magnetic field and the number of lines of force passing through the material is less than if they were passing through a vacuum of the same size and volume (Figure 1.9).
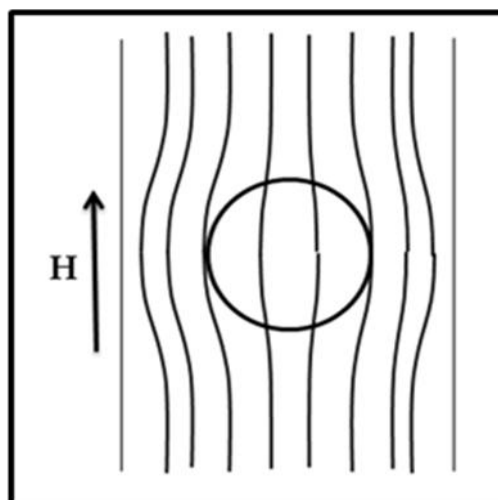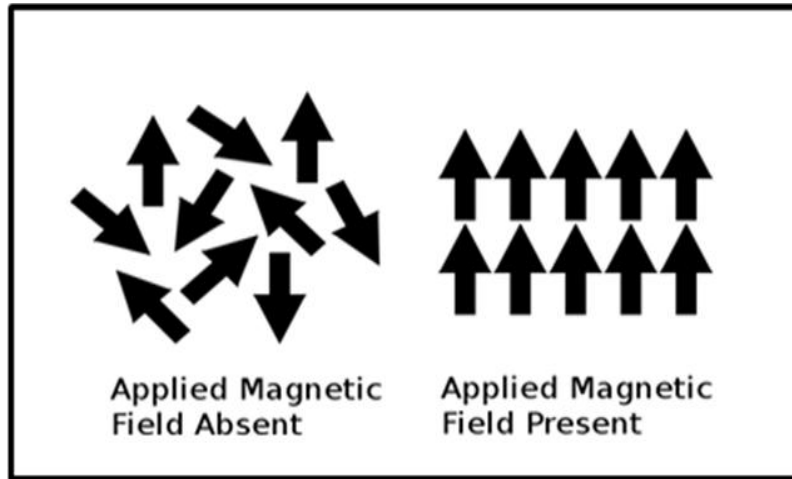

Figure 1.9. Diamagnetic material in an applied magnetic field.

(ii) Paramagnetism

A paramagnetic material consists of atoms or ions, each of which has a net magnetic moment. When the material is placed in an external magnetic field, the number of lines of force passing through it is slightly more than a vacuum of the same shape and size (Figure 1.10). The atomic moments are disordered in the absence of an applied magnetic field and cancel each other, so that the net magnetization of the substance is zero. As a magnetic field is applied, there is a tendency for each atomic moment to turn toward the direction of the field. If there is no opposing force, complete alignment of the atomic moments would be produced and as a whole, the sample would gain a very large magnetic moment in the direction of the field (Figure 1.11). With an increase in temperature, the thermal agitation also increases, resulting in an increased difficulty in aligning the magnetic moments. The effect of an increase in the temperature is to increase the randomizing effect of thermal agitation and thus to decrease the susceptibility [Cullity (1972)].

Figure 1.10. Paramagnetic material in an applied magnetic field.

Figure 1.11. Paramagnetic moment in the absence and presence of an applied magnetic field.

The variation of paramagnetic susceptibilities with temperature is described by Curie's law

$$\chi = C/T \tag{1.7}$$

where χ is a material's susceptibility, C is the Curie constant and T is temperature. This equation indicates that the susceptibility of paramagnetic materials (χ) is inversely proportional to their temperature, i.e. that materials become more magnetic at lower temperatures. Curie's law is only suitable to systems that contain non-interacting magnetic moments. Paramagnetic substance will have a positive susceptibility and permeability greater than one. In Curie's law, it is assumed that individual magnetic moments do not interact with each other, however acted only by the applied magnetic field and thermal agitation. Weiss modified Curie's law by using the idea of a molecular field.

$$\chi = C/T - \theta \tag{1.8}$$

This equation is known as the Curie-Weiss law, where θ is a measure of the strength of the magnetic interactions.

(iii) Ferromagnetism

In a ferromagnetic substance, all the atomic moments are essentially aligned giving a net magnetic moment even in the absence of an applied magnetic field as shown in Figure 1.12 [West (2003)]. The existence of a spontaneous magnetic moment suggests that electron spins and magnetic moments are arranged in a regular mode. All ferromagnets have a maximum temperature where the ferromagnetic property disappears as an effect of thermal agitation. This temperature is called the Curie temperature (T_C). Ferromagnetic materials are paramagnets above the T_C.

Below T_c Above T_c

Ferromagnetic $\leftrightarrow$ Paramagnetic
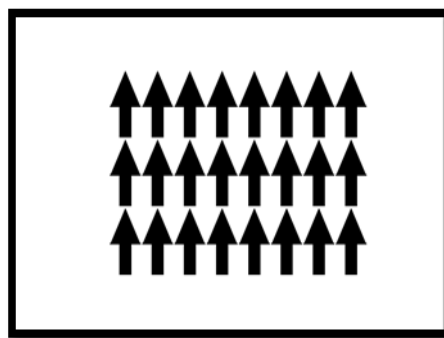
Figure 1.12. Ferromagnetic material.

(iv) Antiferromagnetism

In the case of antiferromagnetic substances, the spins are ordered in an antiparallel arrangement with zero net magnetic moment (Figure 1.13) at temperatures below the ordering or Neel temperature (T_N). Above the Neel temperature, antiferromagnetic materials become paramagnetic that is, the thermal energy becomes large enough to destroy the macroscopic magnetic ordering within the material.
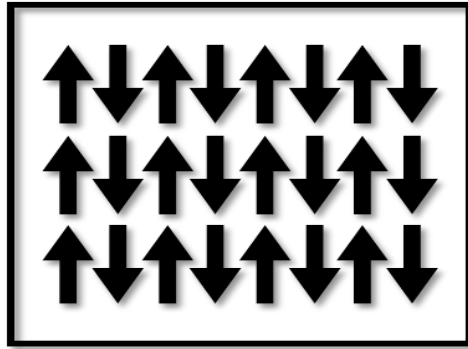
Figure 1.13. Antiferromagnetic material.

(v) Ferrimagnetism

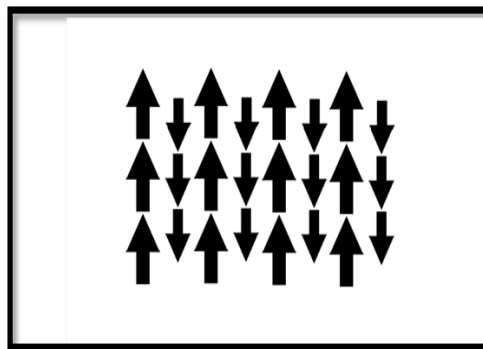The magnetic moments are aligned oppositely and have different magnitudes due to being made up of two different ions giving a net magnetic moment (Figure 1.14). Ferrimagnetism is called uncompensated antiferromagnetism [Cullity (1972)]. Ferrimagnetic materials (ferrites and magnetic garnets) are paramagnets above the Curie temperature.

Figure 1.14. Ferrimagnetic material.

(vi) Superparamagnetism

Superparamagnetism is a form of magnetism, which appears in very fine magnetic particles (small ferromagnetic or ferrimagnetic nanoparticles) [Liu *et al.* (2000), Song and Zhang (2004)]. It will exhibit a remnant magnetization and coercivity of zero. Superparamagnetic materials are important in the field of hard disk drives and ferrofluids. Superparamagnetic materials play an important role in many areas of technology such as magnetic resonance imaging, cell, DNA and protein separation, RNA fishing, targeted

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drug delivery, magnetic hyperthermia, magnetofaction, high sensitivity sensors, etc. [Skumryev *et al.* (2003), Batlle *et al.* (2002)]. Superparamagnetism illustrates the state of a single-domain-sized grain when thermal energy is sufficient to overcome barriers to a reversal of magnetization. These barriers arise from magnetoelastic, magnetocrystalline and shape anisotropy, all of which are proportional to grain volume (V). When the energy barriers are large with respect to thermal energy, the magnetization is blocked and the probability of spontaneous reversal becomes negligible. When the barriers are relatively low, thermal excitations can result in reversal of the magnetization over very short time scales and the grain is in a superparamagnetic state. It is intermediate between ferro and paramagnetism. Ferromagnetic to superparamagnetic transition occurs when thermal energy becomes greater than the barrier height for the magnetization reversal. The temperature at which the magnetic moment reaches a maximum is called the blocking temperature (T_B). Below blocking temperature T_B, the magnetization will have relatively stable and shows ferromagnetic behavior. While above T_B, the thermal energy will be sufficient to suppress the ferromagnetic behavior and therefore the particles become superparamagnetic. The blocking temperature is associated to the anisotropy energy barrier and is dependent on the volume, particles composition and shape. In general, T_B decreases with size of the nanoparticles. This is due to the truth that the energy barrier separating the low energy states is proportional to volume of the particles [Makhlouf *et al.* (2007)]. For a particle of constant size below the blocking temperature T_B, the magnetization will be stable and shows hysteresis loop. The blocking temperature (T_B) is expressed as:

$$T_B = KV/25k_B \tag{1.9}$$

where K is an anisotropy constant, V is the volume of the particle and k_B is the Boltzmann constant (1.38×10^{-23} J K^{-1}). The coercivity of fine particles depends on their size (Figure 1.15) [Handley (2000)].

Superparamagnetic (SP): Below a critical size (r_o), the coercivity is zero because of thermal effect, which is strong enough to spontaneously demagnetize the assembly of magnetic particles.

Single-domain (SD): For $r_o < r < r_c$, the particles become single domain and in this size range, the coercivity reaches a maximum. In a single-domain particle, all the spins are aligned in the same direction and the particle is uniformly magnetized [Issa *et al.* (2013)]. Since there are no domain walls to move, the magnetization will be reversed through spin rotation relatively than through the motion of domain walls. This results in large coercivity of the nanoparticles. Multi-domain (MD) is observed for $r > r_c$ and in this case, the coercivity decreases as the particle size increases and the coercivity H_c is found to vary with size as $\sim 1/r^n$. The comparison of magnetization curves of ferromagnetic, superparamagnetic and paramagnetic materials are shown in Figure 1.16.
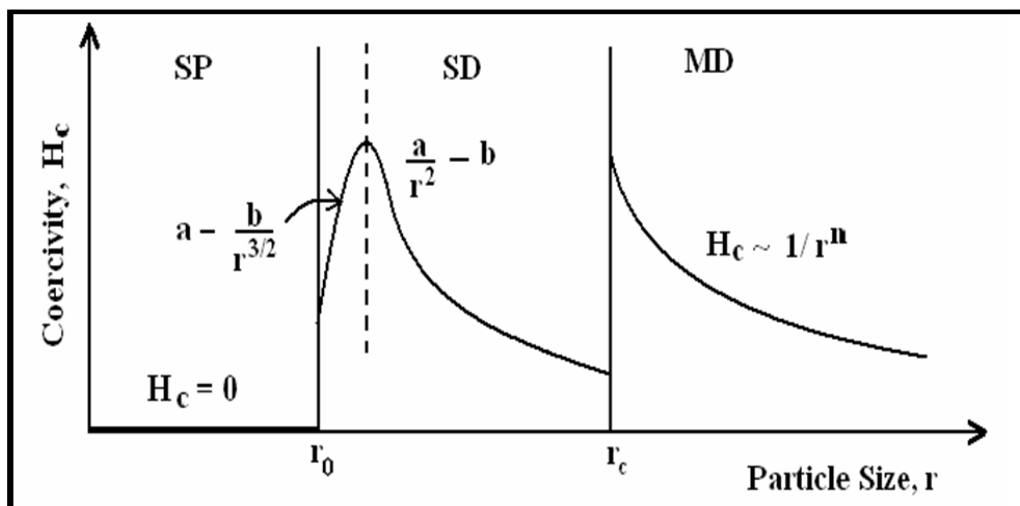
Figure 1.15. The size dependence of coercivity exhibited by magnetic particles: $H_C = 0$ below superparamagnetic (SP) particle size limit r_o, single-domain behavior (SD) between r_o and the single domain limit r_c and multidomain behavior (MD) for $r > r_c$ [Handley (2000)].
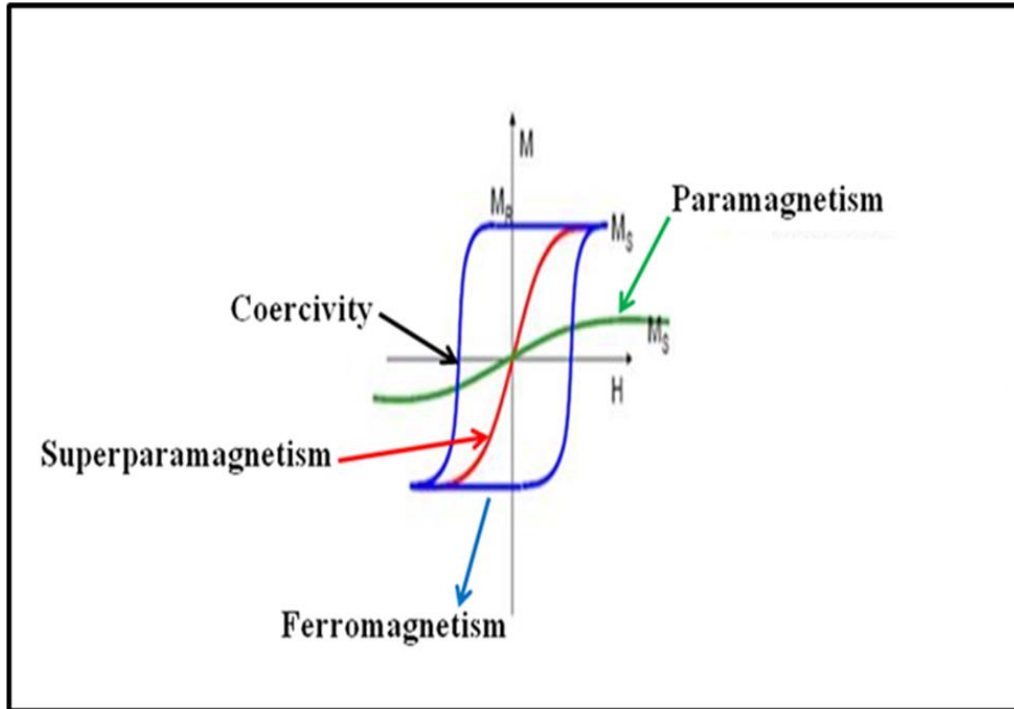
Figure 1.16. Comparison of magnetization curves of ferromagnetic, superparamagnetic and paramagnetic materials.

Magnetic nanoparticles are of great interest for technological applications in various fields, such as magnetic energy storage [Frey *et al.* (2009)], catalysis [Lu *et al.* (2007)], magnetic fluids [Taylor *et al.* (2013)], biomedicine [Thomas *et al.* (2013)] and water treatment [Yavuz *et al.* (2006)]. Magnetic nanoparticles are also used to enhance the capacity of magnetic storage devices for example computer hard discs and magnetic tapes [Skumryev *et al.* (2003)].

1.6.2. Optical properties

One of the most interesting and practical features of nanostructured materials is their optical properties. Optical properties of nanomaterials are applied in various applications such as solar cell photocatalysis, optical detector, laser, sensor, imaging, phosphor, display and biomedicine. In nanostructured semiconductors materials, both linear (one exciton per particle) and non-linear optical (multiple excitons) properties arise consequently of transitions between electron and hole discrete or quantized electronic

levels. As the size of semiconductor and metal becomes smaller or equal to its Bohr radius, the space for motion of exciton is reduced and as a result, the optical band gap energy is increased. The optical properties of nanostructured materials depend on parameters for example size, shape, surface characteristics and additional variables including doping and interaction with the surrounding environment. The effective mass theory (EMA) is the most significant and common theory to explain the size dependence of the optical properties of nanosize semiconductors [Brus (1983)]. The nanostructured metals show significant surface plasmon resonance (SPR) where the electrons of conduction band oscillate at the frequency of alternating electric field incident over the material. This result provides rise to tunable color variation with particle size and shape from visible to near infrared region. The emission of light of a specific wavelength corresponding to the incident radiation is a function of the size of nanostructures [Link *et al.* (2003)]. Moreover, the increased value of energy level spacing is an important decisive factor for such behavior in semiconductor nanoparticles. As a consequence of increased optical band gap value for semiconductor nanoparticles upon reduction in particle size, the absorption edge is shifted toward shorter wavelengths (blue-shift). Thus, semiconductor nanoparticles with different sizes emit various colors after excitation with radiation [Lewis (1993)]. In bulk metals, the valence and conduction bands overlap, but in metal nanoparticles there is a gap between valence and conduction bands. Optical absorption characteristics of nanosized oxides are also influenced by non-stoichiometry defect. Common point defects in nanostructured oxides concern oxygen or cation vacancies [Kang *et al.* (2001)]. The materials exhibit various color when they are converted to nanoparticles. For example, bulk gold appears yellow but its nanostructures show several color such as; red, purple or orange depending on its size and shape (Figure 1.17) [Kreibig *et al.* (1995)].
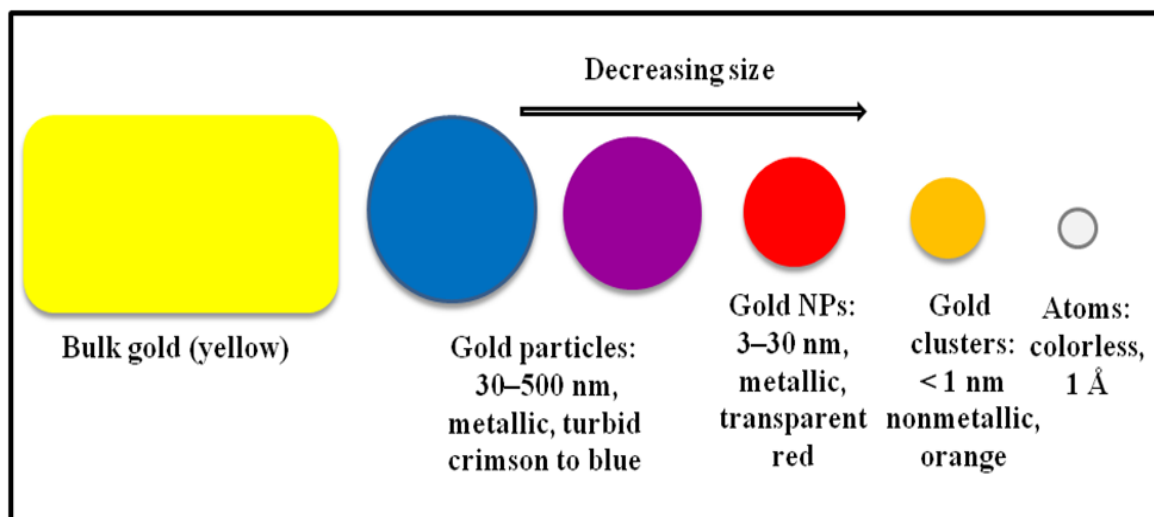
Figure 1.17. Size dependent emission from gold nanoparticles.

1.6.3. Catalytic properties

The nanostructured materials contain a large fraction of the atoms on its surface. The large fractions of the atom, high surface energy, spatial confinement and reduced imperfections are responsible to increase its reactivity and catalytic activity. In addition, the other factors like high surface area to volume ratio, the variation in geometrical structure and unique electronic structure significantly affect the catalytic properties [Rao *et al.* (2002)]. The percentage of atoms occupying on the surface increases on decreasing particle size. This makes nanoparticles more reactive. The most important features essential for their application as catalysts are (i) adsorption of the reactant molecules at surface sites, (ii) bond breaking of the adsorbates, (iii) rearrangement of the adsorbed reaction intermediates and (iv) desorption of the molecules [Somorjai (1978)]. Various surface processes are dependent on the particle size and surface structure. Catalysis using nanostructured materials increase the rate, selectivity and efficiency of chemical reactions. The entire catalytic reaction proceeds through adsorption. Diffusion is extremely fast on catalyst surfaces and requires a much lower activation energy than desorption. The catalytic reactions involve charge transfer of either electrons or protons.

Different oxide composites have been established to be potential catalysts for various important reactions due to different centers present in the same material and their acidity or basicity [Philipp *et al.* (1992)]. The acidity of a surface has a great effect on catalytic performance of an oxide material. Catalyst supports are employing to increase the mechanical stability of the catalyst and the surface area of the active compound [Lu *et al.* (2009)]. Depending on the support, the activity of the catalyst can be superior to that of bulk materials. One of the expected reasons for enhanced activity of supported catalyst may be due to structural effects.

The effect of a catalyst is following:

- Lower activation energy of the reaction.

- Provides an alternate reaction pathway to obtain the products.

- Increases the rate of a reaction since it takes less energy to initiate the forward reaction.
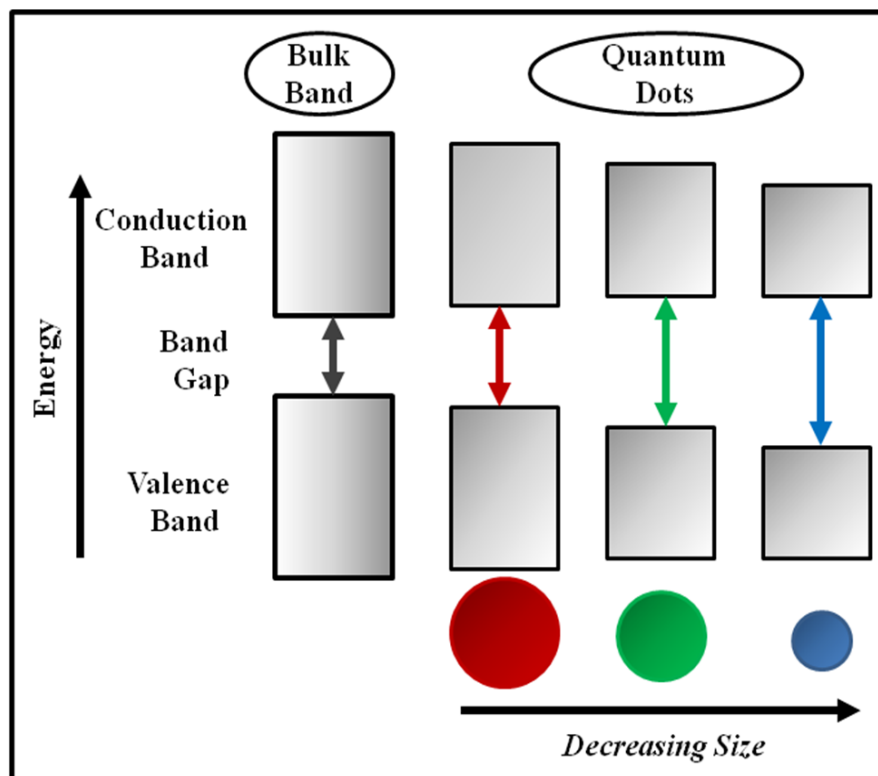
1.6.4. Structural properties

Structural features include lattice symmetry and lattice parameters are very much influenced by size and shape. Bulk materials are usually stable with well defined crystallographic structures. The crystal structure of nanomaterials is same as bulk structure but the change in lattice parameters. In nanomaterials, inter atomic spacing is decreases than bulk due to presence of long range electrostatic forces and the short range core-core repulsion [Schoiswohl *et al.* (2004)]. The deviation in thermodynamic stability with particle size may also induce structural transformation and modification in lattice parameters. Nanostructures should have low value of surface free energy for structural stability. The phase of material is very stable due to low surface free energy at nanosize [Song *et al.* (2003)]. Increase the surface to volume ratio goes along with small particle size that generates excess stress or strain that causes structural perturbation in the lattice

[Cammarata *et al.* (1989)]. Size dependent structural distortions allied with differ in cell parameters [Ayyub *et al.* (1988)].

1.6.5. Electronic properties

The nanomaterials have different electronic structure with various energy level separation and charge carrier density depending on its size and shape. Therefore, they show several electronic properties from their bulk form [Yoffre (1993)]. Because the size of the nanostructured materials becomes comparable with the de Broglie wavelength of the electrons, the quantized nature of the energy states is the main cause in the increase of band gap energy as illustrated in Figure 1.18. This explains the reason for transformation of conductive material to insulator.

Figure 1.18. Quantization of energy levels depends on particle size.

1.6.6. Antimicrobial properties

The antimicrobial activity of the nanostructured materials is well-known to be a function of the surface area in contact with the microorganism. The small size and the high surface

to volume ratio (large surface area) of the nanostructured materials increase their interaction with the microbes to perform a wide range of antimicrobial activities. The expanding applications of nanomaterials as antimicrobials in industries, textiles, medicine, cosmetics and food packaging have been described. Oxidative stress induced by reactive oxygen species (ROS) especially hydrogen peroxide, superoxide anion, hydroxyl radical and hydroxyl ion production in nanostructured materials is concern to be the most important mechanism of their antibacterial activity [Li *et al.* (2012)].

1.7. Oxide based materials related to the present work

A brief description of some oxide based materials considered in the current study has been discussed in somewhat more detailed.

1.7.1. Copper oxide (CuO)

Copper oxide has attracted specific attention due to low cost, abundant resources, non-toxicity and easy preparation in different shapes of nanosized dimensions. Copper oxide is an important p-type semiconductor with a narrow band gap (1.2 eV) exhibits various interesting properties [Marabelli *et al.* (1995)]. Copper oxide has been broadly studied because of its different applications such as photocatalysts [Vaseem *et al.* (2008)], dye-sensitized solar cells [Wanga *et al.* (2010)], gas sensors [Choi and Choi (2000)], field emission devices [Teo *et al.* (2008)] and lithium -ion battery electrode materials [Li *et al.* (2010)]. Although, a few works have explored the CuO application as pseudocapacitor electrodes [Zhang *et al.* (2011)]. Nanofluids of CuO nanoparticles have excellent thermal conductivity appropriate for their applications as heat transfer fluids in machine tools [Chang *et al.* (2005)]. CuO crystal structures have a narrow band gap giving important photocatalytic or photovoltaic properties and photoconductive functionalities [Xu *et al.* (1999)]. These applications depend on the size, morphology and specific surface area of the CuO particles are significant and is also strongly dependant on the synthesis

techniques. The preparations of CuO nanomaterials with various morphologies have importance in both experimental and practical fields.

CuO nanomaterials exhibit different morphologies such as nanotubes [Cao *et al.* (2003)], nanowires [Jiang *et al.* (2002)], nanoleaves [Zhao *et al.* (2011)], dandelion-shaped hollow structures [Liu *et al.* (2004)], nanoellipsoids [Zhang et al. (2005)], nanoshuttles [Wang *et al.* (2010)], peanut-like patterns [Zhang *et al.* (2004)] and nanoplates [Zhou *et al.* (2006)]. Various processing routes have been developed for synthesizing CuO nanoparticles such as chemical vapor deposition [Ottosson and Carlsson (1996)], sol–gel [Gartner *et al.* (2004)], pulsed laser evaporation [Chen *et al.* (2009)] and hydrothermal method [Dar *et al.* (2009)].

1.7.2. Zinc oxide (ZnO)

Zinc oxide nanoparticles have been focus of research due to their unique properties, such as optical transparency, electric conductivity, piezoelectricity and near-UV emission [Chen *et al.* (2008)]. ZnO with a wide band gap (3.3–3.6 eV) is an important n-type semiconductor with the large excitation binding energy of 60 meV at room temperature [Kim *et al.* (2005)] and excellent chemical and thermal stability. Zinc oxide nanoparticles are used for numerous applications such as in solar cells as semiconductor [Hosono *et al.* (2005)], UV lasers [Huang *et al.* (2001)], sensors [Wan *et al.* (2004)], field emission devices [Wang *et al.* (2006)], varistors [Singhal *et al.* (1997)]. It is also a significant material for catalytic applications, in luminescent and electronic industry and in the production of pigments, cosmetics and pharmaceutical [Li *et al.* (2007)]. Due to wide band gap of ZnO, makes it capable of absorbing a larger fraction of the solar spectrum than TiO_2 and as a result it has been suggested that ZnO photocatalysts is the preferred choice as the photocatalytic degradation agent [Sakthivel *et al.* (2003)].

Zinc oxide nanoparticles possess a large surface-to-volume ratio that may exhibit stronger antimicrobial activity and has higher stability than organic materials. ZnO nanostructures exhibit variety of morphologies including nanowires, nanotubes and hollow spheres.

Zinc oxide nanoparticles have been prepared by different methods such as sol–gel processing [Mondelaers *et al.* (2002)], solution precipitation [Wang *et al.* (1999)], spray pyrolysis [Tani *et al.* (2002)], hydrothermal route [Pal and Santiago (2005)], microwave heating process [Bu (2013)] and sonochemical method [Siddiquey *et al.* (2012)].

1.7.3. Nickel oxide (NiO)

Nickel oxide is a very promising transition metal oxide material and has attracted increasing attention because of its particular catalytic, electrical, optical, anomalous electronic and magnetic properties. NiO is a very essential p-type semiconductor with a stable wide band gap (3.6–4.0 eV) [Yang *et al.* (2008)]. It is used in a variety of fields such as gas sensors, catalysis, electrochromic films, fuel cell electrodes, magnetic materials, super capacitors, dye-sensitized solar cells and also as water treatment adsorbents [Mahmood *et al.* (2011)]. As a result of the novel physical and chemical properties of NiO different nanostructures such as nanoparticles, nanosheets, nanorods, nanowires and porous solids [Xing *et al.* (2004)] of nickel oxide were synthesized. Hierarchically structured metal oxide exhibited excellent performance in the removal of heavy metal ions contaminated wastewater. The ingestion of contaminated wastewater by humans causes vomiting, skin irritation, pain and acute diarrhea. The flower like nanostructures NiO has been reported as an efficient sorbent for the removal of heavy metal ion in wastewater [Tiwari *et al.* (2012)].

In the recent past researchers have been synthesized NiO nanoparticles by different methods such as sol–gel, surfactant-mediated synthesis, polymer-matrix assisted synthesis

[Deki *et al.* (2003)], thermal decomposition, microwave irradiation [Yang and Lian (2010)] and reverse micellar method [Ahmad *et al.* (2006)].

1.7.4. Cobalt oxide (Co$_3$O$_4$)

Cobalt oxide nanoparticles are important transition metal oxide both for technological applications and physical studies. Among the metal oxides, cobalt oxide is the most attractive one since it has three well-known polymorphs: the cobaltous oxide (CoO), the cobaltic oxide (Co$_2$O$_3$) and the cobaltosic oxide (Co$_3$O$_4$). Compared to another two polymorphs, Co$_3$O$_4$ is the most stable phase and is a p-type semiconductor with direct optical band gap of 3.95–2.13 eV. Co$_3$O$_4$ belongs to spinel crystal structure formed from a cubic close packing array of oxide ions, in which Co(II) ions reside in the tetrahedral sites and Co (III) ions occupy the octahedral sites. In current years, Co$_3$O$_4$ has attracted large interest due to its potential applications as heterogeneous catalysis [Pudukudy and Yaakob (2014b)], lithium rechargeable batteries, magnetic materials, electrochromic devices and gas sensors [Li and Xu (2005)]. It is well known that the structure, size, and morphology extensively influence the properties and application of the materials. Co$_3$O$_4$ is usually considered to be a remarkable anode material for next-generation Li-ion batteries because of its high theoretical capacity (890 mAh g^{-1}). Mainly, one dimensional (1D) nanostructured Co$_3$O$_4$ arrays increasing directly on conductive substrates are expected to have high performance in energy storage systems due to their high surface-to-volume ratio and rapid electron transportation [Jiang *et al.* (2010)].

Different methods including, sol–gel, thermal decomposition, microemulsion [Liu *et al.* (2002)], electrodeposition, solvothermal and hydrothermal [Jiang *et al.* (2010)] techniques have been developed to prepare Co$_3$O$_4$ nanostructures with diverse

morphologies, such as nanotubes, nanowires, nanobelts, nanocapsules, nanoboxes and nanosheets.

1.7.5. Zinc aluminate ($ZnAl_2O_4$)

Oxide spinels consist of a very large group of structurally associated compounds many of which are of extensive technological significance. The zinc aluminate with spinel structure has attracted interest due to its combination of advantageous properties such as high thermal stability, high mechanical resistance, low temperature sintering ability, hydrophobicity, low surface acidity, better diffusion and chemical resistance. Thus, it is employed as high temperature ceramic material [Tzing and Tuan (1996)] and optical coating. In addition, $ZnAl_2O_4$ is a well-known wide band gap semiconductor (3.8 eV) and large excitation binding energy (60 meV), as a result $ZnAl_2O_4$ used as UV transparent conductors, dielectric and optical materials [Gaudon *et al.* (2009)].

$ZnAl_2O_4$ is an important mixed oxide with a normal spinel AB_2O_4 structure consists of an arrangement of closed packing array presenting tetrahedral interstices for A and octahedral interstices for B, occupied by the bivalent and trivalent ions respectively (Figure 1.19) [Farhadi *et al.* (2010)]. It is commonly used as a catalyst or support in various catalytic reactions such as transesterification, dehydrogenation, hydrogenation, dehydration, isomerization and acetylation [Farhadi *et al.* (2010)]. $ZnAl_2O_4$ spinel oxide is non-toxic, inexpensive, very stable materials with strong resistance to acids and alkalis and has high melting points and relatively high surface areas.

Many techniques for the preparation of $ZnAl_2O_4$ nanoparticles have been reported such as coprecipitation, hydrothermal, sol–gel, template assisted synthesis [Wang and Wu (2005)] and solid-state reaction [Hong *et al.* (1995)].
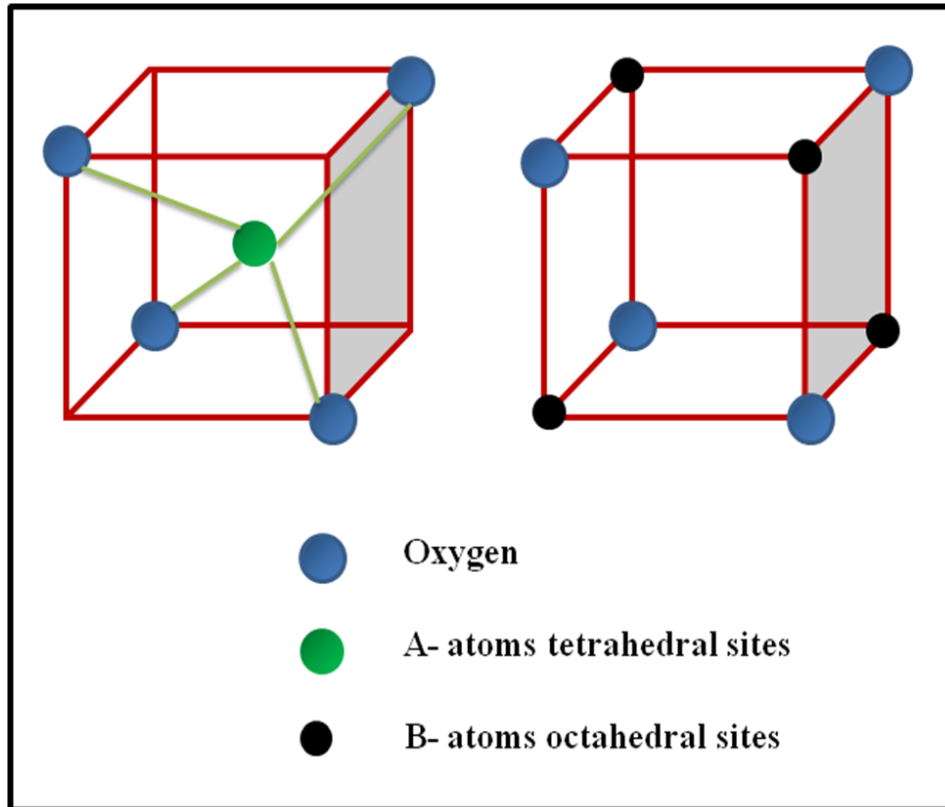
Figure 1.19. AB_2O_4 normal spinel structure.

1.7.6. Zinc ferrite (ZnFe$_2$O$_4$)

Among various nanomaterials, magnetic nanoparticles zinc ferrite are of particular interest for their attractive scientific and technological features in different fields such as magnetic recording, ferrofluids, magnetic resonance imaging (MRI), hot gas desulphurization, catalyst, photocatalyst, drug delivery and pigments etc. [Ikenaga *et al.* (2004), Chen *et al.* (2009)]. Except these applications spinel ferrites are also employed in various electronic devices due to their high permeability at high frequencies, high mechanical hardness, chemical stability and practically low cost. The spinel ferrites are greatly appropriate for computer memories, logical devices, transformer cores, recording heads etc. The spinel ferrites with structural formula of MFe_2O_4 (M is a divalent metal ion) has a unit cell with 32 oxygen atoms in a cubic closest packing and tetrahedral and octahedral sites available for cations [Millot *et al.* (2003)]. But in the inverse spinel structure, the M^{2+} cations are replaced by half Fe^{3+} ions in the tetrahedral sites, the second

half of Fe^{3+} ions left behind at the octahedral sites. Bulk $ZnFe_2O_4$ has a normal spinel structure with the Zn^{2+} ions without magnetic moment in the tetrahedral sites, which makes antiferromagnetic behavior. Though, it has been confirmed that both the crystallite size and synthesize process can affect the magnetic properties of nanocrystalline zinc ferrite. Various methods such as ball milling, coprecipitation, auto-combustion, sol–gel, ultrasonic cavitation, hydrothermal, reverse micelles process and microemulsion [Hochepied *et al.* (2000)] techniques have been employed to synthesize zinc ferrite.

1.8. Objective of the present research work

In perspective of above discussed studies on unique properties of nanostructured materials mostly, metal oxide and mixed metal oxide nanostructures and their applications in different fields of science and technology, it has been found that these nanostructured materials are of great significance due to its tendency to fabricate unique shape, morphology and size dependent physical and chemical properties. However, expensive preparation methods, tedious procedures, complicated steps and agglomeration problems of the nanostructures synthesis intricate task the synthesis of controlled shape and size and therefore their possible applications in different field are observed. An extensively controlled preparation of desired shape, morphology and size depending upon its applications of the nanostructured materials with high purity is still a large challenge for the scientific community. The world wide researchers have been still trying to develop a simple and efficient way to synthesize highly controlled shape and size of the nanoparticles. In this context, a simple and low cost and environment friendly for the large-scale production of metal oxide and mixed metal oxide nanostructured materials and studies on their optical, magnetic, catalytic and antifungal properties have not been addressed in details in the literature. The influence of calcination

temperature on the morphology, crystallinity, optical band gap, specific surface area and pore volume of the nanoparticles has been investigated.

In the present work, formation of high purity samples at the nano level with high surface area and control of the size, shape, homogeneity and agglomeration of nanoparticles, which is one of the primary aims of this thesis.

The purpose of this work is to synthesis, characterize and find applications of metal oxides and mixed metal oxides nanoparticles. Optical and magnetic properties of these materials were also investigated.

Therefore, the objective of the research work presented in the current thesis can be summarized under the following bullet points:

- ➢ To synthesize pure nanocrystalline CuO with dandelion-like morphology using simple and low cost synthesis method at low temperature in short precipitation time and its catalytic reactivity for the reduction of 4-nitrophenol has been explored.

- ➢ To develop an efficient and low cost synthesis method to prepare zinc oxide (ZnO) nanoparticles and study their optical properties. The antifungal activity of the ZnO nanoparticles against pathogenic *Candida albicans* was tested. Also, study their antifungal activity as function of concentration of nanoparticles.

- ➢ To prepared pure nanocrystalline CuO–ZnO mixed metal oxide with unique morphology using an easy, low cost, safe and environment friendly for the large-scale production and study their optical properties. The nanocrystalline CuO–ZnO mixed metal oxide powder has also been explored as catalyst for reduction of 4-nitrophenol.

- ➢ To synthesize porous nanocrystalline NiO with a hexagonal sheet-like morphology using simple and economical synthesis method in short time at low

calcination temperature and study their optical properties. The chemical activity of the samples was tested by catalytic reduction of 4-nitrophenol.

➢ To synthesize pure nanocrystalline ZnO–NiO mixed metal oxide using simple, economical, environment friendly and study their optical and magnetic properties. The chemical activity of the samples was also tested by catalytic reduction of 4-nitrophenol.

➢ To synthesize single-phase nanocrystalline zinc aluminate ($ZnAl_2O_4$) spinel powder without using any chelating agent and study their optical properties. Its catalytic activity was also tested for the reduction of 4-nitrophenol.

➢ To synthesize single-phase nanocrystalline zinc ferrite ($ZnFe_2O_4$) spinel powders using an easy and low cost in short time without employing any surfactant/chelating agent and study their optical properties. The antifungal activity of the nanocrystalline zinc ferrite powders was tested against pathogenic *Candida albicans*.

➢ To synthesize pure Co_3O_4–ZnO mixed metal oxide nanoparticles using a simple, inexpensive and surfactant-free process in short time followed by calcination at low temperature and studied their optical as well as magnetic properties.

➢ Characterization of all the synthesized metal oxide and mixed metal oxide nanoparticles via using various analytical techniques in order to study their main properties.